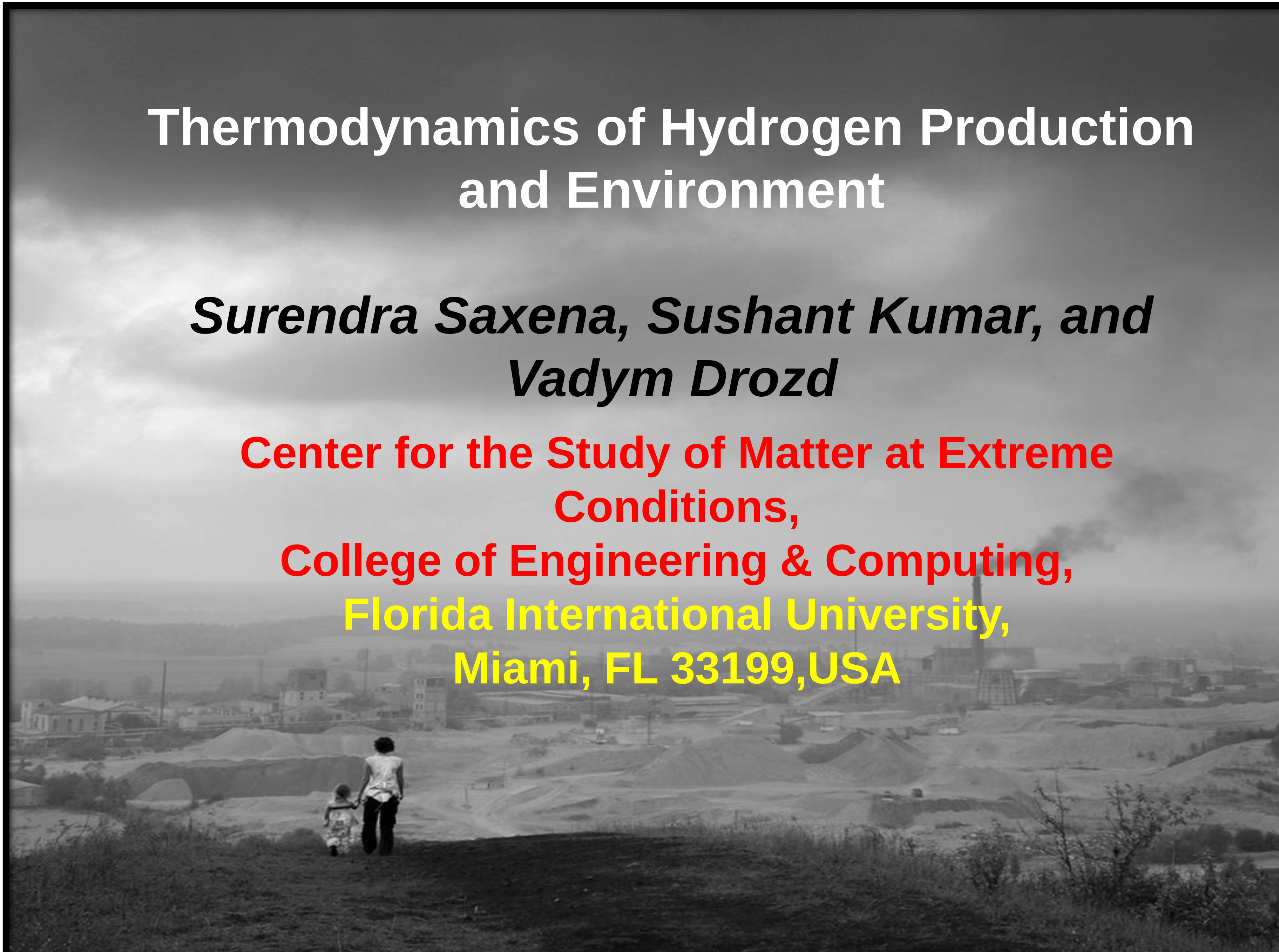
Thermodynamics of Hydrogen Production and Environment

Surendra Saxena, Sushant Kumar, and Vadym Drozd

Center for the Study of Matter at Extreme Conditions,
College of Engineering & Computing,
Florida International University,
Miami, FL 33199,USA

