



ASSOLOMBARDA



POLITECNICO
MILANO 1863

Nanomateriali e processi intensificati per applicazioni nell'oil & gas e non solo

Speaker

Maurizio Masi

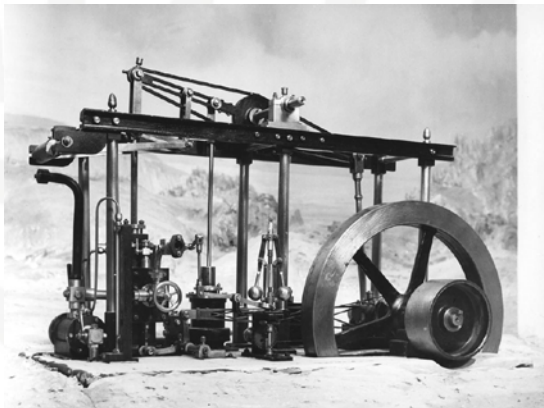
7 ottobre 2015

Modello POLIMI R&D con imprese: JRC

dal modello di trasferimento tecnologico a quello di sviluppo congiunto di tecnologia

Non esiste una relazione lineare tra la scienza e la tecnologia: sovente la tecnologia precede la scienza (grande eccezione progetto Manhattan & pila atomica)

- ☐ *Macchina a vapore vs termodinamica*
- ☐ *Aeroplano vs teorie strato limite fluodinamico*
- ☐ *La pila vs l'elettromagnetismo*
- ☐



Modello POLIMI R&D con imprese: JRC

dal modello di trasferimento tecnologico a quello di sviluppo congiunto di tecnologia

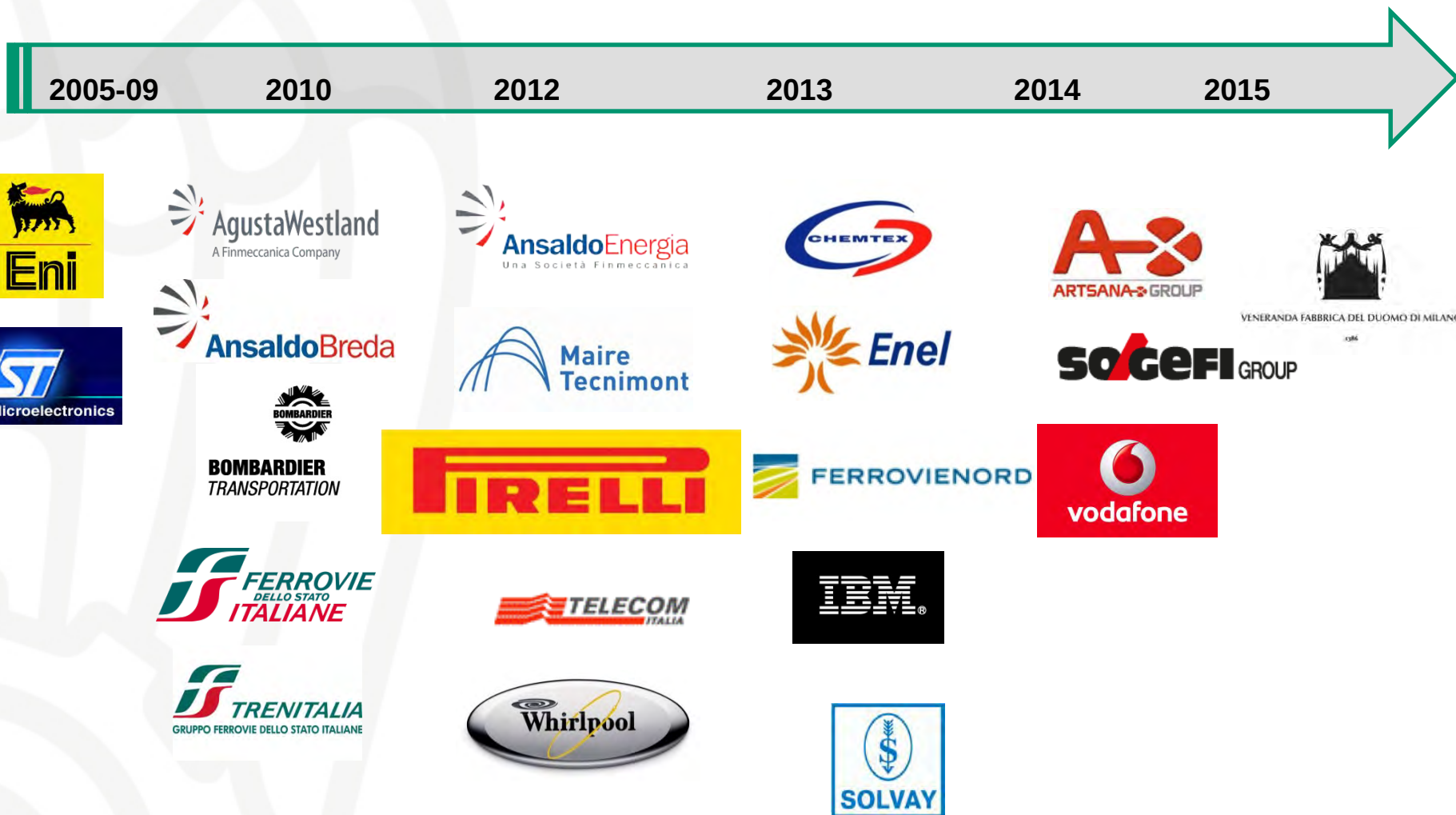
realisticamente è raro l'evento di una scoperta scientifica che conduca a tecnologie innovative da rivoluzionare i mercati. L'innovazione tecnologica è sostanzialmente fondata sulla ricerca incrementale

Joint Research Centers:

