CENTER FOR ADVANCED PROCESS DECISION-MAKING

New Directions for Process Systems Engineering

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NEW MEMBERS

We would like to welcome Ecopetrol as a new member of the CAPD. Ecopetrol, the main oil company in Colombia, is based in Bucamaranga. The contact person will be Ariel Uribe.

We are also pleased to welcome back to the CAPD, Bayer Corporation, whose membership has been re-established through the Graduate Fellowships that they have provided to the Department of Chemical Engineering. The contact person from Bayer will be Sanjay Joshi.

ANNUAL REVIEW MEETING

Please take note that the next **Annual Review Meeting** will take place on **March 8-9, 2010**. This will be followed by the meeting of the special group on **Enterprise-wide Optimization on March 10**. We will hold a reception on Sunday, March 8, in the newly renovated 4th floor of Doherty Hall, next to the new **CAPD Conference Room**. The first day of the meeting, Monday, March 8, will consist of overviews given by Larry, Ignacio, Nick and Erik, followed by a discussion with industrial participants, and a poster session by the students. As we did last year, we will host a group dinner that evening at Monterey Bay Fish Grotto Restaurant. The second day, Tuesday, March 9, is devoted to final year student presentations. In the afternoon, 1:30 to 4:30 PM, there will be a special session on **Enterprise-wide Optimization**. Please let us know of any suggestions on topics that you may have.

NEW CYBERSITE ON MINLP

We would like to invite you to participate as a beta-user in the CMU-IBM Cyberinfrastructure Collaborative site for MINLP: http://www.minlp.org, that has been funded by the National Science Foundation under Grant OCI-0750826.
http://www.nsf.gov/awardsearch/showAward.do?AwardNumber=0750826

The major goal of this site is to create a library of optimization problems in different application areas in which one or several alternative models are presented with their derivation. In addition, each model has one or several instances that can serve to test various algorithms. While we are emphasizing MINLP models, you may also wish to submit MILP and NLP models that are particularly relevant to problems that also have MINLP formulations. The site is intended to provide a mechanism for researchers and users to contribute towards the creation of the library of optimization problems, and to provide a forum of discussion for algorithm developers and application users where alternative formulations can be discussed as well as performance and comparison of algorithms. The site also provides information on various resources, meetings and bibliography.

We are hoping that you can help us to expand the library of test problems, and to provide us with feedback on this site. Any comments that you have will be welcome. Please send them to: minlp@andrew.cmu.edu. We are hoping to complete the beta-test by September 1, 2009, so we will appreciate your contribution by that date.

ENTERPRISE-WIDE OPTIMIZATION

The meeting of the EWO group will take place on September 29, 2009. The group is currently composed of the following companies: ABB, Air Products, BP, Dow Chemical, ExxonMobil, NOVA Chemicals, PPG, Praxair and Total. 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: Larry Snyder; UPitt: Andrew Schaeffer,). Companies that might be interested in joining this group in fiscal year 2010, 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/

NEW SPECIAL INTEREST GROUP ON ENERGY

With the growing emphasis on developing and maintaining energy-efficient and sustainable processes, we at the CAPD at Carnegie Mellon are interested in establishing a special interest group on energy systems.

This special interest group is driven by the success of the active enterprise-wide optimization (EWO) initiative within the CAPD. Within the EWO, member-driven projects are developed in the areas of planning, scheduling, real-time optimization and inventory control of process systems. Moreover, over the last two years, the CAPD has developed close collaborations with the National Energy Technology Laboratory (NETL). This collaboration has allowed us to leverage our research in modeling, optimization and control in a number of areas related to energy systems.

The proposed Energy Systems Initiative (ESI) would allow us to expand our current activities in the development of energy-efficient and sustainable processes. Especially geared toward CAPD members, we plan to structure the ESI along the same lines as the EWO initiative with company-centered projects conducted within a special interested group composed of researchers and practitioners. Moreover, with your collaboration, we envision establishing a broader research base in the energy area, by jointly exploring new funding initiatives. While Ignacio Grossmann will continue to lead the EWO effort, Larry Biegler has agreed to lead the new ESI effort.

At this stage, we would like to solicit your interest, feedback and suggestions for such an initiative. We would especially be interested in any suggestions for projects and ideas on the organization, structure and topics related to this initiative. Our intention is to hold an initial organizational meeting before the end of this calendar year.

CAPD SHORT COURSE

-The **CAPD Short Course**: http://capd.cheme.cmu.edu/shortcourse/index.html will take place on **May 20-26, 2010**. The course, **Optimization Modeling and Integrated Process Operations** is organized in two parts consisting of 6 modules which can be taken in any combination (e.g. 1, 2, 3 or all 6):

I. Optimization Modeling to be taught from Thursday through Saturday (May 20-22) will focus on modeling and algorithms with applications to process optimization, process synthesis and molecular design:
   a) Nonlinear programming (Biegler, Thursday, May 20)
   b) Mixed integer and disjunctive programming (Grossmann, Friday, May 21)
   c) Global optimization and optimization under uncertainty (Sahinidis, Saturday, May 22)

II. Integrated Process Operations to be taught from Monday through Wednesday (May 24-26) will focus on three major decision levels in plant and enterprise-wide optimization:
   d) Mixed-integer models for planning and scheduling (Grossmann, Monday, May 24)
   e) Integrating computation, communication and control in complex process networks (Ydstie, Tuesday, May 25)
   f) Differential/algebraic models for real time optimization (Biegler, Wednesday, May 26)

The material in each module is independent and self-contained and can be taken in any combination. A detailed description of the topics covered in the course is given in: http://capd.cheme.cmu.edu/shortcourse/shortcourse_details.htm. Recall that CAPD members receive a 25% discount. For details see: http://capd.cheme.cmu.edu/shortcourse/index.html
If you are interested in attending this course, please contact Laura Shaheen at 412-268-6344, or e-mail: lr23@andrew.cmu.edu.

GENERAL NEWS

The CAPD Newsletters can now be accessed thorough the webpage http://capd.cheme.cmu.edu/newsletters.html. All registered users of CAPD can access these by using their email addresses as userid and password. We also welcome any suggestions you may have for our webpage http://capd.cheme.cmu.edu

Larry Biegler, Ignacio Grossmann and Art Westerberg have been selected as recipients for the 2009 Warren Lewis Award for the contributions in chemical engineering education. They will receive the award at the Annual Meeting in Nashville in November 2009.

Larry Biegler served on the funding panel for PDE-constrained Optimization for the German National Science Foundation in March. In May he was a visiting professor at Zhejiang University in Hangzhou, China where he presented a short course on Nonlinear Programming and Applications in Design, Control and Operations. He also served as an evaluator of the chemical engineering graduate program at the University of Waterloo. In addition, Larry has been named the Hougen Visiting Professor at the University of Wisconsin and will give the Hougen lecture, entitled *Advanced Nonlinear Programming Methods for Chemical Process Optimization* on Sept. 22, 2009, as well as a series of short course lectures this fall at the University of Wisconsin. More information can be found on http://www.engr.wisc.edu/che/hougen2009.html

Ignacio Grossmann gave two talks at the INFORMS Computing Society Meeting in January: "Global Optimization of Bilinear and Concave Generalized Disjunctive Programs," and "Cyber-MINLP: A Virtual Environment for Problem Formulations and Algorithmic Developments." He also gave the talk "Tightening the Linear Relaxation of a Mixed Integer Nonlinear Program using Constraint Programming," at the CPAIOR 2009, in May at Carnegie Mellon. He then gave the plenary talk "Scope for the Application of Mathematical Programming Techniques in the Synthesis and Design of Sustainable Processes," at the FOCAPO meeting in Breckenridge, Colorado and the talk. "Optimal Design of Large-Scale Supply Chain with Multi-Echelon Inventory and Risk Pooling under Demand Uncertainty," at the ESCAPE-19 meeting in Cracow, Poland. Ignacio gave two seminars: "On the Scope of Discrete-Continuous Optimization in Process Systems Engineering," Department of Industrial and Systems Engineering, at Lehigh University in January, and "Optimal Synthesis and Planning of Sustainable Processes," at INGAR, Santa Fe, in July. Ignacio participated in the advisory board meetings of chemical engineering departments at Penn State, Princeton and Purdue. He also participated at the Technology Advisory Board meeting at Dow Chemical in July. Finally, he headed the 5th year evaluation committee of the Dean of Engineering at CMU.

Nick Sahinidis gave an invited talk on "Derivative-free Optimization Algorithms and Software" at the 2009 Computational Management Science conference in Geneva, Switzerland, in May 2009. Nick has completed the special issue he edited on global optimization for the journal *Optimization Methods and Software.* This issue includes 19 papers. Nick is currently serving on the scientific program committees of the following conferences: (1) Computational Management Science, Vienna, Austria, July 2010; (2) Foundations of Systems Biology in Engineering (FOSBE 2009), Denver, Colorado, August 2009; (3) 1st International Conference on Information Technology in Bio- and Medical-Informatics (ITBAM'10), Bilbao, Spain, Aug 30-Sept.3, 2010. Along with Chris Floudas, he co-organized the global optimization cluster for the 2009 International Mathematical Programming Symposium, Chicago, Illinois, August 2009.

Erik Ydstie presented a three day short course on adaptive control at NTNU in Trondheim in Feb 2009 as part of his duties as Professor II in the institute of Cybernetics in the Electrical Engineering Department at NTNU. He gave a plenary talk at the Gassmaks conference in Trondheim on using process systems engineering tools to improve oil and gas production in sub-sea fields. He gave a seminar on adaptive control at McMaster University in connection with the spring review meeting of the MACC. Erik also gave an invited talk in Department of Chemical and Petroleum Engineering at the University of Kansas. In June he served as Ph.D. examiner for Audrey Favache who defended her thesis on thermodynamics and process control at the University in Louvain la Neuve. He gave a talk at the Kvaerner Engineering in Kristiansand and continued working on due diligence for solar cell supply chain problems for Hydro Solar. Erik is currently leading iLS in its efforts to commercialize adaptive control systems. iLS currently has four full time and four part time employees, mainly working in the area of electric power generation and process modeling. In April Erik attended the advisory board of the Chemical Engineering Department at Worcester Polytechnic Institute. In May he attended the advisory board of the ACS Petroleum Research Fund.

Congratulations to Dr. Jeff Siirola. Research Fellow at Eastman Chemical and member of the NAE, who has been appointed as Adjunct Professor of the Department of Chemical Engineering, given his extensive interactions with the department. http://www.cheme.cmu.edu/people/associatedfaculty.htm

Congratulations to **Mohit Aggarwal** who successfully defended his Ph.D. thesis on stability of equilibrium processes. He has joined Air Products in Allentown.
Congratulations to **Brian Baumrucker**, student of Larry, who successfully defended his Ph.D. exam in May. He will be joining ExxonMobil Engineering and Research Center in Fairfax, VA.

Congratulations to **Bora Tarhan**, student of Ignacio, who successfully defended his Ph.D. exam in April. He will be joining ExxonMobil Upsteam Research Center in Houston.

Congratulations to **Fengqi You** who has accepted a faculty position at the Department of Chemical and Biomolecular Engineering. Fengqi will be defending in late October and will then do a postdoc at San Diego with Bernard Palsson and later at Argonne before joining Northwestern.

Congratulations to **Luis Miguel Rios**, student of Nick, who completed his Ph.D. degree at UIUC in May 2009 and has since joined Nick's group at CMU as a postdoc.

Congratulations to **Xuan Shi**, Nick's recent MS student, who accepted a job with Elite Consulting Group, New York, NY.

Congratulations to **Yiqi Zhu**, Nick's recent MS student, who accepted a job with Bloomberg, L.P., New York, NY.

Congratulations to **Alex Smith**, Nick's former Ph.D. student and postdoc, who accepted a job with Pavillion Technologies in Austin, TX.

Welcome to **YoungJung Chang**, former Ph.D. student of Nick and former postdoctoral student of Costas Maranas; YoungJung has joined Nick's group as a postdoc.

Congratulations to **Danan Wicaksono**, student of Nick, who completed his MS thesis in August 2009 on protein-ligand docking with algebraic optimization models.

Roger Rocha from Petrobras, who spent one year and one half as a researcher in Ignacio's group working in large-scale supply chain optimization, has returned to Brazil where he will be completing his Ph.D. degree at the Pontific Catholic University in Rio**.**

Dr. Edwin Zondervan from the PSE group at Eindhoven, has returned to his country after a two-month stay with Ignacio's group where he worked in the area of optimization of power systems.

Welcome to **Dr. Mariano Martin** from Salamanca, Spain, a Fulbright scholar, who has joined Ignacio's group. He will be working on the optimization of cellulosic-based bioethanol processes.

CAPD e-News. We sent on April 30 our e-newsletter. On a yearly basis, we issue 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 which contain short announcements as well as information that we think will be useful to the CAPD members, such as schedules of future professional meetings. We would appreciate receiving feedback or suggestions for improving the e-Newsletter.

UPDATED VIRTUAL LIBRARY ON PROCESS SYSTEMS ENGINEERING
This library http://cepac.cheme.cmu.edu/pasilectures.htm was initially created from the workshop, Pan American Advanced Studies Institute (PASI-2005) on Process Systems Engineering that took place on August 16-25, 2005, in Iguazú, Argentina. The library has been updated with material from the second workshop PASI-2008 on Emerging Trends in Process Systems Engineering that took place in Mar del Plata, Argentina, August 12-21, 2008. The goal of both these workshops was to provide a state-of-the-art review

and to bring together faculty and Ph.D. students from various countries in the Americas (U.S., Canada, Mexico, Argentina, Brazil, Chile, Colombia and Venezuela). The PASI-2005 workshop covered the following areas:

- Optimization, Process and Product Design, Process and Supply Chain Operations, Process Dynamics and Control, and material on these topics can be found in:
http://cepac.cheme.cmu.edu/pasi2005/slides/index.htm
while the PASI-2008 covered these areas: Advanced Modeling Tools, Biosystems Engineering, Multiscale Design of New Materials, Complex Engineering Systems, Sustainability, New Energy Systems, Enterprise-wide Optimization. Material on these topics can be found in:
http://cepac.cheme.cmu.edu/pasi2008/slides/index.html

The virtual library, http://cepac.cheme.cmu.edu/pasilectures.htm, consists of the Powerpoint slides of the presentations of each topic, which are largely tutorial in nature. These are complemented with background articles that provide comprehensive reviews. Exercises, as well as MATLAB and GAMS files are also available, including comprehensive exams for each workshop that contain questions with answers. Members of the CAPD should find the material to be helpful since it contains useful overviews of areas that are of current interest and that are not normally found in textbooks and reference texts.

WEBSITES/PROCESS SYSTEMS DIRECTORY

In addition to the Virtual Library on PSE, we are happy to report that the CAPD newsletter is distributed in electronic form. We would appreciate receiving feedback from our member companies about 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. Work is under way to update and modify our website. Other websites of interest are Erik's http://mongol.cheme.cmu.edu/, which contains a link to Industrial Learning Systems website, Ignacio's http://egon.cheme.cmu.edu, Larry's http://dynopt.cheme.cmu.edu, and Nick's http://www.andrew.cmu.edu/user/ns1b/ 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 large-scale dynamic optimization, particularly for nonlinear control and estimation. The past few months have seen the following applications.

Dynamic optimization tools, ultimately for on-line use, have been applied that are centered on IPOPT, which continues to be developed and improved at IBM. These have seen a number of applications ranging from detailed fuel cell models, advanced gas adsorption separation, polymer reactors and processes, gas pipeline networks and nonlinear model predictive control. These build on sensitivity-based optimization formulations for Nonlinear Model Predictive Control (NMPC) and Moving Horizon Estimation (MHE). These approaches also exploit the simultaneous approach as well as recent NLP features in IPOPT. The components of this work are detailed in three reprints listed below. This approach has also been extended by **Rui Huang** to the control of air separation columns with detailed dynamic models. Also, both Rui and Rodrigo Lopez Negrete have made advances in the extension of estimation and robust control methods. As a result, large dynamic optimization problems used for NMPC and moving horizon estimation (MHE) have *on-line computation costs reduced by two to three orders of magnitude!* In addition, robust stability properties have been proven and offset-free control can be achieved. A number of preprints are listed below that describe these results.

Related to this work is the development of specialized decomposition strategies within the IPOPT framework**. Brian Baumrucker** recently completed his thesis; he developed interesting optimization formulations that incorporate complementarity constraints and allow a class of discrete decisions to be modeled within a wide variety of NLP problems. This approach is not restricted to particular NLP solvers. The general framework is described in a reprint listed below. Moreover, this approach has been demonstrated for the scheduling and optimization of pipeline distribution systems. A preprint that describes this approach is also listed below.

Reduced order modeling strategies have been developed for large-scale PDE-constrained optimization. These are based on a snapshot-based decomposition and the isolation of principal components (i.e., eigenfunctions) that constitute the dominant elements of the solution space. Using these components as basis functions, one can create accurate reduced order models (ROMs) that are much smaller and easier to solve than the original. This approach, originally due to Karhunen and Loeve has been used in two ways in this research group. In the first, we have applied ROM strategies to Fluent-based models to create reduced order optimization models for gasifiers and combustors. As described in the reprint listed below and implemented by **Yi-dong Lang**, they make use of empirical input-output relationships described by neural network models. In the second approach, ROM strategies have been applied to pressure-swing adsorption (PSA) models.

Finally, **Anshul Agrawal and Sreeram Vetukuri** have made a number of advances in the synthesis of PSA systems for CO2 capture. Notable advances include the development of a dynamic optimization superstructure for the development of complex PSA cycles. This is coupled with the development of novel and efficient optimization algorithms. These advances have led to two studies that describe the use of PSA systems for CO2 capture at high purity and recovery at low energy costs. These studies deal with pre-combustion and post-combustion streams.