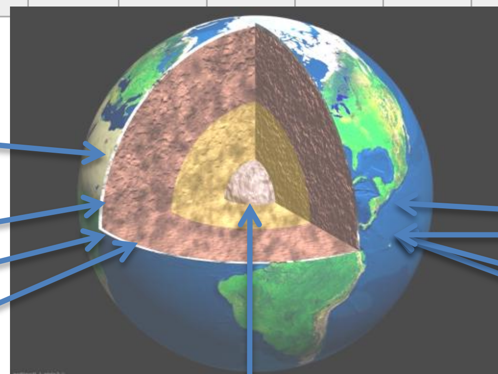


We live on an oxidized planet

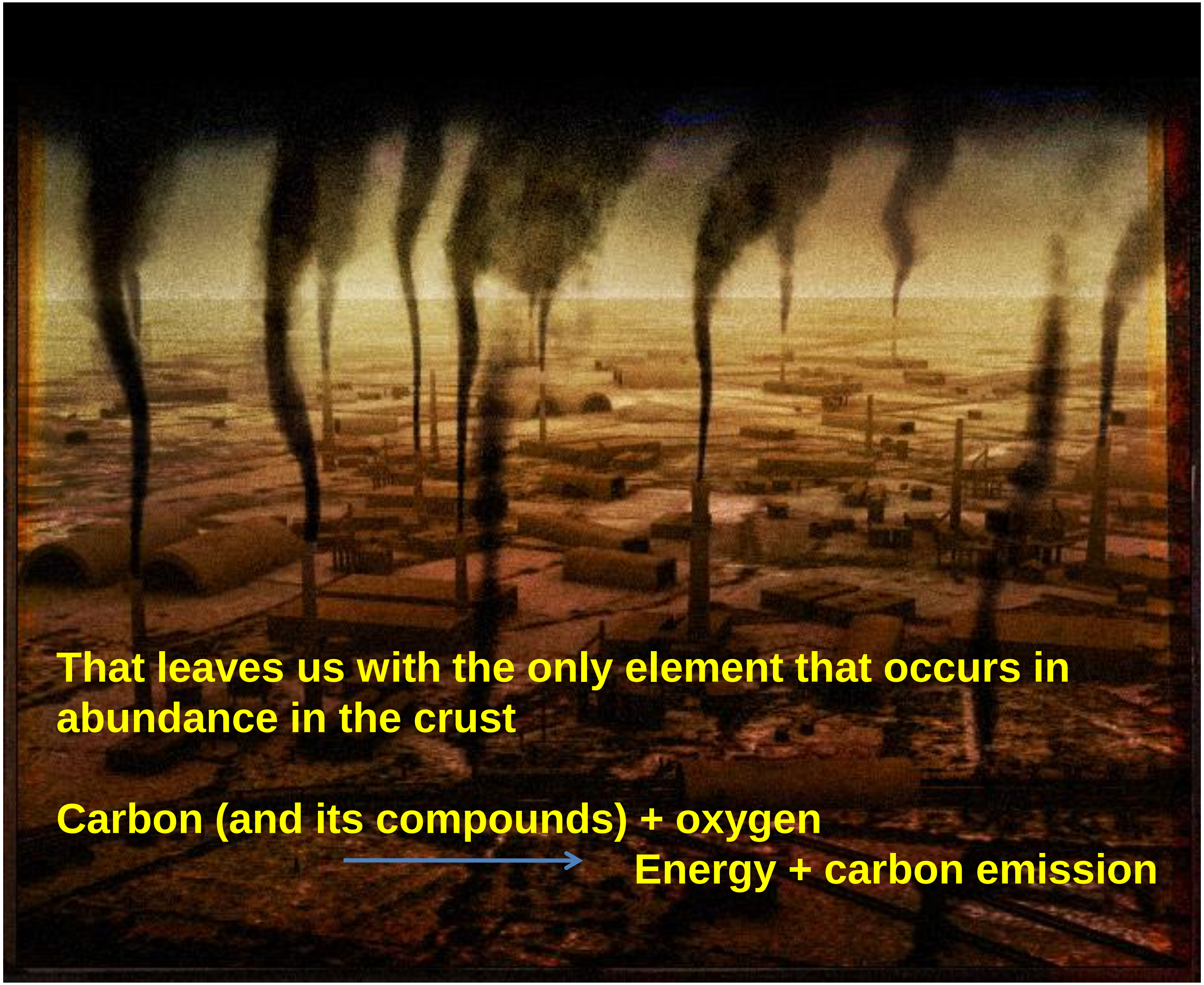
All we needed is one element occurring in abundance to solve our energy problem! Throw any of these elements in water and hydrogen comes out:

Metal + Water = Hydrogen + Oxide

Explore key information about the chemical elements through this periodic table



Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids																			



That leaves us with the only element that occurs in abundance in the crust

Carbon (and its compounds) + oxygen $\longrightarrow$ Energy + carbon emission

Hydrogen is the lightest and most abundant element on the earth. As far the energy value is concerned, the use of each gram of hydrogen when burnt provides 142 kJ of energy according to the reaction

$H_2 + 0.5\ O_2 = H_2O\ \Delta H = -284$ kJ/mole (300 K)

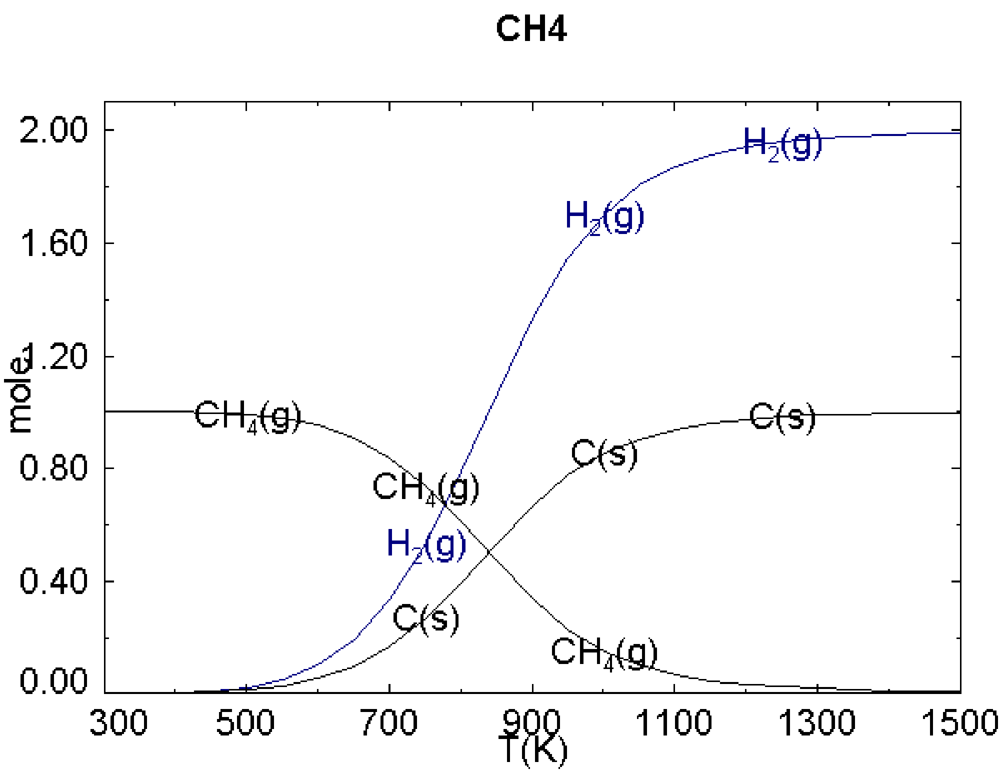
Type	Energy kJ per gram	CO2 per gram
Carbon	**32.79**	**3.67**
Methane	54.0	2.75
Diesel	42.82	3.1
Gasoline	47.3	3.28
H2	142.0	0.0

Sources of hydrogen

Water and natural gas (hydrocarbons) are the two sources of hydrogen

- Water electrolysis
- Carbon + Water reaction
- Methane and other hydrocarbons dissociation and/or reaction
- Metals + water

