ECN

Energy research Centre of the Netherlands

TU Delft

Delft University of Technology

Advanced Membrane Reactors in Energy Systems
Development of novel membranes for membrane reactors.

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www.ecn.nl

GCEP meeting, Stanford University, June 13-16 2005

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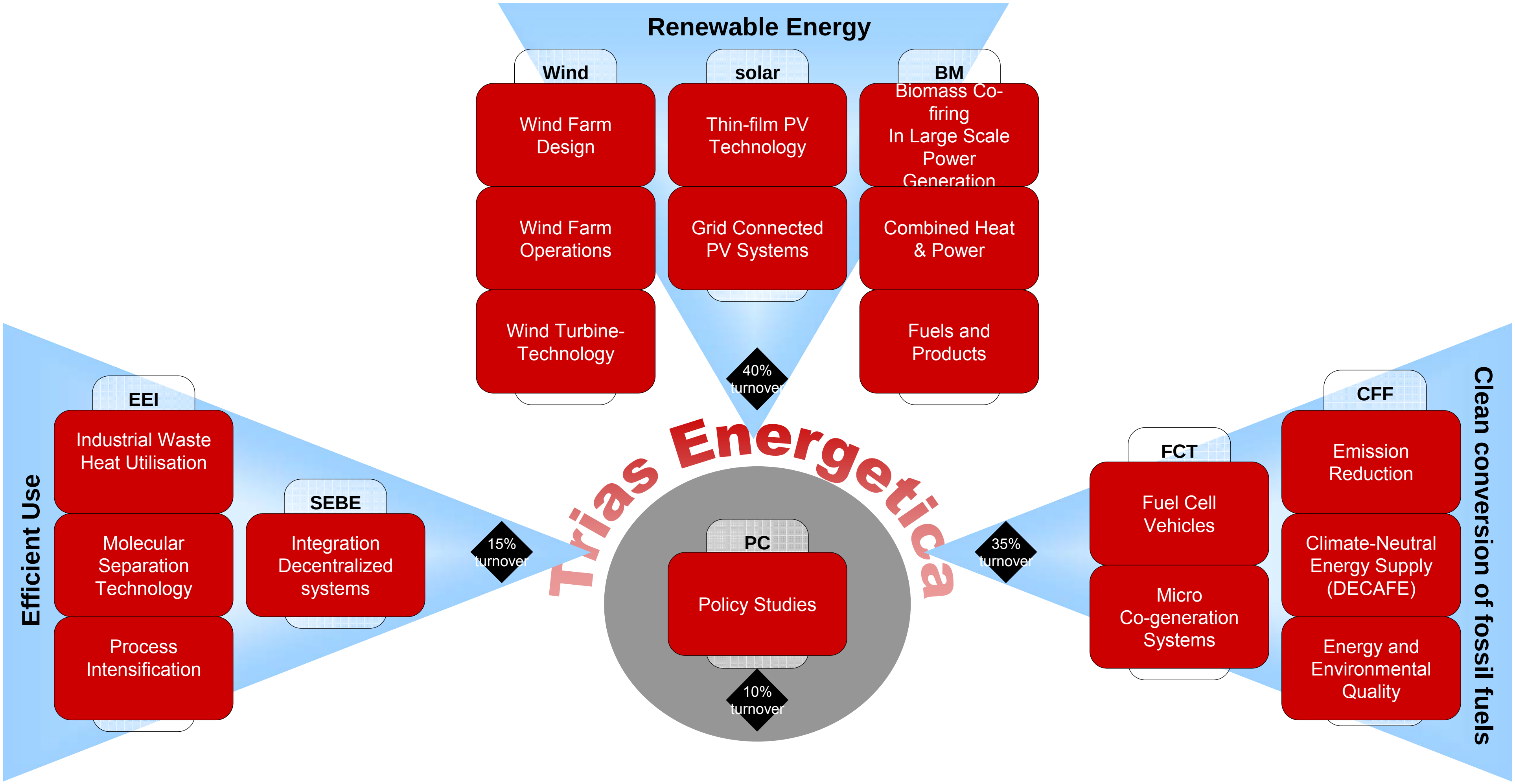
ECN: an overview of activities

Mission statement :

" To develop high level knowledge and technologies needed for the transition towards a sustainable energy supply "

