EARTH ENERGY RENEWABLES

Conversion of Citrus Peel to High Value Chemicals

Production of short and medium-chain fatty acids from citrus by-products and residues

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Clearwater Beach, FL

Citrus residues – Challenge and opportunity

Processing citrus generates large amounts of by-products, residues & waste

Processing of oranges produces ~ 55% juice, 45% other

Source: E. Grant, Citrus World, *AngusJournal*, Feb 2007, 234-238.

By-products & residues from orange processing

Product	kg/box Oranges*
Dry pellets (10% H_2O)	4.0
Molasses (72 °Brix)	1.4
Essential oil/d-limonene	0.3
Pulpwash soluble solids	0.3
Pectin (150 grade)	1.3
Frozen pulp	2.0
Flavonoids	0.2

* 90 lb or 40.8 kg/box, 55% Juice

Source: RM Goodrich, JR Braddock, Doc. FSHN05-22, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, UF, 2006.

Citrus residues dried, pellitized for cattle feed

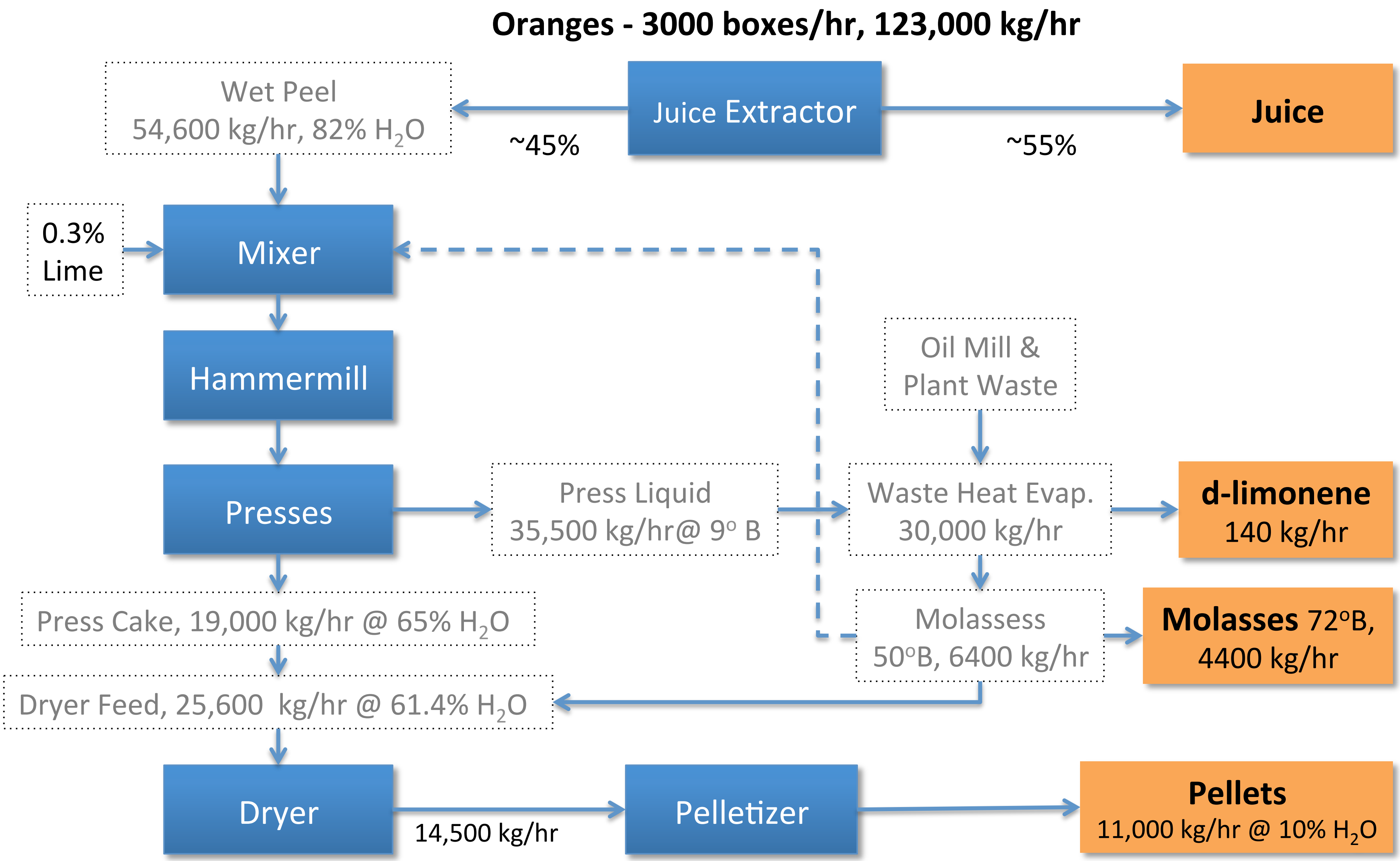
Processing citrus residues as cattle feed

- Most citrus residue is milled, dried and pelletized for use as cattle feed sold in US and Europe
- Energy intensive
- Current market price ~ $130/ton
- Cost of milling/drying/pelletizing $50 - $90*
- Profitability is modest
- Is the *" intent of the feedmill …. the least cost disposal of this (waste) material?"*

*Source: Kris Bevill, Biomass Magazine, http://biomassmagazine.com/articles/1531/freshly-squeezed-ethanol-feedstock

Source: E.Grant, CitrusWorld, Angus*Journal,* Feb 2007, 234-238.

Typical process flow for drying citrus residues



Source: RM Goodrich, JR Braddock, Doc. FSHN05-22, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, UF, 2006.

Consider production of biogas from citrus residues?

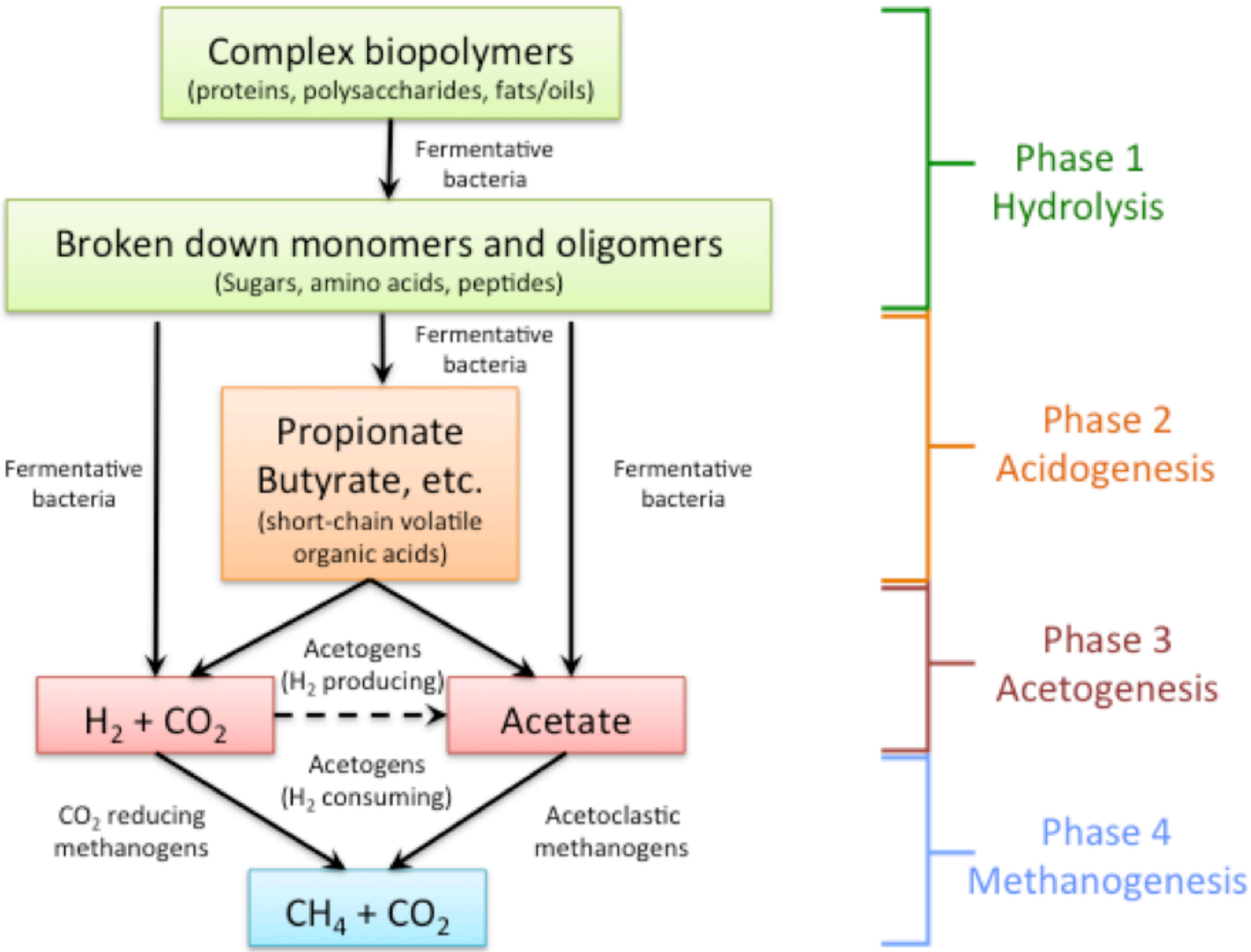
Can we convert orange waste to biogas by Anaerobic Digestion (AD)

