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FINAL REPORT

Training Course on Sustainable Industrial Development: Process Simulation and Optimization Techniques

A training course on process simulation and decision support systems within the framework of the industrial sustainable development

Rabat, Morocco
18-22 September, 2000

organized by

ICS-UNIDO

in collaboration with the

Laboratoire d'Analyse et de Synthèse des Procédés Industriels (LASPI), Ecole Mohammadia d'Ingénieurs, Université Mohammed V-Agdal, Rabat, Morocco

BACKGROUND

One of the premier goals of Subprogramme 2.1 of ICS-UNIDO, which specifically deals with decision support systems issues, is the transfer of knowledge on decision support systems towards developing countries. In this area the Subprogramme acts as a "knowledge collection centre" to gain expertise on general issues typical of the area such as process simulation, decision support systems and geographical information systems and to acquire skills in using the relevant informatics tools which implement the general ideas. The Subprogramme promotes the development of participatory initiatives in the field of monitoring systems, risk analysis and assessment, and the effective transfer of technology in response to environmental problems caused by industrial activities.

In the specific area of Process Simulation and Optimization Techniques, the topic has been presented and illustrated by specialists in a series of meetings and specialised workshops in 1998 and 1999. These included: an Expert Group Meeting on Modelling in Chemistry and Chemical Industry held in Trieste, Italy from 14-16 October 1998, a Workshop on Industry and Environmental Management held in Hanoi, Vietnam from 19-24 October 1998, a Workshop on Industrial Pollution Assessment and Prevention in Mediterranean Coastal Areas held in Izmir, Turkey from 18-20 November 1998, and a Consultation Workshop on the Preparation of Didactic Material for Integrated Coastal Area Management held in Trieste, Italy from 10-12 March 1999. On top of these activities, two specific Training Courses on Process Simulation and Optimization Techniques have been carried out in Trieste, Italy, focusing on Sustainable Industrial Development (21-23 July 1999) and on Essential Oil Extraction (12-19 October 1999). Both Training Courses presented the state of the art in process simulation and optimization techniques, as well as in control system, dynamic simulation and included case studies, exercises and hands-on sessions. In March 2000 ICS organized the first training course on process simulation directly in one of the developing country. The training course organized in Montevideo followed the same structure of lectures and exercises and hands on computers hardware and software: the training course organized abroad is particularly important for the mission of ICS-UNIDO on one side, but it is very difficult to organize because of the necessity of setting up the necessary environment far from the Trieste laboratories.

During this "evangelisation" activity, an issue which was highlighted as a major problem in this area was the lack of adequately trained personnel in the technical communities and a lack of knowledge of the possibilities of process simulation and optimisation techniques in the decision making environments. In recognizing the urgent need for developing human resource capabilities, ICS-UNIDO is giving much importance to the training-of-trainers in the field of process simulation and optimisation techniques, with particular attention to the role of such topics within the framework of sustainable industrial development.

Well-trained personnel would be an invaluable asset to environmental and planning agencies, which deal with complex environmental issues and problems, as well as the protection and conservation of the environment on a daily basis. Such interdisciplinary knowledge would also bring a better appreciation and understanding of the magnitude of the potential risks involved.

JUSTIFICATION

In the Third Millennium, "sustainability" is increasingly becoming a key social, political, scientific and engineering issue. Indeed, there are increasing signs that sustainability will become a major new paradigm influencing the society of tomorrow and the engineering it requires. With their knowledge of chemistry and physics, mass and energy flows, and process technology, chemical engineers are in a pre-eminent position to play a major role in implementing sustainable development. This role is wide. Traditionally, it concerns the design and operation of chemical process plants. Nowadays, it also concerns ethical and rational public policy involving science and technology.

The sustainable development can very simply be defined as a process in which one tries not to take more from nature than nature can replenish. It can be obtained without sacrificing the numerous benefits that modern technology has brought, provided that technology respects the imposed constraints. Engineers are asked to do this by designing new processes and/or by modifying existing processes aiming at using renewable resources and producing by products that can be returned to the earth.

Decision support systems are a set of decision-making tools that are designed to help decision-makers to take appropriate steps in the development of new ideas and new concepts. A complete decision support system is made up by different components, the most important being the experience and the knowledge. Informatic tools, such as Geographical Information Systems, modelling tools and optimization techniques are of great help in the process of establishing a knowledge base for the decision makers.

Process Simulation can play a dramatically important role in the decision support system in the framework of sustainable development by allowing engineers to perform process screening and a priori analysis on the feasibility of a given industrial plan as well as performing simulation of performances of waste water treatment and air pollution control. Integration of three fundamental topics: (i) steady state process simulation, (ii) environmental simulation, and (iii) process control can give, within the framework of the sustainable development theory, a solution for a decision-making system in developed and developing countries.

For these reasons, there exists the urgent need to transfer consciousness and familiarity with informatic tools and techniques implementing the three general topics mentioned above. In this respect, ICS-UNIDO organized a Training Course, covering various aspects of process simulation and optimization techniques following the same structure of the Training Course of Montevideo (March 2000) and adjusting some topics and case studies to the specific geographical area of interest.

OBJECTIVES

- To set-up a training course considering process simulation within the framework of sustainable industrial development, to be used during the present course, and to be considered for the development of training courses to be made available to developing countries;

- To present the necessary background and basic principles necessary to understand and use the informatic tools implementing process simulations, process control and optimisation techniques;
- To describe and teach "how to use" specific programs by means of demo and hands-on sessions;
- To explain how to tackle a simulation problem by showing the sequential steps to be considered in the development of a simulation and optimization strategy;
- Participants will gain perspective and insight into the potential applications of simulation and optimization techniques, as well as experience in the use of specific computer tools that are currently available.

OUTPUTS

- Training material in the form of Power Point slides to be used as rough material for training modules and to be distributed "as is" to the participants;
- A training course structure on Process simulation and optimization techniques;
- A set of examples of application of the topic discussed in the course to be distributed to the participants.

STRUCTURE OF THE COURSE

- The Training Course was held at the Laboratoire d'Analise et de Synthèse des Procedés Industriels (LASPI), Ecole Mohammadia d'Ingénieurs, Université Mohammed V, Rabat, Morocco.

- The Training Course was organized in morning sessions in which theoretical and basic subjects were presented in form of formal lectures. Each afternoon (excluded the first day of the course) an electronic workshop session was held in which participants practiced on fundamental techniques for solving on-the-job problems. Some of the afternoon session were devoted to working in small groups on the solution of case study problems using the computing facilities. LASPI provided a suitable room, as well as 12 networked personal computers, printer, projector and other equipment for the practical part of the Training Course.

- All the activities were organized under the responsibility of the Programme Officer of the Area of Earth, Environmental and Marine Sciences and Technologies, Mr. G. Longo and the TC was carried out according to the attached programme.

CONCLUSIONS AND RECOMMENDATIONS

The training course was directed to technologists, planners and decision-makers working in close contact with industry, particularly engineers, scientists and managers interested in the state-of-the-art applications of computer-based techniques for modelling chemical process. The pre-requisites included a working knowledge of chemical engineering and/or experience in the process industry and a familiarity with the use of computers to solve engineering problems.

The final selection was made under the responsibility of ICS Programme Officer and LASPI representative, and in accordance with the objectives of the training course and the profile of the candidates. Twenty participants from: Algeria, Cameroon, Egypt, Ethiopia, Kuwait, Nigeria, Sudan, Tunisia and Morocco attended the training course.

At the end of the training course, the most important messages to the participants to carry home were the following:

- Informatic tools may be useful in the chemical process simulation environment;
- Sustainable industrial development can be obtained by combining Process simulation, Environmental simulation and Process control;
- Process simulation is a simple tool to be used by trained people with engineering knowledge;
- Process simulation is a tool that does not interpret results: the presence of a trained engineer is essential;
- It is possible and desirable to apply process simulation in the entire life cycle of the plant.

In order to have an opinion on the training course by the participants, an evaluation questionnaire was distributed. Some of the comments are reported here below and in addition some statistics were prepared and attached to this report. As a general consideration, the hands-on part was found by all of them the most useful.

IMMEDIATE FOLLOW-UP

- Setting up of a Web site containing all the training course material.
- Setting up of a mailing list of the participants of the training course to facilitate contacts among them.

LIST OF ANNEXES

- Aide-Mémoire
- List of participants
- Statistics
- Presentation by lecturers

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ECOLE MOHAMMADIA D'INGENIEURS

Financial statement

The budget of the training course is based on the participation of 20 foreign candidates, of which 6 from Morocco, and of 2 European lecturers.

The summary is as follows:

		Amount in US$
1.	Air tickets Foreign participants from: Algeria, Cameroon, Egypt, Ethiopia, Kuwait, Nigeria, Sudan, Tunisia 2 European lecturers	**11,797**
2.	DSA	
	16 participants x 7 nights	13,511
	2 international lecturers x 7 nights	2,000
	Subtotal	**15,511**
3.	Fees for 2 international lecturers	**2,000**
4.	Rent of 1 LCD projector 7 days x 200 US$	**1,400**
7.	Rent of 3 PC machines and 10 SDRAM 64 MO	**1,200**
8.	Stationery 25 folders, 25 badges, 25 pens and 25 notebooks	**327**
	Photocopies of Training Course documentation	**322**
9.	Local transportation 5 days x 100 US$	**568**
11.	Communication facilities (mail, fax and phone)	**475**
	Total	**33,604**

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AIDE-MÉMOIRE

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BACKGROUND

One of the premier goals of Subprogramme 2.1 of ICS-UNIDO, which specifically deals with decision support systems issues, is the distribution of knowledge on decision support systems towards developing countries. In this area, the Subprogramme acts as a "knowledge collection centre" to gain expertise on general issues typical of the area such as process simulators, decision support systems and geographical information systems, and to acquire skills in using the relevant informatics tools which implement the general ideas. The Subprogramme also acts as a prime mover to facilitate the development of participatory initiatives, as well as direct action in the field of monitoring systems, risk analysis and assessment, and the effective transfer of technology in response to environmental problems caused by industrial activities.

In the specific area of Process Simulation and Optimization Techniques, the topic has been presented and illustrated by specialists in a series of meetings and specialized workshops in 1998 and 1999. On top of these activities, two specific training courses on process simulation and optimization techniques have been given in Trieste focusing on Sustainable industrial development (21-23 July, 1999), and on Essential oils extraction (12-19 October, 1999). Both training courses presented the state of the art in process simulation and optimization techniques, as well as in control systems, dynamic simulation, and included case studies, exercises and hands-on sessions. The experience gained during this activity together with the suggestions received from the participants advised us to organize locally the training courses providing lectures and process simulation laboratory directly in the hosting country. The first experiment has been done in South America (Montevideo, Uruguay) in March 2000 and it has been very successful. The present activity continues on this line and brings the course on "process simulation and sustainable development" to Morocco.

During this "evangelization" activity, an issue which was highlighted as a major problem in this area is the lack of adequately trained personnel in the technical communities and a lack of knowledge of the possibilities of process simulation and optimization techniques in the decision-making environments. In developing countries, it is often the case that professional personnel, notwithstanding they are already thinly spread, are occasionally expected to perform functions beyond their technical remit. In recognizing the urgent need for developing human resource capabilities, ICS-UNIDO is attaching much importance to the training-of-trainers in the field of process simulation and optimization techniques, with particular attention to the role of such topics within the framework of sustainable industrial development.

Well-trained personnel would be an invaluable asset to environmental and planning agencies, which deal with complex environmental issues and problems, as well as the protection and conservation of the environment on a daily basis. Such interdisciplinary knowledge would also bring about a better appreciation and understanding of the magnitude of the potential risks involved.

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The sustainable development, which can very simply be defined as a process in which one tries not to take more from nature than nature can replenish, can be obtained without sacrificing the many benefits that modern technology has brought. The only problem is that technology respects the imposed constraints. Engineers are asked to do this by designing new processes and/or by modifying existing processes aiming at using renewable resources and producing by products that can be returned to the earth.

Decision support system is a set of decision-making tools that are designed to help decision-makers to take appropriate steps in the development of new ideas and new concepts. A complete decision support system is made up by different components, the most important being the experience and the knowledge. Informatics tools, such as geographical information systems, optimization techniques and modeling tools are of great help in the process of establishing a knowledge base for the decision-makers.

Process simulation and Optimization Techniques can play a dramatically important role in the decision support system in the framework of sustainable development by allowing engineers to perform process screening and a priori analysis on the feasibility of a given industrial plant, as well as performing simulation of performances of waste water treatment and air pollution control. Integration of three fundamental topics (i) steady state process simulation, (ii) environmental simulation and (iii) process control can give, in the framework of the sustainable development theory, a solution for a decision making system in developed and developing countries.

For these reasons, there exists the urgent need to transfer consciousness and familiarity with informatics tools and techniques implementing the three general topics mentioned above. In this respect, ICS-UNIDO shall be organizing a Training Course, covering various aspects of process simulation and optimization techniques.

OBJECTIVES

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STRUCTURE OF THE COURSE

The Training Course is organized in morning sessions in which theoretical and basic subjects will be presented in form of formal lectures. Each afternoon (excluded the first day of the course) an electronic workshop session will be held in which participants will practice on fundamental techniques for solving on-the-job problems. Some of the afternoon sessions will be devoted to working in small groups on the solution of case study problems using the computing facilities.

PARTICIPATION

The Training Course is directed to technologists, planners and decision-makers who are working in close contact with industry, particularly engineers, scientists and managers interested in state-of-the-art applications of computer-based techniques for modeling chemical process.

The prerequisites include a working knowledge of chemical engineering and/or experience in the process industry and a familiarity with the use of the computer to solve engineering problems.

TENTATIVE PROGRAMME

During the course the following topics will be covered:

- Sustainable industrial development and industrial ecology
- Process simulation fundamentals and techniques
- Environmental applications of process simulation
- Thermodynamic modeling: data banks, physical property determination, phase equilibria models
- Steady state process simulation: user environment
- Single stage unit operations
- Steady state process simulation: process with reaction
- Steady state process simulation: complex unit operations: distillation, crystallization, reaction
- Steady state process simulation: application to simple processes
- Optimization techniques
- Fundamental of Process Dynamics and Control
- Case studies

DOCUMENTATION

The documents available for the course shall be:

- Aide-Mémoire
- Programme and list of participants
- Power Point slides (hardcopy) of all lectures and examples
- Any other relevant documentation

LANGUAGE

The Training Course will be conducted in English; no translation facilities will be available.

TIME AND VENUE

The Training Course will be held at the Laboratoire d'Analyse et de Synthèse des Procédés Industriels (LASPI) from 18 to 22 September 2000.

FINANCIAL ARRANGEMENTS FOR ICS-UNIDO FUNDED PARTICIPANTS:

The Course is financially supported by ICS-UNIDO. Round-trip economy air-transportation from the airport of departure will be arranged for participants invited by ICS-UNIDO; prepaid tickets or otherwise will be issued as necessary. Daily subsistence allowance (DSA) to cover board and lodging will also be provided upon arrival to Rabat. Hotel reservation will be made for all participants upon request.

The participants will be required to bear the following costs: all expenses in their home country incidental to travel abroad, including expenses relating to passport, visa, and any other miscellaneous items.

ICS-UNIDO will not assume responsibility for any of the following costs, which may be incurred by the participant while attending the Training Course:

- compensation for salary or related allowances during the period of the meeting;
- any costs incurred with respect to insurance, medical bills and hospitalisation fees;
- compensation in the event of death, disability or illness;
- loss or damage to personal property of participants while attending the Course.

VISA ARRANGEMENTS

Participants are requested to arrange for their visa, if one is necessary, as early as possible in the Moroccan Embassy in their home country. In case of difficulties, please advise the contact persons (details below).

CONTACT PERSONS

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Further details about the Training Course and travel instructions will be provided upon request.

Training Course on Sustainable Industrial Development: Process Simulation and Optimization Techniques

Rabat, Morocco, 18-22 September 2000

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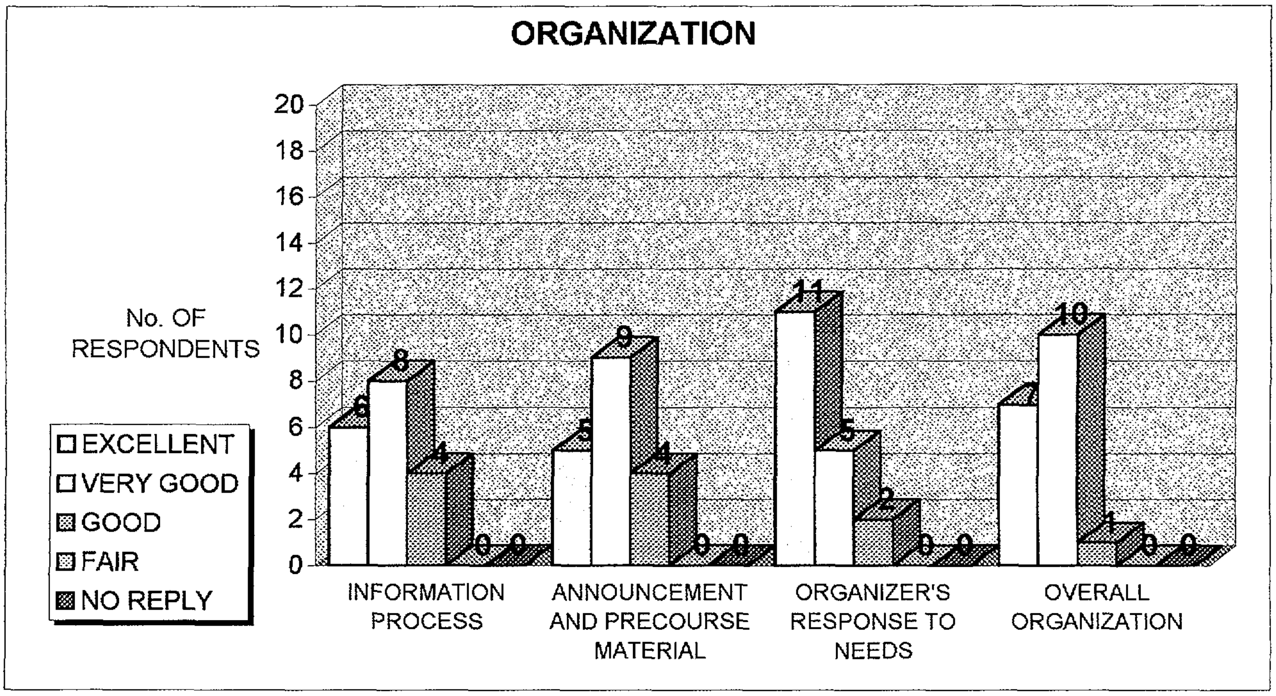
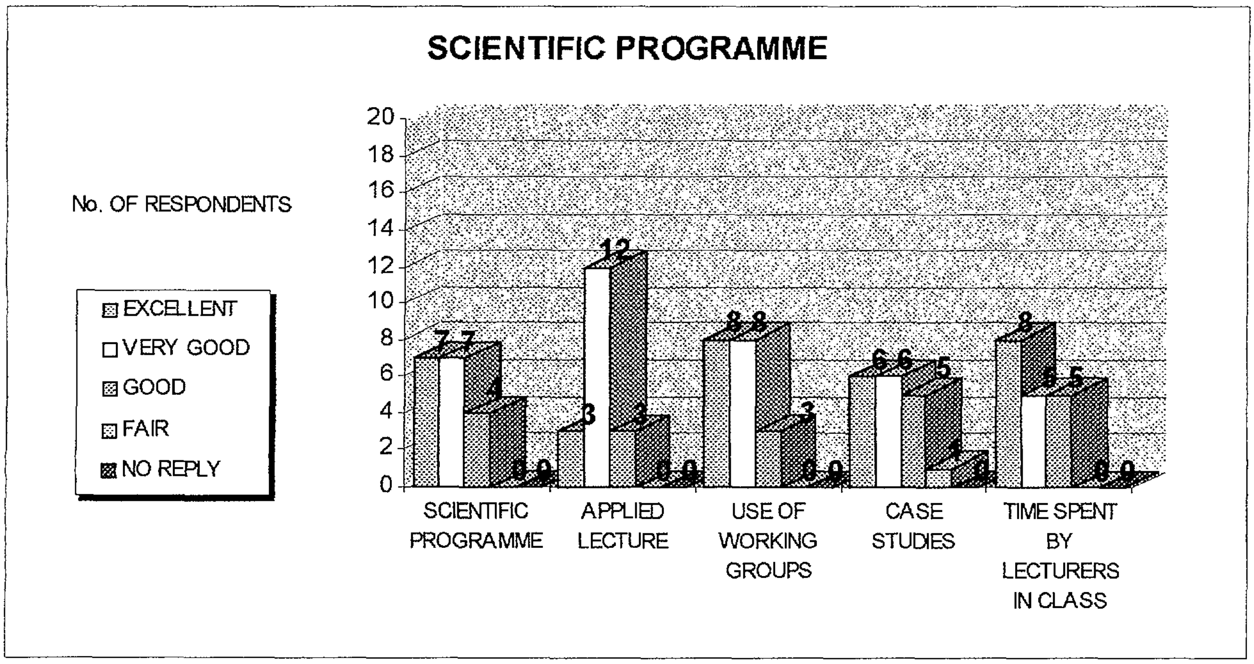
Training Course on "Sustainable Industrial Development: Process Simulation and Optimization Techniques", Rabat, Morocco
18-22 September 2000

EVALUATION





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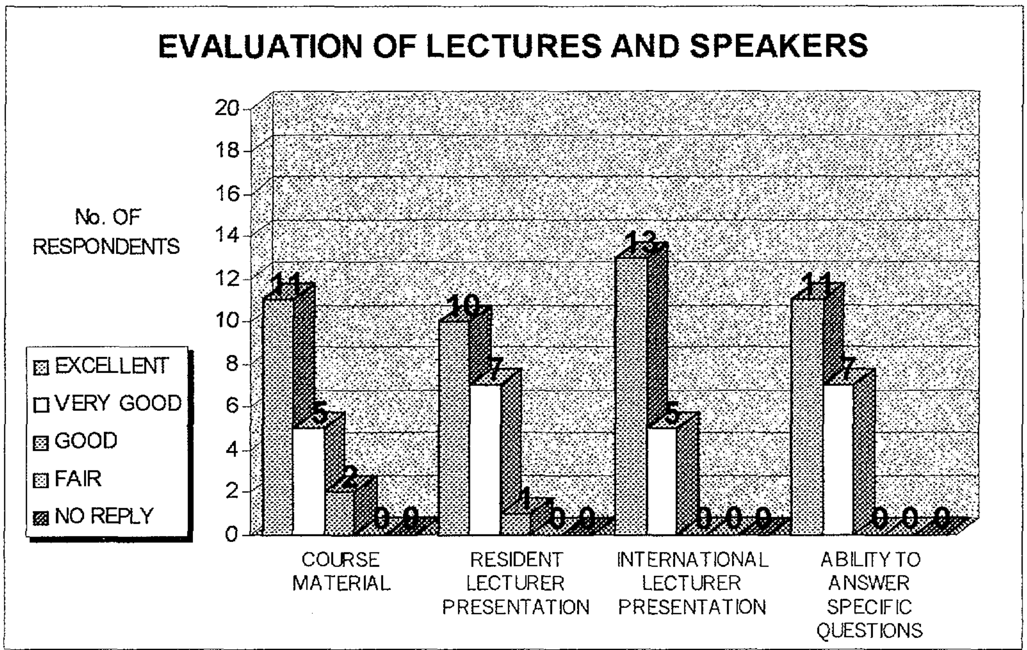
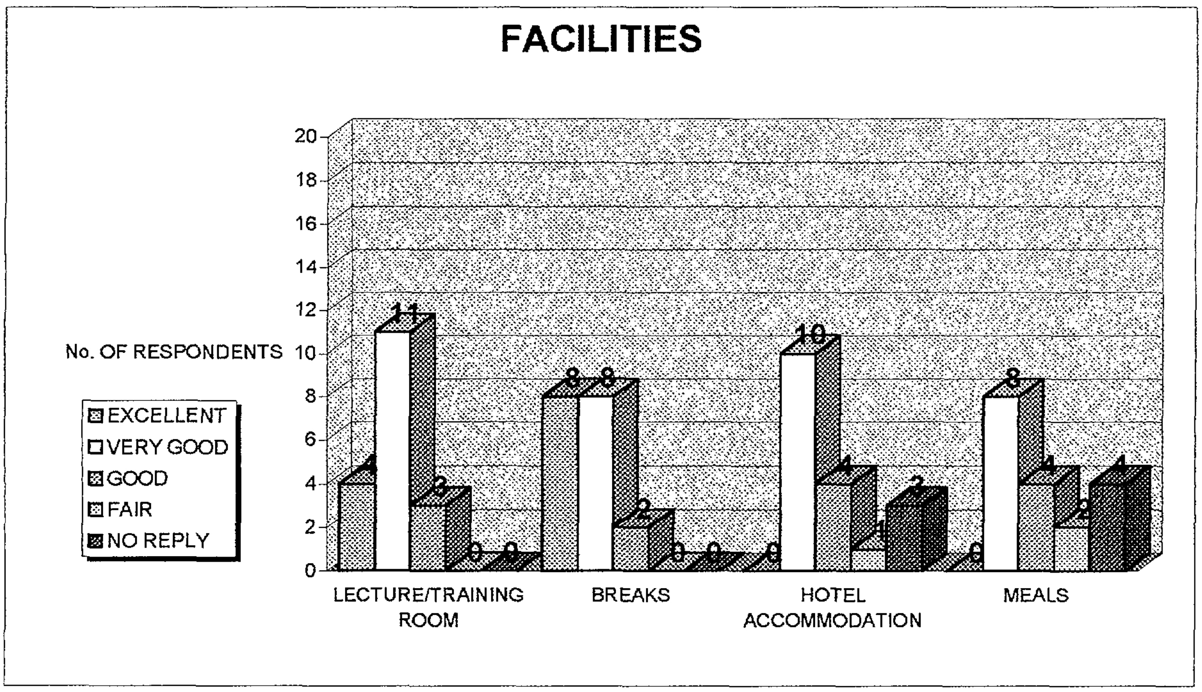
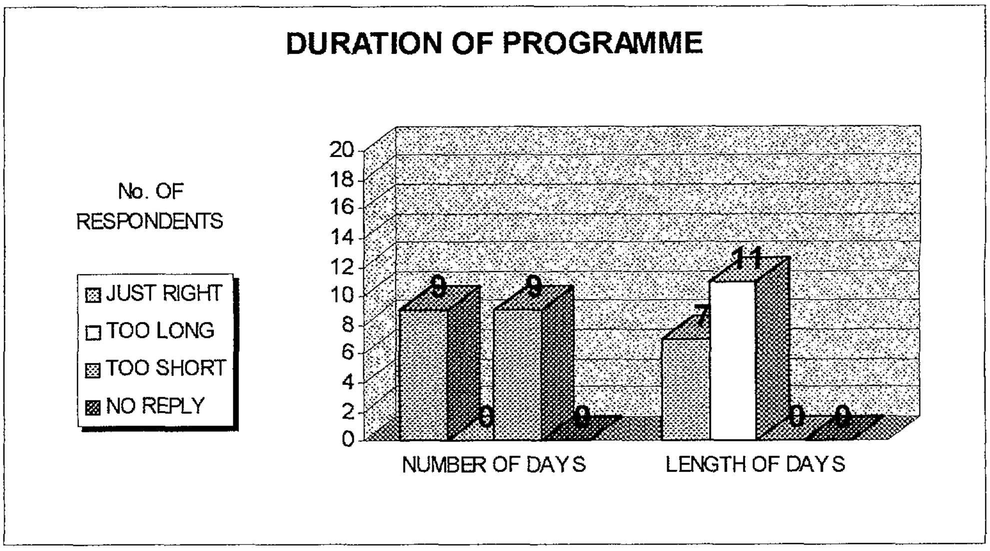
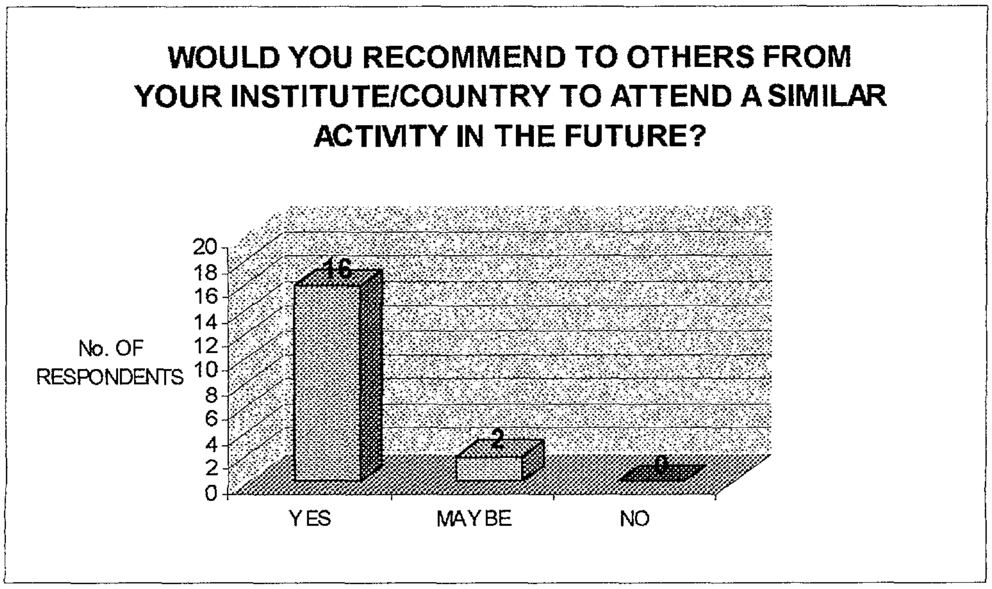


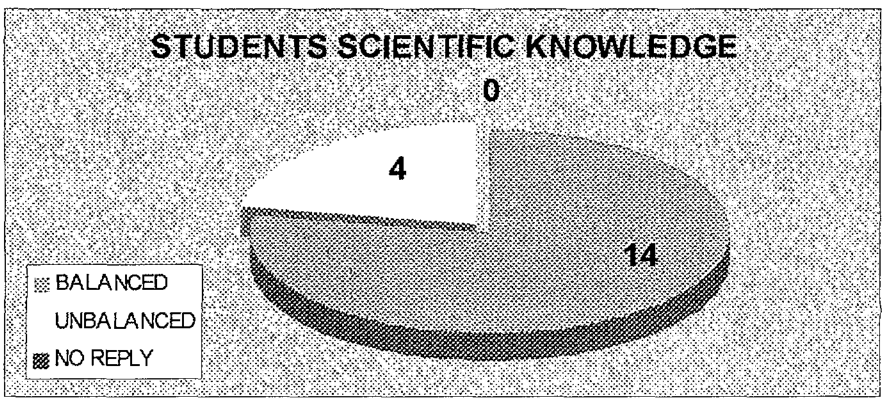


Training Course on "Sustainable Industrial Development: Process Simulation and Optimization Techniques", Rabat, Morocco
18-22 September 2000

EVALUATION







International Centre for Science and High Technology

Gennaro Longo

Programme Officer

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International Centre for Science and High Technology

ICS

Autonomous Institution operating within UNIDO legal framework

International Centre for Science and High Technology

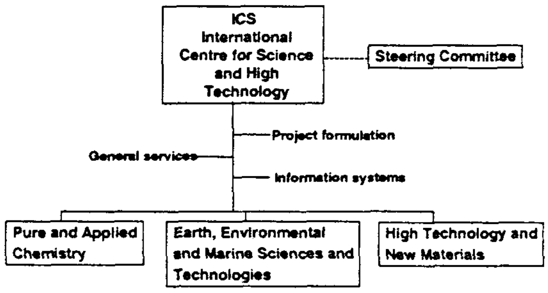
Funded by Nobel prize-winner Prof. Abdus Salam in 1988

Supported by Italian Government

Headquarters: Trieste, Italy (within the Area Science Park)

International Centre for Science and High Technology

Institutional Structure



International Centre for Science and High Technology

Steering Committee

- Italian Government representatives
- Representative of Developing Countries
- UNIDO representative

International Centre for Science and High Technology

Objectives of ICS

- to foster and facilitate the transfer of technology in specific high-tech areas to developing countries
- to provide high-tech SMEs in developing and transition-economy countries with advanced tools and services for the enhancement of their sustainability and competitiveness

International Centre for Science and High Technology

Project proposals

- traditional training activities at ICS support the identification and formulation of projects, which are submitted to donors for funding
- project proposals are identified and implemented with the support of experts and fellows from industries or institutions

International Centre for Science and High Technology

General Framework

- training courses
- scientific workshops
- high-level seminars
- fellowships
- publications and training packages

International Centre for Science and High Technology

Networking

Identification in various regions of the world, selection and evaluation of partner institutions willing to offer

co-operation and support

International Centre for Science and High Technology

Cooperation with different International and high-level Organizations:

→ **UNIDO** (United Nations Industrial Development Organization)

→ **UNEP/MAP** (Mediterranean Action Plan)

→ **MCSD** (Mediterranean Commission for Sustainable Development)

→ **CEI** (Central European Initiative)

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Training Activities 1988-1999

266 Workshops, courses, conferences

8754 Participants (including individual training & expert group meetings)

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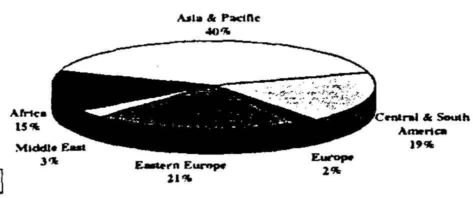
Training for Developing Countries



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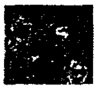
Fields of Activity


Pure and Applied Chemistry


Earth, Environmental and Marine Sciences and Technologies


High Technology and New Materials

International Centre for Science and High Technology

Pure and Applied Chemistry

- Catalysis and sustainable chemistry
- Biodegradable plastics 
- Remediation
- Combinatorial Chemistry and Technologies

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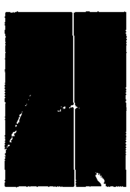
High technology and New Materials

- ***high technology***
  laser applications and optical technologies for industry and medicine
- ***new materials***
  composite materials for low-cost housing
- ***photovoltaic solar energy***
  diffusion of pv systems and applications
- ***telecommunication technologies***
  radio communications, fixed, mobile, satellite and rural networks



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Earth, Environmental and Marine Sciences and Technologies

- impact analysis of industrial development
- sustainable industrial exploitation of natural resources
- forecasting and monitoring
- process simulation

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Environment subprogrammes

- Technologies for sustainable industrial development
- Coastal Zone Management
- Industrial Utilization of Medicinal and Aromatic Plants

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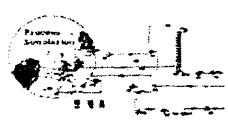
Technologies for sustainable industrial development

- Reinforce decision-making process for sustainable industrial development
- Exploit modern technical tools:
  - Process simulation
  - Remote sensing
  - GIS
  - Image processing



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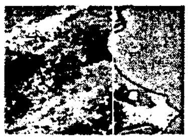
Coastal Zone Management

- Sustainable development of coastal economics
- Integration of scientific, economic, legislative aspects
- Application of decision support systems for:
  - industrial siting
  - resource management and control
  - control and monitoring of pollution
  - marine navigation control



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Industrial Utilization of Medicinal and Aromatic Plants

- Consolidation of existing technology for developing countries
- Technical assistance in product R&D
- Raising government awareness

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Training Course on

Sustainable Industrial Development: Process Simulation and Optimization Techniques

International Centre for Science and High Technology

Training Course on

Decision Support Systems: Process Simulation and Optimization Techniques

Maurizio Fermeglia

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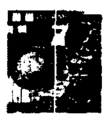
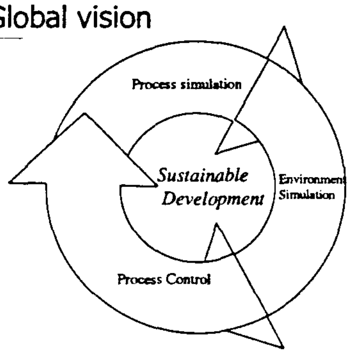


The motivation

- Sustainability and Chemical Engineering
  - Knowledge on chemistry, physics, mass and energy flows, process technology, computer science
  - Traditional Role: design and operation of chemical process
  - New Roles: ethical and rational public policy involving science and technology
- The sustainable development is a process in which one tries not to take more from nature than nature can replenish
  - Technology respects the imposed constraints
  - Engineers are asked to design new processes and/or modifying existing processes aiming at
    - Using renewable resources
    - Producing by products that can be returned to the earth
- Focus on Process Simulation and Optimization techniques
  - Lack of adequately trained personnel in the area
  - Lack of knowledge on the possibilities in the decision making environments
  - Process simulation as a Decision Support System for describing and for optimizing the process
  - Training people and introducing Process Simulation in developing countries

The Global vision



The objectives of the course

- To set-up a training course structure considering process simulation within the framework of sustainable industrial development, to be used during the present course, and to be considered for the development of a training package to be made available to developing countries;
- To present the necessary background and basic principles necessary to understand and use the informatic tools implementing process simulations, process control and optimisation techniques;
- To describe and teach 'how to use' specific programs by means of demo and 'hands on' sessions;
- To explain how to tackle a simulation problem by showing the sequential steps to be considered in the development of a simulation and optimisation strategy;

Benefits for the Participants

- Participants will learn the basic principles of the sustainable chemical technology
- Participants will gain perspective and insight into the potential applications of simulation and optimisation techniques
- Participants will gain experience in the use of specific computer tools that are currently available.
- Participants will gain experience by the presentation of case studies of interest.