ECN's research areas



ECN Energy Efficiency in Industry

Separation technology

Membranes: dense and porous

- Dewatering of organics
- Air-separation
- Hydrogen membranes

Waste heat technology

Heat pumps: solid sorption, thermo acoustic

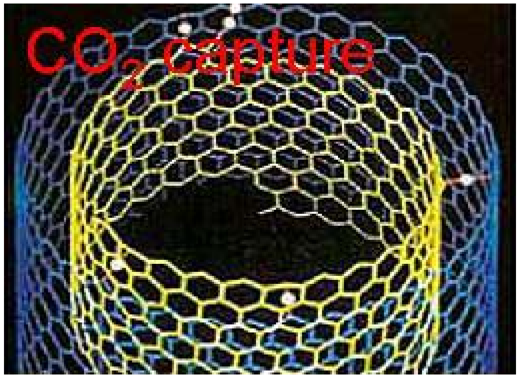
- Heating
- Cooling
- Storage

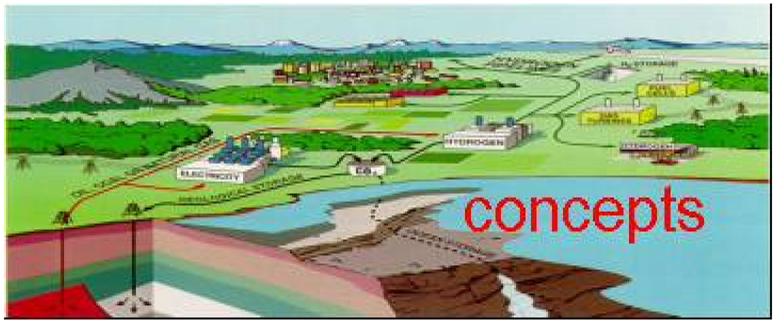
Process intensification

Membrane reactors, hex reactors

ECN Clean Fossil Fuels

- System concepts and technology assessments
- CO2-capture technologies
- H2-technology
- Stirling micro-cogeneration
- Fuel cell technology i.e. PEMFC and SOFC
- Emission reduction
- Environmental research





CO_2 capture activities

GT + membrane reformer

GT + oxy-fuel

Ceramic membranes

On-site H_2 production
membrane reactor

Systems Engineering

SOFC + afterburners

Sorbents ↔ **SOFC components**

Sorption enhanced reforming

Sequestration

- Mineral-fixation
- Bio-fixation

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Delft University of Technology

TU Delft: an overview of activities

Delft Institute for Sustainable Energy (DISE) coordinates the research on sustainable energy of the Delft University of Technology.

The research program focuses on the production, storage, fundamental aspects and utilization of electrical energy and hydrogen.

Hereto, advanced 3D-nano-structured solar cells and small wind turbines are being studied for de-centralized conversion and also storage of sustainable energy in the built environment. Rechargeable Li-ion batteries are being studied for the storage of electrical energy.

Sustainable energy sources, like solar and wind energy, can also be stored via electrolysis of water to form hydrogen.

Hydrogen, as an energy carrier, can be converted into electrical energy using a fuel cell. The safe storage of hydrogen is a prerequisite for the introduction of a Hydrogen Economy.

DISE's projects are focusing on:

- novel nano-structured solar cells
- novel nano-structured functional materials for rechargeable batteries
- novel photo-electrochemical (PEC)cells
- integration of the hydrogen storage concept in PEC-cells

