Production of Bio-based Fuels and Chemicals Using Novel Process Platforms

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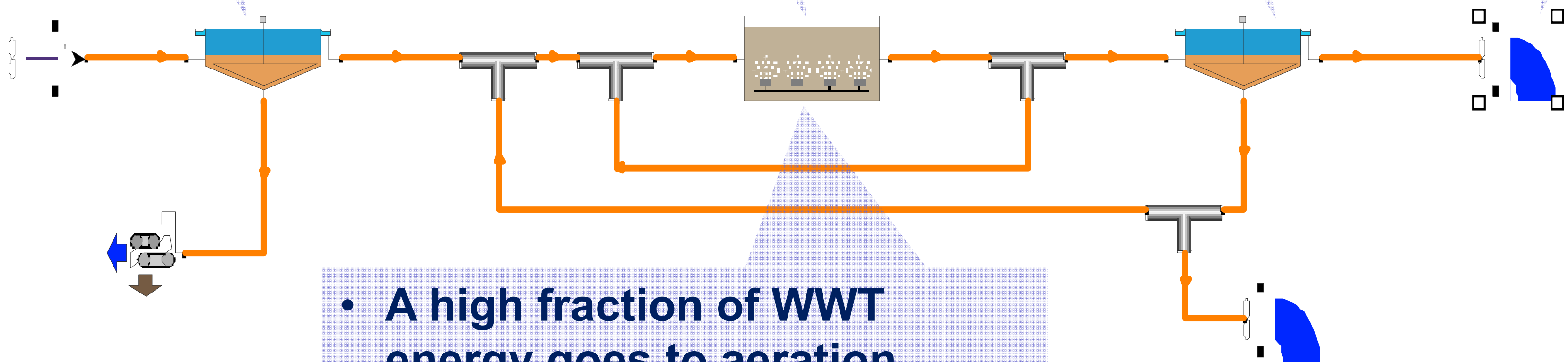
The quest for clean water- today

Solids, inerts separation

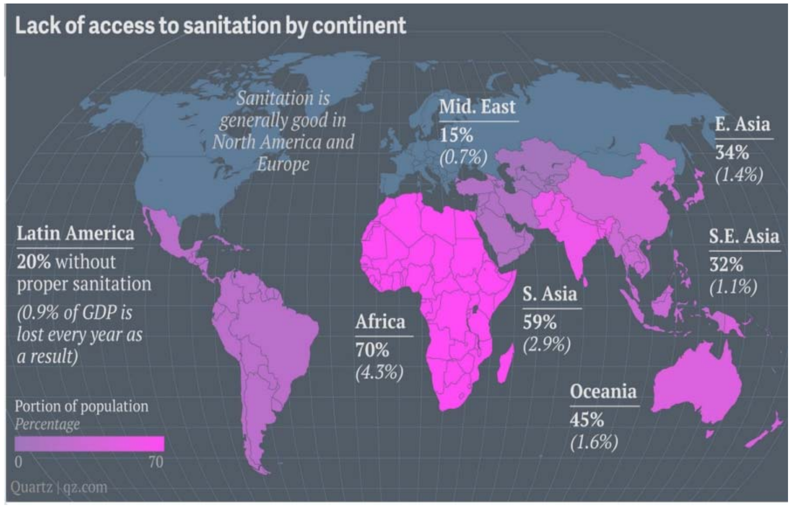
Aerobic C &N removal

Recycle of bacteria

Disinfection and discharge

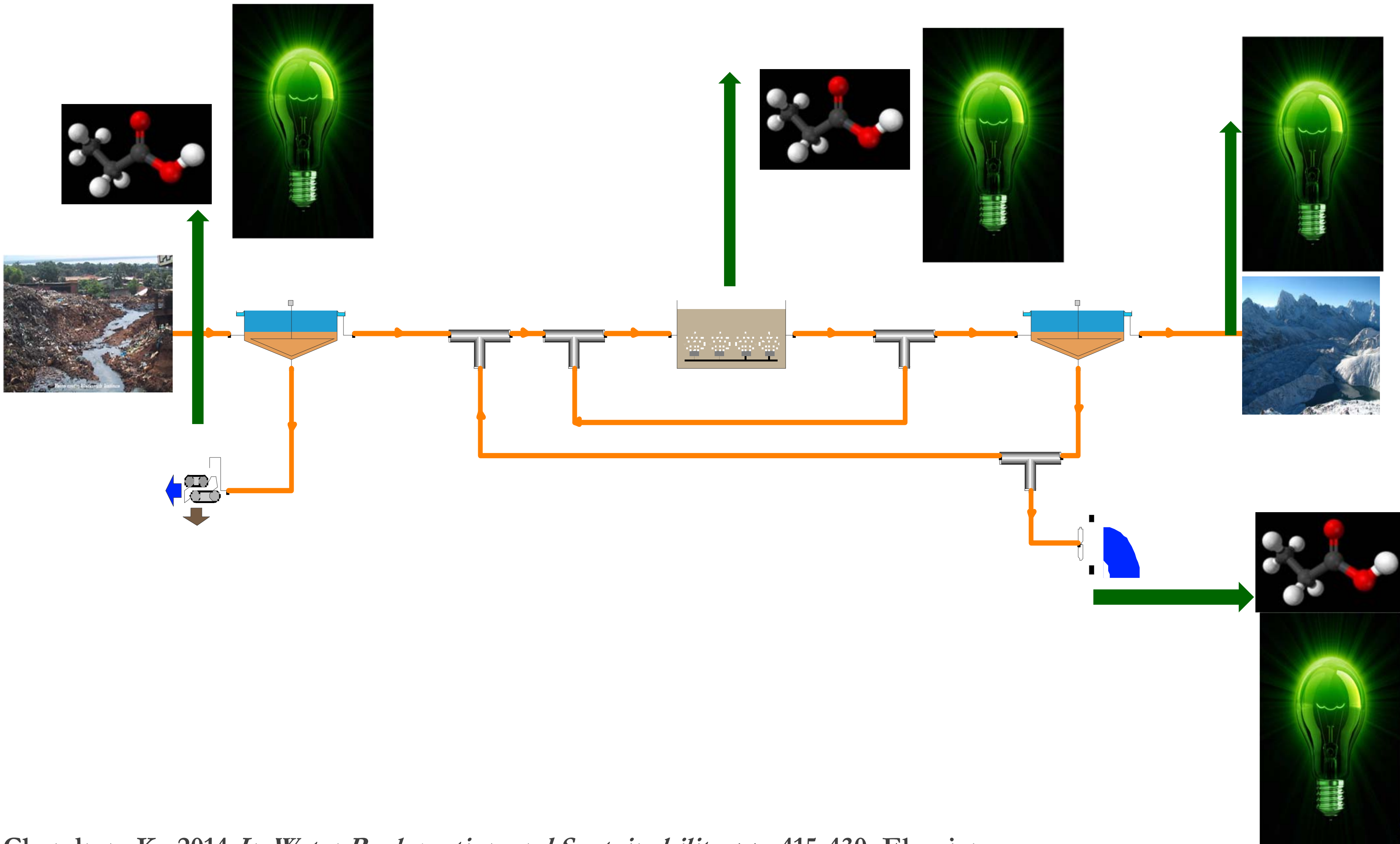


- A high fraction of WWT energy goes to aeration
- $MM in organic chemical purchase
- Bacteria could produce unwanted products (N_2O)



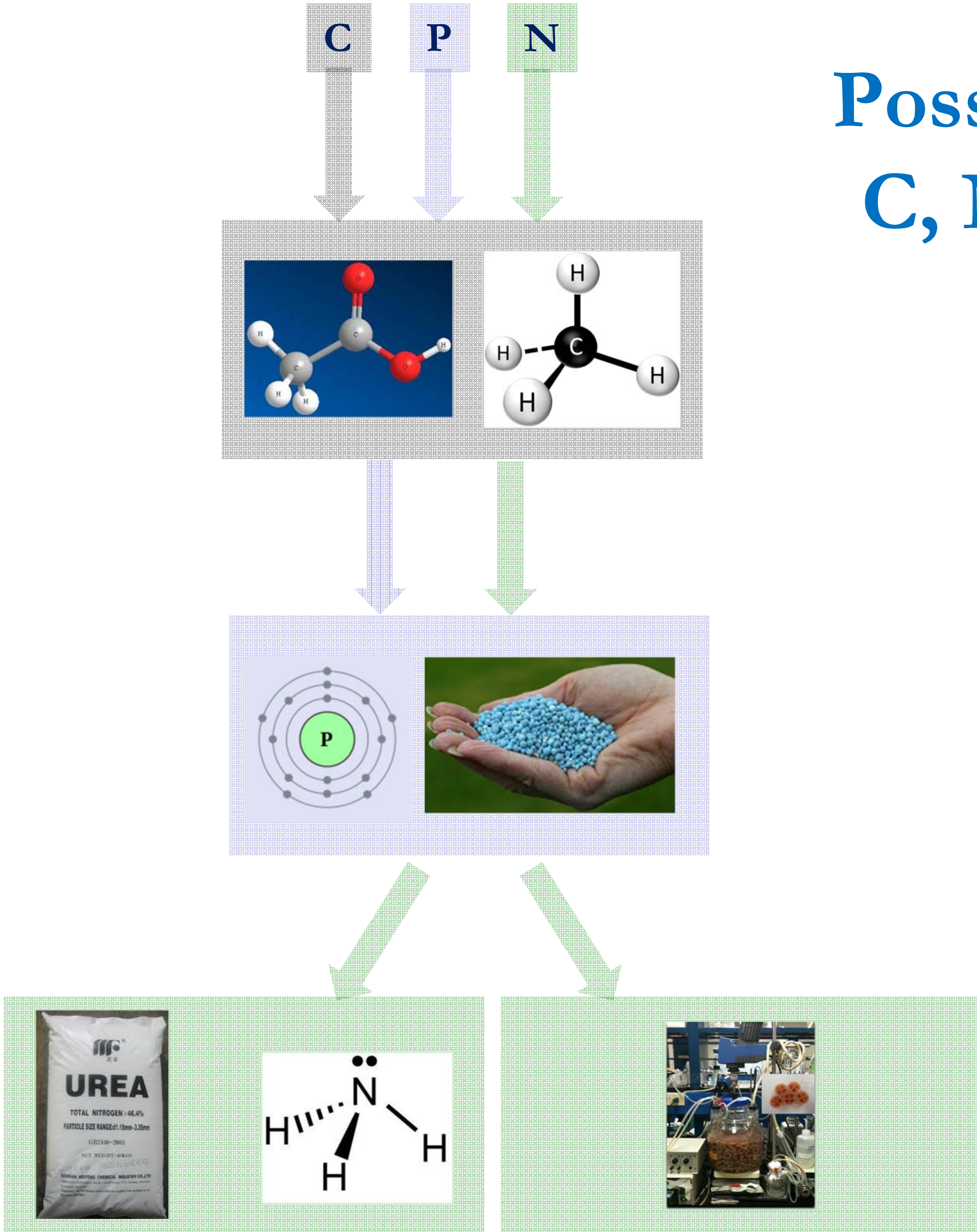
Is it possible to link sanitation with higher value chain biofuels and commodity chemicals?

