Energy and Green House Gas Mitigation Technologies

Japan Society for the Promotion of Science-Imperial College London-University of Tokyo Symposium on Climate Change

Thursday 28th and Friday 29th September 2006

Imperial College London, South Kensington Campus, London SW7 2AZ

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Novel Solvents for CO_2 Capture & Separation

Energy & Green House Mitigation Technologies
Japan Society for the Promotion of Science
Imperial College, 29 September 2006

George Jackson
Department of Chemical Engineering
Molecular Systems Engineering/Centre for Process Systems Engineering

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Outline

- Molecular Systems Engineering
- Advanced thermodynamic modelling (SAFT)
- Separation and Capture of CO_2 in Natural Gas
  - ✓ Chemical adsorption (amines)
  - ✓ Membranes
  - ✓ Physical solvents (hydrocarbons?)
- Thermodynamics and Fluid Phase Equilibria
  - ✓ Methane, hydrocarbons, and carbon dioxide
  - ✓ Validating the SAFT model
- Process Modelling
  - ✓ Design of separation process
  - ✓ Optimisation of process: maximise gas sales
- Conclusions/Future Challenges
  - ✓ Couple CO_2 separation with enhanced oil recovery (EOR)
  - ✓ Double benefit: EOR and CO_2 sequestration
  - ✓ Examine post combustion CO_2 capture

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Research Team

- Molecular Systems Engineering (MSE)

Emmanuel Keskes

Dr Claire S Adjiman

Dr Amparo Galindo

Prof George Jackson

Sponsor: Schulmberger Cambridge Research

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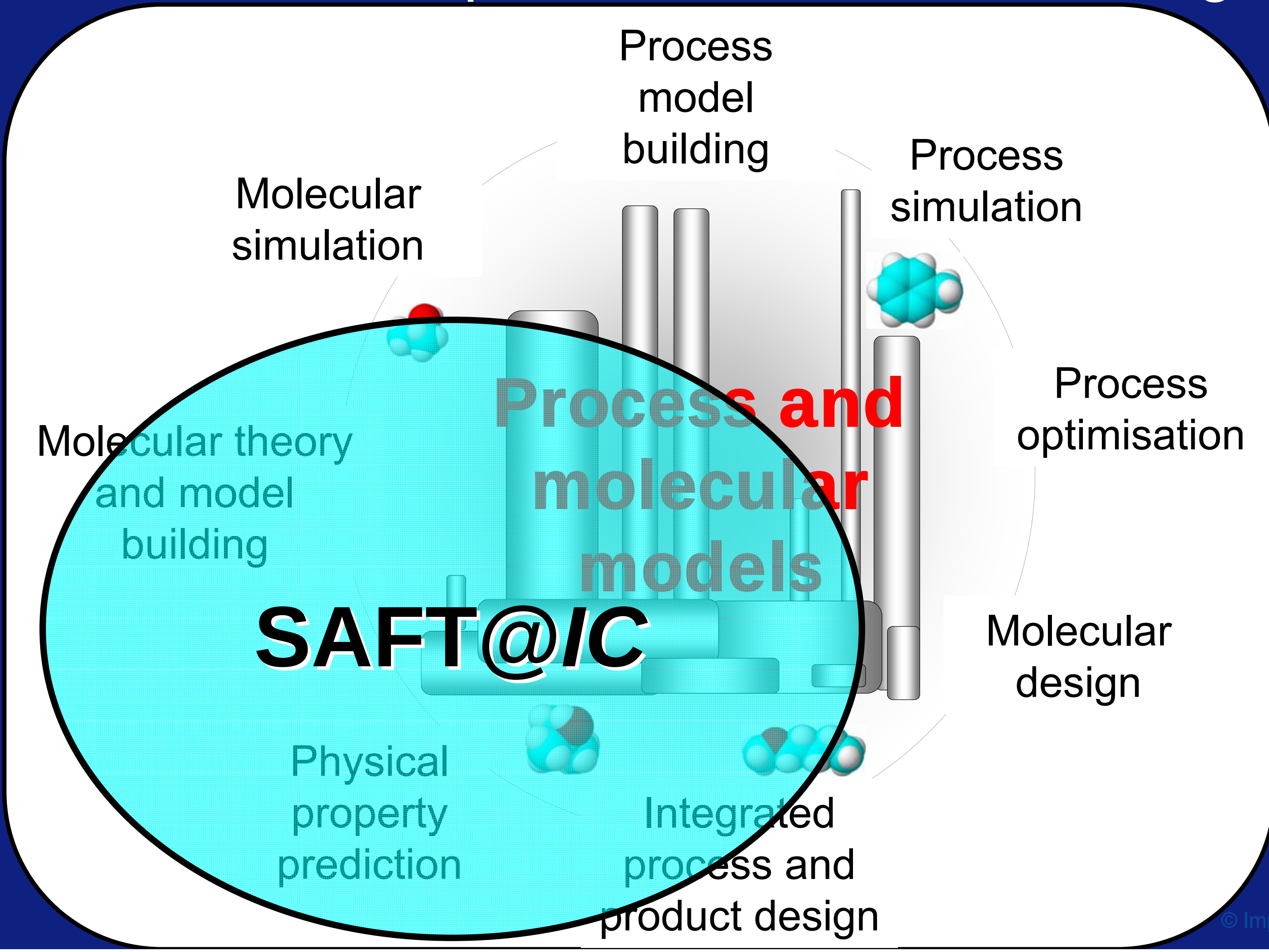
Molecular Systems Engineering

- Model-based process and molecular engineering



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Statistical Associating Fluid Theory (SAFT)

- Original Theory (1989-90)
  Chapman, Gubbins, Jackson, Radosz,
  ***Fluid Phase Eq.*, 52, 31 (1989);**
  ***Ind. Eng. Chem. Res.* 29, 1709 (1990)**

- SAFT-VR variable range potentials (1997)
  Gil-Villegas, Galindo, Whitehead, Mills, Jackson,
  Burgess, *J. Chem. Phys.*, 106, 4168 (1997)

- Numerous other incarnations (PC-SAFT etc.)
  Müller, Gubbins, *Ind. Eng. Chem. Res.* 40, 2193 (2001)
  Economou, *Ind. Eng. Chem. Res.* 41, 953 (2002)

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SAFT-VR

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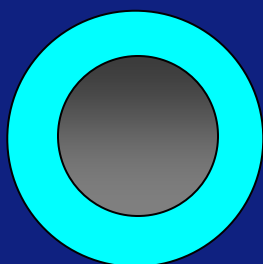
SAFT-VR