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

In the area of optimization, **Juan Pablo Ruiz** has developed a partitioning scheme for GDP problems and applied it to quadratically constrained quadratic programs. He has also completed a review paper with Ignacio on GDP for the IMA meeting on MINLP. In collaboration with **Francois Margot, Pietro Belotti, Larry Biegler, Nick Sahinidis**, **Jon Lee and Andreas Waechter at IBM,** as well as the NSF project on Cyberinfrastucture for MINLP, we have produced the cybersite http://www.minlp/org which has been launched in beta phase. The site currently contains 7 problems whose detailed formulations and input files are available on that site. **Aldo Vecchietti** has continued to update the website for LOGMIP http://www.logmip.ceride.gov.ar/ which is now available in GAMS (http://www.gams.com/dd/docs/solvers/logmip.pdf).

Ravi Kamath has completed a manuscript for the simulation and MINLP optimization of distillation columns using an aggregate model, which compares favorably with the detailed MINLP models by J. Viswanathan. **Jose Caballero** has completed a manuscript on hybrid distillation/membrane columns that resulted from a joint project with Lyondell. **Elvis Ahmetovic** has completed a manuscript on a comprehensive NLP/MINLP for process water networks that can handle multiple feedwater streams, recycles within units, and sources and sinks of water. **Mariano Martin**, has started a new project on design and optimization of cellulosic bioethanol via gasification. In collaboration with Elvis, Mariano has performed water network optimization in a corn-based ethanol plant. **Gonzalo Guillen's** paper on the design and planning of hydrogen supply chains for vehicle use has been accepted for publication.

Bora Tarhan, who finished his Ph.D. degree in April, has completed two novel working papers, one on Scenario Tree Generation for Gradual Uncertainty Resolution, and the other on Improving Dual Bound for Stochastic MILP Models using Sensitivity Analysis. **Vijay Gupta**, a new Ph.D. student that will follow Bora's line of work, has developed a reduction scheme to reduce the number of non-anticipativity constraints in multistage stochastic programming. **Sebastian Terrazas** has completed the first draft of a manuscript in collaboration with Dow on a novel MILP model for optimizing the availability of process networks with uncertain demands and process availabilities in which capacity expansions and intermediate storage tanks are considered. In addition to using the Expected Stochastic Flexibility as a metric, a major

novelty has been the use of Markov chains and basic random process theory to capture the discrete-event nature of the storage problem. In collaboration with Praxair, **Fengqi You** has developed an optimization strategy for tank sizing and vehicle routing that relies on the use of a continuous approximation for vehicle routing to simultaneously optimize the problem of tank selection. **Sylvain Mouret** has been developing interesting generalizations and unification of models for different types of time representations for scheduling models (single-operation and multiple-operation sequencing with synchronized and fixed times). **Abdul Alattas** in a collaboration project with BP, has been testing a number of formulations and numerical schemes for optimizing a cascaded model for CDU that incorporates steam stripping columns in which inversion of temperatures in the rectifying section can be successfully predicted. **Ricardo Lima** has developed a novel scheduling model for PPG for the production of tinted glasses in which long transition times can be accounted for, and handled over boundaries corresponding to time periods. Also, a complex compatibility and recycling profile of waste glass (cullet) formed during the transitions is rigorously handled. **Roger Rocha**, a postdoctoral fellow from PETROBRAS, has completed a manuscript on cascaded knapsack inequalities for production-inventory-distribution problems that effectively exploit the structure of these problems. **Pedro Castro** and **Fengqi You** completed a manuscript that deals with Dinkelbach's algorithm for solving linear fractional MINLP problems that relies on solving a sequence of MILP problems. The application was shown on two cyclic scheduling problems. Finally, **Rosanna Franco** is completing two new interfaces: continuous scheduling of parallel units based on the model by Muge Erdirik-Dogan, and steam and power plant based on a model developed by Ravi Kamath and Joan Carles Bruno.

Nick Sahinidis' Group

There have been a number of major new developments from Nick Sahinidis' group since the previous newsletter.

1. In global optimization, **Xiaowei Bao** has completed a computational experimentation with multiterm, as opposed to single term, relaxations for quadratic constraints and found that these relaxations expedite BARON significantly for the solution of quadratically constrained quadratic programs. A related paper has appeared in *Optimization Methods and Software*. Since completion of this paper, we have been working towards an implementation of multiterm relaxations for general nonconvex optimization problems.
2. **Joe Elble** has completed an extensive computational study on scaling of linear programs prior to the application of the simplex algorithm. The main finding is that equilibration appears to be the best scaling method; more complex scaling procedures do not seem to provide advantages.
3. Two papers have been accepted on parallel computing on Graphics Processing Units (GPUs).
4. **Yan Zhang** has completed the development of a CO2 sequestration model, along with a computational implementation of the model that can be used for risk assessment studies.

Erik Ydstie's Group focuses on solar cell systems, process modeling, nonlinear and adaptive control. In the area of adaptive control, we have been working on developing a new approach to adaptive PID control which is based on global optimization and frequency domain specifications for the closed loop performance. The controller has been tested in simulation studies by **Venkat Nadndivida** (MS student). Experimental studies carried out in the Rothfus lab show that the method is robust and suitable for on-line applications. **Juan Du** has continued her work on nonlinear control theory. She has developed a better understanding for how inventory control can be used for selecting measurements in complex chemical process systems. **Michael Wartmann** has been back at the Shell research labs in Delft working self-optimizing control of oil fields. He has developed some new optimization principles based on the Tellegen theorem which appear to have very broad applicability. He is currently investigating whether the idea can be used to speed up global optimization by using Tellegen's theorem as a redundant constraint. This work is being supported by Tor Heirung (MS exchange student from NTNU), **Mohit Aggarwal** completed his Ph.D. thesis on modeling and stability of equilibrium chemical processes. He applied the concepts to bio-gasification processes, the Alcoa carbothermic aluminum process, and coal gasification. **Zhaojia Lin** (MS Student) is developing a simulation study to test his ideas in the area of process invariants and she extending the method to multi-stage systems. **Rocco Panella** joined the research group (co-supervised by Dennis Prieve). He has made good progress on an experimental program aimed towards developing flexible, dye sensitized solar cells. **Keyu Li** has developed a new approach for adaptive PID control with feedforward from

measured disturbances which has been extensively tested in simulation studies. **Chengtao Wen** has developed distributed, dynamic simulation models for coal fired power plants. The approach for distributed dynamic simulation is based on the method developed by Vianey Garica-Osorio in her Ph.D. with Erik in 2004. The method is based on the use of asynchronous recording controllers which record and control the simulation error. Chengtao's work is supported by Simon Markowski (MS student). **Sudhir Ranjan** made significant progress in developing experimental verification of a new process for continuous production of silicon wafers for solar cells. He has shown that it is possible to float a very thin (0.1mm) layer of molten silicon on a molten tin covered by a glassy slag. The melt solidified to form a small wafer of Silicon <111>. **Sukumar Balaji (Bala)** developed multi-phase simulation models to study the process dynamics. The Ydstie research group has obtained funding from NSF, which includes funding for experimental equipment, to continue the work with a new Ph.D. student in the fall of 2009. Bala has also developed models for the chemical looping process under study by DOE.

STATUS OF RESEARCH PROJECTS

Larry Biegler's Group

General Frameworks for Large Scale Optimization Strategies and Applications

Researcher: **Victor M. Zavala (Ph.D. completed Fall, 2008)**
Student: **Hans Pirnay**
Visitor: **Kexin Wang, Zhejiang University (Ph.D. completed Fall, 2008)**

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. In his Ph.D. thesis, 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. By exploiting the structure of these networks, discretized problems with up to millions of variables could be solved in only a few CPU minutes. More recently, this approach has been extended, by using either a Schur complement strategy for multi-scenario problems or advanced sparse decomposition strategies for general problems. Using an efficient pre-processing step, small subproblems can be derived and design scenarios can be identified more precisely and efficiently. This approach is described in the reprints below.

Finally, the new version of IPOPT continues to updated and maintained. 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 in the following ways:

- Multi-scenario problems 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.
- More recently, Victor Zavala has demonstrated this approach on a large-scale parameter estimation problem, executed on parallel processors and show essentially perfect speedups with this approach. A reprint that describes this approach is listed below.
- The structure of IPOPT has been expanded to deal with NLP sensitivity. This approach very quickly provides an estimate of the solution of a perturbed NLP problem. As a result, it is very useful for quickly solving a sequence of problems that change only slightly from the previous one. More recently, Hans Pirnay has developed a flexible code and interface for this feature, to be released in the near future in the COIN-OR/IPOPT distribution. This is applied below to develop a very fast strategy for Nonlinear Model Predictive Control (NMPC).

- The reduced-space, FORTRAN version of the IPOPT code has been extended by **Kexin Wang** to included recent developments in the IPOPT project. This will also allow the incorporation of recent penalty-based barrier methods developed by Chen and Goldfarb to be adapted to the reduced space approach. In addition, Kexin has recently implemented and tested a new restoration phase for the reduced space approach. This approach deals with linearly dependent constraint gradients along with rapid detection of infeasible constraints.

A number of reprints that describe these features, by Victor Zavala, are listed below.

Mathematical Programs with Equilibrium Constraints (MPECS)

Researchers: **Brian Baumrucker (Ph.D. completed May, 2009)**
Krishna Iyengar (MS started Fall, 2008)

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.

This project builds on the Ph.D. work of Arvind Raghunathan and Brian Baumrucker. 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; it has also enjoyed widespread use in projects with the McMaster University. 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.

In extending MPEC optimization formulations, **Brian Baumrucker** has considered the development of good MPEC formulations that model discrete decisions. He has explored these with the ROMeo real-time optimization package along with 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, he has investigated complementarity formulations in distillation columns and real-time optimization formulations with switching variables.

More recently, Brian has extended this approach to dynamic optimization problems, where switching conditions can occur at any point in time. This class of hybrid dynamic systems provides an interesting challenge; it can lead to very large MINLP problems but can be treated in a straightforward way using MPEC strategies. On one problem, dealing with the optimal trajectory of a racing car, results were obtained that represented significant improvements over literature values. Finally, Brian has adapted this approach to the operation and scheduling of dynamic pipeline models. Working with colleagues from Air Products,

Brian has shown that complementarity formulations embedded within a dynamic optimization formulation can solve very large optimization problems (with the equivalent of many thousands of switching variables) within only a few CPU minutes. This allows the optimal exploitation of inventory in pipelines in order to reduce energy and other operating costs, while still meeting customer demands. Moreover, this allows a number of interesting electricity pricing structures to be considered in the optimal scheduling of pipeline operations. The results of this work are described in a preprint listed below. **Krishna Iyengar** will continue this pipeline scheduling study through the consideration of a number of multi-period scenarios.

Simultaneous Optimization of Differential-Algebraic (DAE) Systems

Researchers: **Victor Zavala (Ph.D. completed August, 2008)**
Rui Huang (Ph.D. started Fall, 2006)
Weijie Lin (Ph.D. started Fall, 2006)
Rodrigo Lopez Negrete de la Fuentes (Ph.D. started Fall, 2007)
Yi-dong Lang (Jiansu Research Institute, Nanjing, China)

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. 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://www.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.

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. A MATLAB framework has been coupled to the AMPL modeling language and domain specific prototypes have already been developed and work very well.

Large-scale Parameter Estimation for Polymerization Processes

In a project funded by ExxonMobil Chemicals, **Victor Zavala** completed his thesis on a developed multi-stage dynamic optimization problems for grade transition and nonstandard 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. Moreover, using the NLP sensitivity approach described above, Victor showed in his thesis that the covariance matrix from a maximum likelihood formulation can be extracted easily from IPOPT using a few additional back-solves of the KKT matrix. This allows statistical inference to be added efficiently to parameter estimation studies. This has recently led to a novel moving horizon estimation scheme which is described in three reprints below.

Weijie Lin is working on process model development for an advanced polymer product. The approach is similar to the moment models developed by Victor, but with more complex features dealing with the polymer structure. Weijie's work has shown the importance of parameter estimation for this large-scale model in order to demonstrate structurally dependent features (e.g., gel effect, cage effect, glass effect) on the polymer reactions. This also allows her to develop MW distributions of the complex polymer network. So far, she has developed novel particular models that deal with polymer kinetics and growth. She has compared this model with industrial data and completed a detailed parameter estimation study. As a result, she has been able to validate the model and also suggest future directions for the experimental program as well. With the successful completion of this work, Weijie has also investigated optimal control strategies that improve the product quality and reduce production time. Preliminary results indicate significant performance gains (around 15%) can be obtained with quite different, novel operating strategies for operation of the polymer process. This work is described in a preprint listed below.

Nonlinear Model Predictive Control Strategies

In less than two decades, Nonlinear Model Predictive Control (NMPC) has evolved from a conceptual framework to an attractive, general approach for the control of constrained nonlinear processes. These are based on the on-line solution of optimization problems for control. One such approach, which we conducted with researches in Switzerland, is listed as a reprint below. The advances in NMPC were realized both through better understanding of stability 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 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. Over the past year, 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. These are described in a reprint below. This leads to an NMPC strategy called the Advanced Step NMPC Controller. Demonstrated on a large-scale polymer process, the Advanced Step Controller leads to on-line calculation effort that is reduced by over two orders of magnitude. As described in the reprint below, we have been developed a general Lyapunov-type stability analysis for this approach that demonstrates nominal stability, input to state stability and robustness margins to noise and model mismatch. This recent development has been extended to moving horizon estimation (MHE) for parameter and state identification and yields the same dramatic improvements in performance. A further reprint is also listed, where Victor shows the potential of combining both fast NMPC and MHE steps in one to yield controllers that are tolerant to noisy data and drifting model parameters. This paper was a featured presentation at the NMPC '08 Conference in Pavia, Italy.

Rui Huang, has recently adapted this work to NMPC distillation control and advanced power plant systems. His preliminary work has demonstrated that the Advanced Step NMPC also reduces on-line calculation time by about two orders of magnitude. The resulting application deals with a detailed air separation (double) column with about 1500 DAEs and an NLP with over 100,000 variables and equations. Although the problem can be solved in less than 4 CPU minutes, the on-line computation is still very much faster. Rui's results indicate that the NMPC controller requires only a single second of CPU time. This work is described in the reprint listed below. More recently, Rui has considered robust extensions of NMPC that follow two parallel tracks. First, the original NMPC strategy has limited robustness (*input-to-state stability* or *ISS*) and this can be extended through the use of multi-scenario optimization problems, which can be solved on-line with a fast sensitivity-based approach. This approach is demonstrated in two preprints that are listed below. Second, disturbances and model mismatch can be addressed by embedding observers within the NMPC formulation. This has been analyzed and a related *input-to-state practical stability* (ISpS) has been demonstrated for this formulation. This work benefits from a collaboration with **Prof. Sachin Patwardhan** at IIT-Bombay, an expert on nonlinear control and identification. Three preprints are listed below which describe this work.

Finally, **Rodrigo Lopez Negrete** is extending this model-based estimation and control approach to stochastic processes with uncertainties in states and outputs. This work also benefits from a collaboration with **Prof. Sachin Patwardhan** at IIT-Bombay, an expert on nonlinear control and identification. Currently, Rodrigo has adapted recently developed Unscented Kalman Filter (UKF) methods, which deal with non-normal noise structures, to the MHE formulation described above. In recent tests, Rodrigo has shown that this strategy has superior performance to Kalman Filter updating approaches as well as previous MHE strategies. Working with Prof. Patwardhan, Rodrigo continues to refine this approach and also is also extending this MHE strategy to incorporate recently developed particle filter and ensemble filter strategies. A preprint that describes this approach is listed below.

Large-Scale Optimization for Fuel Cell Models

Researchers: **Parag Jain (Ph.D. started Fall, 2005, joint with Prof. M. S. Jhon)**
Robert Smith (Ph.D. started Fall, 2008, joint with Prof. M. S. Jhon)

In his thesis project, Cong Xu initiated the investigation of 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, we 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. 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.

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. In his thesis work, **Parag Jain** has extended previous modeling and optimization work for Hydrogen PEM 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. The results of this work are listed in a reprint below.

In addition, Parag has extended this work to assess the role of platinum distribution in the catalyst layer. As discussed in this reprint, this approach leads to an exponentially damped Pt profile in the catalyst layer that leads to significantly higher power densities for the PEM Fuel Cell. Moreover, these results lead to novel optimization-based strategies for improvements in membrane design coupled with catalyst loading. Finally, Parag has extended this approach to fully 3D models of the integrated MEA and its coupling with the gas channel. Finally, Parag's current work is to extend these concepts to multi-scale modeling and to incorporate molecular dynamics models to improve the water and proton transport properties of the polymer membrane. **Robert Smith** has recently joined the group and will continue this direction on the project.

Dynamic Optimization for Semi-Closed Process Models

Student: **Sree Ram Raju Vetukuri (Ph.D. started Fall, 2006)**
Collaborator: **Prof. Andrea Walther (Technical University of Dresden)**

This project explores the application of recent developments in automatic differentiation and nonlinear programming to semi-closed process models, including systems solved with DAE integrators. This sequential optimization approach for dynamic systems has been the competing strategy to the simultaneous optimization approach adopted in our group. It has advantages for problems where error control is especially important, where many time steps are needed and where these need to be adjusted frequently during the integration. Recent years have seen the development of efficient sensitivity strategies to obtain accurate first and even second derivatives for use in dynamic optimization algorithms. However, this approach becomes inefficient when there are many degrees of freedom. For instance, in the optimization of Pressure Swing Adsorption units, Ling Jiang developed an efficient sequential dynamic optimization approach. However, when several hundred inputs were considered in the model, the optimization required hundreds of CPU hours.

