

NEW DEVELOPMENTS IN SEED OILS AND THEIR INDUSTRIAL APPLICATIONS

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Cargill Industrial Oils & Lubricants

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Presentation Outline

➤ Introduction

- Production
- Market Drivers
- Structure, Classification
- Reactivity (Oxidation rate)

➤ Conventional Oils

➤ Biotech. Oils

➤ Applications

- Lubricants - Chemical Modifications
- Paints & Coatings - Chemical Modifications

➤ Conclusions

Average annual production of oils and fats (MM tonnes)

Oil type	1976-80	1996-00	2016-20
World total	52.6	103.5	175.8
Soybean	11.2	22.9	37.1
Palm	4.2	20.2	45.8
Canola/sunflower	7.2	21.7	38.8
Other veg. oils	12.8	18.0	26.2
Animal fats	17.2	20.7	27.9

Market Drivers

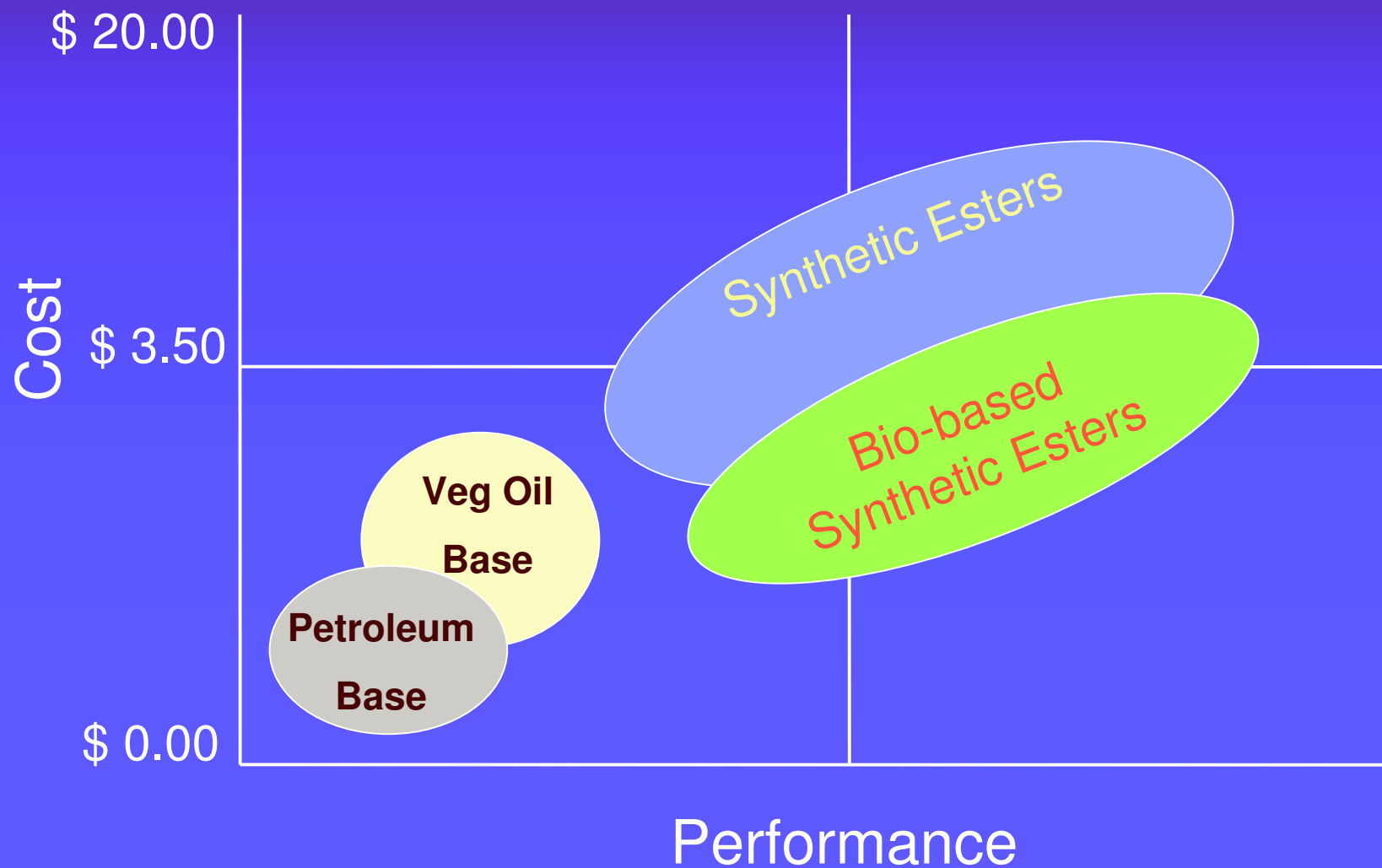
- Price
- Performance
- Regulations (VOC)
- EHS (Bio-degradability)
- ?

Marketing Advantage

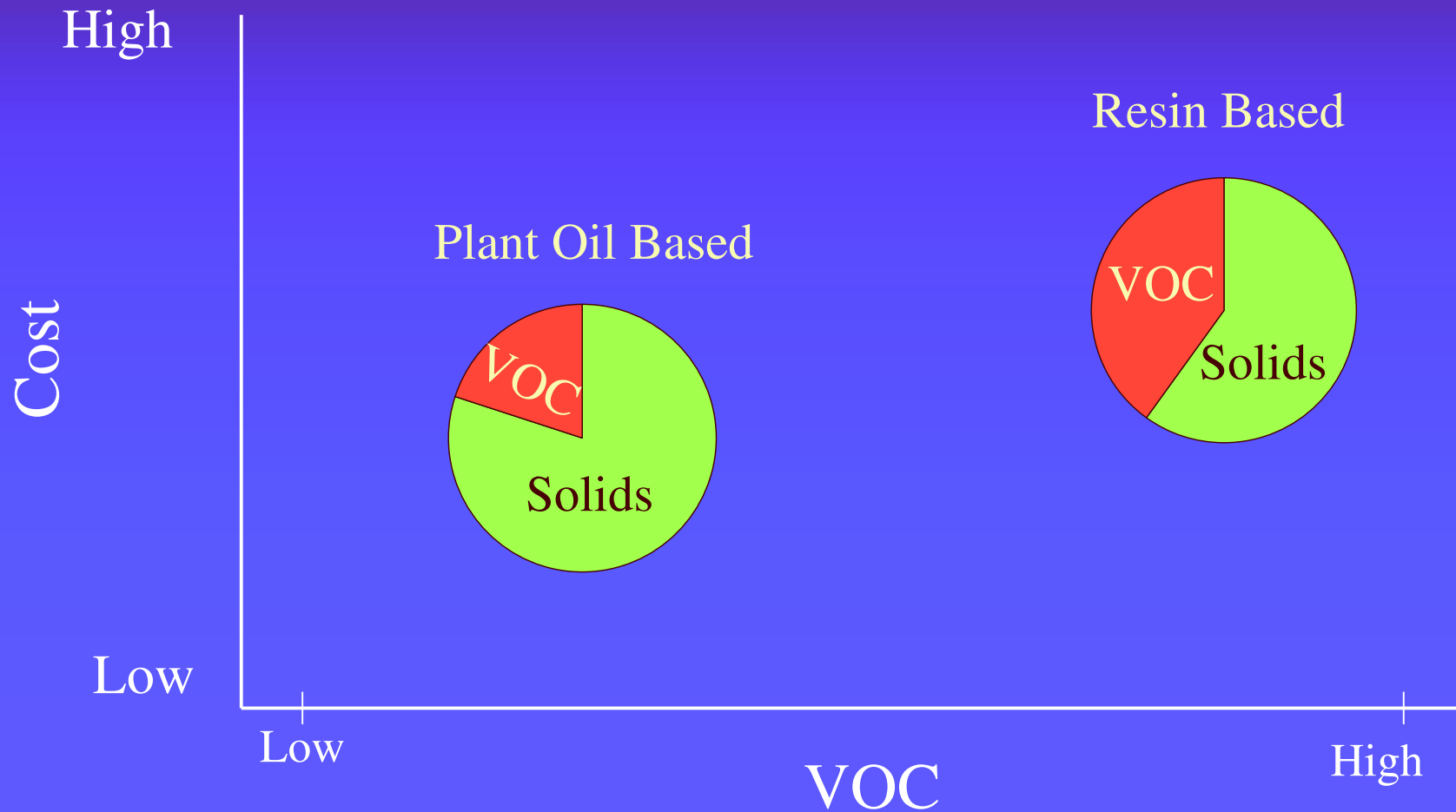
Average Relative Price (range)

Petroleum base stock - Lubes:	1 X / Kg
Synthetic base stock - Lubes:	4 to 10 X / Kg
Resins - Coatings:	3 to 6 X / Kg
Plant Oils:	1 to 2 X / Kg
Bio-based Synth. Esters:	2 to 5 X / Kg

