12-5 hydrogen production and energy storage

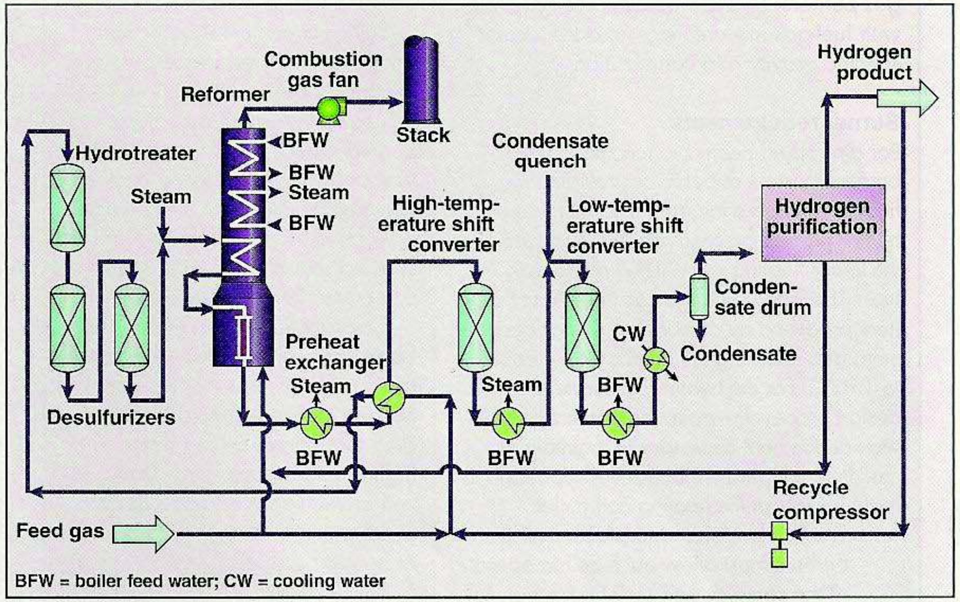
- technical processes and cost

Hydrogen Production By Steam Reforming

Management of the gas is critical for petroleum refiners

Ray Elshout
Energy Systems Engineering

Steam reforming of natural gas at petroleum refining facilities is the predominant means of producing hydrogen in the chemical process industries (CPI). Areas where hydrogen is heavily consumed include ammonia production, the cryogenics industry and methanol production (Table 1)[*1*]. Because hydrogen needs within various sectors of the CPI are at their highest



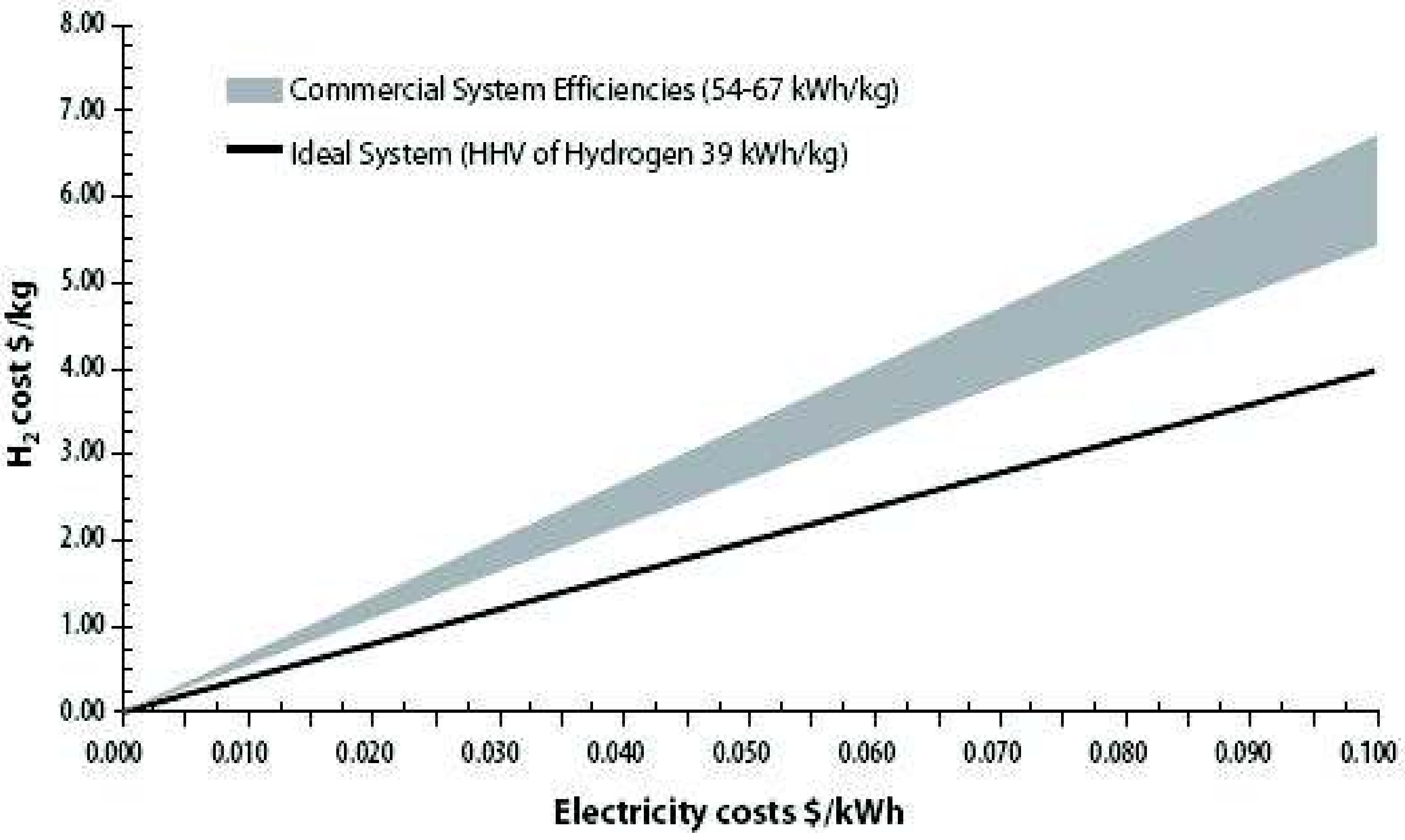
BFW = boiler feed water; CW = cooling water

FIGURE 1. **Steam-methane reforming is still responsible for the bulk of hydrogen production in petroleum refineries**

diesel fuel. Management of hydrogen is | hydrogen from the users requiring

NREL (DOE)
National Renewable Energy Laboratory

Figure 1. Hydrogen costs via electrolysis with electricity costs only



Hydrogen cost

- To day the cheaper hydrogen is produced by **steam-methane reforming**
- $CH_4 + H_2O$------$3H_2 + CO$ (755-1080K) Δ=206MJ
- *from CH4 Cost 400$/T*
- **Hydrogen from electrolysis** :1800-2000$/T for an electrical power at 50$/MWh

efficiency of the electrolyser for hydrogen production

- CEA/ENSMP thesis R.Rivera-Tinoco 30 march 2009
- conversion rate:
- 75% at high temperature electrolysis (EPR temperature)
- NREL (innovation for our energy future)-DOE
- **water to hydrogen conversion efficiencie:80 to 95%**
- 56% for Proton’s proton exchange membrane(PEM)
- 73% for Stuart’s and Norsk Hydro’s bipolar alcaline systems
- 64% for Avalence and Teledyne units
- **75% to 85% second generation of solid oxide electrolyser cells (SOECs)**
- -

estimation cost for Hydrogen

- **from DOE**

100kg/day 8.09$/kg - **1000kg/day 4.15$/kg**

to reach 3.00$/kg the electricity cost must be below than 4¢ to 5.5¢ per kWh

from Riso National Lab (Denmark)

