CENTER FOR ADVANCED PROCESS DECISION-MAKING

New Directions for Process Systems Engineering

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GENERAL NEWS

CAPD e-News. We sent on April 30 our third e-newsletter. As we indicated previously, we now issue on a yearly basis two extensive newsletters with detailed descriptions of the projects in August and January, while the two others are brief e-Newsletters in April and October that contain short announcements as well as information that we think will be useful to the CAPD members. We would appreciate receiving feedback or suggestions for improving the e-Newsletter.

Larry, Ignacio and Steinar attended the PSE/ESCAPE meeting that took place in Garmisch-Partenkirchen. Papers from this meeting are given in the CAPD report series. **Larry Biegler** is the new Programming Chair for the AIChE CAST Division and also the new chair for the International PSE Organization. He will be spending a sabbatical this fall at the University of Heidelberg. This fall he will also be a plenary speaker at the Fast NMPC IFAC Workshop in Grenoble, France and the Veszprém Optimization Conference: Advanced Algorithms (VOCAL) in Hungary. **Ignacio Grossmann** became member of the Chemical Engineering advisory boards of Penn State, Purdue and Princeton. He was also elected as next chair of the Chemical Engineering section of the National Academy of Engineering. He is also running as a candidate for Director of AIChE in this year's elections. He will also be a keynote speaker at the 3rd Interamerican Congress of Chemical Engineering that will take place in Buenos Aires on October 2-4.

Congratulations to our Ph.D. students who successfully defended their Ph.D. exam over the last 6 months: **Ashish Agrawal**, student of Ignacio has become a postdoc in Systems Biology at Yale; **Michael Bartovsky**, student of Steinar; and **Eduardo Dozal**, student of Erik, **Soumitra Ghosh**, student of Ignacio has joined Bayer Corp; **Shivakumar Kameswaran**, student of Larry is joining United Technologies; **Carl Laird**, student of Larry has accepted a position at Texas A&M and is spending a year at the University of Pittsburgh Medical School as a postdoc; **Anton Pfeiffer**, student of Steinar Hauan joined Northrup. **Nick Sawaya**, student of Ignacio, will be defending in two weeks and is joining ExxonMobil.

Professors Arturo Jimenez and **Vicente Rico-Ramirez,** both from Instituto de Celaya in Mexico, will be spending their sabbatical year at the department with the PSE group as Fulbright scholars. **Ricardo Lima**, graduate of University of Porto in Portugal has joined Ignacio Grossmann's group as a postdoc for two years, and will be working in the area of process synthesis. **Gonzalo Guillen**, graduate from Polytechnic University of Catalunya and recipient of a Fulbright scholarship, is joining Ignacio's group as a postdoc, where he will be working in the area of Enterprise-wide Optimization. **Mariano Martin** from the University of Salamanca, Spain, will take part in an internship with Ignacio from August to November, 2006. **Euclides Almeida Neto** from PetroBras is spending a year in Larry's group working on on-line dynamic optimization. **Francesca Pallazzi,** who worked in Ignacio's group for 6 months in the area of design under uncertainty of fuel cells, has returned to EPFL, Lausanne, where she is a Ph.D. student of Francois Marechal.

2006 ANNUAL REVIEW MEETING

The Annual Review Meeting took place on **March 13-14, 2006**. We had a total of 31 representatives of the member companies. Participants included new members of the CAPD: NOVA Chemicals, PETROBRAS, PPG and TOTAL. On Sunday March 12 we had a reception at the Danforth Lounge in the University Center. The first day of the meeting consisted of overviews given by Larry, Ignacio, Erik, Steinar and Gary, followed by a discussion with industrial participants, and a poster session by the students. There was also a dinner that evening at Le Mont Restaurant. The second day was devoted to final year student presentations and to general discussions about the CAPD. The feedback that we received was very positive, and we are most grateful for the continued support by the companies of CAPD. We should note that the Annual Review meeting for next year has been scheduled for **March 12-13, 2007.**

ENTERPRISE-WIDE OPTIMIZATION INTEREST GROUP

The CAPD has established the special interest group on Enterprise-wide Optimization that is part of the project **"Computational Models and Algorithms for Enterprise-wide Optimization (EWO) of Process Industries"** that has been funded by the Pennsylvania Infrastructure Technology Alliance. The participating companies are ABB, Air Products, BP America, Dow Chemical, and ExxonMobil. These companies have supplied case studies that are being undertaken by the EWO faculty and students. The project involves a total of 7 Ph.D. students, and 5 faculty (CMU: **Larry Biegler**, **Ignacio Grossmann**, **John Hooker**; Lehigh: **Jeff Linderoth**; UPitt: **Andrew Schaeffer**). The last a meeting of this group took place on **March 15, 2006**, immediately after the CAPD Meeting. Companies who might be interested in joining this group in fiscal year 2006, please contact Ignacio Grossmann. The membership fee to this group is $12,500 for members of the CAPD. A description of the EWO project can be found in http://egon.cheme.cmu.edu/ewocp/

2006 CAPD SHORT COURSE

The short course, ***Process Modeling and Optimization for Process Engineering*** took place on **May 31- June 6**, **2006**. We were very pleased with the outcome of this course, as we had a total of 12 attendees from around the world, both from industry and academia. The course included the following three modules:

a) Conceptual Design - taught on Wednesday and Thursday (May 31-June 1), with focus on process synthesis, particularly azeotropic and reactive distillation, and design of micro-scale systems.

b) Optimization - taught on Friday and Saturday (June 2-3), with focus on modeling and algorithms for nonlinear programming and mixed integer programming including disjunctive programming and applications to process optimization.

c) Process Operations - taught on Monday and Tuesday (June 5-6), with focus on differential/algebraic models for real time optimization and parameter estimation, and on mixed-integer programming models for process scheduling and supply chain management.

The course includes extensive workshops where participants obtain hands-on experience with various software packages. Course materials include extensive notes, the GAMS software, documentation and case study, and our textbook "Systematic Methods of Chemical Process Design." For next year the course will be offered on **June 6-12, 2007.** The course can be taken in any combination of modules. A detailed description of the modules can be found in http://capd.cheme.cmu.edu/shortcourse.html. If you are interested in attending this course next summer, please contact Toni McIltrot at 412-268-3573, or e-mail: tm2l@andrew.cmu.edu.

VIRTUAL LIBRARY ON PROCESS SYSTEMS ENGINEERING

The Pan American Study Institute on Process Systems Engineering that was organized by **Ignacio Grossmann** took place in Iguazu, Argentina on August 16-25, 2005. The workshop addressed four major areas: Optimization, Process and Product Design, Process and Supply Chain Operations, and Process Dynamics and Control. A major outcome of the PASI conference was the development of virtual library on Process Systems Engineering covering the four areas. The library consists of the Powerpoint slides of the presentations, background articles, as well as exercises and MATLAB and GAMS computer files for various applications, and a practice exam with solutions. The virtual library can be found in, http://cepac.cheme.cmu.edu/pasilectures.htm

WEBSITES/PROCESS SYSTEMS DIRECTORY

We are happy to report that the CAPD newsletter is distributed in electronic form. We would appreciate receiving feedback from our member companies of our CAPD website, **http://capd.cheme.cmu.edu.** This website provides a number of interesting items including information about individual groups, industrial success stories, software

available from the group, etc. We plan to update and modify our website in the next few months. Other websites of interest are Erik's http://mongol.cheme.cmu.edu/, Ignacio's http://egon.cheme.cmu.edu, Larry's http://dynopt.cheme.cmu.edu, Steinar's http://www.andrew.cmu.edu/user/steinhau/ . Also, the department maintains the website of CEPAC (Chemical Engineering Pan American Collaboration), the organization that has been formed to promote collaboration between the US and Argentina, Brazil and Chile. You can find in **http://cepac.cheme.cmu.edu/country.htm** a listing of all universities and researchers with links in the process systems area in the US, Argentina, Brazil, Canada, Mexico and Chile.

EXECUTIVE SUMMARY

Larry Biegler's Group

Since the last newsletter, a number of advances have been made in application of large-scale optimization, particularly for dynamic systems. The past few months have seen the following applications.

Some time ago, we proved an equivalence of the optimality conditions for optimal control and our simultaneous nonlinear programming formulation based on orthogonal collocation on finite elements. **Shiva Kameswaran** has recently extended this work to deal with final time constraints. Shiva was a finalist for the Best Student Paper Award at the ACC meeting in June. The reprint that describes this work is listed below. Moreover, **Shiva Kameswaran** has applied dynamic optimization to develop ramping strategies for fuel cell power plants. A paper that describes this effort is also listed below.

Dynamic optimization tools, ultimately for on-line use, have been applied that are centered on IPOPT. **Victor Zavala** has made strong advances in parameter and system identification for large-scale polymerization processes. This is described in a preprint listed below. In addition, Victor and Carl Laird have developed a formulation for Nonlinear Model Predictive Control (NMPC) that extends the work of Bock and coworkers to the simultaneous approach. As a result, large dynamic optimization problems used for NMPC have on-line computation costs reduced by two orders of magnitude! A paper that describes this work is listed below. For system identification, **Carl Laird** has expanded the source detection approach for municipal water networks through a novel MINLP strategy that allows specification of a restricted number of contaminant sources. An MIQP formulation that addresses this problem is described in a reprint listed below. Related to this work is the development of specialized decomposition strategies within the IPOPT framework. As described in the preprint below, this is demonstrated on large-scale multi-scenario problems with parallel computing architectures. Finally, for periodic adsorption applications**, Yoshi Kawajiri** is currently exploring optimization strategies for Simulated Moving Bed applications, the liquid-solid analog of PSA. In previous work, he has shown substantial improvements in productivity for these systems through an efficient dynamic optimization formulation. As a follow-on to this work, three papers are listed that describe a extended optimization formulations for this challenging problem.

Enabling Software From Larry Biegler's Group

Highlights of **Larry Biegler's group** include further development of the interior point nonlinear programming algorithm, IPOPT, in a number of directions. **Andreas Wächter**, now at IBM, developed a novel and very efficient barrier (interior point) NLP method, based on many of our earlier SQP concepts. In the general purpose framework, it adopts a sparse decomposition of the KKT matrix, and has been tested on thousands of applications with up to a quarter of a million variables. It has also been used to solve problems that incorporate a number of specialized decomposition strategies and for a wide variety of applications with up to 2 million variables. IPOPT is available under an Open Source software license and the source code can be downloaded from http://www.coin-or.org/Ipopt/index.

Carl Laird and **Andreas Wächter** have migrated the FORTRAN code for IPOPT into an object-oriented code written in C++. The resulting C++ package was released for public distribution last August and was recently updated last month to version 3.2.1. The code contains a much simpler interface to modeling environments as well as a more efficient implementation of the algorithm. Finally, the object-oriented code allows for greater flexibility, especially in adopting additional linear solvers and advanced decomposition strategies.

The IPOPT code has already been interfaced to a number of modeling systems including:

- **AIMMS** –This GAMS-like system has a number of extended features including a full graphical user interface for the development of specific user applications. Moreover, it provides exact first and second derivatives and exploits the full capabilities of IPOPT. **Yi-dong Lang** has nearly completed the interface to this system and is currently testing the interface. A similar interface to GAMS is also planned for January.
- **AMPL** – This GAMS-like system is the standard development platform in the Biegler group, has been available for the past two years and can be downloaded from the COIN-OR webpage. It has extensive features for linking to MATLAB and other environments in Unix and Windows. It also provides exact first and second derivatives and exploits the full capabilities of IPOPT.
- **CAPE-OPEN** – IPOPT has been developed under the MINLP object class and has been demonstrated with the CO-Tester. A paper that describes this interface along with a reprint is listed below.
- **MATLAB** – **Claas Michalik** and **Steinar Hauan** developed an IPOPT object that directly links to MATLAB. This object accepts exact first and second derivatives and exploits the full capabilities of IPOPT. Testing of this interface is currently underway.
- **ROMeo** – Recently, **David Ternet** of Simulation Sciences developed an interface between IPOPT and ROMeo, a widely used process modeling and optimization tool for real-time applications. While ROMeo provides only provides exact first derivatives, it works well with the limited memory BFGS option in IPOPT.
- **Bonmin** – As described below, joint work with researchers at IBM, Tepper as well as Ignacio's and Larry's groups have integrated IPOPT and CBC to develop a public domain MINLP code. Developed principally by Dr. Pierre Bonami, the code has been tested on a suite of convex and nonconvex MINLP problems and is being public released.

In addition, **Yi-dong Lang** has developed a user-friendly version of dynamic optimization methods. In particular, they have extended these codes to exploit sparsity and are using them to tackle dynamic optimization problems including batch polymerization, crystallization and parameter estimation. This software, called *DynoPC,* runs under Windows with a GUI interface. It has been distributed to several CAPD members and can now be downloaded on the same website as IPOPT. Currently, this approach is being extended to include updated versions of IPOPT and will be enhanced further by the development of a number of interfaces to optimization modeling platforms including CAPE-OPEN. A paper that describes this work is listed below.

Ignacio Grossmann's Group has been involved in the following developments:

In the area of optimization **Nick Sawaya** has found the exciting theoretical property that it is possible to obtain stronger relaxations for generalized disjunctive programs than the previous convex-hull by Lee and Grossmann. He has used this as a basis for developing novel cutting planes. Also, in collaboration with **Larry Biegler, Gerard Cornjuelos and Pierre Bonami** the open source code *bonmin* for MINLP optimization, that implements the branch and bound, outer-approximation and LP/NLP based branch and bound method, has been completed and is now available in the COIN-OR library. **Lorena Bergamini** has developed a new variant of the global optimization algorithm for MINLP and GDP using novel MIP models for piece-wise linearizations and a more effective search strategy. **Aldo Vecchietti**, continues to work on LOGMIP, a GAMS-based code for disjunctive programming (http://www.ceride.gov.ar/logmip/). **Ashish Agrawal** completed the writing of his Ph.D. thesis in which he emphasized the use of type theory for modeling of discrete and continuous models.

In the area of process synthesis **Ramkumar Karuppiah** has completed the work on a novel method for the global optimization for the synthesis of integrated process water systems that must operate under multiple scenarios. The proposed method relies on generating cuts from a decomposition scheme that relies on Lagrangean relaxation. In a joint collaboration project with **Cargill**, **Andreas Peschel and Ramkumar Karuppiah** developed an optimization model for optimizing the design of corn-based ethanol plants. **Jose Caballero** completed the manuscript on structural consideration for the synthesis of heat /thermally integrated columns. In a joint collaboration project with **Mike Domach, Soumitra Ghosh** has completed a manuscript on a strategy for selecting NMR Precursors and Analytes applying concepts of the Analytical Hierarchy Process by Setty.