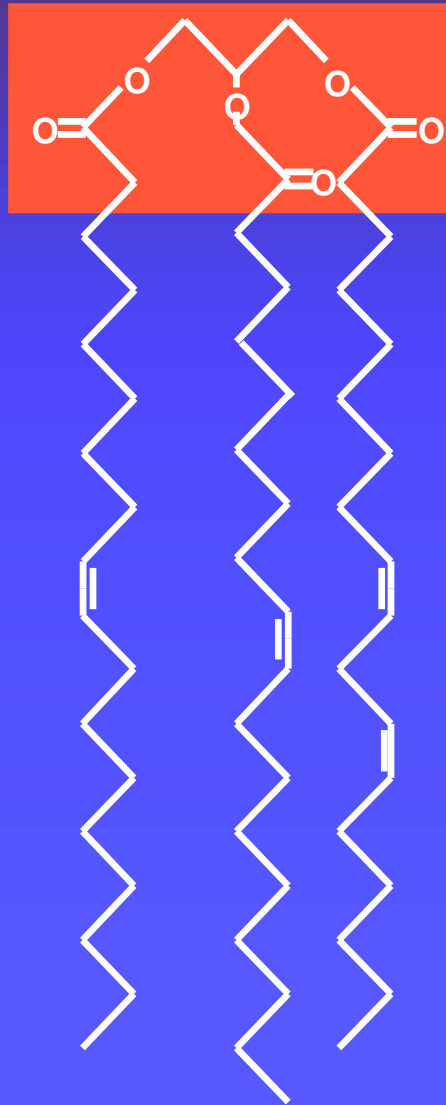
Cost Vs Performance



Opportunity



Triacylglycerol (Plant oils)



← Slightly Polar Ester

← Nonpolar Hydrocarbon

Types of Oils - Applications

I. Drying oils: Linseed oil, Tung oil

(Iodine Value = >150)

APPLICATIONS: Paints and Coatings, Inks, Resins

II. Semi Drying oils: Soybean, Sunflower oil

(Iodine Value = 110 - 150)

APPLICATIONS: Any application with average performance

III. Non Drying oils: Palm oil, Coconut oil, olive oil

(Iodine Value = <100)

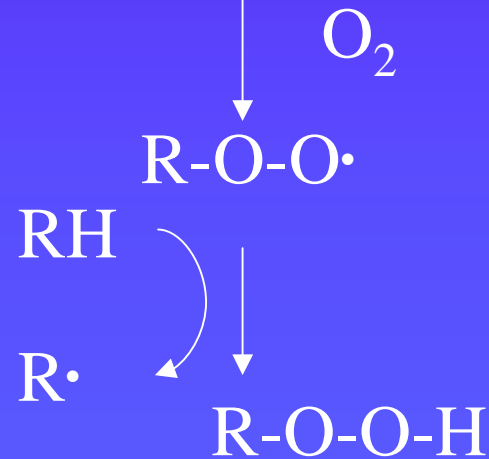
APPLICATIONS: Lubricants, Heat Transfer fluids

Drying = Free Radical Oxidation

Initiation



Propagation



Homolytic Cleavage of Peroxide

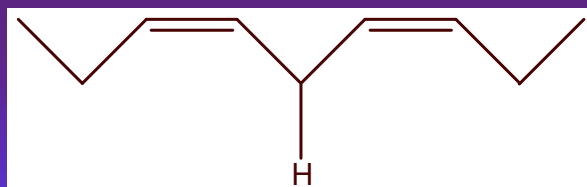
Combination of Radicals

Cross-Linked Products (Polymerization)

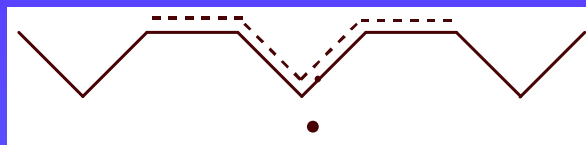
Termination



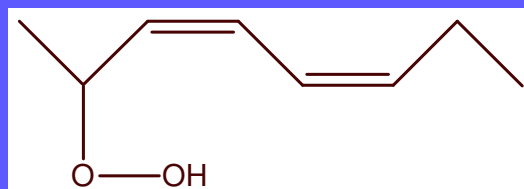
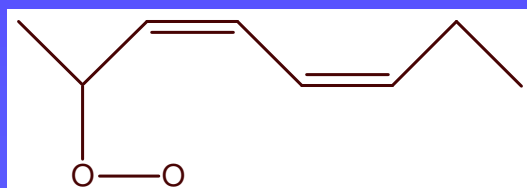
Oxidation - Mechanism