The GCEP project: General

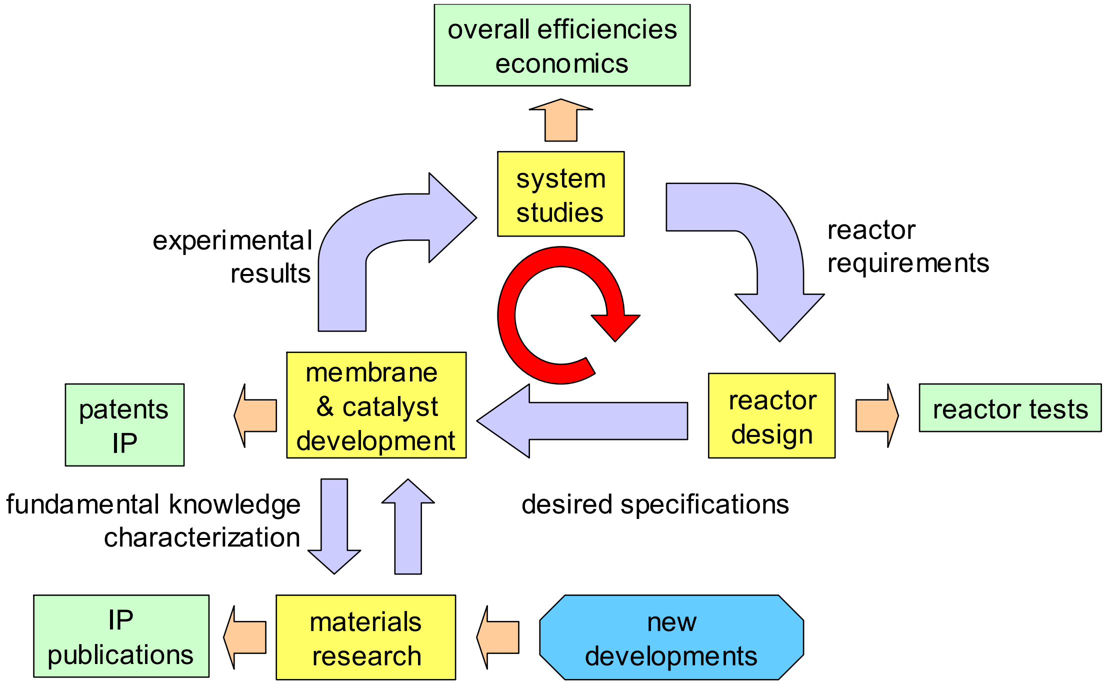
Objective

The purpose of this project is to develop H_2 and CO_2 membranes to allow combination of natural gas reforming with H_2 or CO_2 separation in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation.

Advantages:

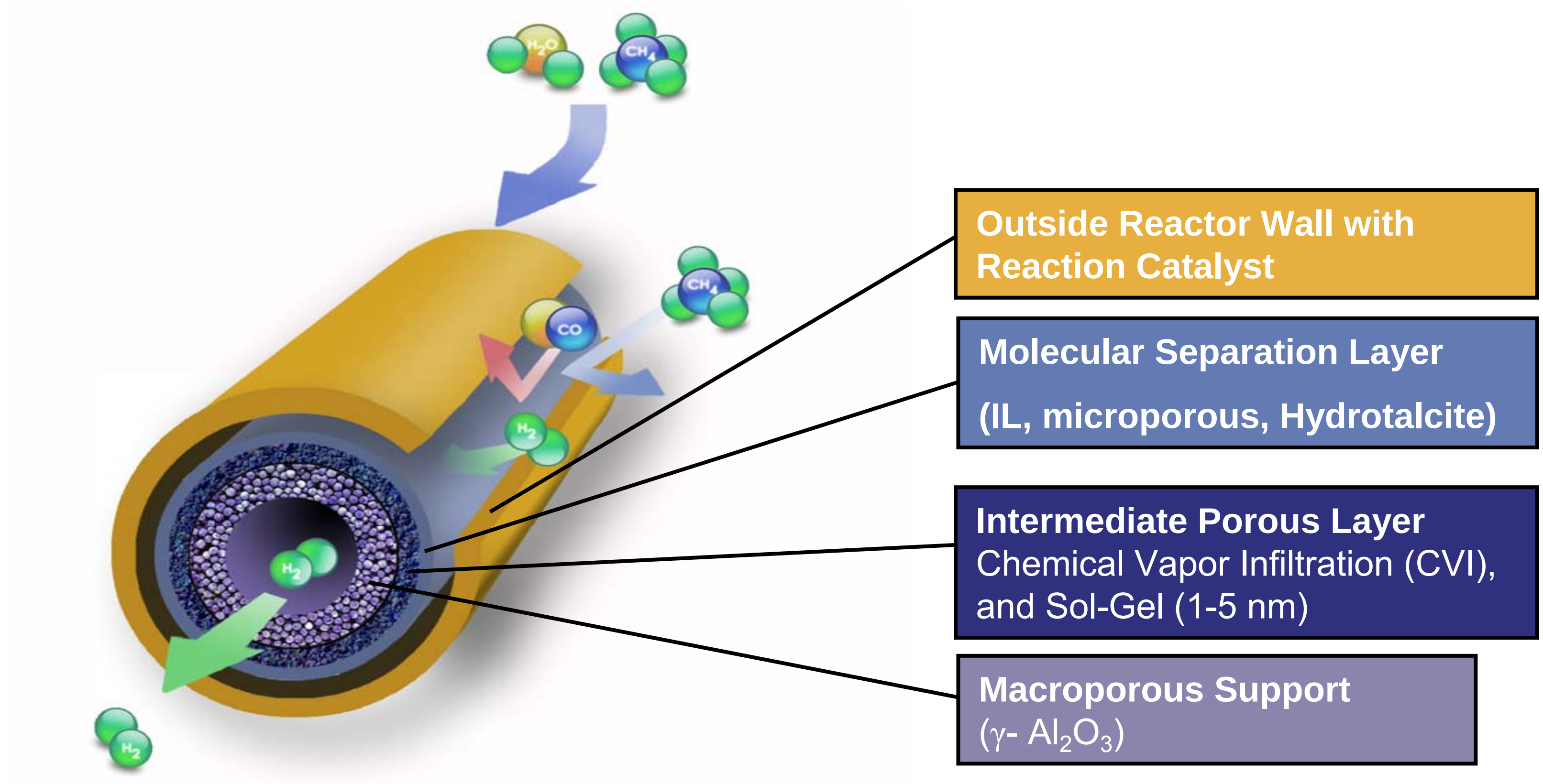
- eliminating the requirement of water gas shift reactors: cost reductions;
- offering higher conversion efficiencies at lower temperatures;
- decreasing primary energy use for CO_2 separation/capture in power generation.

