Advanced School on the Present and Future of Bioenergy

Fermentations coupled to chemical catalysis to increase the product portfolio in the biorefinery

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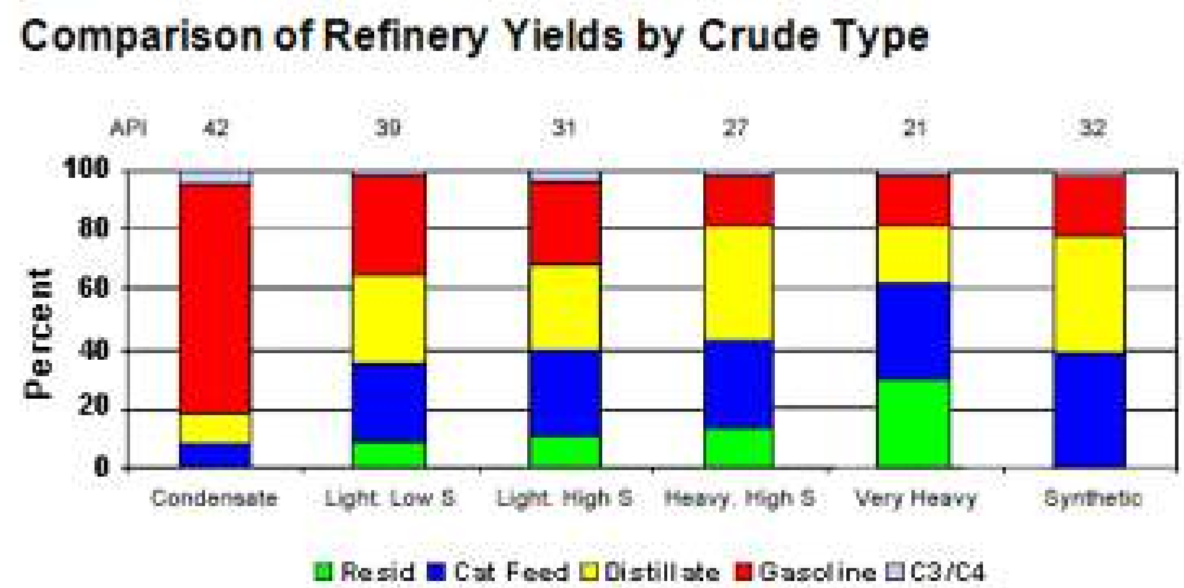
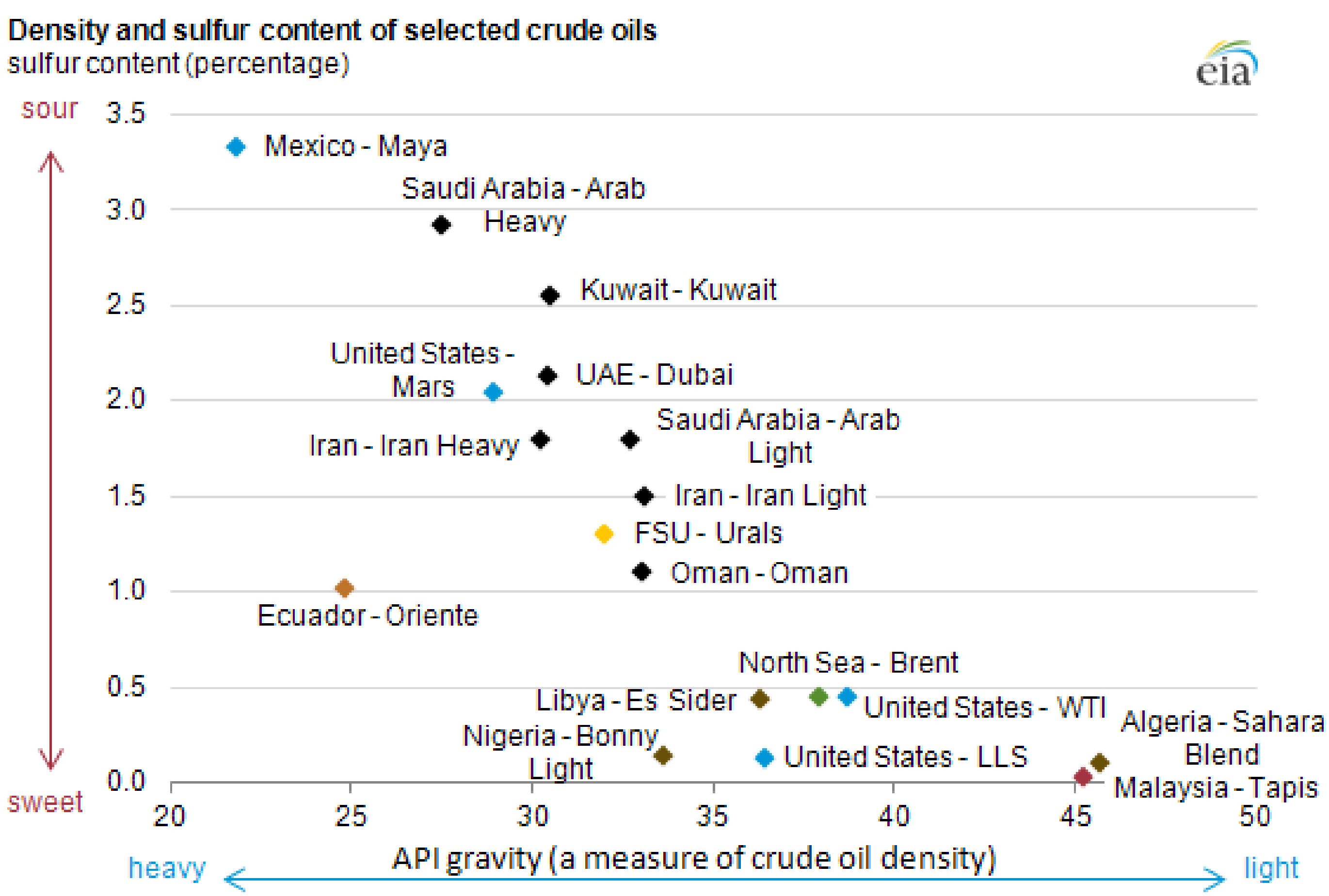
Energy Biosciences Institute

