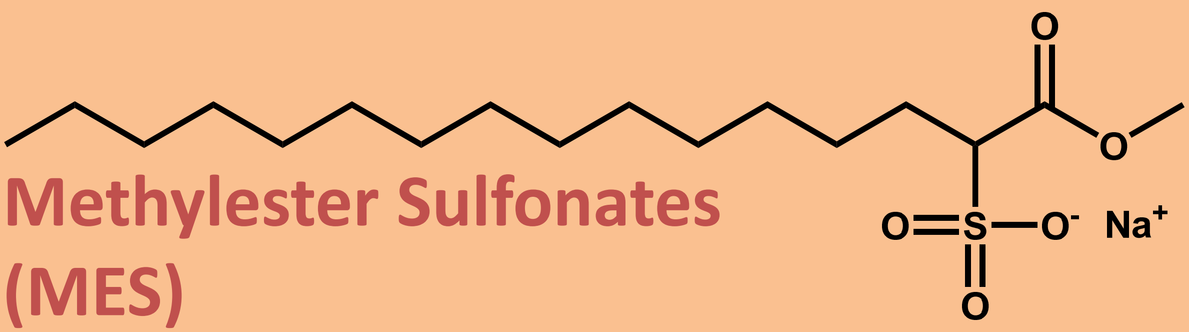
Biobased Surfactants: A Useful Biorefinery Product That Can Be Prepared Using Green Manufacturing

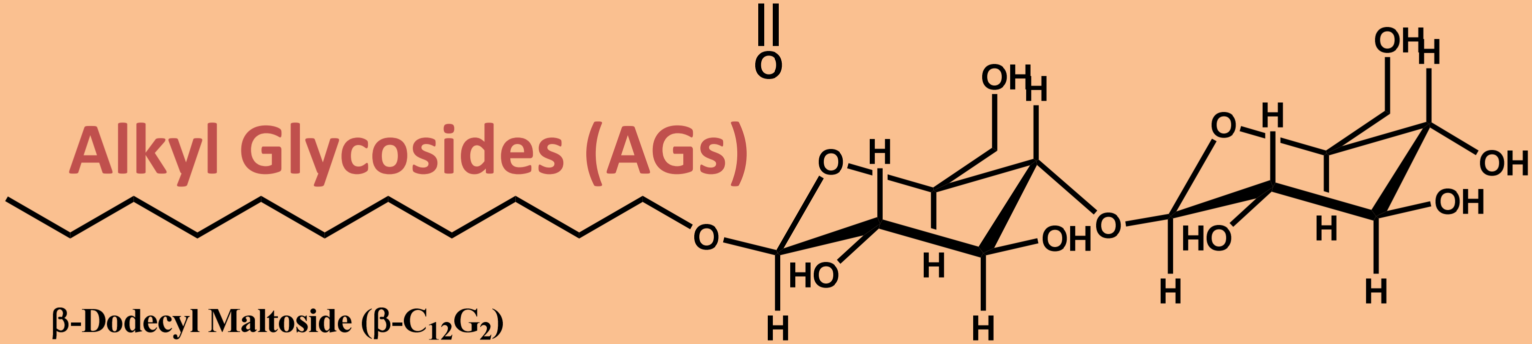
Douglas G. Hayes
Dept Biosystems Engineering & Soil Science
Univ. Tennessee, Knoxville, TN 37996 USA
dhayes1@utk.edu

Outline

1. Overview of Biobased Surfactants (a viable biorefinery commodity)
2. Perspectives for enzymatic preparation of biobased surfactants
3. Overview: Lipase-catalyzed synthesis of sugar esters



Methylester Sulfonates (MES)



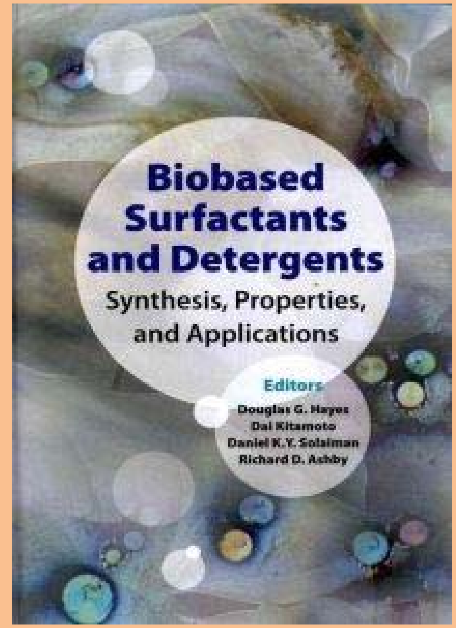
Alkyl Glycosides (AGs)

β-Dodecyl Maltoside (β-$C_{12}G_2$)

Biobased Surfactants: An Economic Perspective

- **Surfactants and Detergents: $24.3 Billion / 14 MMT (2012)**
  - **Household detergents: ~42%, Industrial surfactants: ~29 %, Personal Care: ~16%, Pharmaceuticals: ~7%**
  - **Market share between regions: 30.5% = Europe, 28.5% = North America, 26.3% = Asia / Pacific**
- **Biobased Surfactants: $4.86 Billion / 3.5 MMT (2012)**
  - **~25% of Surfactants and Detergents market**
- **Market share between regions : 46% = Europe, 28% = North America, 18% = Asia / Pacific**
- **Prediction for 2017**
  - **Asia / Pacific will be largest regional consumer of surfactants and detergents**
- **Biobased Surfactants will account for 27.8% of overall market, with the greatest region of growth being Asia / Pacific**
- (courtesy: MarketsandMarkets, Pune (India)