This bottleneck has recently been addressed by a recent SQP-type algorithm that uses exact right hand sides of the KKT equations, along with Jacobian-vector and Hessian-vector products, but computes only inexact Jacobians. Using leading edge technology in automatic differentiation, these quantities can be computed orders of magnitude faster than with the standard sequential approach. Profs. Andreas Griewank and Andrea Walther have recently developed a globally convergent SQP that uses inexact Jacobians, called TR1. Based on a composite trust region strategy, this approach has recently been applied to periodic adsorption processes as well. **Sreeram Vetukuri** has extended this approach using ADOL-C for automatic differentiation and CVODES for sensitivity calculations of first and second derivatives, and interfacing to TR1. Preliminary results on a small SMB system show the potential of this algorithm for reducing CPU time. More recently, he has extended this approach to Pressure Swing Adsorption (PSA) systems that have more complex dynamic behavior, with a broader spectrum of time scales, and more complex mass transfer and equilibrium behavior. The resulting approach has led to a more comprehensive and efficient approach to PSA optimization.

This work feeds into the developed of efficient separation strategies for CO2 capture. Here, the pre-combustion gases CO2 and hydrogen are separated and CO2 is sequestered. Alternately, post-combustion gases CO2 and nitrogen can be separated and CO2 sequestered. Either of these separations can be performed effectively by pressure swing adsorption (PSA) units, which operate dynamically and require the calculation (and subsequent optimization) of cyclic steady state behavior. Such models were considered in the PhD thesis of Ling Jiang. While her optimization approach was very successful for large-scale PSA units, it still required many hours of CPU time, and therefore requires custom reduced order models (ROMs).

Over the past year, both Anshul Agarwal and Sreeram Vetukuri have developed a novel superstructure for the evaluation of CO2 capture strategies using PSA. Following on recent work by Ritter, Webley and their coworkers, this approach captures a number of different PSA steps (e.g., pressurization/depressurization, adsorption/desorption, pressure equalization, light and heavy product recycle) through the formulation of an optimal control problem. Preliminary results indicate that the superstructure is rich enough to predict both high purity and high recovery of captured CO2. It is therefore quite useful in predicting the suitability of different sorbents and operating strategies for PSA. This work is described in two preprints listed below.

Reduced Order Models for PDE-based Units in Power Plant Flowsheets

Researcher: **Yi-dong Lang (Jiansu Research Institute, Nanjing, China)**
Students: **Anshul Agarwal (Ph.D. started Fall, 2005)**
Adam Malacina (MS completed May, 2008)
Jyoti Swankar (MS started Fall, 2008)

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 are IGCC-based coal-fired power plants that include 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 (POD) and Principal Components Analysis (PCA). This approach allows for a tremendous reduction in computing effort for the process flowsheet. Yi-dong has considered a PCA based approach coupled with an efficient experimental design approach along with a neural network solver to determine an input output model. Using an NETL-based Fluent combustor model, he has developed accurate reduced order models (ROMs) that capture the behavior of the Fluent model over a wide input range, but with require about two orders of magnitude less execution time. As a result, these models are quite suitable to incorporate within FutureGen process flowsheet.

Adam Malacina recently completed his MS thesis and has joined UOP. In his MS thesis he applied and extended Yi-dong's approach to a FutureGen gasifier model, also developed in Fluent. While the gasifier model was somewhat more involved than the combustor model, the PCA-based approach worked very well and led to an accurate reduced order model for further process optimization. This work is described in the preprint listed below. The work on reduced order modeling and optimization will be extended to further 3D PDE applications through the MS work of **Jyoti Swankar.**

Optimal Synthesis of Integrated Gasification Combined Cycle (IGCC) Systems
New developments: Models for air separation unit, multistream exchanger

Student: Ravi Kamath [Ph.D. started Jan 2007]

Ravi is developing a comprehensive synthesis model for IGCC plants, with the possibility of polygeneration and CO_2 sequestration. Integrated Gasification Combined Cycle (IGCC) technology for future power plants has attracted great interest because of its capacity to not only achieve a higher thermal efficiency but also capture CO_2 more economically than a conventional coal-fired plant. However, IGCC technology has higher capital costs than coal-fired plants and is economically viable only if operated with CO_2 capture. Ravi's project aims at evaluating the techno-economic performance of an IGCC plant. We assume that we are given a type (rank, quality, composition, physical state) of coal, net output power, location of site, ambient conditions for utilities like air and water and other requirements like co-production of hydrogen or chemicals and extent of carbon capture. The objective is to determine the optimal structural configuration and operating parameters of the IGCC plant that minimize the investment and operating cost, while meeting the constraints for environmental emissions. An important related decision will be the minimum amount of CO_2 to be captured.

As a first step, Ravi developed a comprehensive superstructure that includes potential alternative technologies. The goal is to determine the optimal configuration and operating parameters for the IGCC flowsheet by formulating a mixed-integer nonlinear programming (MINLP) problem. Because of the large number of alternatives, we intend to apply the methodology developed by Mark Daichendt that involves optimizing the entire flowsheet at different levels of complexity using a combination of aggregated and detailed models. Here, Ravi developed simplified models for coal gasification and for the utility section. For coal gasification he developed a model based on Gibbs energy minimization that can be modified to match the performance of real gasifiers. This is done by adding equilibrium reactions as constraints, or additional specifications to match outlet compositions. He has obtained very good results for the Shell, GE and ConocoPhilips entrained gasifiers. The prediction of the main eight species is in close agreement with published data.

Ravi also developed an MINLP model for combined cycles that extends the MINLP model by Bruno. The basic idea consists of postulating a superstructure for the specified power and heating demands. The superstructure is modeled as an MINLP in which pressures and temperatures of steam, enthalpies, and turbine efficiencies are treated with nonlinear models. For an example with an electricity demand of 500 MW, 2 mechanical power demands, and steam demands at high, medium and low pressure, Ravi was able to obtain good results from the MINLP model that involved 44 0-1 variables, 1275 continuous variables and 1309 constraints.

In the last few months Ravi has concentrated on the development of the flowsheet and optimization model for the Air Separation Unit (ASU), which supplies high pressure oxygen (> 95% purity) to the gasifier and medium pressure nitrogen to the gas turbine. A real industrial flowsheet for air separation involves 2 complex columns which are thermally integrated in such a way that heat load of the condenser of high pressure (HP) column matches that of the reboiler of the low pressure column. Also included in the flowsheet are multiple feeds and side-draws that are heat-integrated using two multi-stream heat exchangers. The step-wise construction of the flowsheet can help in understanding why such a complicated heat integration involving multiple streams is preferred over a simple configuration by evaluating material and energy costs at each step in the flowsheet construction. Since writing rigorous models from the start could lead to convergence problems, Ravi tried to focus on the use of simplified or short-cut type models for the complex distillation columns. Ravi extended the Edmister model for counter-current cascades by replacing some of the poor approximations by more realistic constraints based on physical insight. The result of this work is an aggregate model for a counter-current cascade of trays in a distillation column whose performance closely resembles that of rigorous models of Aspen Plus. Just like the rigorous tray-by-tray model, our proposed model does not require knowledge about key components or about whether it behaves as an absorber or a stripper. Ravi has demonstrated the efficacy of this model using both simulation and optimization case studies. Test problems involve distillation of binary and ternary systems with ideal or mildly non-ideal thermodynamics. In the case of simulation case studies, the outlet conditions at the top and bottom are analyzed for a given set of input parameters (e.g. number of trays, column pressure, reflux ratio etc.). In the case of optimization case studies, the objective is to determine the optimal feed locations and/or optimal number of trays that minimize capital and/or energy costs while meeting the specified purity requirements. Results for the simulation case studies show that the outlet conditions predicted by the aggregate model are in close agreement with that of the rigorous model. For the optimization case studies, a rounding heuristic can be used i.e. the number of stages in the cascades can be relaxed as continuous variables and their optimal value can then be rounded to the nearest integer. In most cases, the integer solution obtained by this rounding heuristic was found to be the same as the integer solution of the MINLP model. Thus, use of integer variables can be eliminated for the aggregate model and its solution provides a good approximation to that of rigorous model (often missing by only one or two trays).

Ravi then started to develop models for the multi-stream heat exchangers (MHEX). It is to be noted that modeling MHEX is not trivial because of two reasons: a) Matches between hot and cold streams are not known *a priori* b) Since the matches are not known; it is not clear how to apply the criterion of minimum temperature driving force. Moreover, MHEX have complex hardware designs and the streams involved typically undergo phase change during heat transfer. There is hardly any simulation or optimization based process models for MHEX available in the open literature which takes care of issues like violation of

minimum temperature driving force or temperature cross-overs. Optimization of flowsheets containing one or more MHEXs can be regarded as a case of simultaneous optimization and heat integration where the inlet and outlet streams conditions of MHEXs are optimized simultaneously along with the rest of the process variables in order to minimize overall cost while satisfying the constraints imposed by external process as well as feasible heat transfer constraints inherent for MHEXs. Ravi has developed a general nonlinear equation-oriented model for MHEX which is based on pinch technology for heat integration. A special feature of the model is its capability to detect phase changes and accordingly calculate enthalpies. Candidate streams which are capable of phase changes are split into three substreams corresponding to superheated (SUP), two phase (2P) and subcooled (SUB) regions. This splitting is based on dew point and bubble point temperatures of the stream that may change during the course of the optimization as pressure and composition of the stream are treated as process variables and can be optimized. From the point of view of heat integration, each of the above substreams can be treated as an independent stream with an associated heat load and inlet and outlet temperatures. The inlet and outlet temperatures of substreams are assigned appropriate values using a disjunctive representation involving Boolean variables (Raman and Grossmann, 1994) where the Boolean variables are associated with the phase of parent stream at the inlet and outlet conditions. The disjunctions can be formulated either as a discrete-continuous model involving binary variables (Lee and Grossmann, 2000) or as a continuous model by solving an inner minimization problem with complementarity constraints (as described in the MPEC project above). Also, when a candidate stream does not change its phase, the inlet and outlet temperatures of irrelevant substreams are manipulated in such a way that the associated heat loads are set to zero. It is to be noted that this representation assumes that the enthalpy of the streams can be approximated as a piecewise linear function of temperature in each of three regions. If necessary, the two phase region in particular can be split further into more segments to improve this approximation. Ravi has demonstrated the capability of this model for MHEX using the PRICO (Poly Refrigerant Integrated Cycle Operations) process for LNG production (Lee et al., 2002). Although the PRICO process is a relatively simple process involving a single mixed refrigerant circulating in a simple cycle, it incorporates most of the components present in more complex LNG liquefaction processes. The proposed model is used within a mathematical programming formulation to determine the optimal operating conditions and composition of mixed refrigerant that minimizes the shaft work required for vapor compression.

Using these equation-oriented models, Ravi is currently implementing the superstructure for the ASU flowsheet in GAMS which can be solved as a simulation problem or also as an optimization problem. Then, he plans to focus on other sections of the IGCC plant such as acid gas cleaning and CO_2 absorption. Both of these projects were presented at the PSE 2009 meeting and preprints of this work are listed below.

Ignacio Grossmann's Group

Cyberinfrastructure for MINLP Optimization

New developments: **New website: http://www.minlp.org**

Student: **Juan Pablo Ruiz [started Jan 2007]**
Collaborators: **Larry Biegler, Nick Sahinidis, Francois Margot, Pietro Belotti (Lehigh)**

With funding from NSF, we have created a beta-version of a cyberinfrastructure environment for virtual collaboration for developing and collecting tools for MINLP, including a library of challenging MINLP test problems, with bibliography, web resources, and information on meetings. The objectives of the project are also to develop algorithms, formulations for predicting tight lower bounds, and open-source software for solving large-scale nonconvex MINLP problems (e.g. Couenne). We also aim to test the software with challenging problems arising in real-world applications, in engineering, operations, finance and biology.

One of the main components of the website is a collection of MINLP problems in which instead of simply providing input files in GAMS, AMPL, AIMMS or similar, we have a library of problems where we introduce them first in their qualitative form by describing the problem statement, presenting one or several formulations with detailed derivations, data for one or several instances, and results for one or several solvers. For each instance input files will be provided. As indicated in the last newsletter we had developed

the following MINLP optimization problems: a) Supply chain inventory problem (You, Grossmann), b) Water treatment network (Ruiz, Grossmann), c) MPEC formulation for some discrete constraints (Baumrucker, Biegler), d) X-Ray diffraction (Smith, Sahinidis), e) Cyclic scheduling (Castro). Two recent additions are a) Unit commitment problem (Zondervan, Grossmann), b) Polygeneration in energy systems (Liu, Pistikopoulos, Liu). Two additional problems are under way by Fengqi You (optimal batch design, Dinkelbach's algorithm). We hope that you have a chance to visit our site in http://www.minlp.org and let us know about your feedback.

Pietro Belotti, a Visiting Assistant Professor at Lehigh, has been developing *Couenne* an open-source code for solving nonconvex NLP and MINLP problems. The goal is to develop both approximate as well as rigorous methods that rely on the use of convex envelopes and bound tightening strategies. The rigorous method relies on a spatial branch-and-bound method for bilinear, linear fractional and concave separable functions. Pietro has written the code CouenneSolverInterface that allows the implementation of various bound tightening techniques, and branching strategies. Last few months have concentrated on extensive testing of branching decisions. We should note that *Couenne* is available in the COIN-OR library: http://www.coin-or.org/projects/Couenne.xml

Algorithms for Nonlinear Disjunctive Programming

New Developments: Redundancy for Strengthening Lower Bounds; New LOGMIP website

Student:	**Pablo Ruiz [started Jan 2007]**
Research collaborator:	**Aldo Vecchietti [Researcher at INGAR]**
	Juan Ruiz

The project of Juan is concerned with the global optimization of non convex Generalized Disjunctive Programs. These problems arise, for instance, in the design of pooling problems, in the synthesis of integrated water treatment networks, or generally in the synthesis of process networks with multicomponent flows. Juan's work has, as a major objective to improve the computational efficiency of disjunctive spatial branch and bound methods by combining the relaxation strategies proposed by Tawarmalani & Sahinidis (2002) for nonconvex MINLPs with the results in the work of Sawaya & Grossmann (2007 to obtain tighter relaxations for Linear GDPs.

The basic approach consists of first relaxing the non convex terms in the GDP using suitable convex under/over linear estimators and the convex nonlinear terms with suitable linear outer approximators Tawarmalani & Sahinidis (2002) and introducing them as part as the disjunctive set. Since the corresponding relaxation leads to a linear GDP problem, the next step then consists of performing basic steps which involve intersecting disjunctions in order to obtain tighter relaxations. Of course there are many options that are possible on how to perform the intersections. To address this issue Juan has developed a set of sufficient conditions under which basic steps are not necessary. Using these propositions as a basis as well as other properties, he has developed a
procedure that relies on the following rules: 1. Basic steps are applied between disjunctions with at least one variable in common (The more variables in common the more tightening can be expected). 2. If non convex terms are outside the disjunctions, apply basic steps by introducing them in the disjunctions (if nonconvex terms are inside disjunctions less tightening can be expected). The solution method then consists in first applying this reformulation procedure, leading to a tight relaxation, then applying the bound contraction method by Juan Zamora, and finally applying a branch and bound procedure similar to the one that Sangbum Lee had developed in which branching is performed first on the discrete variables.

Juan has applied the above procedure to Bilinear GDP and Concave. Following the method described above, Juan has applied his reformulation to several process systems problems, such as the design of wastewater treatment networks, pooling networks, distillation sequences with pooling integration, HEN with discontinuous investment cost and retrofit of HEN. In all these problems there were significant improvements in the lower bounds. This in turn led to a significant reduction in the number of nodes in three of these problems. Juan has written a paper on this work which is listed at the end of the newsletter.

As a direct application of the above framework, Juan is currently developing a technique to strengthen the relaxation of general mixed integer nonlinear programs. The main idea consists in splitting the domain of the nonconvex terms and representing this split with a set of disjunctions. This leads to a nonconvex GDP that can exploit the theory developed to find better relaxations. For the case of Quadratically Constrained Quadratic Programs he can show that this new relaxation is different from what it can be obtained by using traditional techniques such as RLT (Sherali and Alameddine, 1992).

In another interesting line of work Juan he has explored the idea of including redundant equations in the formulation in order to strengthen the lower bounds. The motivation comes from the fact that when nonconvex terms are replaced by convex envelopes this leads to a significant relaxation of the feasible region. This in turn means that constraints that are redundant in the original model may not be redundant in the relaxation. Typical case is in a process network when bilinearities in mixers are replaced by McCormick envelopes. In this case the total mass balance, originally a redundant constraint, becomes non-redundant in the relaxation and hence provides a cut. This work is still preliminary but Juan has tested this idea on 4 problems including 2 electric power networks, one process network and one batch process. The improvements in the lower bounds ranged between 36 and 93%. Among other real case studies, he is using this technique to strengthen the relaxation in a muliperiod blend scheduling problem within a more general framework that combines logic based outer approximation with Lagrangean decomposition. Finally, Juan wrote with Ignacio a review paper on Generalized Disjunctive Programming which was recently submitted for publication.