The structure of the course

- Traditional sessions in the morning
  - Basic principles and fundamentals
    - Sustainable industrial development
    - Process Simulation
    - Matyhematical modelling
    - Dynamic simulation and control
  - Inside ...
    - Thermodynamic modeling and data banks
    - User interface
    - Complex unit operations
    - Case studies
  - Specific topics
    - Batch distillation
    - Environmental applications
- Hands on sessions in the afternoon
    - User interface and physical properties
    - Single stage unit operations
    - Complex unit operations
    - Dynamic simulation

Training Course on Sustainable Industrial Development, Process Simulation and Optimization Techniques — Rabat, 11 September, 2000 - slide 7

Agenda...

- Sustainable industrial development
  - Sustainability: why? what? how?
  - Scenarios and goals
  - Master equations, indicators and tools
  - Implications for education
  - Sustainable chemical technologies
  - The role of chemical engineers
  - The role of chemical engineering education
  - A few examples
  - Conclusions

Training Course on Sustainable Industrial Development, Process Simulation and Optimization Techniques — Rabat, 11 September, 2000 - slide 8

...Agenda ...

- Process simulation fundamentals
  - Process simulation goals and definitions
  - Benefits and applications of process simulation
  - Numerical strategies
  - Process simulation: the procedure
  - The results obtainable with process simulation
  - Dynamic simulation
  - Process simulation as a decision support system
- User interface
  - User interface description and general concepts
  - Advanced operability
  - Engineering workflow integration
  - Hardware and operating system
  - A survey of the existing software

Training Course on Sustainable Industrial Development, Process Simulation and Optimization Techniques — Rabat, 11 September, 2000 - slide 9

... Agenda ....

- Data banks, physical properties and phase equilibrium
  - User environment and data banks (demo)
  - Physical Properties and Phase Equilibria
  - Fugacity end Fugacity coefficients
  - Equations of state by integration and derivation
  - Activity coefficient models
  - Henry's law approach
  - Comparison between two approaches
  - Classification of the most common GE models and EOS
  - Model selection criteria
  - Conclusions
- Single stage flash and environmental applications
  - Flash
  - General statements and strategy
  - Main features of an environmental policy
  - Pollution prevention techniques and Process simulation
  - Applications and examples

...Agenda...

- Industrial applications
  - Capacity and selectivity
  - Stage processes
  - Continuous contact processes
  - Distillation columns
  - Absorption and stripping columns
  - Degrees-of-freedom analysis
  - Example: simulation of tray distillation columns
  - Simple example with a Process Simulator
- Complex Separation units
  - Ternary Liquid-Liquid Equilibrium (LLE) diagrams
  - Single- and multi-stage extraction devices
  - Fluids at supercritical conditions
  - Extraction with supercritical fluids
  - Potentials of dense gases in the chemical and process industry
  - Precipitation & crystallisation with dense gases as antisolvents

... Agenda ....

- Industrial case studies
  - Production of Propylene Oxide in a Reactive distillation column
  - Solvent Extraction of ε-Caprolactam
  - Off-gas Packed Column Reactive Absorber
  - Feed Change Analysis in a Oil Refinery Plant
  - LPG plant
- Batch distillation
  - Batch processes & batch distillation
  - Differential ("simple") distillation
  - Modeling of batch rectifiers
  - Operation of batch rectifiers
  - Slop cut handling
  - Alternative configurations

... Agenda

- Process Dynamics and Control
  - Objectives and jargon of process control
  - Process modeling
  - Dynamics of linear systems
  - *Conventional feedback control*
  - Improved control schemes (cascade and feedforward)
  - Multivariable systems
- Examples and case studies
  - Recovery of cyclohexane from a hydrogenation reactor
  - Distillation of methylcyclohexane with phenol
  - Phosphoric acid production

The Program

- Monday, 18 September 2000 - Morning Session

08.30 – 09.00	Registration
09.00 – 09.20	Opening, welcome address, Mr. R. Long, LATU
09.20 – 09.45	Welcome address, presentation of ICS, Mr. G. Longo, ICS-UNIDO
09.45 – 10.15	Presentation and scope of the Training course, Mr. M. Fermeglia, ICS-UNIDO
10.15 – 10.30	Short presentation of the participants
10.30 – 10.35	*Information on local arrangements*
10.35 – 11.00	Coffee break
11.00 – 12.30	Sustainable industrial development, Mr. A. Bertucco, University of Padua, Italy
12.30 – 14.30	Lunch break

- Monday, 18 September 2000 - Afternoon Session

14.30 – 16.00	Process Simulation fundamentals and techniques, Mr. M. Fermeglia
16.00 – 16.30	Coffee break
16.30 – 18.00	Steady State Process Simulation: user interface and philosophy, Mr. M. Fermeglia

The program

- Tuesday, 19 September 2000 - Morning Session

09.00 – 10.30	Data banks, physical property calculation, thermodynamic and phase equilibria models, Mr. M. Fermeglia
10.30 – 11.00	Coffee break
11.00 – 12.30	Single stage operations and environmental applications, Mr M. Fermeglia
12.30 – 14.30	Lunch break

- Tuesday, 19 September 2000 - Afternoon Session

14.30 – 16.00	Hands-on: Thermodynamics and single stage unit operations, Mr. M. Barolo, University of Padua, Italy, Mr. A. Bertucco, Mr. M. Fermeglia
16.00 – 16.15	Coffee break
16.15 – 17.30	Hands-on (continuation)

The program

- Wednesday, 20 September 2000 - Morning Session
  - 09.00 – 10.30 Industrial applications of process simulation: counter-current separation units (distillation, absorption, stripping), Mr. A. Bertucco
  - 10.30 – 11.00 Coffee break
  - 11.00 – 12.30 Complex separation units: conventional and supercritical fluid extraction, Mr. A. Bertucco
  - 12.30 – 14.30 Lunch break
- Wednesday, 20 September 2000 - Afternoon Session
  - 14.30 –16.00 Hands-on: industrial applications, Mr. M. Barolo, Mr. A. Bertucco, Mr. M. Fermeglia
  - 16.00 – 16.15 Coffee break
  - 16.15 – 17.30 Hands-on (continuation)

The Program

- Thursday, 21 September 2000 - Morning Session
  - 09.00 – 10.30 Industrial case studies, Mr. A. Bertucco
  - 10.30 – 11.00 Coffee break
  - 11.00 – 12.30 Modelling, simulation and optimization of industrial plants, Mr. T. Bounahmidi
  - 12.30 – 14.30 Lunch break
- Thursday, 21 September 2000 - Afternoon Session
  - 14.30 – 16.00 Batch distillation, Mr. M. Barolo
  - 16.00 – 16.15 Coffee break
  - 16.15 – 17.45 Hands-on: batch distillation, Mr. M. Barolo, Mr. A. Bertucco, Mr. M. Fermeglia

The Program

- Friday, 22 September 2000 - Morning Session
  - 09.00 – 10.30 Fundamentals of Process Dynamics and Control: Part I, Mr. M. Barolo
  - 10.30 – 11.00 Coffee break
  - 11.00 – 12.30 Fundamentals of Process Dynamics and Control: Part II, Mr. M. Barolo
  - 12.30 – 14.30 Lunch break
- Friday, 22 September 2000 - Afternoon Session
  - 14.30 – 16.00 Hands-on: fundamentals of process dynamics and control, Mr. M. Barolo, Mr. A. Bertucco, Mr. M. Fermeglia
  - 16.00 – 16.15 Coffee break
  - 16.15 – 17.30 Hands-on (continuation)
  - 17.30 – 18.00 Closure, Mr. G. Longo

Logistic

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Process Simulation Fundamentals and Techniques

Maurizio Fermeglia

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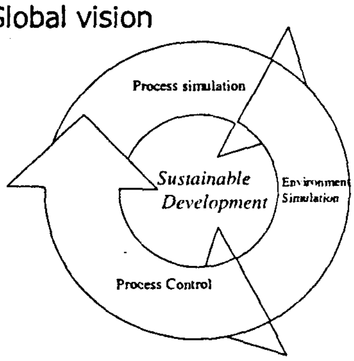
The Global vision



DICAMP - CASLAB

- Department of Chemical, Environmental and Raw Material Engineering - University of Trieste
  - Fundamental studies on Transport Phenomena (Diffusion, Rheology,..), Phase Equilibria (VLE, LLE, GLE) and kinetics
  - Applied studies on separation processes, waste treatments, supercritical fluid extraction, technologies for food production, new materials,...
- Computer Aided Systems Laboratory
  - Process synthesis design and modeling
  - Prediction of thermo physical properties
  - Computational chemistry and physics
  - Data Base development and Web distribution techniques

Agenda

- Process simulation goals and definitions
- Benefits and applications of process simulation
- Numerical strategies
- Process simulation: the procedure
- The results obtainable with process simulation
- Dynamic simulation
- Process simulation as a decision support system

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Solving Material and Energy Balances using Flowsheeting Codes

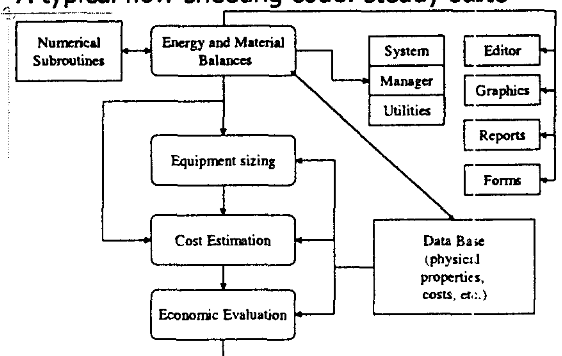
Flowsheeting: steady state process material and energy balances
Flowsheeting Package or Code: the computer code for solving the material and energy balance
Equations in time domain or in space domain

Process Simulation

- Process: a group of operations that transform input streams into product streams by means of chemical-physical transformations
- Simulation: the mathematical representation of the reality by using a computer
- Dynamic process: a process which is studied in the time domain rather than in steady state

- Thermophysical properties: the crucial point
- Data Banks: the basic value
- Unit operations: mathematical modelling
- Other modules such as optimization, numerical procedures,...
- Cost estimation methods
- ....

A typical flow-sheeting code: steady state



Mathematically speaking

- n non linear material balances equations
- 1 energy balance non linear equation
- set of differential - algebraic equations (dynamic simulators)
- In presence of:
  - Very many components;
  - Complex thermo-physical models for phase equilibrium calculations
  - A high number of subsystems (equipment)
  - Rather complex equipment (distillation column,...)
  - Recycle streams
  - Control loops

The fundamentals

- Different possibilities for process simulation
  - Steady state simulation
  - Dynamic simulation
  - Integrated steady state - dynamic simulation
- Different philosophy
  - Process analysis
  - Process synthesis
- Process simulation impact on industry
  - The way engineering knowledge is used in processes
  - The design procedure of the process (plant)

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From a traditional way of using process simulation ...

Flow sheet design
Equipment Critical parameters definition (such as distillation column stages, column diameter,...)

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... to the comprehensive use of Process simulation in the entire 'life' of the plant

Control strategies design
Process parameters optimization (--> 'better' processes)
Time evolution of the process (start up and shut down) (--> risk analysis)
Operator training
Definition of procedure to reduce the unsteady state operations
Process synthesis and design
Data Acquisition and Interface to ERP systems

Benefits of process simulation

- Partial or total replacement of Pilot Plant operations
  - Reduction of the number of runs
  - Runs planning
- Reduction of Time to market for the development of new processes
  - New processes
  - Modification of existing processes (different solvent,...)
  - Production of new materials
- Fast screening of process alternatives to select the best solution
  - economic aspects
  - environmental aspects
  - energy consumption aspects
  - flexibility of the proposed process

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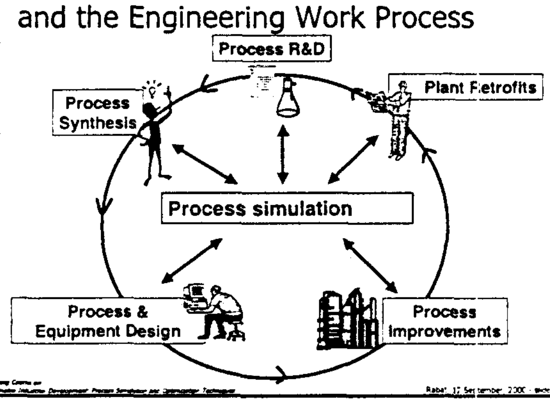
Industrial Processes are complex

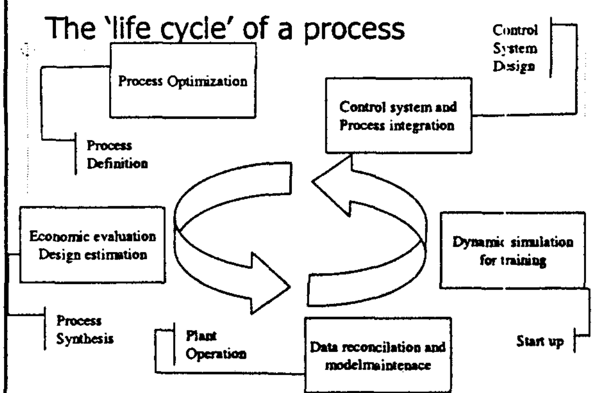
To get those benefits one must
CRITICALLY SIMPLIFY THE PROCESS

➔ The need of engineering knowledge and experience

Process simulation and the Engineering Work Process



The 'life cycle' of a process



Numerical strategies

- Equation oriented strategy - simultaneous solution
  - Write down the entire set of equation
  - Identify the constraints
  - Solve the non liner system
- Sequential Modular approach
  - Each subsystem is solved independently, starting from the first one
  - Output streams for the solved subsystems are input streams for the next subsystem
  - Problems for the recycle streams (of material, energy and information)
- Combination of the two extreme approach
  - Equation can be lumped into modules
  - Modules can be represented by polynomials that fit input-output information

Equation oriented flow-sheeting ...

- Solution of a set of non liner equations with constraints
- Definition of the matrix of the stream connection (process matrix)
- Definition of the inequality constraints
  - Linearization of non-linear equations
  - Process limits for Temperature, Pressure, concentration
  - Requirements that variable be in a certain order
  - Requirements that variables be positive or integer
- Define the procedure for determining the order in solving the equations
- The treatment of feedback (recycles)

Equation oriented flow-sheeting

- Method of solution
  - Newton Raphson
  - Secant
- Tearing = selecting certain output variables from a set of equations as known values so that the remaining variables can be solved by serial substitution
- Partitioning = partition of equations into blocks containing common variables
- Definition of initial guess
- Scaling the variables (the same order of magnitude)
- Scaling the equations (the same deviation from zero)

Sequential modular approach

- Most common approach
- Each unit operation is described by a subroutine (or DLL)
- *The output of a module is the input of the next module*
- Other subroutines take care of
  - equipment sizing and cost estimation
  - numerical calculations
  - handle recycle calculations
  - optimize and serve as controllers for the whole set of modules
- Tearing is the process of solving the recycles by deciding which stream should be interrupted and guessed
- Partitioning
- Fortran or C++ codes

Rabat, 12 September 2000 - slide 19

Advantages and disadvantages

- Advantages of sequantial modular approach
  - The flow-sheet architecture is easily understood because it closely follow the process
  - *Individual modules can easily be added and removed*
  - Modules of different levels of accuracy can be substituted
- Drawbacks of sequantial modular approach
  - The input of a module is the output of a module: you cannot arbitrarily introduce an output or input
  - The modules need extra time to generate derivatives (perturbation of the input)
  - *The modules may require a fixed procedure for the order of solution: slow convergence*
  - Parameter specification is done with control loops: possibility of introducing nested loops
  - Phase equilibrium instability during the convergence of the process

Rabat, 12 September 2000 - slide 20

Steady state simulators: the core product

- Steady-state simulator are directly used in
  - process design
  - evaluating process changes
  - analyzing what-if scenarios
- And is the basis for:
  - dynamic simulation
  - process synthesis with Pinch technology
  - detailed equipment design
  - off-line and on-line equation-based optimization
  - application technologies for vertical markets, e.g. polymers

Rabat, 12 September 2000 - slide 21

Process simulation: the procedure

- Identify the problem
- Obtain all the relevant information
  - Get process data: flow rates, operative conditions, concentrations
  - Get thermodynamic data:
    - In house data
    - Data Banks (Dechema, ...) or literature
    - Through test run on laboratory / pilot plant
    - Via estimation methods (be suspicious
  - Get kinetic data
    - Directly from pilot plant
    - from excess Gibbs energy calculations (if possible)
    - directly from plant data
  - TIP: avoid a rigorous definition of kinetic model and use concept of yield and conversion wherever possible and reasonable, at least in the firsst stage of the development

... Process simulation: the procedure ...

- Select the software
  - Steady state simulation
    - AspenPlus
    - ChemCad III
    - Design 2000
    - Hysim
    - Pro II
    - .....
  - Dynamic simulation:
    - Speedup - Aspen custom model
    - Hysis
    - Protiss
    - gPROM and ABACUSS
    - ....
  - Integrated solution
    - Aspen Dynamic, Hysis, Pro II, ...
- Select the Hardware

... Process simulation: the procedure

- Training
  - Basic course on process simulation
  - Thermodynamic, phase equilibria and model selection
  - Specific topics in thermophysical property calculation
    - Electrolytes
    - Polymer systems
    - Kinetic data and kinetic modeling
  - Specific topics in unit operation modeling
    - heat exchangers design
    - Batch distillation and reaction
    - heat integration
  - Dynamic process simulation
  - Economic factors, cost analysis and energy consumption
  - Environmental impact
  - Batch process modelling
  - Control system

Process simulation: the logic procedure

- Components definition
- Physical - Chemical properties definition
- Flow sheet connectivity
- Feed conditions definition
- Unit operation internal definitions
- Process specification definition
- Control parameters
- Equipment Hold up definition

Results obtainable

- Validation of phase equilibria models for the real system to be used in similar conditions
- Verification of the process operating conditions
- Information on intermediate streams (not measured)
- Enthalpy balances information
- Verification of the plant specifications
- Influence of the operative parameters on the process specifications
- Process De-bottleneking for each individual section
- A priori Identification of process control strategies and tuning of instrumentation
- Possibility to verify security systems behavior for variation of process condition

Problems involved

- Availability of all the required thermodynamic proerties of the pure components involved
- Definition of an accurate thermodynamic model (Equations of state or Excess Gibbs energy model)
- Availability of all the necessary unit operations modules
- Necessity of defining dummy operations, non always easy to identify
- Tear streams identification to achieve rapid convergence if in presence of recycles
- Necessity of defining user models and user thermo (In C++ ar FTN)

Dynamic Simulation

- What is dynamic?
  - dynamic simulation accounts for process transients, from an initial state to a final (steady) state
- Why dynamic simulation?
  - predicted transient behavior of processes under different conditions
  - can be used for
    - process design and development
    - advanced control
    - training plant personnel
    - optimizing plant operations
    - process reliability / availability studies

Dynamic simulation: process design and development

- Gives the design engineers a tool to conceptualize and verify process design by simulating
  - different design alternatives
  - operative conditions
  - safer process design can be accomplished quicker and more cost-effectively
  - developing and testing alternative control schemes used to model a chemical process in basic regulatory control schemes as
    - Internal Model Control (IMC)
    - Model Predictive Control (MPC)

Dynamic simulation: advanced control

- Advanced control of processes includes
  - Regulatory mode: responsible for
    - disturbance rejection
    - bringing the process set point
  - Transition mode: responsible for manipulating setpoints for controllers
    - start up
    - shut down

Dynamic simulation: training plant personnel

- Disturbances can be modeled and operator response can be monitored in an easy, cost effective way
  - DCS systems - control panel simulated by an external dynamic simulator
  - networked workstation - central server provides access to problem data base
  - standalone PC (see above)

Dynamic simulation: optimizing plant operations

- By using an appropriate objective function (product quality) dynamic simulation can optimize (off-line or real time):
  - operating efficiency
  - profit or cost
  - environmental impact

Dynamic simulation: process reliability / availability studies

- Determining
  - failure propagation speed
  - equipment reliability
  - equipment availability

Characteristics of a dynamic simulator

- Components
  - Thermodynamic / Physical properties
  - Unit operation models
  - Numerical solvers
- Mathematically
  - Consist of large systems of ordinary differential and algebraic equations
- Computationally intensive
  - Solver issues: speed - robustness
  - Mathematical problems: non-linear - sparse - stiff
- Approaches
  - Equation based approach
  - Sequential modular approach

Applications of Dynamic Simulation

- Continuous Processes
- Concurrent process and control design
- Evaluation of alternative control strategies
- Troubleshooting process operability
- Verification of process safety

- Batch Processes
- Design of batch and semi-continuous processes

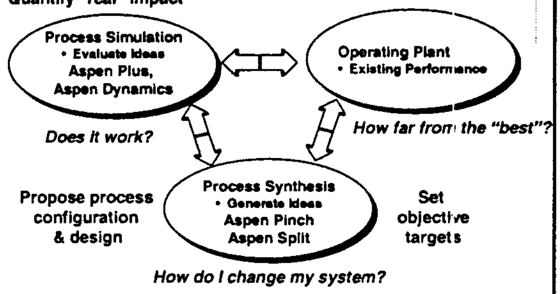
- Online Applications
- Calculation of inferential measurements
- Identification for model-based control
- Decision support

Benefits of Dynamics Modeling

- Capital avoidance and lower operating costs through better engineering decisions
- Throughput, product quality, safety and environmental improvements through improved process understanding
- Increased productivity through enhanced integration of engineering work processes

Integration of Process Synthesis & Process Simulation

Quantify "real" impact



What Process Simulation can do ... and cannot

- Basic 1: apply the degree-of-freedom analysis
- Basic 2: write & solve material+energy balances
- Special: sensitivity analysis and optimisation

HOWEVER

- no equipment design nor momentum balances
- models of some important units missing
- convergence not sufficient for meaningful results
- a PS is a tool: it cannot interpret results

Potentials of the PS in the process industry

- Basic 1: representing plant operating conditions
- Basic 2: process development and revamping
- Advanced: on-line process operation and control
- Advanced: operator training (regular and safety)

TIPS FOR A SUCCESSFUL SIMULATION:

- verify thermodynamic and kinetic data reliability
- select suitable property models and parameters
- calibrate simulation results on pilot plant runs

Cautions in using a process simulator: it is nonsense ...

- to run a PS without an accurate selection of the property models
- to select a good property model without knowing the value of its parameters
- to use predictive models anyway; one good experimental property datum is always better

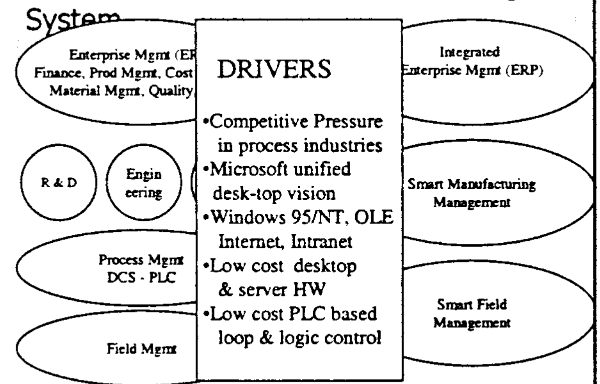
... and note that

- Avoid the GIGO (garbage in gospel out) approach
- The best available model might not be the best choice

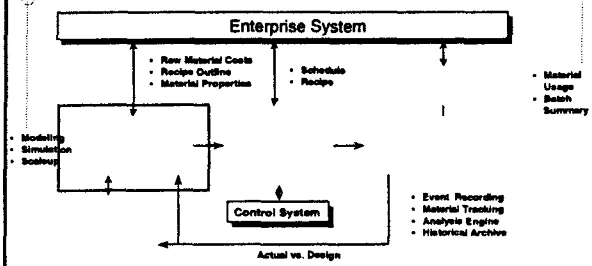
Process Simulation and Decision Support Systems

- Three layers of activities in the smart manufacturing system
  - Management control
  - Process simulation
    - Off-line
    - On-line
  - Control system
- Information distribution is made through interoperability of the software
- In Process simulation crucial point is optimization
  - Use Active x objects to export optimum solutions to other software

The birth of the Smart Manufacturing System



Example: an Integrated Batch Solution



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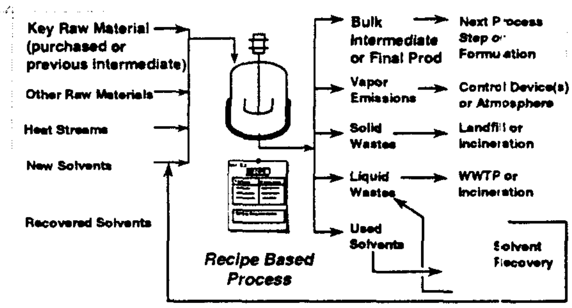
General Batch Process



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Enterprise wide solutions

- Smart manufacturing system
  - Operates at the plant leve
- Enterprise optimization
  - Optimize consumtions and flow of materials at the enterprise level
- Syupply chain
  - Extend across the supply chain management

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In Summary we went through ...

- Process simulation goals and definitions
- Benefits and applications of process simulation
- Numerical strategies
- Process simulation: the procedure
- The results obtainable with process simulation
- Dynamic simulation
- Process simulation as a decision support system

Conclusions

- Process simulation is a powerful methodology for
  - Material and energy balances in steady state conditions
  - Material and energy balances in dynamic condition
  - Investigation of process dynamics and batch process
  - Implementation of a control strategy
- Process simulation is applicable in different field of the process engineering
  - Analysis of existing processes (optimization, debottlenecking,...)
  - Synthesis of new processes (solvent selection, environmental impact,...)
  - Operator training, process dynamics start up and shut down ...
- Process simulation is applicable in the framework of environmental impact study and sustainable development
  - What if analysis
  - Safety analysis
  - New and cleaner processes investigation

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Process simulation is a simple and helpful tool...

... to be used by chemical engineers that fully understand the process

... Never let a kid play with a kalasnikof....

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Sustainable Industrial Development

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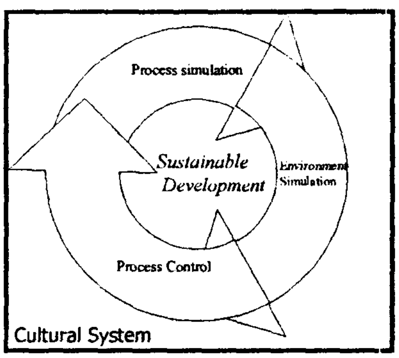
Agenda

- Sustainability: why? what? how?
- Scenarios and goals
- Master equations, indicators and tools
- Implications for education
- *Sustainable chemical technologies*
- The role of chemical engineers
- The role of chemical engineering education
- A few examples
- Conclusions

The Global vision



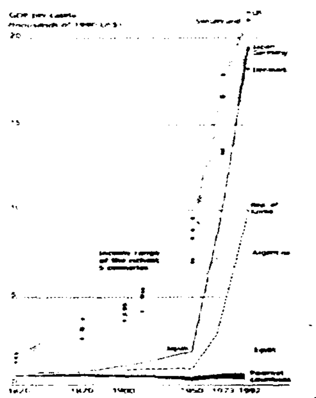
Why: human fertility

Country	Children per women	Country	Children per women
Italy	1.24	Canada	1.74
Spain	1.27	England	1.78
Germany	1.30	China	1.92
Holland	1.59	Sweden	2.01
France	1.70	U.S.A.	2.05

- *Total world population expected to be around 10 billion by year 2050*
- *The larger growth expected in the less developed countries*

Why: rich & poor

- *Widening gap between peoples since the early 19th century*



Why: some fundamental points

All people want to share prosperity
All people have the right to do it
The 'developed' countries are a minority, but give a major contribution to the depletion of natural resources
World population is growing, average lifetime is increasing

Why: some fundamental points

Pollution has become a daily issue also for human health (not only for the environment) in many parts of the world
Energy and materials are being consumed at a rate which could not be applicable to the total world population
We will come to fight about the same (limited) resources
This situation cannot last any longer:
it is not sustainable

What: some definitions

- *"Humanity has the ability to make development sustainable, to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs" (The Bruntland Report, 1987)*
- *"Sustainable development is the means of improving the quality of human life while living with the carrying capacity of the supporting ecosystems" (UNEP)"*
- *What about sustainability of industrial (chemical) productions? "Sustainability in Chemical Engineering means a continuous effort to protect and improve ecosystems, social balance and economic prosperity by a systematic and integral improvement of environmental protection, raw material exploitation, energy efficiency, safety, and health protection in all kinds of material conversion processes and material production" (EFCE definition)*

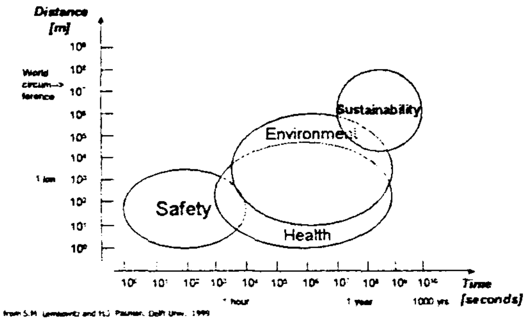
NOTE: a necessary yet not sufficient condition:
A sustainable industrial process must be safe anyway

How: some fundamental points

- *achieving safety in production activities*
- *ensuring human health*
- *protecting the environment*
- *running the world ecosystem in steady-state conditions*

this is the goal of sustainability

Inter-relation with time scale



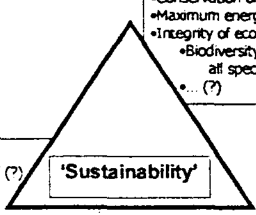
Scales of (Un)sustainability

Whom/what is sustainability concerned with?

