

Evolution of Surfactant Technology and Feedstocks

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Homecare Markets Conference

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Cutting Edge Technology - 1982



Agenda

- Evolution of Surfactant Technology
- Trends in Feedstock Economics
- The Sustainability Problem
 - and a Revolutionary Solution
- Conclusion

Surfactant Technology

Surfactants are Simple

Hydrophobe

- Linear Alkyl Benzene (LAB)
- Detergent Alcohols
- Alpha Olefins
- Nonyl Phenol
- Fatty Acids
- Methyl Esters
- Fats and Oils
- ..

Hydrophile

- Sulfur Trioxide
- Ethylene Oxide
- Ammonia (Amines)
- Chloro-acetic Acid
- ..

Simple Technology Matrix

	<u>Hydrophobe</u> Oleo, Petro or GTL	<u>Hydrophile</u>
Derivation	<p>Alcohol – Petrochemical (Ethylene) Oleochemical (Davy, Lurgi) GTL (Sasol)</p> <p>LAB - Jet Kero -> n-paraffin HF, AlCl₃, UOP Hi 2-Phenyl, Lo Tetralin</p> <p>LAO - Ethylene Oligomerization</p> <p>Fats/Oils Animal / Vegetable</p>	<p>SO₃ Mined or Recovered Sulfur</p> <p>EO Purified EO vs MEG for PET value chain: Pipeline vs railcar vs truck “Natural” EO</p> <p>-NH₂ Oleo or Petro derived</p> <p>MCA ..or SMCA</p>
Combination / Processing	<ul style="list-style-type: none"> • Sulfonation <ul style="list-style-type: none"> – Multi-tube Film /Oleum / Ice-Cold / Annular Ring – Vacuum Neutralization • Ethoxylation <ul style="list-style-type: none"> –Conventional Stirred Tank (CSTR) –Enhanced Loop Reactor • Drying / Granulation / Pelletization 	

Evolution of Surfactants

The last 3 decades have been spent tweaking existing products – with an eye to HS&E

- BAB → LAB
- DTDMAC → Ester Quats
- NPE → LAE
- **Low** color – all products
- **Low** dioxane Ethoxylates, SLES, ALES
- **Low** Carbonyl Detergent Alcohols
- **Low** tetralin LAB
- Nitrosamine **Free**
- Animal **Free**
- Sulfate **Free**
- “**Natural** vs Synthetic” Rise of Oleo Alcohols
- Emergence of GTL

Anionic Surfactants – Current Standards

➤ QUALITY STANDARD WILL BE AFFECTED BY THE INCREASING “SPECIALIZATION” IN USING ANIONIC SURFACTANTS

PRODUCT	AM (%)	F.O. (on 100% AM)	Na ₂ SO ₄ (on 100% AM)	%Klett Color (on 5% AM sol.)
LABSO ₃ H	97.5 - 97.7	0.8 - 1.0	0.5 - 0.6 (♦)	10 - 20
FAS (12-14 nat.)	70 - 75	0.8 - 1.0	0.8 - 1.2	5 - 10
FAS (13-15 synt.)	70 - 73	1.0 - 1.2	0.9 - 1.3	15 - 25
FAS (16-18 nat.)	68 - 70	1.5 - 1.8	1.2 - 1.7	35 - 50
AES-2EO (*)	70 - 73	0.5 - 1.0	0.6 - 1.1	3 - 10
AES-3EO (**)	70 - 73	0.8 - 1.0	0.6 - 1.0	5 - 15
AOS (14-16/14-18)	70 - 75	1.0 - 1.6	1.0 - 1.5	25 - 40
MES (12-14/16-18)	68 - 70 (***)	0.8 - 1.5	1.5 - 1.8	40 - 50 (****)

(♦) : As H₂SO₄ content

(*) : 1,4 Dioxane content of max. 30 ppm (on AM basis) with FO = 2% max. (on AM)

(**) : 1,4 Dioxane content of max. 30 ppm (on AM basis) with FO = 2,5% max. (on AM)

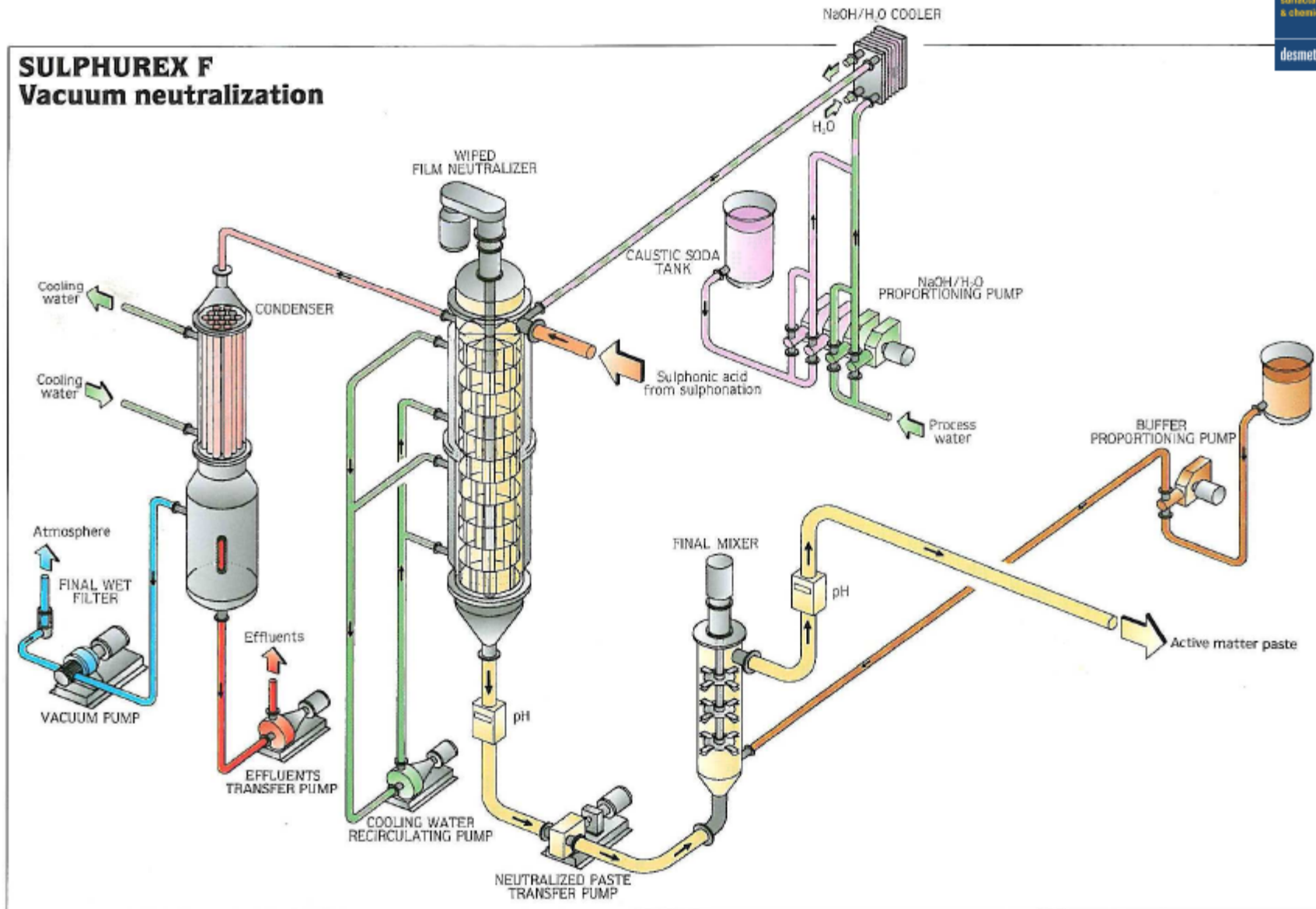
(***) : Di-salt content = 5% max. (on tot. AM)