Aldo Vecchietti: LOGMIP and DICOPT

Aldo has developed at INGAR the LogMIP code, an extension of the GAMS modeling language for posing logic/disjunctive problems. The syntax developed involves the use of IF THEN ELSE statements to represent the disjunctions, including embedded ones. The definition of disjunctions over sets and subsets can also be specified. 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 also automated the logic-based OA algorithm by Metin Turkay, which is suitable for nonlinear GDP process network problems. GAMS is releasing LOGMIP in the new version 22.8 For the corresponding manual see: http://www.gams.com/dd/docs/solvers/logmip.pdf. Aldo has updated the page for LOGMIP. See: http://www.logmip.ceride.gov.ar/ Juan has also been collaborating with Aldo, and has spent part of the summer in Washington DC working with GAMS on what it will be the basis for a further development of Disjunctive Programming solvers (LOGMIP, EMP).

Optimal Synthesis of Integrated Gasification Combined Cycle (IGCC) Systems

New developments: **Manuscript on group method for distillation columns**

Student: **Ravi Kamath [Ph.D. started Jan 2007]**

This is a project that is jointly supervised by Ignacio Grossmann and Larry Biegler.
Ravi is developing a comprehensive synthesis model for IGCC plants, with the possibility of polygeneration and CO2 sequestration. Integrated Gasification Combined Cycle (IGCC) technology for future power plants has attracted great interest because of its capacity to not only achieve a higher thermal efficiency but also capture CO2 more economically than a conventional coal-fired plant. However, IGCC technology has higher capital costs than coal-fired plants and is economically viable only if operated with CO2 capture. Ravi's project aims at evaluating the techno-economic performance of an IGCC plant. We assume that we are given a type (rank, quality, composition, physical state) of coal, net output power, location of site, ambient conditions for utilities like air and water and other requirements like co-production of hydrogen or chemicals and extent of carbon capture. The objective is to determine the optimal structural configuration and operating parameters of the IGCC plant that minimize the investment and operating cost,

while meeting the constraints for environmental emissions. An important related decision will be the minimum amount of CO2 to be captured.

As a first step, Ravi developed a comprehensive superstructure that includes potential alternative technologies. The goal is to determine the optimal configuration and operating parameters for the IGCC flowsheet by formulating a mixed-integer nonlinear programming (MINLP) problem. Because of the large number of alternatives, we intend to apply the methodology developed by Mark Daichendt that involves optimizing the entire flowsheet at different levels of complexity using a combination of aggregated and detailed models. Here, Ravi developed simplified models for coal gasification and for the utility section. For coal gasification he developed a model based on Gibbs energy minimization that can be modified to match the performance of real gasifiers. This is done by adding equilibrium reactions as constraints, or additional specifications to match outlet compositions. He has obtained very good results for the Shell, GE and ConocoPhilips entrained gasifiers. The prediction of the main eight species is in close agreement with published data.

Ravi also developed an MINLP model for combined cycles that extends the MINLP model by Bruno. The basic idea consists of postulating a superstructure for the specified power and heating demands. The superstructure is modeled as an MINLP in which pressures and temperatures of steam, enthalpies, and turbine efficiencies are treated with nonlinear models. For an example with an electricity demand of 500 MW, 2 mechanical power demands, and steam demands at high, medium and low pressure, Ravi was able to obtain good results from the MINLP model that involved 44 0-1 variables, 1275 continuous variables and 1309 constraints.

In the last few months Ravi has concentrated on the development of the flowsheet and optimization model for the Air Separation Unit (ASU), which supplies high pressure oxygen (> 95% purity) to the gasifier and medium pressure nitrogen to the gas turbine. A real industrial flowsheet for air separation involves 2 complex columns which are thermally integrated in such a way that heat load of the condenser of high pressure (HP) column matches that of the reboiler of the low pressure column. Also included in the flowsheet are multiple feeds and side-draws that are heat-integrated using two multi-stream heat exchangers. The step-wise construction of the flowsheet can help in understanding why such a complicated heat integration involving multiple streams is preferred over a simple configuration by evaluating material and energy costs at each step in the flowsheet construction. Since writing rigorous models from the start could lead to convergence problems, Ravi tried to focus on the use of simplified or short-cut type models for the complex distillation columns. Ravi extended the Edmister model for counter-current cascades by replacing some of the poor approximations by more realistic constraints based on physical insight. The result of this work is an aggregate model for a counter-current cascade of trays in a distillation column whose performance closely resembles that of rigorous models of Aspen Plus. Just like the rigorous tray-by-tray model, our proposed model does not require knowledge about key components or about whether it behaves as an absorber or a stripper. Ravi has demonstrated the efficacy of this model using both simulation and optimization case studies. Test problems involve distillation of binary and ternary systems with ideal or mildly non-ideal thermodynamics. In the case of simulation case studies, the outlet conditions at the top and bottom are analyzed for a given set of input parameters (e.g. number of trays, column pressure, reflux ratio etc.). In the case of optimization case studies, the objective is to determine the optimal feed locations and/or optimal number of trays that minimize capital and/or energy costs while meeting the specified purity requirements. Results for the simulation case studies show that the outlet conditions predicted by the aggregate model are in close agreement with that of the rigorous model. For the optimization case studies, a rounding heuristic can be used i.e. the number of stages in the cascades can be relaxed as continuous variables and their optimal value can then be rounded to the nearest integer. In most cases, the integer solution obtained by this rounding heuristic was found to be the same as the integer solution of the MINLP model. Thus, use of integer variables can be eliminated for the aggregate model and its solution provides a good approximation to that of rigorous model (often missing by only one or two trays). Ravi has produced a manuscript on this work which is listed at the end of this newsletter.

Ravi has also developed models for the multi-stream heat exchangers (MHEX). It is to be noted that modeling MHEX is not trivial because of two reasons: a) Matches between hot and cold streams are not known a priori b) Since the matches are not known; it is not clear how to apply the criterion of minimum

temperature driving force. Moreover, MHEX have complex hardware designs and the streams involved typically undergo phase change during heat transfer. There is hardly any simulation or optimization based process models for MHEX available in the open literature which takes care of issues like violation of minimum temperature driving force or temperature cross-overs. Optimization of flowsheets containing one or more MHEXs can be regarded as a case of simultaneous optimization and heat integration where the inlet and outlet streams conditions of MHEXs are optimized simultaneously along with the rest of the process variables in order to minimize overall cost while satisfying the constraints imposed by external process as well as feasible heat transfer constraints inherent for MHEXs. Ravi has developed a general nonlinear equation-oriented model for MHEX which is based on pinch technology for heat integration. A special feature of the model is its capability to detect phase changes and accordingly calculate enthalpies. Candidate streams which are capable of phase changes are split into three substreams corresponding to superheated (SUP), two phase (2P) and subcooled (SUB) regions. This splitting is based on dew point and bubble point temperatures of the stream that may change during the course of the optimization as pressure and composition of the stream are treated as process variables and can be optimized. From the point of view of heat integration, each of the above substreams can be treated as an independent stream with an associated heat load and inlet and outlet temperatures. The inlet and outlet temperatures of substreams are assigned appropriate values using a disjunctive representation involving Boolean variables (Raman and Grossmann, 1994) where the Boolean variables are associated with the phase of parent stream at the inlet and outlet conditions. The disjunctions can be formulated either as a discrete-continuous model involving binary variables (Lee and Grossmann, 2000) or as a continuous model by solving an inner minimization problem with complementarity constraints (as described in the MPEC project above). Also, when a candidate stream does not change its phase, the inlet and outlet temperatures of irrelevant substreams are manipulated in such a way that the associated heat loads are set to zero. It is to be noted that this representation assumes that the enthalpy of the streams can be approximated as a piecewise linear function of temperature in each of three regions. If necessary, the two phase region in particular can be split further into more segments to improve this approximation. Ravi has demonstrated the capability of this model for MHEX using the PRICO (Poly Refrigerant Integrated Cycle Operations) process for LNG production (Lee et al., 2002). Although the PRICO process is a relatively simple process involving a single mixed refrigerant circulating in a simple cycle, it incorporates most of the components present in more complex LNG liquefaction processes. The proposed model is used within a mathematical programming formulation to determine the optimal operating conditions and composition of mixed refrigerant that minimizes the shaft work required for vapor compression.

Using these equation-oriented models, Ravi is currently implementing the superstructure for the ASU flowsheet in GAMS which can be solved as a simulation problem or also as an optimization problem. Then, he plans to focus on other sections of the IGCC plant such as acid gas cleaning and CO2 absorption. Both of these projects were presented at the PSE 2009 meeting and preprints of this work are listed below.

MINLP Synthesis of Separation Systems

New developments: **Optimization of hybrid distillation/membrane columns**

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

This was a short project in collaboration with Lyondell. The motivation is that the separation of olefins (e.g. ethylene, propylene) from paraffins (e.g. ethane, propane) is performed almost exclusively by cryogenic distillation. Since this technology is highly energy intensive, there is a strong economic incentive to explore alternative separation technologies with lower energy consumption. In this project Jose addressed the design and optimization of hybrid separation system consisting of a distillation column and a parallel membrane separation unit. He used the separation of ethylene and ethane as a representative case study for which he developed a mathematical programming approach to optimize and retrofit the hybrid separation system. Due to the complexity of the models, a two stage approach was used. First, Jose developed a shortcut model that allows determining whether the hybrid system could be of interest and the order of magnitude of the energy savings that can be expected. Second, a superstructure optimization approach was developed that uses rigorous models for both the column and the membrane using a process simulator (Unisim.Design) and state of the art MINLP solvers.

The most relevant result that emerged is that the maximum energy savings depend on both the separation capacity of the separator (i.e. selectivity in a membrane) and on the flow to obtain that separation. For a given separation factor, there is a maximum possible energy saved in the column and a minimum flowrate of the permeate in the vapor needed to obtain that separation. The flowrate of the stream withdrawn from the column has a lower impact on the energy saved. Once the economic potential of the hybrid design was established, a rigorous model was developed using a superstructure in a process simulator that includes the distillation column, compressor, cooler and all the potential locations for feeding and withdrawing the streams. A rigorous membrane model was developed in Matlab. The results obtained show an interesting economic potential in the use of hybrid systems in cryogenic separation. In the case study used in this paper, savings up to 30% in energy are possible and around 20% in total annualized cost. The manuscript describing this work is listed at the end of the newsletter.

Water Management Networks in Biofuel Plants

New development: **Generalized models for optimizing integrated water networks**
Post-doctoral fellow: **Elvis Ahmetovic (started September 15, 2008)**

This is a new project by Elvis Ahmetović in which he has been investigating the issue of water consumption in biofuel plants. He has especially concentrated in bioethanol plants for which he has gathered literature and data on water consumption, lost water in cooling towers, water reuse and wastewater treatment in these plants. The objective is to minimize the consumption of freshwater in these plants. He used the mass and energy balance of the Cargill case study on bioethanol developed by Ram Karuppiah, and co-workers as well as closed loops for cooling tower and steam system to minimize water efficiency (gallon of water per gallon of bioethanol produced) in this plant. As the water efficiency that has been reported has been above 3 gallons of freshwater per gallon of bioethanol produced, he has been investigating the concepts of water reuse, regeneration and recycle that can be applied to improve water efficiency in this plant.

In order to achieve this goal, he first developed a general superstructure and a model for the global optimization for the design of integrated process water networks along the lines of Karuppiah's model. The developed superstructure consists of multiple sources of water, water-using processes, wastewater treatment and water pre-treatment operations. The unique features are first, that all feasible interconnections are considered between them, including water reuse, water regeneration and reuse, water regeneration recycling, local recycling around process and treatment units. Second, multiple sources of water of different quality that can be used in the various operations are included. Third, the superstructure incorporates both mass transfer and non-mass transfer operations. His model of the integrated water network is formulated either as a Nonlinear Programming (NLP) and as a Mixed Integer Nonlinear Programming (MINLP) problem for the case when 0-1 variables are included to model the cost of piping and/or selection of technologies for treatment. The MINLP model can be used to find optimal network designs with different number of streams in the piping network. In addition, Elvis proposed to represent the bounds on the variables as general equations obtained by physical inspection of the superstructure and using logic specifications needed for solving the model. In the proposed models he also incorporated the cut proposed by Karuppiah and Grossmann (2006) to significantly improve the strength of the lower bound for the global optimum.

Elvis has also proposed special strategies for solving large scale problems to global or near global optimality. When the objective is to minimize the total network cost without specifying a maximum number of piping connections, the NLP problem is solved first where the 0-1 variables as well as the upper and lower bound constraints are excluded from the model. Once the solution of the NLP is obtained, all zero flowrates are fixed in the network before solution of reduced the MINLP. In the case when a maximum number of pipe segments are specified, the relaxed MINLP problem is solved first. The 0-1 variables of the streams in the network with zero value are fixed at zero and the reduced MINLP is solved in the second stage. The proposed strategies can effectively solve large-scale problems and in most cases, to global optimality. The largest problem solved involved 6 process units, 3 treatment units, 4 freshwater sources, and 3 contaminants. Furthermore, the proposed strategies allow to readily obtain networks of

varying degrees of complexity by limiting the number of piping connections. Elvis has completed a manuscript on this work that is listed at the end of the newsletter.

In cooperation with Mariano Martin, Elvis has also been investigating application of the proposed water network superstructure and the global optimization model to biofuel plants. The results will be published in the next newsletter.

Optimal Design of Biofuel Plants

New development: **Preliminary superstructure for cellulosic bioethanol**

Post-doctoral fellow: **Mariano Martin (started June 1, 2009)**

This is a new project by Mariano Martin, a Fulbright Scholar from the University of Salamanca in Spain, that has as a general objective the synthesis and optimization of biofuel plants. He has started to address the production of bioethanol from using lignocelluloses as raw material. The superstructure consists of four major parts.

The first ones is the gasification of the raw material. Two different technologies have been implemented: (1) Indirect gasification where the combustion of char provides the energy by heating sand which is transferred to the gasifier (2) Direct gasification of the raw material with steam and oxygen, to avoid the dilution of the gas. The gas generated must be cleaned form solids as well as other compounds like Hydrocarbons, NH3, CO2 or H2S generated in the gasification. Furthermore the composition of the gas must be adjusted to a molar ratio of CO : H2 of 1. The hydrocarbons are partially removed in the tar where they are reformed or partially oxidized. In case of working at high pressure, solids are removed in a ceramic filter and later the gas is expanded generating energy. If the indirect lower pressure method of gasification is used, the solids are removed together with NH3 in a wet scrubber and the compressed. The last traces of Hydrocarbons are removed in a PSA system with a bed of Silica gel. At this point the composition is adjusted in terms of CO and H2. In order to do so Water Shift reactor, bypass and PSA for H2 (with a bed of oxides) can be used. The splitting fraction will depend on the performance of the gasifier and the tar reformer.

After the composition adjustment CO2 and H2S is removed. The three technologies considered for this task are (1) the absorption of the sour gases in Monoethyl amine (MEA), (2) A PSA system with a bed of Zeolite 5A and (3) The use of a membrane permeable to CO2 and also using MEA as carrier. Selexol is another possible technology but the solvent is more expensive and the working pressure is also higher that the ones used in the whole flowsheet. This superstructure has two solutions depending on the synthetic path selected. In case of using catalytic synthesis, H2S must be completely removed from the gas due to its poisonous effect on the catalyst. However, bacterial can handle the presence of H2S. Once the gas is purified, two paths are considered: (1) Fermentation path where the syngas is fermented in a stirred tank reactor. Water must be removed. A beer column reduces drastically the amount of water accompanying the ethanol and later four technologies are evaluated to dehydrate the ethanol: (1) Distillation to the azeotropic point, (2) Adsorption in corn grits (3) The use of molecular sieves with a bed of Zeolite 13 X and (4) perevaporation. The second path for the synthesis of ethanol is the high alcohols synthesis production. A catalysts based on the one used for the production of methanol is used. The purification of ethanol is carried out using a sequence of distillation columns. Two sequences considered, direct and indirect.

Mariano is at the stage where he has modeled the above superstructure with shortcut models in GAMS. Preliminary results will be reported in the next newsletter. Finally, Mariano has co-authored a paper with Ramkumar Karuppiah on a heuristic approach for reducing dimensionality in two-stage stochastic programming models. That paper is listed at the end of the newsletter.

Design for Sustainability

New development: Completed manuscript for hydrogen supply chains for vehicle use

Post-doctoral fellow: Gonzalo Guillen [University Roviri e Virgili, Tarragona]

The aim of this work has been to develop tools based on mixed-integer modeling techniques that can facilitate the adoption of more sustainable alternatives for a wide range of problems arising in PSE.

Gonzalo developed a model for the design of sustainable chemical supply chains that takes into account the uncertainty associated with the impact assessment model. The environmental impact is measured through the Eco-Indicator 99, which has been developed for Life Cycle Impact Assessment. This strategy covers the entire life cycle of the product, process or activity, including extracting and processing of raw materials; manufacturing, transportation and distribution; reuse and maintenance; recycling and final disposal. The variability of the Eco-Indicator 99 under uncertainty is controlled by reducing the probability of exceeding a specified target level. Gonzalo formulated this problem as a bi-criterion MILP. The objectives are maximizing the net present value (NPV) and minimizing the probability of an Eco-Indicator 99 value below a given target. The inclusion of the latter criteria gives rise to a chance-constraint whose deterministic equivalent is analytically obtained. The resulting multi-objective model is reformulated as a parametric MILP. The probability associated with the Eco-Indicator 99 is treated as the main objective whereas the NPV is constrained to be greater than an epsilon value. By parametrically changing this epsilon value, the entire set of Pareto optimal solutions of the problem can be generated. The parametric MILP is solved by decomposing it into two sub-problems and iterating between them. The first sub-problem is a parametric LP, while the second sub-problem is a MILP where the epsilon parameter is relaxed as a variable. This MILP includes parametric cuts and logic cuts that are derived from previous explored solutions. Using the proposed model and solution procedure Gonzalo solved several case studies related to a supply chain in Tarragona, Spain, with possible expansions and distributions in Central Europe. The results show how environmentally friendlier solutions in the face of uncertainty in the damage model can be obtained by systematically trading-off the economic benefit of the process. The proposed decomposition strategy can provide the whole set of Pareto optimal solutions in a fraction of the CPU time required in the standard ε-constraint method. The manuscript on this work appeared in *AIChE J*.