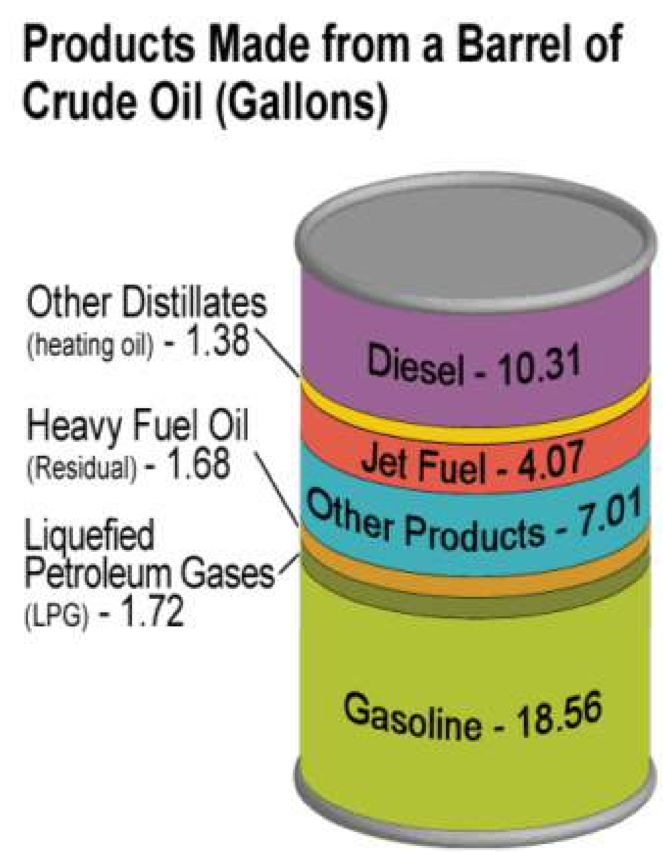
bp

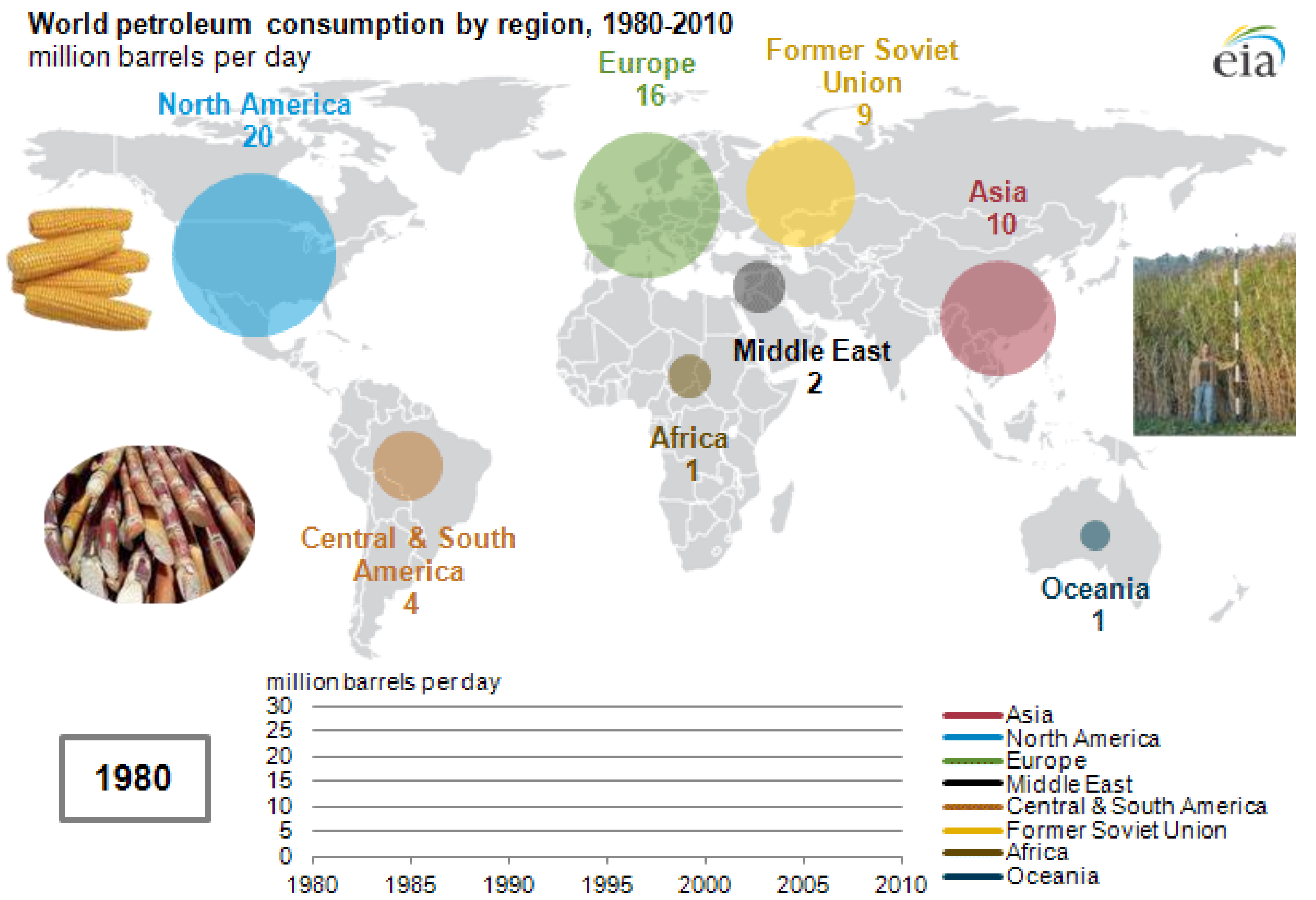
Versatility of a oil refinery

BP's Castellón oil refinery in Spain







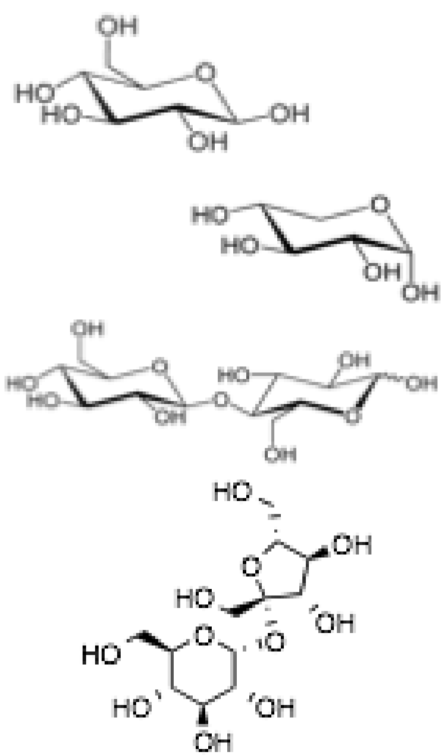


http://www.eia.gov/todayinenergy/detail.cfm?id=5130#

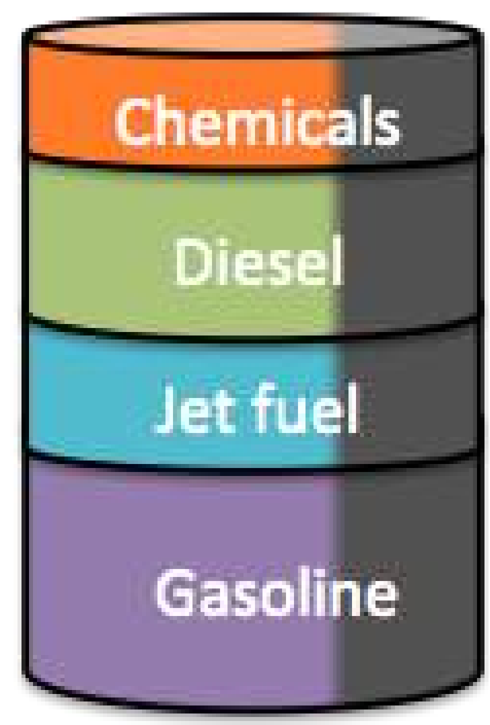
Overall goal of biofuel production

Use a variety of saccharides

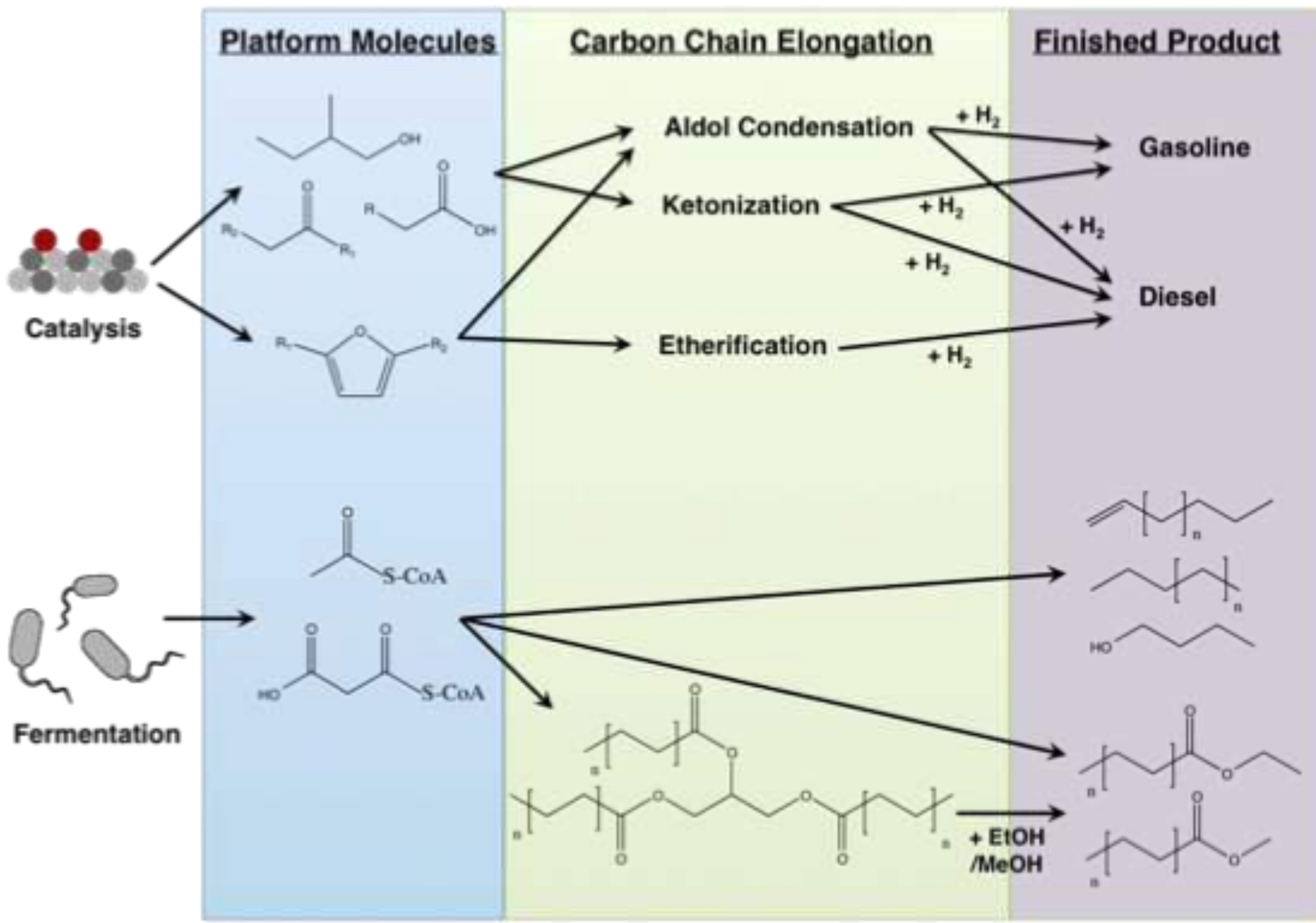
Produce a variety of drop-in products



*** Insert technology here**



Sugar-derived advanced biofuel technologies



Overall goal of biofuel production

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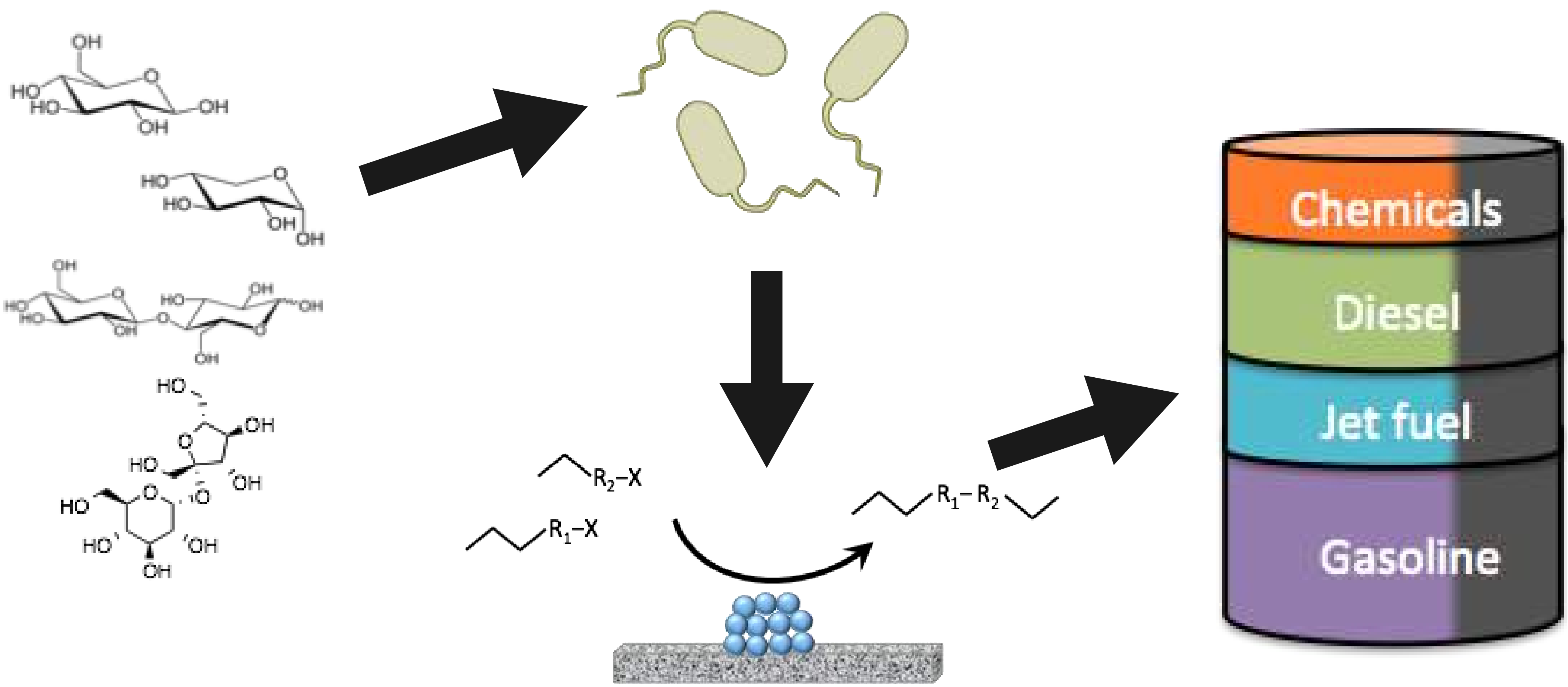
Produce a variety of drop-in products



ACS Catalysis
Review
pubs.acs.org/acscatalysis

Bridging the Chemical and Biological Catalysis Gap: Challenges and Outlooks for Producing Sustainable Chemicals

Thomas J. Schwartz,[†] Brandon J. O'Neill,[†] Brent H. Shanks,[‡] and James A. Dumesic*,[†]

[†]Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States
[‡]Department of Chemical and Biological Engineering, Biorenewables Research Laboratory, Iowa State University, Ames, Iowa, United States

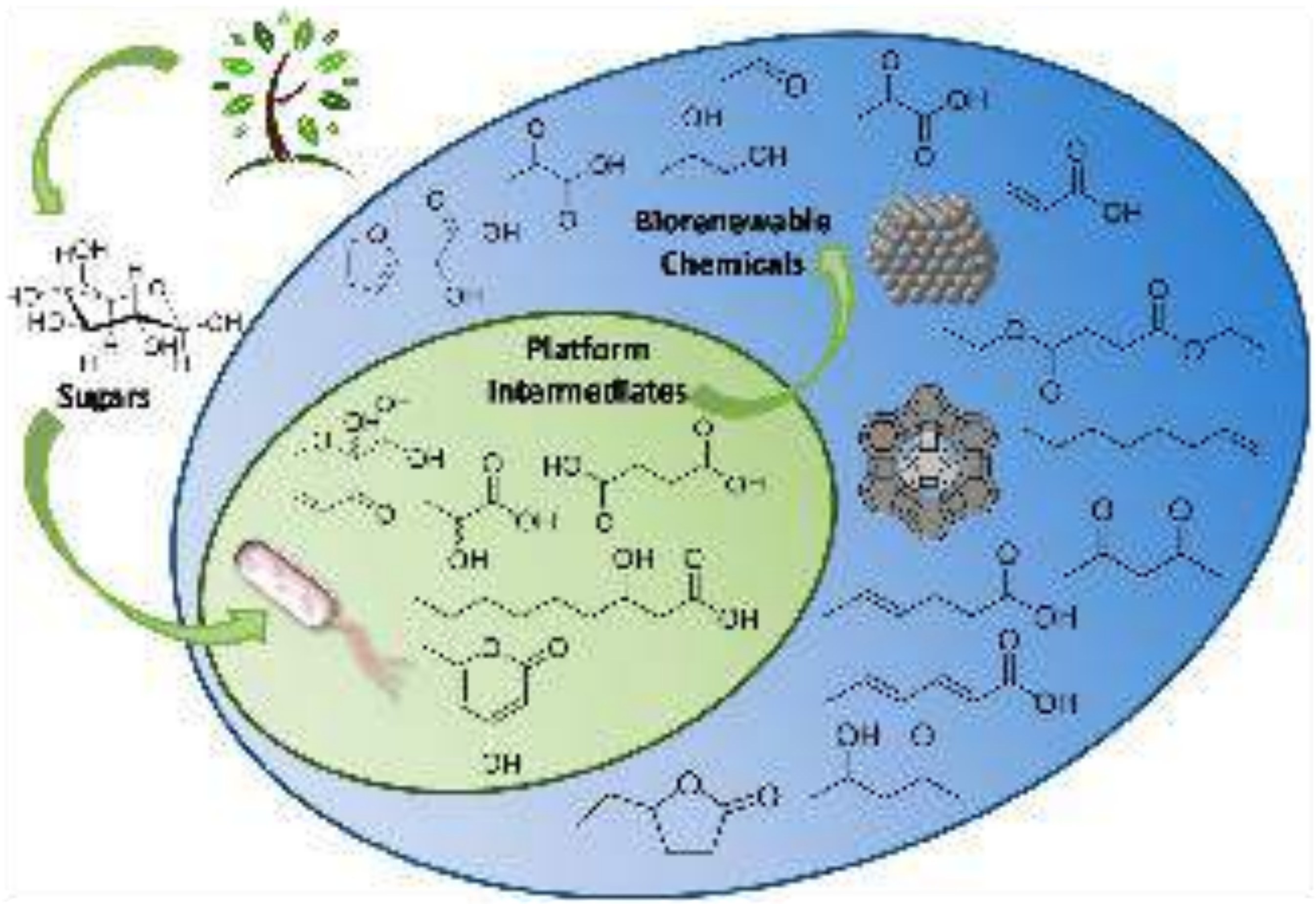
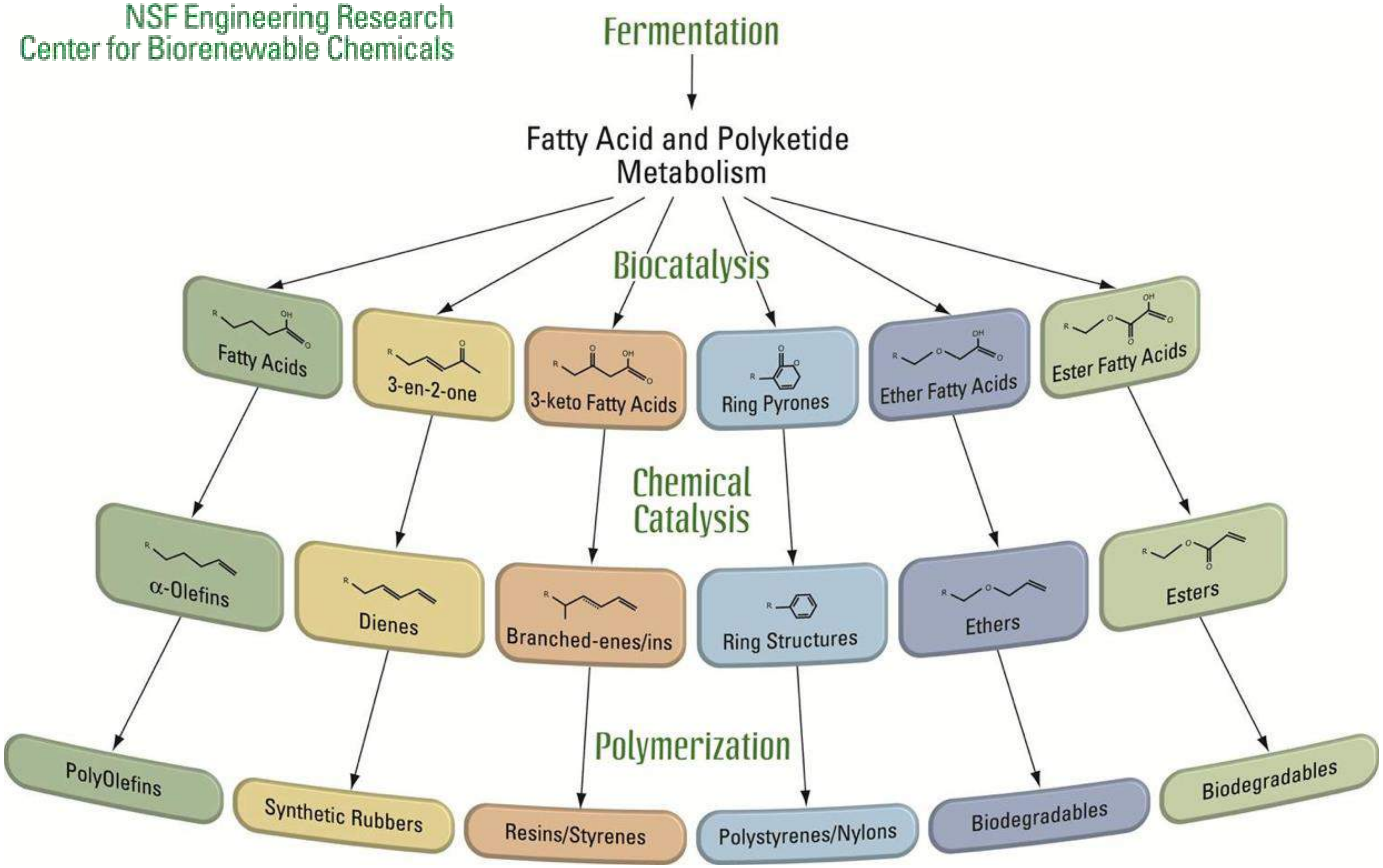


