

Interesterification

Interesterification (IE) is the process of re-arranging the fatty esters within and between triglycerides resulting in most cases, a change in the physical properties of the oil/fat.

Interesterification of oil changes its molecular composition.

Interesterification of triacylglycerol molecules;

Fatty acid distribution is randomized, resulting in the change of the physical property of the oil. Randomization of lard improves its plastic range and thus makes it a better shortening than natural lard.

Interesterification may be either random or directed.

Interesterification involves an exchange of acyl group among triglycerides.

Acyl groups may exchange positions within a triglyceride or among triglyceride molecules.

If A, B, and C are the molar percentages of fatty acids A, B, and C for a commercial oil,

Then, molar percentage of glycerides containing only 1 acid is: % AAA = $A^3 : 10,000$

Molar percentage of glycerides containing 2 acids is: % AAB = $3A^2B : 10,000$

And molar percentage of glycerides containing 3 acids is: % ABC = $6ABC : 10,000$

Random Esterification

The random or chemical IE is the most applied IE modification process of oils and fats as it is simpler, cheaper and easier to carry out compared to directed or enzymatic IE.

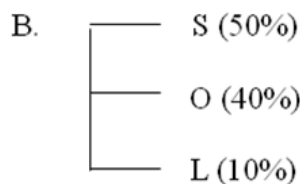
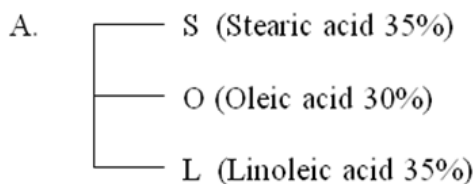
Chemical IE can be carried out by applying the following conditions:

- heat at $> 300^{\circ}\text{C}$;
- heat with caustic soda at 200°C ;
- heat with sodium methoxide or ethoxide at 80°C - 100°C ;
- heat with metallic sodium at 100°C - 120°C ; and

Table: Interesterification catalysis

Type	Example	Required Dosage (% Oil Weight)	Time
High Temperature (120°C - 260°C)			
Metal Salts	Acetates, Carbonates, Chlorides, Oxides of Zn, Fe, etc	0.1%-0.2%	0.5-6 Hours under vacuum
Alkali Hydroxides	NaOH, KOH, LiOH, or Sodium Hydroxide + Glycerol	0.2%	45 minutes- 1.5 Hour under vacuum
Metal Soaps	Sodium Stearate + Glycerol	0.5%-1%	1 Hour under Vacuum
Low Temperature (25°C - 270°C)			
Metal Alkylates	Sodium Methylate	0.1%-1.0%	5-120 Minutes
Alkali Metals	Na, K, Na/K Alloy	0.2%-0.5%	3-120 Minutes
Alkali Metal Hydrides	Sodium Hydride	0.2%-0.5%	30-120 Minutes
Alkali Metal Amides	Sodium Amide	0.15%-0.2%	10-60 Minutes

Random Interesterification



After random interesterification, the triglyceride compositions are:

Sample A		Sample B	
Triglyceride	%	Triglyceride	%
SSS	= 4.3	SSS	= 12.5
OOO	= 2.1	OOO	= 6.4
LLL	= 4.3	LLL	= 0.1
SSO	= 11.0	SSO	= 30.0
SSL	= 12.8	SSL	= 7.5
OOS	= 9.5	OOS	= 24.0
OOL	= 9.5	OOL	= 4.8
LLS	= 12.8	LLS	= 1.5
LLO	= 11.0	LLO	= 1.2
SOL*	= 22.0	SOL*	= 12.0

*Total triglycerides containing 3 different fatty acids.

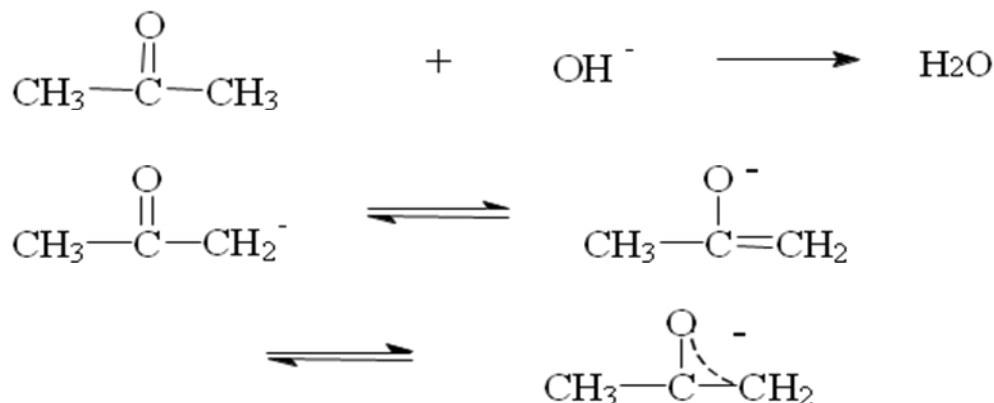
Interesterification can be carried out to an equilibrium condition, at which point the fatty acids assume an almost random distribution among triglycerides.

