CAPE and Thermodynamic Property Packages: Air Liquide approach

Philippe Arpentinier
CENTRE DE RECHERCHE CLAUDE-DELORME

CO-LaN – Interoperability Showcases – Cannes, March 9, 2006

Content

CAPE and Thermodynamic Property Packages:
Air Liquide approach

- History of thermodynamic modelling and process simulation tools at Air Liquide
- Evolution of Air Liquide business since the 90s
- Current difficulties
- Conclusions and future steps

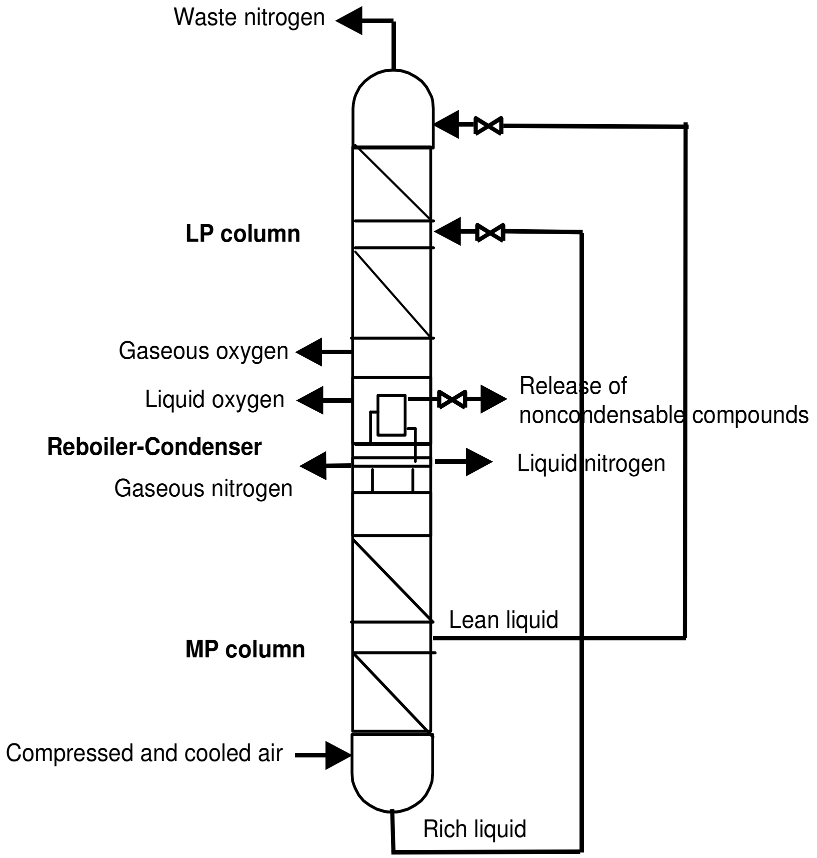
1960 – 1988: In-house development

- Thermodynamic properties of pure substances
  - 1976: Publication of Gas Encyclopaedia (Elsevier - ISBN 0-444-41492-4 -2nd reprint 1992, 3rd reprint 2002)
    - *138 monographs of gases (physical, thermodynamic and transport properties – flammability - biological properties - precautions in handling and storage - leak detection and analysis – material compatibility)*
    - N_2, O_2, Ar, CO_2, H_2, CH_4, C_2H_4, C_2H_2, C_3H_8, NH_3
      - Detailed P-T tables (phases equilibrium, vapor pressure, density, compressibility factor, enthalpy, entropy, heat capacity, viscosity, thermal conductivity)
      - Two types of equation used to generate data for a given substance: empirical correlation dedicated to each property or PVT equation of state (virial development) calibrated on measured values from literature
      - High accuracy (generally lower than 0.1%) due to large number of experimental points on which calibration is done
- Thermodynamic properties of mixtures
  - 1970 -1972: Development of thermodynamic equation of state dedicated to air cryogenic distillation (N_2, O_2, Ar)
    - *Empirical equation of Benedict-Webb-Rubin [1], mixing rules of Starling [2]*
    - *Regression of pure substance parameters and binary interaction coefficients on in-house experimental values*
  - 1972 -1975: Development of thermodynamic equation of state dedicated to natural gas liquefaction and CO separation and purification by methane washing
    - *Modification of Redlich-Kwong equation of state [3] to reproduce more accurately liquid phase properties along the saturation curve*
    - *Regression of binary interaction coefficients on experimental values from literature*
    - *Maximum number of constituents: 20 among 39*

[1] Benedict M, Webb GB, Rubin LC, *J. Chem. Phys.*, 1949, 8, 334-344.
[2] Starling KE, *Hydro. Process.*, 1971, 101-104.
[3] Redlich O, Kwong JNS (1949) Chem. Rev., 44, 233-244.