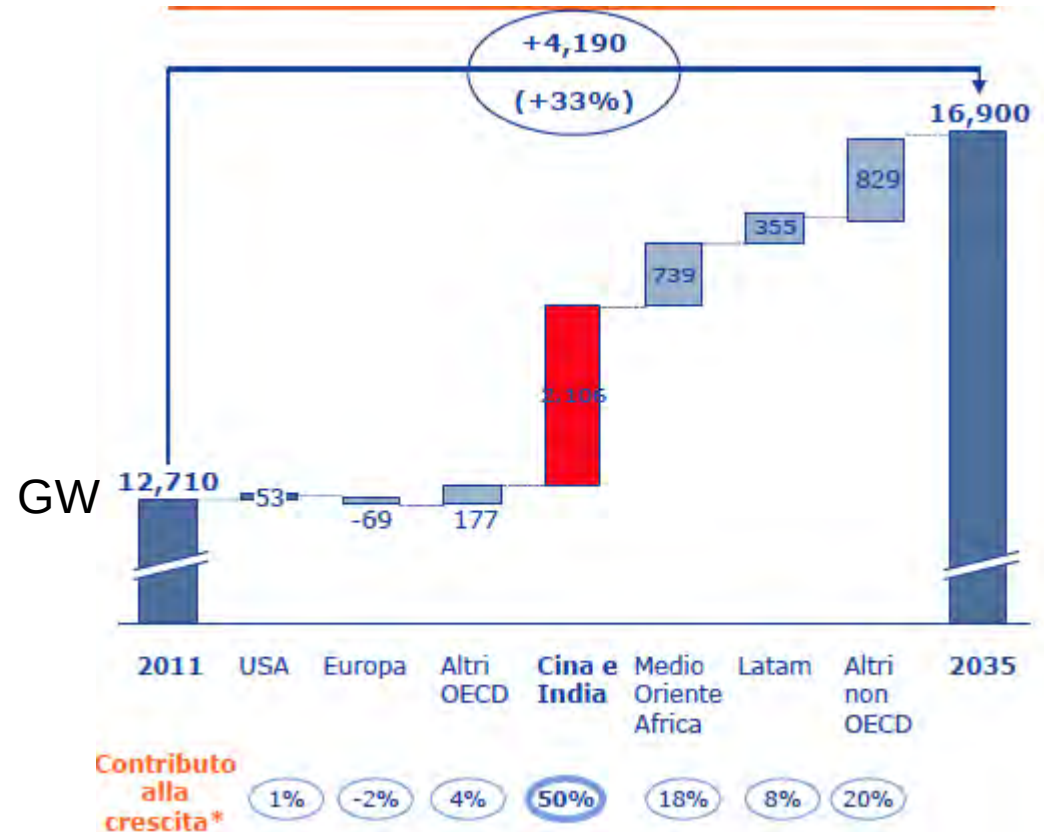
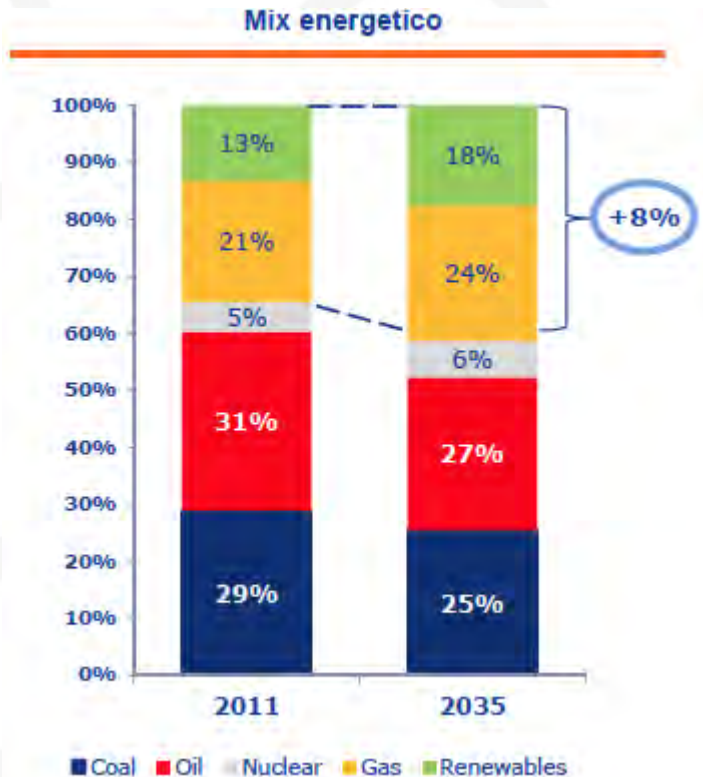
fornire continuità all'attività di ricerca di medio termine, multidisciplinare, sotto condizioni già stabilite da un contratto tipo, che diventi un semplice ordine di servizio per le singole attività (riduzione dei tempi di attivazione) e che regoli gli aspetti di proprietà intellettuale e costi standard

- accessi facilitati ai laboratori dell'Ateneo*
- formare una nuova figura di Ricercatore che si muova tra le metodologie della ricerca accademica e le esigenze della realtà industriale*

Modello POLIMI R&D con imprese: JRC



Scenario energetico nei prossimi 25 anni (IEA)



- ❑ dominio delle fonti fossili (81 → 76% ; 10.3 → 12.8 TW **+24.3% !!**)
- ❑ limitato contributo delle fonti rinnovabili (incluso idroelettrico)
- ❑ impatto dei paesi emergenti

Esempi sviluppati in ambito JRC

Esistono ampi margini di sviluppo per nuove tecnologie in ambito oil&gas

- ❑ *Development of Smart Material for tertiary recovery (with ENI)* 
TRL 5-7
- ❑ *Amphiphilic magnetic nano-particles and aggregates for the removal and capture of hydrocarbons* 
TRL 5-6
- ❑ *RTILs for oil industry: Desulfurization of oil without H₂* 
TRL 3-4



ASSOLOMBARDA

Prof Maurizio Masi
Direttore del
Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”
Politecnico di Milano
Piazza Leonardo da Vinci 32
20133 Milano

