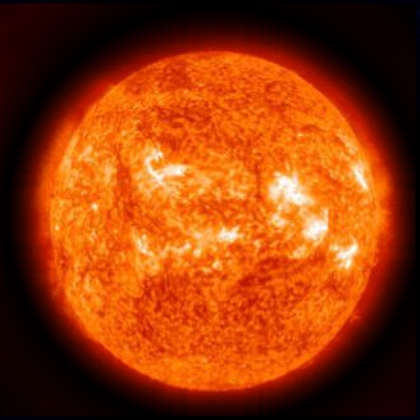
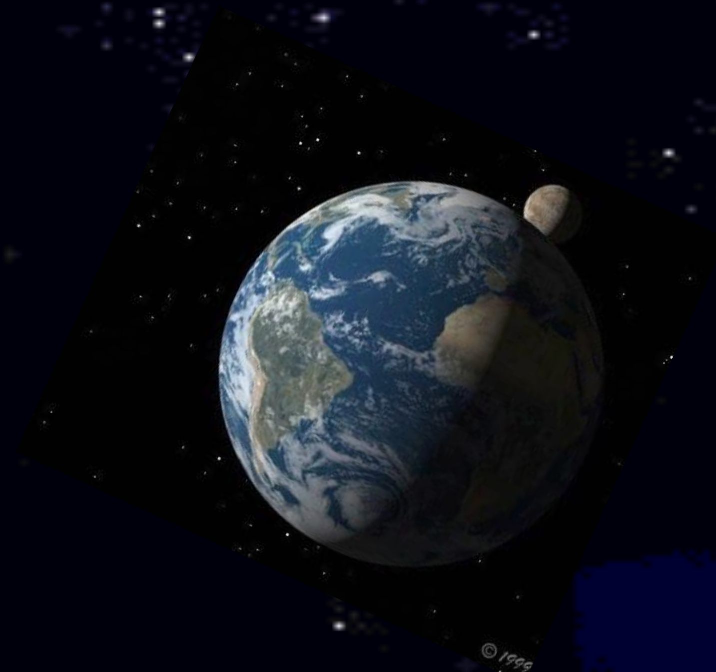


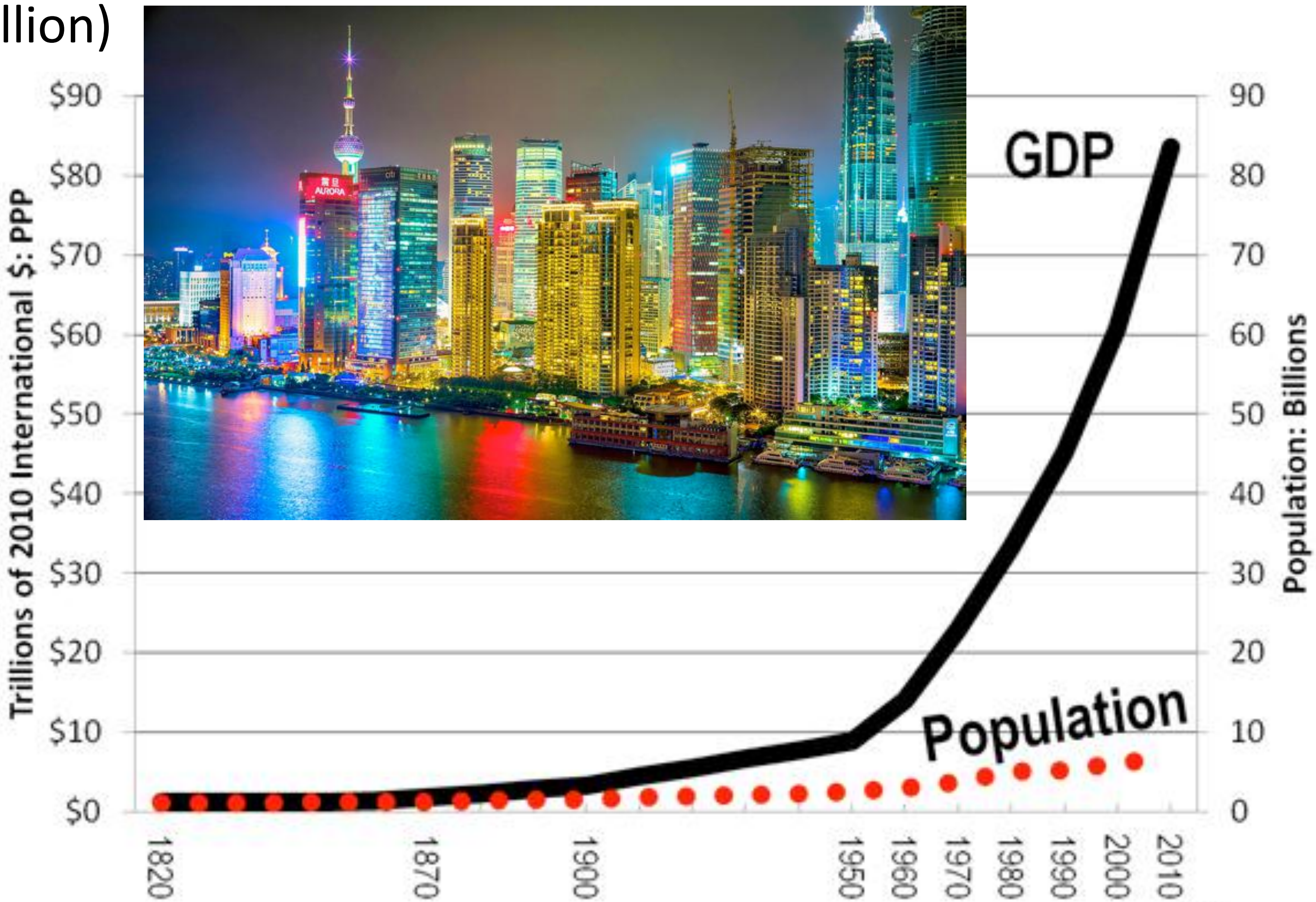
Plan B: Fossil Fuels Without CO_2

Eric McFarland
U.C. Santa Barbara



Unimaginable, Increasingly Egalitarian, Global Prosperity

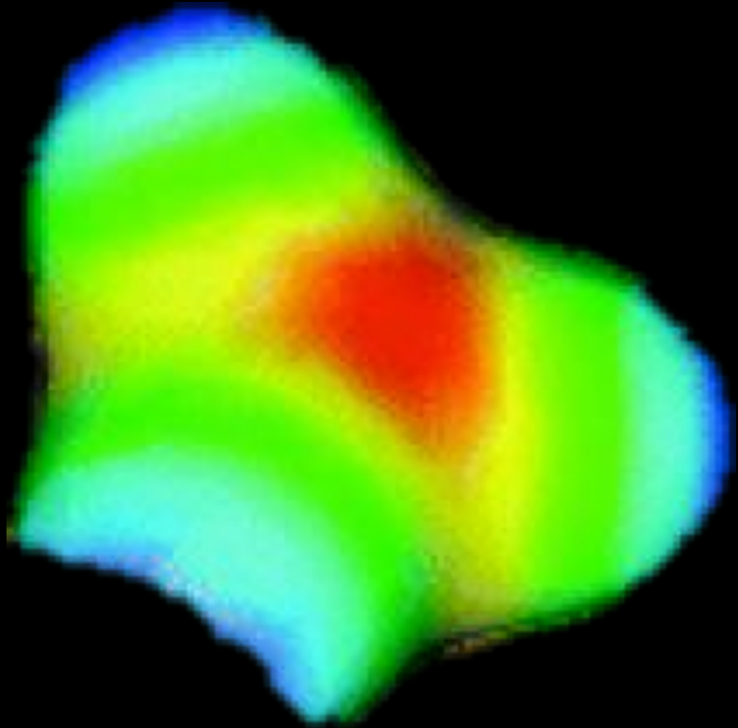
Global GDP ($Trillion)

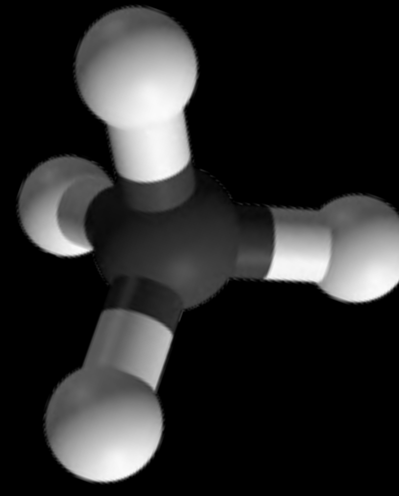


IMF

Made Possible By Abundant Low Cost Fossil Hydrocarbons

Prosperity has been possible because of our use of solar energy stored in the carbon of fossil fuels



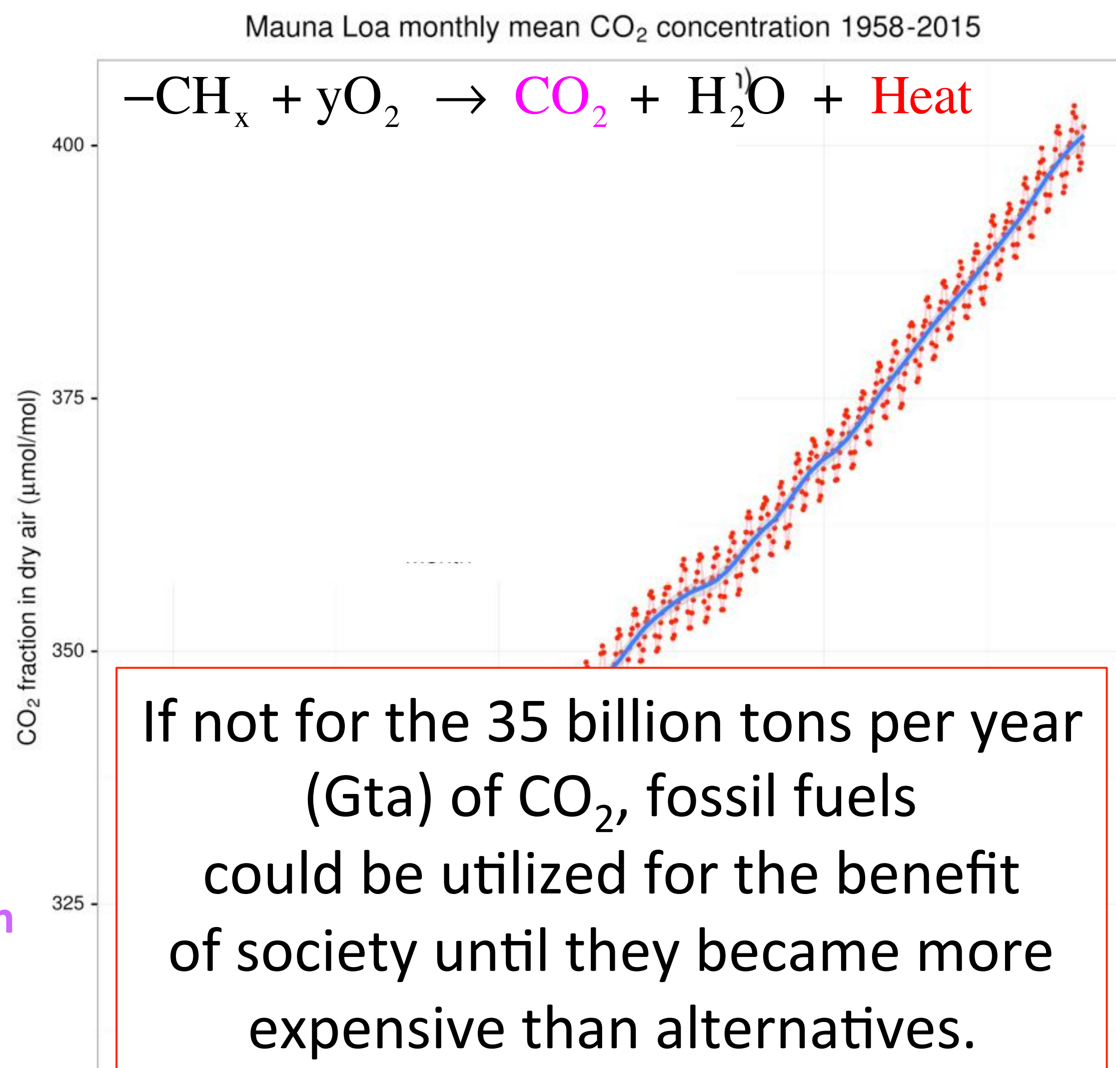


There is no evidence that economically sustainable alternatives to fossil fuels exist today; atmospheric CO_2 continues to rise

55 GJ/ton
2.8 tons CO_2/ton
51 kg CO_2/GJ

45 GJ/ton
3.2 tons CO_2/ton
71 kg CO_2/GJ

20-30 GJ/ton
2.3 tons CO_2/ton
92 kg CO_2/GJ



If not for the 35 billion tons per year (Gta) of CO_2, fossil fuels could be utilized for the benefit of society until they became more expensive than alternatives.

→"Transition Option"

Someday, increasingly rare fossil resources will be too costly to burn.

Probably before then, the CO_2 emissions from combustion will cause harm to parts of our global ecosystem and people.

Global Diversified Risk Management

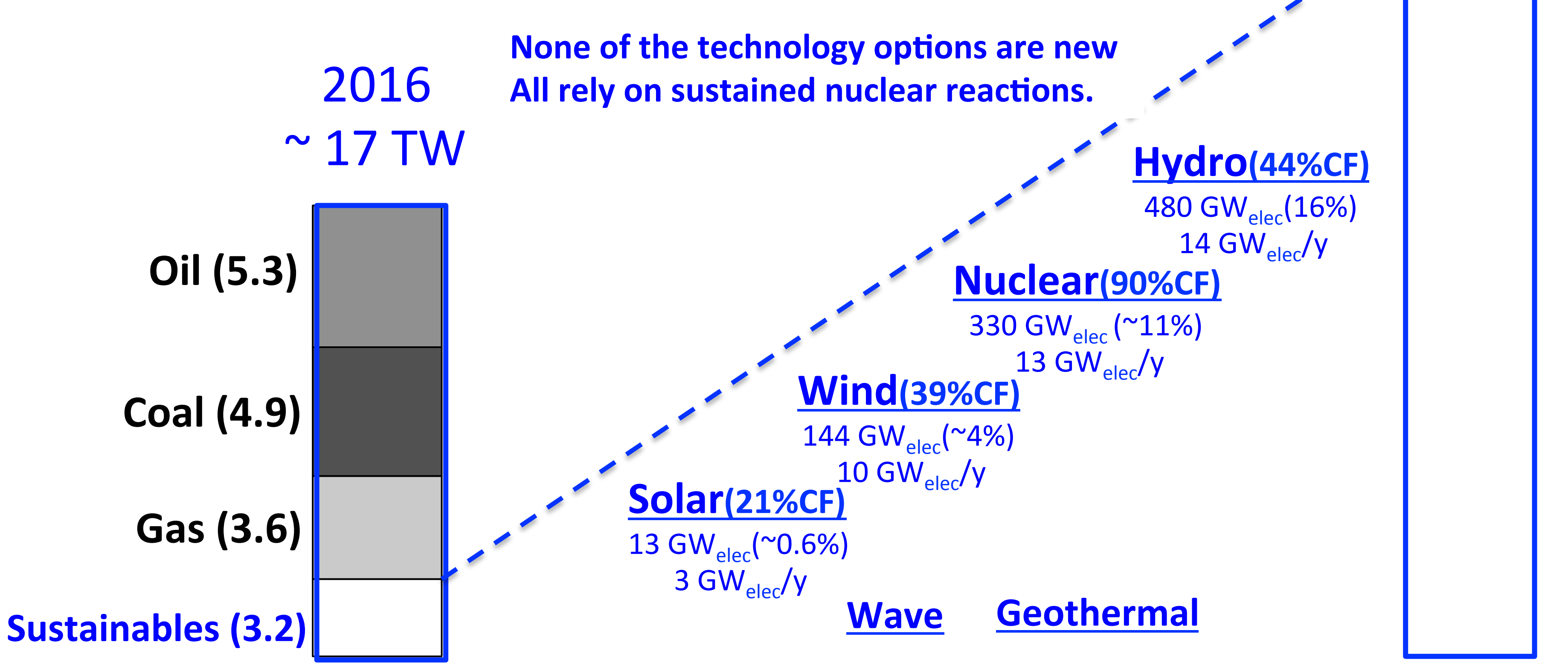
- Protect Against Fossil Fuel Price/Supply Risk
- Address Environmental and Climate Risk

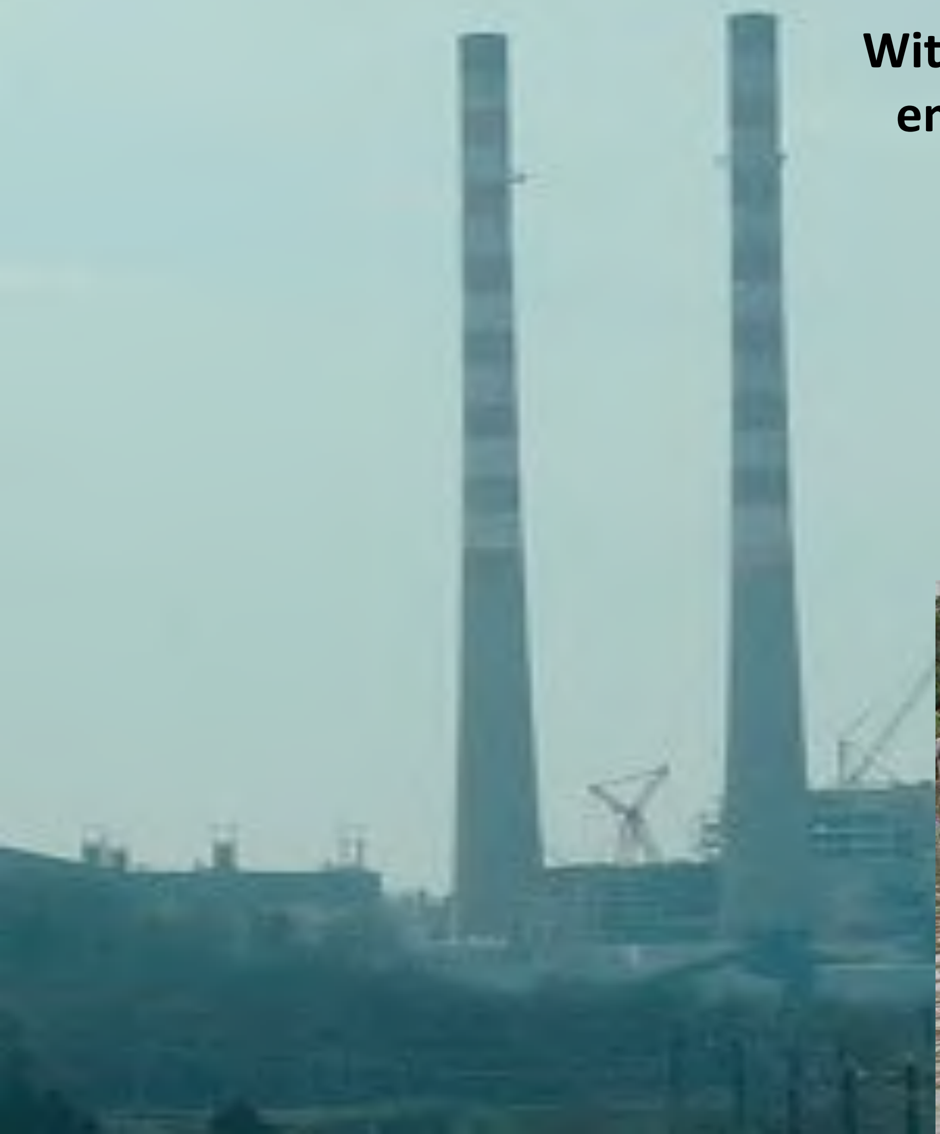
→ **Increase Efficiency**

→ **Increase CO_2-free power generation**

2XXX??