- Microbial consortium break down bio-polymers, carbohydrates, and proteins to bio-gas (CH_4, CO_2, H_2S)
- Biogas can be used for energy content (heat, electricity generation)
- Undigested material can be composted and used as a fertilizer/soil

Citrus waste is highly digestible, but

- Citrus residue is rapidly converted into volatile fatty acids (VFAs) resulting in low pH
- d-limonene in citrus is an antimicrobial capable of causing failure of AD at low concentrations
- Methanogens (methane forming archaea) in the consortium are most susceptible to low pH and d-limonene

Anaerobic digestion is a biological process



Source: CB Clifford, www.e-education.psu.edu/egee439/node/727, ©Penn State University

Intermediate acids and d-limonene are problems

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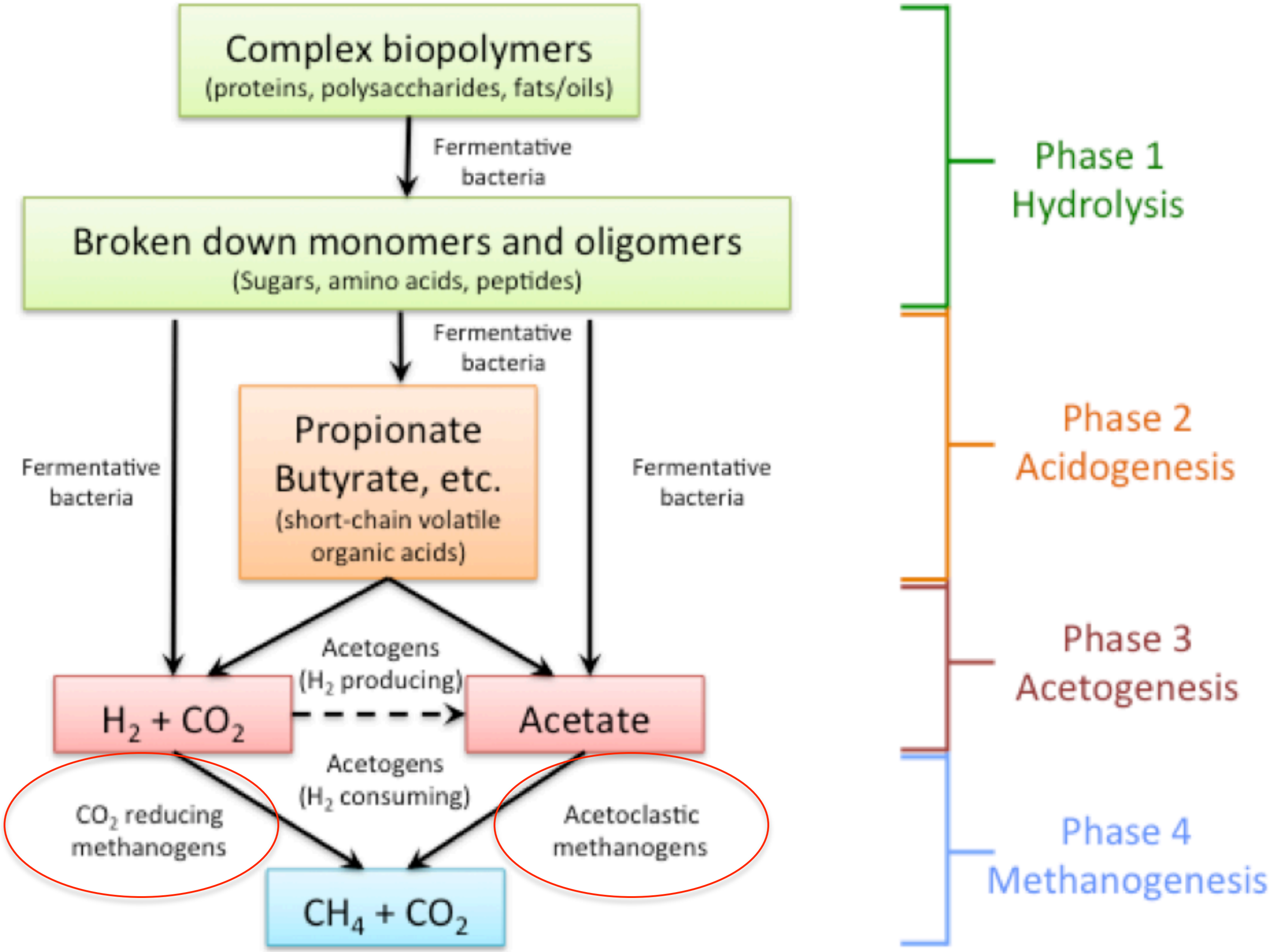
Source: R. Wikandari et al., Biogas Production from Citrus Waste by Membrane Bioreactor, **Membranes**, 2014, 4, 596-607.