Gonzalo extended this technique to account for uncertainty in the coefficients that are used in the damage model of the Eco-indicator 99. The difficulty here is that the approach of using the chance constraint for minimizing the probability of an Eco-Indicator 99 value below a given target, gives rise to a nonconvex problem. The resulting bi-criterion non-convex MINLP has been solved by applying the epsilon constraint method. To guarantee the global optimality of the Pareto solutions, Gonzalo developed a novel branch and bound strategy that exploits a number of mathematical properties such as relating the original objective which is non-convex to a simplified objective that has a unique solution. Furthermore, he has also shown how to obtain in a clever way a tight upper bound. He rigorously proved several properties that form the basis of the algorithm. The method was also successfully applied to similar problems as the one in the first paper. The manuscript on this work has been submitted to *Computers & Chemical Engineering.*

In recent work Gonzalo has addressed with Fernando Mele the design of hydrogen supply chains for vehicle use with economic and environmental concerns. The work is based on a case study considered by Almansoori and Shah (2006) in which they considered the cost of these supply chains. The problem is as follows. Given a set of available technologies to produce, store and deliver hydrogen, the problem consists of determining the optimal design of the production-distribution network capable of satisfying a specified hydrogen demand. The design task is formulated as a bi-criterion MILP, which simultaneously accounts for the minimization of cost and environmental impact. The environmental impact is measured through the contribution to climate change made by the hydrogen network operation. The emissions considered in the analysis are those associated with the entire life cycle of the process, and are quantified according to the principles of Life Cycle Assessment (LCA). To expedite the search of the Pareto solutions of the problem, Gonzalo used a bi-level algorithm in the spirit of Ramesh Iyer's work. The main result that emerged from the case study is that one can sacrifice a modest amount in the economics so as to improve the

environmental impact. This was done by replacing steam reforming by biomass gasification and not using compressed gas for storage. The manuscript that has emerged from this work was submitted to *AIChE J.*

Finally, for the FOCAPD-2009 meeting Gonzalo co-authored a review paper on the scope of mathematical programming techniques in the synthesis and planning of process systems. A reprint of that paper is enclosed with the newsletter.

Design and Planning of Deep-Water Oilfield Development under Uncertainty

New Developments: **Scenario tree generation for gradual uncertainty resolution**

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

Bora Tarhan successfully defended his Ph.D. exam in April and will join ExxonMobil, Upstream Research Center in Houston. His project dealt with the design and planning of gas and oil fields under uncertainty.

As a first step, Bora addressed the problem where a network of candidate processes is given over a specified time horizon described by multiple time periods in which product demands are specified. The major uncertainties are involved in the yields of each process, which are described by discrete probability distribution functions. 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, 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 of 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 mixed-integer/disjunctive programming model that is composed of scenario linking and non-anticipativity constraints. For simplicity he assumed that the time required for a pilot plant study corresponds to one time period. To solve this problem Bora developed a dual Lagrangean branch and bound method.

For the deep-water oilfield development problem, Bora has considered a number of reservoirs where each contains several possible well sites. Some of these have to be drilled and exploited for oil over a planning horizon. The oil field infrastructure can be composed of Floating Production Storage and Offloading (FPSO) and/or Tension Leg Platform (TLP) facilities. The FPSO can be either a small FPSO, converted from a retiring oil tanker, or a large FPSO, newly constructed grassroots facilities. An FPSO can produce, store and offload the produced oil to other tankers. Unlike FPSO, a TLP cannot produce oil; it possesses only drilling and oil recovering capability. TLP and FPSO facilities can be connected through pipes. There are two options for drilling wells: sub-sea well or TLP well. Drilling ships are used to drill sub-sea wells, so there is no need to have an FPSO or a TLP facility present to drill a sub-sea well. A sub-sea well has to be connected to an FPSO facility, whereas a TLP well has to be connected to a TLP. The problem consists of selecting investment and operation decisions such as selection of the type, location of facilities, time to build them, selection of wells to drill, the time to drill each well, time to connect each well to the facilities and production from the wells. The uncertainties are in the sand quality, size of the reservoir and breakthrough time. The goal is to maximize the expected net present value of the project.

Bora has developed in cooperation with Vikas Goel from ExxonMobil an MINLP model with a reservoir model where the oil rate decreases linearly or nonlinearly, and the water-to-oil ratio follows a nonlinear function with the cumulative oil production. In the proposed model the facilities and wells of the original problem are aggregated. Instead of deciding which well to drill or which facility to build, the decisions are how many wells or facilities to build. To account for the fact that uncertainties are not revealed immediately, Bora incorporated a number of rules that specify when the uncertainty is revealed, either in terms of number of items (e.g. number of wells) or in terms of time of production. Because of the aggregation, variables for connection of facilities and wells are disregarded, and lengths to wells are underestimated in order to guarantee that the model predicts an upper bound on the detailed model. This model is similar to the process networks model with the exception that each scenario is a non-convex MINLP. The steps of the algorithm are essentially the same, except that each subproblem is solved using

BARON as the global optimization algorithm. Since this greatly increases the computational expense Bora has developed a hybrid scheme where only the first and last subproblems are solved to global optimality, while the intermediate iterations are solved with the outer-approximation algorithm (OAA in AIMMS). He considered first the case of one reservoir with linear production profile over a 10 year period. The best solution from the stochastic program had an expected NPV of $\$6.37 \times 10^9$ which is higher than the expected value (mean value) solution ($\$5.81 \times 10^9$). In the optimal solution, the model predicts start building two small FPSO facilities, one TLP and drilling 9 subsea wells. Depending on the future outcomes the investments range from building up to 21 TLPs and 8 additional small FPSOs (best case) to only drilling subsea wells (worst case). Bora also solved a problem with a nonlinear profile in which the maximum net present value of the stochastic program obtained was $\$4.59 \times 10^9$ versus $\$3.76 \times 10^9$ of the expected value. As for computational requirements the first problem required 3.6 hrs of CPU-time with the hybrid scheme vs. 9 hrs when global optimization is applied at each iteration. In the second problem the computing time was reduced from 120 hrs down to only 2.6 hrs. Bora produced a manuscript on the hybrid strategy that is listed at the end of the newsletter.

In addition to the above work, Bora has investigated the problem of how to most effectively update the successive MILPs that are involved in the solution of the Lagrangean subproblems. An interesting feature is that only the coefficients in the objective function are changed at each iteration. Bora has developed a method that relies on using concepts of sensitivity analysis for MILP and that have been developed by John Hooker. Basic idea is that one can develop a set of inequalities to predict changes in the objective for changes in the coefficients of the objective. These inequalities are applied at terminal nodes of the branch and bound tree to predict the maximum change in the objective. Bora has produced a working paper that we hope to complete by the next newsletter.

Finally, Bora has proposed an algorithm for generating scenario trees for multistage stochastic programs involving endogenous uncertainties and gradual uncertainty resolution. The algorithm iteratively optimizes a non-convex nonlinear programming model to generate the resolution profiles from the root node towards the leaves. In the nonlinear program the goal is to minimize the skewness and kurtosis distances between the prior and posterior distributions, while satisfying constraints related to Bayesian reasoning and propositions presented in Dias (2002). A crucial point for generating resolution profiles is to decide on the number of steps for uncertainty resolution, the amount of uncertainty reduction at each step, and the number of outcomes (news) at each step. Once the resolution profile is generated, it can be converted to a scenario tree. Bora successfully demonstrated the proposed algorithm on three examples for generating resolution profiles and scenario trees for yield of a process and reservoir size of an oil field. Bora has written a manuscript on this work which is listed at the end of the newsletter.

Solution Strategies for Multistage Stochastic Programming

New Developments: **Reduction scheme for non-anticipativity constraints**

Students: **Vijay Gupta (Ph.D. started January 2009)**

Vijay Gupta, a new PhD student, has started to address the effective solution of Multistage Stochastic Programming problems with endogenous parameters. His long term goal is to develop effective algorithms for problems that involve a very large number of scenarios.

As a first step he has considered a multistage stochastic programming model for the long-term planning of process networks considering endogenous uncertainty in process yields. The key issue with this model is that the model size increases exponentially with increase in the number of uncertain parameters and/or its realizations due to the presence of non-anticipativity constraints in the model. Therefore, the problem either may take very long time or even become intractable to solve directly using commercial solvers. To address this issue, Vijay has proposed a theoretical property that when combined with previous results by Vikas Goel, significantly reduces the problem size. The property specifically states that the maximum number of scenario pairs (s, s') required to represent the non-anticipativity are $p(S - S^{p-1/p})$. As an example, in a problem involving 9 scenarios for 2 uncertain parameters 72 scenario pairs for the non-anticipativity constraints are required for the original model. With Vijay's approach that can be reduced to only 12 pairs.

In this way the reduced model can be solved directly in reasonable time compared to the original model. However, even with the proposed reduction scheme one might generate problems that prove to be too large to be solved directly. Therefore, Vijay has proposed two solution strategies to handle large-scale problems in this class. The first strategy is a time constraint heuristic approach where the non-anticipativity constraints are only included up to a pre-specified time period instead of the complete planning horizon. The resulting model turns out to be significantly smaller than the original one and provides the global optimum if no investments take place beyond the prespecified time. The second strategy is a Lagrangean decomposition algorithm that decomposes the problem into scenarios. The lower bound in this algorithm is obtained by solving the Lagrangean relaxation of the problem and the upper bound is generated by using a heuristic based on the solution of the relaxed problem. Preliminary numerical results for a process network have been very encouraging and shown to be significantly faster than the full-space method.

Multisite Planning and Scheduling of Multiproduct Plants

New developments: **Numerical and analytical comparison of Spatial vs. Temporal Lagrangeandecomposition.**

Students: **Sebastian Terrazas Moreno [Ph.D. started on Jan 2008]**
Philipp Trotter [RWTH-Aachen student, Jan 2009 – June 2009]

Philipp and Sebastian worked on numerical and analytical comparisons of temporal and spatial decomposition schemes on a production and distribution planning problem. They also exploited the economic interpretation of the Lagrange multipliers of both decompositions in order speed up the convergence of the Lagrangean duals. They dealt with a model that involves a network of continuous multiproduct manufacturing sites that supply a set of common products to a variety of markets. The planning horizon spans several months, adding a temporal dimension to the spatial distribution given by the multi-site network. In order to make a representative numerical study, Phillip used different production models to describe the manufacturing sites, starting with an LP model similar to the capacitated lot sizing problem, and finishing with a MILP model that included production set-up times and costs. He also ran different problem instances where he varied the production capacities, product demands, product prices and costs. Philipp looked at the duality gap between the spatial and temporal decomposition and the original (full space) problem. Using 6 instances of a problem that involved 6 time periods, 3 products, 3 production sites, and 3 markets, spatial decomposition resulted in an average gap of 3% while temporal decomposition resulted in a 1% gap. Furthermore, using a cutting plane algorithm, temporal decomposition converged, in average, in 1500 iterations, while spatial decomposition took 3500 iterations. One of Philipp's main contributions is a set of algorithms that bounded the optimal value of the Lagrange multipliers in spatial and temporal decomposition. The bounds correspond to the range of possible transfer prices in the decomposition schemes. In order to identify this price range it was necessary to identify each time period in the model as limited by the market demand or limited by the production site capacity. By using Philipp's algorithms, the average number of iterations required for solving the 6 problem instances mentioned above was reduced significantly. The number of iterations went from 3500 to 500 for spatial decomposition and from 1500 to about 450 in temporal decomposition.

Finally, Sebastian worked on a theoretical comparison of the strength of the bounds provided by temporal and spatial decomposition. He used the technique of Fourier-Motzkin elimination to project both decomposed formulations onto the space of the integer variables and the product sales. This idea revealed that the feasible region of temporal decomposition is contained in the feasible region of spatial decomposition. In the case where the optimal solution involves the maximization of the sales, this comparison rigorously shows the superiority of temporal decomposition. There is work in progress to try to extend this result to the case of profit maximization, where sales of all products are not necessarily maximized.

Integrated Chemical Sites Subject to Discrete and Continuous Uncertainties

New developments: **Bi-criterion MILP formulation for the optimal design of a reliable integrated chemical manufacturing site**

Student: **Sebastian Terrazas Moreno [Ph.D. started on Jan 2008]**

We have worked on this project in close collaboration with John Wassick and the Process Optimization group at The Dow Chemical Company. During the last months we worked on developing an optimization formulation for the design of reliable integrated chemical manufacturing sites, subject to random process failures and fluctuations in supply and demand. Thanks to our collaboration with Dow we were awarded a research grant by *Imagine That Inc.* that consists of a license for Extendim. This modeling software is used for continuous processes affected by discrete events (e.g. component failures). Extendim, which is routinely used in the Process optimization group at Dow, allowed us to compare the predicted optimization results with those obtained by the simulator.

The bi-criterion MILP formulation developed for the optimal design of an integrated site maximizes the *expected stochastic flexibility* (E(SF)) and minimizes the capital investment. The E(SF) is a probabilistic measure of the system's ability to tolerate continuous and discrete uncertainties. The set of Pareto-optimal solutions are obtained by solving the proposed problem repeatedly for different values of available capital investment. This is equivalent to applying the ε-constrained method to the bi-criterion optimization problem. The main design decisions considered are (i) total capacity, and set point for intermediate storage tanks, (ii) extra capacity addition to existing processes, and (iii) addition of parallel processing units. The formulation includes some novel features. It uses Markov chains and basic random process theory to integrate the effect of intermediate storage to the framework for evaluating and optimizing expected stochastic flexibility E(SF). It also proposes an approach for integrating superstructure optimization in the determination of optimal E(SF) in the design of process networks.

Sebastian tested the optimization formulation on a small process network consisting of 4 processes and 3 chemicals, and also on a section of an integrated process provided by Dow. In the first case study the set of Pareto-optimal solutions go from a value of 0.87 to a value of 0.96 through the addition of storage tanks and extra processing capacity. An E(SF) of 0.98 or more was only achievable by addition of parallel processing units in the plants of the integrated site. The second case study involved multiple failures for each plant in the integrated site; some of them were partial failures, causing only a reduction in processing rate. As a consequence the optimal design for E(SF) up to 0.90 included multiple parallel units and no storage tanks. Further increases up to 0.98 included intermediate storage tanks after some of the plant in the integrated site. The simulation of Pareto-optimal designs of the second case study yielded a differences of 0 to 0.05 when compared against the E(SF) predicted by the optimization formulation.

Design and Operations of Responsive Supply Chains

New Development: **Analysis of stochastic inventory management in terms of responsiveness**

Student: **Fengqi You [Ph.D. started Jan 2006]**

The goal of this project, which is being performed 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 and inventories across the supply chain. The motivation is that most optimization models assume that material can be transferred instantaneously. In that way response times that are a function of safety stocks are not taken into account. It is our major goal to establish the trade-offs between economics and deterministic and probabilistic response times or lead times.

As a first step, Fengqi addressed the long term design problem of a supply chain, for which he developed a superstructure model with dedicated and multiproduct continuous plants. The time horizons considered are

of the order of years, and no inventories are considered (worst case for response). The problem was posed as a bi-criterion optimization problem in which the objectives are to maximize net present value and to minimize lead time. To reflect lead times for different choices of topologies Fengqi considered constraints that measure the duration of the longest time path of chemical flows from a supplier to a customer by way of manufacturing sites. The proposed constraints involve transportation times and residence times in processes. For dedicated plants the times are simply constants, while for multiproduct plants they correspond to cycle time plus residence time minus its processing time. For the case of multiproduct plants, the model leads to a nonconvex MINLP problem. Fengqi obtained results on a production network for polystyrene resins that involves a dedicated process (styrene), and two multiproduct plants (solid polystyrene and expandable polystyrene). Three potential plant sites are considered, with two suppliers, and up to 5 customers. The solution involving shortest lead time of 8.85 days had an NPV of $158 million, while the longest lead time was 14.42 days at a much higher NPV of $1,261 million.

Fengqi extended the above problem to a probabilistic model for stockout. Instead of using a deterministic lead time that only relies on transportation and production times with zero-inventory, Fengqi proposed an expected lead time that represents the expected value of time delays incurred by transportation and production across the supply chains, and accounting for inventories in the distribution centers. This expected lead time is then used as a quantitative measure of supply chain responsiveness. This probabilistic model for the safety stock levels accounts for demand uncertainty. This probabilistic constraint is reformulated as deterministic constraints. Fengqi obtained analytical expressions for triangular and normal distributions of the demands. The bi-criterion optimization model was solved with the ε-constraint method, but Fengqi developed a hierarchical algorithm for the solution of the resulting large-scale MINLP by decoupling of the decision-making levels (strategic and operational). Fengqi solved two examples related to the styrene problem described above. The results show that small changes in expected lead time can lead to significant changes in the net present value and the network structure, which in turn suggests the importance of integrating responsiveness into the design and operations of process supply chain network. An interesting by-product of the model is a trade-off curve of safety stock versus expected lead time, which provides very useful information. Fengqi's manuscript reprint is included in this newsletter.

Fengqi has also analyzed the project on multi-echelon stochastic inventory management from the point of view of responsiveness, and concluded that the maximum guaranteed service time is also a measure of responsiveness for supply chains with multi-echelon inventories. Comprehensive analysis and comparison between the two responsiveness measures show that the maximum guaranteed time, which accounts for the optimal safety stocks in each stage of a multi-echelon supply chain, represents an upper bound to the expected lead time.

