Direct Production of Bioplastics and Chemicals from Carbon Dioxide and Solar Energy

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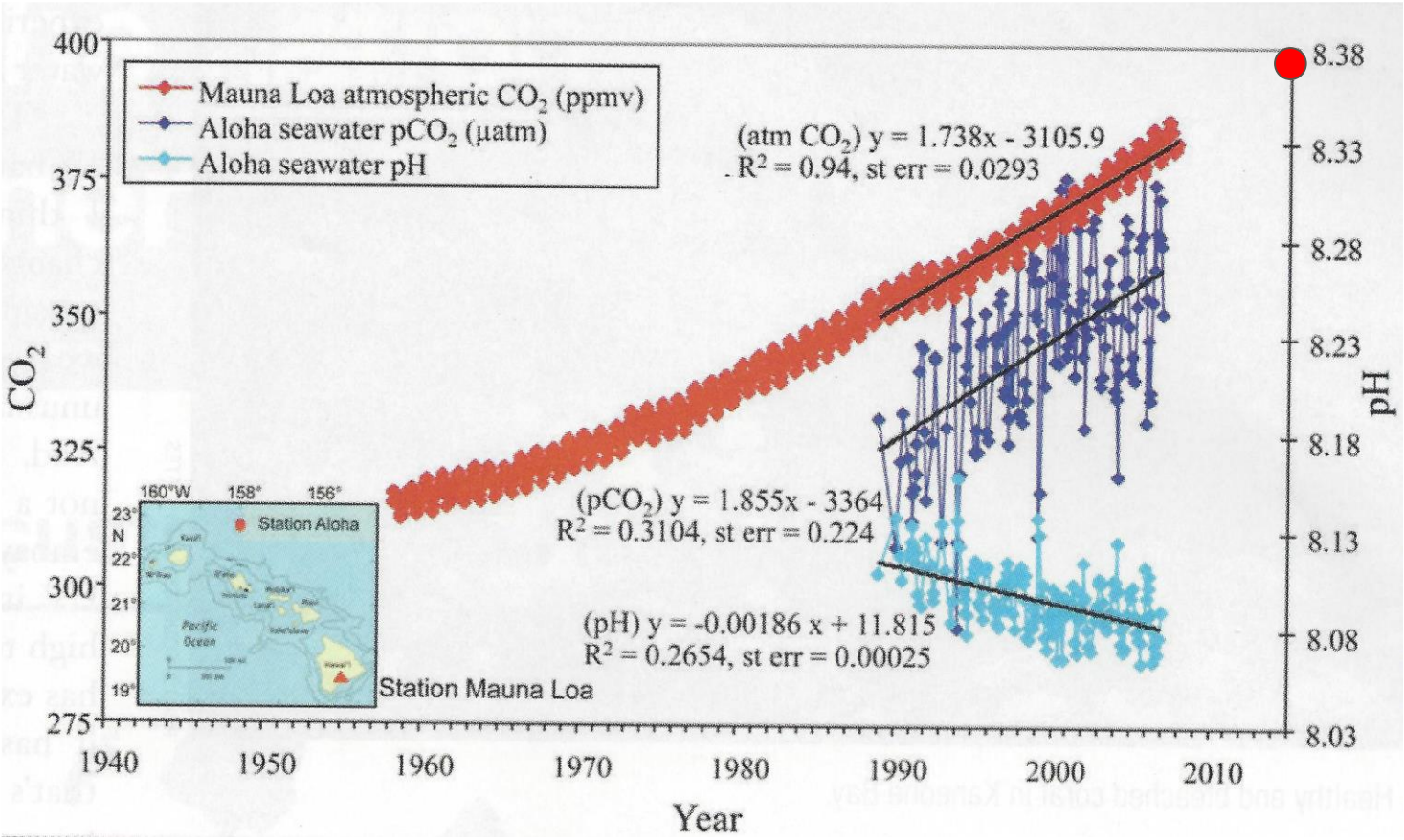
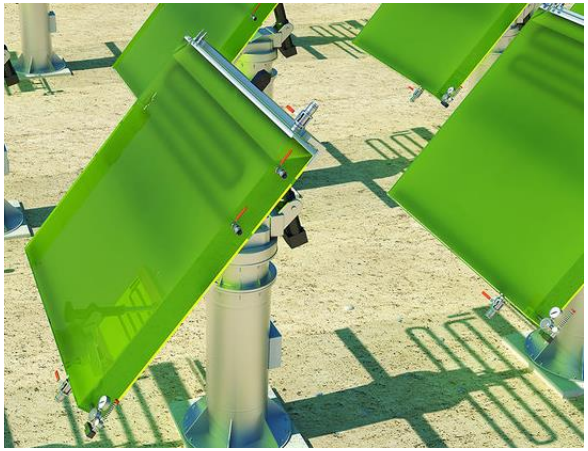
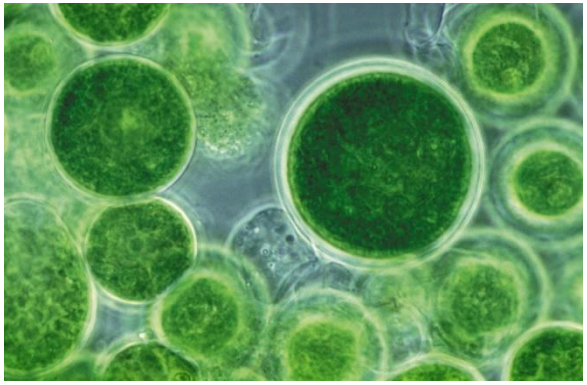
Trend of CO_2 in air and seawater