30+? TW



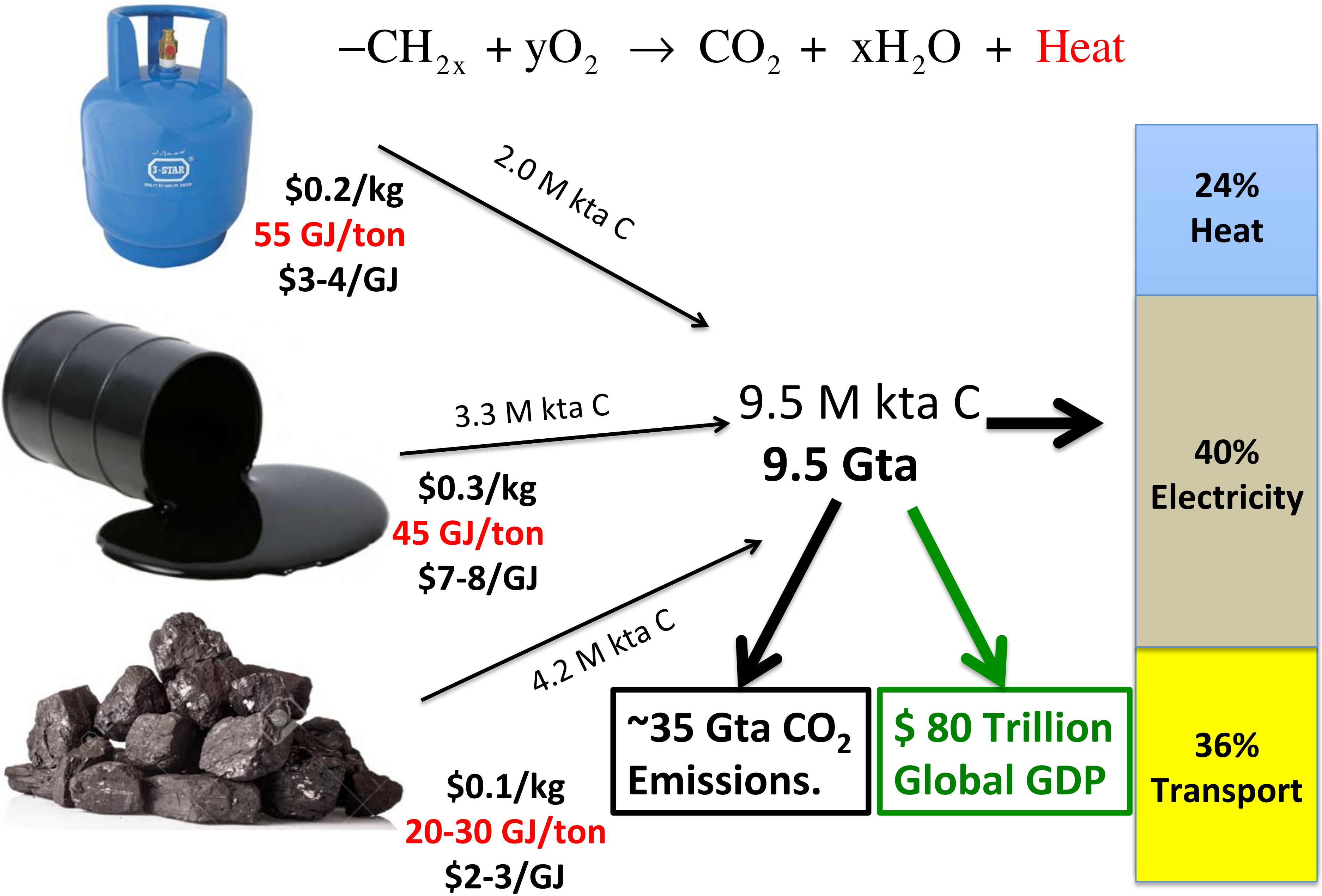


Without cost-effective options, significant CO_2 emission reductions will not be achievable.

If severe consequences occur, <u>the poor will be harmed far worse than the wealthy.</u>

~ 9.5 Gta of C in Hydrocarbons Are Combusted For Low Cost Heat

$$-CH_{2x} + yO_2 \rightarrow CO_2 + xH_2O + \text{Heat}$$



Present "Strategy": Hydrocarbon Combustion For Low Cost Heat

$$-CH_{2x} + yO_2 \rightarrow CO_2 + xH_2O + \text{Heat}$$

Massive Existing Infrastructure
Global Trade Relations
Known Scale-up

Reserves **140 Gt +++** — Gas

Reserves 250 Gt + — Oil

Reserves 1,000 Gt + — Coal

→ **9.5++ Gta C** →

35+ Gta CO_2 Emissions

$ 80+Trillion Global GDP

24% Heat

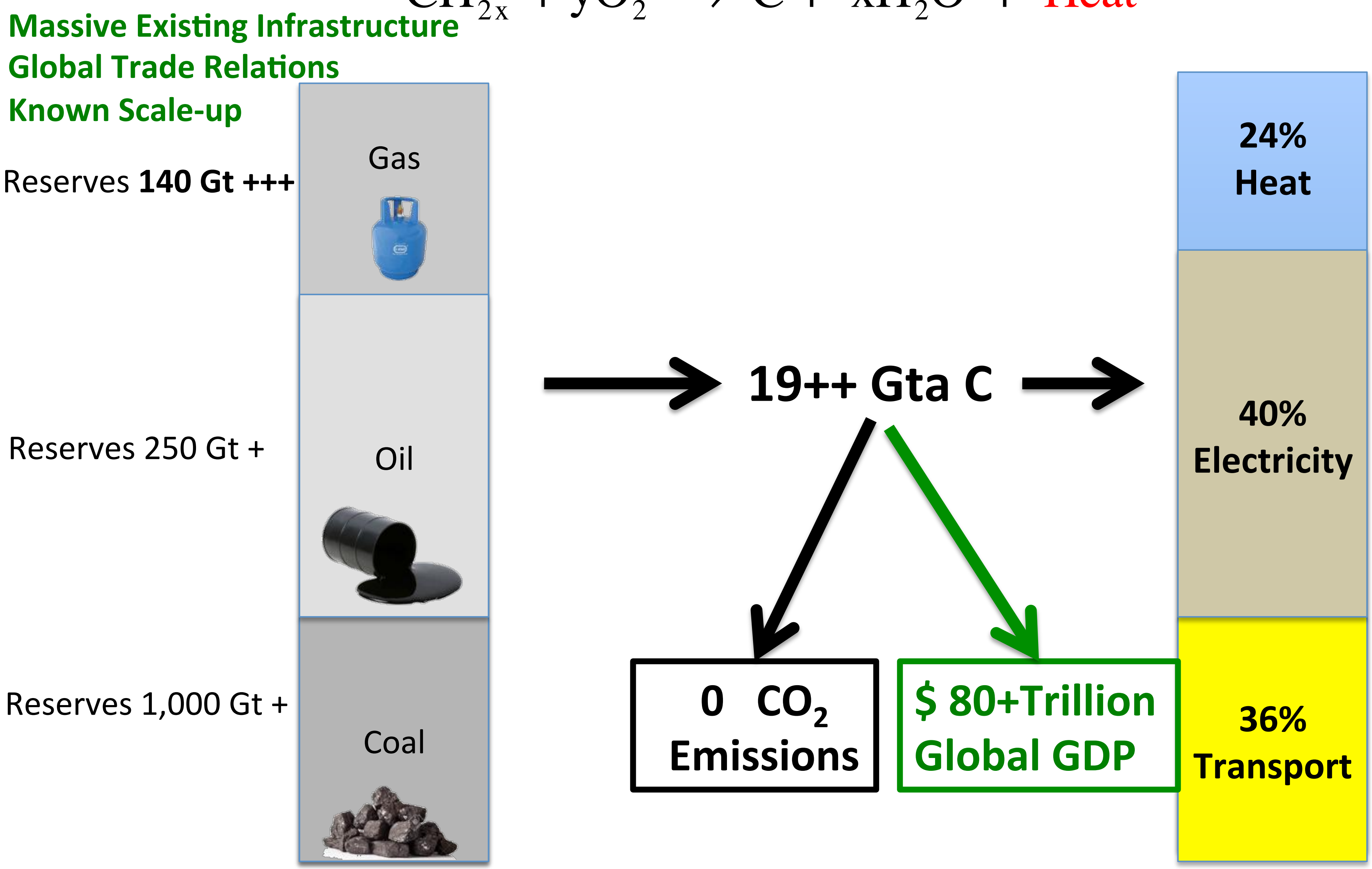
40% Electricity

36% Transport

BUT, if…….

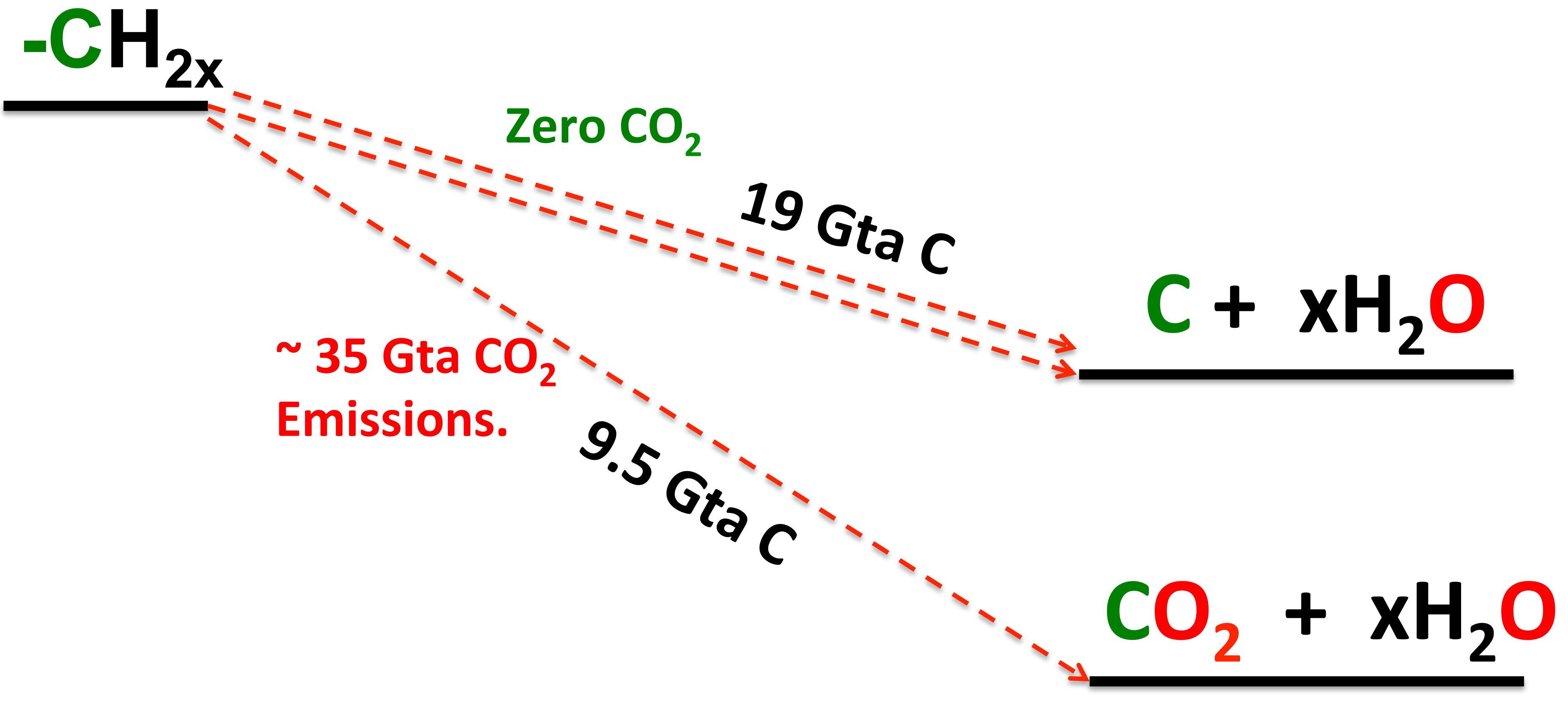
Plan B: Hydrocarbons for Low Cost Heat Without CO_2

$$-CH_{2x} + yO_2 \rightarrow C + xH_2O + \text{Heat}$$



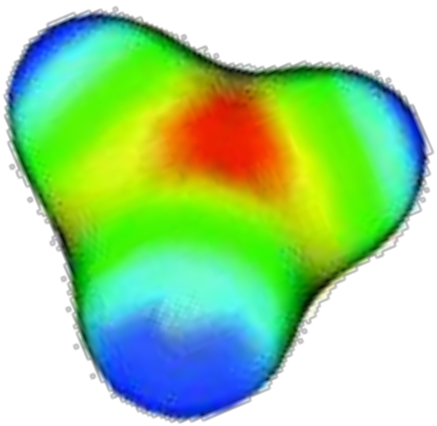
Plan B: ~2x fossil resources **For Heat**

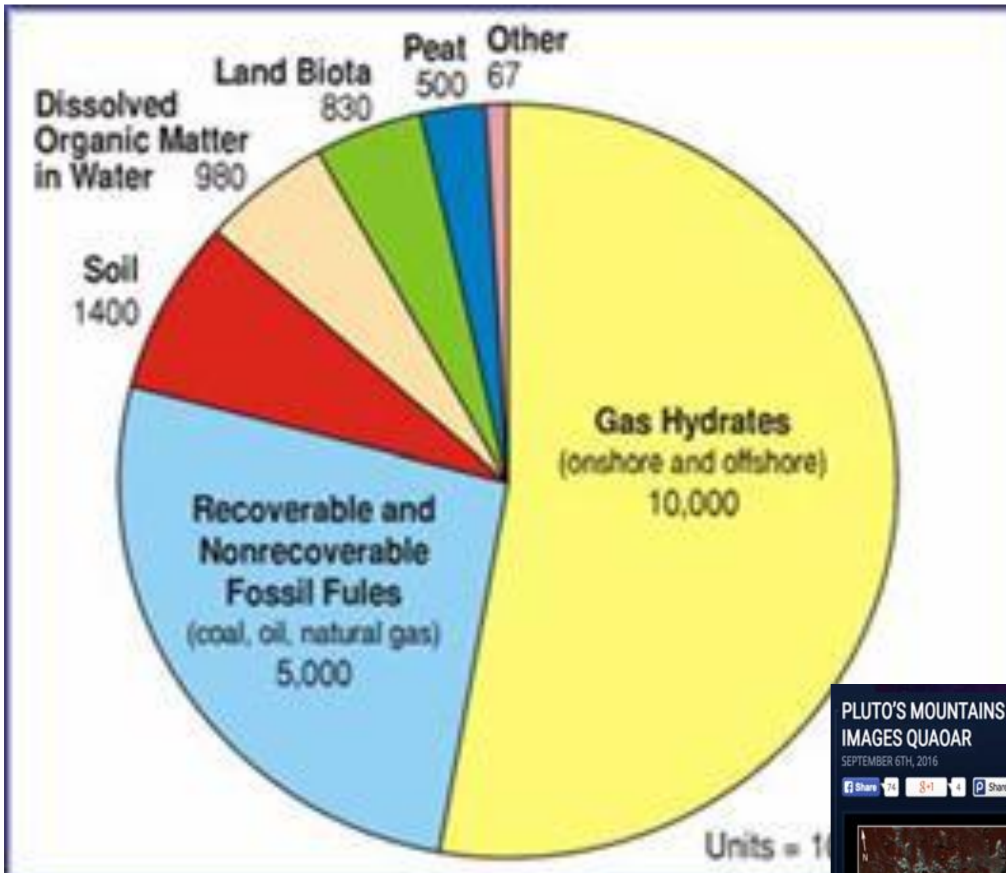
More strategic use of our fossilized solar resources may be more reasonable than no use at all or CCS.

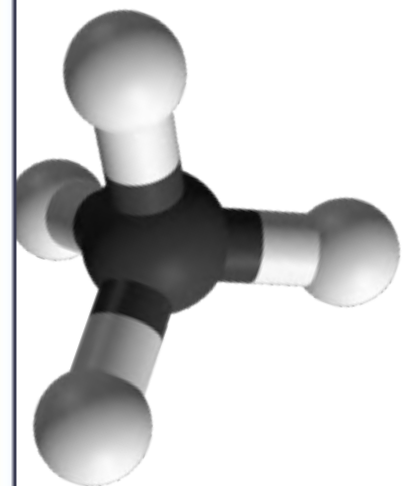


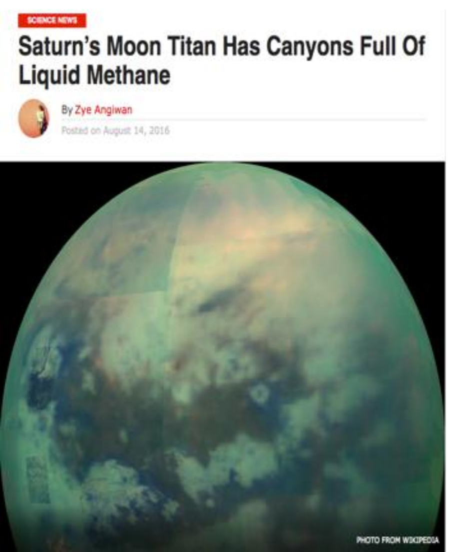
Massive Quantities of Methane are Available

