

# Re-Designing Metabolic Infrastructure for Carbon Management

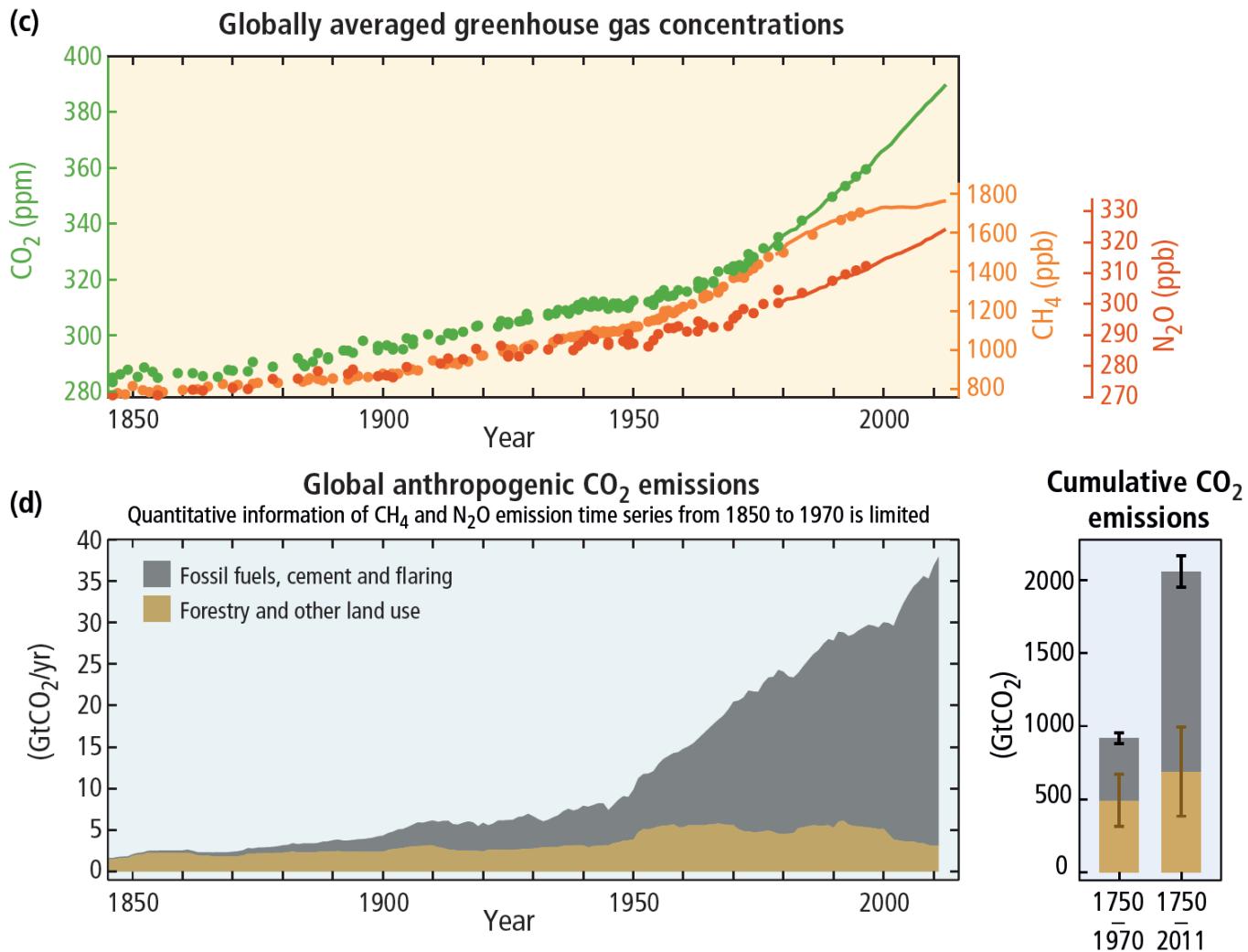
James C. Liao

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Taipei, Taiwan

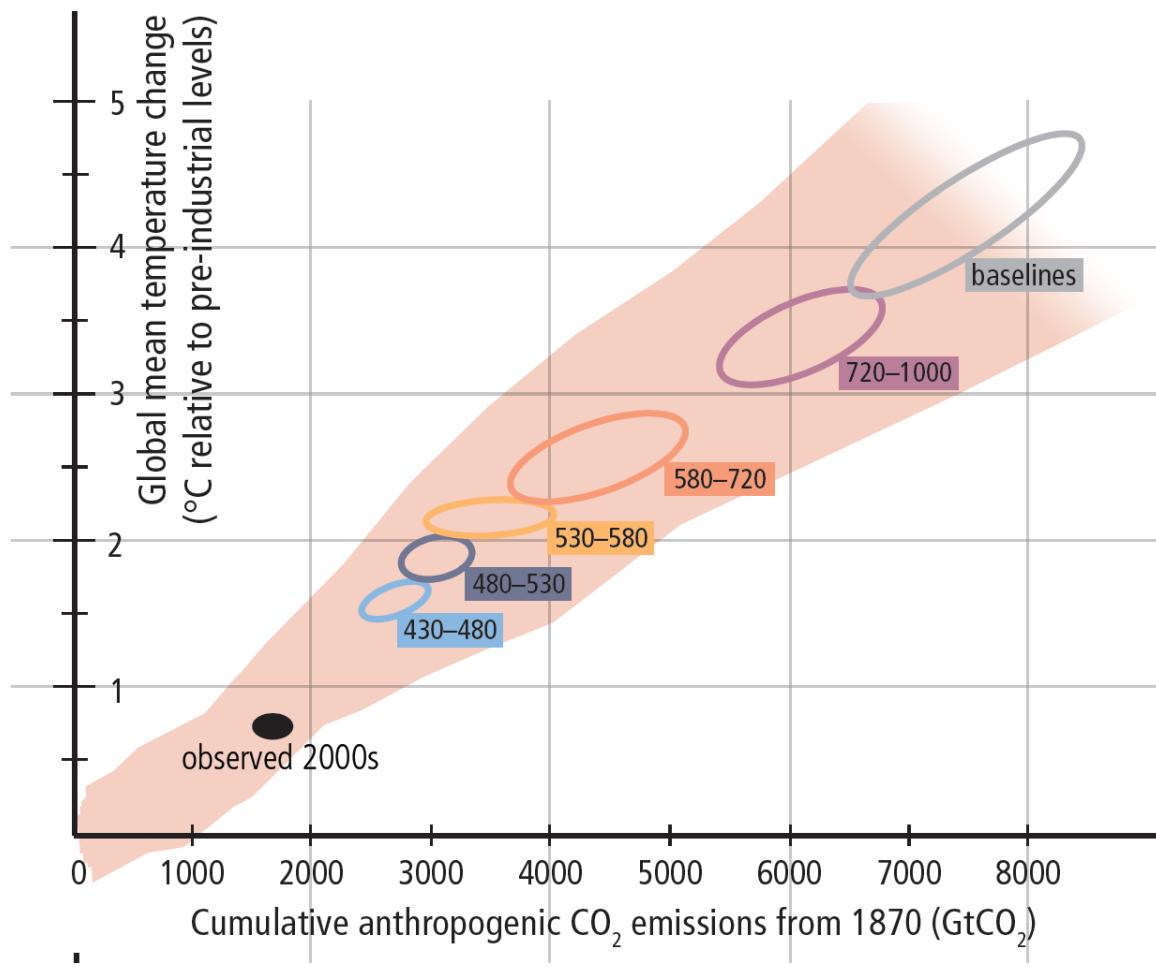


# IPCC Climate Change 2014 Synthesis Report

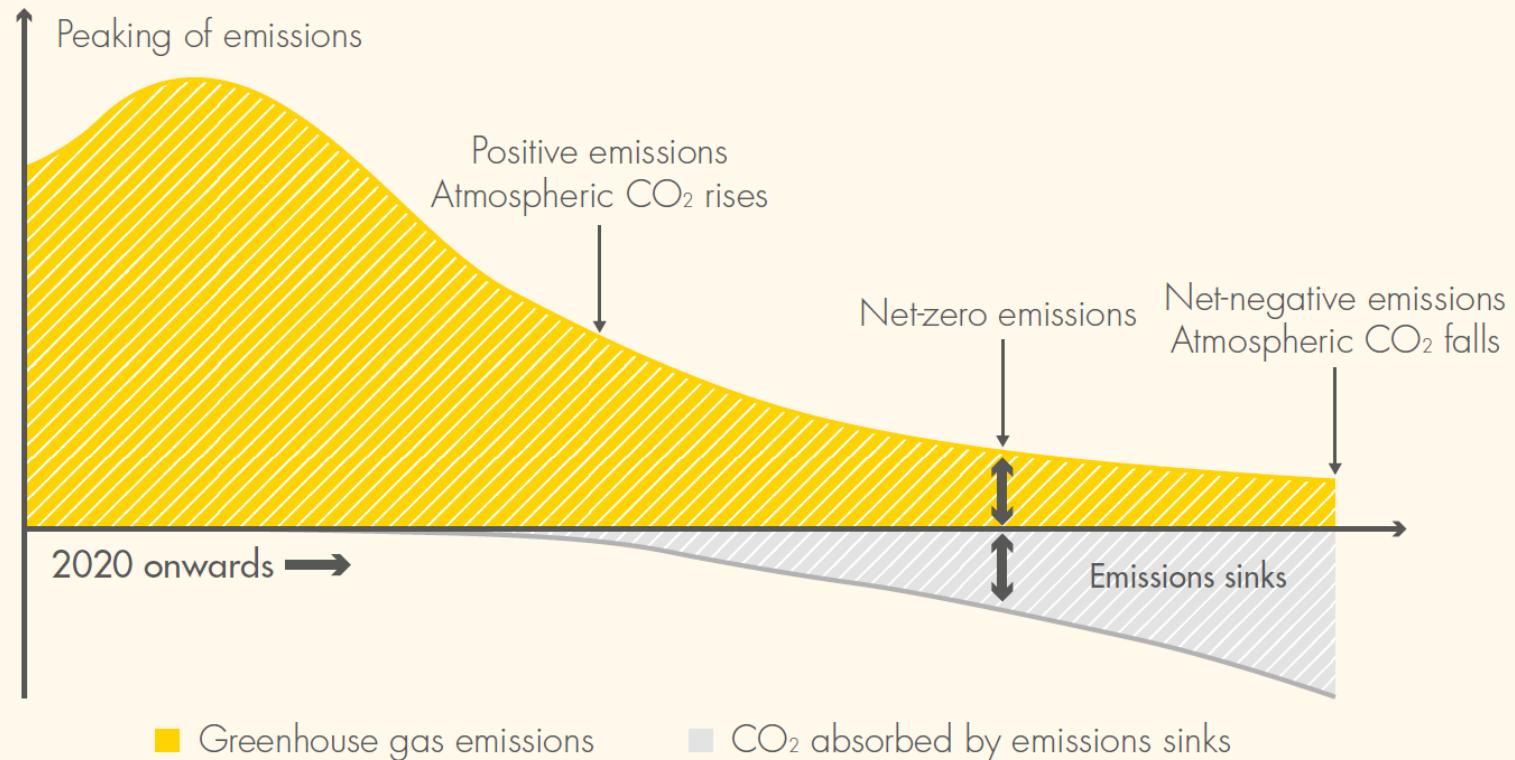


# IPCC Climate Change 2014 Synthesis Report

Risk from climate change depends on cumulative CO<sub>2</sub> emissions

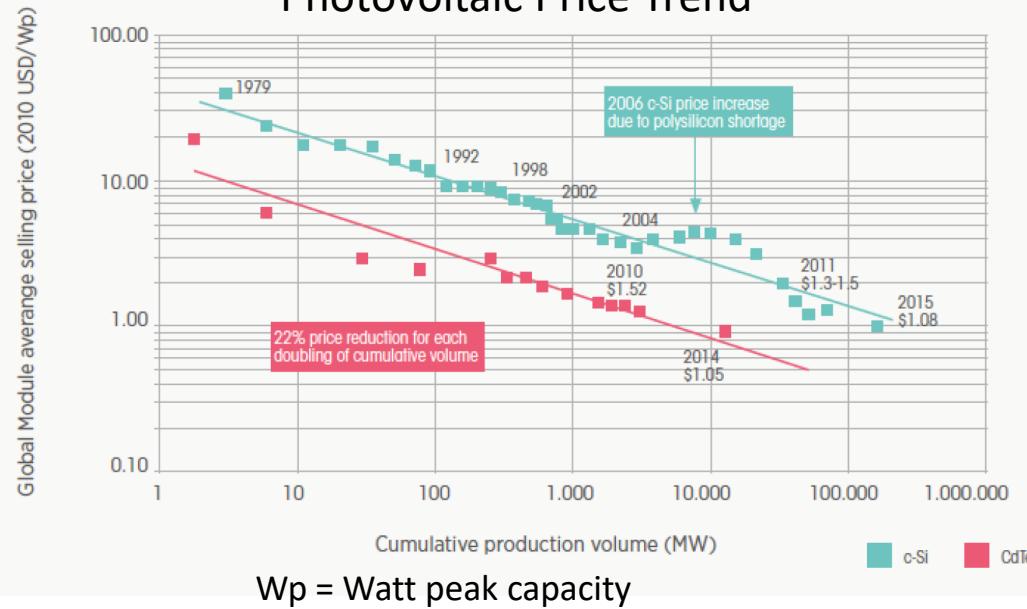


THE PARIS AGREEMENT CALLS FOR AN EARLY PEAK IN EMISSIONS, THEN A DECLINE TO NET-ZERO EMISSIONS DURING THE SECOND HALF OF THE CENTURY