Abstraction of H atom

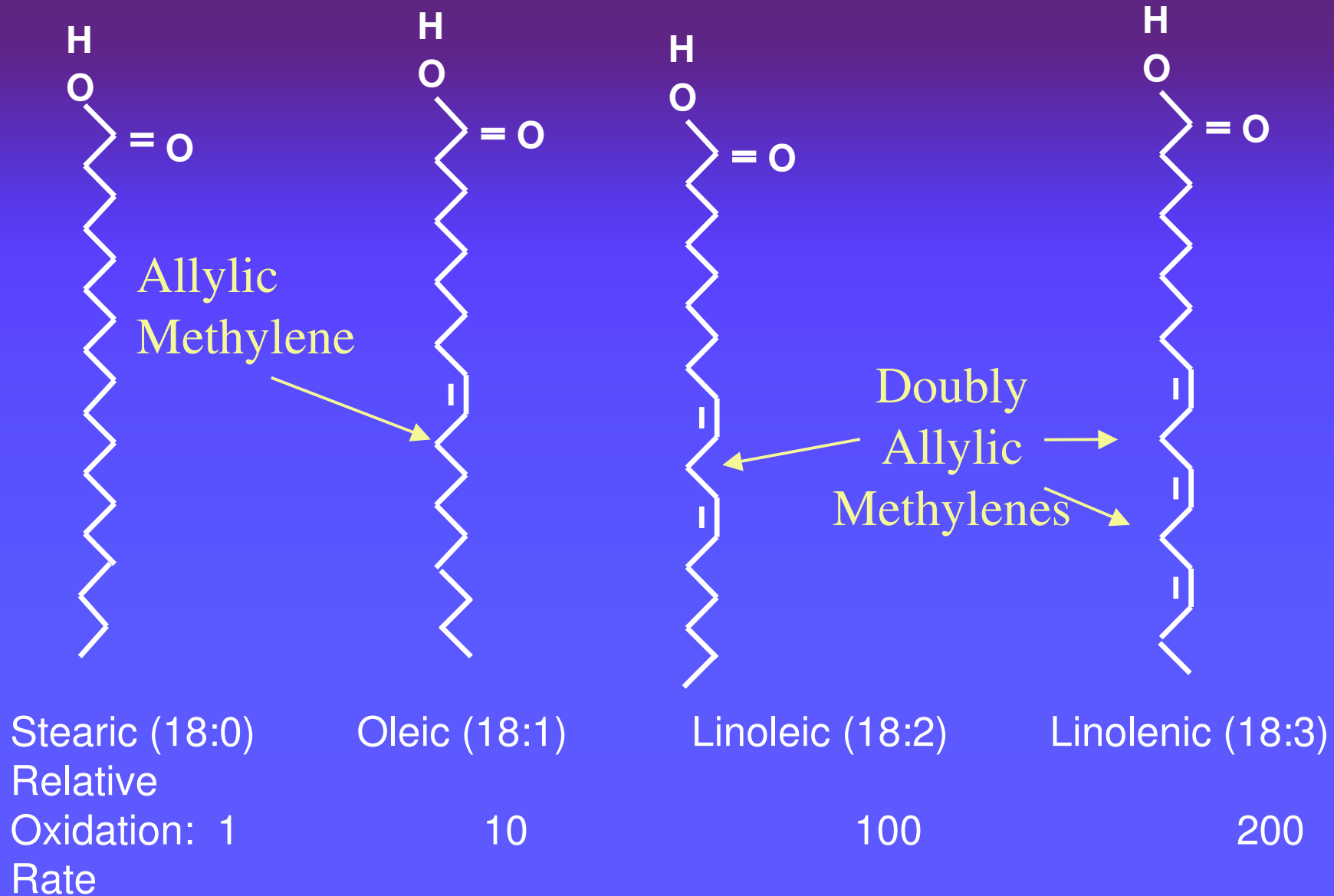


Resonance
Stabilization



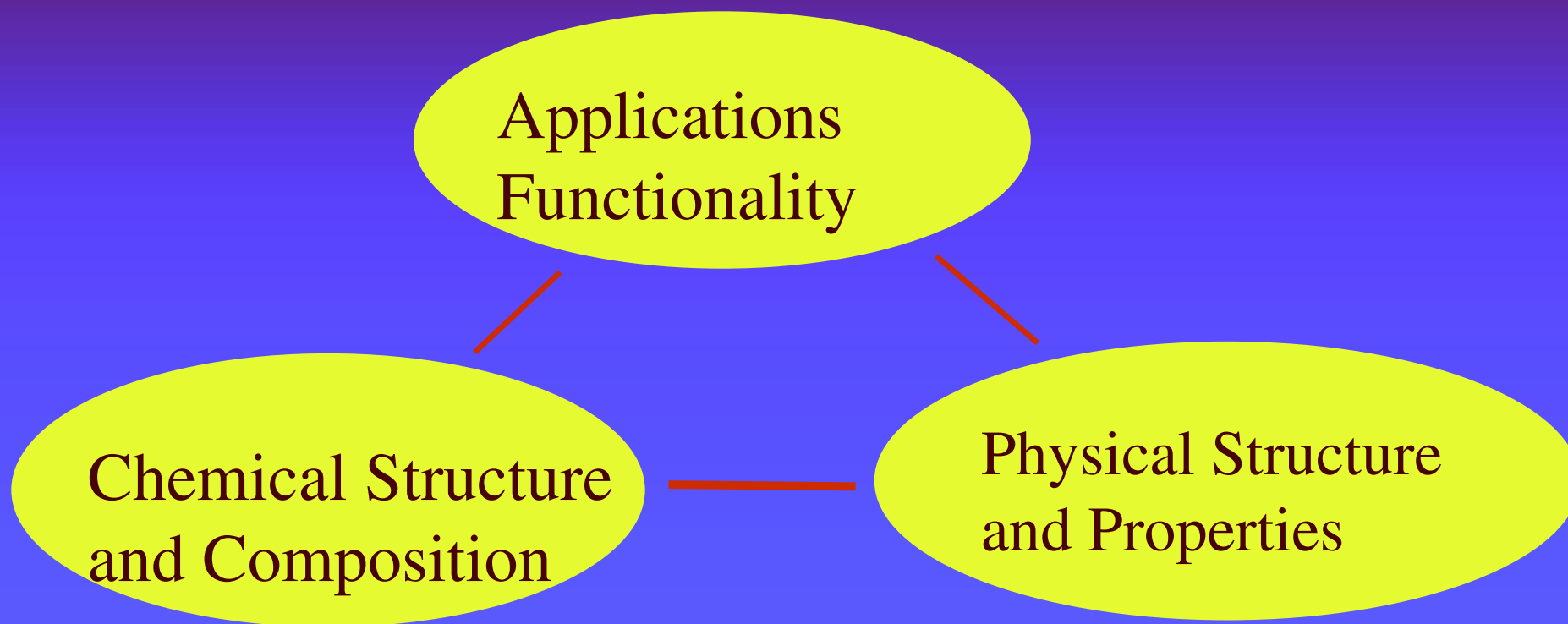
Hydroperoxide

Fatty Acids - Rate of Oxidation



Properties VS. Functionality

Understand the connection between the application and market value



In depth understanding of molecular origins of structure-properties-functionality relationship

Understanding the chemical structure physical properties relationship

Creating the desired functionality through chemical modification and capturing it through New Product Development

Properties VS. Functionality

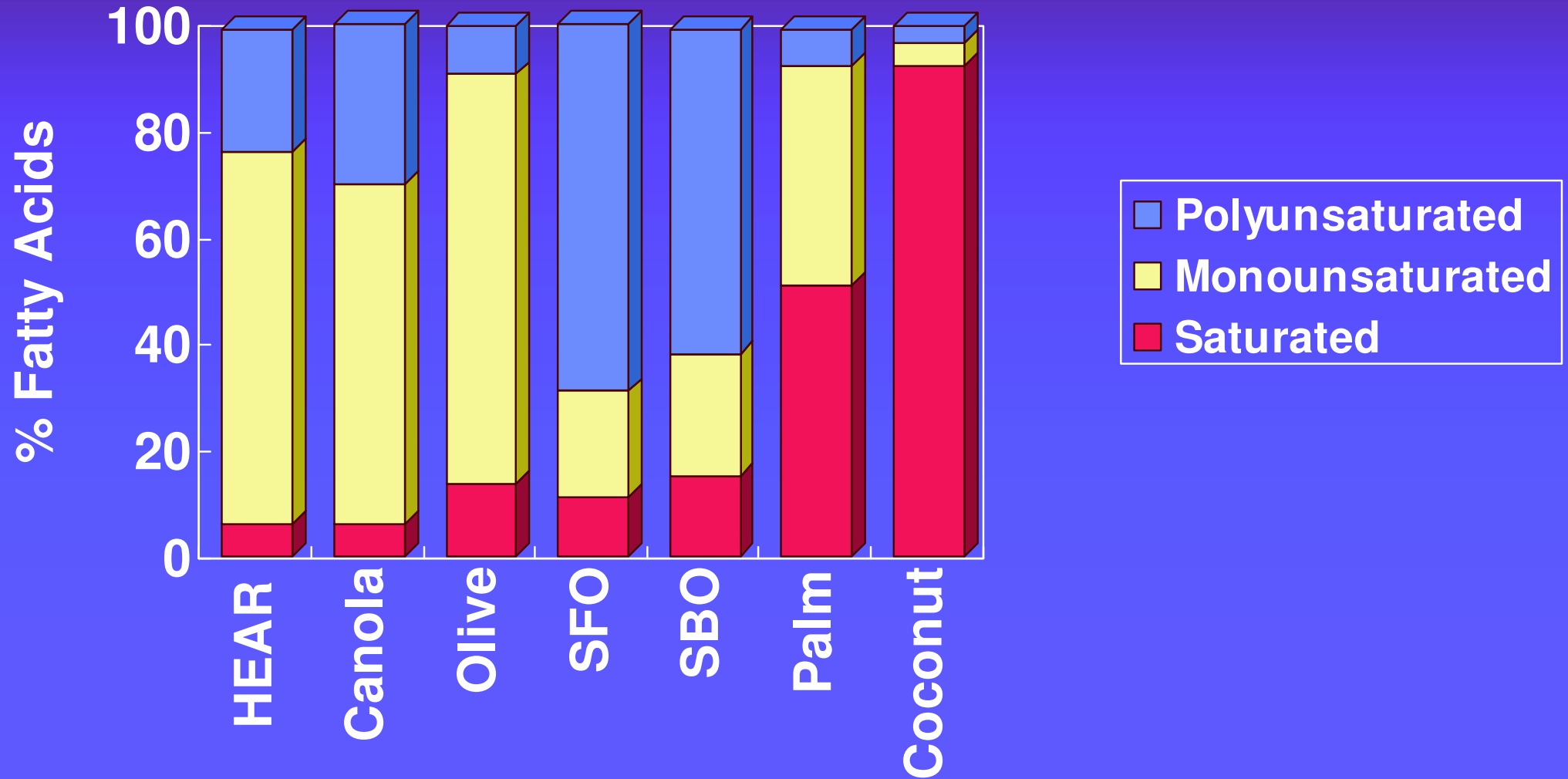
➤ Molecular Property

- Reactivity
- Iodine Value
- Chain length
- conjugation
- Sap. Value
- Acid Value
- Peroxide Value
- Polarity
- Solvency
- Hydrophobicity
- Mol. Weight
- Mol. Packing
- Heterogeneity

➤ Derived Functionality

- Appearance/Color
- Viscosity (flow properties)
- Volatility (VOC)
- Low Temp. Behavior(m.p./f.p.)
- Drying (film formation)
- Adhesion
- Tack/Rub-off
- Lubricity
- Oxidative Stability(shelf-life)
- Compatibility
- Biodegradability

Composition of Plant Oils



Plant Oils - Lubricants

Advantages

- ✓ Excellent boundary lubrication
- ✓ Good viscosity and viscosity index
- ✓ High flash point
- ✓ Biodegradable, nontoxic
- ✓ Environmentally friendly, renewable