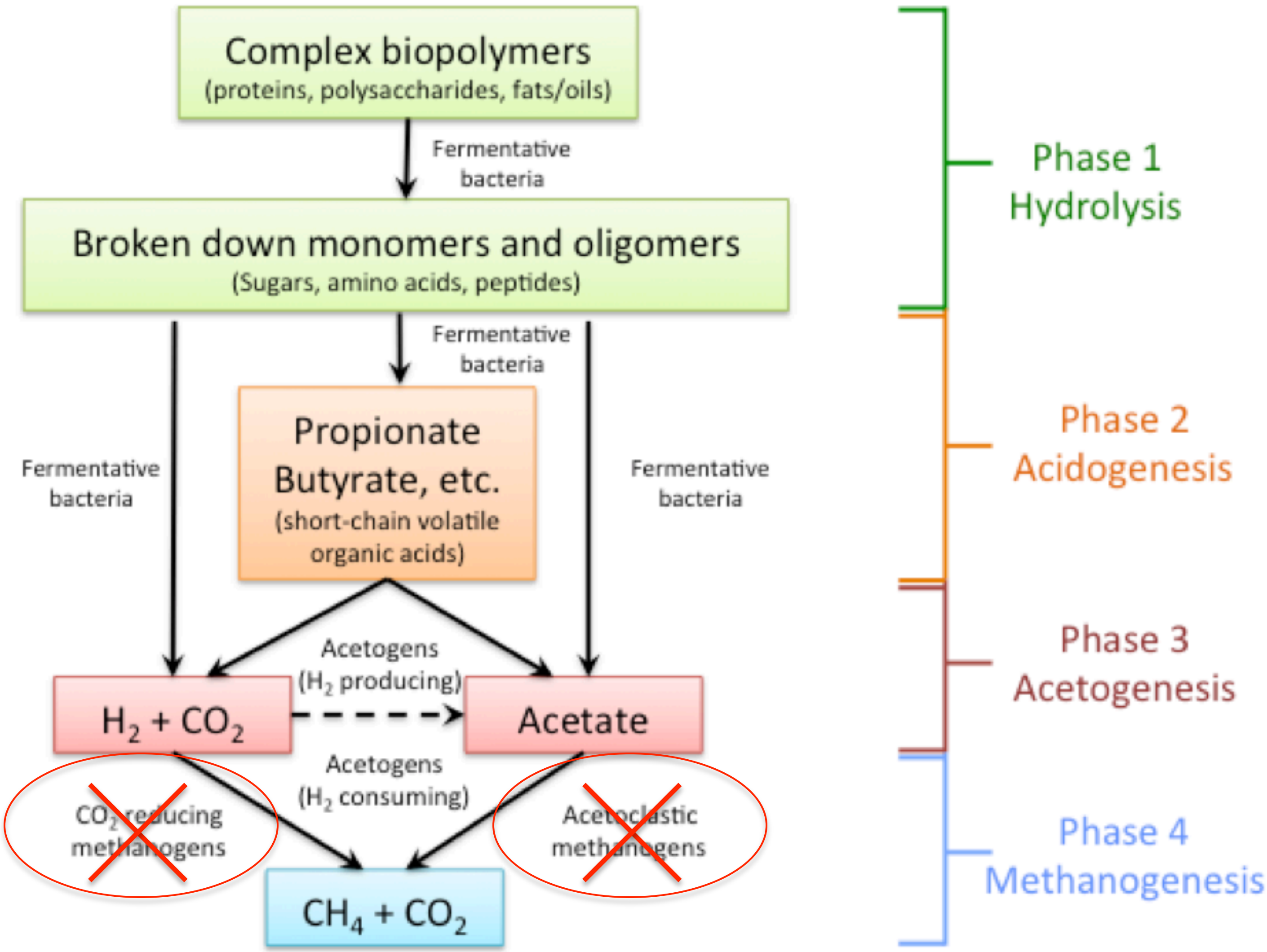
Methanogens are inhibited by d-limonene, acids



Methanogens are fragile and shut down easily

Source: CB Clifford, www.e-education.psu.edu/egee439/node/727, ©Penn State University

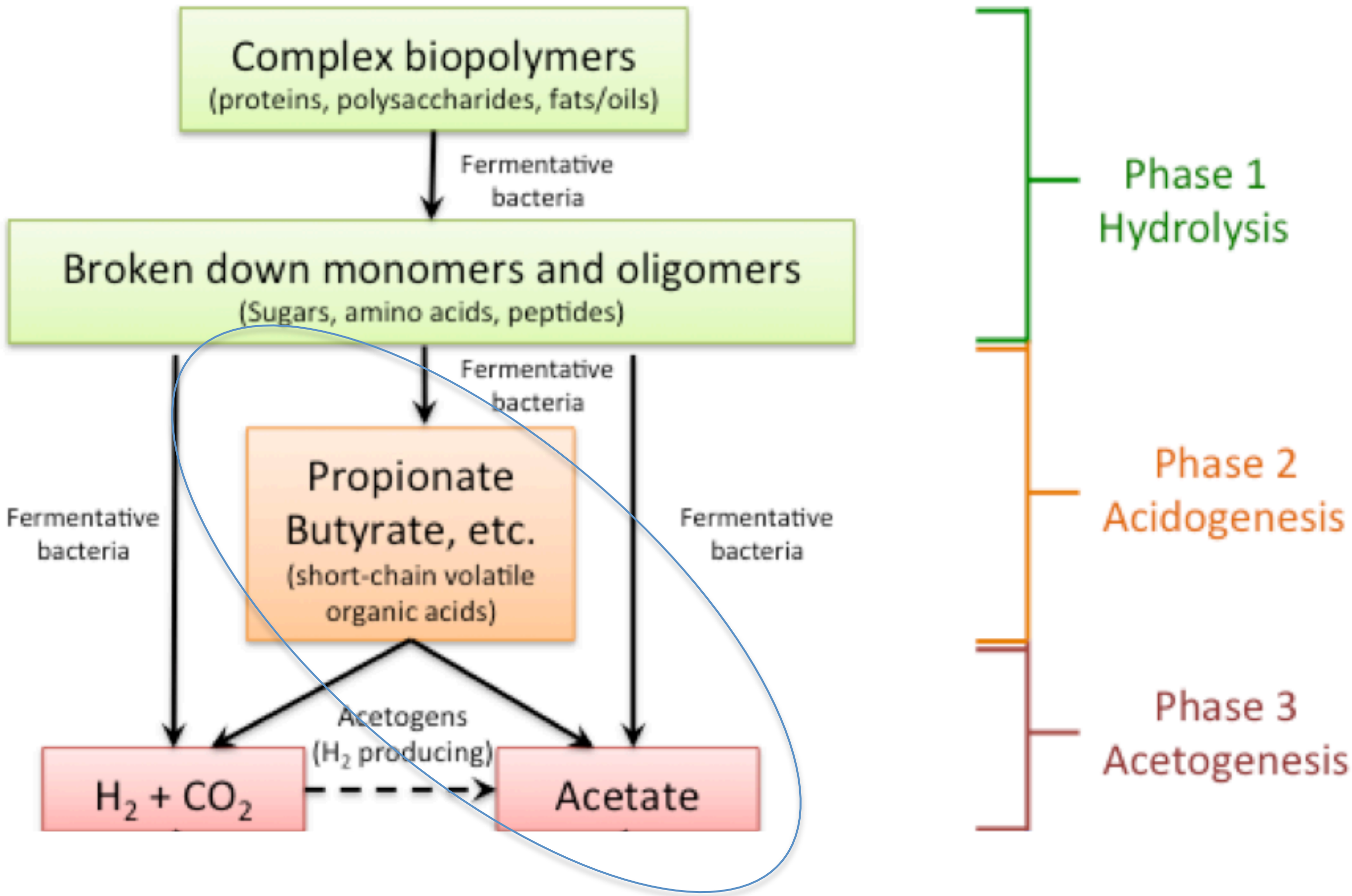
d-limonene is not needed to inhibit methanogens



We can adjust operating conditions or use additives to inhibit methanogens

Source: CB Clifford, www.e-education.psu.edu/egee439/node/727, ©Penn State University

On purpose production of volatile fatty acids



Fermentation broth relatively rich in $C_2 – C_8$ volatile fatty acid salts

$C_2 – C_8$ volatile fatty acids are 20 to 30 times more valuable than methane

A novel, simple, low-cost route to volatile fatty acids

FEEDSTOCK

Food Waste

Orange Peels

Palm Oil Mill Effluent

Bakery Residuals

Sugar Mill Vinasse

BIO CONVERSION

Modified Anaerobic Digestion

PRODUCTS

C_2 – C_8 Organic Acids

Short/Medium-Chain Fatty Acids

Volatile Fatty Acids (VFAs)