Worldwide > 7000 tcf Natural Gas Reserves (non-hydrate) ~ 250 TW-y





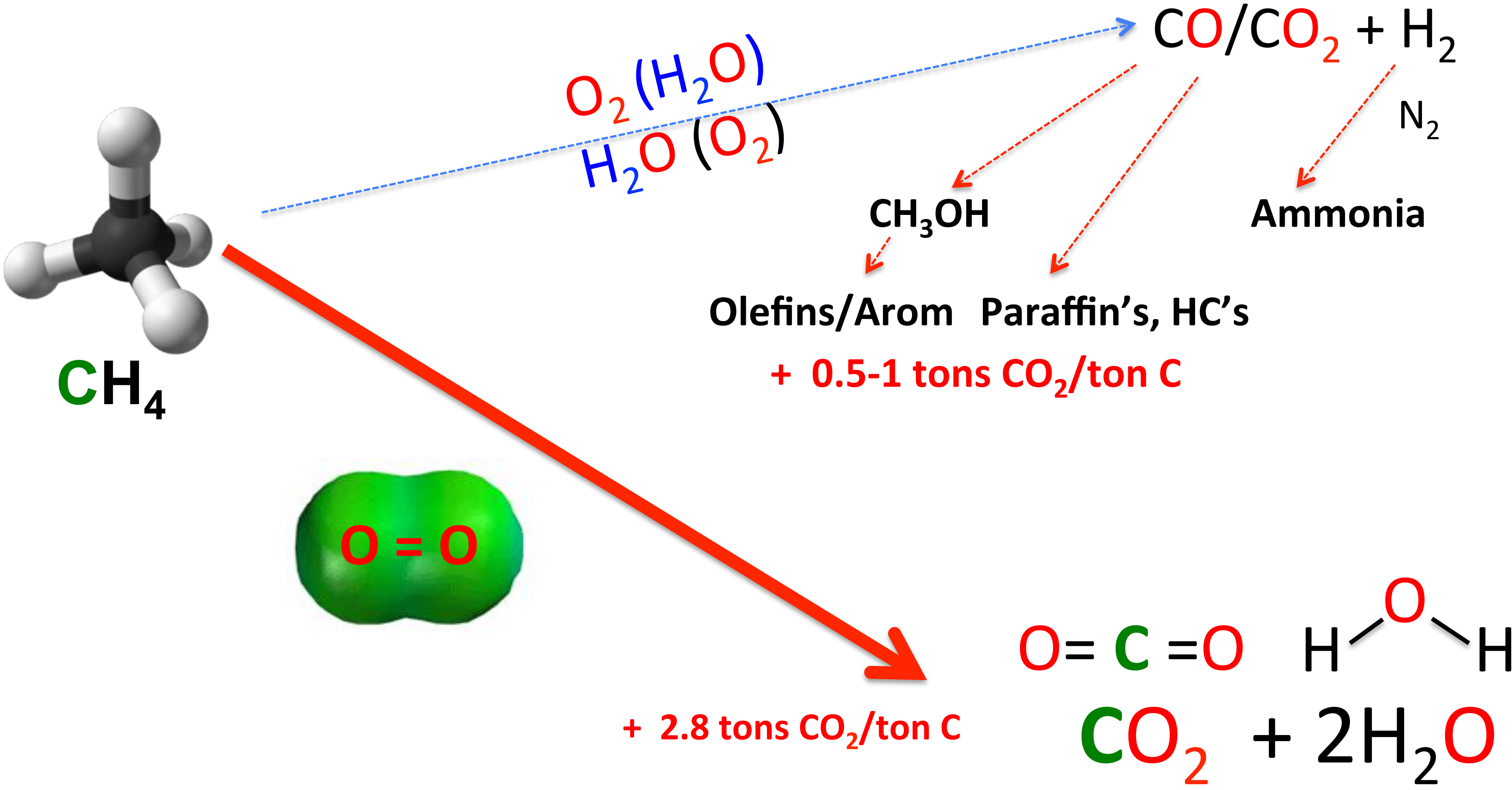




Natural Gas Utilization: Past = Present

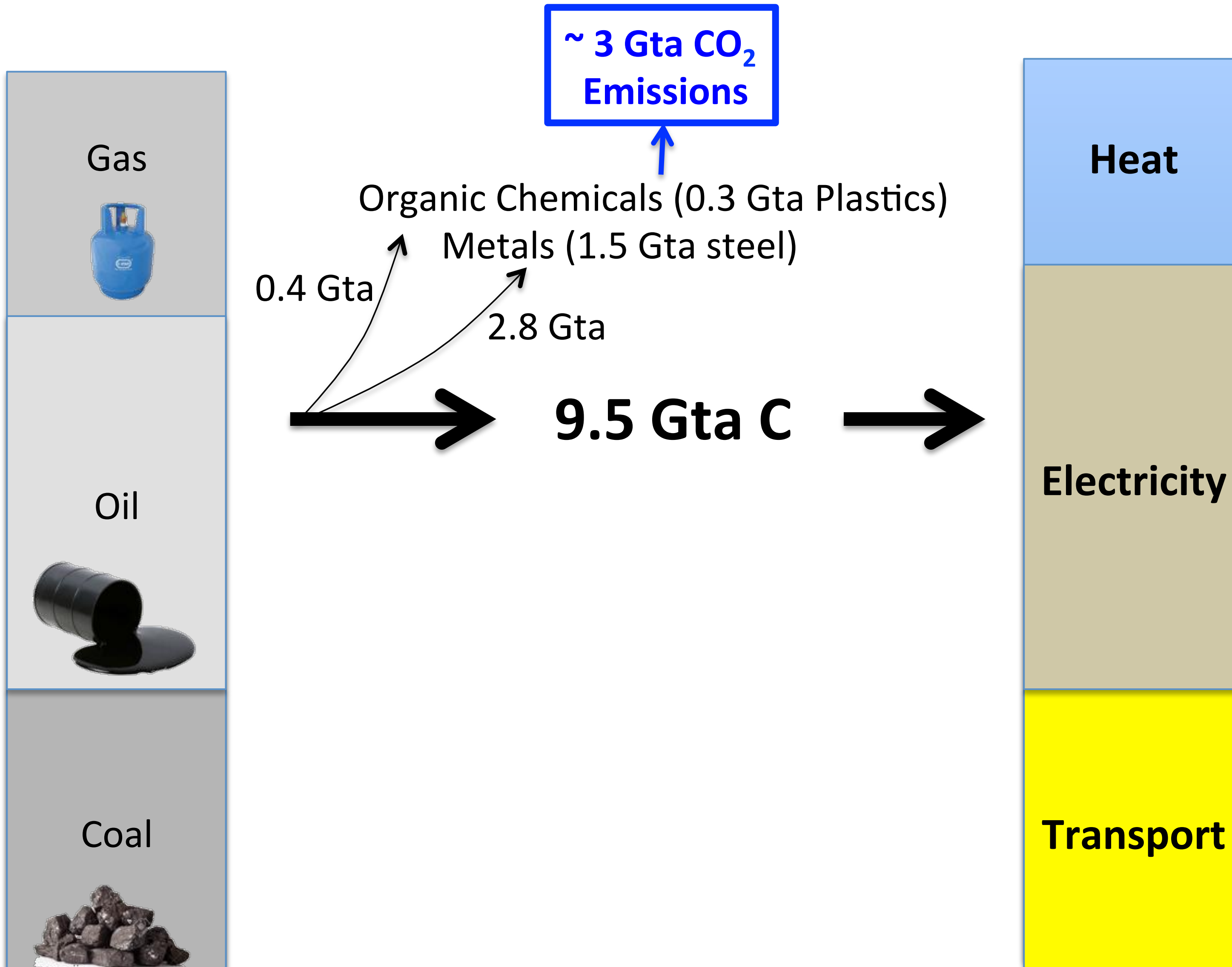
~ 2 Gta of methane is burned in abundant oxygen to produce heat

+ small contribution to the 0.4 Gta of organic chemicals made largely from petroleum.

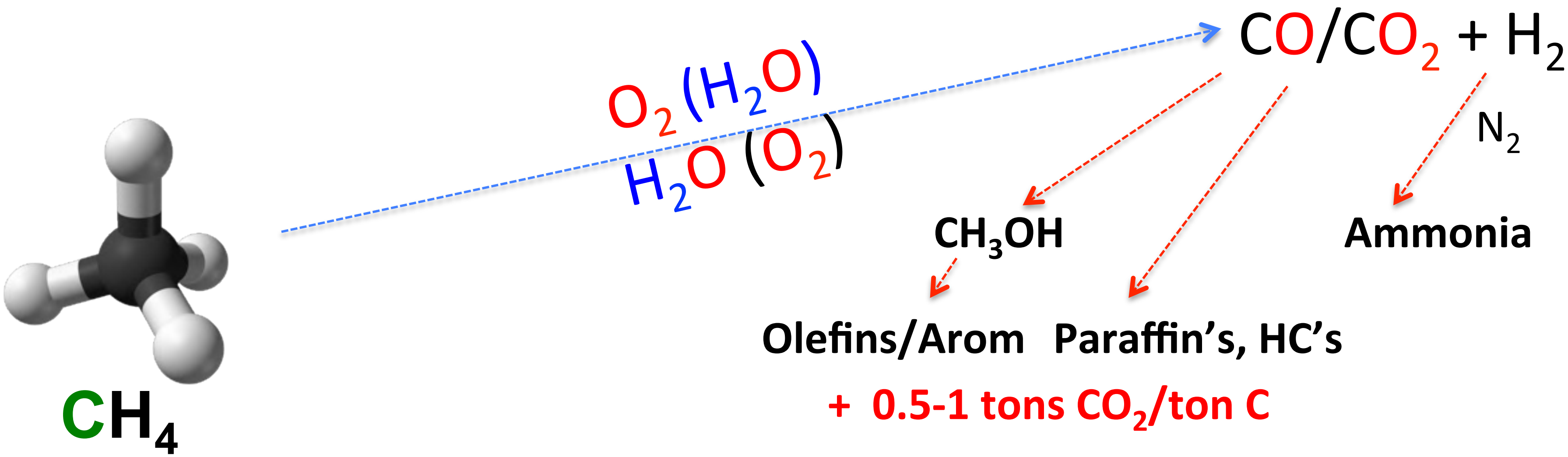


Sustainable Chemical Production Is A Relatively Minor Problem

But potentially large opportunity



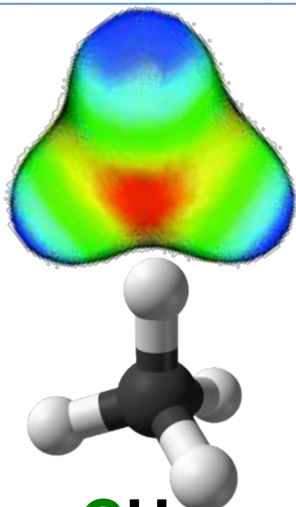
"Selective" Partial Oxidation of Methane for Chemicals



Selective Partial Oxidation of Methane for Chemicals

Oxidative Coupling of Methane over Lithium-Promoted Zinc Oxide Catalyst

Ikuya MATSUURA, Yasuhide UTSUMI, Miyuki NAKAI, and Takao DOI
Faculty of Science, Toyama University, Toyama 930



CH_4

$C^{(-4)}$

Academic "Holy Grail"

$$CH_4 + \frac{1}{2}O_2 \longrightarrow \frac{1}{2}C_2H_4 + H_2O$$

Oxidative Coupling of Methane (OCM)

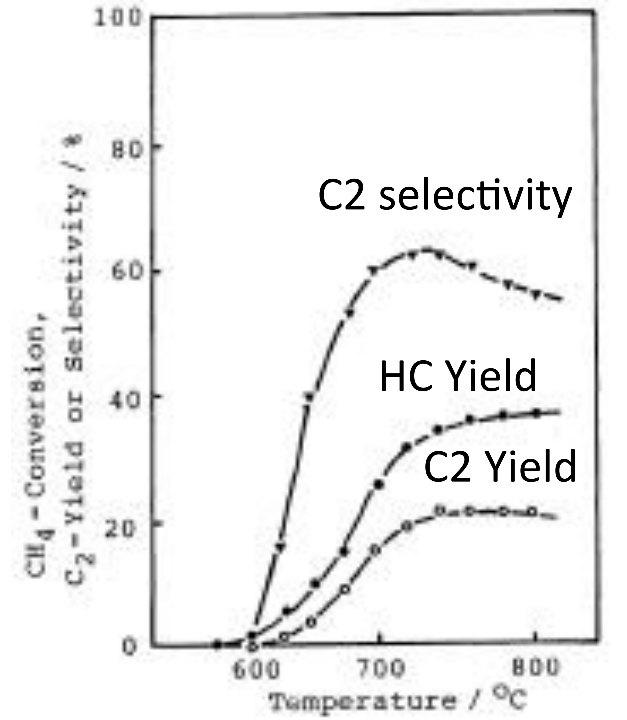


Fig. 2. Amount of CH_4 converted with reaction temperature over 12.5 mol % Li-promoted ZnO. CH_4= 262 Torr, O_2 = 124 Torr. ●, total; o, $C_2H_4+C_2H_6$; ▼, C_2-selectivity.

Chemistry Letters, 1986, 3, p 1981-1984

To Dream the Impossible Dream

OCM With O_2: Thermochemically and Kinetically Not Sensible (*Bell-Evans-Polanyi)*

$$CH_4 \xrightarrow[O-M]{k1} C^{-2} \xrightarrow[O-M]{k2} \rightarrow\rightarrow CO_x + H_2O$$

$$CH_4 \xrightarrow[O_2]{\text{gas phase}} \longrightarrow \rightarrow\rightarrow\rightarrow\rightarrow CO_x + H_2O$$

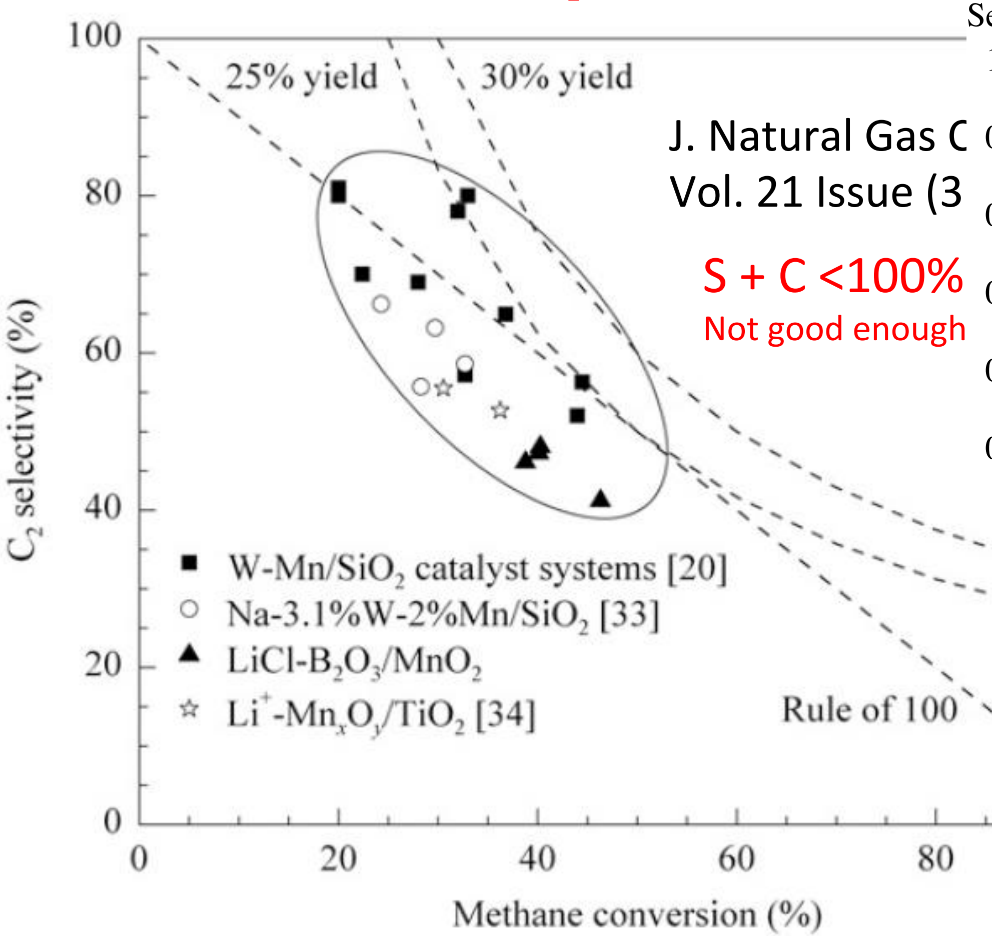
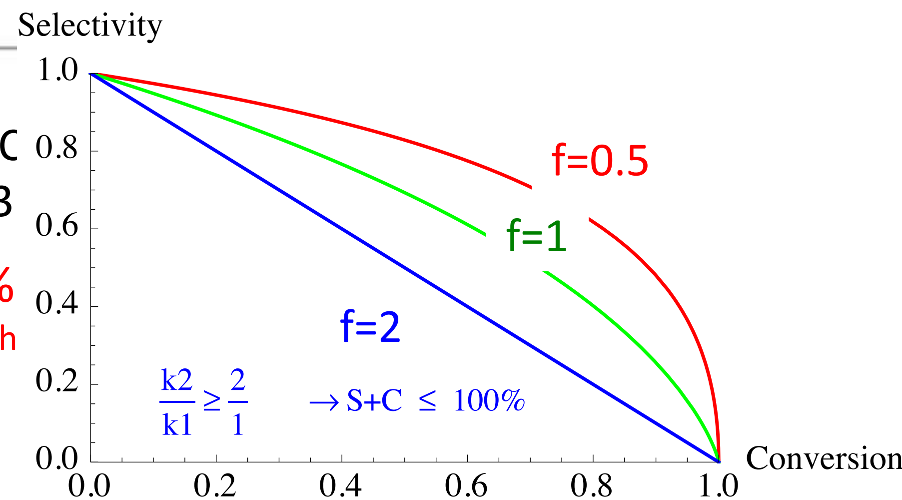
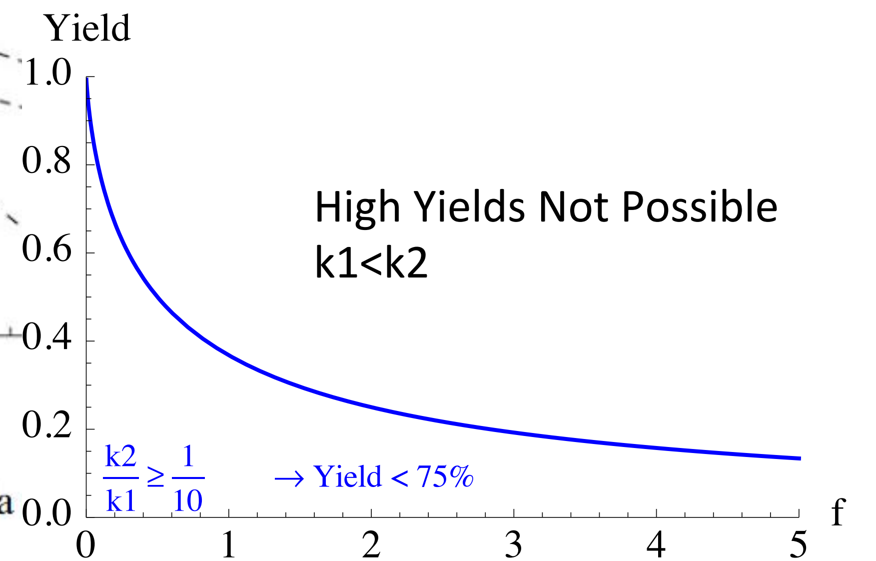