Motivation for biobased surfactants

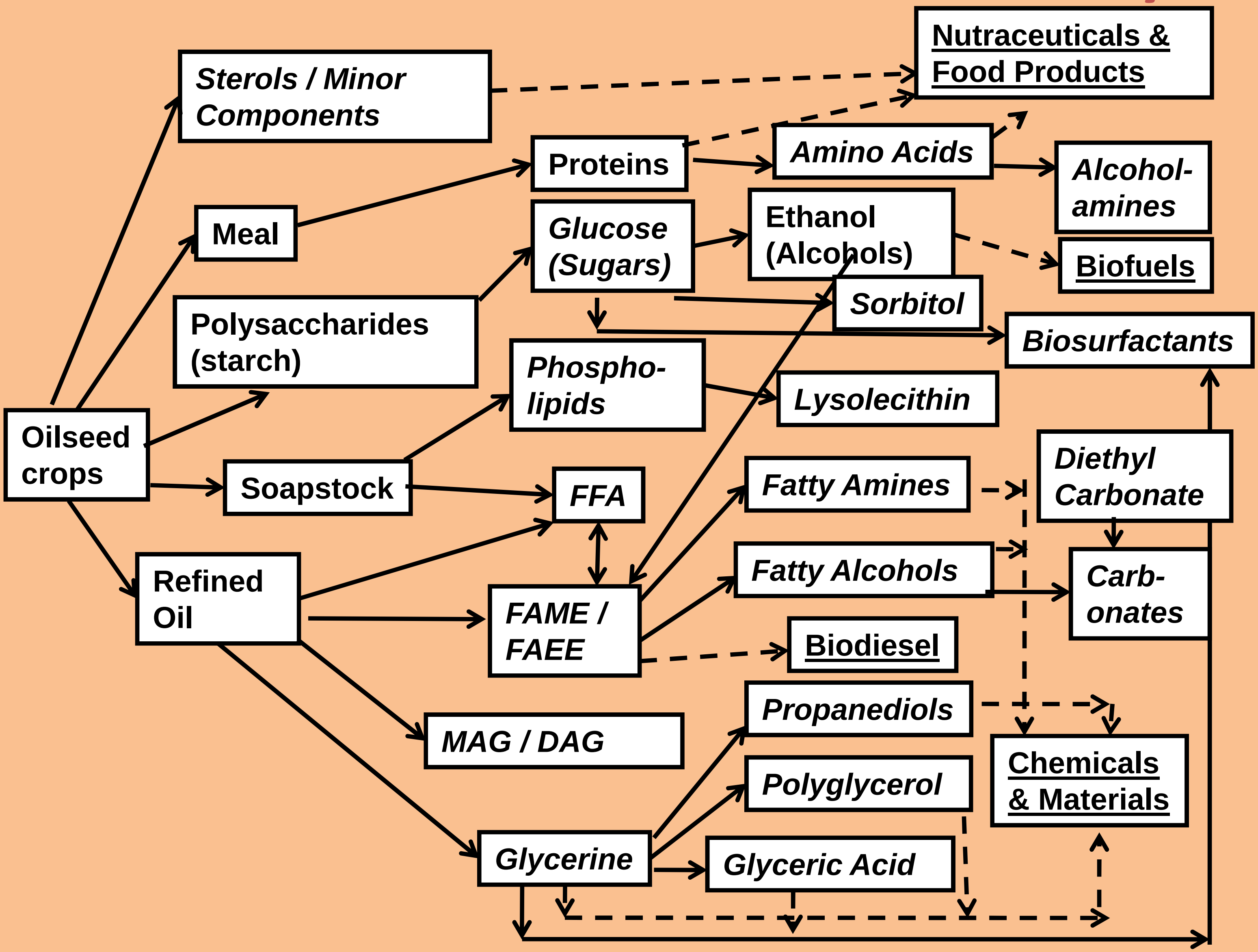


- Synthetic feedstock price surging ($140/bbl for crude oil)
- Production costs (and biodegradability) for biobased ≈ petroleum-based
  (US DOE, *Technology Roadmap for Plant / Crop-Based Renewable Resources* 2020)
- Consumer (and seller) demand for eco-friendly and sustainable products
- Biodiesel → more abundant feedstock supply (fits "biorefinery" model)
- Reduced greenhouse gas (e.g., CO_2) production using biobased feedstocks (a more environmentallly-sustainable beginning-of-life)

Biobased Surfactants: Eco-Friendlier?