The GCEP project: General



Task 1.	System analysis and thermodynamic evaluations	Executed by ECN
Task 2.	Hydrogen membrane research & development	Executed by TUD
Task 3.	CO_2 membranes research & development	Executed by ECN+TUD
Task 4.	Catalyst screening	Executed by ECN
Task 5.	Reactor modelling and design	Executed by ECN

The GCEP project: General



The GCEP project: General

Cooperation TUD-ECN:

- Mutual consent on new post docs/PhD: do they fit in the team
- Mutual access to analytical/test facilities
- Joint scientific reporting to GCEP
- Progress meetings: once every 8 weeks

The project: Tasks ECN

Task 1: System analysis and thermodynamic evaluations

- Aspen+/exergy assessments of membrane processes. Sets boundary conditions for operational window of the membranes

Task 3a: CO_2 membranes R&D

- Material choice (hydrotalcites, calixarenes etc.), characterisation, membrane formation, separation tests, etc.

Task 4: Catalyst screening

- Screening of commercial catalysts, kinetics,stability and coke formation

Task 5: Reactor modelling & design

- Reactor model development (transport models, hydrodynamics etc) to be used as a “plug-in in Aspen+

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The project: Tasks TU Delft

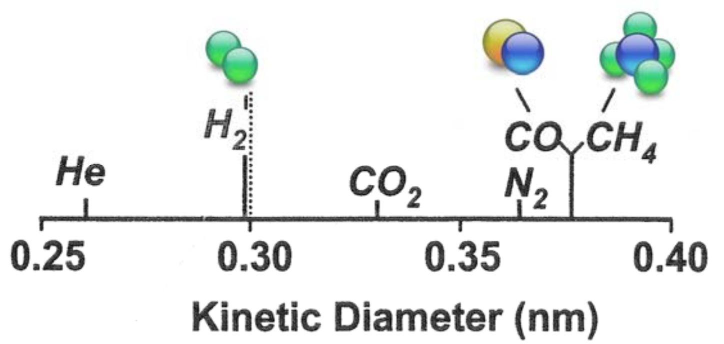
Development of a Nano-Structured Ceramic Membrane for High-Temperature Hydrogen Permselectivity

- Hydrogen production through steam reforming of natural gas:

$$CH_4 + H_2O \xrightarrow[\text{catalyst}]{800^\circ C} 3H_2 + CO \quad \Delta E = 206 \text{ kJ/mol}$$

The application of high-temperature ceramic membrane reactors to this steam-reforming reaction has the potential to achieve similar conversion efficiencies as those attained in conventional reactors at a significantly lower temperature of about 500ºC.

- Nano-structured ceramic layer for hydrogen separation based on differences in kinetic diameter



The project: Tasks TU Delft

Task 2: Hydrogen membranes research and development

- Modify CVD reactor for Chemical Vapor Infiltration and Atomic Layer Deposition

- Materials and Catalyst selection, characterization and membrane formation

- Study steam reforming reaction and in-situ hydrogen separation

The project: Tasks TU Delft

The Goals are:

1. Thermal stability: T @ 500°C

2. H_2 permeability: 10^{-6}~10^{-5} mol/m^2.s.Pa

3. H_2 perm-selectivity: α (H_2/N_2) ~ 1000

The project: Tasks TU Delft

Task 3b: Ionic liquids R&D

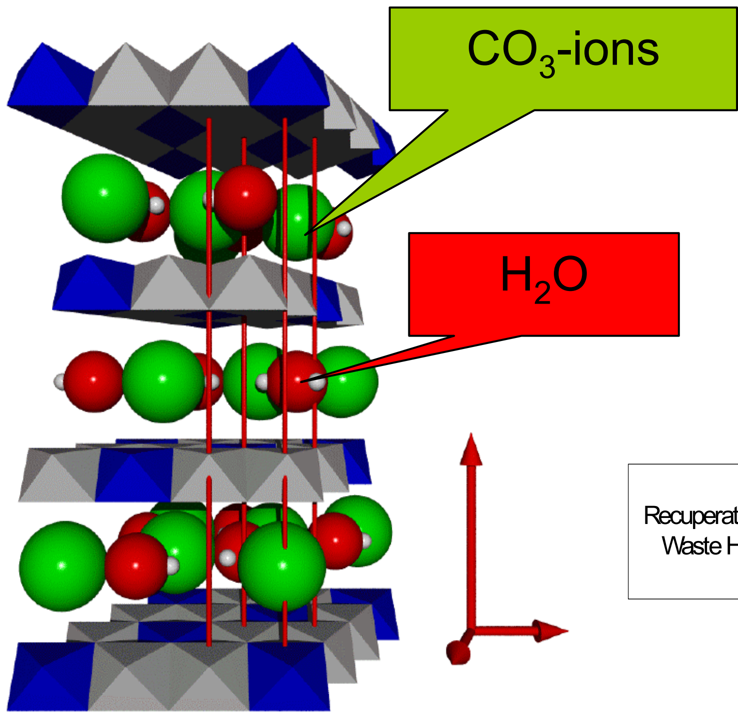
- Simulation of thermodynamic,structural and transport behavior