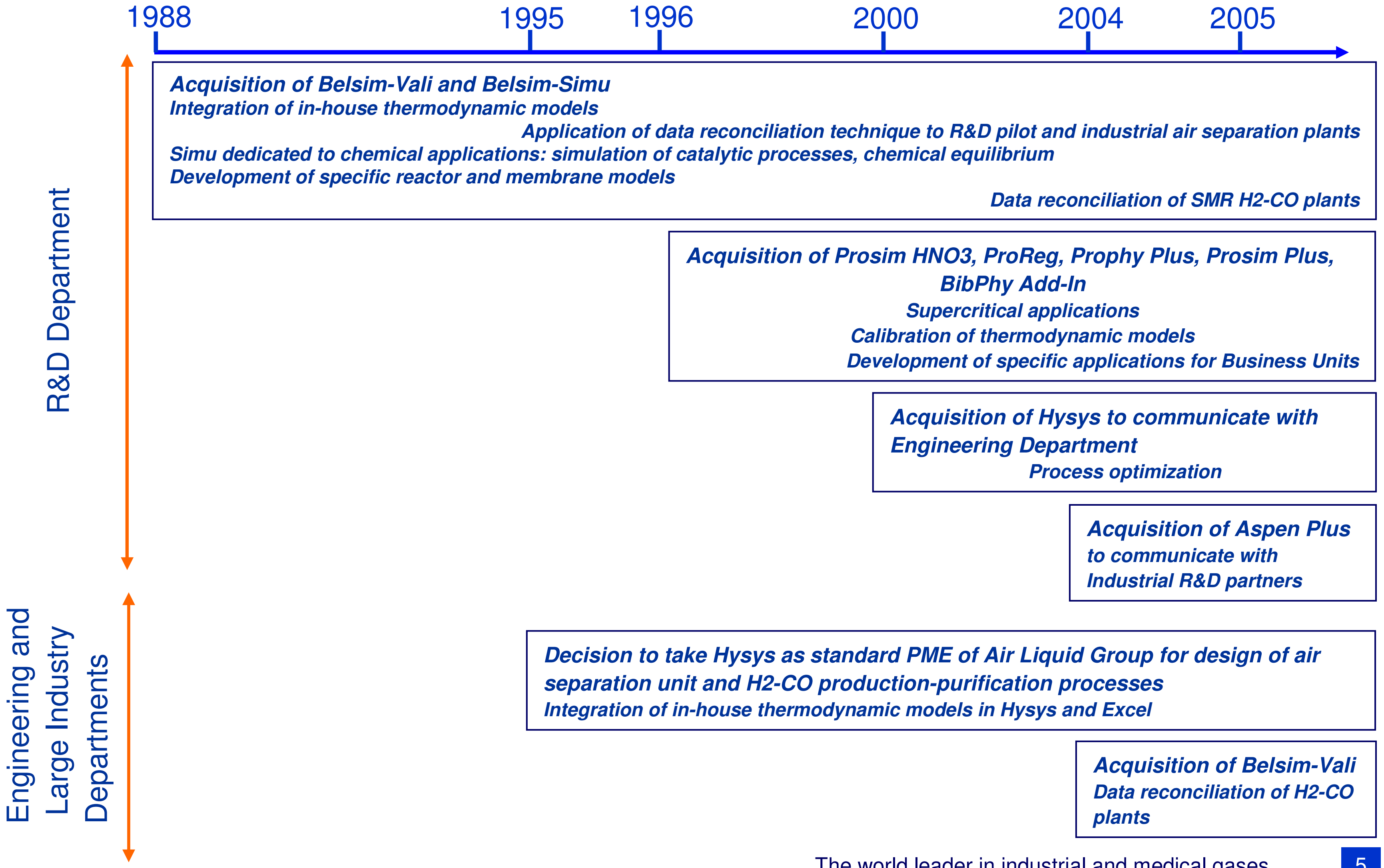
1960 – 1988: In-house development

- Process simulation tools
  - Development of model dedicated to the simulation of conventional double column apparatus for air distillation
  - Development of unit operation models of equipments associated to air distillation columns
    - *Brazed aluminum plate–and–fin heat exchanger*
    - *Compressor, pump, expander*
  - Development of absorption column and stripper models for CO separation application