4.8 $/Gj for H2 production assuming an electricity price of 3.6$/Gj (equivalent to 29$/barrel oil) to 7.8 $/Gj for CH4 production (48$/barrel oil) or 71 cents /kg H2 using HHV at 950°C for SOECs

if we take into account the degradation propertie of HHV it gives 108 cents/kg or 46$/barrel

from ENSMP/CEA (2009) thesis R.Rivera-Tinoco

for a 1.5 kg/s hydrogen production and a cost of electricity between **40to 50 euros /MWh**

the cost is between **1.9 to 2.2 euros /kg H2**

(electrolyser 900°C with high temperature water 523K from EPR)

notice the price of crude oil barrel is between 72 to 112$/barrel in 2010

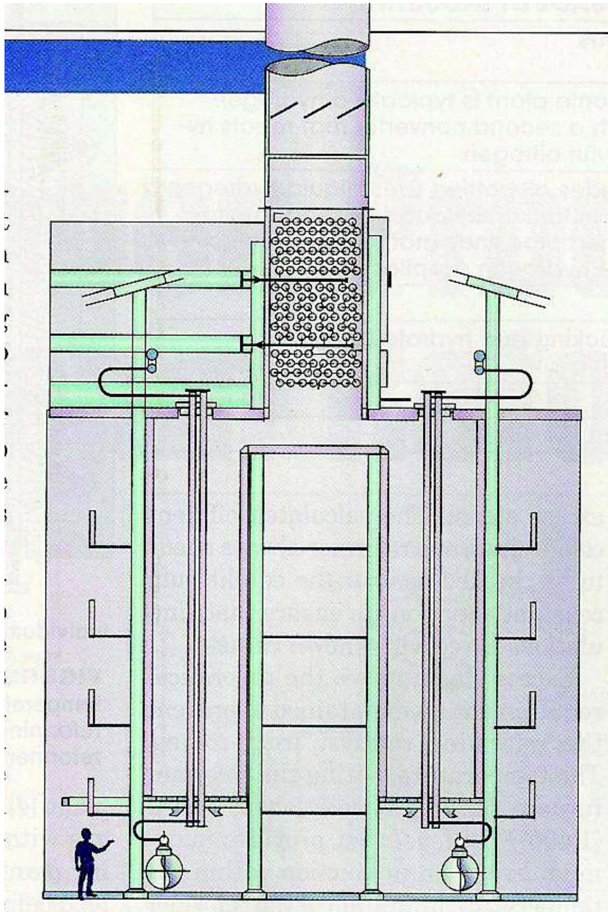


FIGURE 3. A typical reformer furnace could have over 300 burners

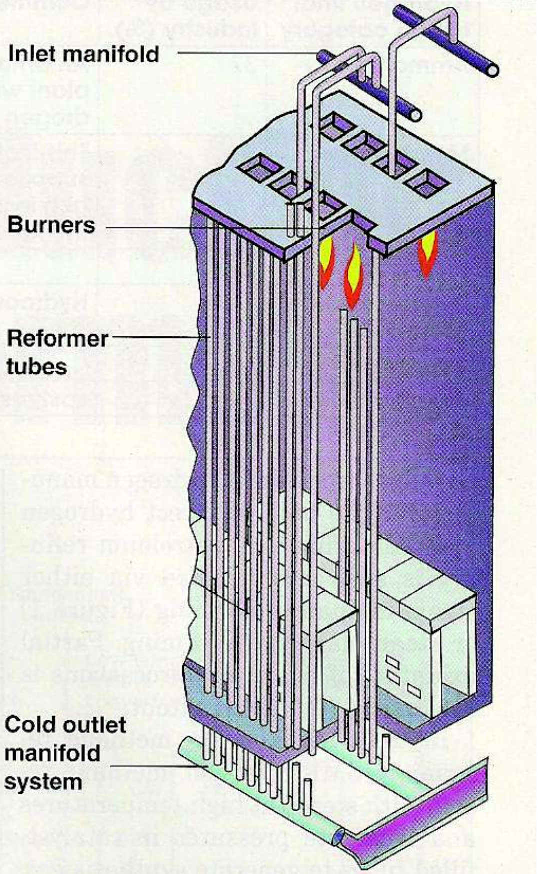


FIGURE 4. Hydrogen plants with single heaters and capacities up to 100,000 ft^3/d have used a down-firing approach

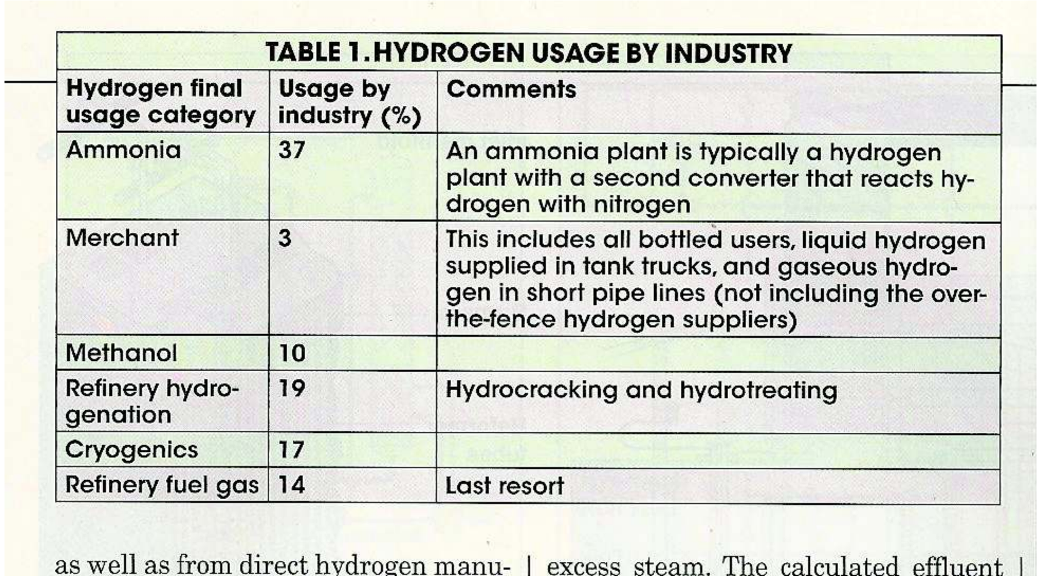


TABLE 1. HYDROGEN USAGE BY INDUSTRY

Hydrogen final usage category	Usage by industry (%)	Comments
Ammonia	37	An ammonia plant is typically a hydrogen plant with a second converter that reacts hydrogen with nitrogen
Merchant	3	This includes all bottled users, liquid hydrogen supplied in tank trucks, and gaseous hydrogen in short pipe lines (not including the over-the-fence hydrogen suppliers)
Methanol	10	
Refinery hydrogenation	19	Hydrocracking and hydrotreating
Cryogenics	17	
Refinery fuel gas	14	Last resort

as well as from direct hydrogen manu-

excess steam. The calculated effluent

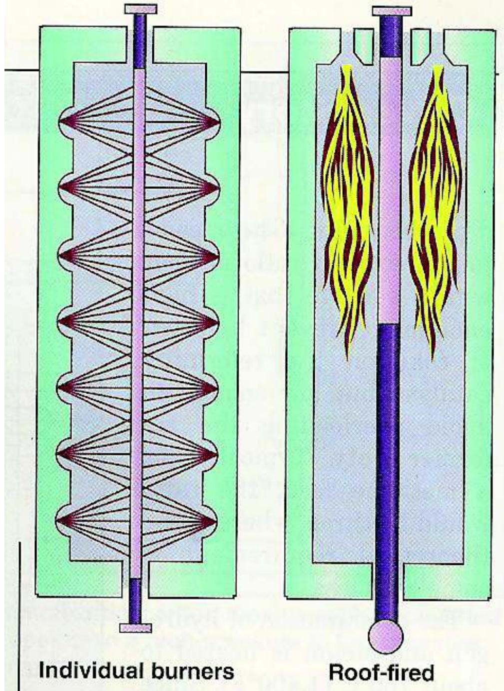


FIGURE 2. Maintaining a tube-wall temperature that is hot enough for the reforming reaction is a critical factor in reformer heater design

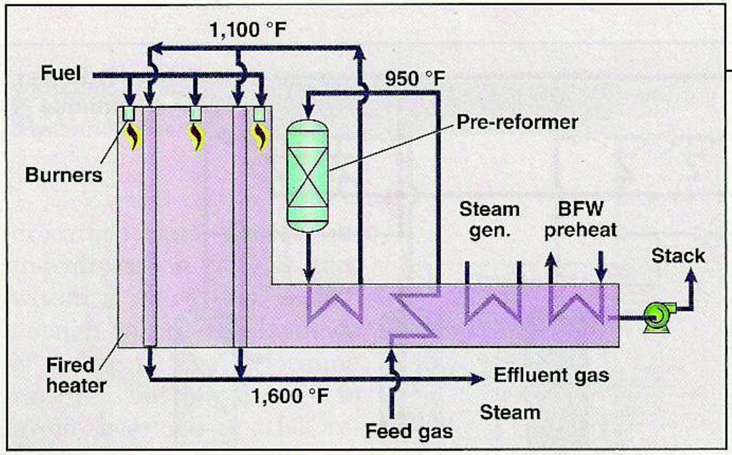


FIGURE 7. A pre-reformer breaks down heavier hydrocarbons into methane ahead of the reforming reactions