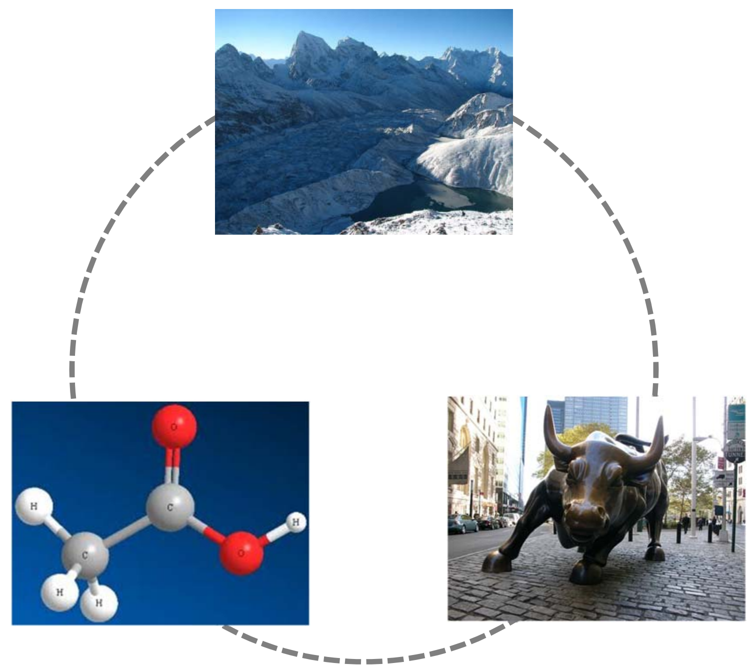
Engineered Resource Recovery from 'Waste' Streams



Chandran, K., 2014 *In Water Reclamation and Sustainability*, pp. 415-430, Elsevier

Possible flowsheet for C, N and P recovery

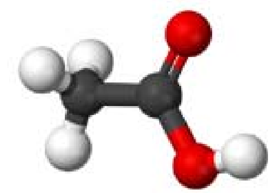


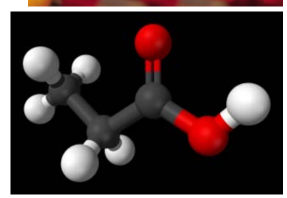


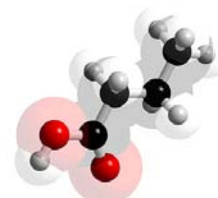
Recovery of C, N and P

All based on anaerobic technologies

Biofuels







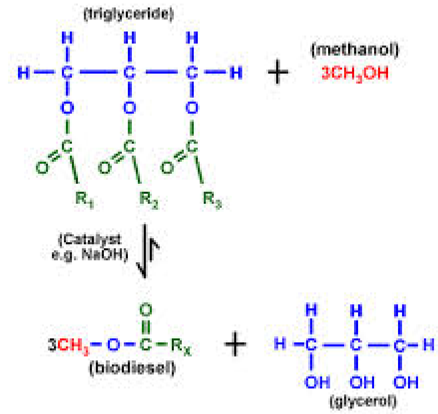
Commercial chemicals

Bioplastics

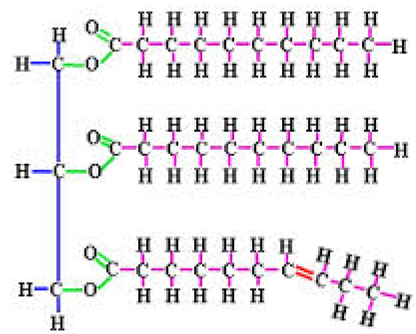
Biofertilizers

Fecal sludge to biodiesel

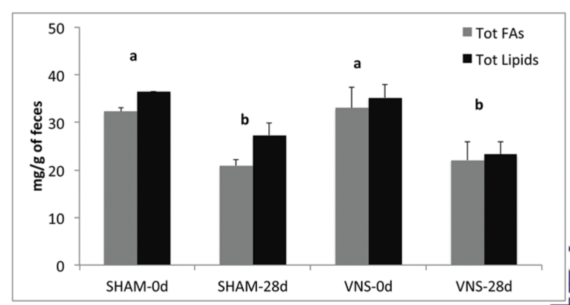
- Biodiesel

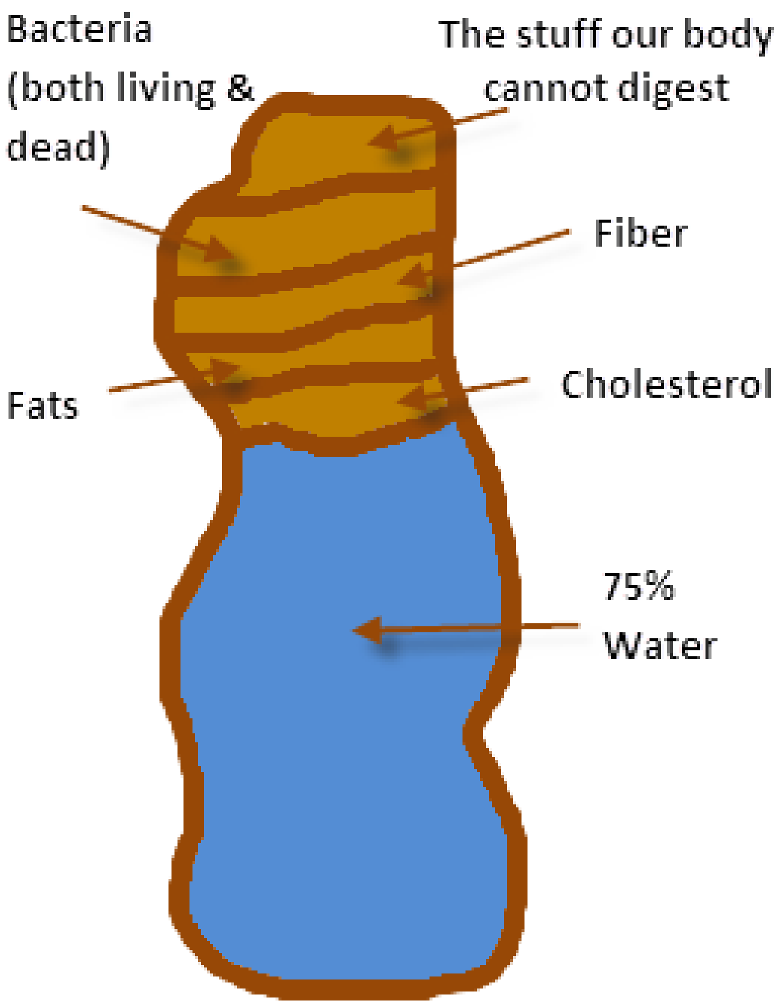


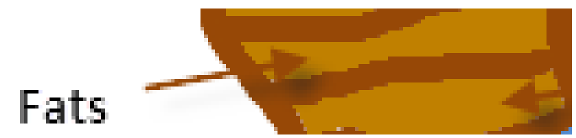
- Lipids

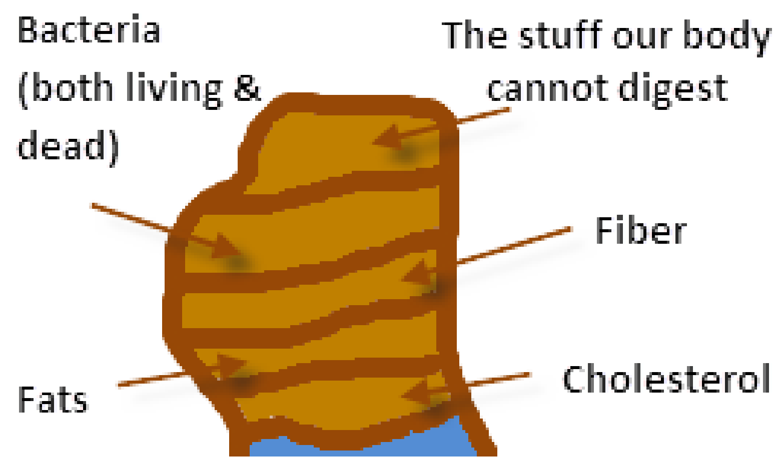


- Lipids in fecal sludge

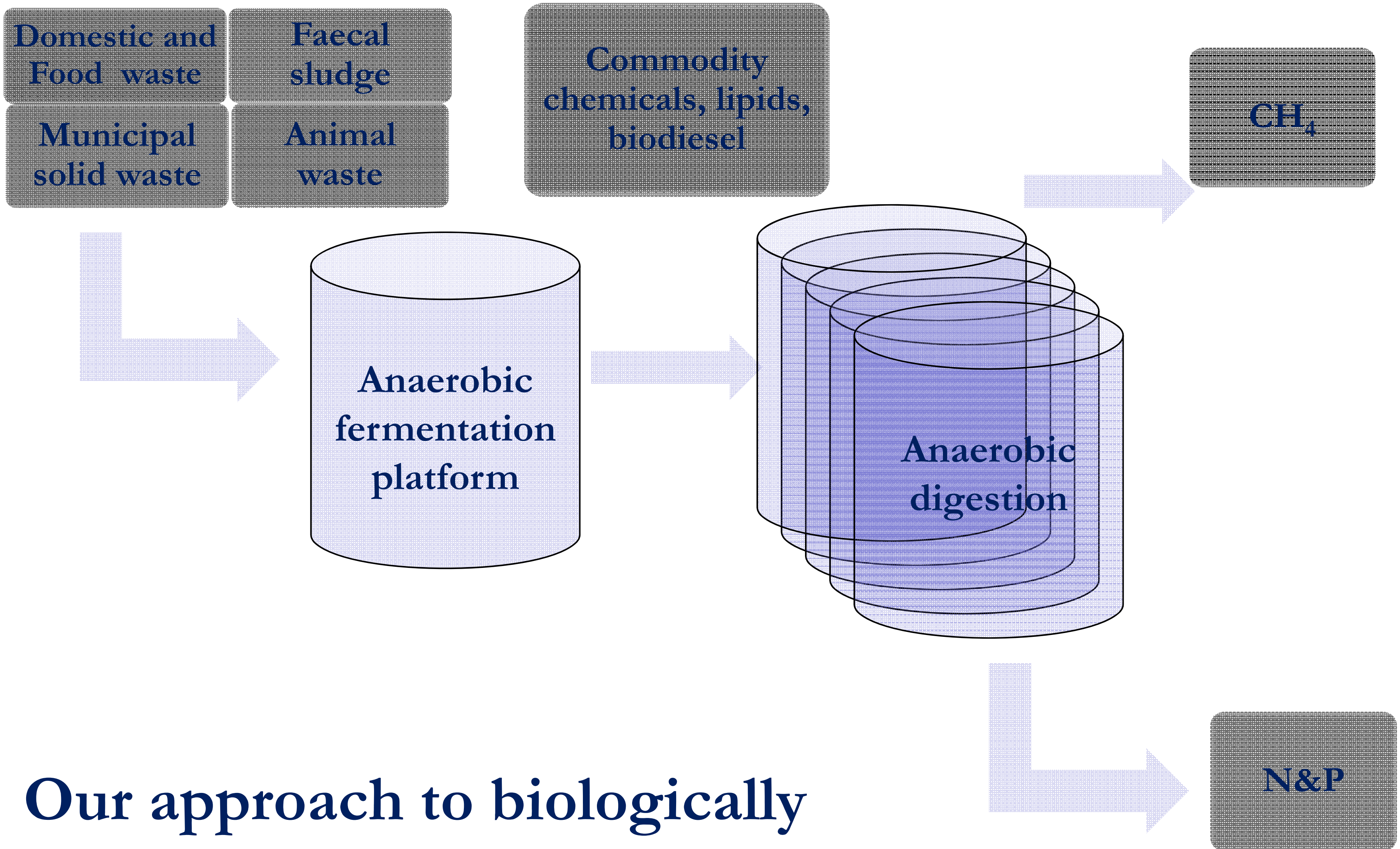








Biodiesel process agnostic to 'waste' stream?