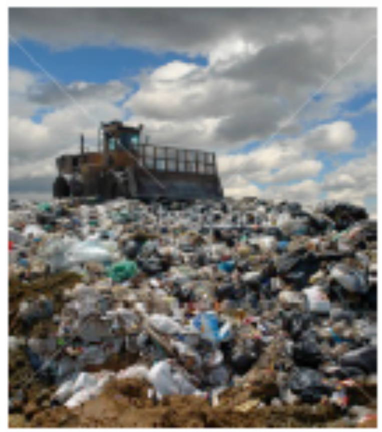
- Acetic acid
- Propionic acid
- Butyric acid
- Isobutyric acid
- Valeric acid (Pentanoic)
- Iso-valeric acid
- Caproic acid (Hexanoic)
- Heptanoic acid
- Caprylic acid (Octanoic)

Derivatives

Any bio-degradable residue or waste as feedstock

Over 30 Feedstocks Successfully Tested

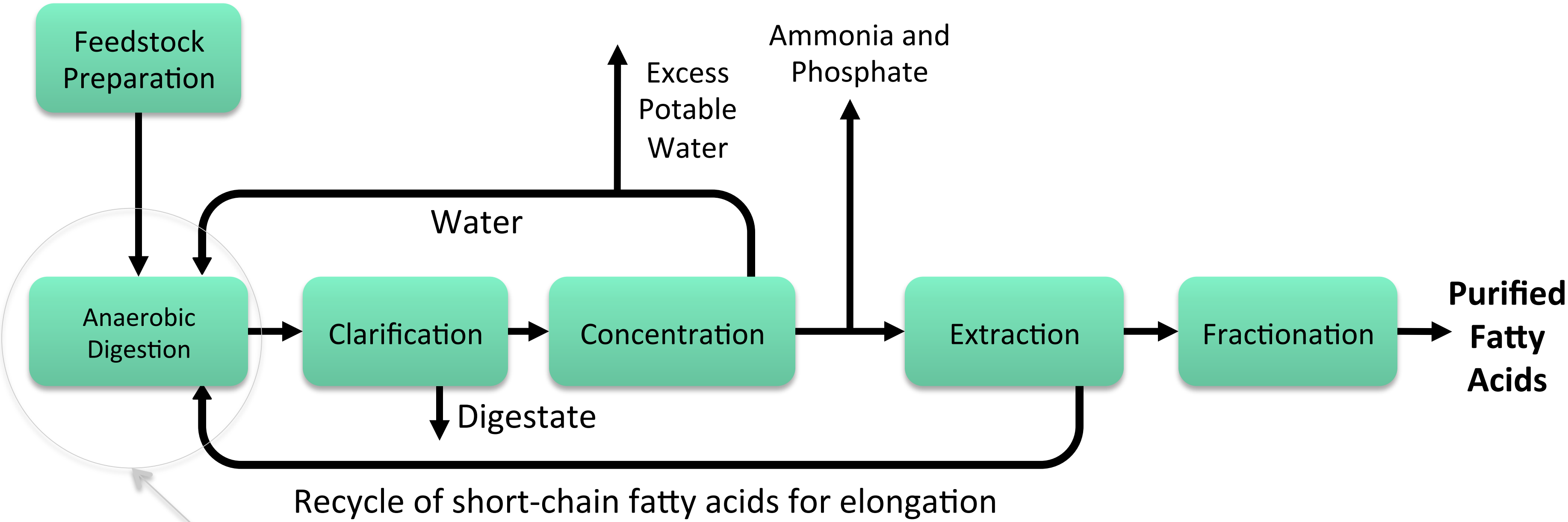
- Orange peel
- Corn Whole Stillage
- Corn Thin Stillage
- Bakery residuals (raw)
- Bakery resids (dried)
- Food wastes
- Paper fines/sludge
- Paper-mill fines
- Sugarcane bagasse
- Glycerol
- Raw Glycerin
- Corn Stover
- Rice Straw
- Cotton gin trash
- Water hyacinth



- Oil Palm empty fruit bunch
- Palm oil mill effluent
- Whole stillage
- Sugarcane molasses
- Sorghum stalks
- Municipal sewage sludge
- Cellulosic municipal solid waste
- Bio-sludge (chem plant WWTP)
- Chicken manure
- Cattle manure
- Sugar beet pulp
- Lipid-extracted micro-algae
- Whole micro-algae
- Pulp-mill molasses
- Switchgrass

Anaerobic digestion to produce VFAs

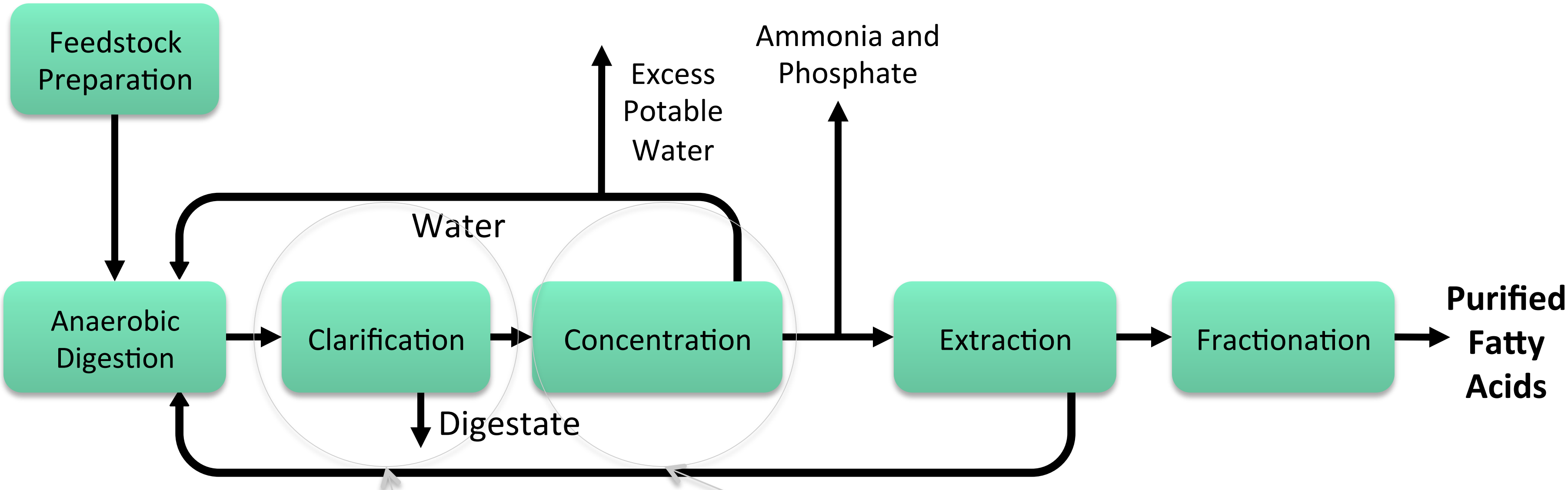
Innovative integration of mature, well-understood technologies



Anaerobic Digestion

- CH_4 production is inhibited
- Non-sterile process with natural cultures (microbial consortium)
- VFAs are thermodynamically favored
- Robust operating with high yields
- Result: Broth of salts of acids, undigested feed, micro-organisms