Bora Tarhan, has developed a Lagrangen-based branch and bound for the optimal planning of process networks with uncertain yields and in which time varying uncertainties are considered as well as possibility of installing pilot plants for reducing uncertainty. He has developed a formulation and solution method that represent an extension of the work of Vikas Goel. **Muge Erdirik** has developed in collaboration with Dow as part of the EWO project a new continuous time model for the scheduling of parallel reactors. She has also developed a novel planning model that provides very tight bounds despite significant changeover times. **Fengqi You,** a new PhD student, has started a new project in Enterprise-wide Optimization dealing with responsiveness in supply chains. **Pedro Castro** has been investigating various formulations for single and multistage problems with parallel units for handling changeovers. Also, in conjunction with Carlos Mendez and ABB (Iiro Harjunkoski and Marco Fahl) he has completed the work on a sequential decomposition strategy for complex multistage batch plants. The manuscript on a comprehensive review of batch scheduling that was prepared mostly by **Carlos Mendez** in collaboration with ABB has been published in *Computers and Chemical Engineering*. In a collaboration with **Antonio Flores-Tlacuahuac** from Mexico, he has completed the work on a combined scheduling and dynamic optimization model for a multiproduct CSTR reactor in order to account for optimal control in the transitions. The work by **Minhwan Park** and **Fernando Melle** on cost models for purchase contracts in supply chain optimization problems has just been published by *Ind. Eng. Chem. Research*. Finally, **Rosanna Franco** has joined our group to replace Gabriela Garcia in the development of interfaces.

Steinar Hauan's Group

In the last semester, we have had good progress on our MEMS based biosensor thanks to the efforts by Mike Bartkovsky (experimental focus) with help from faculty and student collaborators in ECE. In brief, we have fabricated, processed and characterized our latest (4th) generation sensor design and demonstrated that it is capable of detecting mass changes with high reproducibility and sensitivity. Some practical tasks related to operation in liquid remain, but the first of (presumably) many sets of sensor runs have been completed. Optical imaging techniques have also verified the presence of higher order vibrational modes where, in fact, the signal-to-noise ratio is better than when the device operates in its fundamental (1,1) frequency. Jane Valentine (theoretical focus) has developed a first optimization framework that seeks to determine the optimal use of these frequencies in the simultaneous detection of multiple species on a single membrane.

Murni Ahmad has completed her modeling work on flowsheets using liquid-liquid extraction for protein separation from water and polymer mixtures. Since April, she has spent a substantial portion of her time in the wet-chemistry lab and carried out a number of phase separating experiments. In the last step of her upcoming thesis, these experiments will be used to determine binary interaction parameters for her thermodynamic models subsequently to be used in basic flowsheet optimization.

Over the last semester, Xiang He has increased the complexity in her microscale Lab-on-a-Chip (LoC) systems. Previously, most of her systems and those studied by Anton Pfeiffer consisted of a single unit operation -- albeit multiplexed to pack several such operations on a single chip -- she has designed and optimized several multifunctional chips wherein mixing, injection and separation are considered in combination with each other. It appears that many of the systems in the open literature are unnecessary complex and often also significantly overdesigned. Enabled by our system-level simulation framework and library of unit operation, a goal for the next few months is to develop a set of practical design guidelines that only invokes the more complex designs when actually required.

Israel Owusu (Distributed Enterprise Resource Planning) and Scott Turnberg (Optimal Design of hybrid reactive separation systems) have both spent the majority of their last 6 months on computer implementations, i.e. coding. Scott has also been doing an internship in Dow over the summer.

Congratulations
Anton Pfeiffer and Mike Bartkovsky both successfully passed their Ph.D. defenses and are now alumni of the group.

Gary Power's Group

Professor Gary Powers and Masters student, Denny Jacob have completed a study testing the validity of procedures for the hydro-testing of piping systems for off-shore oil platforms. Hydro-testing is done to detect leaks in piping systems due to defective welds, valve seals, etc. In this study, Mr. Jacob constructed a modular logic model of the steps and equipment in hydro-testing procedures used by the American Petroleum Institute and numerous construction companies. The models included failures of the sensors, equipment, humans and procedures. The system model was verified against system specifications using the model checking system SMV, Numerous faults that have occurred in testing off-shore piping systems were detected as well as several faults that have not occurred yet. Case studies were performed to indicate how the hydro-testing procedures could be improved. Data from current testing procedures will be gathered to validate the models and suggested improvements.

Erik Ydstie's Group

The Ydstie research group works on developing advanced modeling and control system methods for chemical processes. The work is distributed along two distinct axes. The first axis concerns how to use process physics and passivity based control theory to develop distributed simulation and control methods for chemical process networks. We are especially interested in developing methods that integrate physics, computation and communication in coherent and stable ways. The second axis is based on the idea of incorporation learning and adaptivity in control and optimization. We are especially interested in studying how we can learn and adapt simple representations of optimal control (discrete and continuous decision making) in complex systems.

Christy White has developed an efficient way to represent and model particulate processes. She has developed inventory control approaches for such processes and a general approach for state and parameter estimation. The problem she is working on is motivated by the direct reduction Saline to form high purity silicon for the photo voltaics industry.

Kendell Jillson has developed very efficient methods for how to model and integrate very complex process networks in a stable manner. He has developed methods that show how such systems can be designed to be self-stabilizing and self optimizing. He is currently adapting the modeling paradigm so that it can be used to represent bio-processes.

Eduardo Dozal has developed a new method for real time optimization which can be used to solve complex problems in non-convex optimization. The method works by filtering out "surface roughness" and embedding the high dimensional problems in a low dimensional input output representation of the system to be optimized. The objective of this research is to develop methods for optimal control of systems which do not rely on full state feedback.

Yuan Xu joined the research group in January. He is working on stability analysis, distributed simulation and batch chemical control. He uses passivity based methods and integrates it with non-equilibrium thermodynamics. His application domain is the carbothermic reduction of aluminum oxide to form aluminum.

STATUS OF RESEARCH PROJECTS

Larry Biegler's Group

General Frameworks for Large Scale Optimization Strategies and Applications

Researcher: Carl Laird (Ph.D. started Fall, 2001)

As a result of several generations of Ph.D. students, we now have a number of very efficient NLP algorithms including rSQP, full-space SQP, parameter estimation, data reconciliation and multiperiod optimization. As described above, the most recent incarnation is IPOPT, with continuing development by Andreas Wächter. This

code has become a core algorithm for many of the research projects described below. Three reprints that describe the basic algorithm as well as the convergence properties are listed below. In addition, Carl Laird has applied IPOPT and the AMPL interface to develop a novel source detection strategy for municipal water networks as an important application for barrier methods. This optimization problem is developed to detect attacks on networks and to determine optimal control and remediation strategies. Such networks are typically over several hundred to many thousands of nodes and require the incorporation of both spatial and temporal behavior. This difficult problem was reformulated as a DAE system with time delays. Moreover, because the hydraulic equations could be decoupled from the species mass balance, a novel preprocessing strategy renders the nodal constraints to be *linear* and the resulting problem can be solved easily using our simultaneous optimization strategies for dynamic optimization (see below). By exploiting the structure of these networks, discretized problems that represent actual municipal networks with up to 300,000 variables could be solved in only a few CPU seconds. More recently, this approach has been extended, by using an MIQP strategy, to a more robust one that promotes unique solutions. Using an efficient pre-processing step, small subproblems can be derived and attack scenarios can be identified more precisely and efficiently. This approach is described in the preprint below. Finally, Carl spent the past summer with Andreas Wächter at IBM to complete development on the next version of IPOPT. Designed in C++, this code is object oriented and flexible to deal with a wide variety of linear solvers, new barrier algorithms, and a variety of globalization strategies and decomposition approaches. Moreover, as noted above, the new code provides a much easier interface to modeling environments. Carl has expanded the IPOPT code to accommodate multiperiod problems. These are essential to deal with process optimization under uncertainty and have a structure that can be decomposed through Schur complements and can be completely parallelized on distributed memory machines. Carl has obtained some excellent results with this decomposition that validate these properties. Detailed results of this implementation are given in the paper listed below.

Mathematical Programs with Equilibrium Constraints (MPECS)

Researchers: **Juan Arrieta (Ph.D. started Fall, 2002)**
Brian Baumrucker (Ph.D. started Fall, 2004)

MPECs represent an exciting new field in mathematical programming. While applications of MPECs have long been recognized in game theory, transportation planning, economics and engineering design, little work has been done in developing efficient algorithms for their solution In process engineering, these problems stem from bilevel and multilevel optimization problems as well as optimization of hybrid (discrete and continuous) systems. Included in this class are optimization problems with phase equilibrium constraints, as in equilibrium stage processes.

The MPEC problem is essentially a nonlinear programming problem augmented by complementarity conditions. The addition of these conditions leads to a violation of convergence assumptions for most nonlinear programming algorithms (e.g., linear independence of the constraint gradients) and can cause these algorithms to fail. On the other hand, the barrier method described above has a straightforward extension to these problems. As a result, complementarity constraints can be incorporated with little additional cost in the algorithm. In fact, all of the features that contribute to the efficient performance of IPOPT can be invoked directly for the solution of the MPEC problems. The resulting algorithm based on IPOPT has been developed further and refined for a number of challenging dynamic optimization applications in process engineering. Our work in this area includes the following:

Arvind Raghunathan recently completed his Ph.D. and has accepted a position with United Technologies. In his research, he has incorporated the MPEC formulation into the IPOPT code, now called IPOPT-C, along with algorithmic modifications to treat the complementarity constraints more efficiently. This code has been interfaced to the AMPL modeling system and has been tested on a set of library MPEC problems. Our results show that this implementation compares well against competing barrier algorithms such as LOQO.

Arvind tested this approach on a number of process optimization problems with phase equilibrium constraints. These include distillation optimization problems with disappearing vapor and liquid phases on equilibrium stages, dynamic systems with switching conditions, such as overflows and phase disappearance in distillation columns and metabolic network systems. For the latter, we have considered parameter estimation problems for dynamic fermentation systems for wine production. These results show that this approach leads to better and more uniform performance than the smoothing approach used in our previous studies.

Current work by **Juan Arrieta** deals with modeling and optimization of dynamic biological systems that are based on cellular models. Such systems are large-scale extensions of MPECs. Moreover, they have interesting modeling features since state dependent constraint functions with discontinuities also need to be treated through MPEC formulations. Moreover, **Brian Baumrucker** is currently considering the development of good MPEC formulations that model discrete decisions. He is currently working with the ROMeo real-time optimization package and is exploring formulations for complementarity conditions within real-time optimization models. In particular, he has shown that penalty-based NLP formulations have worked very well on these models. Moreover, with these formulations, one is able to decouple problem-specific optimization algorithms from the optimization model and rely on general purpose optimization solvers. In addition to the ROMeo comparison described above, he is investigating complementarity formulations in distillation columns with mass transfer limitation.

Simultaneous Optimization of Differential-Algebraic (DAE) Systems

Researchers: **Juan Arrieta Camacho (Ph.D. started Fall, 2002)**
Shivakumar Kameswaran (Ph. D. completed August, 2006)
Victor Zavala (Ph.D. started Fall, 2004)
Yi-dong Lang (Jiansu Research Institute, Nanjing, China)
Prof. Antonio Flores Tlacuahuac (Unversidad Iberoamericana)

The topic on simultaneous solution and optimization strategies for large-scale, dynamic optimization problems incorporates a number of projects. In the past, we have applied this approach to optimization problems for batch reactors, process dynamics and tray-by-tray batch distillation and large-scale dynamic flowsheeting models. Moreover, we have tackled dynamic examples successfully with this approach that cause any sequential dynamic optimization method to fail. It can occur in open-loop unstable systems that arise in optimal control and nonlinear MPC, dynamic parameter estimation and the optimization of runaway reactors. Prof. Antonio Flores, a research colleague from the University of Iberoamericana, has demonstrated the advantages of this approach on a number of challenging polymerization processes. Moreover, he has recently extended this to consider the application of global optimization strategies for these problems. A reprint that describes this approach is listed below. Moreover, the following research projects are currently being addressed in our group.

Dynamic Optimization Platforms

We have developed two complementary modeling frameworks for dynamic optimization, one based on reduced space and one on full space. First, over the past four years Yi-dong Lang has developed a stand-alone Windows modeling system for dynamic optimization called ***DynoPC***. Written for Windows with a Visual Basic user interface and with heavy integration of graphical, simulation and automatic differentiation tools, this software package incorporates our advances in dynamic optimization, particularly IPOPT and the elemental decomposition. This program continues to be distributed to interested research groups both in academia and industry and can be downloaded from http://coin-or.org Current developments with *DynoPC* include ESO interfaces that are compliant with recently developed CAPE-Open protocols. This leads to an interface compatible with a number of existing process models and modeling environments. In particular, Yi-dong has recently completed a polymer reactor study that was modeled in *gProms* and solved with *DynoPC*. This problem had over 300,000 variables and was solved in about an hour of CPU time. Further reformulations of this system, using a simple partitioning strategy, have led to an optimization problem that is much better conditioned and can now be solved in only about 1000 CPU secs. Finally, DynoPC has been extended to solve the dynamic optimization problem for moving finite elements. A paper that describes *DynoPC* and the moving finite element approach is listed below.

Second, we have been using IPOPT in a full space framework linked to the AMPL modeling environment. As detailed in many of the studies listed below, this framework has been extremely powerful and flexible in solving a wide variety of problems. We are currently adopting a MATLAB framework and have coupled it with the AMPL modeling language. Domain specific prototypes have already been developed and work very well.

Consistency and Convergence of Simultaneous NLP Formulations for Dynamic Optimization

Does the solution of the discretized NLP converge to the solution of the original optimal control problem? What are the particular problem classes and assumptions for which this can be shown? This has been an interesting and long-

standing research problem. Back in 1989, we have developed some consistency results based on the work of Reddien (1976) for Gauss collocation schemes. In addition, Lagrange multipliers from the KKT conditions have a direct relationship to adjoint variables from the Euler-Lagrange equations. However, more powerful convergence results are difficult to show and usually apply only to well-conditioned linear-quadratic control problems. Nevertheless, despite limited convergence results, very good performance is usually obtained with simultaneous optimization strategies.

Recently, Shiva has revisited some of the theory in order to derive properties for Radau and Lobatto collocation. Both of these methods (while of lower order) tend to behave much better than Gauss collocation. We have recently derived order conditions for these methods and have related their convergence properties to the more general class of boundary value solvers. Moreover, these have been verified by a number of example problems. Currently, Shiva has extended this approach to problems with final time constraints. As described in a paper below, final time constraints allow the same high order rates of convergence as long as they possess a controllability property. This is also illustrated in a case study.

Nonlinear Model Predictive Control Strategies

In less than two decades, Nonlinear Model Predictive Control (NMPC) has evolved from a conceptual framework to an attactive, general approach for the control of constrained nonlinear processes. These advances were realized both through better understanding of stablity and robustness properties as well as improved algorithms for dynamic optimization. The above dynamic optimization algorithms have been applied extensively in Nonlinear Model Predictive Control (NMPC). This strategy is also being extended to large-scale models for polymerization processes. In a project funded by ExxonMobil Chemicals, **Victor Zavala** has begun to develop multi-stage dynamic optimization problems for grade transition and defouling operations. For this, he has developed a detailed reactor model of a polyolefin reactor, which includes a complete kinetic description that is used for parameter estimation using actual process data. Using AMPL and IPOPT, Victor has extended this model to multiple data sets as well as EVM problems (where errors in both inputs and outputs are considered). Applying this approach to a large number of data sets, Victor was able to estimate kinetic parameters quite well; the scatter of the data was reduced by an order of magnitude, compared to previously fitted models. This approach is described in a paper listed below.