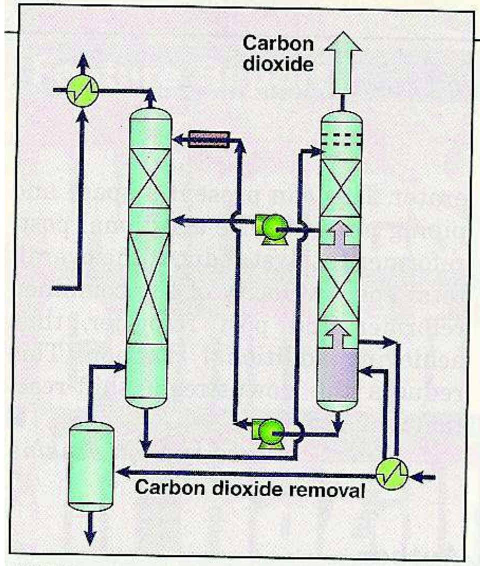


FIGURE 5. Most older units remove carbon dioxide from the hydrogen-rich gas with a solvent

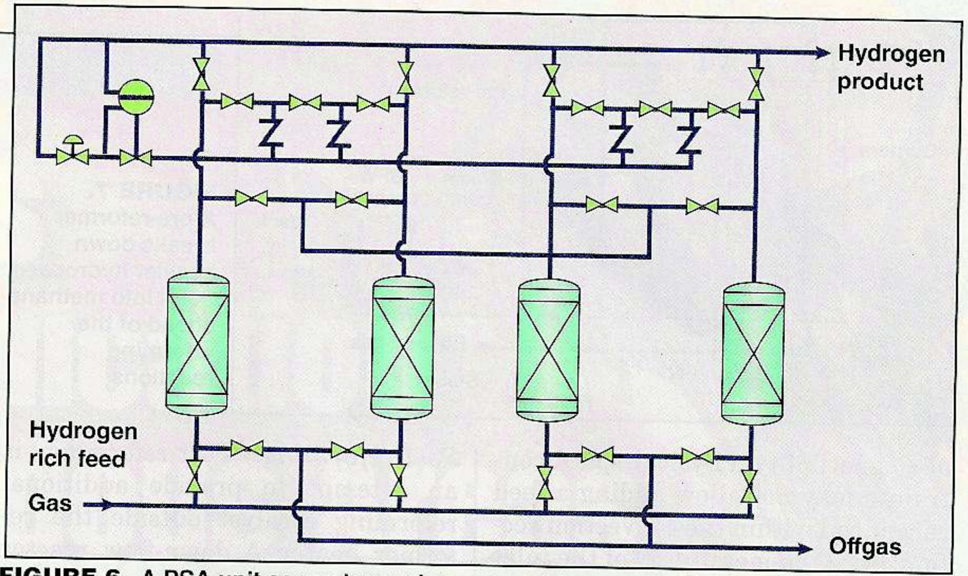


FIGURE 6. A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants

steam generator. BFW is fed through

Hydrogen purification

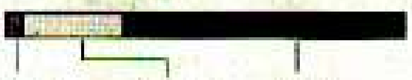
New cements for CO_2 storage

- new cements are able to Storage 0.6 ton
- of CO_2 per ton of cement
- It gives a positive material balance for CO_2

The Remix for a Planet Growing Warm

A Typical Concrete Mixture

BOX GIRDER



4% silica fume — 25% fly ash — 71% Portland cement

- 29 percent reduction in CO_2
  - *Silica fume reduces permeability to salt from road surface, protecting the rebar.*

PIERS

69% slag — 16% fly ash — 15% Portland cement

- 85 percent reduction in CO_2
  - *Fly ash adds strength.*

FOOTINGS

42% slag — 18% fly ash — 40% Portland cement

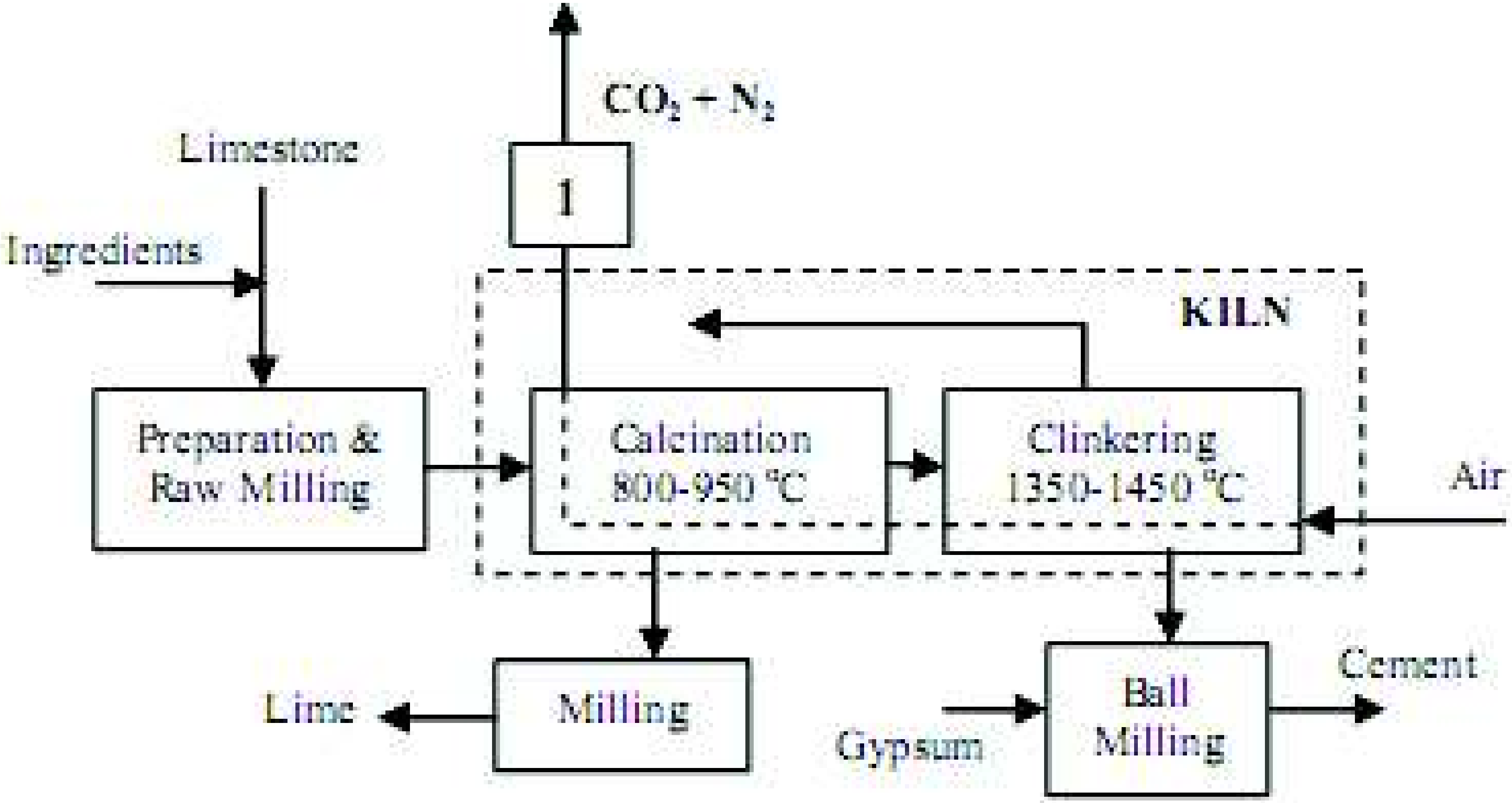
- 60 percent reduction in CO_2
  - *Slag improves resistance to corrosive sulfates in the soil.*

Sources: Kevin A. MacDonald, Cemstone Products Company; Richard D. Stehly, American Engineering Testing

The New York Times
SCIENCE & TECHNOLOGY

Mars 2009

Lime and cement processing



Flow sheet of a typical, state-of-the-art process for the manufacture of lime and cement.
After a preparation and raw milling step, lime is produced through calcination within a kiln.
Cement is produced in a further clinkering step and much more elevated temperatures.
Most CO_2 is produced from the decomposition of carbonates and burning of kiln fuel.
Final products are obtained following fine milling steps.

