Modification of Edible Fats and Oils

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Why Modified Lipids ?

- Improves Oxidative Stability
- Alter the Melting Properties
- Alter the Crystallization Properties
- Economic Advantages:

Less Expensive Oil → More Expensive Oil

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Modification Methods

1) Hydrogenation

2) Fractionation

3) Interesterification

4) Physical Blending

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Hydrogenation

- Treatment of Fats and Oils with Hydrogen
- A Catalyst and Heat must be present
- Exothermic Reaction
- Converts Liquid Oils into Solid or Semi- Solid Products
- Improves Oxidative Stability
- Imparts desired Physical Properties (melting point, SFC)

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Hydrogenation: Principle

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Possible Reactions during Hydrogenation

- **Complete Saturation:**

  18:3 → 18:2 → 18:1 → 18:0

- **Partial Hydrogenation**

- **Geometric Isomerization:**

  cis → *trans*

- **Positional Isomerization:**

  cis → *trans*

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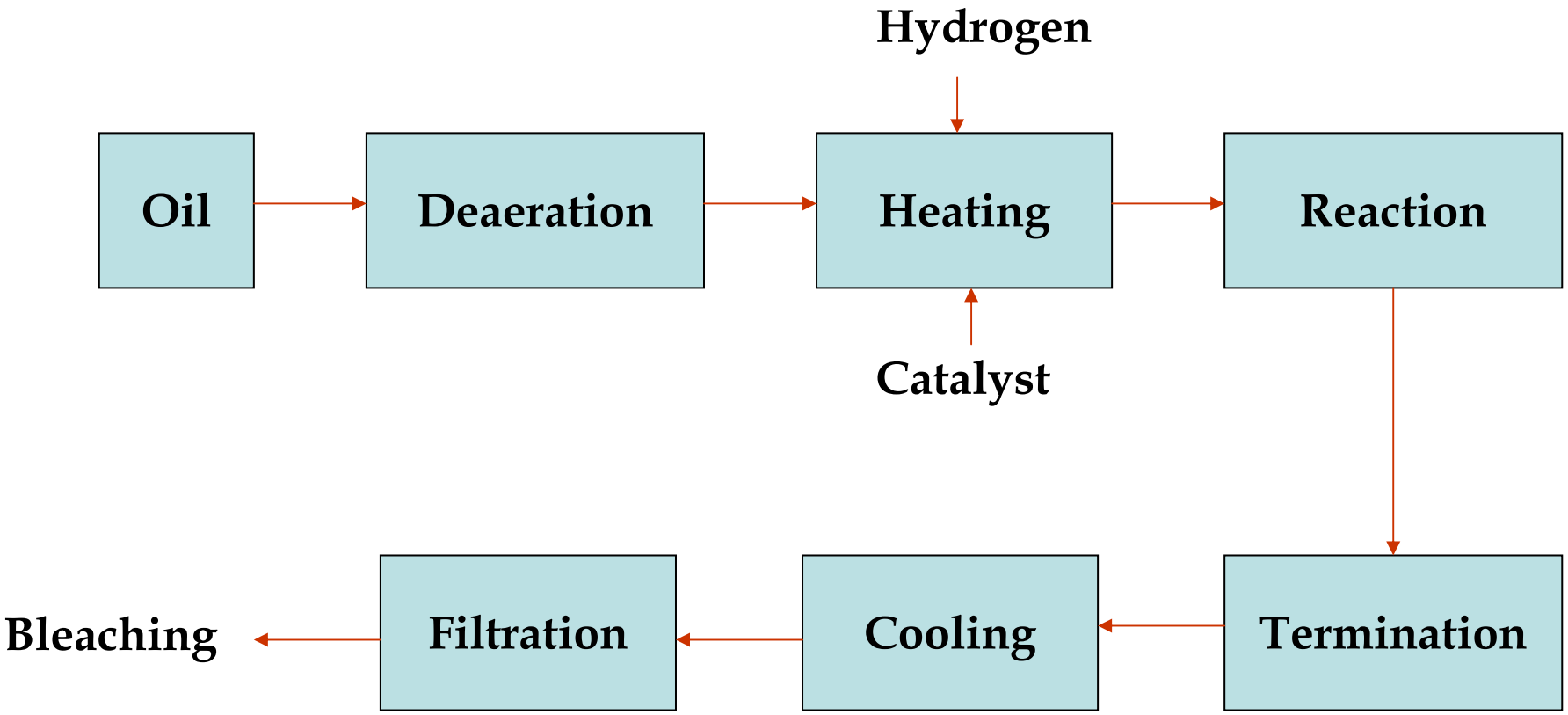
Hydrogenation