Clarify broth and concentrate the VFAs



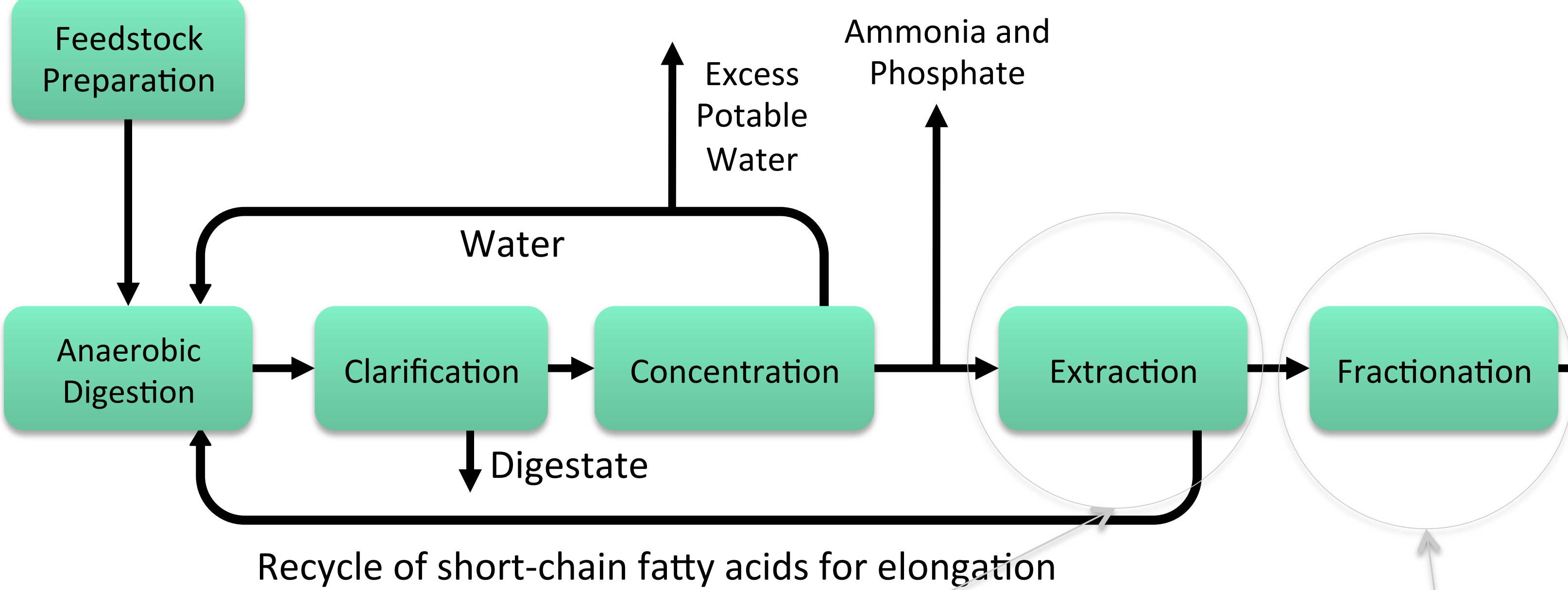
Clarification

- Centrifugation to remove large solids
- Ultra-filtration to remove small solids
- Clarified broth

Concentration

- Reverse Osmosis
- Increase fatty acid salt concentration 4x
- Concentrated clarified broth

Extraction and fractionation to recover purified VFAs



Extraction

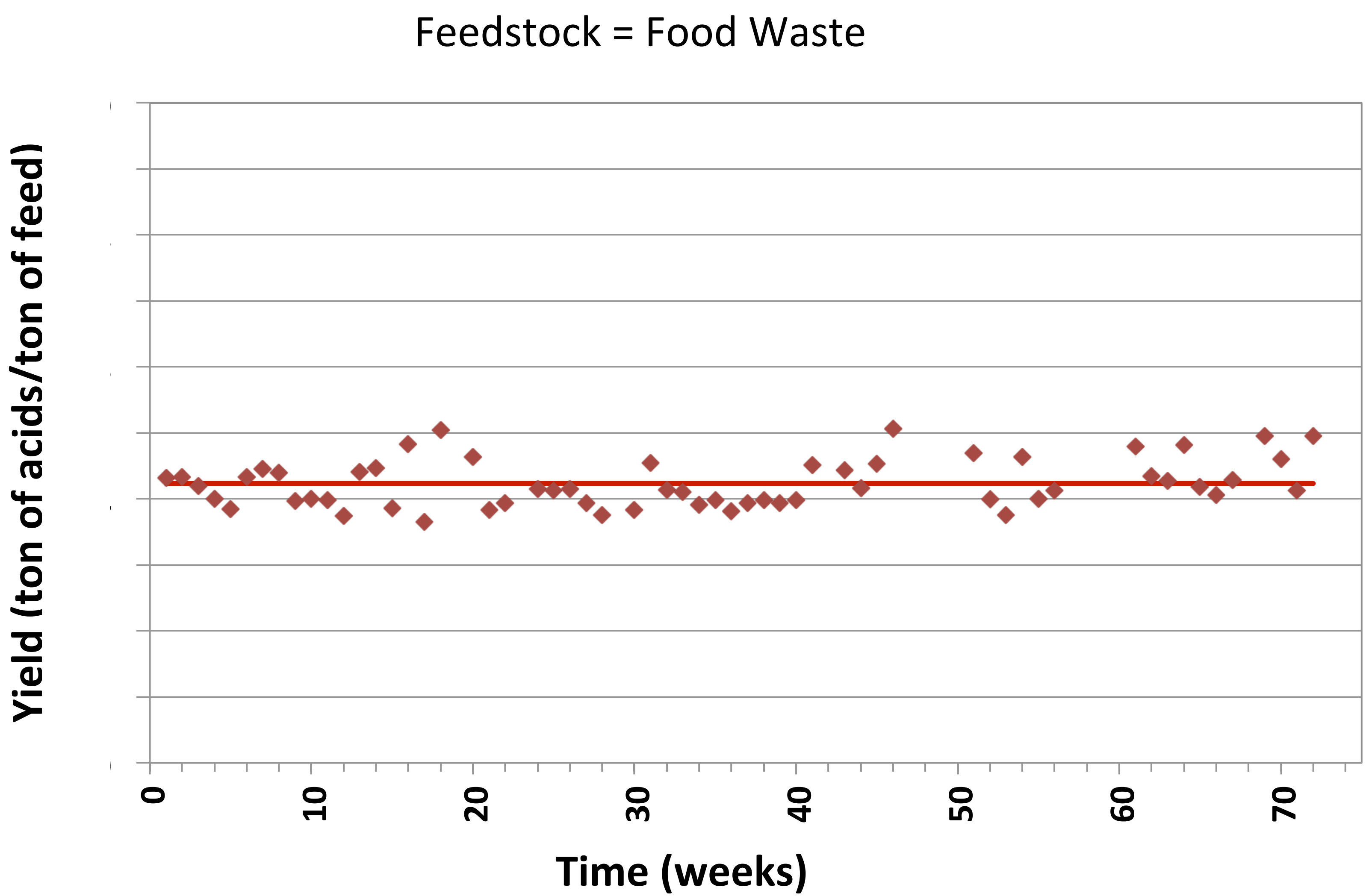
- Proprietary Intellectual Property
- Solvents: Clean
- Simple, efficient, and effective
- Clean mixed acid stream

Fractionation

- Distillation
- Separation based on boiling points
- Distinct, purified acid streams