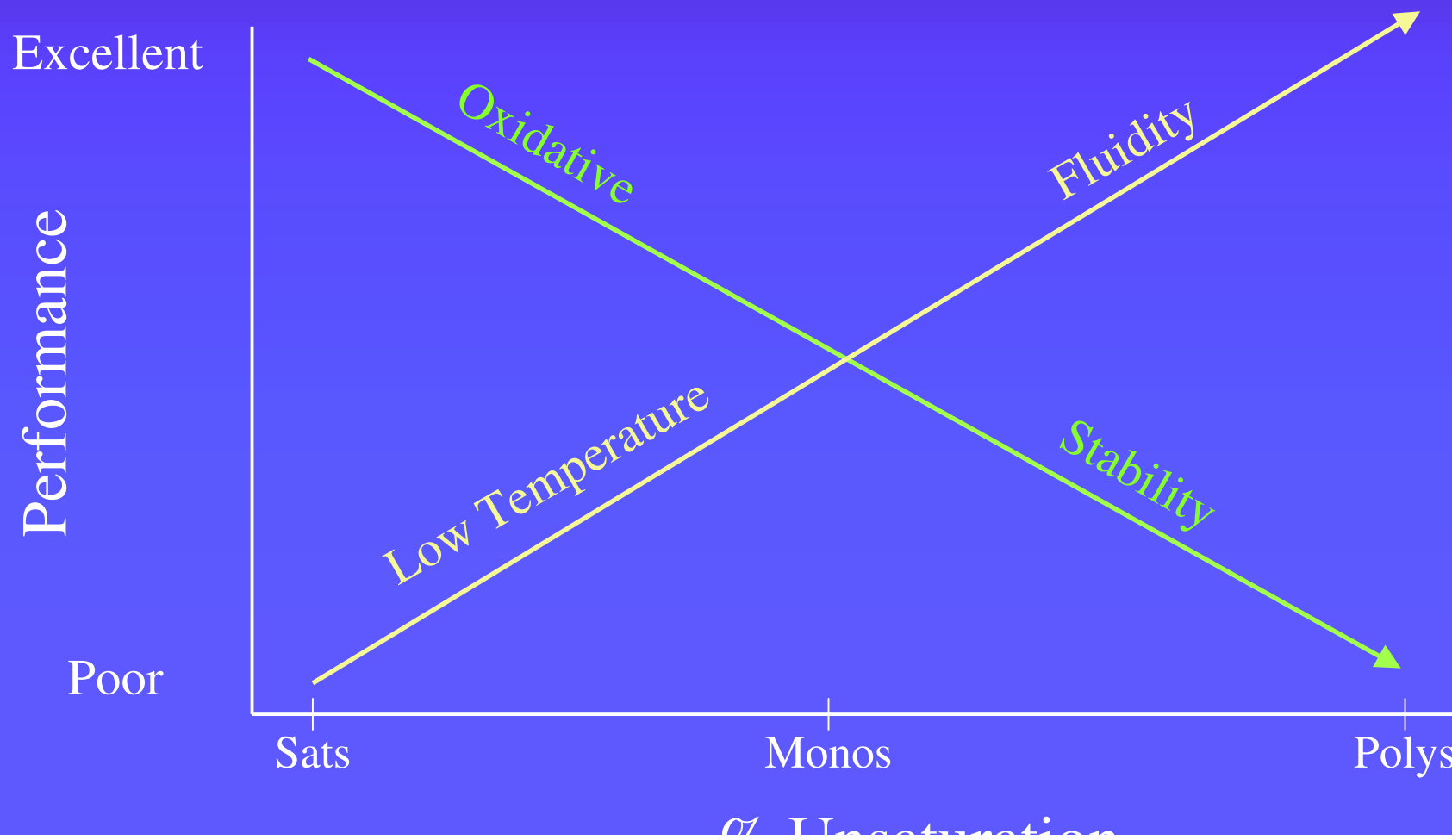
Limitations

- *Poor oxidative stability*
- *Poor low temperature properties*
- *Lack of viscosity range*
- *Limited additive technology*

TAG - Low Temperature VS. Oxidative Stability

Property	C18:0 TAG	C18:1 TAG	C18:2 TAG	C18:3 TAG
Iodine value	0	86	173	261
Mol Wt.	892	886	880	874
Melt Temp.	74 °C	5 °C	-11 °C	-24 °C
Oxidation	Low 1	Mod. 10	High 100	V. High 200