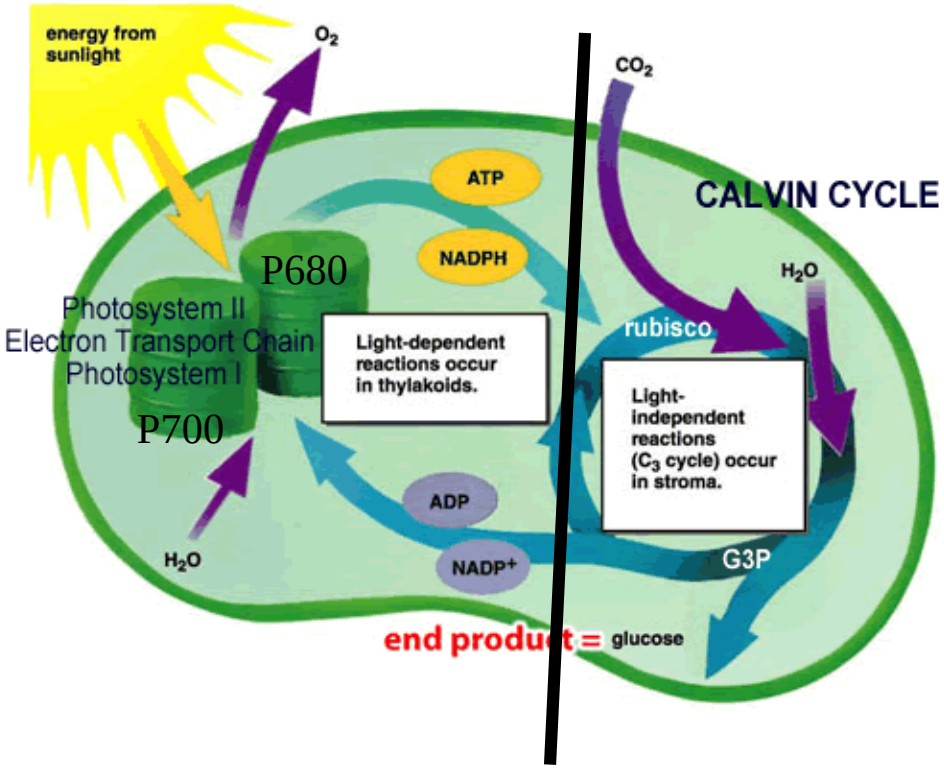
Global CO_2 breaches 400 ppm– C&EN, May 18, 2015