- Monomeric segments (repulsion/attraction)



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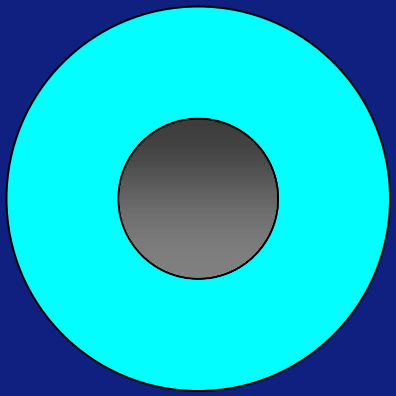
SAFT-VR

- Monomeric segments (repulsion/attraction)



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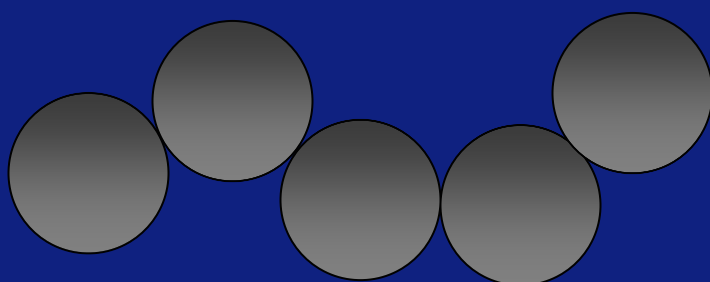
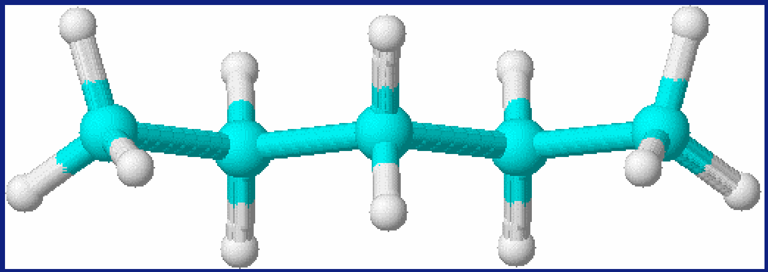
SAFT-VR

- Monomeric segments (repulsion/attraction)

- Nonspherical molecules (chains)





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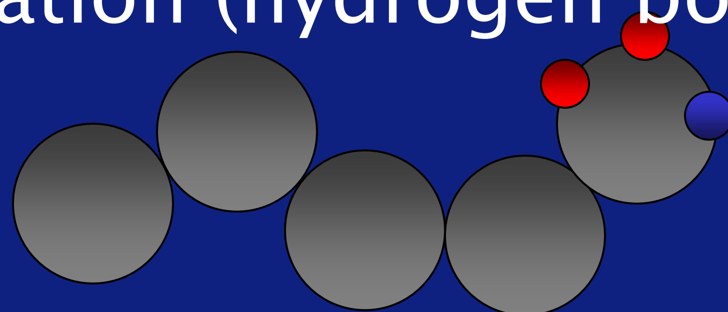
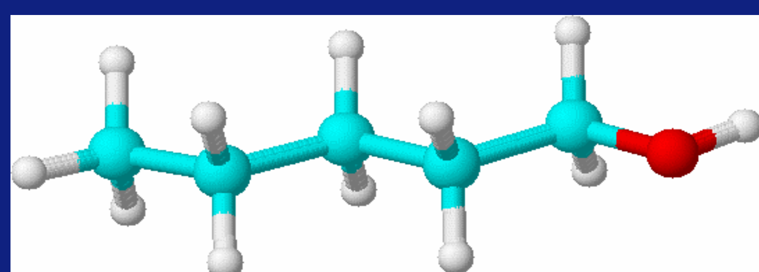
SAFT-VR

- Monomeric segments (repulsion/attraction)
- Nonspherical molecules (chains)
- Association (hydrogen bonding, chem. equil.)





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CO_2 Separation and Capture

- Wellhead natural gas can contain 30-70% CO_2
- Large throughput: 100-1000 MMSCFD
  CO_2 30-700 MMSCFD
- Typical power station: 11 MM tonnes CO_2/year
  CO_2 570 MMSCFD
- How to best separate such large volumes of gas?
- What is best option for sequestering CO_2?

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CO_2 Separation and Capture

Standard technologies

- Amine extraction – chemical association.
  High selectivity >99%, but energy intensive, bulky, and toxic (ecological concerns).
  Not appropriate for large levels of CO_2.
- Membranes (polymers) – physical separation.
  Compact and large throughput, but typically less selective (5-20% CO_2 in product stream).
  Physical/chemical deterioration can occur.

Possible alternative

- Hydrocarbon solvents – physical absorption.
  Cheap, tunable selectivity, less energy intensive.

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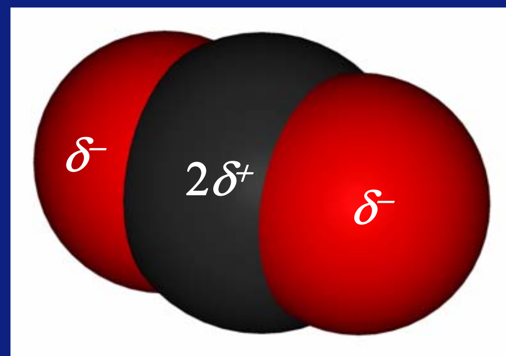
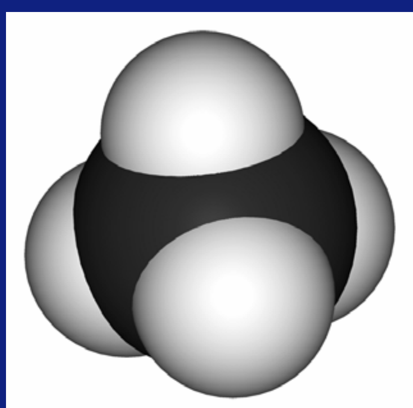
Thermodynamics and Fluid Phase Behaviour