- Reduced greenhouse gas (e.g., CO_2) production during manufacture (↑ BB feedstock by 24% → ↓ CO_2 by 8%)
- Replacement of alkylphenyl ethoxylates, APEs, phosphate builders, solvents (more environmentally sustainable end-of-life)
- Increased acreage of palm oil, e.g. →
  - Loss of biodiversity
  - Loss of animal habitat
  - Deforestation
  - Roundtable for Sustainable Palm Oil
- Chemically derivatized biobased surfactants similar to synthetics in terms of biodegradability

Biobased Surfactants and the Biorefinery

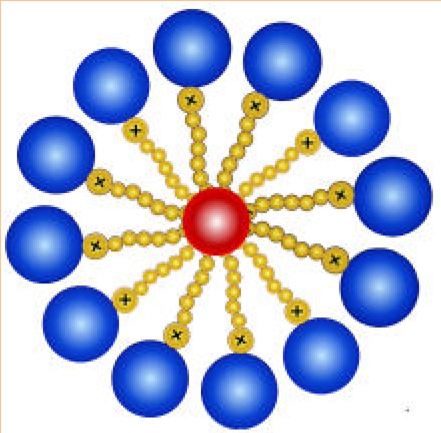


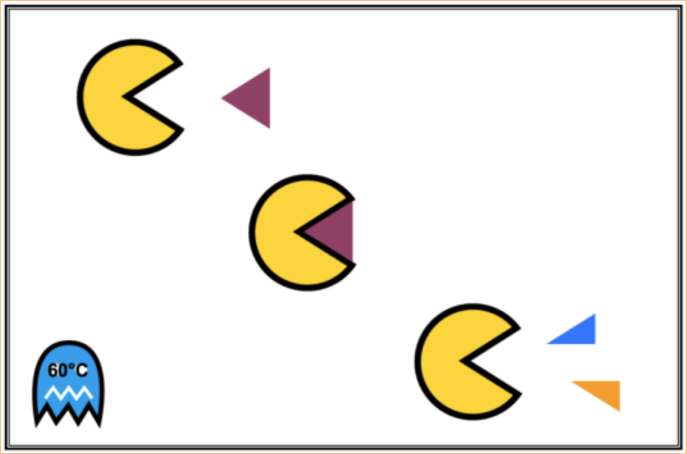
Barriers to Biobased Surfactants

- Increasing prices of oleochemical feedstocks
- Reliability of oleochemical feedstocks
- Price fluctuations of oleochemical feedstocks
- Need for uniform world-wide biobased and eco-friendly labeling
- Need for a domestic oleochemical feedstock suitable for S+D

New Trends for Biobased Surfactants

- Increased use of biobased building blocks for hydrophile
- New and improved biosurfactants: new organisms, genetic modification
- Increased use of low-cost feedstocks: glycerin, used cooking oil, municipal waste, lignin
- Increased development of new biobased surfactants for drug delivery
- Green Manufacturing: Use of enzymes as catalysts





Fatty Acyl Feedstocks for Biobased Surfactants

- **Ideal for food and pharmaceutical use: oleyl (18:1)**
- **Ideal for industrial use: C_{12}-C_{16}, no double bonds**
  - **Palm Kernal Oil (48% 12:0, 18% 14:0, 8% 16:0)**
  - **Palm Stearine (54% 16:0, 5% 18:0, 1% 14:0. 33% 18:1, 7% 18:2**
  - **Coconut (48% 12:0, 16% 14:0, 8% 16:0)**
    - ***Cuphea (enriched in 8:0 – 14:0)***
    - **Common Seed Oils (18:1-rich; significant 16:0+18:0 content)**
    - **Tallow (23-27% 16:0, 15-23% 18:0, 3-4% 14:0, 36-43% 18:1)**
    - ***Jatropha (14.7% 16:0, 6.9% 18:0; 42.4% 18:1 35.2% 18:2)***
    - ***Soapnut (4.7% 16:0; 1.5% 18:0, 7.0% 20:0, 52.6% 18:1, 23.9% 20:1)***
    - ***Algal oils (42% 16:0, 5% 18:0, 26.0 18:1, 14% 18:2)***
      - **Hydroxy fatty acids: castor (lesquerella, dimorphotheca)**
      - **Epoxy fatty acids: vernonia, epoxidized soybean**