Our approach to biologically refining organic streams

Anaerobic Digestion

Complex organic polymers

↓ Hydrolysis

Sugars, amino acids

↓ Acidogenesis

Volatile fatty acids (VFA)

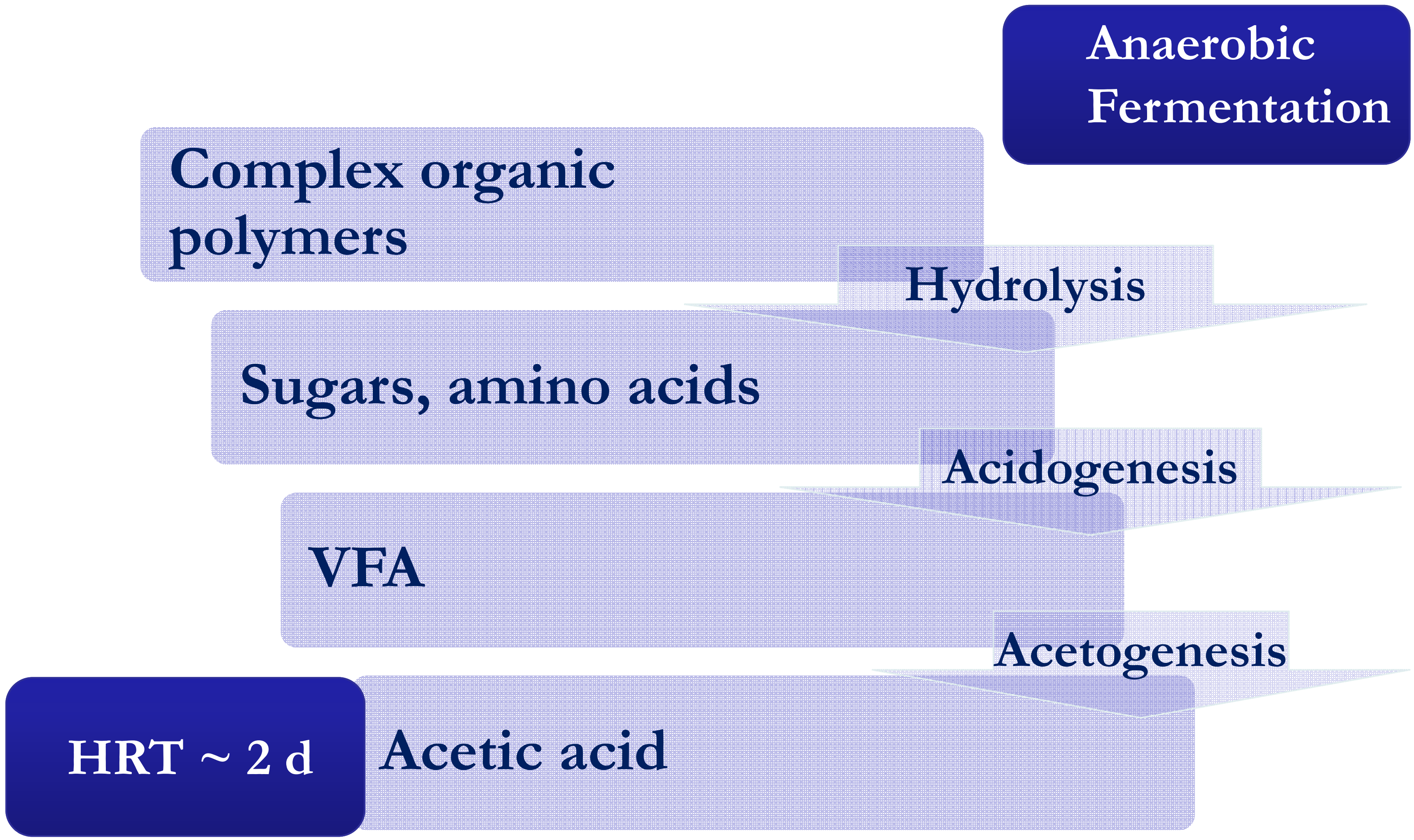
↓ Acetogenesis

Acetic acid

↓ Methanogenesis

Methane

HRT > 10 d



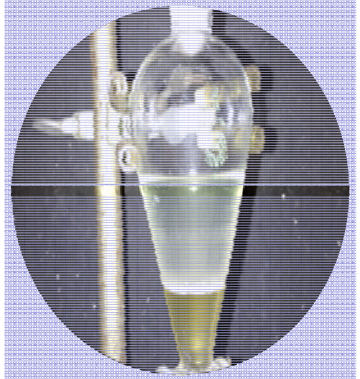
- Fermentation is more advantageous than just anaerobic digestion
- Fermentation can be incorporated into existing digestion processes

Overview of our process

Organic waste

Anaerobic fermentation to produce volatile fatty acids (VFA)

Convert VFA to lipids



Harvest and extract lipids

Convert lipids to biodiesel

Conversion of VFA to Lipids

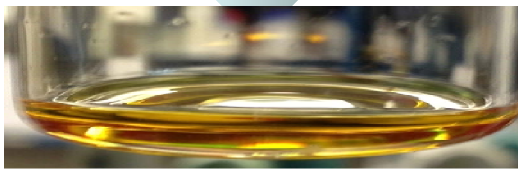
- Different COD sources
  - VFA from food waste fermentation
  - Synthetic VFA
  - Glucose
- Different initial VFA concentrations

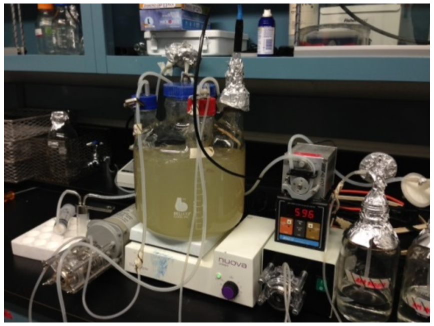
6:1:3 acetate, propionate, butyrate. 2 day HRT

- Different feedstock composition
  - Excess N: COD:N = 5:1
  - Limiting N: COD:N = 25:1, 50:1, 125:1, 250:1

Lipid content of *Cryptococcus albidus*

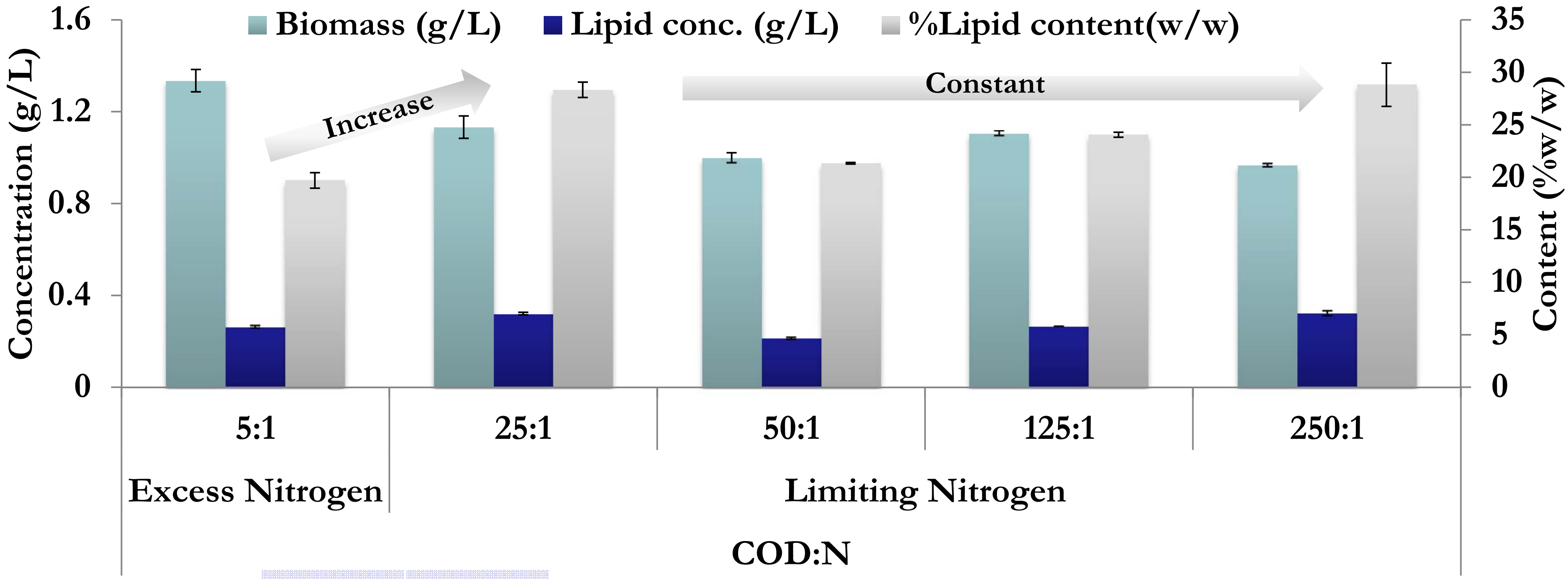
Batch process





Chemostat

Effect of feedstock composition

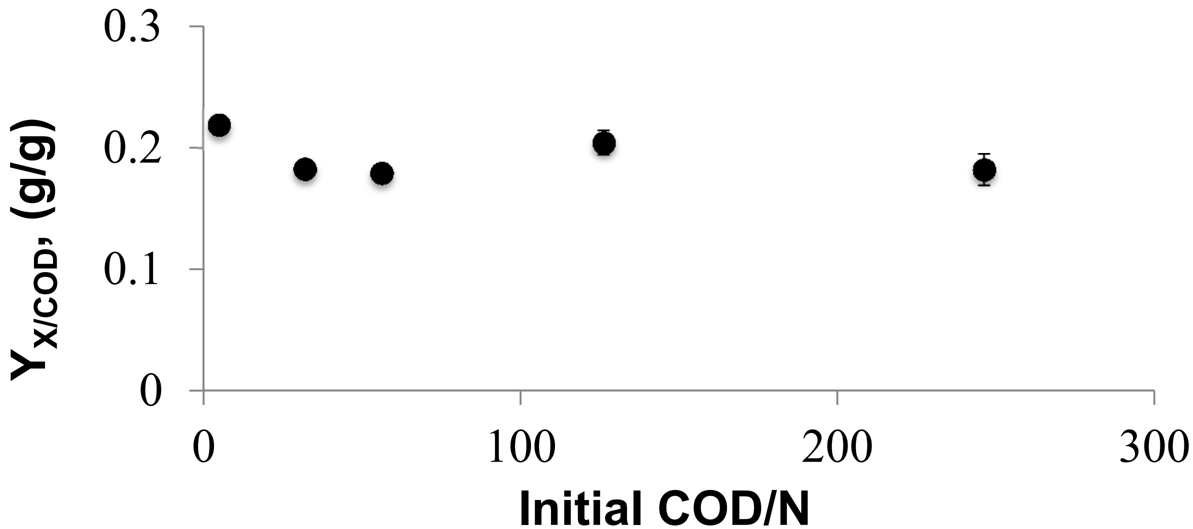


	COD: N	μ_m (h^{-1})
	5:1	0.041
Limiting Nitrogen	25:1	0.043
	50:1	0.039
	125:1	0.036
	250:1	0.023

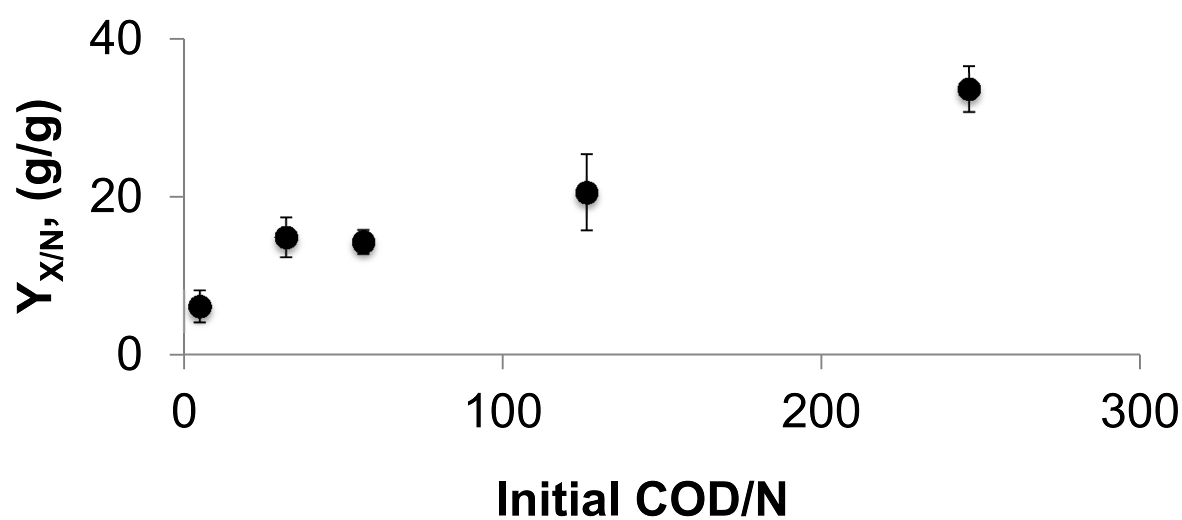
Process can handle variability in influent feedstock