CO_2 fixation via photosynthesis



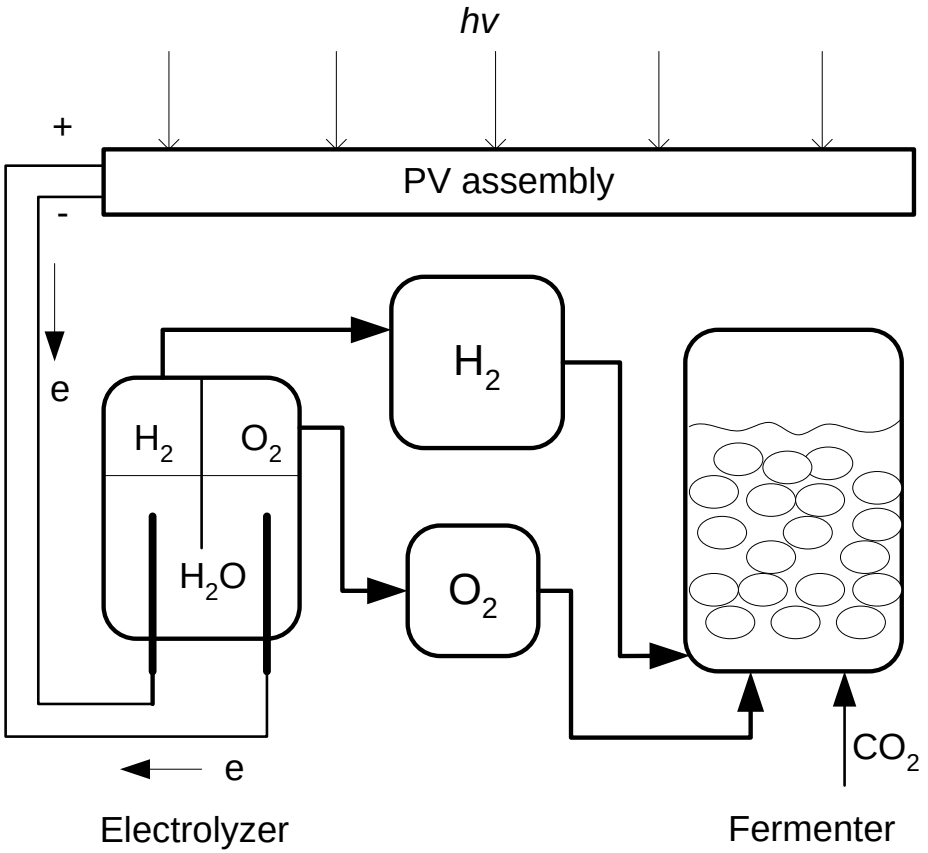


$$CO_2 + H_2O + h\nu \rightarrow CH_2O\ (biomass) + O_2$$



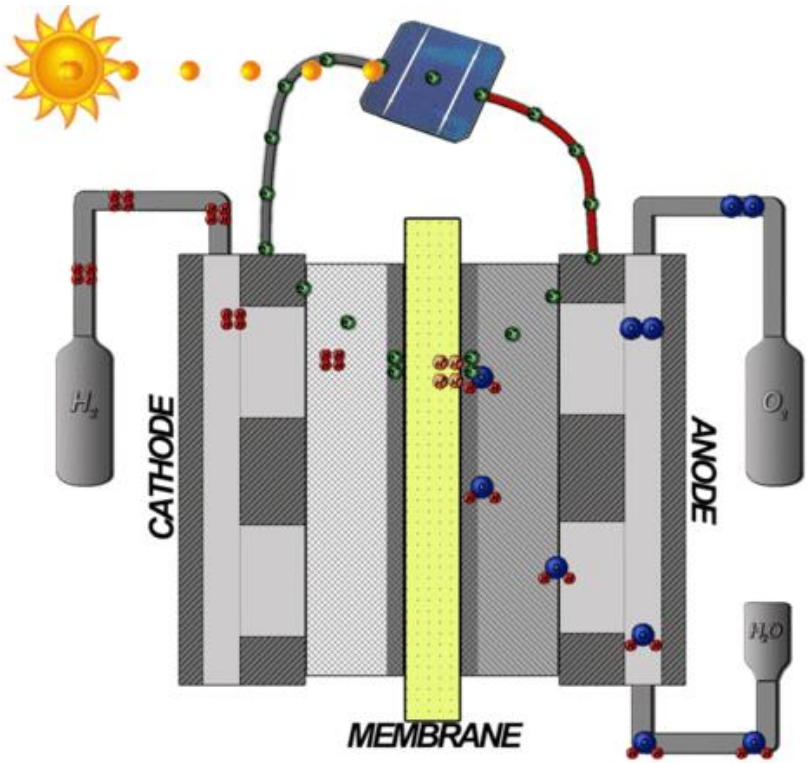
The light capture and CO_2 fixation are tightly coupled and should be decoupled!

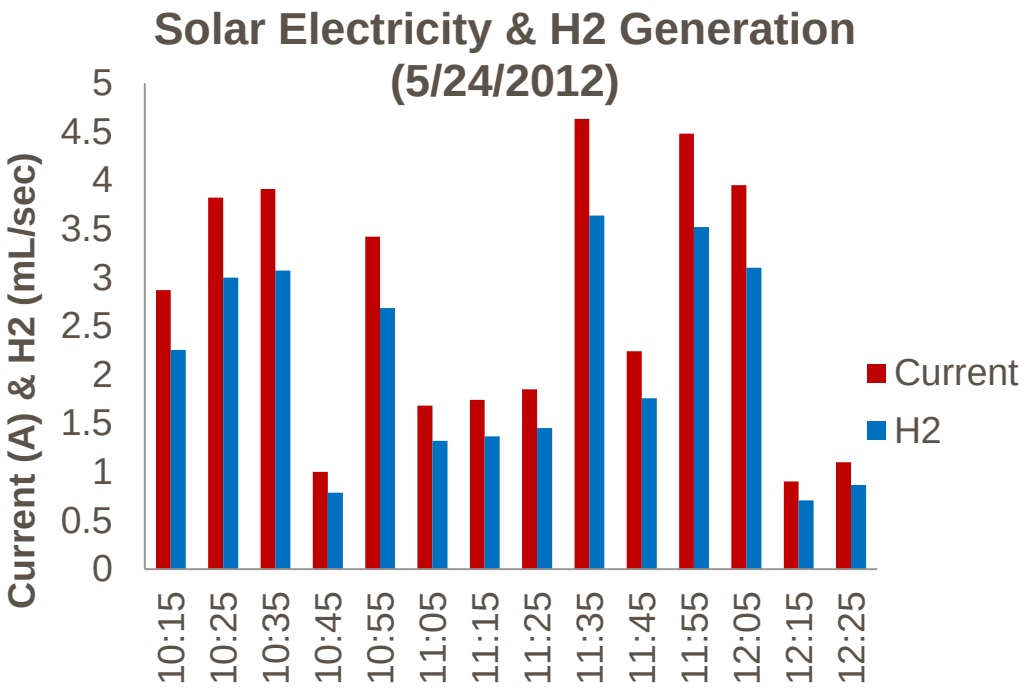
Artificial photosynthetic system



$$CO_2 + H_2O + h\nu \rightarrow CH_2O \text{ (biomass)}$$

H_2 from Intermittent solar energy



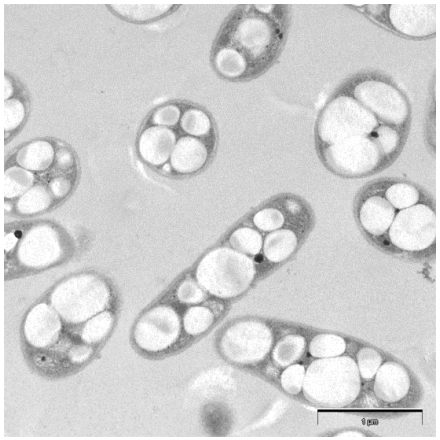


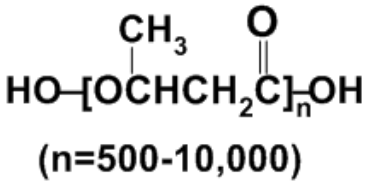
Anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+(aq) + 4e$