Biocatalytic Synthesis of Biobased Surfactants: Advantages

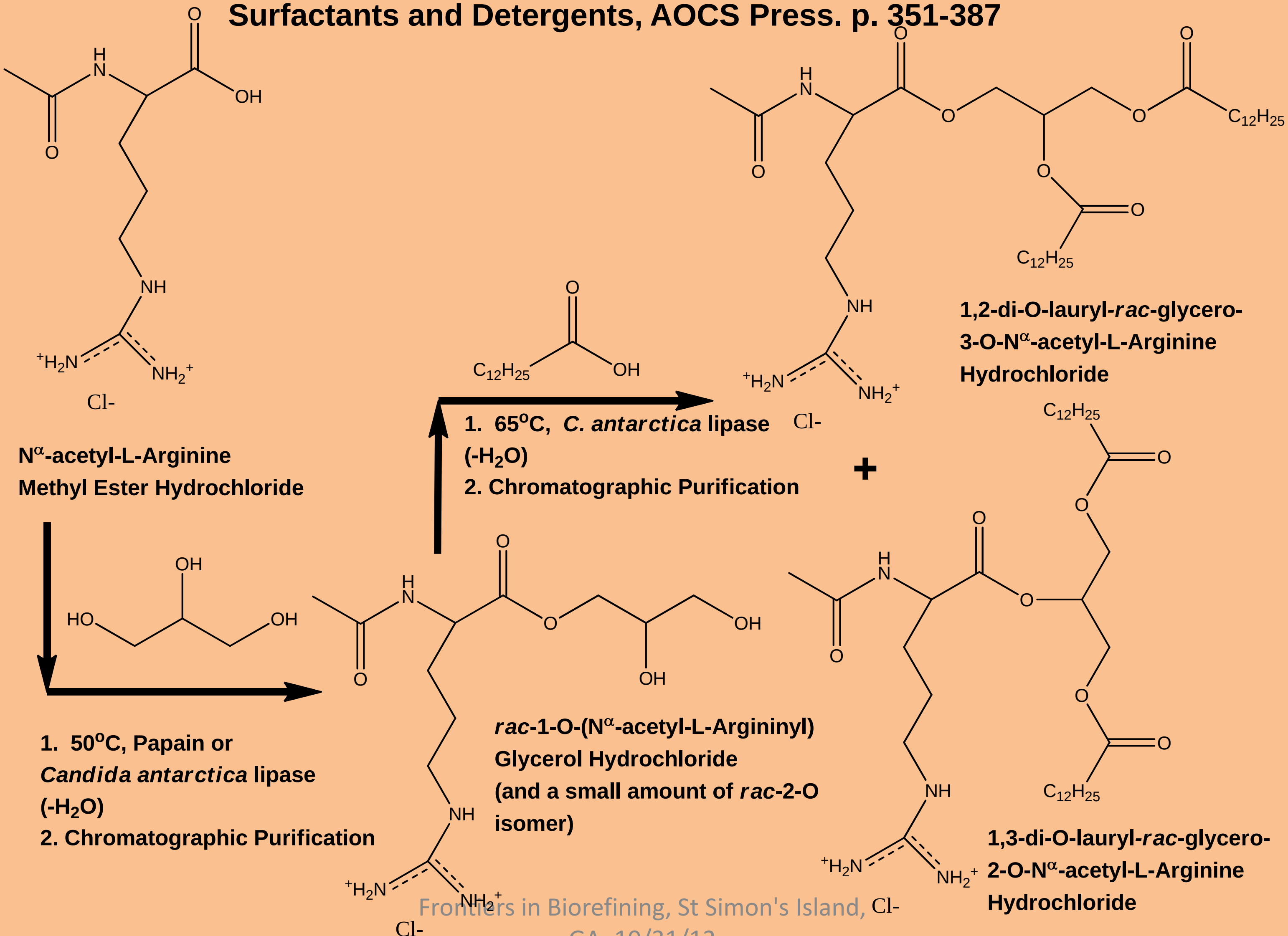
- **Lower energy use (lower temperature, ambient pressure) → reduced CO_2**
- **Lower amounts of waste products and by-products**
- **Lower amounts of reactants (near-stoichiometric ratios; no excess reactants)**
- **Absence of toxic metal catalysts or acids /bases → improved safety**
- **Can result in lower solvent usage**
  - **→ Enhanced performance as per Life Cycle Assessment**
- **Product distribution more narrow (regioselectivity, stereoselectivity)**