Nucleation of calcium carbonate clusters

Denis Gebauer, Antje Völkel, Helmut Cölfen*

SCIENCE 322,1819-1822 (2008),www.science mag.org /cgi/content/full/322/5909/1819/DC1

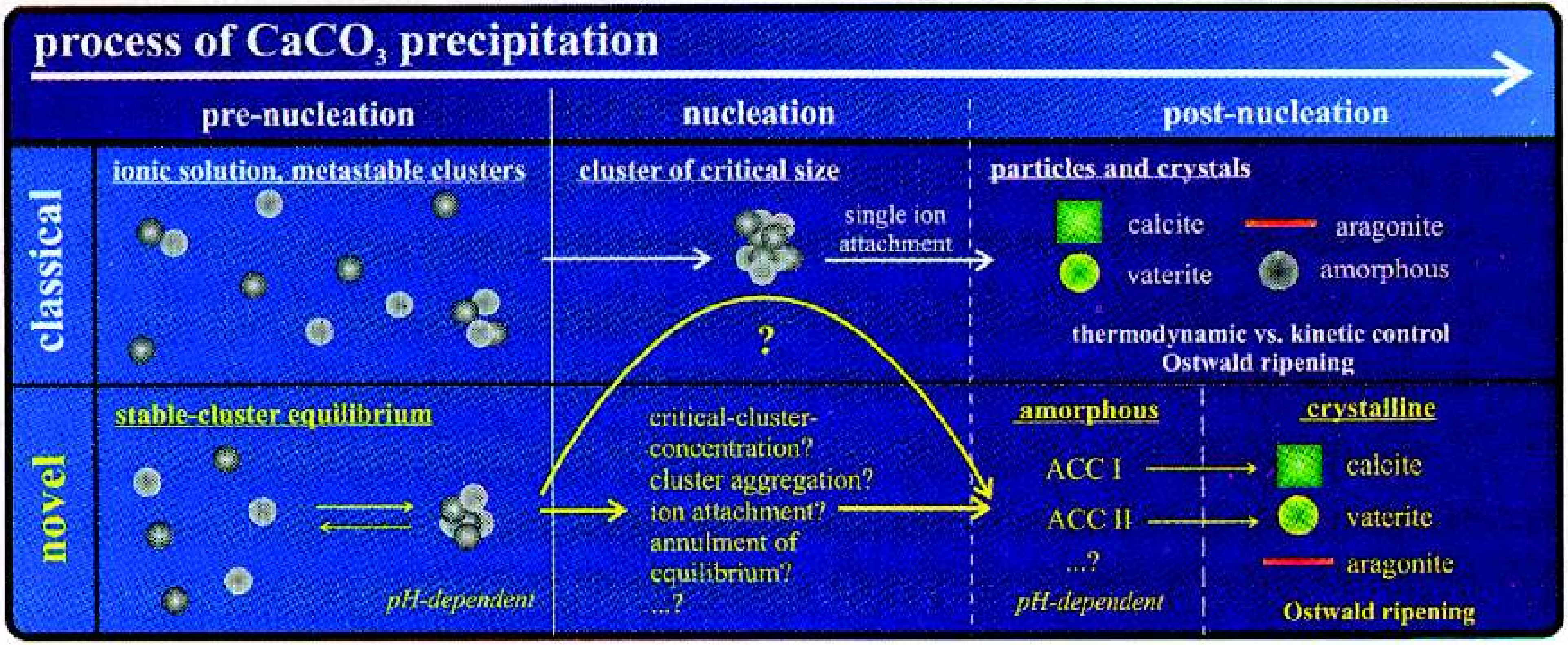


Fig. 4. Schema of the classical and novel view on precipitation (not to scale). Prenucleation-stage calcium carbonate clusters provide an early precursor species of different ACC phases giving rise to an alternative crystallization-reaction channel.

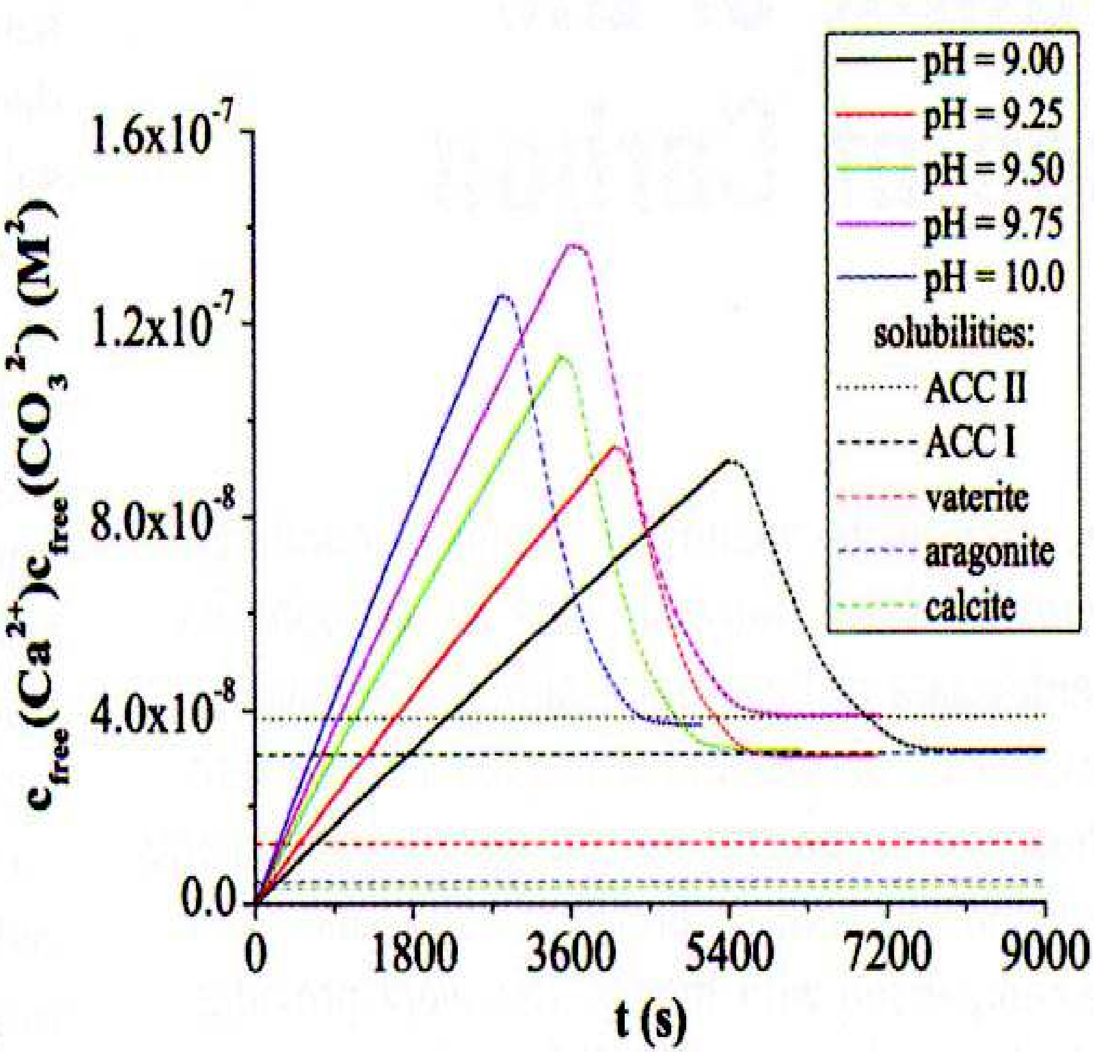


Fig. 3. Time development of the free ion product. Shown are averaged values obtained from a sample of three measurements. Because averaging is not appropriate during nucleation, the particular developments are indicated by dashed lines. We find two different ACC phases with solubility products of ~3.1×10^{-8} M^2 (ACC I) and ~3.8×10^{-8} M^2 (ACC II), corresponding to the pH dependency of the prenucleation cluster equilibrium. Also given are the solubilities of vaterite, aragonite, and calcite (27) (SOM section 2.5.)