In addition, we recently adapted the real-time iteration approach developed in the context of multiple shooting (Diehl et al. (2006); Bock et al. (2006)) to a collocation-based approach with a full space nonlinear programming solver. In the paper below, we show that straightforward sensitivity calculations from the KKT system also lead to a real-time iteration strategy, with both shifted and non-shifted variants. This approach is demonstrated on a large-scale polymer process, where on-line calculation effort is reduced by over two orders of magnitude. This recent development is being analyzed further and will be applied to a number of on-line applications that include state estimation and economic optimization.

Finally, through collaborations with D. Subramanian and T. Samad at Honeywell, Inc. Arvind Raghunathan had been pursuing an important research problem on conflict resolution of aircraft trajectories. Given a set of aircraft with starting points, destinations, protection zones and obstacles, what are the optimal trajectories that lead to the best performance or minimum fuel consumption? Moreover, detailed flight models are employed that limit the maneuverability of these aircraft. This problem leads to a nonconvex dynamic optimization problem. Moreover, protection zones lead to disjunctive constraints that have been modeled through convex hull formulations. The resulting problems are discretized using collocation on finite elements and solved using IPOPT. More recently, Juan has also extended this approach to a number of more complicated aerospace models including satellite trajectories and NMPC variations of these trajectories. His recent work has shown that our approach generates optimal solutions significantly faster than competing methods. A paper that describes this approach will be included in the next newsletter.

Large-Scale Optimization for Fuel Cell Models

Researchers: **Cong Xu (Ph.D. completed Spring, 2005, joint with Prof. M. S. Jhon)**
Shivakumar Kameswaran (Ph. D. completed August, 2006)
Parag Jain (Ph.D. started Fall, 2005)

Cong Xu recently completed his PhD and is doing postdoctoral studies. For his thesis project, he has been investigating optimization problems arising in fuel cell applications, including Direct Methanol Fuel Cells (DMFCs) and Hydrogen PEM fuel cells. In particular, he has extended simple DAE models for fuel cells to consider optimal flow patterns and minimization of contamination effects due to membrane crossover, and he has extended these models to consider sensitivity and optimization calculations. In particular for DMFCs, Cong Xu and Peter Follmann have compared and critically assessed several literature models and have explored the crossover phenomenon. By applying our dynamic simulation and optimization tools, they were able to develop dynamic feeding strategies for these systems that greatly reduce contamination due to methanol crossover. These systems have been modeled and optimized with a variety of FORTRAN, MATLAB and MAPLE-based tools, such as OCC. The results show that the optimal design of DMFCs can be achieved without pulsed operation. Here crossover is significantly reduced and the power density is correspondingly increased. The efficiency of these processes can also be improved through flowsheet optimization strategies as well as heat integration of the process units. This approach is based on conventional flowsheet optimization schemes within Aspen/Plus along with simultaneous optimization and heat integration strategies. The application to fuel cell based processes leads to interesting trade-offs between the fuel cell, the rest of the flowsheet and the heat recovery system. A reprint that describes this approach is listed below.

Dynamic optimization has also been applied by Shiva Kameswaran to develop ramping strategies for fuel cell power plants. In a project funded by Fuel Cell Energy, Inc. and DOE, Shiva has demonstrated significant improvements in maintaining power levels with more energy efficient operation. Using AMPL and IPOPT, he has incorporated detailed models of the entire power plant and has demonstrated this approach both for parameter estimation and optimal control. This approach was presented at the recent AIChE meeting and a paper that describes this work is listed below.

Finally, Parag Jain has begun to extend previous modeling and optimization work for Direct Methanol Fuel Cells. He has applied a comprehensive two-dimensional computational model of a PEM fuel cell that accounts for major transport processes including membrane electrode assembly (MEA) and gas distribution channels. Additionally a water transport model in the membrane has been developed and incorporated into the full PEM fuel cell model. Using AMPL and IPOPT, Parag is using this model to develop a detailed optimization case study. In the future, we expect this effort to be validated through experimental facilities at the University of Connecticut.

Reduced Order Models for PDE-based Units in Power Plant Flowsheets
Researcher: **Yi-dong Lang (Jiansu Research Institute, Nanjing, China)**
Student: **Anshul Agarwal (Ph.D. started Fall, 2005)**

Process simulation has become an essential capability that spans most tasks in process engineering, design and analysis. Simulation programs such as Aspen Plus, Pro/II and HYSYS are integrated into core engineering design activities. However, due to computational limitations, current process simulators usually deal with lumped parameter models that often do not capture detailed spatial characteristics of process units, including fluid flow and transport processes. As a result, they can suffer accuracy limitations and the loss of predictive capability. To overcome this difficulty, we are working with NETL on the Advanced Process Engineering Co-Simulation (APECS) project. Within this framework, process flowsheeting models (in Aspen Plus) have been successfully combined with computational fluid dynamics (CFD) models (using Fluent) to model multiphase systems, such as gasifiers and turbines within power plants. Current efforts are also focused on the inclusion of other distributed parameter custom models. In particular, an important, and challenging, application for this activity is the FutureGen Cycle, a 275 MW coal-fired power plant that includes hydrogen generation and CO2 recovery, and requires multi-phase, spatially distributed models within its simulation environment.

To extend these NETL activities, we are developing and applying integrated optimization strategies that provide powerful tools for model development and process improvement. So far, these optimization problems are small-scale and efficient, and robust optimization algorithms are available that can be implemented easily. These features have led to the relatively easy and widespread adoption of optimization strategies. On the other hand, optimization strategies for CFD and distributed parameter models have seen far less development and this currently represents an important and challenging research activity. For APECS, which incorporates these models, we believe that optimization strategies will perform a key role in the development of advanced energy processes, such as the FutureGen Cycle. To provide a vehicle for the research tasks in this project, we consider the model components of the FutureGen Cycle flowsheet. This process includes a number of unit operations for coal gasification and

byproduct (e.g., ash/slag and sulfur) separation; multiphase CFD models are needed for this purpose. Yi-dong Lang has been working with colleagues at Fluent Corp. to develop reduced order CFD models based on Proper Orthogonal Decomposition. This approach allows for a tremendous reduction in computing effort for the process flowsheet.

Moreover, feeding the gasifier with oxygen is an air separation unit (ASU) that is a significant energy consumer that must be optimized. Further downstream, the byproduct gases CO2 and hydrogen are separated and CO2 is sequestered. These separations can be performed effectively by pressure swing adsorption (PSA) units, which also require custom reduced order models. Anshul Agarwal has begun to develop reduced order models for these units as well using a novel space-time discretization.

Optimization and Control of Periodic Adsorption Processes
Student: Yoshi Kawajiri (Ph.D. started Fall, 2003)

Simulated Moving Bed (SMB) chromatography was developed in the 1960s as a realization of continuous chromatographic separation. Since then, SMB has been gaining attention in food, sugar, and petrochemical applications. In more recent years, SMB has been recognized as an attractive technology for enantiomeric separations in the pharmaceutical industry. An SMB system is realized by connecting multiple columns in a cycle. The feed and desorbent are supplied continuously between columns, and at the same time extract and raffinate products are withdrawn. Counter-current operation is "simulated" by switching these inlet and outlet streams intermittently in the direction of the liquid flow. As with PSA this system is characterized by a Cyclic Steady State (CSS), where the concentration profiles in the columns change dynamically but repeat the same pattern in every cycle.

Over the past three years, **Yoshi Kawajiri** has been investigating efficient optimization strategies for these systems. Here optimization methods can be based on the single-discretization approach to discretize the Partial Differential Equations (PDEs) only in the spatial domain and then integrate the resulting Differential Algebraic Equations (DAEs) in time. On the other hand, the full-discretization approach discretizes the PDE both in time and spatial domain, leading to a large-scale Nonlinear Programming (NLP) problem. Yoshi has compared both approaches and found that the latter approach has shown tremendous improvements in the productivity of SMB systems. Moreover, these were obtained almost two orders of magnitude faster than with the single discretization (sequential) method used in gProms. The approach was applied to optimization of SMB systems with steady and time-varying feeds (i.e., PowerFeed), both for linear and nonlinear isotherms. This efficient approach also allows us to consider the design and control much more complex SMB systems. In particular, Yoshi has developed two superstructure SMB systems, one for a single step and the second over a full cycle, that allow for the optimization of a number of novel, recently reported designs, as well as some new ones. These superstructures lead to well-defined and easily solved problem formulations and lead to innovative designs with improvements in productivity. Moreover, through the formulation and solution of multi-objective optimization problems, we confirm that our approach has the potential to find more advantageous operating schemes than the standard SMB or PowerFeed operating schemes. Finally, we also show that these multi-objective solutions can be related to a class of profit maximization problems for SMBs. This is described in three papers listed below.

<u>Ignacio Grossmann's Group</u>

Open-Source Code for MINLP Optimization

New developments: **Open source code *bonmin* is now available in COIN-OR**

Post-doctoral fellow: **Pierre Bonami (Tepper)**

Collaborators: **Larry Biegler, Gerard Cornjuelos (Tepper), Francois Margot (Tepper)**

Students: **Nick Sawaya, Carl Laird, Jennifer Njoroge**

This project has been a collaboration with researchers at IBM (Andreas Wächter, Andy Conn, Joantahn Lee, Andrea Lodi). The main objective has been to develop open source code for solving MINLP problems.

We have initially restricted ourselves to solving MINLP problems that have a convex relaxation. The postdoctoral fellow Pierre Bonami developed the code *bonmin* that solves MINLP problems with the NLP-based branch and bound, outer-approximation and the LP/NLP based branch and bound method. Both the outer-approximation and the LP/NLP based branch and bound method are based on our previous work (Duran and Grossmann, 1986; Quesada and Grossmann, 1992). The implementation provides a single computational framework for the three methods. When no linearizations are performed the method reduces to NLP-based branch and bound. When linearizations are performed this can be done by completing the LP-based branch and bound at each cycle followed by the NLP subproblem. When the LP-based branch and bound is not completed, the NLP subproblems can be solved at intermediate nodes, for instance at integer feasible nodes like in the original Quesada and Grossmann method. The LP/NLP based branch and bound has been extended to a more general branch and cut scheme in which NLP subproblems do not have to be solved at only integer feasible nodes, but they can be solved at any intermediate node. For convenience we have termed this method "hybrid." The code makes use of the following open source codes: IPOT from Andreas Wächter and Larry Biegler, and CLP or CPB from the COIN-OR library.

Pierre has tested his code with close to two hundred test problems. Nick helped to build most of the convex MINLP problems of this library, which include batch design, retrofit planning, layout and trim loss problems. Carl Laird also contributed with some water contamination problems that involve a large number of continuous variables. The test problems are available in the webpage: http://egon.cheme.cmu.edu/ibm/page.htm The performance of the open source code was compared with both SBB, the branch and bound code in GAMS, and DICOPT, the outer-approximation method that is also available in DICOPT. The computational results on a representative subset of 38 the 200 problems showed the following trends. DICOPT solved 20 of the 38 problems the fastest and in less than 3minutes. Among these was a retrofit planning problem with 576 0-1 variables, 2720 continuous variables and 4980 constraints. The hybrid method (i.e. branch and cut) proved to dominate for the remaining 18 problems in terms of speed and successful completion. Among these was a problem with 14 0-1 variables, 107,222 continuous variables, and 107,209 constraints. It is also interesting to note that the hybrid method always dominated the NLP-based branch and bound as well as the open-source outer-approximation method. A paper that will describe the large set of test problems with an explanation of them is being prepared by Nick, Carl and Pierre.

Our next major step in this project will concentrate on handling nonconvexities in an "ad-hoc" manner, that is without performing rigorous global optimization. For this purpose the undergraduate student Jennifer Njoroge has assembled a collection of about 20 test problems that correspond to synthesis and scheduling problems. The initial results indicate that *bonmin* can be applied with little modification to nonconvex problems, with the proviso that convergence to a feasible or optimal solution is not always achieved.

Algorithms for Nonlinear Disjunctive Programming

Student:	**Nicolas Sawaya [Ph.D., to complete end of Aug 06]]**
Visitor:	**Lorena Bergamini [Ph.D. Jan 03]**
Research collaborator:	**Aldo Vecchietti [Researcher at INGAR]**
New Developments:	**Superior relaxation is shown to dominate previous convex hull relaxation**
	New variant for global optimization method

Nicolas Sawaya

The objective of Nick's project has been to develop novel solution methods for nonlinear generalized disjunctive programs (GDP). A major objective in Nick's work has been to develop effective cutting plane methods for linear GDP problems. The other objective has been to develop an integrated framework for solving nonlinear GDP problems. However, in a surprising development Nick has found that it is possible to obtain stronger relaxations than the one based on the convex hull by Lee and Grossmann.

The first step in Nick's research work was to develop a solution method for linear GDP problems that relies on cutting planes, and that can be embedded within a branch and cut algorithm. The major steps of the algorithm are to

first solve the big-M relaxation. Next, we formulate and solve a separation problem in which we minimize the difference between a feasible point in the convex hull relaxation and the solution of the big-M problem. Here we can use the 1, 2 or infinity norm, with the first and last leading to linear objectives. If the difference in the separation problem is small or even zero this is a clear indication that the both the big-M and the convex hull relaxations are essentially identical. If, on the other hand, the difference is not small one can derive a cutting plane. The derivation of successive cutting planes continues until the improvement in the lower bound of the big-M model with the cutting planes lies within a tolerance. The idea is then to switch to a branch and bound method. Nick applied his cutting plane technique to three major problems using the infinity norm. The first is the strip packing problem that consists of fitting a set of rectangles in a roll of fixed width in order to minimize its length. Here the proposed cutting plane method led to order of magnitude reductions in the CPU time compared to both the big-M and convex hull formulation. Nick also solved a 10 process retrofit problem, and extension of a model that Jennifer Jackson formulated, and he also addressed a job-shop scheduling problem with up to 10 jobs and 8 stages. The cutting plane technique was not very helpful in both cases, although in the retrofit problem it did improve substantially the performance of the big-M reformulation.

Nick has also been investigating the use of cutting planes for solving nonlinear disjunctive problems. He has considered as a first step nonlinear GDP problems that are reformulated as big-M MINLPs and solved them through branch and bound. Nick has recently tested this method on a retrofit planning problem, where he obtained 50% reduction in CPU time in rge application to a retrofit problem.