Figure 7. Applicability of the rule of 100 to experimental data or higher

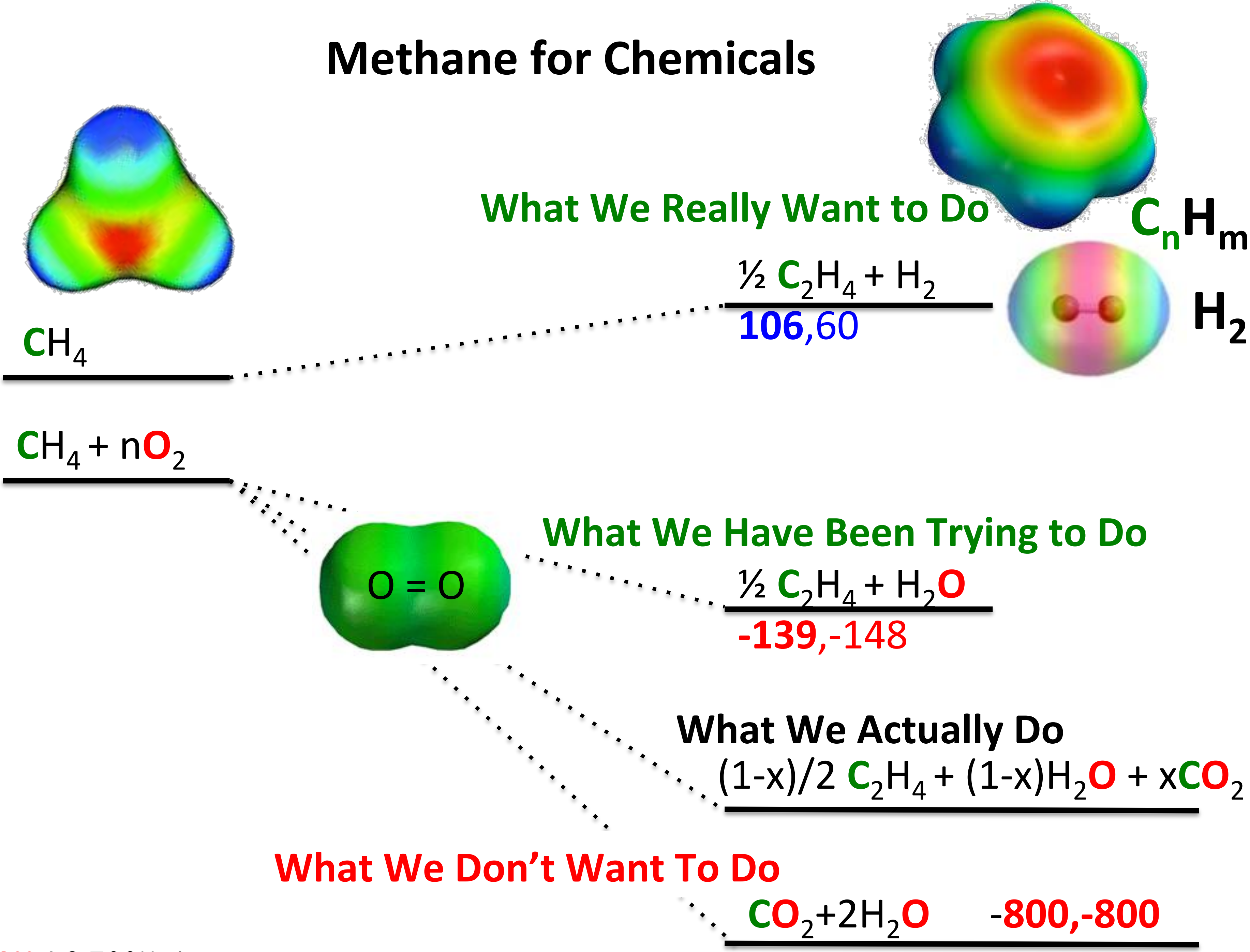
J. Natural Gas C
Vol. 21 Issue (3

S + C <100%
Not good enough



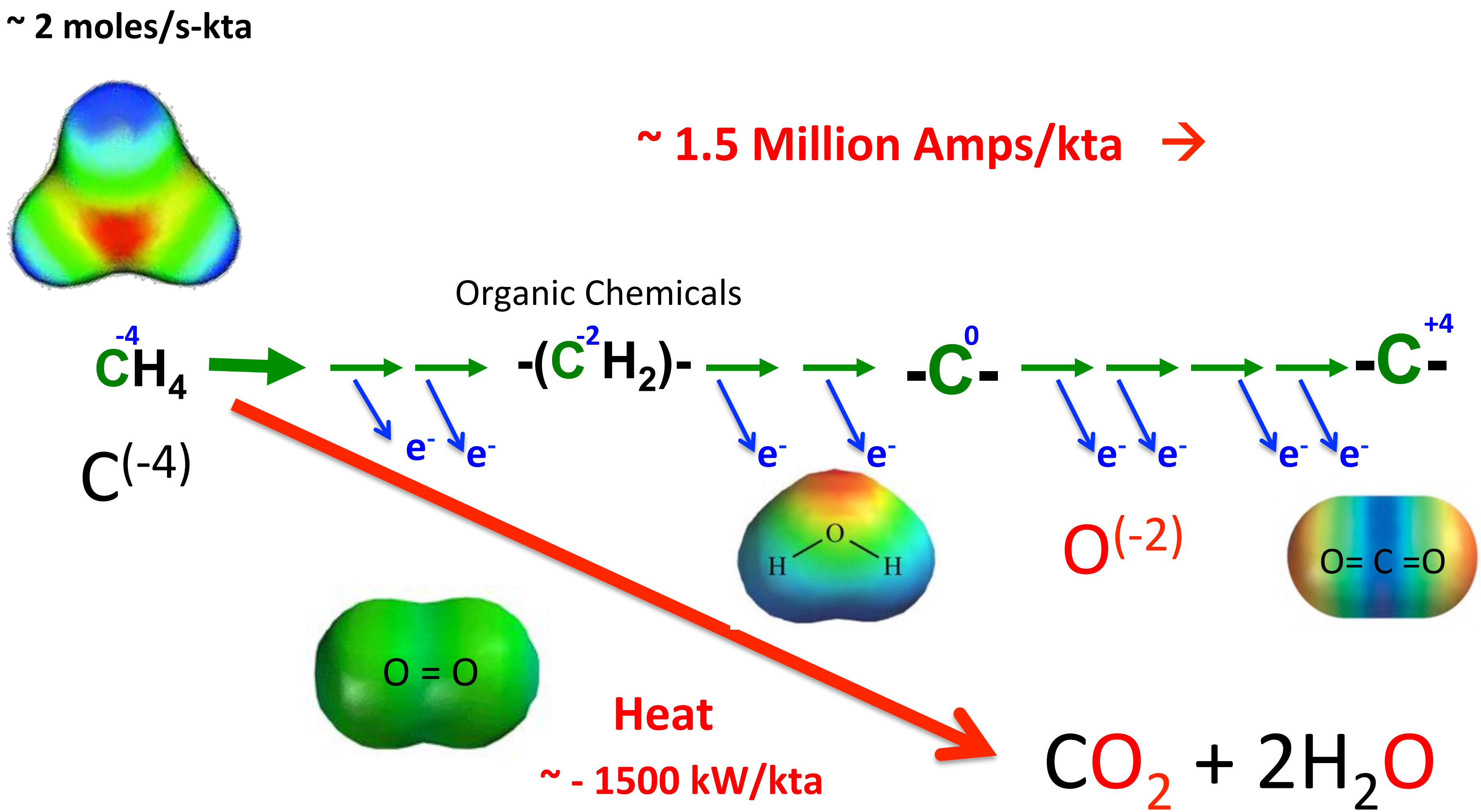


Methane for Chemicals

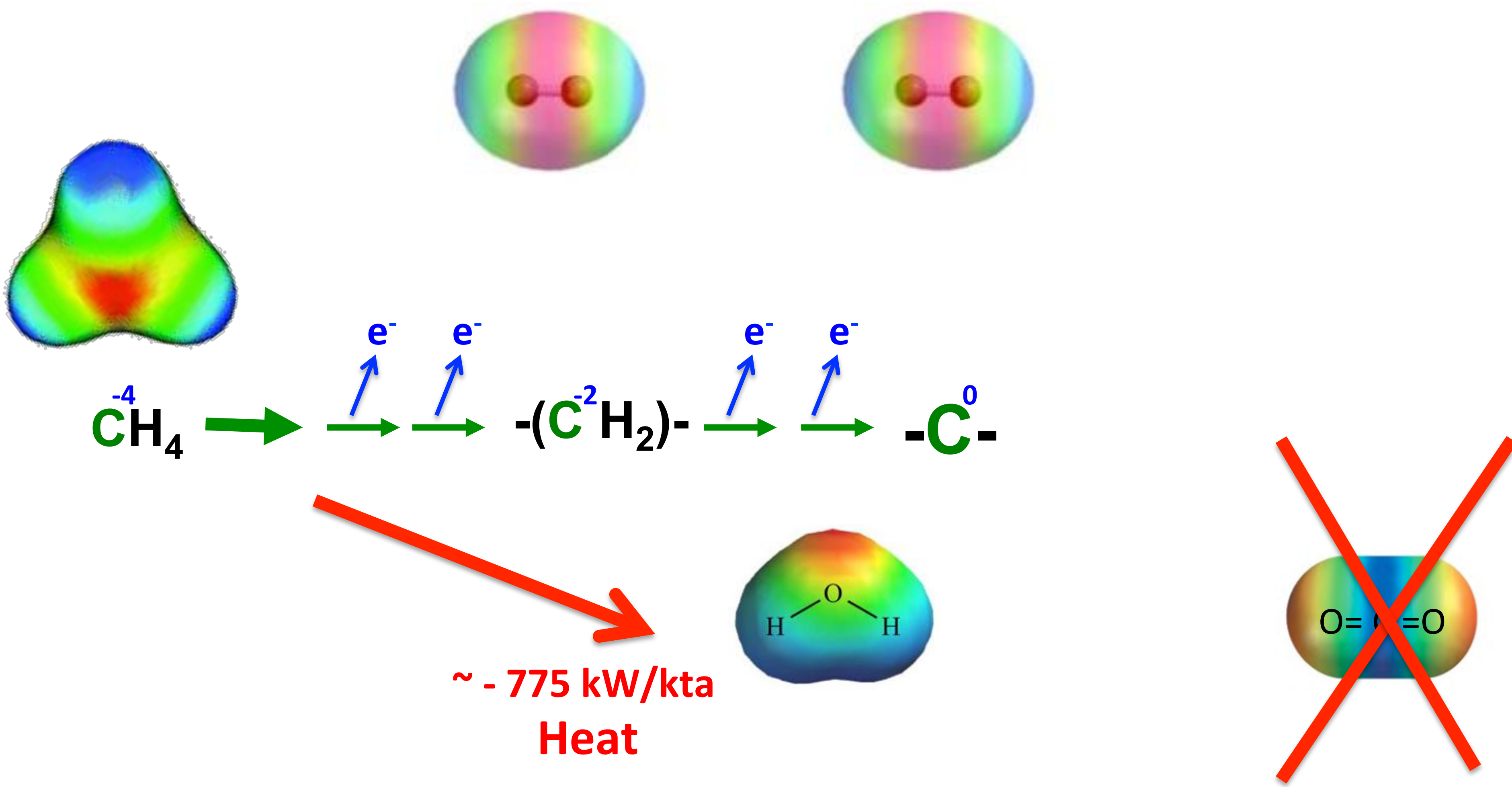


ΔH,ΔG 700K, 1atm

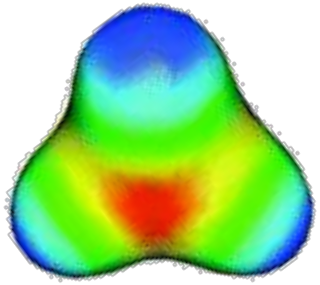
Philosophical approach → maintain the electron's chemical potential

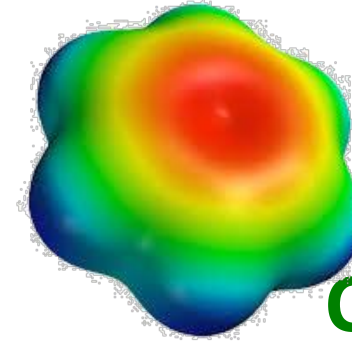


Do not allow complete C oxidation: Different Reaction Environments



Methane for Organic Chemicals





C_nH_m

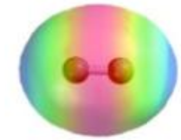
$CH_4 + nX_2$

I_2

Cl_2

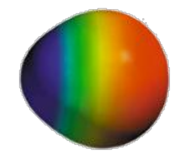
O_2

½ $C_2H_4 + H_2$ **106**,60



H_2

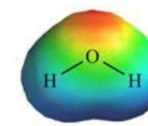
½ C_2H_4 + 2HI **94**,36



2HX

½ C_2H_4 + 2HCl **-80**,-137

½ $C_2H_4 + H_2O$ **-139**,-149



H_2O

Oxygen is not the only electrophile !

ΔH,ΔG 700K, 1atm

Halogens Suppress Complete Oxidation

flame retardants:

1) Oxidative dehydrogenation +

2) Suppresses oxycombustion

$-CH_2-CHBr-CH_2-$ - - - --- - - $CH_2-CH_2-CH_2-$

↑T

Hydrodebromination(ODH)

$-CHBr-CH_2- \rightarrow -CH=CH- + HBr$

$HBr + O_2 \rightarrow HOO^* + Br^*$

$HOO^* + HBr \rightarrow H_2O_2 + Br^*$

$H_2O_2 \rightarrow 2OH$

$OH + HBr \rightarrow H_2O + Br^*$

$HCl + O_2 \rightarrow HOO^* + Cl^*$

$HBr + O_2 \rightarrow HOO^* + Br^*$

$HI + O_2 \rightarrow HOO^* + I^*$

HI is the fastest

Alkylhalides are Easy To Make and Easy To Separate

Oxyhalogenation/Dehydrohalogenation for Partial Oxidation

Fredrick Rust, Industrial & engineering chemistry

1949 vol:41 iss:11 pg:2595

Oxidation of Hydrocarbons Catalyzed by Hydrogen Bromide

SUMMARY

FREDERICK F. RUST AND WILLIAM E. VAUGHAN

Shell Development Company, Emeryville, Calif.

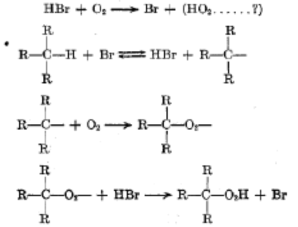
The gas phase, homogeneous oxidation of the lower hydrocarbons is greatly modified by the presence of hydrogen bromide. In the presence of this catalyst ethane is converted principally to acetic acid, straight-chain paraffins mainly to ketones, and branched-chain compounds chiefly to stable peroxides. The character of the product is determined principally by the most reactive carbon-hydrogen linkage in the molecule. In these reactions the reactivities of these linkages increase markedly in the order—primary, secondary, and tertiary. The introduction of oxygen under these conditions is accompanied by a low degree of carbon-carbon bond scission, the operating temperatures are low, and the conversions and yields high.

THE availability of vast quantities of natural gas and petroleum hydrocarbons attaches more than ordinary importance to their economic utilization as sources of industrial chemicals. An obvious and especially attractive method of using the lower paraffins is their direct oxidation with gaseous oxygen. Extensive prior research has given evidence of the mechanism of oxidation and it is thought by many to involve the generation of free radicals which react with oxygen to form peroxy bodies. These are, apparently, generally unstable under the extreme reaction conditions necessitated by the inherent stability of the paraffin toward oxygen and thus decompose, perhaps violently, with carbon skeleton breakdown. The present study has revealed that addition of a third component, hydrogen bromide, lowers the reaction temperature, stabilizes the reactive peroxy intermediates, and, thus, so modifies the oxidation chains that the undesired degradation reactions are minimized.

These oxidations not only are characterized by discreteness of reaction, but also in some cases lead to products not previously derived in quantity from reactions with oxygen. High yields of relatively simple mixtures are obtained at temperatures far below those usually encountered in hydrocarbon oxidations. The joint participation of hydrogen bromide and oxygen in photochemical chain reactions involving olefins was demonstrated earlier in these laboratories (*9*). This paper summarizes the laboratory results obtained with several types of hydrocarbons and the mechanisms developed to explain the various kinds of principal products derived therefrom. The experimental data will be given in greater detail in succeeding papers (*1–3, 7*).

The hydrogen bromide–catalyzed oxidation of paraffins containing *tertiary* carbon-hydrogen linkages (*2*) appears to proceed by a relatively simple chain reaction, which is fundamental to the oxidations of the other types of compounds. (In accordance with general acceptance, tertiary carbon-hydrogen bonds or tertiary hydrogen atom involve a carbon-hydrogen linkage wherein the other three valences of the carbon are satisfied by three other carbon atoms. The same interpretation is applicable to secondary and primary.) In general it can be said that branched chain compounds are converted in high yield to stable organic hydroperoxides; this is a characteristic which distinguishes these oxidations from others of the past, inasmuch as such a product in major amount has not been reported heretofore. For example, the oxidation of isobutane, the simplest member of the series, at temperatures as low as 160° C. produces *tert*-butyl hydroperoxide in yields as high as 75% based on the consumed oxygen from a 10 to 10 to 1 mixture of isobutane, oxygen, and hydrogen bromide under conditions where 87% of the oxygen is reacted. *tert*-Butyl alcohol and di-*tert*-butyl peroxide (*6, 10*) are also formed. Breakdown of the carbon skeleton during the oxidation is minor. Further, the hydrogen bromide catalyst is regenerated semiquantitatively; losses are attributable to oxidation to bromine or to formation of organic bromides, the possibilities for the production of which will be apparent from a consideration of the following mechanism developed to explain the principal reaction:

$$HBr + O_2 \longrightarrow Br + (HO_2 \ldots\ldots ?) \qquad (1)$$



(2)

(3)

(4)

It is seen that the over-all reaction is simply:

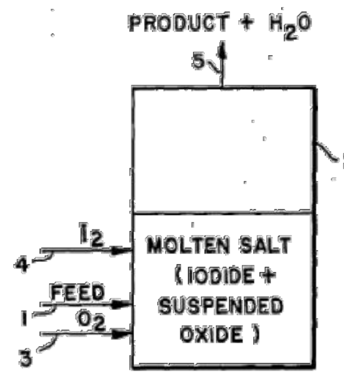
$$(R)_3CH + O_2 \xrightarrow{HBr} (R)_3COOH \qquad (5)$$

Equation 1, a chain-initiating step which probably occurs largely at the wall, generates a bromine atom. The bromine atom, in reacting with a molecule of a tertiary hydrocarbon or derivative, attacks virtually exclusively the tertiary hydrogen atom, forming hydrogen bromide and the tertiary-alkyl radical (Equation 2). The latter may, with due consideration for the probable reversibility of the previous reaction, undergo an association reaction with oxygen (Equation 3) and the peroxy radical thus produced is stabilized as the hydroperoxide molecule by an exchange reaction with hydrogen bromide (Equation 4). By this process a bromine atom is regenerated and reactions 2, 3, and 4 may be repeated. Of course, the chain can be interrupted at any point by destruction of the carrier radicals, as by inelastic collision with the walls or by the association of two radicals. It is apparently reaction 4 which distinguishes these oxidations from others which are less clean-cut, for without such a hydrogen donor, the peroxy radical apparently cannot become a stable molecule and instead breaks down with varying degrees of carbon-carbon bond scission. Further and important is the specificity of the

March 5, 1963 M. NAGER 3,080,435

DEHYDROGENATION PROCESS

Filed July 18, 1960



Shell 1960's (I_2-ODH)

- 90% Sel., 80% Conv.

More Separable Intermediates

React for Show, Separate for Dough

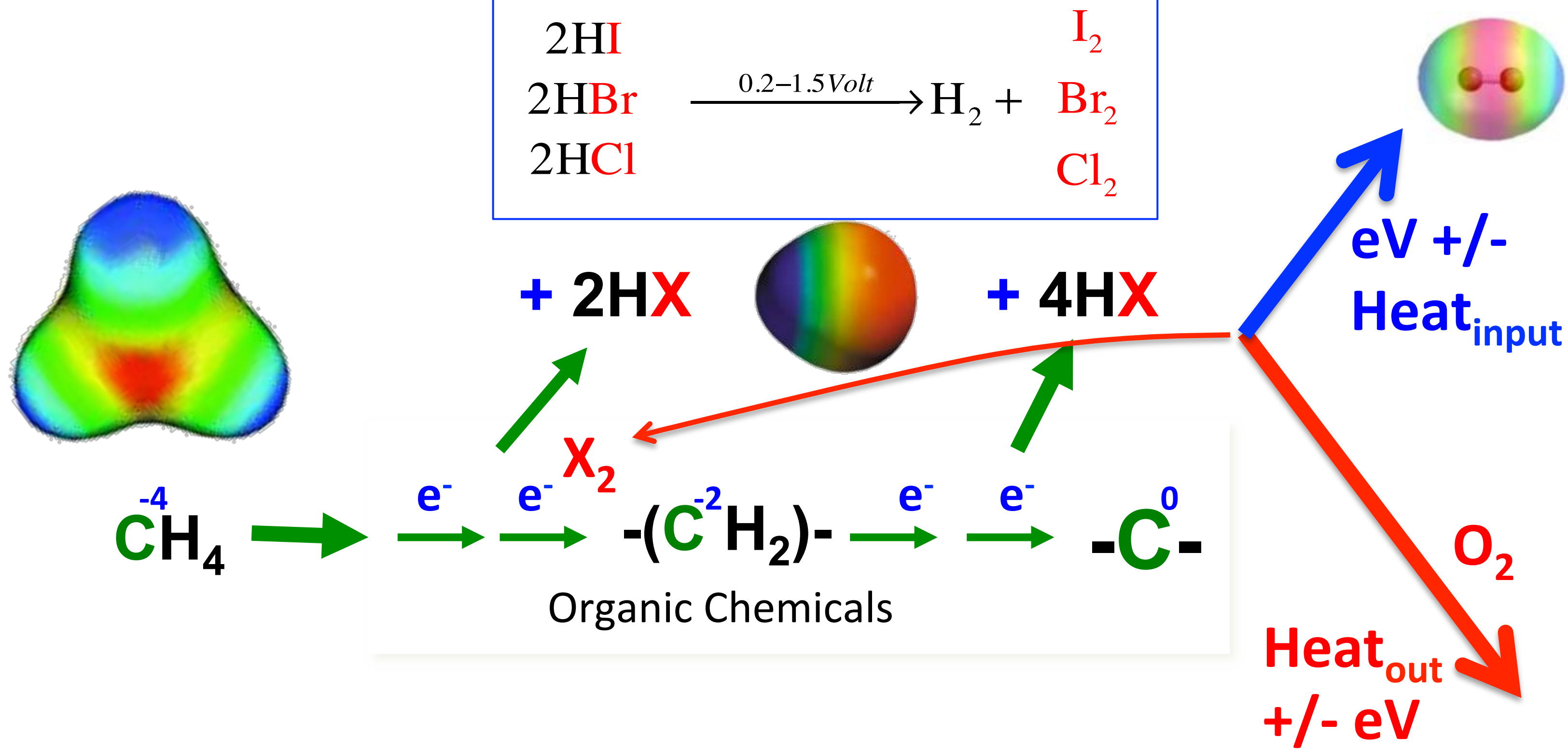
$$CH_4 + XY \rightarrow H_3C\text{-}X/H_nC_m + HY$$

XY	Intermediates	HY
O_2	CH_4 , N_2, CO_x CH_yO_x	H_2O, H_2
S	CH_4 CH_3SH CS_2	H_2S, H_2
NO_x	CH_4 N_2, NO, CO_x	H_2O
SO_x	CH_4 SO_2 CH_3SO_3H	H_2O SO_2 H_2SO_4
I, Br, Cl	CH_4 $CH_n\text{-}X_m$	HX, H_2

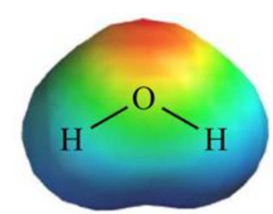
Less “efficient” or less direct reaction pathways with more separable products are often more desirable than more reaction efficient and direct pathways.