- *Time scale: generations (centuries)*
- *Spatial scale: planet earth*
- *Biological scale: all life forms (eco-systems)*
- *'Social scale':*
  - *All societes*
  - *Equity*
  - *Quality of life*

A sketch for sustainability: which goals

Environmental goals:
- Human health protection
- Conservation of non-renewable resources
- Maximum energy and material efficiency
- Integrity of ecosystems
  - Biodiversity, i.e. total protection of all species (?)
- ... (?)



Social goals:
- Population 'control' (?)
- Social mobility (?)
- Equity (?)
- Participation of women (?)
- Cultural identity (?)
- Institutional development (?)
- ... (?)

Economic goals
- Efficiency
- Growth (?)
- Equity (?)
- ... (?)

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Master Equation 1

Unsustainability Impact =

(Population)
x
(GDP per population)
x
(Unsustainability impact per GDP)

Note: *'Environmental Impact'* and *'Unsustainability Impact'* are inter-changable

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Master Equation 2

Environmental Impact =

(Number of people)
x
(Production per person)
x
(Consumption and pollution per unit of production)

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Master Equation 3 (engineers)

Annual Impact on the Environment =

(Environmental Impact per Unit of Resource
x
(Resource Use per Unit of Product)
x
(Product Demand per person per Year)
x
(Number of People)

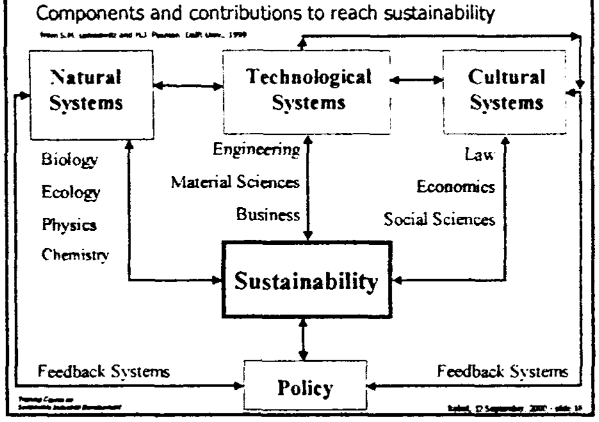
Indicators of (Un)sustainability

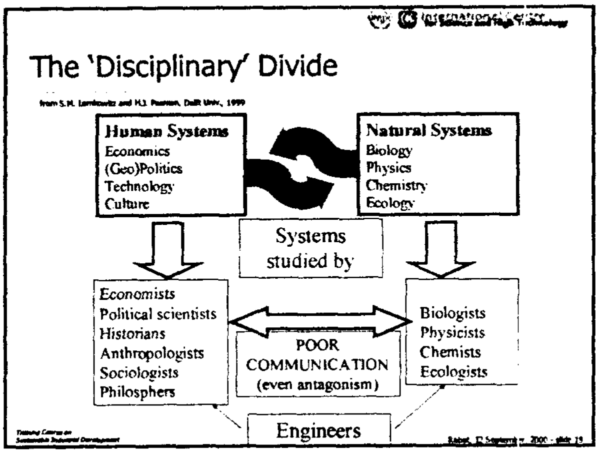
- *population growth*
- *food production*
- *energy: resources, reserves*
- *climate patterns*
- *emissions/concentrations (CO_2, CH_4, NO_x, SO_2, CFCs)*
- *deforestation*
- *loss of habitat*
- *loss of bio-diversity*
- *social indicators:*
  - *income equity: (inter)national*
  - *crime, suicide*
  - *mass emigration*

Tools for Achieving Sustainability

- *from short term to long term perspective*
- *the 'big picture': systems approach*
  - *economics (internalizing 'external costs')*
  - *laws ('wastes' or 'residuals')*
  - *education (modifying norms/values)*
  - *stabilizing population*
  - *promoting equity*
  - *dematerializing economic development*

Components and contributions to reach sustainability

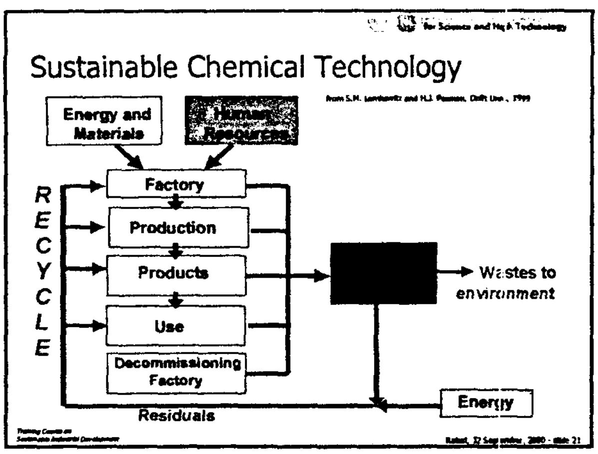




A Fundamental Question for Education

- *Is good education 'subversive'?*
- *University 'education' versus 'training'*
- *Education stimulates questioning of basic tenets, such as functioning of modern capitalism. That is, it stimulates ideas.*
- *Difference between:*
  - *'What is true'*
  - *'What is good'*
  - *('Facts' versus 'Values')*
- *Value questions: stress 'balance' rather than 'objectivity'*
- *Importance of dialog!*

Good education stresses 'critical ref ection'



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Sustainable Chemical Technologies should enable environmentally sound processes and products

- *with less amount of residues* (in air, water and soils)
- *with higher selectivity and yields* (less by-products)
- *with less resource consumption* (dematerialization)
- *under safer conditions* (no risks nor toxic compounds)
- *more based on renewable raw materials* (biomass)
- *more economical*

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Chemical Engineering and Sustainability

For any product, throughout its life cycle, it must be ensured:

- Minimum resource and energy use
- Minimum emissions

In addition: useable residuals (recycled) instead of wastes

This is called **'Industrial Ecology'**

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The (huge) role of Chemical Engineers: Reducing unsustainability/GDP

- *Dematerialization*
- *'zero' is the goal (no pollution no waste)*
- *renewable resources*
- *Life Cycle Analysis (LCA) approach*
- *sustainability design tools*
- *'industrial ecology'*
- *democratization technology*

Chemical Engineers for Sustainable Chemical Technologies: we know what and how to do

- *We have the basic knowledge about concepts that can be easily extended to sustainability (SHE knowledge):*
  - *mass and energy balances*
  - *interactions between chemicals and the environment*
  - *safety (safe design and loss prevention)*
  - *effects on health*
- *We have the tools to make calculations and predictions: they are called Process Simulators and Environmental Simulators*
- *BUT we must be aware that we cannot solve the problem alone (by ourselves): we need interactions with other disciplines on an equal basis level*

The importance of Education in Chemical Engineering

- *Chemical Engineering is an essential 'tool' for sustainability!*
- *'Sustainability' can be easily integrated into Chemical Engineering*
- *It is important to present broad, integrated systems-based approach (avoid 'reductionism'!)*
- *Introduce 'sustainability' via core courses. Deepen via elective courses*
- *Use project-based education; stress:*
  - *Broad, systems-based analysis*
  - *Solution through design and simulation (consider entire life cycle)*
  - *Publication and dissemination of results*
- *Encourage participation of 'stakeholders' (industry, government, NGOs) in the educational process*

Directions summary

- *First, avoid wastes*
- *Second, reduce them in quantity, if it cannot be avoided*
- *Third, recycle, if it cannot be further reduced*
- *Fourth, contain, if it cannot be recycled*
- *Fifth and final, treat it if no other possibility is open*
- *For 'zero waste' first of all a chemistry effort is needed*
  So called green chemistry *aims at developing reactions to make products without producing wastes*

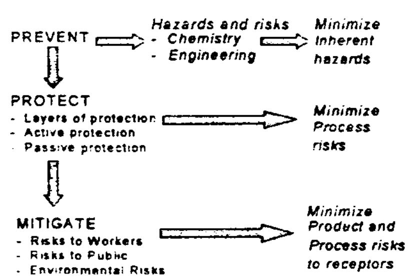
An example: the Kyoto Protocol to the UN Convention on Climate Change (CO_2)

- *Has aim of "the stabilisation of greenhouse gases at a level that will prevent dangerous anthropogenic interference with the climate system"*
- *Contains legally binding committments to limit or reduce greenhouse gas emissions*
- *Industrialised countries must reduce emissions within the period 2008-2012 by at least 5% below 1990 levels*
- *Allows inclusion of biological sources and sinks as well as fossil fuel emissions*

An example: the phase out of chloro-fluoro-carbon (CFC) compounds

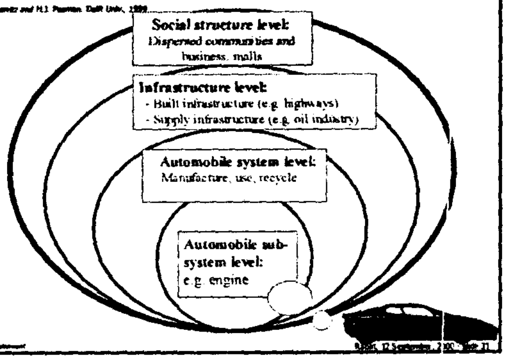
- *The depletion of the atmospheric ozone layer was a very strong fact that lead to the Montreal Protocol in 1987*
- *the use of CFCs for any application was banned by the year 1996*
- *A huge world market in current formidable expansion (refrigeration, conditioning,...) was forced to look for more sustainable alternatives in a 'very' short time*
- *New compounds (HFCs, HC) and mixtures were found out soon to substitute CFCs in the transition period*
- *Research was stimulated about 'natural' (environmentally benign) refrigerants*
- *the commitment is to replace completely all ozone-harmful compounds by 2030*

An Example: Hierarchical approach to safety and environmental risk reduction



An Example: the Automotive System

from S.M. Jansbewitz and H.J. Paulin, Delft Univ., 1999



An Example: Solvent substitution in the chemical and process industry

- *In the production of fine chemicals generates considerable waste volumes (roughly 15 kg per kg of product)*
- *It is essential to reduce this amount by using different (I.e. more sustainable) solvents*
- *Dense gases can lower the energy consumption and enable much easier recovery of products*
- *It is proposed to study extensively the use of compressed gases as alternate solvents and antisolvents in the chemical and process industry*
- *Water and carbon dioxide are the most promising ones, and are natural*
- *The technical feasibility of this change can be profitably achieved by process simulation*

Summary of Directions for Sustainability

- *Substitution of fossil fuels*
- *zero emissions*
- *low energy processes*
- *low impact products (recyclable)*
- *focus on basic needs*
- *Instruments of change: legislation, taxation, "responsible care"*
- *Tools for change: life-cycle analysis, environmental impact analysis, working with natural systems*

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A Challenge for Chemical Engineers

- *To bring the SHE issues at the design stage*
- *To make some steps forward:*
  - *from safe processes*
  - *to safe products*
  - *to sustainable processes and products*
- *Always remember that chemical engineering is necessary but not sufficient*

Preliminary conclusions: present situation

- *Present world* unsustainable
- *Increasing polarization:*
  - *ageing minority rich*
  - *youthful majority poor*
  - *rapid growth poor*
- *Pollution on world scale: possible climate change*
- *Loss of bio-diversity*

Preliminary conclusions: development

- *Steady state: ability of future generations to meet needs is not harmed*
- *Social-economic equity for present and future*
- *Limits to population, consumption, waste (social, technological, environmental constraints)*
- *Protection of Nature for its own sake ('intrinsic value')*

All of these are **crucial achievements**

Conclusions

- Awareness of the huge problem in front of us (culture)
- Dissemination of knowledge about sustainable technologies (ideas, projects)
- Formulation of short- and medium- time range projects
- High and constant pressure on politicians and decision makers
- Application of technical tools (Process simulators) for the assessment of sustainability in chemical productions

Essential role of and challenge for chemical engineers

A tip from last century greatest scientist

"It is not enough that your science should add to the sum of human knowledge: concern for man himself must always be your goal, concern for the great unsolved problems of the distribution of goods and the division of labour, that the creation of your mind may be a blessing, and not a curse, to mankind. Never forget this among your diagrams and equations"

Albert Einstein

However, never forget:

"Antea edere, deinde philosophare"

Some Latin writer, 2000 years ago

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Acknowledgments

The author is grateful to Dr. Saul M. Lemkowitz *and* Dr. M.J. Pasman *from Delft university of Technology, for their help in the preparation of this lecture*

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Process simulation: User Interface and Phylosophy

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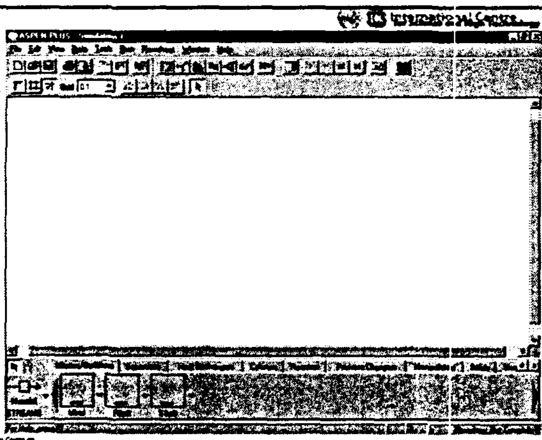
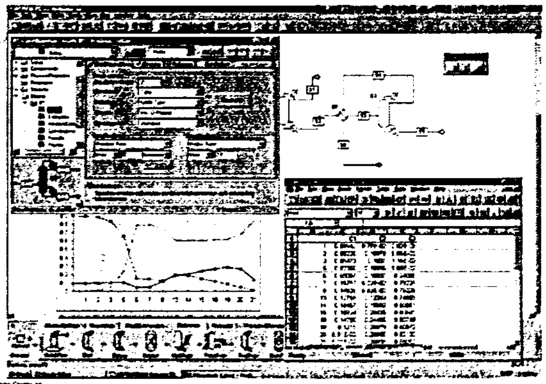
Agenda

- User interface description and general concepts
- Advanced operability
- Engineering workflow integration
- Hardware and operating system
- A survey of the existing software



ASPEN PLUS 10



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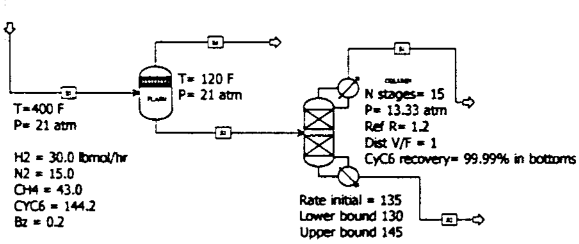
DEMO Time

Introduction to process simulation
Flowsheet definition
Component selection
Property selection
Run base case

Cyclohexane recovery study

Goal 1: to obtain a cyclohexane recovery of 99.99%
Goal 2: to maintain a flow rate in S1 of 30 lbmole/hr



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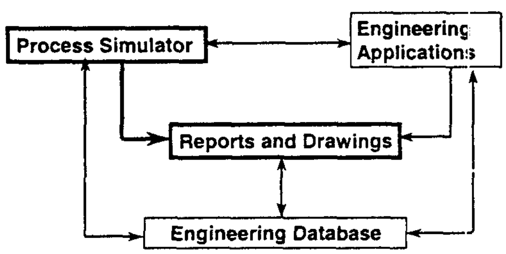
From Base Case to ...

Design Specifications inside blocks
Design specifications outside blocks
Sensitivity analysis
Case studies
Optimization

Engineering Workflow Integration



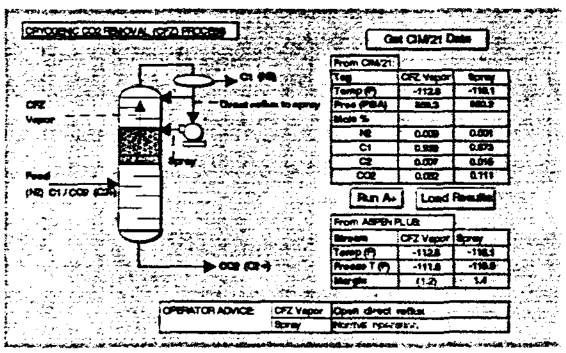
Windows Interoperability

- Two-way data transfer between the software and other Windows applications via copy, paste, paste link
- Access to all inputs & results
- Access to plots and flow sheet graphics
- Copy data tables and spreadsheets into the simulator for DRS, Data-Fit, etc
- Windows Interoperability - Benefits
  - Quick and error-free ad-hoc transfer of the simulator results to other Windows applications
  - *Easier preparation of reports and results*
  - Multitier applications
- OLE Automation and DCOM – COM+ technology

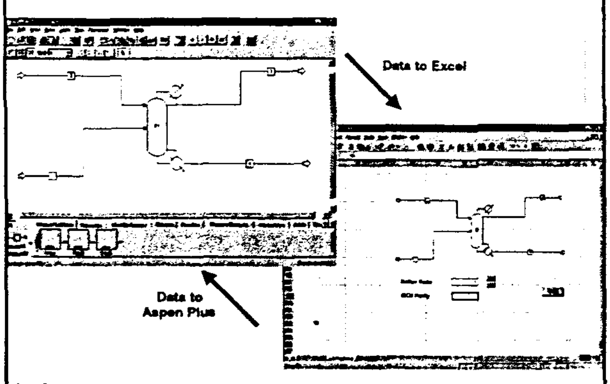
CAPE-OPEN Standard

- The objective of the Global CAPE-OPEN (GCO) project is ***to deliver the power of component software and open standard interfaces in computer-aided process engineering***
  - Develop additional open standard interfaces for CAPE components
  - Adapt existing software so that it complies with the CO standard
  - Develop methods, training and support tools for helping users to take advantage of the availability of CO-compliant components
- Results of CAPE-OPEN
  - global acceptance as a standard for communication between simulation software components in process engineering
  - availability of software components offered by leading vendors, research institutes, and specialized suppliers which will enable the process industries
  - open new markets for suppliers of CAPE components.
  - major breakthrough as compared to the current state-of-the-art, which is that of no integration at all.

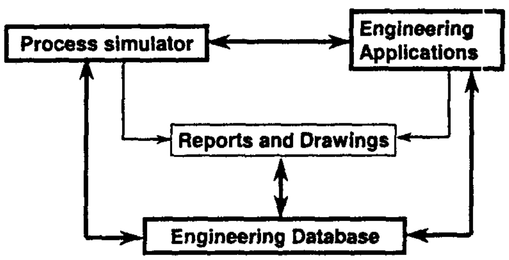
Example - Column Advisor



Custom User Interface



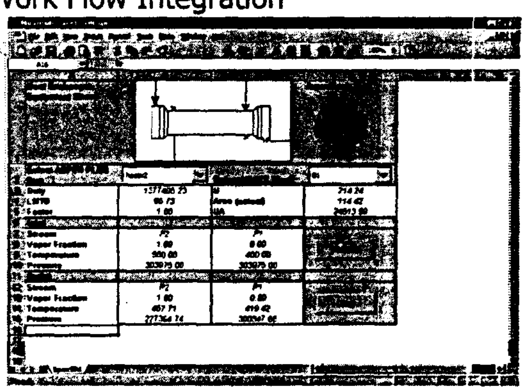
Engineering Workflow Integration



Workflow Integration

- Supported interfaces to specific 3rd-party engineering applications
  - equipment design (B-JAC, HTRI, HTFS)
  - engineering databases (Aspen Zyqad, PASCE)
  - costing packages (ICARUS)
  - *in-house technologies*
- Workflow Integration - Benefits
  - Support for engineering infrastructures that integrate engineering work processes
  - Error-free data transfer into 3rd party Windows engineering programs
  - Quick and consistent use of simulation results throughout the engineering lifecycle
  - Improved engineering quality

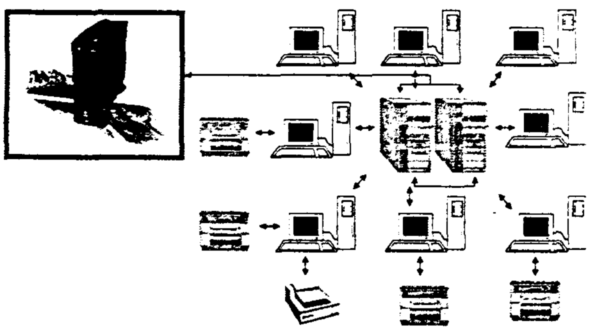
Work Flow Integration



The Hardware and Operating systems

- Operating Systems
  - Client - server solutions
  - Client is Windows NT 4.0 and WIN2K
  - Server is Windows NT or UNIX
  - Office environment
- Hardware
  - Client: PC Intel Pentium II 400Mhz - 32-64 MB RAM - SCSI Disks 8 GB - High quality monitor and video board (reasonable requirements)
  - Server: Intel or RISC based systems - 512 MB RAM - SCSI RAID Disks, BU unit, ... (OS NT or UNIX Sun SGI)
- Networking scheme and architecture
  - License server service
  - Installation point and file server
  - Computational server

The virtual lab → C.A.-S. Lab
HW and SW structure



A survey of process simulation software

- Stady state simulators
  - Aspen Plus (Aspentech)
  - PRO II (Sim Sci)
  - Hysys.Process (Hyprotec – AEA Technology)
  - Chem CAD
  - Process
  - .....
- Dynamic simulators
  - Speedup → Aspen Dynamics (Aspentech)
  - Batch model and DynSim (Sim Sci)
  - Hysys.Plant (Hyprotec – AEA Technology)
  - gPROMS (PSE)
  - ABACUS (MIT)
  - .....

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Thermodynamic and phase equlibria modelling

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Agenda

- User environment and data banks (demo)
- Physical Properties and Phase Equilibria
- Fugacity end Fugacity coefficients
- Equations of state by integration and derivation
- Activity coefficient models
- Henry's law approach
- Comparison between two approaches
- Classification of the most common GE models
- Classification of the most common EOS
- Model selection criteria
- Conclusions

Data Banks in Aspen +

- AQUEOUS databank
  - Contains parameters for 900 ionic species
  - It is used for electrolytes applications
  - the key parameters are the aqueous heat and Gibbs free energy of formation at infinite dilution and aqueous phase heat capacity at infinite dilution.
- AQU92 databank
  - Contains parameters for 900 ionic species (previuos version of A+)
- ASPENPCD databank
  - Contains parameters for 472 organic and some inorganic compounds. This databank has been superseded by the PURECOMP databank (previous versions of A+)
- INORGANIC databank
  - Contains thermochemical data for about 2450 (mostly inorganic) components. The key data are the enthalpy, entropy, Gibbs free energy, and heat capacity correlation coefficients.

Data Banks in Aspen +

- **PURE10 databank**
  - Contains parameters for over 1727 (mostly organic) components. This is the main source of pure component parameters for ASPEN PLUS. The databank is based on the data developed by the AIChE DIPPR data compilation project, parameters developed by AspenTech, parameters obtained from the ASPENPCD databank, and other sources. For most simulations, the PURE10 databank contains all the property parameters you need. The parameters stored in the databank can be categorized as:.
    - Universal constants, such as critical temperature, and critical pressure
    - Temperature and property of transition, boiling point and triple point
    - Reference state properties, enthalpy and Gibbs free energy of formation
    - Coefficients for temperature-dependent thermodynamic properties, such as liquid vapor pressure
    - Coefficients for temperature-dependent transport properties, such as liquid viscosity
    - Safety properties, such as flash point and flammability limits
    - Functional group information for all UNIFAC models
    - Parameters for RKS and PR equations of state
    - Petroleum-related properties, such as API gravity and octane numbers
    - Other model-specific parameters, such as the Rackett and UNIQUAC parameters

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Data Banks in Aspen +

- **SOLIDS databank**
  - Contains parameters for 3314 solid components. This databank is used for solids and electrolytes applications. This databank is largely superceded by the INORGANIC databank, but is still essential for electrolytes applications.
- **COMBUST databank**
  - The COMBUST databank is a special databank for high temperature, gas phase calculations. It contains parameters for 59 components typically found in combustion products, including free radicals. The CPIG parameters were determined from data in JANAF tables for temperatures up to 6000K (JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan, 1979). Calculations using parameters in the ASPENPCD and PURECOMP are generally not accurate above 1500K.

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DEMO

User Environment
Data Banks
Retrieval of components from Data banks

Modeling Phase Equilibrium

- The goals of the modeling are both to correlate existing data and to predict phase equilibrium
- An ideal model would
  - use easily measured physical properties to predict phase equilibrium at any condition
  - it would be theoretically based.
- No such model exists, and any single model cannot treat all situations.

Correlation and Prediction

- Correlation
  - regressed parameters
  - semi-empirical equations
  - fitting of portions of the phase diagram even with high accuracy
- Prediction
  - physical significance of the parameters
  - theoretically based models need the introduction of additional adjustable parameters
- The general conclusion is that modeling is still case specific
- Some Problems to be solved
  - critical points
  - the multi-component mixtures
  - polar - polar and polar - non polar interactions
  - association and solvation

Phase Equilibrium relationships

$$T^{(1)} = T^{(2)} = \ldots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = \ldots = P^{(\pi)}$$

$$\mu_1^{(1)} = \mu_1^{(2)} = \ldots \mu_1^{(\pi)}$$

....

$$\mu_m^{(1)} = \mu_m^{(2)} = \ldots \mu_m^{(\pi)}$$

Form Chemical Potential ... to Fugacity

$$\mu_i(T,P)=\mu_i^0+RT\ln\frac{f_i}{f_i^0}$$

$$\mu_i^{(\alpha)}=\mu_i^{0\alpha}+RT\ln\frac{\hat{f}_i^{\alpha}}{f_i^{0\alpha}} \qquad i=1,2,\ldots\ldots,m$$

$$\alpha=1,2,\ldots\ldots,\pi$$

$$\mu_i^{01}+RT\ln\frac{\hat{f}_i^{(1)}}{f_i^{01}}=\mu_i^{02}+RT\ln\frac{\hat{f}_i^{(2)}}{f_i^{02}}=\ldots\ldots=\mu_i^{0\pi}+RT\ln\frac{\hat{f}_i^{(\pi)}}{f_i^{0\pi}}$$

Phase Equlibrium in terms of fugacity

$$T^{(1)}=T^{(2)}=\ldots=T^{(\pi)}$$

$$P^{(1)}=P^{(2)}=\ldots=P^{(\pi)}$$

$$f_1^{(1)}=f_1^{(2)}=\ldots f_1^{(\pi)}$$

....

$$f_m^{(1)}=f_m^{(2)}=\ldots f_m^{(\pi)}$$

Fugacity coefficient and Equilibrium

- Fugacities are more convenient than chemical potentials...
- ... but equilibrium is best expressed in term of fugacity coefficients
- When using EOS VLE is expressed by

$$\hat{\Phi}_i=\frac{\hat{f}_i}{Px_i}=\frac{\hat{f}_i}{P_i}$$

$$\hat{\Phi}_i^L x_i=\hat{\Phi}_i^V y_i \qquad i=1,2,\ldots,m$$

Equation of State by integration

- Equation of State is a function ...

$$F(P,V,T,y_1,\dots y_{N-1}) = 0$$

- Fugacity is obtained by integration

$$RT\ln\varphi_i = \int_0^P\left(\bar{V}_i - \frac{RT}{P}\right)dP$$

$$RT\ln\varphi_i = \int_v^\infty\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{V}\right]dV - RT\ln Z$$

.. but may by obtained by differentiation

$$RT\ln\hat{\Phi}_i = \left(\frac{\partial nA^r}{\partial n_i}\right)_{n_j,T,V} - RT\ln Z$$

$$F = \frac{nA^r(V,T,\bar{n})}{RT}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,n} = -\frac{P}{RT} + \frac{n}{V}$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,n} = -\frac{nS^r(T,V,\bar{n})}{RT} - \frac{F}{T}$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V} = \ln\hat{\Phi}_i + \ln Z$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,n} = -\frac{1}{RT}\left(\frac{\partial P}{\partial V}\right)_{T,n} - \frac{n}{V^2}$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,n} = -\frac{nC_V^r}{RT^2} - \frac{2}{T}\left(\frac{\partial F}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial^2 F}{\partial n_i \partial n_j}\right)_{T,V} = \left(\frac{\partial\ln\hat{\Phi}_i}{\partial n_j}\right)_{T,P} + \frac{\bar{V}_i}{RT}\left(\frac{\partial P}{\partial n_j}\right)_{T,V} - \frac{1}{n}$$

$$\left(\frac{\partial^2 F}{\partial T\partial n_i}\right)_{V} = \left(\frac{\partial\ln\hat{\Phi}_i}{\partial T}\right)_{P,n} - \frac{1}{T} + \frac{\bar{V}_i}{RT}\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial^2 F}{\partial T\partial V}\right)_{n} = -\frac{1}{RT}\left(\frac{\partial P}{\partial T}\right)_{V,n} + \frac{P}{RT^2}$$

$$\left(\frac{\partial^2 F}{\partial V\partial n_i}\right)_{T} = -\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V} + \frac{1}{V}$$

Activity coefficient and Henry's law approach

- **Vapour phase fugacity: $f_i^v = P\, y_i\, \phi_i^v$**
- **Liquid phase fugacity: $f_i^l = (f_i^l)_{id}\, \gamma_i$**
- **where: $(f_i^l)_{id} = R_i(T,P)\, x_i$**
- **If pure liquid exists $R_i =$** $\lim_{xi\to 1}\frac{f_i^L}{xi} = f_i^L\, puro$

  If not : $R_i =$ $\lim_{xi\to 0}\frac{f_i^L}{xi}$

- **f_i pure =** $p_i^o \times \Phi_i^o \times \exp\int_{p^o}^{P}\frac{v_i^L dP}{RT}$ → $\exp\left[\frac{v_i^L(P-p^o)}{RT}\right]$

- **In most cases (low P) ==> $P\ y_i\ \phi_i^v = p_i^o\ \gamma_i\ x_i$**

Henry's law approach

- For supercritical components the fugacity at the reference liquid state cannot be calculated because the vapour pressure is not defined.
- An hypothetical reference state H_i is defined for the component i at infinite dilution:

$F_i^L = x_i \gamma^*_i H_i$ $\gamma^*_i = 1$ as $x = 0$

$\gamma^*_i = \gamma_i / \gamma^{**}_i$

- Therefore $\mathbf{P}\ \mathbf{y_i}\ \phi_i^V = x_i H_i \gamma_i / \gamma^{**}_i$
- Simplified Henry's law: $\mathbf{P}\ \mathbf{y_i} = x_i H_i$

Types of VLE Phase behaviour

- Ideal systems
  - Systems that obey the Raoult's law
  - Consist of molecules of the same size and shape and intermolecular forces
  - Mixtures at low pressures that may be assumed as ideal mixtures (hydrocarbons, isomers,...)
  - Ideal mixtures cannot form azeotropes or multiple liquid phases
- Non ideal systems
  - Due to interactions between functional groups creatinf non randomness in the mixture
  - Due to energy effects created by size and shape differences
  - Is accounted for activity coefficients

Types of VLE Phase behaviour

- Effects of non ideality
  - gamma > 1 because molecules are dissimilar and tend to aggregate more with molecules of the same species, creating large local concentration. Ge is positive. Positive deviation from ideality
  - gamma is large: liquid may split into two phases
  - gamma < 1 when attractive forces between dissimilar molecules are stronger than the forcess between the like molecules. Ge is negative. Negative deviation from ideality
  - if gamma < may have chemical complexes (ammonia water system)

Two Approaches: Gamma - Phi versus Phi - Phi

GAMMA PHI

- Pros
  - Reliability at low pressure
  - Very good for describing polar mixtures
  - Simplicity
  - Easy programming and low CPU time
- Cons
  - Valid only at low pressure
  - Parameters of the model are highly correlated
  - Consistency at the critical point

PHI PHI

- Pros
  - Continuity at the critical point (one model)
  - Parameters are non so strongly correlated
  - Applicable in an high T and P range
  - Describes volumetric properties as well as equilibrium
- Cons
  - Complexity and high CPU time
  - Polar and low pressure mixtures

Excess Gibbs energy expressions

- Starting point: Excess Gibbs Energy

$$RT \ln\gamma_i = \left(\frac{\partial n_T g}{\partial n_i}\right)_{T,P,n_j \neq i}$$

- **Margules two suffixes:** $g^e = A x_1 x_2$
- **Redlich Kister**

  $g^e = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \ldots\ldots]$
- **Whol:**

$$\frac{g^E}{RT(x_1 q_1 + x_2 q_2)} = 2a_{12} z_1 z_2 + 3a_{112} z_1^2 z_2 + 3a_{122} z_1 z_2^2 + 4a_{1112} z_1^3 z_2 + 4a_{1222} z_1 z_2^3 + 6a_{1122} z_1 2 z_2^2 + \ldots\ldots$$

- **Van Laar:**

$$\frac{g^E}{RT} = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2}\left(\frac{\sqrt{a_1}}{b1} - \frac{\sqrt{a_2}}{b_2}\right)^2$$

Excess Gibbs Energy expressions

- Wilson: Ge = RT(-x1ln(x1+x2 L12)- x2ln(x2+x1 L21))

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1}\right]$$

$$\Lambda_{12} = \frac{\nu_2}{\nu_1}\exp\left[-\frac{(\lambda_{12} - \lambda_{11})}{RT}\right]$$

Problem: miscibility gap $0 < \left(\frac{\partial^2 g^e}{\partial x_1^2}\right)_{T,P} + RT\left(\frac{1}{x1} + \frac{1}{x2}\right)$

- UNIQUAC
- NRTL
- UNIFAC

EOS are used in Process Simulators

- Process Synthesis more than analysis
- Sophisticated unit operation models (SFE)
- Fill gaps in multi-component systems
- High Pressure Predictions
- Use of simple models applicable to wide range of systems
- Predicted phase behavior must show the same trend as real behavior

↓

- Define the functional relation for pure components
- Define the extension to mixtures (mixing + combining rules)

Volume calculation for Equation of state

- Simple for cubic equations but not trivial
  - Cardano analytical method
- Crucial for non cubic equation
- Method must be robust and efficient
  - Most of the time the code runs in the volume calculation routine
  - Sometimes the initial guess is not good due to the bad initial guess of the equilibrium calculation
  - ... the same for a bad parameter estimation
- Method should always gives an answer
  - .. with an error code
- Method should be EOS independent

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Numerically speaking: ... solution of a non linear equation

.. in which the unknown is the volume (or the density) and the equation is the EOS written in terms of Pressure = ...