Fluidity VS. Oxidative Stability of Plant Oils



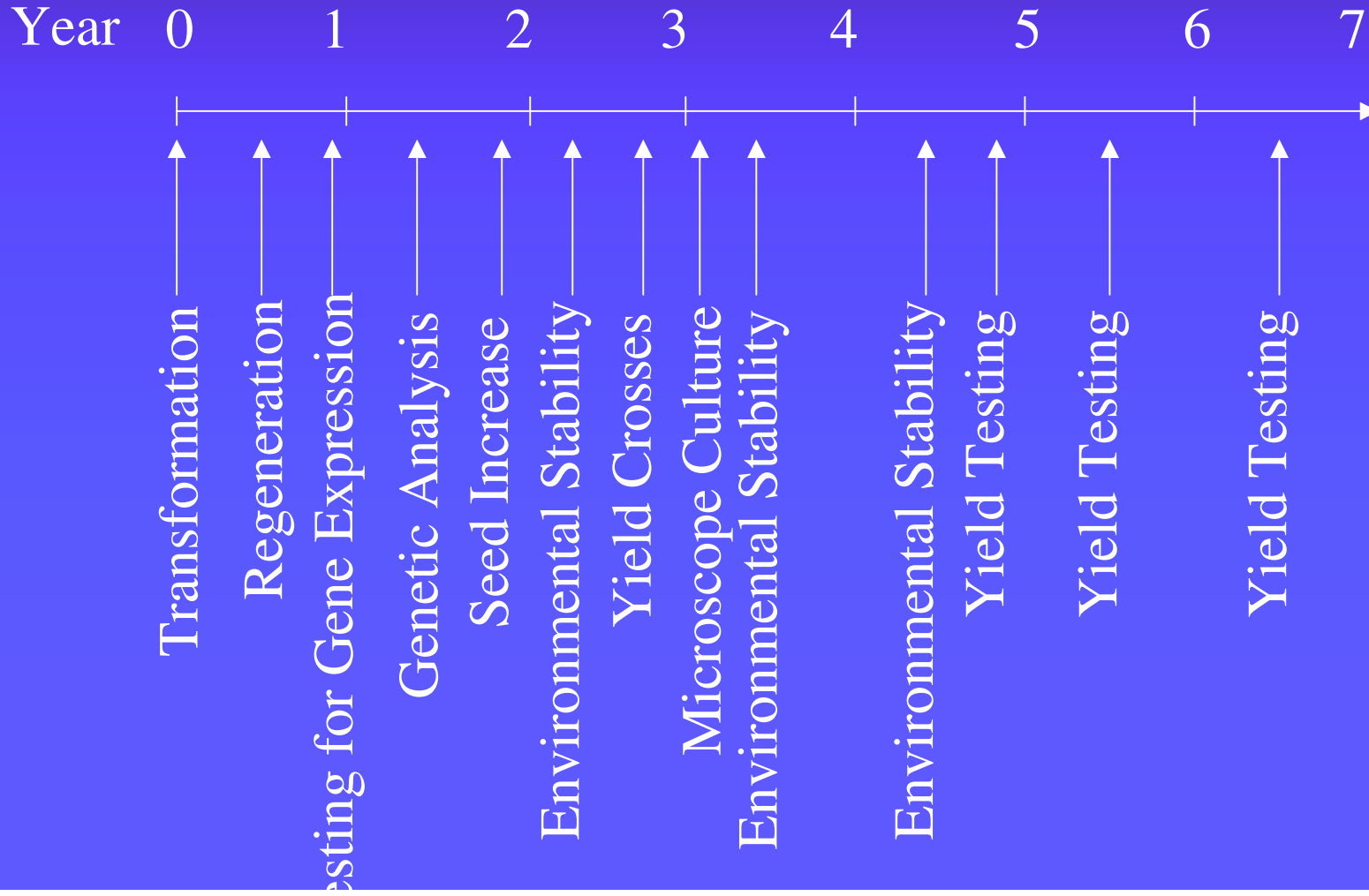
Identity Preserved (IP) Oils

- ❖ Genetic Modification
- ❖ Hybrid Production

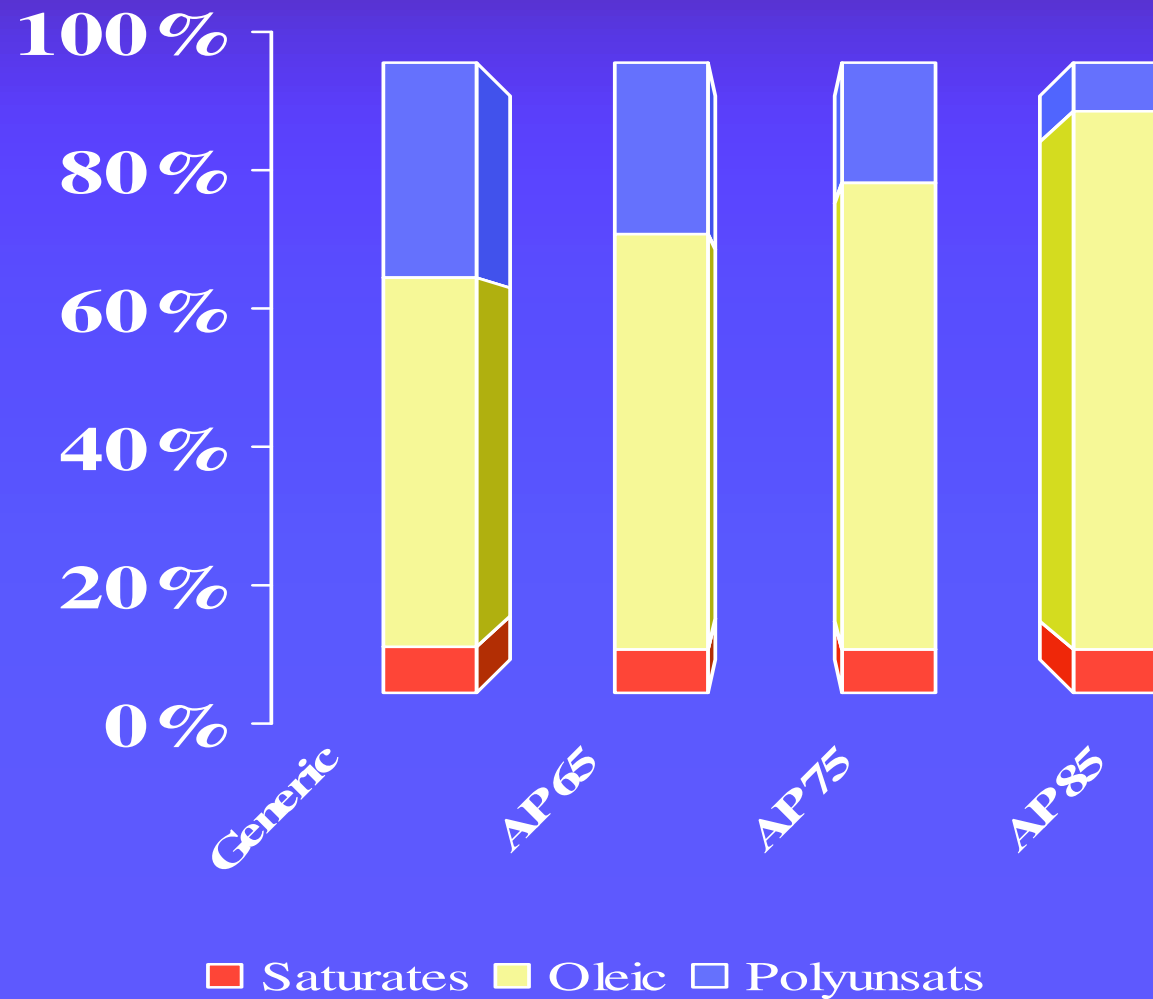
Requirements of IP Development

- Genetic Analyses
- Trait Stability Testing
- Variety Development
- Hybrid Development
- Disease Resistance
- Oil Yield
- Herbicide Tolerance
- Fungal Tolerance

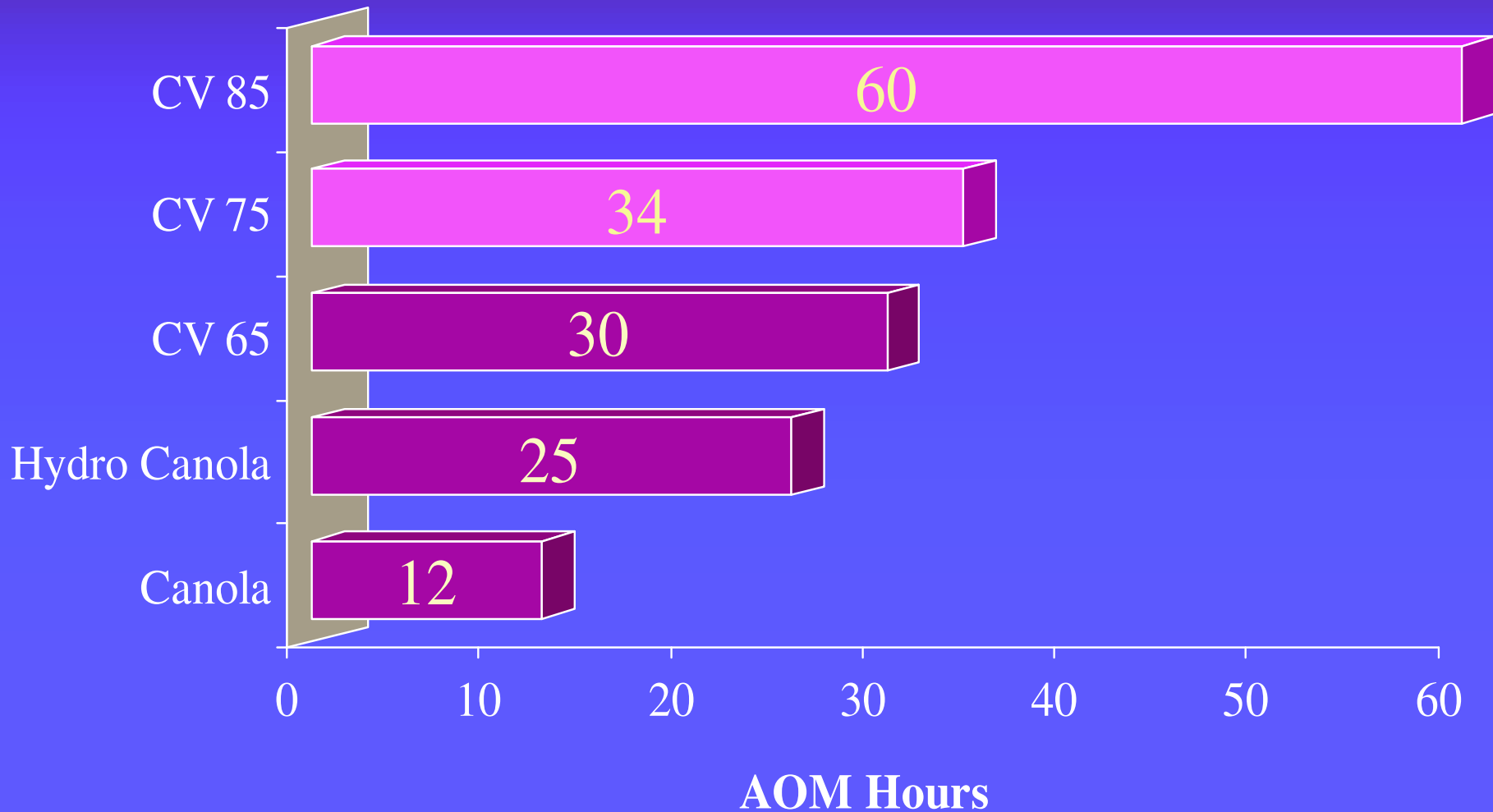
Time Line for IP Development



High Oleic Canola Oils

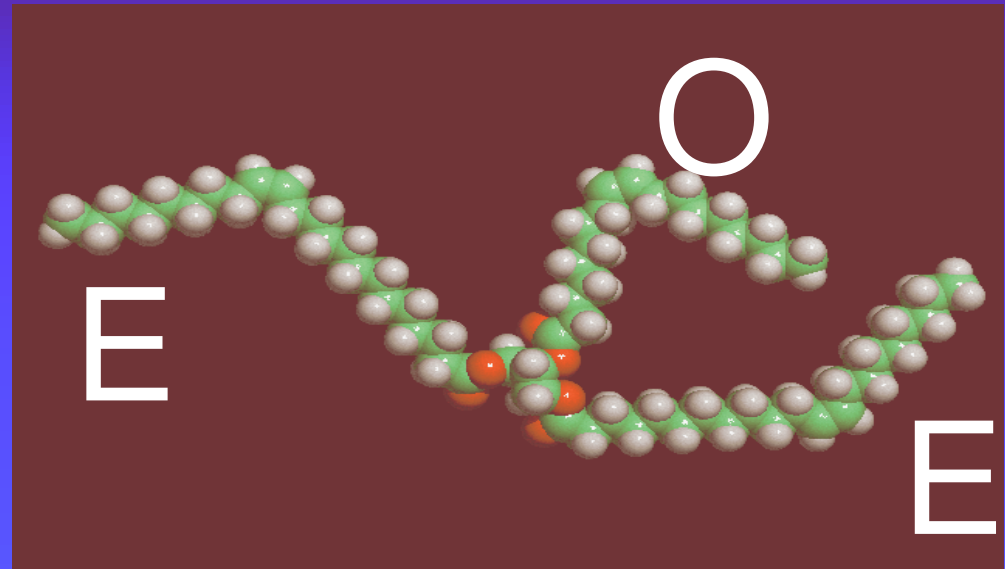
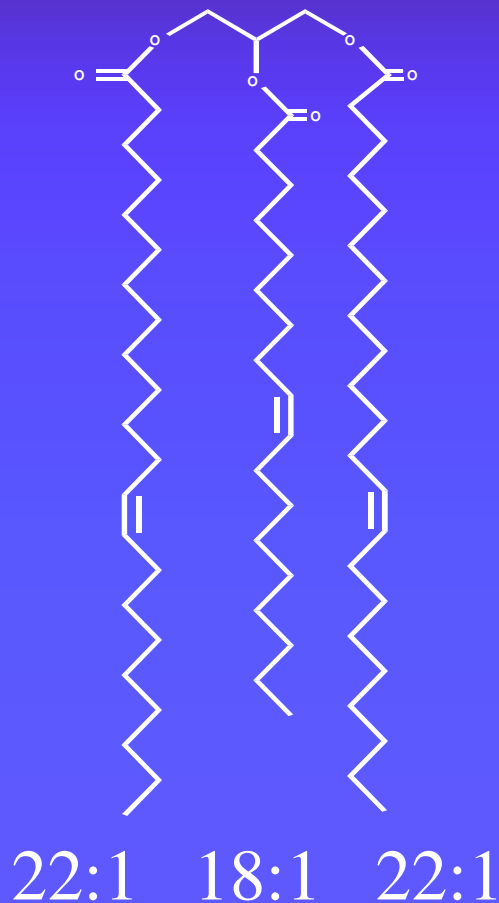