Reaction Mechanisms

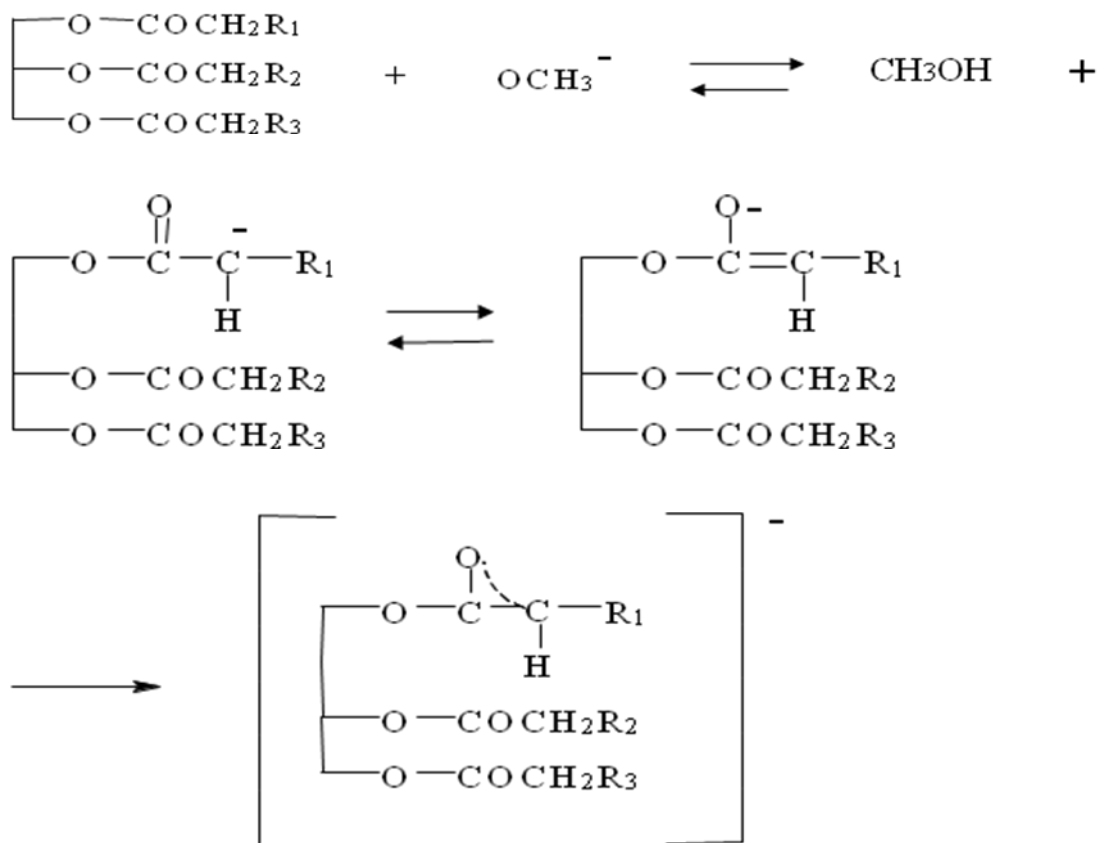
1. The formation of enolate ion
2. The formation of Beta-Keto ester
3. Interesterification

Catalyst Function in Interesterification

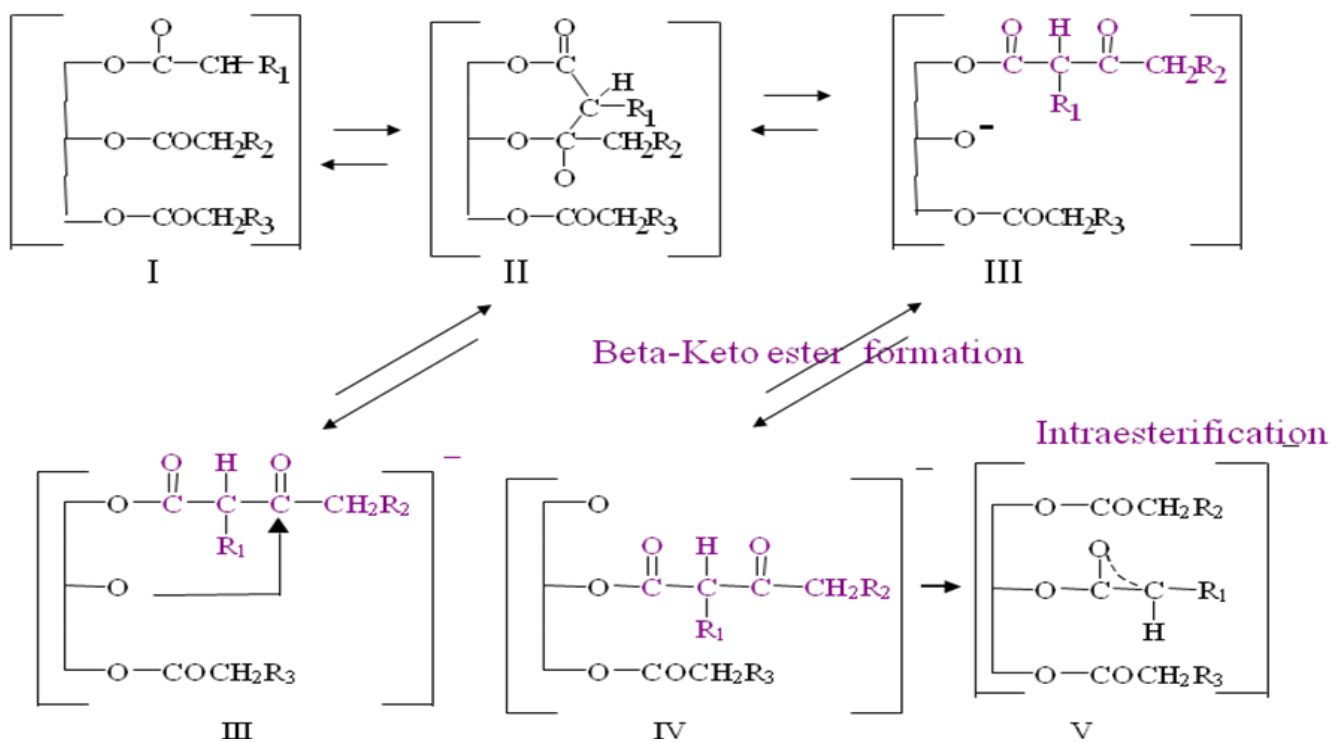
Initial removal of an α -proton by the base catalyst leads to the charge delocalized enolate anion.