Enzymes Useful for Surfactant Synthesis

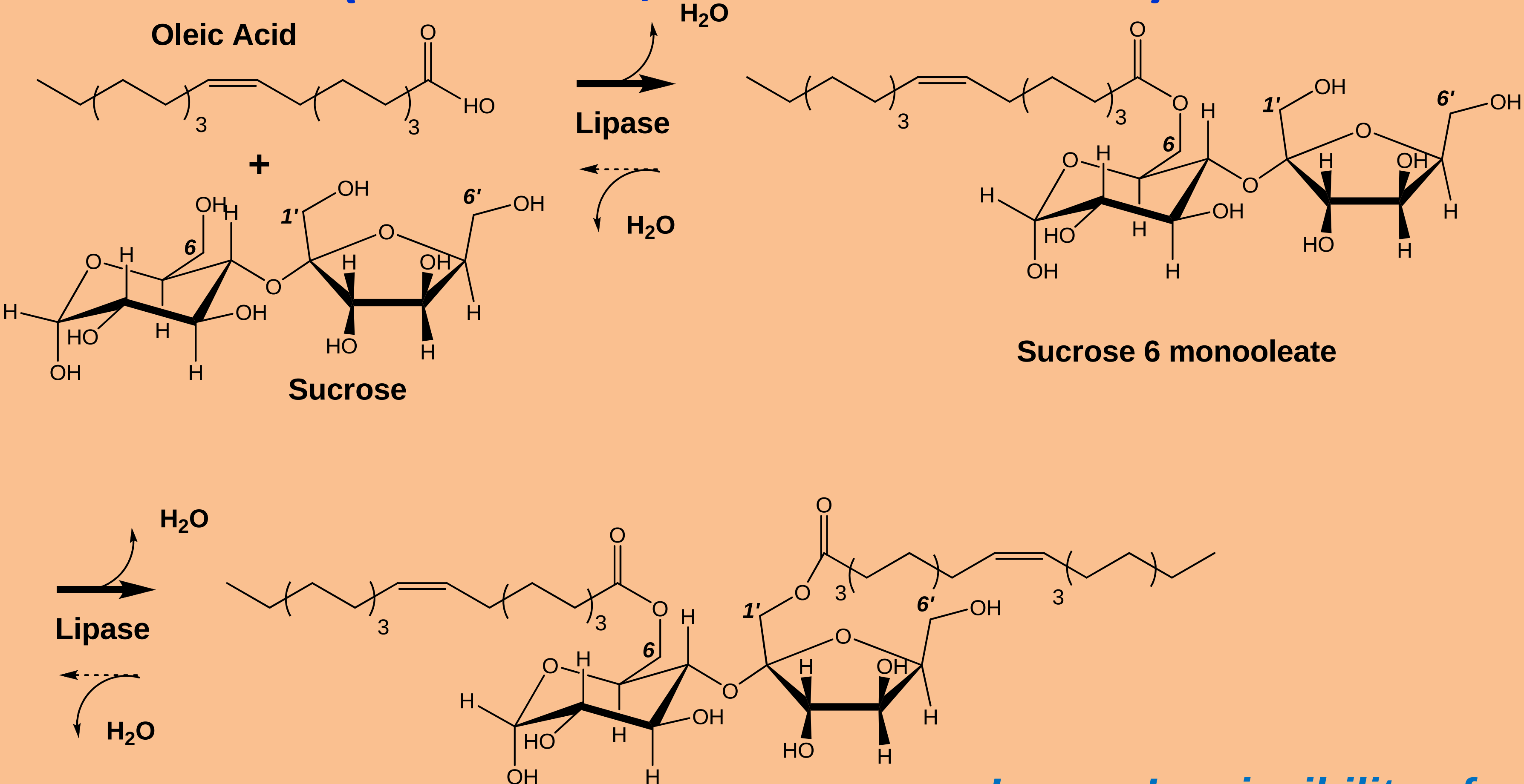
Enzyme	Surfactant or precursor
Alcohol dehydrogenase	Aldehyde or ketone (from fatty alcohol)
α-Amylase	Alkyl polyglucosides
Glucosidase	Alkyl glucosides
Glucosyl transferases	Alkyl polyglucosides
Lipases	Fatty acid esters (polyol, polyglycerol), fatty amide-based, lysophospholipids, carbonates, amino acid-based
Papain	Amino acid surfactants
Phospholipases	Tailor-made phospholipids

Lipase-catalyzed synthesis of di-O-alkyl, O-(N$^{\alpha}$-acetyl-L-argininyl) glycerol

Infante et al., 2009, in Hayes et al (Eds), Biobased Surfactants and Detergents, AOCS Press. p. 351-387



Saccharide-Fatty Acid Esters via Lipase (Dr. Ran Ye, PhD Dissertation)



Sucrose 6, 1' dioleate

Issue: Immiscibility of saccharide & fatty acid

Saccharide-Fatty Acid Esters : Applications

- **Biodegradable emulsifiers for use in foods, cosmetics, and pharmaceuticals**

- **Possible anti-tumor activity, antimicrobial and insecticidal activity**

Suspension / Supersaturated Solution-Based Bioreactor System

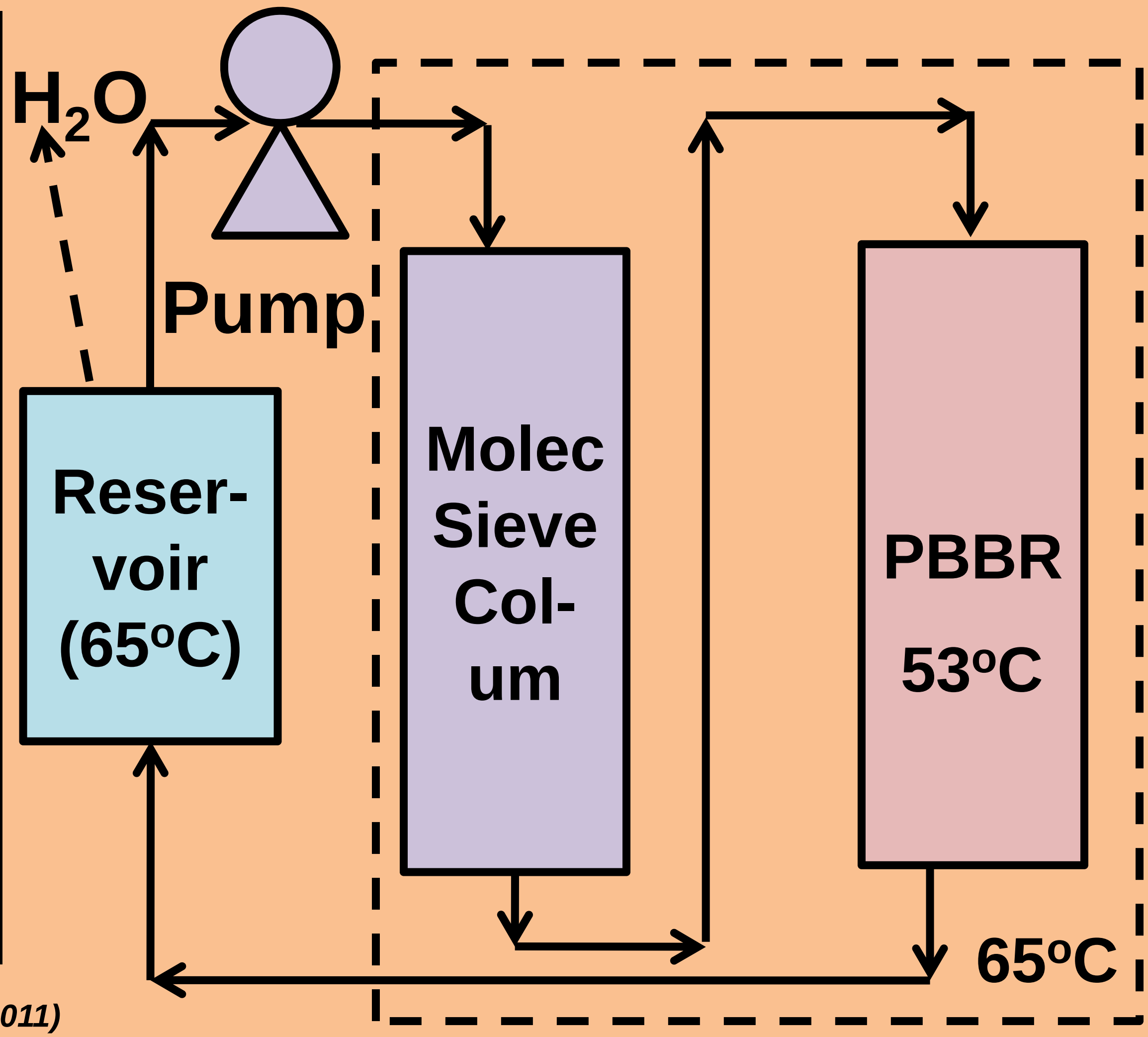
Immobilized *Rhizomucor miehei* lipase (Lipozyme-IM, Novozymes, Inc.)