3 TPD methane-inhibited AD demonstration plant

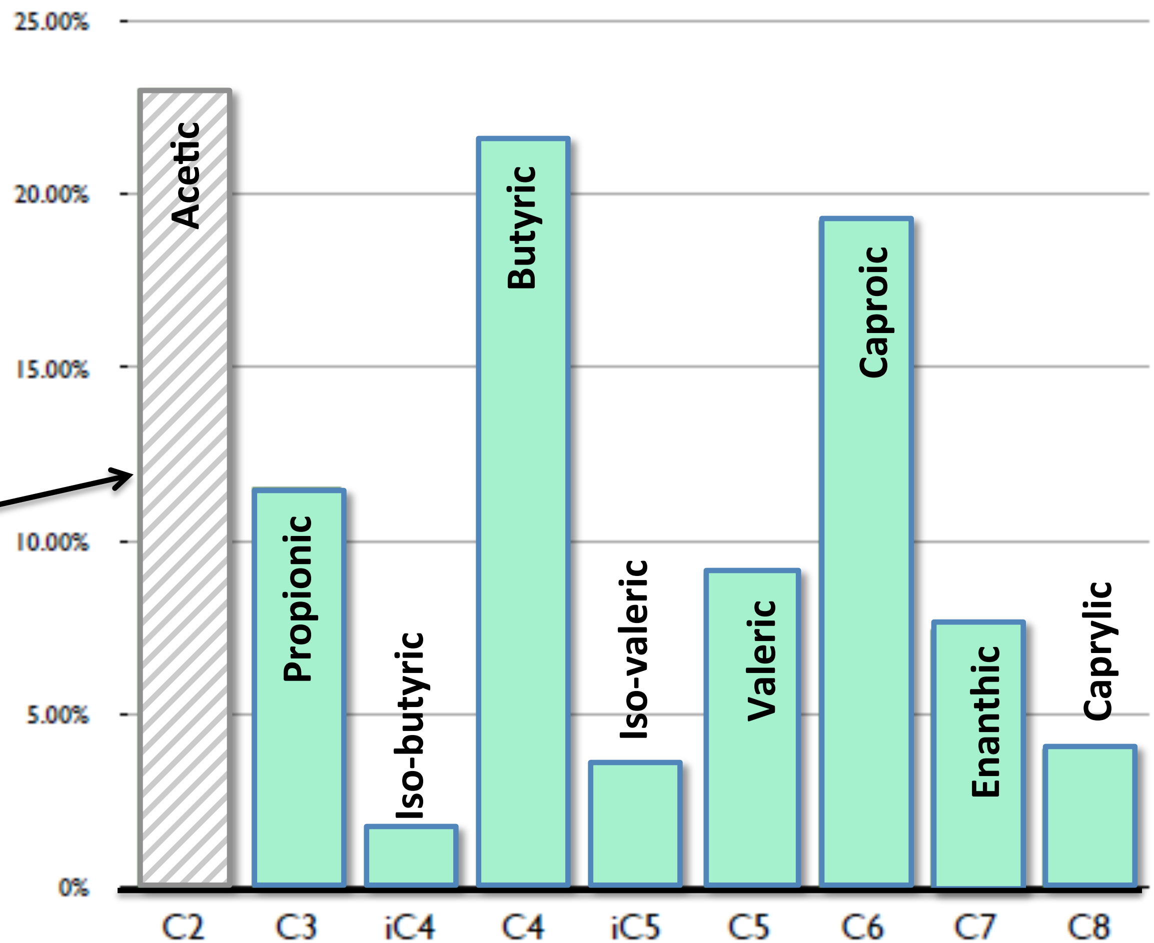
Demonstration plant yield of fatty acids – 72 weeks



Distribution of C_2 - C_8 acids from food waste

Typical Fatty Acid Profile in Anaerobic Digestion Broth

Acetic acid can be recycled to elongate it and, thus, eliminate it, thereby increasing C_3-C_8 acids.



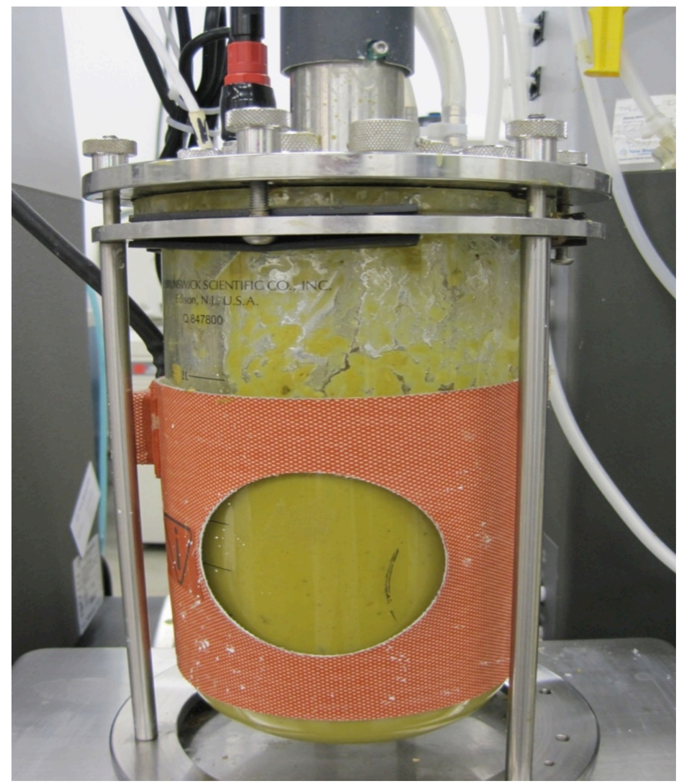
The product distribution can be shifted to shorter or higher average chain lengths by employing different feedstocks or modifying operating conditions.

Citrus residues to volatile fatty acids

- Pressed orange peels fermented in a semi-continuously operated chemostat
- Fresh substrate and water added daily; liquid and solids were removed daily
- Inoculum from laboratory food scrap fermentations