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Hydrogenation: Monitoring the Reaction

- H_2 Consumption
- Refractive Index
- Iodine Value
- Melting Properties:
  - Melting Point
  - SFC

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Hydrogenation Variables

- Reaction Temperature
- Pressure
- Agitation
- Catalyst Type
- Catalyst Concentration
- Reaction Time

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Impact of Hydrogenation Variables

Increase of:	Saturate Formation	Trans Isomer Formation
Catalyst Dosage	Decrease	Increase
Agitation Speed	Increase	Decrease
Temperature	Decrease	Increase
Pressure	Increase	Decrease

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Hydrogenation Conditions Affecting Selectivity

Selective Hydrogenation	Nonselective Hydrogenation
High temperature (170°C)	Low temperature (120°C)
Low hydrogen pressure (1 Atm)	High hydrogen pressure (>3 Atm)
High catalyst (0.05% Ni)	Low catalyst (0.02% Ni)
Selective catalyst	Nonselective catalyst
Low agitation	High agitation
High trans fatty acids	Low trans fatty acids
Steep SFC Curve	Shallow SFC Curve

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Hydrogenation: Feedstock Oil Quality

Parameter	Specification
Peroxide value	< 0.5 meq/kg
p-Anisidine value	< 10
Free fatty acids	< 0.05%
Moisture	< 0.05%
Soaps	< 25 ppm
Phosphorus	< 2 ppm

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Effect of Hydrogenation on Soybean Oil Composition

Fatty Acid (%)	RBD oil	Partially Hydrogenated and Winterized oil
16:0	11	9
18:0	4	4
18:1	21	49
18:2	54	35
18:3	9	3

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Hydrogenated Oil End Products: Examples

- Liquid Oils – Brush Hydrogenation
- Margarine Bases – Partial Hydrogenation
- Shortening Bases – Partial Hydrogenation
- Stearin - Total Hydrogenation
- Coating Fats – Partial Hydrogenation

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Fractionation

- Separates Fats and Oils into Fractions with different Melting Points
- Three Major Processes:

(a) Dry Fractionation

- Gradual cooling of oil w/o solvent
- includes winterization and dewaxing

(b) Solvent Fractionation

- Crystallization performed in diluted solutions
- Solvents: Acetone, Hexane & IPA

(c) Detergent Fractionation

- Addition of detergent solution into crystallized oil
- An electrolyte is also added

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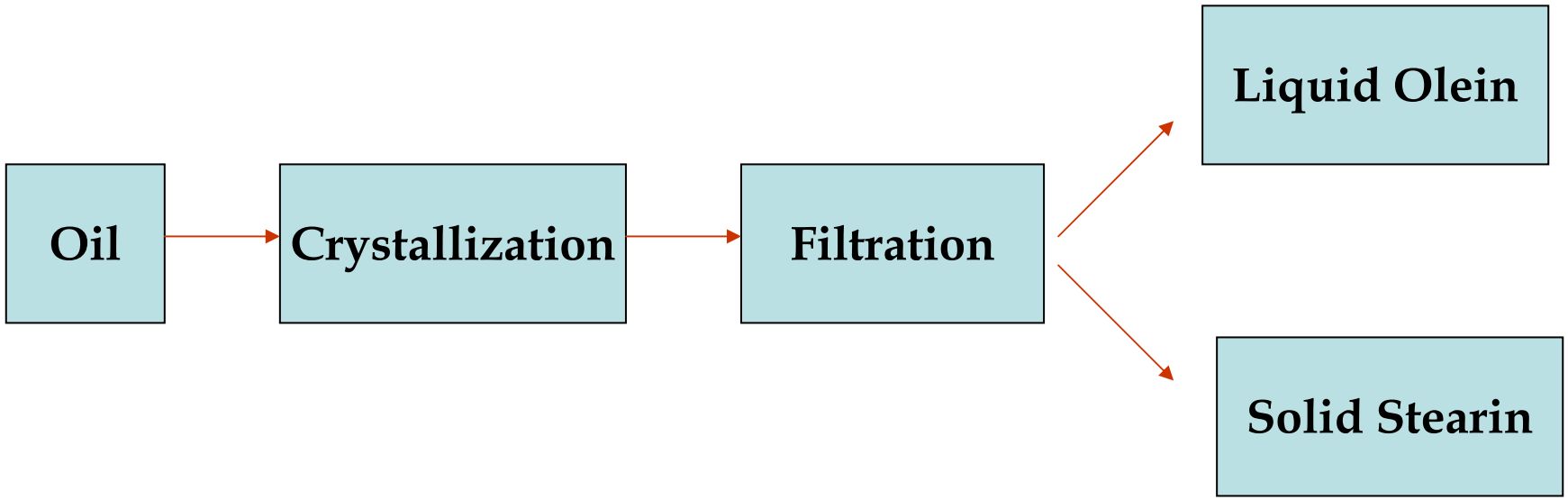
Fractionation Principle