SCIENCE 322,1819-1822 (2008),www.science mag.org /cgi/content/full/322/5909/1819/DC1

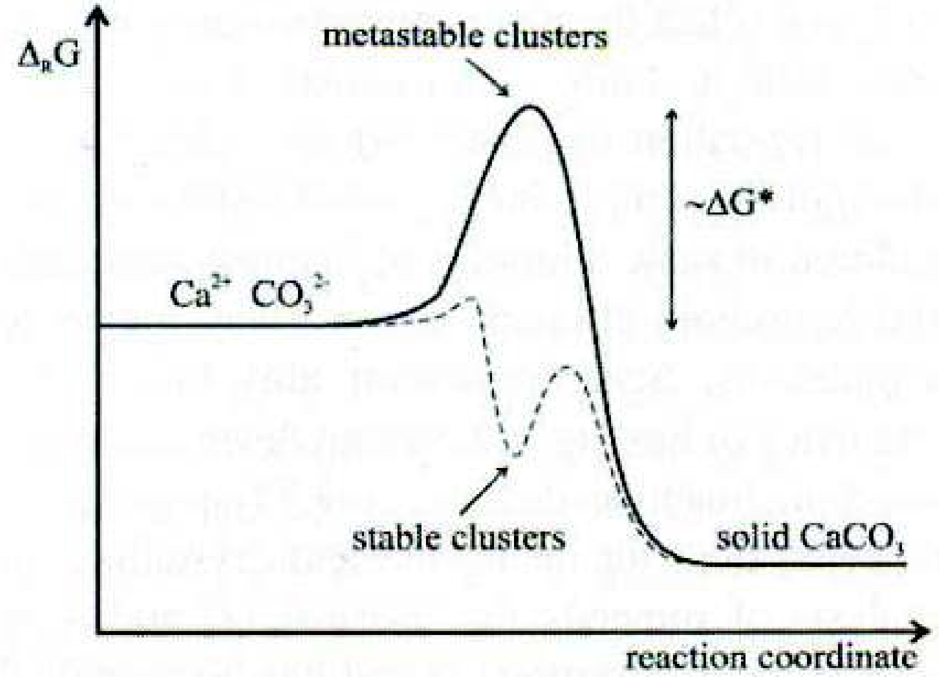
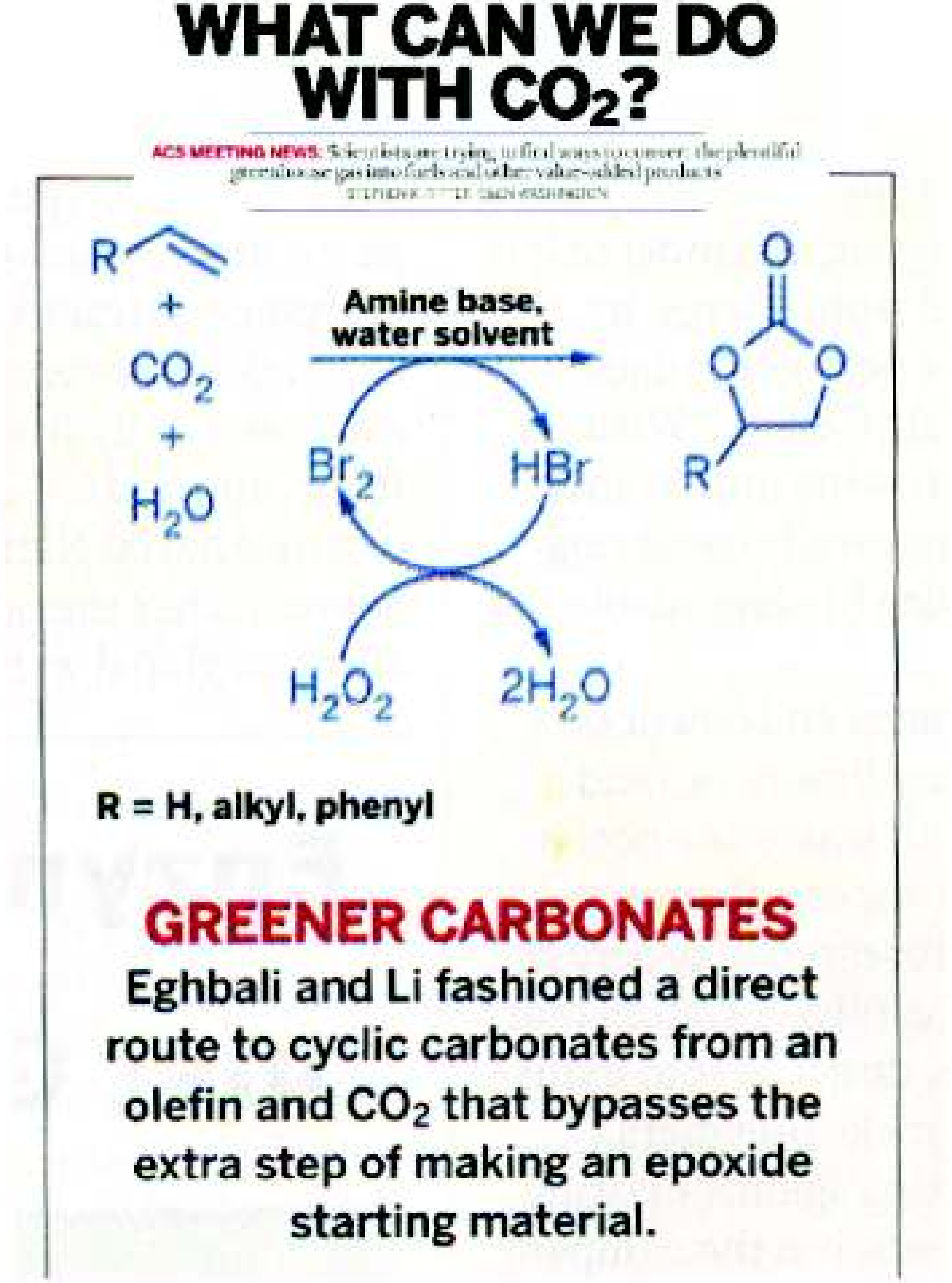


Fig. 2. Schematic illustration of the free reaction enthalpy $\Delta_R G$ versus the reaction coordinate. In the classical view (bold line), metastable clusters form and nucleation occurs when the critical nucleation enthalpy ΔG^* is overcome. In fact, stable clusters (dashed line) are formed with an activation barrier negligible compared to thermal energy. The structure and depth of the indicated minimum remain unknown, as well as the height of the activation barrier for nucleation.

SCIENCE 322, 1819-1822 (2008), www.sciencemag.org/cgi/content/full/322/5909/1819/DC1

Polymer synthesis from CO_2

- One of the main field for CO_2 polymerisation is to produce **polycarbonate** material which are biodegradable molecules and are able to storage 50% of CO_2 in the weight
- It decreases the consumption of hydrocarbons of 50%



WHAT CAN WE DO WITH CO_2?

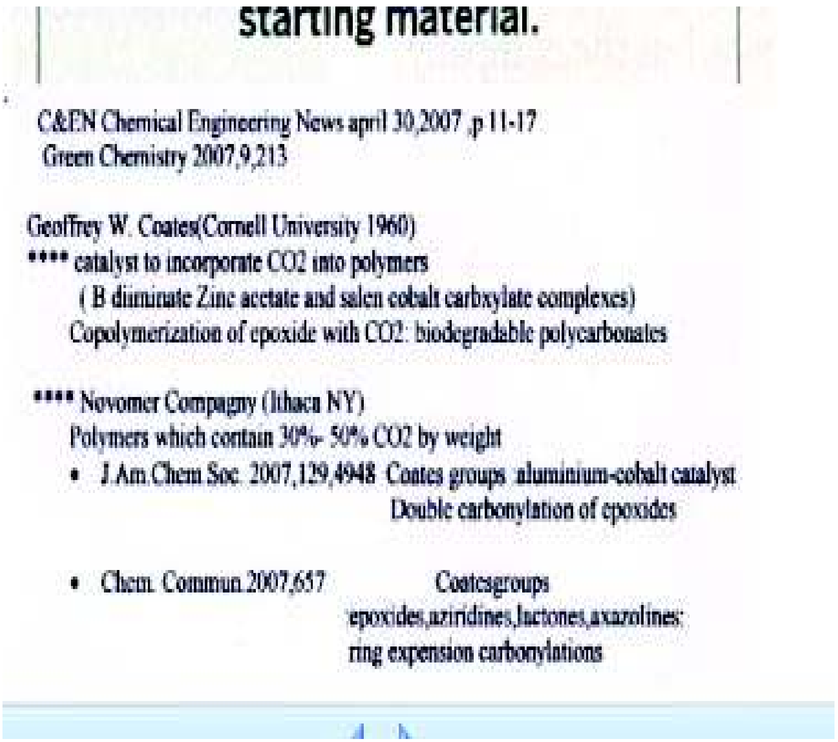
ACS MEETING NEWS: Scientists are trying to find ways to convert the plentiful greenhouse gas into fuels and other value-added products

R = H, alkyl, phenyl

GREENER CARBONATES

Eghbali and Li fashioned a direct route to cyclic carbonates from an olefin and CO_2 that bypasses the extra step of making an epoxide starting material.

Polymer synthesis with
CO_2 give polycarbonates
Which can storage 50%
Of CO_2 in weight



starting material.