Transfer of Hydrogen (e^-) to Hydrogen Halide Offers Significant Process Flexibility and Preserves Chemical Potential

$$\left.\begin{array}{l}2HI\\2HBr\\2HCl\end{array}\right.\xrightarrow{0.2-1.5\,Volt} H_2 + \left.\begin{array}{l}I_2\\Br_2\\Cl_2\end{array}\right.$$

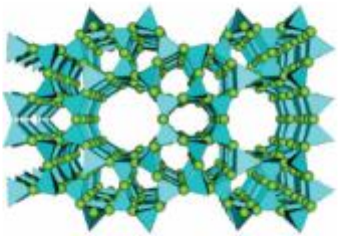


$$\left.\begin{array}{l}2HI\\2HBr\\2HCl\end{array}\right. + \frac{1}{2}O_2 \longrightarrow H_2O + \left.\begin{array}{l}I_2\\Br_2\\Cl_2\end{array}\right. + \text{Heat (or eV)}$$



Alkylhalides Are Readily Transformed Into Organic Chemicals Using Known Alcohol Pathways (MTO,MTG)

$$CH_3Br \rightarrow (-CH_2-) + HBr$$



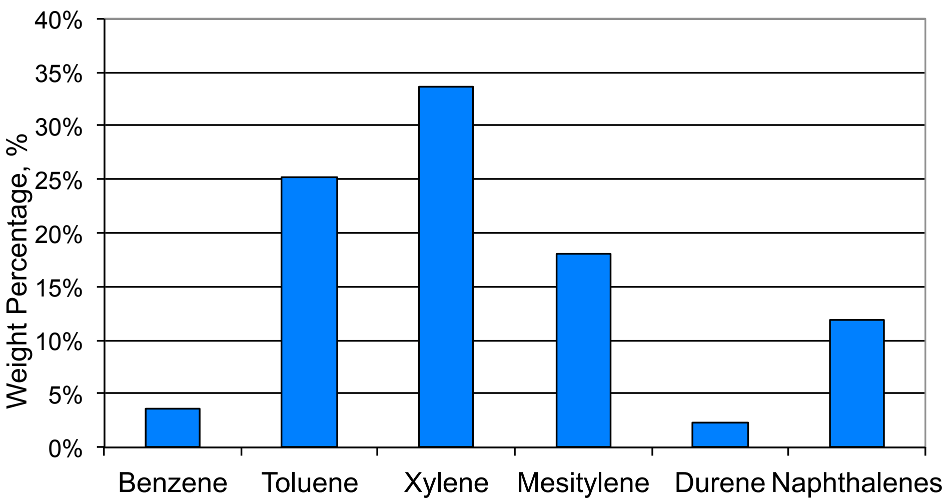
SAPO → Light Olefins (ethylene/propylene)

ZSM5 → Aromatics

Table 1 Product distribution for SAPO-34 at different temperatures

Catalyst, SAPO-34
Condition, 2.0 s, 0.2PCH_3Br

	C mol selectivity, %				
	400 °C	425 °C	450 °C	475 °C	500 °C
CH_4	1.3	2.1	3.2	4.8	8.2
C_2H_4	19.4	24.3	29.7	34.4	40.2
C_2H_6	0.3	0.4	0.6	0.8	1.0
C_2H_4/C_2H_6	64.7	60.8	49.5	43	40.3
C_3H_6	39.3	35.9	32.5	27.1	24.1
C_3H_8	7.0	5.2	4.8	3.6	2.4
C_3H_6/C_3H_8	5.6	6.9	6.8	7.5	10.1
C_{4-6}	14.0	13.3	10.4	9.6	6.5
BTXM +	2.8	4.4	3.7	3.1	3.7
RBr	8.9	9.1	9.2	7.9	5.1
Coke	7.0	5.3	5.9	8.6	8.9

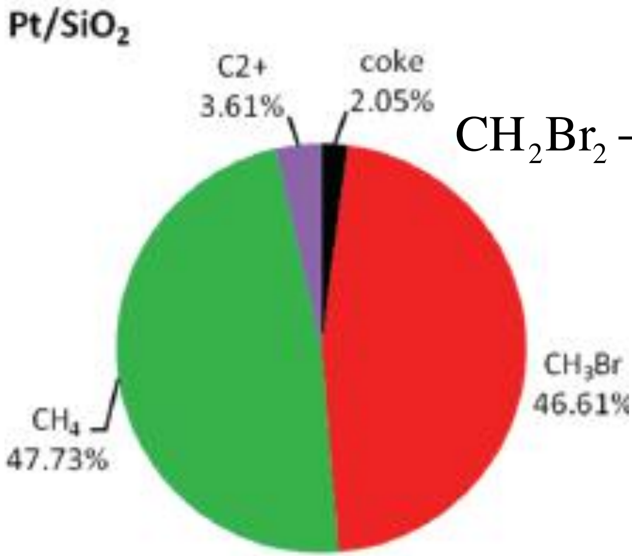


Phys. Chem.Chem.Phys. **2011,** 13,2550

Chem.Com. **2004**, 566, 658

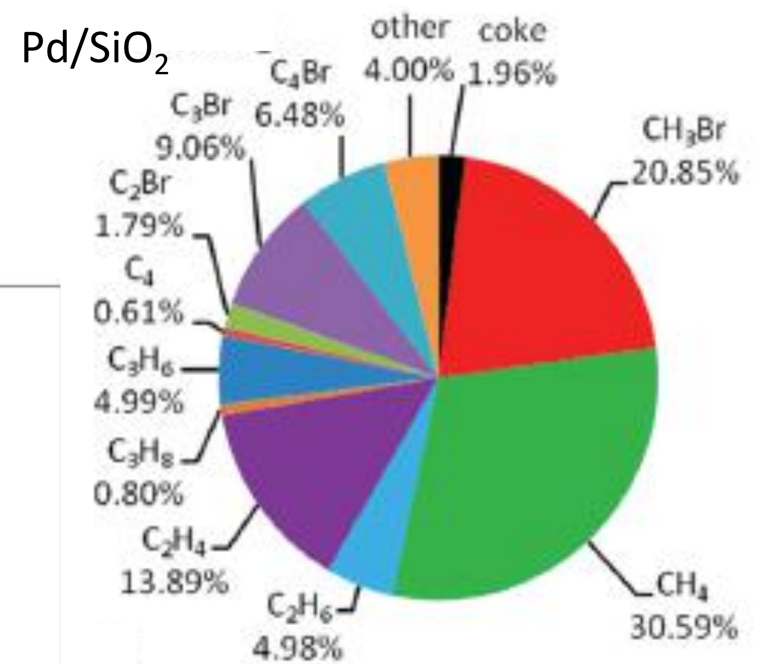
Polyhalides ? Interesting New (old) Chemistry

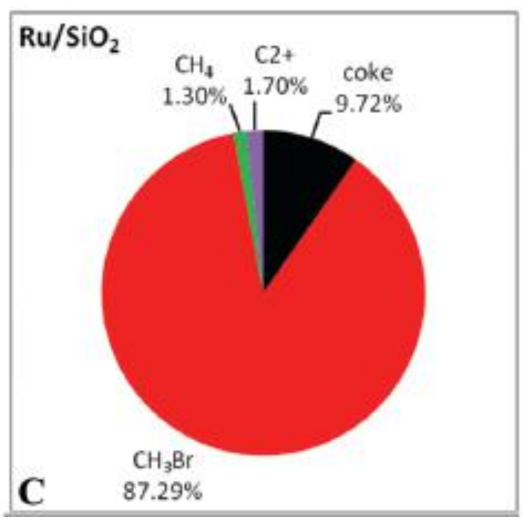
$$nCH_2Br_2 \rightarrow -C_nH_m + 2nHBr$$

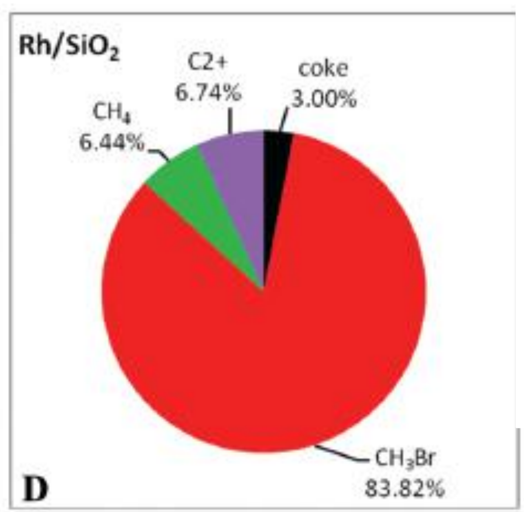


$$CH_2Br_2 \xrightarrow{H_2} CH_3Br \xrightarrow{H_2} CH_4$$

$$CH_2Br_2 \xrightarrow{H_2} {}^*CH \xrightarrow[-HBr]{} {}^*C_2H_5 \xrightarrow[-HBr]{} {}^*C_nH_m$$

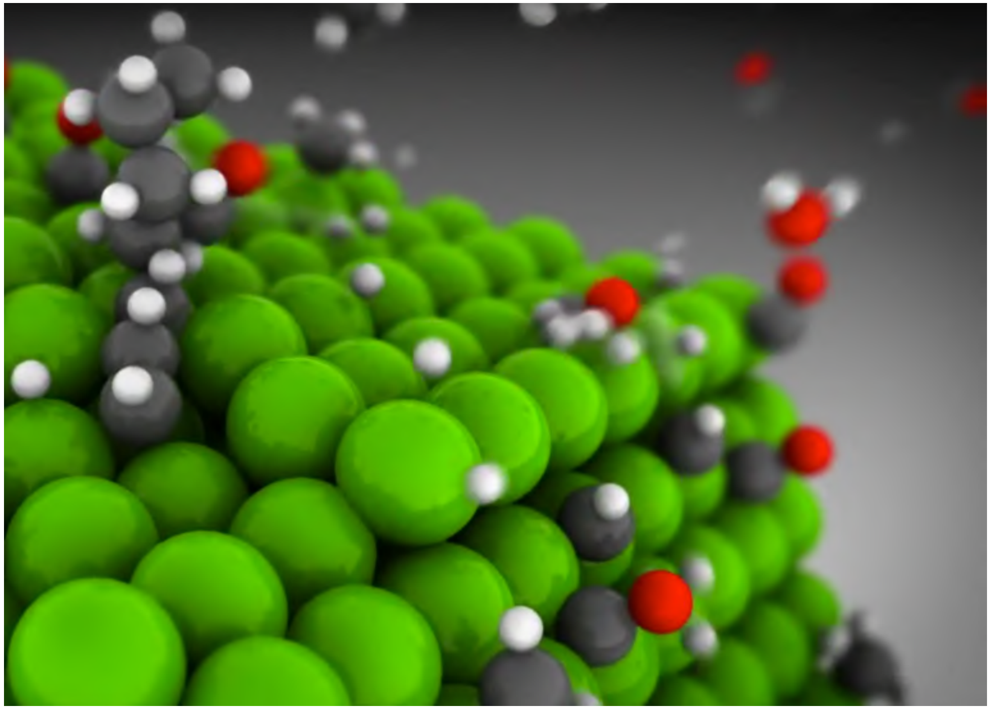






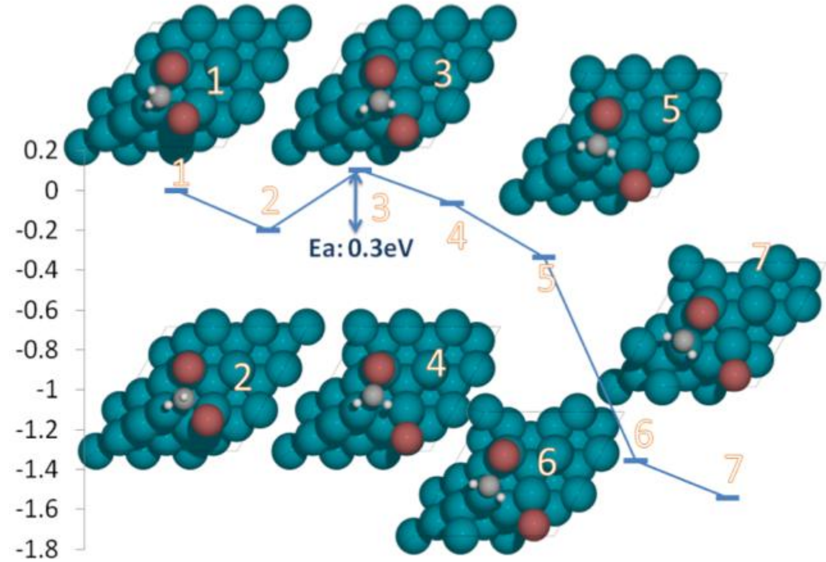
ACS Catal. (2012), 2, 479–486

What you want on surfaces for oligomers are -CH and -CH_2 (Fischer-Tropsch)

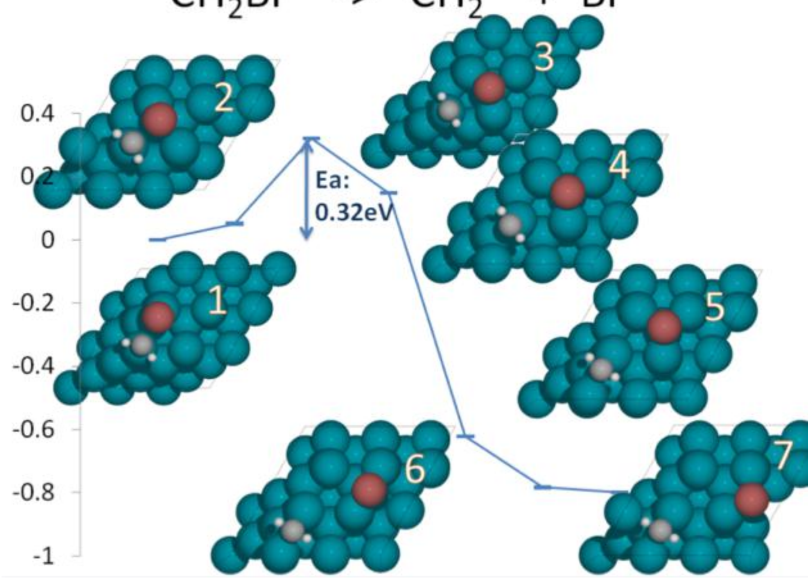


https://www.youtube.com/watch?v=44OU4JxEK4k

CH_2Br_2 -> CH_2Br^* + Br^* (E_a= ~0.3eV)

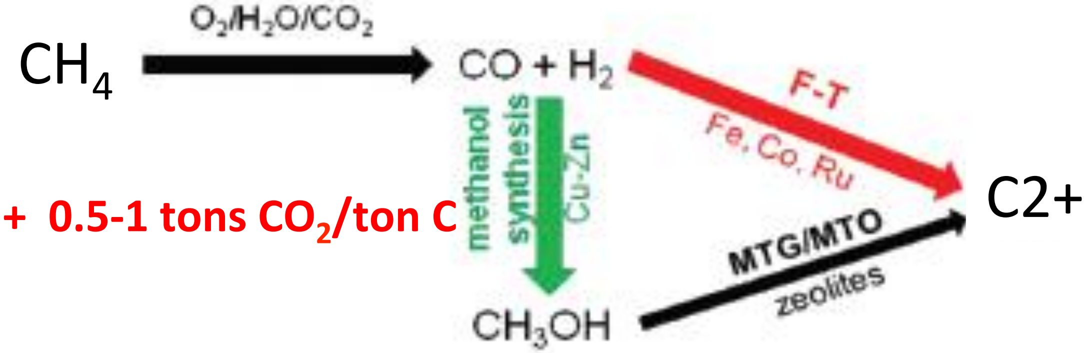


CH_2Br^* -> CH_2^* + Br^*

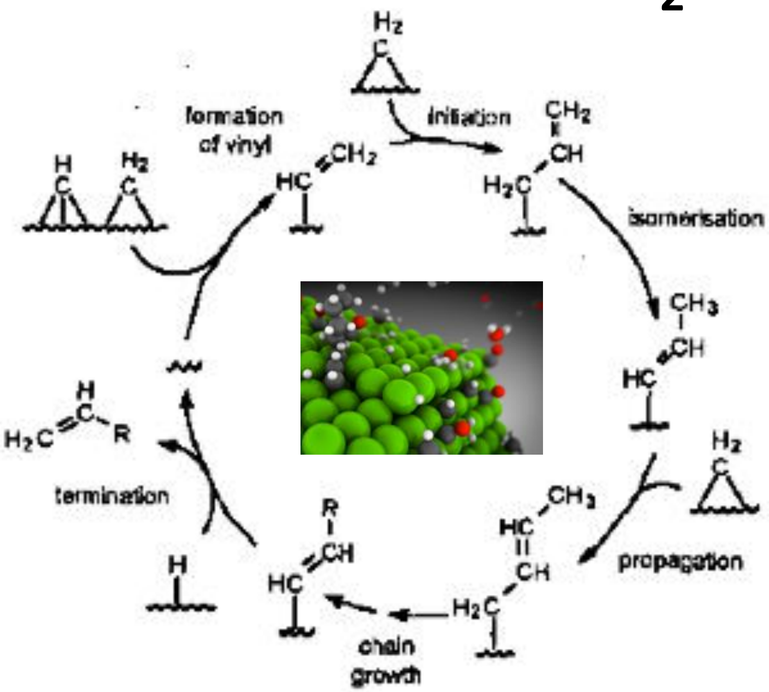


ACS Catal. (2012), 2, 479–486

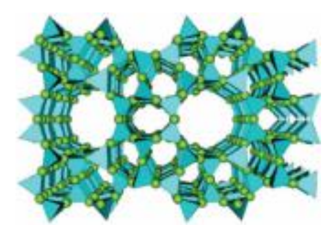
A General Platform for Methane Conversion without CO_2

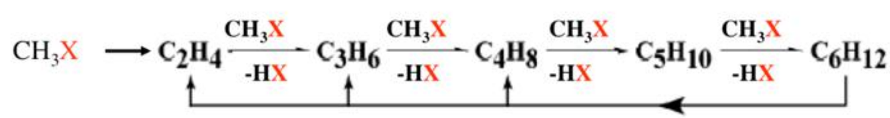


+ 0.5-1 tons CO_2/ton C

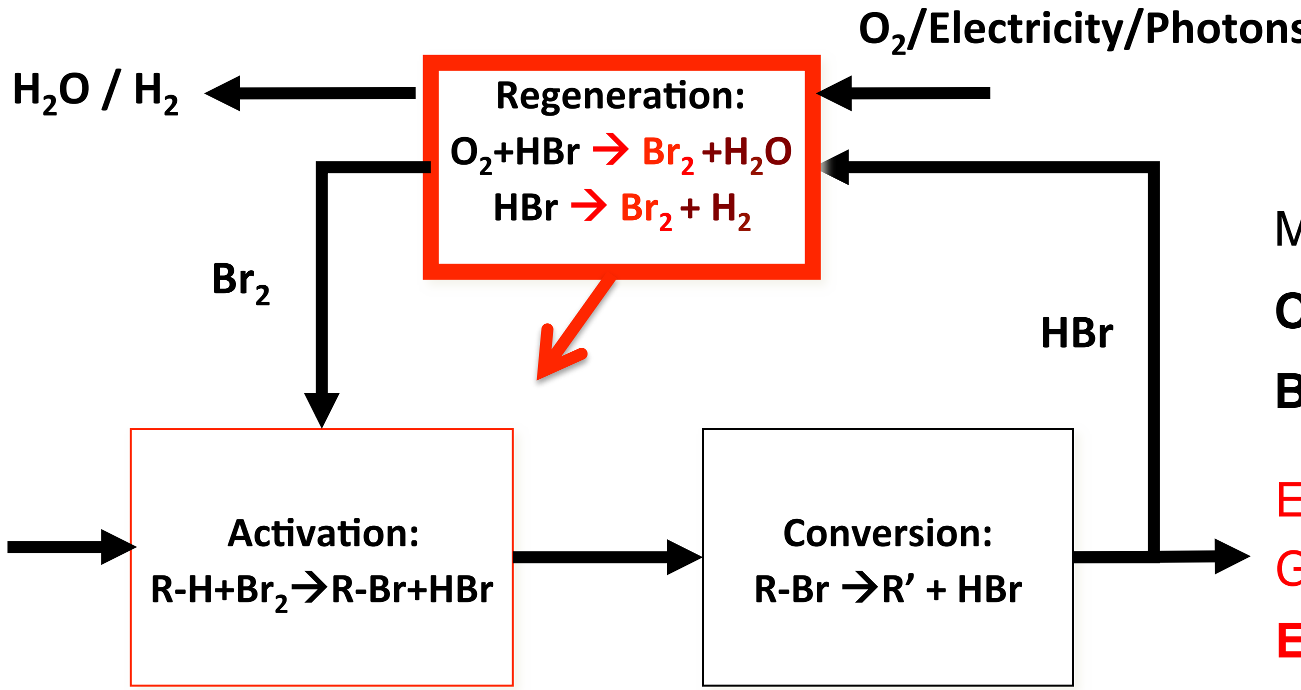


No CO_2





Demonstrated Br_2/HBr Platform



Methane

Ethane

Propane

Methanol/DME

Olefins

BTX+

Ethanol

Glycol

Ethylene

BTX+

Propanol

Propylene

BTX

Olefins

Ethoxylates

Without CO_2

But …….