As received

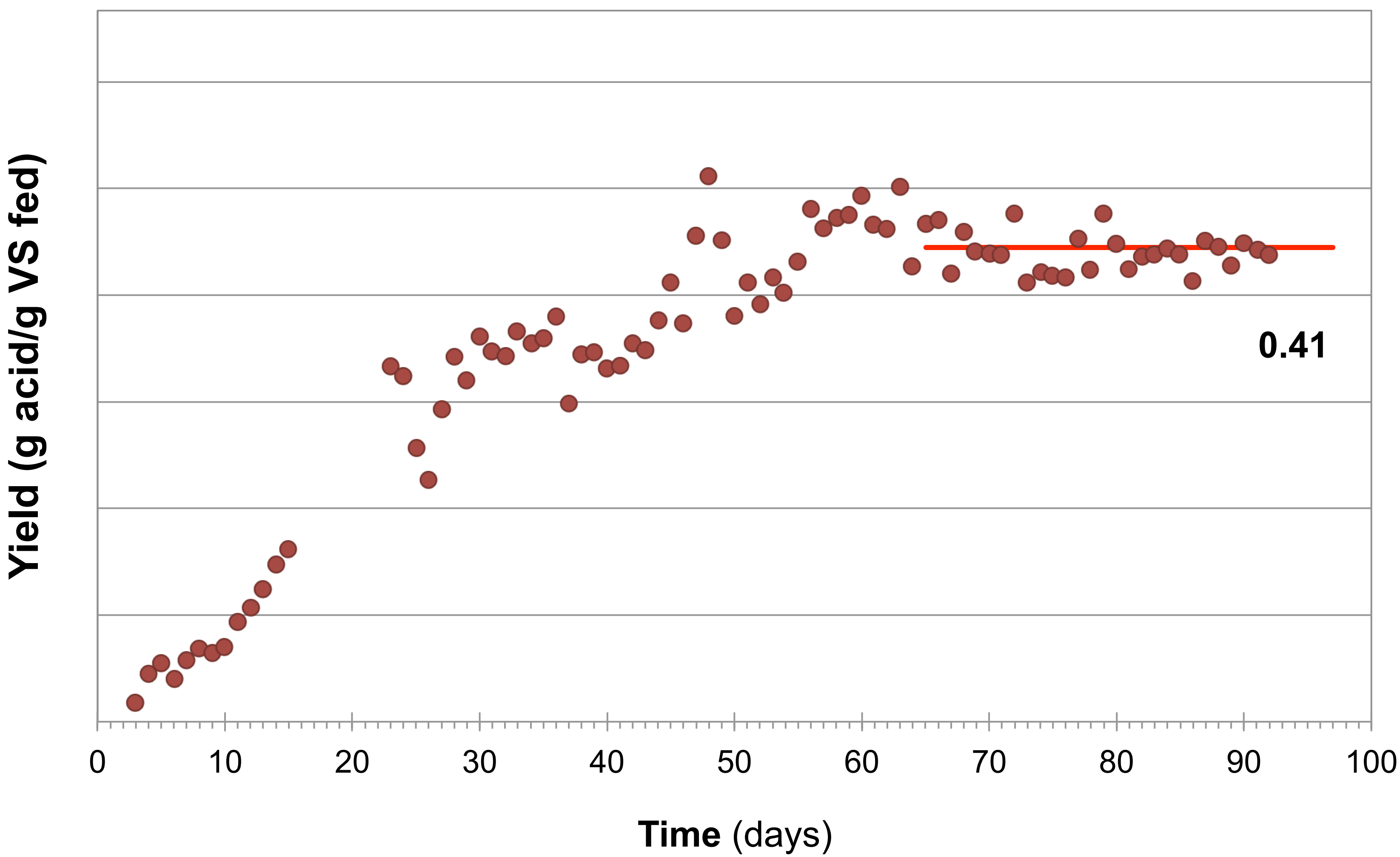
Ground for use



Composition of pressed orange peel

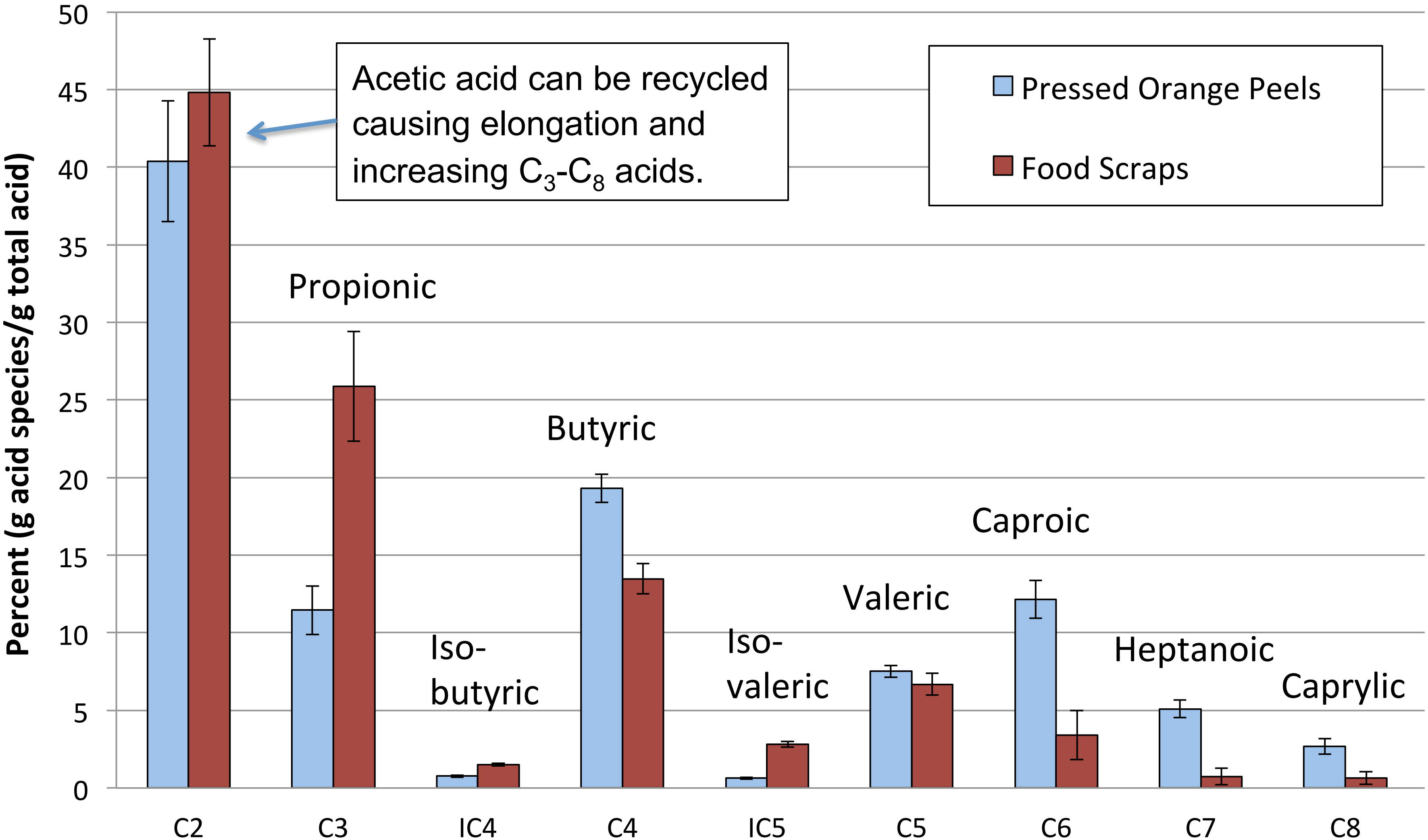
Component	Percentage
Moisture (wet basis)	63.6
Ash (dry basis)	6.2
Crude Protein	23.1
Polymeric Carbohydrates	24.0
Free Sugars	8.6
Hexane Extractives (fats)	2.7
Other extractives	35.4

Yield of VFAs from pressed, dried citrus peel



Addition of pectinase, cellulase, hemi-cellulase resulted in thinning of the broth and increased yields of ~20%

Distribution of VFAs from citrus peel



The product distribution can be shifted to shorter or higher average chain lengths by modifying operating conditions.

Many existing applications & markets for VFAs

Propionic Acid

Butyric Acid

Valeric Acid

Caproic Acid

Heptanoic Acid

Caprylic Acid

Animal Feeds
Feed Preservatives
Food Preservatives
Herbicides
Pharmaceuticals

Cellulose Acetate
Butyrate Propionate
(CAB/CAP)

Flavor and Fragrance

Neopolyolesters (NPE)