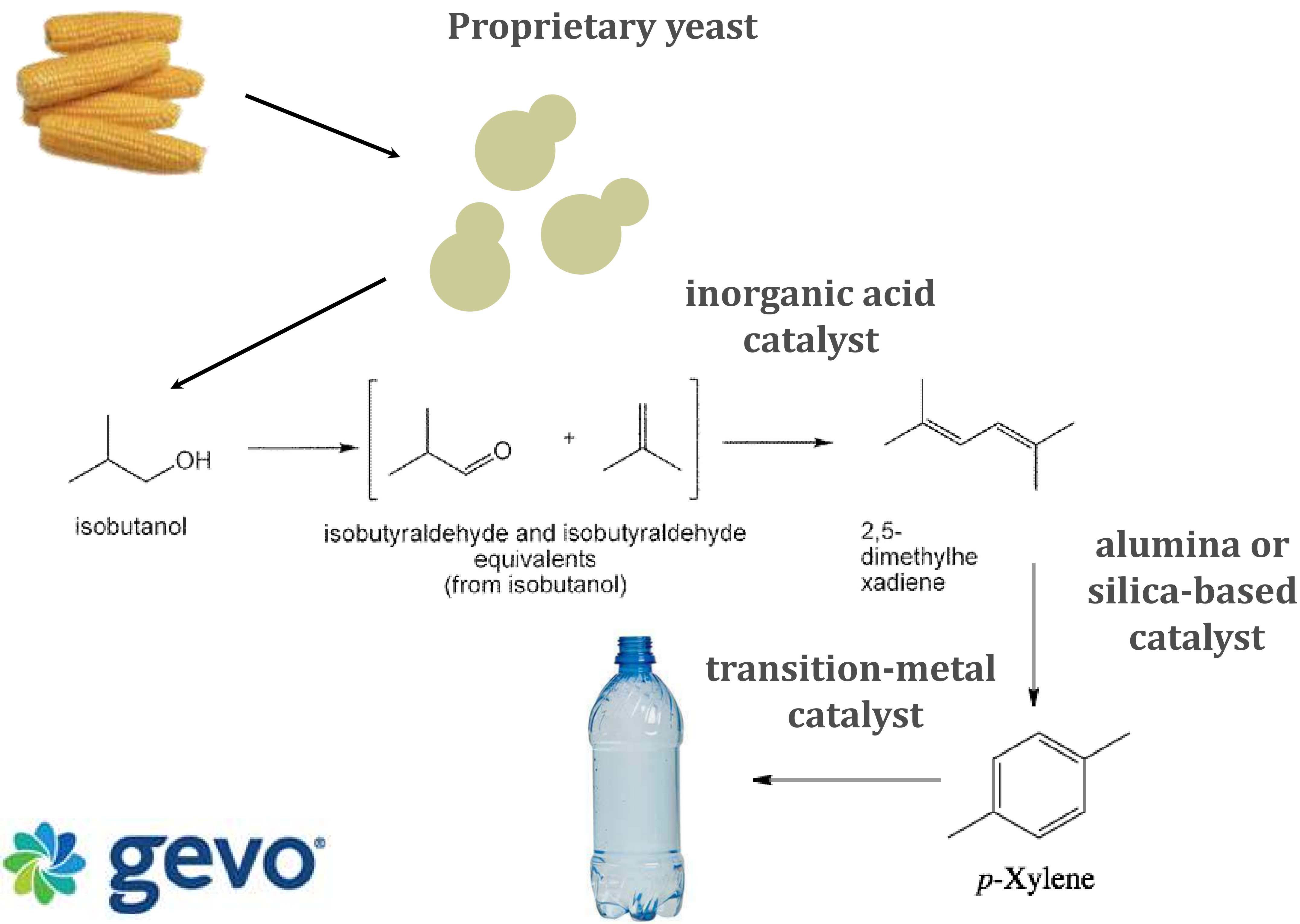
Figure 3. Overview of the coupling of chemical and biological catalysis for production of biorenewable chemicals.

Published: May 15, 2014

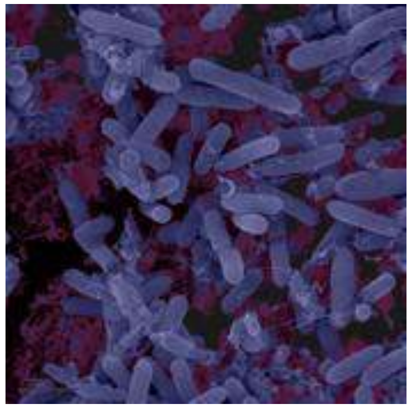


http://www.cbirc.iastate.edu/research/testbeds/

Gevo's integrated process for sugar to para-xylene



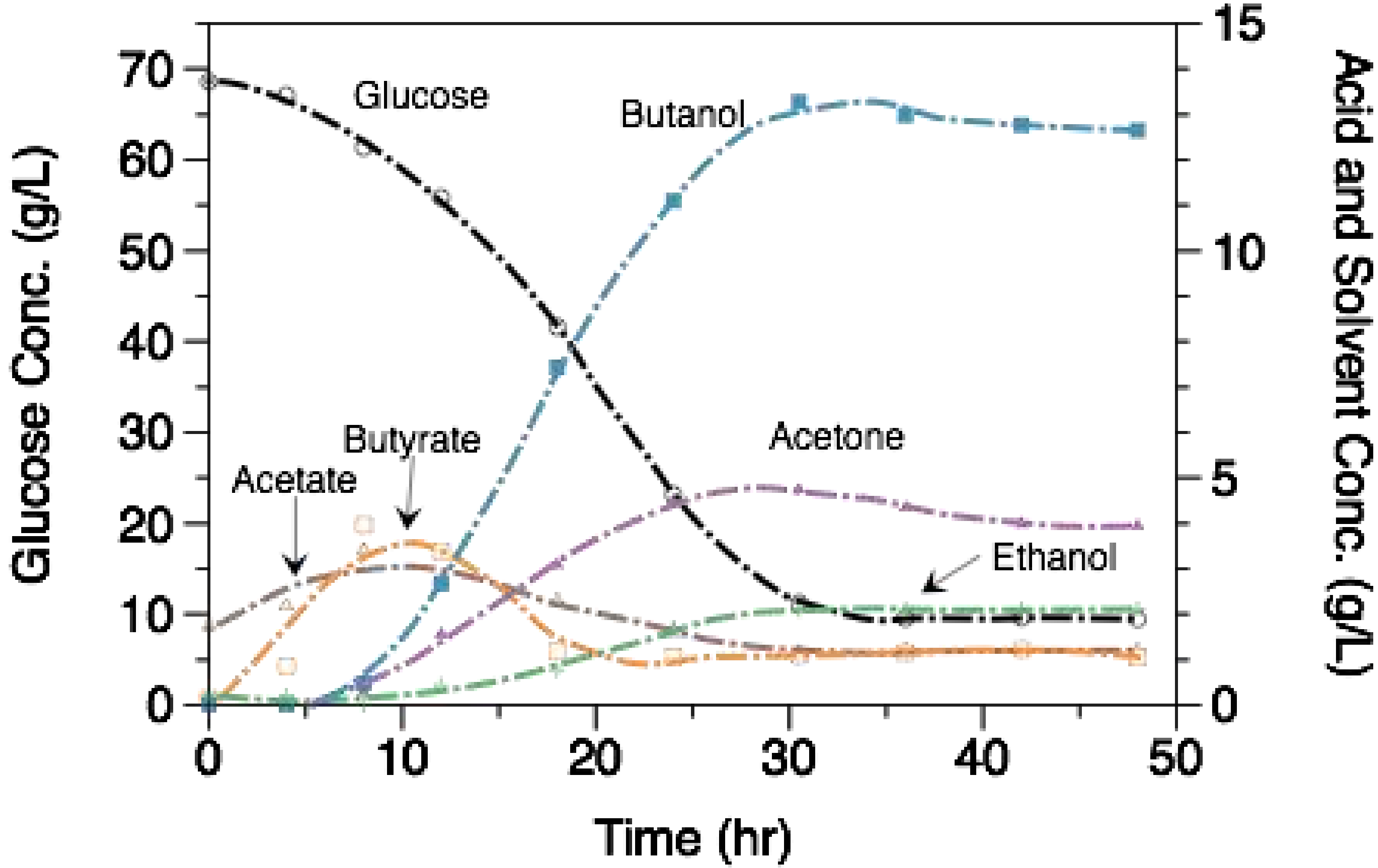
gevo



Clostridium acetobutylicum

Acidogenic phase

Solventogeni c phase



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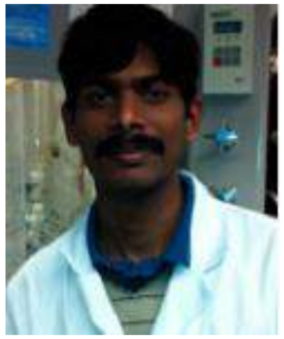
www.hallowellco.com

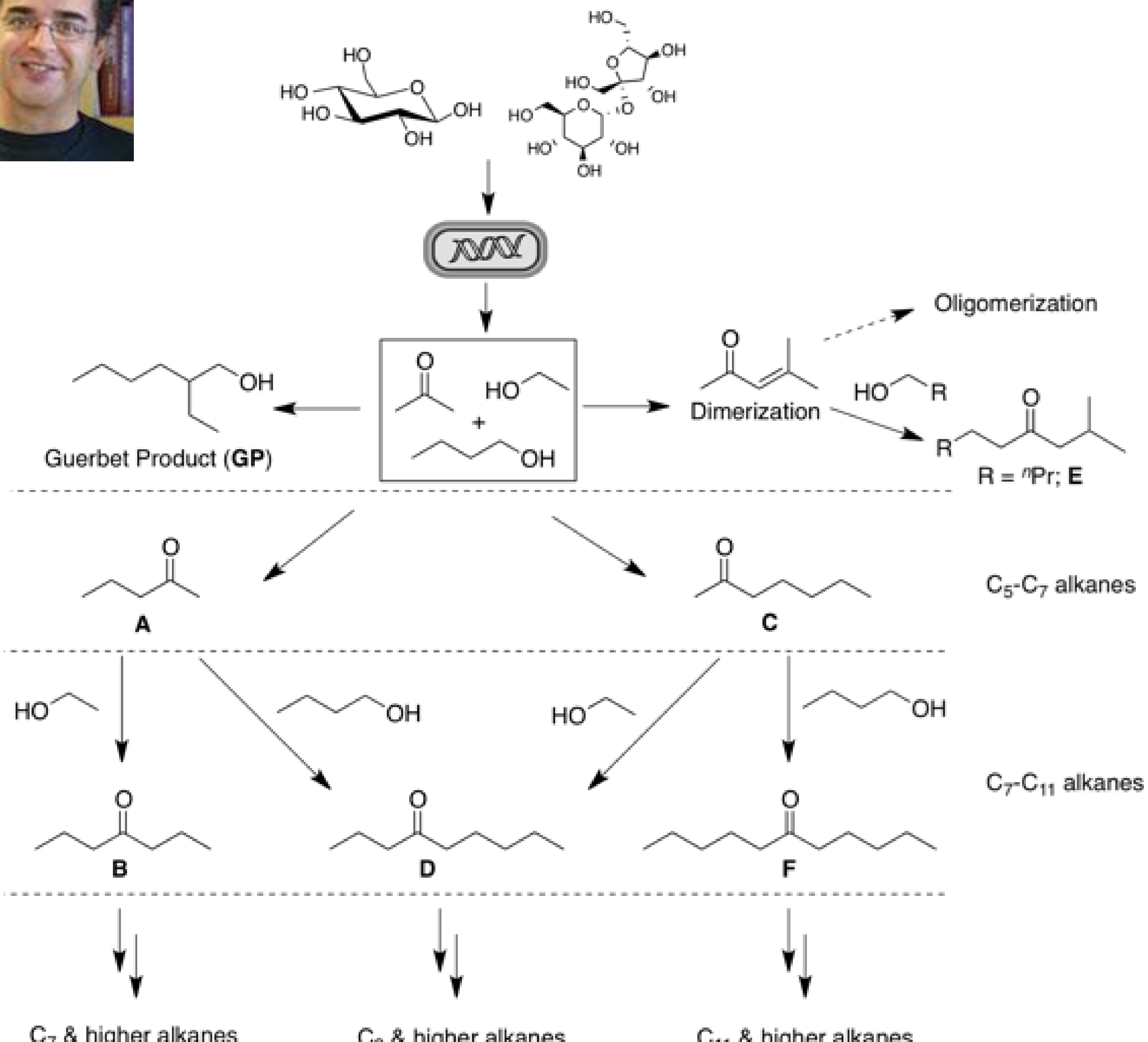
Integrated Process Design 1.0: ABE to Ketones