(****) : Color figures after bleaching

Further reduction to 10ppm via Vacuum Neutralization

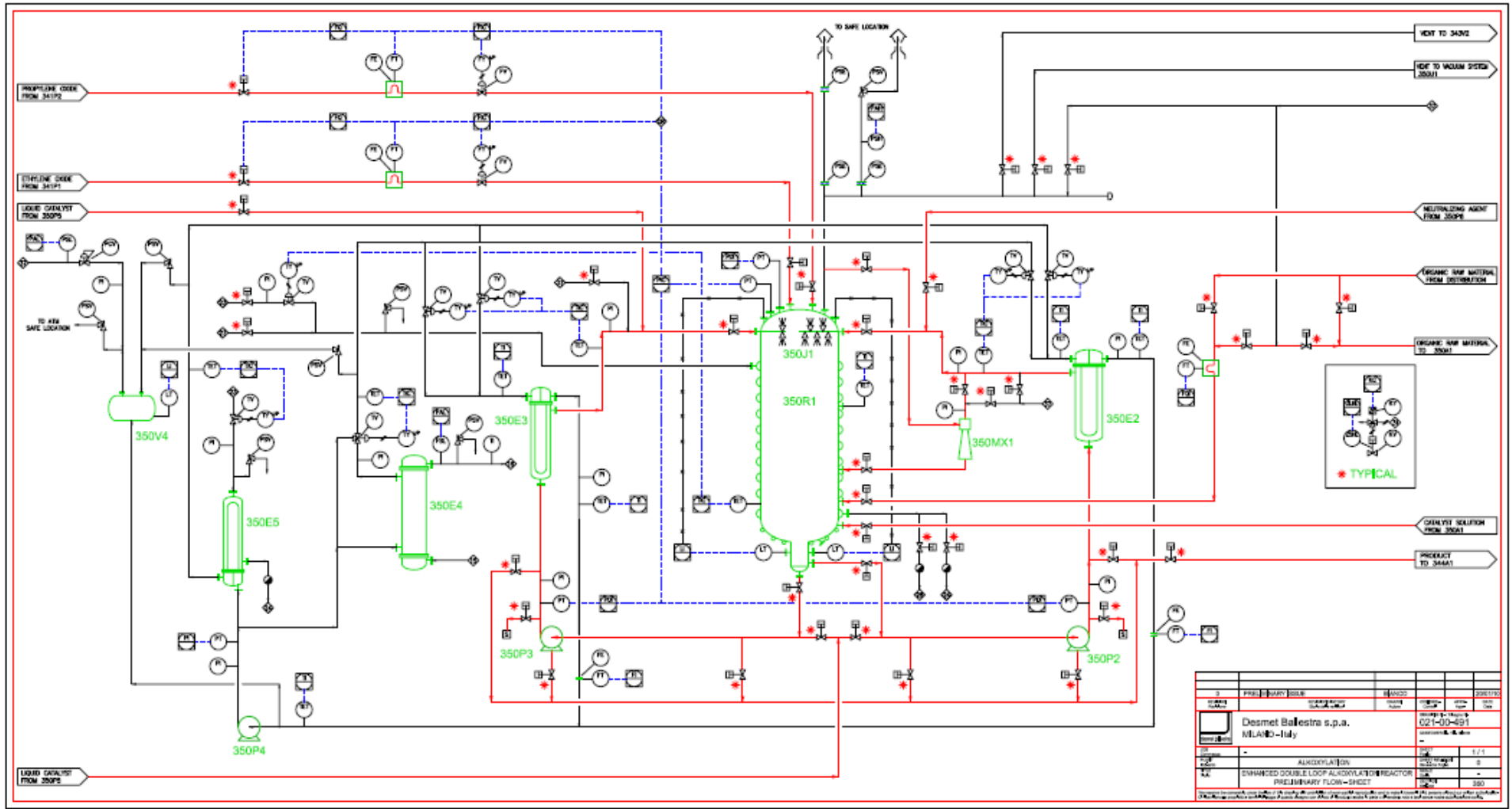
Source: Ballestra

Anionic Surfactants – Dioxane Reduction



Source: Ballestra

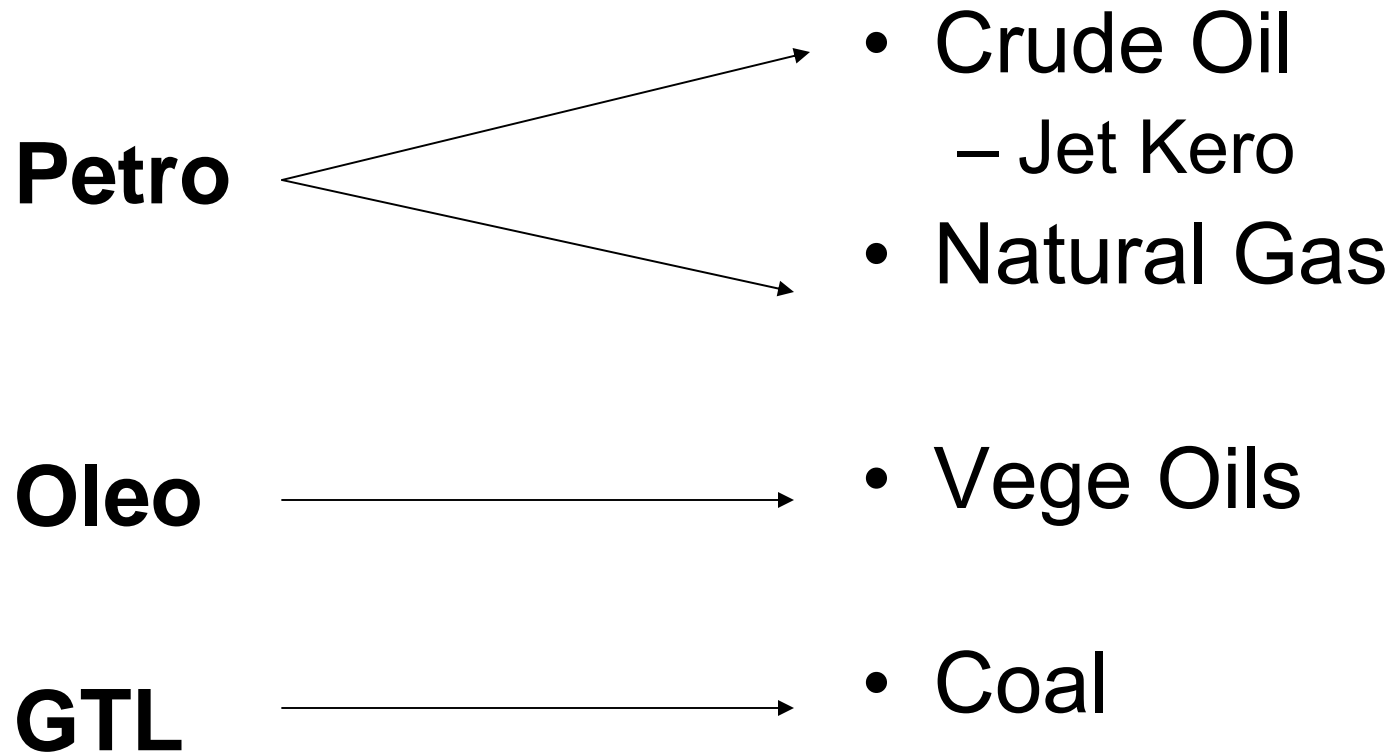
Nonionic Surfactants – State of the Art Ethoxylation



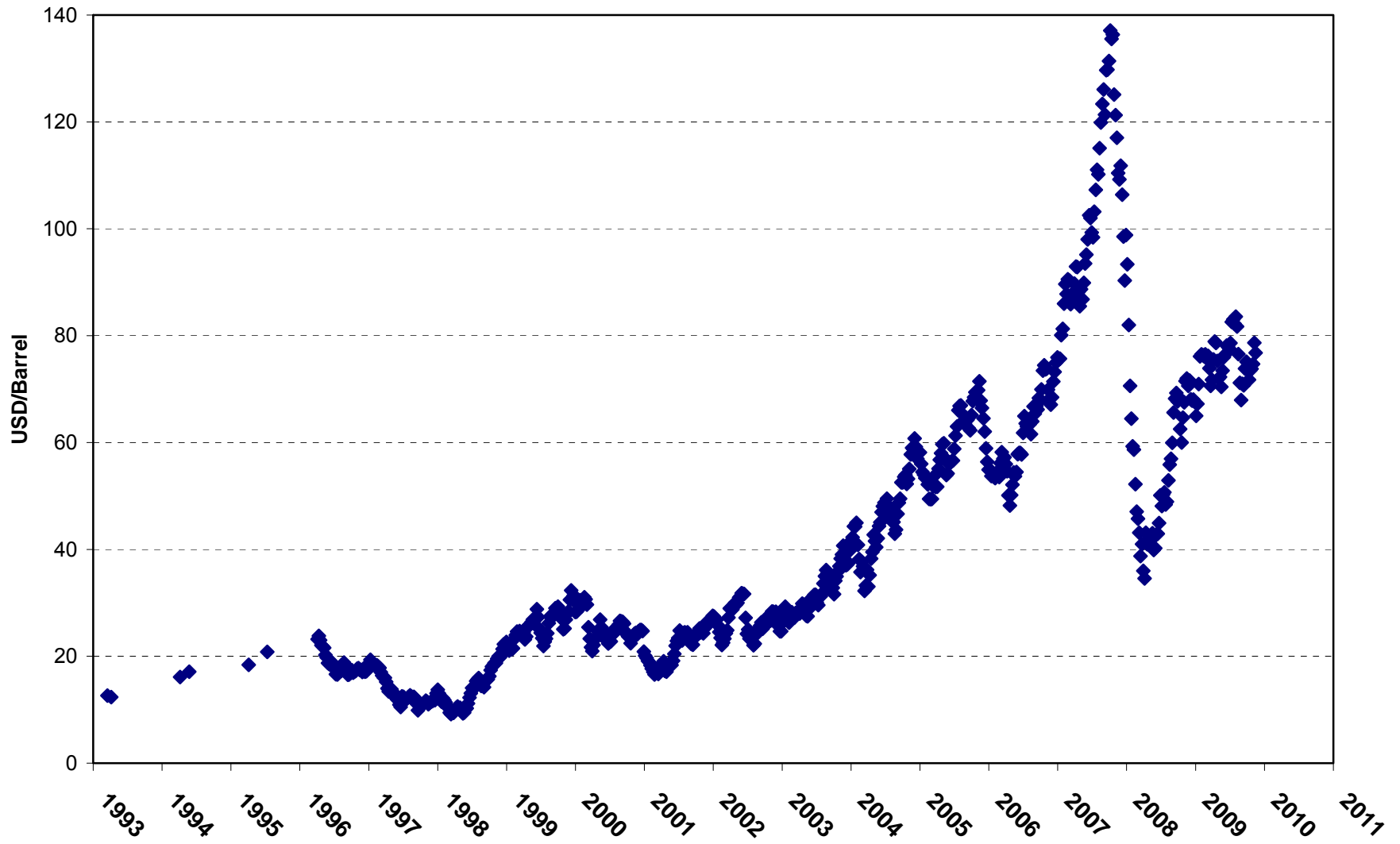
Source: Ballestra

Feedstock Economics

Two Decades of Cost Drivers

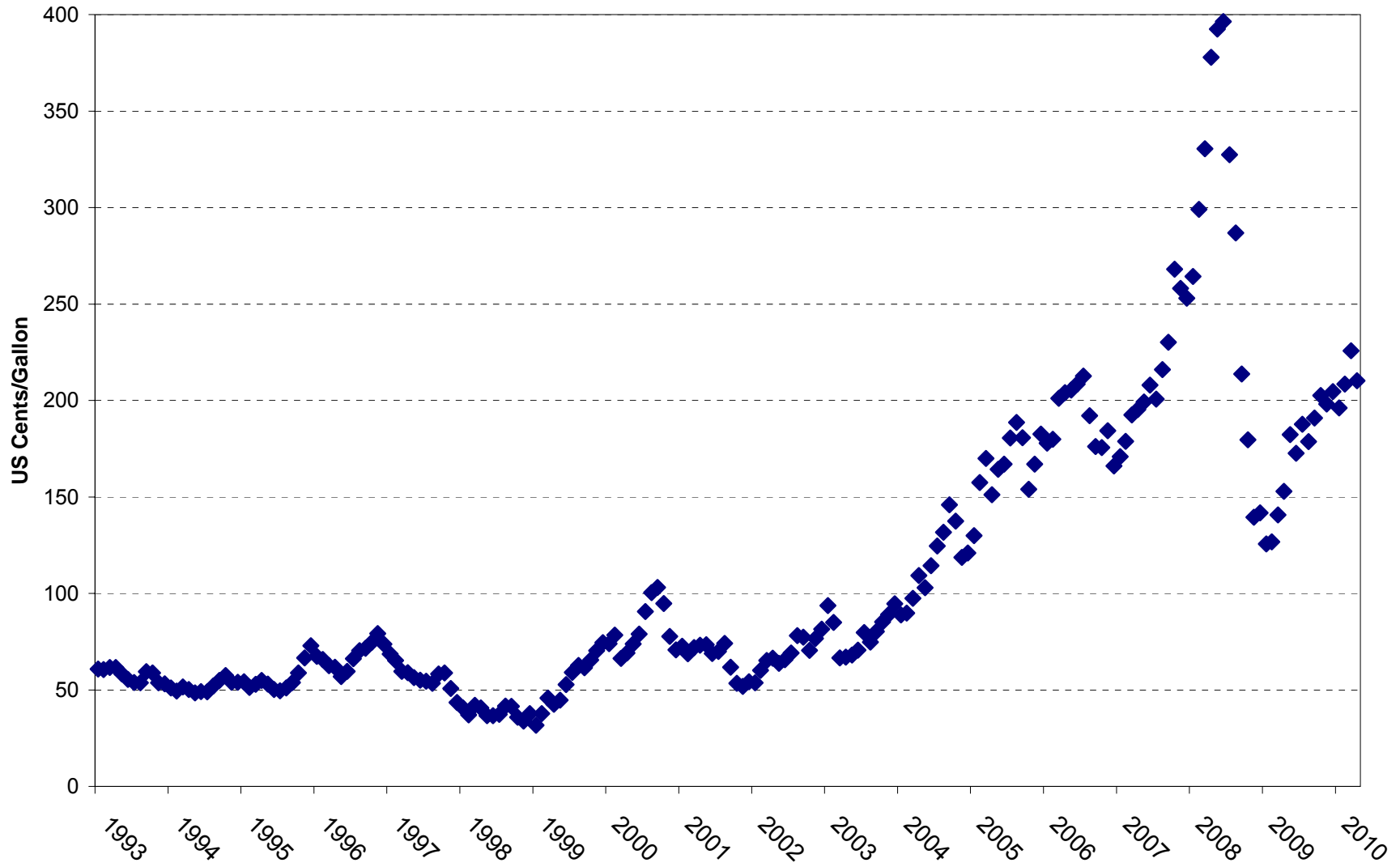


World Avg Crude Oil Spot Price (USD/BBL)