Vajpeyi and Chandran, 2015 BRT

EFFECT OF NITROGEN CONCENTRATION ON YIELD COEFFICIENTS

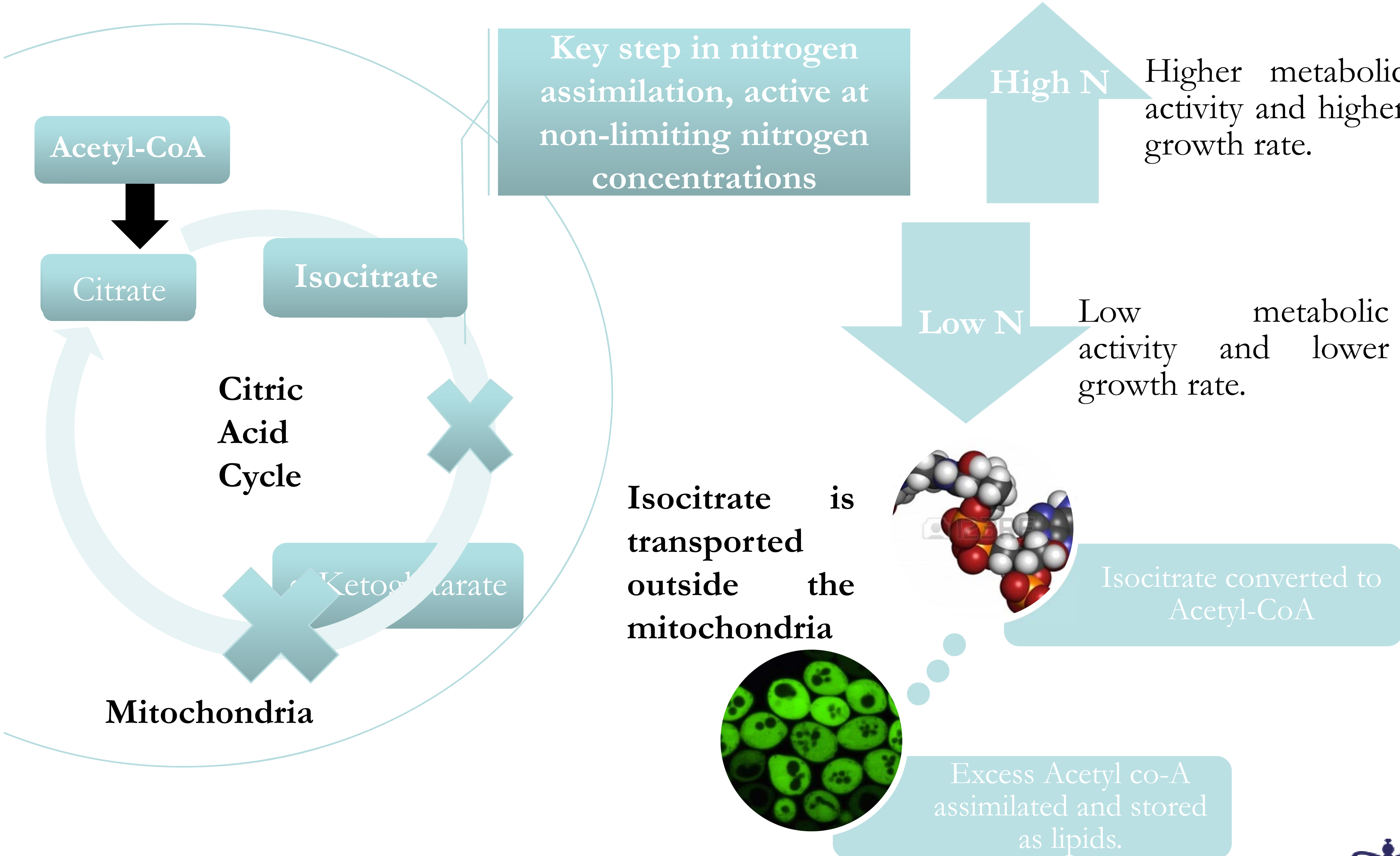


Cultures become more efficient in carbon uptake and storage (as lipids) with increasing N-limitation

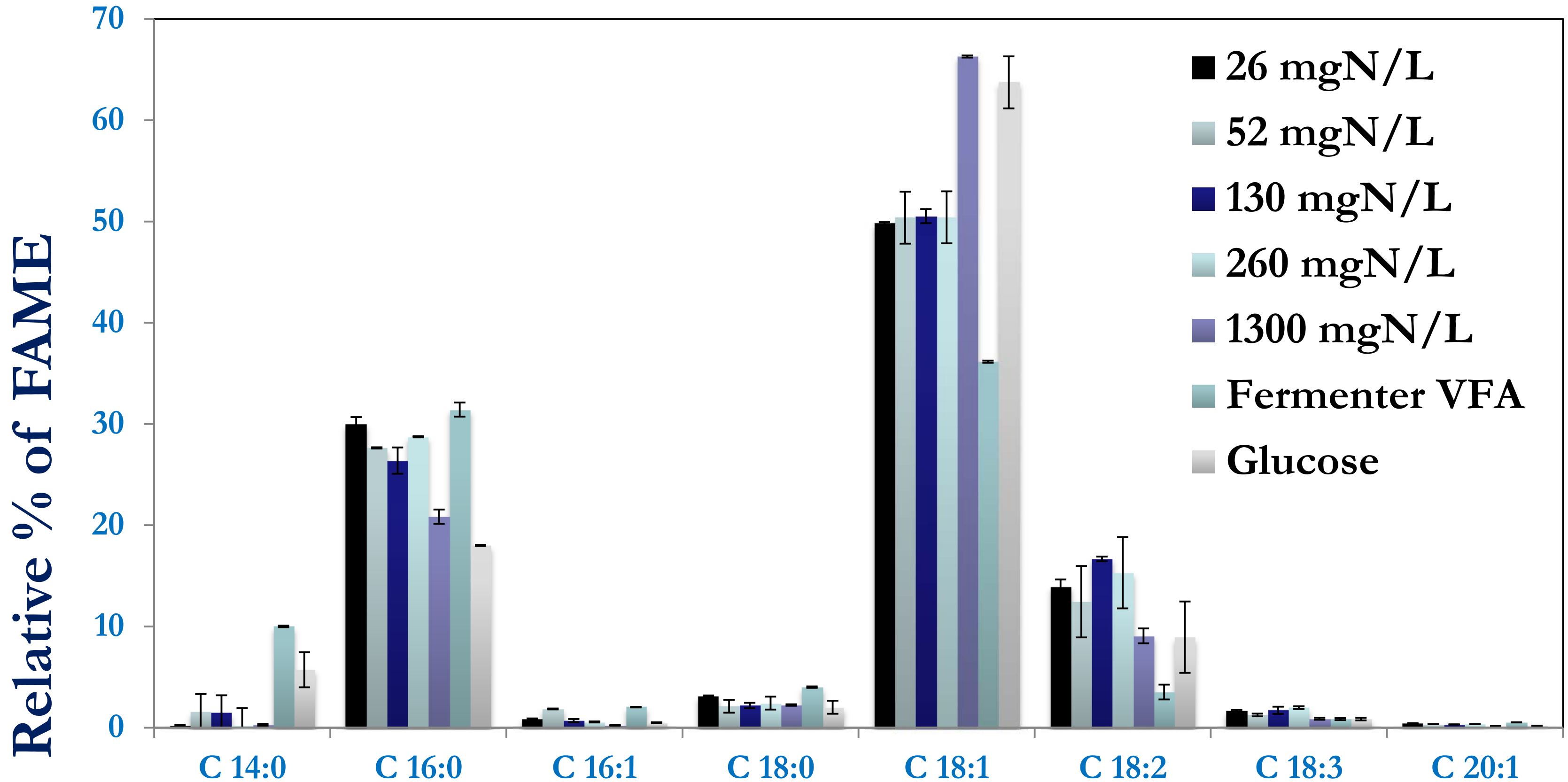


Vajpeyi and Chandran, 2015 BRT

METABOLIC EFFECT OF NITROGEN CONCENTRATION



Lipid Composition



Major fatty acids accumulated are palmitic (C16:0), oleic (C18:1), and linoleic acid (C18:2)

Similar to soybean oil and jatropha oil, predominant feedstocks for biodiesel production in the US and the EU

Vajpeyi and Chandran, 2015 BRT

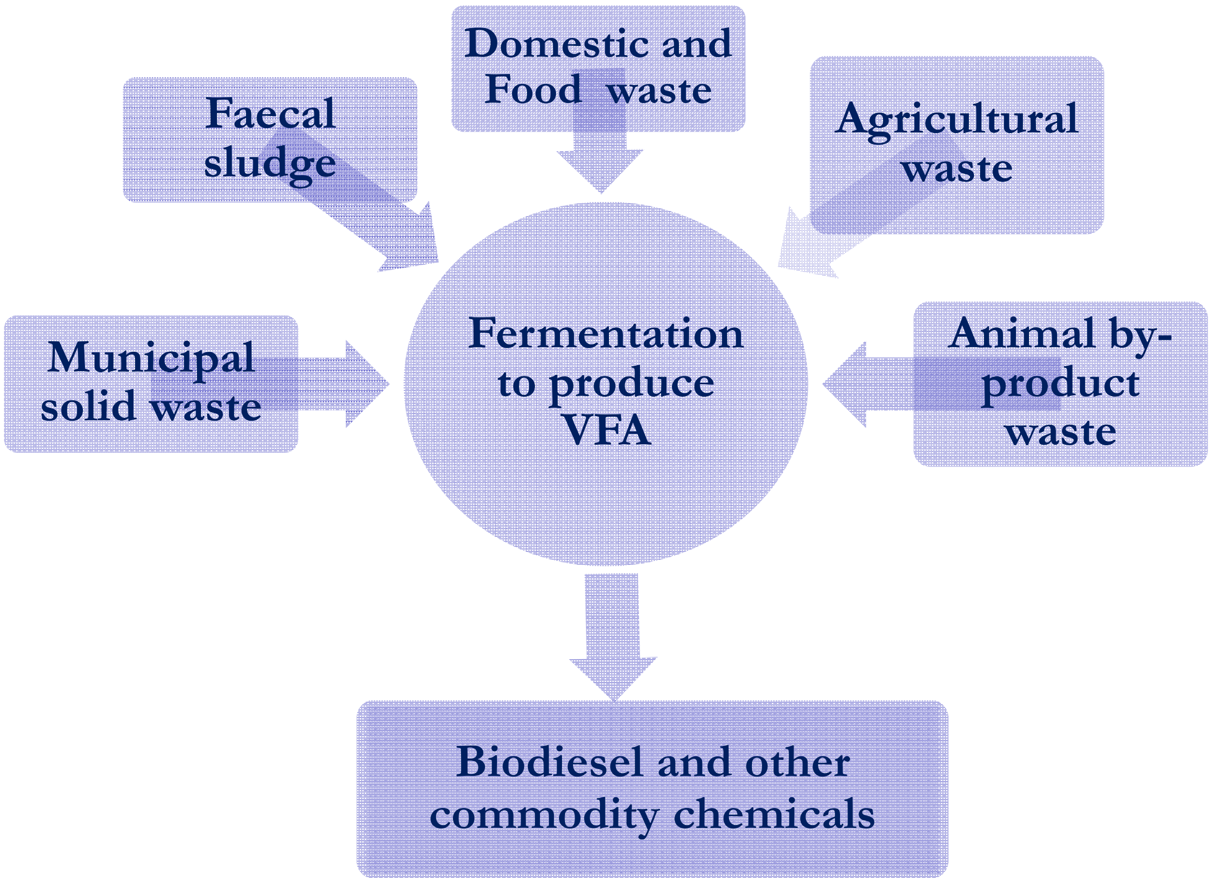
Economic analysis

Cost of biodiesel production	
Carbon source cost	$30/ton (Much lower if sludge comes in pre-fermented, as in Kumasi, GH)
Lipid yield from *C. albidus* (kg lipid/ton VFA)	40.96 (lowest observed value during our studies)
Lipid cost ($/lb)	0.33
Gross cost ($/L biodiesel)	0.71
Gross cost ($/Kg biodiesel)	0.81

Not competing with biodiesel industry, rather making sanitation enterprise energy neutral or energy positive