C&EN Chemical Engineering News april 30,2007 ,p 11-17
Green Chemistry 2007,9,213

Geoffrey W. Coates(Cornell University 1960)
**** catalyst to incorporate CO2 into polymers
(B diiminate Zinc acetate and salen cobalt carbxylate complexes)
Copolymerization of epoxide with CO2: biodegradable polycarbonates

**** Novomer Compagny (Ithaca NY)
Polymers which contain 30%- 50% CO2 by weight

- J.Am.Chem.Soc. 2007,129,4948 Coates groups aluminium-cobalt catalyst
  Double carbonylation of epoxides

- Chem. Commun.2007,657 Coatesgroups
  epoxides,aziridines,lactones,axazolines:
  ring expension carbonylations

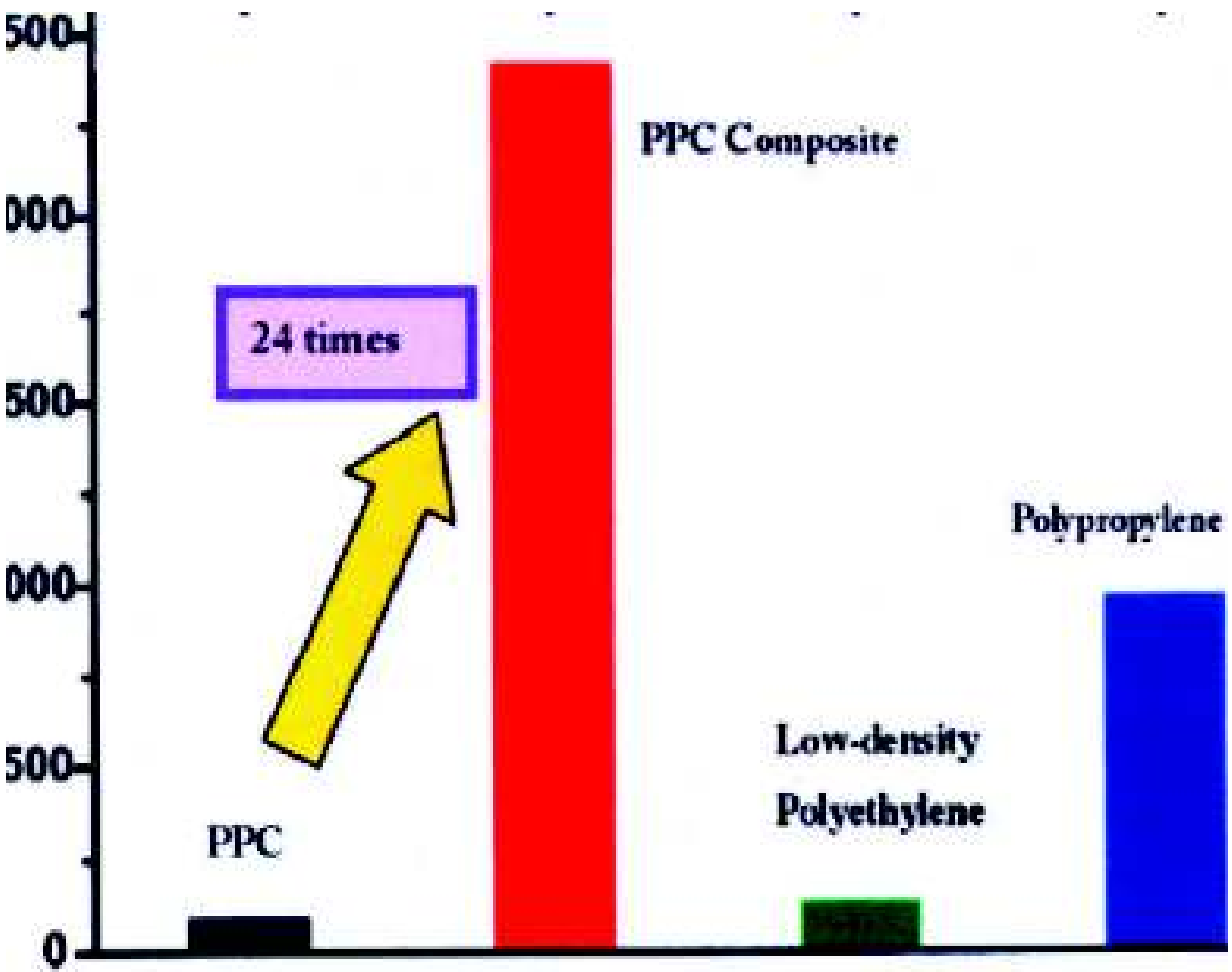


Figure Modulus data for PPC, PPC composite, and general-purpose plastics

Significant Property Improvement of plastic made from carbone dioxide
AIST Nov 18,2008
Hiroshi Shimizu,Li Yongjin,Nanotechnology Reseach Institute .Dir Nobutsugu Minani
Of National institute of Advanced Industrial Science and Technology (AIST)
President Hiroyuki Yoshikawa

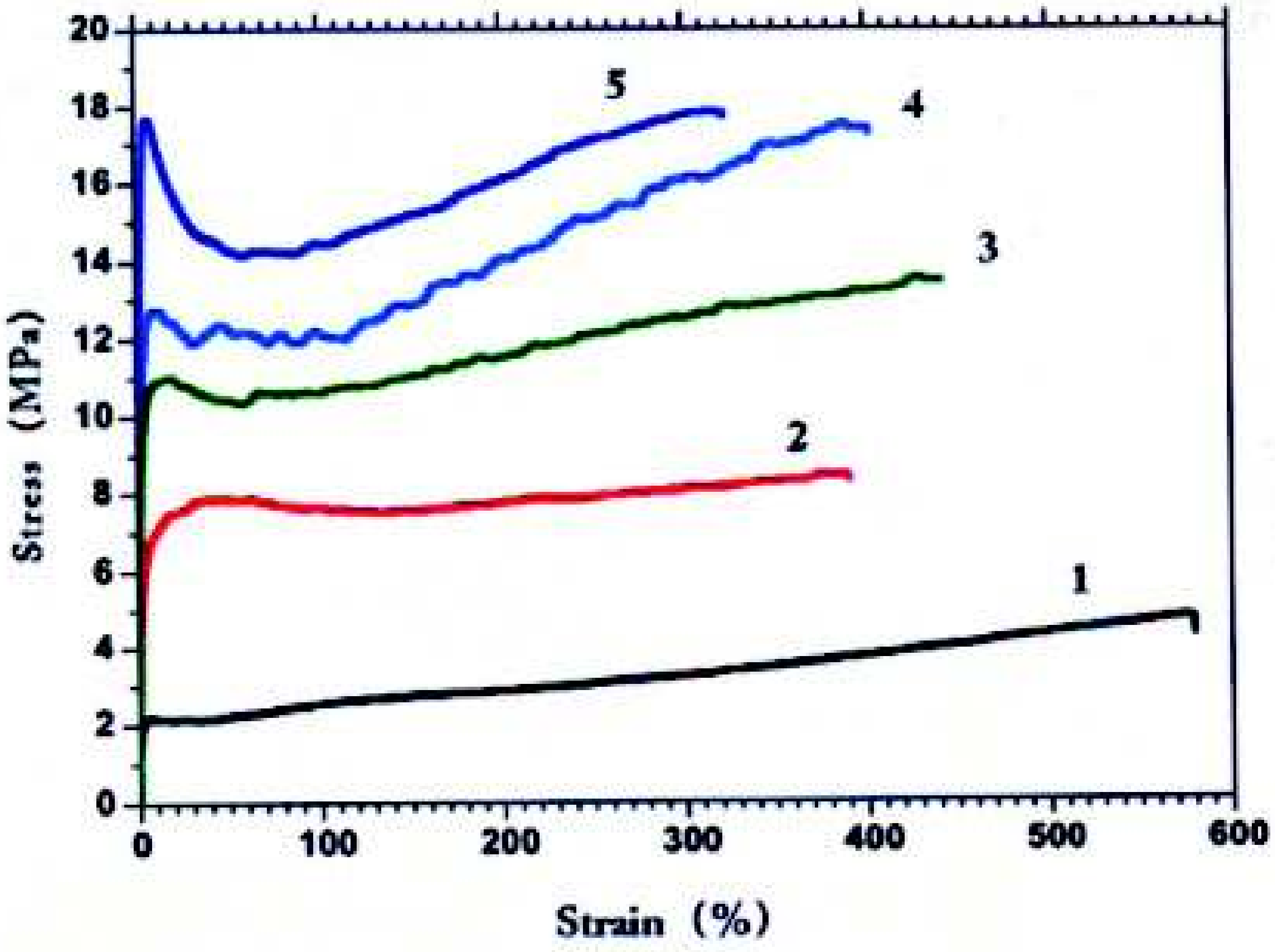


Figure 1 Stress – strain curves of PPC and PPC composites

[Curve 1: pure PPC, Curves 2 to 5 : PPC composites, (2 : PPC/X=70/30, 3 : PPC/X/Y=70/30/2.5, 4 : PPC/X/Y=70/30/10, 5 : PPC/X/Y=70/30/5)]