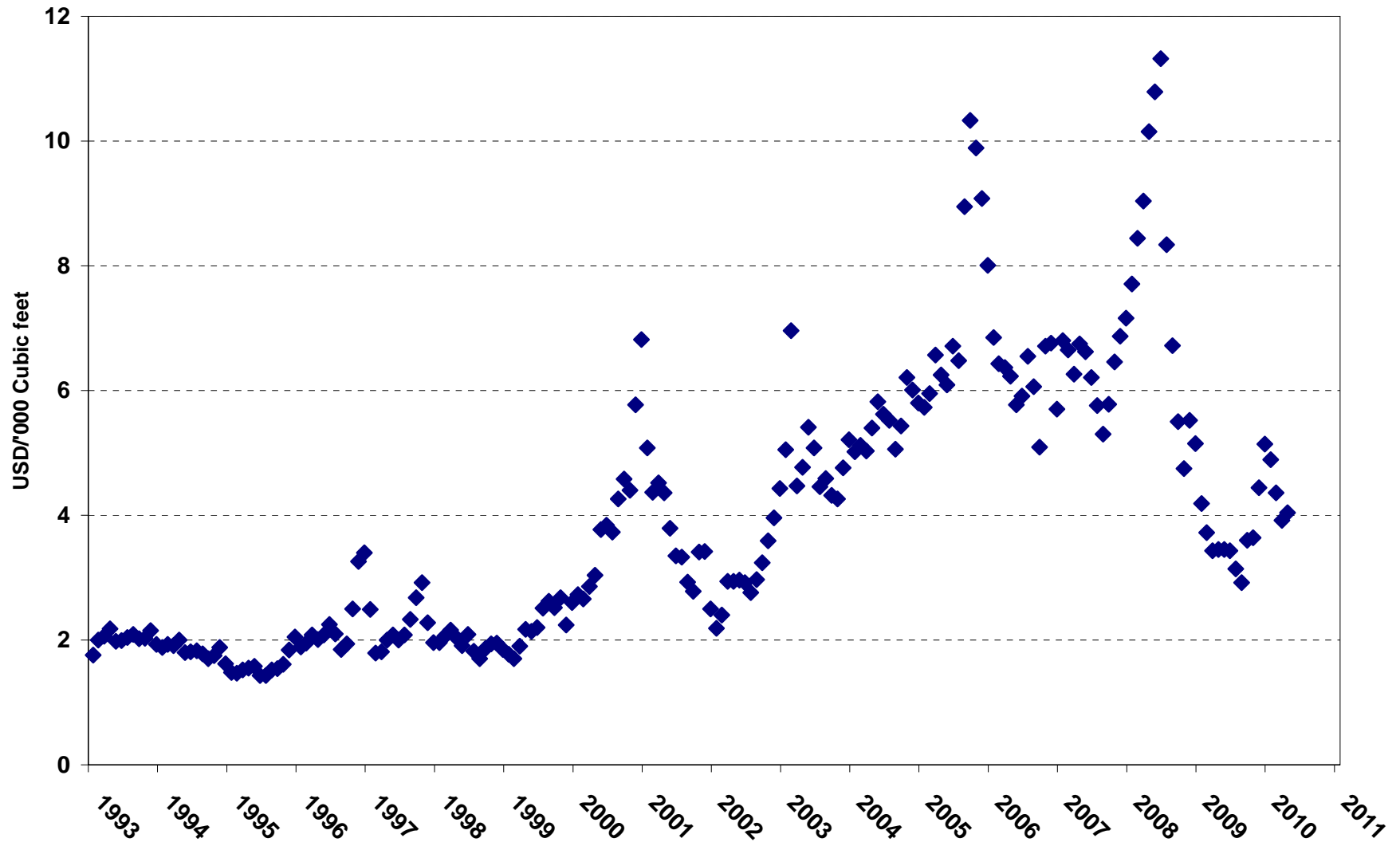
Source: US Energy Information Administration

Jet Kero (Singapore) US Cents/ Gallon



Source: US Energy Information Administration

US Natural Gas Wellhead Price (USD/'000 Cubic Feet)



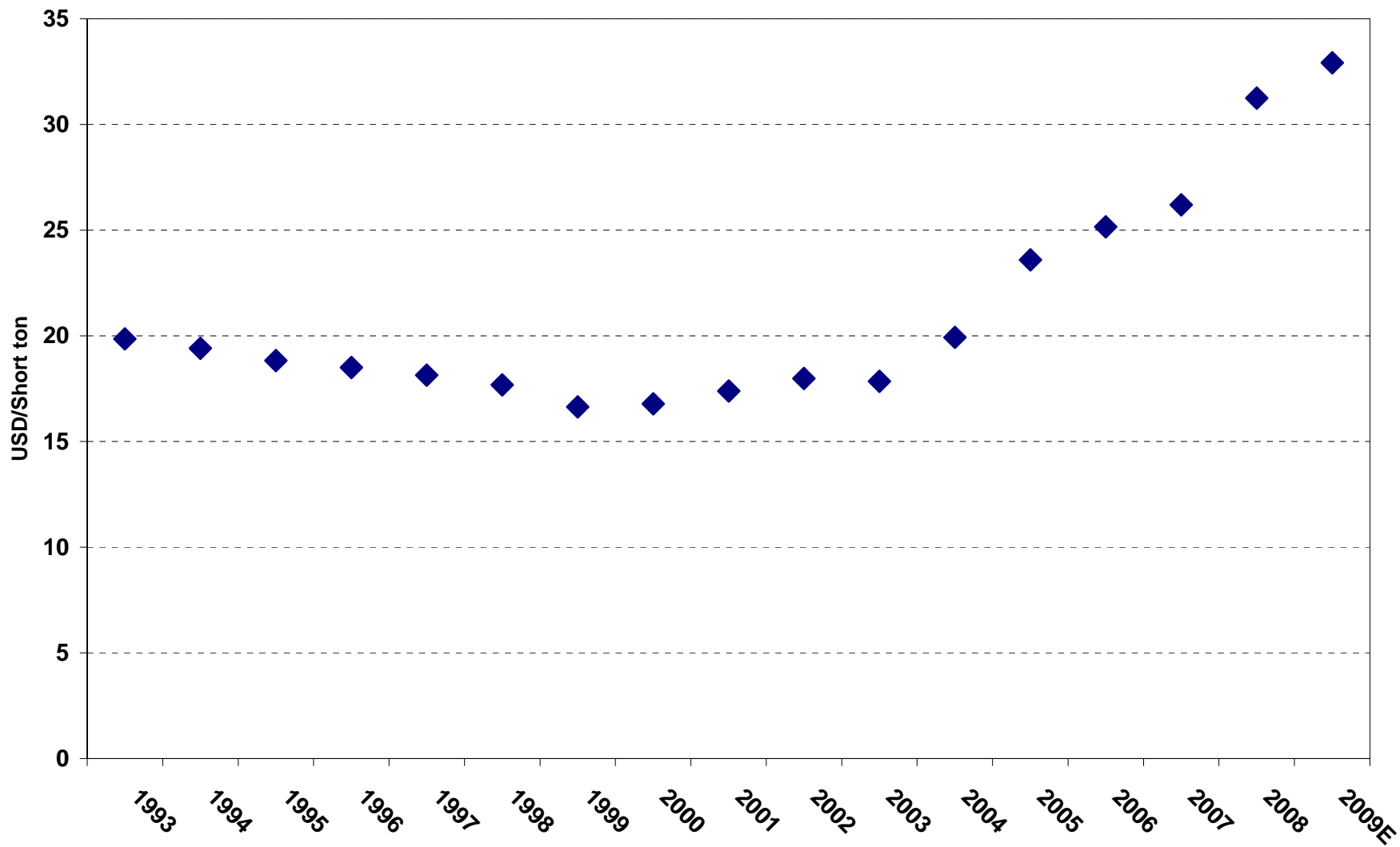
Source: US Energy Information Administration

Historical Price Relationship between CBOT Soybean Oil and Bursa Malaysia Crude Palm Oil Futures, 1995-Present