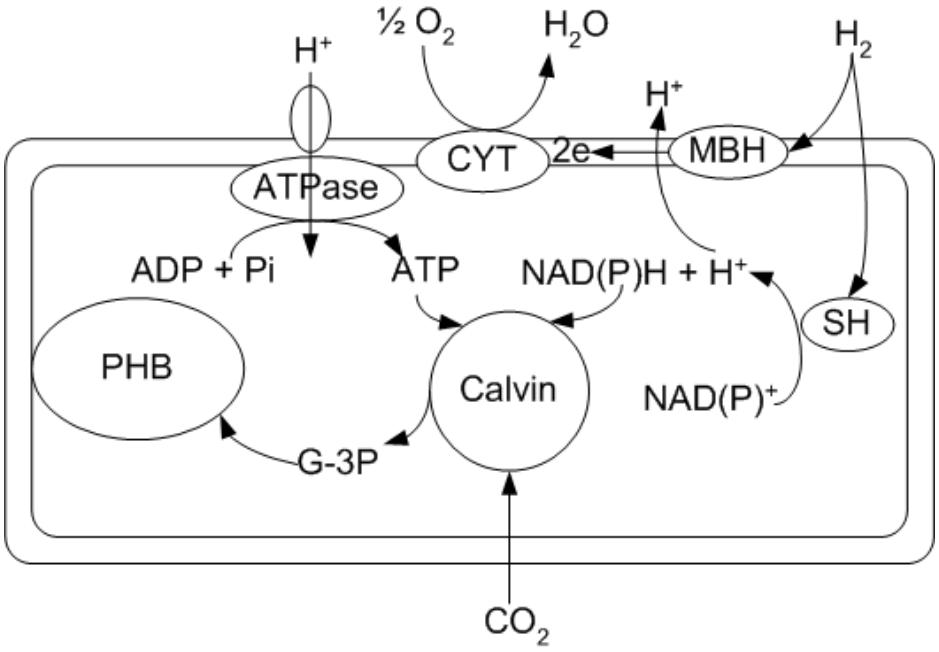
Cathode: $4H^+(aq) + 4e \rightarrow 2H_2\ (g)$

Overall: $2H_2O(l) \rightarrow O_2(g) + 2H_2\ (g)$

CO_2 Fixation by Autotrophic Bacterium







H_2/CO_2 = 6 mole/mole (energy efficiency 28%)

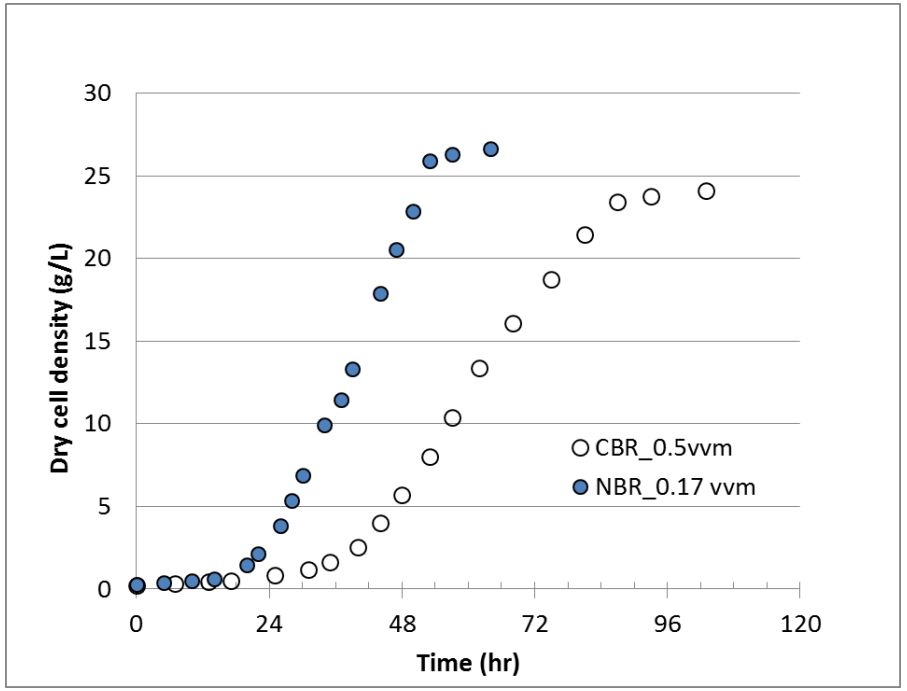
For biomass synthesis (51 wt% C):

$$CO_2 + 6H_2 + 1.94O_2 + 0.19NH_3 \rightarrow CH_{1.74}O_{0.46}N_{0.19} + 5.42H_2O$$

For PHB synthsis (56 wt% C):

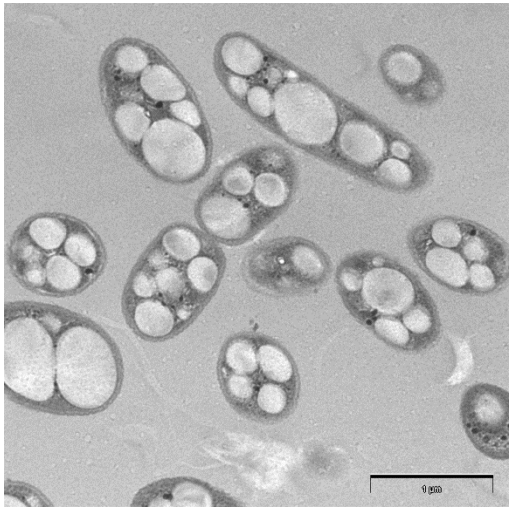
$$CO_2 + 6H_2 + 1.875O_2 \rightarrow CH_{1.5}O_{0.5} + 5.25H_2O$$

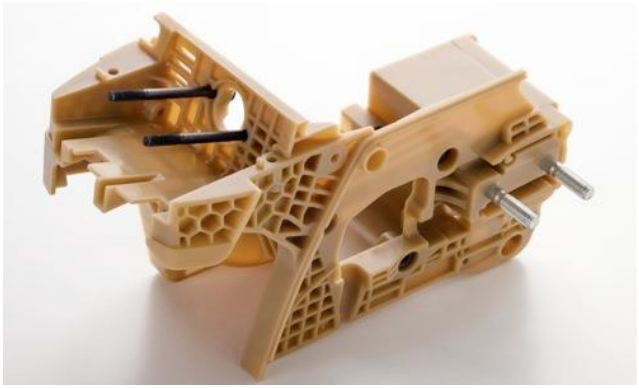
Conventional versus Novel Bioreactors

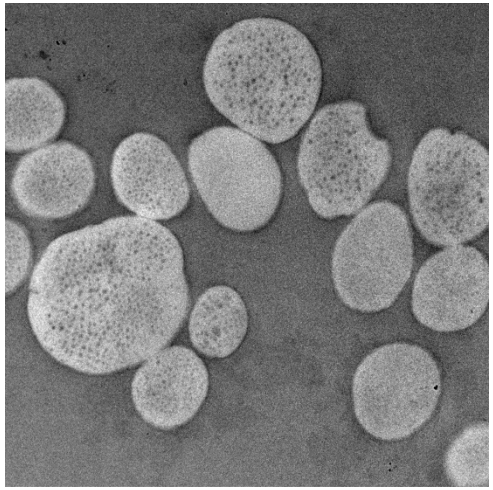


	Conventional BR	Novel BR
Cell growth rate (g/L.hr)	0.23	0.42
CO_2 fixation rate (g/L.hr)	0.55	0.98
Cell density (g/L)	24	27
PHB (wt%)	59	52
PHB yield (g/g H2)	0.1	0.38