Source: Shell schematic

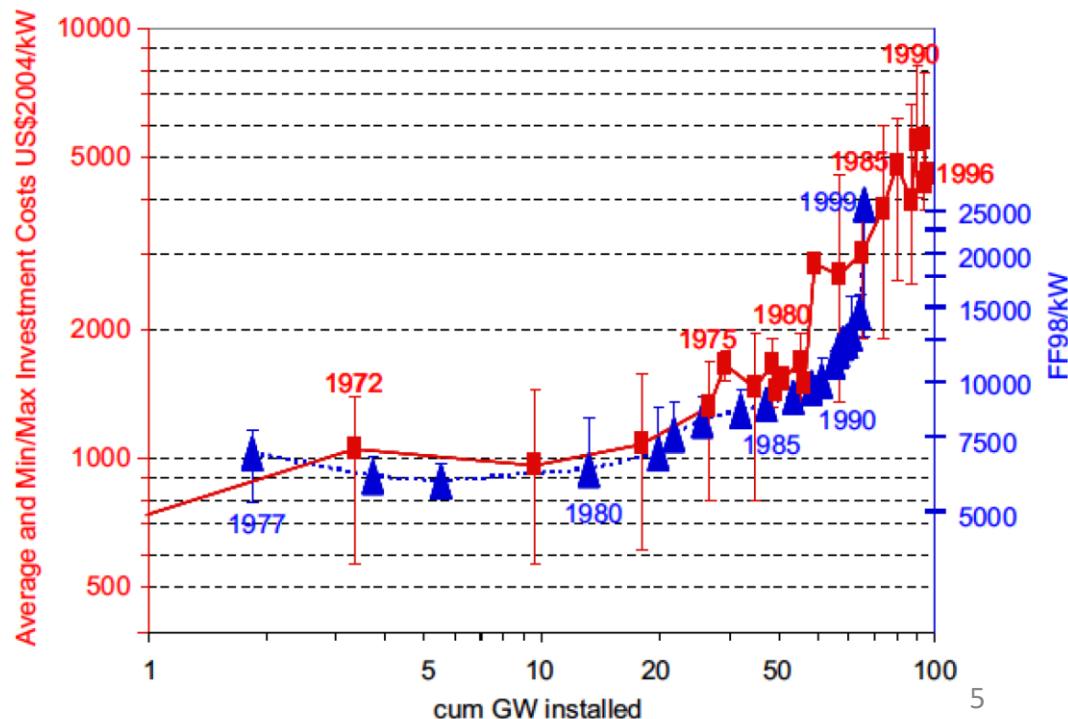
## Photovoltaic Price Trend



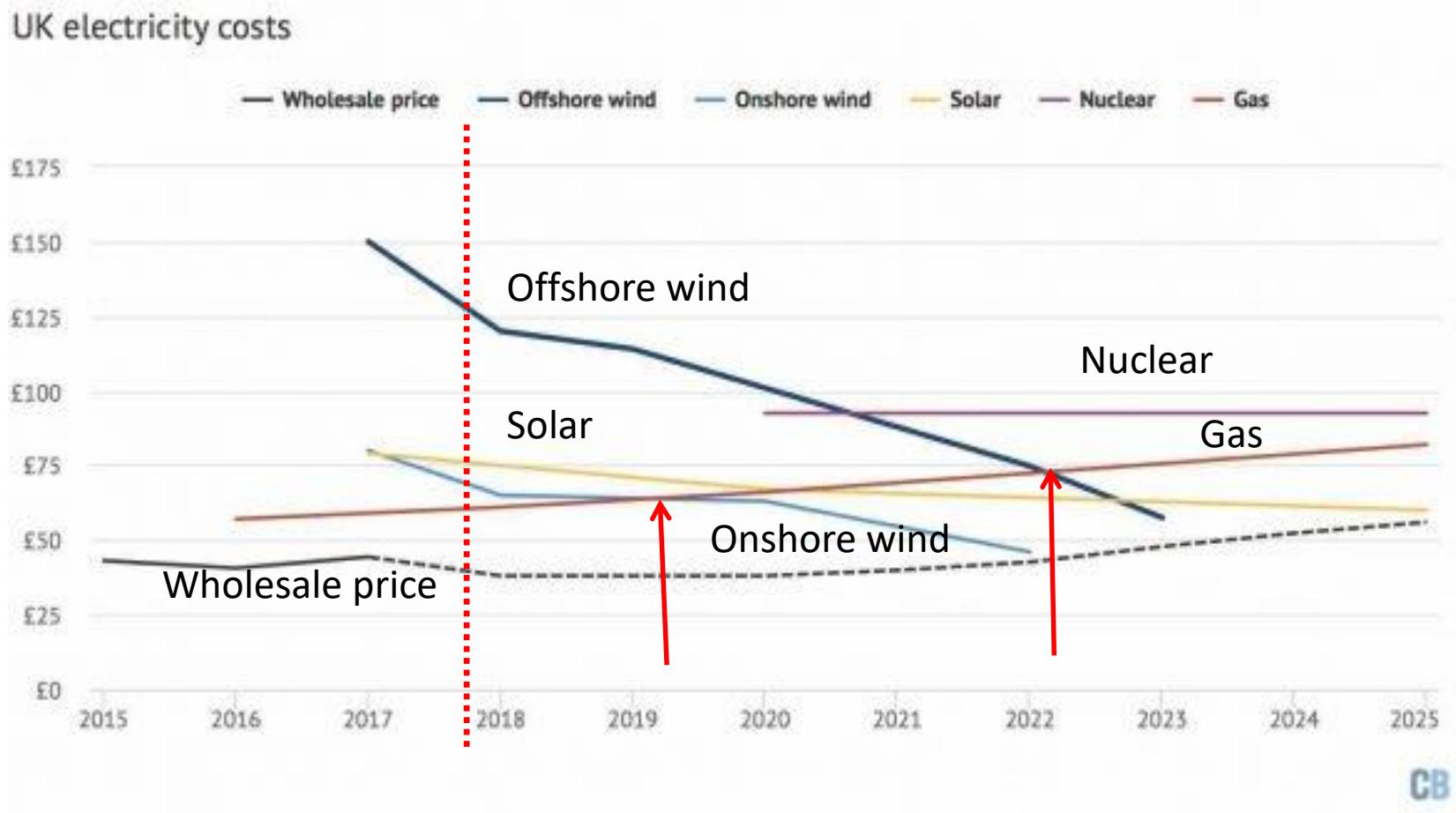
Wp = Watt peak capacity

Cost of nuclear plants (\$/kW) in the US and France (Grubler, 2010)

Learning or experience curves of photovoltaic (PV) modules made from crystalline-Si and CdTe (IRENA, 2012).



# UK auction reveals offshore wind cheaper than new gas

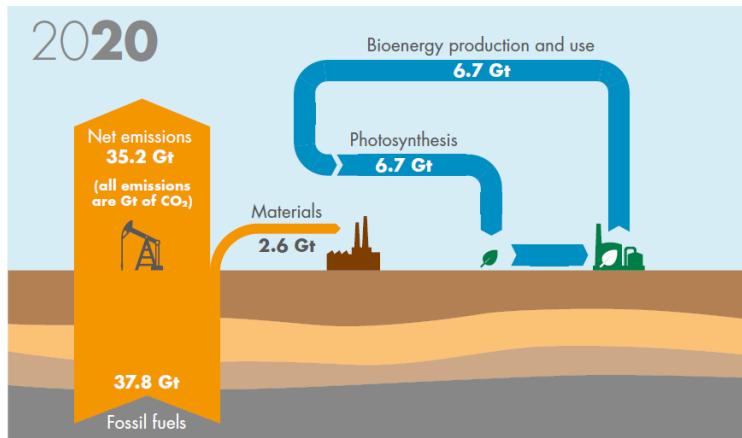


<https://www.carbonbrief.org/analysis-uk-auction-offshore-wind-cheaper-than-new-gas>

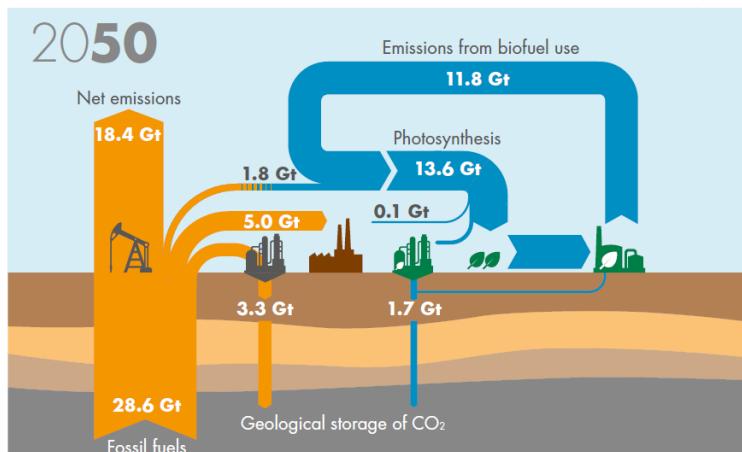
# Shell SKY Scenarios

## THE EVOLVING ENERGY SYSTEM CO<sub>2</sub> BALANCE SHEET IN SKY

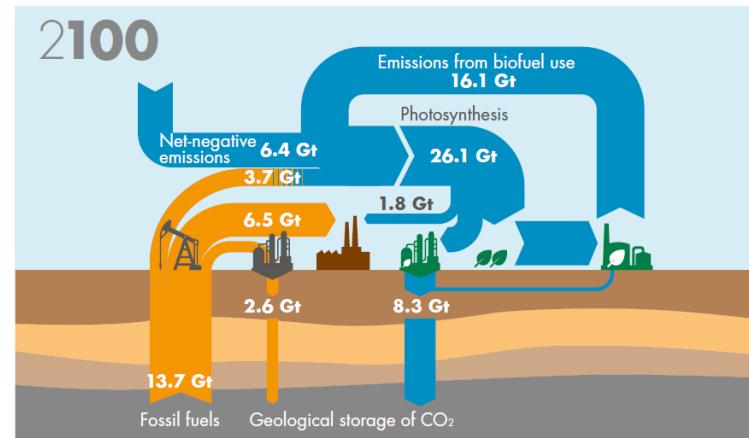
▲ Fossil fuel production    ■ CCS    ▲ Biofuel production    ▲ Bioenergy with CCS    ■ Carbon in products    ▲ Growing biomass



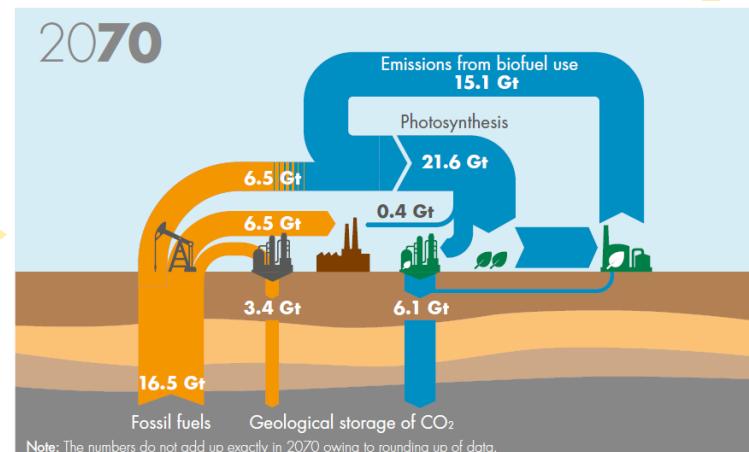
Today, most carbon in fossil energy production is burned and emitted to the atmosphere, while the CO<sub>2</sub> absorbed by wood and other plants used for energy is also returned to the atmosphere.