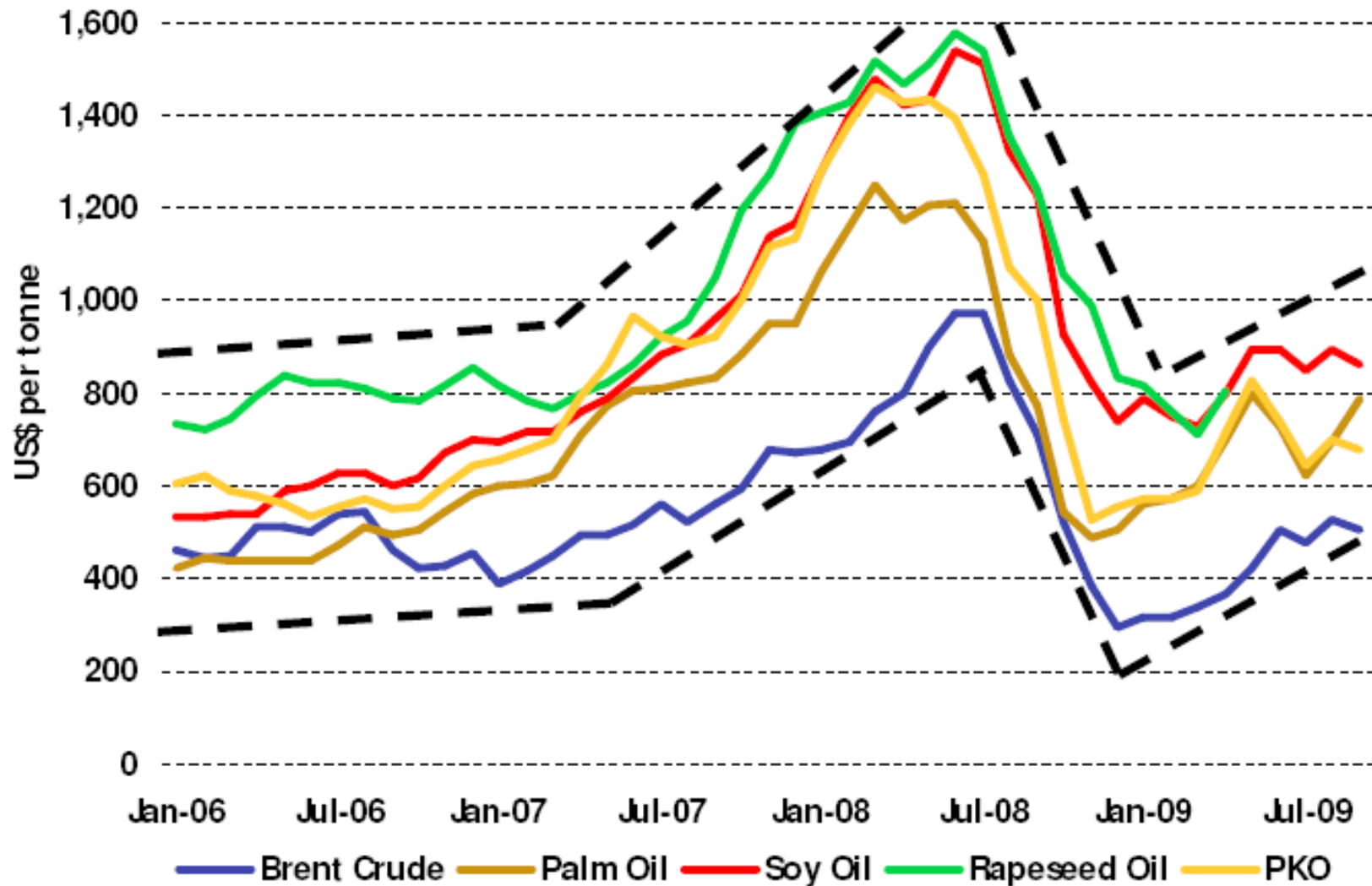
Source: MPOB

Average US Coal Price (USD/Short ton)



Source: US Energy Information Administration

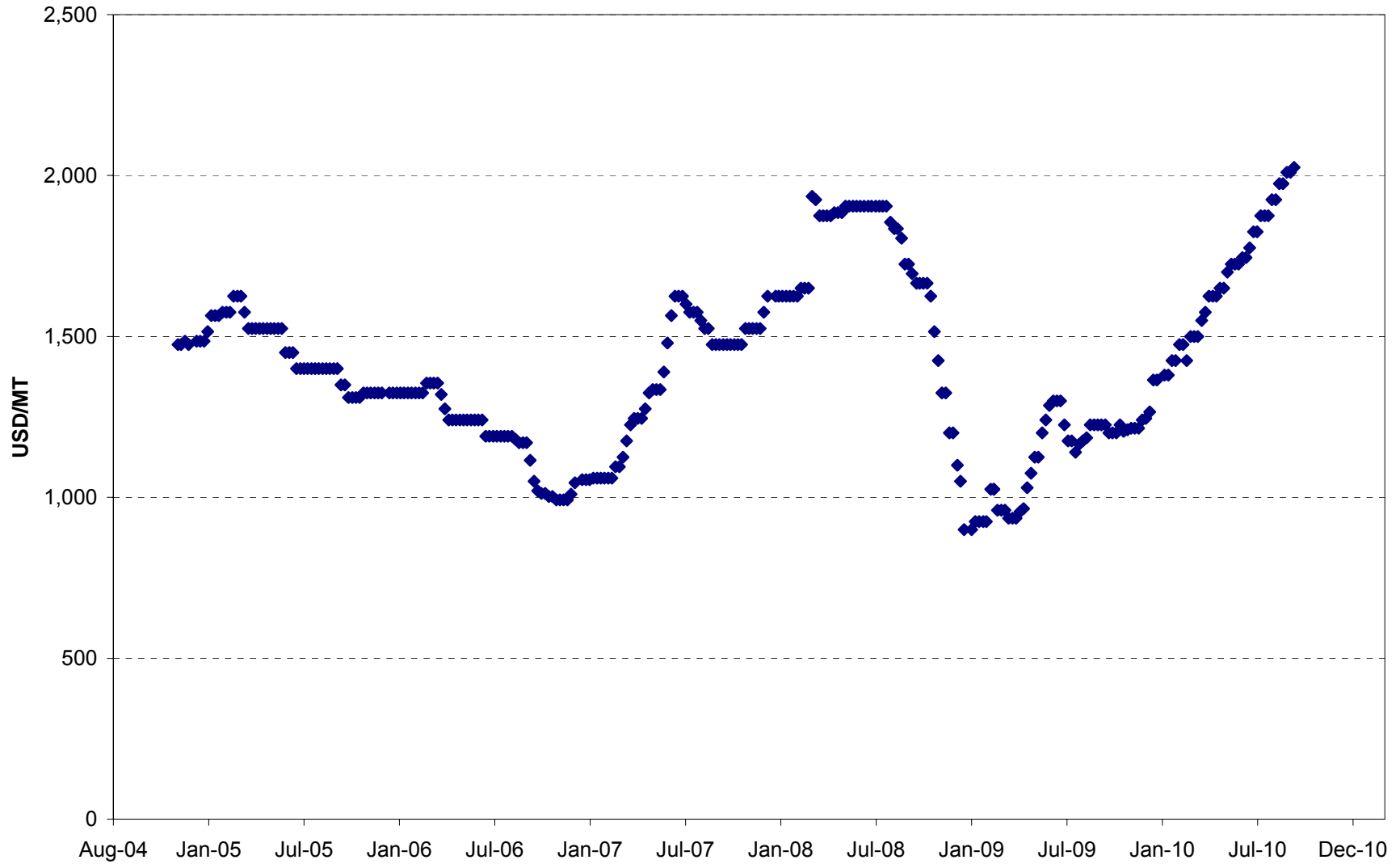
Vege Oil Prices Moving in a Band with Crude Oil



Source: LMC International: The Outlook for Oleochemicals, 2020

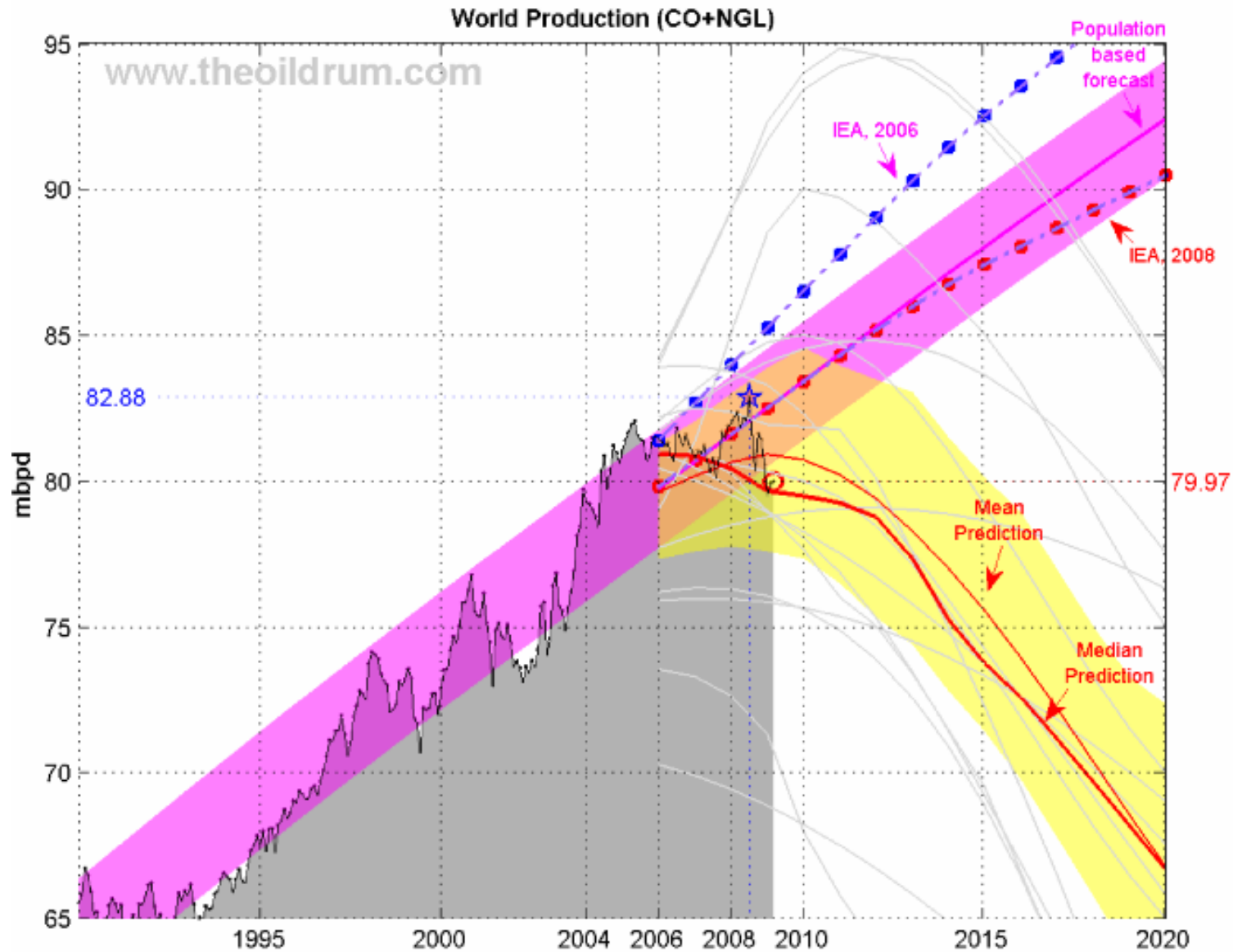
Feeds through to Alcohol and Beyond

Lauryl Alcohol Pricing (FOB SE Asia)