Chem. Com. **2004**, 2100

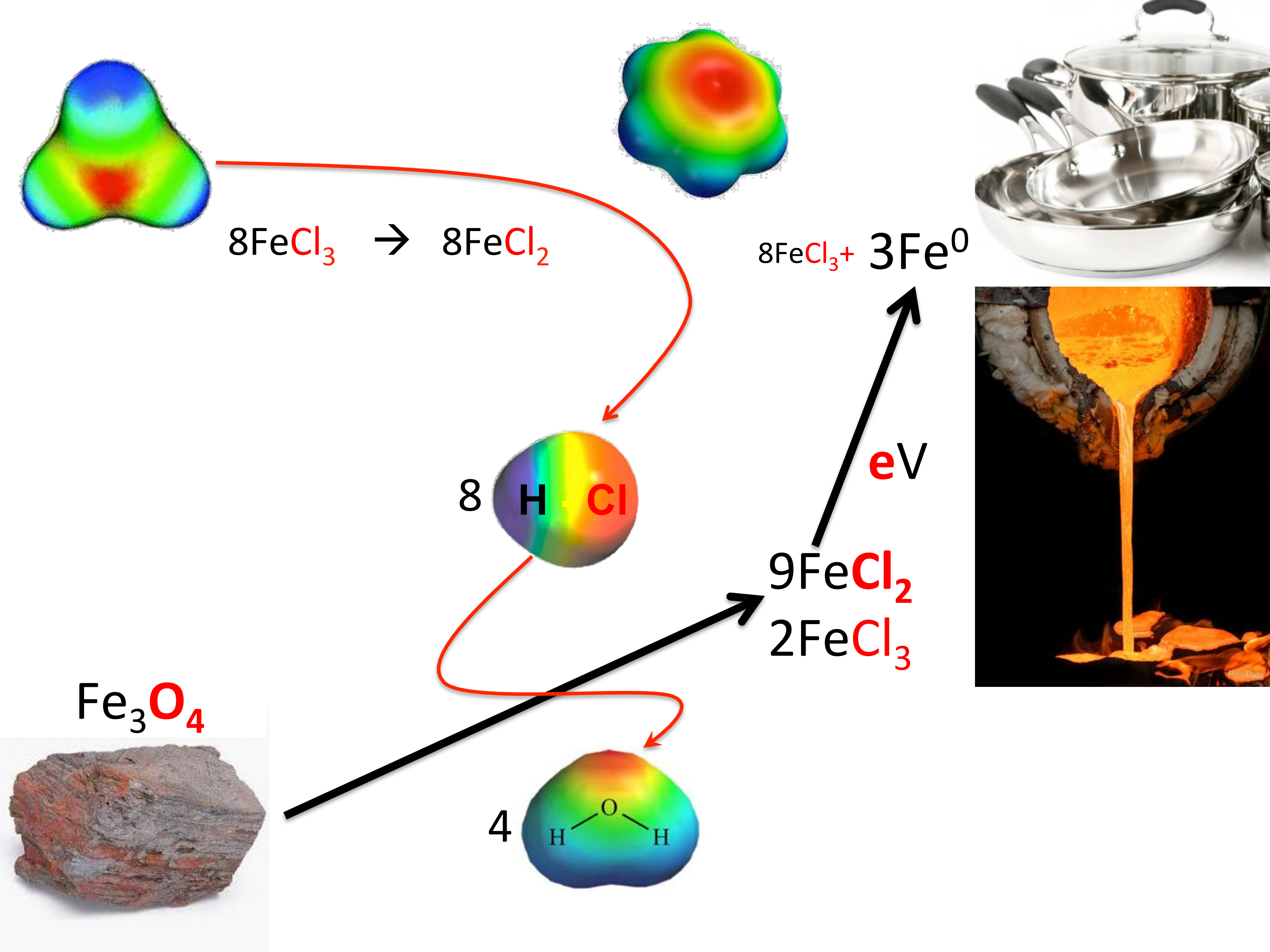
Catalysis Today **2004**, 98, 317

Chem.Com. **2004**, 566, 658

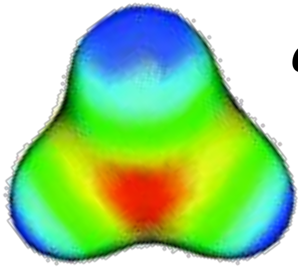
Phys. Chem.Chem.Phys. **2011**, 13,2550

ACS Catal. **2012**, 2, 479–486

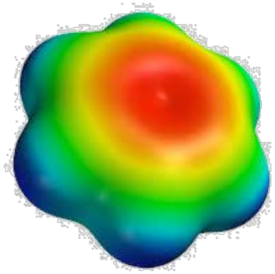

2 Gta
Fe3O4

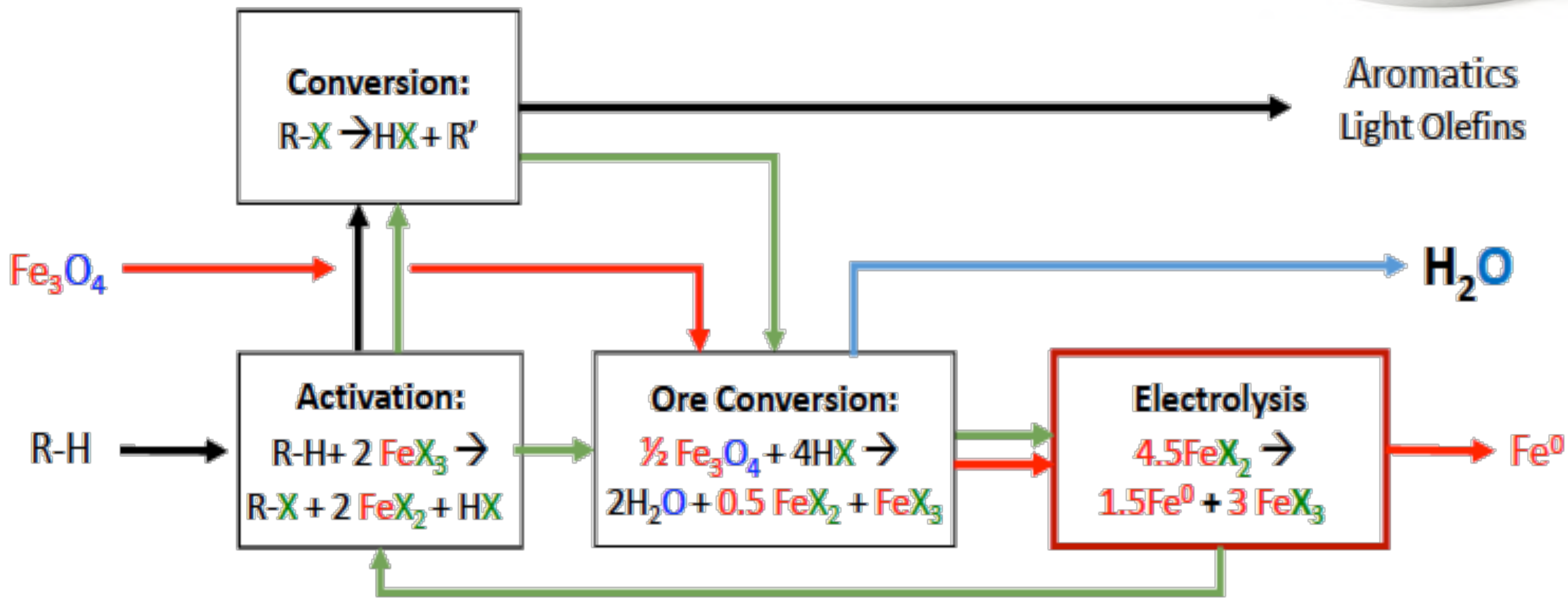


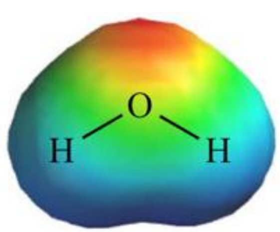
8FeCl3 → 8FeCl2
8FeCl3+ 3Fe0
8 H - Cl
eV
9FeCl2
2FeCl3
Fe3O4
4 H O H



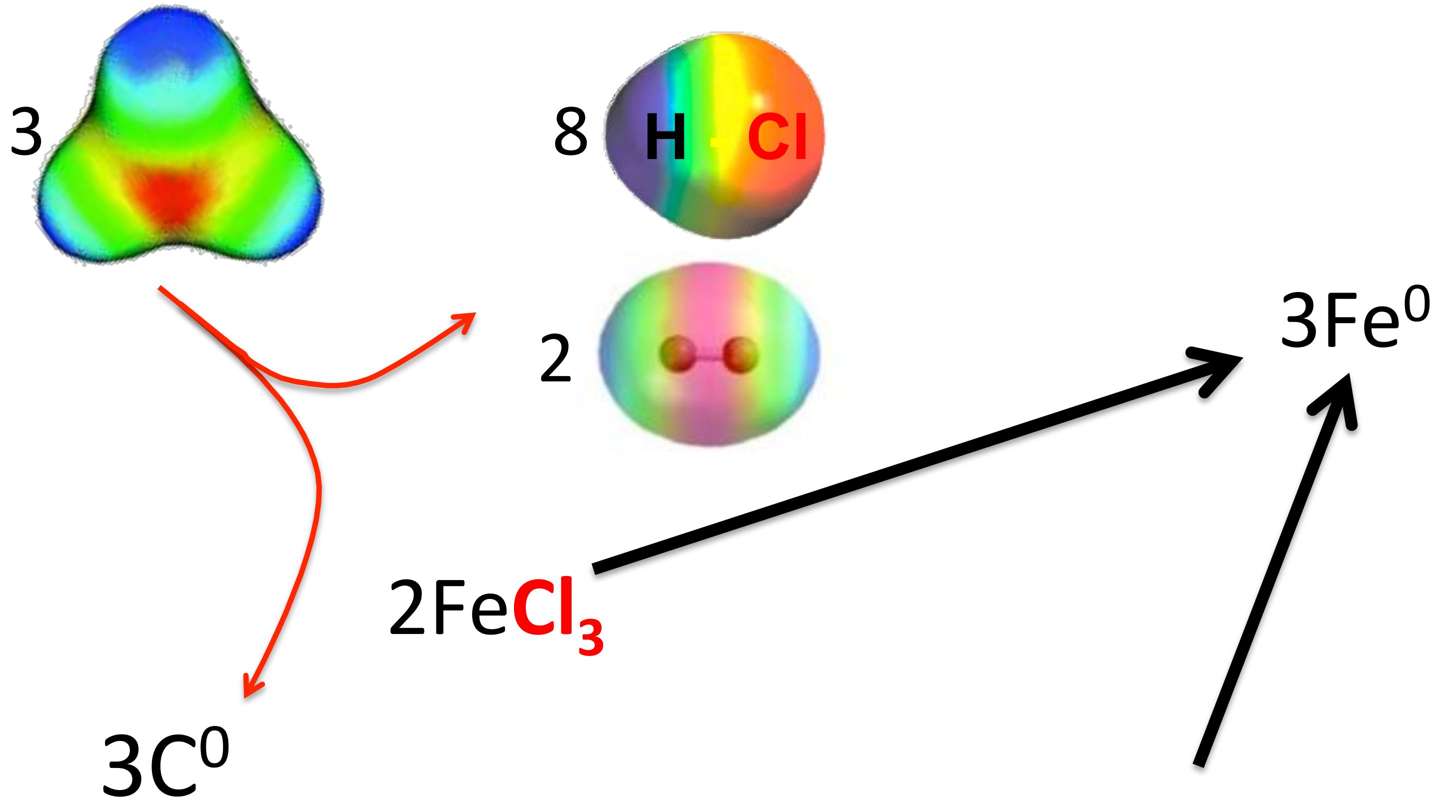
In Press
Chemical Engineering Journal







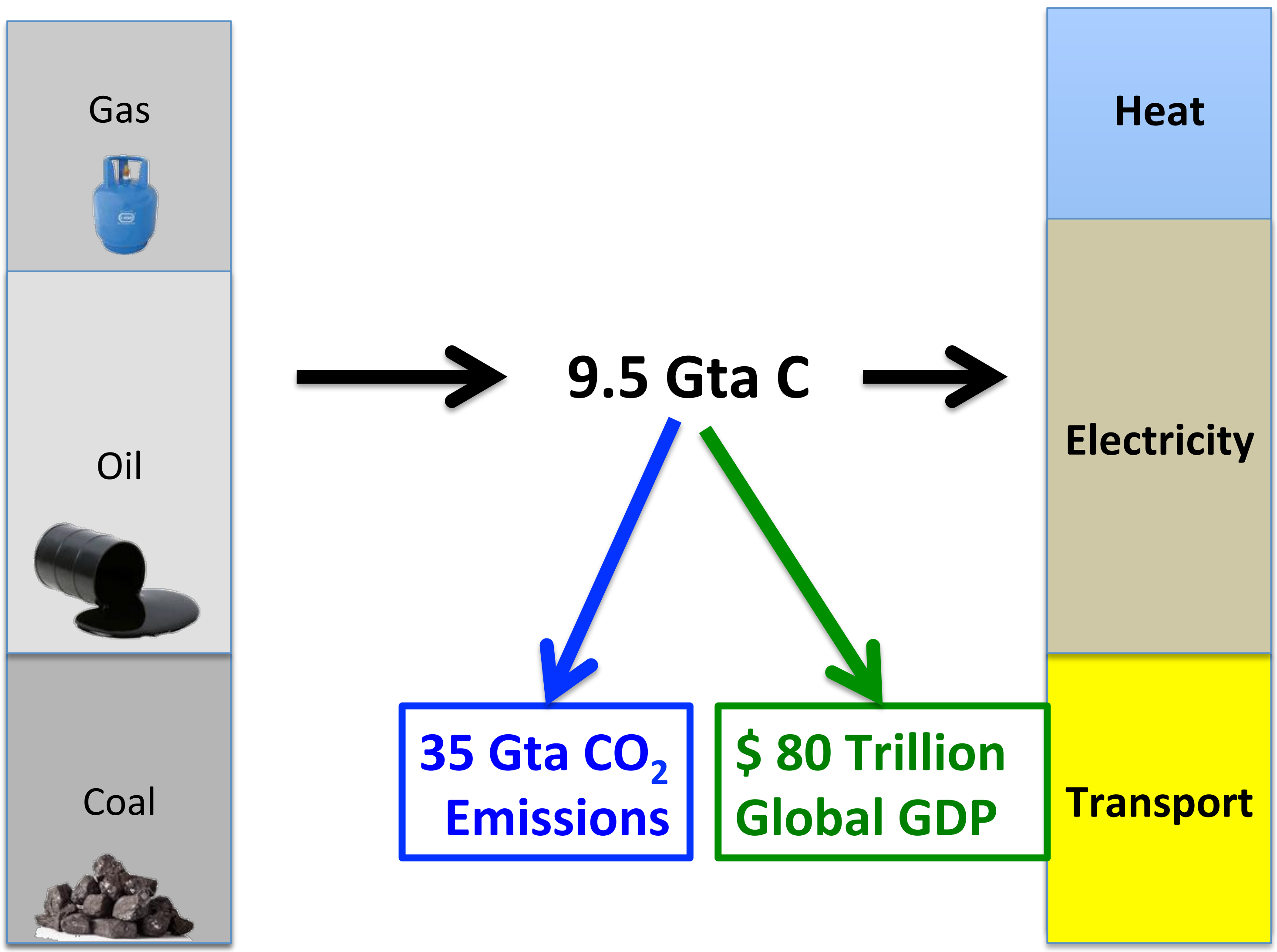
But …… you still need CO_2 free electricity



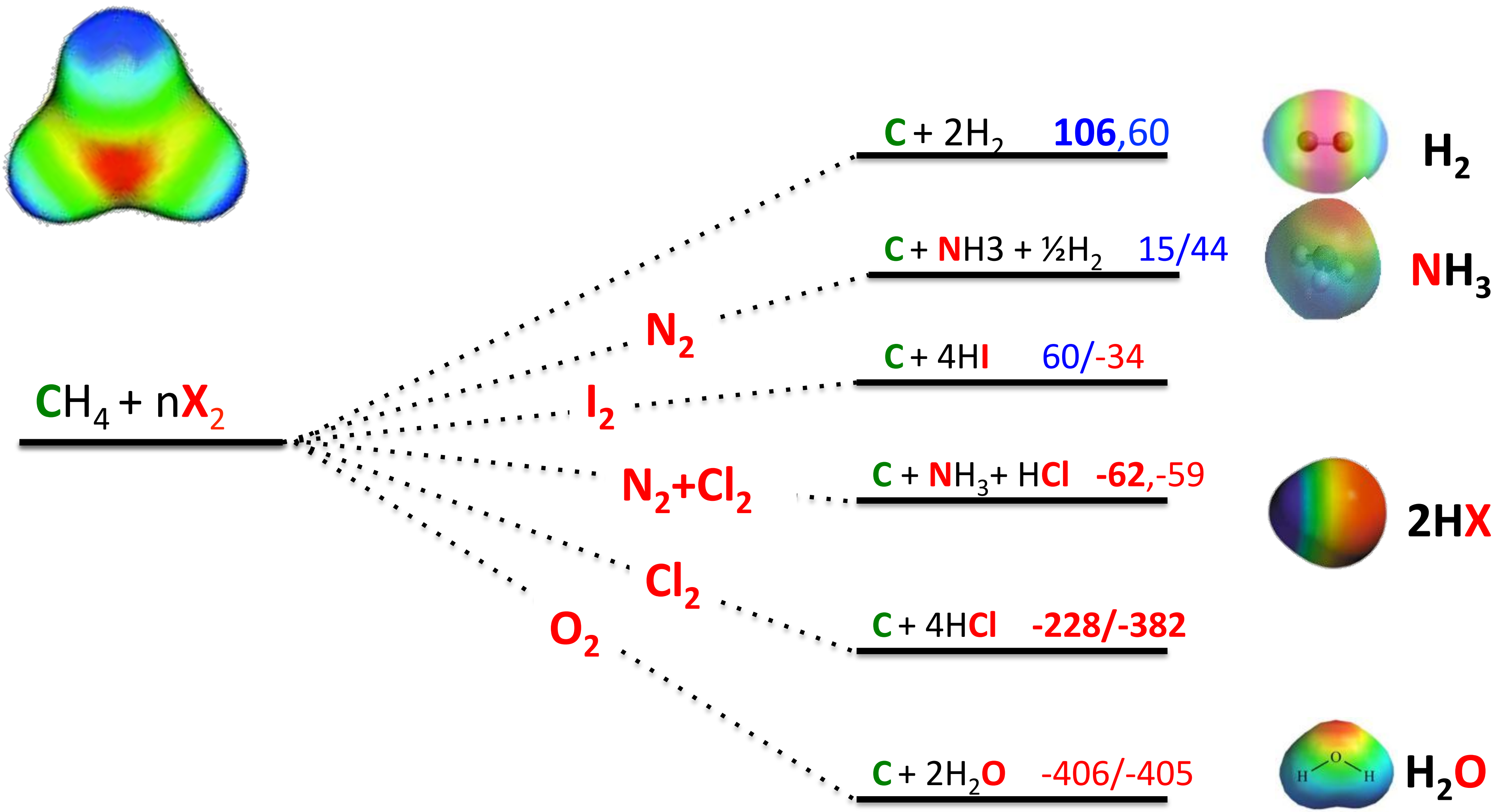
Halogen Facilitated Thermal Reduction

$$3CH_4 + 2FeCl_3 + FeCl_2 \rightarrow 3C + 3Fe + 8HCl + 2H_2$$

Interesting chemistry, but the few Gta of CO_2 from chemical production is NOT the problem