In Sky, in 2050, the storage of CO<sub>2</sub> is rapidly scaling up. There are equal contributions from the embedded carbon in materials production and CCS. Fossil energy CCS leads the way, but bioenergy CCS (BECCS) is close behind.



In Sky, at 2100, the bioenergy system has reached its resource base limit and is twice the size of the fossil energy system in CO<sub>2</sub> terms. The active management of CO<sub>2</sub> means that the total energy system is providing a drawdown of CO<sub>2</sub> from the atmosphere.



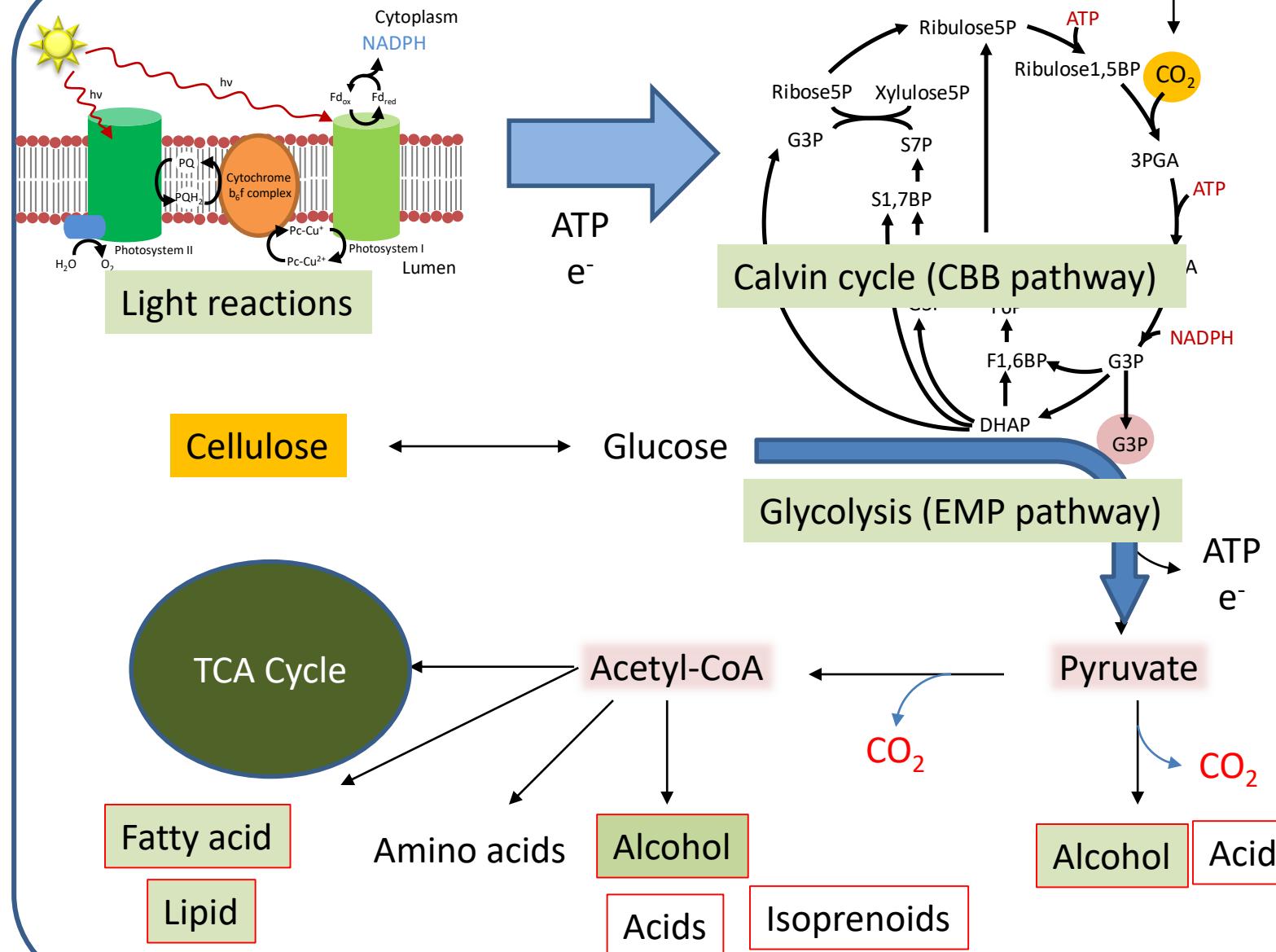
Note: The numbers do not add up exactly in 2070 owing to rounding up of data.

In Sky, in 2070, the energy system has achieved net-zero emissions. Fossil energy production is less than half today's level. Alongside direct CCS and the use of carbon for materials, the remaining fossil energy emissions are fully offset by captured CO<sub>2</sub> from an expanded bioenergy system.

# Biological Carbon Capture and Utilization

- Avoid CO<sub>2</sub> release during fermentation  
Bogorad et al. Nature 2013, Lin et al. PNAS 2018
  - Conventional Fermentation: Sugar → alcohol + CO<sub>2</sub>
  - Reductive Fermentation: Sugar + Reducing agent → alcohol
- Increase CO<sub>2</sub> fixation by photosynthesis  
Yu et al. Nature Comm. 2018
- Develop non-photosynthetic CO<sub>2</sub> fixation  
Li et al. Science 2012

# Pathways to Life



# Theoretical Energy and Mass Yields



energy %

mass %

2540       $2 \times 1235 \text{ kJ/mol}$ 

97.24%

51%



2540      2455 kJ/mol

96.6%

41%



2x 2540      4543 kJ/mol

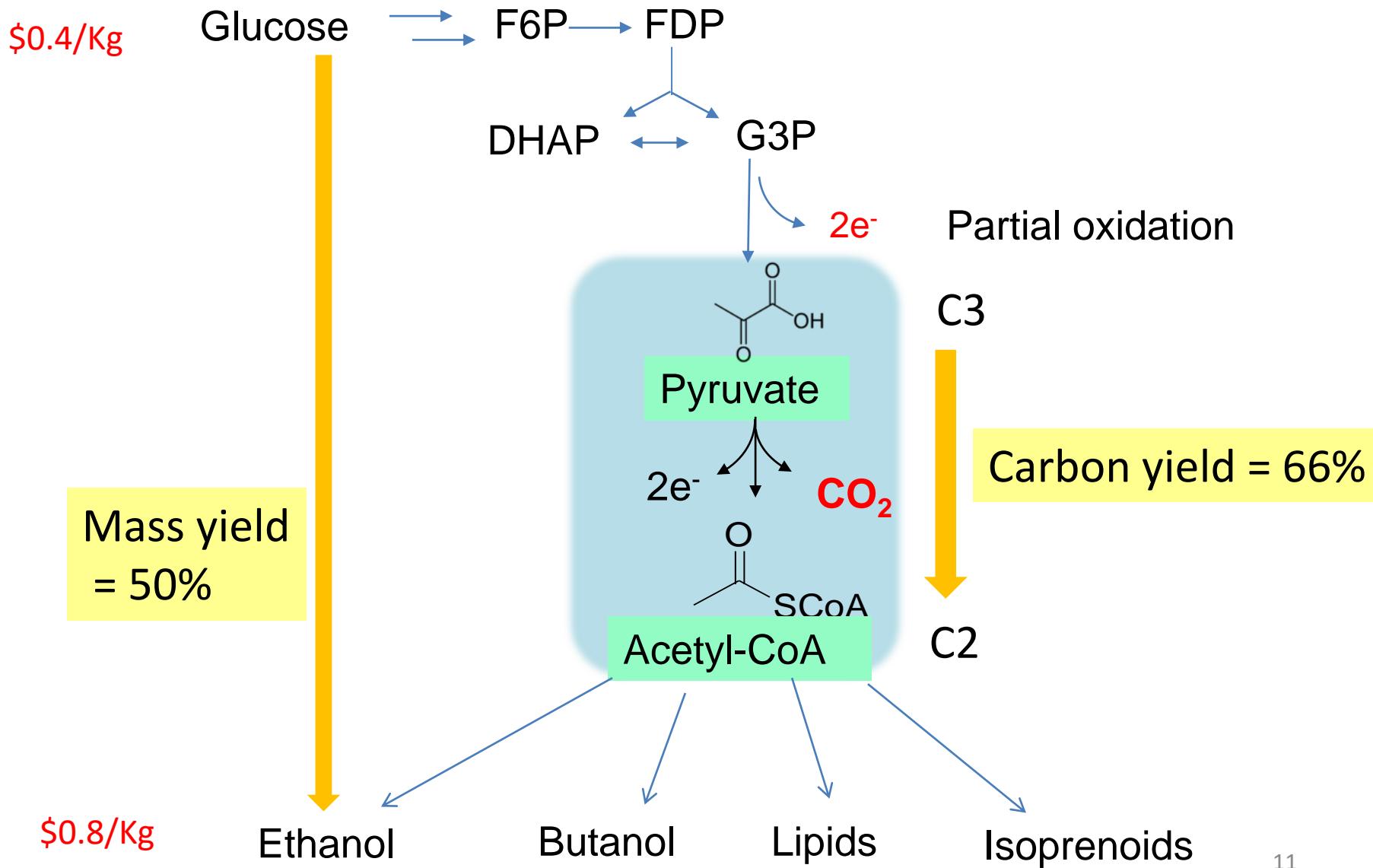
89.4%

27%

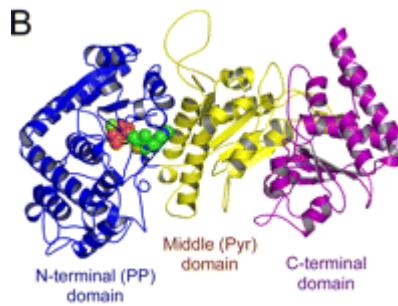
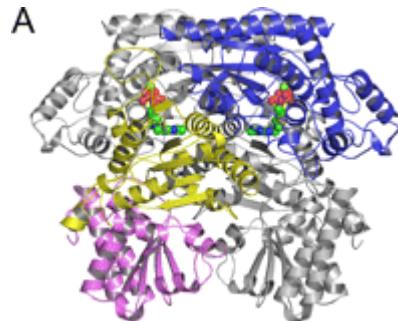
Jet fuel