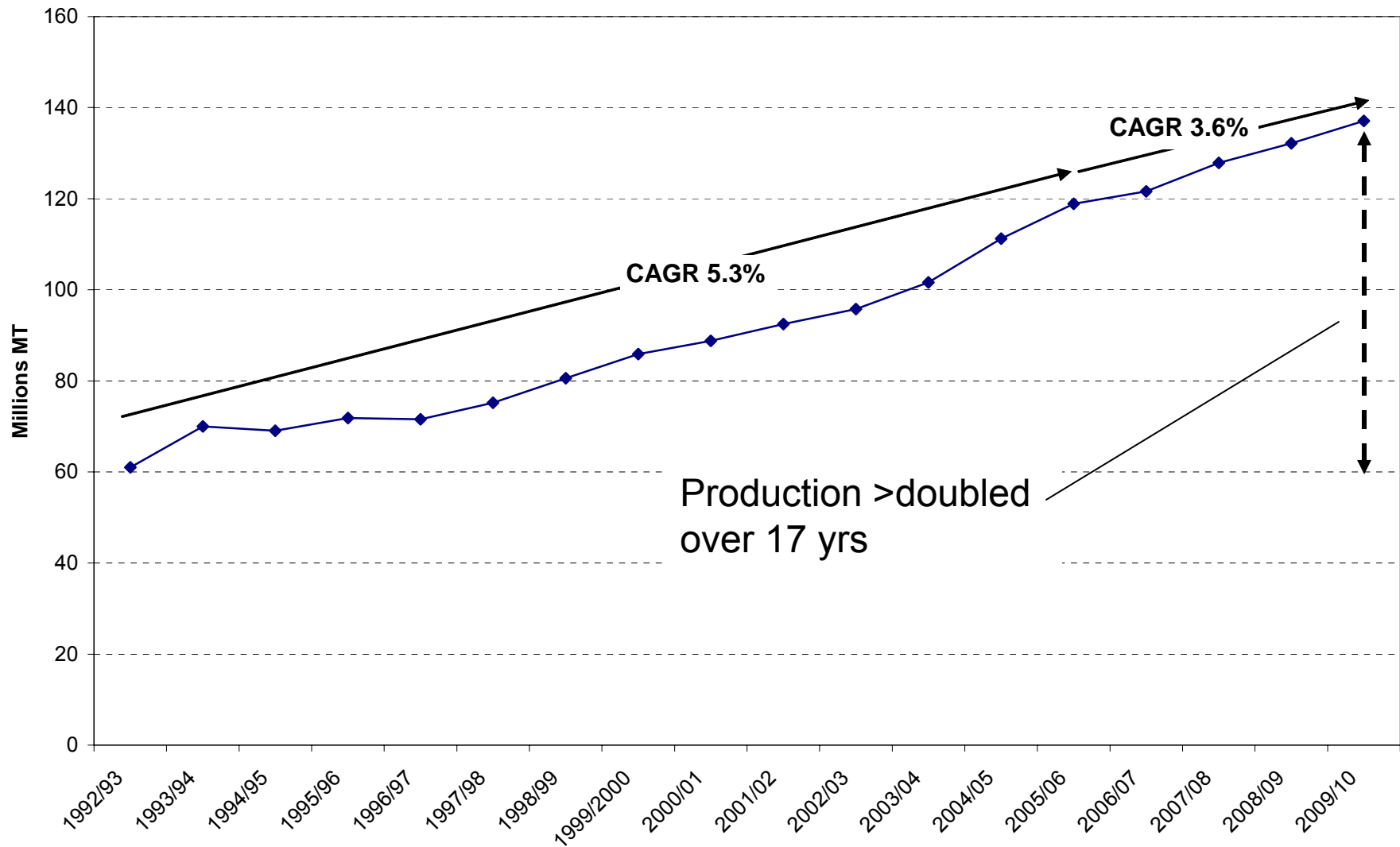
Sustainability

Sustainability Problem 1 – Peak Oil



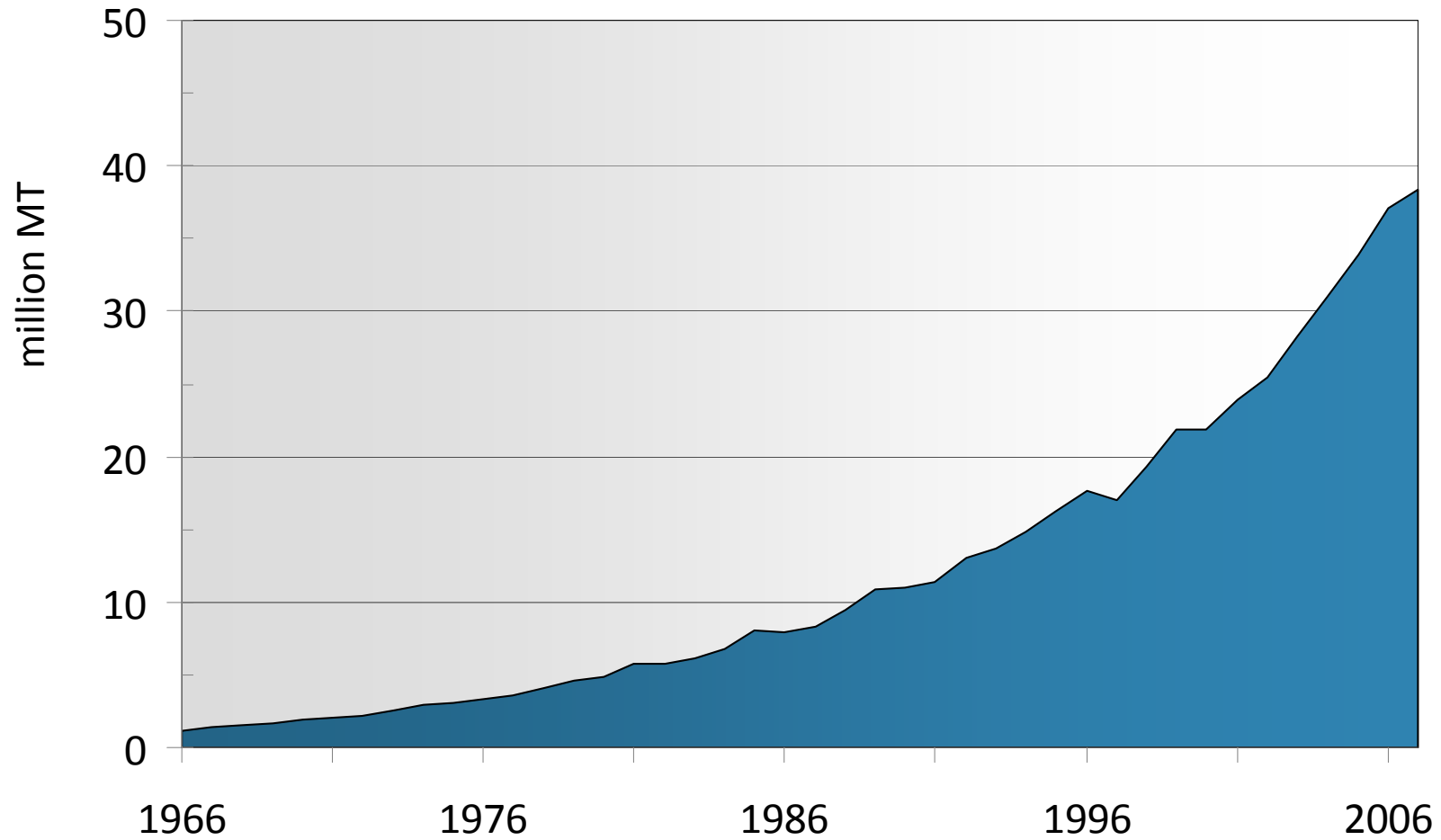
World oil production (EIA Monthly) for crude oil + NGL.

Vegetable Oil Growth



Includes: Palm, PKO, Soybean, Rapeseed, Sunflower, Peanut, Cottonseed, Coconut, Olive

Palm Oil Growth



Source: Oil World, MOPB, MPOC

Palm Oil Sustainability

The Roundtable on Sustainable Palm Oil:

- Promotes the growth and use of sustainable oil palm products through global standards
 - *Respect for rights of land owners, farm workers, smallholders and their families*
 - *No primary forests or high conservation value areas sacrificed for new palm oil plantations*
- *Formed in 2004: Today 360 Members including*
 - *Oil Palm Growers, Consumer Goods Companies, Retailers, Investors and others*

Source: **RSPO**

So – is it time for a revolution?



From this.....

.....to this

Biomass to solve “Peak Oil”?

3 Generations of Bio Fuels and Chemicals

- **1: Vegetable Oil / Corn / Sugar Derived**
- **2: Non-food crops / Jatropha / Bio-Mass**
- **3: Algae – “Industrial Farming”**

Sources of Petro/Oleo-Alternatives

<u>Crop</u>	<u>Oil Yield (L/ha)</u>	<u>Land Area Needed (M ha)^a</u>	<u>% of existing US Crop Area^a</u>
Corn	172	1,540	846%
Soybean	446	594	326%
Canola	1,190	223	122%
Jatropha	1,892	140	77%
Coconut	2,689	99	54%
Oil Palm	5,950	45	24%
Microalgae ^b	136,900	2	1.1%
Microalgae ^c	58,700	4.5	2.5%

- a) For meeting of all transport fuel needs of USA
- b) 70% oil by weight in biomass**
- c) 30% oil by weight in biomass**

Source: "Biodiesel from Microalgae", Biotechnology Advances (25), 2007, Yusuf Chisti

Oil Content of some Microalgae

<u>Microalga</u>	<u>Oil Content (% dry Weight)</u>
Botryococcus braunii	25 – 75
Chlorella sp.	28 – 32
Cryptocodinium cohnii	20
Cylindrotheca sp.	16 – 37
Dunaliella primolecta	23
Isochrysis sp.	25 – 33
Monallanthus salina	>20
Nannochloropsis sp.	31 – 68
Neochloris oleoabundans	35 – 54
Nitzschia sp	45 – 47
Phaeodactylum tricornutum	20 – 30
Schizochytrium sp.	50 – 77
Tetraselmis sueica	15 - 23

Source: "Biodiesel from Microalgae", Biotechnology Advances (25), 2007, Yusuf Chisti

Commercial Activity

Nascent but real

- **Microalgal Biomass Market = 50 – 100 KMT/yr**

<u>Algae</u>	<u>Annual Prod.</u> <u>(MT Dry)</u>	<u>Countries</u>	<u>Applications</u>
Arthrospira	3,000	China, India, USA, Myanmar, Japan	Human and animal nutrition, cosmetics, phycobiliproteins
Chlorella	2,000	Taiwan, Germany, Japan	Human nutrition, aquaculture, cosmetics
Dunaliella Salina	1,200	Australia, Israel, USA, China	Human nutrition, cosmetics, β - Carotene
Aphanisomenon flos- aquae	500	USA	Human nutrition
Haematococcus pluvialis	300	USA, India, Israel	Aquaculture, astaxanthin
Cryptocodinium cohnii	240	USA	DHA Oil
Shizochytrium	10	USA	DHA Oil