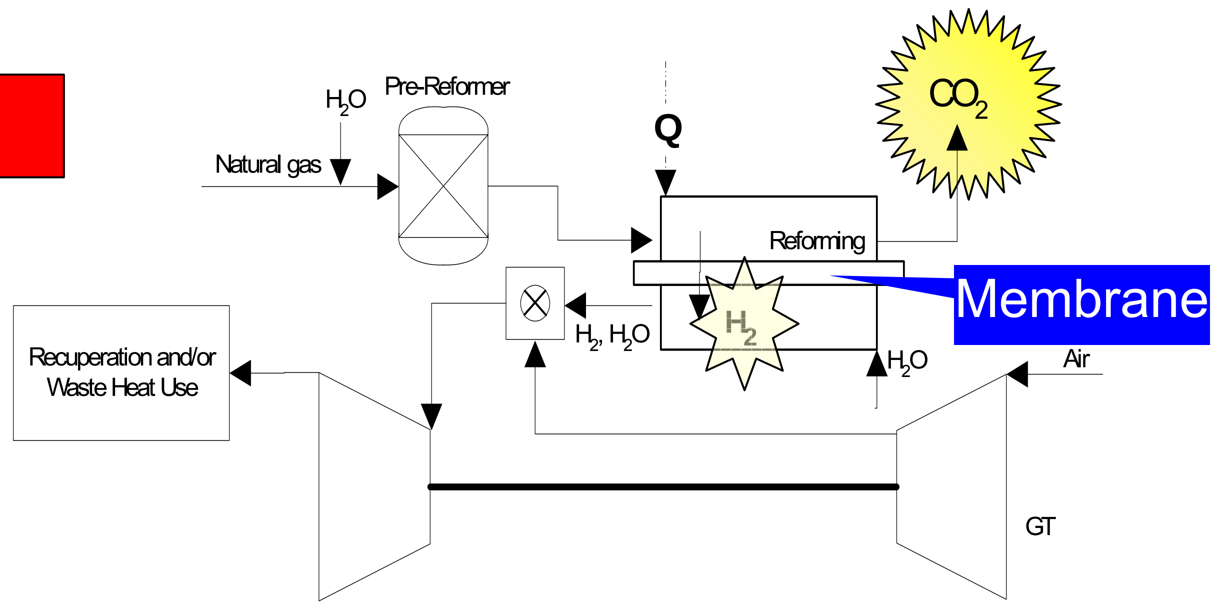
- Quantum chemical calculations to investigate inter-ionic interactions