# Oxidative Glycolysis

## Embden-Meyerhof-Parnas (EMP) pathway



# Non-oxidative Glycolysis (NOG)



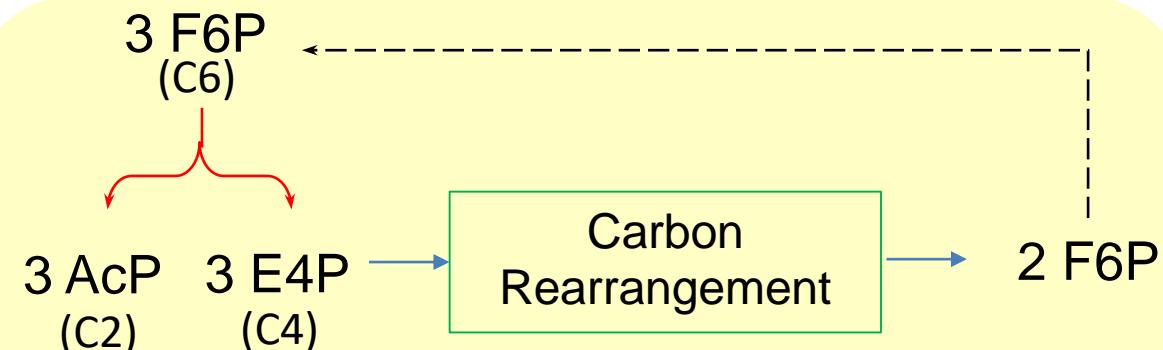
*Bifidobacterium breve.*

Phosphoketolase

$F6P \rightarrow AcP + E4P$

$X5P \rightarrow AcP + G3P$

Glucose → F6P

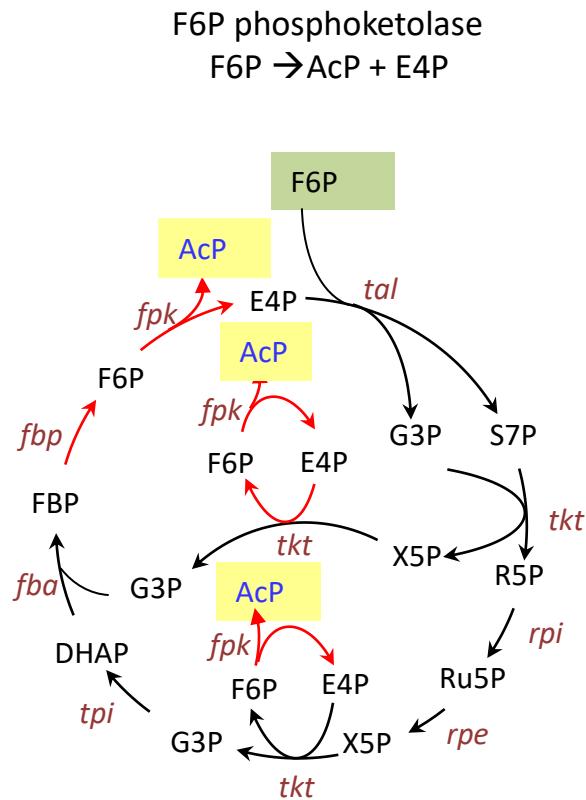


3 AcCoA

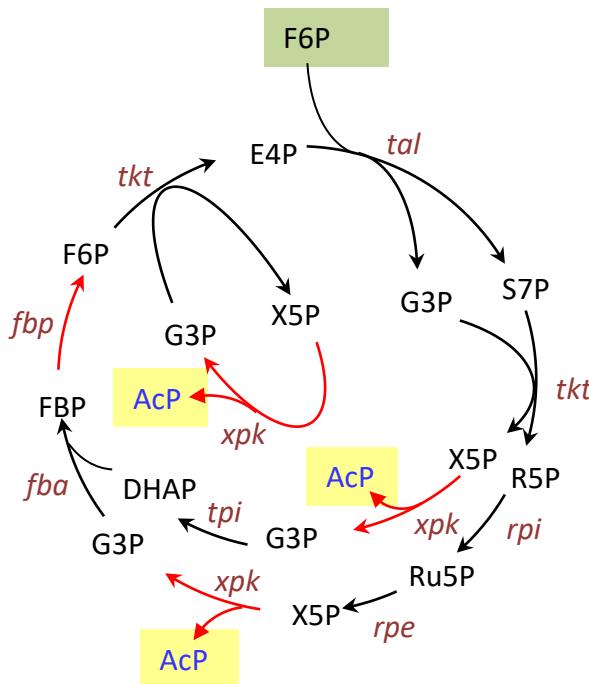
Ethanol  
Butanol  
Acetate

Carbon yield = 100%

# Two Modes of Non-Oxidative Glycolysis (NOG)

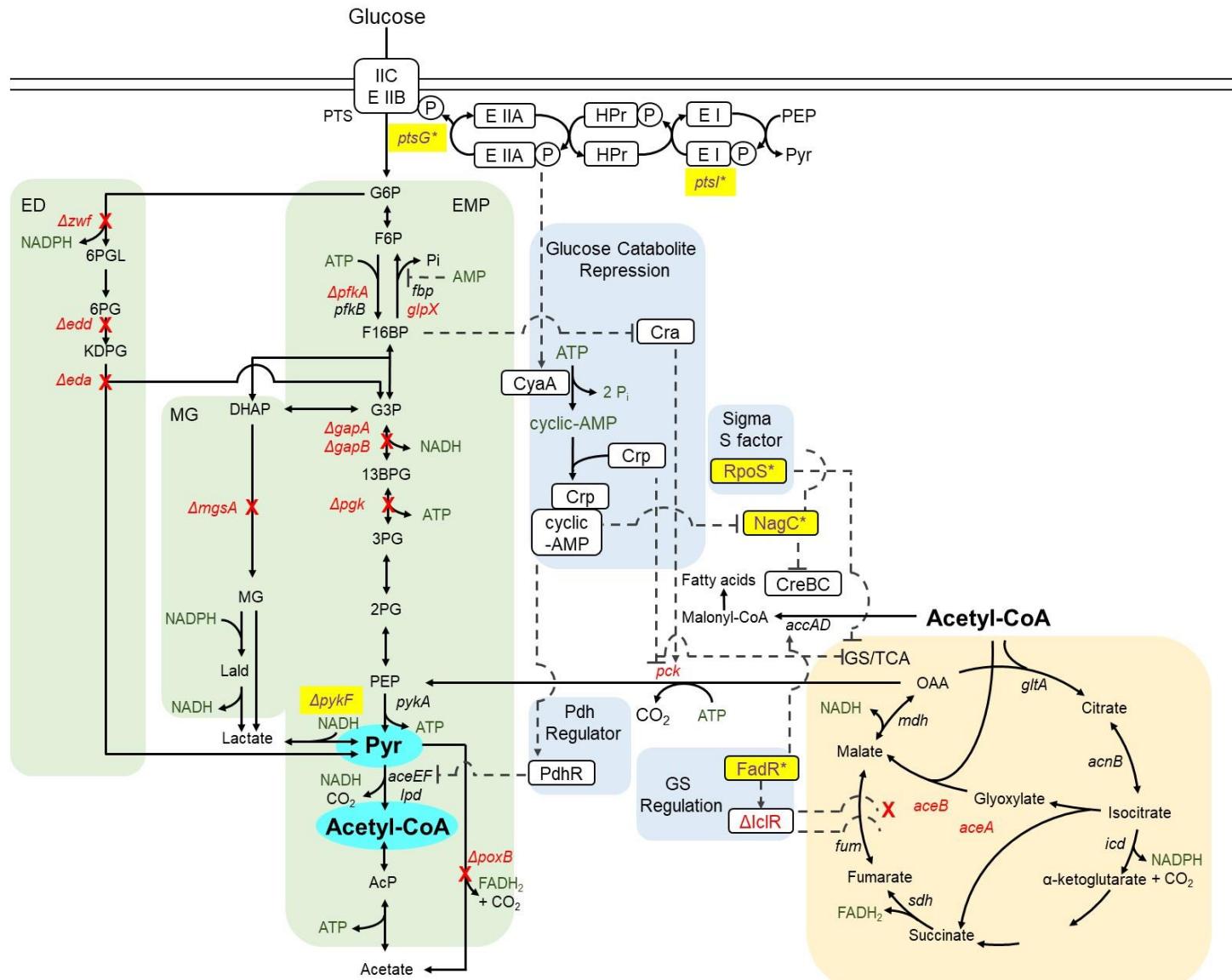


X5P phosphoketolase  
 $\text{X5P} \rightarrow \text{AcP} + \text{G3P}$

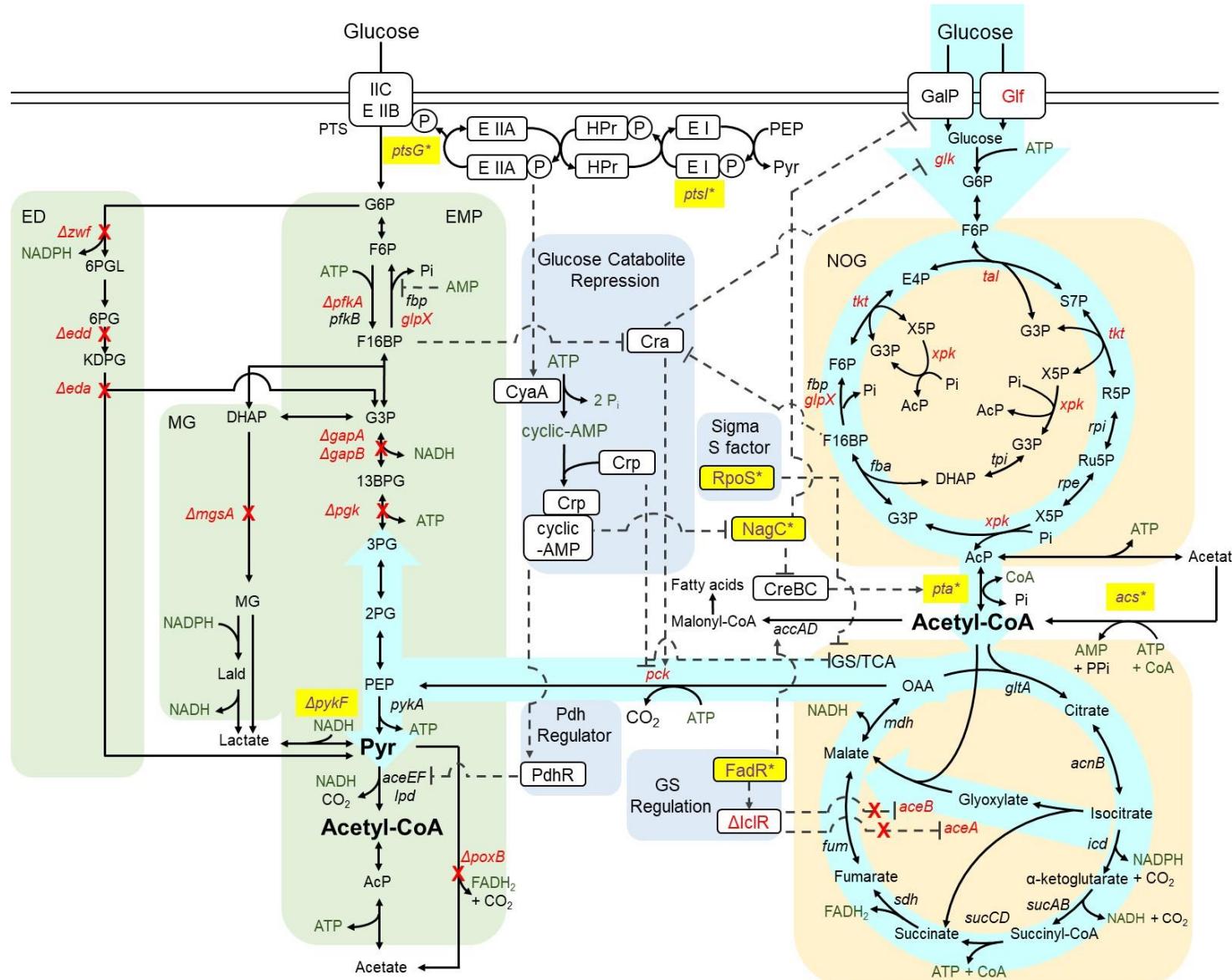


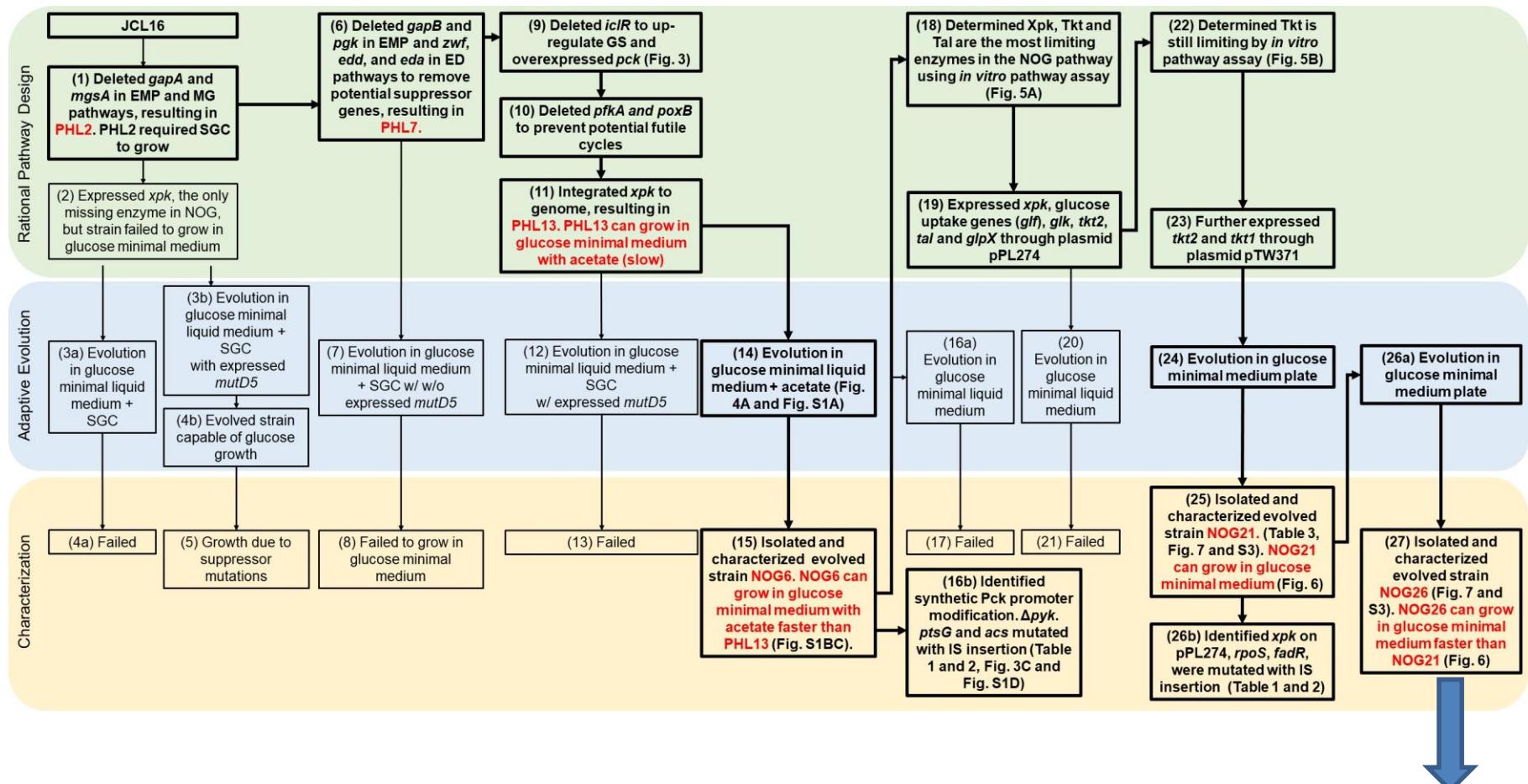
Net reaction:  $\text{F6P} \rightarrow 3 \text{ AcP}$

# Construction and Evolution of an NOG *E. coli* strain



# Construction and Evolution of an NOG E. coli strain





# Economy of oxidative and non-oxidative glycolysis for making ethanol

Traditional  
fermentation



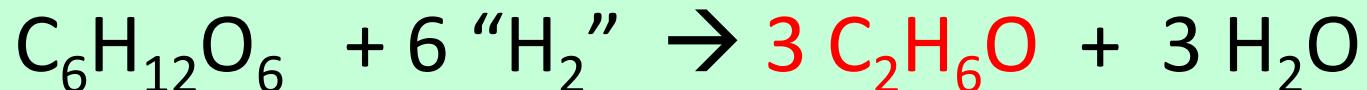
sugar price = \$0.4/Kg

ethanol price = \$0.75/Kg

<http://www.nasdaq.com/markets/sugar.aspx>

(Formate)

NOG



When

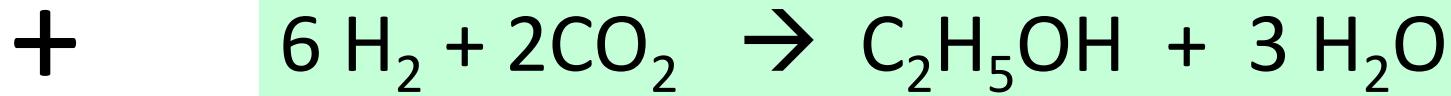
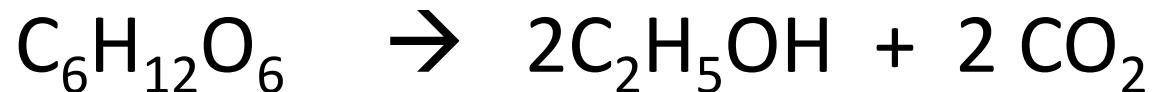
$$\frac{\text{sugar price}}{\text{H}_2 \text{ price}} > \frac{12}{90} (= 0.133)$$

Then it makes sense to use NOG + H<sub>2</sub>.

H<sub>2</sub> price < \$3/Kg