An important issue in the application of the convex hull is how implement the constraint $\lambda\, g(\nu/\lambda)\le 0$ for the case when λ goes to zero and when g is nonlinear and convex. In our previous work we had used the simple approximation $(\lambda+\varepsilon)\, g(\nu/(\lambda+\varepsilon)\le 0$. This however can give rise to problems depending on how ε is selected. The problem here is that if ε is set too small there are difficulties with accuracy. If ε is somewhat large then if a disjunct term does not apply and the inequalities are violated it may make the approximation infeasible. Nick had proved that a rigorous approximation that avoids both problems is given by $(\lambda_{jk}+\varepsilon)g_{jk}(\nu_{jk}/(\lambda_{jk}+\varepsilon))\le \max_{\nu_{jk}\in(0,U_{jk})}(\max\ (\varepsilon g_{jk}(\nu_{jk}/\varepsilon),\ \varepsilon g_{jk}(\nu_{jk}/(1+\varepsilon))))$, where the basic idea is that the term on the right hand side represents a relaxation that can be made arbitrarily small. Since the constraints are convex, the maximization on the right hand side can be computed by evaluating the functions at the extreme points for each inequality which are few for sparse problems. In this way the actual expression can be simplified to, $(\lambda_{jk}+\varepsilon)g_{jk}(\nu_{jk}/(\lambda_{jk}+\varepsilon))\le \max\ (\varepsilon g_{jk}(0),\ \max_{\nu_{jk}\in(0,U_{jk})}\varepsilon g_{jk}(\nu_{jk}/(1+\varepsilon)))$. Nick however, also found an alternative expression given by $(\lambda_{jk}+\varepsilon)(g_{jk}(\nu_{jk}/(\lambda_{jk}+\varepsilon))+g_{jk}(0)(\lambda_{jk}-1))\le 0$, which is easier to implement. Nick was able to show that in fact the latter expression is superior compared to the first one in terms of accuracy, under most circumstances. The exceptions rarely hold true. Nick has successfully tested this approximation scheme in several examples (analytical, process network, safety layout) using values of $10^{-7}\le\varepsilon\le 10^{-4}$. The results have shown that very good approximations are obtained with both methods, although the second approximation outperforms the first. Based on input by Kevin Furman from ExxonMobil, Nick has been considering the alternative convex expression $((1-\varepsilon)\lambda_{jk}+\varepsilon)g_{jk}(\nu_{jk}/((1-\varepsilon)\lambda_{jk}+\varepsilon))-\varepsilon g_{jk}(0)(1-\lambda_{jk})\le 0$ which not only circumvents the infeasibility that arises in the original Grossmann & Lee expression, but, when $0 < \varepsilon < 1$, it is exactly equivalent to the (true) CH expression at $\lambda = 0$ or 1, regardless of the value of ε within that range. Nick has numerically tested the various schemes concluding that the Furman approach seems to work best.

In the recent months Nick has studied in great detail some of the pioneering papers by Egon Balas on disjunctive programming. In doing so, he established a bridge between the generalized disjunctive programming (GDP) model that we have been considering and the disjunctive model by Balas. The major difference is that the GDP model is more general in that it includes Boolean variables for establishing the truth of the disjunctions and logic relations between the discrete decisions. The major point that emerged from Nick's analysis is that there is actually a way of obtaining a stronger relaxation of the GDP problem:

$$
\begin{aligned}
&Min\ Z = \sum_{k \in K} c_k + f(x) \\
&s.t. \qquad r(x) \le 0 \\
&\bigvee_{j \in J_k} \begin{bmatrix} Y_{jk} \\ g_{jk} x \le 0 \\ c_k = \gamma_{jk} \end{bmatrix} \qquad \forall k \in K \qquad \text{(GDP)} \\
&\Omega(Y) = True \\
&0 \le x \le U, c_k \in \mathbf{R}^1_+,\ Y_{jk} \in \{True, False\}\ \ \forall j \in J_k, \forall k \in K
\end{aligned}
$$

The main point is that in the work by Lee and Grossmann we considered the convex hull reformulation by taking the convex hull directly on the disjunction as shown above. It turns out, however, that if we take the convex hull by introducing the global constraints $r(x) \le 0$, we actually constrain the definition of the convex hull which in turn leads to a stronger relaxation. Furthermore, for the linear case, one can show that by defining the relaxation in that form the cuts that are generated are facets of the actual facets of the true convex hull. While the theory is very elegant, a drawback is that the straightforward extension of the previous convex hull leads to a very large problem due to additional disaggregated variables in the Boolean variables. To circumvent this problem Nick has devised a scheme that is equivalent to considering only a partial DNF representation, and that uses the logic explicitly to avoid the definition of many disaggregated variables. The preliminary results on the strip packing problem have been very encouraging. The improvement in the lower bound is typically 50-80%! These improved lower bounds however do not always translate to great reductions in CPU time. Our conjecture is that this is due to the fact the strip packing problem has only one variable in the objective, and that the performance becomes very sensitive to the branching rules. We expect to have full numerical results and the paper completed in our next newsletter.

Lorena Bergamini

Lorena, a Ph.D. student from INGAR in Argentina working under the direction of Pio Aguirre and who spent one semester with us, developed a new deterministic algorithm for the global optimization of process networks that are formulated as Generalized Disjunctive Programs and that involve nonconvexities. The global optimization algorithm relies on the use of piecewise MILP approximations (no spatial branch and bound search). Also, the method is based on the Logic-Based Outer Approximation (OA) algorithm developed previously by Metin Turkay and that overcomes difficulties related to singularities that are due to zero flows. The method developed by Lorena is capable of handling nonconvexities, while rigorously guaranteeing the global optimality of the synthesis of process networks. This is accomplished by constructing a master problem that is a valid bounding representation of the original problem, and by solving the NLP subproblems to global optimality. Lorena assumed that the functions involved are sum of convex, bilinear, and concave terms. In order to rigorously maintain the bounding properties of the MILP master problem for nonconvex problems, piecewise linear under and overestimators for bilinear, and concave terms are constructed over a grid with the property of having zero gap in the finite set of points. The set of these approximation points are defined over subdomains defined by bounds of variables and solution points of the previous NLP subproblems. For bilinear terms, the convex envelope by McCormick is used. Disjunctions are used to formulate the convex envelope in each subdomain, and the convex hull of these disjunctions is used to provide the tightest relaxation. Linear fractional functions are treated in a similar way. Piecewise linear subestimators replace the concave terms. The NLP subproblems are also solved to global optimality using a reduced MILP master problem. Since the NLP subproblems are reduced problems, involving only continuous variables related to a process with fixed structure, the variable bounds can be tightened thereby enhancing the underestimators.

Lorena has recently developed an improved version of the algorithm described above. The main ides is to first use an alternative mixed-integer representation for the piece-wise linear approximations using a so-called delta method that has the nice property that the polytope has integer values for all extreme points, which is not the case in the traditional lambda MIP model, which is the “textbook” model that we had used previously. Two other modifications in Lorena’s algorithm have been to solve to feasibility rather than to optimality the associate MILP subproblems, and to only obtain a local NLP solution as an upper bound rather than a full global solution. Lorena has applied her technique to water treatment networks, integrated water networks, heat exchanger networks and to

distillation sequences with aggregated models. In all cases the improvements in computational times were quite substantial compared to the initial method.

Aldo Vecchietti: LOGMIP and DICOPT

Aldo and his students at INGAR in Argentina are developing the LogMIP code, which is as an extension of the GAMS modeling language for posing logic/disjunctive problems. The main features of LogMIP are several language constructs in order to concisely formulate GDP problems. The syntax developed involves the use of IF THEN ELSE statements to represent the disjunctions, including embedded ones. An interesting related development has also been to show that logic constructs that are commonly used in Constrained Logic Programming (CLP), such as implications for constraints (e.g. $g(x) \leq 0 \Rightarrow f(x) \leq 0$) can be systematically converted in the form of disjunctions. The intent is also to be able to accommodate hybrid models that are partly expressed as disjunctions and partly as equations in algebraic form. Aldo has completed in LogMIP the definition of disjunctions over sets and subsets. The conditional statement operator WITH in conjunction with other operators: relational operators (<, <=, =, >, <=), logical operators (and, or) and sets operators (ord, card, in) or using a subset definition are used to control de disjunction's domain defined over a set. As for the propositional logic, the special constructs ATLEAST, ATMOST, EXACTLY are defined to specify that the sum over a subset of variables with a given cardinality is at least, at most or equal to one. Also, LogMIP can now accept logic propositions in symbolic form without the need of translating them into linear inequalities.

For solving linear disjunctive/hybrid problems LOGMIP can automatically generate the convex hull relaxation and big-M transformation for linear problems. Aldo has implemented LogMIP in the IDE version of GAMS and tested it with several problems that include jobshop scheduling and the retrofit MILP model from Jennifer Jackson. The latter has yielded very impressive numerical results. Aldo found that the big-M formulation of the retrofit planning problem takes about 1745 nodes with OSL, while convex formulation through LOGMIP only requires 9 branch and bound nodes!. For solving nonlinear disjunctive/hybrid problems Aldo has also automated the logic-based OA algorithm by Metin Turkay, which is suitable for nonlinear GDP process network problems. Work is under way to implement the reformulations for nonlinear GDPs. The LogMIP Website is now also available, http://www.ceride.gov.ar/logmip/. The Website includes now some explanation about LogMIP, the User's manual, solvers and examples downloads, references and links.

Aldo has recently added a capability in DICOPT for handling more effectively infeasible NLP subproblems. In the current version an integer cut is simply added if the NLP is found to be infeasible. This is often very ineffective as the integer cut is quite weak, especially as the dimensionality of the 0-1 variables increases. What Aldo has done is to allow the addition of linearizations of the infeasible NLP subproblems. When using a solver like CONOPT the linearizations will be derived at a point where the infeasibility is minimized. This option is rigorous for the case of convex MINLP problems. For nonconvex problems there is the risk of cutting off optimal solutions. To solve problems in GAMS with linearization in infeasible NLPs the following option must be defined: infeasder 1. By default infeasder is 0. In this case DICOPT runs like the previous version (just with the integer cut with NO linearization on the infeasible points). This new option has shown to significantly improve the performance of DICOPT in several problems, which often did not converge with the old version. This performance has also been verified by Nick Sawaya on several difficult convex layout problems that tend to produce infeasible NLP subproblems.

Modeling of Hybrid Systems and Mixed-integer Programs

New developments: Type theory as a modeling framework

Students: Ashish Agarwal [Ph.D., completed May 07]

Ashish has completed his Ph.D. degree and joined Yale as a postdoc in the area of Systems Biology. The initial objective of Ashish's project was to develop a new hybrid systems framework for modeling supply chain networks. The basic idea in Ashish's project has been to rely on a hybrid dynamic systems representation that combines differential equations to capture the continuous dynamics and automata to capture the discrete dynamics. Each

automaton describes the space and dynamics of a single discrete variable. The continuous dynamics is used to represent material flow, while the discrete dynamics is used to model scheduling decisions. The hybrid dynamic representation is then applied to a supply-demand network in order to provide a formal representation of the system, determine the optimal operating conditions, scheduling deliveries, selecting between outsourcing and production, and performing a dynamic allocation of resources. Ashish developed a representation based on automata than can be systematically transformed into one with finite states, then to a disjunctive programming model, and finally into a mixed-integer linear program. In this way an important accomplishment is that one can systematically derive the mixed-integer linear programming model describing the supply demand optimization network problem. Ashish has tested the model formulation on a small supply chain optimization problem demonstrating that the model can be expressed in very compact form. Ashish has completed a manuscript describing this work.

In the second part of his work, with the collaboration of Professor Bob Harper from Computer Science, Ashish investigated the use of Type Theory as a systematic formalism based on logic for proving correctness of formulations for mathematical optimization. The basic idea in type theory is to rigorously define the different variable and operator types using logic constructs to ensure that all transformations of data, variables and equations are "well-formed." In this way one can use such a representation to define mappings as is for instance the case of the reformulation of generalized disjunctive programs to mixed-integer linear programs. Furthermore, one can use type theory as a basis for developing software that has a strong foundation, and that is more likely to be free of errors. Ashish has applied this formalism to generalized disjunctive programming problems for transforming them automatically into MILP models. This has required a sophisticated theoretical development based on type theory that in turn he has used as a basis for software development. Asish used the language ML for developing the software and has demonstrated the application to several GDP models that can be automatically converted into MILP problems. Ashish is in the process of converting several chapters of his thesis into papers that will be submitted for publication.

Global Optimization of Integrated Process Water Systems

New developments:	**Generalization of method for multiscenario optimization under uncertainty** **Completed paper on optimization algorithm for membrane systems**
Students:	**Ramkumar Karuppiah [Ph.D. started Jan 04]**
Visitor:	**Eugenio Bringas (Univ. Cantabria, Spain, Sept-Dec 05).**

Ram's project has dealt initially with the global optimization for the synthesis of process water systems that integrate the water reuse section for processes with the distributed water treatment section for a given number of pollutants. The initial objective has been to find for given sets of processes and given treatment units the optimal configuration of the system that minimizes the use of freshwater, or more generally that minimizes the total cost. Ram has assumed for the processes units that they are either characterized by fixed contaminant loads, or by variable loads that obey mass exchange constraints in terms of concentrations. For the treatment units fixed recoveries are specified. Ram has considered the extension to synthesis for multiple scenarios in order to handle uncertainties in the contaminant loads and recoveries in the treatment units. This work he has generalized to generic multiscenario problems.

For the synthesis of the integrated water system, Ram developed a superstructure that involves for a given number of process units and treatment units all possible alternatives for interconnection of process and treatment units, and mixing and splitting of streams. The model corresponds to an NLP model with bilinearities in the mixers given by the product of flows times concentrations in ppm of the contaminants. Ram developed a global optimization algorithm that relies on combining spatial branch and bound search, with piecewise linear approximations inspired by the work of Lorena Bergamini. The motivation is that piecewise linearizations improve the quality of the lower bound, but they do it at the expense of introducing additional 0-1 variables. For this reason it is sensible to still use a spatial branch and bound search, but strengthened by piecewise linearizations for a fixed (modest) number of intervals. To also strengthen the quality of the lower bound, Ram has derived a valid cut that represents overall mass balances for each of the contaminants. The algorithm also relies on bound tightening and on branching only on the flows. The bisection rule is used for partitioning. Ram has tested his method with several examples. In one problem involving 4 process units and 3 treatment units the NLP had 195 variables and 151 constraints. CONOPT

either did not converge, or if it did, the best it found was 186.18 ton/hr. Our proposed method converged to the global optimum of 170.39 ton/hr, requiring only 10.3 secs solving the problem at the root node. BARON in contrast required 3490.5 seconds and 9656 nodes. Ram has also extended the model to general cost functions and selection of treatment units, which gives rise to an MINLP model due to 0-1 variables that are needed to model these units. The reprint of Ram's manuscript is included in this newsletter.