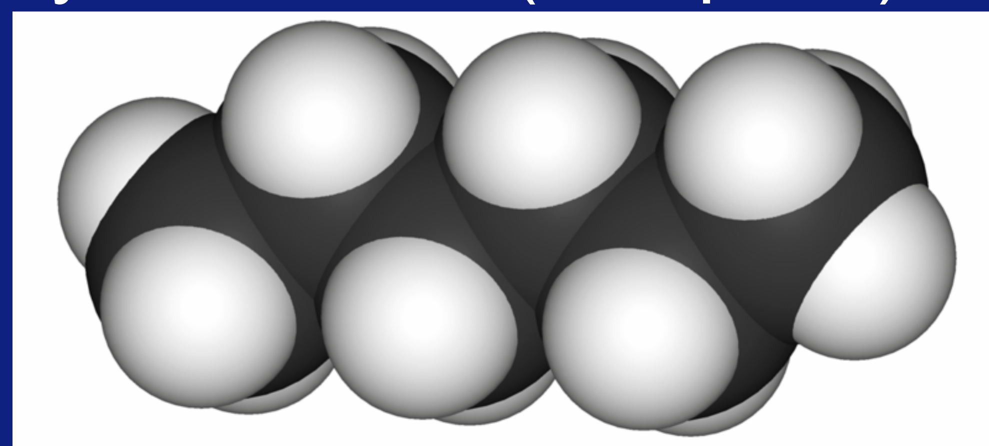
Carbon dioxide CO_2 (quadrupolar)



Methane and higher hydrocarbons (non-polar)



methane



n-hexane

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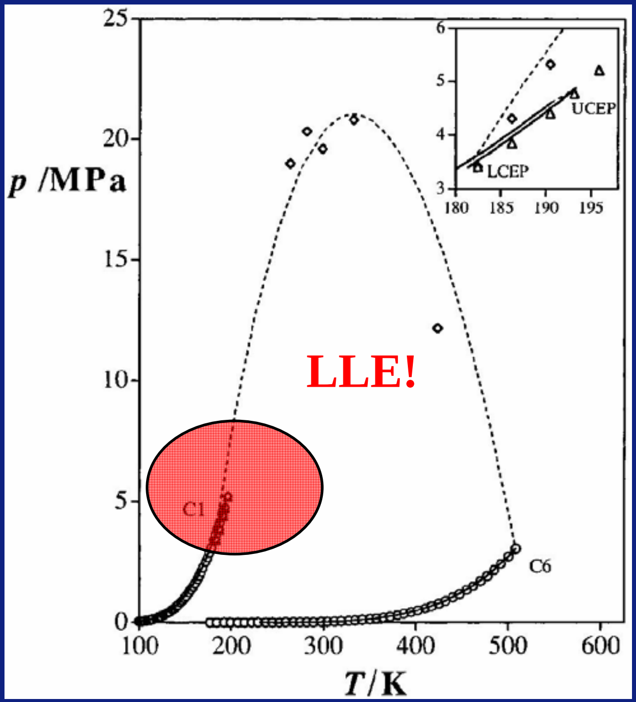
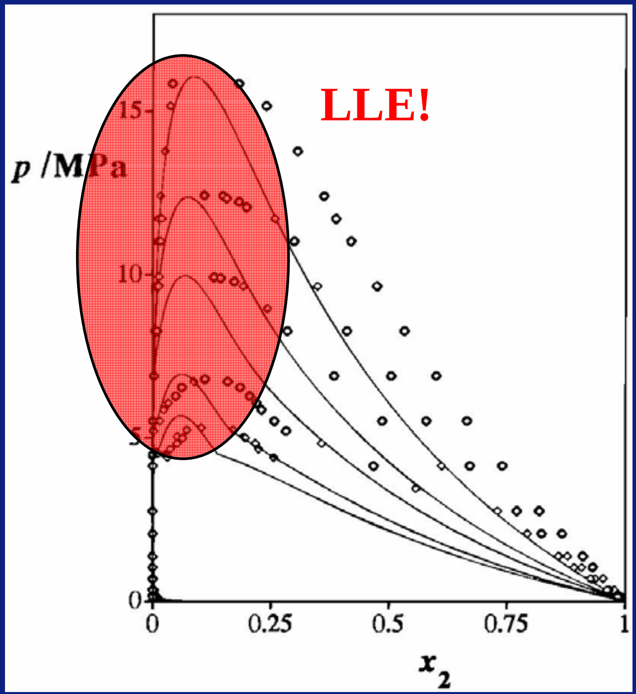
Thermodynamics and Fluid Phase Behaviour

Fluid phase behaviour of CH_4 in higher alkanes





methane + *n*-hexane

Liquid-liquid immiscibility above ~ 5 bar

McCabe, Gil-Villegas, Jackson (1998)

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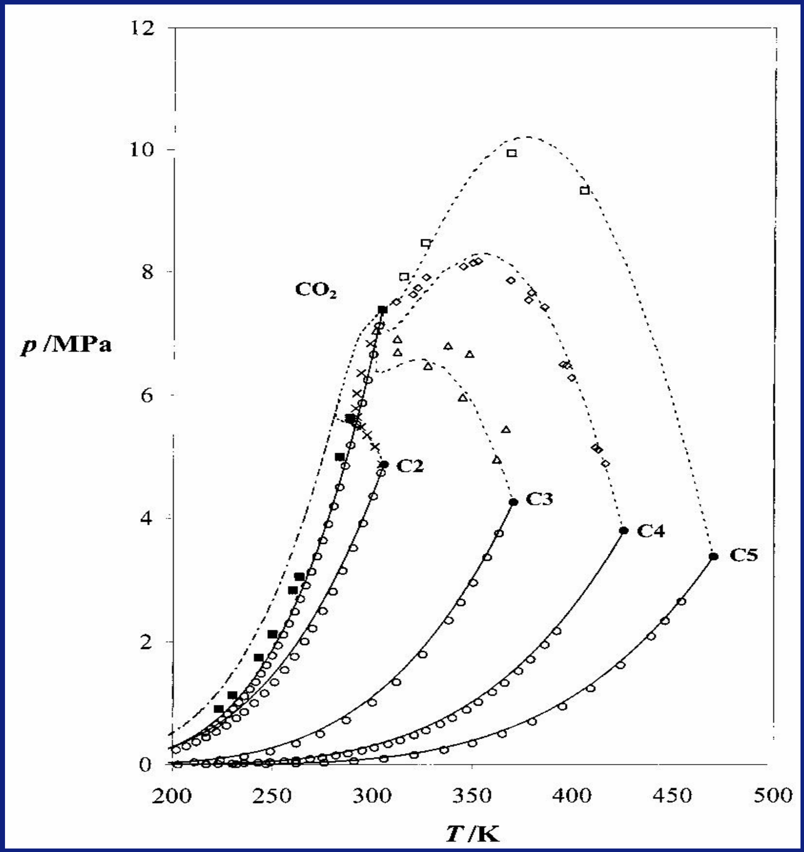
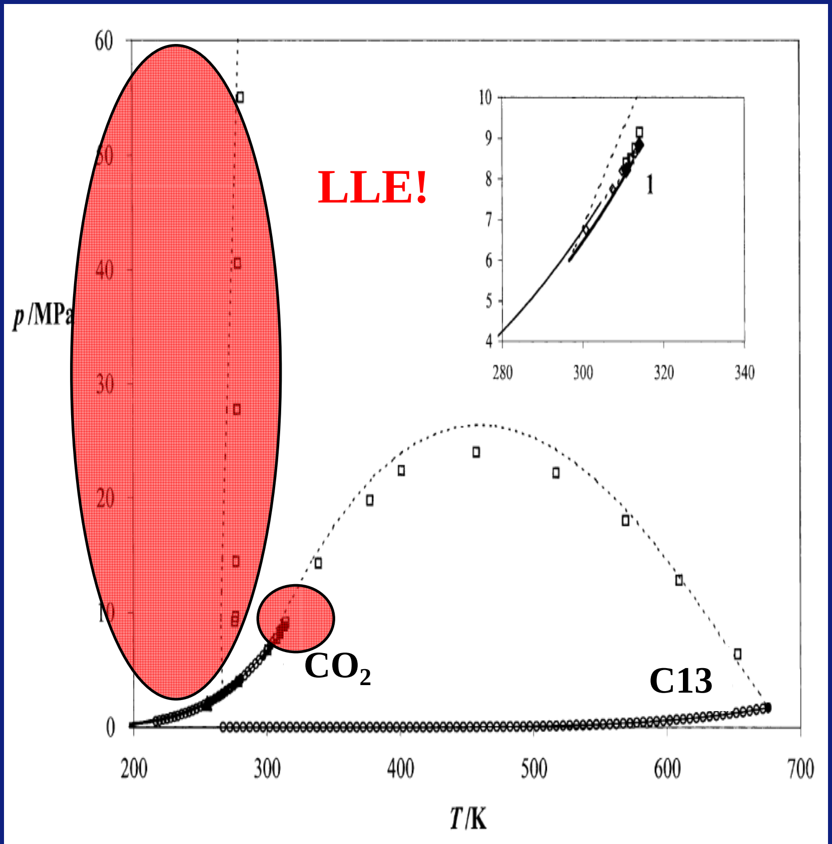
Thermodynamics and Fluid Phase Behaviour