Polyethylene/
Propylene Glycol
(PEG/PG) Esters

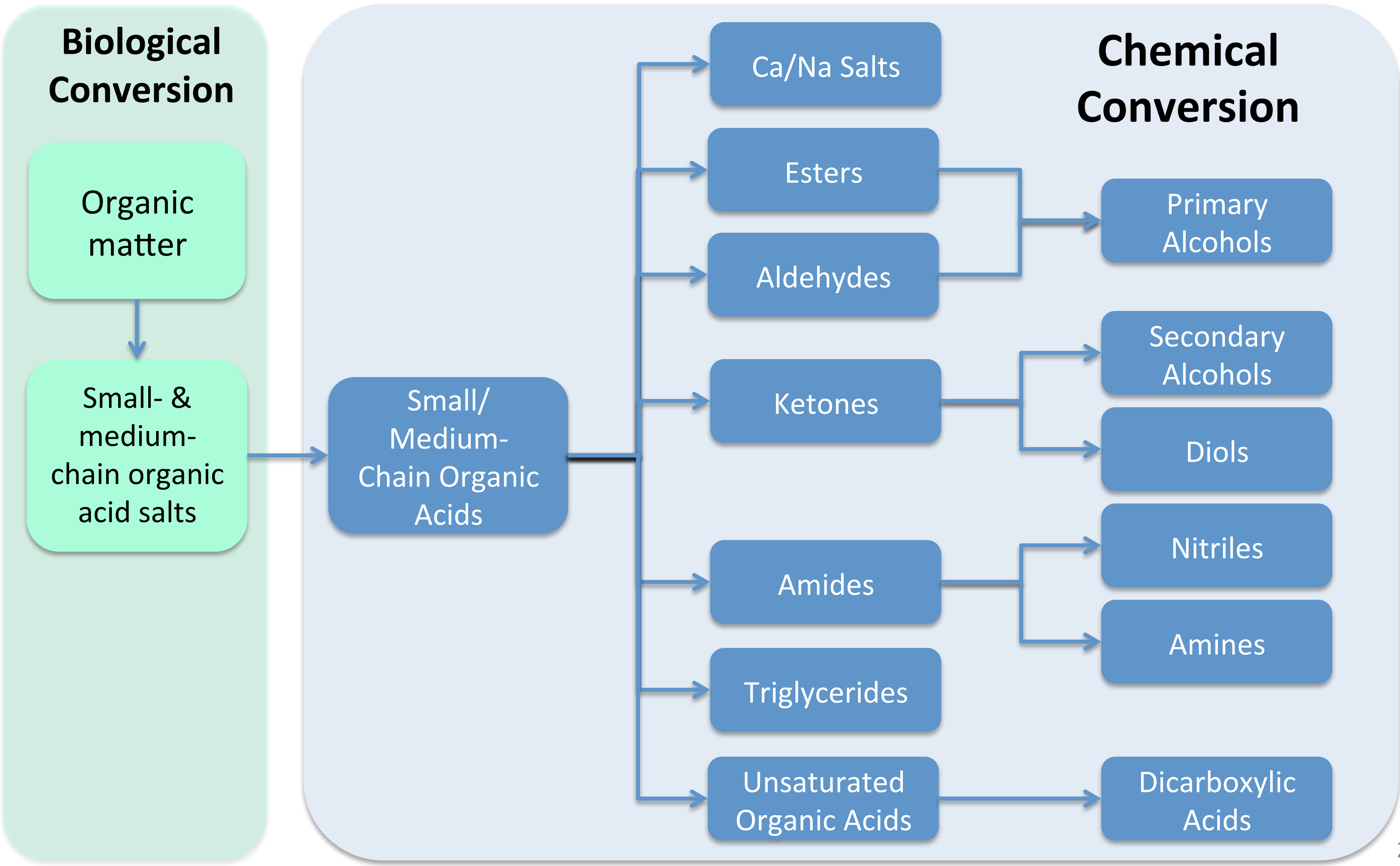
Resins
Rheology
Modifiers
Coatings
(Automotive)

Lubricants

Emulsifiers
Thickeners
Resin Plasticizers
Viscosity Control
Wetting Agent
Emolients

Organic acids - easily converted into derivatives

Basis for a new bio-chemical platform



Derivatives markets are orders of magnitude larger

	Flavor & Fragrance	Animal Feeds	Feed & Food Preservatives	Pers'l Care, Cosmetics	Herbicides, Pesticides, Fungicides	Pharma	Cleaners, Detergents	Surfactants	Coatings, Adhesives	Plasticers	Solvents, Siccatives	Plastics , Resins	Lubricants	Fuels
Fatty acids/salts	✔	✔	✔		✔			✔	✔	✔	✔		✔	
Esters	✔	✔		✔			✔	✔	✔	✔	✔		✔	
1^{o} alcohols	✔			✔			✔		✔			✔		✔
2^{o} alcohols					✔	✔					✔			✔
Ketones						✔					✔			
Dicarboxylic acids				✔						✔		✔	✔	
Diols				✔	✔							✔	✔	
Amides						✔					✔	✔		
Amines, Nitriles						✔					✔			
Olefins							✔					✔		
Alkanes														✔

Techno-economic analysis

Parameter	Medium-chain Fatty Acids	Medium-chain Fatty Acids	Medium-chain Fatty Acids
Feed Input, dry TPD	30	130	260
Feed Input, actual (dry basis) MT/yr	9,410	40,800	81,500
CAPEX	$19,600,000	$60,400,000	$101,500,000
Product Price, $/kg	$3.00	$3.00	$3.00
Revenue, $/yr	$12,700,000	$55,000,000	$110,100,000
Total OPEX (no depreciation), $/yr	$3,900,000	$11,500,000	$20,200,000
EBITDA, $/yr	$8,800,000	$43,500,000	$89,900,000
ROI based on EBITDA	45%	72%	89%
Payback time based on EBITDA	2.2	1.4	1.1
Production cost (no depreciation) $/ton	$847	$571	$500
EBITA, $/yr	$7,600,000	$39,900,000	$83,800,000

Margin potential: Cattle feed vs. VFAs

Assuming a facility processes 75,000 boxes of oranges per day during the ~6 month harvest season. Each box produces 4 kg dry peel (10% water) or 3.6 kg bone dry peel.

Peel Waste to Cattle Feed

Market Price = $130/ton

Operating Cost = $50 - $90/ton*

Assume $130/ton market price and $50/ton operating cost

Revenue Potential = ~$7,000,000

Cost of Production = ~$2,700,000

Margin Potential = ~$4,300,000

*Source: Kris Bevill, Biomass Magazine, http://biomassmagazine.com/articles/1531/freshly-squeezed-ethanol-feedstock

Peel Waste to Organic Acids

Market Price = $1000 - $7000/ton acid

Operating Cost (w/o feedstock) = ~$750/ton acid

Assuming: Ave Mkt Price = $3000/ton acid

Revenue Potential = ~$67,000,000

Cost of Production = ~$17,000,000

Margin Potential = ~$50,000,000

Earth Energy Renewables

1995

University Research

Texas A&M MixAlco Process Prof. Mark Holtzapple 1995 to 2007; '96 EPA Green Chem Award

2007

Lab & Pilot

Terrabon, Inc. Fermentation Tests Bench-scale 2 – 10 L and 4000 gal pilot

2009

Demo

Terrabon, Inc. Demonstration Scale plant 100,000 GPY Bryan, TX

2011

DARPA

Terrabon Inc. Jet fuel Demo Plant under DARPA contract 2011

Over $70 Million Invested

2012

Earth Energy Renewables LLC

Earth Energy acquires all assets, demo plant, & IP Nov '12. Keeps key tech and ops staff.

2015

Production of Pure Acids and Their Benchmarking

EER pivots toward high value short- & med-chain organic acids based on same core process.

Focus on secondary alcohols, hydrocarbons

Focus on organic acids

Facilities located near Texas A&M University

Lab, pilot and demonstration scale operations

Take-home messages

1. **Technology has the potential to be disruptive in some industries**
   - Simple, robust process based on mature unit-ops; No new-to-world technologies
   - Proven in part at pilot scale and in part at demonstration scale
2. **Citrus processing residues are promising feedstock**
   - Readily digestible by anaerobic digestion; High yields
   - Already aggregated in central locations
3. **Markets for volatile fatty acids and derivatives are large and global**
   - VFAs by EER process qualify as natural products
   - VFAs can be converted to a wide range of other valuable chemicals
   - Process has potential to serve as basis for a new chemicals platform
4. **Potential for substantial economic returns**
   - Favorable economic structure
     - Low capex/opex, feedstock cost, high yield, high product price
   - Profitable at small scale; Industrial markets benefit from economies of scale

This is not another citrus waste to ethanol story!

Generating more value from citrus processing residues

“Simplicity is the ultimate sophistication”

Leonardo Da Vinci