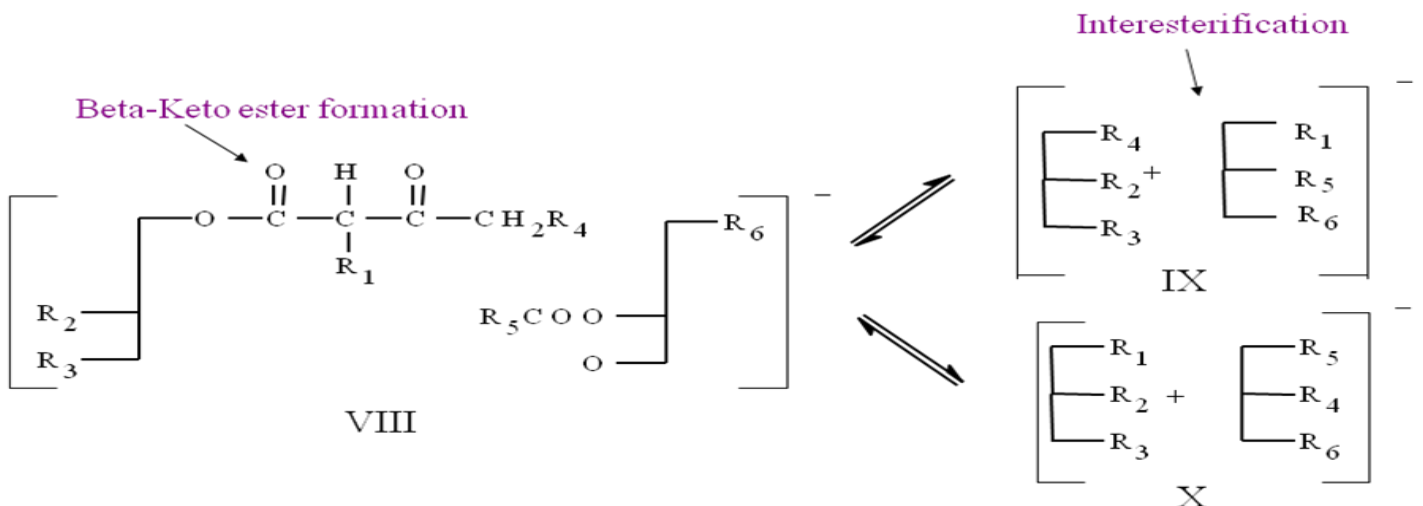
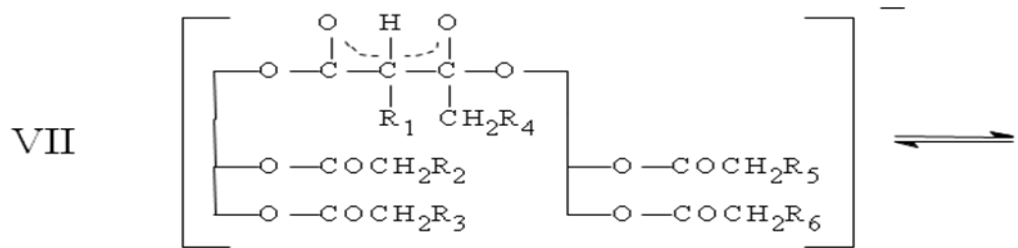
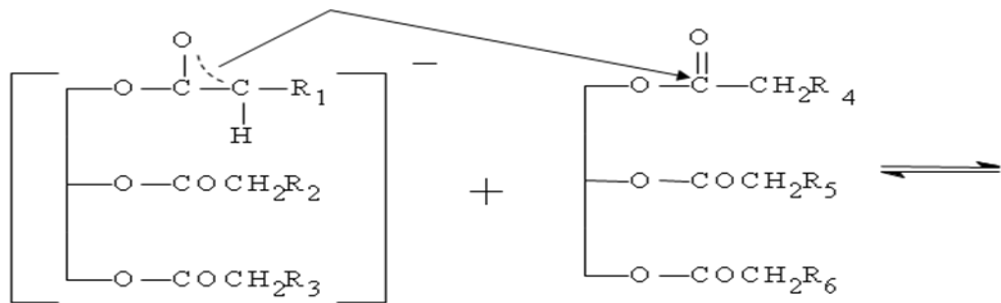