Tel. +39 022399 3201/3131
Fax. +39 022399 3280/3180
Email: maurizio.masi@polimi.it
Web: www.chem.polimi.it

www.assolombarda.it
www.farvolaremilano.it
www.assolombardanews.it
 [@assolombarda](https://twitter.com/assolombarda)
 [company/assolombarda](https://www.linkedin.com/company/assolombarda)
 [AssolombardaTV](https://www.youtube.com/AssolombardaTV)
 [@assolombarda](https://www.instagram.com/assolombarda)



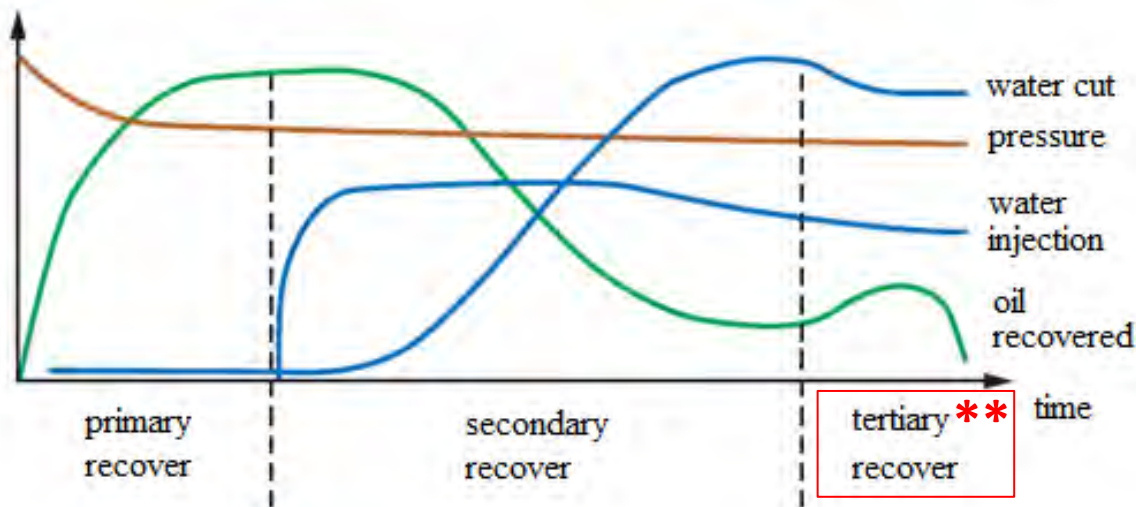
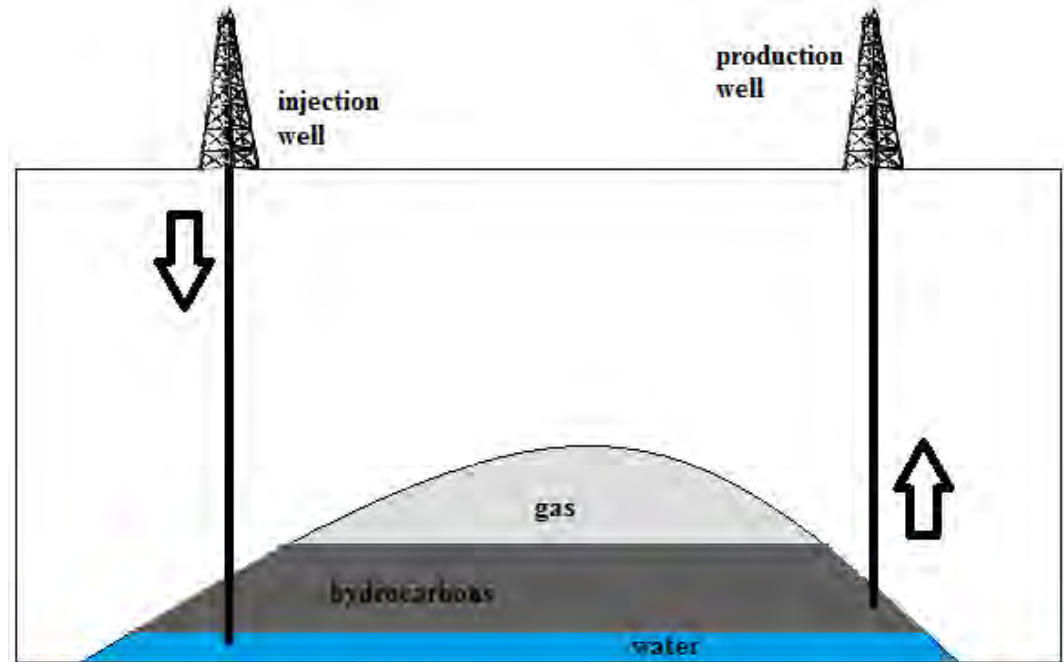
Part 1. “Development of Smart Material for tertiary recovery”

- **Smart Materials through Production Well**
 - Inverse emulsion of high absorbent Hydrogel via FRP (free radical polymerization)*