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Table 1 Mechanical properties at room temperature (25°C)

Sample	Modulus(MPa)	Strength(MPa)	Elongation at break(%)	Tg (°C)
PPC	101	4.8	578	30.4
PPC/X=70/30	1564	8.4	390.6	36.7
PPC/X/Y=70/30/5	**2431**	**17.9**	**322**	**39.8**
Low-density polyethylene	142	16.6	616	-128
iso-polypropylene	979	26.1	1077	-0.1

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President Hiroyuki Yoshikawa

CO2 for ENERGY STORAGE

- **energy storage** from decarbonated sources

- *** *technical and financial data*
- *** *capture unit from exhaust gas*
- *** *thermodynamic data*
- *** *Redox processes and catalysist material*

CO_2 a good candidat for
ELECTRICAL ENERGY STORAGE

Great advantages of chemical plant with REDOX reactions for carbon recovery:large chemical facilities

- **OXY + ne ---$\Rightarrow$ RED**
- $CO_2 + H_2 \longrightarrow CH_4 + 2\,H_2O$
- $\longrightarrow CH_3OH + H_2O$
- $\longrightarrow$ F.T. process

- **The key step is hydrogen production**

energy management and electrical storage

- evolution of the fossil carbon fields (including coal, petroleum, gas)

°**electrical energy storage**

°**carbon recovery**

°**energy cost and energy storage cost**

°**geopolitical problems** of the energy resources

European set plan 2008

a reversible storage of CO2 capture

gives **carbon resources**

for the futur of our civilization

Financial aspects

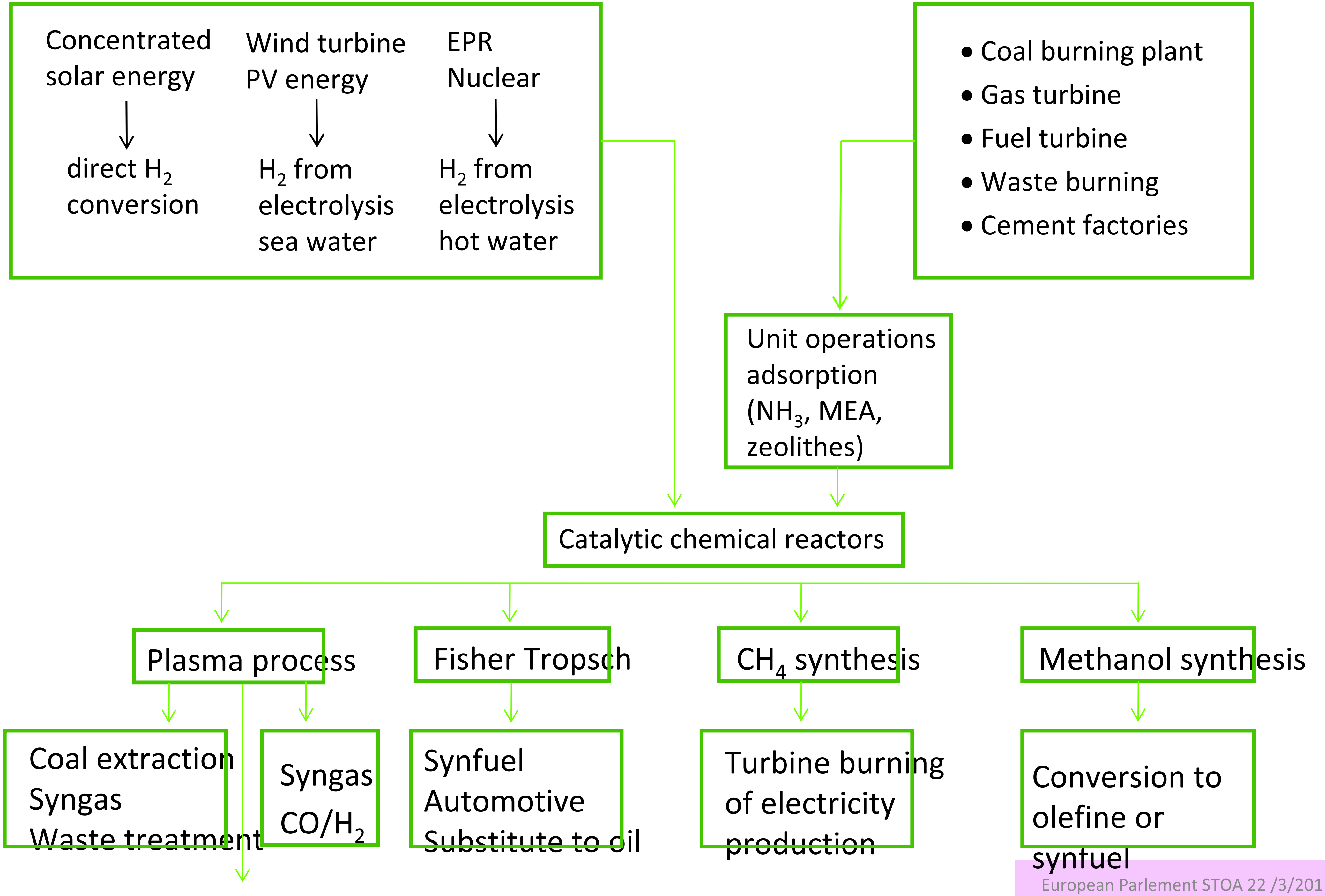
one of the main working parameters is

how much

it was the deal of Kyoto program for
carbon dioxide regulation
it is the challenger of

Cancun conference

this week (30 nov-7 dec 2010)



Concentrated solar energy → direct H_2 conversion

Wind turbine PV energy → H_2 from electrolysis sea water

EPR Nuclear → H_2 from electrolysis hot water

- Coal burning plant
- Gas turbine
- Fuel turbine
- Waste burning
- Cement factories

Unit operations adsorption (NH_3, MEA, zeolithes)