# Reductive Fermentation (H<sub>2</sub>-assisted CO<sub>2</sub> fixation)

Traditional fermentation

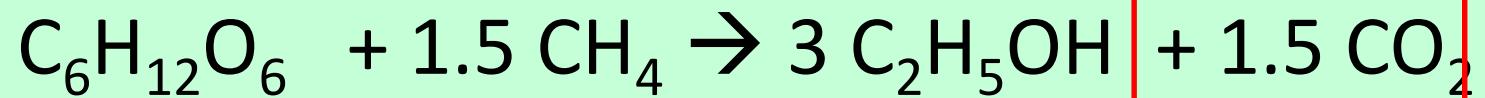
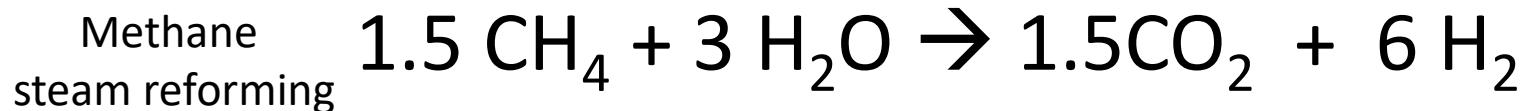
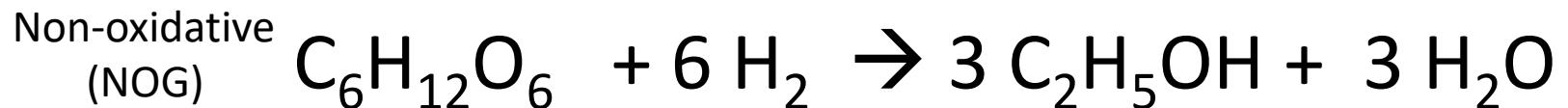


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NOG: Reductive  
fermentation



# CO<sub>2</sub> Saving



# Methane upgrading

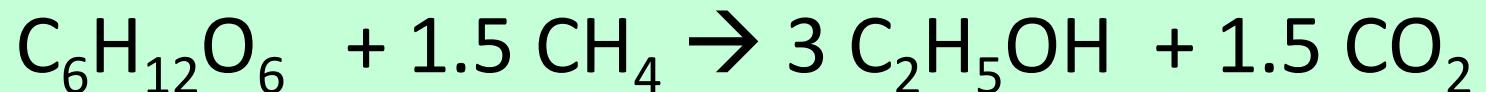
Traditional  
Fermentation  
+

Methane  
upgrading



---

NOG  
+  
Steam  
Reforming



Natural gas price ~ \$3/mmBTU, Ethanol price ~\$0.8/Kg

$$\frac{\text{Price of 1 mol of C}_2\text{H}_5\text{OH}}{\text{Price of 1.5 mol of CH}_4} = 9.6$$

# Methane upgrading

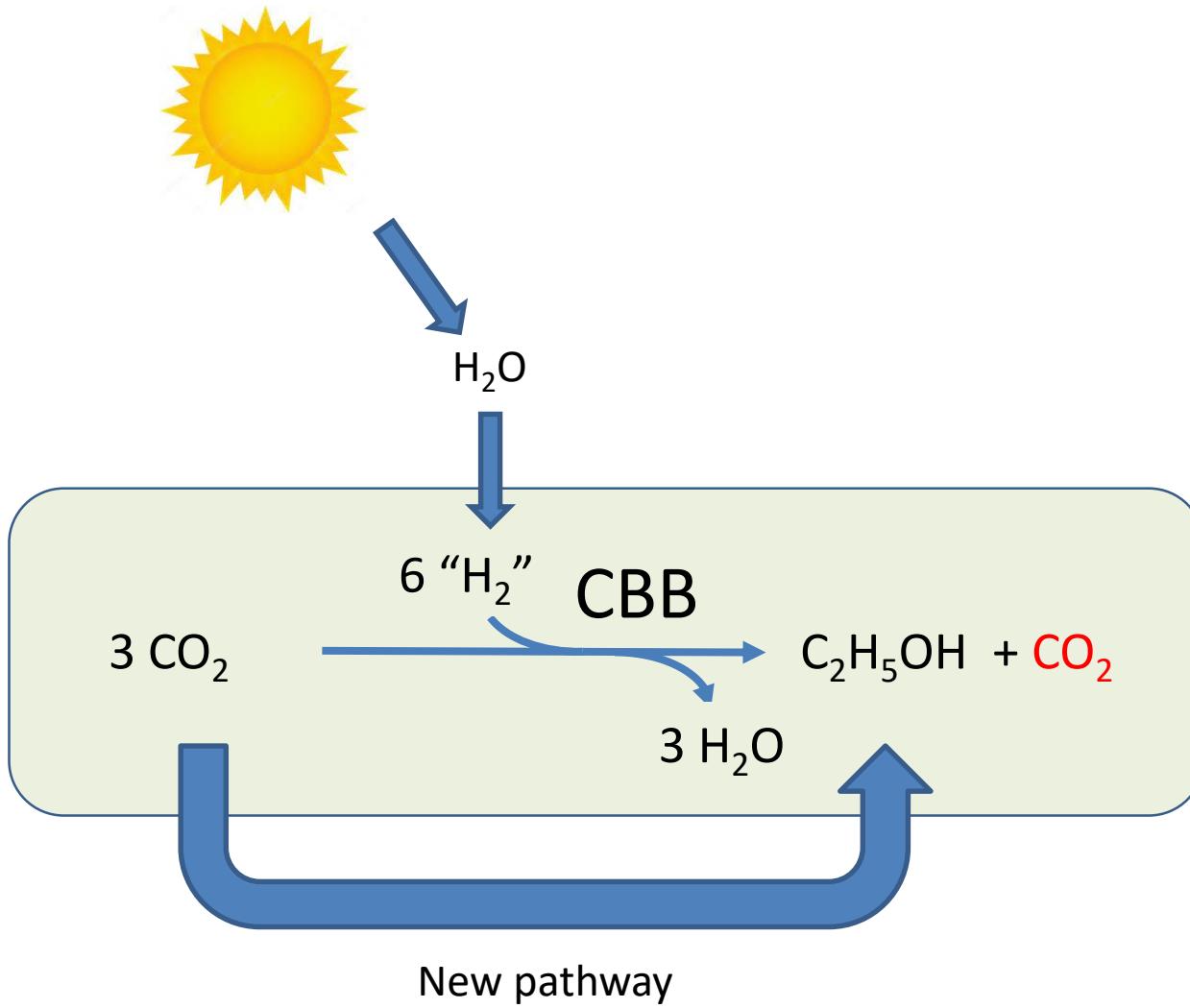
Reactions	$\Delta G^\circ$ (kJ/mole)	Energy* efficiency	Carbon <sup>#</sup> yield	Comment
1) $C_6H_{12}O_6 \rightarrow 2 C_2H_6O + 2 CO_2$	-228.4	0.97	66.70%	Current fermentation
2) $0.5 CO_2 + 1.5 CH_4 \rightarrow C_2H_6O$	100.05	1.03	133%	Proposed Methane upgrading ( $\Delta G^\circ > 0$ )
3) = 1)+2) $C_6H_{12}O_6 + 1.5 CH_4 \rightarrow 3 C_2H_6O + 1.5 CO_2$	-128.35	0.99	80%	Proposed reductive fermentation
4) $2CH_4 + O_2 \rightarrow C_2H_6O + H_2O$	-309.1	0.77	100%	REMOTE

\*Energy efficiency is calculated from the lower heating value (LHV) of combustion of products divided by the LHV of the reactants.