The problem: Rapid and robust convergence

A classification of the different Equations

- Cubic Equations of State: the van der Waals family
  - Van der Waals
  - Soave Redlich Kwong
  - Peng Robinson
  - Volume translation
- Virial equation of state
  - BWR
- Corresponding state
- Perturbation theory
  - The Perturbed Hard Chain Theory
  - The Perturbed Hard Sphere Theory
  - The SAFT Equation

Cubic EOS

- Widely used, simple, rapidly solved analytically
- Easily extended to binary and multi-component systems
- Mixing rules are crucial
- All are derived from van der Waals theory

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

- Pure Component parameters are constrained to:

$$\left(\frac{\partial P}{\partial V}\right)_C = \left(\frac{\partial^2 P}{\partial V^2}\right)_C = 0$$

Van der Waal equation from Partition function

- The partition function is defined as:

$$Q = \frac{1}{N!}\left(\frac{1}{\Lambda}\right)^{-3N}\left(V_f\right)^N\left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N q_{r,v}{}^N \qquad P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,Ni}$$

- L De Broglie wavelength, function of molecular mass and temperature, it is related to molecular dimension
- N number of molecules
- Vf Free Volume = V-b
- E0 Intermolecular potential
- qr,v molecule degree of freedom

$$V_f = V - \frac{N}{N_A}b = f(\rho)$$

$$E_0 = -\frac{2aN}{VN_A^2} = f(\rho)$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Soave Redlich Kwong Equation

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

Redlich Kwong Equation

$$a = \left[1 + mT_r^{1/2}\right]^2 \cdot a_c$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

m is a function of the acentric factor

Soave Equation

Peng Robinson Equation

- Original

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

- Volume translation

$$P = \frac{RT}{v-b} - \frac{a}{(v+c)(v+b+2c)}$$

$$\tilde{V} = V + \sum_i c_i n_i \qquad c_i = \sum_i c_i x_i$$

$$c_i = f\left(T_{Ci}, P_{Ci}, Z_{RAi}\right)$$

Cubic Equations for Mixtures

- Mixing rule for the a parameter

$$a_m = \sum_i \sum_j x_j x_i a_{ij} \qquad a_{ij} = (1-k_{ij})\sqrt{a_i a_j}$$

- Mixing rule for b parameter

$$b_m = \sum_i x_i b_i \qquad b_m = \sum_j \sum_i x_i x_j b_{ij}$$

- The fugacity coefficient for SRK

$$\ln\left[\frac{\hat{f}_i}{x_i P}\right] = \ln \hat{\varphi}_i = \frac{b_i}{V - b_m} - \ln\left[\frac{PV}{RT}\left[1 - \frac{b_m}{V}\right]\right] - \frac{2\sqrt{a_m a_i}}{RTV}$$

Huron-Vidal Mixing Rules

- Huron and Vidal (1979) used a simple thermodynamic relationship to equate the excess Gibbs energy to expressions for the fugacity coefficient as computed by equations of state:

  GE =RT ln φ - Si xi RT ln φ i *

- Equation is valid at any pressure, but cannot be evaluated unless some assumptions are made. If Equation is evaluated at infinite pressure, the mixture must be liquid-like and extremely dense. It can be assumed that:

  V = b and VE = 0

- Combining results in an expression for a/b that contains the excess Gibbs energy at an infinite pressure:

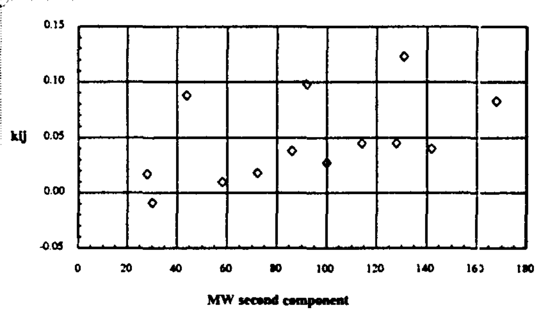
$$\frac{a}{b} = \sum x_i \frac{a_i}{b_i} - \frac{1}{\Lambda} G_\infty^E(p=\infty) \qquad \Lambda = \frac{1}{\lambda_1 - \lambda_2} \ln\left(\frac{1+\lambda_1}{1+\lambda_2}\right)$$

- The parameters and depend on the equation-of-state used.

Features of the Cubic Equations of state

- Three parameters for pure components: Tc, Pc, w
- The main advantage is the flexibility and the easy of use
- The main disadvantage is its accuracy in the PVT space for both pure components and mixtures
- The applicability is questionable when critical properties are not known (high molecular weight such as polymers)
- Group contribution (Soave, 1994)
- Volumetric properties are not accurate in the close vicinity of the critical point
- The physical meaning of the parameters is questionable
- Mixture parameters are difficult to predict
- They are a very powerful and useful correlation tool

Binary interaction parameters for SRK



VIRIAL EQUATION OF STATE

- Sound theoretical foundation
- Free from arbitrary assumption
- Remarkably general provided the intermolecular potential obeys certain well-defined restrictions
- Takes the interaction into account
  - The second virial coefficient considers interaction between two molecules
  - The higher order coefficients follows in an analogous manner
- The coefficients B, C, .. can be calculated 'a priori' from statistical mechanics

Virial Equation of State

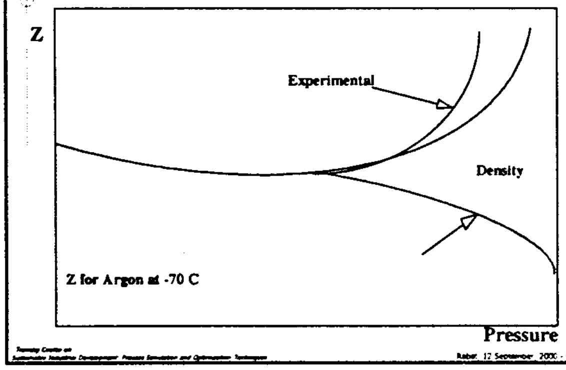
- Density expansion

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ \dots$$

- Pressure expansion

$$Z = 1 + B'P + C'P^2 + D'P^3 + \ \dots$$

The importance of the coefficients



Benedict Webb Rubin Equation

- Many constant for the pure component properties
- Problems for the mixtures in defining the mixing rules

$$P = RT\rho + \left(B_0RT - A_0 - C_0/T\right)\rho^2 + \left(bRT - a\right)\rho^3 +$$
$$+\ \alpha a\rho^6 + \left(c\rho^3/T^2\right)\left(1+\gamma\rho^2\right)\exp\left(-\gamma\rho^2\right)$$

- Very good for the description of pure components
- Very accurate for multi-property
- Very problematic in the extrapolation and mixture calculations

CORRESPONDING STATES THEORY

- Derived by van der Waals - most important result
- Based on the critical constraints
  - Variables v, T and P are related by a universal function such that F(Tr,Pr,Vr) = 0
- The EOS for any one fluid is written in reduced coordinates, that equation is also valid for any other fluid.
- The original formulation is a two parameter theory
  - Only for simple molecules
  - In which the force field has a high degree of symmetry
  - Typically small, non polar substances
- For more complex molecules it is necessary to introduce an extra parameter (at least)

ASSUMPTIONS OF CORRESPONDING STATES

- Two parameters approach
  - The partition function is factored as Q=Qint Qtrans and Q int is independent of volume
  - The classical approximation is used for Q trans i.e. no quantum effects are considered (H2 He, Ne)
  - The potential energy is described by the sum of the interactions of all possible pairs of molecules and depends only on the distance
  - The potential energy of a pair of molecules is represented by a universal function of the intermolecular distance
- Three parameters approach
  - Assumption 3 is relaxed: we use an average potential wherein we have averaged out all the effects of symmetry
  - Assumption 4 is abandoned: each molecule (or class) has a characteristic parameter

Corresponding States Theory: Pure Components

- $F(T_r, V_r, P_r) = 0 \quad z = \Im(T_r, P_r, X)$

- Leach Leland Formulation

$$\frac{A^r(T,V,x)}{RT} = \frac{A_0^r(T_0,V_0)}{RT_0} \qquad T_0 = \frac{T}{f_{\alpha\alpha}} = \frac{T}{(T_C/T_{C0})\Theta_{\alpha\alpha}}$$

$$V_0 = \frac{V}{h_{\alpha\alpha}} = \frac{V}{(V_C/V_{C0})\Phi_{\alpha\alpha}}$$

- Other formulation

$$Z = Z_0 + \frac{\omega}{\omega^r}\left(Z^r - Z^0\right)$$

Corresponding States Theory: Mixtures

- For mixture the definition is the same

$$F(T_r, V_r, P_r) = 0 z = \Im(T_r, P_r, X)$$

- One has to define the pseudo critical properties

Tcm , vcm, wm

- Mollerup approach
- Plocker extension to mixtures of Lee Kesler eq.
- Shape factor methods of Leland

Motivation for non cubic EOS

- EOS is a reasonable choice for HP calculations
- Cubic Equations are not suitable for predictions
  - TC e PC are questionable for 'natural systems'
  - Binary kij are difficult to predict
  - The physical basis of Cubic EOS is poor
- Perturbation theory gives indications
- Perturbed Hard Chain - Perturbed Hard Sphere Chain
  - Theory more complex and gives better model
  - Parameters become 'predictable'
  - Higher complexity is balanced by good computer codes

The basic theory: the van der Waals PF

- The partition function

$$Q = \frac{1}{N!}\left(\frac{1}{\Lambda}\right)^{-3N}\left(V_f\right)^N\left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N q_{r,v}{}^N$$

• N	number of molecules
• L	De Broglie wavelength, function of molecular mass and temperature, it is related to molecular dimension
• Vf ≈ V-b	Free Volume
• E0	Intermolecular potential
• qr,v	molecule degree of freedom

The Gererilzed van der Waals Partition Function

- The partition function is modified (Beret Prausnitz) considering q r,v = q r,v (ext) q r,v (int)
  - External degrees of freedom = 3 (transl.) * c (transl. equivalent)
  - External (=influenced by density) contributions from rotation and vibrations
  - Internal contributions depend only on Temperature

$$q_{r,v}(ext) \propto \left(\frac{V_f}{V}\right)^{c-1} \qquad P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$Q = \frac{1}{N!}\left(\frac{V_f}{\Lambda^3}\right)^N\left(\frac{V_f}{V}\right)^{N(c-1)}\left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N\left[f(T)\right]^N$$

The Carnaham Starling Equation

- Perkus Jevick

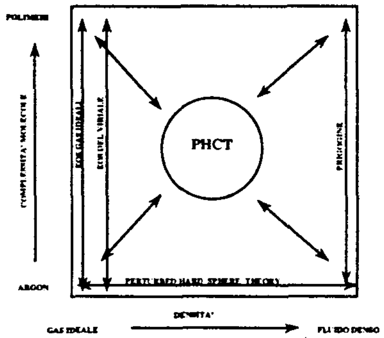
$$\frac{V_f}{V} = \exp\left[\frac{\xi(3\xi-4)}{(1-\xi)^2}\right]$$

$$\xi = 0.74\frac{v_0}{v} \qquad v_0 = \frac{\sigma^3}{\sqrt{2}}N_A$$

- Carnahan - Starling Equation:

$$P = P^{IG} + P^{HS} + P^{ATT} = \frac{RT}{v} + \frac{RT}{v}\left[\frac{\xi(4-2\xi)}{(1-\xi)^3}\right] - \frac{a}{v^2}$$

The Perturbed Hard Sphere Theory



PHCT Equation: an Overview

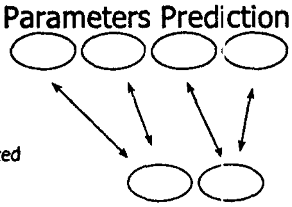
- Reference Term
  - CS Term (with v* parameter) + c
- Perturbation Term
  - Low Density Term (Second Virial)
    - Dispersion, Dipole moment, Quadrupole moment
  - High Density Term
    - Dispersion (Monte Carlo Simulation)
    - Polar (Gubbins and Twu)
- Parameters: c, v*, T*
  - Based on Bondi Volume
  - Based on Correlation with MW
  - For Polymers and Petroleum Fractions

PHCT Equation: Extension to Mixtures

- Reference Term
  - Linear mixing rule for c and v*
- Second Virial Term
  - Binary parameter in cT* mixing
- Dense-Fluid Term
  - Binary parameter in cT* mixing
  - Temperature dependent k
  - Asymmetric k
- Parameters: kij
  - Defined in terms of segment-segment
  - Constant within classes

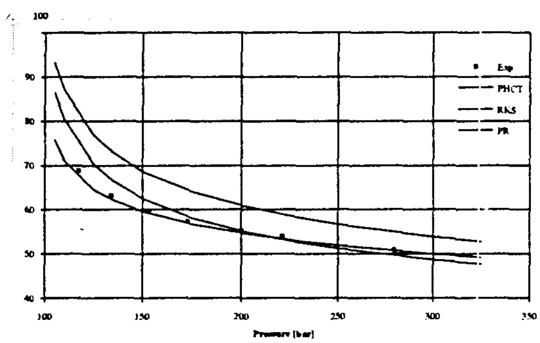
Binary interaction Parameters Prediction

- Site - Site Interaction

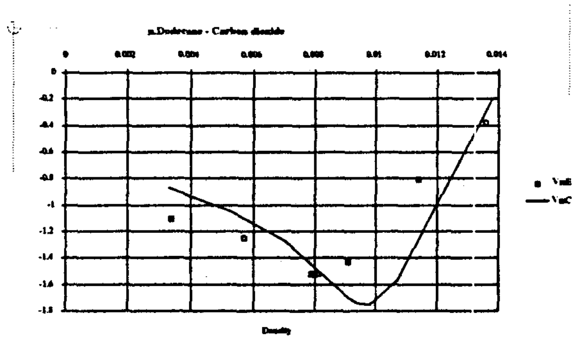


- Parameters Characterized
  - Carbon Dioxide
  - Methane
  - Light Hydrocarbons (Ethane, Propane, Propylene, Ethylene)
  - Heavy Hydrocarbons (Alkanes, Aromatics, Naftens,..)

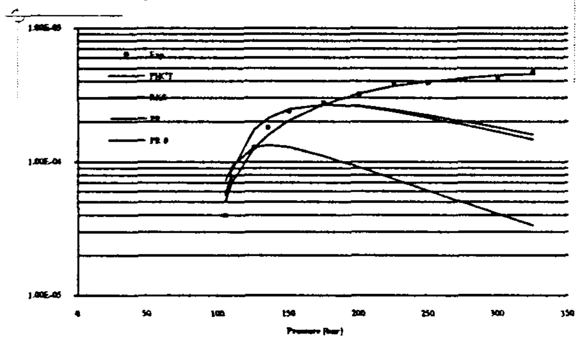
Mixture Volume: CO2 - Octacosane (313 K)



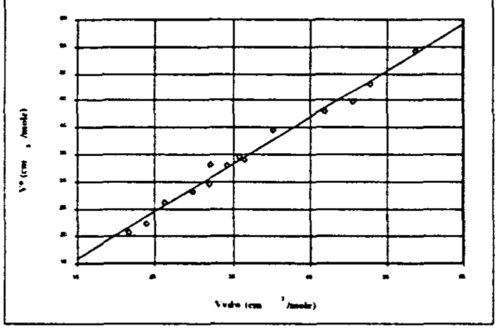
Partial Molar Volume



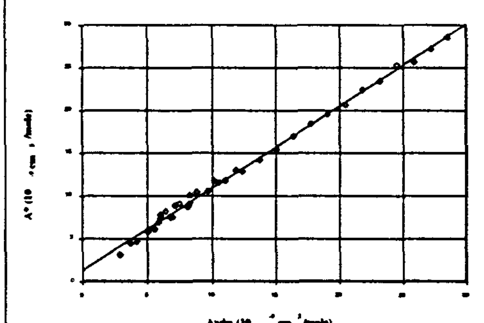
Solubility in CO2: Octacosane at 318 K



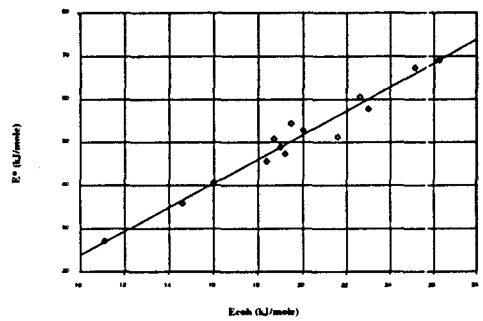
Pure Component Parameter V*

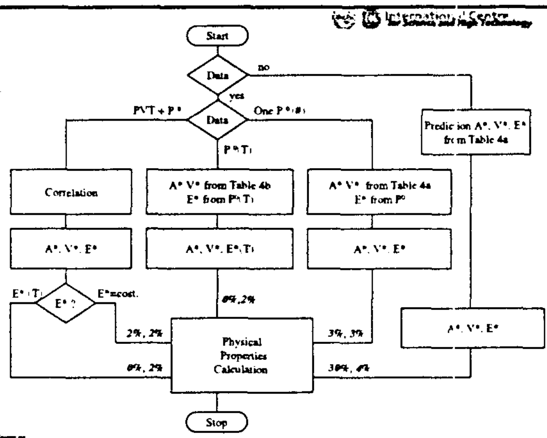


Pure Component Parameter A*



Pure Component Parameter E*





Conclusions

- For low pressure systems use Excess Gibbs energy models
  - Preferably UNIQUAC and NRTL
  - Careful to the values of the parameters
- Use the Henry's law approach for the incondensable components
- Use EOS for high pressure systems
  - The big question today is still
    ..... cubic or non cubic this is the problem
  - Cubic Equations of state are used for '[illegible]' mixtures and for hydrocarbon and also with polar compounds
  - Cubic equations of state are nothing more than a correlation tool for '[illegible]' systems such as polymers, dense gases,...
  - Non cubic equations of state are superior, provide volumetric properties but are complex
- Use UNIFAC for undefined components, or use the correlations for the pure component parameters of non cubic EOS
- In the intermediate region use the MHV2 Huron and Vidal method for combining EOS and activity coefficients models

Recommendations for model selection

- Oil and Gas Production
  - Reservoir systems PR-BM, RKS-BM
  - Platform separation PR-BM, RKS-BM
  - Transportation of oil and gas by pipeline PR-BM, RKS-BM
- Refinery
  - Low pressure applications (up to several atm) Vacuum tower, atmospheric crude tower BK10, CHAO-SEA, GRAYSON
  - Medium pressure applications (up to several tens of atm) Coker main fractionator, FCC main fractionator CHAO-SEA, GRAYSON, PENG-ROB, RK-SOAVE
  - Hydrogen-rich applications Reformer, Hydrofiner GRAYSON, PENG-ROB, RK-SOAVE
  - Lube oil unit, De-asphalting unit PENG-ROB, RK-SOAVE

Recommendations for model selection

- Gas Processing
  - Hydrocarbon separations Demethanizer C3-splitter PR-BM, RKS-BM, PENG-ROB, RK-SOAVE
  - Cryogenic gas processing Air separation PR-BM, RKS-BM, PENG-ROB, RK-SOAVE
  - Gas dehydration with glycols PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, SR-POLAR
  - Acid gas absorption with Methanol (RECTISOL) NMP (PURISOL) PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, SR-POLAR
  - Acid gas absorption with Water Ammonia Amines Amines + methanol (AMISOL) Caustic Lime Hot carbonate ELECNRTL
  - Claus process PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, SR-POLAR

Recommendations for model selection

- Petrochemicals
  - Ethylene plant Primary fractionator Light hydrocarbons Separation train Quench tower CHAO-SEA, GRAYSON PENG-ROB, RK-SOAVE
  - Aromatics BTX extraction WILSON, NRTL, UNIQUAC and their variances
  - Substituted hydrocarbons VCM plant Acrylonitrile plant PENG-ROB, RK-SOAVE
  - Ether production MTBE, ETBE, TAME WILSON, NRTL, UNIQUAC and their variances
  - Ethylbenzene and styrene plants PENG-ROB, RK-SOAVE –or– WILSON, NRTL, UNIQUAC and their variances
  - Terephthalic acid WILSON, NRTL, UNIQUAC and their variances

Recommendations for model selection

- Chemicals
  - Azeotropic separations Alcohol separation WILSON, NRTL, UNIQUAC and their variances
  - Carboxylic acids Acetic acid plant WILS-HOC, NRTL-HOC, UNIQ-HOC
  - Phenol plant WILSON, NRTL, UNIQUAC and their variances
  - Liquid phase reactions Esterification WILSON, NRTL, UNIQUAC and their variances
  - Ammonia plant PENG-ROB, RK-SOAVE
  - Fluorochemicals WILS-HF
  - Inorganic Chemicals Caustic Acids Phosphoric acid Sulphuric acid Nitric acid Hydrochloric acid ELECNRTL
  - Hydrofluoric acid ENRTL-HF

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Recommendations for model selection

- Coal Processing
- Size reduction crushing, grinding SOLIDS
- Separation and cleaning sieving, cyclones, precipitation, washing SOLIDS
- Combustion PR-BM, RKS-BM (combustion databank)
- Acid gas absorption with Methanol (RECTISOL) NMP (PURISOL) PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, SR-POLAR
- Acid gas absorption with Water Ammonia Amines Amines + methanol (AMISOL) Caustic Lime Hot carbonate ELECNRTL
- Coal gasification and liquefaction See Synthetic Fuel table

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Recommendations for model selection

- Power Generation
  - Combustion Coal Oil PR-BM, RKS-BM (combustion databank)
  - Steam cycles Compressors Turbines STEAMNBS, STEAM-TA
  - Acid gas absorption See gas processing.
- Synthetic Fuel
  - Synthesis gas PR-BM, RKS-BM
  - Coal gasification PR-BM, RKS-BM
  - Coal liquefaction PR-BM, RKS-BM, BWR-LS
- Water and Steam
  - Steam systems Coolant STEAMNBS, STEAM-TA
- Mineral and Metallurgical Processes
  - Mechanical processing: Crushing Grinding Sieving Washing SOLIDS
  - Hydrometallurgy Mineral leaching ELECNRTL
  - Pyrometallurgy Smelter Converter SOLIDS

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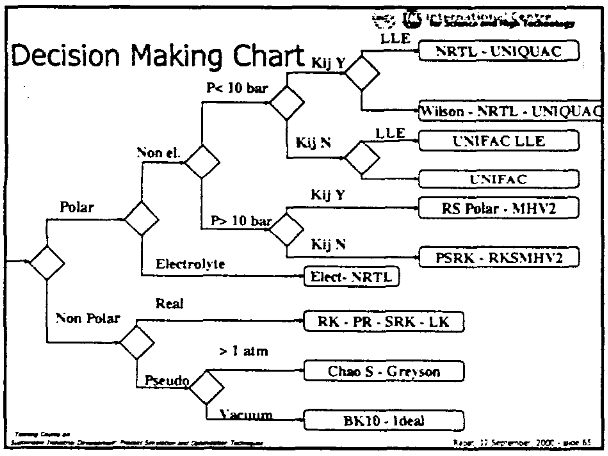
Recommendations for model selection

- Environmental
  - Solvent recovery WILSON, NRTL, UNIQUAC and their variances
  - (Substituted) hydrocarbon stripping WILSON, NRTL, UNIQUAC and their variances
  - Acid gas stripping from Methanol (RECTISOL) NMP (PURISOL) PRWS, RKSWS, PRMHV2, RKSMHV2, PSRK, SR-POLAR
  - Acid gas stripping from: Water Ammonia Amines Amines + methanol (AMISOL) Caustic Lime Hot carbonate ELECNRTL
  - Acids Stripping Neutralization ELECNRTL

Decision Making Chart



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Environmental applications of process simulation

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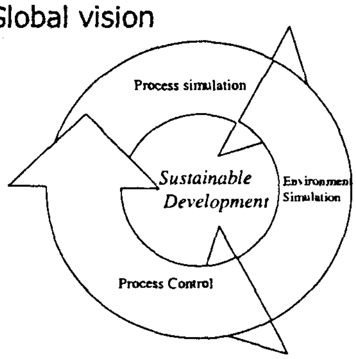
The Global vision



Agenda

- General statements and strategy
- Main features of an environmental policy
- Pollution prevention techniques and Process simulation
- Applications and examples

The general context and motivations

- Pollution Prevention in the Chemical Industry
  - Increasing cost of waste disposal
  - Growing number of environmental regulations
- Environmental policy as an integral component of the corporate strategy

Environmental concern and wastes ...

- Waste minimization at their source leads to ...
  - cost savings
  - improved product yield and quality
  - reduced pollution
  - safer workplace conditions
  - fewer waste management needs
  - conservation of natural resources
- Waste treatment is often needed
- End-of-pipe approaches are more expensive but still necessary

Features of an environmental Policy ...

- Leadership
  - Combination of plant manager and health officer
  - Responsability for setting goals for reduction in generation of specific chemical wastes
- Material Balance: aims at accounting for every quantity of a chemical that is:
  - shipped to the process
  - created or destroyed in the process
  - delivered as a product from the process
  - released as gaseous, liquid, or solid waste

... Features of an environmental Policy

- Cost accounting: assigns the pollution cost to individual process, such as:
  - pollution control
  - waste disposal
  - regulatory compliance
  - lost materials
  - insurance
  - future liabilities
  - public and customer relations dealing with waste issues
- Employee involvement at all levels
  - from top manager to production and maintenence workers
  - workers need training

Pollution prevention tecniques

- Process changes
- Operation changes
- Equipment changes
- Chemical substitution
- Product substitution

Pollution prevention: Operation changes

- involve improving plant operations
  - material handling and equipment maintenance
  - better control of material use
  - employee practices
- to minimize
  - spills
  - process upsets
  - excessive use of chemicals
  - or other problems that can generate wastes
- in every stage of the process
  - storing
  - moving
  - mixing
  - reacting chemicals

Pollution prevention: other techniques

- Equipment changes
- Chemical substitutions
  - involve using raw materials that create fewer toxic and hazardous wastes during production process without necessarily changing the process itself
  - aiming at substituting hazardous and toxic materials
- Product changes
  - involve designing the end product so its manufacture creates less toxic and hazardous waste
  - can be achieved without changing the fundamental manufacturing process (ex. : pellets rather than powder)

Benefit of Process Simulation

- The modeling of a chemical process enables to efficiently analyze the process in terms of environmental impact
- Modelling plays an integral role in company's environmental policy

Results in terms of environmental impact

- Compute the operating conditions to meet the discharge requirement
- Compute the performance, capital and operating costs for each equipment item
- Compute the properties of materials in a waste treatment process
- Prepare an integrated flowsheet that considers design constraints
- Automatically maximize performances, within process constraints
- Fit the parameters of the waste treatment models to experimental data
- Perform sensitivity calculations

Results in terms of modelling as integral role

- Complete material balance
- Identification of the costs and savings potential of pollution prevention options
- Effective vehicle of communication among managers, engineers, and production workers to describe the impact of making processes, operations or equipment changes.
- What if scenarios can be evaluated
- Model allows accurate support of pilot plant tests
- Process simulation aids the engineer in understanding the process design and in evaluating process alternatives
- The waste treatment process can be optimized to identify the operating conditions which achieve the most effective and economic treatment within regulatory constraints

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SOME EXAMPLES AND APPLICATIONS

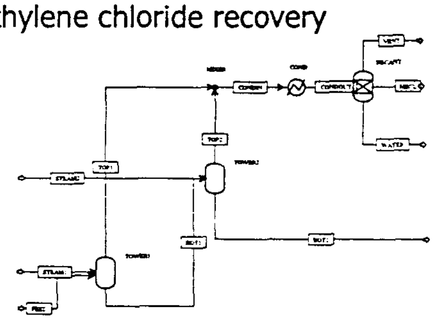
Coke oven gas desulfurization

- Goal:
  - lower the hydrogen sulfide content of purified coke oven gas from coke plant
- Simulation
  - identify ways of optimize process parameters to lower sulfur content
  - identification of new process conditions
- Results
  - decrease of sulfur dioxide emissions of 360 tons per year
  - 30% of the sulfur dioxide emissions reduction

Optimizing steam consuption for solvent recovery

- Goal
  - recovery of methylene chloride from waste
- Simulation
  - calculation of the steam consumption
  - identification of the optimum conditions
- Results
  - savings in steam usage realized without any major process or equipment changes

Methylene chloride recovery



Defining process conditions of a sour water stripping system

- Goal
  - a Chinese Design Institute was contracted to design a high sulfur sour water treatment process within a very tight timeframe
- Simulation
  - electrolyte containing complex system
  - evaluation of different process schemes
- Results
  - process conditions and sensitivities of key process variables were defined with only two person-months effort

Improving the operations of a Waste water treatment plant

- Goal
  - debottleneck the plant and determine how operating variables can be manipulated to improve effluent quality
- Simulation
  - identification of the clarifier as the bottelneck unit
- Results
  - additional capacity and operating changes in the clarifier can improve the capacity of the plant
  - evaluation of the impact of the plant loading on the effluent quality
  - study alternative operating tecniques (changing residence time, recycle, level of biomass) to lessen toxicity

Evaluating alternative process configurations to meet environmental regulations

- Goal
  - a dye producer applies single stage reverse osmosis to purify effluents
  - new modules are to be added to meet regulations
- Simulation
  - simulation of all possible new configurations (six months work estimation in a pilot plant)
  - comparison in terms of process economy and performances
- Results
  - optimum design found in two weeks
  - savings of 5 months investments
  - environmental regulations were met on schedule

Identify the design of an industrial sludge incinerator

- Goal
  - design an incinerator for industrial sludge
- Simulation
  - identify optimum design with the minimum heavy oil addition as a function of sludge humidity
- Results
  - optimal design which saved 30% in heavy oil consumption over previous design was identified

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Process simulation is a simple and helpful tool...