Supply Chain Optimization under Uncertainty

New Development: **MILP model for capacity planning with reactor transformation and construction lead time**

Student: **Fengqi You [Ph.D. started Jan 2006]**

As indicated in the last newsletter, this was a collaboration project with Dow Chemical in the context of the Enterprise-wide Optimization. The major goal was to develop optimization models and algorithm for chemical supply chain optimization under various types of uncertainties and risks. Based on an internship at Dow Chemical in Midland, Fengqi addressed the risk management for supply chain operations under uncertainty. In this work, Fengqi worked with John Wassick to develop a two-stage stochastic linear programming approach for the tactical planning of a global multi-product chemical supply chain that is subjected to uncertainties in production reliability and customer demands. Monte Carlo sampling and the associated statistical methods are applied and incorporated into the stochastic programming model to avoid the large number of scenarios required. A simulation framework was also developed to assess the potential improvement of using stochastic programming in the supply chain planning process compared with traditional deterministic approaches. The results of the case study show that on average cost savings of 5.70% could be achieved by using the stochastic programming model on a monthly basis. To solve the large scale case study effectively, a multi-cut L-shaped solution method is developed that can achieve

significant savings in CPU times. To explicitly consider the risks included in the global supply chain planning process, Fengqi studied four risk management models by using different risk measures. A real world case study was presented to demonstrate the effectiveness of the proposed models and algorithms. Computational studies suggest that probabilistic financial risk management model and downside risk management model are more effective in reducing high cost risk compared with the popular variance management and variability index management models. Fengqi has completed a manuscript on this work which has been accepted for publication and is listed at the end of the newsletter.

As a second step, Fengqi has been considering a project on capacity planning with reactor transformation, which is also provided by Dow Chemical in the context of the Enterprise-wide Optimization. In this problem, we are given a production-distribution system with a number of production sites and customers. Each production site has some production trains. We are also given a number of products that can be categorized into a few product families. There are some types of production trains available, and each type of production train can produce a certain given product family. The actions of capacity modification includes adding a new production train in a new or existing production site, removing an existing production train, and convert an existing production train from producing one product family to producing another product family. Construction lead times for each capacity modification actions are given and should be taken into account. Fengqi has developed an MILP model for the deterministic case. A resulting challenge is that the MILP model has a large number binary variables and logic constraints due to the "reactor transformation" constraint. Fengqi is now working on developing an efficient algorithm to solve the large scale MILP problem. Fengqi is also working on is to address demand uncertainty for this problem.

Integrated Supply Chain Design and Stochastic Inventory Management

New Development: **Large-scale supply chain design with multi-echelon stochastic inventory**

Student: **Fengqi You [Ph.D. started Jan 2006]**

Fengqi has been working on a classical operations management problem for joint location-inventory problem inspired by the work of Shen, Coullard, and Daskin (2003). The problem is as follows. The locations of the supplier and the customers are known and the distances between them are given. The supplier to customers lead time is assumed to be the same for all the customers. A number of candidate sites are given to locate the distribution centers (DC), and there are fixed setup costs when distribution centers are established. Each customer has a normally distributed demand which is independent of other customers' demands. Each DC can connect to more than one customer, but each customer should be only assigned to exactly one distribution center to satisfy the demand. Linear transportation costs are incurred for shipments from supplier to DC and from DC to customer. Most of the inventory in the network is held in the DCs, where the inventory is managed with a (Q, r) policy with type I service. Inventory costs are incurred at each DC and consist of working inventory and safety stock. The customers only maintain a small amount of inventory whose costs are ignored. The objective is to determine how many DCs to locate, where to locate them, which customers to assign to each DC, how often to reorder at the DC, and what level of safety stock to maintain to minimize the total location, transportation, and inventory costs, while ensuring a specified level of service. Fengqi first reformulated the model as an MINLP problem. Using its convex relaxation model for preprocessing, he developed a local optimization heuristic method to obtain near-global optimal solutions very quickly. Based on this model, Fengqi also proposed a Lagrangean relaxation and decomposition algorithm for the global optimization of the model. He obtained numerical results for examples ranging from 33 to 150 customers. The reprint on this work is included in this newsletter.

Fengqi extended the above problem for supply chains with multi-echelon inventory systems in the presences of uncertain customer demands. By using the guaranteed service approach (Graves and Willems, 2000) to model the multi-echelon stochastic inventory system, the stochastic nature of the problem is captured and imbedded into an equivalent optimization model for simultaneously optimizing the transportation, inventory and network structure of a multi-echelon supply chain under demand uncertainty. The model determines the supply chain design decisions such as the locations of distribution centers (DCs), assignments of each downstream node to its upstream node, shipment levels in each arc of the supply chain

network, and inventory decisions including the pipeline inventory and safety stock in each node of the supply chain network. The model also captures risk-pooling effects by consolidating the safety stock inventory of downstream nodes to the upstream nodes in the multi-echelon supply chain. Fengqi first formulated this problem as an MINLP with a nonconvex objective function including bilinear, trilinear and square root terms. By exploiting the properties of the basic model, Fengqi reformulated the problem as a separable concave minimization program. A tailored spatial decomposition algorithm based on Lagrangean relaxation, piecewise linear approximation and the model property is developed to obtain near global optimal solutions (below 1% gap) with reasonable computational expense. Two examples on industrial gases supply chain and performance chemical supply chain are presented to illustrate the applicability of the proposed model. Computational examples for industrial gas supply chains with up to 5 plants, 100 potential distribution centers and 150 customers are presented to illustrate the performance of the algorithm. Fengqi' manuscript is listed at the end of this newsletter.

Stochastic Vehicle Routing and Tank-sizing

New Development: Continuous approximation model for capacitated inventory-routing problem

Students: **Fengqi You [Ph.D. started Jan 2006]**
Elisabet Capon [UPC, Barcelona, Sept-Nov 2008]

This is a project in collaboration with Praxair in the context of the Enterprise-wide Optimization. The objective is to optimize asset allocation in the merchant liquid supply chain by incorporating operating decisions. Specifically, given is a set of customers over a long time horizon (typically 5 years). The problem is to determine the optimal fleet and storage capacity allocation over time with the objective of minimizing capital and operating costs. Fleet capacity can be reallocated and increased in the short term by converting trailers from one product to another and/or by hiring third party carriers and in the long term by acquiring new fleet. Storage capacity can be modified by relocating and installing new tanks at storage facilities and at customers. An inventory of discrete size tanks may be available. A major feature of this problem is that Praxair manages inventory for the customers, i.e. it determines who receives a delivery each day, by which route and what the size of that delivery is. Thus, the distribution planning problems associated with such vendor managed re-supply policies are known as inventory routing problems (IRP). The typical objective of an IRP is to minimize operating (distribution and inventory) costs. Even though the IRP is a long-term problem, almost all proposed solution approaches solve only a short-term version of the problem to make it easier.

To integrate the long term strategic tank sizing decision with the short term routing decisions, Fengqi developed a continuous approximation model for this problem. The basic idea to approximate the capacitated vehicle routing or delivery cost in the strategic level, so as to tradeoff the inventory capital cost (tank sizing). Computational results on a toy problem have shown that the CPU time can be reduced from around 20 minutes by using the detailed integrated model to 20 seconds by using the continuous approximation model with the same optimal solution on tank sizing. To improve the computational efficiency of the detailed routing problem, Elisabet and Fengqi have developed a simultaneous route selection and tank sizing model. The model still captures the tradeoff between capital cost of tank sizing and the operating cost of vehicle routing, while simultaneously predicts the optimal tank size for each customer and the routes to be used in the detailed routing. Using only the routes selected by this model, the detailed routing problem can be solved effectively without the need to explore all the alternative routes between customers. Computational study of a toy problem shows that this method can save more than 20% CPU time for solving the detailed routing problem.

Fengqi is now working on the stochastic version of this problem. A novel computational framework is developed to address customer demand uncertainty. By integrating the stochastic inventory approach with continuous approximation, the proposed computational framework simultaneously predicts the optimal tank sizing decisions and optimal safety stock levels for all the customers after solving the upper level problem. The detailed vehicle routing decisions are then obtained by solving the lower level problem for each time period and each customer cluster. Uncertainties from the adding and losing customers are currently under

investigation by using stochastic programming approach. An efficient algorithm to reduce the computational effort of the resulting large scale stochastic integer programming is also being developed.

Optimal Scheduling of Crude Oil Operations

New development: **Integration of CP for symmetry breaking constraints**

Student: **Sylvain Mouret [Ph.D. started Jan 2007]**

Sylvain is working on an Enterprise-wide Optimization project funded by Total through the collaboration with Pierre Pestiaux. The specific problem that Sylvain is addressing is the scheduling of crude oil operations in the front-end of a refinery that is composed of crude marine vessels, storage tanks, charging tanks and CDUs. Crude vessels unload crude oil into storage tanks during a time window depending on the arrival time to the refinery. These crude-oils are then mixed into charging tanks before being distilled by CDUs which separate the charged oil into fractions such as gas oil, gasoline, kerosene, heating oil and residues. Given arrival times of marine vessels, capacity limits of tanks, flow rate limitations, initial key components concentrations in vessels and tanks, components concentration ranges as part of distillation specifications, demands for each mixed oil, and a time horizon, the objective is to determine time and volume variables of all crude-oil transfer operations in order to maximize the gross margins of distilled mixed oil.

Sylvain has developed a novel continuous time model for this scheduling problem that relies on the idea of postulating a given potential number of priority-base slots. The proposed approach consists of assigning specific transfer operations to the ordered set of slots. The objective used is to maximize the gross margins of crudes that need to be processed to satisfy given demands. By introducing 0-1 variables for assignments, and continuous time, volume and level variables, and imposing precedence constraints that enforce non-overlapping operations (e.g. inlet and outlet of a given tank), the problem can be formulated as an MILP provided the constraints on compositions for blending are relaxed. Once the solution is obtained for this problem, an NLP subproblem is solved with fixed 0-1 variables to enforce the composition constraints. This yields an upper bound, which surprisingly Sylvain has found to be very tight, and in many instances with zero-gap. This is of course is only true for the objective of maximizing the gross margins of distilled mixed oil.

One feature in the proposed MILP model, however, is that it has many degenerate or "symmetric" solutions which leads to the enumeration of a larger number of nodes. Sylvain has addressed the symmetry challenge by using a regular language, and its corresponding Deterministic Finite Automaton (DFA), in order to restrict the possible sequences of operations assigned to the set of time-slots. This restriction is can then be added to the model under the form of linear network flow constraints as explained in Côté et al. (2007). Sylvain has applied this solution approach to several problems from the Lee et al. (1996) paper obtaining very encouraging results. In the smallest problem the proposed method is one order of magnitude faster than DICOPT and two orders of magnitude faster than BARON. As for the solution of the four problems, in three of them the gap was 0%; the one that was not had a gap of 3.3%. The computing times ranged between 2 sec and 82 sec. The article describing this work is listed in this newsletter. It will be published in Industrial and Engineering Chemistry Research in 2009.

Sylvain has also developed an integrated hybrid approach using CP to handle the logic constraints including the symmetry-breaking constraints. This approach consists in use using inference techniques at each node in order to extend the branching decisions to more than one variable whenever it is possible. The hybrid approach has been tested on the 4 instances of a crude-oil operations scheduling problem from Lee et al. (1996.) The results show that, even though the hybrid approach is slightly less effective in terms of reducing the search space, it leads to 60% average improvement in CPU time. This is due to the fact that constraint propagation of logic constraints is much cheaper than solving the node relaxation of a LP containing complex logic constraints. The largest problem had 3 vessels, 6 storage tanks, 4 charging tanks and 3 CDUs. Postulating 30 slots the problem was solved in 560 sec (21 nodes) using the pure MILP approach while it was solved in 146 sec (91 nodes) using the hybrid MILP-CP approach. The integration of CP has been taken one step further by using it in order to strengthen the linear relaxation of the MILP.

CP inference techniques have been used, at each node, in order to get tight bounds of continuous variables involved in bilinear terms. These tight bounds can then be used to generate McCormick cuts (based on McCormick under and over estimators of bilinear terms). Sylvain used this approach on the Lee et al. (1996) problems where the objective is to minimize logistics costs, including storage costs. In continuous-time formulations, storage costs appear in the objective function as bilinear terms (volume * storage duration), thus resulting in poor linear relaxations (relaxation gap over 100%). The use of CP has allowed reducing the average optimality gap from 14% to less than 4% while keeping the computational expense small (CPU time increase by 9%). A copy of this manuscript is enclosed with this newsletter.

Finally, Sylvain, is also developing generalizations of scheduling models beyond the crude oil problem, based on representations that range from single-operation and multiple-operation sequencing. The goal is to let scheduling modelers define high-level parameters to describe any problem which can then be used in very different yet comparable time representations and corresponding mathematical models. This principle has successfully been applied to Constraint Programming where scheduling problems are described using the Resource-Activity paradigm. Many real-world constraints can be modeled while powerful CP filtering algorithms have been developed to efficiently solve these problems. The same approach could be brought to mixed integer (non)linear programming where tight and/or compact formulations are automatically generated from a high-level description of the scheduling problem.

Planning of Refinery Operations

New development: Modeling and testing of steam stripping column

Student: Abdulrahman Alattas [Ph.D., started Jan 2007]

Abdulrahman's project is a joint collaboration with BP through Ignasi Palou-Rivera in the Enterprise-wide Optimization project. The major objective is to develop refinery planning models that incorporate nonlinear process models, in contrast to the common fixed yield models that lead to robust LP models that are prevalent in industrial practice (e.g. PIMS).

The specific problem that Abdulrahman is addressing is for complex refinery configurations for processing heavy crudes. The crude is introduced into the crude distillation unit (CDU) that can include the atmospheric distillation column and the vacuum distillation column and produces the first cuts of the crude. These include the overhead fuel gas, straight-run naphtha, straight-run gasoline, straight-run light distillate, straight-run gas oil and the bottom residue. Along with the CDU, the configuration of interest includes the following process units: naphtha reforming unit that produces

reformed gasoline and fuel gas from straight-run naphtha, catalytic cracking unit that produces fuel gas, gasoline and fuel oil from straight-run light distillate and straight-run gas oil, residue hydrotreating unit that treats the bottom residue to blending quality, and product blending units that combine different intermediate product streams to produce the desired final products: premium gasoline, regular gasoline, diesel, fuel oil and residue. The objective of the planning model is to determine the types, quantities and mixing strategies for the different crude oils available for purchase, so that the refinery will meet the objectives of maximizing profits while meeting specific demands over a specified time period. Abdulrahman implemented both fixed-yield models and swing-cuts models in order to assess their relative benefits. The swing cuts model, which can also be formulated as an LP, can be thought of a model that has the flexibility of transgressing the fixed boundaries of the fixed yields models within certain limits. In a specific instance Abdulrahman found that the swing cuts model can predict a solution with 10% improvement in the profit, largely due to different decisions in the purchase of crudes.

Abdulrahman initially implemented an extension of the aggregate distillation models proposed by Jose Caballero. This required the CDU to be represented through cascaded columns, including columns with steam stripping. The initial aggregated model, however, did not include steam stripping. It was tested in a mixture with 10 to 20 hydrocarbons in conventional distillation columns. Since this led to significant convergence problems, often yielding infeasible NLP solutions, Abdulrahman derived valid linear inequalities for the flows of vapor and liquid, since these obey complex relations given the thermal

integration of streams in the cascaded columns. These inequalities significantly improved the robustness of the solution of the NLPs. Abdulrahman was able to solve up to 4 cascaded columns with up to 20 components.

The next major step has been to replace on the cascaded columns by one with steam stripping columns. Initial attempts to use several common models were not successful in overcoming convergence problems. Moreover, we also found surprisingly little in the literature on how to model these columns as they can be regarded as absorbers. After many trials, Abdulrahman has developed a simplified aggregate model that resolves some of the typical simplified assumptions not applicable to steam distillation. The new aggregate model proved more difficult and required more initialization steps, however, it successfully reproduced the effect of having an inversion of temperature (i.e. bottoms lower temperature than feed temperature). Optimizations of individual steam strippers have proved to be fairly robust and accurate. Abdulrahman is now implementing this model as part of the cascaded columns in order to represent the CDU column. The next phase will involve including the cascaded column model for the CDU into the refinery planning model and running it for different crude oils. The new NLP planning model will then be compared LP planning model. Additional NLP models will also be investigated, including a CDU fractionation index (FI) model.

Planning for Petroleum Allocation

New development: Paper on multidimensional knapsack constraints

Post-doctoral fellow: Roger Rocha [started September 2007]

This project involves Roger Rocha from Petrobras, who is visiting the CAPD for two years, regarding applications in Enterprise-wide Optimization. The main objective of this work is to investigate a mathematical programming approach to solve the Petroleum Allocation Problem at Petrobras. Petroleum allocation must be programmed so that sufficient supplies of required crude oil reach refineries along the planning horizon. This must be done by taking into account strategic planning and operational constraints along the petroleum supply chain as follows. Crude oil can either be locally produced or imported from abroad. Local crude oil comes from production sites, mostly offshore, and is transported either by tankers or pipelines. Imported oil is only transported by tankers. After reaching maritime terminals, crude oils are either exported or shipped to Petrobras refineries. At the refineries, petroleum is processed in crude distillation units (CDUs) on daily scheduled production campaigns. These campaigns are defined by consumption rates of different petroleum categories, duration, release date, and deadlines to completing them. Roger proposed an MILP formulation of the problem that relies on a time/space discretization network. The formulation involves some inequalities which are redundant to the mixed integer model but not necessarily to LP relaxation. As the model itself was not able to solve industrial size instance of the problem, not even to find a feasible after 15 days of computation, he implemented a heuristic to find an initial feasible solution by fixing some variables associated with the hardest part of this model and solving the remaining part. In order to improve the solution quality we use a local search method by optimization called local branching, that in most of the case studies could find a solution guaranteed to be no more than 10% of optimality in less than 5 hours. The manuscript describing this work is listed in this newsletter.