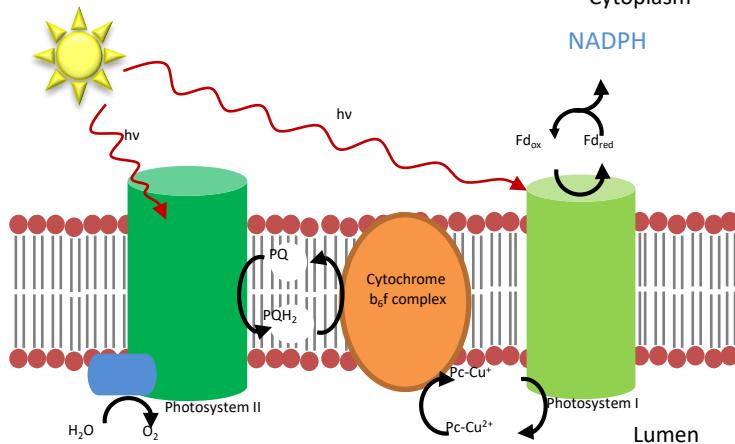
!  $\Delta G_f^\circ$  and  $\Delta H_{LHV}^\circ$  values were taken from Table 2

# Carbon yield calculation does not include  $CO_2$ .

# Augmented CO<sub>2</sub> fixation



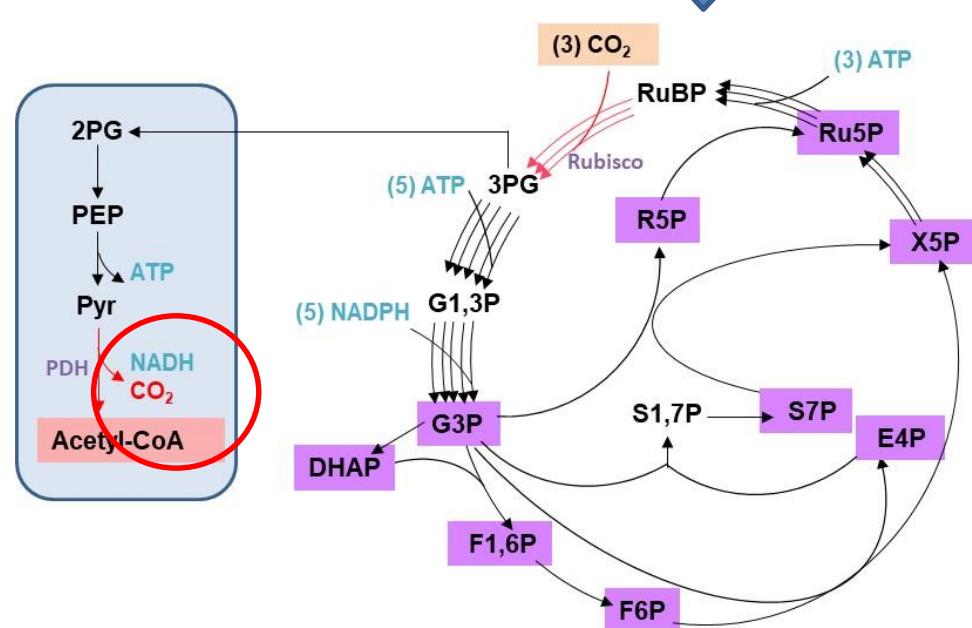
# $\text{CO}_2$ fixation by Calvin-Benson-Bassham (CBB) cycle



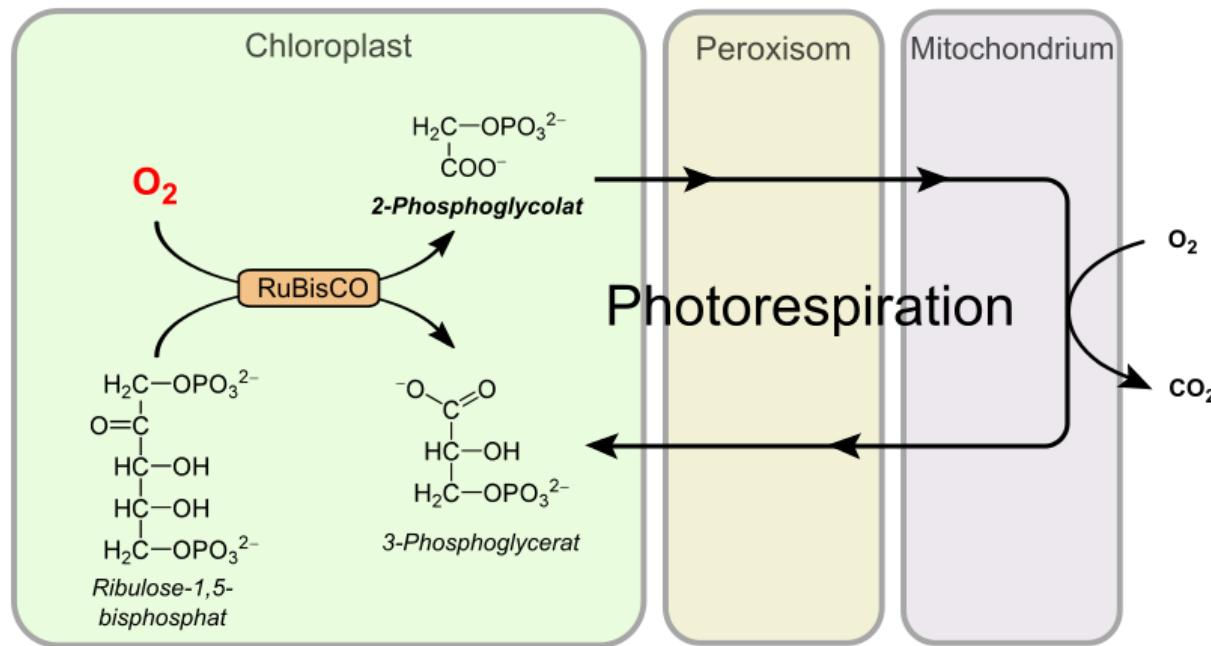
ATP, NADPH

$3\text{CO}_2 \rightarrow 1 \text{ pyruvate}$

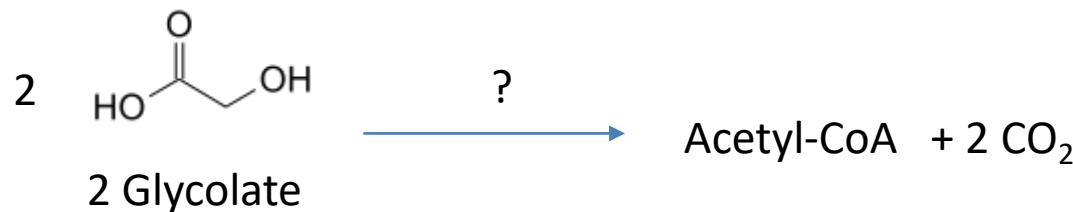
$3\text{CO}_2 \rightarrow 1 \text{ Acetyl-CoA} + \text{CO}_2$