As a next step in his research, Ram has considered the extension of the above problem to the case when the water system must operate under multiple scenarios in which the loads in the units as well as the recoveries in the treatment units are uncertain, and therefore change in each scenario. This problem gives rise to a two-stage stochastic programming problem. The first stage costs include the investment cost for piping which depends on the maximum flowrate allowable in a pipe, and the design cost of each treatment unit, which is dependent on the maximum flow of wastewater handled by that treatment unit. The operating costs of the network appear in the second stage, which include the cost of obtaining freshwater for use in the process units, the cost of pumping a certain flow of water through the pipes and the operating costs in the treatment units. The difficulty of the global optimization for the nonconvex multiscenario problem is that the corresponding NLP or MINLP becomes much larger. Furthermore, 0-1 variables must be introduced for the piping in order to control the potential complexity in the configurations for each period. Ram developed a solution method that is based on a branch and cut algorithm. The basic idea consists in performing a spatial branch and bound where cuts are generated at each node using a Lagreangean decomposition scheme. These cuts are obtained by globally optimizing each scenario independently. These cuts are then added to the original problem that is convexified by constructing convex envelopes for the non-convex nonlinear terms leading to an MILP that is solved to predict a rigorous lower bound to the global optimum. A heuristic is used for the generation of good upper bounds. These lower and upper bounds are converged within a specified tolerance in a spatial branch and bound algorithm. Ram considered a problem with 2 process units and 2 treatment units and 10 scenarios. The MINLP model involved 28 binary variables, 868 continuous variables, 1044 constraints and 490 non-convex terms. The application of the proposed algorithm yields an expected cost of $651,653.06, which is the global solution to the problem. The lower and upper bounds converge within 1% tolerance at the root node of the branch and bound tree. The proposed algorithm takes a total of 62.8 CPUsecs to solve while BARON could not verify optimality of the upper bound after 10 hours of CPU time.

Ram has been able to generalize the above cited branch and cut algorithm for generic multiscenario problems, and that work is described in a paper that has been submitted recently for publication.

Eugenio Bringas

The aim of the work by Eugenio, which was conducted in collaboration with Ramkumar, was to obtain the globally optimal design of an emulsion pertraction plant, that consists of a prespecified number of hollow fiber modules (MOD), mixers (MU) and splitters (SU), with various possible interconnections between the units. The specific objective of this work has been to identify the interconnections of the superstructure and the flowrates and the contaminant compositions of the streams, such that we meet the discharge composition regulations using a minimum area of the membranes. In order to address this problem, Eugenio proposed a superstructure for the aqueous feed solution and the emulsion stream which flow counter currently inside a hollow fiber module where the transfer of contaminant takes place between the aqueous phase and the emulsion phase. In the postulated structure, the aqueous phase flows continuously, while the emulsion phase operates in batch mode.

In order to solve the associated superstructure optimization problem, Eugenio and Ram have developed a two-stage approach in which a simplified version of the model is first solved to rigorous global optimality. In a second stage the rigorous model is solved by using as a starting point the solution of the problem in the first stage. The global optimization algorithm relies on a spatial branch and bound algorithm in which tight lower bounds on the global optimum are generated though cuts obtained from Lagrangean decomposition, similar to the work of Ram for multiscenario optimization. The only difference is that in this case the Lagrangean relaxation of is decomposed into two subproblems pertaining to the aqueous phase and to the stripping phase which are optimized independently for fixed values of the multipliers. Eugenio applied this technique to a system consisting of 2, 3 and 4 membrane modules. As one might expect the proposed method becomes more competitive as the size of the problem increases. The manuscript that describes this work is listed below and has been submitted for publication.

Optimal Design of Corn-based Ethanol Plants

New developments: **Superstructure optimization model**

Students: **Ramkumar Karuppiah [Ph.D. started Jan 04]**
Visitor: **Andreas Peschel (RWTHm Aachen)**

This project has been initiated with the exchange student Andreas Peschel and Ramkumar Karuppiah in collaboration with Cargill. The objective has been two-fold: a) Develop short-cut models for corn-based ethanol plants; (b) Develop a superstructure optimization model to determine the extent to which the design of these plants can be improved.

In this work, we have addressed the problem of synthesizing corn-based bio-ethanol plants. In such plants, fuel ethanol is produced using corn-kernels as the feedstock. Fuel grade ethanol has to be 100 % pure before it can be blended with gasoline to be used in automobiles. However, conventional distilleries produce an azeotropic mixture of ethanol and water (95 % ethanol – 5 % water), which has to be purified further for making fuel ethanol. The main challenge in the way of producing fuel ethanol commercially is that the process is very energy intensive and requires large amounts of steam and electricity for use in the rectifiers to get an azeotropic mixture of ethanol and water and requires the use of expensive molecular sieves to get 100 % pure ethanol. Furthermore, the waste stillage from the fermentation units, which is rich in volatile organic compounds, and the other wastewater streams in the plant have to be treated before disposal, which, in turn requires energy intensive units like centrifuges and dryers. Due to the high costs involved in this process, currently it is not economically feasible to produce fuel ethanol commercially and sell it in the open market without subsidies. If the economics of the process have to be improved, we would need use process synthesis tools similar to those being used in the petrochemical industry to design optimally operating plants, rather than use ad-hoc or empirical approaches to build such systems. We look at the problem in a way to reduce the operating costs of the plant and minimize the energy usage and maximize the yields of the plant.

In order to design such a bio-ethanol plant, Andreas and Ram proposed a superstructure optimization approach where first a fixed configuration of flowsheet is considered by embedding the various process units involved in ethanol production. These units are interconnected to each other through network feed flows and other utility streams. The objective is to optimize the structure, determining the connections in the network and the flow in each stream in the network, such that we minimize the energy requirement of the overall plant while trying to maximize the yields. For this purpose, heat integration and water re-use possibilities are included. We also try to exploit different options for feedstock and processing technologies. The optimization of the system has been formulated as an MINLP, where the model that is optimized involves mass and energy balances for all the units in the system. Andreas and Ram have optimized an example network for such a corn-ethanol plant. The paper describing the results is currently being written.

Disjunctive Optimization Techniques for the Synthesis and Design of Separation Synthesis

New developments: **Structural considerations in heat integrated/thermally coupled columns**

Collaborators: **Jose Caballero [Associate Prof., Univ. Alicante]**

This project deals with a modeling framework for separation systems based on the State-Task Network (STN) and State Equipment Network (SEN) representations. These models are formulated with generalized disjunctive programming (GDP) models that explicitly handle discrete and continuous variables. The intent has been to develop whenever possible optimization approaches that can make use of tray by tray models. In the recent past Mariana Barttfeld from Argentina concentrated on MINLP and GDP models for single columns and complex column configurations. Jose Caballero in Spain has been working on the analysis and synthesis of thermally integrated columns using short-cut techniques for predicting the performance of the columns. In the most recent work he has developed a solution strategy for optimizing columns using a process simulator.

In the past Jose has addressed the issue of systematically generating all the configurations for thermally coupled distillation columns, including those that are structurally equivalent. In addition, the goal is to identify structures that

are "easy to control" in the sense that interconnections of the columns flow from high to low pressure. Jose developed a set of logic propositions that can be expressed as constraints in a GDP model to define the search space for these thermally integrated columns. Jose also derived equations to calculate the number of thermodynamically equivalent configurations for a given sequence of tasks. Jose developed a novel superstructure for synthesizing non-azeotropic mixtures with the Underwood-Fenske-Gilliland approximations. The synthesis approach considers alternatives from conventional sequences, in which each final distillation column has a condenser and a reboiler, to fully thermally coupled distillation sequences going through all possible intermediate combinations. In order to perform the optimization of the superstructure Jose formulated the problem as a disjunctive programming problem, and developed a two-stage solution procedure. In the first one a sequence of tasks is optimized, and then in a second stage the best configuration in actual columns is extracted among all the thermodynamically equivalent configurations. The model has proved to be robust and reliable.

In his recent work Jose has been investigating a strategy for determining optimal design of distillation columns using a process simulator (ASPEN) and using the disjunctive programming framework. A major motivation has been to avoid the need of explicitly handling the thermodynamic equations as has been the case in Mariana's work. The idea in Jose's model is to adopt the Logic-Based Outer-Approximation Method in which the NLP subproblem is given only by the existing trays in the column. For this Jose uses the optimization capability in ASPEN to optimize a column with fixed number of trays. In order to define the MILP master problem Jose performs numerical perturbations on the degrees of freedom (usually only two variables). In addition he performs a sequence of simulations by adding and deleting trays in each section in order to evaluate the economic potential of these decisions which are modeled as 0-1 variables in the MILP. The largest problem that Jose applied it was to a mixture of 2-propanol, 1-propanol, i-butanol and 1-butanol. A column with 70 trays was postulated (feed in tray 35). The optimum was found in 3 major iterations. The design yielded a column with 27 trays (tray 24 to 57) and was solved in about 1 min CPU-time.

Jose has most recently dealt with the synthesis of mixed thermally coupled-heat integrated distillation sequences. The approach considers from conventional columns (each distillation column with a condenser and a reboiler) to fully thermally coupled systems (only one reboiler and one condenser in the entire system). Jose has considered the generation of the superstructure generation using a representation based on separation tasks instead of equipment. To derive all feasible structures, ranging from thermally coupled to simple columns, Jose has written the logic using propositions in Conjunctive Normal Form (CNF). Converting these propositions into Disjunctive Normal Form (DNF) yields each of the feasible design alternatives. The problem is that this transformation is non-trivial. However, Jose considered three possible approaches. One is to pose the CNF logic as a constrained logic programming problem. In this case by using OPL one can in fact generate all solutions to the CNF propositions that are equivalent to each of the clause in DNF form. The second approach is to convert the CNF logic into linear inequalities and pose the problem as an integer program with zero objective. In this case by using BARON one can find all the solutions to the integer program, which again represent each term in the DNF form. The reason this development is significant is that w have now a systematic way of generating the DNF logic for superstructures. The third approach is a recursive ad-hoc procedure on the graph of the superstructure that Jose implemented in MATLAB. A disjunctive programming formulation that incorporates the logic constraints was developed by Jose. The model is based on the Fenske, Underwood Gilliland equations. However, the disjunctive formulation allows easily the use of any other shortcut, aggregated or even rigorous model without almost modifying the structure of the formulation. Rather than solving the problem with a general purpose algorithm Jose has developed a specific solution method that consists first of solving the MINLP problem (big-M reformulation of GDP) with DICOPT assuming no heat integration. Fixing the sequence of states from the first MINLP, the heat integrated problem is solved with SBB. The algorithm then sets up an OA master problem from which the nest sequence of states is generated and iterated with the MINLP problem with fixed sequence of states. Jose has tested this algorithm in 3 examples including, 5 hydrocarbons, alcohols, and aromatics. The interesting feature in the examples is that the method generates structures with both thermal integration and heat integration, and only thermal integration as seen below. The manuscript on this work has just been accepted for publication.

Synthesis of Crystallization Processes

Post-doctoral fellow: Ricardo Lima (started July 2006)

Ricardo, the new postdoc from Porto in Portugal, intends to work on the systematic generation of superstructures for crystallization and study an effective solution method for the associated MINLP problem.

Optimization Approaches for Metabolic Engineering

New developments: Selection of screening strategies for NMR analytes with Analytical Hierarchical Process

Student: Soumitra Ghosh (Ph.D., completed May 06) (supervised jointly with Mike Domach)

Soumitra completed his Ph.D. degree and has joined Bayer Corp. His project was on metabolic engineering in collaboration with Mike Domach. The first part of Soumitra's work involved the development of a software package for systematically identifying all the alternate optima that arises in the LP problem for maximizing yield in metabolic networks. The methods he implemented were a recursive MILP method that was developed by Sangbum Lee and a depth-first enumeration method. These methods can provide information on product yield horizons and the optimal "target" values of fluxes to achieve in metabolic networks. These methods can also elucidate the metabolite trafficking possibilities in tissues. While methods that enumerate flux scenarios are useful for the "front-end" analysis of metabolic engineering problems or probing the possibilities in tissue physiology, the evaluation of actual data from a tissue or engineered cells is ultimately needed to verify the veracity of theoretical predictions and mechanistic hypotheses. This gives rise to an inverse problem in which NMR data are used to best fit a linear combination of fluxes that minimizes a sum of squares deviation. However, this nonlinear programming problem is problematic because it is highly non-convex due to the bi-linear and tri-linear terms that arise in the isotopomer distribution vectors. Therefore, in order to obtain reliable results the NLP must be solved to global optimality. For this purpose Soumitra developed a formulation that involves using the results of the "front-end" analysis (MILP solutions) to provide tight bounds in the global optimization of the inverse-problem of data-to-fluxes. Soumitra applied the code BARON by Nick Sahinidis for deterministic global optimization and obtained good results. He applied this method on an E. coli bacterial mutant that has had pyruvate kinase activity deleted with 17 reversible reactions. The problem involved 910 variables and 897 constraints, and was solved by BARON in about 3 hours. It should also be noted that linking flux distribution forecasting with spectra-to-fluxes calculations provides a potential means for assessing the utility of different analyte sets for ascertaining the net values of metabolic fluxes.

In the last part of his Ph.D. work Soumitra developed a two-tiered computational approach for screening NMR analyte sets for their ability to report on metabolic fluxes. After obtaining the flux bounds via MILP, analytes are first screened for the ability of their NMR spectra to differentiate between different extreme point (or linear combinations of extreme point) flux solutions. Then, the analytes are screened for whether they provide unique flux values or multiple flux solutions. The effect of noise in NMR data is also considered as a factor in the ability of an analyte set to faithfully provide a correct flux solution as opposed to an alternative solution. The screening strategies were successfully implemented in a small hypothetical problem and in the E. coli system. An additional aspect that Soumitra has considered is the sensitivity problem of the inferred metabolic pathway with noise measurements in the NMR spectra. His has formulated this problem as an NLP problem to determine the maximum of the minimum deviations in the different peaks of the spectra given that the pathway fluxes lie within a given tolerance. With this additional measure and economic considerations of analyte selection that is driven by the material and labor costs associated with their isolation, there are different trade-offs that one can consider in the selection of the analytes. In order to address this problem Soumitra has applied the Analytic Hierarchy Process or AHP by Saaty. In simple terms the AHP leads from simple pairwise comparison judgments to the priorities in the hierarchy. Soumitra considered the performance of each NMR analyte according to the following criteria: (i) extreme point comparison (ii) abundance data based on both cytosolic content and frequency in proteins , (iii) Multiple Global Optima Test. Glutamate ranked first overall, followed by Alanine, and OAA (aspartate). This ranking was consistent with the results of the structured methodology used in this work. Soumitra completed the manuscript on this work which is listed below in the references.

Strategies for Reduction of Time-Varying Uncertainty in the Planning of Process Networks

New Developments: **Solution method for Disjunctive/MILP model**

Students: **Bora Tarhan (Ph.D. started January 2005)**

The project of Bora Tarhan follows the line of work of Vikas Goel for the design and planning of gas and oil fields under uncertainty. As a first step Bora has been addressing a different stochastic optimization problem that in principle is simpler to model in order to prepare the ground for the complex gas and oil field problem. The problem is as follows. A network of candidate processes is given over a specified time horizon that is described by multiple time periods in which product demands are specified. It is assumed that major uncertainties are involved in the yields of each process, which are described by probability distribution functions. We consider that the uncertainty can be reduced with the potential investment in pilot plants, which delays the introduction of a process but provides more accurate process information on the yields. In addition, it is assumed that once a process is installed, the uncertainties in the yields decrease with time to reflect the experience and improved understanding in the operation of the process. The problem then consists in making planning decisions for process selection, capacity expansions, and possible investment in pilot plants in order to maximize the expected net present value over the specified time horizon.