Fluid phase behaviour of CO_2 in higher alkanes





carbon dioxide + *n*-alkanes

Varying degrees of immiscibility in fluid

Blas and Galindo (2002)

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Fluid phase behaviour of CO_2 and CH_4 in higher hydrocarbons

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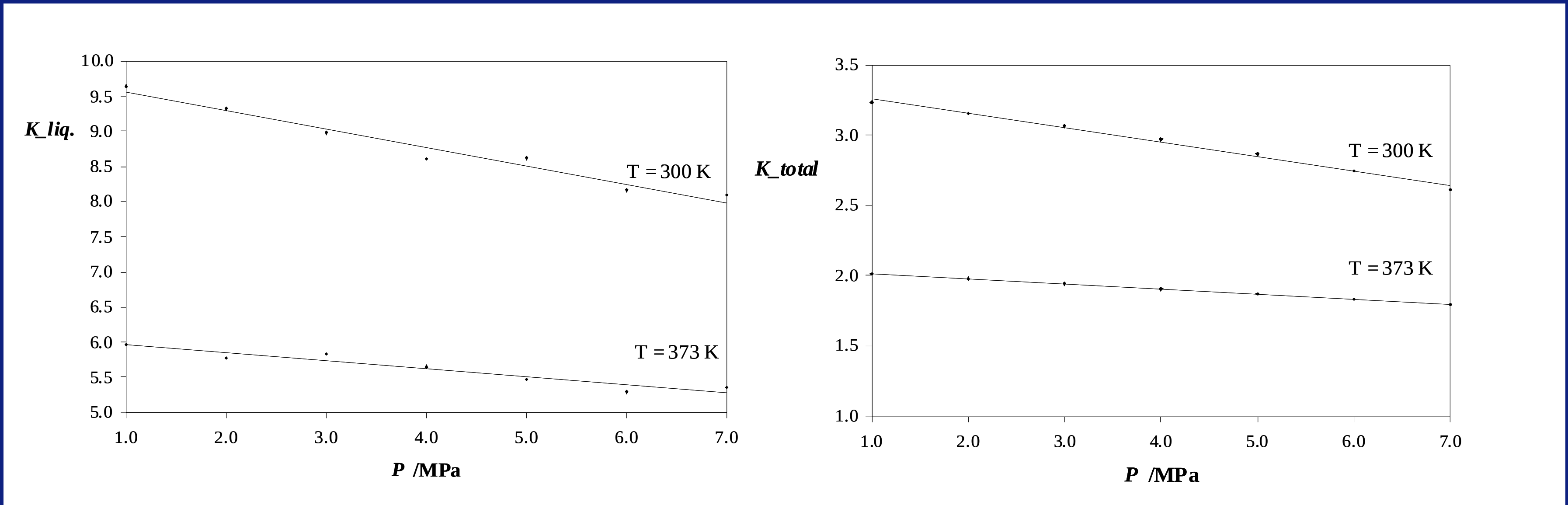
Thermodynamics and Fluid Phase Behaviour

Absorption of CO_2 /CH_4 in hydrocarbon solvent



carbon dioxide + methane + *n*-hexadecane

Gas stream $K\_gas = y(CO_2):y(CH_4) = 3:1$

Overall selectivity in *n*-hexadecane $K\_total > 3$

Keskes, Adjiman, Galindo, Jackson (2006)