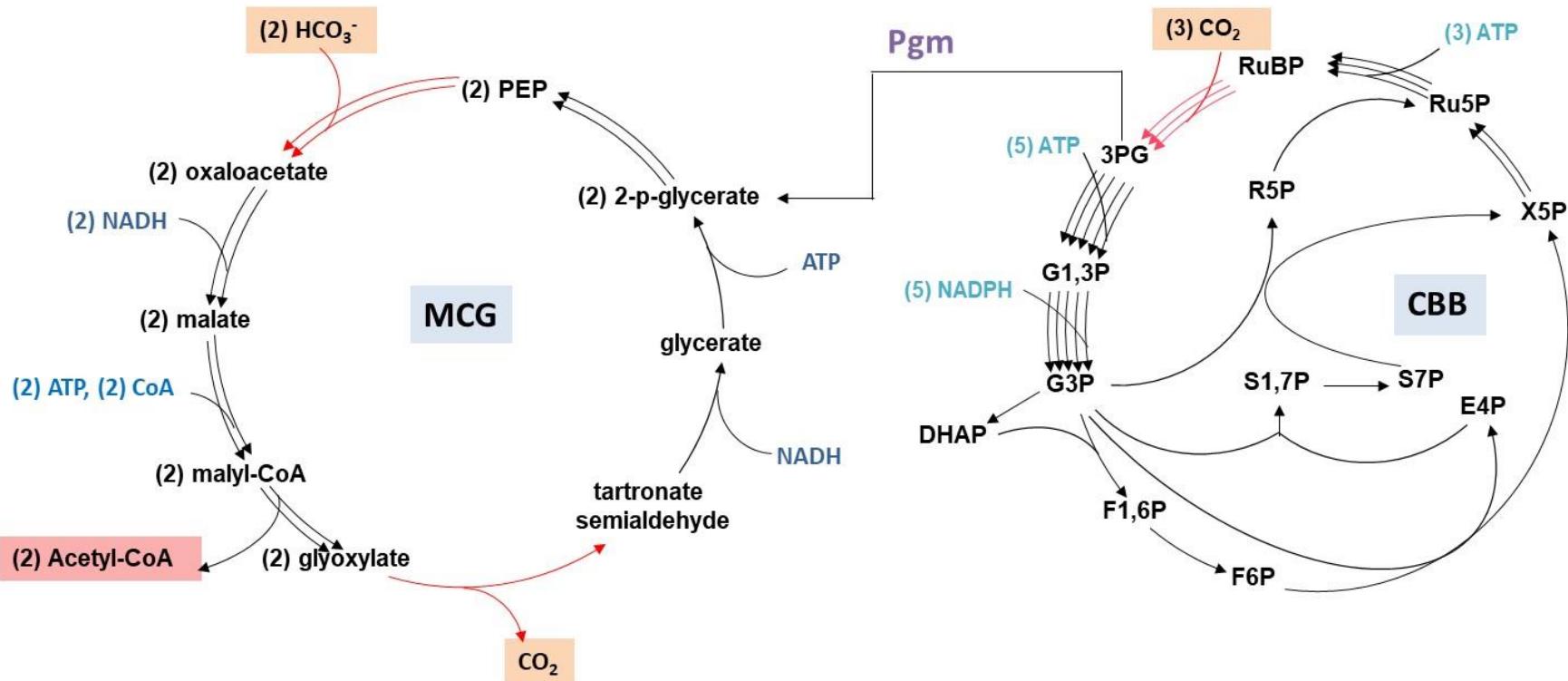
# Photorespiration



From Wikipedia



# MCG augments CBB pathway



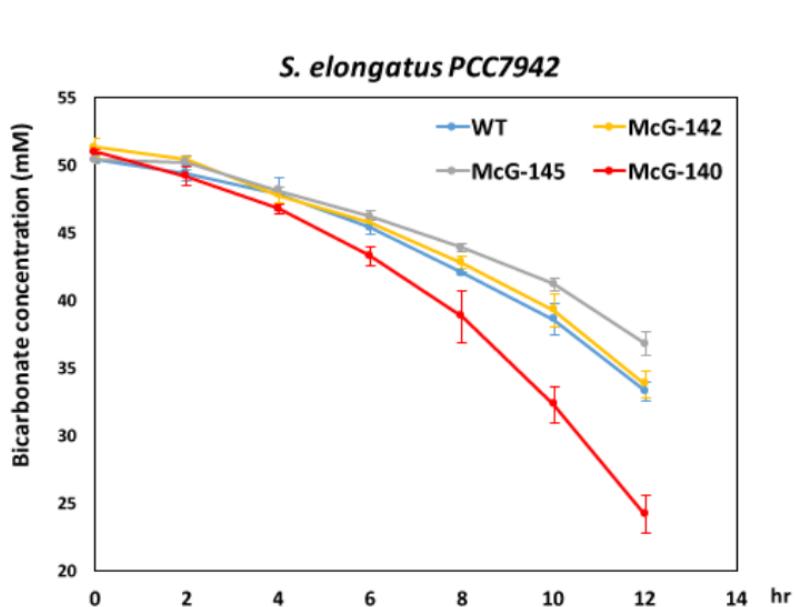
Per Ac-CoA Synthesis from CO <sub>2</sub>	NAD(P)H consumption	ATP consumption	Rubisco turnover	The theoretical carbon yield
CBB+ PDH	4	7	3	66% (Ac-CoA/C3)
CBB+ NOG	4	6	2	100% (1.5 Ac-CoA/C3)
CBB+ MCG	4	5.5	1.5	100% (2 Ac-CoA/C3+C1)

**Table 2 Comparison of ATP/NADH consumption and carbon yield among different pathways in assimilation of glycolate to produce acetyl-CoA**

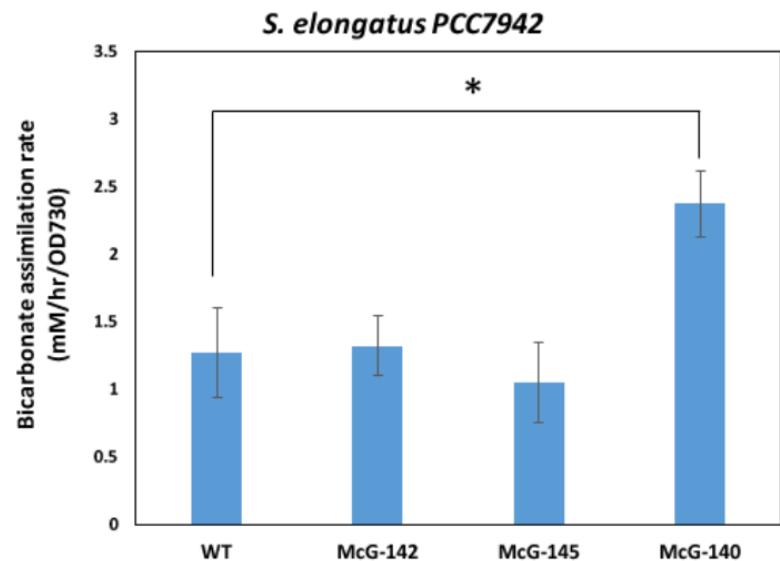
Per Ac-CoA synthesis from glycolate	NAD(P)H consumption	ATP consumption	The theoretical carbon yield
Native photorespiration pathway <sup>41</sup>	0	0	50% (1 Ac-CoA/2 glycolate)
The bacterial glycolate assimilation route <sup>41</sup>	-2	0	50% (1 Ac-CoA/2 glycolate)
The MCG pathway	1	2	100% (1 Ac-CoA/1 glycolate)

The MCG pathway can convert one glycolate to produce one acetyl-CoA without net carbon loss. The bacterial glycolate assimilation route converts two glycolate to only one acetyl-CoA

# MCG in *S. elongatus* increases CO<sub>2</sub> fixation



f



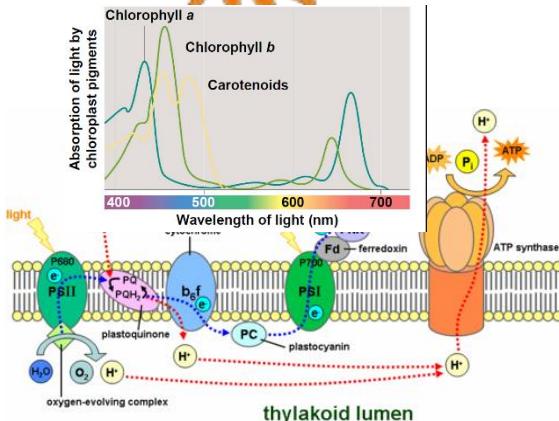
# Challenges of Algae and cyanobacteria: Photobioreactor is expensive



# Decouple Light and Dark Reactions



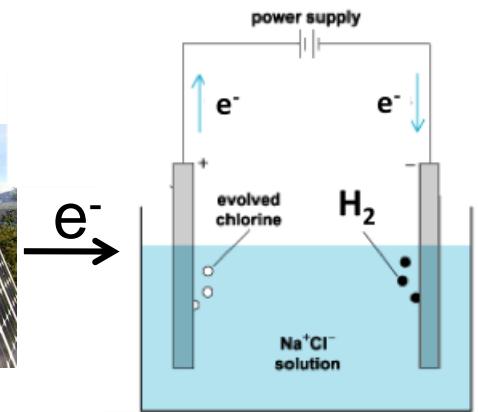
## Light Reactions



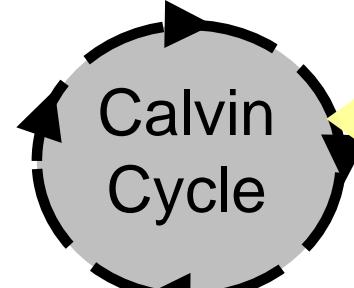
PV



Electrochem



NADPH ATP



NAD(P)H  $\leftarrow H_2$

Biofuel

Energy efficiency

0.3 % (practical)

5.7% (theoretical)

Energy efficiency

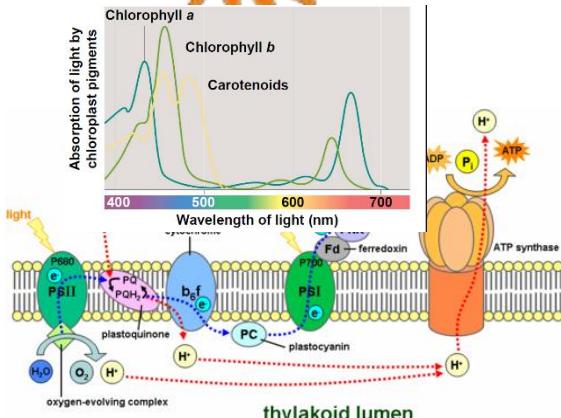
2.9% (practical)

9% (theoretical)

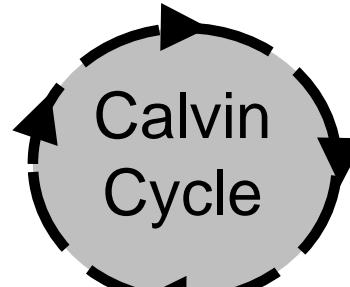
# Decouple Light and Dark Reactions



## Light Reactions



NADPH ATP



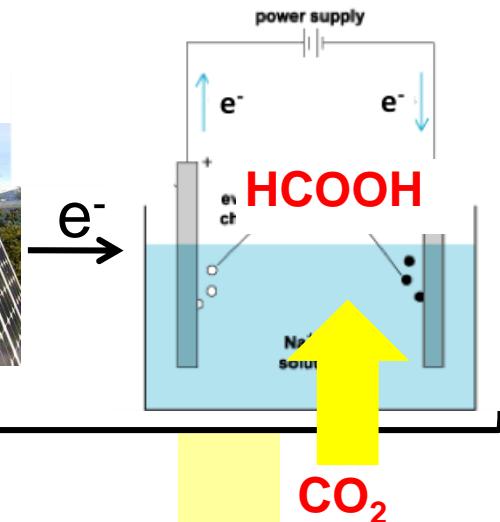
Biofuel



PV



Electrochem



Energy efficiency

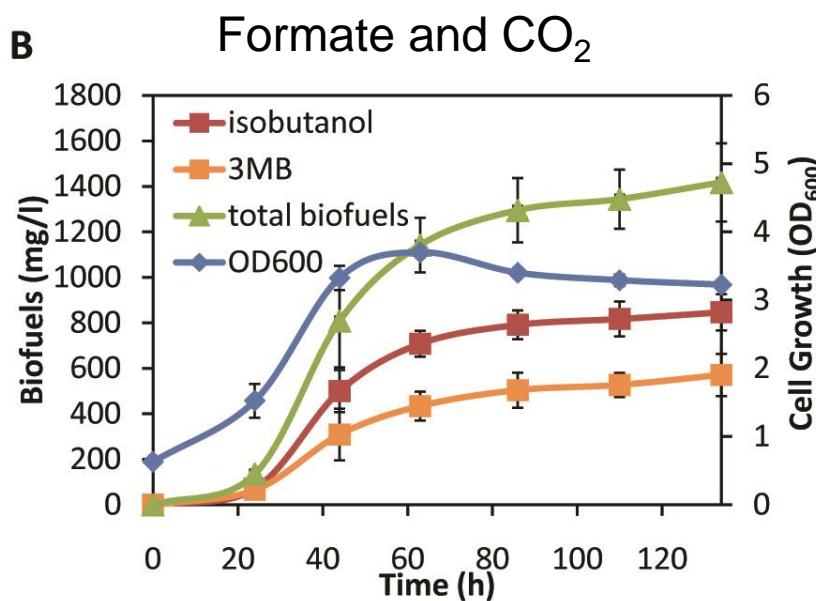
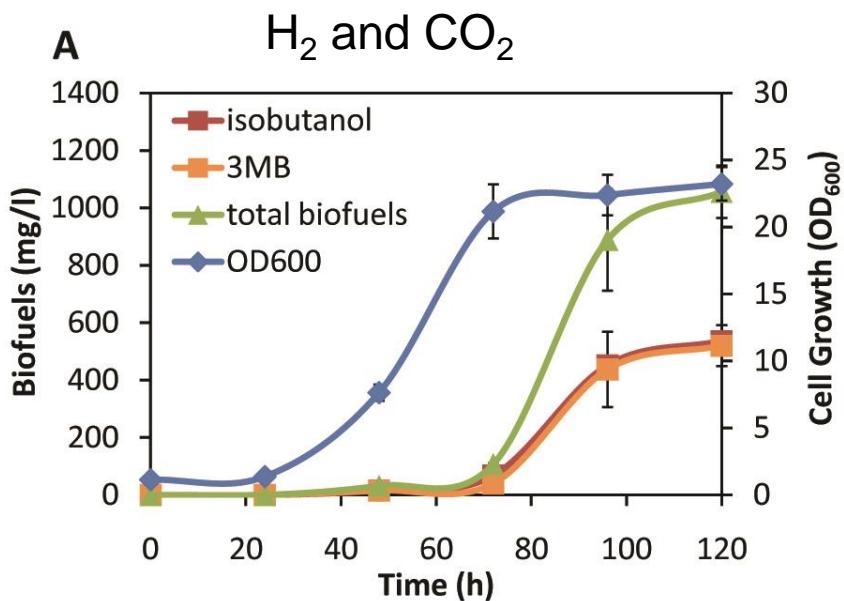
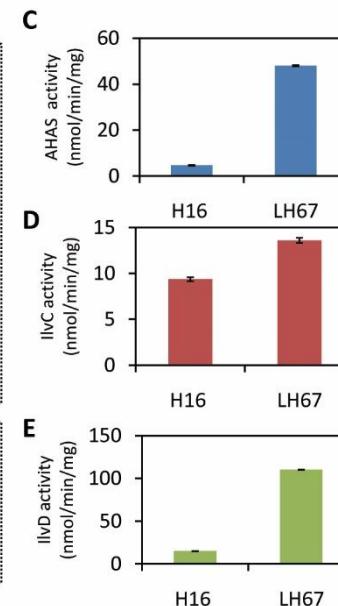
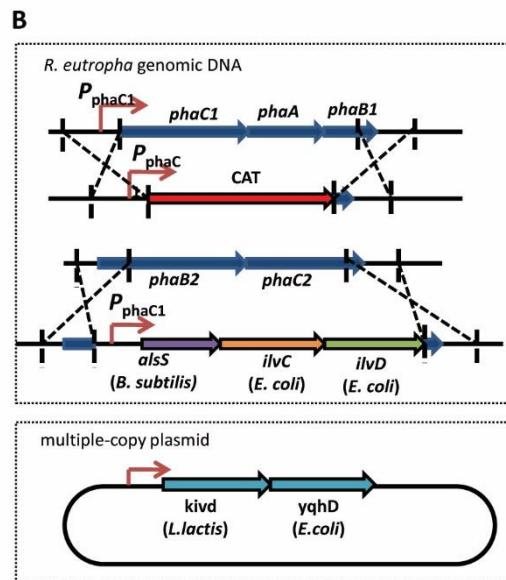
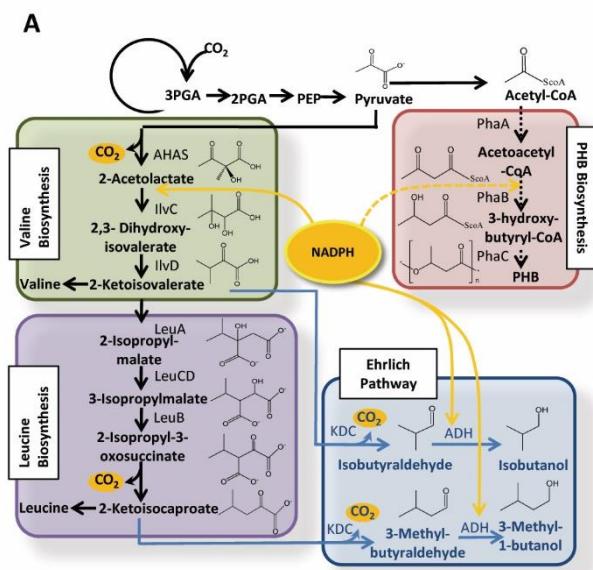
0.3 % (practical)