Oxidative Stability of H.O.Canola



Canola - Structured Oils

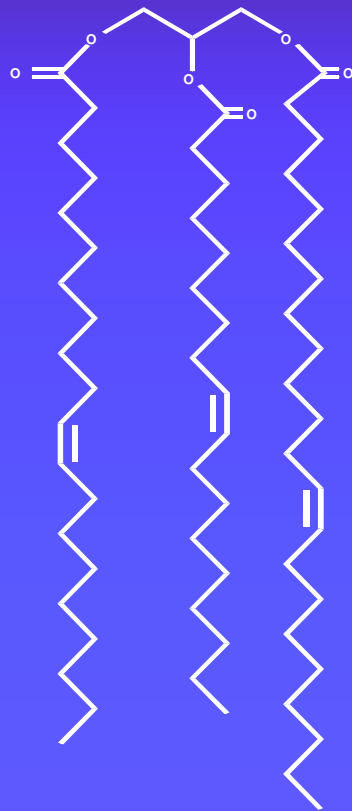
(1,3-Dierucoyl-2-Oleoyl-*sn*-Glycerol, EOE)



Advantages:

- Chemical Feedstock
- Good Lubrication Properties

Canola - Structured Oils



20:1 18:1 22:1

Heterogeneous Chain Length Oils

Advantages:

- High oxidative stability
- Good low temperature properties
- Low friction coefficient