Enolate Ion Formation



Mechanism for Intramolecular Ester-Ester Interchange





CHEMICAL INTERESTERIFICATION CATALYST : NaOCH₃

- Trivial names: Sodium methoxide; Sodium methylate
- Very alkaline catalyst (stronger than NaOH)
- Very reactive : exothermic decomposition into NaOH and CH₃OH in presence of moisture
- Hazardous product, requiring care full handling and controlled storage
- Available in powdered form for interesterification, or dissolved in MeOH (25%) for biodiesel production

Catalyst Inactivation;

Type	Poison		Catalyst inactivated (% on oil)		
	level		Na	CH ₃ ONa	NaOH
Water	0.01 %		0.013	0.03	
fatty acid	0.05 %		0.004	0.01	0.007
peroxide	1.0		0.0023	0.0054	0.004
total catalyst inactivated			0.0193	0.0454	0.0011

INTERESTERIFICATION PROCESS

Addition of the catalyst

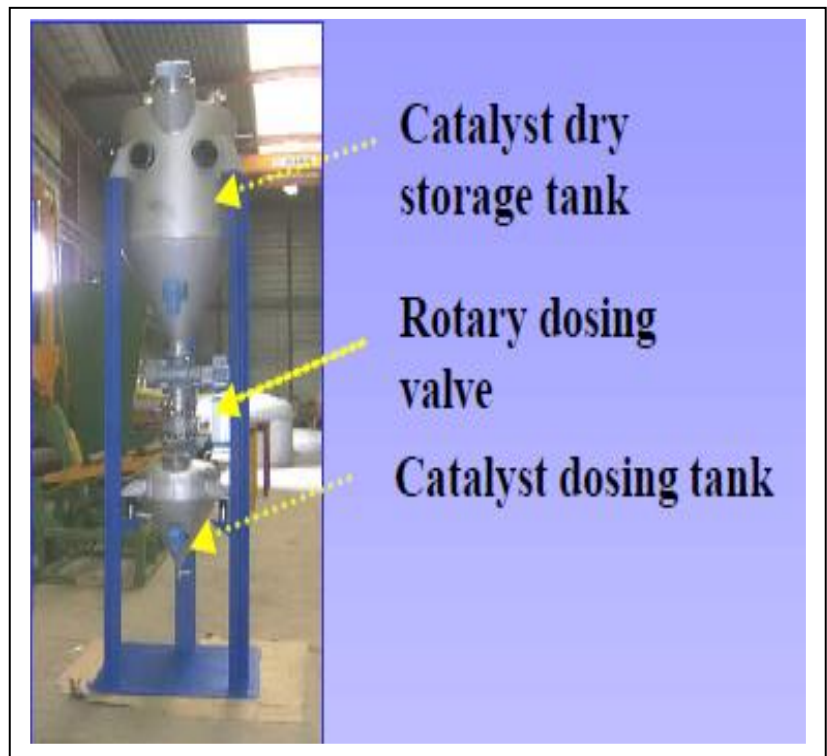
- Addition of 0.05-0.1% NaOCH₃
- Aggressive' catalyst
- Avoid direct contact



Automatic dosing

Start of the reaction

- Formation of deep red-brownish color
- Usually appears shortly after catalyst-addition (few minutes)



Catalyst dry
storage tank

Rotary dosing
valve

Catalyst dosing tank

Randomisation usually occurs quite fast (10-15 min.)

- Industrially reaction time is longer : 30-60 min.
- No quick on-line method to check completion/status of the reaction
- Once 'Randomization' is reached, reaction will continue (until destruction of catalyst),
- Too long reaction will darken oil & give color fixation

• Side reactions leading to oil loss (catalyst related)

1 mole NaOCH₃ gives 1 mole FAME & 1 mole Na-soap

1 mole FFA ← acid catalyst inactivation

% (FAME + FFA) = +/- 10 * % NaOCH₃ added

- Oil loss during post bleaching = 0.3 * % bleaching earth
- Oil loss during deodorisation = +/- 1.3 * % (FFA+FAME)

0.1% of NaOCH₃ catalyst
0.5% bleaching earth → Overall oil loss : 1.5%

CHEMICAL INTERESTERIFICATION :

Process Stages

1. Neutralisation: FFA $\xrightarrow{\text{NaOH}}$ FA soaps (no removal)
2. Drying: H₂O < 100 ppm; preferably < 50 ppm
120°C; < 20 mbar
3. Reaction with catalyst: 90-100 °C during 30 min. at 20 mbar max. 0.1 %; preferably 0.05% catalyst
4. Reaction stop: water / acid / acid activated silica
5. Bleaching : 0.2-0.5% Bleaching earth