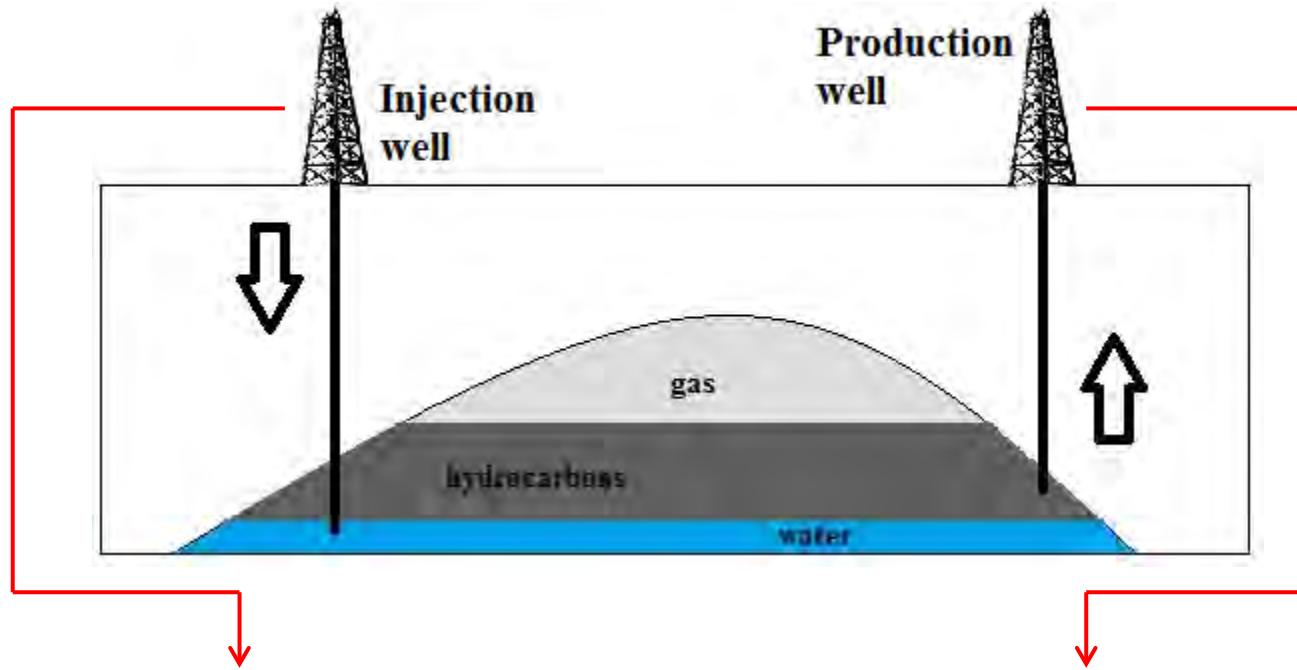
* Patent pending eni



Structure of an oil extraction site



**** EOR method
&
Water Shut-off
method**



Smart Materials through Injection well

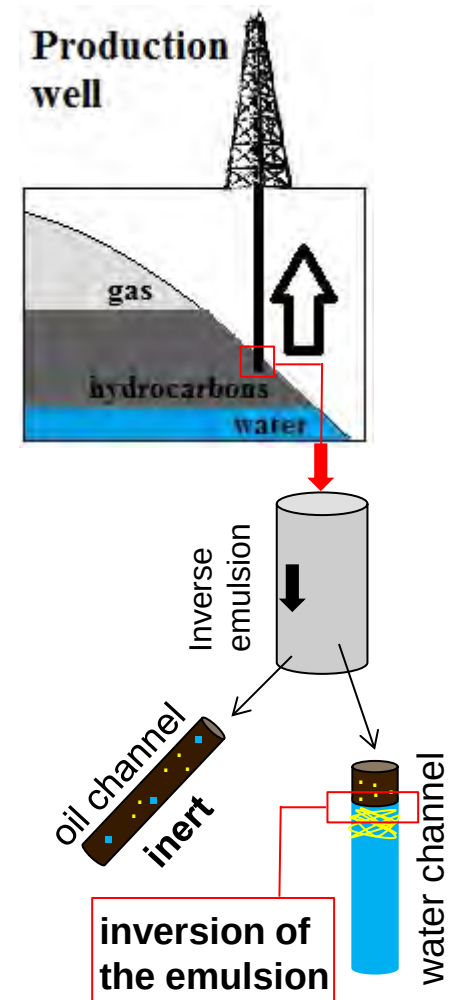
- Thermoresponsive Polymer
- Emulsions in water of Polymer with degradable shell

Smart Materials through Production well

- Inverse emulsion of high absorbent Hydrogel via FRP
- Inverse emulsion of viscosifiers polymers (eg. Cellulose, Starches)

Requirements:

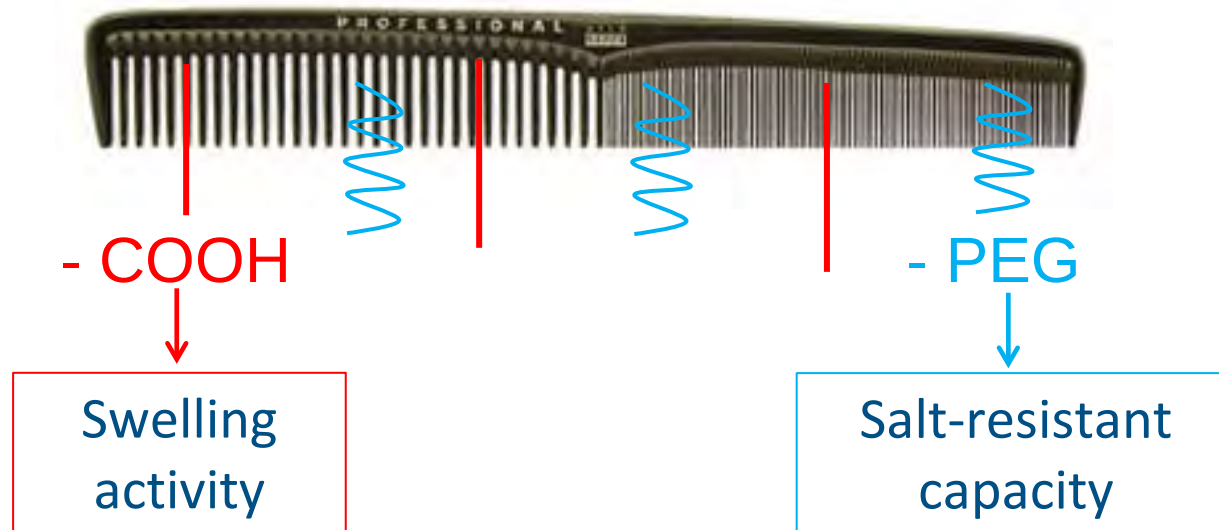
- **Action selectivity.** Smart materials act after the inversion of emulsion only in contact with appropriate quantities of water, and not indistinctly in the oil well (e.g. irreducible water).
- **Salt resistant capacity.** The specific chemical structure of smart materials (e.g. PEG and/or OH- moieties) allows them to swell in contact with water with high amounts of salt dissolved (eg. 90 g / l NaCl) and enhance significantly its viscosity.
- **Application range.** the possibility to organize the hydrogels in micro and nano particles allows their application to a variety of oil wells, from the porous one to the fractured.