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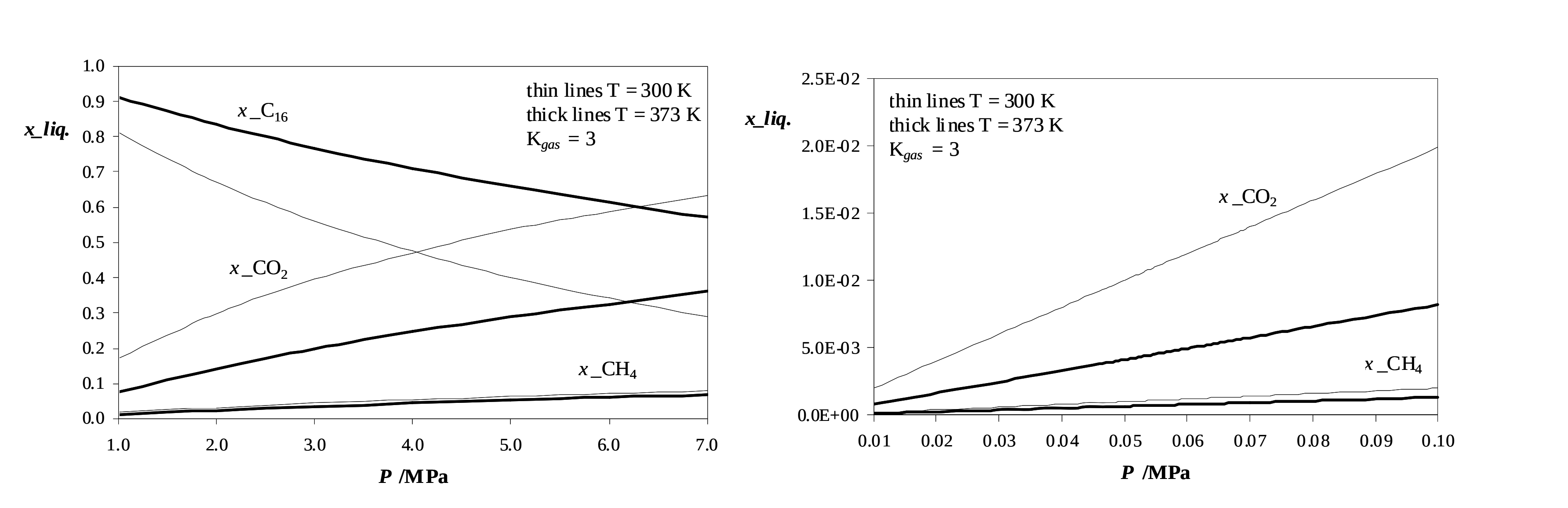
Thermodynamics and Fluid Phase Behaviour

Absorption of CO_2 /CH_4 in hydrocarbon solvent



carbon dioxide + methane + *n*-hexadecane

Gas stream y(CO_2):y(CH_4)=3:1

Temperatures ~ 300 K   Pressures > 5 bar

Keskes, Adjiman, Galindo, Jackson (2006)

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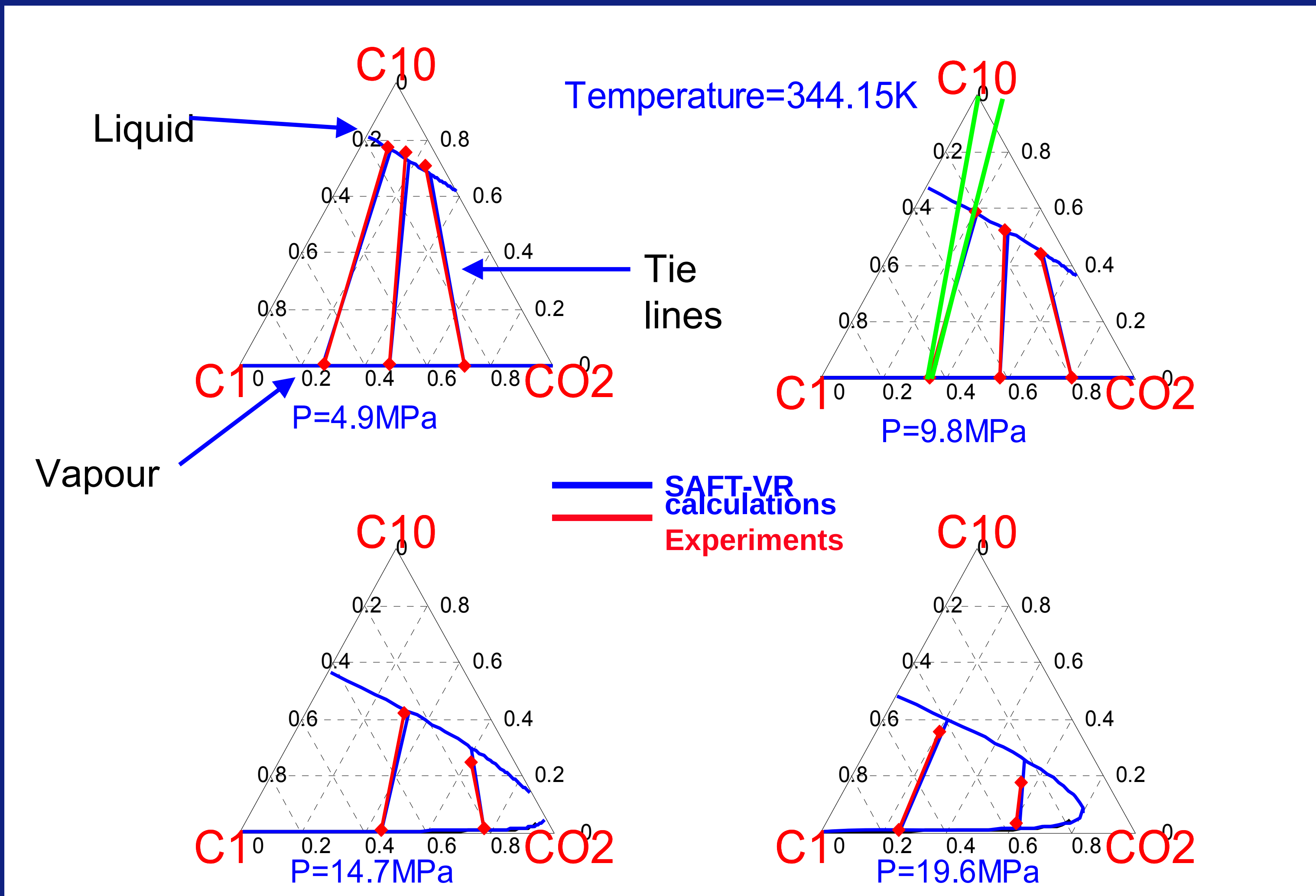
Thermodynamics and Fluid Phase Behaviour

Validation of theory with experiment



Keskes, Adjiman, Galindo, Jackson (2006)

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CO_2 Separation and Capture from CH_4

Process Design

- Find the design
  - equipment size,
  - operating conditions,
  - solvent: which alkane? alkane mixtures?

  that gives the best economic performance, given feed, purity and environmental constraints.
- Process and solvent should be designed simultaneously.
- Require accurate description of thermodynamics at high pressure.