We Want CO_2-free Low Cost Fuels and Heat

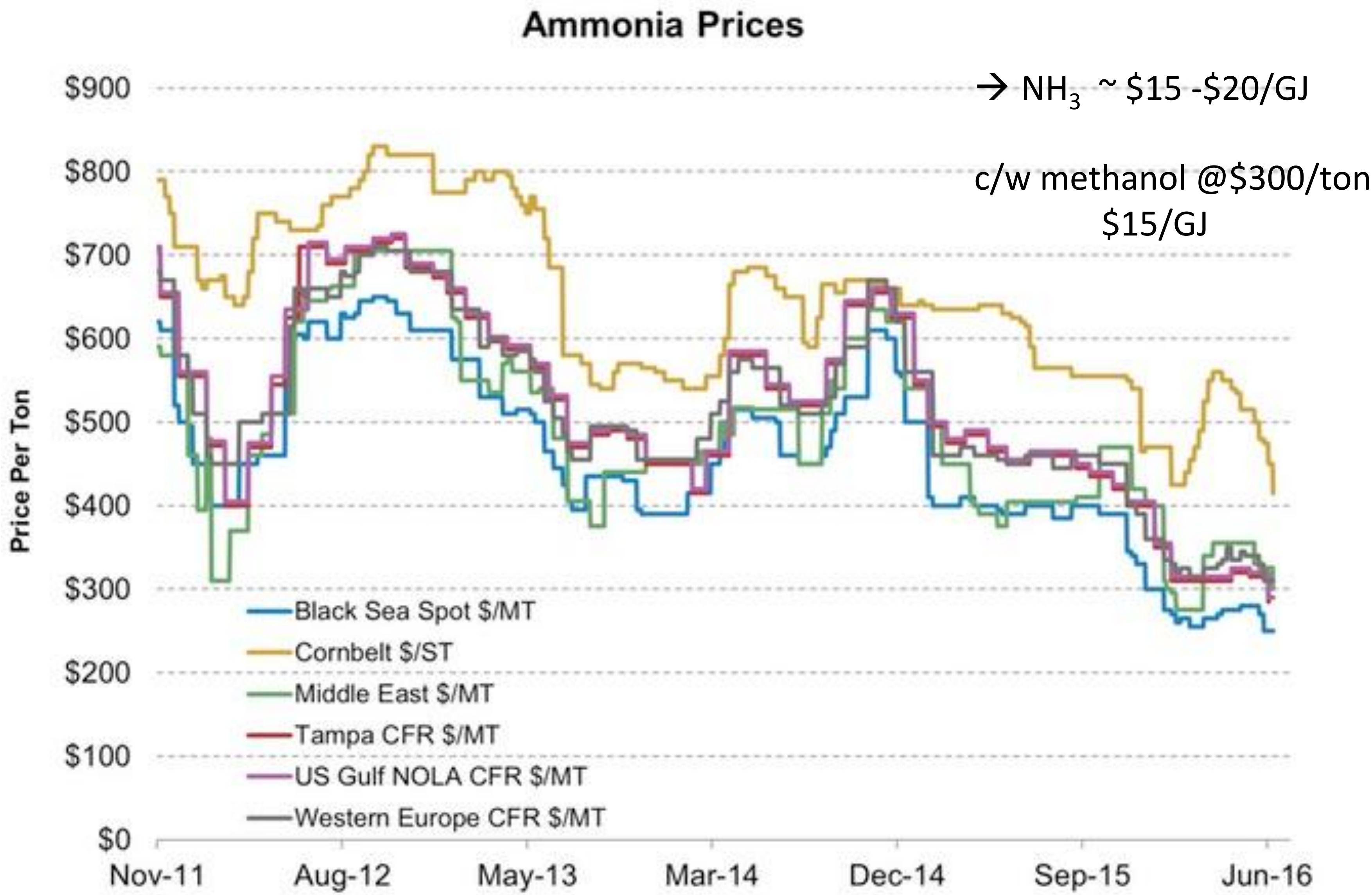


ΔH,ΔG 700K, 1atm

CO_2 free combustion

$$\frac{3}{2}O_2 + 2NH_3 \rightarrow N_2 + 3H_2O$$

Heat of Combustion ~ Methanol



Increased NH_3 production → Decreased Food Prices

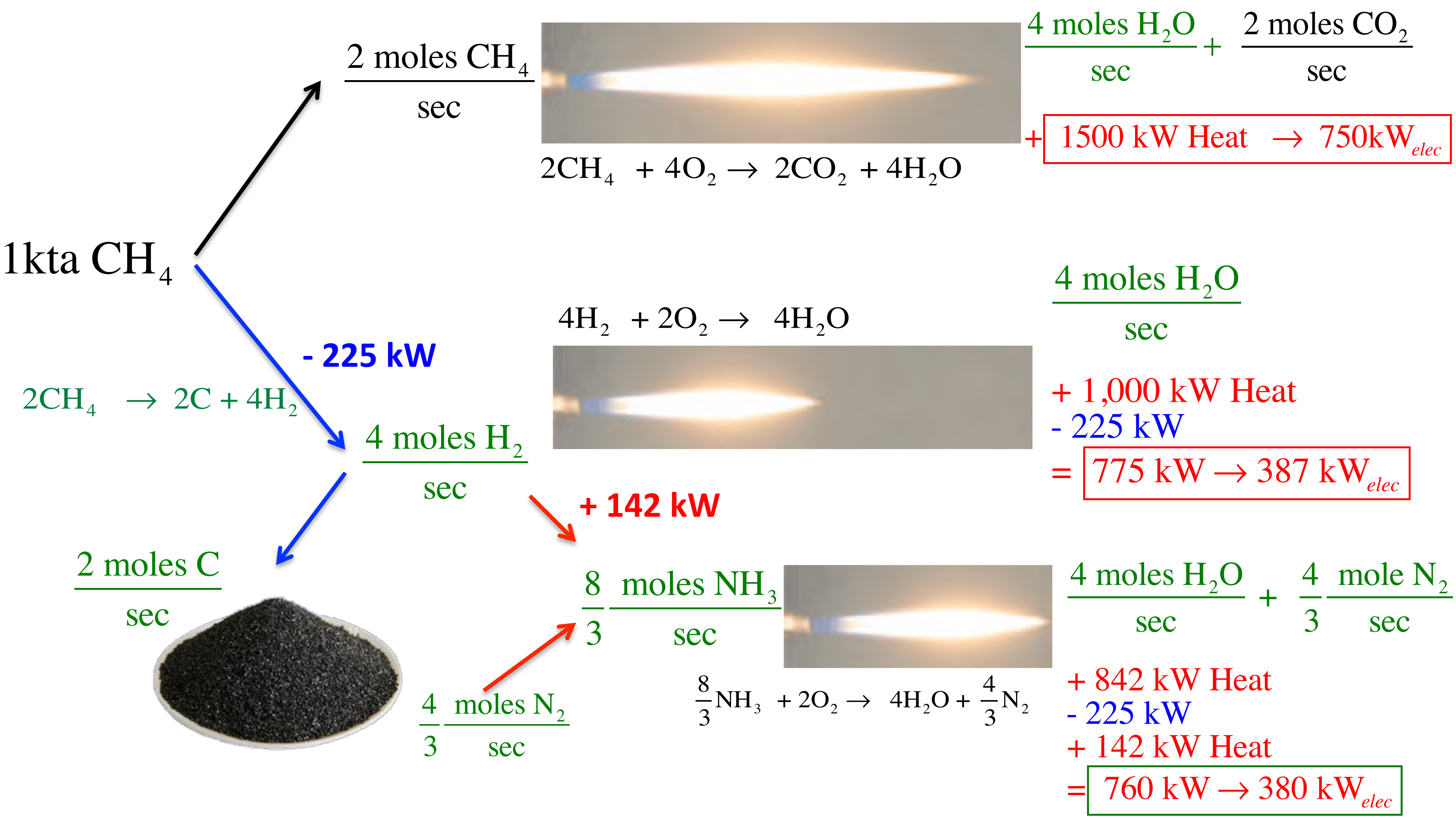
Hydrogen as the ultimate sustainable electron acceptor $CH_4 \rightarrow C + 2H_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$CH_4 \rightarrow C + 2H_2$

$2H_2 + O_2 \rightarrow 2H_2O$

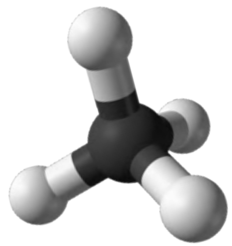
Less Heat but No CO_2



2X operating cost. How much more capital?

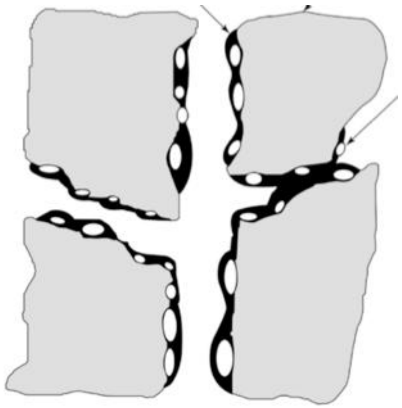
The Carbon "Problem"

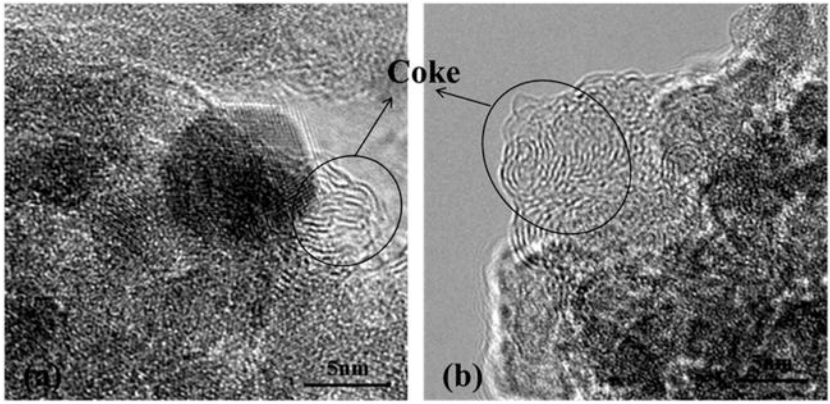
$$CH_4 + n\mathrm{X} \rightarrow C + H_4\mathrm{X}_n$$



CH_4

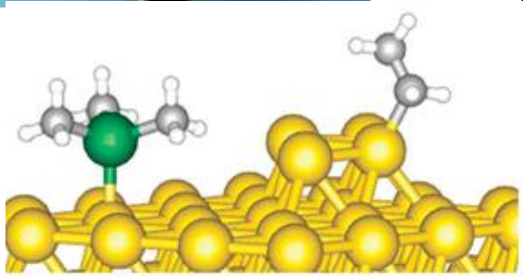
(C^{-4})

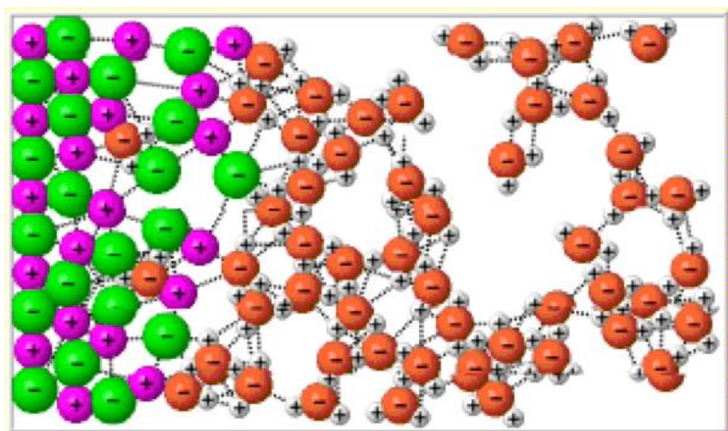


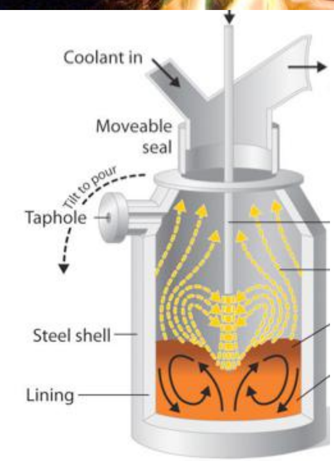


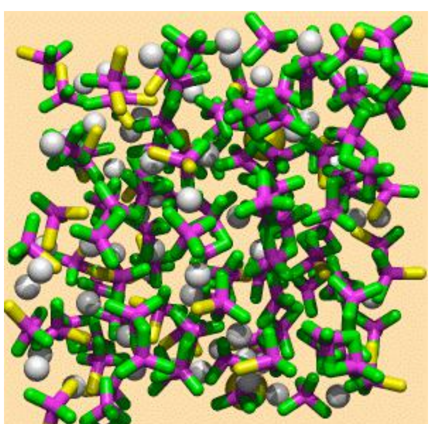
Inspired By Nature

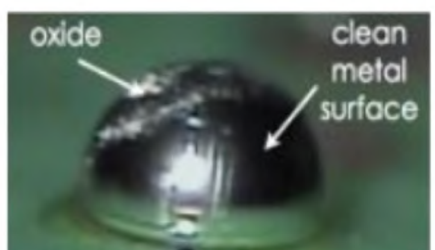
Understanding and Controlling Reactions and Processes in Complex Melts

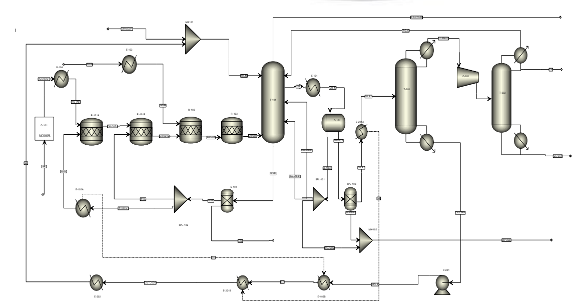






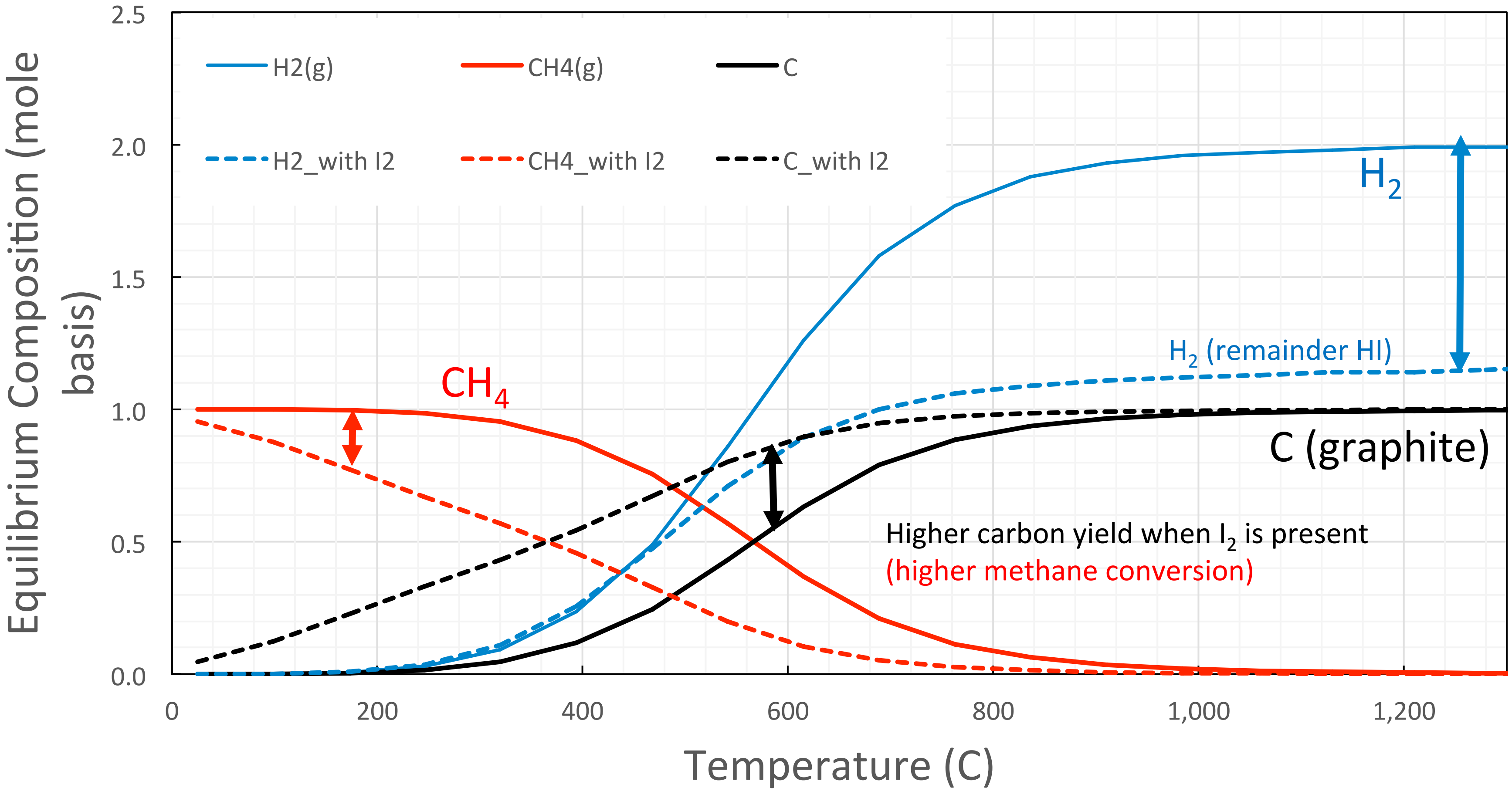






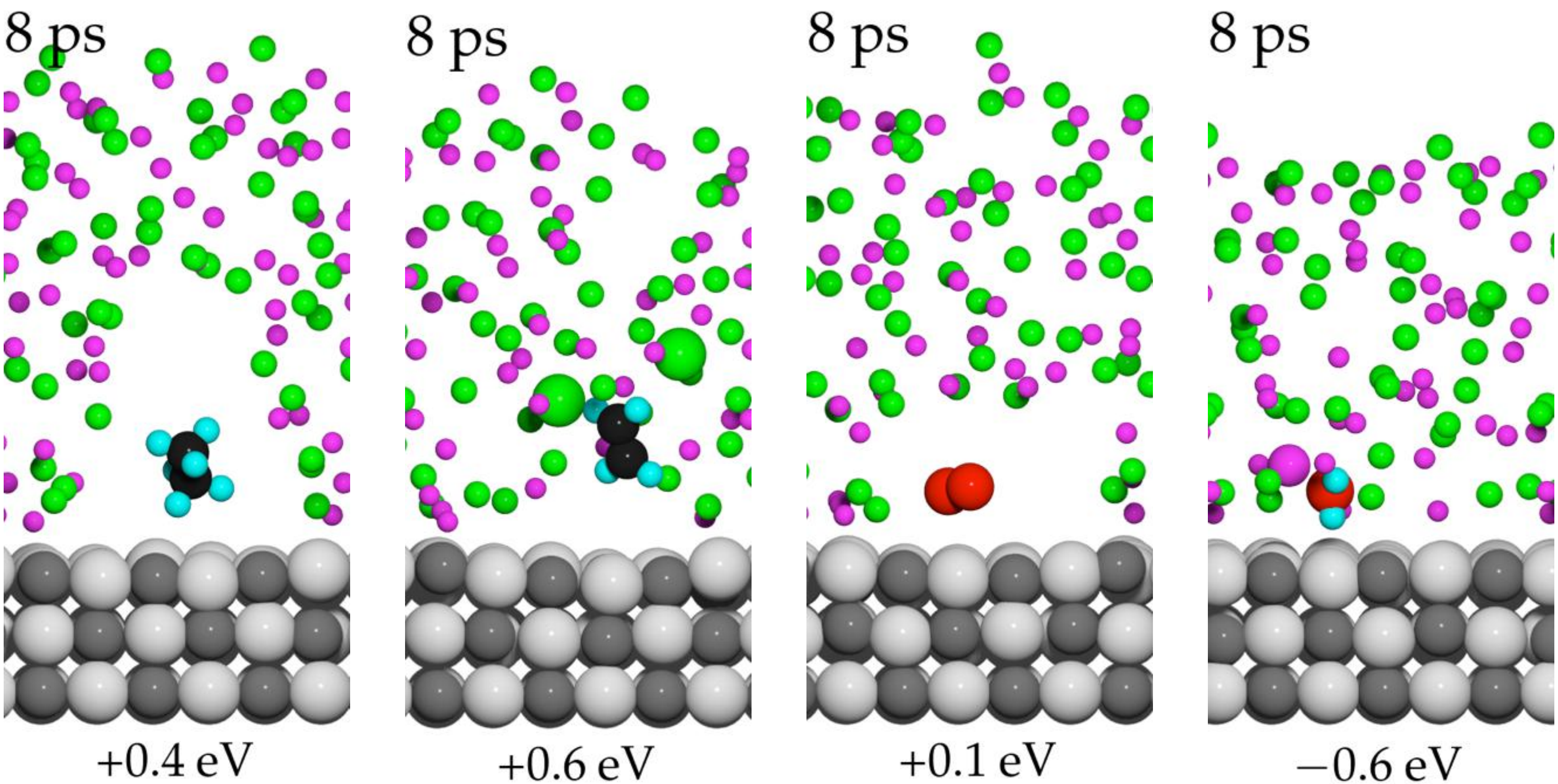
Hydrocarbon Chemistry in Molten Halide Salts

Equilibrium for pyrolysis favored at lower temperature when halogens present



Molten salts used for environmental control of reactive surface sites

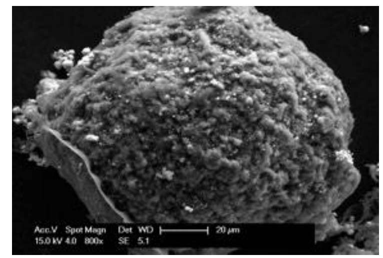
Ethane **Ethylene** **Oxygen** **Water**