Solvent-Free Suspensions: Preparation

•<u>Stirring</u>: 80ºC, 800 rpm, 6 hr

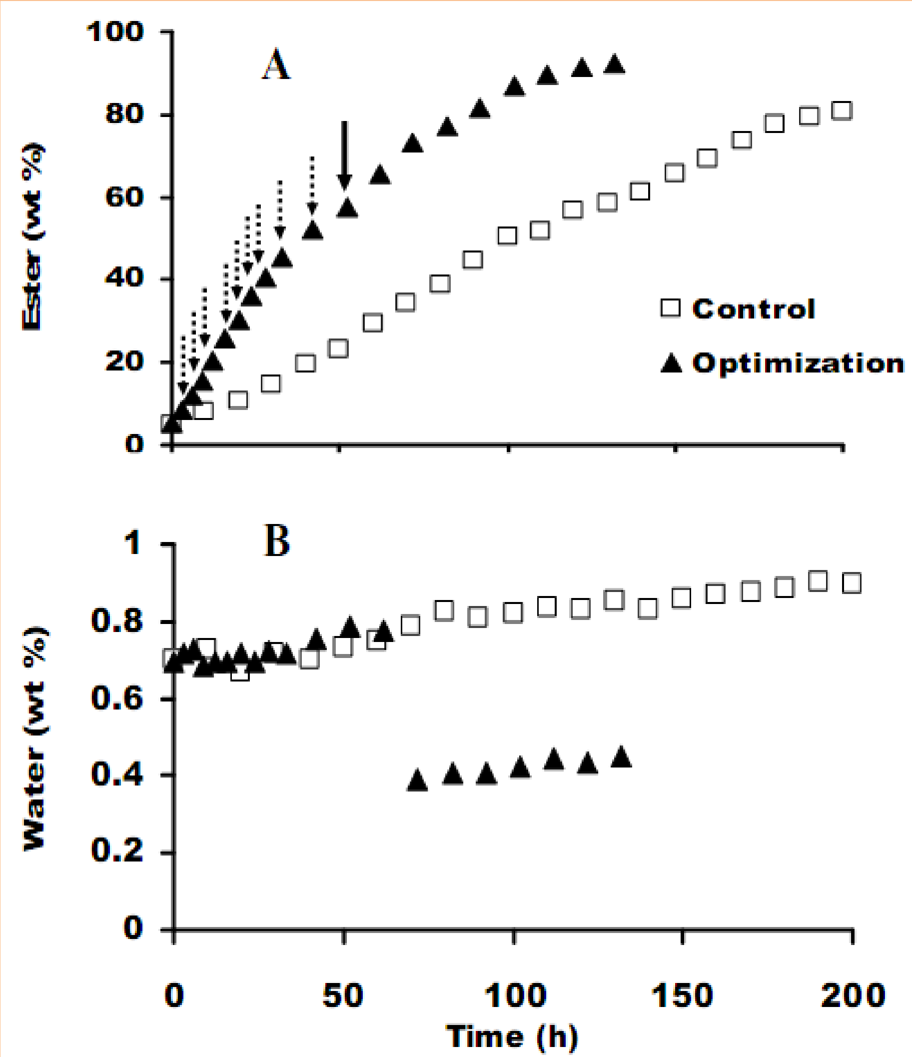
•<u>Centrifugation</u>: 800 rpm, 30 s

•<u>Usage</u>: at specified intervals, system stopped; suspension remade



Ye, and Hayes, *JAOCS* 88 (9):1351–1359 *(2011)*

Optimization of Bioreactor System (Fructose Oleate Synthesis)