Inverse emulsion of high absorbent Hydrogel via FRP

Selected Material :

Copolymeric high absorbent hydrogels of acrylic, methacrylic acid and its pegylated esters micro and nano organized in inverse emulsions (in hydrocarbon based solvents e.g. Diesel, Kerosene, Gasoline).





Nano-Hydrogels

Diameter : 100 nm to 250 nm

PDI : < 0.2

Concentration : 20% $w_{\text{polymer}}/w_{\text{tot}}$

Inverse emulsion

Diameter : 120nm

PDI : 0.15

water



gasoline

Polymer- water solution

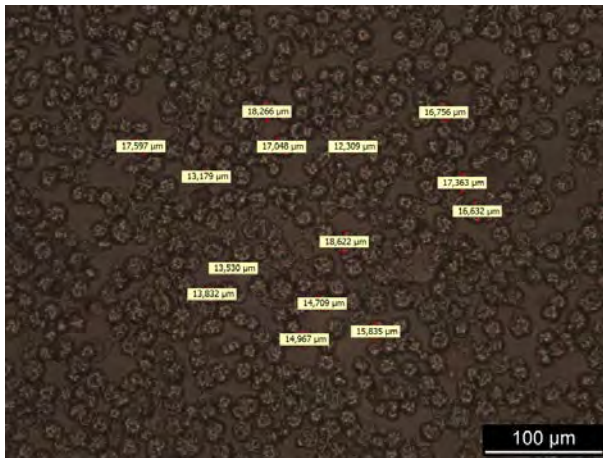
Diameter > 380nm

(Sx) inverse emulsion contacted with water, NaCl 85 g/L.

(Dx) sample after inversion of the emulsion



Micro-Hydrogels



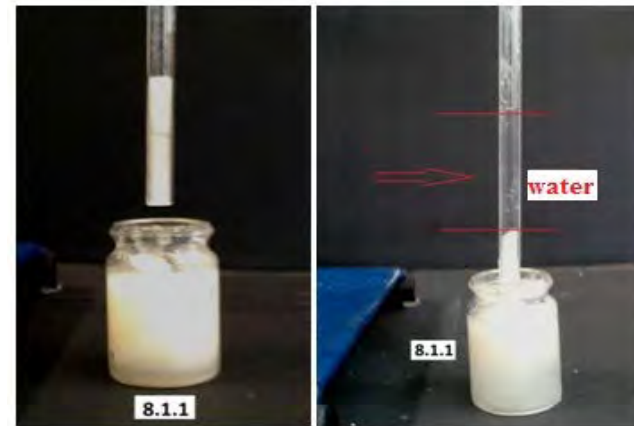
Micro-gel in inverse emulsion



Micro-gel after contact with water (NaCl 85g/L)



Micro-gel contacted water (NaCl 85g/L);
Micro-gel emulsion : water = 1:2

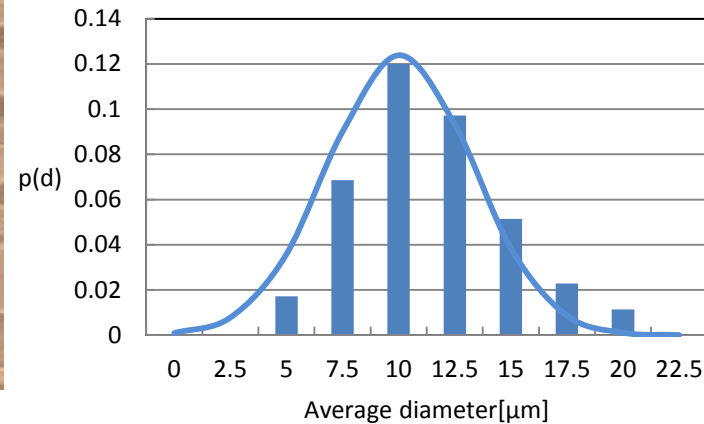
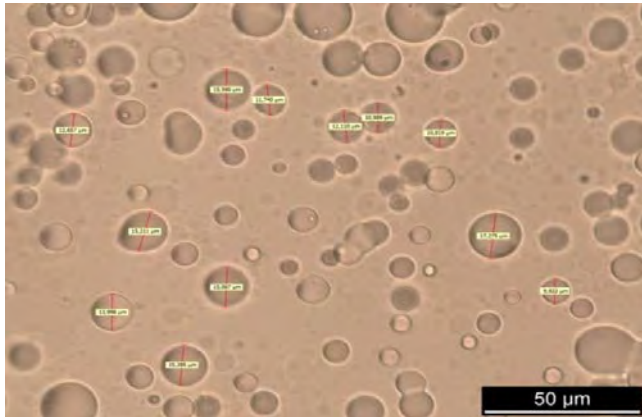


Application of micro-gel through
a 0.12 inches tube

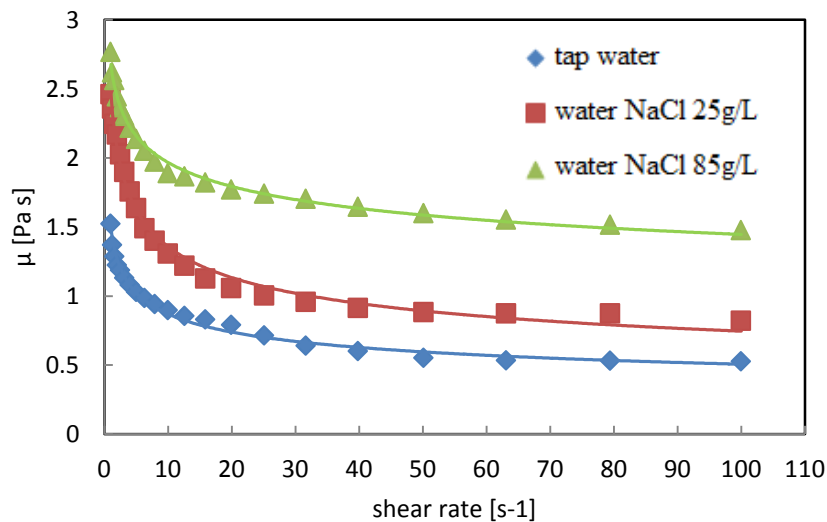


Inverse micro-emulsion

- produced monodispersed micro-particles with a massive concentration of dispersed phase of 15%