In order to capture all the complex trade-offs, Bora developed a new mixed-integer/disjunctive programming model that is composed of scenario linking and non-anticipativity constraints that are similar in spirit to Vkas's model. However, one importance difference is the time varying uncertainty. For simplicity Bora considered that this uncertainty is revealed over two time periods. Furthermore, he assumed that the time required for a pilot plant study corresponds to one time period, meaning that it reduces the uncertainty to only one time period. Obviously this scheme is rather restrictive but we have adopted it only as an initial assumption that we intend to relax at a later stage. In order to solve this special multi-stage stochastic program he initially reformulated it as a mixed-integer linear program, which can be solved through an LP-based branch and bound. However, this approach is restricted to smaller instances. Therefore, Bora has developed a dual Lagrangean branch and bound method, also similar in spirit to the work by Vikas Goel. The corresponding subproblems are obtained by relaxing the disjunctions and transferring the first period non-anticipativity constraints to the objective function with Lagrange multipliers. The resulting model can be rewritten as independent subproblems for each scenario. The overall objective is to find the minimum upper bound by updating the multipliers. The branch and bound involves branching over both discrete and continuous variables that are involved in the non-anticipativity constraints. Bora has successfully applied this method to a small 3 process network, with one existing process and two with new technologies and for which investment of pilot plants can be considered. A 10 year horizon was considered. If one were try to reformulate this problem as a single MILP it involves 7360 0-1 variables, 8,841 continuous variables and 85,139 constraints. Using CPLEX after one week the best solution that could be obtained had a net present value of $61.5 million. With the proposed method a solution of $80.14 was found in 10 hours of CPU time with a gap of 3%. The proposed solution did not select pilot plants to reduce the uncertainty, and proposed expanding Process I up to a capacity of 10 tons/day and making an additional expansion of 4.49 tons/day at time period 1 if the yield turns out to be 69%. If the yield for Process I is found to be 81% then an expansion of 2.98 tons/day is made also at the time period 1. Bora has completed the manuscript on this work and is listed in the references.

Simultaneous Planning and Scheduling of Multiproduct Plants

New developments: **Development of aggregate and detailed models for parallel batch reactors**

Students: **Muge Erdirik [Ph.D. started Jan 2004]**

Muge's project deals with the simultaneous planning and scheduling of multiproduct plants. The initial objective in her work has been to consider the case of a single processor on which a number of products must be produced continuously over a given number of time periods. Sequence-dependent changeovers are given and due dates are assumed to take place at the end of each time period. The objective is to determine a production plan and schedule in order to maximize the profit (income minus inventories and changeovers).

To address the scheduling problem described above, Muge has first developed a detailed MILP scheduling model using the concept of slots. This model, however, can only solve problems with few time periods, meaning it cannot be used to solve planning problems that typically require long time horizons. A simple approach to circumvent this problem is to develop an aggregate planning model that is simpler to solve but does not include all details such as changeovers. Well-known limitations of such an approach are inconsistencies between planning and scheduling and loss of optimality. Therefore, our objective has been to develop an iterative scheme that relies on aggregated models but that is guaranteed to converge to the same solution as if we had solved the detailed scheduling model. In order to accomplish this objective Muge developed an aggregated MILP model that underestimates the changeover times and includes 0-1 variables for deciding what products may be produced in a detailed schedule. The iterative scheme consists in solving a sequence of aggregated MILP planning models and detailed scheduling models with fixed assignment of products to be produced at each time period. In addition to using a simple integer cut, Muge has developed superset, subset and capacity cuts that eliminate a larger number of alternatives. The idea of the supercuts is to eliminate those alternatives that involve a larger number of products than the current assignment. These can be eliminated on the basis of optimality arguments. Likewise the idea of subset cuts is to eliminate subsets of alternatives from the current assignment. These are eliminated on the basis that subsets are considered in the detailed scheduling level since the 1-assignments are treated as upper bounds; only the 0 assignments are fixed. The capacity cuts take into account the potential effect of changeovers in limiting the production. For the cases where the detailed scheduling model with fixed assignments can still be expensive to solve, we can resort to a rolling horizon solution approach or on a temporal decomposition scheme. Muge has tested extensively her solution method. She considered two major cases: high lower bounds for the demands bound, low lower bounds for the demands. In the former case the schedule is forced to produce more products in each time period, and hence is more difficult to solve. She considered 5 products and a time horizon ranging from 4 to 24 weeks. In the 4 week problem (120 0-1, 987 continuous, 906 constraints) the proposed method converged to the optimum in 207 secs while the detailed model over the 4 weeks did not terminate the search after 6000 secs (8% gap of bounds) and obtained a suboptimal solution. In the case of low demand the proposed method converged in 4.6 secs versus 525 secs for the simultaneous approach. In the 24 week problem (720 0-1, 5907 continuous, 5526 constraints) the proposed method converged within 6% of the optimum in 3190 secs while the detailed model did not terminate the search after 4000 secs (18% gap of bounds) and obtained an inferior solution. In the case of low demand the proposed method converged in 8 secs within 4% of the optimum while the simultaneous approach did not terminate after 3000 secs but found a slightly better solution. Muge has completed a manuscript which has been published in *I&EC Research*.

Based on an internship that Muge spent at Dow Chemical in Midland, she has been addressing the simultaneous multisite planning and scheduling problem for batch reactors. This problem is in fact the case study that was selected by Dow for the Enterprise-wide Optimization project. The specific problem can be stated as follows. It is assumed that we are given a set of production sites, each with a unique set of raw material costs, raw material availability, storage tanks with associated capacity, transportation costs to each customer, reactors with associated materials it can produce and batch sizes and times for each material it can produce, as well as operating costs for each material, sequence dependent clean out times, and time the reactor is available during a given month. We are also given a set of customers, each with a unique set of demand for desired products, and price paid for each product. Finally, specified are the materials produced: process intermediates and final products. A related issue is the assignment of the limited number storage tanks at a site to particular materials. Generally a tank can store any material produced at a site, but due to the costs associated with setting up an inventory tank for a particular material a tank cannot be arbitrarily switched between products month to month but must be assigned a product for at least 6 months. Another issue is that a final product of one process may be used as a raw material for another process within the site. However, once a final product is fed to the dedicated storage tank, it can not be retrieved back to the plant. Therefore, one has to take into account the issue of intermediate storage as well. The problem is then to determine the monthly production quantities for each reactor and the assignment of materials to storage tanks such that the profit is maximized.

Muge has considered first the case of a single site. For this she proposes a novel continuous time MILP optimization model for scheduling that is based on slot time representation that overcomes some of the major difficulties faced by the STN and RTN discrete and continuous time models. While effective for short-term scheduling, the proposed model becomes computationally expensive to solve for long planning horizons. Therefore, as in the case of the single continuous processor, Muge has devised a rigorous bi-level decomposition algorithm. The problem is decomposed into an aggregated upper level planning and a lower level planning and scheduling problem. The upper

level determines the products to be produced at each time period as well as number of batches of each product, production levels and product inventories. The upper level is based on a new relaxed STN model where the detailed timing constraints and changeovers are replaced by time balances yielding a tight upper bound on the profit. The lower level is solved in the reduced space of binary variables according to the information obtained from the upper level model; therefore it yields a lower bound on the profit. The lower level determines production and inventory levels as well as detailed timing of the sequence of products and associated assignments to processing equipments and storage tanks. The procedure iterates until the difference between the upper and lower bound is less than a specified tolerance. To expedite the search we add logic cuts that arise from the structure of the problem which help reduce the feasible search space for the binary variables and tighten the gap between the solutions of the two levels. The proposed decomposition scheme ensures consistency between the two levels and optimality within a specified tolerance. Application of the proposed solution approach is illustrated with several examples which show that the aggregated upper level model yields very tight bounds, while the slot based scheduling model can be solved very effectively with constraints supplied by the aggregate model. The preliminary results have been very encouraging. In a problem involving 3 products (one intermediate) and 2 batch reactors over a 3 week horizon, the planning problem predicted a profit of $1,071,116, while the detailed scheduling model had an objective of $1,026,832. This is a clear indication that Muge's planning model has excellent approximation for the changeover times. Moreover while the "flat" scheduling model required 7,388 secs to solove, the planning model required 6.2 secs, while the reduced scheduling model only required 0.265 sec. Muge is in the process of testing her method with larger problems, and considering the possibility of various integer cuts when iterations are required between the planning and restricted scheduling model. Future work will also look at the extension to multiple sites.

Design and Planning of Responsive Supply Chains

New Development: Models for planning and design.

Students: Fengqi You [Ph.D. started Jan 2006]

This is a new project that is being performed by Fengqi You, a new PhD student from Tsinghua University in China. The major goal of this project, which is in the context of the Enterprise-wide Optimization initiative, is to develop a comprehensive optimization model that allows the effective integration of long term strategic design decisions for multisite process manufacturing facilities, with short term planning for production and distribution that accounts for the time delays across the supply chain. The major motivation for this project is that virtually all optimization models assume that material can be transferred instantaneously. In that way lead times corresponding to the response times once orders are placed, are not taken into account. It is our goal to establish the trade-offs between economics and lead times.

As first step, in order to understand the issues of delays in short term planning, Fengqi has considered the multiperiod planning of multisite process networks with dedicated plants. Information on transportation times of the raw materials, intermediates and final products are given, as well as the residence times in each process. Supplies can be continuous or intermittent. Fenqui has developed a multiperiod model that determines the optimal amount and timing for the supply of raw materials, as well as the optimal levels of production and inventory on a daily basis given a set of product demands. When the supplies are continuous, the model reduces to a multiperiod LP. When the supplies are intermittent, the model leads to a multiperiod MILP problem. This model can determine the trade-off between initial inventory level and lead times.

As a second step, in order to address the more general long term design problem, Fenqgi has developed a model for designing a multisite network of processes. In contrast to the planning model the time horizons are of the order of years, and zero-inventory levels are considered. The problem is then posed as a bi-criterion optimization problem in which the objectives are to maximize net present value and to minimize lead time. For the case of dedicated plants the problem can be formulated as an MILP, since nonlinear terms defining the lead times can be linearized. For the case of multiproduct plants, Fenqui has considered cyclic schedules over each year in which trade-offs are established between inventories and transitions. This significantly complicates the model and leads to a nonconvex MINLP problem. Fenqui has obtained preliminary results on a network consisting of 3 sites, 4 suppliers, 6 dedicated plants, and over a time horizon of 10 years divided into 3 time periods. The corresponding MILP model had of the order of 200 0-1 variables, 2000 continuous variables and 2500 constraints, requiring about 70 hours of CPU time to

generate the Pareto-optimal surface for the bi-criterion optimization. This plot then shows how the optimal net present value, and therefore the structure of the supply chain, changes with different specifications of the lead time. In both cases, planning and design, the work is still at a preliminary stage.

Cost Models for Contracts in Supply Chain Optimization Problems

New Development: **Disjunctive cost models for a variety of contacts yield effective MILP models**

Visitors: **Minhwan Park (KAIST)**
Fernando Mele (Polytecnic University of Barcelona)

Minhwan and later Fernando, addressed the issue of modeling contracts in supply chain optimization problems motivated by the fact that conventional models usually simply assume fixed prices of the raw materials and products. They considered short and long-term multiperiod production planning of a chemical supply chain network over a given number of time periods. The operation of the network is constrained by existing capacities of all processes in the network, limits in the supplies of raw materials and market saturation of some products. Information is given for different types of contracts that can be made for purchasing raw materials and selling the products. The objective in the short-term planning problem is to determine over a given time horizon, typically weeks or months, the types of contracts for the purchase of raw materials and sales of products in order to maximize the profit, which can be calculated by the data on sales revenues, operating costs, marketing costs, inventory cost and shortfall penalties. For the case of the long-term planning problem, the possible capacity expansion of the processes is considered. In this case, the NPV is optimized. The goal in these problems is to decide (a) which contract to make in the purchase of the raw materials and selling the products in each time period, and (b) whether capacity of each process should be expanded or not in each time period.

Minhwan and Fernando considered the following supply/demand models: fixed price contract, discount contract, bulk discount contract and fixed duration contracts over a specified number of time periods. For each of these contracts disjunctive programming models were proposed which in turn were formulated as MILP models using the convex hull reformulation. These contract models were then incorporated in the corresponding multiperiod MILP models for short and long term planning. These models were applied to a petrochemical complex involving 28 chemicals and 38 processes. Both short term (10 months) and long term (4 years) problems were considered. For the first case when only fixed prices are considered the planning problem reduces to an LP with 12,606 continuous variables and 13,416 constraints. When the four types of contracts are considered for 3 of the raw materials (naphtha, ethylene and acetylene) this gives rise to an MILP with 6160 0-1 variables, 40,606 continuous variables and 46,002 constraints. To our surprise CPLEX took only 0.995 sec to solve this MILP (vs. 0.18 for LP). The explanation is that the disjunctive models are extremely effective and provide very strong LP relaxations. In the long term problem we observed a similar trend. The case of fixed prices involves 152 0-1 variables, 5161 continuous variables and 5269 constraints, while the case of contracts also on the same raw materials involves 2,616 0-1 variables, 12,329 continuous variables and 14,017 constraints. In this case CPLEX actually took less to solve the problem with contracts (0.89 sec vs. 1.2 secs). The results also show qualitatively the advantages of the flexibility provided by the selection of contracts, both in terms of increased profits and in terms of demand satisfaction. The paper describing this work has just been published and is included in the reprints.

Scheduling of Batch Multiproduct Plants

New Development: **Publication of review paper**

Post-doctoral fellows: **Carlos Mendez (started Janaury 2003)**
Pedro Castro (finished July 2005)

Carlos Mendez

In collaboration with Iiro Harjunkoski and Marco Fahl from ABB, and from Jaime Cerda at INTEC, Carlos Mendez who is now back at INTEC in Argentina, completed a very comprehensive review of the area of batch scheduling. In

this paper a general a roadmap is given for classifying the problems as well as the optimization models. The models are then reviewed according to the classification with their main equations from the standpoint of discrete and continuous time STN and RTN models, and from the standpoint of sequential models for multistage plants. Numerical results are presented for discrete and continuous time models for a well-known Kondili example and an industrial size problem proposed by Kallrath from BASF. These results were obtained by our visitors from Barcelona, Anna Bonfill and Gonzalo Guillen. The paper next discusses a series of real world examples to illustrate the considerations that future methods must account for. The paper then reviews academic and industrial research with reference to commercial software. Finally, the paper discusses other solution approaches, the need to use special strategies for large industrial problems, and the area of rescheduling. We believe that his review paper should be very useful for those who want to get acquainted with the batch scheduling area. The reprint of this paper has been included in this newsletter.