Vajpeyi and Chandran, 2015 BRT

Conclusions and implications

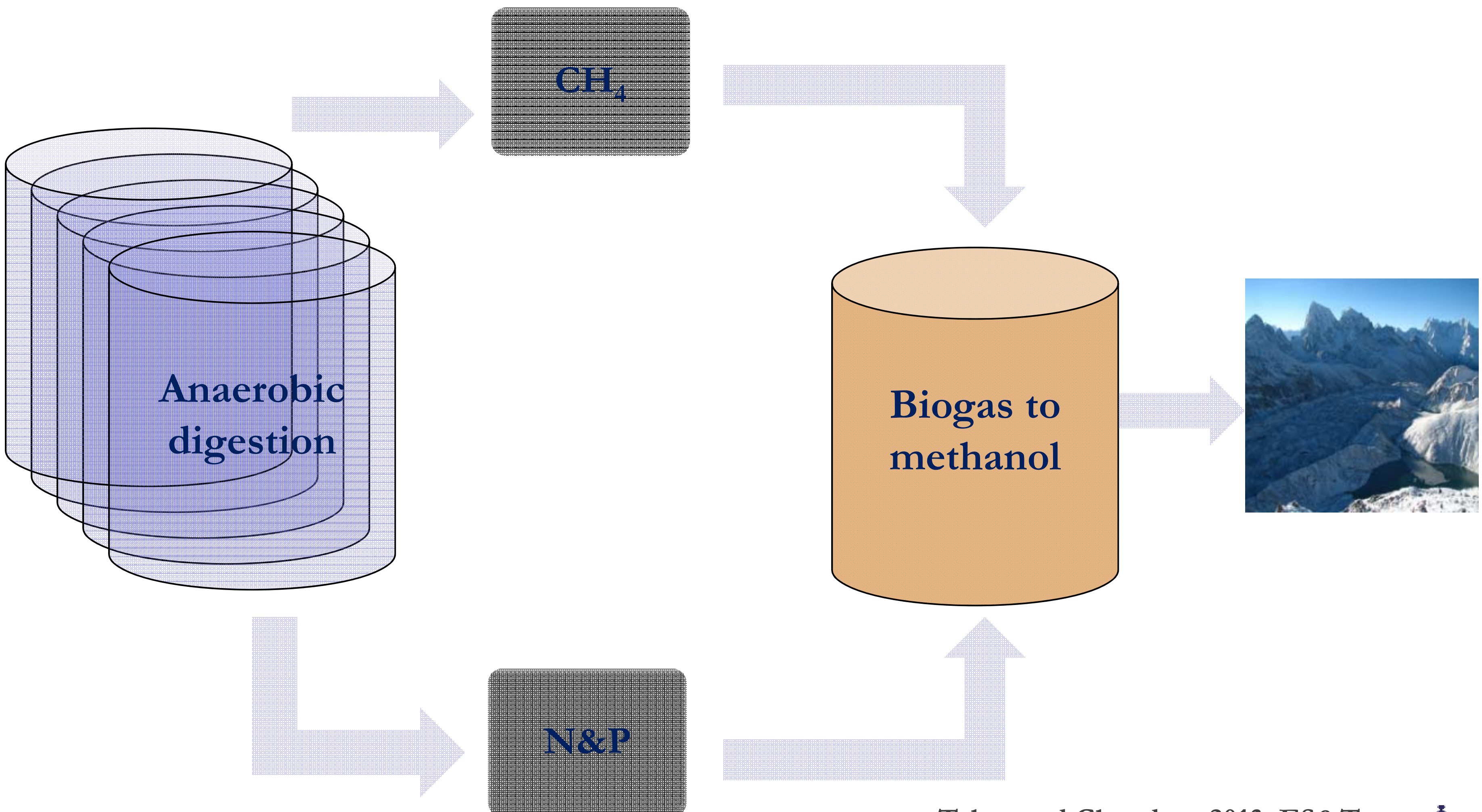


Novel and flexible platform to convert a variety of organic 'waste' streams to biodiesel or other lipid based commodity chemicals

Not reliant upon inherent lipid content- other organic classes can be converted to lipids

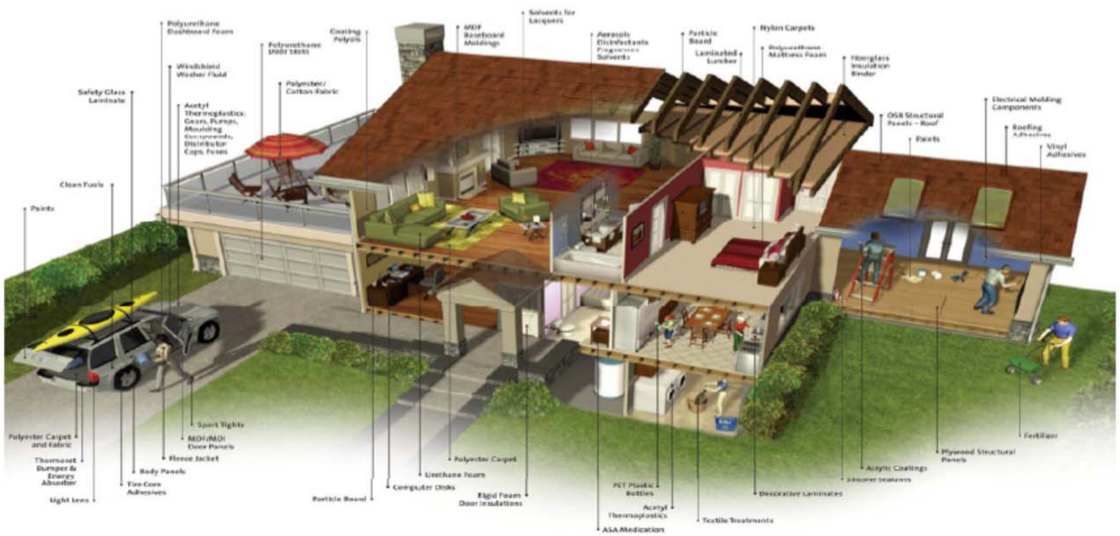
- For biodiesel as the preferred end point, reliance upon agricultural outputs is reduced or eliminated
- Links sanitation practice with energy and chemical recovery
- Mechanistic interrogation underway using a systems approach

Production of bio-methanol by ammonia oxidizing bacteria

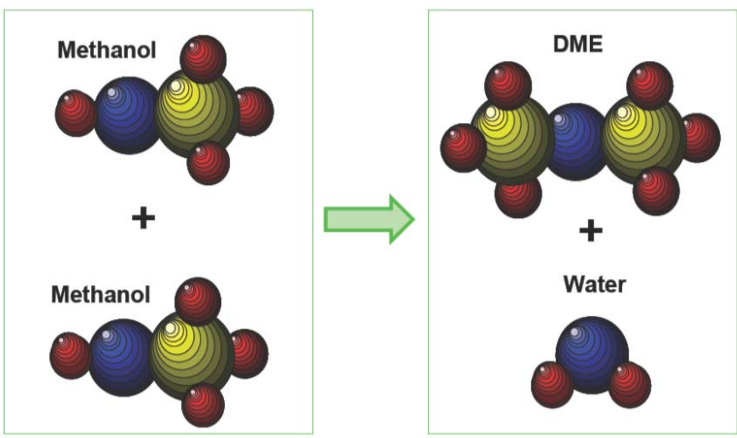


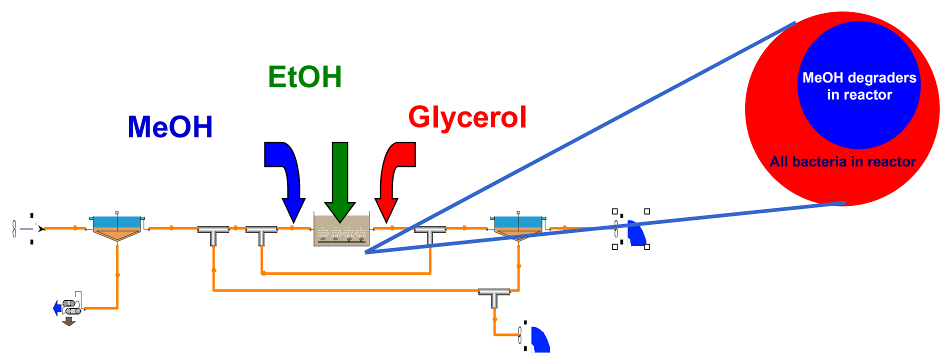
Taher and Chandran 2013, ES&T
Su and Chandran, *unpublished*