Roger developed some valid inequalities which are associated with polytopes that have been extensively studied in the literature. Furthermore, separation routines for strong valid inequalities associated with these polytope are readily available in some commercial solvers. Use of this feature allows a substantial reinforcement of the underlying LP relaxation to be attained. He has tested on some industrial-size instances of the problem involving approximately 40 crude oils, 6 tanker types, 8 maritime terminals involving 12 docks, 11 refineries, and 21 crude distillation units over a time horizon of 72 discretized intervals. Typical instances have 40,000 binary variables, 160,000 continuous variables, and 40,000 constraints. He presented this work at the FOCAPO meeting.

Roger has recently extended this work with “cascading” multidimensional knapsack constraints that can be obtained by reformulation of certain mass balances in supply chain problems. Roger has investigated and tested reformulations to an inventory-production-distribution problem that arises frequently as subproblem of supply chain models. Through an inventory reformulation, Roger identified the special structure of

Cascading Knapsack Inequalities, hidden in the Initial Formulation. This allowed him to use an off-the-shelf MIP solver to solve instances that were out of reach by the Initial Model. Furthermore, capitalizing on this special structure, Roger has proposed tighter reformulations for some special cases of this problem, reducing further the solution times for a large number of instances. An interesting lesson of this work is that although we have nowadays sophisticated MIP solvers capable of solving problems never envisaged before, it is still paramount for the users of MIP solvers to have an understanding not only on the modeling but also on how the MIP solvers work if they are to be able to solve more challenging problems. Roger has produced a manuscript on this work which is listed at the end of the newsletter.

In another exciting development Roger developed a decomposition scheme for problems that can be decomposed into subproblems. The idea is to duplicate variables as one would do in Lagrangean decomposition, but the entire objective is transferred only to the first subproblem while the remaining ones are defined as feasibility subproblems. In the next step disjunctive cuts are generated for the subproblems. Instead of simply using these constraints as cuts, the idea is to use valid inequalities for disjunctions and generate cuts through the reverse polar as per the work by Egon Balas. Roger has tested this idea in the now classic batch scheduling problem of parallel lines by Vipul Jain. Roger has applied his method to this problem and obtained very good results showing that his cuts are stronger than the combinatorial cuts that had been developed by Vipul. The computational results on the petroleum allocation problem have not proved to be as encouraging, although one still obtains reductions of the order of 20-30%.

Planning and Long-term Scheduling of a Multi-product Continuous Process with Recycle

New development: **MILP model for continuous multi-product process with recycling of the waste glass (cullet)**

Post-doctoral fellow: **Ricardo Lima [started July 2006]**

Ricardo's project on Enterprise-wide Optimization has been performed in collaboration with the PPG Glass Business and Discovery Center (GBDC) with the aim of developing a mathematical model for the planning and scheduling of a real-world process for manufacturing tinted glass in a continuous multi-product single stage process with recycling of the waste glass (cullet). The aim of this work is the development and solution of a large scale mixed integer linear programming (MILP) model that has enough accuracy to contribute to real decisions as part of a decision supporting tool. The optimization of the production schedule is driven by high transition costs due to long transition times, in the order of days, and their impact on the profit of the process. The products are characterized by color, which depends on the color of the substrate and the color of a coating if added. The changeover from one substrate to another substrate implies a transition time in the order of days, while the changeover from a specific substrate color to a product with the same substrate with a coating requires a comparatively short changeover. During changeovers, the process produces cullet at the same conditions (energy, raw materials, and production rate). The process scheduling is restricted by: 1) sequence-dependent changeovers between a subset of the products and no changeovers between another subset of products; 2) impositions on the sequence of production and production times between products without changeovers; 3) minimum run lengths due to process control and stability; and 4) by a complex compatibility and recycling profile of cullet.

Ricardo has used as a basis the continuous time slot MILP model proposed by Muge Erdirik-Dogan. Due to the particular characteristics of the process described, Ricardo has proposed several new features that are motivated by this application but that are also generic. The main features are: a) carry-over changeovers across the due dates; b) minimum run lengths across the due dates; c) a rigorous aggregation of the products based on the type of changeovers; d) definition of minimum inventory levels at the end of the time horizon, and e) recycling of material (cullet). The two first extensions are motivated by long changeovers and minimum run lengths that use considerable time of the time period. The cost of adding the first extension is only given by the addition of linear equations, while the second extension requires the addition of binary variables depending on the lengths of the time periods set, and the formulation used, i.e. if the minimum run length is considerably greater than the length of the time period, then binary variables are required. The third extension aggregates the products without changeovers into pseudo-products for the scheduling part of the model, while in the inventory balances and objective function the products are

disaggregated to consider the different selling prices, costs, and production rates. This aggregation eliminates a large number of equations and variables. Each product has a minimum requirement for cullet feed to the process in order to achieve glass quality standards, and to minimize energy costs. An interesting feature is the bidirectional relation between the scheduling, and the cullet generated and consumed, since a given sequence of production generates specific amounts of cullet, but also the quality and quantity of cullet available in storage can restrict the products to be produced. The cullet is generated due to the process yield and during the transitions, creating two major types of cullet, transition cullet and product cullet. The recycling of cullet is characterized by a compatibility matrix between cullet recycled and product to produce, and by specific rates of cullet consumption as a function of the production run. The cullet recycling is modeled using mass balances for the transition cullet and product cullet that is produced and consumed, and inventory balances, since there is a maximum storage capacity. Cullet generated over the storage capacity has to be sold.

Ricardo has developed two solution approaches. The first is based on the direct solution of the MILP model, and the second is based on a rolling horizon strategy. The latter is motivated by the large size of the model and associated computer burden to achieve good solutions. The time horizon for the planning model is twice the length of the time horizon for the scheduling model in order to provide feedback information to the scheduling sub-models of the future demand. In addition, constraints over the inventory levels at the end of the planning time horizon also feedback the information that the demand is not over after the planning time horizon. Due to the long transition times and minimum run lengths, these are also modeled over the due date at the interface between the scheduling and the planning model. Ricardo has solved several case studies to demonstrate: a) the importance of the extensions proposed to the model in terms of inventory levels; b) the influence of the length of the time period in the inventory levels, and sequence of production; c) the impact of different final inventory level constraints at the end of the planning horizon, d) capability of handling recycled material in a scheduling model. The two solution approaches have also been compared in terms of size of the models, and computational efficiency in terms of integrality gaps and CPU time.

Scheduling of Batch Multiproduct Plants

New Development: **Scheduling of cement plants with variable electricity cost application of Dinkelbach's algorithm in cyclic scheduling**

Collaborators: **Pedro Castro (INETI, Portugal)**

Pedro Castro spent four months at Carnegie Mellon, mostly working on an Enterprise-wide Optimization project with ABB dealing with the scheduling of cement plants with variable electricity cost. In addition to this work, Pedro has been collaborating with us for a number of years developing effective computational strategies for effectively solving MILP models for large scale scheduling problems.

As indicated in the last newsletter, with input from Muge, Pedro developed a new mixed integer linear program (MILP) for the optimal short-term scheduling of single stage batch plants with sequence dependent changeovers and optimal selection of the number of batches to produce. It is a continuous-time formulation employing multiple time grids that is based on the resource-task network (RTN) process representation. The main novelty is that aggregated processing and changeover tasks are considered that account for the time required to produce all batches of the product, plus the changeover time to the next product in the sequence. The performance of the new formulation was studied by Pedro through the solution of 12 example problems for the objective of revenue maximization and 4 for the objective of makespan minimization. The new formulation emerged overall as the best performer for the scenario of maximum plant flexibility, where different batches of the same product can be produced in different units. The model developed by Muge with immediate precedence sequencing variables was the fastest but it is not a general scheduling model in the sense that it assumes a single cyclic schedule in each unit, which can be broken, but two or more cyclic schedules per unit may result.

Regarding the ABB project, Pedro considered cement plants that operate semi-continuously. In the final phase of cement manufacturing, clinker is crushed and ground together with additives to obtain cement.

The grades of cement are characterized by their chemical composition and grain size distribution. The grinding process takes place in mills, which are large rotary machines with steel balls that crush the material until the right grain size distribution is reached. According to the grade, the cement is conveyed to silos, where it is stored until dispatch takes place. The energy contract signed by the plant and electricity provider establishes a certain pricing policy. Electricity cost is typically lower during the night and higher during the day. It is also lower during the weekends. The objective in the scheduling problem is to develop a short term schedule (one week) that minimize the total energy cost subject to constraints on resource availability that includes processing units (mills), storage units (silos), and utilities (electricity). Pedro assumed full connectivity between mills and silos even though, in reality, some combinations may not be possible to occur simultaneously. It is also assumed that every silo can store all product grades, in order to increase the flexibility of the model, but only one grade at a time. Normally, the product grade allocated to a silo never changes in its entire life. Pedro developed both discrete and continuous time RTN models for this problem. The development of the continuous model was particularly challenging, although it could be simplified since changeovers were not accounted for. The results showed that the continuous time model can only solve problems of small size. The discrete-time model proved to be more effective since it had a very tight LP relaxation, which allowed it to handle a sufficiently fine time grid to represent the problem data accurately. The goal was to ensure a weekly schedule that accounted for hourly changes in electricity cost, and this has been successfully accomplished. Pedro was able to solve with the discrete model problems of industrial significance (5 mills, 3 products, 3 silos, and hourly changes of electricity cost) with optimality gaps below 1% in less than 5 minutes. Another interesting result was to show that potential cost savings of around 20% can be achieved when applying this scheduling model for cases when plant is operating at around 50% capacity. The manuscript describing this work is listed at the end of this newsletter.

Pedro has also collaborated with Fengqi in the optimization of linear fractional MINLPs, which arise in cyclic scheduling. Fengqi proved convergence properties of Dinkelbach's algorithm for mixed-integer fractional programs. This algorithm conceptually corresponds to Newton's method, although it can also be viewed as a special type of direct substitution method. Fengqi solved problems with up to 2000 0-1 variables and 2000 continuous variables and constraints requiring only about 5 minutes of CPU time. Other solvers like DICOPT, SBB and BARON cannot solve these problems. On the cyclic scheduling problem of Pedro Castro Dinkelbach's algorithm also greatly outperformed DICOPT, SBB, α-ECP and BARON. A manuscript is in preparation on this work.

Software for MINLP Optimization in Design and Scheduling

Research Assistants: Rosanna Franco (started July 2006)

Rosanna Franco has been working on the web-interfaces that are available in:
http://newton.cheme.cmu.edu/interfaces

Rosanna has completed the new interface WATERNET that implements the model by Ram Karuppiah for optimizing the integrated network for water reuse and distributed treatment. See:
http://newton.cheme.cmu.edu/interfaces/indexwater.html

Nick Sahinidis' Group

Nick's work falls into two main thrusts: (1) optimization theory, algorithms, and software and (2) applications of optimization to problems in biology, chemistry, engineering, and medicine. Research in optimization addresses the development of algorithms and software for: (a) global optimization of NLPs and MINLPs, (b) optimization of black-box models, and (c) linear programming. On the applications side, current activities address: (a) crystallographic computing, (b) protein structural alignment, (c) metabolic network modeling and design, and (d) design of compounds with desired properties.

Enabling Software from Nick Sahinidis' Group

Nick continues the development of BARON, primarily in collaboration with his former student **Mohit Tawarmalani**, who is currently an Associate Professor at Purdue's Krannert School of Management. In addition, students in Nick's group address theoretical and computational issues in global/local optimization. Their results are, from time to time, incorporated into BARON. The BARON software is currently available commercially under GAMS and AIMMS. In addition, a full blown version of the GAMS/BARON system is available entirely for free under the NEOS server for optimization. More information about BARON can be found at http://archimedes.cheme.cmu.edu/baron/baron.html.

Software for bioinformatics is also developed and maintained by Nick's group:

- CMOS: software implementing the Xie and Sahinidis algorithm for solving the contact map overlap problem for aligning the 3D structures of proteins
- R3: software implementing the Xie and Sahinidis residue-rotamer reduction for predicting the structure of protein side chains
- SBH: software implanting the Chang and Sahinidis algorithm for finding all near-optimal solutions of the combinatorial problem in DNA sequencing by hybridization

Nick's web site at http://archimedes.cheme.cmu.edu/group/biosoftware.html provides these codes as on-line solvers.

THRUST 1—OPTIMIZATION ALGORITHMS, THEORY, AND SOFTWARE

Algorithms and Software for Global Optimization of NLPs and MINLPs

Student: **Ms. Xiaowei Bao (Ph.D. student in Chemical and Biomolecular Engineering at the University of Illinois, started August 2004)**

Collaborator: **Mohit Tawarmalani (Associate Professor, Purdue University)**

As a result of research that was initiated in 1991, we have developed algorithms and software for global optimization of NLPs and MINLPs. The main results of this work have been:

- A theory of convex extensions that provides a systematic means for developing the functional expression of convex/concave envelopes of nonlinear functions of continuous and integer variables.
- An entirely linear outer-approximation of factorable nonlinear programs. Relying on LP relaxations results in a robust solution approach to global optimization.
- A variety of range-reduction schemes for reducing the search space of integer and nonlinear programs.
- Finite branching schemes for concave minimization and two-stage stochastic integer programs.
- The BARON software for the global optimization of NLPs and MINLPs.

Xiaowei Bao last year initiated work on the global optimization of quadratically-constrained nonconvex quadratic programs. This is a class of optimization problems with applications in various settings, including facility location, multiperiod refinery scheduling and planning, and circle packing problems. The approach that Xiaowei investigated last year relies on branch-and-bound. While standard approaches relax each nonconvex term separately, Xiaowei explored relaxations of entire quadratic constraints. She developed new ways to generate cutting planes for these constraints from the convex envelopes of multilinear functions. Once these cutting planes are added to the root-node relaxation, the performance of BARON on this class of problems improves by several orders of magnitude. A related paper was accepted in *Optimization Methods and Software* and has been accepted subject to minor revisions. Over the past few months, we have been extending this approach to general nonconvex optimization problems and are implementing cutting planes from multilinear relaxations in BARON.

Nick Sahinidis and **Mohit Tawarmalani** are currently maintaining the BARON software. Ongoing work on BARON involves the development of tighter relaxations for MINLPs, work that is expected to be implemented and made available by the end of this coming semester. A current focus has been on replacing BARON's previous LP relaxations by MIP relaxations, where integrality constraints are enforced

on integer variables of the original, possibly nonconvex, MINLP. In a preliminary implementation, the Xpress MIP solver has been used to solve these relaxations and has more than doubled BARON's ability to solve MINLPs from the IBMLib collection of problems. The implementation is expected to be fully functional by the end of this coming semester, including a link to the Cplex MIP solver.

Global Optimization for Problems in Quantum Chemistry

Student: Mr. Keith Zorn (Ph.D. student at CMU, started September 2007)

Keith Zorn has been working on optimization problems in quantum chemistry, in particular Hartree-Fock theory. Quantum mechanics utilizes an explicit description of electron distribution to describe atoms and molecules. Hartree-Fock theory is a branch of quantum chemistry consisting of a series of approximations to the time-independent Schrodinger equation. Typically, Hartree-Fock systems are solved through an iterative Self Consistent Field (SCF) process. SCF, however, is a local solution algorithm that depends upon an initial guess and offers no guarantee of a globally optimal solution. Because of the nonlinear and nonconvex nature of the equations, global optimization is necessary to ensure that the true minimum ground-state energy is discovered. Keith worked on an existing multi-extremal, nonconvex, polynomial programming problem for the calculation of ground-state electronic energy for small, closed-shell, Hartree-Fock systems. The literature has suggested a standard linearization technique based on factorable programming ideas to obtain a lower bound for this problem. Keith has applied the Relaxation Linearization Technique to strengthen the relaxation and expedite solution of the optimization model. Through the introduction of relaxed, redundant constraints before linearization, the root node gap, computational time, and number of required optimization iterations are shown to be significantly reduced. This semester, Keith continued his work on additional RLT relaxations for this problem. He has found that a rather unusual relaxation (high order RLT) considerably tightens the relaxation gap and results in an approach that is over a magnitude faster than other approaches to this problem.

Global Optimization for Machine Learning Problems

Algorithms and Software for Black-box Optimization

Student: Dr. Luis Miguel Rios (postdoc, started June 2009)

This project began with a systematic testing of existing derivative-free algorithms that are capable of optimizing black-box problems. Derivative-free optimization is an area of recent interest and rapid growth, fueled by a growing number of applications, especially in the oil and gas, and chemical process industries. The major challenge is that the objective function in many problems is expensive to evaluate, while no bounds or Lipchitz constants are available, and strategies to directly estimate derivative information are impractical or expensive. The most recent systematic testing of derivative-free algorithms for solving problems of this nature was done 10 years ago. **Luis Miguel Rios** has collected 225 test problems from the globallib and princetonlib collections and solved them under different conditions using 23 different black-box solvers. The main conclusions from this computational study were that: (a) even obtaining a feasible solution cannot be taken for granted for these problems/solvers, (b) larger problems diminish the chances for obtaining good solutions, (c) LGO and MCS are better, on average, than other solvers, (d) all solvers are 'useful' in the sense that there are at least a few problems for which each solver is best in terms of solution quality. Current plans in this line of research include the addition of non-smooth problems in the test set collection. Test problems of black-box models from industry are currently sought.