6. Deodorising: 220-230°C (deodo) / 240-250°C (stripping)

CHEMICAL INTERESTERIFICATION :

Side Reactions

NaOCH₃ : strong 'alkaline' catalyst

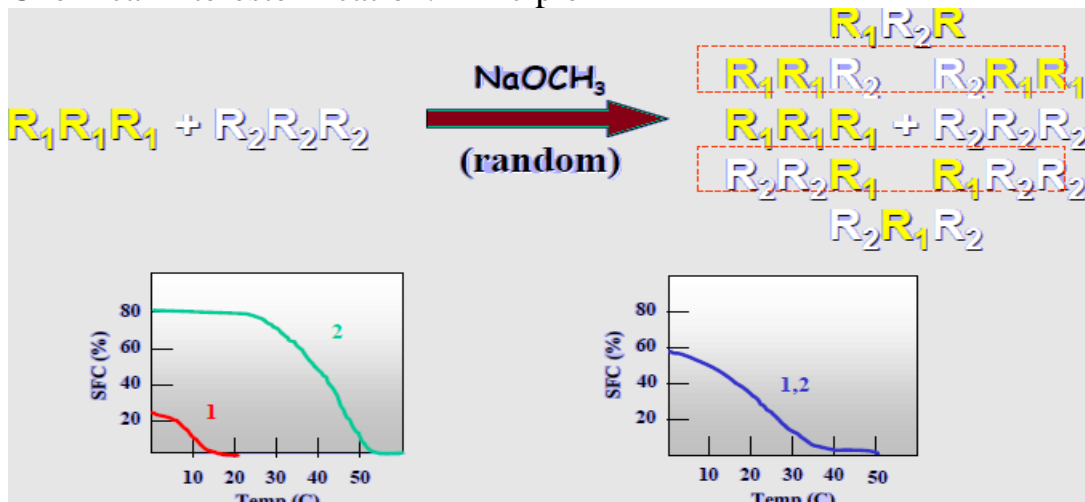
will catalyze also unwanted side-reactions

- Degradation of tocopherols
- Formation of tocopherol esters
- Formation of di-alkyl ketones
- Some formation of phytosterol esters

more side products at higher catalyst conc. & temperature

max. catalyst conc. : 0.1% - max. temperature : 120°C

Chemical Interesterification: Principle



ENZYMATIC INTERESTERIFICATION

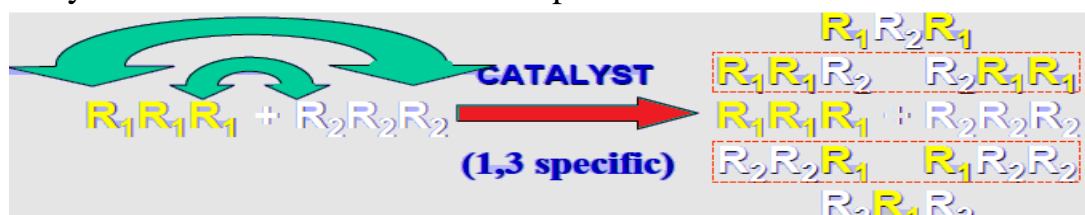
Enzyme : Lipozyme TL IM

- Triacylglycerolhydrolase (also named Lipase)
 - Lipase from Thermomyces lanuginosus. (in past from pancreas)
 - sn-1,3 specific and heat stable (max. temp. : 75°C)
- % X at 1,3 = [% X in Original Triglyceride] – [% X at 2 position]

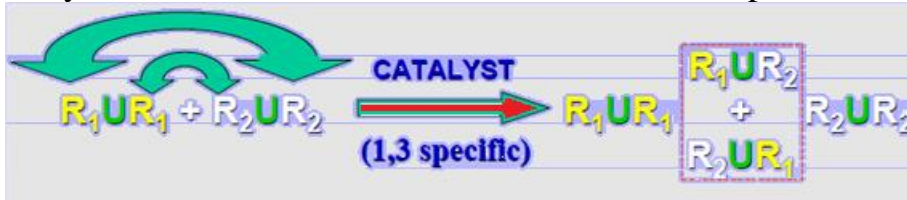
Immobilized

- For use in fixed bed processes
- No enzyme in finished oil product
- Enables re-use of enzyme for better process economy
- Stabilizes the enzyme

Enzymatic Interesterification: Principle



Enzymatic Interesterification of SUS Fats : Principle



Enzyme inactivation due to : (stability)

Enzymatic Interesterification

Enzyme : Lipozyme TL IM

Process temperature (max. 70°C)

Radicals (Peroxides)

Polar impurities (phosphatides, soaps)

Secondary oxidation products : ketons, aldehydes...