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CO_2 Separation and Capture from CH_4

Process Achitecture

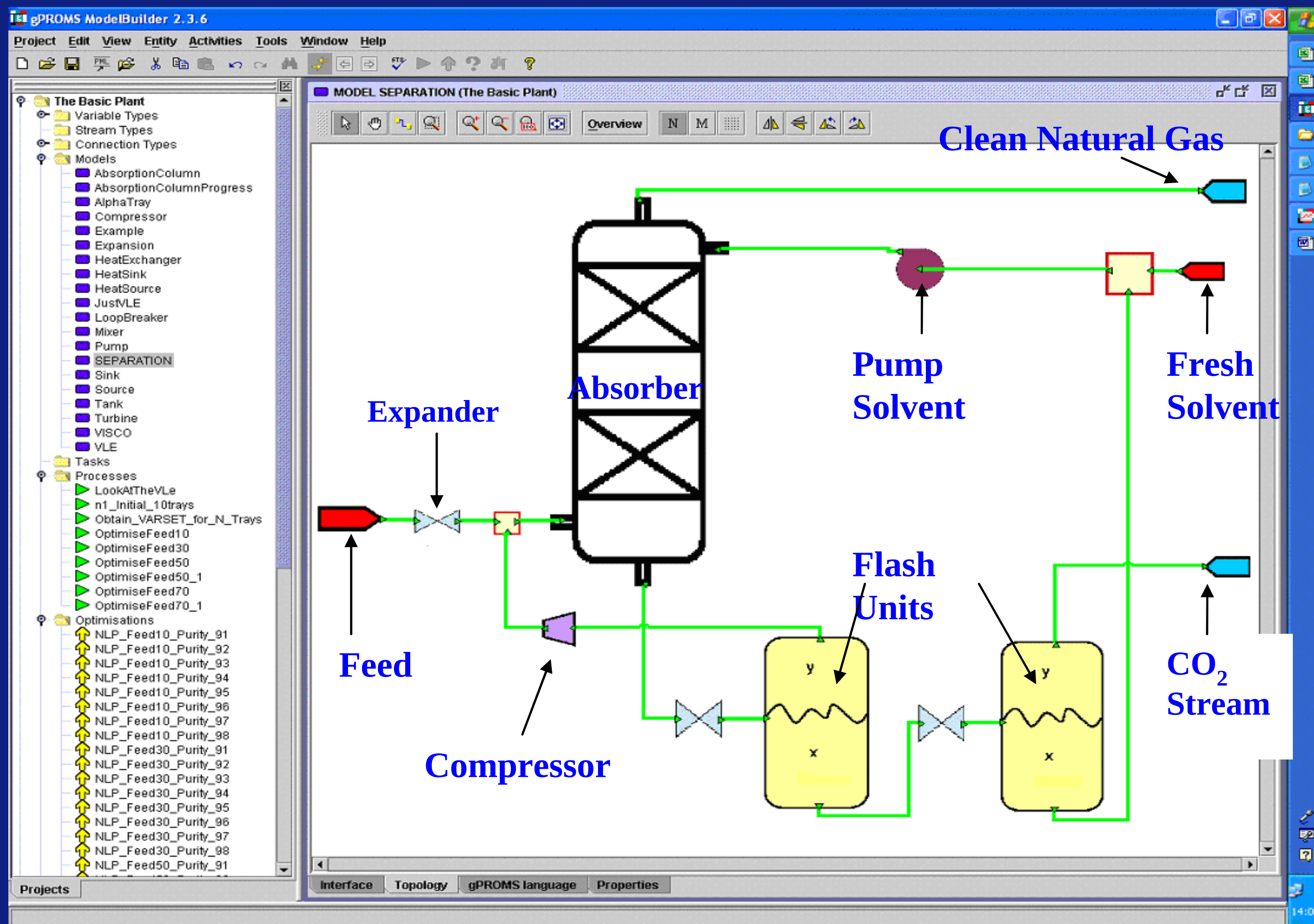
gPROMS Interface

High pressure absorber

2 Flash units

1 for Recycle

1 for CO_2 pure stream



Keskes, Adjiman, Galindo, Jackson (2006)

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CO_2 Separation and Capture from CH_4
Process Optimisation - Objective

The objective is to maximise the profit of the separation plant:

$$\text{Maximise (Profit NPV = Natural Gas Revenue - Total Separation Costs)}$$

$$\text{or}$$

$$\text{Minimise (Lost Revenue for } CH_4 \text{ in } CO_2 \text{ Stream + Total Separation Costs)}$$

- Natural gas revenue = Present value of natural gas annual sales
- Total separation cost = CAPEX + Present value of OPEX

Assumptions:

- Fixed interest rate = 5%
- Fixed gas price = 10 USD / Millions BTU
- Project life is 15 years

Keskes, Adjiman, Galindo, Jackson (2006)

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CO_2 Separation and Capture from CH_4

Process Optimisation – Variables & Constraints

Optimisation Variables

n-alkane solvent C_nH_{2n+2}	n (real) ≤ 14
Recycling pressure	P1
Absorption pressure	P0
Solvent recirculation rate	F_solvent

Main Optimisation Constraints

Natural gas purity spec > 97% (mol/mol)
Absorber height < 50 m
Tower cross section < 30 m^2
Liquid temperature > 10K + melting of pure solvent

Keskes, Adjiman, Galindo, Jackson (2006)

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CO_2 Separation and Capture from CH_4

Case-Study: Grissik (Indonesia) - Air Liquide

FEED:

- Composition
  - CO_2: 30%
  - CH_4: 70%
- Rate:
  - 1000 mol/s
  - = 68 MMSCFD
- Pressure
  - 7.96 MPa
- Temperature
  - 301.5 K