Current Technology – 2 Examples

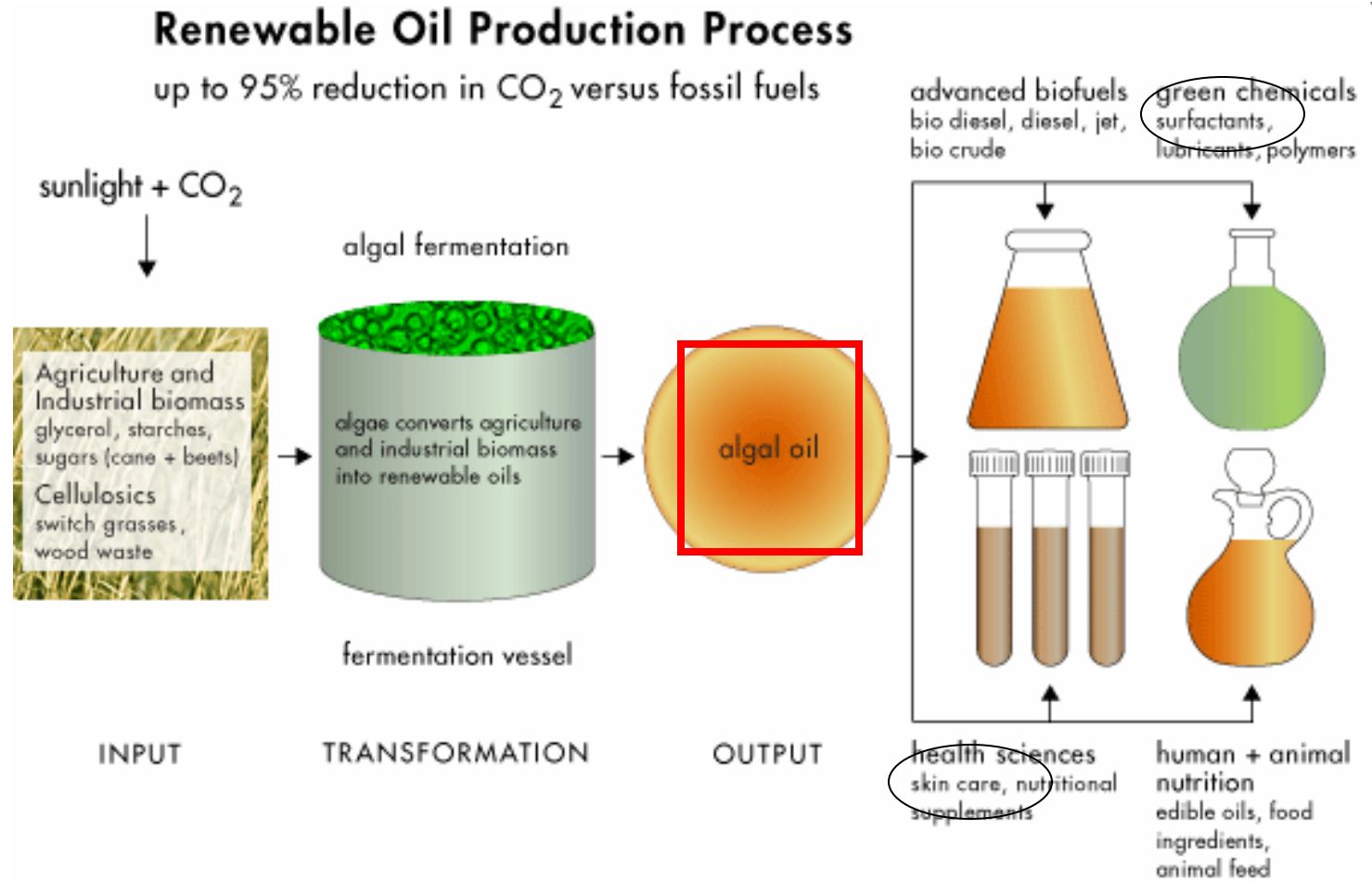
- **Solazyme**



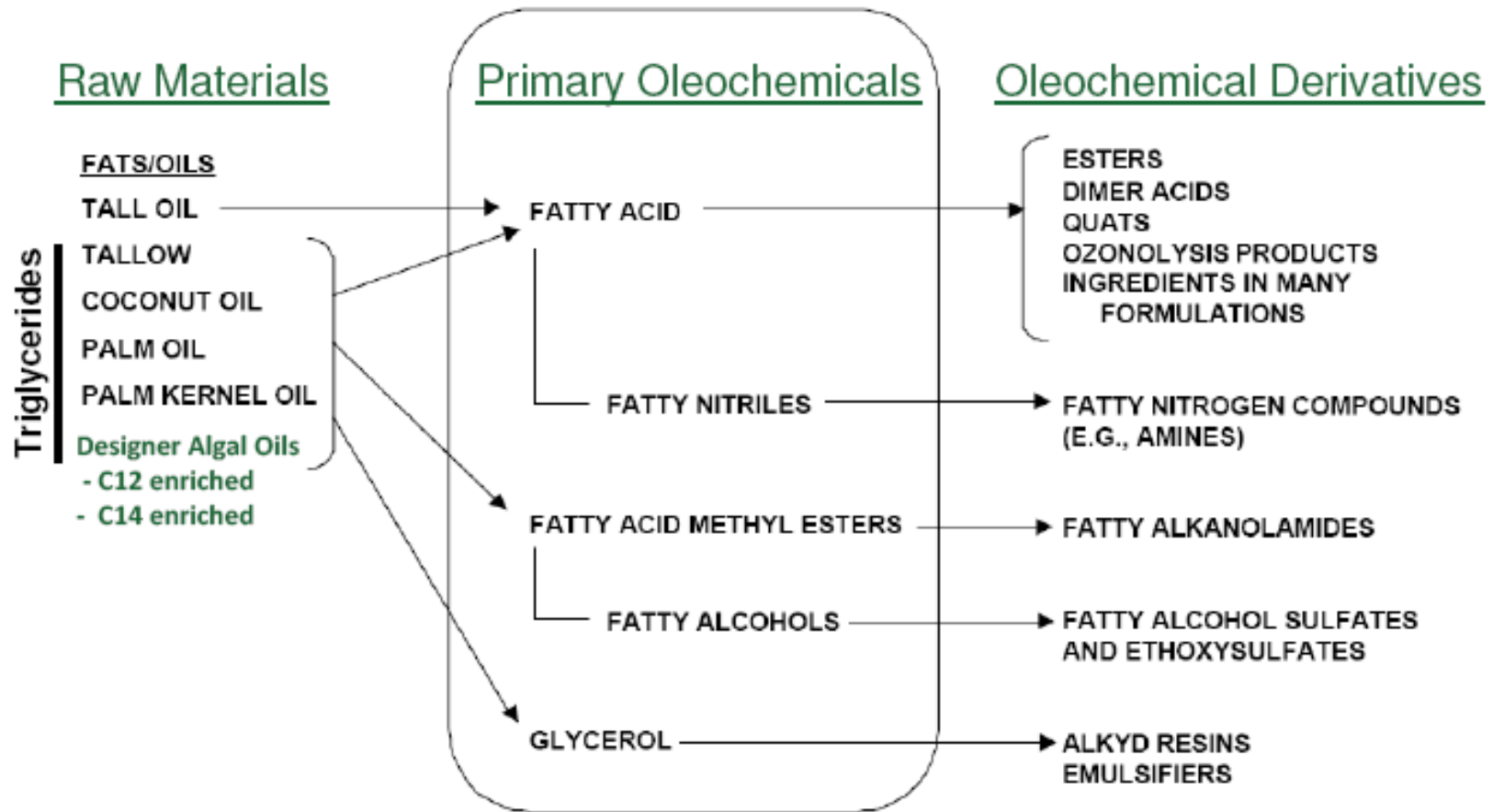
- **Elevance**



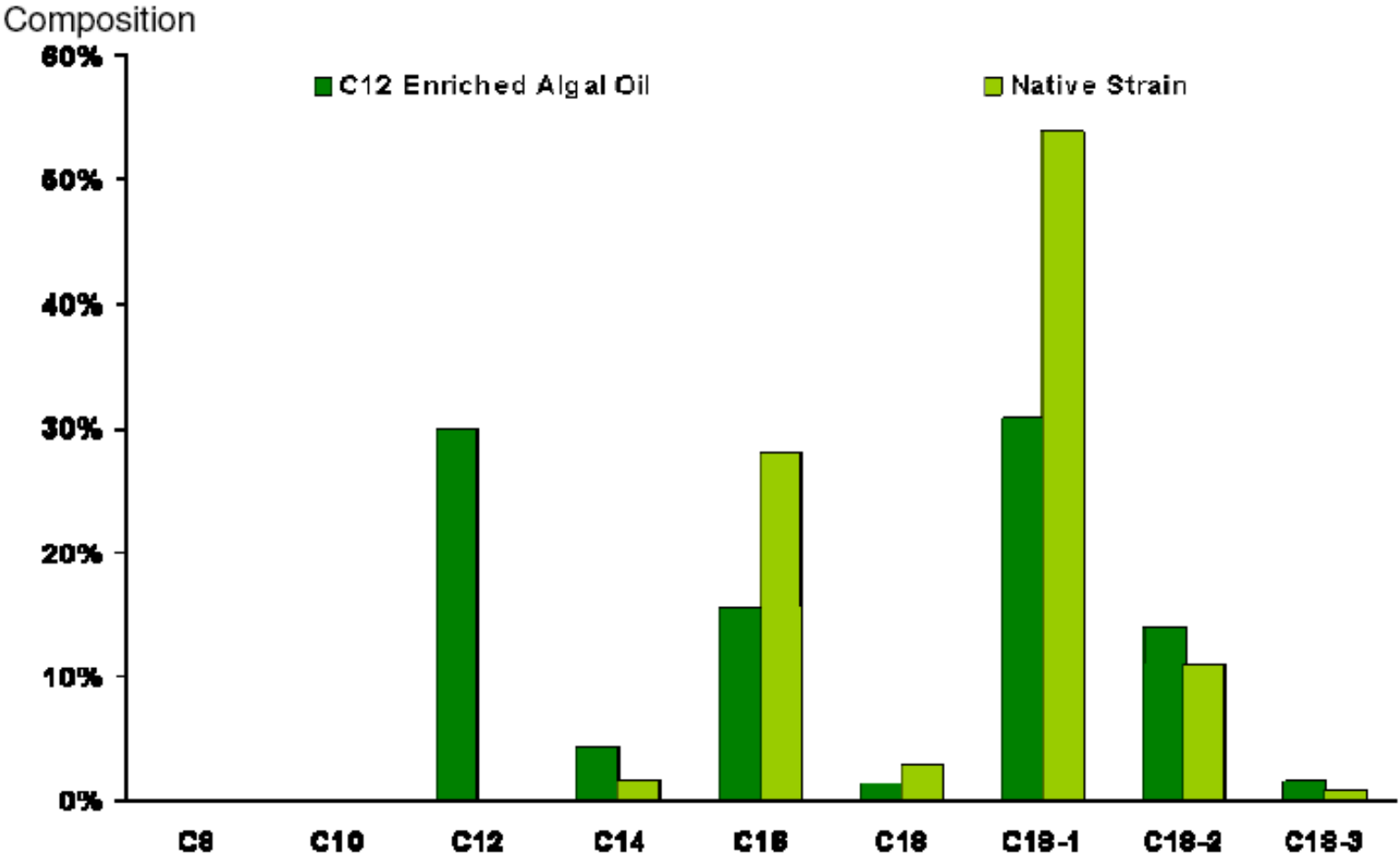
Solazyme - Algae plus Biomass -> Algal Oil