Thermodynamics of dissociation of methane



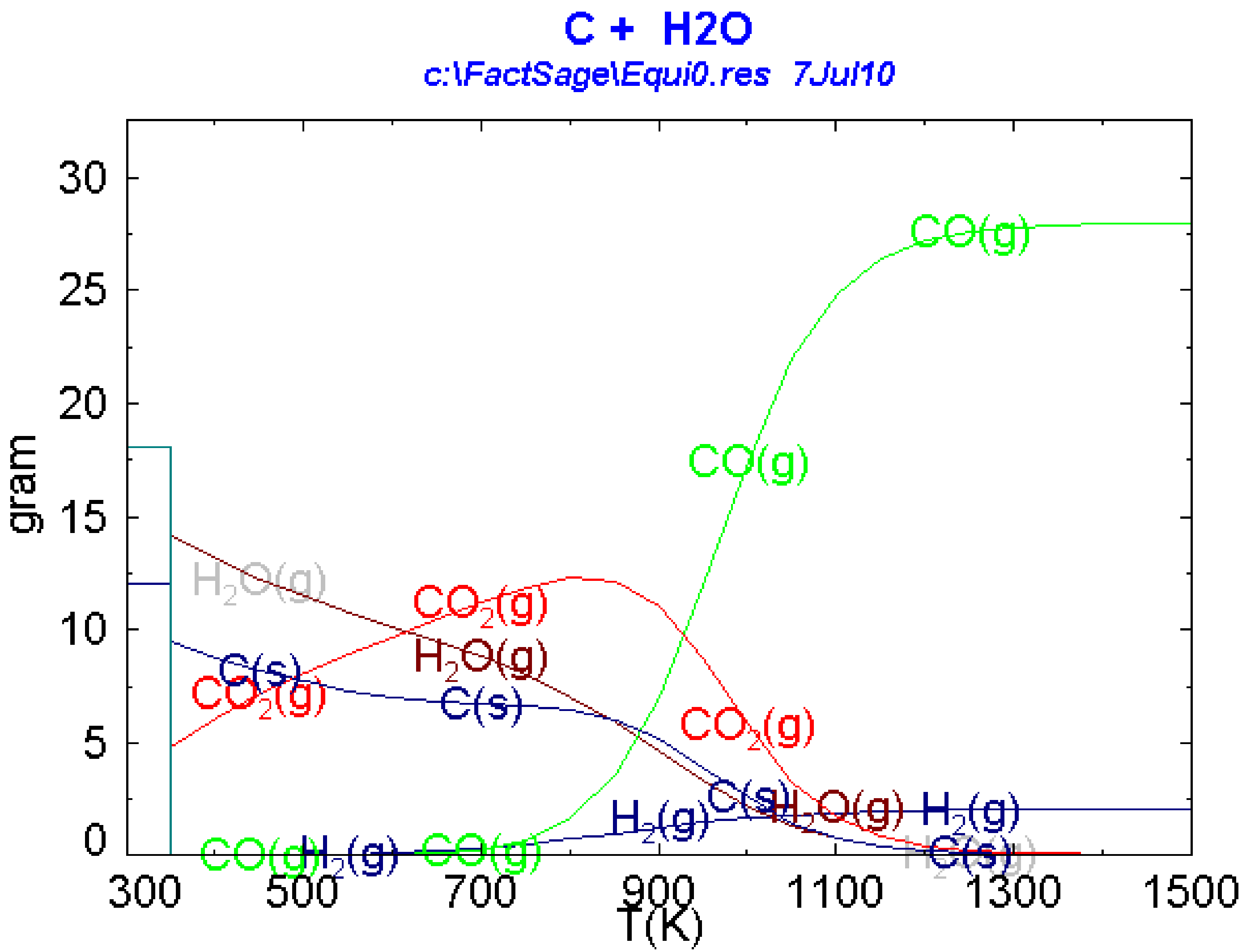
Methane can be dissociated into carbon and hydrogen over a suitable thermodynamic path by use of catalysts. For the reaction CH4 = C + 2H2 ΔH =130 kJ (1100 K)

Fig. shows the phase relations for CH4. To dissociate 16 grams of methane, we need to burn about 4 grams of carbon which gives us about 15 grams of CO_2 for each 4 grams of hydrogen.

For 1 g H2 we have 4 g CO2

There is a vast amount of activity in this area of research as reviewed by Shah et al. [1].

Gasfier reaction C + H_2O = CO +H_2



The process of coal gasification has many reaction steps.
In a simplified scheme, the total energy is given by the two reactions:

C(graphite)+ H_2O(l) = CO(g) + H_2(g) ΔH = 250.3 kJ at 1500 K

CO(g, 1500K) +H_2O (l) = CO_2(g) + H_2(l) ΔH = -6.65 kJ at 1000 K

The combined reaction is C+ 2H_2O = CO_2 + 2H_2 ΔH = 243.6 kJ

Industry must use temperatures as high as 1800 K

The total CO_2 produced in producing 1 gram of hydrogen is 11 grams process related and 6.78 grams for heating totaling 17.78 grams.