Trace elements (e.g. Nickel)



Quality of Incoming oil is important : degummed – bleached-(deodorised)

Enzyme productivity : kg EIE oil/kg enzyme

Depending on incoming oil quality

For good quality oil : min. 2500 kg EIE oil/kg enzyme

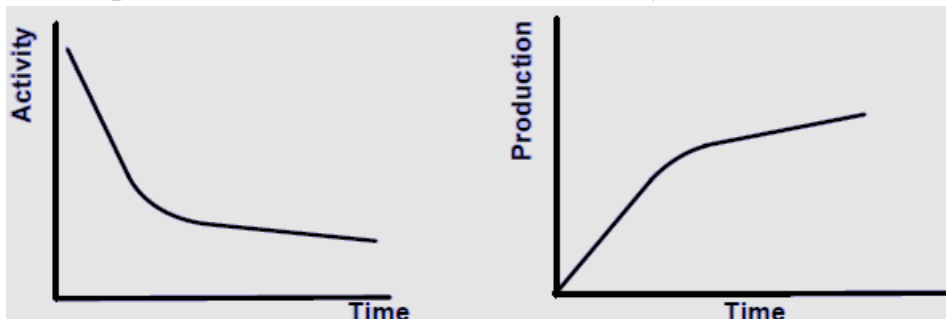
Productivity up to 4000 kg EIE oil/kg enzyme in pilot tests

Enzymatic Interesterification : Operation

1. Single Fixed Bed Reactor

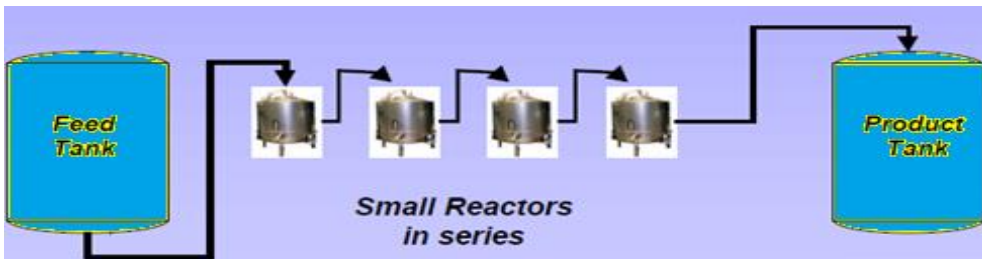
Enzyme Activity decreases over time

- Flow to be adjusted to maintain conversion
 - Max. Initial flow : 10 kg IE oil / kg catalyst.hr (blend dependent)
 - Regular analyses of the conversion required
 - Low production rate at the end of the enzyme's lifetime



2. Multiple Fixed Bed Reactors in Series

- Different enzyme activity in each reactor
 - Lowest enzyme activity in first reactor : GUARD EFFECT
 - Highest enzyme activity in last reactor
 - Average production rate : **1-2 kg IE oil / kg enzyme.hr**

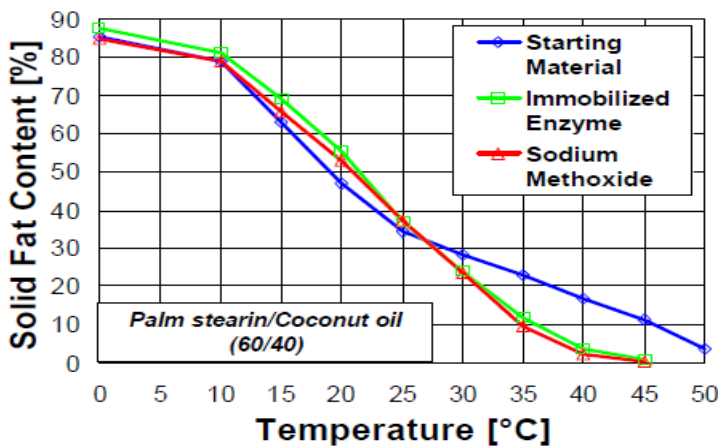
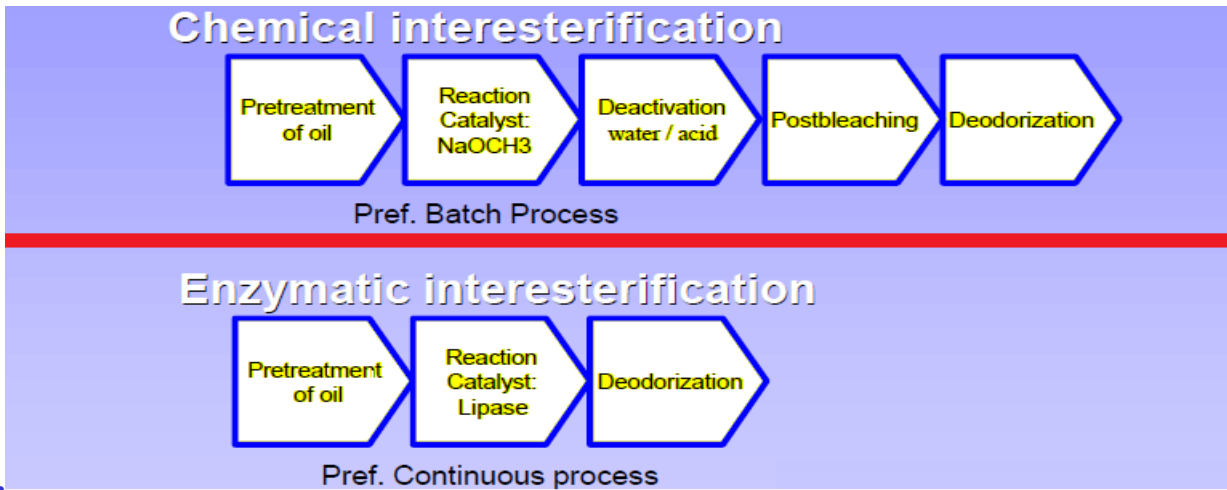


Chemical Interesterification \Rightarrow Batch
 Enzymatic Interesterification \Rightarrow Continuous

Process Comparison Chemical vs. Enzymatic Interesterification

Less steps with enzymatic process

Being able to control the melting characteristics, enzymatic interesterification can produce fat with physical properties similar to fat produced using chemical interesterification.