A Bioplastic of 100% CO_2 Carbon





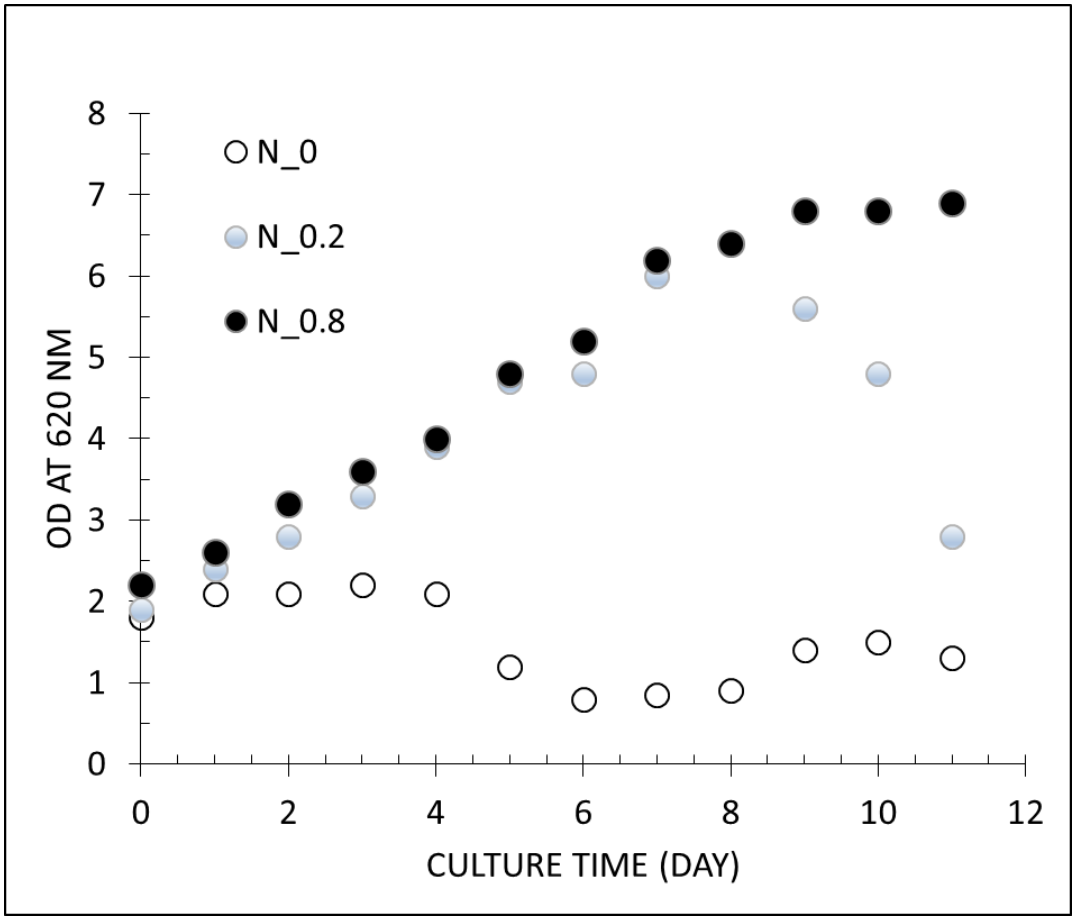


Fate of residual biomass?