Gasoline

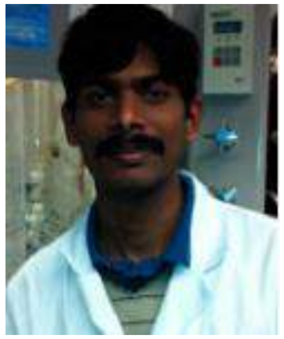
Jet

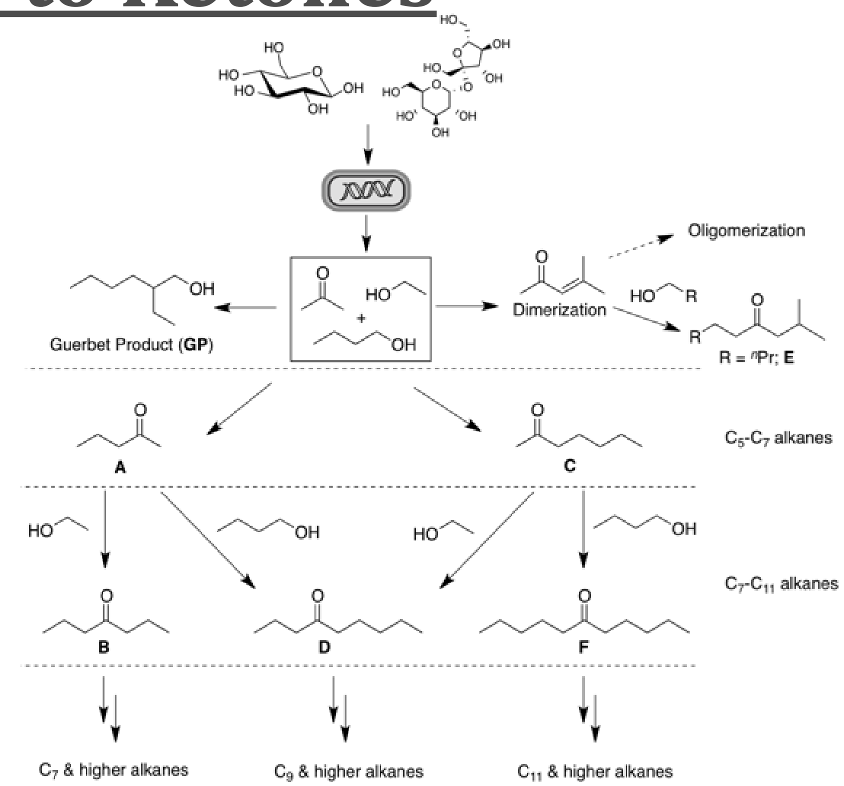
Diesel

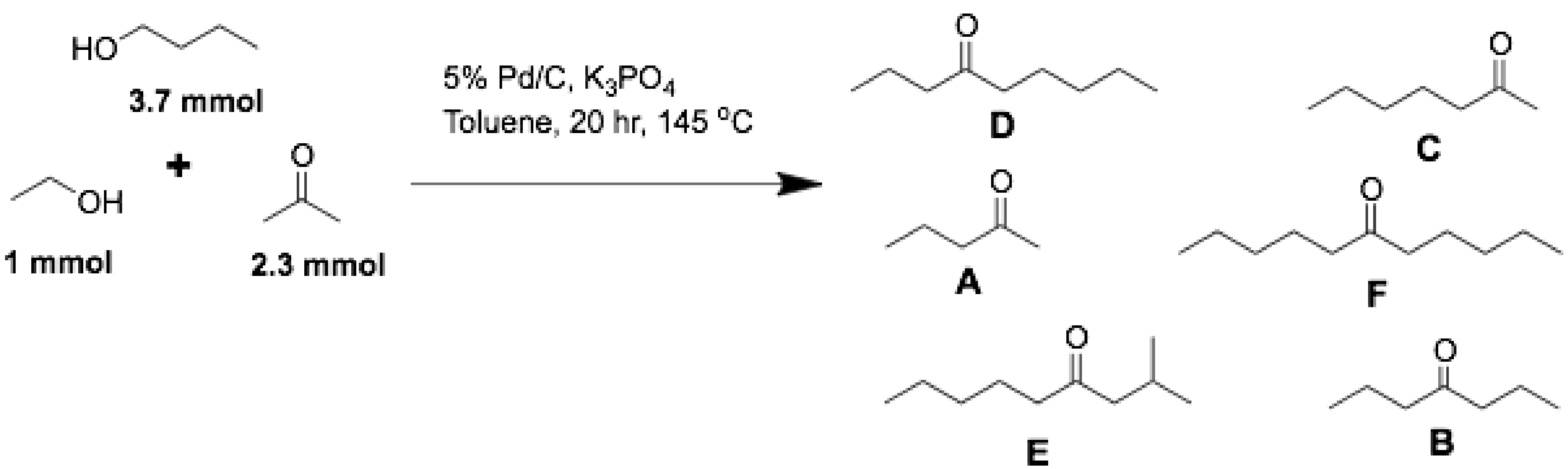


Nature, 2012 (**491**)

Integrated Process Design 1.0: ABE to Ketones







Nature, 2012 (**491)**

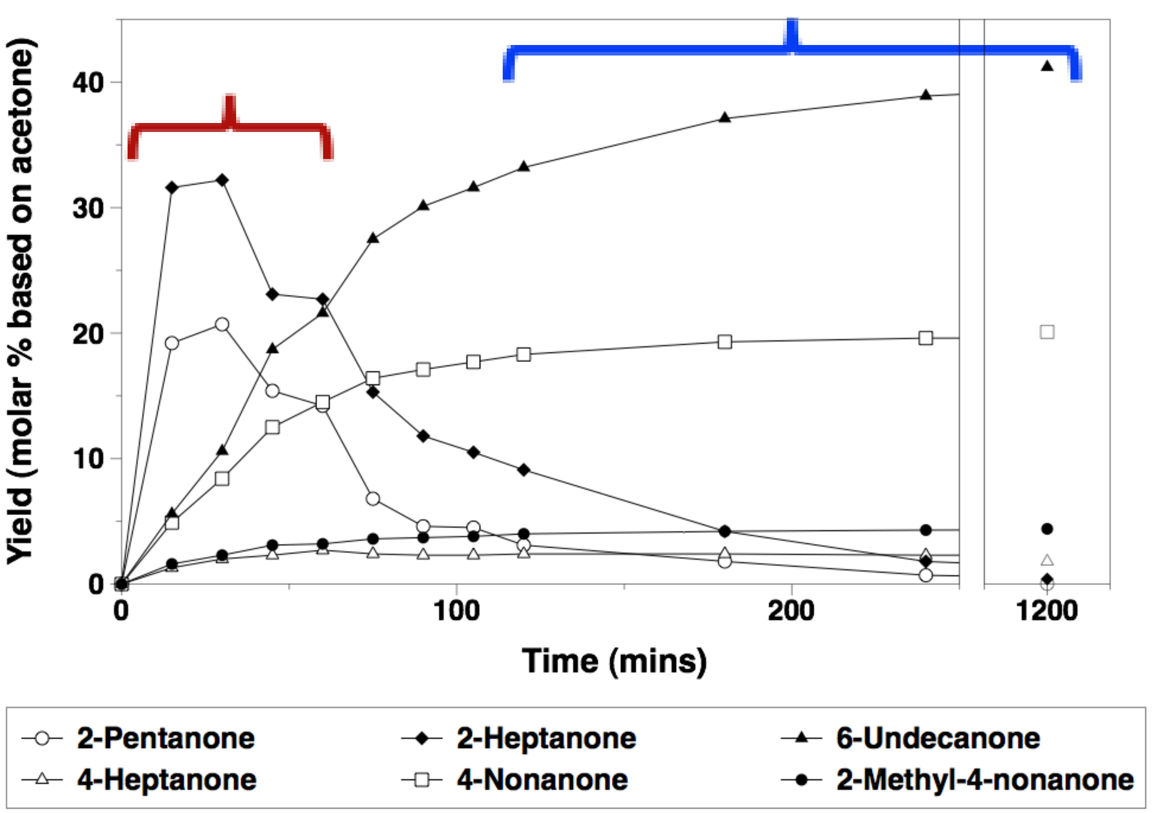
Tuning the reaction for gasoline or jet/diesel products

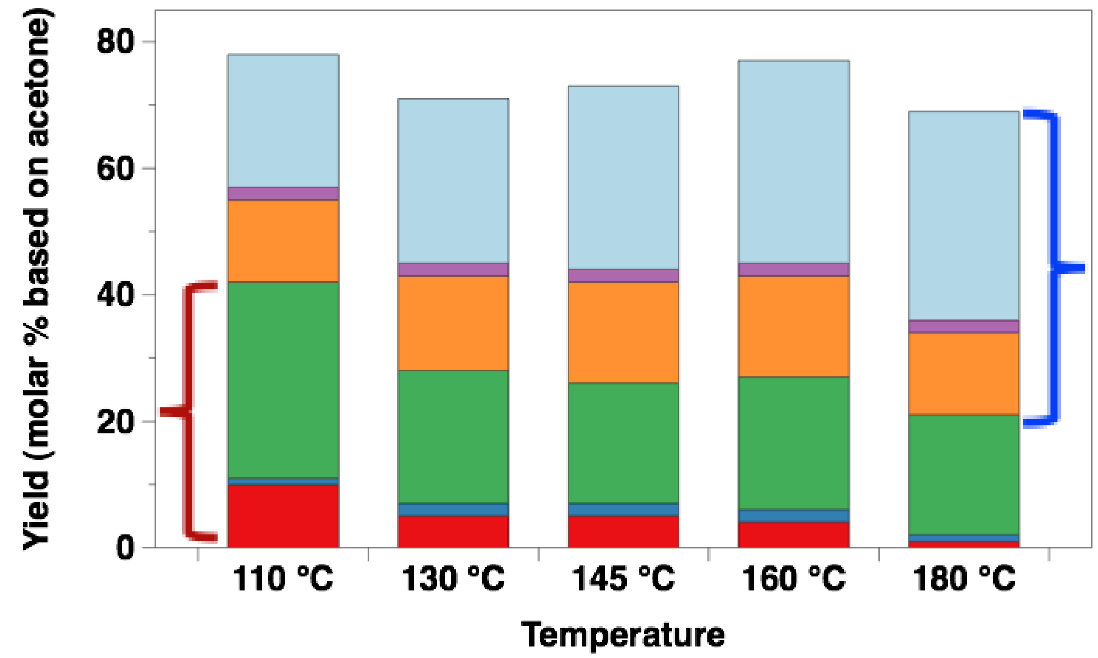
Reactor conditions for gasoline precursors:

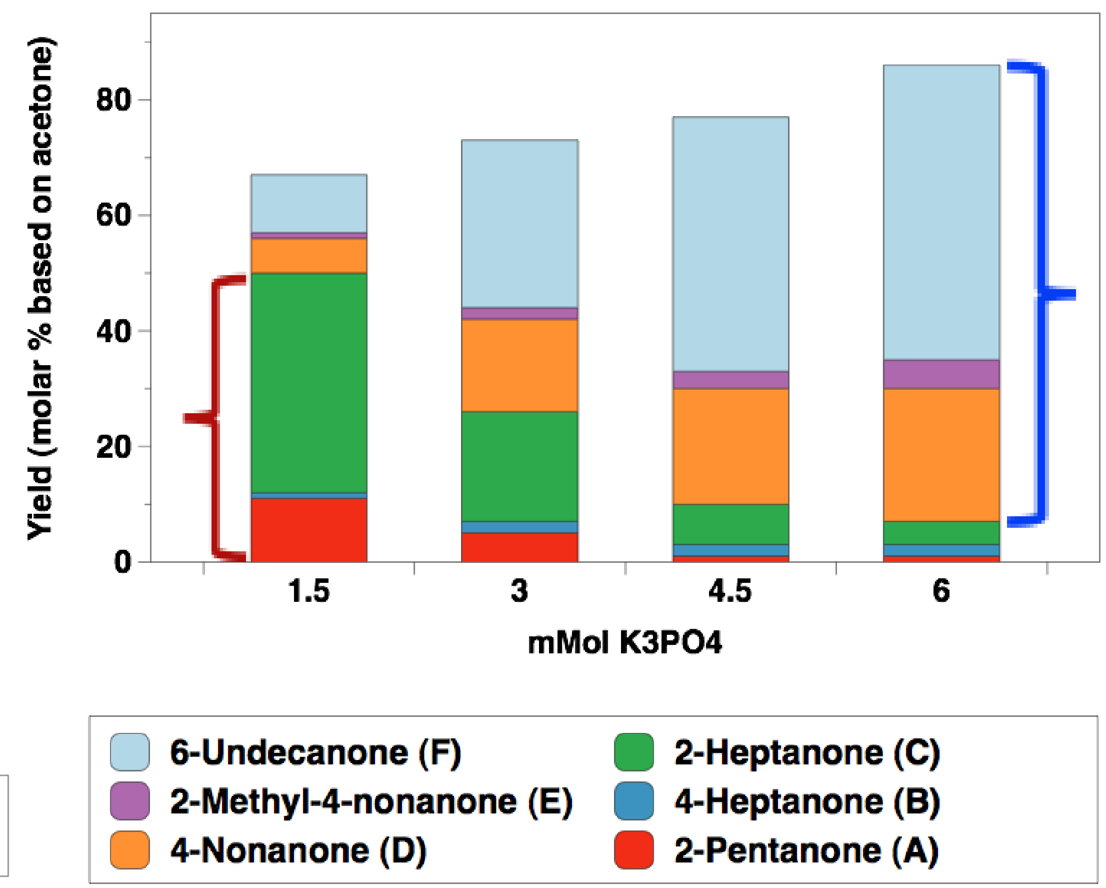
- ⇓ temperature
- ⇓ base loading
- ⇓ retention time

Reactor conditions for jet/diesel precursors:

- ⇑ temperature
- ⇑ base loading
- ⇑ retention time

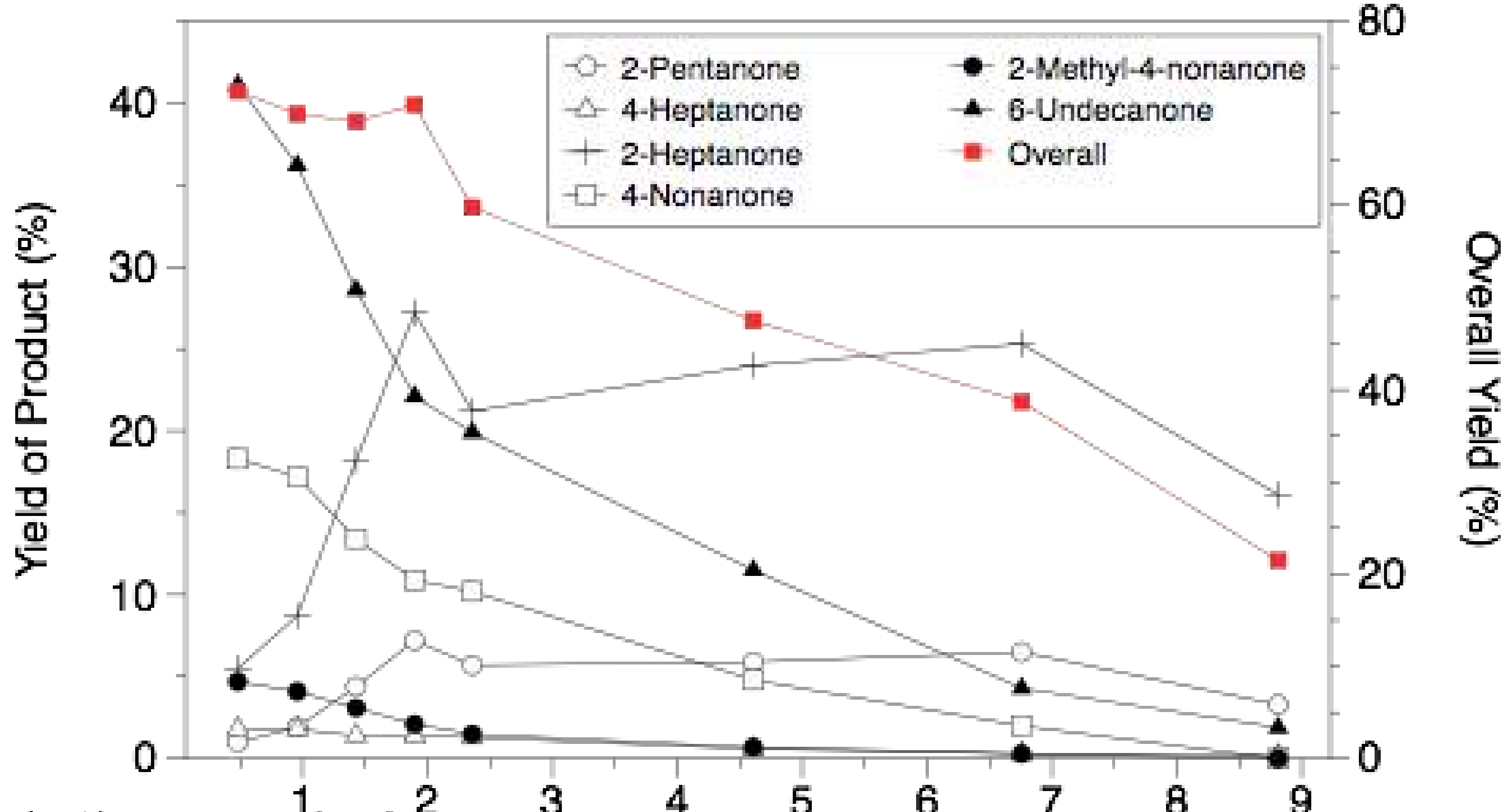






Pazhamalai Anbarasan et al., Nature, 2012 (**491**)

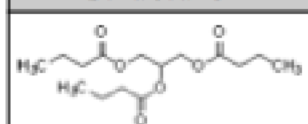
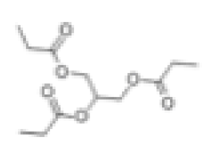
Integration of fermentation and catalysis



$$K_{D_i} = \frac{[\text{species } i \text{ in extractant phase}]}{[\text{species } i \text{ in aqeous phase}]}$$

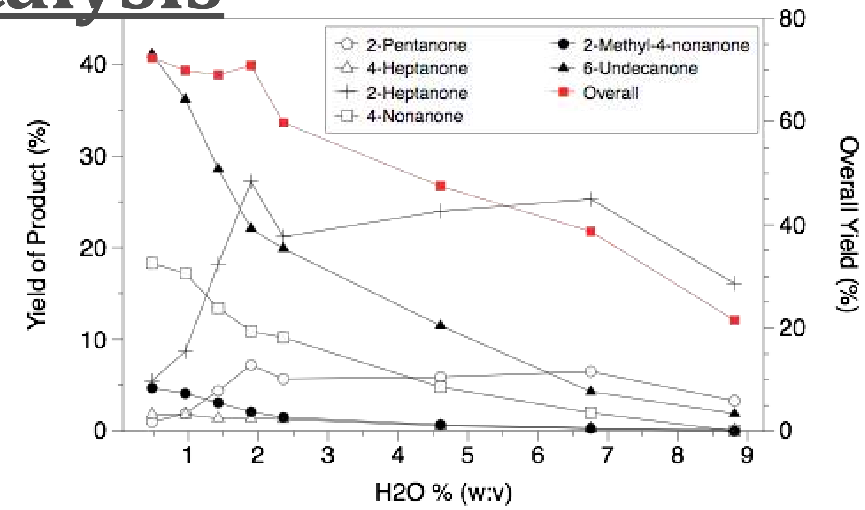
Extractant Properties:

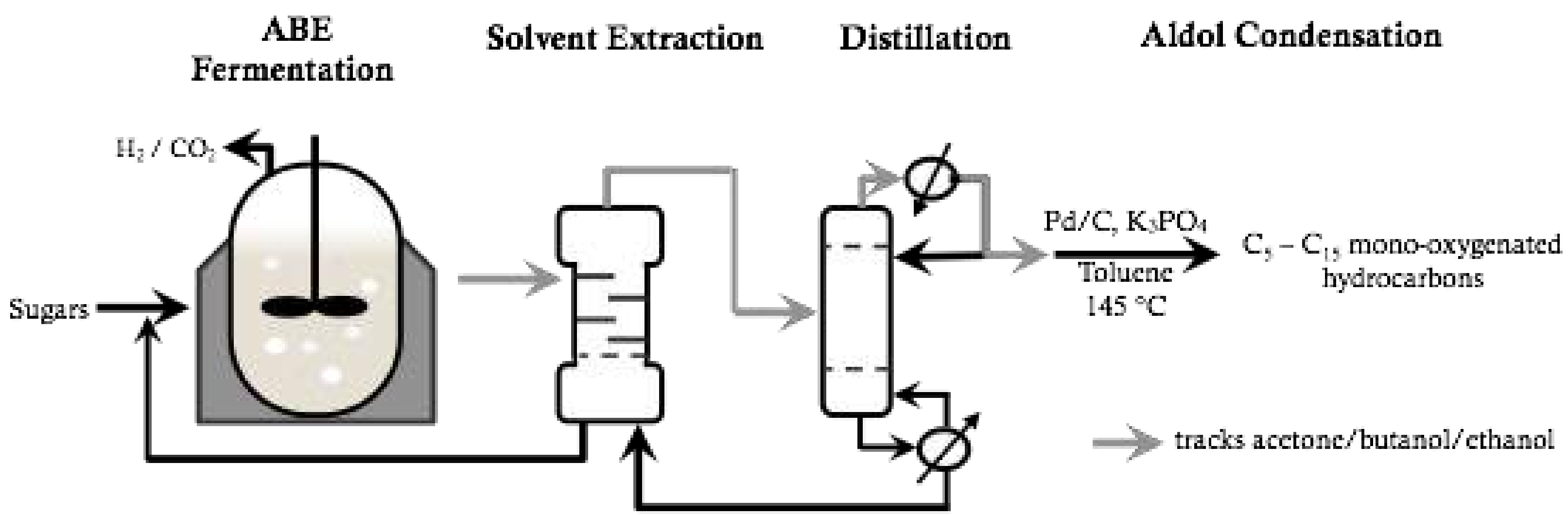
1. High K_D for acetone and 1-butanol
2. Non-toxic
3. Water immiscible
4. High boiling point

Extractant Structure	Name	Acetone K_D	Butanol K_D	Ethanol K_D
	Glyceryl Tributyrate	1.0 ± 0.04	2.6 ± 0.04	0.19 ± 0.02
	Glyceryl Tripropionate	1.1 ± 0.04	2.4 ± 0.05	0.25 ± 0.02
	Oleyl Alcohol	0.35*	3.6*	0.25*

(*) indicates values taken from literature

Integration of fermentation and catalysis





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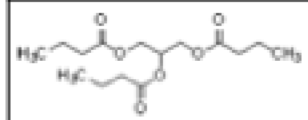
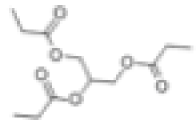
	Glyceryl Tributyrate	1.0 ± 0.04	2.6 ± 0.04	0.19 ± 0.02
	Glyceryl Tripropionate	1.1 ± 0.04	2.4 ± 0.05	0.25 ± 0.02
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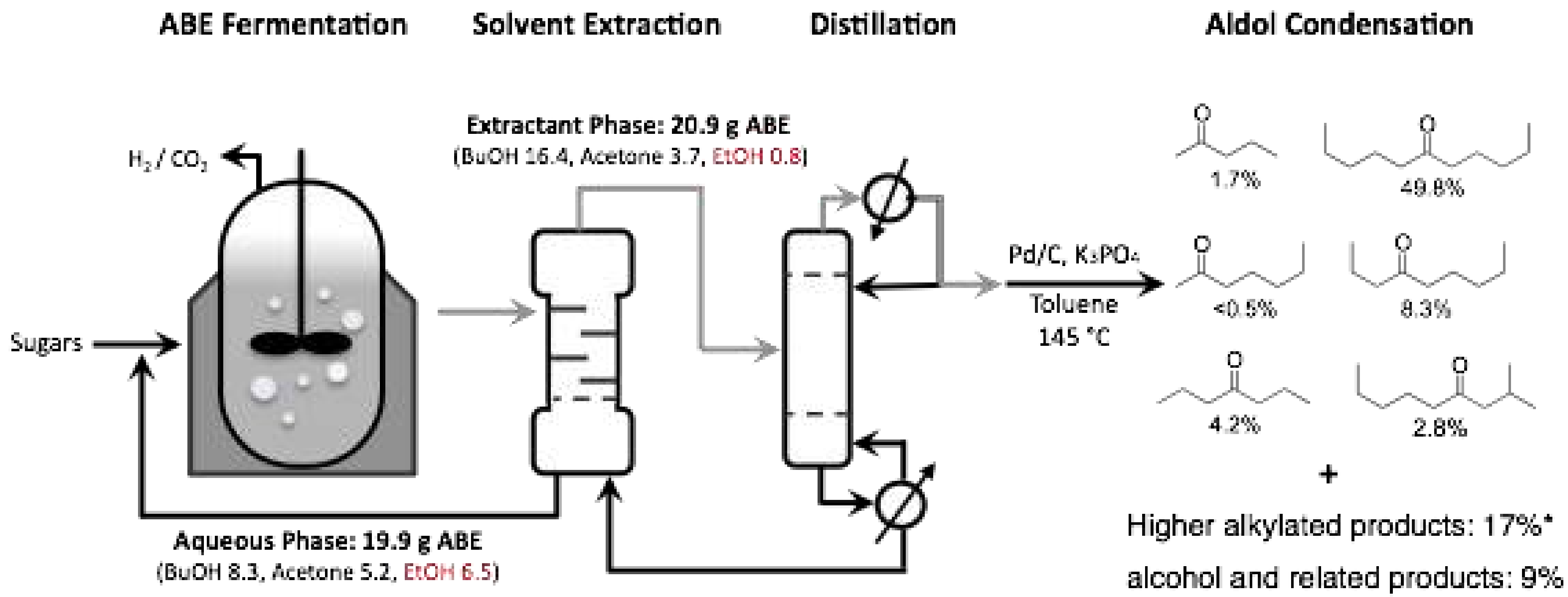
ABE to ketones process performance



105 g glucose
1.6 g acetate

40.8 g of ABE
(≈ 90% Theoretical)

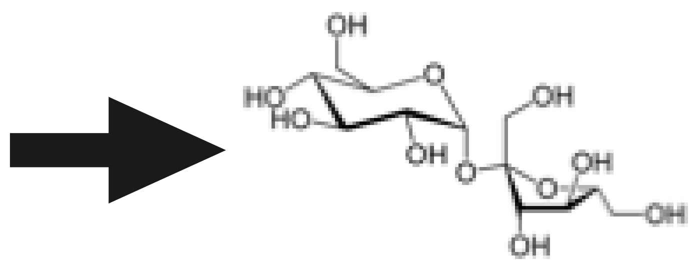
93% Molar Yield on Acetone
(97% Conversion)

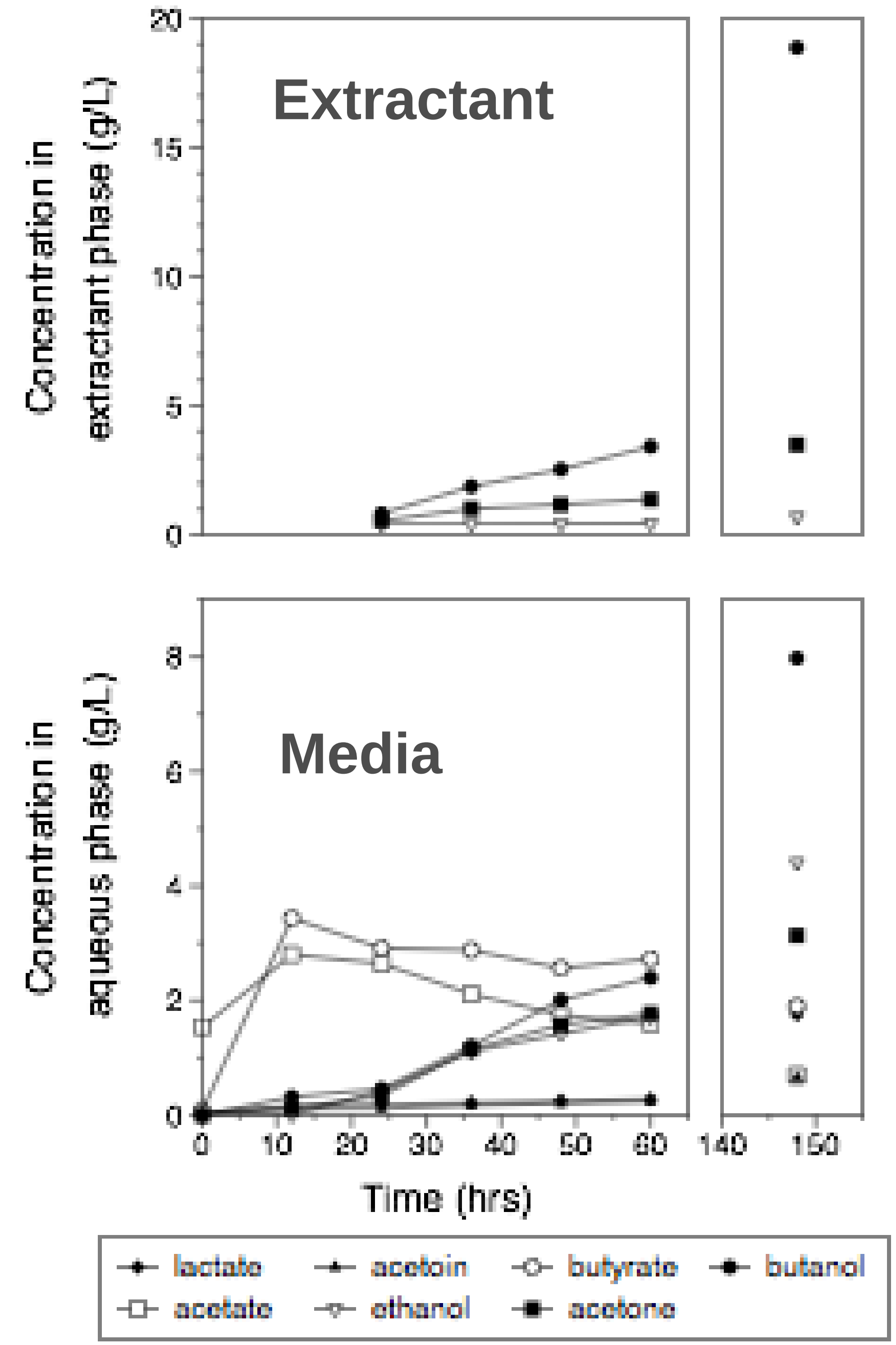
Alkylated Products C_7+	Reaction Mass (mg)	Total Mass[a] (g)
4-Heptanone	2.8	0.2
2-Heptanone	7.6	0.7
4-Nonanone	48.5	4.2
2-Methyl-4-nonanone	0.8	0.1
6-Undecanone	89.9	7.7
Higher MW products	22.2	1.9
Alcohols and other products	61.7	5.3
Overall	**233.5**	**20.0**