Catalytic chemical reactors

Plasma process

Coal extraction
Syngas
Waste treatment

Syngas CO/H_2

Fisher Tropsch

Synfuel
Automotive
Substitute to oil

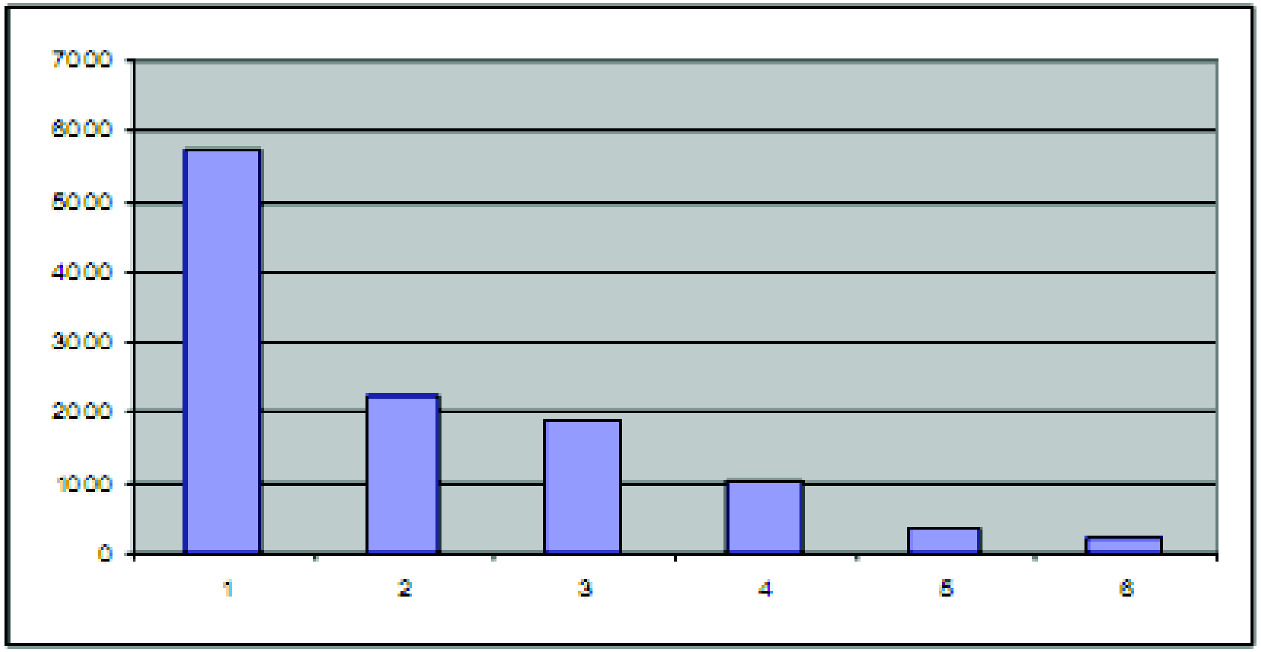
CH_4 synthesis

Turbine burning of electricity production

Methanol synthesis

Conversion to olefine or synfuel

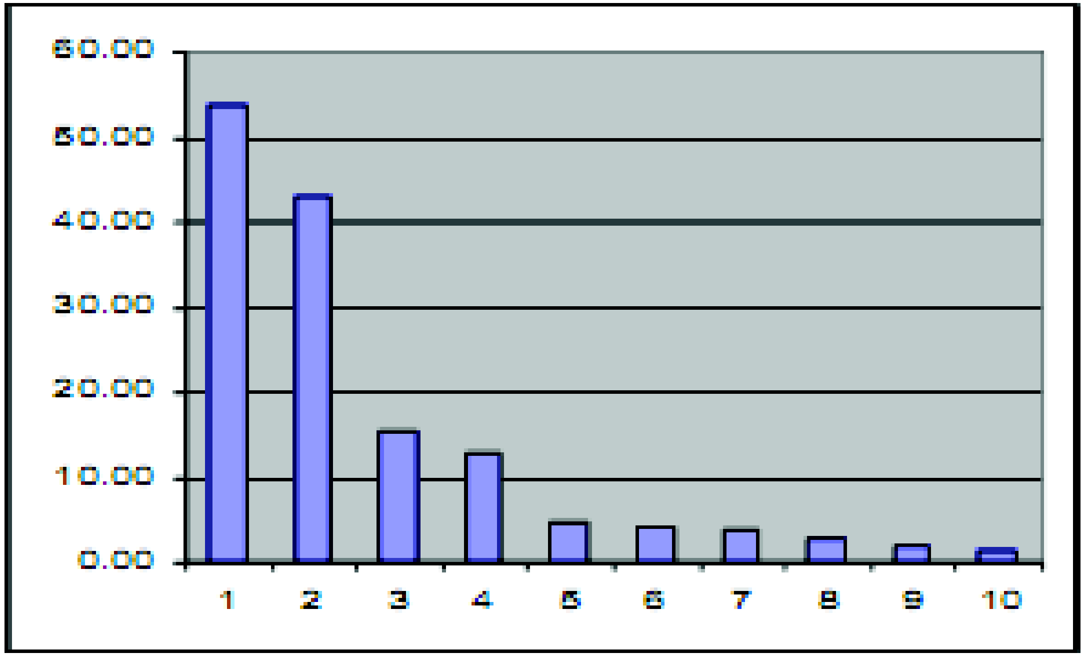
Total emissions USA 2002 in MMt (10^6t)



1. Total US	5752	%
2. Electric Power	2250	39
3. Transportation	1868	32
4. Industrial Processes	1042	18
5. Residential Homes	365	6
6. Commercial Buildings	227	4

. U.S. 2002 CO_2 emissions in MMt: Total, Electric Power, Transportation, Industrial, Residential and Commercial

Total emissions USA 2002 in MMt (10^6t) (non –energy related processes)

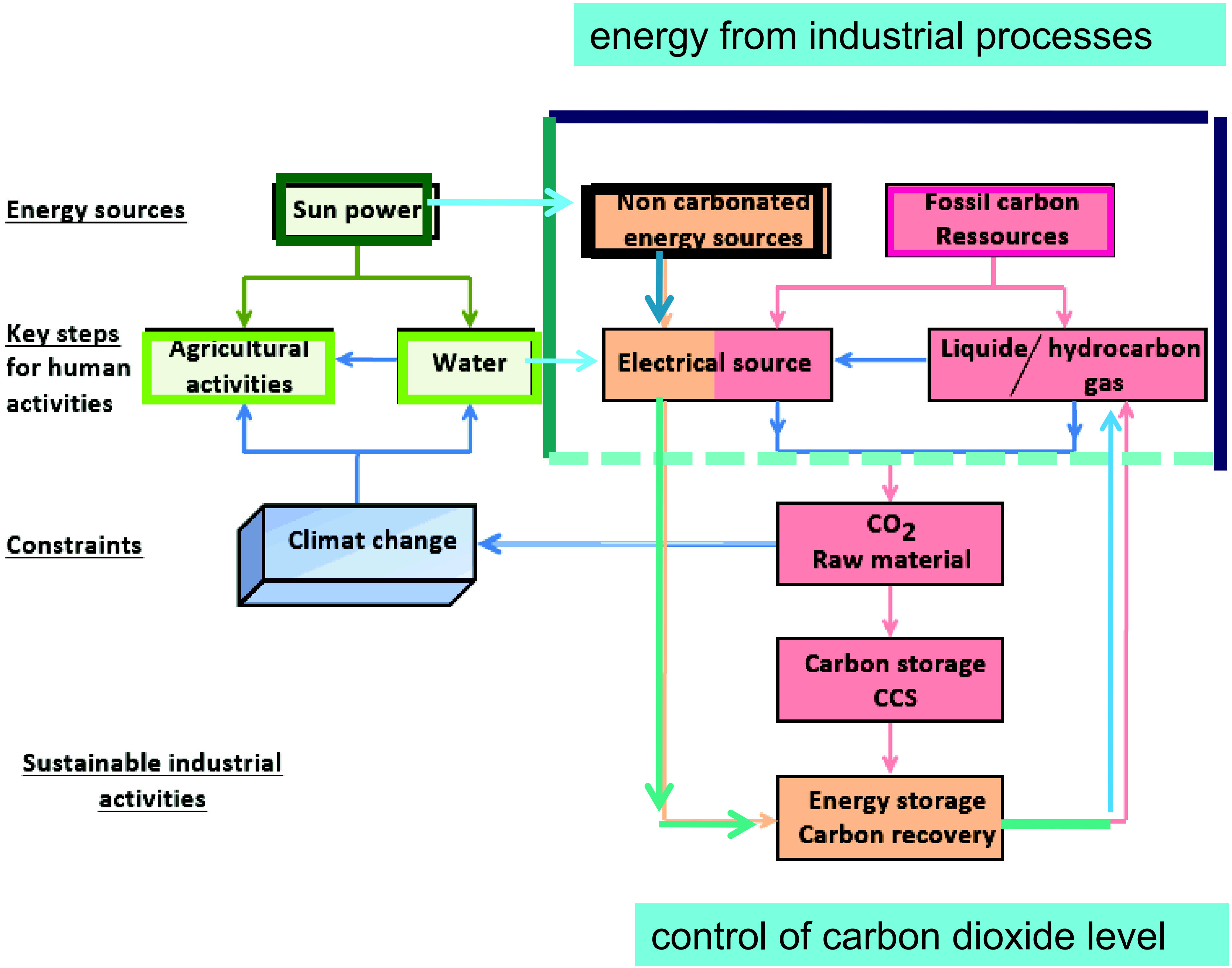


1. Iron and Steel Production	53.76
2. Cement Manufacture	43.03
3. Ammonia Manufacture & Urea Application	15.56
4. Lime Manufacture	12.98
5. Limestone and Dolomite Use	4.72
6. Aluminum Production	4.22
7. Soda Ash Manufacture & Use	4.08
8. Petrochemical Production	2.78
9. Titanium Dioxide Production	2.01
10. Phosphoric Acid Production	1.38

3. U.S. Industry 2002 CO_2 emissions in MMt: non-energy related processes.

energy efficiency of coal energy processes

- coal burning system for electrical power station
- in the main countries 30%
- new plants 37%
- supercritic news plants 45 to 58%



energy from industrial processes

Energy sources

Key steps for human activities

Constraints

Sustainable industrial activities

Sun power

Agricultural activities

Water

Climat change

Non carbonated energy sources

Fossil carbon Ressources

Electrical source

Liquide / hydrocarbon gas

CO_2 Raw material

Carbon storage CCS

Energy storage Carbon recovery

control of carbon dioxide level

Fourth Part

- main ways for **energy storage from electron to carbon recorvery** by using CO2 molecule
- **Electron to chemical synthesis** :Hydrogen + CO2
- to Methanol
- to Methane
- to synfuel by FT processes
- **electron to plasma processes**
- thermal or non equilibrium plasmas
- **Photon to thermolysis** of water or CO2 dissociation