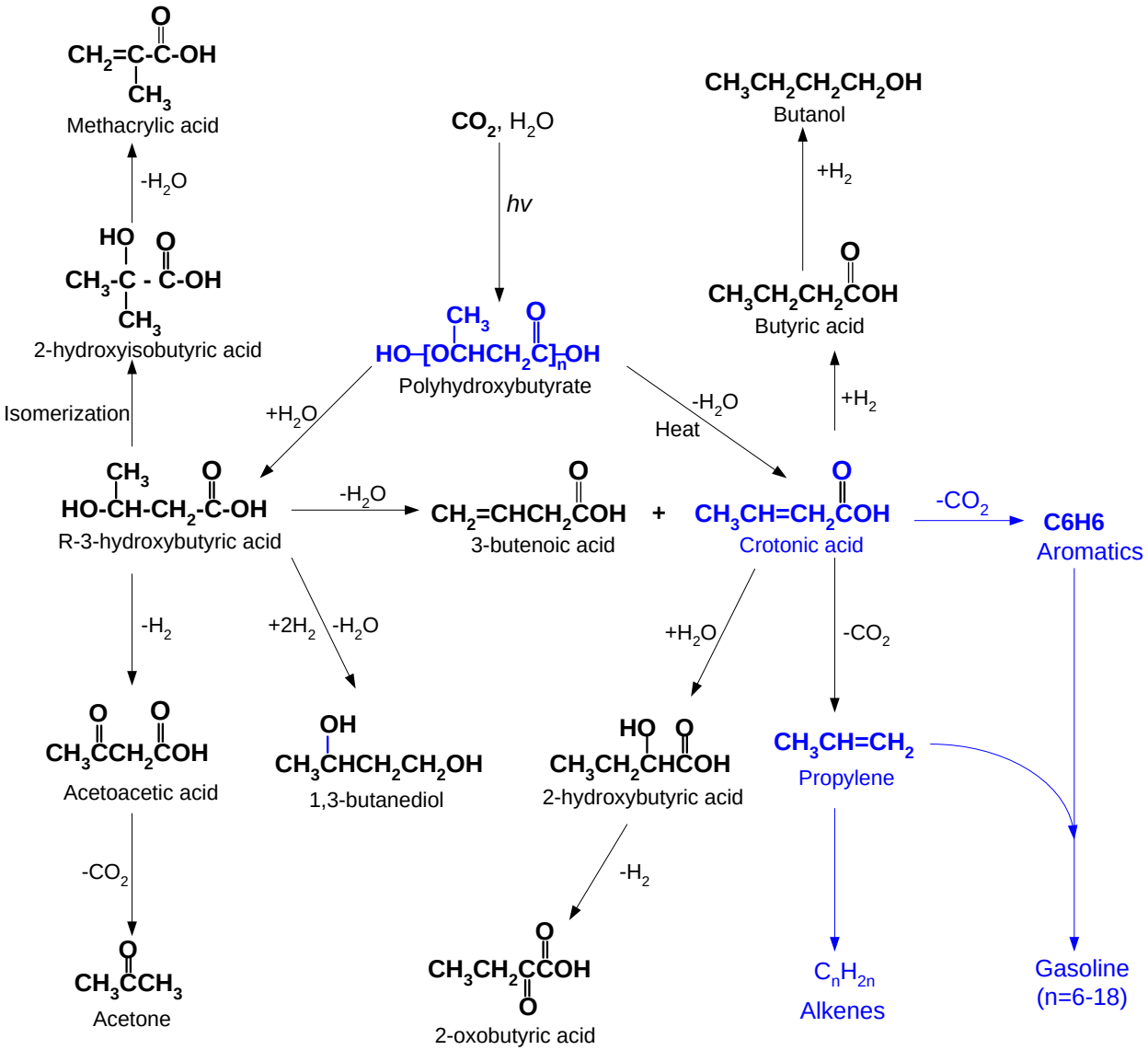
Residual biomass as nutrients in CO_2 fixation

$$CO_2 + 6H_2 + 1.94O_2 + 0.19NH_3 \rightarrow CH_{1.74}O_{0.46}N_{0.19} + 5.42H_2O$$

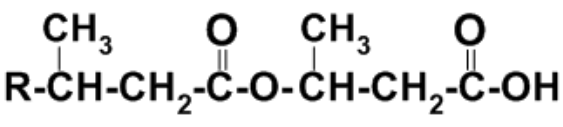
After PHB recovery, the residual cell mass becomes N-rich hydrolysates.