* Values determined using FID response factor, [a] Total Mass values based on fermentative production and recovery of 153.5 mmol Acetone, 333.8 mmol Butanol, and 158.7 mmol Ethanol

Nature, 2012 (**491**)

Extractive fermentation with sucrose



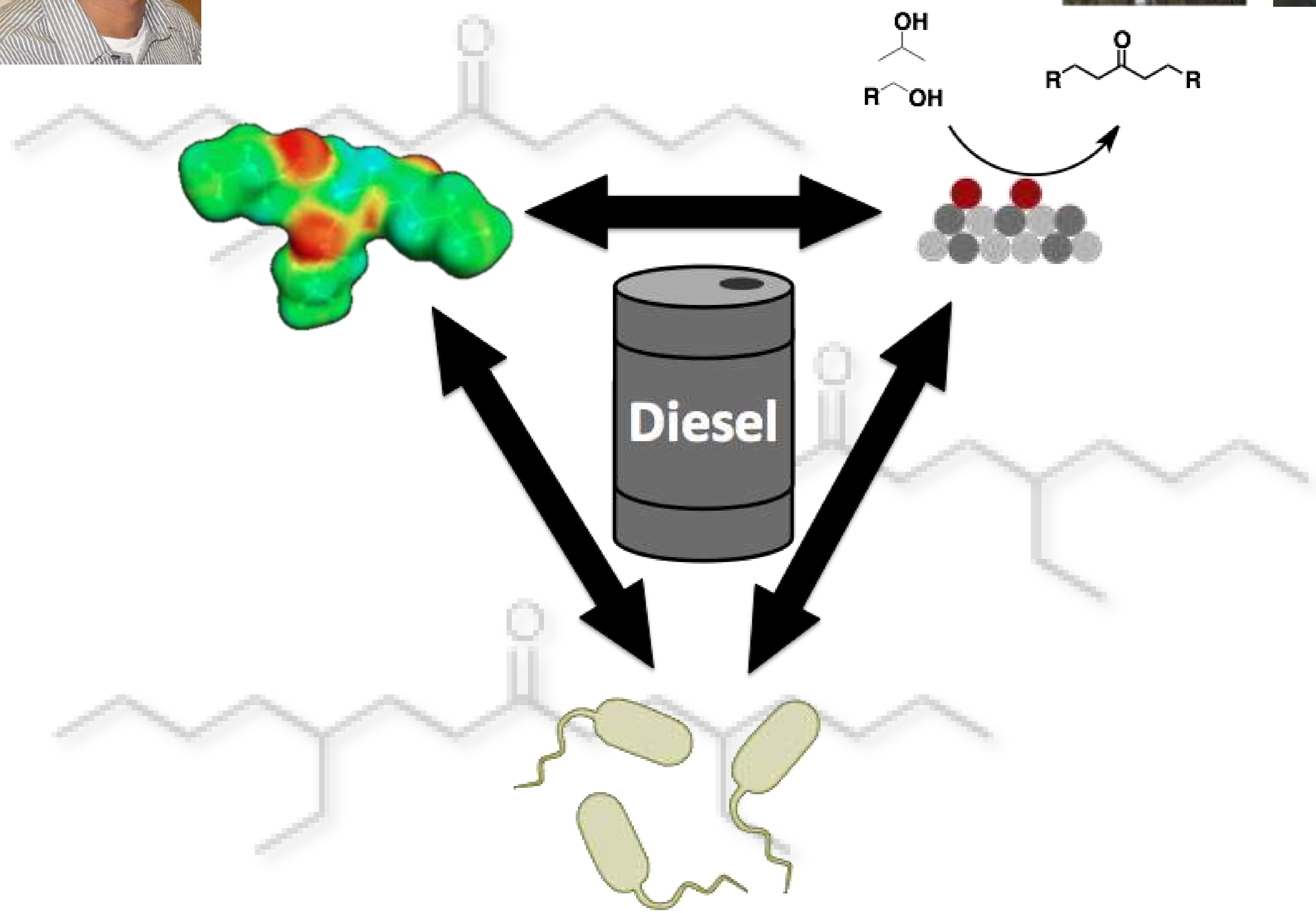


Fermentation Conditions:

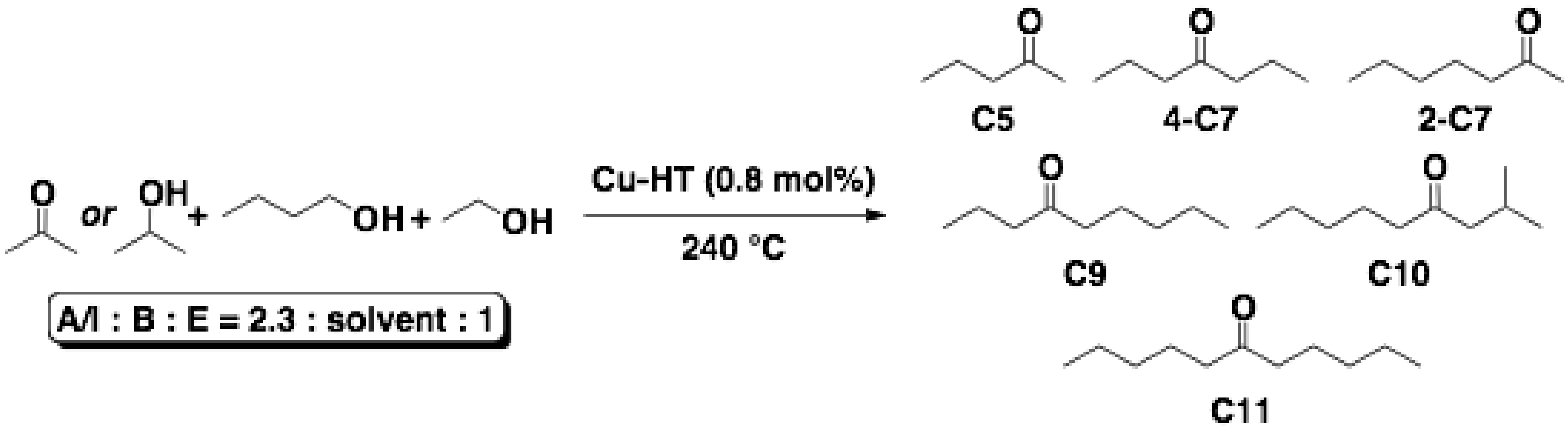
- Fed-batch (Initial sucrose conc. 60 g/L)
- 50 mL 1:1 volume ratio of media:tributyrin (shake flasks)
- pH controlled at ≥ 4.8 for first 12 hours
- concentrated media (500 g/L sucrose) added periodically
- tributyrin added once pH began to increase (~16 hrs)
- incubated in an anaerobic chamber

Nature, 2012 (**491)**

Integrated Process Design 2.0: Tailoring products and chemistry



Sanil Sreekumar et al. ChemSusChem 2014

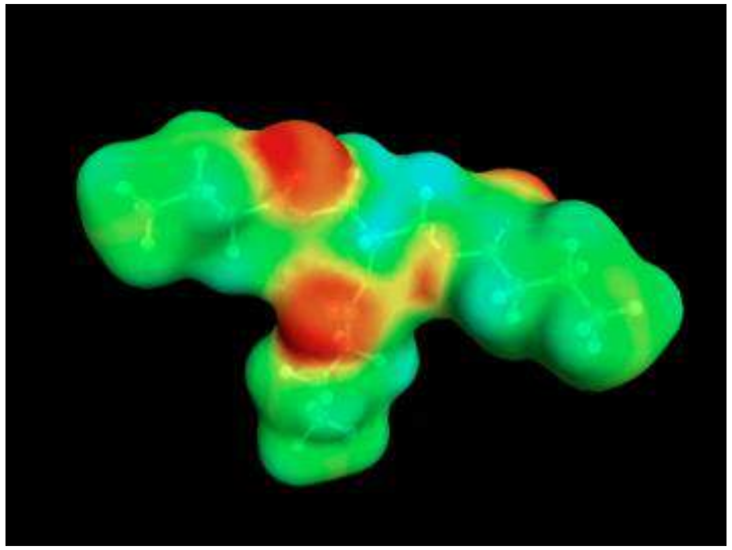


Entry	Reaction	C5 (%)	2-C7 (%)	4-C7 (%)	C9 (%)	C10 (%)	C11 (%)	Alcohols (%)	Yield (%)	C11+[a] (wt%)
1	ABE	1.9	1.0	23.5	4.2	0.4	35.5	9.1	73	14
2	IBE	1.0	1.9	24.0	1.9	0	21.8	11.1	61	25

[a] C11+ include mainly C13 and C15.

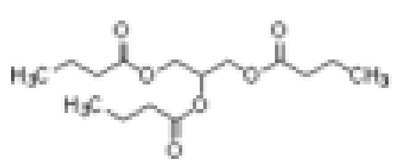
Sanil Sreekumar et al. ChemSusChem 2014

Investigating LLE w/ Quantum Chemistry



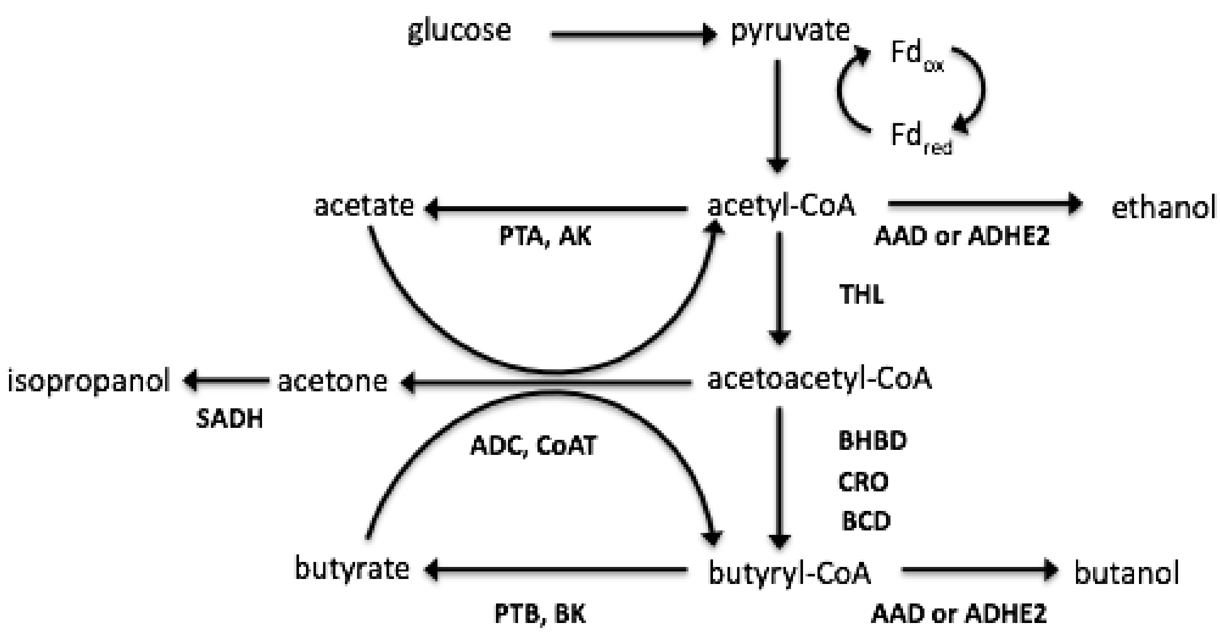
Solute	γ_∞ in Oleyl	γ_∞ in Tributyrin
Acetone	1.14	0.71
Isopropanol	1.48	2.71
Ethanol	1.18	3.61

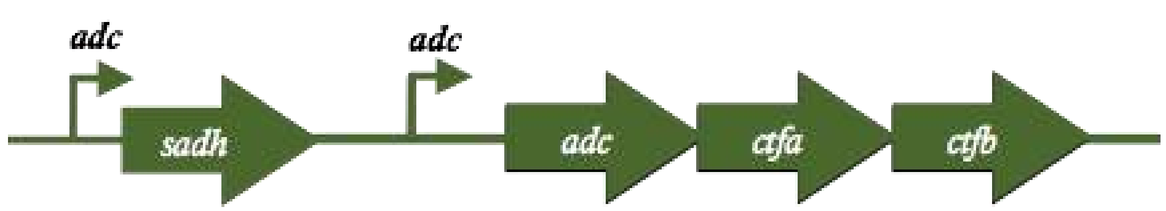
Using COSMO-RS we were able to predict LLE behavior by measuring γ_∞ (values closer to 0 = more ideal mixing)

Extractant Structure	Name	IPA K_D	Butanol K_D	Ethanol K_D
	Glyceryl Tributyrate	0.3	2.6	0.19
	Oleyl Alcohol	0.8	3.5	0.25