5.7% (theoretical)

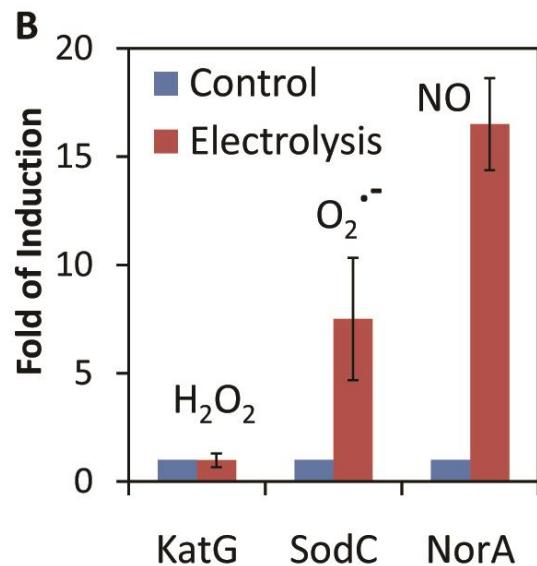
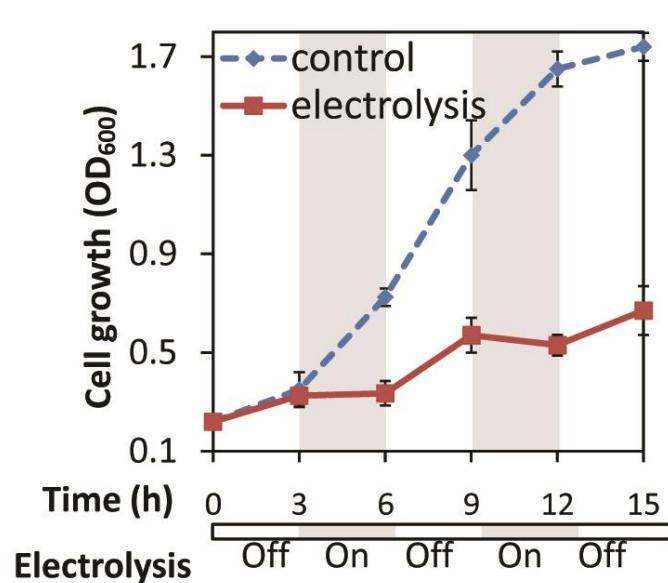
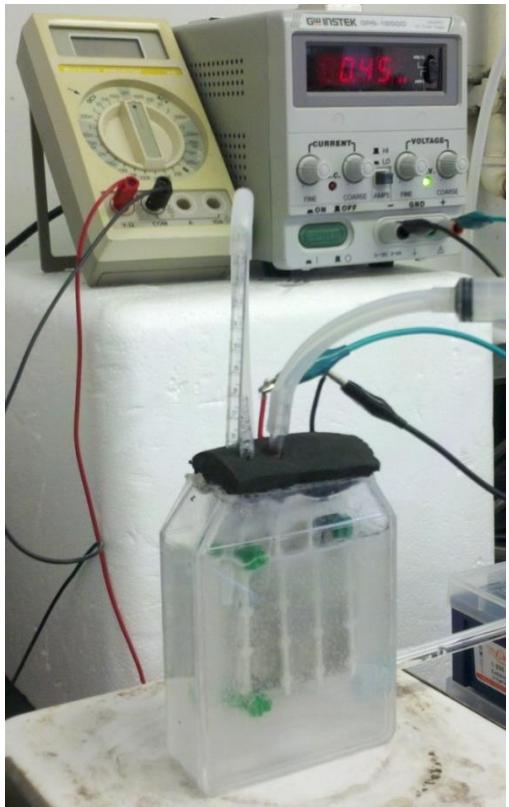
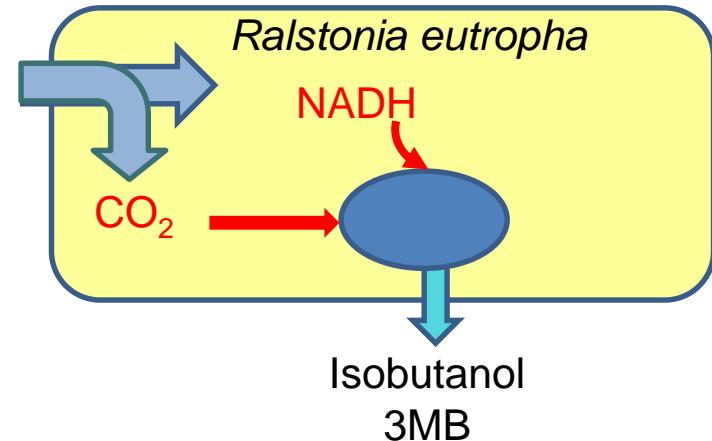
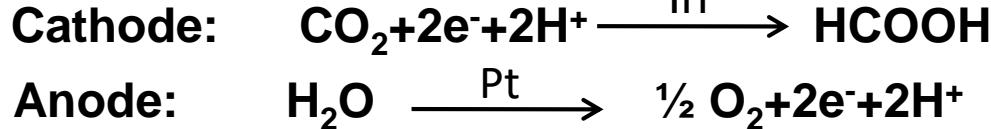
Energy efficiency

2.9% (practical)

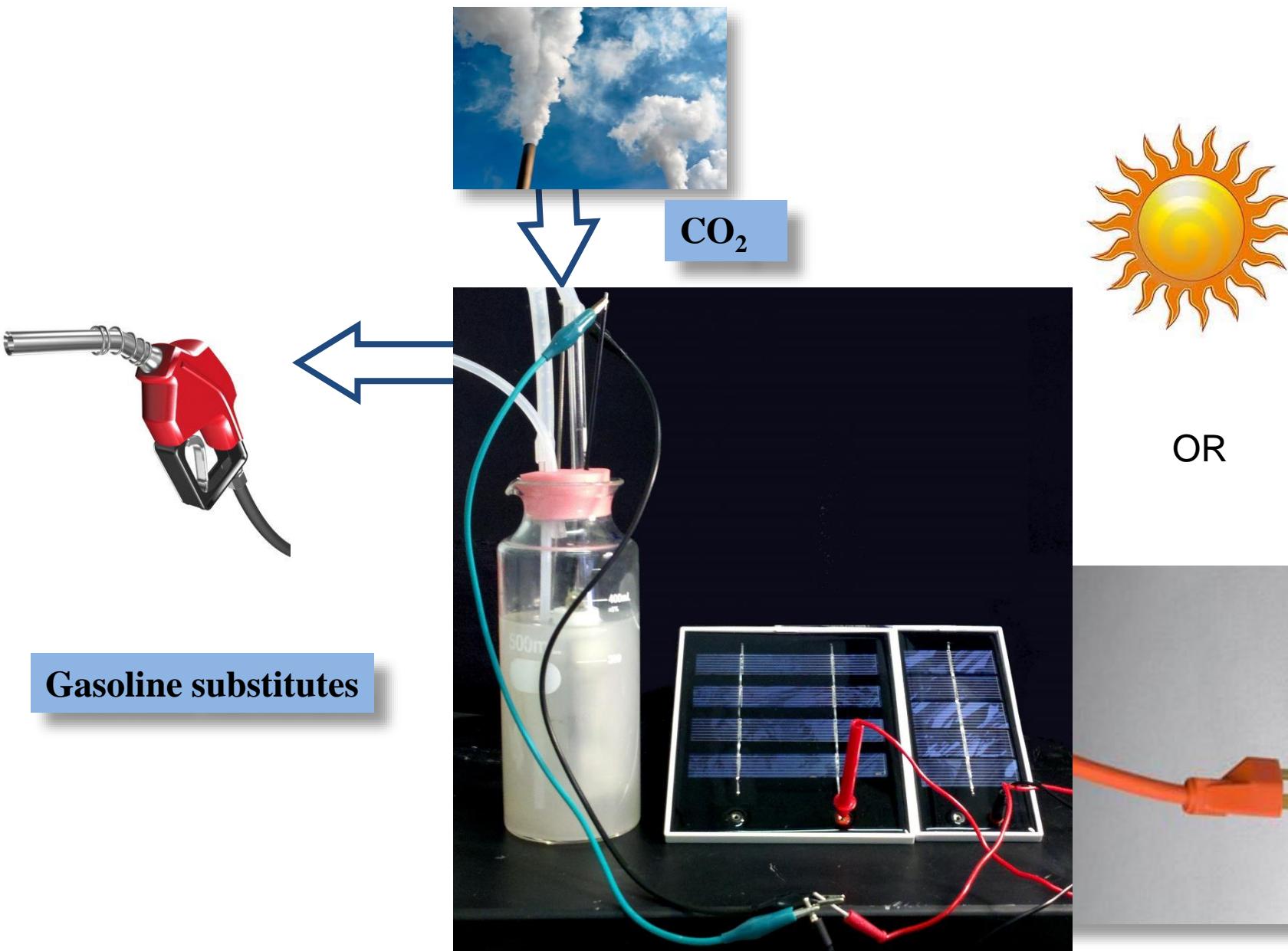
9% (theoretical)



# Electricity-powered CO<sub>2</sub> fixation for Isobutanol synthesis



# Integrated Electro-microbial fuel Production



Thank you.