Pedro Castro

Pedro Castro has returned to INETI in Portugal. He made important contributions with a continuous RTN model (Resource Task Network) in his Ph.D. in Portugal, and used it as a theme for his research at Carnegie Mellon. Pedro first examined the single stage problem with parallel lines, a problem that Vipul Jain addressed in his Ph.D. thesis. Pedro also found like Vipul Jain that the MILP and CLP models increases exponentially with problem size, while the hybrid MILP-CP method attains reductions of several orders of magnitude in the larger instances. He then also found that his continuous time RTN model exhibits exponential behavior. However, he found if that he does not use a common time grid for the parallel stages, but that rather uses a multiple time grids for each stage, then the RTN MILP model can be solved almost as fast as the hybrid model. He solved problems ranging from 12 orders and 3 units, up to 30 orders and 5 units for the cost minimization case. This was a truly a surprising result because it comes to show again the impact that alternative formulations can have in solving MILP problems. Another interesting result that emerged was that Pedro solved the discrete time model with up to about 400 time intervals in order to obtain exact or very close approximations. The surprising point here was that while the discrete time model was slower for the smaller problems, it did not experience an exponential increase in time. In fact the times ranged from 2.5 to 27 seconds for all the test problems. Pedro also examined the performance when the objective is minimization of earliness. In this case the discrete model performed the best followed by constraint programming. This comes to show the importance of objective functions in scheduling problems. This paper has been published and is available as a reprint of this newsletter.

In the next phase Pedro investigated the optimal scheduling of multistage plants. In this case he performed a non-trivial extension of the multi-time grid RTN MILP model for a single stage. He also examined in detailed a sequential MILP model that had been proposed previously by Harjunkoski and Grossmann. He performed extensive numerical experiments using as objective functions cost minimization, minimization of makespan, and earliness minimization. The problems ranged from 6 orders, 4 units, 2 stages to 10 orders, 8 units, 4 stages. His results showed that constrained programming tended to be the more effective solution method for makespan minimization. The sequential model proved to be best for earliness minimization, while the proposed model performed best for the cost minimization criterion. On an overall basis, the discrete RTN model was also competitive. Here again the discrete-time formulation was shown to have very good performance, particularly for total earliness minimization, despite generating very large MILPs when considering the exact problem data. The trend that was also observed is that continuous time models were more effective in small to medium size, while discrete time was better for the larger problems. The main conclusion was that for the multistage case not a single model proved to be the dominant one. This work also led to a manuscript that has been published.

The extension to handling changeovers in multistage plants Pedro has completed recently by developing two new continuous-time formulations for the short-term scheduling of single/multistage plants. The formulations rely on the use of multiple time grids, one per equipment resource. While one formulation uses binary variables linked to such tasks, giving rise to 4-index binary variables, the other maintains the 3-index binary variables of the previous model and changes one set of constraints to make it possible to handle sequence dependent changeovers. Both formulations were shown to be very efficient in single stage problems with the most surprising result coming from the fact that the 4-index binaries formulation was found to be slightly better than its 3-index binaries counterpart, despite featuring a number of binary variables that can be up to one order of magnitude larger. This behavior results from the use of tighter timing constraints (measured by a lower integrality gap) by the former, where all tasks that can be

executed in a given unit and time interval are aggregated into the same set of constraints, whereas the 3-index binaries formulation has the corresponding constraint disaggregated due to the need to consider one task defining order index in the constraint domain. As the number of stages increases, the performance of the developed multiple time grid formulations decrease steadily and feasibility may even be compromised. The other goal was to provide a critical review of other approaches that are suitable for this specific type of scheduling problem. These included an RTN-based discrete-time formulation, a continuous-time model with global precedence sequencing variables, a constraint programming model and a hybrid MILP/CP model. A total of 39 examples were solved and the results, together with those of the two previous works, allowed us to identify the main features, strengths and weaknesses of each approach, which were thereafter summarized in a comprehensive table. Overall the best model proved to be the continuous-time formulation with global precedence sequencing variables. The paper describing this work is listed in the references.

Pedro was also involved in a challenging industrial pharmaceutical problem that was supplied to us by ABB through Iiro Harjunkoski and Marco Fahl. This problem had the feature that it is multistage, but with very significant changeover times, and with complex operating rules. Both, 30 and 50 order problems proved to be unsolvable with known existing MILP methods. Pedro and Carlos proposed two alternative heuristic decomposition approaches for the efficient and fast solution of large industrial scheduling problems. Both use the concept of decomposing the full problem into several subproblems, each featuring a subset of the orders. The main difference lies in linking the consecutive subproblems. While the first approach completely freezes the schedule of the pre-assigned orders and ensures feasibility for the remaining through machine release dates, the second approach allows for more flexibility by only fixing the assignments and relative positions of the previously scheduled orders. The second approach was found to be more robust and seems better suited for the solution of this specific type of problem. Using both approaches Pedro and Carlos were able to obtain solutions that are often very close to the global optimum. The results for the solution of a 30-order problem show that the proposed decomposition methods are able to obtain solutions that are 35% better than those obtained by the solution of the full problem, on a fraction of the computational time.

Simultaneous Scheduling and Control

New development: **MINLP model for cyclic scheduling of multiproduct CSTR reactor**

Collaborator: **Antonio Flores-Tlahuacac (Professor U. Iberoamericana)**

This is a collaboration with Antonio Flores from the Universidad Iberoamericana (Ignacio's alma mater). Antonio, being a control person, has been motivated by the idea of using dynamic models for control in scheduling problems. Given our interest in the area of scheduling, we decided to join forces in a work in which the basic idea is to combine a scheduling optimization model, with a dynamic model for the optimization and control of the transitions. In this work we have addressed the simultaneous scheduling and control problems for a continuous stirred tank reactor (CSTR) that produces multiple products within a cyclic schedule that involves sequence dependent transitions. We formulated the problem as an optimization problem. Integer variables are used to determine the production sequence and continuous variables take into account production times, cycle time and inventories. The scheduling part of the model is similar to our previous work with Jose Pinto. Because, dynamic profiles of both manipulated and controlled variables are also decision variables, the dynamic part of the model is formulated with DAEs. The resulting problem can then be cast as a Mixed-Integer Dynamic Optimization (MIDO) problem in which the objective function includes income from sales of products, inventory costs and transition costs that takes into account through quadratic deviation terms, the amount of off-specification material produced during product transition. To solve the MIDO problem the MIDO problem is transformed into an MINLP using orthogonal collocation, where initial guesses on the duration of the transitions must be provided. These are then revised in a subsequent optimization. Because of the highly nonlinear behavior embedded in chemical process models, the resulting MIDO formulation gives rise to an MINLP problem featuring hard nonlinearities such as multiple steady-states, parametric sensitivity, bifurcation and even chaotic dynamics.

Antonio has tested the proposed model on several example problems. In one the problem consists of scheduling 5 products, each of them having 3rd order kinetics in the CSTR, the predicted cycle time was 127 hours using a sequence B $\rightarrow$ A $\rightarrow$ E $\rightarrow$ C $\rightarrow$ D, in which the dynamics of the transitions was explicitly accounted for with . It

should be noted that the solution of the resulting MINLP was quite difficult to converge, but was accomplished by solving a sequence of MINLPs where the transition times are fixed in an iterative fashion. Antonio is exploring the application of this approach to real world polymerization problems.

Software for MINLP Optimization in Design and Scheduling

Research Assistants: Rosanna Franco (started July 2006)

Rosana Franco has joined our group as a research assistant. As a first step she will update some of the web-interfaces that Gabriela Garcia has developed and that are available in:
http://newton.cheme.cmu.edu/interfaces

The current list of programs that we have available, most of them in our website, are the following:
(description in http://egon.cheme.cmu.edu)

Synthesis:

SYNHEAT	MINLP synthesis heat exchanger networks (Yee) Also includes transshipment model for targeting (Papoulias)
STEAM	MINLP Model for the synthesis of combined cycles for utility plants (Bruno) Model includes correlations for steam, efficiencies and cost data
GLOBESEP	Global NLP optimization for synthesis of separation networks and single feed/mixed products (Quesada)
WATER	Global NLP Model for synthesis of wastewater treatment configuration (Galan)
EXTRACTOR	Disjunctive MINLP for synthesis of liquid-liquid extraction systems (Reyes)
GDP-DISTILL	GDP Model for the optimal selection of number of trays and feed tray location in distillation columns using tray-by-tray model (Barttfeld)

Batch design:

BATCHSPC	MINLP and MILP models for multiproduct batch plants single product campaigns (Kocis, Voudouris)
BATCHMPC	MILP model for multiproduct batch plants mixed-product campaigns (Birewar, Voudouris)

Scheduling:

STN State-Task-Network MILP formulation for scheduling multipurpose batch plants. Both the the Kondili, Pantelides and Sargent (1993) model and the Maravelias and Grossmann (2003) are implemented.

PARALLEL	MINLP continuous multiproduct scheduling on parallel lines Features feasibility preanalysis (Sahinidis)
MULTISTAGE	MINLP continuous multiproduct in multistage plants (Pinto)
CYCLE	LP/MILP aggregate flowshop scheduling (cycle time/makespan) Includes loop tracing algorithm (Birewar)
STBS	MILP short term multistage scheduling (Pinto, Bolio)
CRUDEOIL	MILP model for refinery scheduling (Lee, Pinto)
DECAY	MINLP model for scheduling of clean-up of parallel furnaces (Jain)
UTILPLAN	MILPmultiperiod model for utility plants (Iyer)
PRODEV	MILP model for scheduling of tests in new product development (Schmidt, Najimas) MILP for resource scheduling in new product development (Jain, Maravelias)

Planning:

PLANNER	MILP multiperiod model for capacity expansion in process networks (conventional and lot sizing model) (Sahinidis, Norton)
MULTISITE	MILP model for planning the selection of processes and capacity expansion in different geographical location and accounting for transportation costs (Turkay)
GREENPLAN	Bi-criterion MILP model for selection of processes that maximize the net present value and

minimize toxicity (Drabbant)
NETCHAIN Multiperiod MILP for supply chain optimization of multisite facilities with flexible processes, intermittent deliveries, changeovers and inventories (Bok/Iyer)

Steinar Hauan's Group

Flexible Synthesis of High-value Products

Student: Murni Ahmad (MSc Dec 2001, Ph.D. finishing Sep 2006)

BACKGROUND

Co-advised by Todd Przybycien in BME, Murni is working on optimal design and operation of pharmaceutical and biochemical processes. In addition to regulatory constraints imposed on the operation of actual equipment, modeling is further complicated by incomplete knowledge of the biological mechanisms involved and different assessment of time-to-market aspects compared to production of bulk chemicals. A key issue is to capture the economic interactions between efficiently designed processes in new equipment in light of procedural requirements for FDA approval. A problem is that thermodynamic models and parameters are associated with limited validity and large uncertainty. Consequently, individual designs as well as scaleup must be done by a collection of models.

The current focus problem is protein separation by 2-phase aqueous systems. By adding polymer (poly-ethylene glycol, PEG) and selected salts to a water based "protein stew", a liquid-liquid phase split occurs where target proteins partition unevenly between the outputs. This opens for separation schemes based on two-stage extraction with partial recycle of PEG and relevant salts followed by precipitation.

The system is complicated by several factors:

- both liquid phases contain more than 70% water.
- the overall concentration of target protein is very low.
- protein partition coefficients are strongly species dependant and may vary by 2-4 orders of magnitude in a given system.
- the phase behavior is highly sensitive to the molecular weight of the polymer as well as the ionic strength in the solution.
- the phase separation process is kinetically controlled due as proteins interact electrostatically with themselves and each other.

At present, the process has limited use in industry due to incomplete knowledge about thermodynamic models and kinetic parameters. As most extraction processes, however, the economic potential appears promising and our goal is to come up with an optimization framework that is consistent across a range of interesting species.

PROGRESS

Over the last months, Murni has both completed a set of protein separation case studies combining flowsheet simulation with basic optimization of cost and performance. In brief, we can now generate the optimal tradeoff surfaces between protein yield, purity and the cost of phase forming agents. However, these results are highly sensitive to the physical property parameters available. As a consequence, Murni has spent significant parts of the last 5 months in the wet chemistry laboratory and performed measurements of VLLE data to predict both VLLE phase behavior and protein partitioning. This experimental verification will be the last part of her thesis expected to be completed by the end of September 2006.

Agent Systems in Engineering Design and Optimization

Students: John Siirola (Ph.D., completed May 2005), and Israel Owusu (Ph.D., started Jan 2004).

BACKGROUND

The main idea behind agent systems is to enable the study of large-scale engineering and design problems where:

- the models are complex, highly nonlinear and definitely non-convex
- many of the calculations fail routinely
- the problem has many local optimum
- the solution space of discrete alternatives is enormous

The underlying approach asserts that our computing capabilities will increase significantly over the next decade and that the computational resources will be available in the form of distributed computer clusters. We believe this will change our perception of "effective computing strategies": instead of creating algorithms that reach a result in the minimum number of algorithmic steps, it will become more important to be able to use the available -- but distributed --computing resources in an efficient manner. This represents a shift in thinking from CPU time to wall clock time.

A key feature in our approach is the use of an agent-based architecture. In these systems many computational agents – or individually executing algorithms -- attack different or even the same parts of the problem. There are also agents that remove bad solutions. All these agents share total and partial solutions as they progress. This sharing is very low bandwidth relative to the information developed by any agent internally. Experience shows there is considerable synergy among these agents, often reducing the time to find solutions by surprising amounts. For example, an agent may discover another agent has produced a particularly good new point from which it thinks it can make rapid progress. Or it may find a solution that gives it a much improved bound over any it has found by itself. These systems are like creating an army of ants to attack the problem, in the hopes that one of them will reach a desired solution. Parallelism comes by having the agents operate more or less autonomously and in parallel on several computers. But if computing is fast and cheap - why not?

With the completion of John Siirola's thesis, the fundamental implementation of the agent system and its control structure has been established. We have completed preliminary studies of multiobjective optimization for NLP, MIP and (simple) MINLP systems and demonstrated the conditions under which the agent system performs well compared to traditional approaches. We have also established the concept of "Polymorphic Optimization" wherein the agent system simultaneously consider more than one mathematical model of our physical system that each (de)emphasizes a particular aspect of the model.

PROGRESS

Israel has spent most of the last 6 months "buried" in implementational details of the distributed optimization framework. The key steps have been to create modules that encapsulate the different approaches to demand allocation, subproblem solution and information management.

Microscale Chemical Synthesis and Sensing

Microsystems is an extreme case of process intensification with general advantages compared to conventionally sized equipment as follows:

(a) improved conversion and selectivity in chemical reactions due to potentially better control of local mixing and heat transfer as well as a surface to volume ratio,

(b) capacity scaleup by device replication and not change of size avoids normal redesign issues when moving from laboratory equipment to pilot plants to production facilities,

(c) improved safety as the small amount of materials and energy present significantly reduces the potential impact of accidents and spill,

(d) clean and cost-effective production of small volumes through the use of cheap, one-time production equipment with no need for downtime and batch cleanup or risk of contamination, and

(e) reduced requirements for physical space and power.