Average d: 10 μm
Std deviation: 3.2 μm



- Viscosity of water enhanced
- Major enhancement in the most concentrated salt water
- Micro-gel emulsion : water = 1:1

Graph. Viscosity of water after the application of the micro-inverse emulsion



Part 2. “Amphiphilic magnetic nano-particles and aggregates for the removal and capture of hydrocarbons” **

- Removal of hydrocarbons and lipophilic substances dispersed in water
- Removal of hydrocarbons and lipophilic substances in polluted soils
- Extraction of oil and lipophilic from solid systems (e.g. bitumen from tar sands)

- *Phosphate recovery from extinguishing powders*
- *Metals recovery from galvanic wastewaters*

** Patented Polytechnic of Milan

Date : 24/06/2014

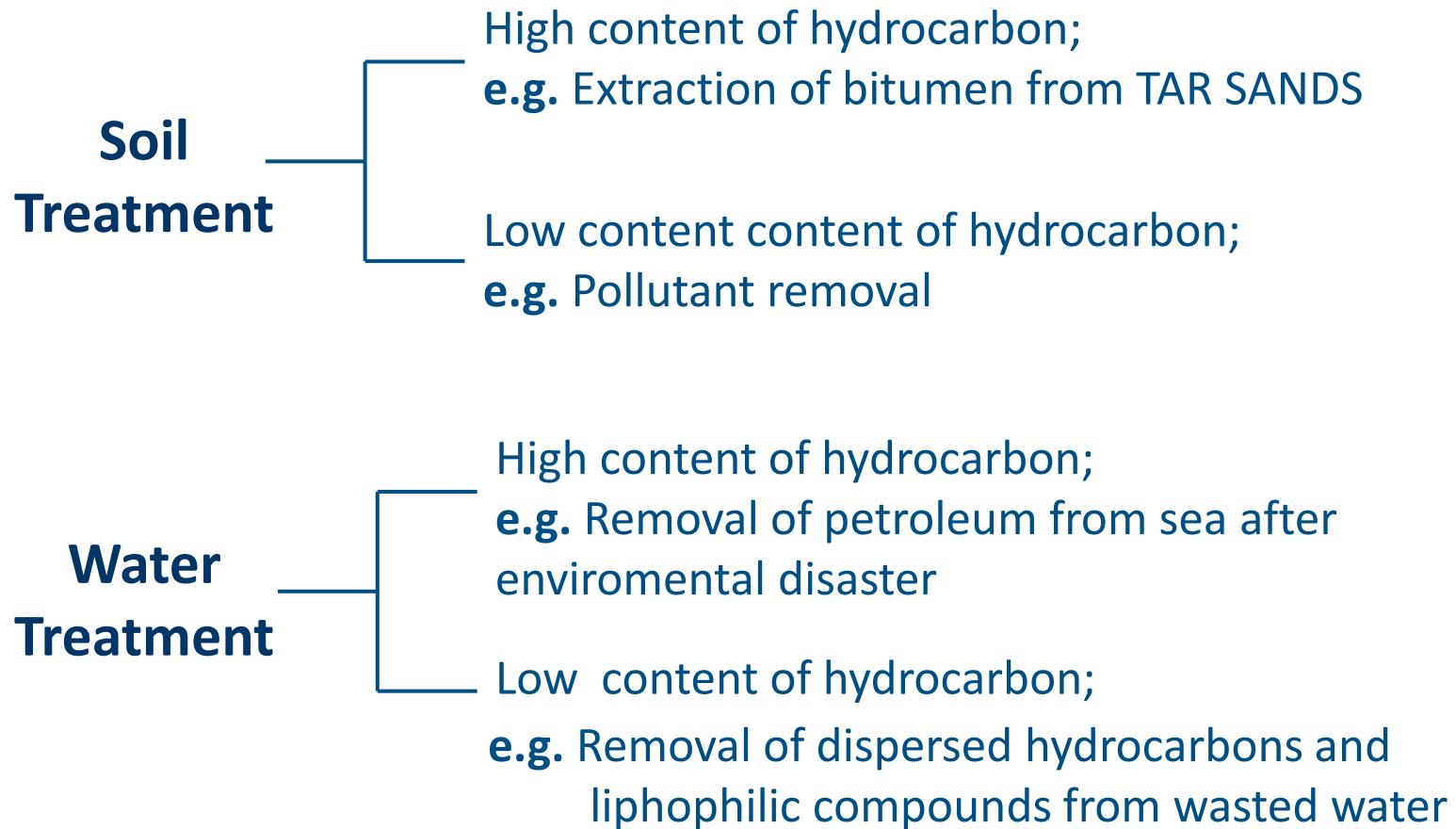
CH.14.001.A

NPs made of magnetite (Fe_3O_4) covalently coated with oleic acid and a sulphonate surfactant.