Steam-Methane-Reformation

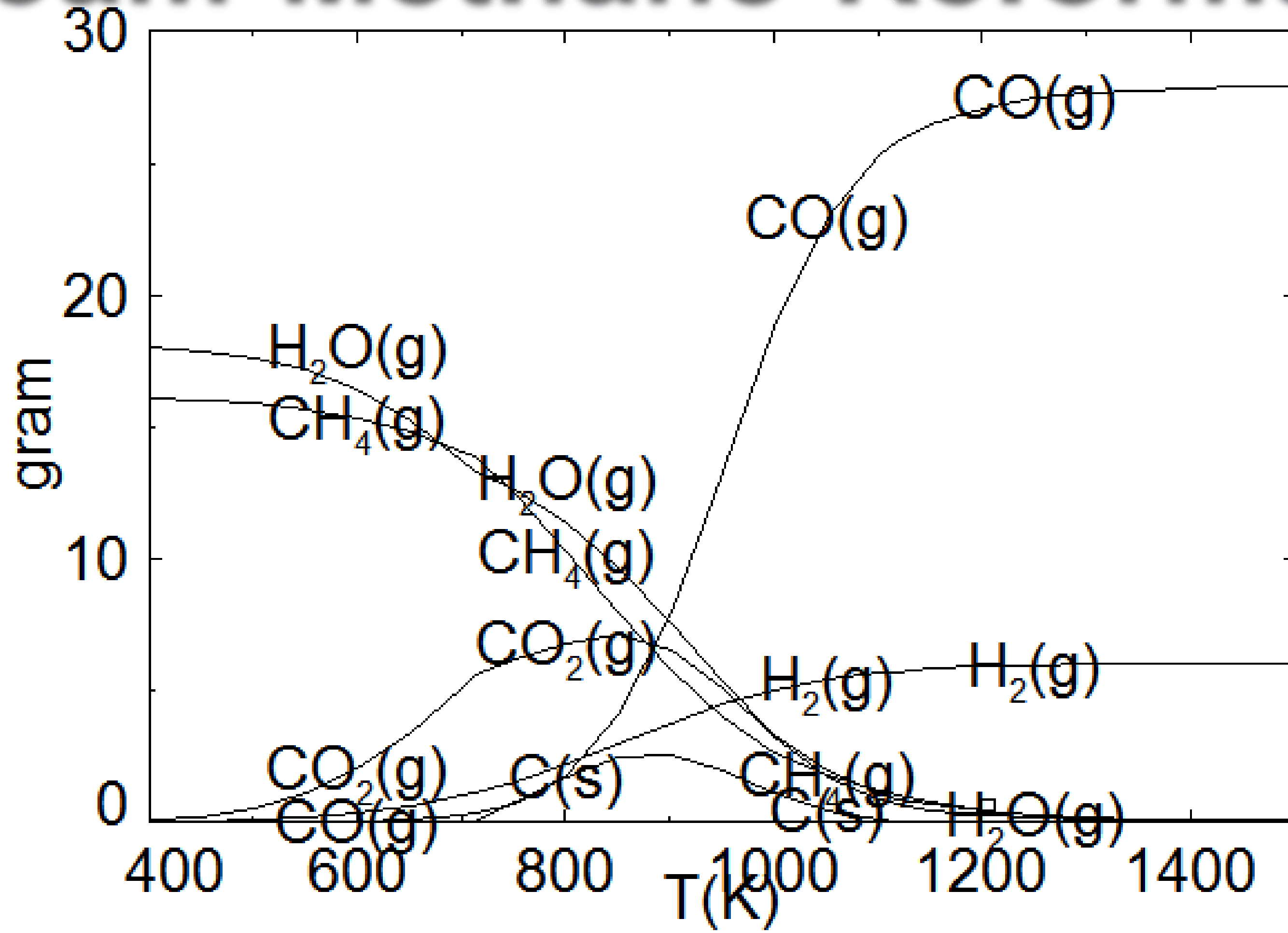


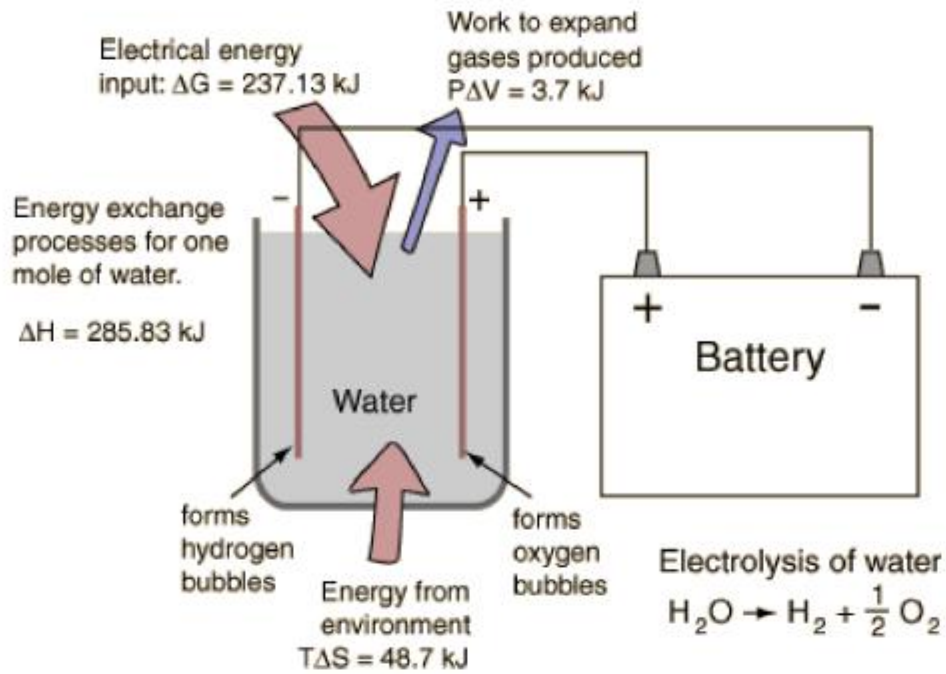
Fig.1. The reaction 16 grams of methane and 18 grams of water produce several grams of hydrogen and nearly 4 times CO, which can be further converted to CO_2 and hydrogen by the water-gas shift reaction. Totally the CO_2 produced by the SMR process is 10.5 grams for every 1 gram of hydrogen.

Thermodynamics of electrolysis

$H_2O = H_2 + .5\ O_2 \Delta H = 285.8$ kJ and $\Delta G = 234.5$ (300 K)

Energy needed from coal: 8.7 grams of coal generating 16 grams of CO2 per gram of hydrogen.

However, the carbon emission penalty is much more because we need to use electrical energy at ambient temperature and ambient pressure; the conversion from coal to electricity may be only 34% efficient and therefore we require a minimum energy of 39.7 and perhaps between 70 to 75 kWh/kg H2 to be obtained from 8 kg of carbon generating some **30 kg of CO2 for each kg of hydrogen**. It is clear that electrolysis of water using fossil fuel for energy is not an option. Therefore, it is not a better method than the SMR technique. The energy has to be provided by alternate energy sources.