[SSS-SSU-SUU-UUU] —Crystallization→ [SSS-SSU] + [SUU-UUU]

Filtration

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Fractionated Fats & Oils

OIL TYPE	REFINING STATE
Palm oil	crude / bleached / deodorized
Palm kernel oil	crude / bleached / deodorized
Soybean oil	bleached / deodorized
Cottonseed oil	bleached / deodorized
Fish oil- Native	crude / bleached
- Hydrogenated	bleached / deodorized
Tallow	crude
Milk fat	crude / deodorized

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Fractionation: Analytical Methods

Analytical Technique	AOCS Method Number
Solid fat content (SFC)	Cd 16b-93
Melting point	Cc 1-25
Cloud point	Cc 6-25
Dropping point	Cc 18-80
Cold test	Cc 11-53
Peroxide value	Cd 8-53
Iodine value (Wijs method)	Cd 1-25
Fatty acid composition (GC)	Ce 16-89
Lovibond color	Cc 13e-92

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Effect of Fractionation on Palm Oil Composition

Chemical Properties	Palm Oil	Palm Olein	Palm Stearin
14:0 (%)	1.0	1.0	1.3
16:0 (%)	44.0	40.0	54.0
18:0 (%)	4.5	4.4	6.0
18:1 (%)	39.0	43.0	32.0
18:2(%)	10.0	11.0	6.0
Iodine Value	53	58	40
Melting Point (^oC)	36.0	22.0	51.0
SFC (%) at 10^oC	50	40	74

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Interesterification

- Rearrange and Randomize the FAs on the Glycerol Molecules

- Why Interesterify ?

  - Achieve Melting Properties that cannot be achieved by Other Methods

  - Replace Hydrogenated Fats

  - Change the Melting Properties

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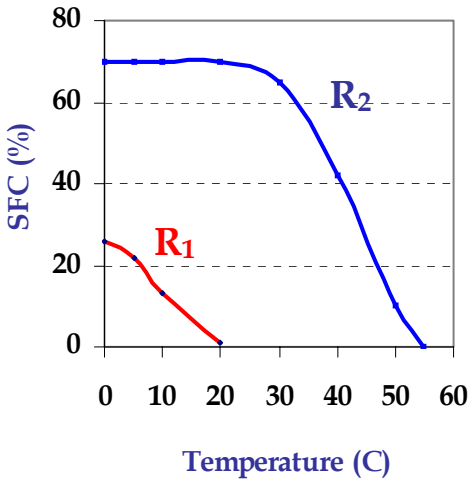
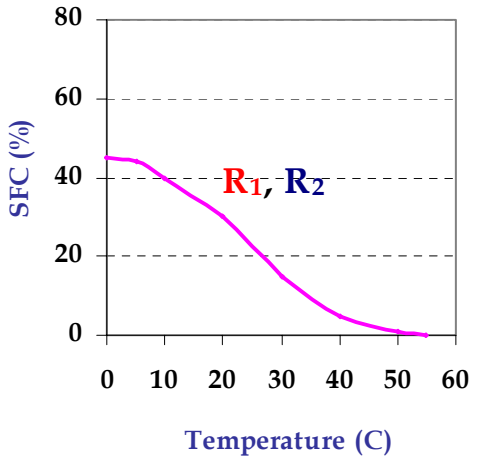
Chemical Interesterification: Principle

$R_1R_1R_1$

$R_1R_1R_1 + R_2R_2R_2$ —Catalyst→ $R_1R_2R_1$ $R_2R_1R_1$ $R_1R_2R_2$ $R_2R_1R_2$ $R_2R_2R_2$





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Chemical Interesterification: Feedstock Oil Quality