Effect Chemical vs enzymatic I.E. on oil quality

PS / SFO	10/90			20/80			30/70			40/60			50/50		
	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz
Color															
Yellow	11	15	10	15	10	9	16	11	8	19	16	8	19	18	10
Red 51/4	1.0	2.0	1.0	1.2	2.3	0.9	1.8	2.2	1.2	2	3	1.4	2.1	3.4	1.0
Tocopherol (ppm)	701	252	505	639	197	412	581	281	426	546	185	425	463	182	366
DAG (%)	1.5	3.9	2.0	1.7	3.7	3.0	1.9	4.5	3.5	2.14	4.2	3.0	2.4	4.9	3.5
Trans fats (%)	0.50	0.67	0.75	/	/	/	0.50	0.62	0.61	/	/	/	/	/	/

- EIE oil has a lighter colour than CIE oil (after pretreatment)
- EIE oil has a higher tocopherol content than CIE oil
- EIE oil has a lower diglyceride content than CIE oil

Frying:

food is placed in hot oil, There are two main methods of commercial frying which are distinguished by the method of heat transfer involved:

1. shallow frying

This method is most suited to foods which have a large surface-area-to-volume ratio (for example bacon slices, eggs, burgers). Heat is transferred to the food mostly by conduction from the hot surface of the pan through a thin layer of oil.

2. deep-fat frying

Deep-frying is a cooking process, with which water containing foodstuff is immersed into edible oils or fats at temperatures between 140 – 180°C. In the first phase, within a few seconds, a thin crust forms, whose structure crucially affects the deep-frying process and the quality of the food with regards to fat absorption and crispness. Fats and oils have a high heat capacity, thereby enabling heat transfer at temperatures far above that of the boiling point of water. Due to the evaporation in the boundary zone between food and oil, the water bound in the food is gradually transported from the inside to the boundary layer into the surrounding oil (mass transfer).

Here heat transfer is a combination of convection within the hot oil and conduction to the interior of the food. All surfaces of the food receive a similar heat treatment to produce a uniform colour and appearance.

Two types

1. Batch
2. Continuous

Changes in frying oil

During frying the combination of prolonged heating and high temperature in the presence of moisture and oxygen causes an interrelated series of reactions – ((types of reaction during deep frying)):

- hydrolysis,
- oxidation

- polymerisation.
- Pyrolysis

These all contribute to the breakdown of fats. There is an increase in saturation of fatty acids, breakdown products are formed and there are texture, colour and flavor changes. There is an exchange of substances between the food and the fat with the food absorbing fat and breakdown products, proteins, and other substances released into the fat.

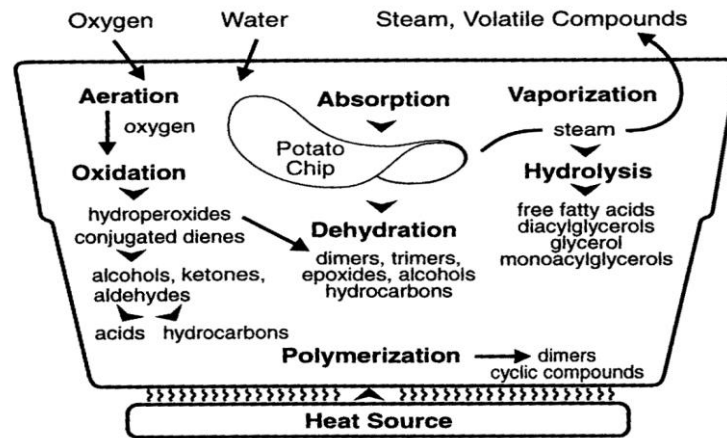
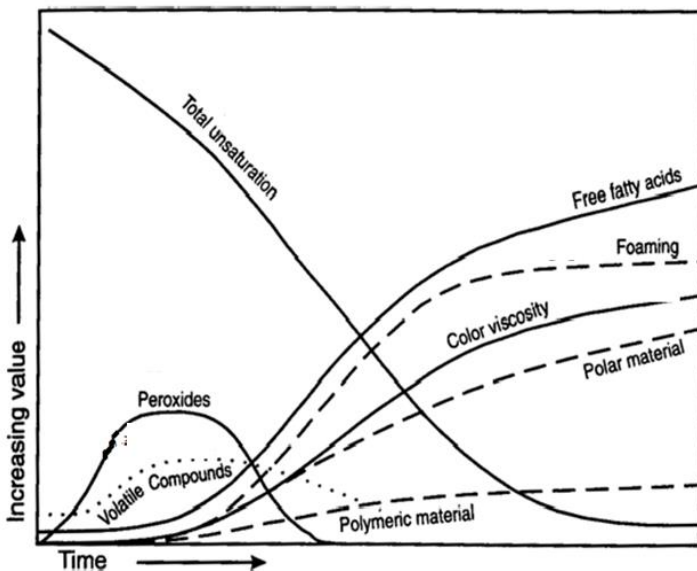