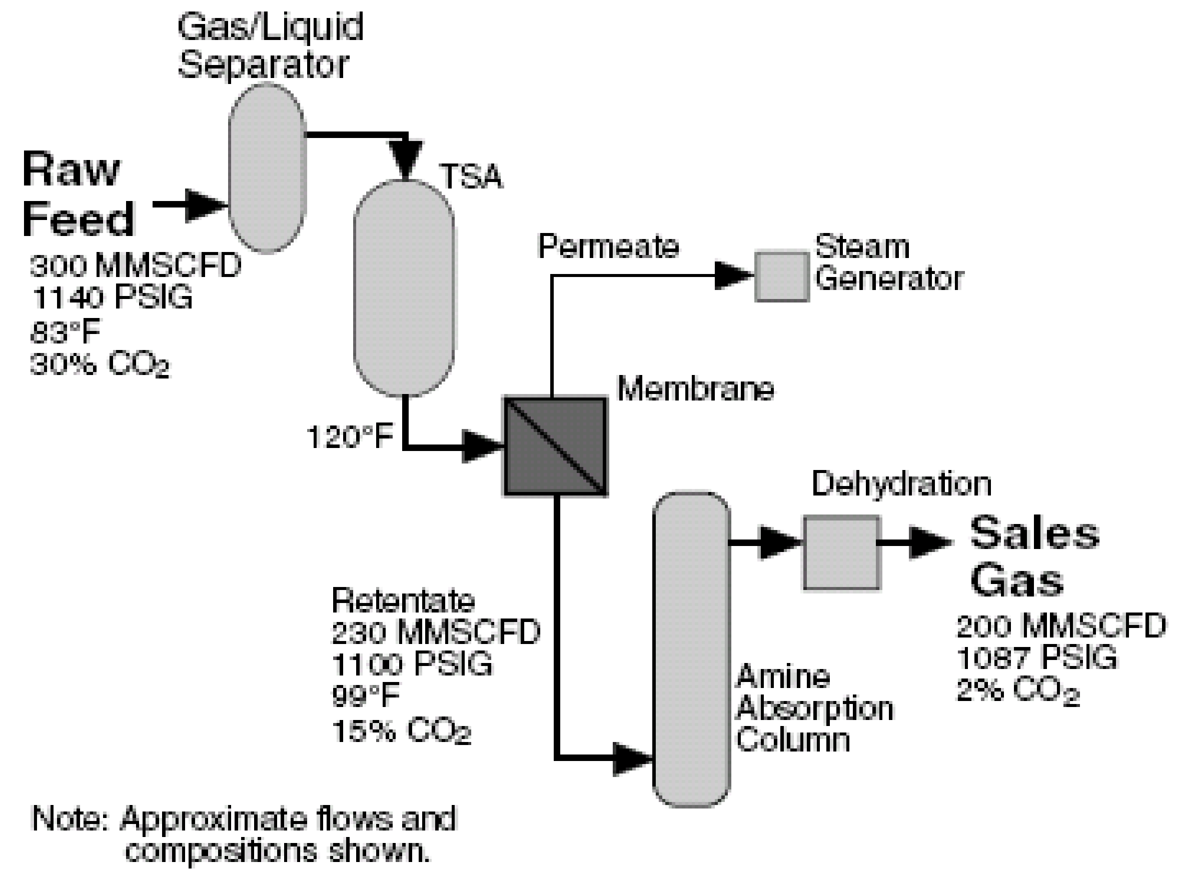

Figure 2. Grissik Process Flow Diagram

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CO_2 Separation and Capture from CH_4

Process Optimisation - 30% CO_2 Feed

Amount of CO_2 in the Feed (mol/mol)	10%	30%	50%	70%
Natural Gas Sales		1829		
Total Separation Cost		82		
CH_4 losses in the CO_2 outlet		107		
Total Operating Cost		42		
Total Capital Investment		40		
CH_4 Recovery		94.5%		
CO_2 Recovery		93.2%		
CO_2 Stream Purity		87.9%		
n-alkane solvent C_nH_{2n+2}		14		
Absorber Pressure (MPa)		4.80		
Recycling Tank Pressure (MPa)		1.99		
Solvent Recirculation Flowrate (100mol/s)		8.6		
Absorption Column Height (m)		30.0		
Absorption Column Section (m^2)		14.5		

Table: Process economics, control variables and absorber dimensions for 4 feed compositions (costs are in MMUSD-2005, Million US dollar bases on 2005 figures)

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CO_2 Separation and Capture from CH_4

Process Optimisation – Range of CO_2 Feeds

Amount of CO_2 in the Feed (mol/mol)	**10%**	**30%**	**50%**	**70%**
Natural Gas Sales	2400	**1829**	1314	793
Total Separation Cost	50	**82**	96	114
Cost of CH_4 losses in the CO_2 outlet	88	**107**	69	36
Total Operating Cost	27	**42**	50	61
Total Capital Investment	23	**40**	46	53
CH_4 Recovery	96.5%	**94.5%**	95%	95.6%
CO_2 Recovery	73.2%	**93.2%**	97.1%	98.7%
CO_2 Stream Purity	69.6%	**87.9%**	95.1%	98.1%
n-alkane solvent C_nH_{2n+2}	14	**14**	14	14
Absorber Pressure (MPa)	4.72	**4.80**	4.75	4.83
Recycling Tank Pressure (MPa)	1.56	**1.99**	1.94	1.93
Solvent Recirculation Flowrate (100 mol/s)	6.4	**8.6**	10.4	12.7
Absorption Column Height (m)	30.1	**30.0**	30.1	30.0
Absorption Column Section (m^2)	8.8	**14.5**	16.1	17.1

Table: Process economics, control variables and absorber dimensions for 4 feed compositions (costs are in MMUSD-2005, Million US dollar bases on 2005 figures)

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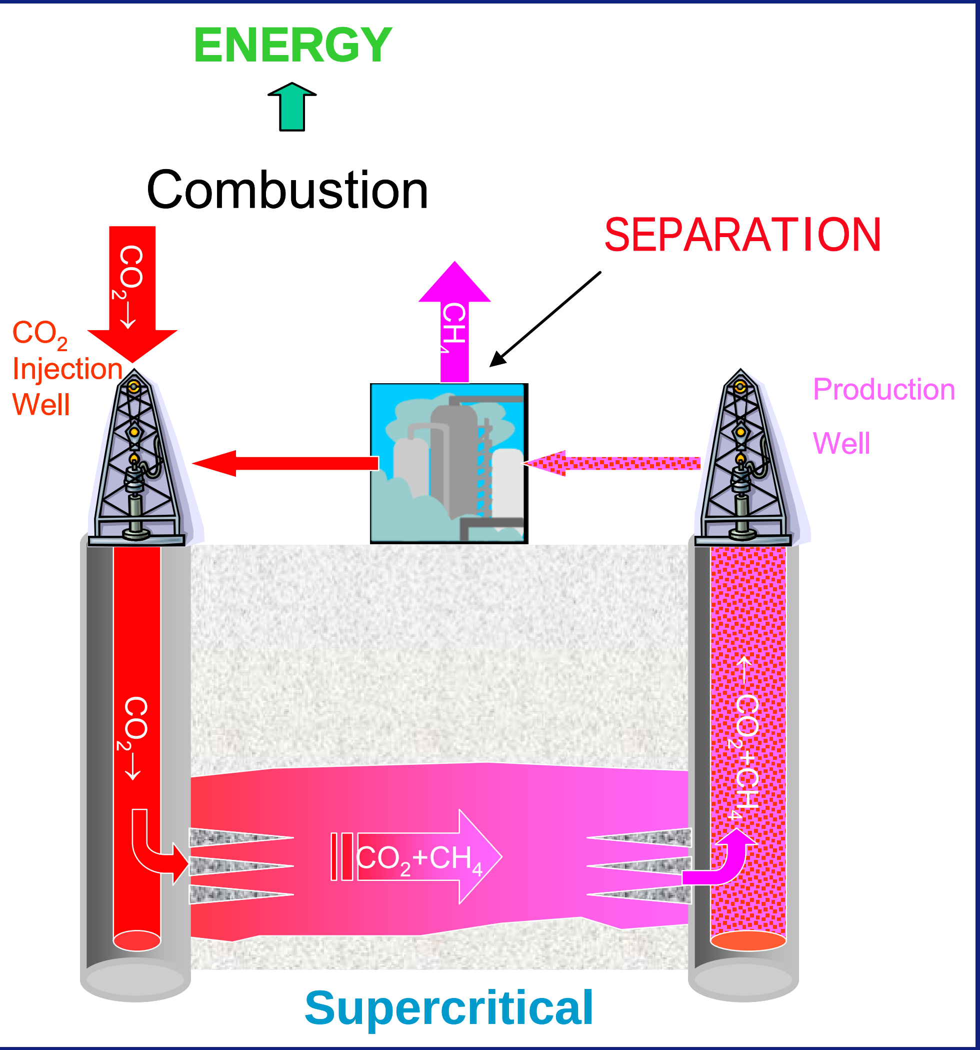
CO_2 Separation and Capture from CH_4