... that may help in solving problems connected to the environmental impact

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Industrial Applications of Process Simulation: Counter-current Separation Units

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Complex Separation Units:

Conventional and Supercritical Extraction

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Agenda

- Ternary Liquid-Liquid Equilibrium (LLE) diagrams
- Single- and multi-stage extraction devices
- Solvent Extraction of ε-Caprolactam
- Fluids at supercritical conditions
- Extraction with supercritical fluids
- Potentials of dense gases in the chemical and process industry
- Precipitation & crystallisation with dense gases as antisolvents

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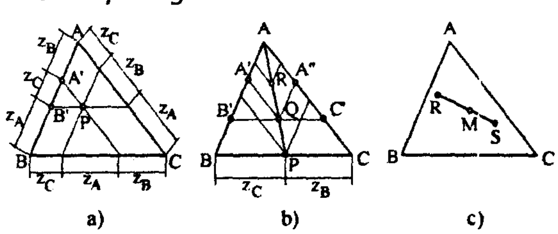
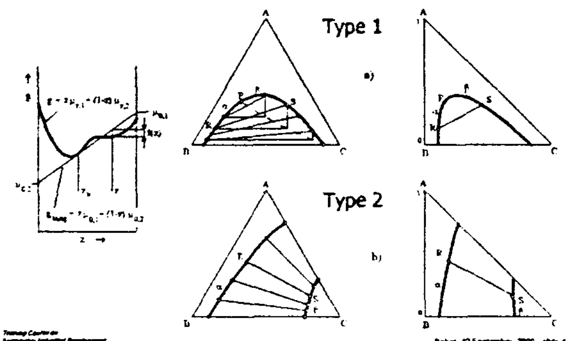
Ternary Diagram Fundamentals

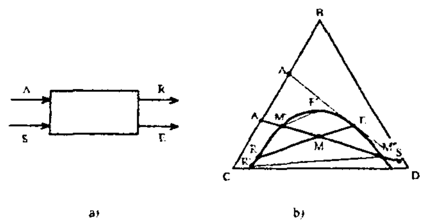


$$\frac{z_{M,A}-z_{R,A}}{z_{S,A}-z_{M,A}}=\frac{z_{M,B}-z_{R,B}}{z_{S,B}-z_{M,B}}=\frac{z_{M,C}-z_{R,C}}{z_{S,C}-z_{M,C}}=\frac{S}{R}$$

Ternary Liquid-Liquid Equilibrium

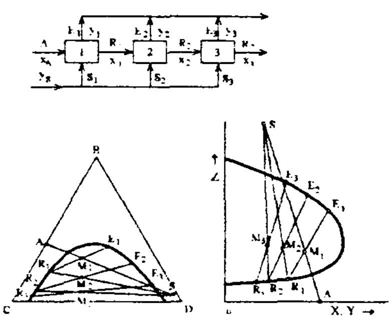


Single Stage Unit (mixer-settler)

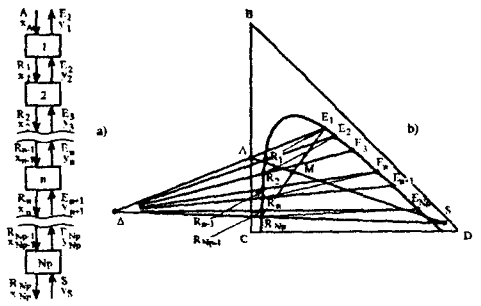


$$\frac{X_{R,A}-X_{M,A}}{X_{M,A}-X_{S,A}} = \frac{S_{AB}}{R_{AB}} = \frac{S(1-x_{S,C})}{R(1-x_{R,C})}$$

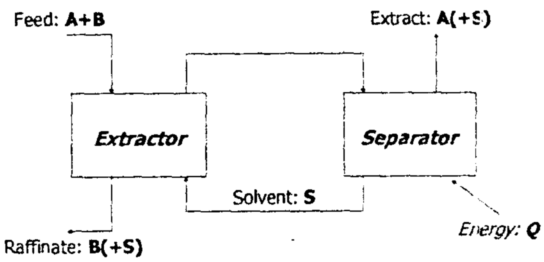
Multistage Unit



Countercurrent Extraction Column



Block Diagram of an Extraction Process



Atmospheric pressure everywhere

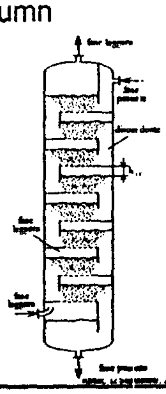
Sieve Tray Extraction Column

Ternary system (at least):

- component of interest
- solvent 1
- extraction solvent

Two phases:

- heavy (pesante)
- light (leggera)



Extraction versus Distillation Operations

Advantages (Pros)

- easier separation (higher selectivity)
- separation of azeotropic mixtures
- less energy required

Disadvantages (Cons)

- an extra-component needed
- much lower plate efficiency
- distillation required downstream

Two operations in-between:

- azeotropic distillation
- extractive distillation

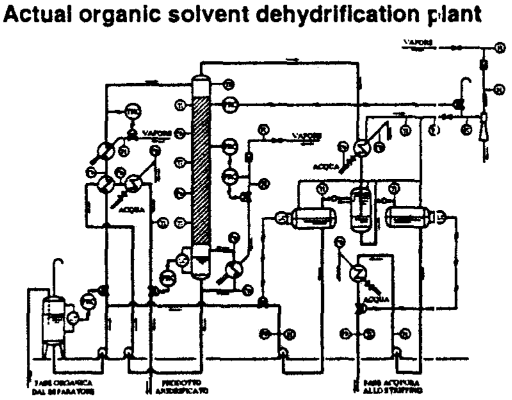
Contents

- Capacity and selectivity
- Stage processes
- Continuous contact processes
- Distillation columns
- Absorption and stripping columns
- Degrees-of-freedom analysis
- Example: simulation of tray distillation columns
- Simple example with a Process Simulator

Our aim: SIMULATION, not design

- Start from the real world (an existing plant)
- Make a plant scheme of the section of interest by means of a process simulator
- Get field data of plant operation
- Try to reproduce the actual operating conditions
- Make necessary adjustments
- When it works, use the 'calibrated' model to make virtual experiments on the real plant
- Do this for both steady-state and dynamic situations

Actual organic solvent dehydrification plant



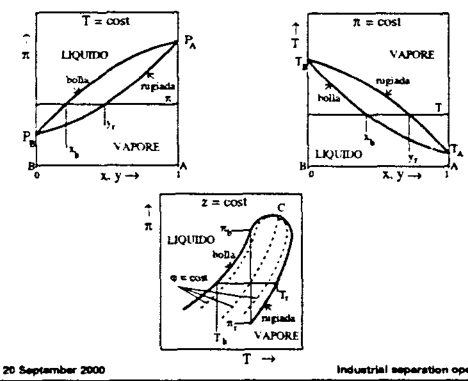
Capacity
(equilibrium ratio)

$$K_i = y_i / x_i$$

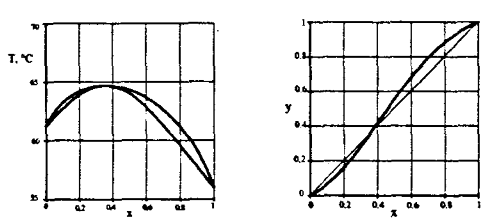
Selectivity
(volatility)

$$S_{i,j} = K_i / K_j$$

Vapor-Liquid Equilibria of Binary Systems

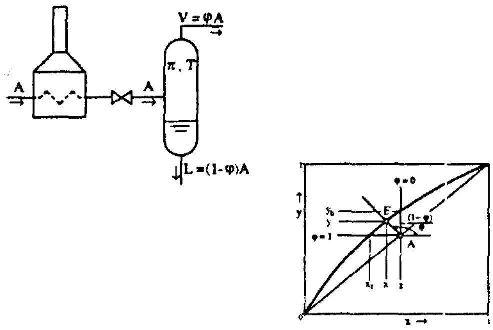


Vapor-Liquid Equilibria of Binary Systems

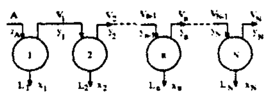


System: acetone-chloroform at π=1 atm

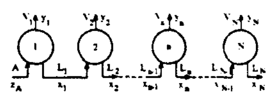
Single stage operation (Flash, mixer-settler,..)



Multiple contact



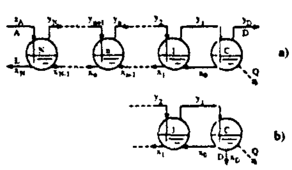
Multiple partial condensation



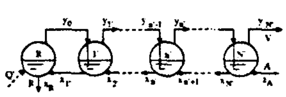
Multiple partial vaporisation

The idea of multistage distillation

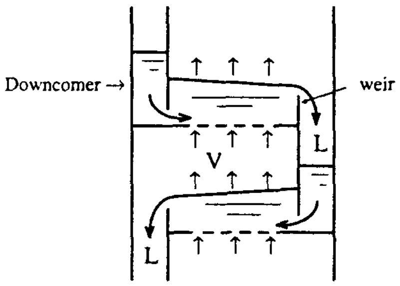
rectifying section



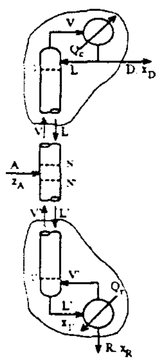
stripping section



The tray as the contact stage



The distillation column: a stack of trays



Material Balances (McCabe hypothesis)

$A=D+R$
$D=V-L$
$R=L'-V'$
$L'=L+(1-\varphi)A$
$V=V'+\varphi A$
$Az_A=Dx_D+Rx_R$
$Vy=Lx+Dx_D$
$V'y=L'x-Rx_R$

Energy Balances (McCabe hypothesis)

$Q_c=\lambda V$
$Q_r=\lambda V'$
$Q_c=Q_r+\varphi A\lambda$

Operating variables in a distillation column

- **Composition of products** x_D, x_R

  $D=A(z_A-x_R)/(x_D-x_R)$
  $R=A(x_D-z_A)/(x_D-x_R)$

- **Reflux ratio** $r = L/D$

  $Q_c=(r+1)\lambda D$
  $Q_r=(r+1)\lambda D-\varphi A\lambda$

- **Number of contact stages** N, N'

  $N=f(r, x_D, x_R)$
  $N'=f'(r, x_D, x_R)$

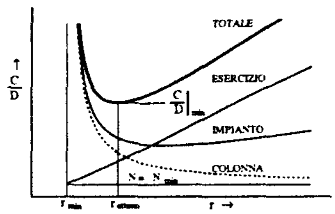
- **Ideal stage assumption** $y_j = K_j x_j$

Operating limits and optimum point

At given x_D, x_R:

$r \rightarrow \infty \qquad N+N' \rightarrow min$

$r = r_{min} \qquad N+N' \rightarrow \infty$



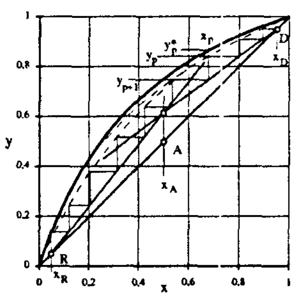
Total costs C versus r

Ideality and reality in a Mcabe-Thiele diagram

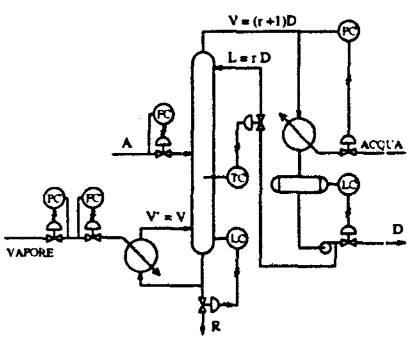
Plate efficiency:

$$E_p = \frac{(y_p - y_{p-1})}{(y_p^* - y_{p-1})}$$

$$y_p^* = K_p x_p$$



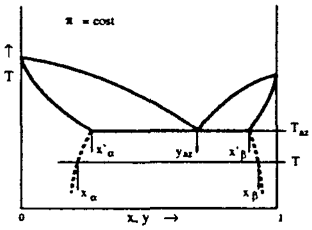
A schematic of a real tray distillation column



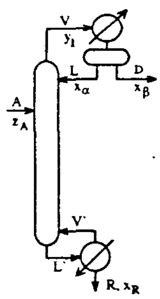
Distillation column with two liquid phases

Binary system with miscibility gap:

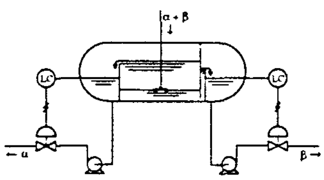
- Liquid-liquid equilibria
- Liquid-liquid-vapor equilibria



Distillation column with two liquid phases



Liquid-liquid phase splitter



Actual organic solvent dehydrification plant

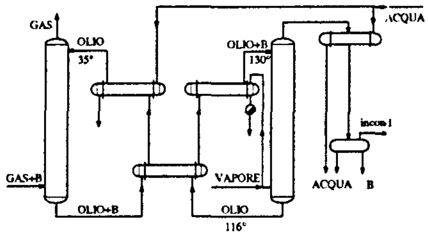
NOTE:

NOT ONLY COLUMNS,
BUT ALSO TANKS,
VALVES, PUMPS AND
HEAT EXCHANGERS

Absorption and Stripping tray columns

Ternary system (at least):

- inert gas (GAS)
- inert liquid (OLIO)
- component B to be exchanged



Continuous contact processes (for distillation, absorption, stripping)

In stage columns the contact between the gas and the liquid phases occurs on the tray.
The exchange area depends on the hydrodynamics

In continuous contact units:

- Packings are used rather than trays
- the gas and liquid phases flow countercurrently
- the liquid forms a film on the packing
- the exchange area can be very high if a proper design of the packing is adopted (structured packings)

Continuous contact processes (for distillation, absorption, stripping)

The material balance around a packing section:

$$Z = \frac{G}{k_g a A} \int_{y_{in}}^{y_{out}} \frac{dy}{y - y_{iface}}$$

Z = packing height
a = specific packing exchange area (wetted)
G = gas flow rate
k_g = gas-side mass transfer coefficient

Continuous contact processes (for distillation, absorption, stripping)

The material balance at a given section:

$$G(y - y_{in}) = L(x - x_{out})$$

From the steady-state assumption on mass fluxes:

$$-\frac{k_l}{k_g} = \frac{y - y_{iface}}{x - x_{iface}}$$

NOTE: The gas and liquid compositions at the interface are always assumed at equilibrium: $y_{iface} = K\, x_{iface}$

A popular equation for continuous contact processes (simplified)

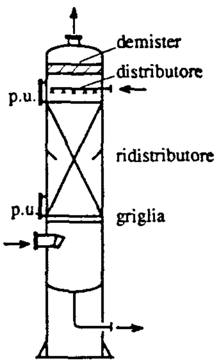
$$Z = NTU_g \times HTU_g$$

$$NTU_g = \int_{y_{in}}^{y_{out}} \frac{dy}{y - y_{iface}}$$

$$HTU_g = \frac{G}{k_g a A}$$

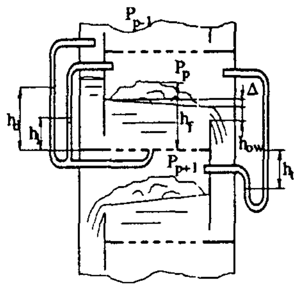
Sketch of an absorption packed column

NOTE:
the liquid and gas distribution through the packed bed is essential for ensuring efficient mass transfer, e.g. to achieve separation



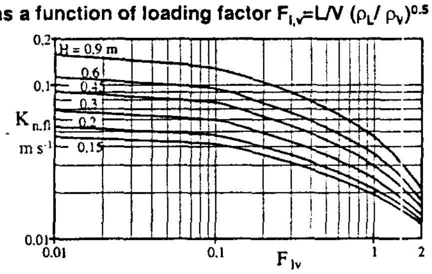
Capacity of tray columns

- Lower operating limit: weeping point
- Upper operating limit: flooding point
- correct operation: gas velocity between 40% and 80% of the flooding value



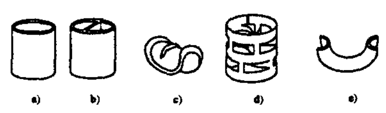
Capacity of tray columns

Fair plot for the calculation of gas flooding velocity as a function of loading factor $F_{l,v}$=L/V $(\rho_L/\rho_V)^{0.5}$



$v_{n,fl}$= $K_{n,fl}$ K_1 K_2 K_3 K_4 $(\rho_L/\rho_V)^{0.5}$ (sieve trays)

Capacity of random packed columns

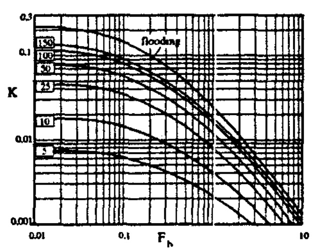


Eckert plot:

flooding and loading as a function of $F_{l,v}$

K= K(ρ_g ,ρ_l ,μ_l , v_n , C_f)

parameteric in pressure drop per unit height



Capacity of structured packed columns

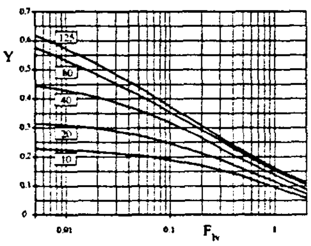
Kister and Gill method:

flooding and loading as a function of $F_{l,v}$

$Y = Y(\rho_g, \rho_l, \mu_l, v_n, C_f)$

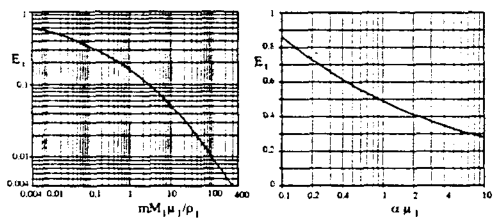
flooding and loading as a function of $F_{l,v}$

parameteric in pressure drop per unit height



How can tray efficiency be calculated?

- It depends on mass transfer, liquid entrainment, ...
- Different methods, rough estimation anyway (average error: ± 30%)
- examples: AIChE method, o'Connor plots,...



a) b)

How can packing height be calculated?

About NTU:

- just perform a numerical integration

About HTU:

- It depends on mass transfer and hydrodynamics
- Different methods, rough estimation anyway (average error: ± 50%)
- examples:
  Bolles and Fair method (random packings)
  Bravo method (structured packings)
  proprietary methods

What is provided by popular Process Simulators?

About tray columns:

- Many methods for the design and rating of tray diameter
- the possibility for the user to provide plate efficiency values

About packed columns:

- many methods for the design and rating of column diameter
- no methods for calculating the column height (except for RATEFRAC®)
- common use of the concept

  HETP=height equivalent of a theroretical plate

  which is indeed an *old and misleading* approach

What is needed to simulate correctly complex separation units ?

- a suitable phase equilibrium model (CRUCIAL)
- accurate values of the equilibrium model parameter (CRUCIAL)
- tray or packing geometric information (OBVIOUS)
- non-equilibrium information (IMPORTANT, but can be adjusted on plant operation data)

NOTE and REMEMBER:

in steady-state simulations, column holdups have no relevance, except for reactive separations

Degrees-of-freedom analysis

- Number of independent variables:

  $N_i = N_v - N_c$

  $N_{unit} = \Sigma N_i + N_a - N_{cs}$

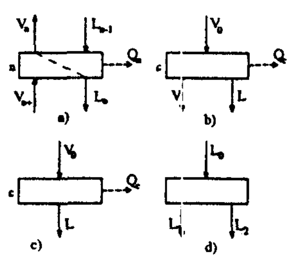
- Simple elements:

  a) $N_i = 2\,Nc + 6$

  b) $N_i = Nc + 4$

  c) $N_i = Nc + 3$

  d) $N_i = Nc + 3$



Degrees-of-freedom analysis

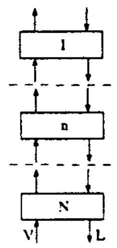
- Series of Np theoretical stages:

  $\Sigma N_r = (2\,Nc + 6)\,Np$

  $N_a = 1$

  $N_{cs} = 2\,(Nc + 2)\;(Np - 1)$

  $\Longrightarrow N_{unit} = 2\,(Nc + Np) + 5$



- Absorber:

  Vapor feed: Nc + 2 variables

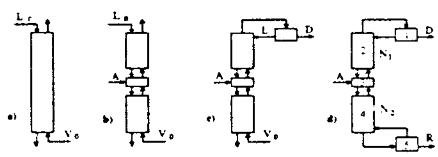
  Liquid feed: Nc + 2 variables

  pressure and heat on each stage: 2 Np variables

  number of plates: 1 variable

  $\Longrightarrow N_{unit} = 0$

Degrees-of-freedom analysis



Complete distillation column:

$\Sigma N_r = 9\,Nc + 2\,(Npe + Nps) + 26$; $N_{cs} = 8\,(Nc + 2)$; $N_a = 0$

$\Longrightarrow N_{unit} = Nc + 2\,(Npe + Nps) + 10$

Pressure on each stage: Npe+Nps+3 variables

Heat duty on each stage: Npe+Nps+1 variables

Feed: Nc + 2 variables $\Longrightarrow N_{unit} = 4$

Degrees-of-freedom analysis

- Which approach? Design or simulation?

  ⟹ Process Simulators use the second one

- Three cases:

1. Columns with both condenser and reboiler (distillation towers, extraction with top and bottom recycles)
2. Columns with no condenser nor reboiler (absorption and sripping columns without reflux)
3. Columns in-between cases 1 and 2

Degrees-of-freedom analysis: application to simulations

1. Distillation towers, extraction with top and bottom recycles:

   2 degrees of freedom

2. Absorption and sripping columns without reflux:

   1 degree of freedom

3. Columns in-between cases 1 and 2: it depends

NOTE: Process Simulators always provide the correct *degrees-of-freedom analysis*

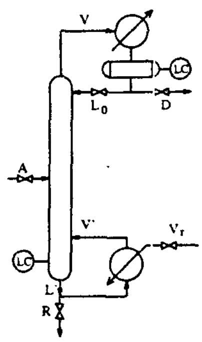
Simulation of a distillation column

- we usually have:

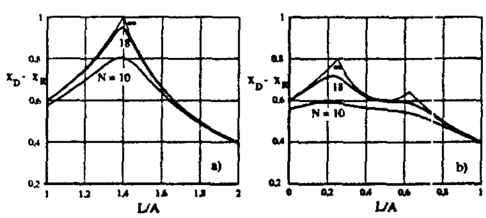
feed: assigned
pressures: assigned
heat duty: no dispersions
Npe, Nps: assigned

$\Longrightarrow N_{unit} = 2$

- for example:
  var1= L
  var2 = V'



Simulation of a tray distillation column



V'/A=2 V'/A=1

Effect of reflux on separation of an ideal binary mixture at two different values of V'/A.

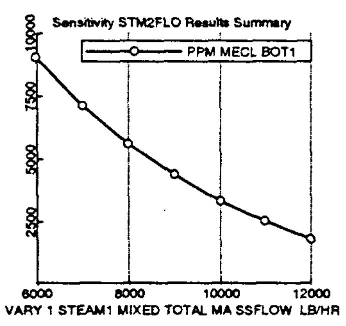
Relative volatility=2, z_A=0.6 and φ_A=0

Simple example with a Process Simulator: Optimizing steam consumption for solvent recovery

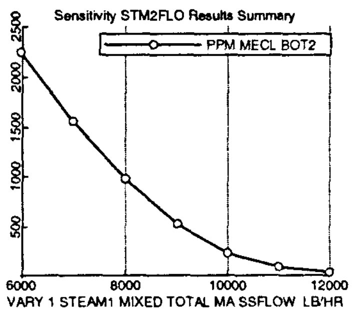
- Goal
  - recovery of methylene chloride from waste
- Simulation
  - calculation of the steam consumption
  - identification of the optimum conditions
- Results
  - savings in steam usage realized without any major process or equipment changes

Process Flowsheet

Bottom flash1 versus primary steam feed rate



Bottom flash2 versus primary steam feed rate



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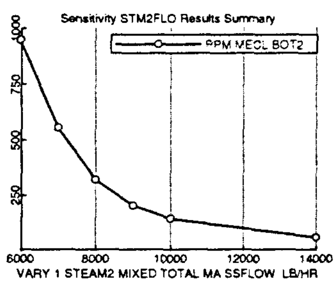
Bottom flash2 versus secondary steam feed rate



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Summary of Results

The distribution of steam consumption between the two towers has an important effect on the removal of Methylene Chloride

The minimum amount of steam required to meet emission specifications (150 ppm) is found by optimization

Total steam (lb/h):
- 15,680 from sensitivity on flash1
- 14,870 from sensitivity on flash2
- 13,055 from global optimization

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Solvent Extraction of ε-Caprolactam

Process Simulator Analysis of the Extraction Section of the production plant PR 16-19 at P.to Marghera

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Scope and Significance

- Current search for the substitution of benzene as the solvent in the caprolactam extraction process
- Need to find out a solvent compatible with the existing plant and production (plant revamping)
- Liquid-liquid equilibrium data required to allow quantitative evaluation of alternatives
- Assessment of possible alternatives through process simulation
- Importance of tuning the Process Simulator to represent correctly operation of the existing plant

Sustainable technology

"Sustainable development is the means of improving the quality of human life while living with the carrying capacity of the supporting ecosystems" (UNEP)

"Sustainability in Chemical Engineering means a continuous effort to protect and improve ecosystems, social balance and economic prosperity by a systematic and integral improvement of environmental protection, raw material exploitation, energy efficiency, safety, and health protection in all kinds of material conversion processes and material production" (EFCE definition)

In the case considered, there is no technical reason to substitute benzene, and no economic reason to change, other than the fact that the existing process might not be sustainable

How to assess sustainability?

Looking for a new process and/or a different solvent

Quantitatively evaluating the new alternatives and comparing them with the existing process from both the technical and economical viewpoints

Therefore:

Accurate process simulation of the existing plant

+

Knowledge of phase equilibria with alternative solvents

=

Technical and economical feasibility

The process basics

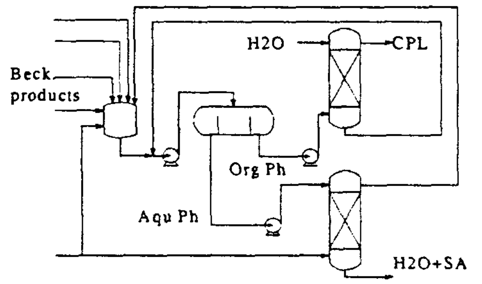
- *Caprolactam (CPL) produced by the Beckmann reaction (rearrangement) of cyclohexanone oxime. Ammonium sulphate (SA) and water (H_2O) are by-products*
- CPL is recovered through solvent extraction: benzene (BZ) is used, with SA as salting-out agent

BZ ⇒ CPL+SA+H_2O ⇒ CPL+BZ+(H_2O)+(SA)

⇒ H_2O+SA+(CPL)+(BZ)

- Ternary and quaternary systems are involved, in the presence of water, organics and electrolytes
- Two lay-outs of the extraction plant can be considered

The process: the extraction section of the caprolactam production plant



Ternary LLE data with different solvents

- CPL distribution coefficient:

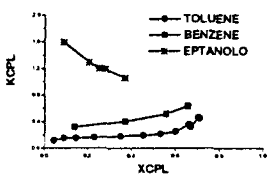
$$K_{CPL} = \frac{X_{CPL,ORG}}{X_{CPL,ACQ}}$$

- CPL-to-water selectivity:

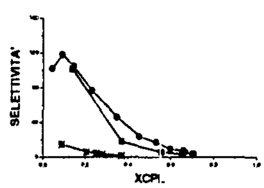
$$\alpha = \frac{K_{CPL}}{K_{H_2O}}$$

- Comparison between benzene, n-heptanol and toluene at 40°C
- Temperature enhances the distribution coefficient (less solvent needed) but lowers the selectivity (more water carried in the organic phase)

Ternary LLE data with different solvents

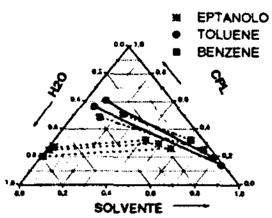


Capacity:
EPT > BZ > TOL

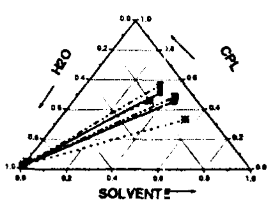


Selectivity:
TOL > BZ >> EPT

Salt effects on ternary LLE diagrams at 40 °C



Ternary system



Quaternary system:
30% w/w of SA

Process Simulation with toluene

- Process Simulator: AspenPlus® rel. 10.1
- Thermodynamic model: ELECNRTL (Chen et al., 1982)
- Simulation units: Radfrac, Flash3, Sep3
- Regression of ELECNRTL binary parameters:
  - CPL-H_2O, TOL-CPL and TOL-H_2O from measured data of the ternary system TOL-CPL-H_2O
  - CPL-SA and H_2O-SA from literature data of the ternary system H_2O-CPL-SA
  - TOL-SA from measured data of the quaternary system TOL-CPL-H_2O-SA

The extraction section as represented by the process simulator

- *See overheads*

Ternary and Quaternary LLE calculations

- Very good correlation of **ternary** LLE data
- **Quaternary** system: the thermodynamic **model** is **not able to account for salt distribution** between phases

Aqueous Phase

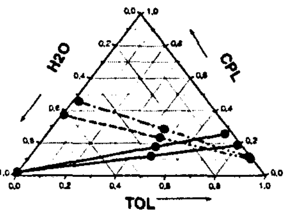
	CPL	H20	TOL	SA
exp.	1,25	63,69	0	34,34
cal.	1,22	63,67	0,03	26,63

Organic phase

	CPL	H20	TOL	SA
exp.	18,91	1,48	80,25	0,72
cal.	18,94	1,51	80,22	8,43

Quaternary LLE calculations

- *At high SA and CPL concentrations the model predicts a wrong CPL distribution between phases*



Simulation results of the extraction section

	kg/h	%w/w	kg/h	%w/w
	TOP 8R1			
	with TOL		*with BZ*	
SA	0	0,00	0 (*0*)	0,00
CPL	**14709**	*16,57*	**15292** (*15290*)	17.03
TOL/BZ	73006	82,23	72968 (*73004*)	81.31
H2O	**1063**	1,20	**1257** (*1490*)	1,66
TOTAL	88778	100	89517 (*89784*)	100
	BOTTOM 8R2			
	with TOL		*with BZ*	
SA	22259	32,66	22260 (*22260*)	33.14
CPL	**630**	0,92	**59** (*61*)	0,09
TOL/BZ	30	0,05	66 (29)	0,04
H2O	45237	66,37	45049 (*44816*)	66.73
TOTAL	68156	100	67434 (*67166*)	100

Simulation results of the extraction section

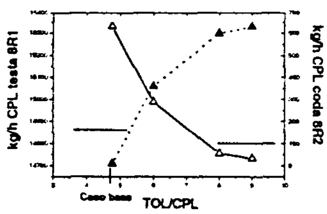
- The simulation is able to **represent correctly** the operation of **the existing plant** (figures in italics)
- At given temperature and feed flow rates, using **toluene instead of benzene** results in:
  - **Less CPL out of 8R1** (top)
  - **Less H_2O out of 8R1** (top)
  - **More CPL out of 8R2** (bottom)

Effect of temperature on the extractor 8R1

	TOP		BOTTOM	
kg/h	*40°C*	*60°C*	*40°C*	*60°C*
H_2O	498	121	10412	10789
TOL	71904	73397	5112	3619
CPL	**9091**	**11945**	20630	17776
SA	0	0	173	173

- At 60°C **more** CPL is recovered from the top

Effect of the solvent-to-feed flow rate ratio



- With TOL, **99.7% of the CPL** entering the overall extraction section can be **recovered** (TOL/CPL of 8.0)
- In the case of BZ **the same recovery** is presently obtained with much a **lower** ratio (BZ/CPL=4.7)

Conclusions for Caprolactam Extraction

- In order to assess the possibility of substituting **benzene** as the extraction solvent in caprolactam production it is **essential to use a process simulator**
- To achieve **quantitative results** the model parameters must be tuned on **reliable LLE** data
- **the subsitution of Benzene with Toluene** as the extracting solvent was **easily evaluated by using the Process Simulator**
- Useful results were obtained even if the presently **best available thermodynamic model** is still **insufficient** to deal with this type of mixtures

Conclusions for Caprolactam Extraction

It was found that:

- Toluene can be used as an alternative, provided higher values of the operating temperature and of the TOL/CPL ratio are adopted
- Toluene reduces the water content in the caprolactam-rich outlet stream, that is the cost of downstream caprolactam dehydrification
- Due to the higher solvent flow rates most of the existing plant has to be re-designed

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Fluids at Supercritical Conditions (SFCs)

What? *(What is it?)*
- A fluid above its critical temperature
- A fluid above its critical pressure
- ... but not too much

Why? *(Why should be used?)*
- It is a wonderful solvent
- It is a clean solvent
- It allows to develop new processes and products

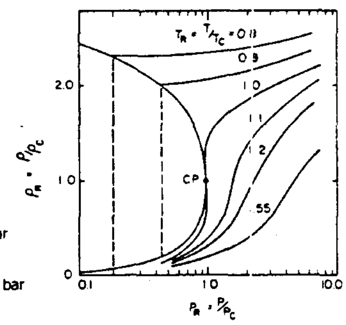
How? *(How is it useful?)*
- As an extraction solvent
- as an antisolvent
- as a reaction medium

Rabat, 12 September 2000 - slide 1

SFCs: basic properties

Density dependence upon pressure and temperature
- high compressibility
- high expansion coefficient

Critical constants
- *Xenon*: T_c=17°C, P_c=57 bar
- *Ethane* T_c=9°C, P_c=50 bar
- CO_2 T_c=31.06°C, P_c=73.81 bar



Rabat, 12 September 2000 - slide 2

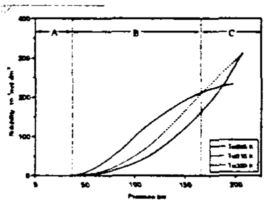
SFCs: basic properties

state	density ρ kg m-3	viscosity η cP (10-3 Pa s)	Diff. coeff. D cm2 s-1	P,T
gas	0.6 2	1 3 × 10-2	0.1 0.4	1 atm, T_{amb}
supercritical	200 500	1 × 10-2 3 × 10-2	0.7 × 10-3	> T_c, P_c
dense gas	400 900	3 × 10-2 9 × 10-2	0.2 × 10-3	> T_c, 4P_c
liquid	600 1600	0.2 3	0.2 × 10-5 2 × 10-5	Org. solvent 1 atm, T_{amb}

Density, viscosity and diffusion coefficient:
- liquid-like density
- *gas-like viscosity*
- intermediate diffusion coefficient

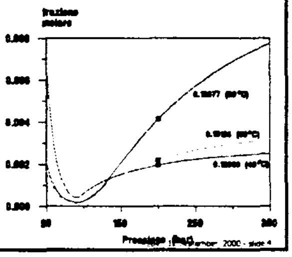
Rabat, 12 September 2000 - slide 3

Solvent behavior of SCFs



In general:

- very low solubility
- crossover pressure



System CO_2**-ferrocene**

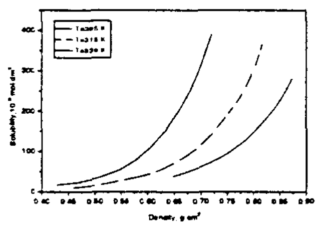
- correlation with PR EOS

Solvent behavior of SCFs

- they behave as **liquid solvents,** but with **lower** capacity and selectivity **performances**
- the **key** variable is the fluid **density:** $S = \rho^A \exp\left[\frac{B}{T} + C\right]$
- Solubility depends also on the **solute:**

$$y = \frac{P^{sat}}{P} E$$

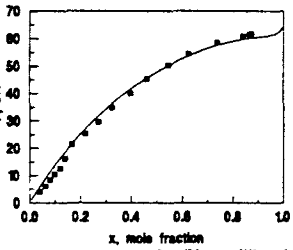
- E=enhancement factor
- **Note**: the values of solubility are **very low**



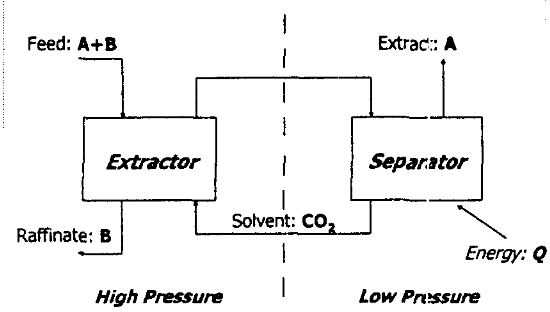
Solvent behavior of SCFs: binary mixtures

System CO_2- **DMSO** (Dimethylsulphoxide): VLE at 298 K

- solubility **of the dense gas in the liquid:** from 0 to 100%
- solubility **of the dense gas in a polymer:** still high
- solubility **of the heavy component in the vapor:** less than 1 part over 1,000
- **homogeneous mixture** (i.e. supercritical) at low pressure (reasonably)



Block Diagram of a SFE Process



Supercritical Fluid Extraction (SFE) as a Unit Operation

Advantages (Pros)

- easier recovery of extracts
- solvent-free products
- less energy required (?)