Applications of methanol



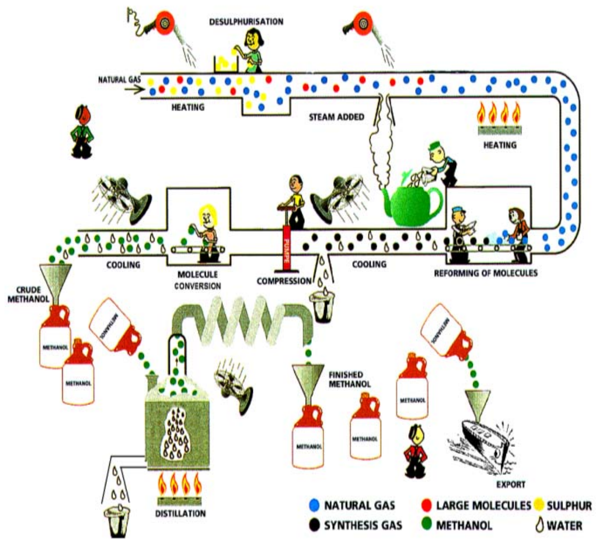
VOLVO:s DME-powered Truck

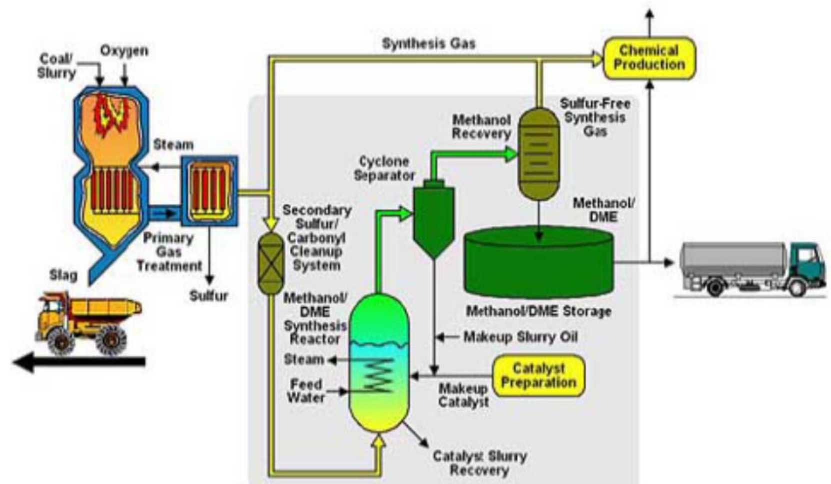


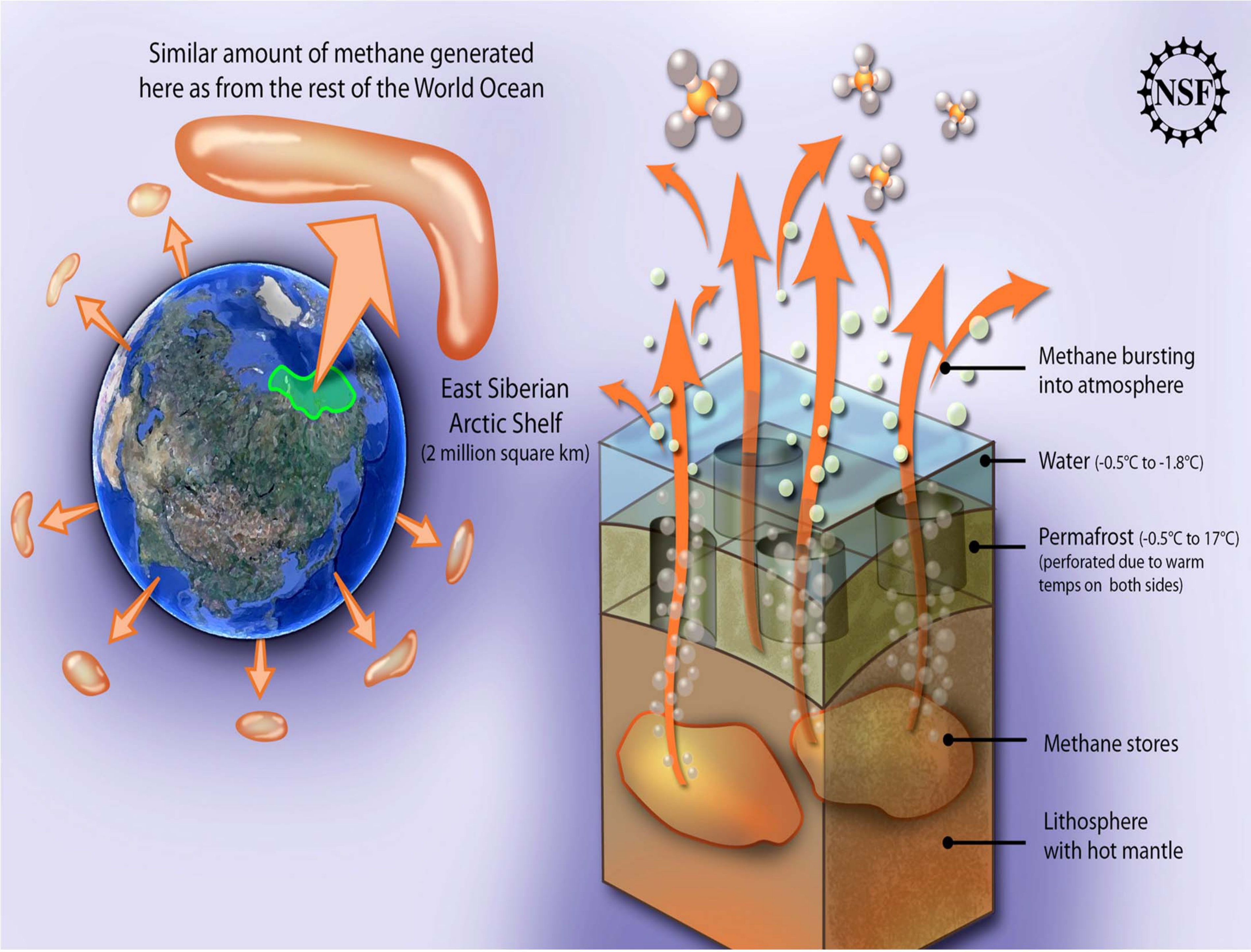


Baytshtok et al., 2008, 2009, Lu et al., 2010, 2011, 2012

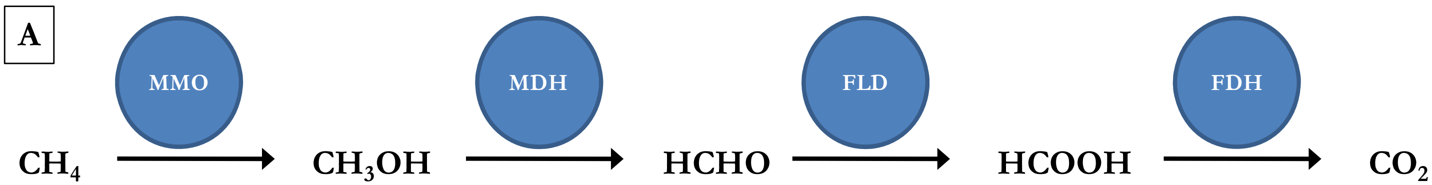
Sources of methanol

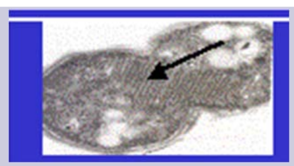
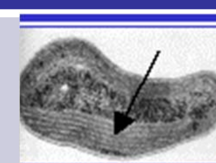




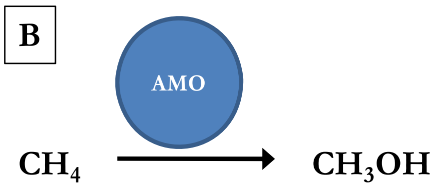

Similar amount of methane generated here as from the rest of the World Ocean
East Siberian Arctic Shelf
(2 million square km)
NSF
Methane bursting into atmosphere
Water (-0.5°C to -1.8°C)
Permafrost (-0.5°C to 17°C)
(perforated due to warm temps on both sides)
Methane stores
Lithosphere with hot mantle

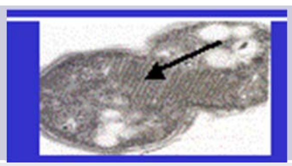
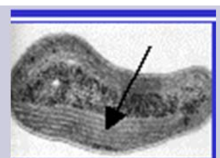
Biological production of methanol



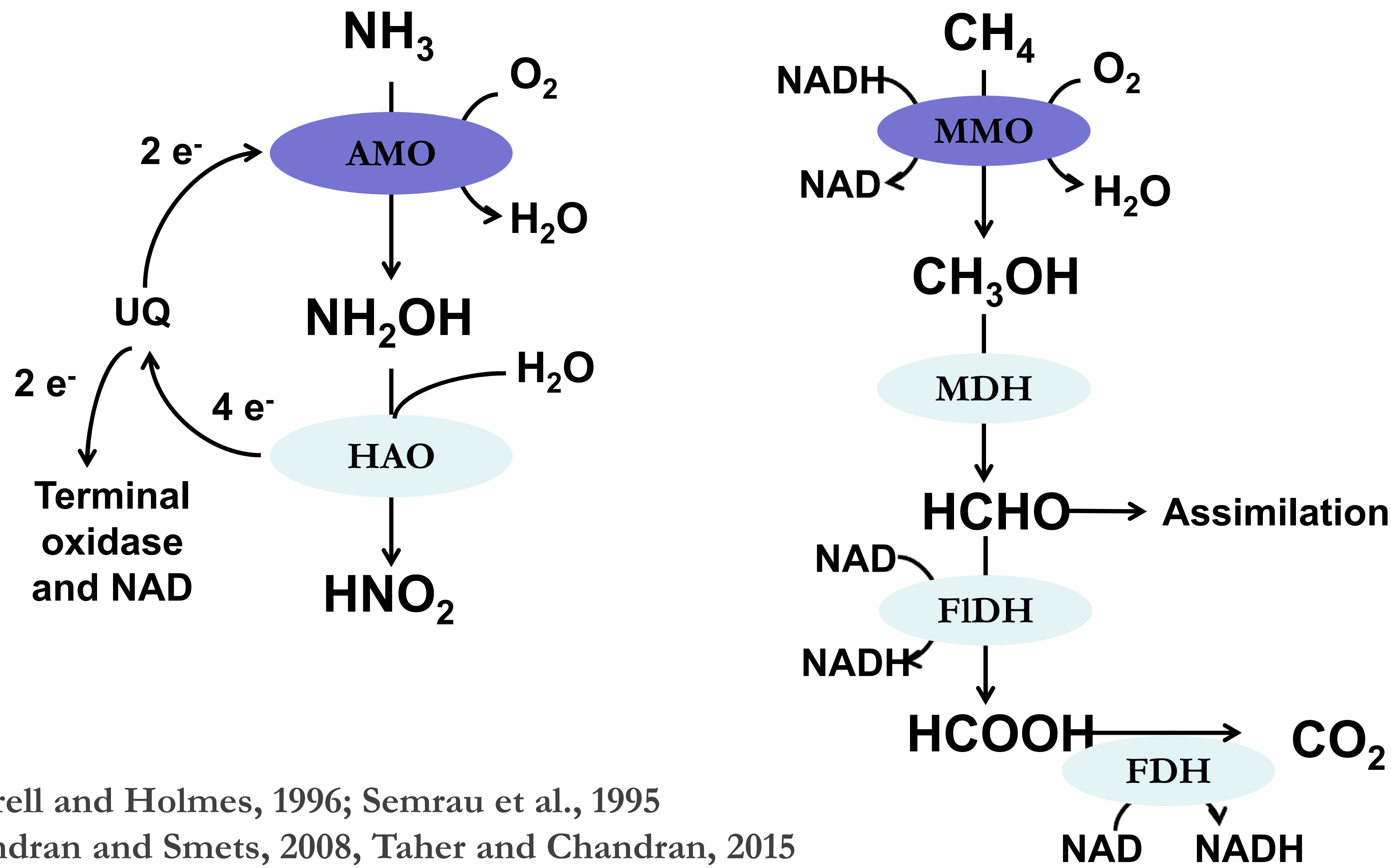
	Type I methanotroph	Type II methanotroph
		
Phylogeny	Gamma proteobacteria	Alpha-proteobacteria
CH4 oxidation and carbon assimilation	Ribulose mono-phosphate	Serine
Monooxygenase	pMMO	sMMO

Biological production of methanol

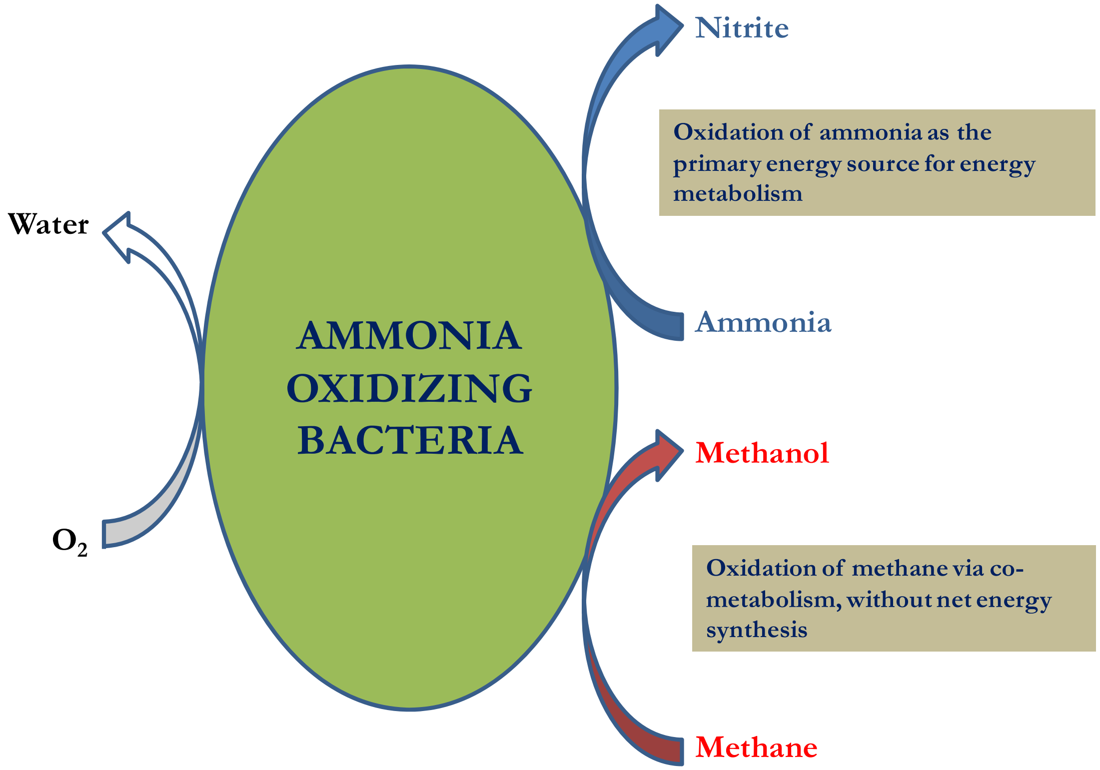


	Type I methanotroph	Type II methanotroph	Ammonia oxidizing bacteria
			
Phylogeny	Gamma proteobacteria	Alpha-proteobacteria	Beta-proteobacteria
CH4 oxidation and carbon assimilation	Ribulose mono-phosphate	Serine	Fortuitous, no assimilation known
Monooxygenase	pMMO	sMMO	AMO

Ammonia and Methane Oxidation



Murrell and Holmes, 1996; Semrau et al., 1995
Chandran and Smets, 2008, Taher and Chandran, 2015
Yu *et al.*, 2010a,b, Khunjar *et al.*, 2015



- Concomitant oxidation of CH_4 and CO_2 fixation
  - Digester gas contains CO_2
  - Foulant for chemical catalyst; but a food source for AOB
  - Moisture- not really an issue
- Prospect of combining C &N cycles

Objectives

- **Develop ammonia oxidation bioreactors for partial oxidation of methane to methanol**

- **Optimize conditions for partial oxidation to CH_3OH**
- **Optimize operation and design to maximize yields**