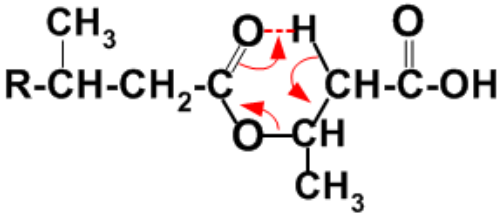


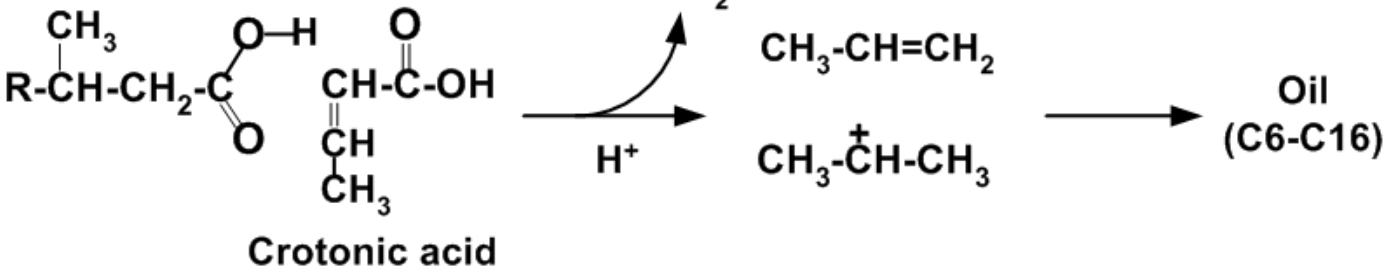
Bio-based chemicals from PHB platform

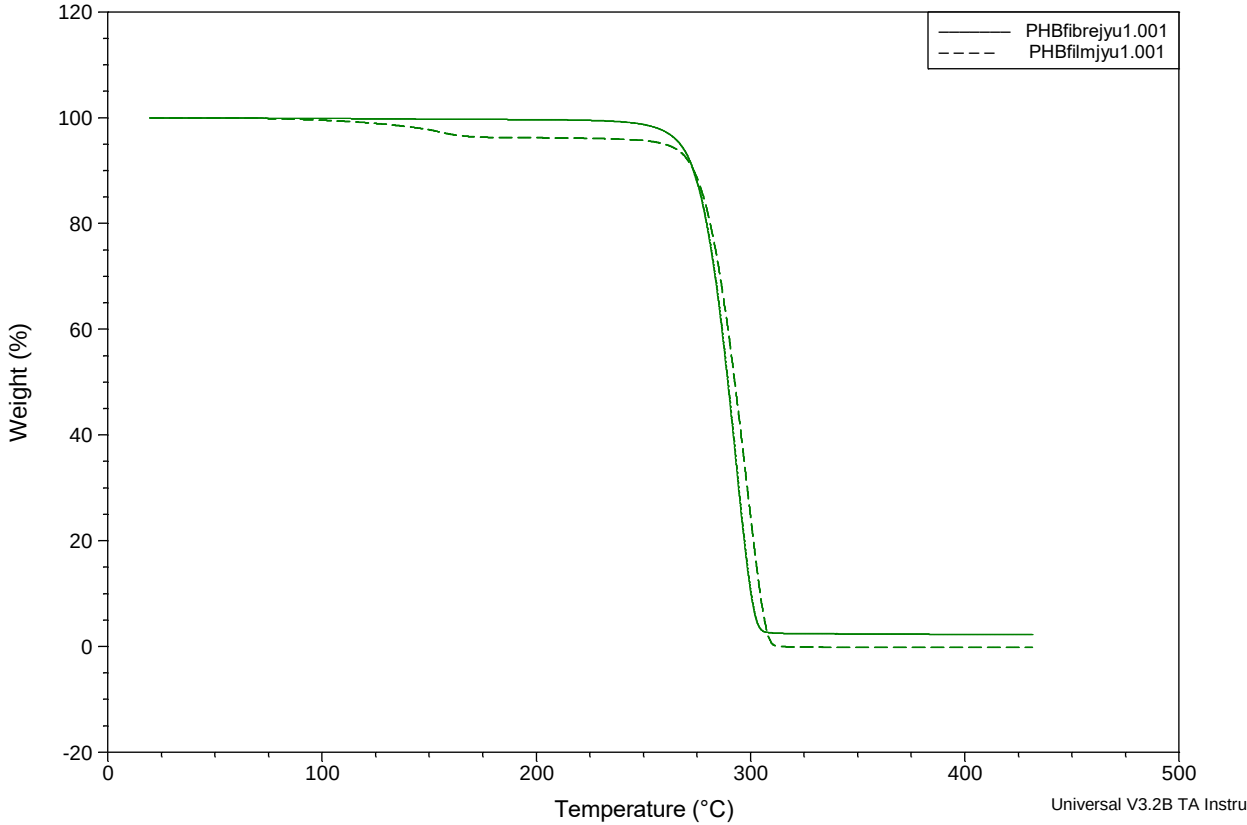


PHB Thermal Degradation & Reaction Mechanism

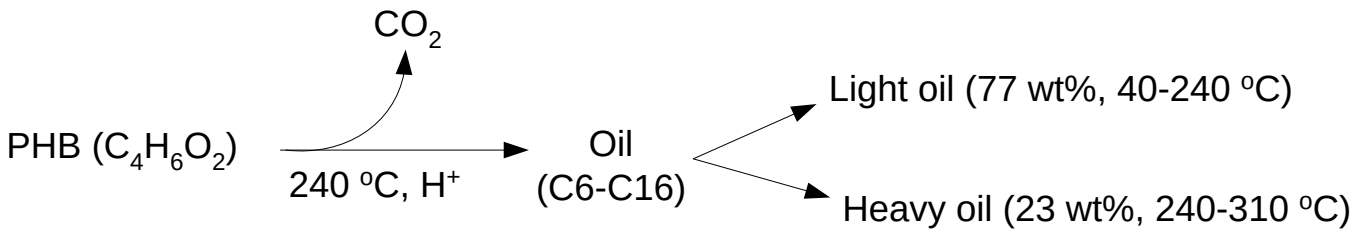








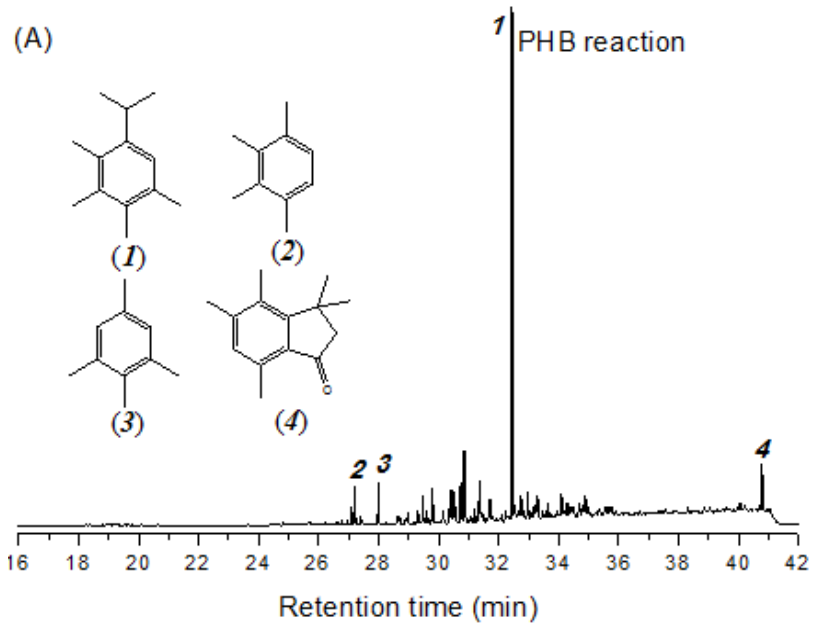
High-grade Biofuels from PHB

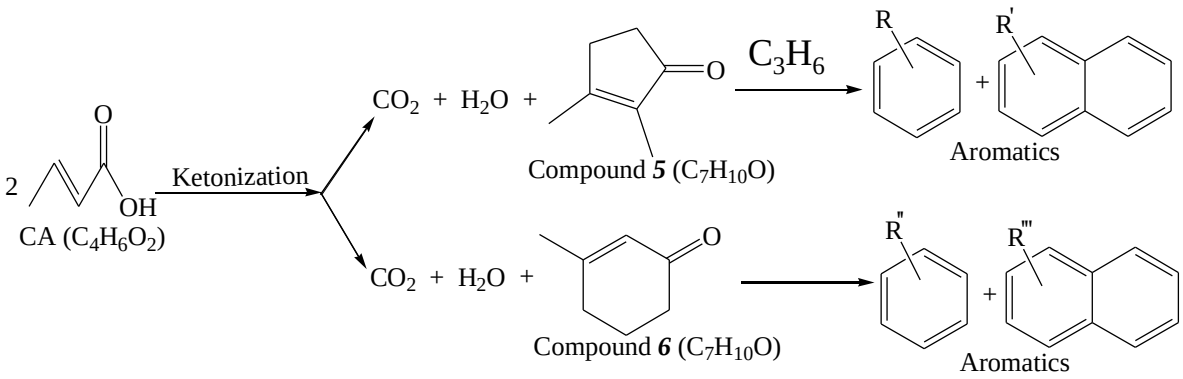


Fuels	Gasoline[a]	Light-oil	Heavy-oil	Biodiesel [b]
BP (°C)	40-240	40-240	240-310	182-338
C (%)	80.40	81.37	79.38	76.96
H (%)	12.30	11.30	9.67	11.85
N (%)	0.15	0.14	0.23	-
O (%)	6.35	7.19	10.72	9.41
HHV (MJ/kg)	41.8	41.4	38.4	39.7

[a] Blind samples of gasoline, light-oil and heavy-oil analyzed by Hazen Research Inc
[b] Properties of biodiesel from references

Aromatics from PHB platform



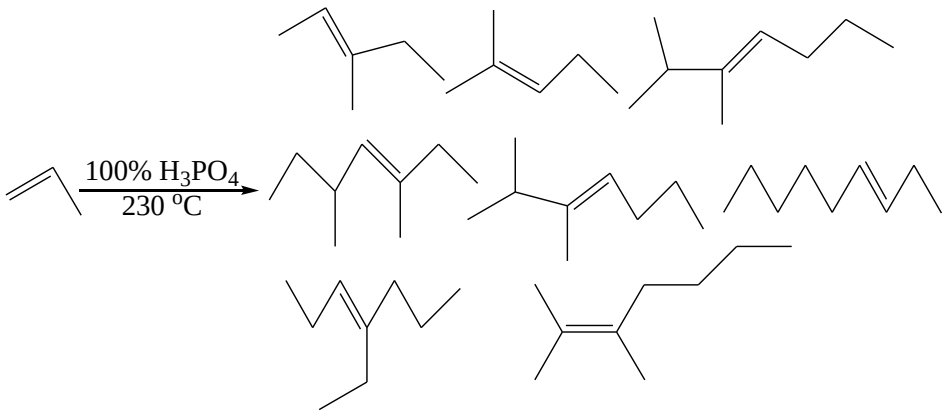


S Kang, J Yu. *RSC Advances* 2015, 5, 3005-30013.

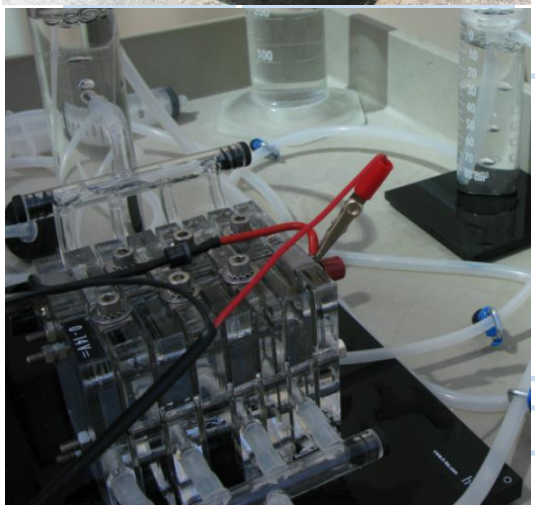
Alkenes from PHB plateform

Catalyst	O-containing Chemicals (%)*	Alkenes (%)*	Benzenes (%)*	Naphthalenes (%)*
A	19.6	2.6	65.8	11.2
B	9.9	57.0	31.1	2.0

*Based on percentage of peak areas in GCMS chromatograms



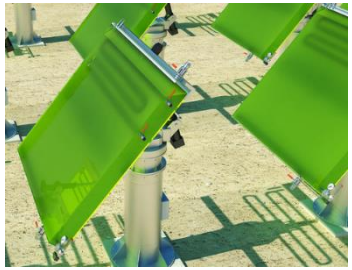
Solar Energy Conversion Efficiency



Solar electricity 17%	• Affordable commercial PV assembly • High efficiency 20-30%