Disadvantages (Cons)

- very low capacity
- lower selectivity
- high pressure equipment needed
- solvent recycle imperative

When SFE can be applied:

- very high value products
- safety and health requirements

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Examples of industrial applications of SFE

caffeine from coffee grains (1977)
hops extracts (1980)
nicotine from tobacco (1982)
essential oils and aromas (1983)
......
ginseng (1995)

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Examples of industrial applications of SFE: pharmaceuticals (last 5/6 years)

- Antiprosthatic from *Serenoa repens* seeds
- Taxol from tree bark
- Octasanol from sugar cane
- EPA from fish oil (now also fractionation)
- Bioactive principles from *Calendula*
- Bioflavons from *Gimkobiloba*

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Industrial applications of SFE to pharmaceuticals: please note!

- SCFs **are poor solvents** of most relevant substances
- SCFs **are good solvents** of common organic solvents
- SCFs **are not selective** either as good or poor solvents
- Capacity/selectivity are improved by adding **cosolvents**
- For **pharmaceuticals** cosolvents are **not** welcome
- Relatively **high pressure** needed: expensive plants, risky operation (non-engineers pressure scare)

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Potentials of dense gases in chemical processes: non-extractive applications of SFCs

- Fractionation of liquid mixtures
- Reactions in supercritical solvents
- precipitation and micronisation techniques
- Impregnation
- Purification and cleaning
- Cromatography with supercritical eluent

Supercritical CO_2 as a reaction solvent

Advantages (Pros)

- enhancement of reactant and product solubilities in the phase where reaction occurs
- increase of chemical reaction rate (especially very close to the critical point)
- reduction of mass transport limitations and of catalyst deactivation for heterogeneously catalysed reactions
- possibility to make continuous the widely used batch processes, with CO_2 acting as mass and energy carrier: thus improving productivity and process controllability

Disadvantages (Cons)

- elevated pressures required (above 200 bar)
- multiphase systems and reactors
- low solubility of reactants

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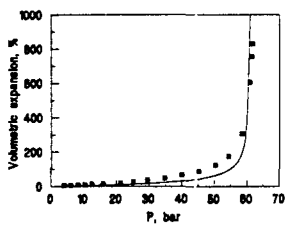
Solvent behavior of SCFs: binary mixtures

System CO_2- **DMSO** (Dimethylsulphoxide): liquid volume expansion at 298 K

- Volume expansion depends on the **solubility** of the dense gas **in the liquid**
- It is a **function of temperature**
- Its value can be **as high as 1,000%!!**
- An important equation:

$$\frac{V-V^0}{V^0}=\frac{v}{v^0_{os}}\left(1+\frac{x}{1-x}\right)-1$$



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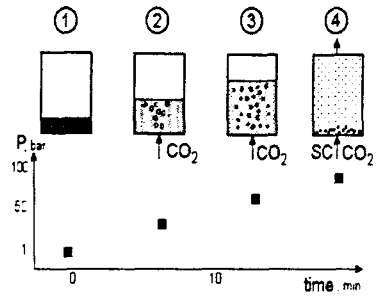
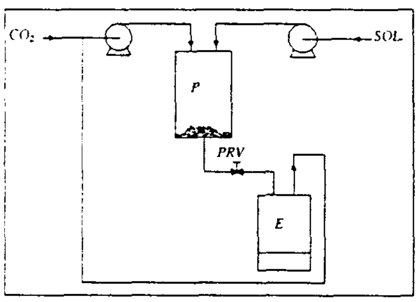
Precipitation by a supercritical antisolvent (SAS)

Step 1: make an organic solution of your solute
Step 2: apply pressure with CO_2
Step 3: CO_2 dissolves in the solution and changes the solvent characteristics: the solute precipitates completely
Step 4: wash out the mixed solvent mixture
Step 5: purify the solid by supercritical CO_2

A scheme of the SAS process (batch)

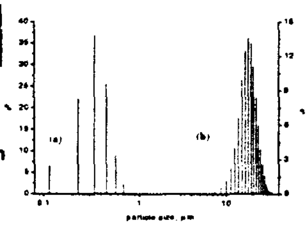


A scheme of the apparatus for SAS (semicontinuos)



SAS process with CO_2: micronization of a biocompatible polymer

S.E.M. picture
(bar=1 μm, x10,000)



Particle size distribution
a) SAS technique
b) conventional technique

Supercritical CO_2 as an antisolvent

Advantages (Pros)

- relatively low operating pressure (engineers)
- complete recovery of the solute as a solid product in a single stage
- relatively low CO_2 consumption
- possibility of tuning the product morphology and cristallinity (micronisation)

Disadvantages (Cons)

- organic solvent to be eliminated from the final product
- very high operating pressure (non-engineers)
- difficulty to change established processes

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Opinions about the future of SCFs

Philosophers

- **Ten years ago:** "**Supercritical Fluids** must offer **better results** with respect to existing technologies; it is important **not to use the solvent scare** to promote their applications" (Val Krukonis)
- **Today:**
  - **the issue** is the search for **clean, natural technologies,** i.e. **sustainable technologies**
  - another **major** issue is saving our life environment, **reducing the need** of polluting materials
  - the **market** is more and more oriented towards "**natural" products**, with low environmental impact
- **In next years:**
  - the above issues will be enforced
  - near critical /supercritical CO_2 is likely to **become an alternate solvent** for many existing productions

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Conclusions from the engineering viewpoint (pharmaceutical applications)

- The development of pharmaceutical technologies working with supercritical CO_2 must be based on the most favourable properties of SCFs, in view of obtaining truly new and valuable products
- Present potentials:
  - extraction of natural bioactive principles
  - controlled drug delivery system production
  - development of biocompatible products
  - use of CO_2 as a purification solvent
  - Preparative SCF Chromatography
  - new chemical syntheses in supercritical CO_2
  - sterilization
- To achieve an industrial level it is essential to assess both the technical and the economical feasibility (promoting a process just because it is based on supercritical CO_2 is not enough)
- *The problem of high pressure in the production plants is a fictitious problem*

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Acknowledgments

Coworkers

- Paolo Pallado, PhD
- Nicola Elvassore, PhD
- Michele Lora, PhD
- Luca Devetta, PhD
- Alberto Striolo, PhD student
- Gianluca Pettinello, Chem. Eng.
- Marco Baggio, Chem. Eng.
- Franco Tessari, Chemist
- Federico Zanette, Chem. Eng.
- Monica Daminato, Chem. Eng. student
- Attilio Venturi, Biotech. student

Companies

- Exenia, Albignasego (PD)
- Fidia Advanced Biopolymers, Abano (PD)
- ...not many more

For those who are interested to know more...

Intern. Symposiums on Supercritical Fluids

- Nice, F, 1988
- Boston, USA, 1991
- Strasbourg, F, 1994
- Sendai, J, 1997
- **Atlanta, USA, April 2000**

Intern. Conf. High Pressure Chemical Engineering

- Erlangen, D, 1984
- Erlangen, D, 1990
- Zürich, CH, 1996
- **Venice, September 2002**

Congressi Italiani sui Fluidi Supercritici

- Amalfi, NA, 1991
- Ravello, NA, 1993
- Grignano, TS, 1995
- Capri, NA, 1997
- Lago di Garda, 13-16 giugno 1999
- **Amalfi, September 2001**

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Industrial Case Studies

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Agenda

- Commercial process simulators
- A few tips before starting with simulations
- Production of Propylene Oxide in a Reactive distillation column
- Feed Change Analysis in a Oil Refinery Plant
- Off-gas Packed Column Reactive Absorber

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Leading Commercial Process Simulators

AspenPlus, AspenDynamics: largely used
Process, ProII: first one; largely used
Hysym, Hysys: well integrated, first for dynamics
Chemcad: special unit operations

Characteristics of a good Process Simulator

- *Flowsheet*: suitable graphic interfaces
- *Components*: large and accurate databases
- *Unit Operations*: reliable models
- *Streams*: any type (multiphase, solids, electrolytes...)
- *Properties*: up-to-date models
- *General*: user friendly (and fool proof)
- *Robustness*: high against user's mistakes
- *Convergence*: fast and safe to the correct solution
- *Accessories*: equipment design, economics, sensitivity analysis, optimisation
- *Flexibility*: linkable to user's routines

What a Process Simulator can and cannot do

- *Basic 1*: apply the degree-of-freedom analysis
- *Basic 2*: write & solve material+energy balances
- *Special*: sensitivity analysis and optimisation

HOWEVER

- no equipment design nor momentum balances
- models of some important units missing
- convergence not sufficient for meaningful results
- a Process Simulator is a tool: it cannot interpret results

Potentials of Process Simulation in the Chemical Industry

- Representing correctly plant operations
- Developing the process (revamping, upgrading,...), by making virtual experiments on a real plant
- *Advanced:* operator training (regular and safety)
- *Advanced:* on-line process operation and control
- *Advanced:* development of alternative, environmentally friendly processes

TIPS FOR A SUCCESSFUL SIMULATION:

- verify thermodynamic and kinetic data reliability
- select suitable property models and parameters
- calibrate simulation results on pilot plant runs

Cautions in using a Process Simulator: it is a nonsense ...

- *to run a Process Simulator without an accurate selection of the property models*
- *to select a good property model without knowing the value of its parameters*
- *to use predictive models anyway; one good experimental property datum is always better*

... and note that

- *The GIGO (garbage in gospel out) approach must be avoided*
- *The best available model might not be the best choice*

Production of Propylene Oxide in a Reactive distillation column

A Process Simulator Analysis of an Industrial Reactive Distillation Column

A. Bertucco[a], F. Bezzo[a], M. Barolo[a], A. Forlin[b]
[a] Istituto di Impianti Chimici, Università di Padova
[b] Centro Ricerche EniChem, Porto Marghera

Why a "reactive" distillation column?

1. *Production* of Propylene Oxide (PO) in a liquid alkaline phase (saponification)

$$2\ CH_3\text{-}CHOH\text{-}CH_2Cl + Ca(OH)_2 \Leftrightarrow 2\ CH_3\text{-}CHOCH_2 + CaCl_2 + 2\ H_2O$$

chlorhydrine, Ca hydroxide, PO, Ca chloride

2. *Separation* of PO from the reactive solution

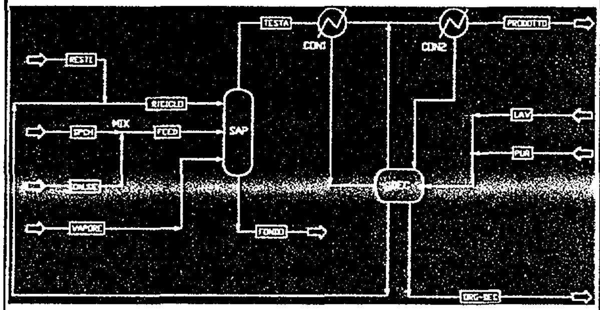
$$CH_3\text{-}CHOCH_2 + H_2O \Leftrightarrow CH_3\text{-}CHOH\text{-}CH_2OH \quad (\textit{to avoid!})$$

PO, Propylene Glycol

⇩

In a "reactive" column both operations can be achieved simultaneously

The plant section considered



flowsheet modeled by Aspen Plus

Thermodynamics

- Main components:
  1. water (H2O)
  2. propylene chlorhydrine (PCH)
  3. propylene oxide (PO)
  4. dichloropropane (DCP)
  5. dichloro-*i*-propylether (DCIPE)
  6. propylene glycol (GLY)
  7. calcium chloride (CACL)
  8. calcium hydroxide (CAOH)

- **Complex system, due to the presence of:**
  - ***water***
  - ***organic compounds* of different polarity**
  - ***electrolytes / salts***

Thermodynamics

- **Electrolytes**
  - **model by Chen *et al.* (1982; 1986), implemented through module ELECNRTL of Aspen Plus**
- **Non-electrolytes**
  - **NRTL by Renon and Prausnitz (1968)**
- ***Salting-out* effect:**
  - **the change in the activity coefficient is calculated as a function of the $CaCl_2$ concentration, according to Carrà *et al.* (1979)**

Chemical kinetics

- Model proposed by Carrà *et al.* (1979)

$r_1 = k_1$ [PCH] (PO production)

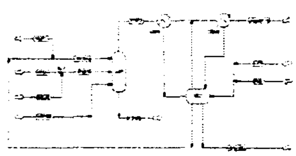
$r_2 = (k_h + k_{oh} [OH^-]) [PO]$ (GLY production)

- Both reactions occur in the liquid phase
- The production of PO is much faster than the GLY formation
- High residence times lead to the formation of by-products

Process Simulation

Column : diameter: 2.75 m
13 2-downcomer trays, feed on the 11th (from bottom)
Murphree efficiency: 0.4
operating pressure: low vacuum

- *Column feed:*



Process Simulation

- **The reactions considered may occur also in the static mixer and in the feed pipe:**

to column

About 60% of PCH reacts *before* entering the column

Process Simulation

- **Comparison with experimental data from the plant (stream PRODOTTO):**

The agreement with test-run data is satisfactory

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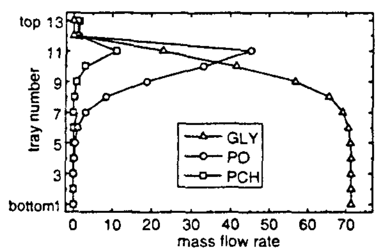
Column simulation

- **Internal liquid flow rates ("scaled" values)**



Below tray no. 5 the PO production is negligible

⇓

no GLY can be formed

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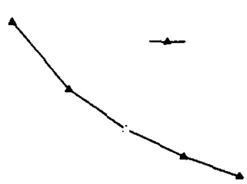
Effect of the stripping steam flow rate

- **Normalised production of *i* in the stream *j*:**



The production of glycol is strongly affected by the steam flow rate value

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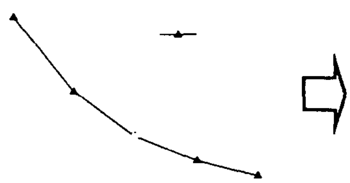
Effect of chlorhydrine temperature



1. The production of PO is not influenced by the energy input to the column
2. *The effect on the by-product is indeed remarkable*

Increasing the column capacity

- In the base case (reference conditions), the column is operated around 50% of flooding; therefore, the feed flow rate can be increased

- *The load may be increased as much as 50%!*
- *The production of GLY decreases!!*

Conclusions for the Reactive Column

- The Process Simulator is able to reproduce the plant steady-state operating conditions with good accuracy
- A large extent of reaction occurs before entering the column
- The PO production is essentially not affected by operating conditions
- The GLY production heavily dpends on the energy input to the column
- The feed flow rate can be increased, with no change for the PO production; the GLY formation is reduced

Solvent Extraction of ε-Caprolactam

Process Simulator Analysis of the Extraction Section of the production plant PR 16-19 at P.to Marghera

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[a] *Istituto di Impianti Chimici, Università di Padova*
[b] *Direzione reparto PR 16-19, EniChem, Porto Marghera*

Feed Change Analysis in a Oil Refinery Plant

Steady-state and Dynamic Simulation of the Topping Section of the I.E.S. Refinery in Mantova

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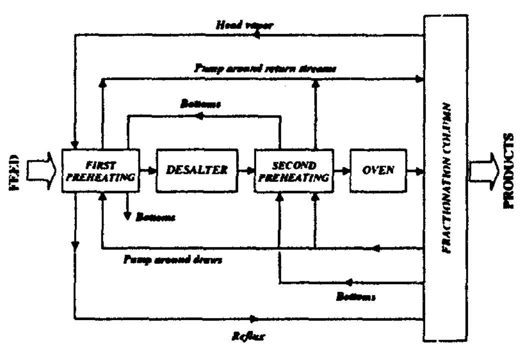
[b]*Raffineria Italiana Energia Servizi, Mantova*

The problem

- Frequent changes of feed due to erratic trend of the oil market
- Need of ensuring quality of required products anyway, by using oil mixtures
- Goal to reduce non-production time during changes
- Demand for better training of plant operators, especially under emergency conditions
- Improved scenarios about the plant safety with respect to the surrounding environment

The Topping section of the Refinery



Process Simulator requirements

- Complex thermodynamics of the system (very many hydrocarbons, water, gases)
- Robust covergence for both the column and the nested loops of heat exchangers
- Perfect reproduction of steady-state operation
- Accurate description of operation under transient conditions

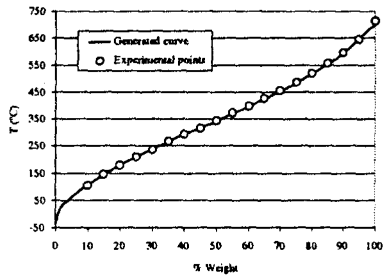
The tools

- T.B.P. curves from the chemical analysis lab
- Plant data of steady-state operation
- Plant data of transient operation during the change of the feed
- A suitable process simulator for both types of situations
- A smart student to run the simulator

The simulation procedure

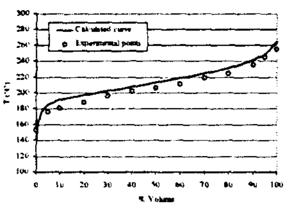
- Check that the thermodynamic model matches the experimental T.B.P. curves
- Retrieve data from the plant operating both at steady-state conditions (test-run 1) and during a feed change (test-run 2)
- Use a suitable process simulator (HYSYS®)
- Reproduce temperature values and profiles in all points of the topping section

Results: thermodynamic model

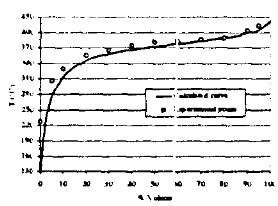


73% Iranian Heavy / 27% Syrian Light oil mixture

Results: steady-state simulation



Kerosene (ASTM D86)



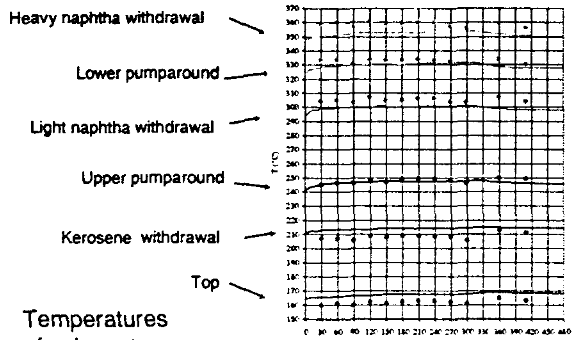
Heavy naphtha (ASTM D1160)

Results: steady-state simulation

tray	T simulated (°C)	T plant (°C)
Top	164,5	159
Kerosene withdrawal	210,9	203
Upper pumparound	241,2	241
Light naphtha withdrawal	293,8	299
Lower pumparound	323,9	328
Heavy naphtha withdrawal	347,6	355
Bottom	365,9	370

Comparison between simulated and experimental temperatures on trays

Results: dynamic simulation



Temperatures of column trays

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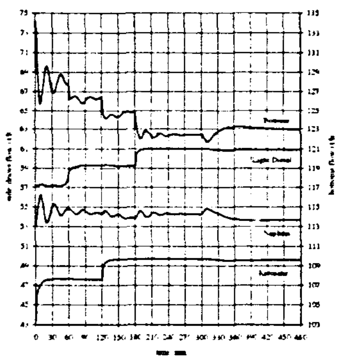
Results: dynamic simulation



Transients of product flow rates

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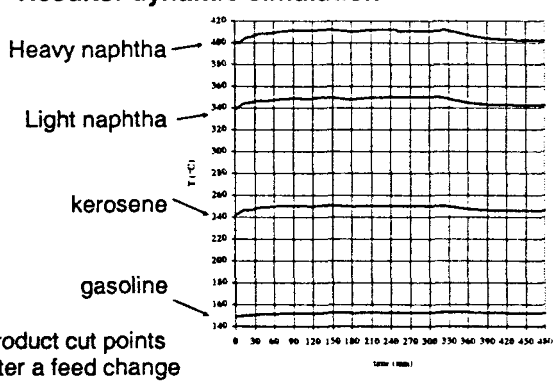
Results: dynamic simulation



Product cut points after a feed change

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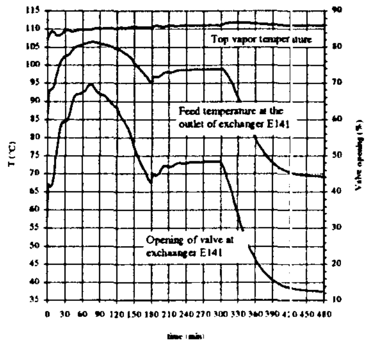
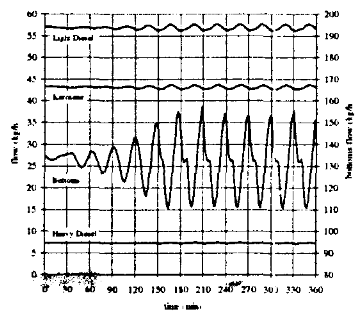
Results: dynamic simulation



Monitoring of unmeasured variables

Results: dynamic simulation



a virtual experiment

Conclusions for the oil refinery topping section

- **the thermodynamic model of the simulator is suitable for treating crude oil mixtures**
- **the simulator reproduces well steady-state operation: it is possible to predict product quality with different oil mixtures in the feed**
- **the simulator is checked under transient condition:**
  - **it is possible to minimize the time lost between two subsequent productions**
  - **it can be used for training of operators**
  - **the plant behavior in emergency situations can be figured out (loss prevention)**

Off-gas Packed Column Reactive Absorber

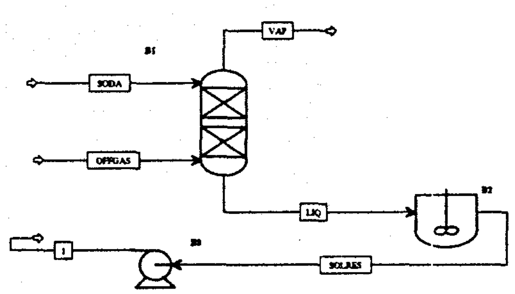
Steady-state and Dynamic Process Simulator Analysis of an Absorption Column of Carbonyl Chloride

M. Barolo[a], A. Bertucco[a], L. Gallo[a], A. Forlin[b]
[a]*Istituto di Impianti Chimici, Università di Padova*
[b]*Direzione reparto PR 16-19, EniChem, Porto Marghera*

The problem

- $COCl_2$ content in an off-gas to be reduced below 0.02 ppm (TLV) in emergency operations
- Packed absorption tower to be used
- Liquid absorbent: NaOH solution (recirculated)
  $COCl_2 + 4\ NaOH = Na_2CO_3 + 2\ NaCl + H_2O$
- Parallel reaction: $COCl_2 + H_2O = CO_2 + HCl$
- Reactive absorption transient operation

The industrial column



Process Simulator requirements

- Complex thermodynamics of the system (electrolytes, water, organic compounds, gases)
- Equilibrium-based or rate-based model ?
- Thermodynamic model parameter values
- Kinetic parameter values:
  - chemical kinetics
  - mass-transport coefficients

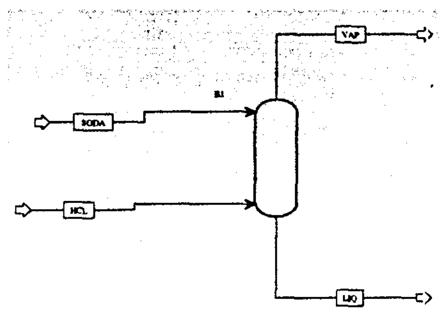
Is there a Process Simulator suitable to deal with this problem?

- Most of them use the equilibrium stage approach
- Only RATEFRAC® has a rate-based model
- RATEFRAC® was unable to converge
- RATEFRAC® is not available for dynamic operation simulations
- Equilibrium stage approach with HETP to be used

The simulation procedure

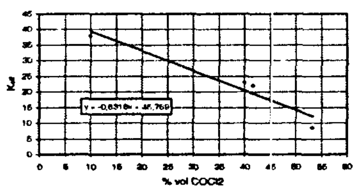
- Retrieve and/or correlate thermodynamic model parameters
- Measure HTU in a lab-scale column operating at steady-state conditions
- Calculate HETP and simulate the lab-scale column with AspenPlus® (stage approach) to tune the kinetic parameter K_{eff}
- Scale HETP and K_{eff} up to the industrial level
- Use Aspen Dynamics® to represent the real plant

The lab-scale column



Results

- Measures of y_{COCL2} in VAP stream as a function of concentration and flow rate of both off-gas and NaOH solution
- Values of the effective reaction constants K_{eff} for $COCl_2$ neutralization:



Results (continued)

... and for HCl formation:

$$(K_{eff})_{HCl} = (K_{eff})_{COCl_2}\sqrt{\frac{D_{HCl}}{D_{COCl_2}}}.$$

- evaluation of HETP and K_{eff} for the industrial plant:

$$(HETP)_{ind} = (HETP)_{pil}\left(\frac{(d_p)_{ind}}{(d_p)_{pil}}\right)$$

$$(k_l)_{ind} = (k_l)_{pil}\left(\frac{\left(\frac{u_L}{a_w}\right)_{ind}}{\left(\frac{u_L}{a_w}\right)_{pil}}\right)^{0.667}\left(\frac{(a_p d_p)_{ind}}{(a_p d_p)_{pil}}\right)^{0.4}.$$

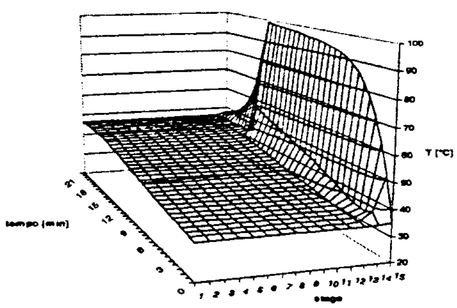
Lab-scale column simulation results

- $COCl_2$ composition profiles in the vapor phase:

Stage	$COCl_2$ [ppm vol]	$COCl_2$ [ppm mass]
1	75	270
2	340	1200
3	1550	5500
4	7010	24600
5	30900	104000

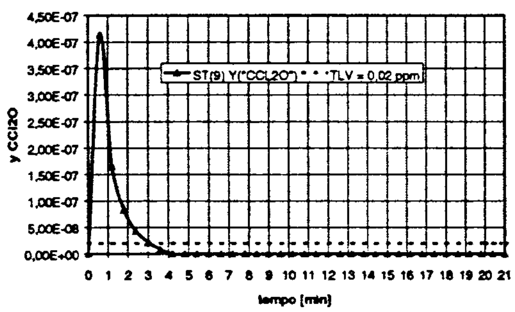
Industrial column simulation results

- Temperature profiles:



Industrial column simulation results

- Composition profiles:



Conclusions for off-gas absorber

- A reactive absorption problem under dynamic conditions was addressed
- an insufficient process simulator was adapted to treat the problem of interest
- the values of parameters were adjusted to phase equilibrium literature data and lab-scale absorption measurements
- the scale-up of these values to the industrial plant scale allowed predictive calculations
- it was shown that the abatment of the undesired compound is well below the safety limits

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General Conclusions

The operation and optimization of industrial plants can be easily tackled by Process Simulators, BUT:

- the values of parameters required by the Process Simulator must be accurate, i.e. consistent with experimental data
- among other properties, it is of paramount importance to represent correctly both the equilibrium behavior and the reaction rates
- without a careful check of how these properties are evaluated, process simulation and optimization is a nonsense and a waste of time
- Process Simulators allow to perform *virtual* experiments on *real* production plants
- Process Simulators allow to perform feasibility analysis of newly proposed processes

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Acknowledgments

- My colleagues Dr. Massimiliano Barolo and Prof. Gian Berto Guarise
- People from industry: Dr. Paola Volpe, Ing. Anna Forlin, Ing. Alfio Rondina, Ing. Giorgio Persi
- My students: Fabrizio Bezzo, Tiziana Carron, Alessio Belmonte, Daniel Berhan, Marco Piazza, Marco Salvato, Luca Ferrari, Lisa Gallo, Carlo Vianello
- the International Centre for Science and Technology of UNIDO in Trieste (first of all Ing. Gennaro Longo and Mrs. Elisa Roa)

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Fundamentals of process dynamics and control

– Part I –

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ICS-UNIDO Training Course on
Sustainable Industrial Development : Process Simulation and Optimization Techniques
(Rabat, Morocco, 18-22 September, 2000)

Objectives of the lectures

At the end of the two lectures, you are expected to:

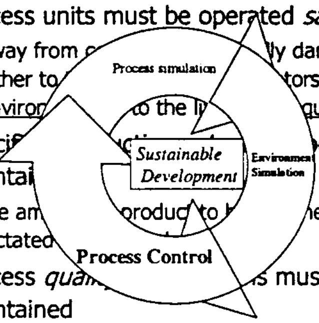
- know the basics of dynamic behavior of (simple) linear systems
- understand the role of process models in control system design
  - ✓controller tuning
  - ✓feedforward control
- apply and tune conventional PID controllers for simple processes
- understand the advantages of cascade control

Agenda for Part I

- Objectives and jargon of process control
- Process modeling
  - first principles
  - empirical process modeling
- Dynamics of linear systems
  - first- and second-order processes
  - time-delay processes
  - inverse-response systems

Operation of processing units

- Process units must be operated *safely*
  - away from ... ly dangerous either to ... tors or to the environ... to the li... quipment
- Speci... e maintai...
  - the am... produc... to ... ed is dictated...
- Process *qua*... s must be maintained
  - out-of-spec products need to be re-processed



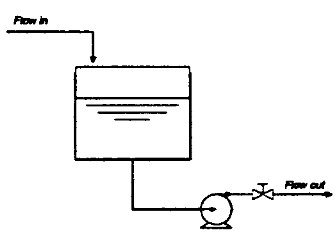
The task of a process control system

① ***Monitoring*** certain variables that indicate process conditions at any time (measurements)

② ***Making*** rational ***decisions*** regarding what corrective action is needed (current state vs. desired state)

③ ***Inducing changes*** in the appropriate process variables to improve process conditions (valves to manipulate)

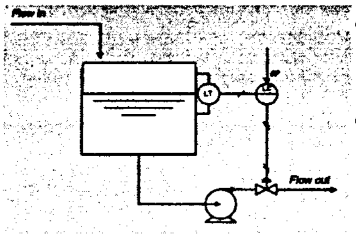
Motivating example: level control



- The inlet flow comes from an upstream process, and may change with time
- The level in the tank must be kept constant in spite of theses changes

If the outlet flow is simply set equal to the inlet flow, the tank may overflow or run empty (because of flow measurement errors)

Introducing a level controller



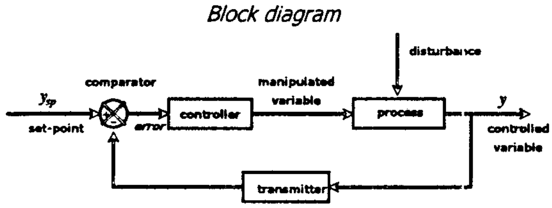
- The level controller (LC) looks at the level (*monitoring*)
- If the level starts to increase, the LC sends a signal to the output valve to vary the output flow (*change*)

This is the essence of *feedback control*

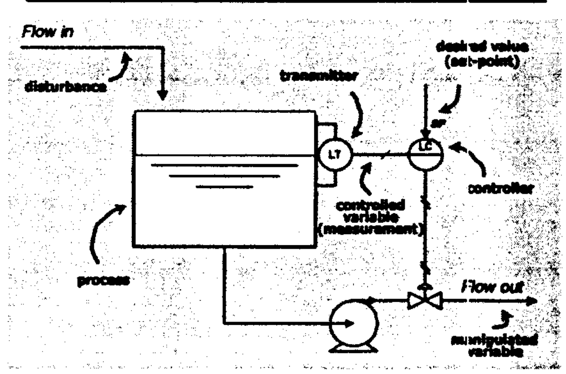
Feedback control

- It is the most important and widely used control strategy
- It is a *closed-loop* control strategy

Block diagram



Back to level control



More on control jargon

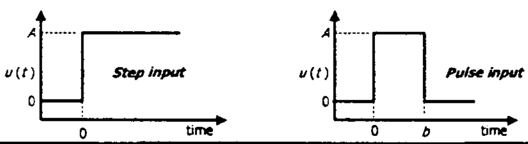
- *Input variables*: independently stimulate the system; they can induce change in the internal conditions of the process
  - *manipulated* (or control) variables ***u; m*** → at our disposal
  - *disturbance* variables ***d*** → we cannot do anything on them
- *Output variables*: measurements ***y***, by which one obtains information about the internal state of the system (e.g. temperature, level, viscosity, refractive index)
- *States*: minimum set ***x*** of variables essentials for completely describing the internal condition of a process (e.g. composition, holdup, enthalpy)

Process dynamics

- Given a dynamic model of the process, it investigates the process response to various input changes

Two elements are necessary:

- a *dynamic model* of the process
- a known *forcing function*



Process models: Why?