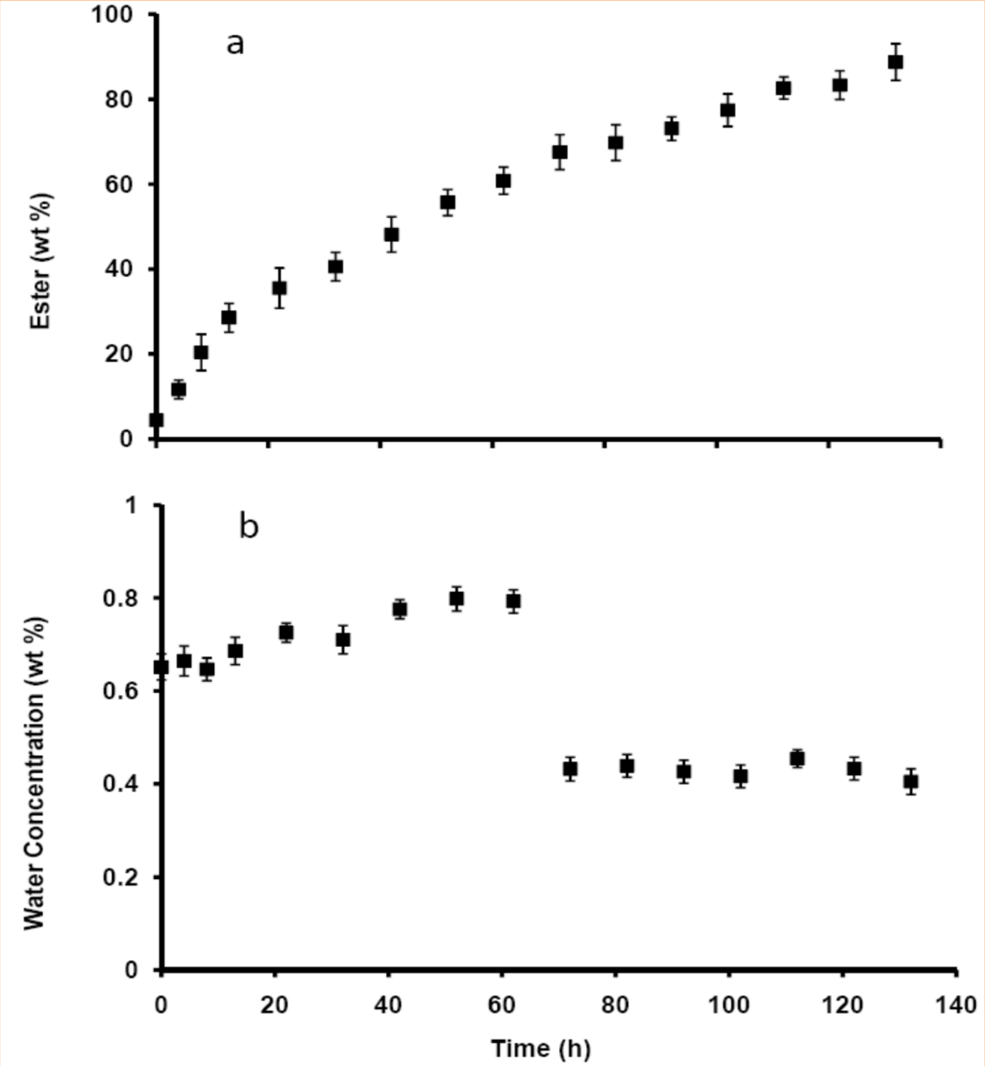


- Dashed arrow →optimized interval time
- Solid arrow →introduction time for water removal approach (off-line, enacted during re-formation of suspensions)
- N_2 (g) bubbling + Vacuum
- Water content ~0.4% w/w is optimal; addition at 60% ester is optimal
- ~ 92 % (0.297 mmol $_{Ester}$ h^{-1} $g_{RML}{}^{-1}$) in 117h

Ye, and Hayes, *JAOCS* 88 (9):1351–1359 *(2011)*

Excellent Enzyme Activity Retention

- No significant changes in the time course of reaction ..
- .. For 4 successive runs using the same lipase preparation