The solvers tested by Luis Miguel have been brought under a unified software interface that allows the user to call any of these solvers through a simple interface. This software platform is currently being tested and will be made available in the near future.

Algorithms and Software for Linear Optimization Problems (LP) and Extensions

Students: **Mr. Deepak Channamariyappa (former M.S. student at CMU, currently visiting researcher)**
Mr. Joseph Elble (Ph.D. student in Industrial Engineering at the University of Illinois)
Dr. Panagiotis Vouzis (postdoctoral researcher at CMU)

Algorithms for solving LPs represent the workhorse of optimization systems for solving large-scale MILPs, NLPs, and MINLPs. While highly successfully commercial software exist for solving LPs, none is guaranteed to provide reliable results in the sense that they are all subject to the effects of floating point arithmetic and round-off errors. The goal of this project is to develop new simplex algorithms and software in order to provide tools that can reliably solve large-scale linear optimization problems even in the presence of round-off errors. Towards this goal, we plan to develop symbolic algorithms for linear programming preprocessing, matrix scaling, and matrix factorization.

The long-term goal of this project is to develop novel algorithms for LPs and make them available via distributed implementations on modern GPUs and FPGAs.

Deepak Channamariyappa has been studying of preprocessing techniques for Linear Programming. These techniques currently represent more of an art rather than science in the field of Linear Programming. The long term goal of this project is to implement and compare the computational performance of different preprocessing techniques. It is expected that this study will be beneficial for the development of useful tools for nonlinear optimization problems as well. This past semester Deepak performed computational experimentations that rely on the presolve routines of the GALLAHAD package. Our main finding was that the sequence in which different presolve techniques are applied to any given LP problem can affect the final outcome of preprocessing, in terms of number of variables/constraints and sparsity of the presolved problem. Current work focuses on identifying an "optimal" presolve sequence.

Panagiotis Vouzis and **Joe Elble** have performed an extensive computational experimentation with advanced computing architectures. For less than $3000, we purchased a standard computer to which we added to Graphics Processing Units (GPUs). The combined system has an output of 1.25 GFLOPS. Panagiotis has been experimenting with parallel implementations of algorithms for the solution of systems of equations. In particular, Panagiotis has implemented Kaczmarz's row projection method (KACZ), one of the first iterative methods used for large nonsymmetric systems. We are finding that while parallelism of KACZ allows considerable CPU time reductions per iteration, it nonetheless increases the number of iterations for this algorithm. In addition, we are finding that developing sparse matrix implementations is more challenging than implementing successful dense matrix implementations. Panagiotis and Joe implemented several iterative methods for solving LPs on the GPU. The main conclusion was that a combination of GPU/CPU implementation significantly outperforms parallel computations on a 16-node Linux cluster. A related paper has been submitted to *Parallel Programming*.

Joe Elble has also been working on the problem of binormalization of a given matrix. Binormalization improves the condition number of a matrix and is important in the context of solving systems of equations. The GPU implementation developed by Joe for the composite Jacobi binormalization algorithm was found to be up to six times faster than a corresponding CPU implementation. The GPU implementation achieves a high rate of parallelism, and clearly scales better in terms of the size of the matrix.

THRUST 2—APPLICATIONS OF OPTIMIZATION IN BIOLOGY, CHEMISTRY, ENGINEERING, AND MEDICINE

Protein Structural Alignment

Student: **Shweta Shah (Ph.D. Student at CMU, started September 2007)**

Aligning proteins based on their structural (3D) similarity is a fundamental problem in molecular biology with applications in many settings, including structure classification, database search, function prediction, and assessment of folding prediction methods. Structural alignment can be done via several methods, including contact map overlap (CMO) maximization that aligns proteins in a way that maximizes the number of common residue contacts. A former student, Wei Xie, developed a reduction-based exact algorithm for the CMO problem. Our approach solves CMO directly rather than after transformation to other combinatorial optimization problems. We exploit the mathematical structure of the problem in order to develop a number of efficient lower bounding, upper bounding, and reduction schemes. Computational experiments demonstrate that our algorithm runs significantly faster than existing exact algorithms and solves some hard CMO instances that were not solved in the past. In addition, the algorithm produces protein clusters that are in excellent agreement with the SCOP classification. An implementation of our algorithm is accessible as an on-line server at http://eudoxus.scs.uiuc.edu/cmos/cmos.html. This algorithm currently represents the state-of-the-art algorithm for the CMO problem.

Shweta Shah, has been working on the development of heuristics for obtaining good solutions at the root node of the branch and bound algorithm that we have developed for this problem. Shweta's computations indicate that our dynamic programming-based bounds can be improved significantly by a randomized greedy heuristic, as well as a heuristic that exploits the presence of specific motifs in the protein structures to be aligned.

Protein-Ligand Docking

Students: Danan Wicaksono (M.S. student at CMU)

A central problem in drug design is to identify small molecules that can bind on certain active sites of a protein and deactivate the corresponding function of the protein. Key to solving this problem is the ability to identify the site on a given protein where a given molecule is most likely to bind. This is frequently accomplished through the minimization of binding free energy. Saurabh Awasthi, who completed his MS thesis in August 2008, used the software package Autodock to provide binding energies for protein-ligand complexes from the protein data bank. He also utilized 14 of the derivative-free optimization solvers used in the work of Luis Miguel Rios (reported above) to find optimal docking positions. He found that solutions provided by Autodock are not locally optimized and that the derivative-free solvers are able to provide improved (smaller) binding energies. Danan Wicaksono is continuing Saurabh's work, and has developed algebraic optimization models for rigid docking. We have found that local solvers, such as MINOS and CONOPT, often provide better solutions than those obtained by AutoDock for this problem.

Design of Drilling Fluids for Extreme Drilling Conditions

Student: Apurva Samurda (Ph.D. student at CMU, started September 2007)

The current drilling fluids market exceeds $3 billion a year but there are no cost efficient and environmentally benign means for drilling under extreme conditions. By extreme conditions, we refer to drilling depths beyond 20,000 ft, pressures as high as 2000 bar, and temperatures as high as 250 °C. The environmental constraints include the requirement for biodegradable fluids that are not toxic to aquatic environments. There are three main families of drilling fluids currently in use: gaseous, aqueous, and non aqueous. The major driver of the drilling fluids market is that different well conditions require different types of drilling fluids to be used for most effective operation. The drilling fluid should possess a number of properties: (1) it should gel under static conditions so as to keep the cuttings suspended when the fluid is not moving; (2) it should have high shear thinning and sufficiently high viscosity for efficient hole cleaning; (3) it should have high annular velocity, which improves transport of cuttings; (4) it should have density that provides a hydrostatic pressure just sufficient to prevent collapse of weak formations into the borehole; (5) it should have suitable pH in order to reduce corrosion; and (6) it should be environmentally benign, i.e., it should have good biodegradability and low aquatic toxicity. It is important to recognize that an optimal drilling fluid must be determined as a function of well *and* drilling conditions. A major challenge for the design of drilling fluids for extreme drilling is that the fluid must be stable under a very

wide range of operating conditions. Furthermore, the fluid must be optimal from an economic standpoint, while having minimal environmental impact. Another major challenge is that the behavior of fluids under extreme conditions is very difficult to predict computationally. Indeed, existing fluid mixture models are complex and highly nonlinear. Since viscosity is one of the primary concerns in the context of drilling fluids, attention of this project has focused on viscosity prediction models. In addition, Apurva has proposed molecular design via an optimization formulation that relies on the inversion of nonlinear property relationships so as to avoid nonlinearities in the underlying property prediction models. In recognition of the fact that drilling fluids are blends, Apurva will be extending these optimization models from the design of pure fluids to blends. Data will be collected from industrial use of drilling fluids in order to calibrate these models. A mathematical model will be developed that will integrate molecule and mixture design with the post-drilling process, i.e., filtering and recycling of the fluid in order to identify and design fluids that minimize environmental impact as well as drilling costs. Finally, optimization algorithms will be developed for handling the nonlinearities that arise in this model from mixture design considerations.

Risk Assessment in CO2 sequestration

Student: Yan Zhang (Ph.D. student, started September 2008)

This project develops and will apply a systematic methodology for risk assessment in CO2 sequestration. We are developing novel Monte Carlo simulation and black-box optimization methods, including parallel implementations, with the goal of reducing the enormous computational effort currently required for probabilistic risk assessment. Yan has developed a semi-analytical model capable of predicting the rate of CO2 leakage to the biosphere as well as spatial CO2 diffusion and reaction with adjacent aquifers and aquitards after injection in an oil/gas reservoir. In the long run, the developed techniques will be integrated with sequestration models and systems, including CQUESTRA and CO2-PENS, and applied to study a number of existing and potential sequestration sites.

Erik Ydstie's Group

Adaptive Control Systems

New developments: Software for adaptive PID control completed. Web based software for continuous time function identification in beta testing stage. Adaptive Model Predictive Control (AMPC) in beta test stage.

Students: **Richard Chan (Post Doc researcher and ILS)**
Keyu Li (PostDoc researcher and ILS)
Venkat Nandivada (MS student)

Keyu Li has developed a software solution for passivity based adaptive feedforward control and automatic tuning of PID controllers. The algorithm is based on a fast algorithm for global optimization to identify first order deadtime models suing real time data and the method to select informative data developed by Wayo in his Ph.D. thesis. The feedforward gains are tuned continuously whereas the feedback (PID) controller gains are updated only intermittently. The PID algorithm is based on fixing the gain and phase margins (user specified) and them optimizing the bandwidth. These problems are solved on-line and provide a novel and robust solution to the adaptive PID control problem. The algorithm has been tested in simulation on an ethylene cracking process and a selective catalytic reactor for NOX reduction in coal fired power plans. The software can be interfaced with standard DCS using the Microsoft OPC interface and is ready for testing in industrial trials. Richard Chan has been working on developing a multivariable adaptive predictive controller which is configurable on the fly. The algorithm uses a classical MPC formulation to define the control signal whereas the models are based on a Laguerre type model formulation which is suitable for robust adaptive control of uncertain and slowly time-varying systems. The algorithm has been tested in simple simulation studies and on the Shell challenge problem.

Modeling and Nonlinear Control

New developments: **New stability results for the reactive, multi-component distillation Continuous time switching lemma, models for chemical looping combustion. Papers submitted on adaptive control systems and nonlinear control**

Students: **Mohit Aggarwal (Ph.D. awarded May 2009)**
Balaji Sukumar (PostDoc)
Juan Du (PhD Student)
Zhaojia Lin (MS student expected 2009)

Mohit has developed stability theory for systems with time-varying reference using an idea called contraction analysis. The theory has application distributed, web-based simulation and control. Mohit has used the theory to develop modeling tools for chemical process systems using invariant groups as a way to develop reduced order models for very complex reacting systems. With the help of Bala he has developed reduced order process models using process invariants for the gasifier in the IGCC process, a bio-gasifier (work with Air Products) and the carbothermic aluminum process. Bala has used the method to develop reduced order models for a chemical looping reactor being developed by Alstohm. Juan Du has extended the infinite switching lemma developed by Wayo for continuous time systems. The lemma is useful for stability analysis of chaotic systems since it can be used to show convergence to invariant (omega-limit) sets without extensive linearization or re-normalization.

Carbothermic Aluminum Production

New developments: **Paper submitted on modeling and control of the VRR**

Students: **Mohit Aggarwal (Ph.D. awarded 2009)**
Balaji Sukumar (PostDoc researcher)

Carbothermic reduction 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. Yuan Xu developed an interface between the ChemApp/FACT thermodynamics program with MATLAB via a MEX Interface. This program allows the model to handle ranges of temperatures and compositions without extra work needed to determine equilibrium constants, activity coefficients, and extent of reactions. Another improvement has been to incorporate computational blocks using the SIMULINK tools in MATLAB and an interface with COMSOL CFD code. 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. The vapor recovery section of the carbothermic aluminum process has been modeled. 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. Mohit has developed a three phase (liquid/solid/gas) multi-scale, simulation model which will be used for system design, scale-up, economic evaluation and control studies. A variety of models have been developed for primary reactor under steady and cyclic operating conditions. Balaji has developed simulation models and control system structures for the entire process. He is now in the process of developing micro-models for studying dust formation and condensation which will help in the control of the reactor process.

Process Networks with Application to Energy Problems

New developments: **Software has been developed for simulation of coal fired power plants**

Students: **Michael Wartman (PhD expected 2010)**
Chengtao Wen (PostDoc Researcher)
Simon Markovski (MS expected 2009)
Tor Heirung (MS expected 2010, NTNU, MSc CMU, 2009)

Michael developed a process analog of the Tellegen theorem of electrical network theory. He 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 Jillson has used the theory to develop control system structures for the IGCC process. He has shown that passivity based control systems can be used to stabilize and control the IGCC. Chengtao Wen has been involved with a modeling team at Emerson process management which has implemented models and developed suing the thermodynamic theory into a complete system for design and evaluation of process control systems in coal fired power plants. Chengtao and Michael are now working on synchronization problems. The idea here is that that the models need to synchronized with on-line data in real time. Chengtao is working on synchronization in the power industry whereas Michael is working synchronization in oil and gas field production

Multi-Scale Modeling of Particulate Processes with Fluid Flow

Student: Juan Du (Ph.D. expected 2011)

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 passivity-based inventory controller maintains a constant mass of a specified size of silicon particles. The results from this research will be published in Powder Technology.

Last year we have matched the model to pilot-scale process data obtained from Solar Grade Silicon LLC in Moses Lake, Washington. We developed an observer for on-line estimation of process states and parameters. The method allows for estimation of particle size distribution in real time. 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. The model and control scheme is being used for scale-up and control system design for production system under current development at SGS. It expected that that when the new process is in operation that it 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.

Dye Sensitized Solar Cells

Student: Rocco Panella, co-supervised by Dennis Prieve (Ph.D. expected 2013)

One of the integral components of dye-sensitized solar cells (DSSCs) is ta porous, ~10 μm thick layer of sub-100 nm oxide particles. Typically, this oxide is titania (TiO_2), which is deposited onto a clear, conducting substrate such as indium tin oxide (ITO). Diffusion of electrons through this film is believed to be dependent on the degree and intimacy of interparticle connectivity in this layer, which is usually achieved through high temperature (~400° C) sintering. Here, we propose a low-temperature method for achieving intimate contact between particles and the conductive substrate via attractive double layer interactions and electrophoresis.

Titania particles have been synthesized via a sol-gel method. Analysis via dynamic light scattering shows a Z-average diameter of 33.9 nm with a standard deviation of 15.2 nm. Using electrophoresis, the pH_{IEP} of these particles was found to be 6. The pH_{IEP} of ITO coated glass slides was found to be 4 using a ZetaSpin apparatus [13]. In order to observe the deposition of the nano-scale particles onto surfaces, we have done preliminary experiments showing that sub-50 nm particles are capable of scattering light from the evanescent wave in a TIRM apparatus; particles were brought close to the working surface via electrophoresis.

The differing isoelectric points of the two materials show that it is possible to adjust the properties of the suspending solution such that the double layer interactions of the materials can help or hinder adhesion of the particles to the surface. The use of an evanescent wave to probe the presence of the nano-particles near a surface is a novel method of tracking surface coverage which warrants further investigation.

Continuous Production of Silicon Wafers for Solar Cells

Students: Sudhir Ranjan (Post Doc)
Sukumar Balaji (PostDoc)

This project aims to develop scientific foundations for a continuous process to produce crystalline Silicon wafers from high purity poly-Silicon. In the new process we float Silicon over a two-layered molten substrate to form a very thin (less than 0.3 mm) Silicon sheet which solidifies to produce crystalline Silicon wafers suitable for solar cells. The production cost will be low relative to expensive wire saw processes since the new process is continuous and does not incur Silicon loss.

In the research we study the stabilization and control of a freezing front on a molten substrate. Systems of this type may exhibit Mullins-Sekerka instability and active control is needed to stabilize the process. In the current research we will develop multi-scale process models capable of representing the instabilities present in the freezing front. The models will be matched to a physical system using experimental data. Control methods will be developed to stabilize the freezing front using our thermodynamics based approach to passivity based control. We focus on the application of the methods to Silicon for making solar cells. A number of new measurement techniques will be tested for the Silicon solidification problem and process parameters needed for process design, scale-up and control will be determined. A thin layer of molten Silicon will be slowly poured on a high-density liquid used as a substrate in micro scale experiments. The physical properties of the substrate will be tuned so that the molten Silicon can be continually cooled and withdrawn in the form a continuous sheet of single-/multi-crystalline Silicon. We will show that the use of molten (liquid) substrate forming three liquid-liquid layer prevents the crystal imperfections, dislocations and grain boundaries present in current continuous, horizontal wafering processes. We will demonstrate that limited purification can be experienced. The simultaneous goal is to develop multi-scale mathematical models to compare the proposed micro-scale experimental results on movement and flow of the molten Silicon over the liquid substrate. Model predictions will be compared with macro-scale experiments.

Solar energy has so far not measured up to its potential due to the high cost of producing high purity Silicon and Silicon wafers. Significant progress has been made in developing cheaper processes for making

high purity poly-silicon in fluid bed reactors. Very limited progress has been made in finding alternatives to the expensive band-saw process for wafering, however. The ideas described in this proposal may contribute towards solving this important problem. The proposed three layer process described in the proposal draws inspiration from the Pilkington glass process which revolutionized the glass industry. Preliminary experiments show that it is feasible to produce silicon wafers in small scale using a similar idea. The most important broader impacts of this research are expected to be found in the area of alternative energy. We also expect that the research will lead to new methods for multi-scale modeling and stabilization and control of solidification fronts. These problems turn up in a number of application areas, including the drying of paints, film processing and coating.

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