Parameter	Specification
Peroxide value	< 1.0 meq/kg
Free fatty acids	< 0.05%
Moisture	< 0.01%
Phosphorus	< 5 ppm

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Chemical Interesterification: Process Steps

1) Pretreatment of Oil: 120°C, < 50 mbar
H_2O < 0.01%

2) Catalyst Addition: 0.05 – 0.1%

3) Reaction: 90-150°C; 15-60 min; < 50 mbar

4) Catalyst Deactivation: water; organic acid; silicate

5) Centrifugation

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Interesterification

- **CHEMICAL: - Random**
  - **Preferred Catalysts:**
    - **CH_3ONa; CH_3CH_2ONa**

- **ENZYMATIC: - Selective**
  - **Lipase-Catalyzed**

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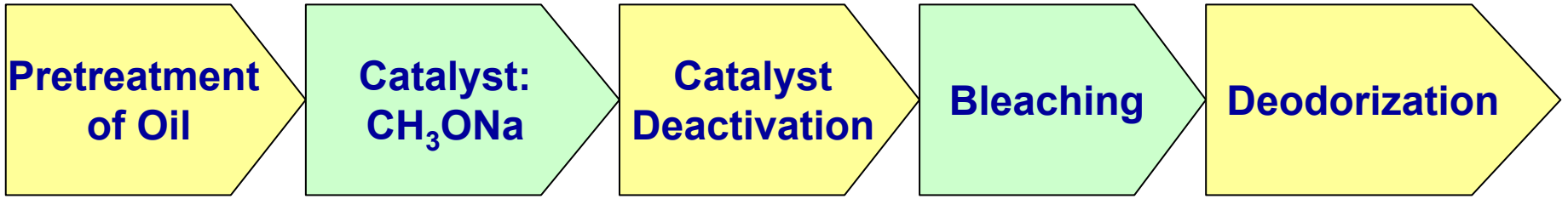
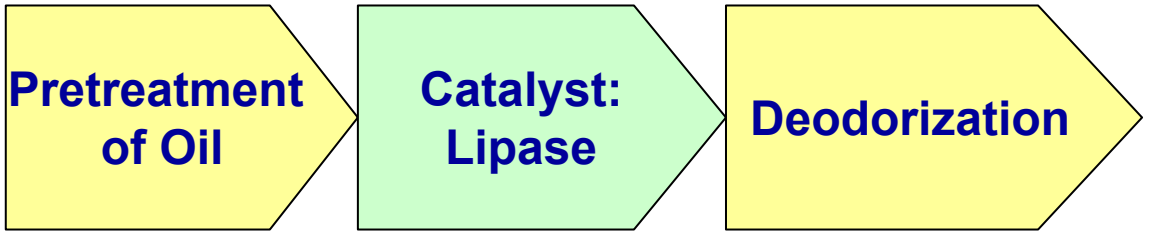
Interesterification: Process Comparison

Chemical Interesterification:



Enzymatic Interesterification:



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Interesterification: Monitoring the Reaction

- SFC
- Melting Point
- Dropping Point
- Cloud Point
- TAG Profile (FT-NIR)

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Interesterification: Current Trends

- Increasing trends to reduce/ eliminate TFA in foods

-Legislation

USA: FDA labeling on*Trans* fats – January 2006

Europe: max 2% in food fats (Denmark)

- Major food processors are replacing TFA by low/zero TFA alternatives
- Increased demand for:

Low trans products: < 5% in food fats

Zero trans products: < 0.5% in food fats

- Alternative technology for partial hydrogenation

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Interesterification: Product Examples

- Low/No Trans Margarines and Spreads
- Low/No Trans Shortenings
- Cocoa Butter Alternative Fats
- Reduced Calorie/ No Calorie Fats
- Milk Fats

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Physical Blending

- Easiest and Most Economical Way to Modify Fat
- Purpose:
  - Increase Stability
  - Alter the Color and Flavor
  - Alter the Melting Properties
- Blend Two Oils with different Melting Curves to achieve Oil with a Specific Melting Properties
- Blends can be Calculated using the SFI Value and Linear Algebra

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Summary

- **Reasons for Modifying Fats & Oils:**
  1) Alter Physical Properties
  2) Improvement of Stability
  3) Economical Benefits

- **Modification Methods:**
  1) Hydrogenation
  2) Fractionation
  3) Interesterification
  4) Blending
  5) Combinations of each of the above

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