Reference
Schroeder
Ch 5

Metal-water reactions

Throw any one of the several metals in water and you have pure hydrogen

$Mg + H_2O = MgO + H_2$ $\Delta H = -316$ kJ (300 K)

recycling of MgO back to magnesium according to

$MgO = Mg + 0.5\ O_2$ $\Delta H = 601$ kJ (300 K)

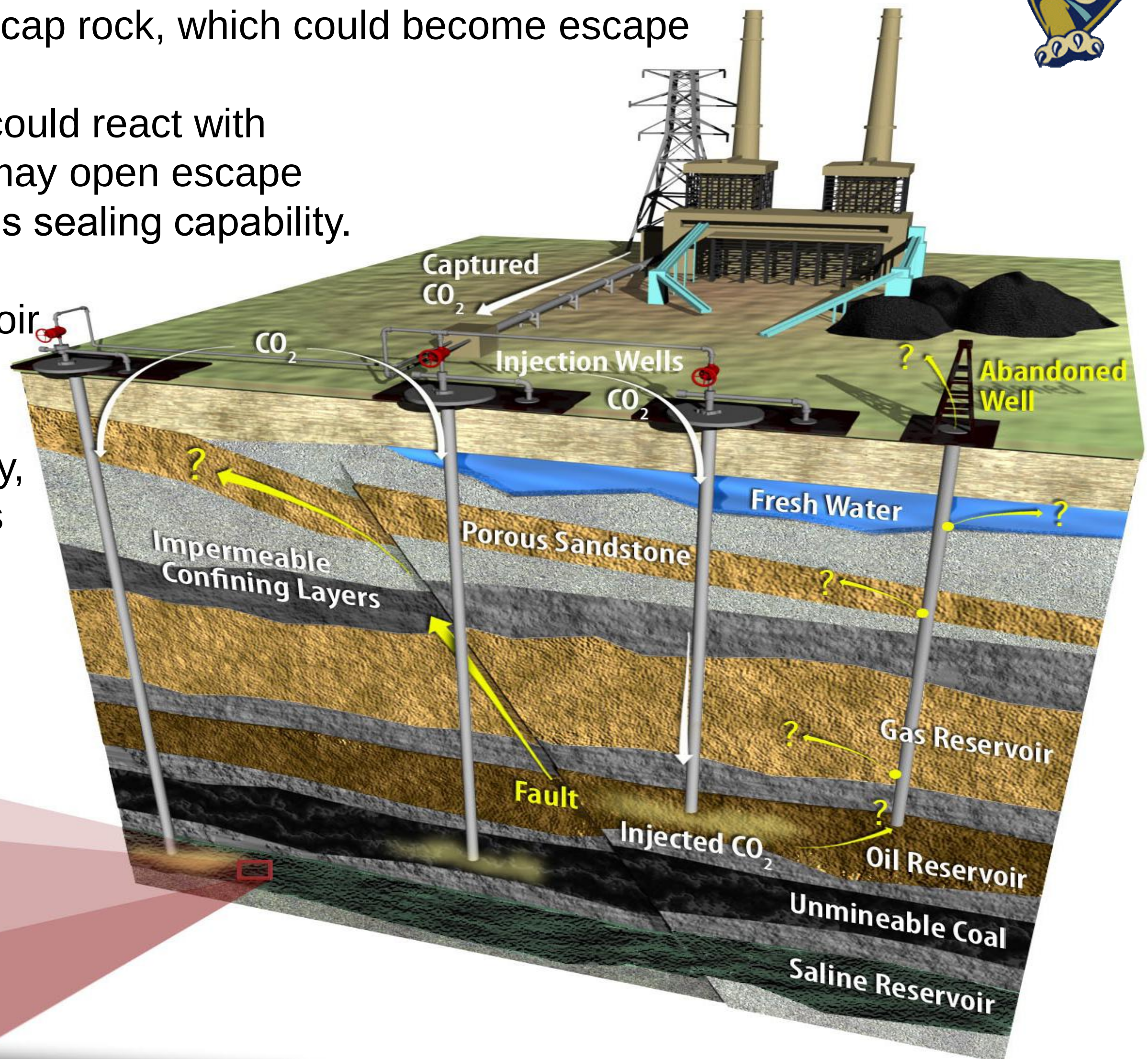
If this were thermal energy from coal, **CO_2 will be ~20 g**
But this has to be electric!

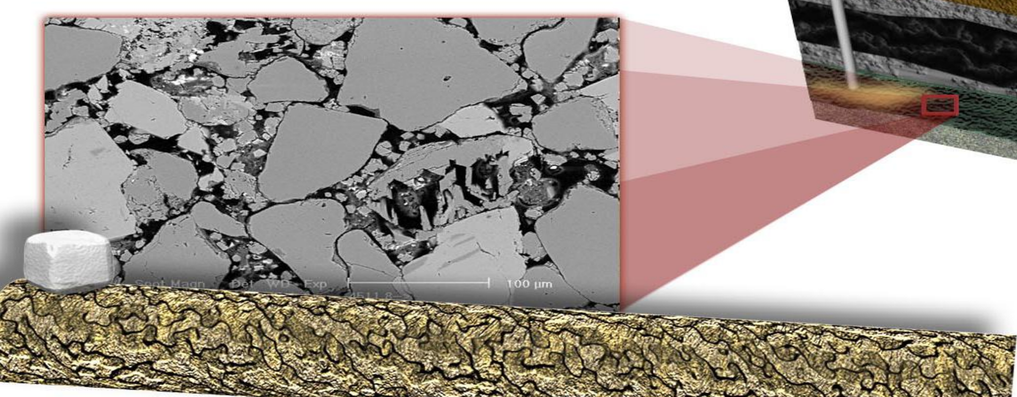
The CO2 could force the native fluids, and any substances these fluids mobilize, into freshwater aquifers or other natural resources.

The increased pressure in the reservoir could cause structural changes in the formation, such as fractures in the cap rock, which could become escape routes.

The CO2 mixed with saline water could react with cement plugging the wells, which may open escape routes or may improve the cement’s sealing capability.

The CO2 could chemically react with minerals in the storage reservoir to create new minerals, which could be good because it immobilizes the CO2 permanently, but could also be bad if it happens quick enough to hamper injection operations.





http://www.lanl.gov/orgs/spo/appliedenergy/docs/geologic_sequestration.pdf

Carbonation, a safe method but….

A carbonation reaction may be represented by

$MO + CO_2 = MCO_3$ (1)

where M can be any metal such as (Ca or Mg). To qualify for this application, the metal oxide has to be

- abundant in the earth's crust
- must react with CO_2 at low temperatures
- must have a reaction kinetics appropriate for the low temperature equilibrium
- must form a carbonate that is stable in the environment at ambient conditions.