Ye, and Hayes, *JAOCS 89 (3) 455-463 (2012)*

Criteria for Sucrose Esters

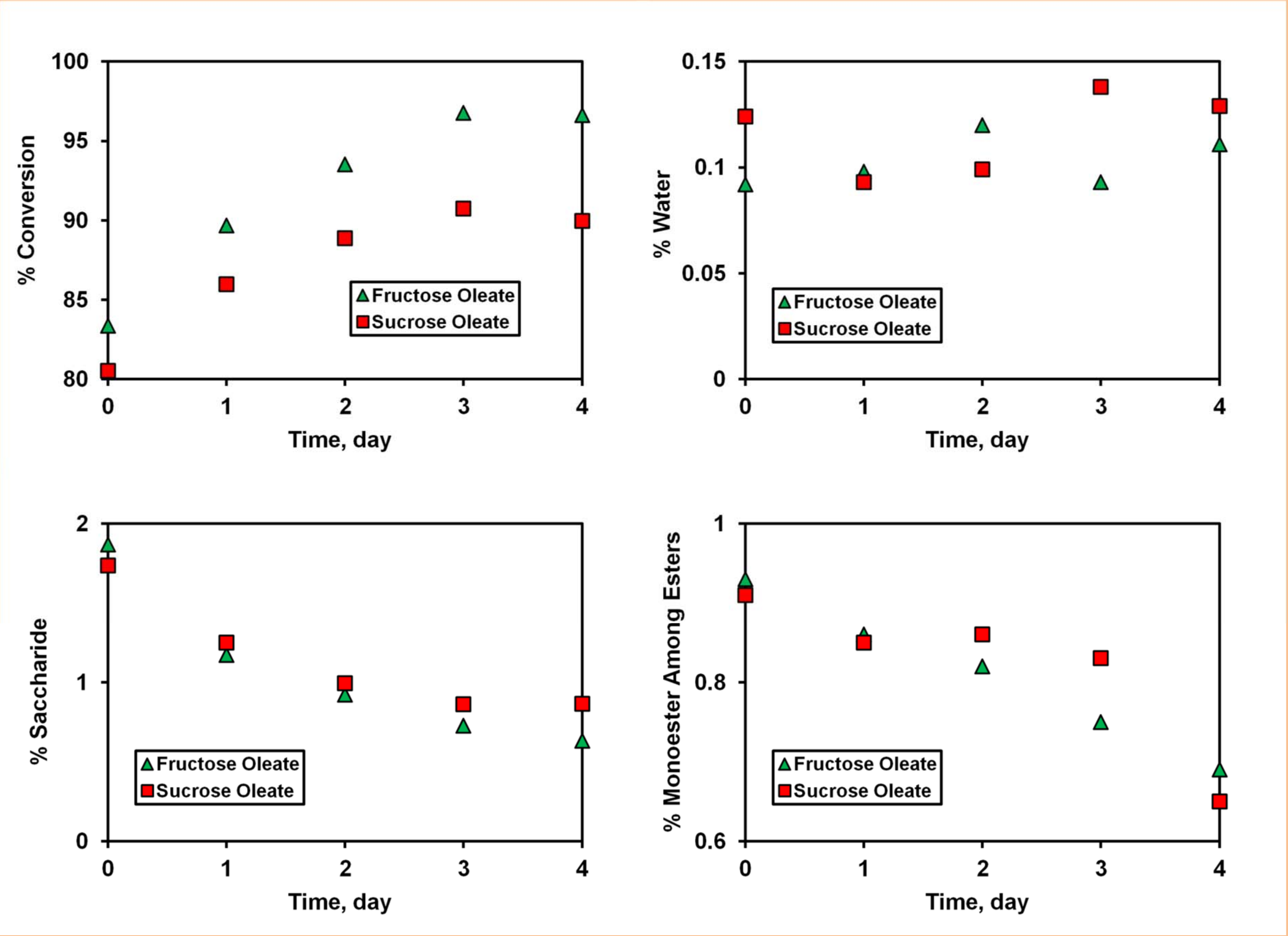
- < 2% sulfated ash
- Specific requirements for solvents (DMF, DMSO, methanol, MEK, etc.
- Acid value < 6 (~3 wt% FFA)
- < 5% free sucrose
- (FAO JECFA Monographs 4, 2007)

Additional Esterification to Increase the Yield (Fructose and Sucrose Oleate)

- **Starting materials**
  - Reaction product from solvent-free biocatalysis
  - Smaller size of sugar crystals (Homogenizer, 12,000 rpm, 1 min)

    → Centrifugation at 800 rpm for 1 min
  - Fructose: 387 nm, Sucrose: 562 nm (~20-40 μm after same treatment, saccharides ”as received”)
- **Reaction conditions:**
  - Closed, stirred batch, system
  - $CaSO_4$-controlled (ultralow water activity; Dang et al., *JAOCS*, 2005 82: 487-493)
  - Immobilized *Candida antarctica* lipase (10 wt%; Novozym 435, Novozymes, Inc, Franklinton, NC USA)
  - 65°C, 4 days

Results: Further Esterification



Physical Properties

Property	Fructose Ester	Sucrose Ester
FFA	3.4 %	10.0 %
Saccharide	0.63 %	0.86 %
Moisture	0.11 %	0.13 %
Ester Profile	69% Mono, 31% Di	65% Mono, 35% Di
HLB (Griffin)	7.2	10.1
Melting Point, ^oC	-12.8 to -17.2	-14.5 to -18.3

Summary

1. **Enzymes are potentially valuable for the sustainable preparation of biobased surfactants**
   a. **Polyol esters (lipases)**
   b. **Amino acid surfactant (lipases, papain)**
   c. **Alkyl glucosides (glucosidase, CGTase)**

2. **Solvent-free enzymic synthesis of saccharide – fatty acid esters nearly reaches standardized specifications without the need for purification.**

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