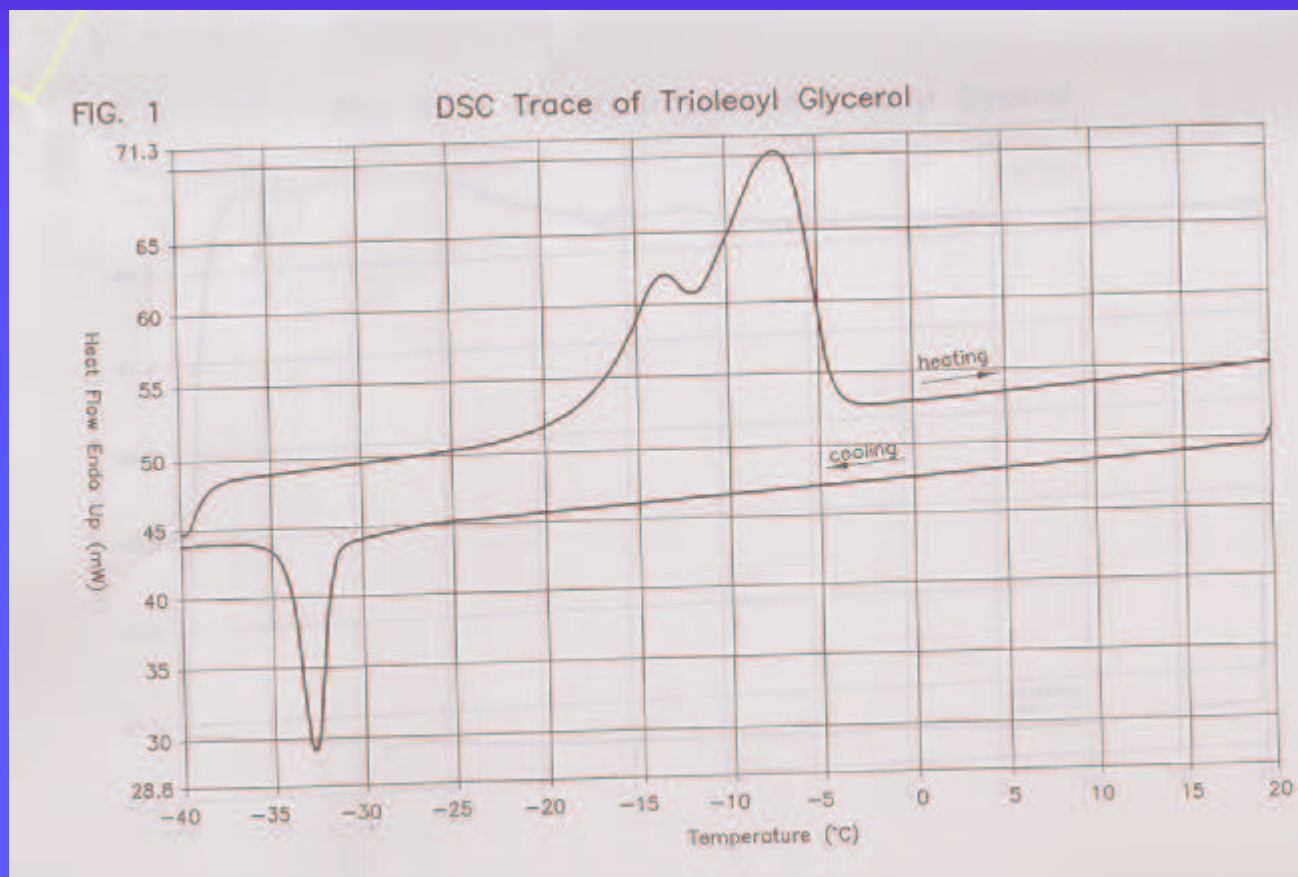
Cyclopropanated Oils



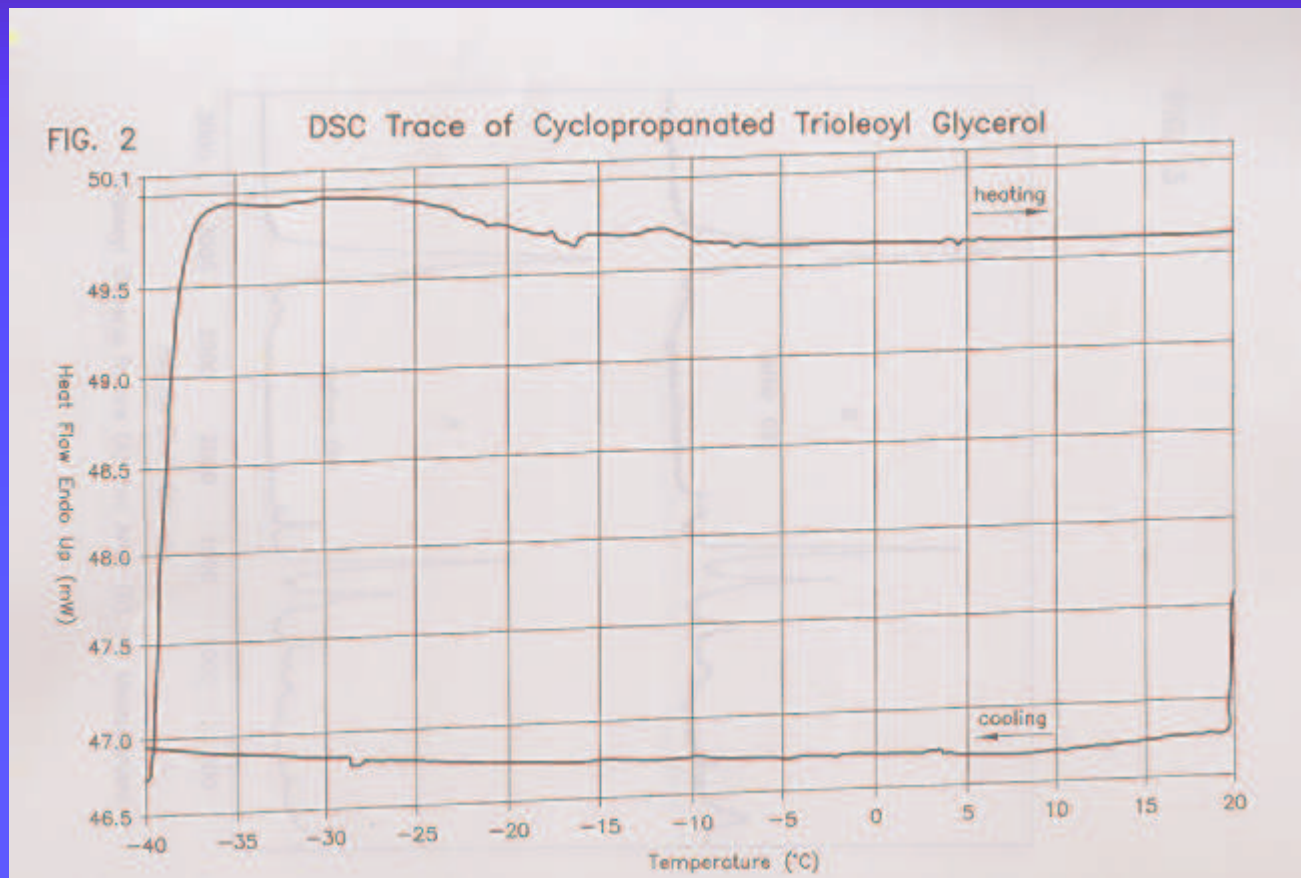
Ref: Kodali & Li US 6,051,539

DSC of High Oleic Oil

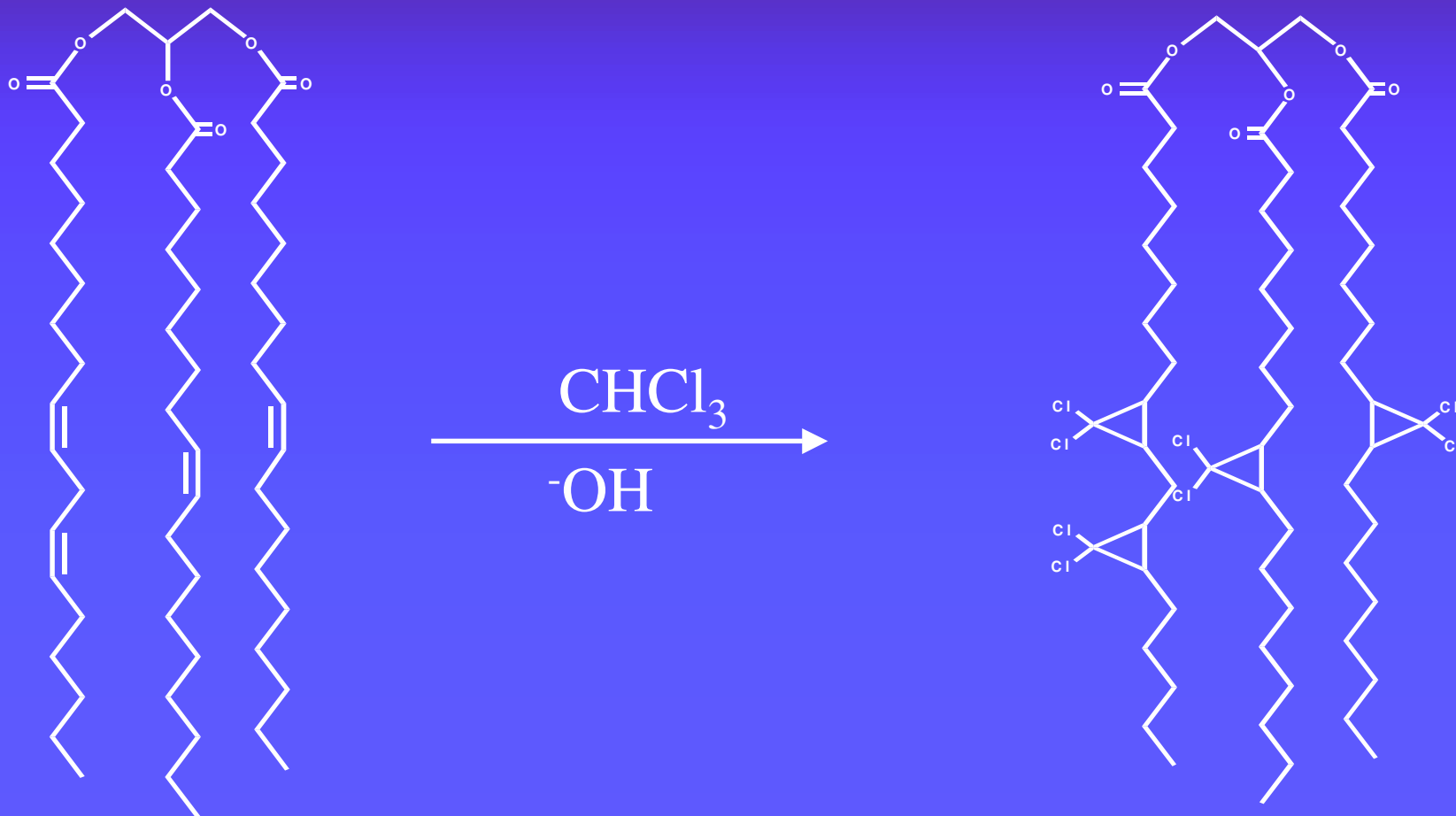
(Melting / Crystallization)



DSC of Cyclopropanated Oil (Melting / Crystallization)