Dolomites: source of MgO and CaO

An oxide + CO_2 = carbonate; as for example

$CaO + CO_2 = CaCO_3$ $\Delta H = -178$ kJ (300 K)

CaO and MgO do not occur freely in nature and are obtained from the carbonates (dolomite, magnesite and limestone) by calcination e.g.:

$CaCO_3 = CaO + CO_2$ $\Delta H = 215$ kJ (700 K) which is a very high temperature process burning 6.5 g of Coal and releasing 24 g of CO2

Some processes (e.g. ZECA by Gao et al., [4]) involve CaO in the reaction to produce hydrogen and are still labeled as zero emission methods, which is highly misleading.

Silicates:

Silicates are oxides of silicon and other metals, form the bulk of earth's crust, but the kinetics of converting them to carbonates is very slow. As an example consider the carbonation reactions of forsterite:

- **$\frac{1}{2}Mg_2SiO_4 + CO_2 = MgCO_3 + \frac{1}{2}SiO_2$**

and serpentine

- **$1/3Mg_3Si_2O_5(OH)_4 + CO_2 = MgCO_3 + 2/3SiO_2 + 2/3H_2O$.**

Both of these reactions are exothermic and favored at low temperatures. In nature magnesite and silica are common in serpentinized ultramafic rocks. Their formation is due to natural CO_2–rich fluids percolating through mineral deposits. Magnesite is stable and not likely to release the bound CO_2 again. Mountains such as the Alps consist of dolomites $(Ca,Mg)CO_3$ and limestones. Unfortunately the kinetics of these reactions is slow and to accelerate the reaction, the silicates must be dissolved in acid or thermally activated, which complicates the process and makes it expensive.

Hydrogen is not a clean fuel….?

The conclusion we can draw from the review above would be that

- we need to produce hydrogen from fossil fuel without carbon emission and
- carbonation, despite its advantages, may not be a practicable global solution to the problem of carbon sequestration.

However, we should consider the carbonates of the alkali metals as described below for a partial solution.

Thermodynamics of modified coal gasification

Process I. CO_2 sequestration and hydrogen production

For existing power stations, where CO_2 is produced,

4 NaOH (c) + C (c) + CO_2(g) = 2 Na_2CO_3 (c)+ 2 H_2 (g) ΔH = -66.2 kJ (600 K) (1)

Process II. CO sequestration and hydrogen production

If CO is actually produced in some quantity in the plant, we could use the CO for producing hydrogen according to the following reaction

2NaOH (c)+ CO(g) = Na_2CO_3 (c) + H_2 (g) ΔH = -119 kJ J(600 K) (2)

Process III. Hydrogen production with zero emission

2 NaOH (c)+ C(c) + H_2O (l) = Na_2CO_3 (c)+ 2 H_2 (g) ΔH = 64.58 kJ (600 K) (3)

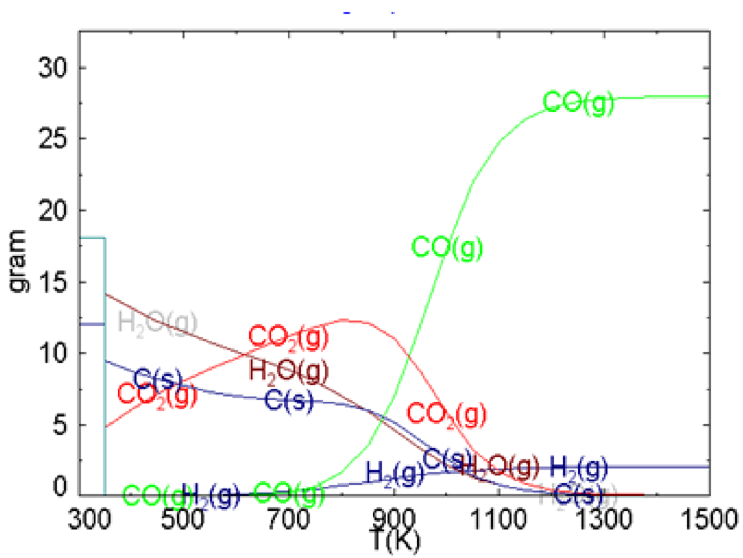
These reactions can also be performed using natural gas (methane)

Reaction (2) was proposed by Saxena [6]. Less amount of solids are required to produce the same amount of hydrogen. This may be helpful if the cost structure of the sodium compound alters in time. In this process 20 kg of NaOH will yield 26.5 kg of Na_2CO_3 for each 1 kg of hydrogen.

6. Saxena, S. K. Drozd Vadym, Durygin Andriy, Synthesis of metal hydride from water. Int J. Hydrogen Eenergy, doi: 10.1016/j.ijhydene.2006.09.032

How is it different from a gasifier technique?

$4NaOH + C + CO_2 = 2Na_2CO_3 + 2H_2$ The reaction (1)