- Material testing

Related R&D results ECN

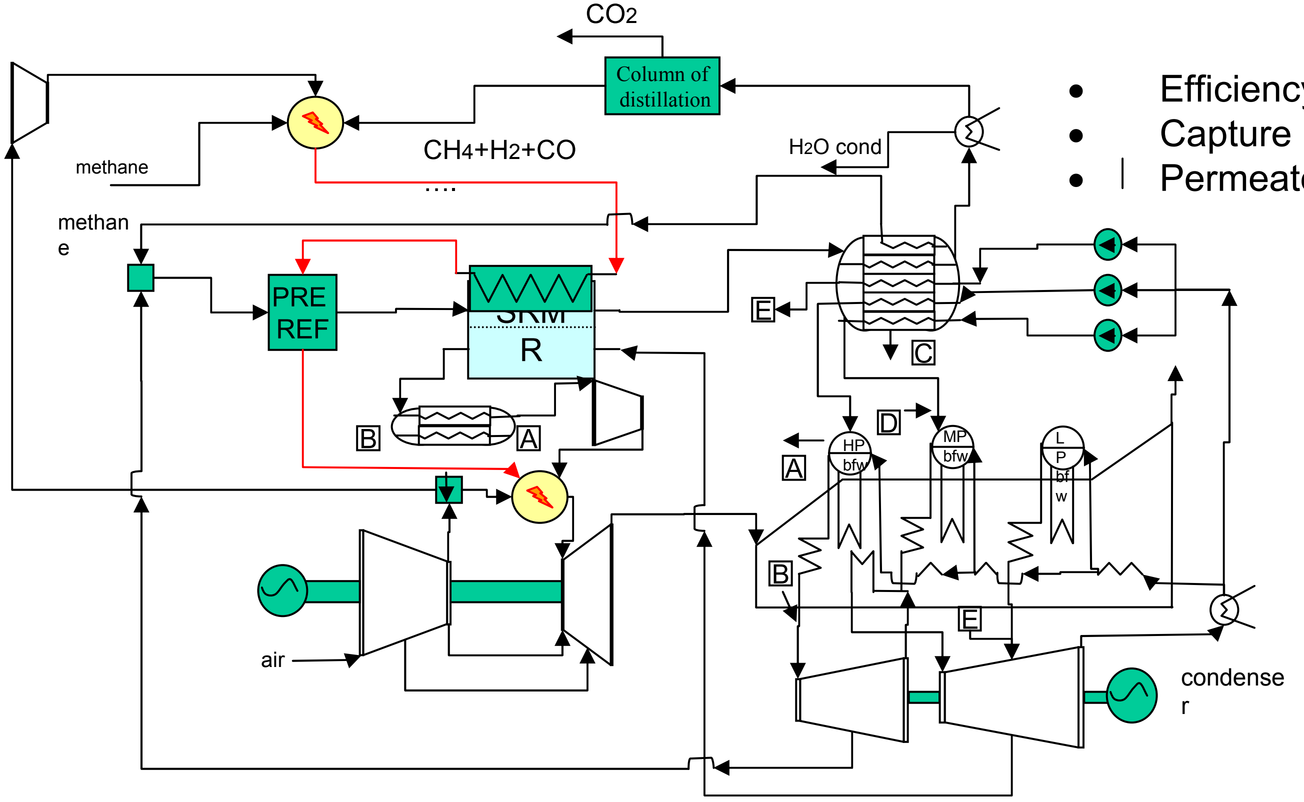
•CO_2 membrane candidate: Hydrotalcite





Related R&D results ECN

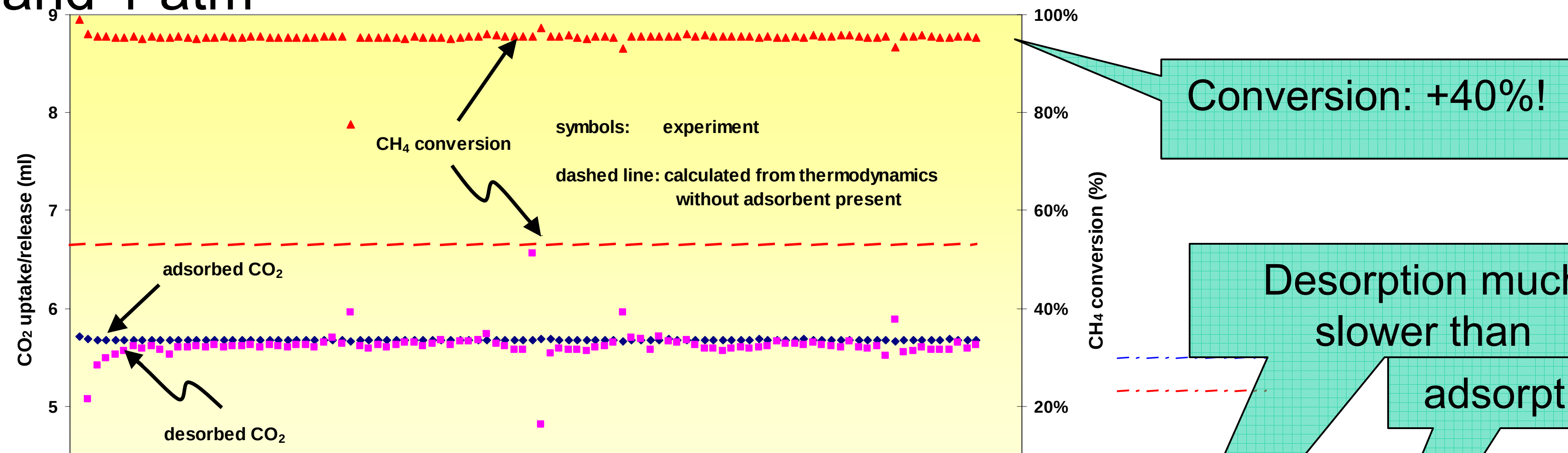
NG membrane reformer combined cycle



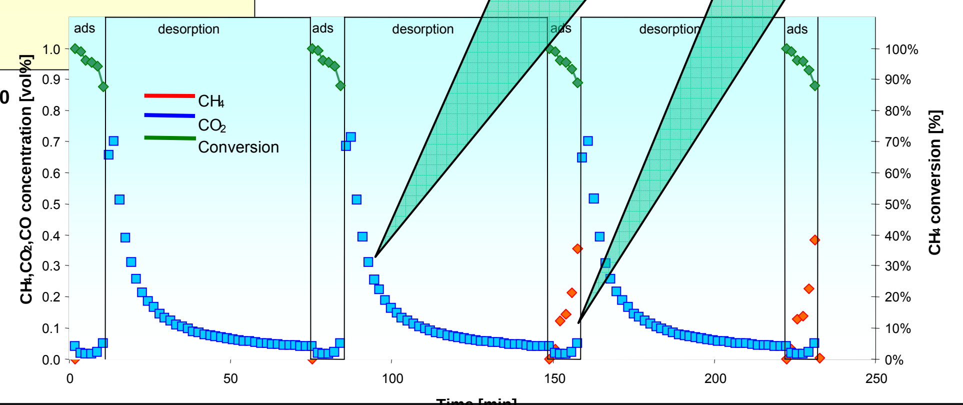
- Efficiency with capture 50+ % LHV
- Capture ratio > 80%
- Permeate combustion looks very attractive

Related R&D results ECN

SERP demonstrated for steam reforming of methane at 400 ºC and 1 atm



adsorption conditions: 25 ml/min, 2.9% CH_4, 17.5% H_2O and 79.5% N_2,, 10 minutes;
desorption conditions: 100 ml/min, 29% H_2O, 71% N_2,, 75 minutes; sample: 1,5 g catalyst, 3,0 g K-promoted htc



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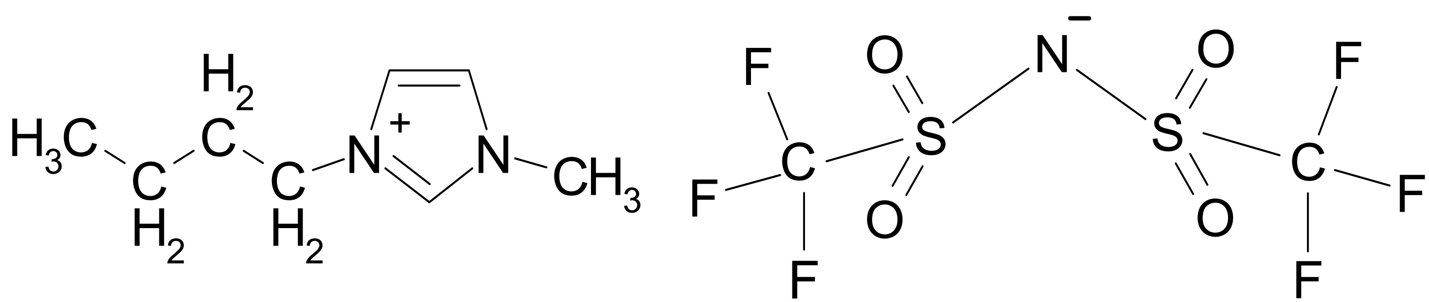
Related R&D results TU Delft

Ionic Liquids:

1-butyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide

Abbreviation: [bmim][Tf2N]



Related R&D results TU Delft

Thermal stability of ionic liquids

Ionic liquid	Temperature onset for decomposition (dried), °C
[bmim][Cl]	254
[bmim][I]	265
[emim][BF_4]	412
[bmim][BF_4]	360/403
[emim][PF_6]	375
[bmim][PF_6]	349
[emim][CF_3CO_2]	150
[emim][Tf_2N]	440/455
[pmim][Tf_2N]	452
[bmim][Tf_2N]	439

Viscosity decreases in the order
Cl-> [PF6]->[BF4]->[Tf2N]-

Ionic Liquid	Viscosity at 25°C, cp
[hmim][Cl]	716
[emim][BF_4]	43
[bmim][BF_4]	233
[hmim][BF_4]	314 at 20°C
[bmim][PF_6]	450
[hmim][PF_6]	585
[bmim][CF_3CO_2]	73
[emim][Tf_2N]	28
[bmim][Tf_2N]	52
[hmim][Tf_2N]	—

ref: Huddleston et al. (2001)