Sanil Sreekumar et al. ChemSusChem 2014

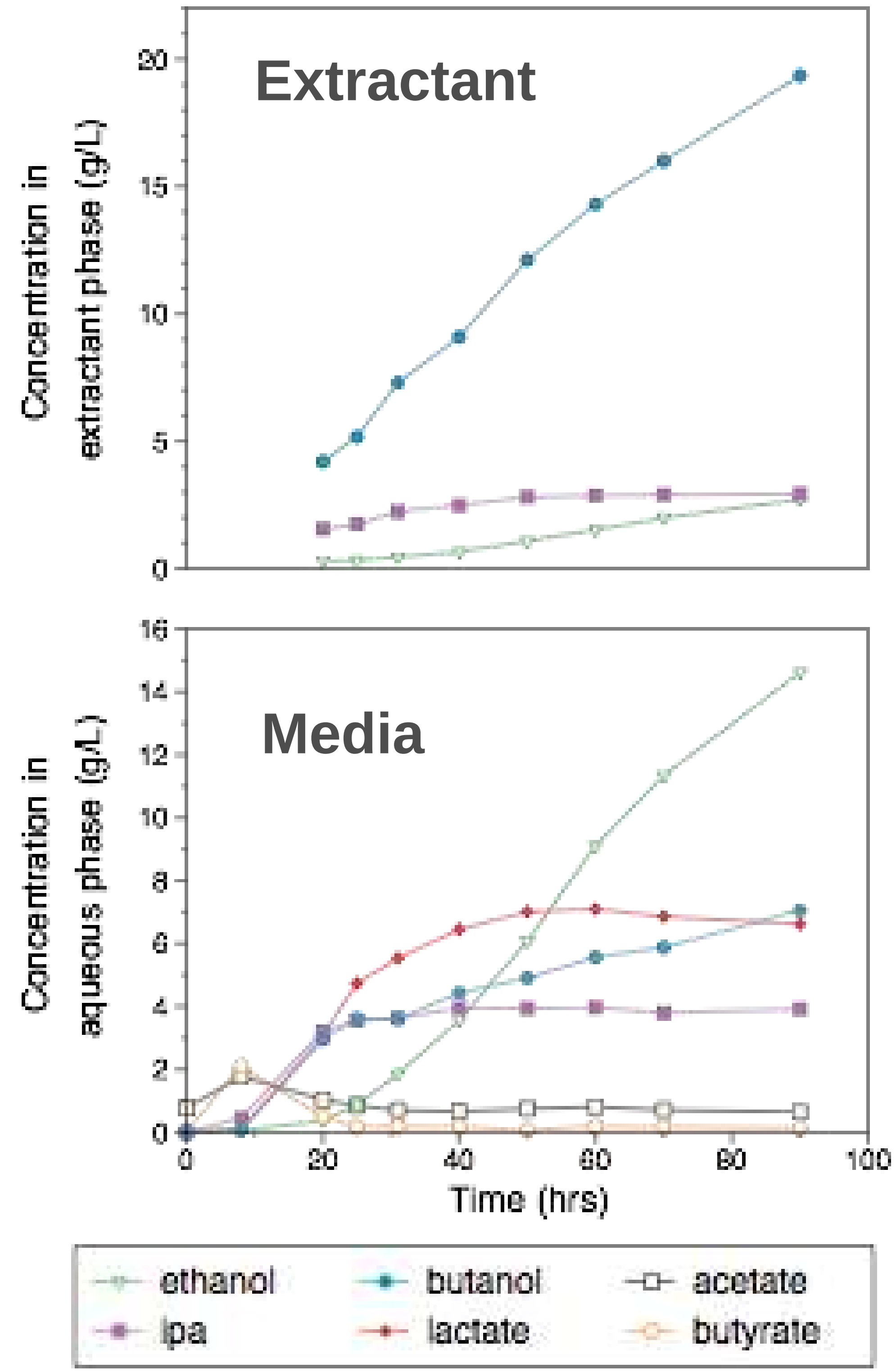
Engineering Clostridia to produce IBE:





- 117 g of glucose consumed
- 39.6 g IBE produced (5.6 g IPA, 17.9 g Butanol, 16.1 g Ethanol)
- IBE yield 0.34 g/g$_{gluc}$ or 78% theoretical

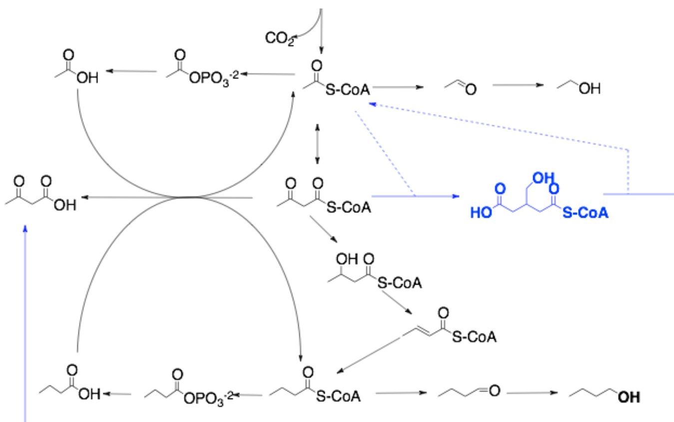
Lee et al. Appl. Environ. Microbiol. **March 2012** vol. 78 no. 5 **1416-1423**