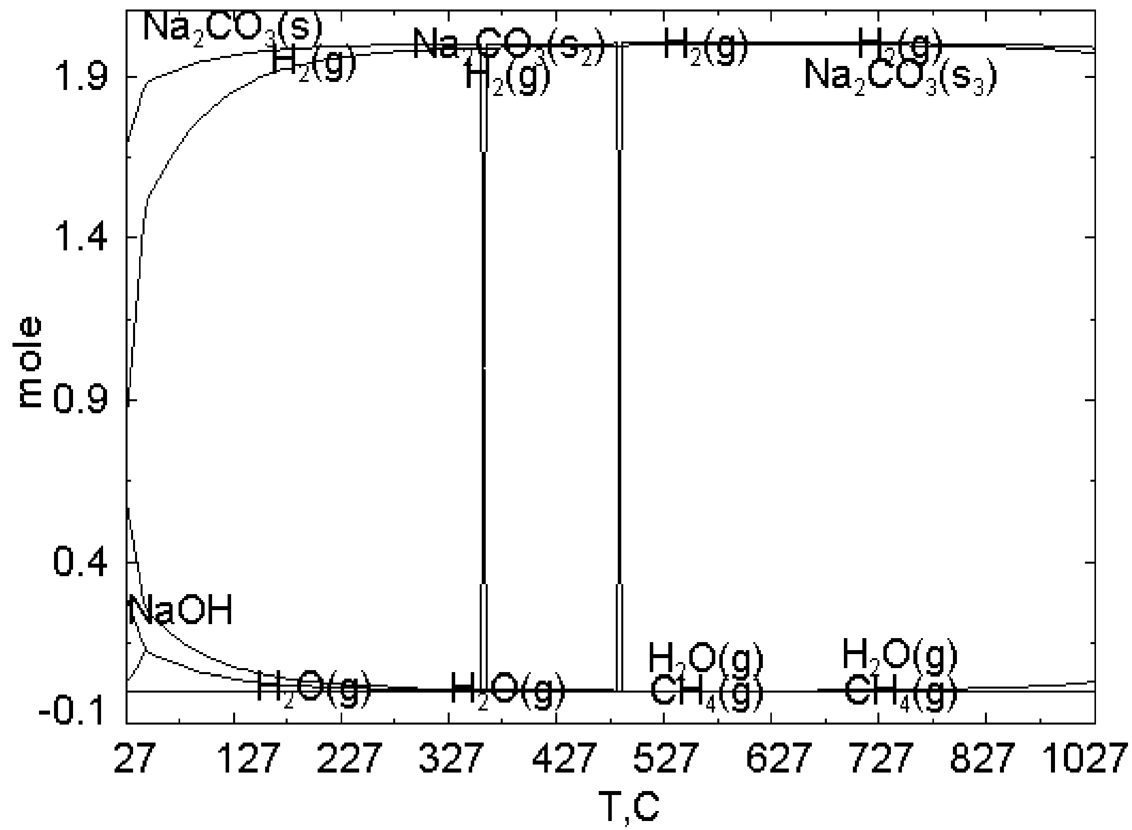
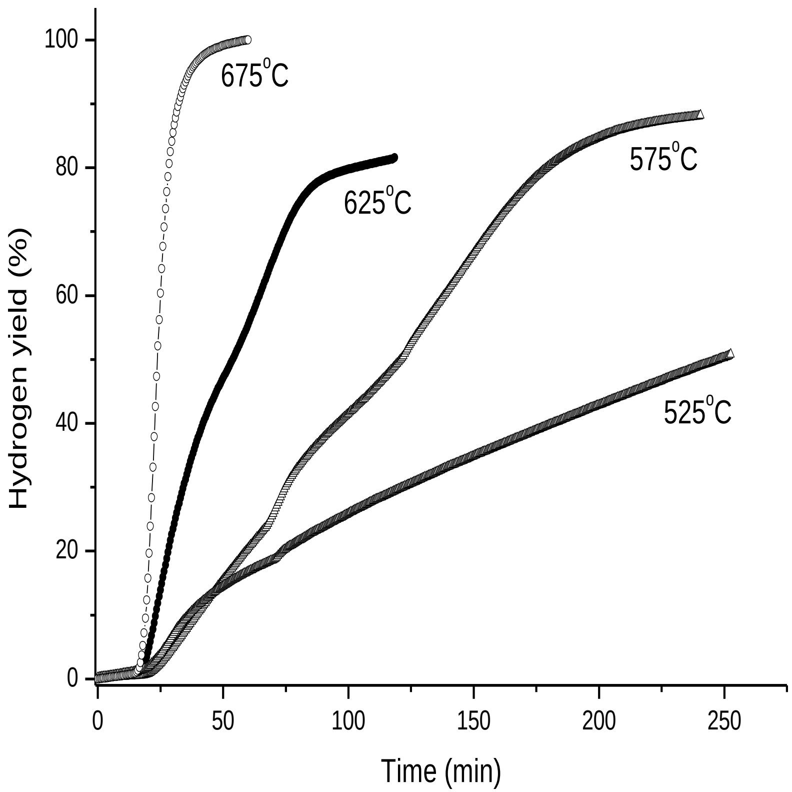