Applications are emerging in the areas of sensor systems, microscale chemical synthesis, high throughput screening, environmental monitoring and medical sciences. The goal of this research is to adapt and expand current algorithms for process design into this new domain. At present, two directions are being actively pursued: (1) microscale fluid flow and chemical reactions, and (2) gravimetric sensing of biological molecules

The overall goal in microscale process design is to find the proper level of modeling detail to capture fluid flow, chemical reactions and heat transfer to address system level issues such as flow configuration, unit layout and operational procedures. With the proper experimental building blocks, we aim at treating these systems as multi-purpose and multi-period batch plants with special methods for dealing with surface-, heat- and end-of-pipe as well as coordination of clustered arrays for high throughput testing and production. There are 3 key issues in this project: (a) identification and modeling of relevant microscale effects, (b) how to generate reduced order models suitable and computationally feasible in a multi-unit optimization framework, and (c) shape- and parameter optimization of the resulting microscale unit operations. One of the key aspects is to understand the underlying physics and capture the behavior in a sufficiently simple model; this is being pursued with collaborators in ECE and ME.

Specific projects:

(a) Microscale Total Analysis Systems

Students: Anton Pfeiffer (Ph.D., graduated Apr 2006) and Xiang He (Ph.D., started Jun 2003)

Collaborators: Tamal Mukherjee (ECE), Jim Hoburg (ECE) and Qiao Lin (ME)

BACKGROUND

Microfabrication process have enabled manufacture of micro-sized channels, pumps, valves, mixer components and reactors. Integration of these components have enabled the creation of on-chip systems that span sample collection, preparation and analysis of biological materials, drug screening and chemical synthesis. Existing lab-on-a-chip systems tends to consist of relatively few components as the development of each such microscale unit operation continues to require empirical optimization and trial-and-error approaches. Long and expensive development cycles are acceptable for high-volume products where the equipment and process life times are measured in years and a few percent performance improvement translates to large profit. However, the wide variety of biological applications such as genomics, proteomics, therapeutics, diagnostics and a wide-array sensor systems implies the need for many customized designs instead of a few high volume products. Our work aims to create computer tools to aid in the development of two types of customized microfluidic devices: (a) integrated system wherein multiple microfluidic components are combined to form a complete single-function analysis system, and, (b) multiplexing systems where independent subsystems are combined physically on the same structure to provide parallel and/or redundant measurements.

The core idea of this work is to reduce the design and verification time for custom-designs from months and years to days and hours by use of component models and software tools for simultaneous performance optimization, layout and routing of the individual chips in question.

PROGRESS

In the spring and summer semesters, we have used our system level Lab-on-a-Chip simulator to take a close look design paradigms for microscale sampling and separation systems. Unlike finite element approaches where evaluating complex design alternatives may take many hours and even days, we are able to quickly assess the performance of each suggested design and generate pareto fronts that identifies the tradeoffs between performance, complexity and size. Although the verification studies are only 80% complete at this point, it appears that most of the experimental LoCs published in the literature are either significantly overdesigned or unnecessarily complex. However, there are cases where the full range of geometric options are necessary for the systems to work at all.

A main goal in the upcoming fall semester is to complete the identification of tradeoff curves and publish a comprehensive set of design heuristics for the optimal design of these systems.

(b) A MEMS-based Gravimetric Biosensor

Students: Michael Bartkovsky (Ph.D., graduated Aug 2006), Jane Valentine (Ph.D., started Jan 2003),

Collaborators: Todd Pryzbycien (Biomedical Engineering), Anna Liao (ECE) and Gary Fedder (ECE).

BACKGROUND

This work aims at creating a MEMS-based device capable of detecting picograms of biological target molecules. The basic principle is to cause a shift in resonance frequency for a polymer membrane by specific chemical functionalization of its surface. The membrane has characteristic dimensions in the millimeter range and prototypes have been used in microphones and speakers by our ECE collaborators.

There are four major tasks in this project:

(a) fabrication of a CMOS/polymer membrane with integrated capabilities for actuation and capacitive sensing.

(b) chemically specific functionalization of the membrane surface such that target molecules get adsorbed with the highest possible selectivity

(c) creating a clamshell packaging in which liquid samples may be brought in contact with the membrane surface.

(d) computer aided optimization of system parameters – including device geometry, functionalization density and scanning frequencies -- for single membranes as well as arrays of such.

PROGRESS

As of July 2006, we finally have a working prototype sensor. In brief, Mike has successfully functionalized the sensor surface with affinity binding groups and measured the resulting frequency shifts arising both from the binding groups themselves as well as from protein covered beads that subsequently bound to the surface. The experiments have been verified using optical techniques and the results are internally consistent and reproducible.

The device sensitivity appears to be even better than our original theoretical predictions. The reasons why are still being investigated, but we speculate that the chemical surface functionalization changes the elastic properties of the membrane structure in a favorable way.

Design of Multiproduct Reactive Separation Plans

Students: Scott Turnberg (Ph.D., started Jan 2005)

BACKGROUND:

Reactive distillation is a multifunctional process combining product conversion and separation inside a single piece of equipment. While the process has been demonstrated to significantly reduce both the capital and energy cost for highly non-ideal physiochemical systems, systematic design methods for generating and comparing design alternatives have been slow to evolve.

This projects seeks to combine recent analytical and algorithmic advances in the theory of reactive separation systems with the design of multiproduct plants for flexible production of acetate and oxygenate series. The main deliverables of the project will be:

(a) an algorithm capable of rigorously determining whether a particular set of reaction and separation tasks may feasibly take place in a single piece of equipment,

(b) a multi-objective optimization approach to assessing the economic trade-offs between the design alternatives generated,

(c) extensive case studies on current sequential and integrated processes to identify the first generation of pilot plant experiments for multiproduct equipment.

It is a goal to carry out the systematic search for solutions in part (c) using the agent system.

PROGRESS

Scott has automated the search for feasible product composition regions in reactive cascades; the next step is to integrate this approach into an agent-based search algorithm. In preparation for this task, he is doing a summer internship at Dow where they are evaluating the possibility of using agent systems for distributed control of process units.

Erik Ydstie's Group

Modeling and Control of Particulate Processes

Student: Christy M. White (Ph.D.)

This research addresses modeling and control of yield and size distribution in particulate processes. We use a novel method for solar-grade silicon production, the thermal decomposition of silane gas in a fluidized bed reactor, as a benchmark. We have developed a model and control scheme for the behavior of particles in a fluidized bed reactor based on silicon production. The model simulates growth of silicon particles with ordinary differential and algebraic equations that track particle movement through discrete size intervals. The model solves quickly and is easily tuned to fit experimental data. The results from this research were published in Powder Technology in March.

After developing an observer for on-line estimation of process states and parameters, we have combined the observer based modeling scheme with inventory control for total mass and seed-mass control for on-line stabilization of the particle size distribution. We presented some results from this work at the Fifth World Congress of Particle Technology Conference in Florida in April. Working with groups from REC Silicon (formerly Solar Grade Silicon LLC) and FLUOR Corporation, we simulated experiments to assist process design and scale-up. We will present results from this effort at the AIChE meeting in November. We continue to perform control studies for the fluidized bed reactor and interact with REC Silicon as they design and build a commercial scale fluidized bed reactor. The new process will provide several competitive advantages relative to the current Siemens process, including higher throughput per process unit, lower capital cost and significantly lower energy usage.

Modeling and Control of Distributed Process Networks

Student: Kendell Jillson (Ph.D.)

We have introduced a novel modeling framework for studying dynamics, distributed control, and optimization of complex chemical process networks. We are interested in developing distributed control systems that self-organize

so that stability and optimality follows as a consequence of how the networks are put together and how they are connected with boundary conditions or other networks.

By considering only the topology of the system, basic conservation principles and the second law of thermodynamics we have developed a multi-component analog to Tellegen's Theorem of electrical circuit theory. This result has been combined with the passivity theory of nonlinear control. It is shown that under certain convexity conditions the network converges to a stationary solution. Under similar conditions, it is shown that the network is self-optimizing in that the entropy production is minimized. Kendell presented this work in July at the 16th IFAC World Congress in Prague and at the AIChE meeting in Cincinnati.

We have also developed a theory for plant-wide control and stabilization of complex process systems. We have developed structural conditions for stability and simulated a recycle-flowsheet with a reactor and distillation column. The paper describing these results have been submitted for review in the *Int. Journal of Process Control*. We have used the network modeling theory to develop a networked model of the biological process of angiogenesis, the growth of new blood vessels. This is signaled by cancerous tumor cells as a way for tumors to increase their uptake of nutrients from the body as they grow. By modeling this problem with our network framework, we hope to gain insight into the system and eventually be able to suggest an optimal treatment strategy for dealing with tumor growth.

Optimal Decision Making by Adaptive Policy Iteration

Eduardo J. Dozal-Mejorada (Ph.D.)

Wayo (Eduardo) has developed an online optimization technique for unconstrained optimization based on adaptive policy iteration. The technique is based on Dynamic Programming. Barto et. al. (1995) describe Dynamic Programming (DP) based reinforcement learning (RL) algorithms such as Sutton's Temporal Difference methods, Watkins' Q-learning, and Werbos' Heuristic DP. In 1994, Bradtke introduced the *Adaptive Policy Iteration* (API) algorithm based on Watkins' Q-learning method and the concept of Policy Iteration. The algorithm successfully solved the problem of adaptive LQ regulation with state feedback. A Kalman filter or full state information is needed for implementation of these methods. The methods cannot easily be applied to partially observable Markov decision processes (POMDP) when the system model is not known for state estimation.

The objective of his research is to develop methods for optimal control of systems which do not rely on full state feedback. The RL approach we develop is motivated by Bradtke's method. The method uses input output data to obtain a corresponding Q-function. The Q-function is estimated recursively by least squares. The estimates are then used to develop reduced order representations of the optimal feedback strategies. The resulting optimal controls do

not require Kalman filtering leading to a novel reinforcement learning based approach. The method works well for systems where most modes have dynamics that dissipate quickly. The use of input output data allows us to focus modeling attention on the low order (observable and controllable) dynamics while the fast (poorly observable) dynamics are allowed to drift and it is therefore suitable for optimal control with wide separation of time constants.

Wayo and Kendell are developing methods for optimization of complex supply chains using Kendell's network theory and Wayo's optimal control approach. They show that by focusing on value added and cost minimization in a distributed supply chain it is possible to achieve global optimality without a central coordinator if the activity rates are positive,

Furthermore, Wayo spent this summer at Shell Global Solutions' Westhollow Technology Center working on MPC. The problem involved distributed control and optimization using SGS proprietary software and algorithms.

Passivity Based Control of Multi-Phase Reactor Systems

Student: Yuan Xu (Ph.D.)

The focus of this research is on passivity-based control of multiphase systems with reaction transport (diffusion and convection). To study this type of system, a metallurgic process has been chosen involving the carbothermic reduction of aluminum. This process takes carbon and aluminum oxide feed to produce aluminum. Work thus far has included developing a model using MATLAB to describe a variation of this process, as is being created by ALCOA, the world's largest aluminum producer. Proportional control is currently being used to explore the controllability, stability, and sensitivity of the system. Future work will be directed toward interfacing the FACT thermodynamics program with MATLAB via a MEX Interface. This will allow for the model to handle ranges of temperatures and compositions without extra work needed to determine equilibrium constants, activity coefficients, and extent of reactions. Another future improvement will be to incorporate computational blocks using the SIMULINK tools in MATLAB. Not only will this give the model a more "user-friendly" interface, but it will also allow for the exploration of modular simulation, where numerous monolithic simulation blocks can be combined and individually interchanged or altered without major recoding needed to modify the overall model.

Thermodynamics and Process Networks

Students: Luis Antelo (Ph.D. Univ of Vigo, Spain)

The aim of this research is to develop new foundations for control and optimization of large integrated, networks of chemical processes. We use the formalism of irreversible thermodynamics and the passivity theory of nonlinear control as a basis for this theory. However, there are severe limitations that need to be overcome when we extend these methods to problems that include coupled fluid flow, heat and mass transfer.

Luis has continued Felipe's work on the flash systems stability and he is currently studying how he can extend these to distillation by combining his ideas on using the Gibbs-Duhem equation with the algebraic methods of Chad Farschman and the Lagrangian/Eulerian decomposition of Duncan Coffey. He has also developed a new theoretical framework for plantwide process control which we are currently testing in simulations. Luis went back to Spain in the beginning of December. He will come back to visit us for three months next fall.

Modeling the Vapor Recovery Reactor in Carbothermic Aluminum Production using Multi-Scale Modeling Methods

Student: Mohit Aggarwal (co-supervised with Prof Lee White) (Ph.D.)

Mohit just joined the group in November. He will start out his PhD by developing a model for the vapor recovery section of the carbothermic aluminum process under development by ALCOA. In this process aluminum is produced in a high temperature (2000C) two stage process. A significant amount of aluminum vaporizes from the

aluminum reactor and this aluminum must be recovered in a vapor recovery column in order to maximize the production yield and save energy. We will model the primary reaction in the column, the gas flows as well as solid transport. The focus is to develop efficient methods to represent the thermodynamics and the multiphase behavior of the VRR. This work is a continuation of Vianey's modeling work (PhD/PostDoc 2004). Mohit will develop a three phase (liquid/solid/gas) multi-scale, simulation model which will be used for system design, scale-up, economic evaluation and control studies.

Adaptive Control using Selective Memory

Student: Priyesh Thakker (M.S.)

Priyesh joined the group in November. He will test a novel method for selective memory in adaptive control in simulation and pilot plant studies starting in January. He will focus attention on control of a steam water heat-exchanger in the unit operations lab at Carnegie Mellon. The method he investigates uses a newly developed technique to decide whether new data are informative or not by using a dual model adaptation concept which was subject to a patent application from CMU in May of 2005.

PUBLICATIONS:

B-06-09
Kawajiri, Y. and L. T. Biegler, "A Nonlinear Programming Superstructure for Optimal Dynamic Operations of Simulated Moving Bed Processes," http://dynopt.cheme.cmu.edu/papers/papers.htm

B-06-10
Victor M. Zavala and Lorenz T. Biegler, "Large-Scale Parameter Estimation in Low-Density Polyethylene Tubular Reactors," http://dynopt.cheme.cmu.edu/papers/papers.htm

B-06-11
Jussi Hakanen, Yoshiaki Kawajiri, Kaisa Miettinen and Lorenz T. Biegler "Interactive Multi-Objective Optimization for Simulated Moving Bed Processes," http://dynopt.cheme.cmu.edu/papers/papers.htm

B-06-12
Kawajiri, Y. and L. T. Biegler, "Large Scale Nonlinear Optimization for Asymmetric Operation and Design of Simulated Moving Beds," http://dynopt.cheme.cmu.edu/papers/papers.htm

B-06-13
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