Applications

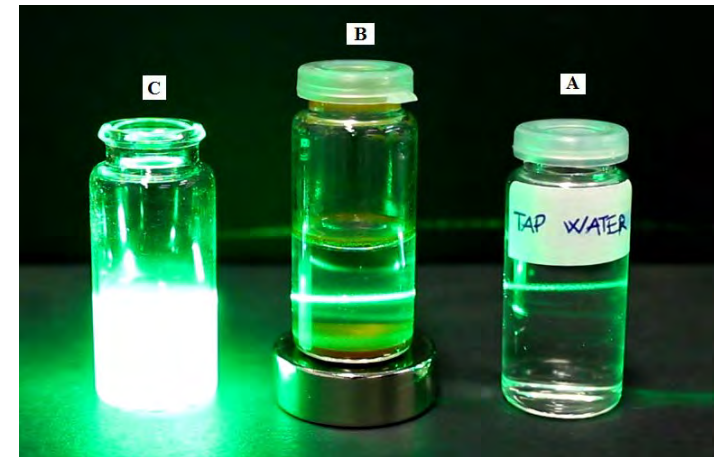




Experimental Pattern

- Treated water wasted with different ppm of crude oil.
- Percentage of dry NPs over the amount of wasted water = 0.2 %.
- Used a magnet to attract te NPs after their application

ppm of crude oil	% dry NPs over the amount of water	% remainig oil in water after treatment
1000	0.2	<10ppm
2000	0.2	<10ppm
3000	0.2	<10ppm



A_ tap water

B_ emulsion : tap water/2000ppm of crude oil after using NPs

C_ emulsion : tap water/2000ppm of crude oil



Advantages

- An applying method relatively simple compared to common treatments used.
- A significant decrease in the costs of treatment of wastewater and contaminated soils.
- The particles are completely recyclable and reusable with performance comparable to the newly synthesized particles, after washing with a solvent for the removal of the hydrophobic/lipophilic phase captured.



Lipophilic compounds, hydrocarbons & metals removal

1

to remove lipophilic substances (i.e. fluorinated species, silicones oils, lubricants, ..) from industrial wastewaters / contaminated soils with the goal of purification



2

To effectively and efficiently remove metals (i.e., Fe, Cr, Zn, Mn, As, B, ...) from polluted waters?



3

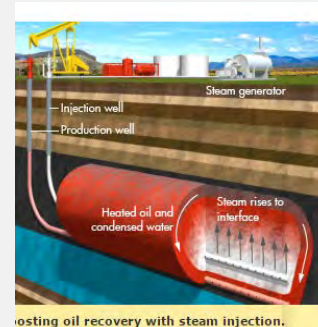
To remove and recover oils from oil & hydrocarbons spills in seawaters or soil, to remediate accidents and environmental disasters



Hydrocarbons extraction

4

To increase oil recovery from oil reservoirs (average 30%) through EOR methods (*Enhanced Oil Recovery*)



5

To optimize hydrocarbons extraction from solid systems like tar sands



More than solvents...

RTILs for oil industry: Desulfurization of oil without H_2



Highway Diesel Fuel



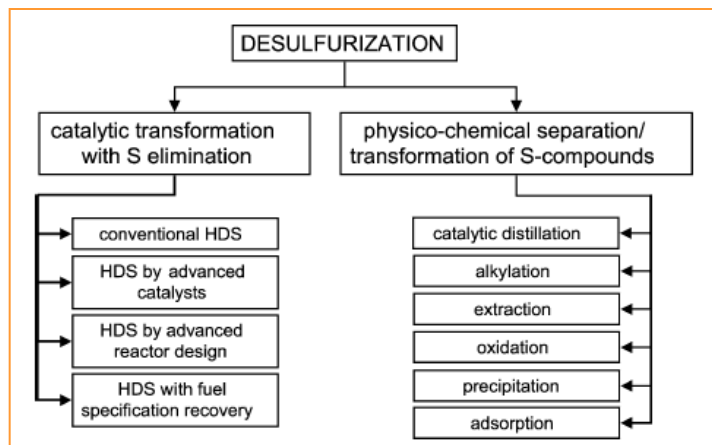
$S < 10 \text{ ppm}$

<http://www.dieselnets.com/standards/eu/fuel.php>



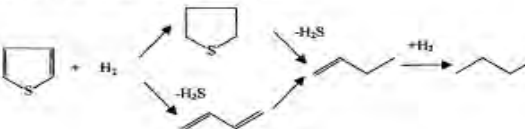
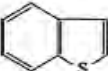
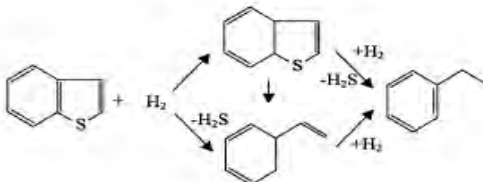
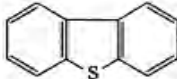
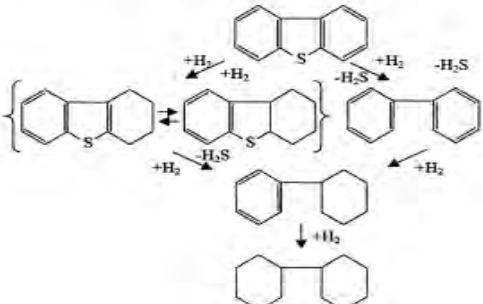
$S < 15 \text{ ppm}$

<http://www.epa.gov/otaq/fuels/dieselfuels/index.htm>



Hydrodesulfurization HDS

Babich & Moulijin
Fuel **2003**, 82, 607

Type of organic sulfur compound	Chemical structure:	Mechanism of hydrogenating reaction ^{a)}
Mercaptanes	$R-S-H$	$R-S-H + H_2 \rightarrow R-H + H_2S$
Sulfides	R^1-S-R^2	$R^1-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Disulfides	$R^1-S-S-R^2$	$R^1-S-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Thiophene		
Benzothiophene		
Dibenzothioephene		



More than solvents...