Fig. Equilibrium in the system 4 NaOH + C+ CO2

Experimental results



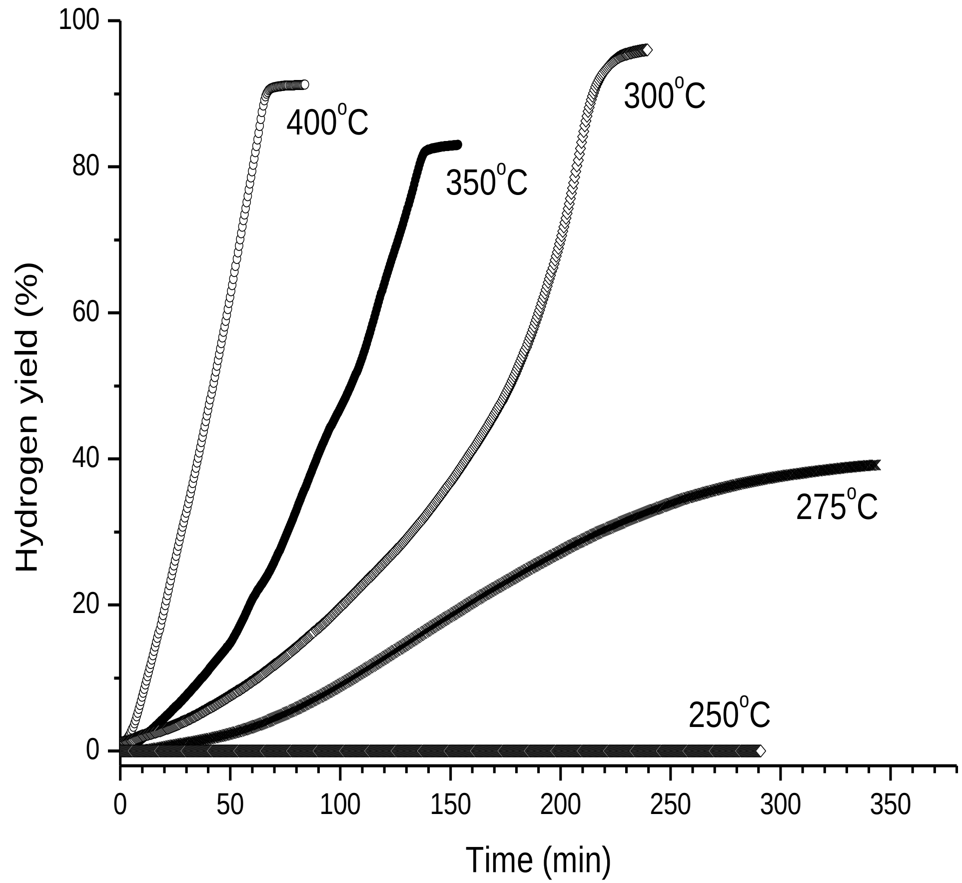
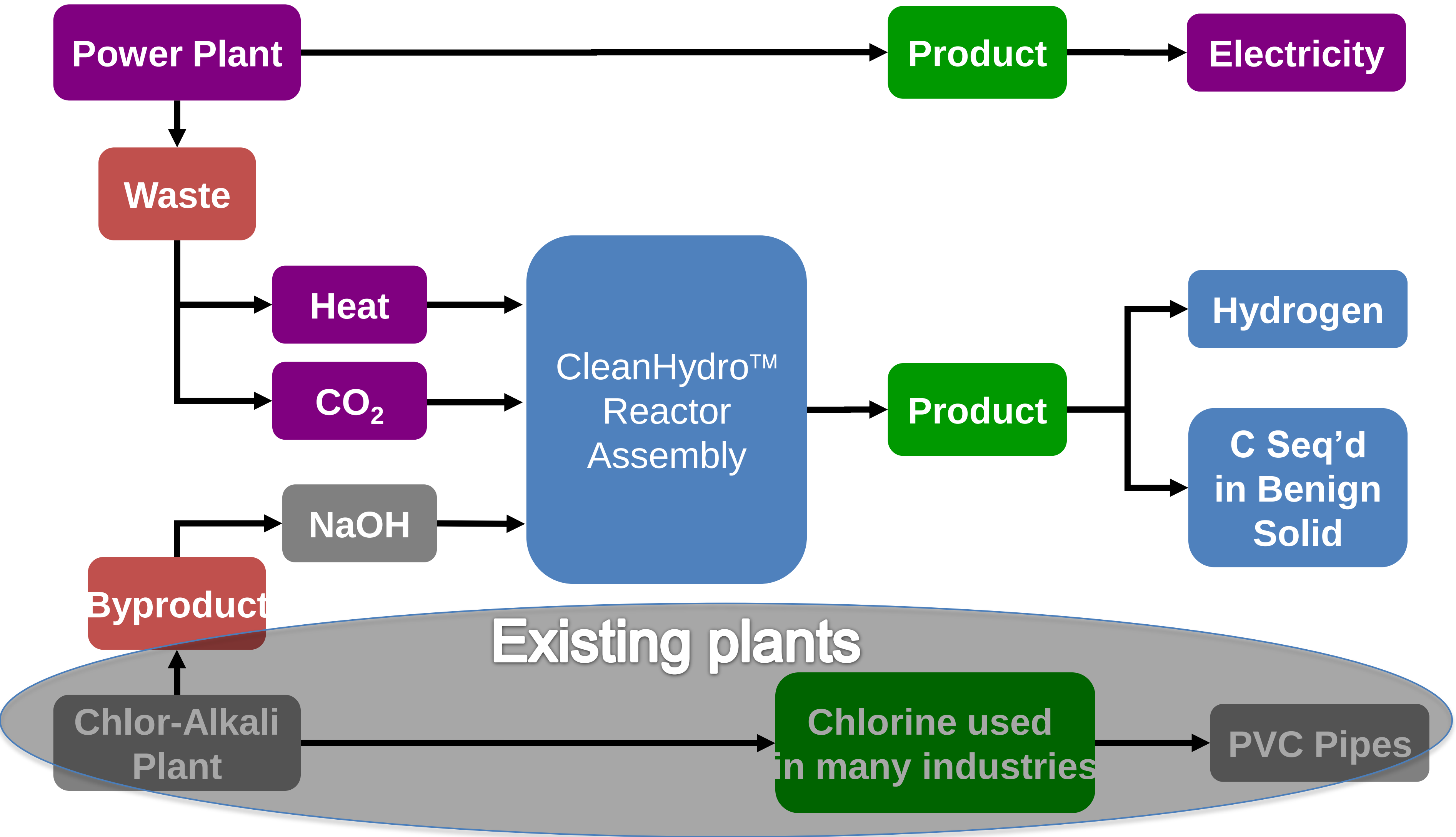


Fig. 4. a. Hydrogen generation in 2NaOH + C + H2O → Na_2CO_3 + $2H_2$ reaction studied at different temperatures. N_2 carrier gas flow rate 50 mL/min.

b. Hydrogen generation in 2NaOH (c) + CO (g) = Na_2CO_3 (c) + H_2(g) reaction studied at different temperatures. N_2 carrier gas flow rate 50 mL/min.

CleanHydro Converts Waste to Hydrogen and Sequestered Carbon



The CleanHydro Value Proposition (plant owner burning coal)

FLORIDA INTERNATIONAL UNIVERSITY

Two-Year Payback Scenario Cost Calculation for a 40 ton/hour NaOH Feed* Reactor

Material	Price $/ton	Tons used	Expenses	Profit $
Coal	45	6	270	
Reactant solid	100	40	4,000	
Product solid	150	53		7,950
H_2	2000	2		4,000
Energy			2,784	
Total			7094	11,950
Profit/hr, $				4,896
Annual profit $				42,888,960
CO_2 sequestered/yr = 192,720 tons				5,781,600
The profit with $30 carbon credit =				48,670,560
Cleaning, maintenance, labor and misc, annual			6,250,000	42,420,560
Capital $			28,500,000	
Time to recover Capital, yrs				<1 yr

*40 tons NaOH+ 6 tons C+ 9 tons of water= 53 tons Na2CO3+2 ton H2

How is this Zero Emission?

- By using the by-product hydroxide from ***the existing plant***, we produce hydrogen.

- No new hydroxide is produced. Hydrogen should increasingly replace oil and gasoline in energy use.

- For example use of hydrogen in fuel-cell based transportation will result in reduction of CO_2 emission.

Conclusions

As yet there are no known methods of hydrogen production that do not involve carbon emission, other than those using non-fossil energy.

Therefore, Hydrogen cannot be used to protect the environment unless it is to be accompanied by carbon sequestration.

Carbonation is not an easy solution and each proposed process must be carefully evaluated: thus a process may not make any sense, if

a. it produces more carbon emission than it sequesters

b. it requires more energy than the power plant is producing

c. it produces other toxic solids and gases

The carbonation process must be economic such that the costs of feed and outputs are well balanced.

Use of NaOH for carbonation when the chlor-alkali balance **is not violated and the products are sellable could help to mitigate 10 to 15% percent of CO_2 in many plants. The hydrogen produced in these reactions is carbon-emission free.**