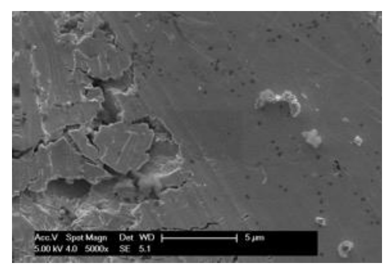


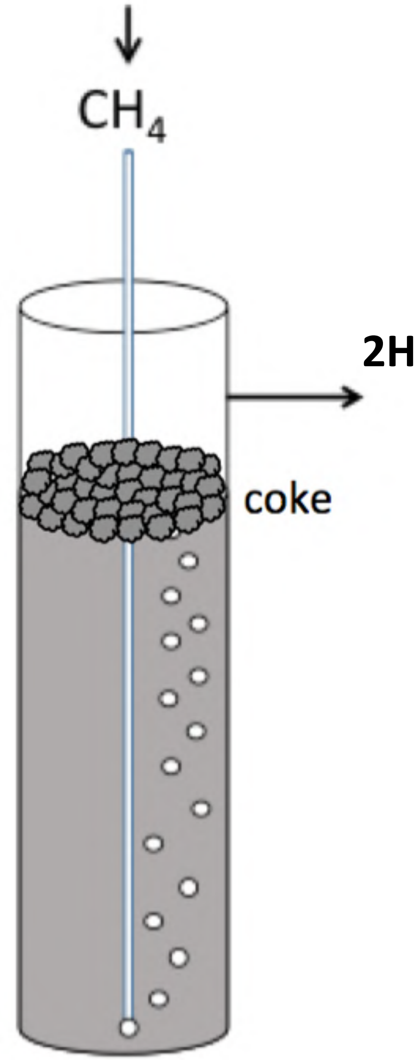
J. Phys. Chem. C, **2015**, *119* (16), pp 8681–8691

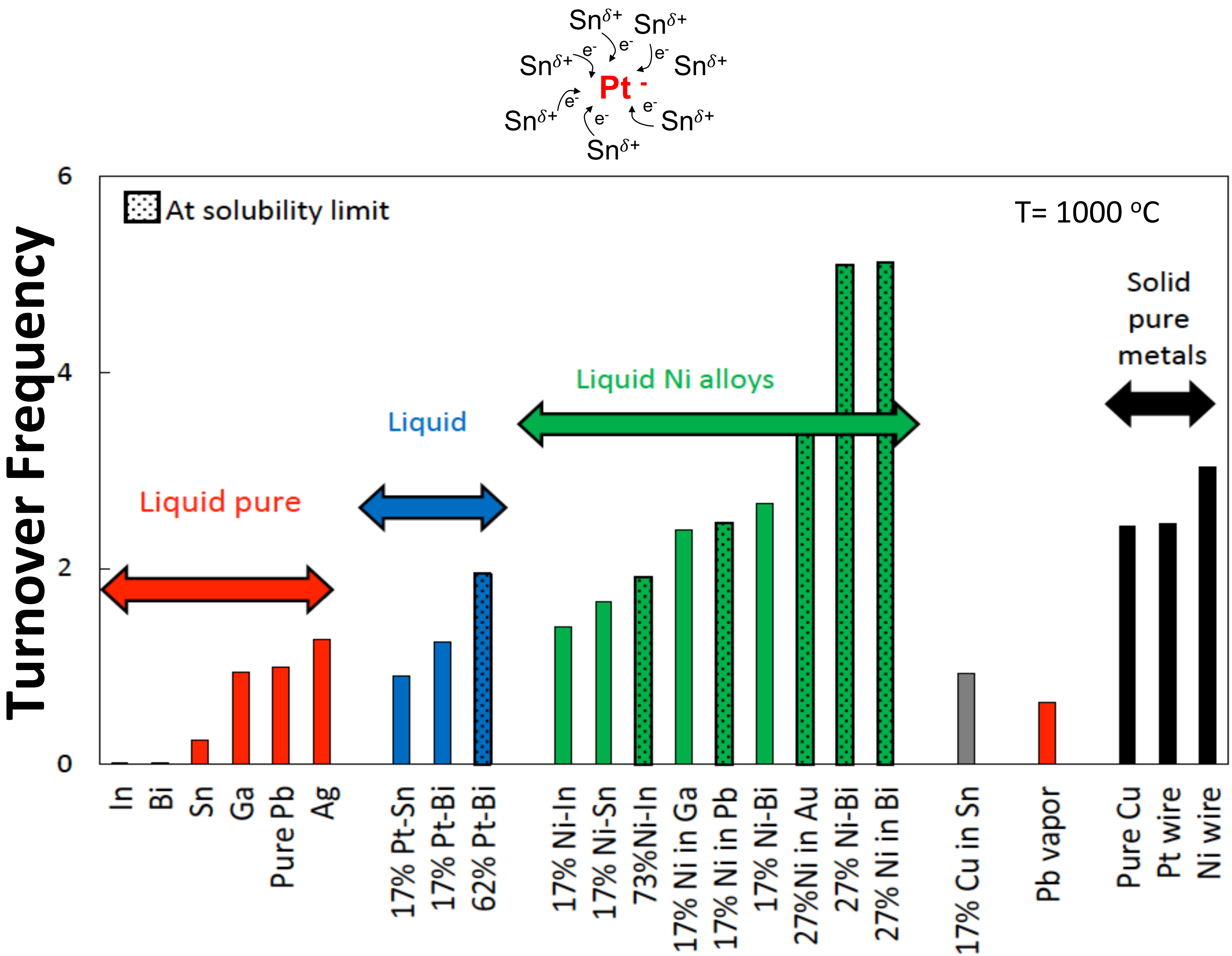
Molten Metal Methane Pyrolysis

$$CH_4 \rightarrow C + 2H_2$$



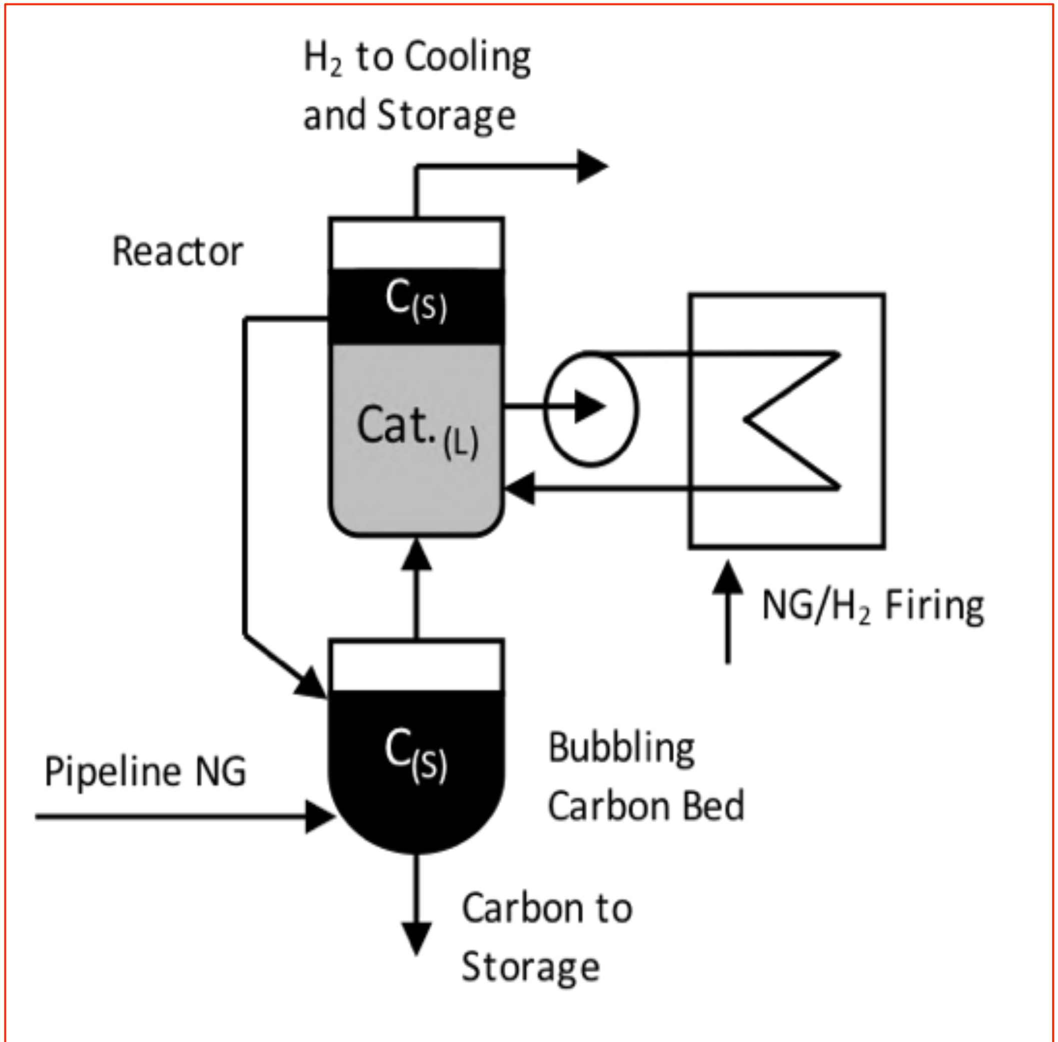


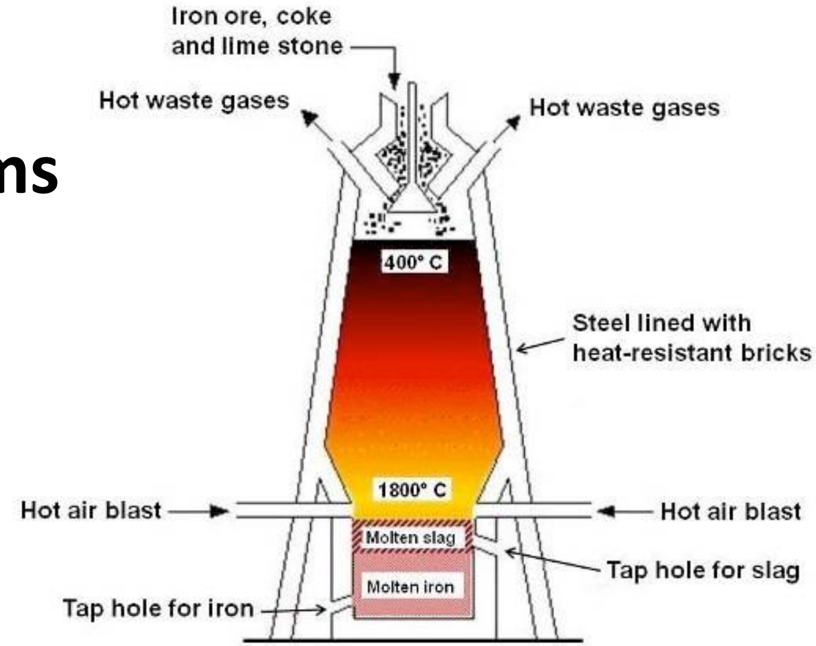




Sn$^{\delta+}$
e$^-$
Pt $^-$
At solubility limit
T= 1000 ^{o}C
Turnover Frequency
6
4
2
0
Liquid pure
Liquid
Liquid Ni alloys
Solid
pure
metals
In
Bi
Sn
Ga
Pure Pb
Ag
17% Pt-Sn
17% Pt-Bi
62% Pt-Bi
17% Ni-In
17% Ni-Sn
73%Ni-In
17% Ni in Ga
17% Ni in Pb
17% Ni-Bi
27%Ni in Au
27% Ni-Bi
27% Ni in Bi
17% Cu in Sn
Pb vapor
Pure Cu
Pt wire
Ni wire

Commercially Practiced Systems





Blast Furnace

Techno-economic evaluation of methane pyrolysis in molten metals; decarbonizing natural gas

$$CH_4 \xrightarrow{heat/catalyst} C + 2H_2 \xrightarrow{H_2 -> Heat} C + \tfrac{5}{3}H_2 + \tfrac{1}{3}H_2O$$

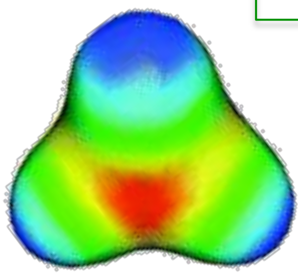
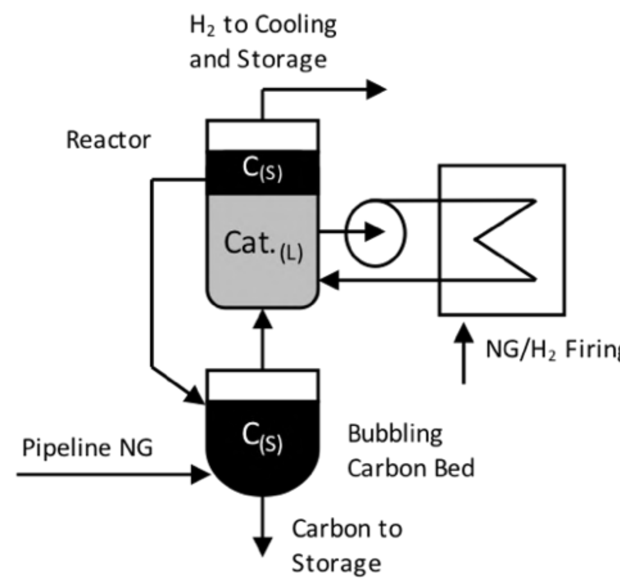
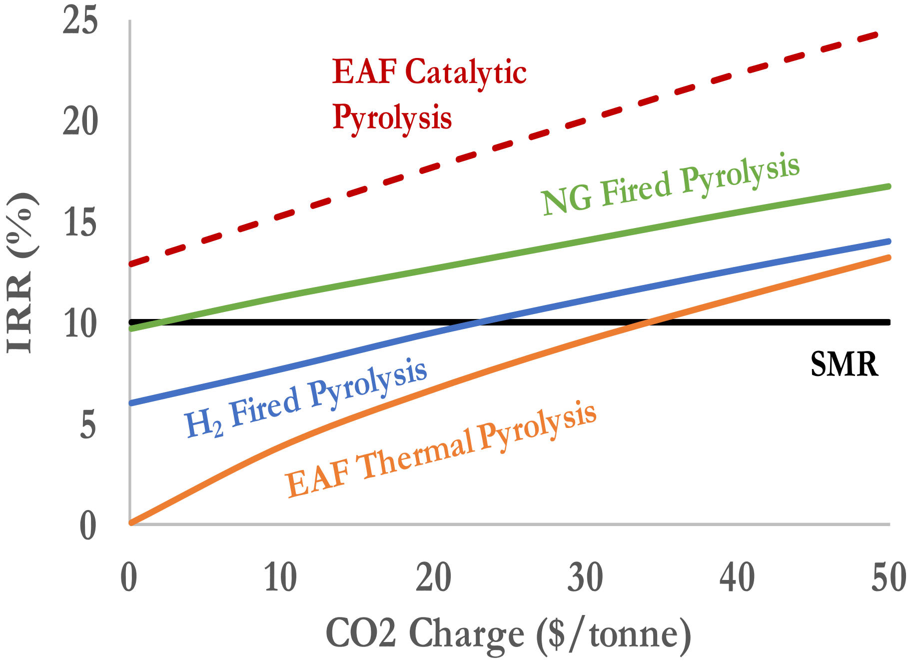


Table 1 – General Economic Assumptions	
Year of analysis	2016
Construction period	2 year
Start-up period	3 months
Revenue during start-up	50% of normal operation
Plant Lifetime	25 years
On-stream factor	91%
Inflation	2%
Discount rate	10%
Plant Salvage Value	No Value
Depreciation	Straight Line
Depreciation period	10 years
Tax rate	35%



Submitted
Chemical Engineering Journal



Thermochemical Hydrogen Production Can Beat SMR

SMR vs Pyrolysis US Gas Price $2/GJ

SMR" adjusted price of H_2 for Internal Rate of Return (IRR) = 10%.

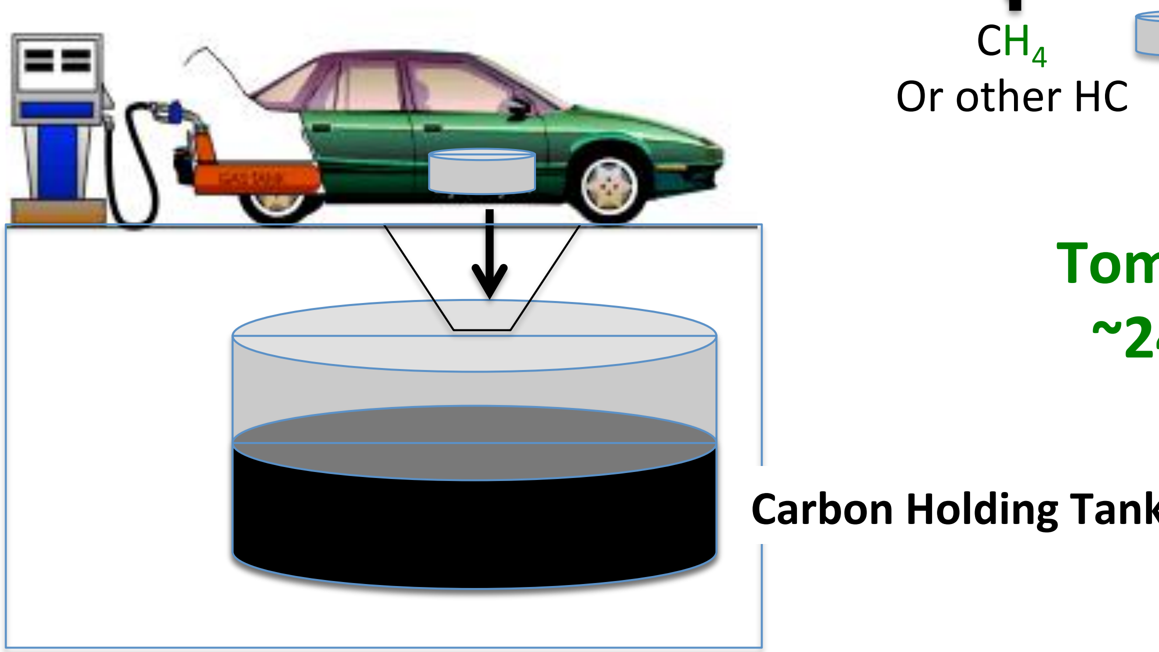
Other's use same H_2 price.

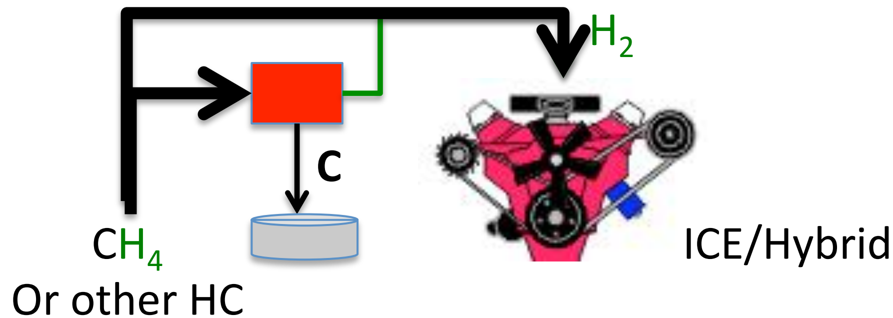
Table 2 – Summary of 200 kta Hydrogen Production Cases

	SMR	EAF Thermal Pyrolysis	EAF Catalytic Pyrolysis	NG Firing Pyrolysis	H_2 Firing Pyrolysis
Natural Gas Capacity (kta)	500	800	800	800	972
Heat Supply	Fired Heater	EAF	EAF	Fired Heater	Fired Heater
Reaction Temperature (°C)	650-1000	1500	1000	1000	1000
Purchase Cost of Equipment ($MM)	79	29	21	55	65
Fixed Capital Investment ($MM)	473	230	170	437	521
Total Cost of Production ($/kg H_2)	0.95	1.12	0.95	0.97	1.10
Tonnes CO_2 emitted per tonne H_2	7.0	3.7	2.9	1.3	0.0
CO_2 Charge to Validate Pyrolysis ($/tonne)	-	38	<0	2	22

A Car of "the future": On Board Thermal Pyrolysis?

Today's ~ 48 mpg hybrid





Tomorrow's ~ 0 CO_2
~24 mpg hybrid**

Challenge: Cost effective modular reactor system

Catalytic converters ~ $100.

Our Grand Challenge: Direct Methane to Ammonia (Fuel and Foods)

$$CH_4 + \frac{1}{2}N_2 + nX \rightarrow NH_3 + C + HX$$

500 kta Haber Bosch Ammonia Facility

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$
$$2N_2 + 3H_2 \rightarrow 2NH_3$$

Summary

- **Fossil hydrocarbons remain the lowest cost source of power and organic chemicals and continue to make possible global prosperity.**

- **We do not, presently, have cost competitive alternatives.**

- **If the global society ever places a meaningful cost on carbon dioxide emissions and continues to unnecessarily restrict innovation in commercial nuclear power, alternative means of using fossil resources may provide the least costly processes for CO_2 emissions reductions until the inevitable increasing scarcity drives up their cost.**

- **Alternative conversion pathways have many interesting fundamental mechanistic questions and practical challenges that should be interesting to chemical scientists, engineers, and students.**

CHEMICAL ENGINEERING
UC SANTA BARBARA

MIT Energy Initiative

Acknowledgements

Ches Upham, Henrik Kristoffersen, Brett Parkinson, Mojgan Zavareh, Horia Metiu, Mike Gordon, Galen Stucky

Questions ?

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