Future needs

- Application of the Kyoto protocol:
  - CO_2 is captured from power plants
  - And then stored in Oil / Gas reservoirs
  - Enhance the production of Oil or Gas
- Increasingly concentration of CO_2
  - Time = 0 ⇒ CO_2 = 0 - 30%
  - Time = 5 years ⇒ CO_2 = 70%
- With increasing CO_2 content
  - Separation cost increases
  - Revenue from NG sales decreases
  - Production will be terminated as soon as separation becomes too expensive

⇒ Improved separation process needed:
- to maximise revenue over project life
- to deal with variable feed
  - Concentration: CO_2 content = 0 - 70%
  - Pressure = 5-10 MPa



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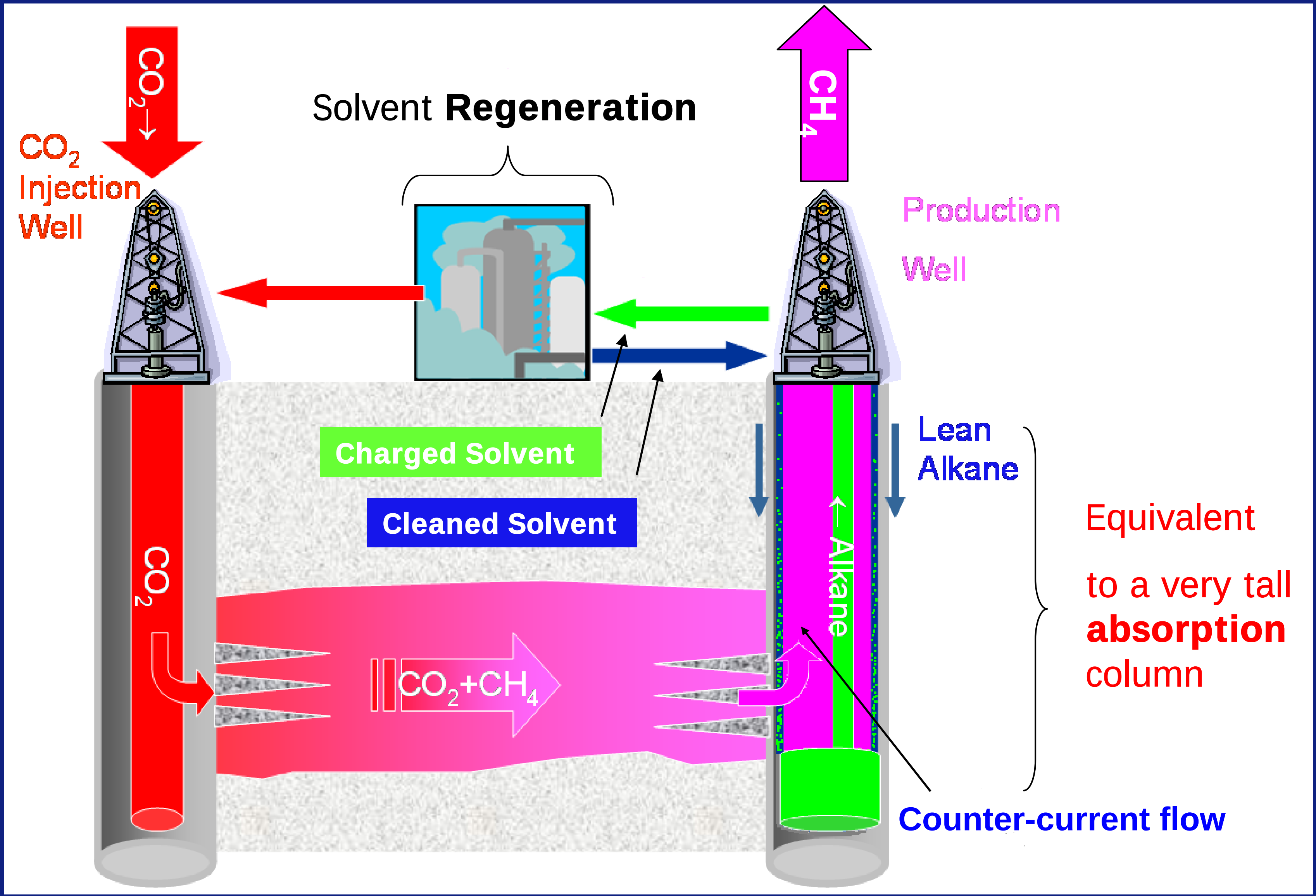
Downhole Separation



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CO_2 Separation and Capture from CH_4

Conclusions

- Hydrocarbons preferentially absorb CO_2 – Physical solvent
- Low temperatures (~25ºC) - High pressure (> 5 bar)
- Higher homologous lead to enhanced selectivity
- Advanced thermodynamic modelling (SAFT)
- Design and optimised CO_2/CH_4 separation process
- Process economically viable
- Very flexible for different CO_2 contents of feed

Future Direction

- Critical comparison - amines and membranes
- Integrate process with EOR (and post-combustion capture)
- CO2 as a reservoir fluid - Downhole separation

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Thank You!

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