- To improve the understanding of the process (whenever possible, avoid using the plant)
- To train plant operating personnel (teach them how to face standard and abnormal situations)
- To design the control strategy for a new process (select which output should be controlled by which input)
- To select the controller settings (get reasonable tuning with computer simulations; then refine it on field)
- To design the control law (if possible, use a process model directly within the control law)
- To optimize the process operating conditions (a steady state model is often sufficient)

Process models: Which?

- We will consider only two classes of dynamic process models
  - *state-space* models
  - *input-output* models

☞ *State-space models* can be derived directly from the general conservation equation:

Accumulation = (Inlet – Outlet) + (Generation – Consumption)

They are written in terms of differential equations relating process *states* to time ⇒ They occur in the "time domain"

Process models : Which? (cont'd)

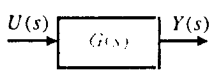
☞ *Input-output models* completely disregard the process states. They only give a relationship between process inputs and process *outputs* ⇒ They occur in the "Laplace domain"

State-space model ⇔ *Input-output model*

$$\frac{d\mathbf{x}(t)}{dt} = f(\mathbf{x}; u; d; t) \quad \text{(states)}$$

$$\mathbf{y} = h(\mathbf{x}) \quad \text{(output)}$$

$$Y(s) = G(s)U(s)$$



$G(s)$ is called *transfer function* of the process

Linear systems

- In the time domain, a linear system is modeled by a linear differential equation.
- For example, a linear, n^{th}-order system is:

$$a_n \frac{d^n y}{dt^n} + a_{n-1} \frac{d^{n-1} y}{dt^{n-1}} + \ldots + a_1 \frac{dy}{dt} + a_0 y = bu(t)$$

Our assumptions:
- the coefficients of the differential equations are constant
- the output y is equal to the state x

Note

- The Laplace-domain representation is possible only for linear (or linearized) systems
- We will assume that the process behavior in the vicinity of the steady state is linear

First-order systems

Time-domain model | *Laplace-domain model*

(Dividing by a_0)

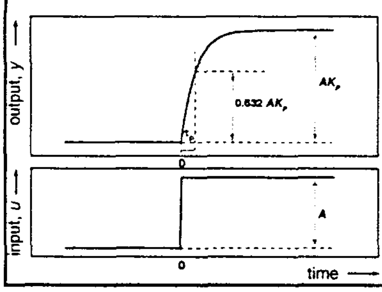
$$\tau_P \frac{dy}{dt} + y = K_P u(t) \qquad Y(s) = \left(\frac{K_P}{\tau_P s + 1}\right) U(s)$$

- K_P is the process *steady state gain* (it can be >0 or <0)
- τ_P is the process *time constant* (it is always >0)

Transfer function of a first-order system: $G(s) = \dfrac{K_P}{\tau_P s + 1}$

Response of first-order systems

- We only consider the response to a *step* forcing function of amplitude *A*



The time-domain response is:

$$y(t) = AK_P\left(1 - e^{-\frac{t}{\tau_P}}\right)$$

It takes ~ 4÷5 time constants for the process to reach the new steady state

Determining the process gain

- An open-loop test can be performed starting from the reference steady state:
  - step the input to the process
  - record the time profile of the measured output till a new steady state is approached
  - check if this profile resembles $y(t) = AK_P(1 - e^{-t/\tau_P})$
  - if so, calculate K_P as:

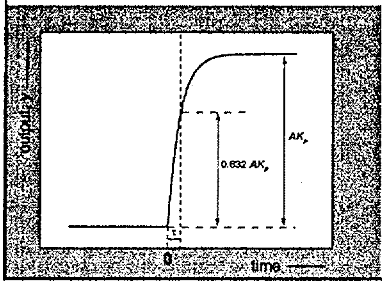
$$K_P = \frac{y_{ss,new} - y_{ss,ref}}{u_{new} - u_{ref}} = \left(\frac{\Delta(\text{output})}{\Delta(\text{input})}\right)_{steady\ state}$$

The gain is a dimensional figure

☞ *The process gain can be extracted from* <u>*steady state*</u> *information only*

Determining the time constant

- From the same open-loop test:
  - determine τ_p graphically (note: it has the dimension of time)



You need ***dynamic*** *information to determine the process time constant*

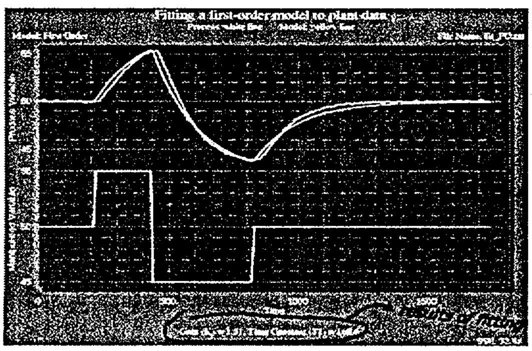
Extracting the values of K_p and τ_p from process data is known as *process identification*

An alternative approach

- State the identification task as an optimization problem:
  - *given a first-order model, find the K_p and τ_p values that allow the model to best-fit the experimental data*
- You will need a computer package to perform the fitting (e.g. Control Station™, Matlab™)
- It is better to step up and down the manipulated input several times to capture the "true" dynamic behavior of the process
- Never trust on the "raw" fitting results only! Always judge the results by superimposing the fitted curve to the process one

An alternative approach (cont'd)

Example using Control Station™



Extension to nonlinear systems

- Strictly speaking, the gain and time constant are independent of the operating steady state *for linear systems* only
- If a true (i.e. nonlinear) system is being considered, the excitation sequence must be such that the process is not moved too far away from the nominal steady state

linear

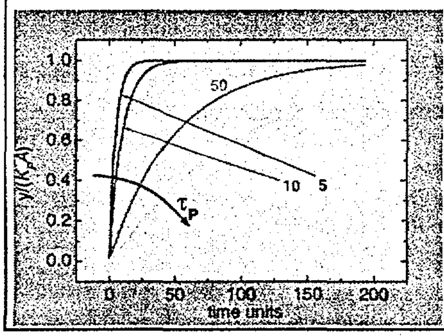
$$K_{P,\text{linear}} = \left.\frac{\Delta y}{\Delta u}\right|_{\text{any steady state}}$$

nonlinear

$$K_{P,\text{nonlinear}} = \left.\frac{\partial y}{\partial u}\right|_{\text{nominal steady state}}$$

Further remarks

"Slow" and "fast" processes



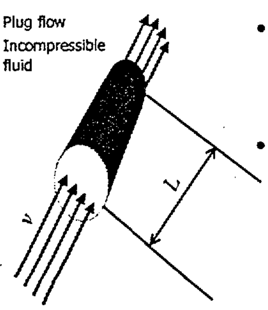
The time needed to approach the new steady state increases with increasing τ_P

Note

For all τ_P's, the output starts to change *immediately* after the input has been changed

Pure time-delay systems

✓ Plug flow
✓ Incompressible fluid

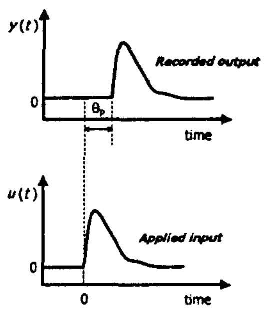


- Many real systems do not react *immediately* to excitation (as first order systems instead do)
- The time needed to "transport" a fluid property change from the inlet to the outlet is:

$$\theta_P = \frac{L}{v} \quad : \textit{dead time or time delay}$$

- Examples: transportation lags (e.g. due to pipe length, to recycle, ...); measurement lags (e.g. gaschromatographs)

Pure time-delay systems (cont'd)



- The process output is simply shifted by θ_P units in time with respect to the input

Models

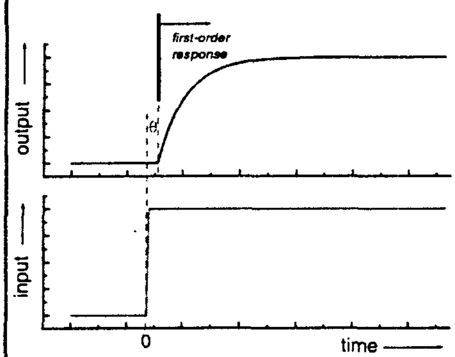
- *Time domain*:

$$y(t) = \begin{cases} 0 \ , & t < \theta_P \\ x(t-\theta_P), & t \geq \theta_P \end{cases}$$

- *Laplace domain*:

$$\frac{Y(s)}{U(s)} = e^{-\theta_P s}$$

FOPDT systems



The dynamic behavior of many real systems can be approximated as *First Order Plus Dead Time* (FOPDT)

Modeling a FOPDT system

- The behavior of a pure time-delay system is simply superimposed to that of a first-order system

$$\tau_P \frac{d\,y(t)}{dt} + y(t) = K_P\, u(t-\theta_P) \Longleftrightarrow \text{Time domain}$$

$$G(s) = \frac{K_P\, e^{-\theta_P s}}{\tau_P s + 1} \Longleftrightarrow \text{Laplace domain}$$

- Approximating a real system as a FOPDT linear system is extremely important for controller design and tuning

Second-order systems

- Time-domain representation: $a_2 \frac{d^2 y}{dt^2} + a_1 \frac{dy}{dt} + a_0 y = bu(t)$

$$\tau^2 \frac{d^2 y}{dt^2} + 2\zeta\tau \frac{dy}{dt} + y = Ku(t)$$

- Laplace-domain representation:

$$\frac{Y(s)}{U(s)} = \frac{K}{\tau^2 s^2 + 2\zeta\tau s + 1}$$

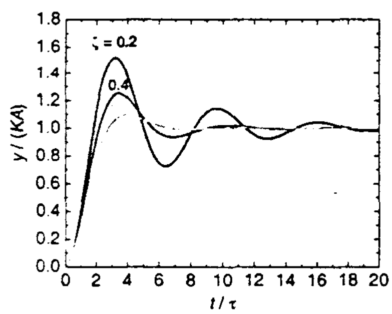
$$\frac{Y(s)}{U(s)} = \frac{K}{(\tau_1 s + 1)(\tau_2 s + 1)}$$

K = process gain

τ = natural period

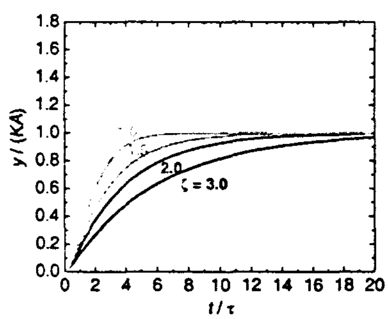
ζ = damping coefficient

Underdamped systems



Open-loop response to a input step disturbance

Overdamped systems



Open-loop response to a input step disturbance

Effect of the damping coefficient

- The value of ζ completely determines the degree of oscillation in a process response after a perturbation

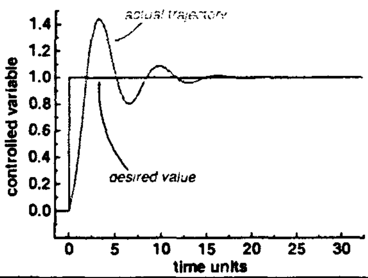
$\zeta > 1$: overdamped, *sluggish* response

$0 < \zeta < 1$: underdamped, *oscillating* response
(the damping is attenuated as ζ decreases)

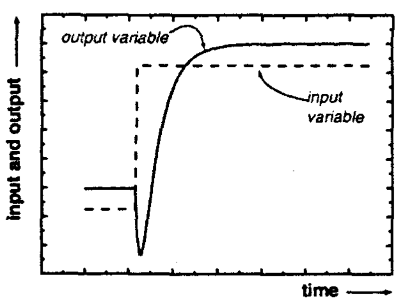
$\zeta < 0$: *unstable* system
(the oscillation amplitude grows indefinitely)

The importance of 2nd-order systems

- Control systems are often designed so that the *controlled* (i.e., closed-loop) process responds as an underdamped second-order system



Inverse-response systems



- There is an *initial* inversion in the response: the process starts moving *away* from its ultimate value
- The process output *eventually* heads in the direction of the final steady state

Inverse-response systems (cont'd)

- Inverse response is the net result of two *i)opposing* dynamic modes of *ii)different magnitudes*, operating on *iii)different time scales*
  - the faster mode has a small magnitude and is responsible for the initial, "wrong way" response
  - the slower mode has a larger magnitude and is responsible for the long-term, dominant response

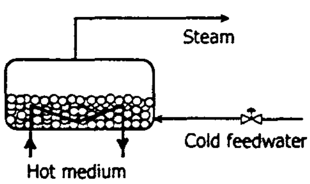
Laplace-domain representation

$$\frac{Y(s)}{U(s)} = \frac{K(\tau_L s+1)}{(\tau_1 s+1)(\tau_2 s+1)}$$

- τ_L is called *lead time,* and in general it may be >0 or <0
- However, a requirement *for inverse response* is $\tau_L < 0$

Is this only theory?

Example process: drum boiler



Disturbance: step increase in the cold feedwater flowrate

Output: level in the boiler

- *In the long run*, the level is expected to increase, because we have increased the feed material without changing the heat supply
- But *immediately* after the cold water has been increased, a drop in the drum liquid temperature is observed, which causes the bubbles to collapse and the observed level to reduce

Summary of Part I

- The need for a control system
- Devising process models:
  - time-domain
  - Laplace domain
- Dynamic behavior of linear systems:
  - first order
  - dead time
  - first order plus dead time (FOPDT)
  - second order
  - inverse response

Fundamentals of process dynamics and control

– Part II –

Dr. Massimiliano Barolo

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Agenda for Part II

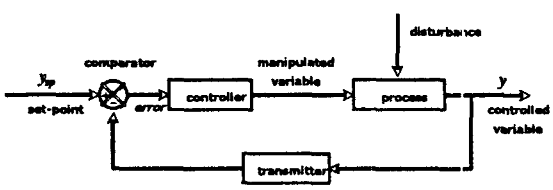
- Conventional feedback control
  - examples of simple controlled systems
  - on-off, P, PI & PID controllers
  - tuning and performance evaluation
- Improved control schemes
  - cascade control
  - feedforward control
- Multivariable systems
  - controller pairing and loop interaction

Feedback control

- The process information (*y*) is fed *back* to the controller
- The objective is to reduce the *error signal* to zero, where the error is defined as:

$$e(t) = y_{sp}(t) - y(t)$$

y_{sp} = set point (target value)
y = measured value



The typical control problems

① Regulatory control

– the task is to counteract the effect of external disturbances in order to maintain the output at its constant set-point (*disturbance rejection*)

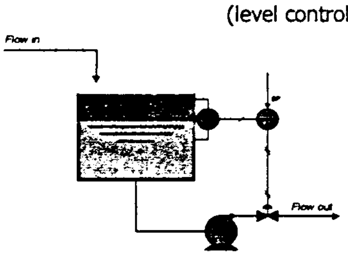
② Servo control

– the objective is to cause the output to track the changing set-point

In both cases, one or more variables are *manipulated* by the control system

Material balance control # 1

Liquid holdup control (level control)



- If the level h tends to decrease, the error $(h_{sp} - h)$ increases
- The controller sends a signal to the control valve actuator
- The flow out is increased
- The level in the tank decreases

Material balance control # 1 (cont'd)

- The controller's job is to enforce the total mass balance around the tank, in order to have neither accumulation nor depletion of liquid matter inside the tank

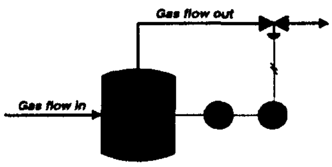
$$\underbrace{\textit{rate of mass out}}_{\text{set by the controller}} = \underbrace{\textit{rate of mass in}}_{\text{unknown to the controller}}$$

☞ The equality is enforced by the controller *regardless of the value of the level set-point*

Material balance control # 2

Gas holdup control

(pressure control)

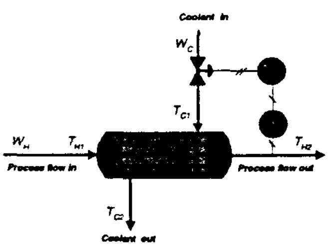


- If the pressure P tends to increase, the error $(P_{sp} - P)$ decreases
- The controller sends a signal to the control valve actuator
- The flow out is increased
- The pressure in the drum decreases

The pressure controller maintains the mass balance in the drum by matching the flow out of the drum to the total mass flow into the drum

Heat transfer control #1

Control of a process stream cooler

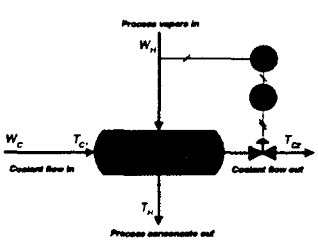


- If the temperature T of the exiting process stream increases, the error $(T_{sp} - T)$ decreases
- The coolant flow is increased by the controller
- The exit temperature of the process flow decreases

Heat transfer control # 2

Condenser control

- The heat of condensation is transferred at a relatively uniform temperature ⇒ the temperature is *not* a good indicator of the heat transfer rate



- The *pressure* of the condensing vapors is used as the controlled variable
- If the rate of heat transfer decreases, less vapor is condensed, and the stream pressure increases
- The controller increases the coolant flow rate

The task of a process control system

once more...

① Monitoring certain variables that indicate process conditions at any time (measurements)

② **Making *rational decisions* regarding what corrective action is needed (current state vs. desired state)**

③ Inducing changes in the appropriate process variables to improve process conditions (valves to manipulate)

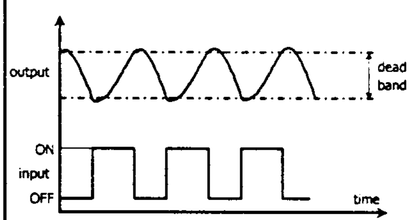
According to what rationale does a feedback control system work?

On-off control: the simplest one

- The control variable is manipulated according to:

$$u(t) = \begin{cases} u_{max}, & \text{if } e \geq 0 \\ u_{min}, & \text{if } e < 0 \end{cases}$$

The final control element is either completely open/maximum, or completely closed/minimum



Widely used as thermostat in domestic heating systems, refrigerators, ...; also in noncritical industrial applic'ns (some level and heating loops)

Summary for on-off control

☺ Advantages
- simple & easy to design
- inexpensive
- easily accepted among operators

☹ Pitfalls
- not effective for "good" set-point control (the controlled variable cycles)
- produce wear on the final control element (it can be attenuated by a large dead band, at the expense of a loss of performance)

Proportional (P) controllers

- The control variable is manipulated according to:

$$u(t) = u_0 + K_C\, e(t)$$

u_0 is the controller bias
K_C is the controller gain

- The controller gain can be adjusted ("tuned") to make the manipulated variable changes as sensitive as desired to the deviations between set-point and controlled variable
- The sign of K_C can be chosen to make the controller output u increase or decrease as the error increases

P-only controllers

$$u(t) = u_0 + K_C\, e(t)$$

- The bias u_0 is the value of the controller output which, in manual mode, causes the measured process variable to maintain steady state at the design level of operation ($e(t)=0$) when the process disturbances are at their expected values
- The bias value is assigned at the controller design level, and remains *fixed* once the controller is put in automatic

$u = u_0 = \text{const}$: at the *nominal* steady state

P-only controllers (cont'd)

$$u(t) = u_0 + K_C\, e(t)$$

What if the disturbance level changes during the process?

- The manipulated input u must ***change*** to guarantee that the process stays at steady state, i.e. $u \neq u_0$

⇩

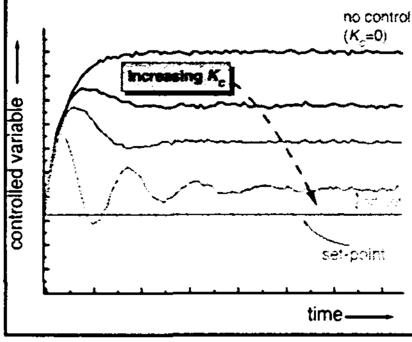
- A steady state error $e \neq 0$ *must* be enforced by the P-only controller to keep the process at steady state: $u_{s.s.} = u_0 + K_C\, e(t) \neq u_0$

⇩

A P-only controller cannot remove off-set

Performance of P-only controllers

Response to a disturbance step change



- Whatever the value of K_c, the offset is reduced with respect to open-loop operation
- Increasing K_c
  - the offset is reduced
  - the system may oscillate
  - the process response is speeded up
- Although the open-loop response may be 1st order, the closed-loop one is not

Summary for P-only control

☺ Advantages
- conceptually simple
- easy to tune (a single parameter is needed, K_C; the bias is determined from steady state information)

☹ Pitfalls
- cannot remove off-set (off-set is *enforced by* the controlled)

PI controllers

P=Proportional , I=Integral

- The P controller cannot remove off-set because the only way to change the controller bias during non-nominal operations is to cause $e \neq 0$
- The rationale behind a PI controller is to set the "actual" bias different from u_0, thus letting the error be zero
- The control variable is manipulated according to:

$$u(t) = u_0 + K_C\left[e(t) + \frac{1}{\tau_I}\int_0^t e(t)\,dt\right]$$

integral action contribution

u_0 is the controller bias
K_C is the controller gain
τ_I is the integral time (also called reset time)

PI controllers (cont'd)

$$u(t) = u_s + K_c\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t)\,dt\right)$$

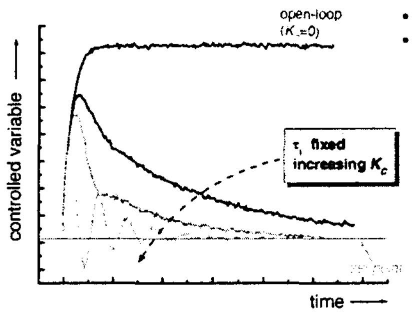
- Note that until $e \neq 0$, the manipulated input keeps on changing because of the presence of the integral term
- The change in $u(t)$ will stop only when $e = 0$

⇩

The integral action can eliminate off-set

Performance of PI controllers

Response to a disturbance step change: effect of K_c



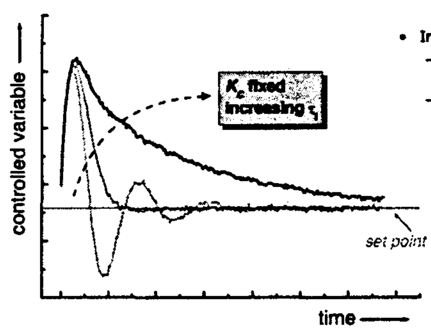
- The offset is eliminated
- Increasing K_c:
  - the process response is speeded up
  - the system may oscillate

CAUTION

For large values of the controller gain, the closed-loop response may be unstable !

Performance of PI controllers (cont'd)

Response to a disturbance step change: effect of τ_I



- Increasing τ_I:
  - oscillations are dampened
  - the process response is made more sluggish

CAUTION

For small values of the integral time, the closed-loop response may be unstable !

Summary for PI control

☺ Advantages

- *steady state off-set can be eliminated*
- the process response can be considerably speeded up with respect to open-loop

☹ Pitfalls

- tuning is harder (two parameters must be specified, K_C and τ_I)
- the process response becomes oscillatory; bad tuning may even lead to instability
- the integral action may "saturate"

PID controllers

P=Proportional , I=Integral , D=Derivative

- *i*) If the error if increasing very rapidly, a large deviation from the setpoint may arise in a short time. *ii*) Sluggish processes tend to cycle
- The rationale behind derivative action is to anticipate the future behavior of the error signal by considering its *rate* of change
- The control variable is manipulated according to:

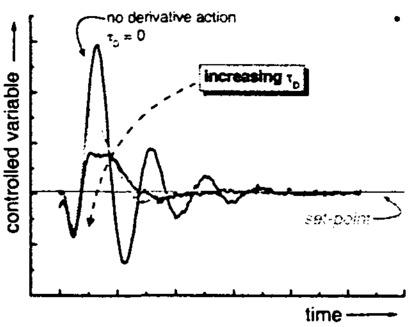
$$u(t) = u_0 + K_C\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t)\,\mathrm{d}t + \tau_D\frac{\mathrm{d}e(t)}{\mathrm{d}t}\right)$$

derivative action contribution

τ_D is called <u>derivative time</u>

Performance of PID controllers

Response to a disturbance step change



- Increasing τ_D :
  - the oscillations caused by the integral action are dampened
  - the process response is speeded up

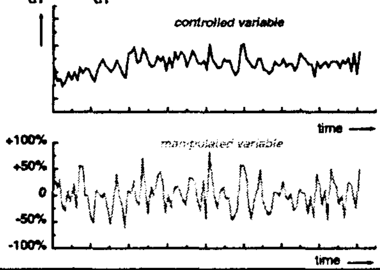
<u>CAUTION</u>

Noisy measurements may disrupt the controller performance !

Beware measurement noise !

- The derivative action requires derivation of the output measurement y with respect to time:

$$\frac{de}{dt} = \frac{d(y_{sp} - y)}{dt}$$



If the measured output is noisy, its time derivative may be large, and this causes the manipulated variable to be subject to abrupt changes ⇒ *Attenuate or suppress the derivative action*

Summary for PID control

☺ Advantages

- oscillations can be dampened with respect to PI control

☹ Pitfalls

- tuning is harder than PI (three parameters must be specified, K_C, τ_I and τ_D)
- the derivative action may amplify measurement noise ⇒ potential wear on the final control element

😐 Use of derivative action

- avoid using the D action when the controlled variable has a noisy measure or when the process is not sluggish ($\theta_P / \tau_P < 0.5$)

Controller selection recommendations

- When steady state offsets can be tolerated, use a P controller (many liquid level loops are on P control)
- When offset *cannot* be tolerated, use a PI controller (a large proportion of feedback loops in a typical plant are under PI control)
- When it is important to compensate for some natural sluggishness in the system, and the process signal are relatively noise-free, use a PID controller

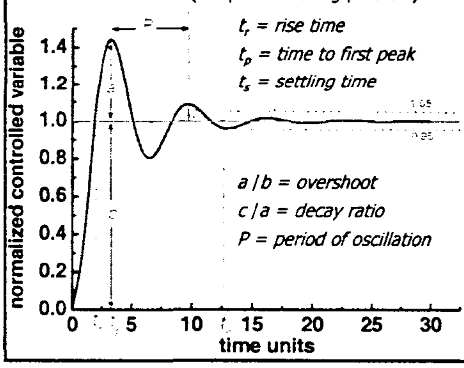
Direct & reverse acting controllers

- Most times, the final control element is a pneumatically-driven valve
  - **air-to-open** valves (also called fail-closed): as the controller output signal increases, the valve opens further
  - **air-to-close** valves (also called fail-open): as the controller output signal increases, the valve closes further

Process gain	Air-to-open valve	Air-to-close valve
Positive	direct acting PID	reverse acting PID
Negative	reverse acting PID	direct acting PID

Performance assessment

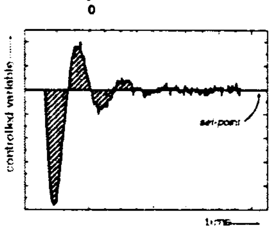
(set-point tracking problem)



A "good" decay ratio is 1/4 ("quarter amplitude" decay)

Performance indexes

$\mathrm{IAE} = \int_0^{\infty} |e(t)|\,\mathrm{d}t$: <u>*integral of the absolute value of error*</u>



IAE corresponds to the shaded area

- The controller's tuning parameters (K_C; τ_I; possibly τ_D) are chosen such that IAE is minimized
- Semi-empirical formulae can be derived based on a FOPDT open-loop identification
- *The optimal controller's settings for load disturbance rejection are different from those for set-point tracking*

Tuning guidelines

- Fit a FOPDT model to the process data obtained by step (or pulse) changes in the manipulated variable
  - the process must begin at the nominal steady state
  - the sampling rate should be at least ten times faster than the process time constant
  - the measured variable should be forced to move at least ten times the noise band
- Determine *initial* values for K_C, τ_I (and possibly τ_D) from suggested correlations
- Never *ever* trust blindly on these settings. Always refine the tuning on-field

Tuning correlations for PI control

(based on FOPDT open-loop identification)

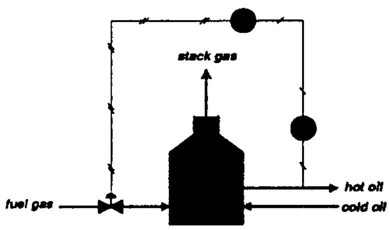
	K_C	τ_I	
IMC for balanced set point tracking and disturbance rejection	$\dfrac{\tau_p}{K_p(\theta_p + \tau_p)}$	τ_p	***Note*** τ_c is the larger of $(0.1\tau_p)$ and $(0.8\theta_p)$
minimum ITAE for set point tracking	$\dfrac{0.586}{K_p}(\theta_p / \tau_p)^{-0.916}$	$\dfrac{\tau_p}{1.03 - 0.165(\theta_p / \tau_p)^{[illegible]}}$	
minimum ITAE for disturbance rejection	$\dfrac{0.859}{K_p}(\theta_p / \tau_p)^{-0.977}$	$\dfrac{\tau_p}{0.674(\theta_p / \tau_p)^{0.680}}$	

$$\mathrm{ITAE} = \int_0^{+\infty} t\,|e(t)|\,\mathrm{d}t$$: *integral of the time-weighted absolute value of error*

Controller tuning can be performed automatically using the "Design Tools" module of *Control Station*™

A disadvantage of feedback control

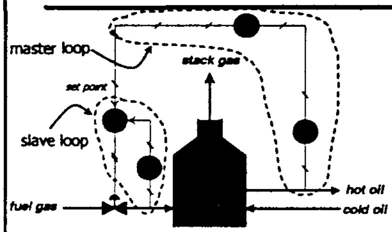
- In conventional feedback control the corrective action for disturbances does not begin until *after* the controlled variable deviates from the set point



If either the cold oil flow rate or the cold oil temperature change, the controller may do a good job in keeping the hot oil temperature at the setpoint

What if the pressure *of the fuel gas* changes?

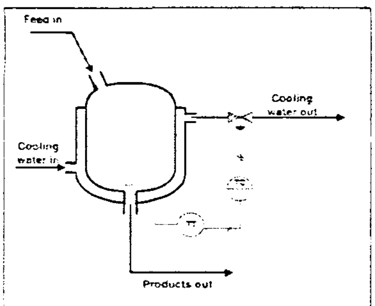
Cascade control # 1



The performance can be improved because the fuel control valve will be adjusted *as soon as the change in supply* pressure is detected

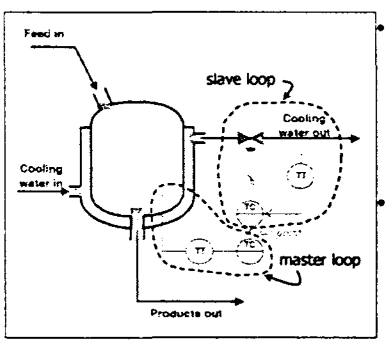
- Two control loops are nested within each other: the *master* controller and the *slave* controller
  - the output signal of the master (primary) controller serves as the set point of the slave (secondary) controller

Cascade control # 1



- The TC may reject satisfactorily disturbances such as reactant feed *T* and composition
- If the *T* of the cooling water increases, it slowly increases the reactor *T*
- The TC action may be delayed by dynamic lags in the jacket and in the reactor

Cascade control # 1 (cont'd)



- The performance can be improved because the cooling water rate will be adjusted as soon as a change in the *jacket* temperature is detected
- This keeps the heat removal rate at a constant level, and the *reactor* temperature is less affected by the unknown disturbance

Tuning a cascade loop

1. Begin with both the master and the slave controllers in manual
2. Tune the slave (inner) loop for set-point tracking first (the tuning guidelines presented before can be used)
3. Close the slave loop, and adjust the tuning on line to ensure good performance
4. *Leaving the inner loop closed*, tune the master loop for disturbance rejection (the tuning guidelines presented before can be used)
5. Close the master loop, and adjust the tuning on line to ensure good performance

A P-only controller is often sufficient for the slave loop

Summary on cascade control

☺ It is used to improve the dynamic response of the process to load disturbances

☺ It is particularly useful when the disturbances are associated with the manipulated variable or when the final control element exhibits nonlinear behavior

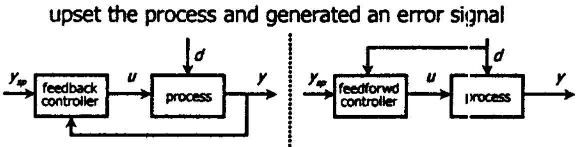
☹ The disturbances to be rejected must be *within* the inner loop

☹ The inner loop must respond *much more quickly* than the outer loop

☹ *Two* controllers must be tuned

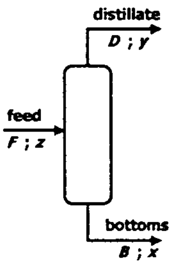
Feedforward control

- Basic idea : measure a disturbance variable *before* it enters the process, and immediately take the corrective action that avoids the process to be upset
- In contrast : a feedback controller does not take a corrective action until *after* the disturbance has upset the process and generated an error signal



feedback control *feedforward control*

Example of feedforward control



Control objective

Use flow D to control the distillate composition y in spite of disturbances in F and z. Measurements of y and x are not available

Steady state mass balances:

$$\begin{cases} F = D + B \\ Fz = Dy + Bx \end{cases} \Rightarrow D = F\frac{z-x}{y-x}$$

If the distillate and bottoms compositions are not available:

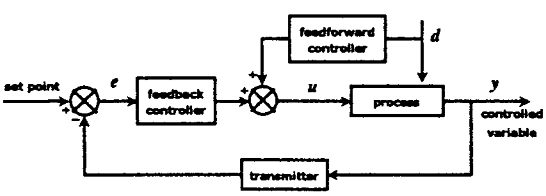
$$D = F\frac{z - x_{sp}}{y_{sp} - x_{sp}}$$: required control law based on pure feedforward action

Disadvantages of feedfwd control

- The disturbance *must* be measured on-line
- *At least* a crude model of the process is needed (it is necessary to know how d affects y)
- If the process model is not perfect, off-set will always result, because the controlled variable is not measured
- The controller may be derived *theoretically*, but it may not be realizable in practice

Feedfwd control with feedbck trim

- A feedback trim ca be used to compensate for modeling errors and unmeasured disturbances (feedback control does not need a process model and can remove off-set)



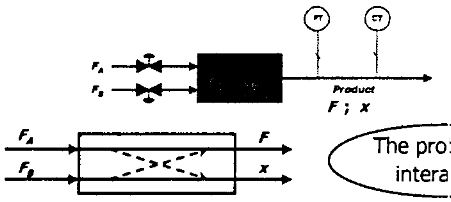
Multivariable systems

- Thus far, Single-Input Single-Output (SISO) systems have been considered
- Most processes are characterized by Multiple Inputs and Multiple Outputs (MIMO)

The <u>input/output pairing</u> problem arises

Which input variable should be used in controlling which output variable?