Algal Oils in Surfactant Value Chain

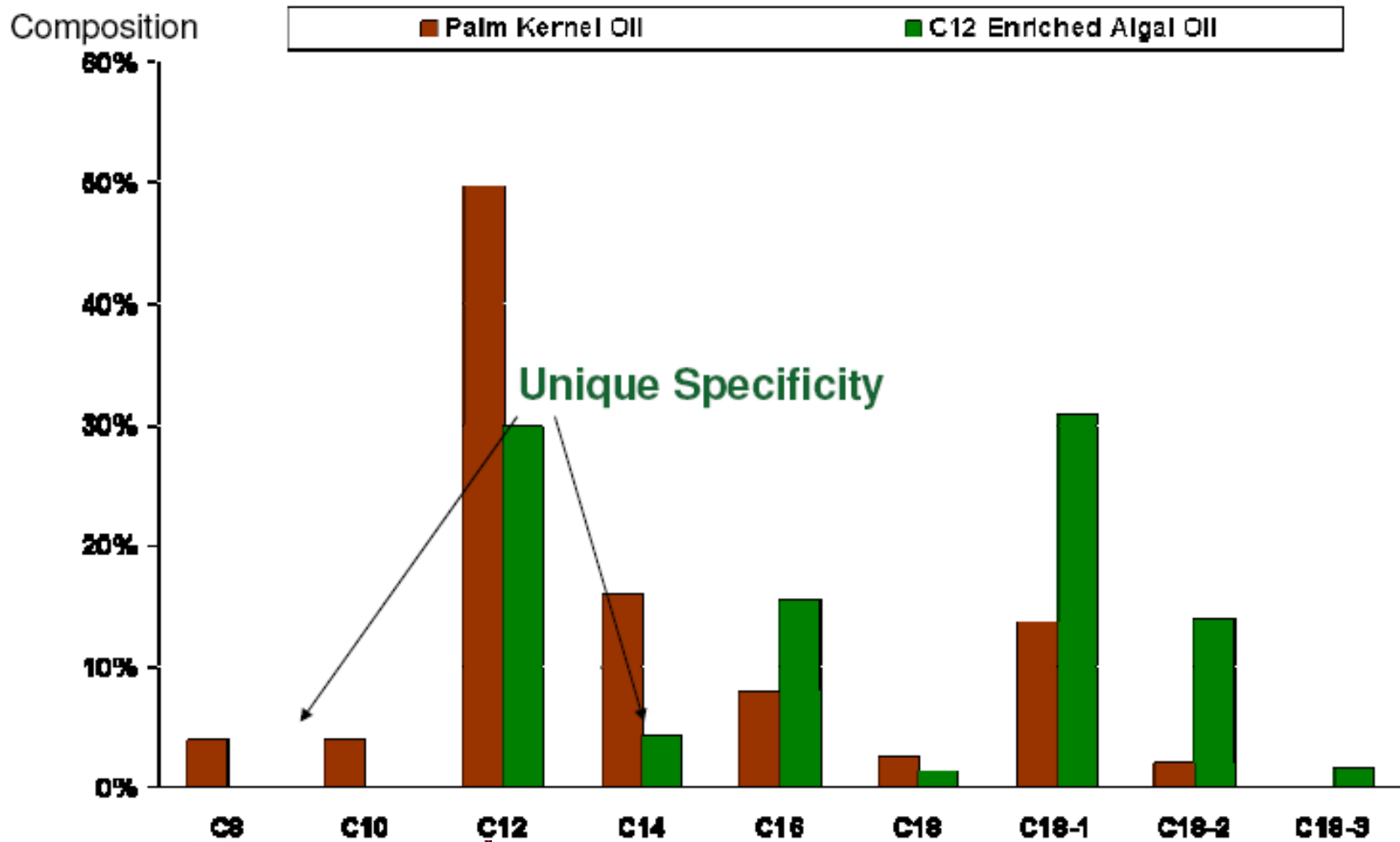


CHAIN LENGTH CONTROL: C12 ENRICHED OIL



Source:  solazyme®

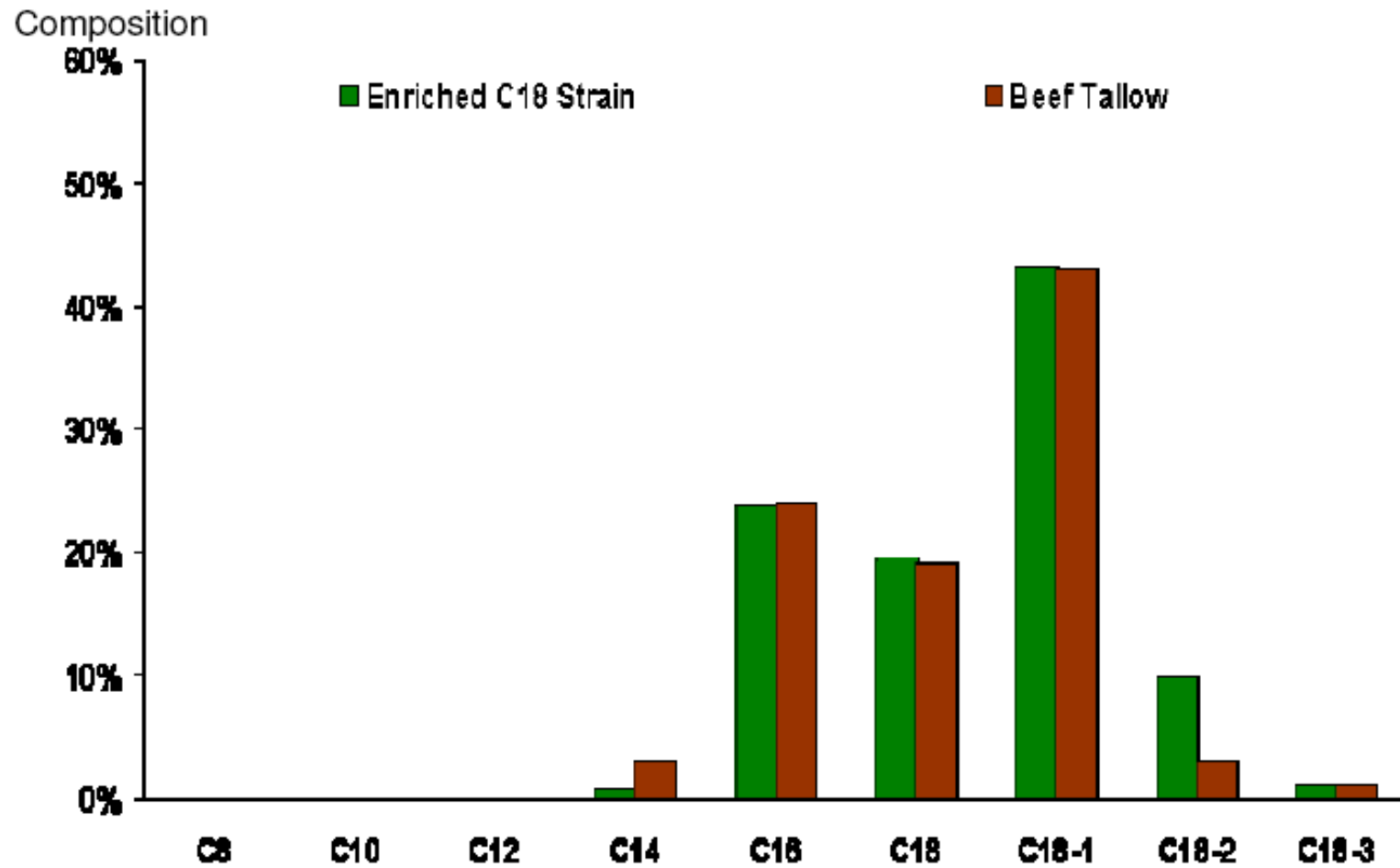
HIGHLY SPECIFIC TRANSFORMATION TECHNOLOGY



Source:

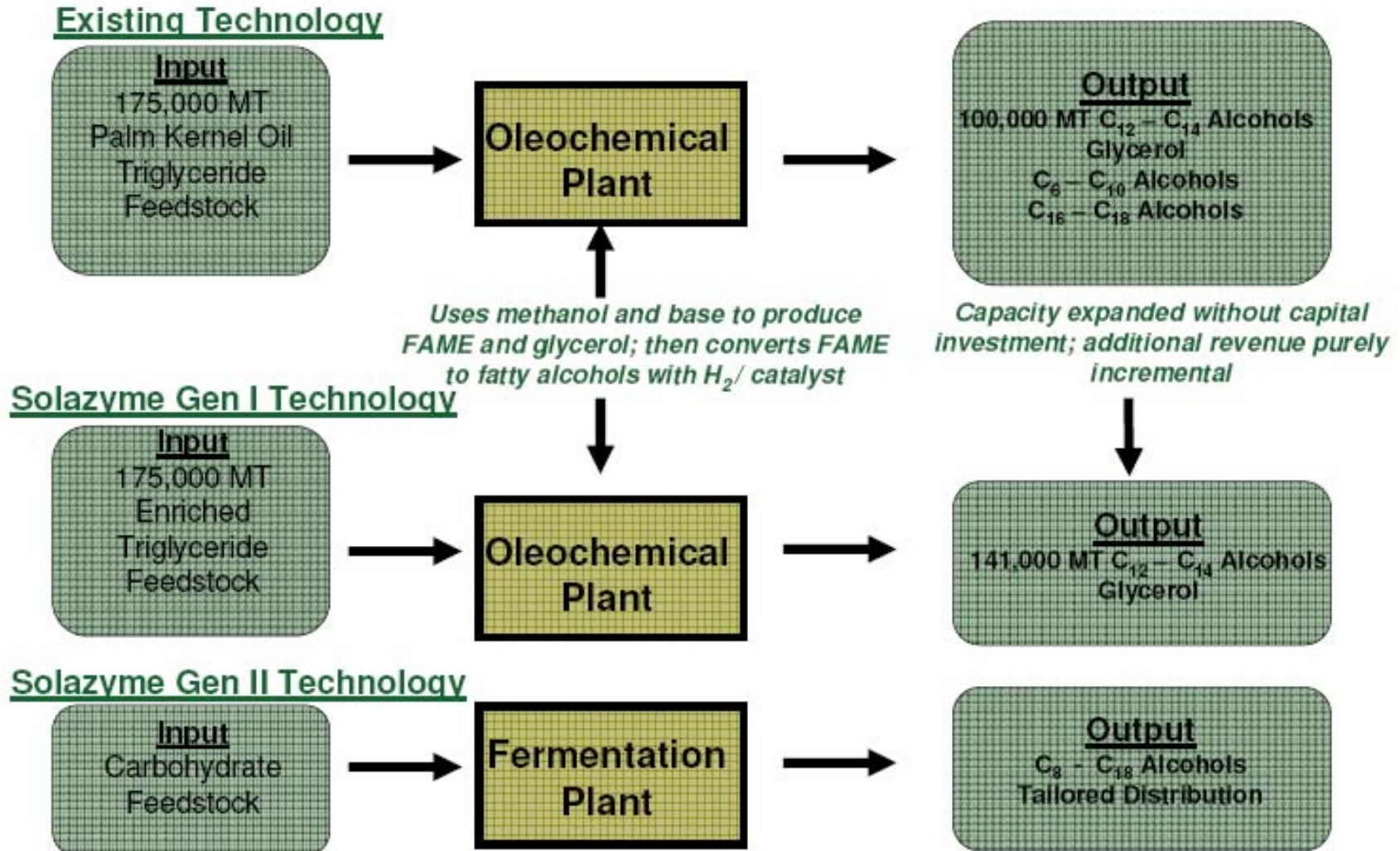


SUSTAINABLE ALTERNATIVE TO ANIMAL FATS

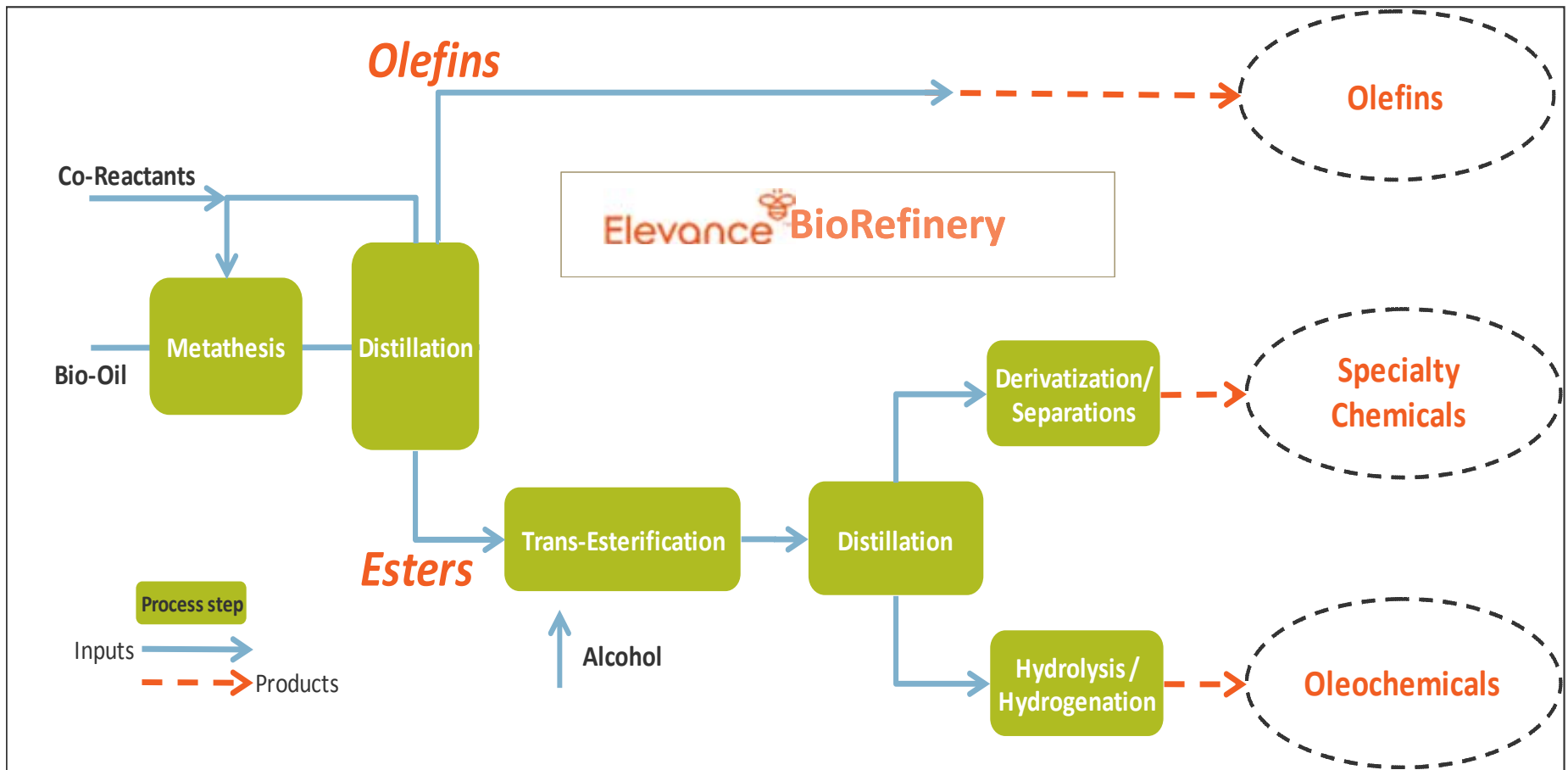


Source:  solazyme®

Next Generation Surfactant Technology



Chemicals from Biomass - Elevance



Source:



The Elevance bio-refinery produces 3 advantaged product streams

Specialty Chemicals

- Novel di-functional products
- Functionality of oleochemicals & petrochemicals in one molecule
- Metathesis is only economic route to manufacture
- 9DA (9-decenoic acid) is a key product

Olefins

- Alpha and Internal olefins
- C10 – C18+
- Unique, high value product distribution vs petrochemical production
- 1 – decene is a key product

Oleochemicals

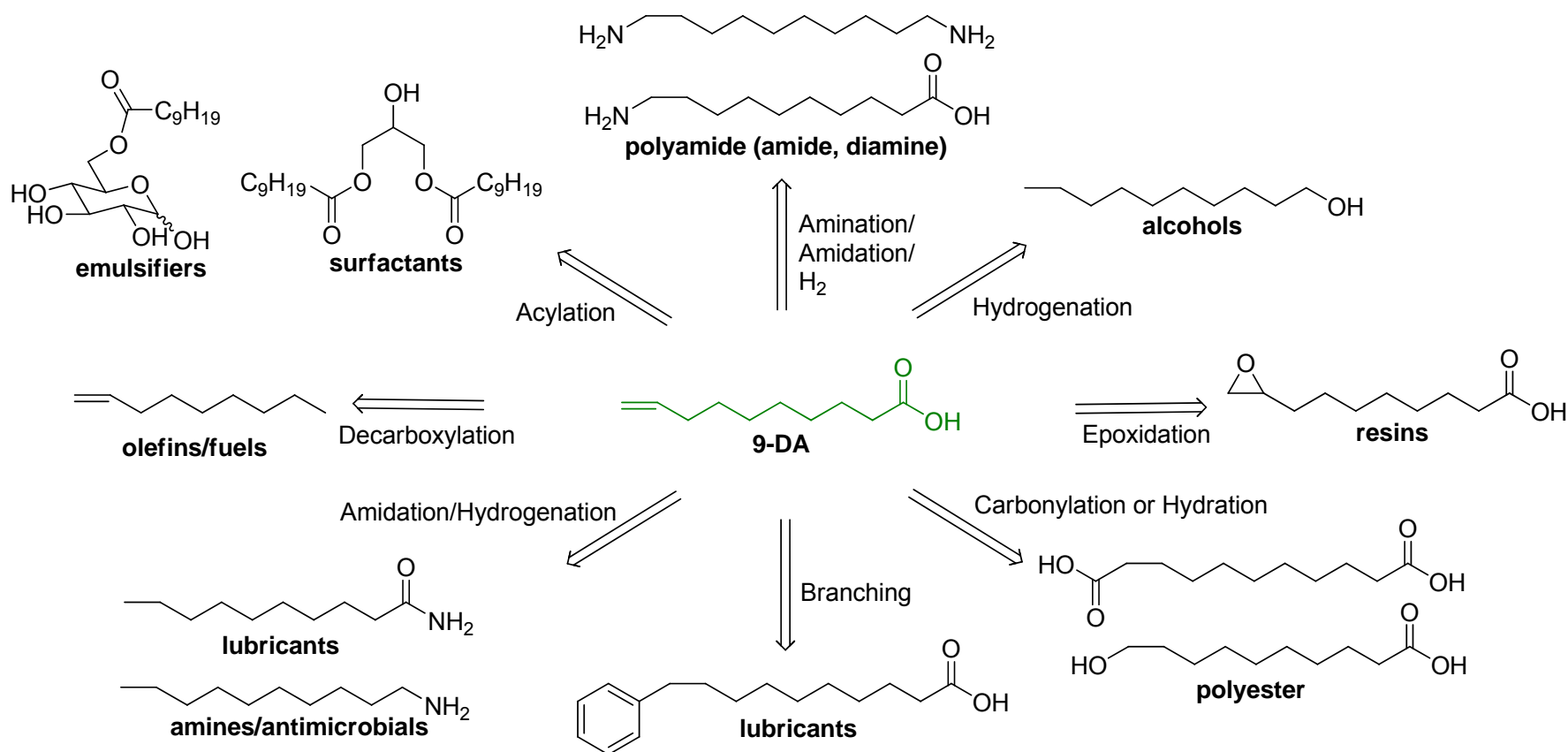
- High distribution of C10 and C12 tri-glycerides , esters or fatty acids
- Process reduces C18 fraction
- Ability to use commodity oils (vs CNO/PKO) to produce lauric & decanoic
- Lauric & capric/decanoic are key products

Source:



Novel di-functional specialty chemicals: 9DA

- The natural product equivalent of a petrochemical building block.
- Possibilities for considerable innovation in a wide variety of markets and applications

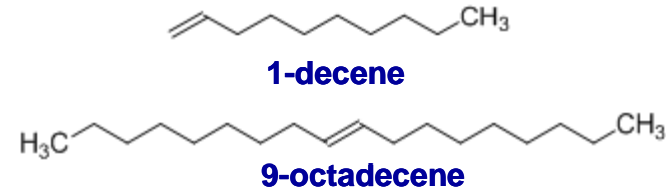


Source:



High value Olefins

C10-C18+ Alpha and Internal Olefins



Specific Products	Example Applications	Specifications & Comments
<ul style="list-style-type: none">• 1-decene	Lubricant & PAO	Standard Industry specs
<ul style="list-style-type: none">• C10 – C18 internal olefins	Oilfield, Surfactants, Paper sizing	Mixed stream or specific cuts
<ul style="list-style-type: none">• 9-octadecene	Oilfield, Paper sizing	High purity, symmetrical olefin

- **Competitive with petrochemical alternatives (quality and cost)**
- **Products available for qualification**
- **Off-take and Supply agreements currently in negotiation**

Source:

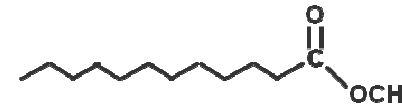


Oleochemicals

Decanoic & Lauric from feedstocks
other than PKO or CNO



Decanoic acid methyl ester



Lauric acid methyl ester

Specific Products

- Decanoic (C10 or Capric) ester/acid
- C12 – 15 ester/acid
- C16 - 18 esters/acids

Specifications & Comments

- Pure cut; standard industry specifications
- Mixed stream
- Mixed stream ; high palmitate (C16)

-
- **Product distributions enable custom blends**
 - **Product available for qualification**
 - **Off-take Agreements & Specifications being established**

Conclusions

- Recent surfactant progress - **Evolutionary**
- Sustainability problem needs **Revolutionary**
- A new surfactant value chain needed
- Algae / Biomass may offer a solution
- A **Revolution** in surfactants is possible

Thanks To



RSPO



Time for..

- Questions.....
- Comments.....

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