Preliminary experiments

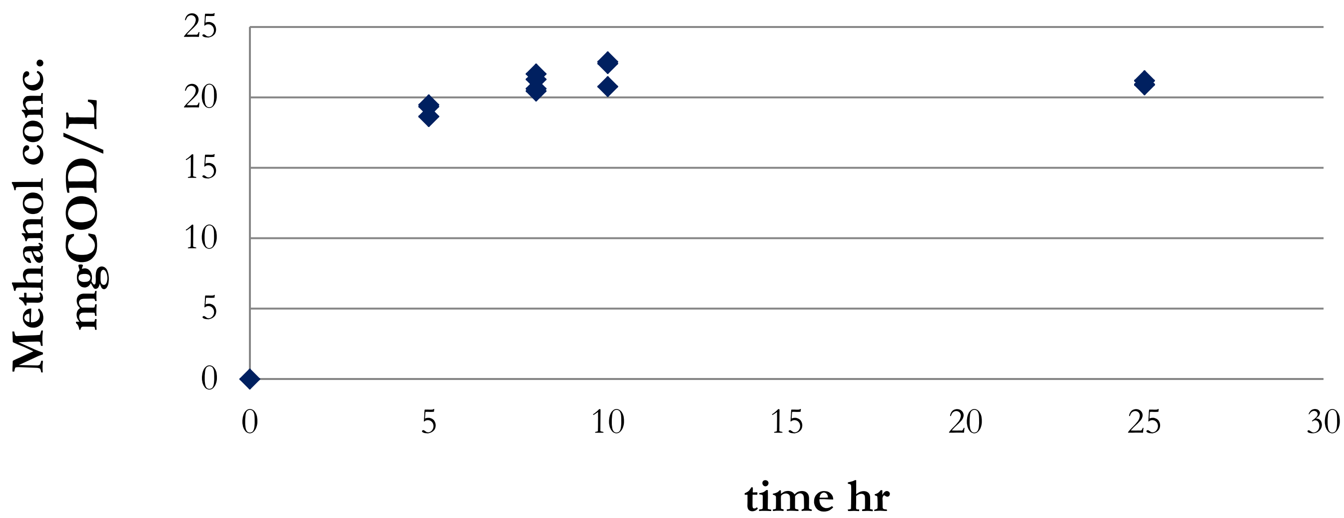
- **Exposing nitrifying activated sludge to different amounts of methane and oxygen**

			t=0 h					t=5 h	
		Biomass mgCOD/L	NH3 (mgN/L)	NH_2OH (mgN/L)	CH4 (mg/L)	O_2 (mg/L)		NH3 (mgN/L)	CH3OH mgCOD/L
Ex1		1352.6	100	0	7.67	26.67		94.58	0
Ex2		1352.6	100	0	11.5	20		96.24	0
Ex3		1352.6	100	0	13.8	16		97.2	0
			t=0 h					t=5 h	
		Biomass mgCOD/L	NH3 (mgN/L)	NH_2OH (mgN/L)	CH4 (mg/L)	O_2 (mg/L)		NH3 (mgN/L)	CH_3OH mgCOD/L
Ex4		1268.4	98.6	1.4	7.67	26.67		93.2	0
Ex5		1268.4	98.6	1.4	11.5	20		95.15	1.49
Ex6		1268.4	98.6	1.4	13.8	16		96.03	2.3

Taher & Chandran, 2013, ES&T

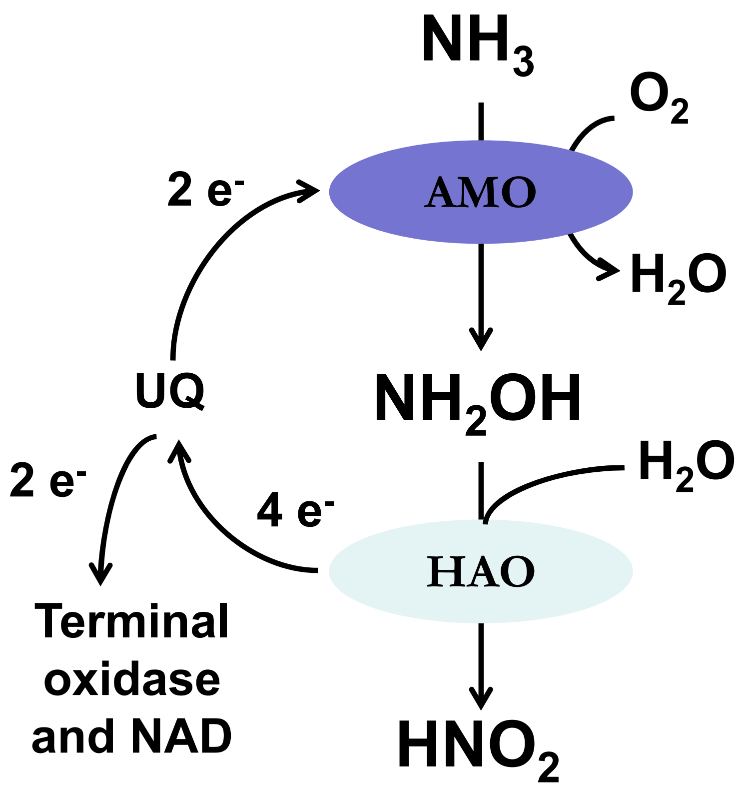
Preliminary experiments

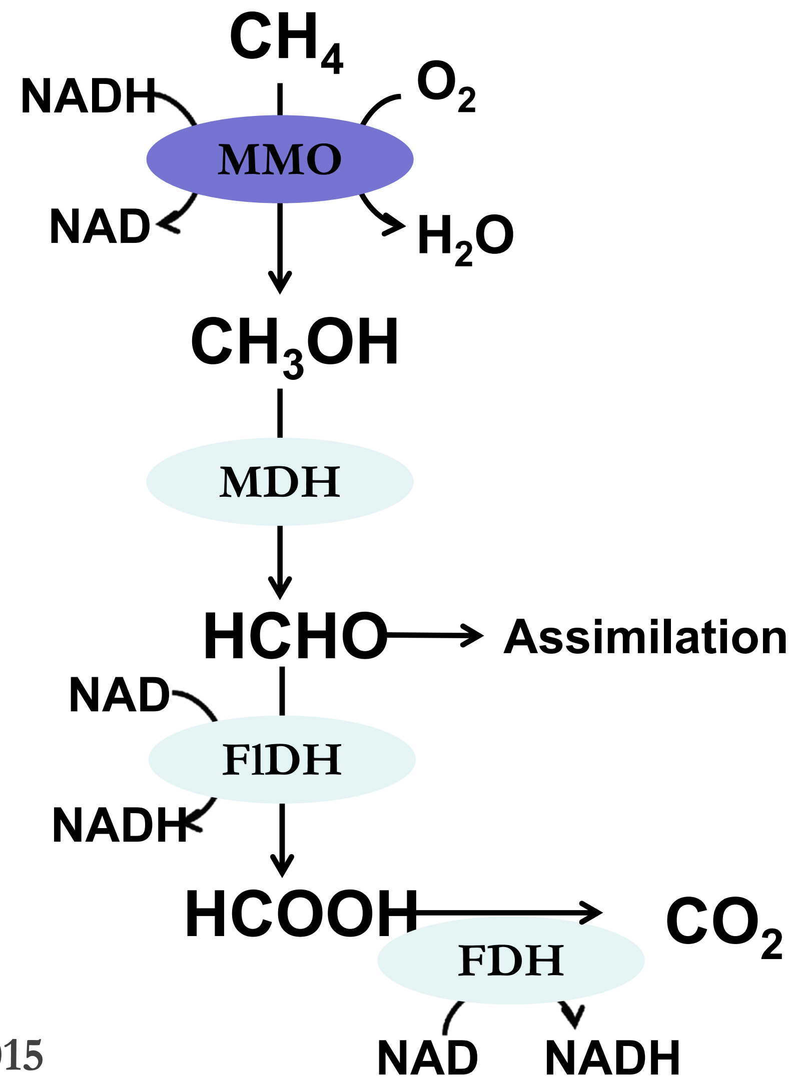
- **Continuous sparging methane (30 ml/min) and oxygen (20 ml/min)**



Taher & Chandran, 2013, ES&T

Ammonia and Methane Oxidation



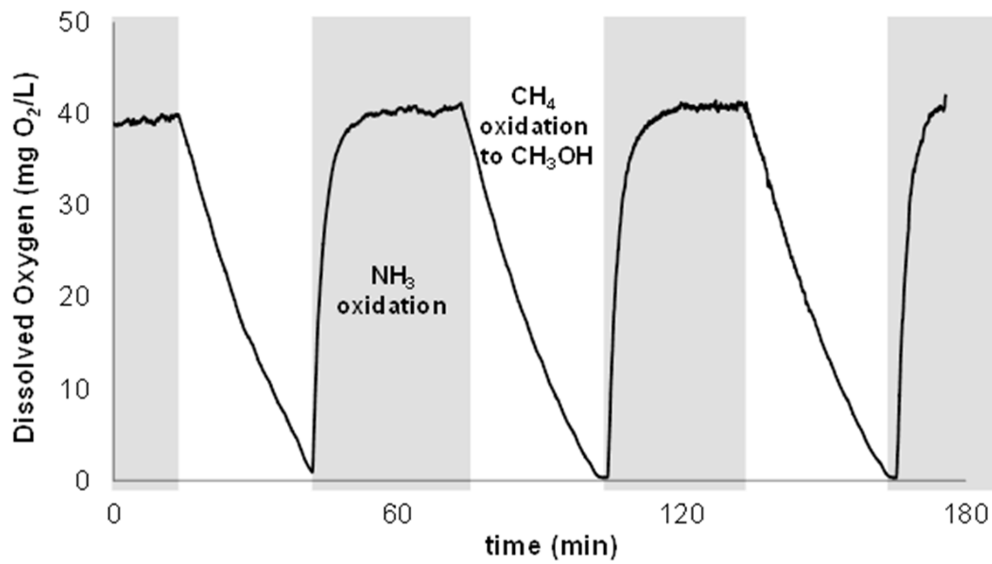


Murrell and Holmes, 1996; Semrau et al., 1995
Chandran and Smets, 2008, Taher and Chandran, 2015
Yu *et al.*, 2010a,b, Khunjar *et al.*, 2015

Improved design

- Issue: competitive inhibition of CH_4 and NH_3 oxidation
  - Rationale: NH_3 needed to activate AMO
  - Solution: isolate NH_3 and CH_4 oxidation
  - Maintain low or zero NH_3 concentrations in solution
- Issue: Limitation of reducing power from NH_3
  - Solution: Create conditions to create electron imbalance
  - OR Supply reductant
  - OR Internally produce reductant
    - Same solution as above BUT
    - Keep NOB in solution