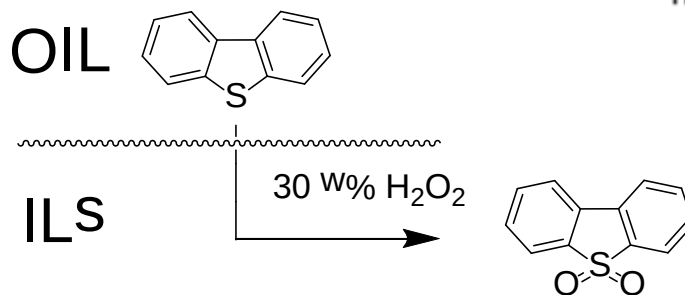
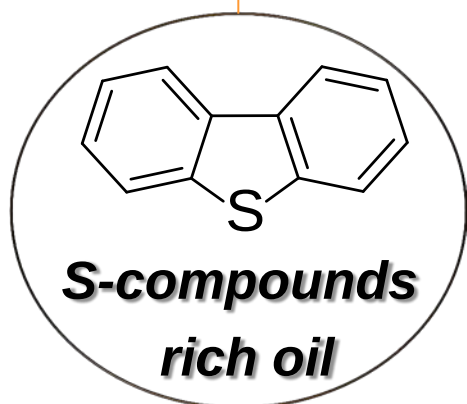
RTILs for oil industry: Desulfurization of oil without H₂



Oxidative desulfurization

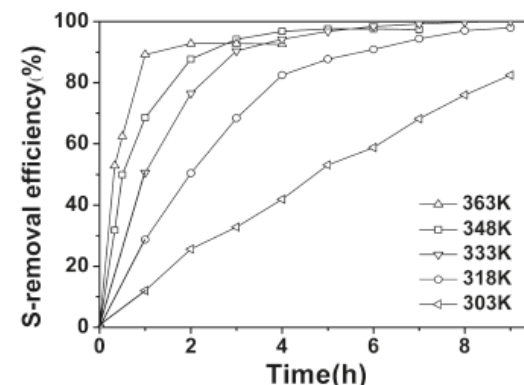
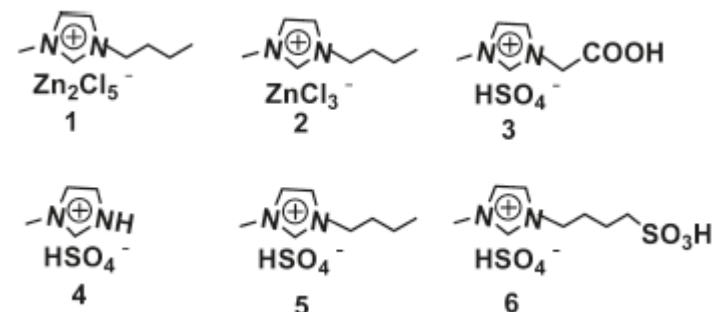
by acidic ILS

(ILs are both extractant and catalyst)



Ge et al.

Ind. & Eng. Chem. Res. **2011**, 50, 13686



Extractive desulfurization by tailored ILs

- Not mixable with oil
- Not flammable
- Selective for S-compounds

Hansmeyer et al. *Green Chem.*, **2011**, 13, 1907

Verdà et al. *Ibidem*, **2011**, 13, 2768



More than solvents...

RTILs for oil industry: Gas separation



Raw natural gas

SOUR

High content of H_2S

ACID

*High content of CO_2
or CO_2+H_2S*

SWEET

Low content of CO_2 and H_2S



**Alkanolamine based processes
(MEA, DEA, MDEA...)**

Carbamate/carbonate formation

***Chemical absorption covers 95% of
gas sweetening in USA***

Karadas et al. *Energy&Fuel* 2010, 24, 5817



Disadvantages:

Loss of reagents

**Transfer of water into the gas stream
Formation of corrosive byproducts by
amine degradation**

**Energy consumption during
regeneration ($4GJ/ton CO_2$)**

Romeo et al. *Appl. Therm. Eng.* 2008, 28, 1039

Karadas et al. *Energy&Fuels* 2010, 24, 5817



More than solvents...

RTILs for oil industry: Gas separation

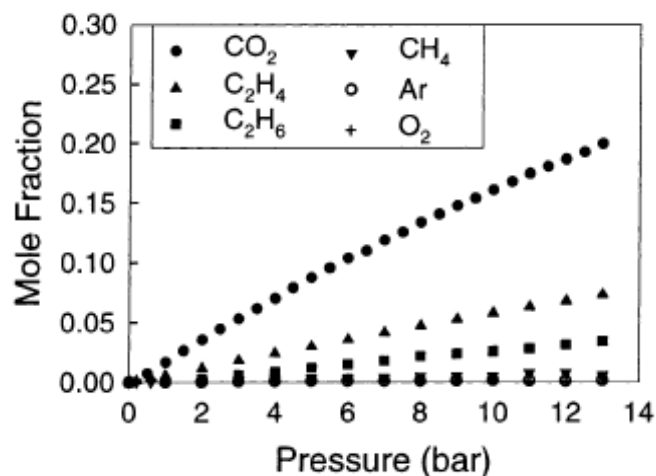


The principle:

Use of RTILs as physical solvents.

High solubility for CO₂

Low solubility for CH₄, N₂, H₂, O₂ ...



Gas solubilities (298 K) in bmim PF₆

$$H_1(T,P) \equiv \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \approx \frac{P_1}{x_1}$$

Ratio of gas pressure over molar fraction
of gas in the liquid phase

TABLE 1: Henry's Constants (bar) for Gases in [bmim][PF₆]

	10 °C	25 °C	50 °C
H ₂ O ¹³	0.09 ± 0.02	0.17 ± 0.02	0.45 ± 0.05
CO ₂	38.7 ± 0.4	53.4 ± 0.3	81.3 ± 0.5
C ₂ H ₄	142 ± 14	173 ± 17	221 ± 22
C ₂ H ₆	284 ± 47	355 ± 36	404 ± 41
CH ₄	1480 ± 110	1690 ± 180	1310 ± 290
O ₂	23 000 ± 15 000	8000 ± 5400	1550 ± 170
Ar	22 000 ± 10 000	8000 ± 3800	1340 ± 220
CO	nondetect (> 20 000)	nondetect (> 20 000)	nondetect (> 20 000)
N ₂	nondetect (> 20 000)	nondetect (> 20 000)	nondetect (> 20 000)
H ₂	nondetect (> 1500)	nondetect (> 1500)	nondetect (> 1500)

Anthony et al.

J. Phys. Chem. B, 2002, 106, 7315-7320