History of thermodynamic modelling and process simulation tools at Air Liquide

1988 – 2004: Acquisition and use of commercial Process Modelling Environment (PME)



Acquisition of Belsim-Vali and Belsim-Simu
Integration of in-house thermodynamic models
Application of data reconciliation technique to R&D pilot and industrial air separation plants
Simu dedicated to chemical applications: simulation of catalytic processes, chemical equilibrium
Development of specific reactor and membrane models
Data reconciliation of SMR H2-CO plants

Acquisition of Prosim HNO3, ProReg, Prophy Plus, Prosim Plus, BibPhy Add-In
Supercritical applications
Calibration of thermodynamic models
Development of specific applications for Business Units

Acquisition of Hysys to communicate with Engineering Department
Process optimization

Acquisition of Aspen Plus
to communicate with Industrial R&D partners

Decision to take Hysys as standard PME of Air Liquid Group for design of air separation unit and H2-CO production-purification processes
Integration of in-house thermodynamic models in Hysys and Excel

Acquisition of Belsim-Vali
Data reconciliation of H2-CO plants

Overview of the current situation

- Cohabitation of four PMEs: Hysys, Belsim, Prosim, Aspen
- Different versions of in-house thermodynamic models
- Specific Process Modelling Components (PMC) compliant with only one PME
- Continuation of in-house development: Matlab®, Excel®, Fortran
  - Development of specific PMCs by R&D and transfer to Engineering Department or Business Unit (Centralized production facilities and Cylinder filling plants)
  - Development trough academic collaboration (PhD, …)

Content

CAPE and Thermodynamic Property Packages: Air Liquide approach

- History of thermodynamic modelling and process simulation tools at Air Liquide
- Evolution of Air Liquide business since the 90s
- Current difficulties
- Conclusions and future steps

Evolution of Air Liquide business since the 90s

Diversification

- ✓ Strong increase of H_2-CO business
  - Modelling, design and operation of H_2-CO production plants by steam reforming of natural gas
    - *Reactors: pre-reformer, reformer, water-gas shift reactor*
    - *Separation units: water condensation from syngas,CO2 removal (amine washing), CO separation (methane washing)*
  - Hydrogen purification by membrane or PSA: dew point of HC-H_2S-H_2 mixtures
- ✓ New projects linked to CO_2 capture, purification and sequestration
  - CO2 separation from oxy-combustion gases or blast furnace by PSA or distillation
- ✓ Cylinders: a more and more accurate demand
  - Deregulation of natural gas distribution
    - *Increase of the demand of natural gas mixture used for analyzer calibration*
    - *Recommendation to supply complete phase envelop of the mixture (dew and bubble curves, critical point location)*
  - Liquid mixture for petrochemical industry
    - *Prediction of liquid phase composition evolution during cylinder blow-off*

Health and Electronics

- ✓ High purity (ppm-ppb) and high accurate mixtures (0.1%)

Historical core business

- ✓ Increase of air separation plant capacity: oxygen production > 4 000 t/d
  - Safety: impurities accumulation in air separation units
    - *Formation of solid CO2 and N2O in liquid oxygen*
    - *HC solubility in liquid oxygen*

➔ A more and more complex and diversified demand for thermodynamics and simulation tools

- ✓ Thermodynamic properties
  - Nature of the substances
  - Nature of the mixture
    - *Water-Liquid-Vapor Equilibrium*
    - *Liquid-Liquid-Vapor Equilibrium*
    - *Solid-Liquid-Vapor Equilibrium*
    - *Electrolyte solutions (acid or basic)*
  - Robustness and accuracy of LV equilibrium resolution algorithm
    - *Location of critical point of mixtures*
    - *Convergence around cricondentherm and cricondenbar points*
- ✓ Process Modelling Components
  - Detailed reactor model for steam methane reforming
    - *Kinetic model: gas-solid reaction, diffusional limitations, carbon formation*
    - *Heat transfer by radiation, convection and conduction*
  - Pressure Swing Adsorption model
    - *Time-dependent and cyclic process*
    - *Kinetic of adsorption-desorption*

Content

CAPE and Thermodynamic Property Packages:
Air Liquide approach

- History of thermodynamic modelling and process simulation tools at Air Liquide
- Evolution of Air Liquide business since the 90s
- Current difficulties
- Conclusions and future steps

Current difficulties

General limitations

- ✓ Precarious communication and model transfer between the different CAPE actors
  - R&D and Advanced Technologies Department
  - Engineering Department
  - Business Units
- ✓ Multifaceted contexts
  - R&D: exploratory and development projects, feasibility study, technical support
  - Engineering projects (design and quotation)
  - Industrial plant operation and control