Experimental Design/Setup



- **Maintenance Energy:**

$$m_G = 4.5\exp[\frac{-69000}{R}\left(\frac{1}{T} - \frac{1}{298}\right)]$$ **Tijhuiset al. (1993)**

$$@T = 298^K \quad m_G = 4.5\frac{KJ}{c - molX.H}$$

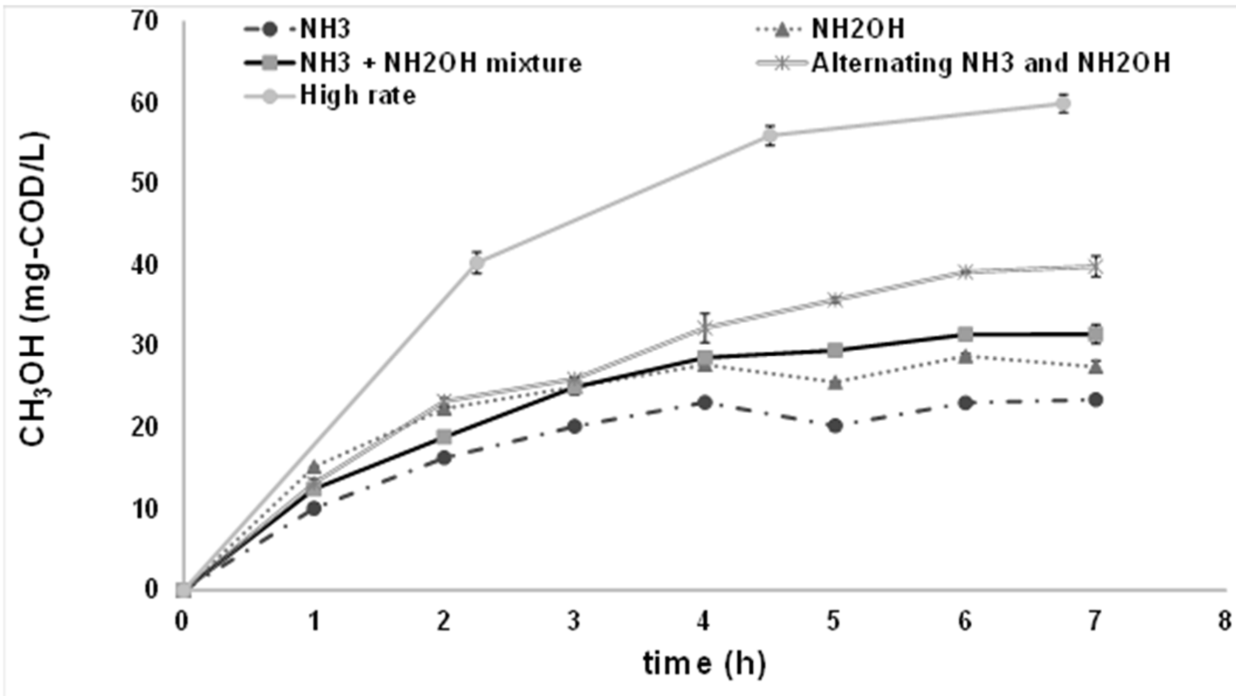
- **Catabolic reaction:**

$$NH_3 + 1.5O_2 \xrightarrow{G^{catabolic} = 274.75\frac{KJ}{molN}} NO_2^- + 2H^+$$

$$m_{NH3} = 0.0072\frac{mgN}{mgCOD.h}$$

Taher & Chandran, 2013, ES&T

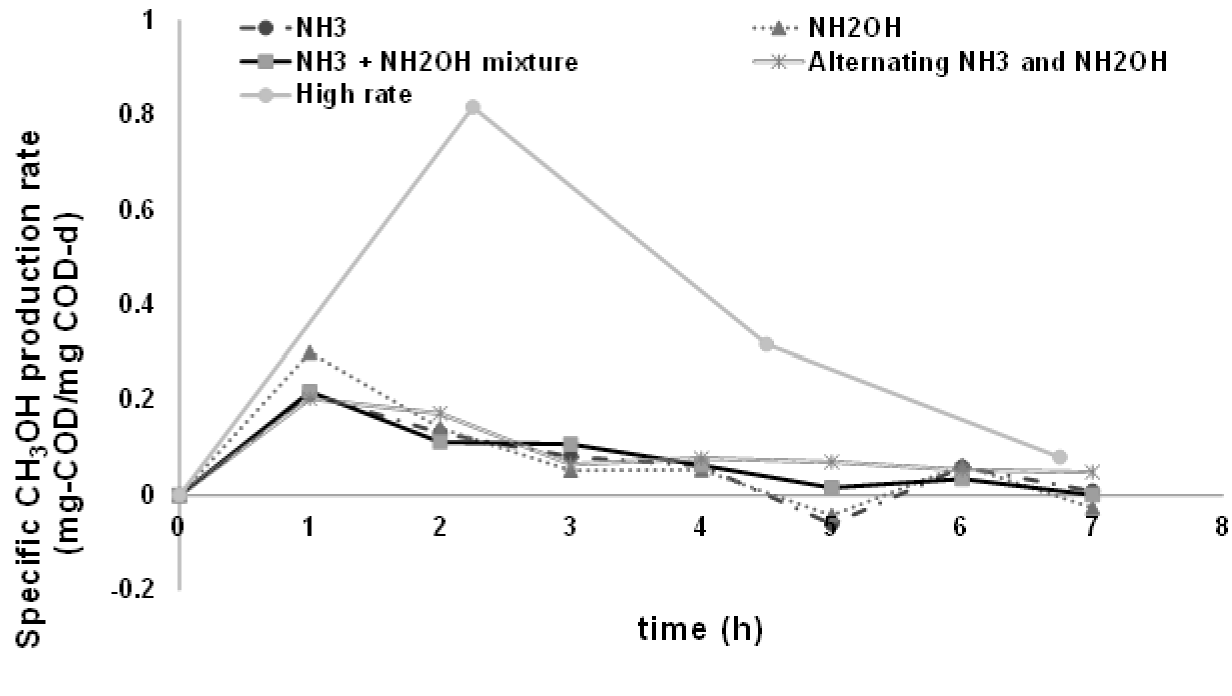
Cumulative CH_3OH production



- Switching between NH_3 and NH_2OH supply gave the highest CH_3OH yield

Taher & Chandran, 2013, ES&T

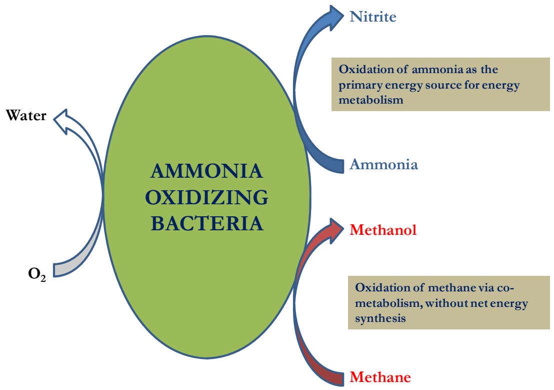
Rate of CH_3OH production

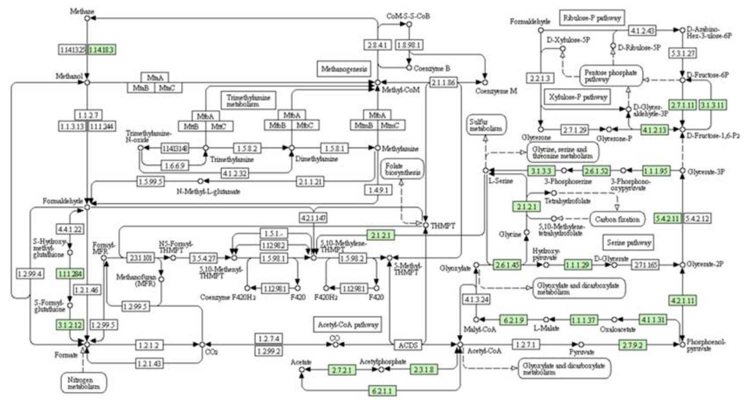


Taher & Chandran, 2013, ES&T

Maximum CH_3OH production rate $\frac{mg\ CH_3OH\ COD}{mg\ biomass\ COD\text{-}d}$	Peak CH_3OH concentration (mg COD/L)	Microbial system used	Reference
0.21	23.47 ± 0.50	Mixed nitrifying cultures NH_3 only feed (FS1)	Taher and Chandran, 2013
0.30	27.50 ± 0.78	Mixed nitrifying cultures NH_2OH only feed (FS2)	
0.22	31.52 ± 1.19	Mixed nitrifying cultures NH_3 and NH_2OH co-feed (FS3)	
0.20	40.71 ± 0.16	Mixed nitrifying cultures NH_3 and NH_2OH alternating feed (FS4)	
0.82	59.89 ± 1.12	Mixed nitrifying cultures NH_2OH only feed with biomass replenishment (high rate)	
0.37	28.8	Pure suspended cultures of *Nitrosomonas europaea*	Hyman and Wood, 1983
0.31-0.54	NA	Pure suspended cultures of *N. europaea*	Hyman et al.,, 1988
0.02-0.1	6.2 ± 4.9	Pure immobilized cultures of *N. europaea*	Thorn, 2007

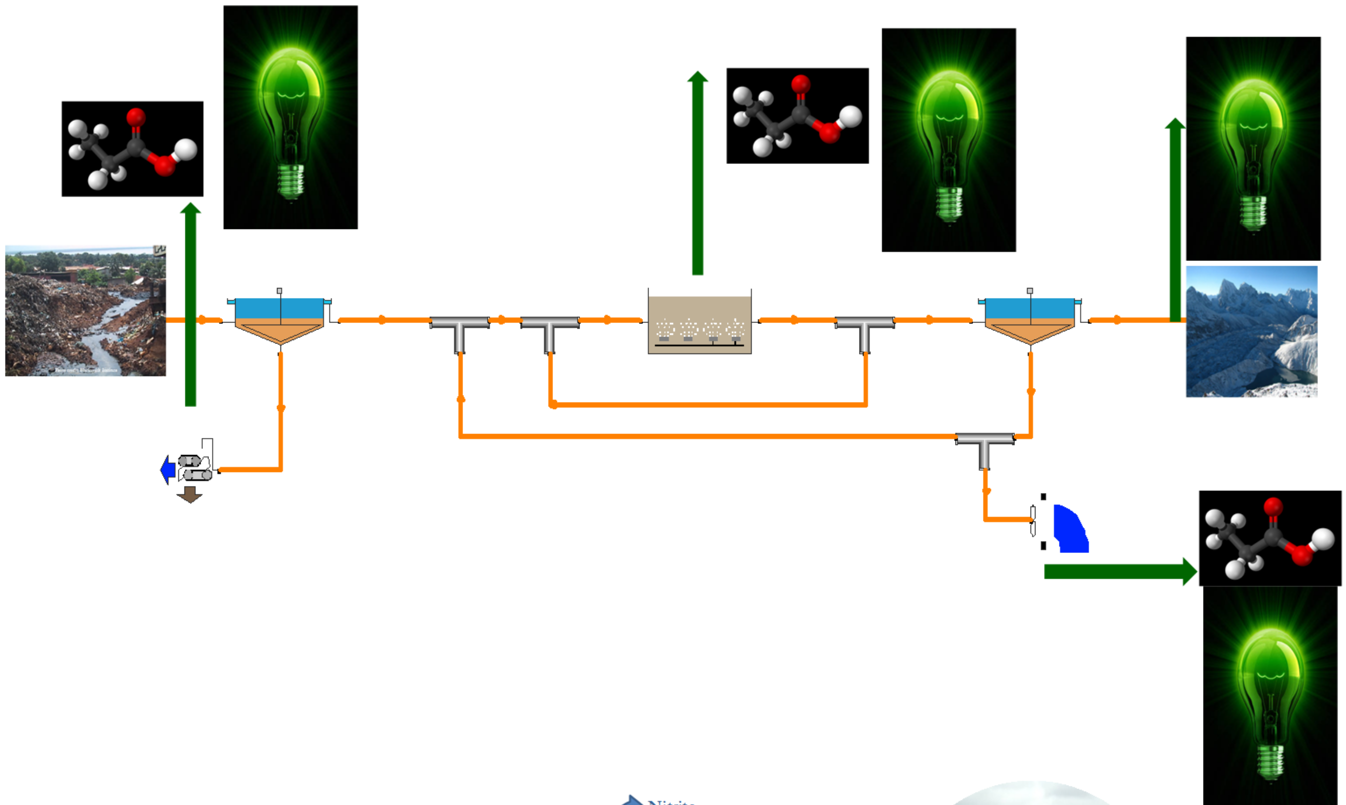
Summary

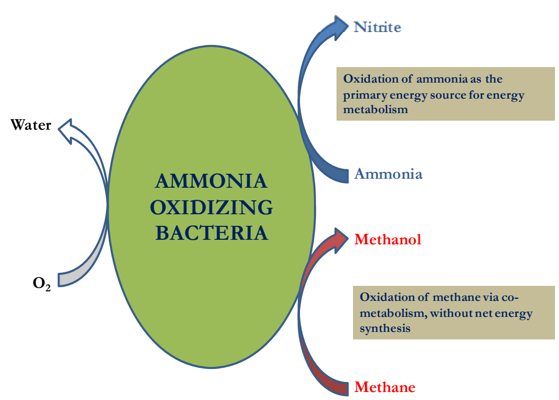




- **Proof of concept developed in batch and continuous mode for converting CH_4 to CH_3OH using AOB**
- **Next**
  - **Understand the system wide impact of CH_4 exposure and conversion in AOB**
  - **Leverage the results of the Paul Busch research to implement process at wastewater treatment plants**
    - Accelerate path towards process engineering and optimization

Water-Energy-Food-Cities





Discussion

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