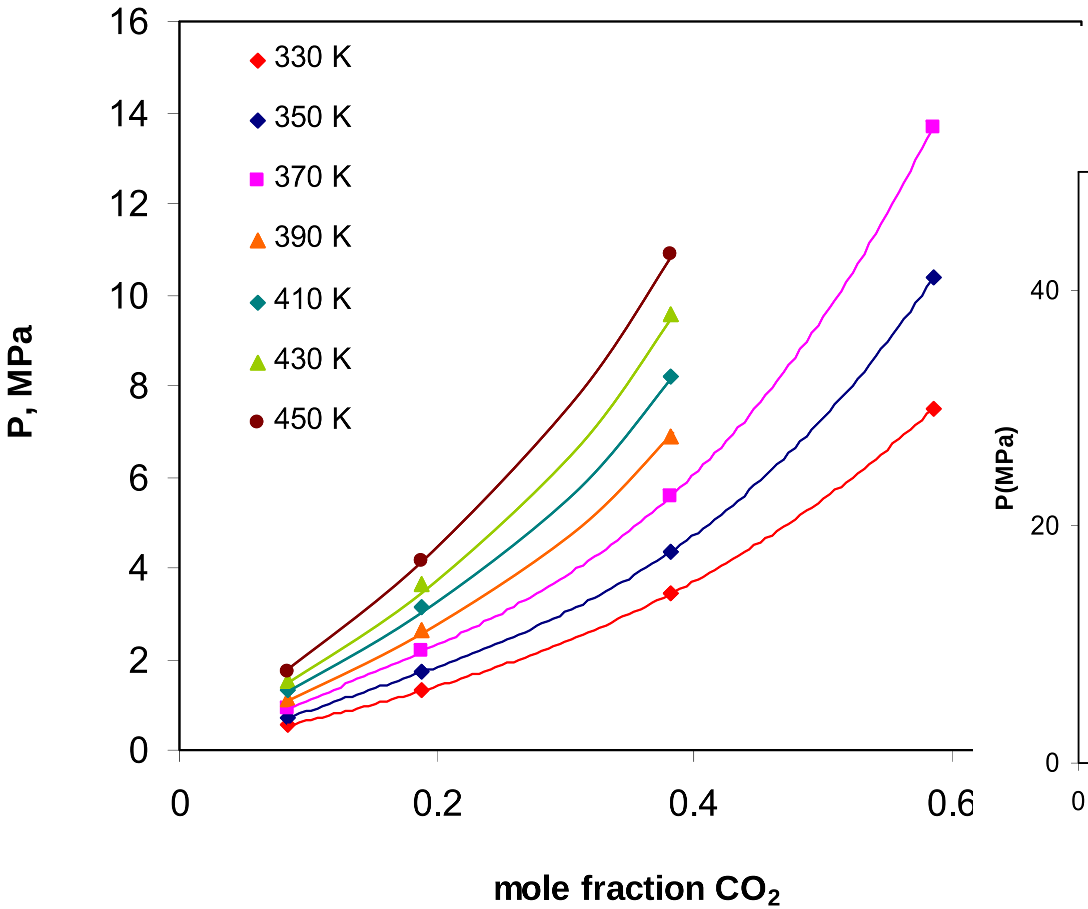
Related R&D results TU Delft

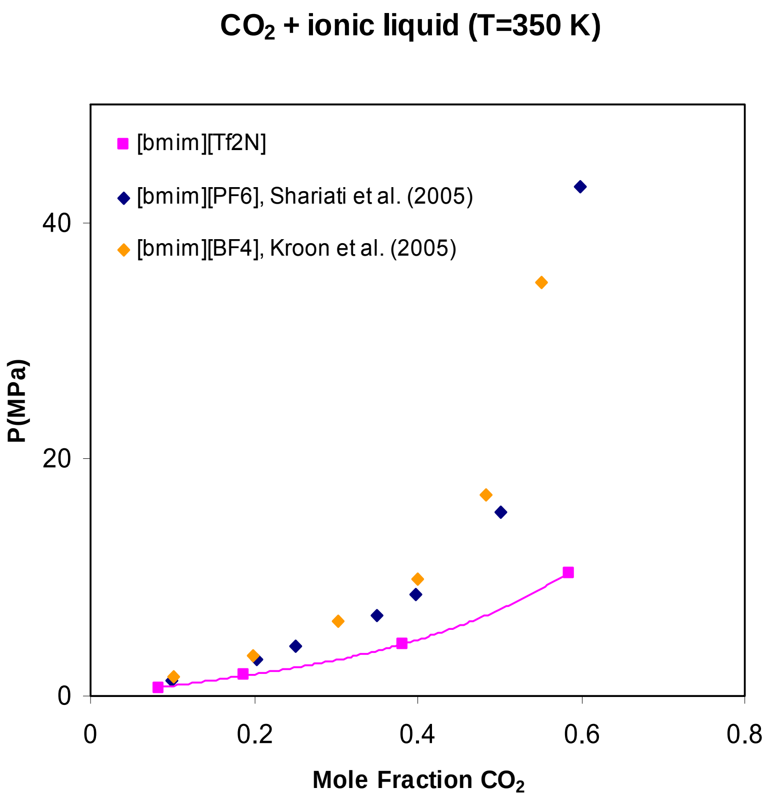
Comparison of the available information on different classes of ionic liquids (ILs) showed that the Tf_2N family is suitable for application as separation medium in reforming and WGS reactions, because it has:

- High thermal stability
- Low viscosity compared to other ILs
- High solubility for CO_2 compared to other ILs
- Low solubility for H_2 compared to other ILs

Related R&D results TU Delft

CO_2 + 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)amid





The Dutch GCEP team

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