Water electrolysis 75%	• Industrial electrolyzer 60-80%
CO_2 fixation 28-41%	• Low efficiency for high rate

A laboratory artificial system's solar energy efficiency 3.6 – 5.2%

Artificial versus Natural Photosynthesis



Photosynthesis	Artificial	Natural [a]
Species	*Ralstonia eutropha*	*Neochloris oleoabundans*
Chlorophyl (wt%)	0	8-25
Cell growth rate (g/L.day)	10.1	0.4
CO_2 fixation rate (g/L.day) [b]	19.6	0.78
Cell density (g/L)	27	2.4
PHB/lipid content (wt%)	52	33
Oil productivity (g/L.day)	5.3	0.13
Scale-up cost	Low	High

a. Li et al. *Appl. Microbiol. Biotechnol*. (2008) 81:629-636
b. Based on 0.53 g C/g dry cell mass

Conclusions

- Biopolyester PHB can be directly produced from CO_2, sunlight and water
- PHB is a bioplastic that can be processed like conventional thermoplastics
- PHB is also a platform material from which hydrocarbon oil, alkenes, aromatics and other small chemicals can be conveniently derived
- The overall solar energy efficiency of artificial photosynthesis is 4-5%
- The artificial system has technical and economic merits over microalgae system

Acknowledgement

- Students and post-doctors for laboratory work
- Office of Naval Research for financial support

Thank You !!!