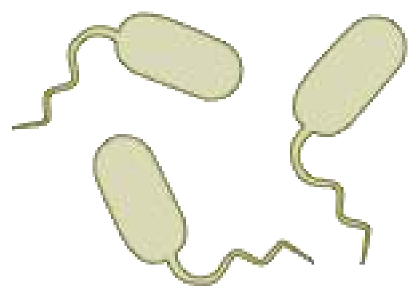


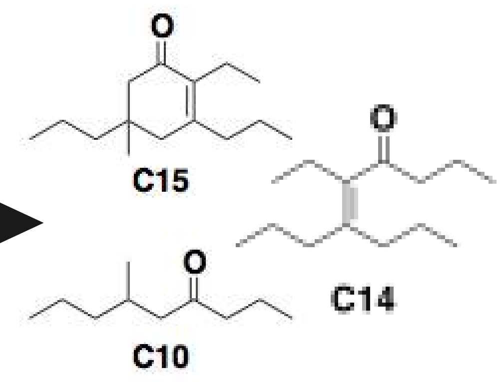
Sanil Sreekumar et al. ChemSusChem 2014

Integrated Process Design 3.0 and beyond: product ratios

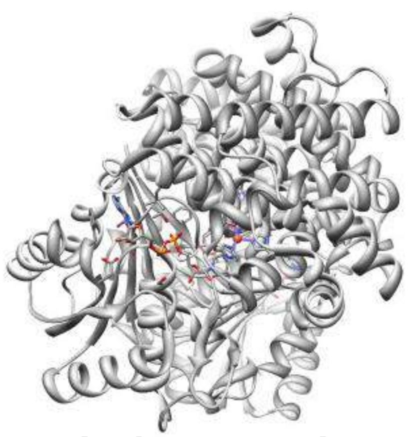
Metabolic Engineering

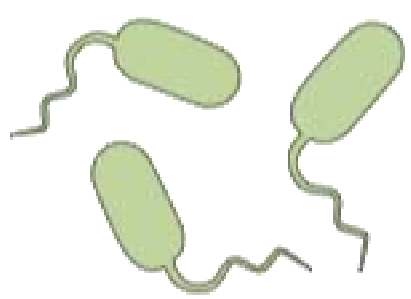


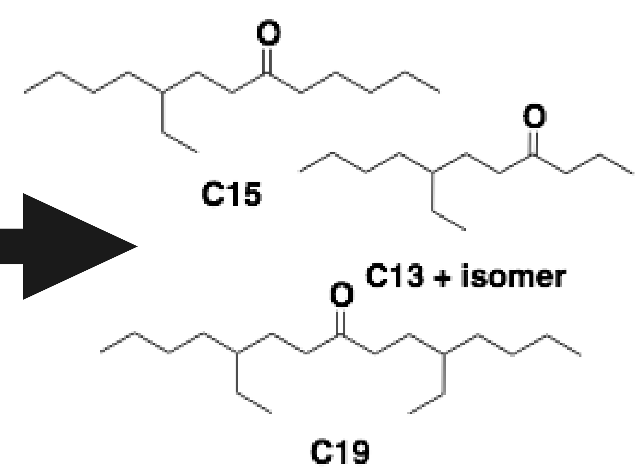




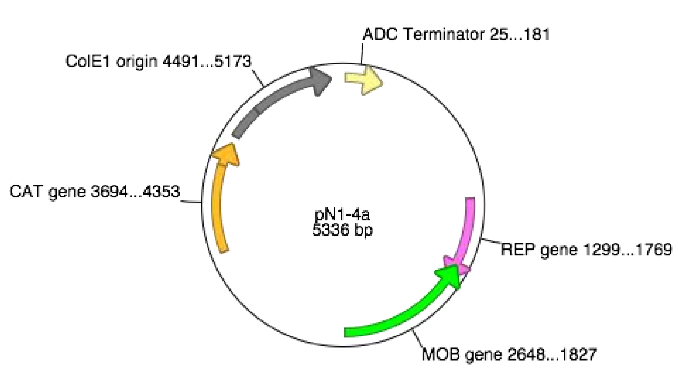
Protein Engineering

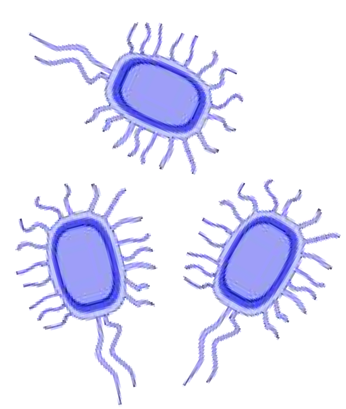


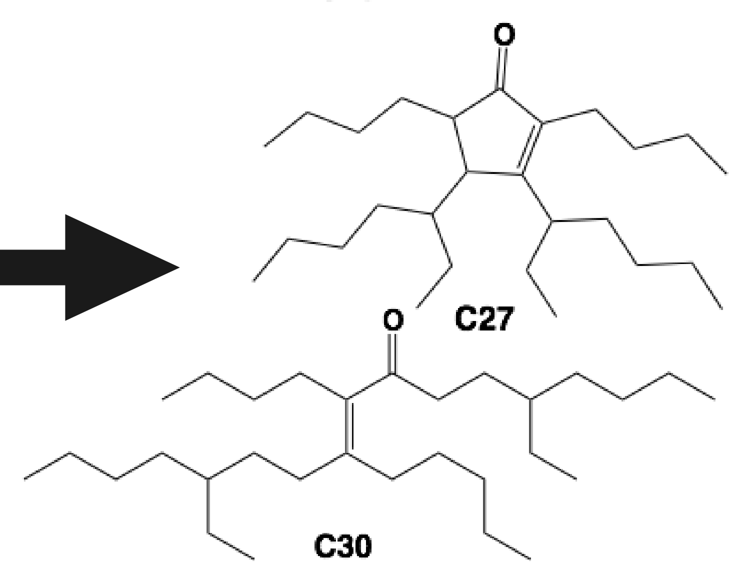




Chassis/Genetic Engineering



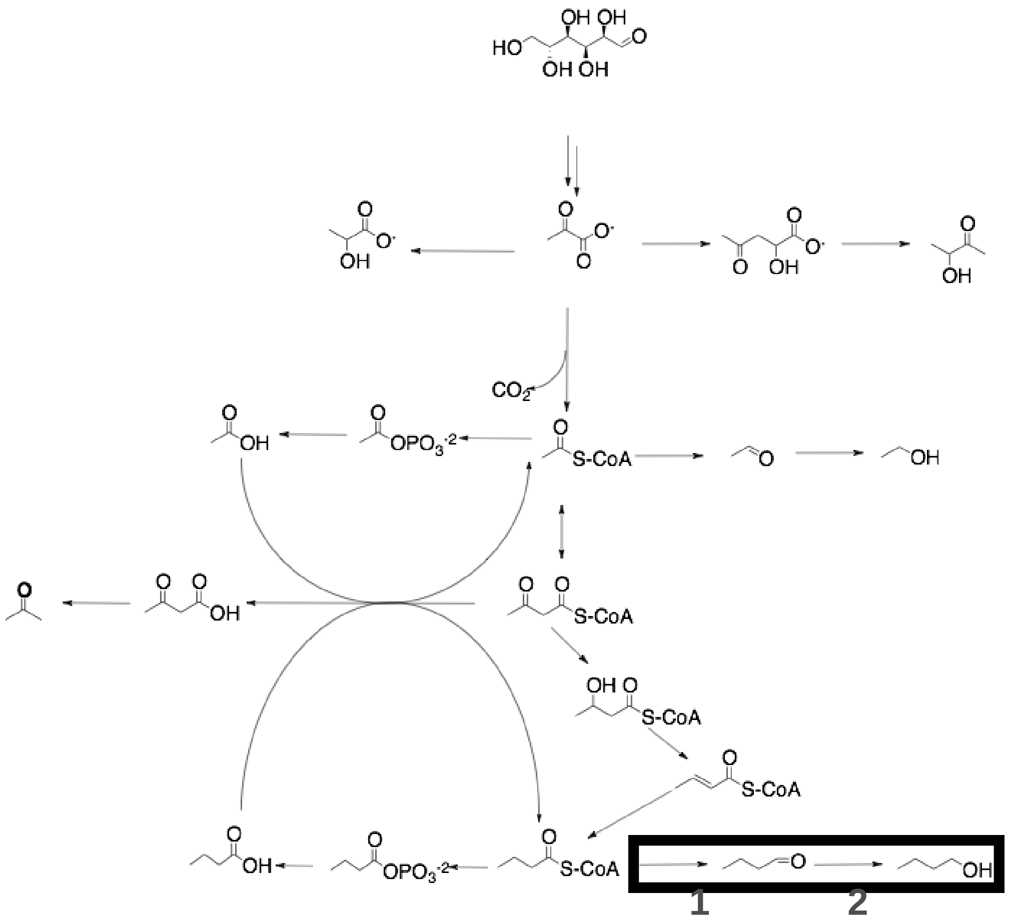


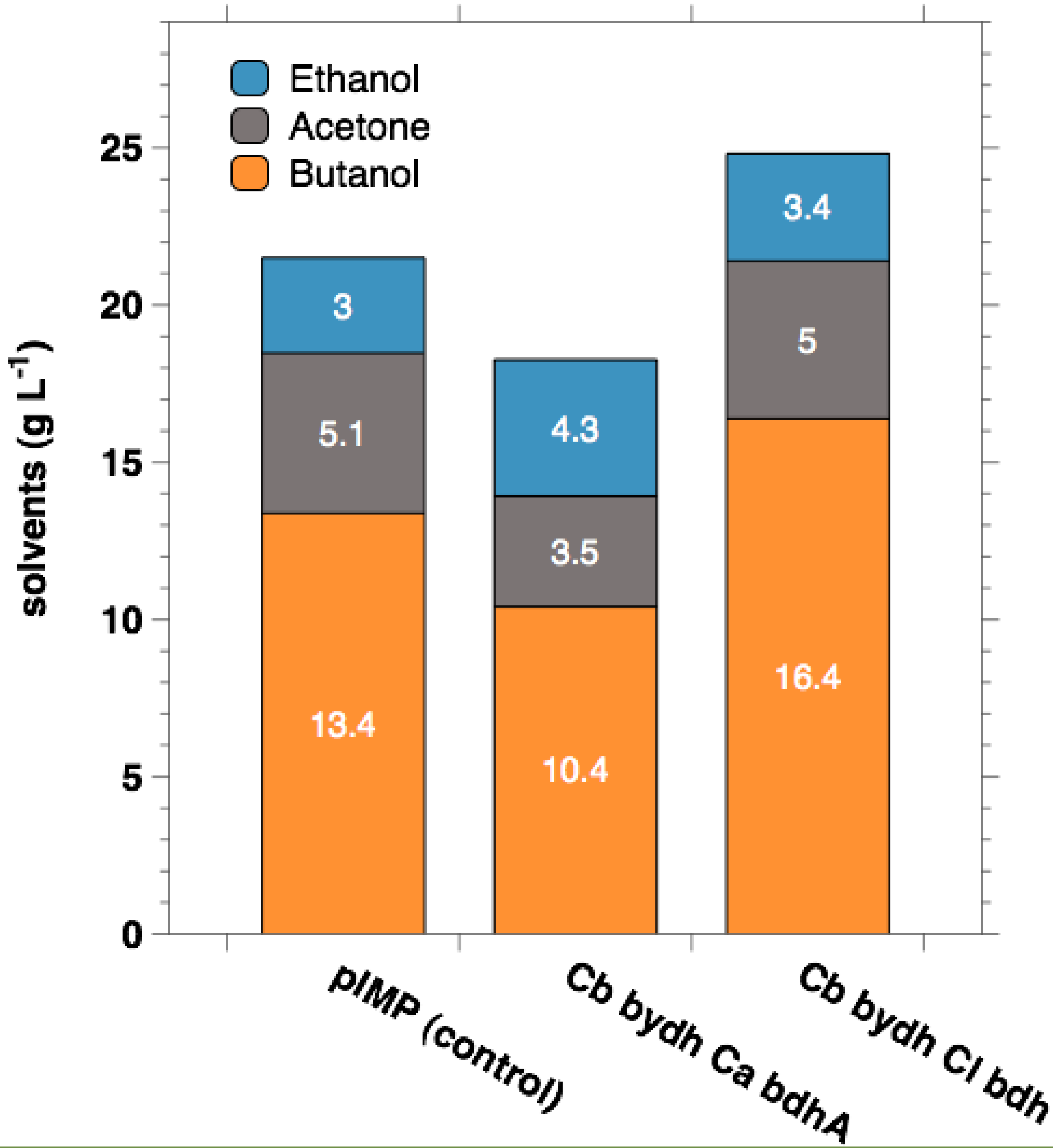


http://777boeing.com/boeing-787-dreamliner/ http://www.manufacturing.net/news/2014/03/walmart-testing-ultra-aerodynamic-semi-trailers http://www.mxindustrial.com/index.php?route=product/product&product_id=490

Metabolic engineering C. acetobutylicum for increased butanol production with heterologous enzymes

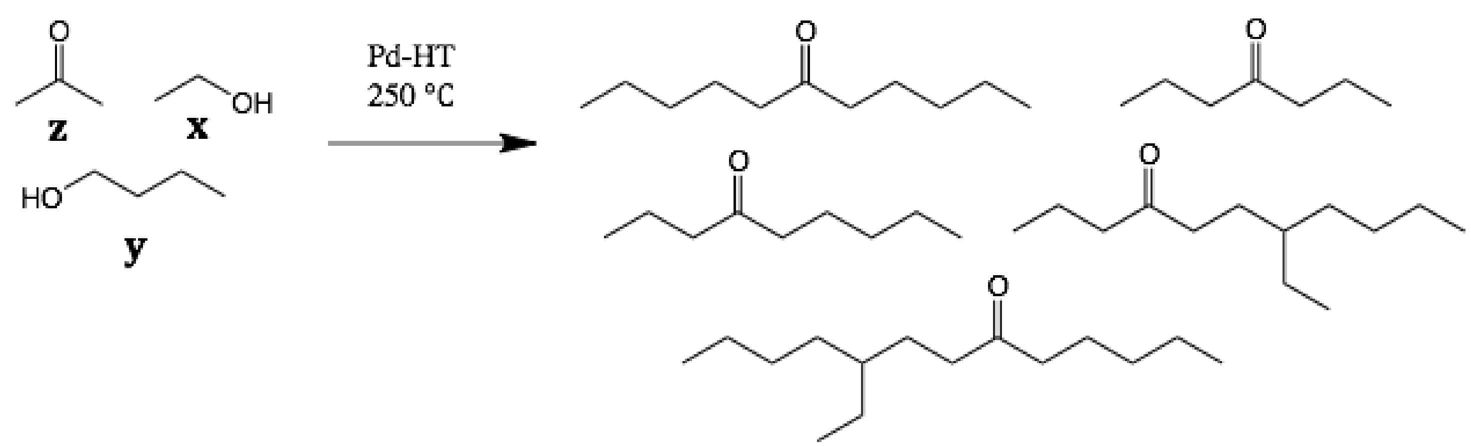
1 *C. beijerinckii* butyraldehyde dehydrogenase (Cb bydh)
2 C. acetobutylicum butanol dehydrogenase A (Ca bdhA)
2 *C. ljungdahlii* butanol dehydrogenase (Cl bdh)





Sebastian Bormann et al. Metabolic Eng. 2014

Tuning the organism for gasoline or jet/diesel products

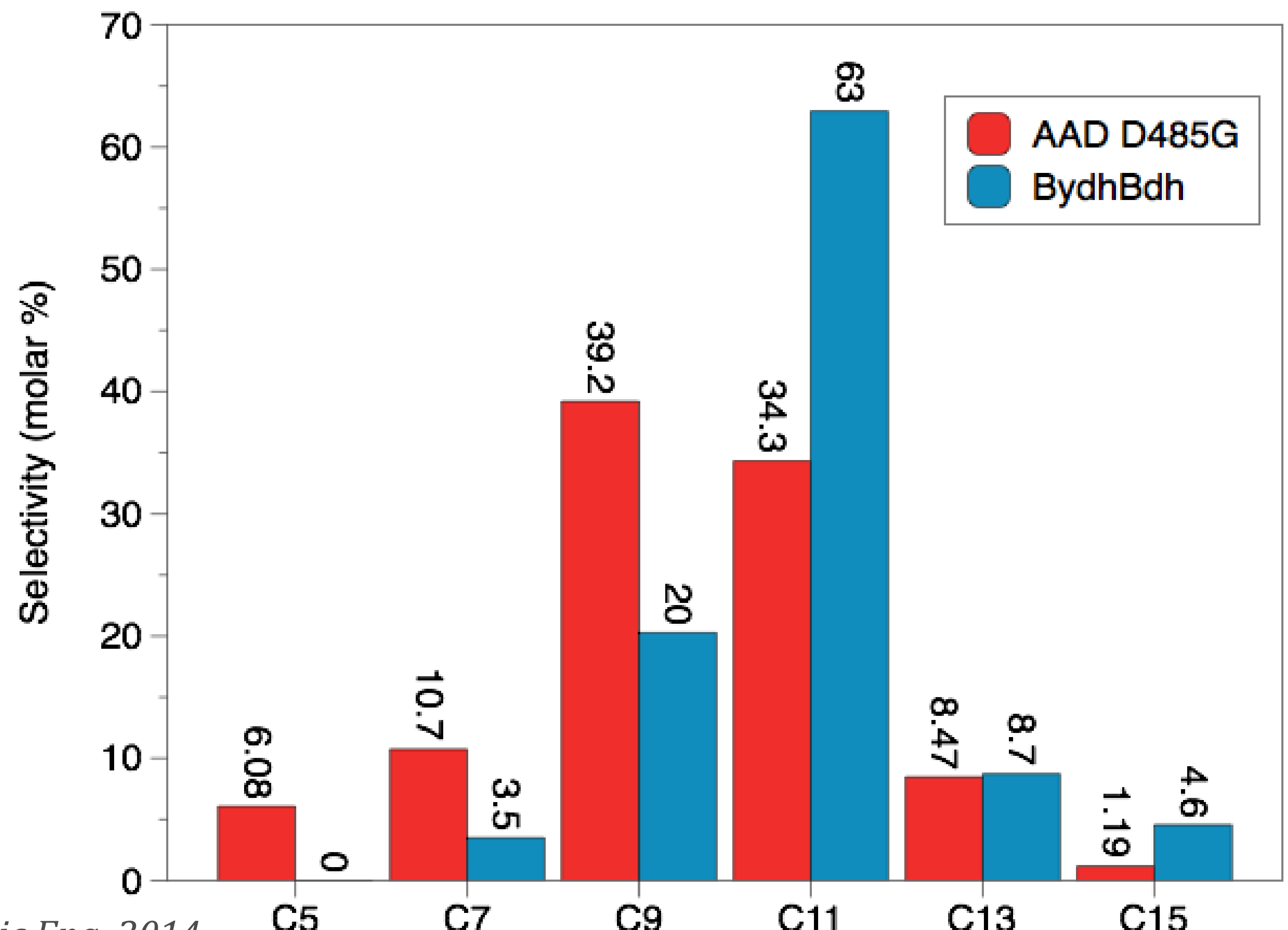


AAD D485G:

14.8 g L^{-1} butanol
5.54 g L^{-1} acetone
13 g L^{-1} ethanol

BydhBdh:

16.9 g L^{-1} butanol
5.4 g L^{-1} acetone
3.6 g L^{-1} ethanol



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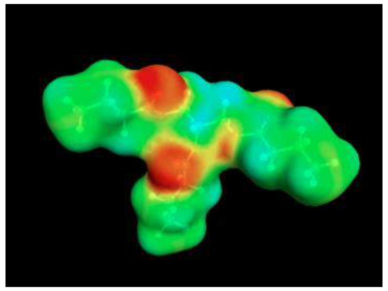
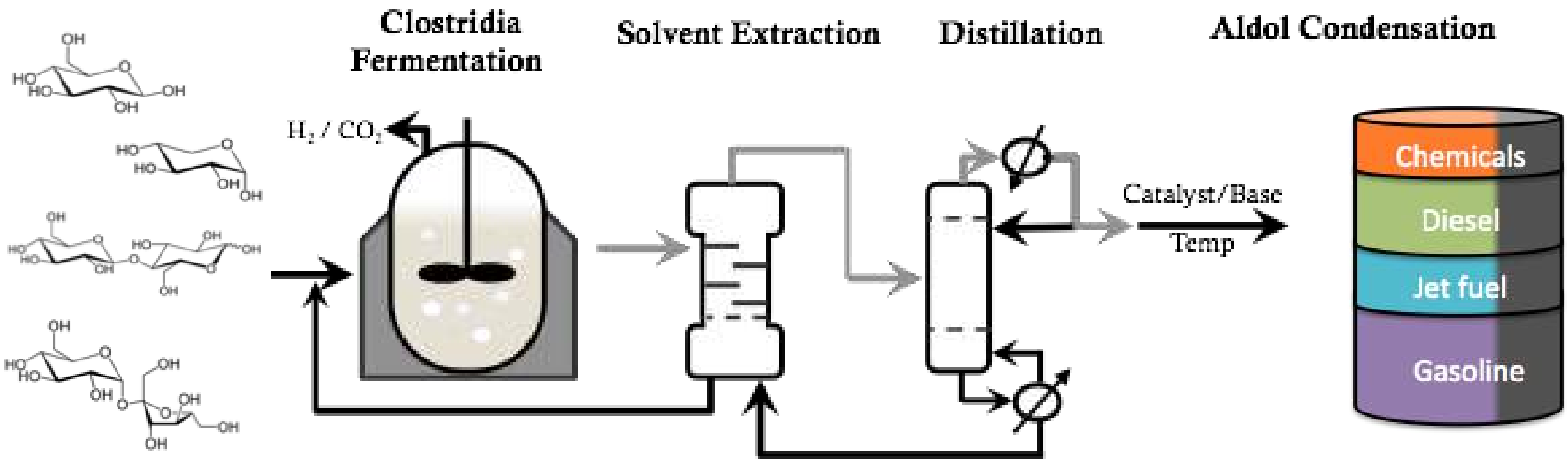
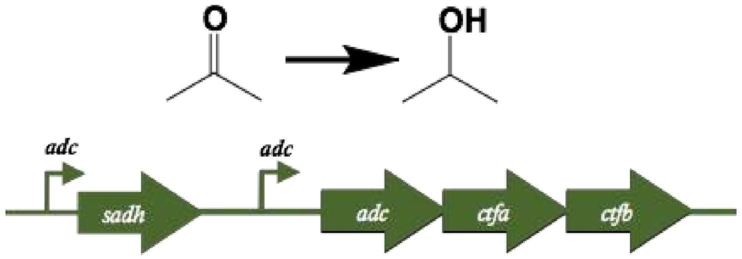
Summary

Identifying Extractants

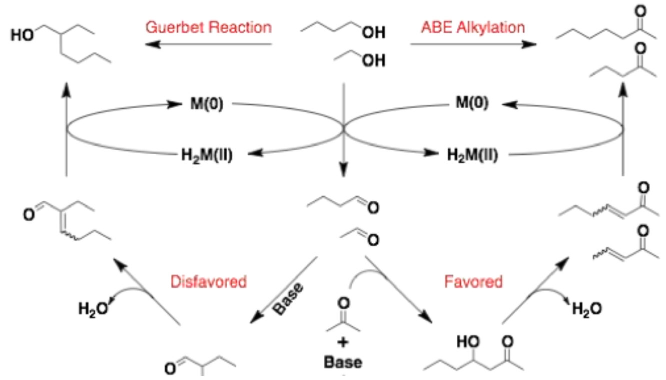




Metabolic Engineering



Catalyst Tuning



Special thanks to:

Energy Biosciences Institute

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