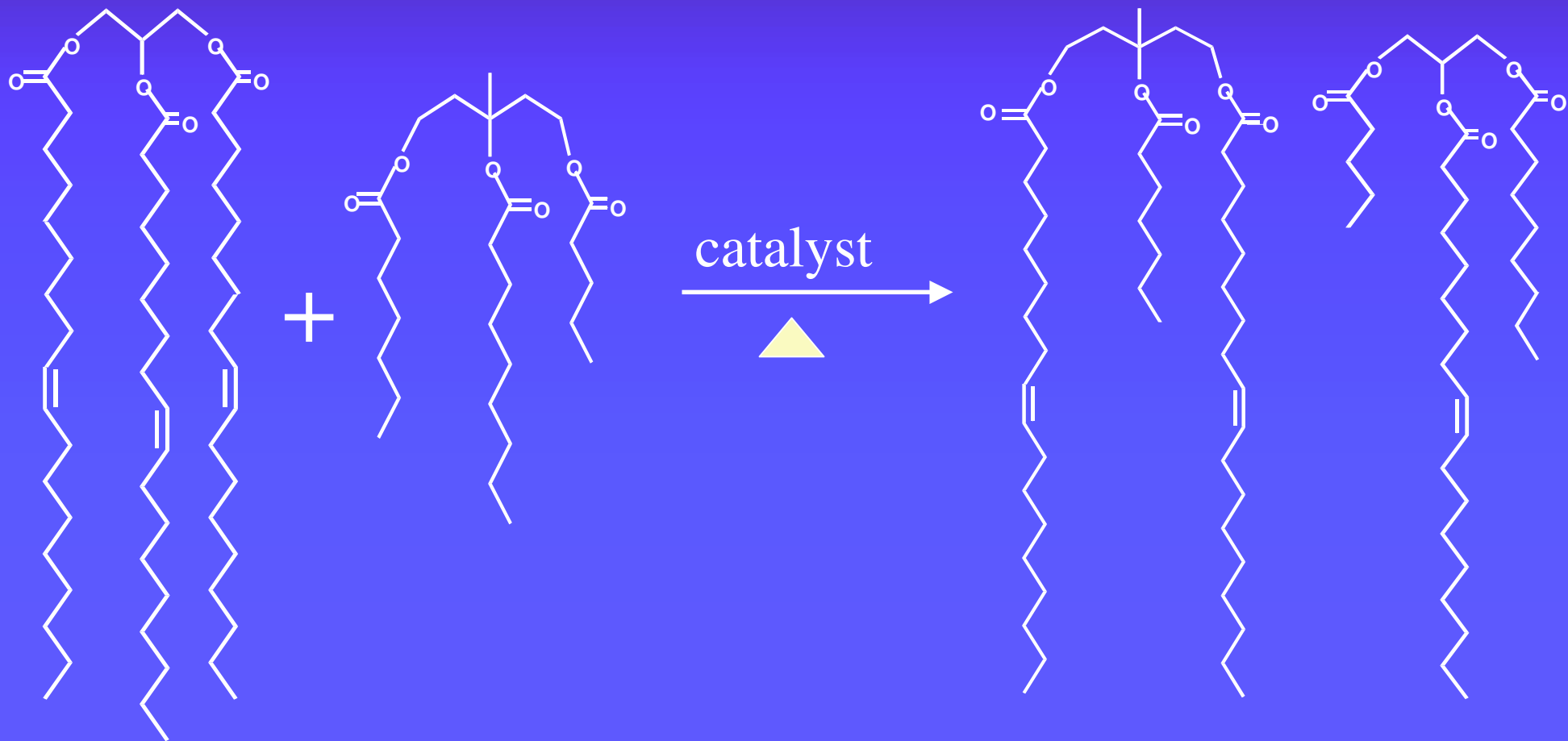


Dichlorocyclopropanated Oils



Kodali & Li US 6,291,409 B1

Heterorogenous Oils



Kodali & Nivens US 6,278,006 B1

Plant Oils - Paints & Coatings

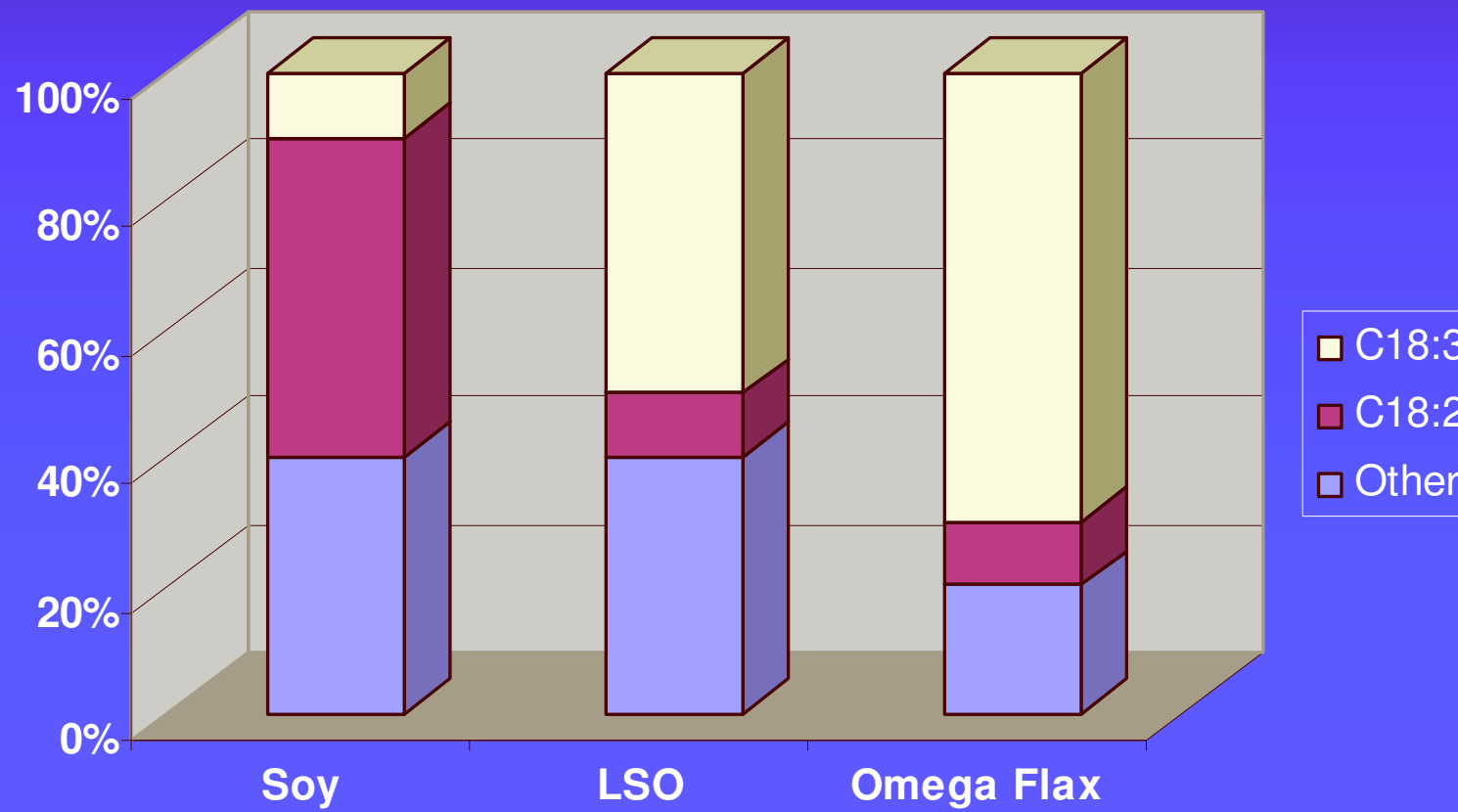
Advantages

- ✓ Low Cost
- ✓ Natural
- ✓ Non Hazardous
- ✓ low / No VOC
- ✓ Renewable

Limitations

- Low Performance / Low Reactivity (slow drying)
- Film Hardness
- Color (Yellowing)

Drying / Semi-Drying Oils



Chemical Modification

Cargill Processes/Products (Viscosity @ 25°C, Cp)

Trans-Ester. Oils - FAME of Soybean, Linseed (15)

Heat Bodied Oils - Soybean Oil, Linseed Oil (400 - 50,000)

Oxidized Oils - Soybean, Linseed Oil (100 - 3,000)

Maleinized Oils - Falkowood-51 (2,000 -3,000)

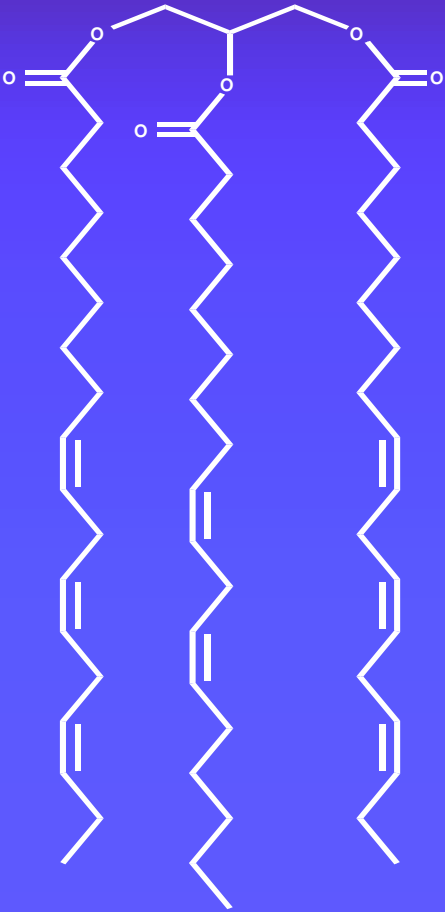
CPD Condensed Oils - Dilulin (300-600)

Solvent Substitutes - FAME

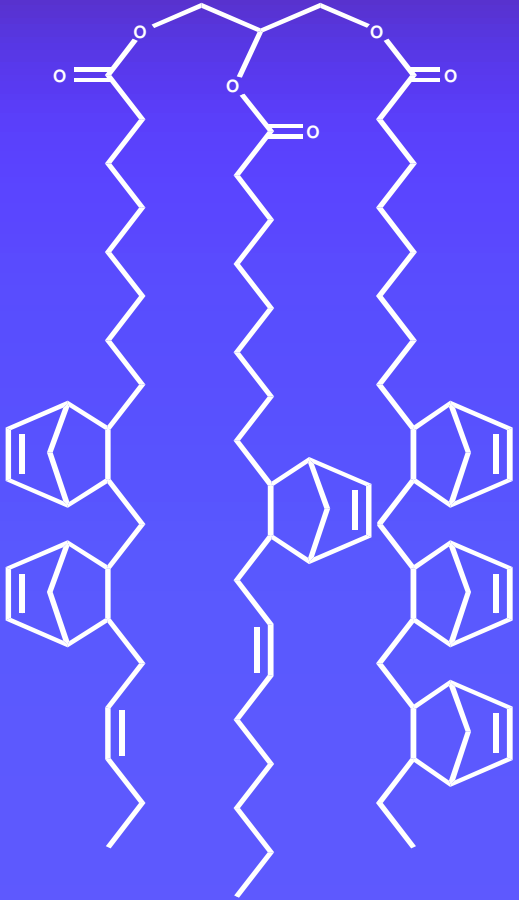
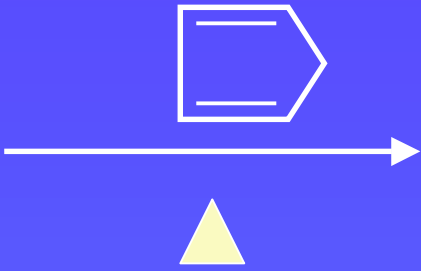
Property	Laurate	Canola	H.O. Canola	SBO	LSO
IV	10	110	95	130	175
Viscosity	15	20	20	20	20
Solvency	High	Moderate	Moderate	Moderate	Moderate
Reactivity	V.Low	Low	V. Low	Low	Moderate
Mol. Wt.	225	300	300	300	300
VOC	Moderate	Low	Low	Low	Low
Lubricity	Moderate	High	High	---	---

CPD Oils - Dilulin

(Reactive Diluents)



ISO



DILULIN

Kodali US 5,693,715

Kodali US 5,288,805

Summary

- ✓ Understanding the structure - properties -functionality relationship is very important to arrive at an oil composition to suit the application
- ✓ Plant oil fatty acid composition can be modified through Bio-technology to make value added products useful in inks, coatings, and lubricants
- ✓ Functional properties like stability and viscosity can be further modified by chemical modification
- ✓ VOC, cost, performance, and environmental factors are major driving forces for using plant oils and their derivatives in inks, coatings, and lubricants

Acknowledgements

- ❖ Scott Nivens
- ❖ Charles Tanger

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