Figure provides Physical and Chemical Reactions during Deep- Fat Frying

<i>Heat, oxygen, moisture, impurities</i>	
Fresh fat	⇒ Degraded fat - breakdown products
	<i>Stability (iodine value) ↓</i>
	<i>Free Fatty Acids (acidity) ↑</i>
	<i>Odour ↑</i>
	<i>Colour darkens</i>
	<i>Taste - becomes poor</i>
	<i>Viscosity ↑</i>
	<i>Foaming ↑</i>
	<i>Surface tension ↓</i>
	<i>Specific gravity ↑</i>

Figure provides an overview of fat as it ages. As oil degrades the specific gravity increases, heat capacity, and surface tension decrease and contact time between the oil and the food increases causing changes in heat transfer. Volatile and non-volatile decomposition products are formed, free fatty acid content increases, iodine value decreases, fat darkens, strong flavors develop, the smoke point is lowered and there is increased foaming and viscosity. It is suggested that potentially harmful compounds may be formed in the food.



Functions of Fat in Food

Fats and oils are not just a caloric powerhouse but they also serve many chemical, physical, and nutritional functions in the foods we eat. Here are ten of the most important functions that fats serve in food.

1. Appearance

Fats and oils can alter a food's appearance by creating a glossy or moist visual texture. The ability of fat to refract light is also responsible for the opaque appearance of milk. Fats also aid in the browning process of many foods, giving them an appealing golden brown color.

2. Emulsions

Fats and oils are an important component in most emulsions. Emulsions are the dispersion of a fat or oil into water (or vice versa). There are many emulsions in the culinary world including salad dressings, mayonnaise, gravies, and cheese sauces. Emulsifying fat into a liquid produces unique flavor and texture qualities.

Emulsions can be conveniently classified according to the distribution of the oil and aqueous phases. A system which consists of oil droplets dispersed in an aqueous phase is called an oil-in-water or O/W emulsion (e.g., mayonnaise, milk, cream, soups, and sauces). A system which consists of water droplets dispersed in an oil phase is called a water-in-oil or W/O emulsion (e.g., margarine, butter, and spreads)

3. Flavor

Fat has the unique ability to absorb and preserve flavors. Oils are often infused with herbs and spices for preservation. Fats also contain compounds that lend specific flavors of their own. The way fat coats the tongue and allows flavors to linger can also alter a flavor experience.

4. Heat Transfer

Fats provide one of the most efficient modes of heat transfer during cooking. From deep fat frying to sautéing in a skillet or wok, hot oil is able to transfer high levels of heat to the surface of food without overheating the interior portions. Using fats and oils to transfer heat also facilitates crust formation

5. Melting Point

The type of fat used in a product often determines the melting point of the final product. A melting point is the temperature at which a substance changes from a solid to a liquid. This characteristic is especially important for items like chocolate, frosting, and salad dressings. Saturated fats, like butter and lard, are solid at room temperature, which makes them perfect for use in solid foods like chocolate and frosting. Vegetable oils are liquid at room temperature, which makes them perfect for use in products like salad dressings. The low melting point of vegetable oils allows salad dressings to stay in liquid form when refrigerated.

6. Nutrition

Fats are the most calorie dense compound in food, weighing in at over twice the calories per gram of proteins or carbohydrates. While this may not be seen as an advantage in today's modern society, the ability to provide energy dense food items is still necessary in many parts

of the world. Fat is an effective method of delivering calories when needed. Fats are also important for delivering fat soluble vitamins such as Vitamins A, E, D, and K. with essential fatty acid.

7. Satiety

Fats play an important role in making foods satisfying or making us feel full. Because fats take longer to digest than carbohydrates or proteins, high fat foods stay in the stomach longer and delay the feeling of hunger.

8. Shortening Power

Shortening is not just the name of a solid, shelf stable fat but it is also the term used to describe fat's ability to make baked goods tender by impeding the formation of gluten strands. Normally, as bread dough is kneaded the gluten (wheat protein) begins to join and form long elastic strands, which give strength and a chewy texture to the bread. When fat is added to dough, like in biscuits and pie crusts, the fat gets in the way of the gluten formation, therefore keeping the final product tender and flakey.

9. Solubility

While fats and oils are not soluble in water, there are other chemical compounds that are only soluble in fats. Many of these fat-soluble compounds are responsible for foods flavor and even vitamin content. Including fat in food allows for maximum flavor and a wider range of nutritional content.

10. Texture

Fats and oils have a texture all their own but are also responsible for tenderizing baked goods via the shortening process . Fat provides a very specific, lubricating mouth feel, which is why most dry crackers or chips are served with high fat content dips or spreads. Emulsions made with fat are responsible for the creamy texture of many items like ice cream, mayonnaise, and other sauces.