A 2×2 MIMO system

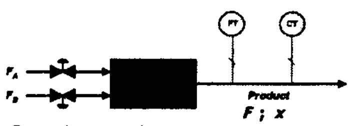


The problem of interaction

- Process interactions may induce undesirable interactions between control loops
- When control loop 1 adjusts u_1 to keep y_1 at its setpoint, it upsets the output y_2
- Control loop 2 reacts by manipulating u_2, thus perturbing y_1 and causing control loop 1 to react

A 2×2 MIMO system (cont'd)

- Because of loop coupling, the control loops may "fight" against each other
- The "best" pairing is the one that keeps loop interaction to a minimum



$$F = F_A + F_B$$

$$x = \frac{F_A}{F_A + F_B}$$

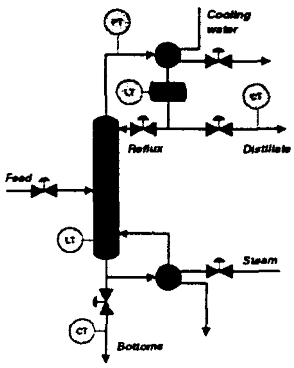
Case 1: $x_{sp} \approx 1$

It follows that $F_A >> F_B \Rightarrow F_A \leftrightarrow F$ ***and*** $F_B \leftrightarrow x$

Case 2: $x_{sp} \approx 0$

It follows that $F_B >> F_A \Rightarrow F_B \leftrightarrow F$ ***and*** $F_A \leftrightarrow x$

A more challenging MIMO system



- Outputs to be controlled:
  - distillate composition
  - bottoms composition
  - top level
  - bottom level
  - column pressure
- Available inputs:
  - reflux rate
  - distillate rate
  - bottoms rate
  - steam rate
  - cooling water rate
  - feed rate

Decentralized control

- Applying single-loop PID controllers to a MIMO process is known as *decentralized control*
- Because of coupling, the tuning of each loop cannot be the same it would be in the absence of the other loops
- In practice, loop "detuning" must be applied

Tuning decentralized controllers

1. With the other loops on manual mode, tune each loop independently until satisfactory performance of the loop is obtained
2. Restore all the controllers to joint operation under automatic control, and readjust the tuning parameters until the *overall* closed-loop performance is satisfactory in *all* loops

- As a start, a single detuning factor F_T may be employed for all loops:

$$K_{C,i}^{MIMO} = K_{C,i}^{SISO} / F_T$$
$$\tau_{I,i}^{MIMO} = \tau_{I,i}^{SISO} \times F_T$$

(for the *i*-th control loop)

Summary of Part II

- SISO systems: conventional controllers
  - the rationale behind P, PI and PID controllers
  - understanding the effect of K_C, τ_I, τ_D
  - controller tuning
- SISO systems: advanced controllers
  - cascade control and feedforward control
- MIMO systems: loop paring and interactions
  - controller tuning

Control Station™

- It is a software for process control, analysis, tuning and **training**
- Developed by Prof. Doug Cooper at the Chem. Eng. Dept. (Univ. of Connecticut, Storrs, CT, U.S.A.)
- Information on the software at the following Internet site:

`http://www.engr.uconn.edu/control/`

Useful references

- Seborg, D. E., T. F. Edgar and D. A. Mellichamp (1989). *Process Dynamics and Control*, John Wiley & Sons, New York (U.S.A.)
- Ogunnaike, B. A. and W. H. Ray (1994). *Process Dynamics, Modeling and Control*, Oxford University Press, New York (U.S.A.)

**For further information,
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Batch distillation

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Italy

ICS-UNIDO Training Course on
Sustainable Industrial Development : Process Simulation and Optimization Techniques
(Rabat, Morocco, 18-22 September, 2000)

Agenda

- Batch processes & batch distillation
- Differential ("simple") distillation
- Modeling of batch rectifiers
  - ⇨ short-cut models
  - ⇨ approximate models
  - ⇨ rigorous models
- Operation of batch rectifiers
  - ⇨ constant reflux ratio
  - ⇨ constant distillate composition
  - ⇨ total reflux
- Slop cut handling
- Alternative configurations

Batch processes

- Batch processing is advantageous
  - for the production of specialty chemicals with high added value
  - when the production cycle is organized in seasonal campaigns
  - when it is required to keep the process inventories low
- The key feature of a batch process is *flexibility*
  - products can be "tailored" to the customer's demand
  - the fast-changing market demand can be accommodated easily
- This is achieved through an inherently *dynamic* operation of the process equipment

Batch distillation

☺ Advantages

- a mixture of *N* components can be separated into *N* products within a single piece of equipment ⇒ *low capital costs*
- a wide variety of feeds can be separated in the same column ⇒ *high flexibility*

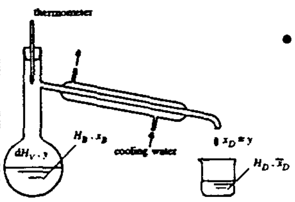
☹ Drawbacks

- consumes more energy than continuous distillation ⇒ *high operating costs*
- unsteady operation ⇒ *hard to understand* for the plant personnel
- large number of degrees of freedom for process optimization ⇒ *hard to understand* for the plant management

Use of batch distillation

- To separate reactants from process inventories (raw materials)
- To separate valuable products from reaction mixtures
- For recovering components that are used in one of the processing steps (e.g., solvents)
- To remove undesired components from an effluent stream
- ...

"Simple" (differential) distillation



- Material balances on a "small" time interval dt:

$$\begin{cases} \mathrm{d}H_V = -\mathrm{d}H_B \\ y\,\mathrm{d}H_V = -\mathrm{d}(H_B x_B) \end{cases}$$

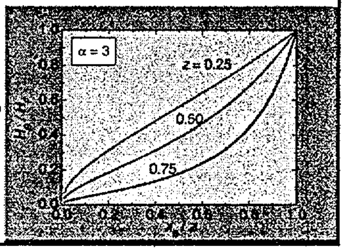
Integrating: $$\ln\frac{H_B}{H_F} = \int_{x_F}^{x_B} \frac{\mathrm{d}x_B}{y - x_B}$$ ***Rayleigh equation***

Limitations of simple distillation

- The following overall balances hold true:

$$\begin{cases} H_F = H_B + H_D \\ H_F z = H_B x_B + H_D \bar{x}_D \end{cases}$$ from which x_D can be calculated

The heavy component cannot be obtained simultaneously pure and *in a large amount*

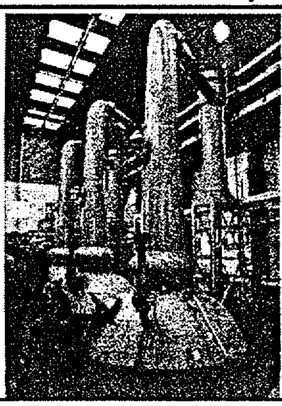


Limitations of simple distillation

- The fractionation obtained in a single batch is not very high
- The fractions obtained usually need to be re-distilled in order to achieve the desired purity

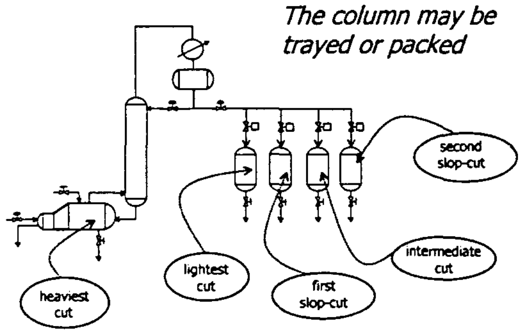
☹ Low product recovery
☹ Large energy consumption

A real-world example



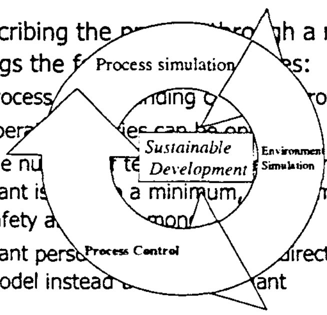
Batch rectifier

The column may be trayed or packed



Modeling and simulation: Why?

- Describing the p... thro...gh a model brings the f... ...s:
  - process ... ...nding ... ...oved
  - oper... ...ies can be op...
  - the nu... ...f te... ...med on the plant i... ...a minimum, ...mproves safety a... ...mon...
  - plant pers... ...irectly on the model instead ... ...ant



Simulation approaches

- Simulation of batch distillation columns can be carried out according to three main classes of models
  - ① Short-cut models
  - ② Approximate models
  - ③ Rigorous models
- Shifting from short-cut modeling to rigorous modeling increases:
  - ⇨ the descriptive capability (ability to represent the "physical" reality)
  - ⇨ the complexity (calculation time)

① Short-cut simulation

☞ It is assumed that the liquid holdup in the column is negligible with respect to the holdup in the reboiler

⇩

1 The dynamic behavior is approximated by a series of steady state operations

2 At every time instant, the simulation is carried out with the same models used for column <u>design</u> (no differential equations need to be solved)

- *binary systems:* McCabe-Thiele
- *multicomp. systems:* Fenske-Underwood-Gilliland

Short-cut simulation (cont'd)

- *Advantages:*
  - fast calculations
  - for binary operations (McCabe-Thiele diagrams), it is possible to "see" how the operation is progressing
- *Pitfalls:*
  - results are not very accurate
  - limited to constant-relative-volatility mixtures
- *Use:*
  - to guide the choice of case studies for more accurate simulations
  - <u>preliminary</u> studies of process design and optimization

② Approximate simulation

☞ Liquid holdup in the column and reflux drum explicitly accounted for

- Further hypotheses:
  - *constant liquid holdup*
  - *negligible vapor holdup*
  - *no heat balances*

  } ⇨ *constant molar rates*

  - ideal trays (or Murphree stage efficiency)
  - perfect mixing of liquids
  - boiling feed
  - total condensation with reflux at the boiling point
  - constant pressure profile

Building an approximate model

1 Choose the most appropriate model for the calculation of vapor-liquid equilibria

2 Locate the regions where liquid matter can accumulate

3 Write down the dynamic material balances

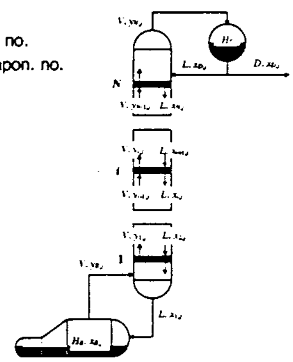
in the absence of chemical reaction

Inlet – Outlet = Accumulation

4 Include the equilibrium relationships and the stoichiometric equations (constraints)

Where does matter accumulate?

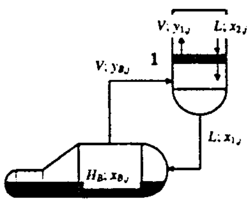
i = tray no.
j = compon. no.



- The accumulation points are located:
  - *in the reboiler*
  - *on the trays*
  - *in the reflux drum*

Material balances in the reboiler

Accumulation = Inlet – Outlet



- total holdup (H_B) : $\frac{dH_B}{dt} = L - V$
- j-th component holdup $(H_B x_{Bj})$:

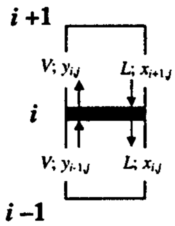
$$\frac{d(H_B x_{B,j})}{dt} = Lx_{1,j} - Vy_{B,j}$$

$$j = 1, 2, \ldots, Nc-1$$

$$x_{i,Nc} = 1 - \sum_{k=1}^{Nc-1} x_{i,k}$$

Material balances on the *i*-th tray

Accumulation = Inlet – Outlet



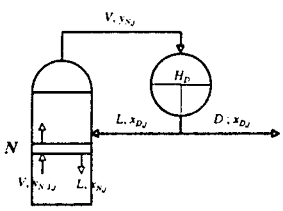
- *total holdup* (H_i)
  - constant ($\Rightarrow L_{i+1} = L_i = L$)
- j-th component holdup ($H_i x_{i,j}$)

$$\frac{\mathrm{d}(H_i x_{i,j})}{\mathrm{d}t} = Lx_{i+1,j} + Vy_{i-1,j} - Lx_{i,j} - Vy_{i,j}$$

$$j = 1, 2, \ldots, Nc-1 \quad ; \quad x_{i,Nc} = 1 - \sum_{k=1}^{Nc-1} x_{i,k}$$

Material balances in the reflux drum

Accumulation = Inlet – Outlet



- *total holdup* (H_D):
  - constant ($\Rightarrow V = L + D$) (perfect level control)
- j-th component holdup:

$$\frac{\mathrm{d}(H_D x_{D,j})}{\mathrm{d}t} = V\left(y_{N,j} - x_{D,j}\right)$$

$$j = 1, 2, \ldots, Nc-1 \quad ; \quad x_{i,Nc} = 1 - \sum_{k=1}^{Nc-1} x_{i,k}$$

Equilibrium and phase constraints

- Thermodynamic equilibrium relationships:

$$y_{m,j} = K_{m,j} x_{m,j} \quad ; \quad m = B, 1, 2, \ldots, N \quad j = 1, 2, \ldots, Nc-1$$

$$K_{m,j} = f(P_m, T_m, x_{m,j}, y_{m,j})$$

K is the equilibrium ratio (e.g., calculated by: NRTL, UNIFAC, EoS, ...)

- Phase constraint equations:

$$x_{i,Nc} = 1 - \sum_{j=1}^{Nc-1} x_{i,j} \; ; \; y_{i,Nc} = 1 - \sum_{j=1}^{Nc-1} y_{i,j} \quad i = B, 1, 2, \ldots, N, D$$

Numerical issues

- It is required to solve a system of differential (dynamic balances) and algebraic equations (equilibrium relationships)
- The column holdups may be significantly different in magnitude (reboiler holdup >> tray holdup)
- Component volatilities may be spread out in a wide range

⇩

- The system of equations is stiff
  - short integration steps
  - implicit integrating schemes
  - calculation times possibly large

Conclusions on approximate models

- *Advantages:*
  - they describe the dynamic behavior with sufficient accuracy
  - no restrictions on the thermodynamic model
- *Pitfalls:*
  - calculation times are larger than with short-cut models
- *Use:*
  - analysis of process feasibility and optimization
  - qualitative studies on the control of the operation

③ Rigorous simulation

- Used when it is required to accurately describe the dynamics of an *existing column*
- They are employed for detailed studies on:
  - process feasibility and optimization
  - automatic control
  - evaluation of energy requirements and fluid dynamic limits of the available column

☞ Almost all of the simplifying assumptions of approximate models are removed

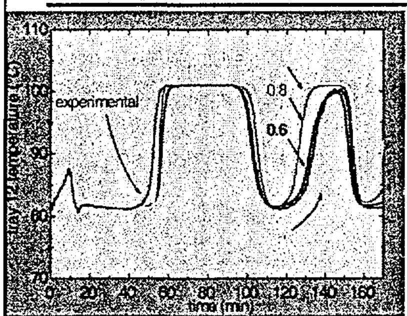
Rigorous simulation (cont'd)

- Equations:
  - enthalpy balances are taken into account
  - tray hydraulics is accounted for
  - the pressure profile is calculated (not assigned)
  - heat losses are taken into account
  - the external flow rates are expressed on mass or volume basis
- Pitfalls:
  - the calculation time increases considerably
  - the model parameters must be accurately determined (e.g., Murphree tray efficiency)

Parameter determination

1. Perform a test run in the plant and register the time profile of a measurable variable (e.g., one or more tray temperatures)
2. Run the model several times with different values of the parameter; save the simulated temperature profiles
3. Choose the "best" value of the parameter
4. Use this value, and check if the model can reproduce the time profile of *another* variable, whose value is measured on the plant

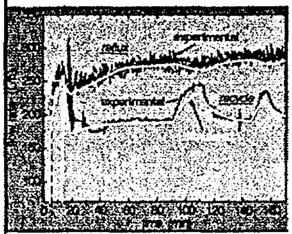
Example: evaluating tray efficiency



- Parameter to be determined: *Murphree tray efficiency*
- Variable recorded in the plant: *temperature on tray #12*

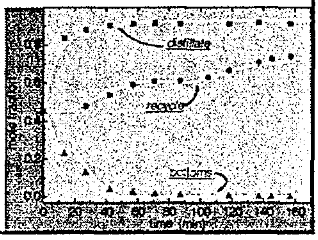
The "best" value is : $E_M = 0.6$

Reproducing other profiles



Flow rate profiles

Composition profiles



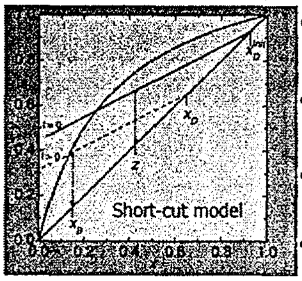
Operation of batch columns

- The most frequent operating procedures are
  - ⇨operation at constant reflux ratio r (with x_D varying during the operation)
  - ⇨operation at constant distillate composition x_D (with r varying during the operation)
  - ⇨operation at total reflux
- Steps shared by all the operating procedures
  - ⇨startup
  - ⇨product removal (main cut) } repeated cyclically
  - ⇨off-cut removal (slop cut) }

The startup phase

- Column and holding tanks cleaned from residuals of previous operations
- Water sent to condenser and steam to reboiler
- Vapor, released from the reboiler, rises through the column, is condensed at the top and accumulated in the reflux drum
- When the top level is OK, reflux returned into the column, and *total reflux* operation started
- Trays filled with liquid and fractionation begins
- Operation progresses until steady state is reached
- The other two steps follow (product and slop removal)

Operation at constant reflux ratio



- Reflux ratio
  $r = L/D$: <u>constant</u>
- Slope of operating line
  $m = r/(r+1)$: <u>constant</u>
- The line shifts down during the operation
- Product specifications:
  $x_B = x_B^{spec}$, $x_D = x_D^{spec}$

It is required to determine which is the reflux ratio and what is the energy consumption

Operation at constant *r* : short-cut

- From the overall balance
$$\begin{cases} H_F = H_B^{fin} + H_D^{fin} \\ H_F z = H_B^{fin} x_B^{spec} + H_D^{fin} x_D^{spec} \end{cases}$$

  and the Rayleigh equation
$$\ln \frac{H_B^{fin}}{H_F} = \int_z^{x_B^{spec}} \frac{d x_B}{x_D - x_B}$$

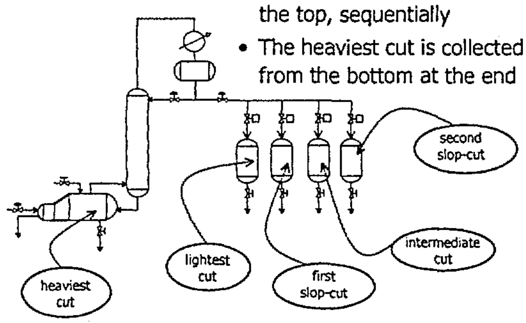
  it is possible to determine the reflux ratio r.

- Heat consumption: $d Q_r = \lambda V \, dt = \lambda (r+1) \, dD$

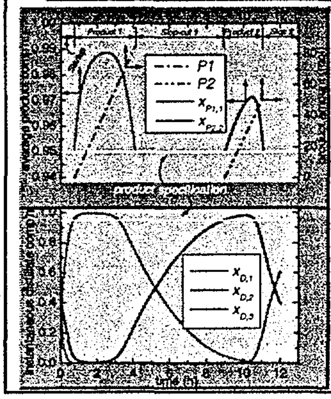
$\Rightarrow \quad Q_r = \lambda (r+1) H_D^{fin}$ $\qquad \lambda$ = latent molar heat of the vapor phase

Collecting the products (r = const)

- Products are collected from the top, sequentially
- The heaviest cut is collected from the bottom at the end



Composition profiles (r = const)



- The concentration "front" progressively moves from the bottom to the top
- First, a product that more than meet the specifications is obtained; then, the dilution increases
- In this case (system with 3 components) 2 slop-cuts are obtained

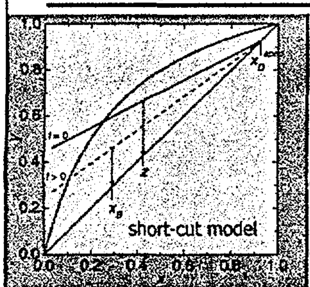
Final remarks (r = const)

☺ Operation at constant reflux ratio is easy to accomplish

- The operation is characterized by a moving composition front
- Switching vessels need to be provided
- A policy for recycling slop-cuts is necessary

☹ It is necessary to provide an on-line measurement or estimation of the average product composition (gaschromatograph; refractive index; density; "virtual" sensors)

Operation at constant x_D



- Reflux ratio:
  $r = L/D$: <u>increases</u>
- Slope of the operating line
  $m = r/(r+1)$: <u>varies (increases) with time</u>
- The line rotates around the distillate specification point
- Product specifications:
  $x_B = x_B^{spec}$, $x_D = x_D^{spec}$

It is required to determine what are the reflux ratios and what is the energy consumption

Operation at constant x_D : short-cut

- Heat consumption:

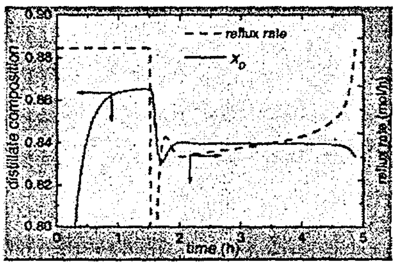
$$dQ_r = \lambda(\dot{V}\,dt) = \lambda\,dV = \lambda(r+1)\,dD$$

$$\Rightarrow \quad Q_r = \lambda \int_0^{H_D^{fin}} (r+1)\,dH_D \quad \Rightarrow$$

it is necessary to correlate the reflux ratio to the amount of product collected

1. For a given r, x_B is found from the McCabe-Thiele diagram
2. From the material balances: $H_D = H_F \dfrac{z - x_B}{x_D^{spec} - x_B}$
3. Then, r is correlated to H_D and Q_r can be calculated

Composition profile (x_D = const)



Accurate control of composition is hard, especially at the beginning and at the end of the operation

Final remarks (x_D = const)

☹ Operation at constant distillate composition is harder than operation at constant reflux ratio

- the reflux rate must be adjusted at every time instant
- conventional controllers may not be adequate

☹ It is necessary to provide an on-line measurement or estimation of the instantaneous product composition (gaschromatograph; refractive index; density; "virtual" sensor)

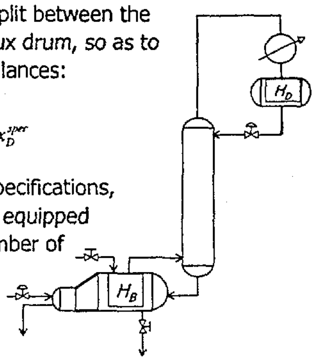
Operation at total reflux

- The feed charge is split between the reboiler and the reflux drum, so as to fulfill the material balances:

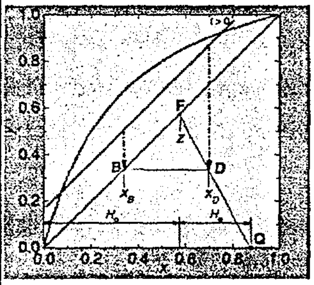
$$\begin{cases} H_F = H_B + H_D \\ H_F z = H_B x_B^{spec} + H_D x_D^{spec} \end{cases}$$

- Given the product specifications, the column must be equipped with a minimum number of trays:

$$N_{min} = \frac{1}{\ln\alpha} \ln \frac{x_D^{spec}(1-x_B^{spec})}{x_B^{spec}(1-x_D^{spec})}$$



Operation at total reflux: short-cut



- Material balances give:

$$\frac{x_D - z}{z - x_B} = \frac{H_B}{H_D}$$, valid at every time instant

- Point Q on the x-axis with abscissa a_Q is defined:

$$\frac{a_Q - z}{z} = \frac{H_B}{H_D}$$

- At any instant, line BD is parallel to the x-axis

Operation at total reflux: short-cut

- Dynamic composition balance:

$$Vy - Lx = H_D \frac{\mathrm{d}x_D}{\mathrm{d}t} \Rightarrow V(y-x) = H_D \frac{\mathrm{d}x_D}{\mathrm{d}t}$$

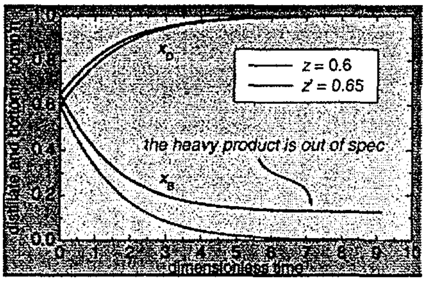
- Heat consumption:

$$\mathrm{d}Q_r = \lambda(\dot{V}\,\mathrm{d}t) = \lambda \frac{H_D}{y-x} \mathrm{d}x_D$$

$$\Rightarrow Q_r = \lambda H_D \int_0^{x_D^{spec}} \frac{\mathrm{d}x_D}{y-x} \Rightarrow$$

At any time, it is necessary to evaluate the distance $(y-x)$ between the operating line and the diagonal

Composition profiles (total reflux)

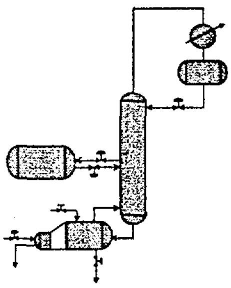


Nominal feed composition:

$z = 0.6$

If the feed composition is not known accurately, one of the products may go out of specification

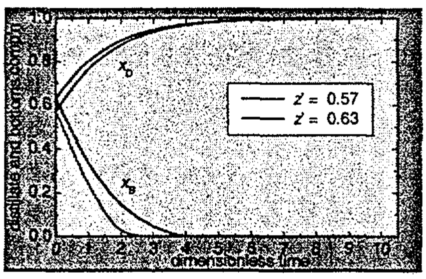
Middle vessel column



The batch column is equipped with two sections (rectifying and stripping), as happens for a continuous column

☞ *The middle vessel "absorbs" the uncertainties on the feed composition*

Composition profiles (middle vessel)



Nominal feed composition:

$z = 0.6$

Both products can be obtained at the desired purity, regardless of the uncertainty on the feed composition

Final remarks (total reflux)

☺ It is the easiest way to operate a batch column: a simple level controller is sufficient

☺ The column always operate at its maximum fractionating capacity

☺ Particularly suited when high-purity products must be obtained

☺ The operation can be interrupted at any time without loosing the separation already achieved

☺ For multicomponent mixtures, it can be repeated sequentially

☺ Introducing a middle vessel ensures that both products are obtained on specification

Slop-cut handling

- From a batch of *N* components, up to *N*−1 slop cuts are obtained, which need to be reprocessed in subsequent batches
- Most frequently employed procedure: *total slop recycle*
  - all the slop cuts of the previous batch are combined with fresh feed in the initial charge to the current batch
  - a pseudo steady state is obtained after some cycles

☺ Minimum tankage need to be provided

☹ The separation already achieved within each slop cut is lost

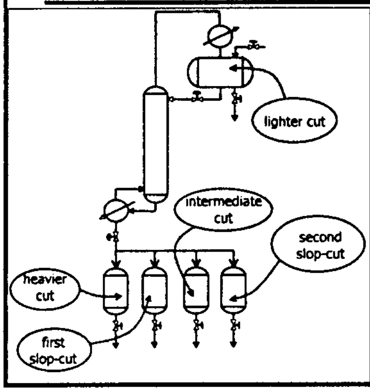
Slop-cut handling (cont'd)

- An alternative procedure: *Multicomponent-binary separation*:
  - only slop cuts with similar compositions are mixed together
  - the mixtures so obtained are distilled separately when a sufficient amount has been collected

☹ More tankage needs to be provided

☺ The separation already achieved within each slop cut is not lost

Alternative configurations

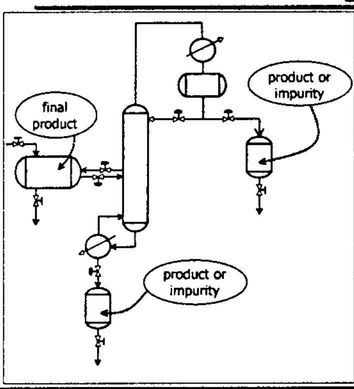


Batch stripper

- The feed is charged to the reflux drum
- Products and slops are removed from the bottom
- The reboiler is smaller

➢ Useful when the amount of light component is low

Alternative configurations



Middle-vessel column

- The feed is charged to the middle vessel
- Products and slops are removed *continuously*
- The reboiler is small

➢ Useful for ternary mixtures and for azeotropic mixtures

Useful references

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- Muhrer, C. A. and W. L. Luyben (1992). Batch Distillation. In: *Practical Distillation Control* (W. L. Luyben, Ed.). Van Nostrand Reinhold, New York (U.S.A.).
- Seader, J. D. and E. J. Henley (1998). *Separation Process Principles*, John Wiley & Sons, New York (U.S.A.)
- Barolo, M. (2000). Batch Distillation. In: *Encyclopedia of Separation Science* (I. D. Wilson et al., Eds.), Academic Press, London (U.K.)

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MODELING, SIMULATION AND OPTIMIZATION OF NON CONVENTIONAL INDUSTRIAL PLANTS

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Training Course ICS - LASPI

Rabat, 18 - 22 September 2000

objectives

- On-line computer sugar process monitoring optimization
- Use of Chemical Engineering approach for sugar process analysis and synthesis (System engineering approach)
- Implementation of research results at industrial scale

Simulation of a Non Conventional Process (1)

- **A non conventional process is that which can not be simulated by commercial process simulator without adding user model(s).**
- **Two types of user models:**
  - Thermodynamic models;
  - Equipment models

Simulation of a Non Conventional Process (2)

- **Development of user models needs R&D work type.**
- **Very often in developing countries, no R&D work is done by production companies, and then process simulation is not used.**

Example: R&D for sugar industry

METHODOLOGY(1)

- **Use of pseudocomponent concept to better characterize industrial sugar juices**
- **Use of thermodynamic models to estimate the properties of sugar solutions**
- **Development of tendency models for sugar juice purification processes**

METHODOLOGY(2)

- Modeling steady and transient regimes of unit operations encountered in sugar factories using a phenomenological approach
- Use of the preceding models to analyze and optimize unit operations separately and globally within sugar factories

METHODOLOGY(3)

- All of these steps were realized in collaboration with national sugar factories, mainly SUNABEL and SURAC
- Exploit the results obtained in the preceding steps to optimize the whole factory using on-line computer

RESULTS

1. Adaptation of Peng-Robinson Equation of State (PR-EOS) for boiling temperature and enthalpy estimation of industrial sugar juices, characterized by pseudocomponents

SUGAR JUICES COMPOSITION

Pseudocomponents used:

Sugar
Nitrogenous compounds
Non-Nitrogenous comp.
Ash

SUCROSE SOLUBILITY

2. Adaptation of UNIQUAC-PITZER-DEBYE-HÜCKEL (UQPDH) model for estimation of sucrose solubility in industrial sugar solutions

CLARIFICATION OF CANE JUICE (1)

3. A general reaction scheme is proposed, in satisfactory agreement with the experimental results, for calcium phosphate precipitation in clarification of cane juice

CANE JUICE CLARIFICATION (2)

Use of the calcium phosphate precipitation scheme to better understand the pre-liming behavior of cane juice

LIME KILN

4. Kinetics modeling of coke combustion and limestone decomposition using thermogravimetry analysis

BEET JUICE PURIFICATION

- Development of a tendency model for the complex reactions involved in pre-liming and liming of beet sugar juice
- Use of this model to optimization study of pre-liming station of a national factory

UNIT OPERATIONS MODELLING

- **Modeling of evaporation stations using Peng-Robinson Equation of State (PR-EOS)**
- **Modeling of crystallizes using population balance**
- **Modeling of RT type diffusers, rotary drier, limer , pre-limer and lime kiln**

SCAPE

- **SCAPE (Software for Computer Process Engineering) is a process simulator of sequential-modular type conceived in our laboratory to satisfy engineering needs of food and mineral industries. The actual developments are oriented mainly to sugar and phosphate industries**

INDUSTRIAL APPLICATIONS (1)

- Sugar losses minimization of RT2 type diffuser
- Study of potential of pulp rotary drier capacity increase
- boiler diagnostic of sugar factories using data reconciliation technique
- heat integration of sugar factories by Pinch Technology

INDUSTRIAL APPLICATIONS (2)

- Batch crystallizers optimization
- Design of a control strategy for evaporation station using its dynamic mathematical model based on PR-EOS
- Use of the same methodology for design control strategies for some other stations