Multiplicity of PMEs

- ✓ Different results with “same thermodynamic model” from different PMEs
  - Origin of differences
    - *Database of pure substance properties*
    - *Version of the equation of state (alpha function) or activity coefficient model*
    - *Mixing rules*
    - *Resolution algorithms of LV equilibrium*
    - *Reference state of enthalpy calculation*
    - *Model or correlation used for the calculation of liquid molar volume and liquid fugacity in standard state*
- ✓ No interoperability between PMEs
  - Standard CMPs of one PME not compliant with the other PMEs
  - CMPs (reactors, membranes) developed by AL in one PME not compliant with the other PMEs

In-house tools

- ✓ Gas Encyclopaedia: e-version available on Air Liquide web site
  - P-T tables of thermodynamic properties exportable in Excel sheet
  - Temperature and pressure interpolations are required
- ✓ In-house simulation models (Matlab®, Excel®, Fortran)
  - Limitations due to isolated use
    - *No possibility of coupling CMPs coming from PMEs or another model*
    - *Requirement: (re-) programming of pure substance properties and equation of state*
    - *Approximate programming of pure substance properties or use of correlations outside their validity range can lead to propagation of errors*
  - Management of versions
- ✓ Thermodynamic models
  - Method of integration in Excel® and in the PMEs Hysys® and Belsim-Vali®
    - *Fraction coming from the original model*
    - *Fraction already programmed in the PME (pure compound properties, solving method, …)*
    - *Different results in different environments*
  - Not available in all environments (PMEs, Excel®, Matlab®, …)
  - Many developers, many users … lead to many versions…even in the same environment
  - Traceability and justification of modifications (mixing rules, binary interaction coefficient calibration, addition of pure components, pure substance parameters)
    - *Increase the distance from initial objective*
    - *Fuzzy validity range*

➔ Difficulties of perpetuation of in-house knowledge and of integration in commercial tools

Content

CAPE and Thermodynamic Property Packages: Air Liquide approach

- History of thermodynamic modelling and process simulation tools at Air Liquide
- Evolution of Air Liquide business since the 90s
- Current difficulties
- Conclusions and future steps

Main actions to improve the existing situation

- ✓ Adoption of a thermodynamic standard usable at each step of process development
  - Database of pure substances properties
  - Database of thermodynamic models and associated resolution algorithms
- ✓ Development of concept of CO “thermodynamic property package” dedicated to given applications
  - Interoperability of packages: PMEs, Excel®, Matlab®
  - Consistency of results throughout different applications
  - Perpetuation of in-house knowledge: database of packages
    - *Detailed description and validity range*
    - *References of experimental values (literature, in-house)*
  - Improvement of accessible information quality for a relevant later re-use
- ✓ Adaptation of existing simulation models to CO standards and new developments CO compliant
  - Compliant with CO thermodynamic property packages
  - Interoperability: PMEs

Conclusions and future steps

September 2004 – November 2005

- Test of Simulis® Thermodynamics (Prosim SA) in R&D
  - Development of a thermodynamic package dedicated to CO2-CO-N2-H2 mixtures
    - *SRK equation of state*
    - *Alpha function of Boston-Mathias*
    - *Calibration of binary interaction coefficients on measurements from literature*
    - *Validation of results on ternary experimental data*
  - Creation of CO property package
    - *Plug tests in Hysys 2004 with the help of Prosim SA, CO-LaN and Hysys hotline*
    - *November 2005: final validation of the package integrability in Hysys 2004 environment*
    - *Deployment of the package in R&D department*

January 2006: Decisions

- Air Liquide R&D thermodynamic standard: Simulis® Thermodynamics associated to DIPPR® database of pure substances
- Test of Simulis® Thermodynamics by Engineering Department

Future steps

- ✓ Test of Simulis® packages in other environments
    - Belsim-Vali®
    - Matlab®
    - Aspen Plus®
- ✓ Creation of a Simulis® packages database
- ✓ Test of an in-house simulation model adaptation to CO standard
- ✓ Deployment of package development methodology
    - Bibliographic study (measurements, modelling)
    - Choice of a thermodynamic profile
    - Evaluation of calibration requirement, if yes
    - Requirement evaluation of additional experimental values in studied conditions
        - *Question: what is the minimum number of supplementary experimental values to be measured to avoid significant errors*
    - Campaigns of measurements
    - Calibration of the model
    - Creation of the package
    - Integration in the package database

AIR LIQUIDE™

Thank you for your attention