Oleochemistry

Oleochemical derivatives

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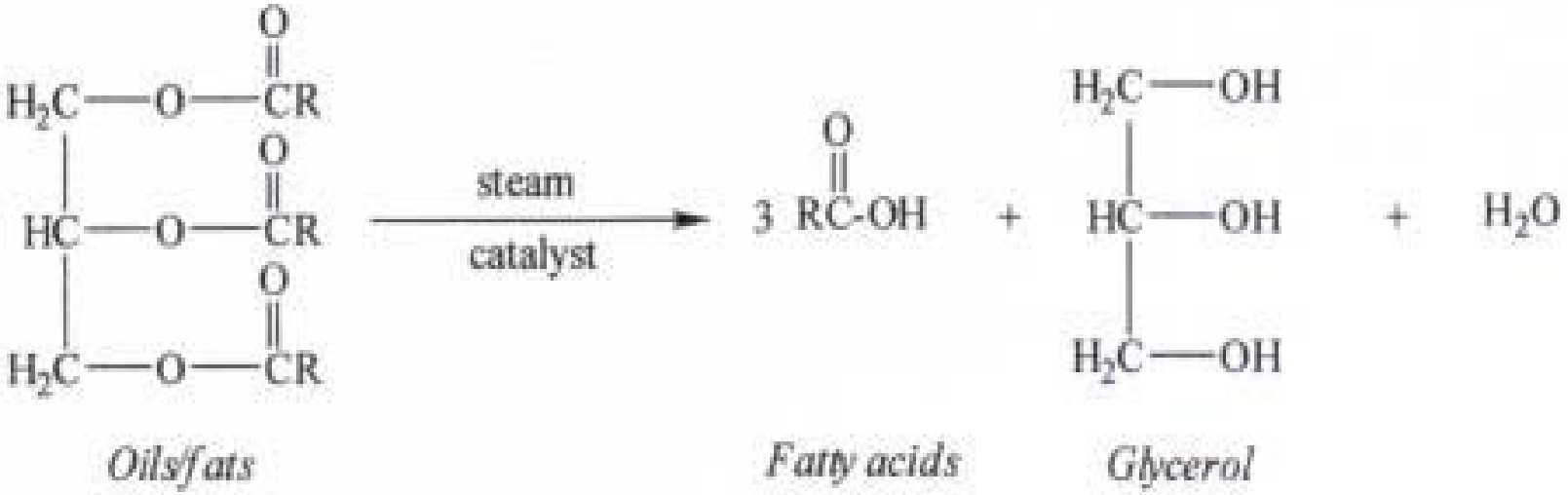
The students should be able to understand:

Oleochemical reactions and their applications

- Five basic products in oleochemicals
  a. Fatty acid
  b. Glycerin
  c. Fatty alcohols
  d. Fatty amines
  e. Methyl esters

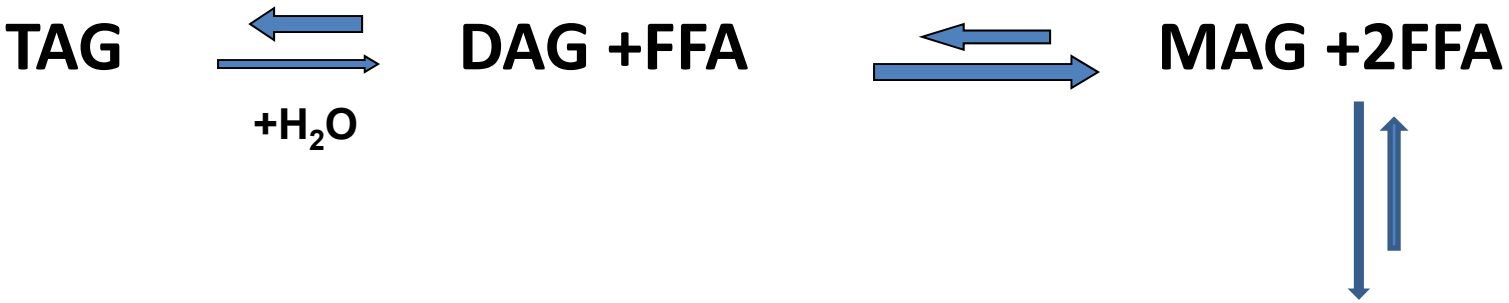
- Oleochemicals industry in Malaysia

Fatty acids production routes



Oil/ Fat Splitting

Hydrolysis by Lipases



More important is to ensure that the lipase channels the reaction towards the DAG rather than the TAG

Saponification

- **Saponification** is a process that used fats to produces soap.
- Technically, saponification comprises of the reaction of base - NaOH for solid soap and KOH for liquid soap- with triglycerides, which are esters of fatty acids.
- The formation of the sodium salt of a carboxylate is called as hydrolysis.
- In addition to soap conventional of saponification reaction will produces glycerol as by product.
- The substances that can be converted into soap are called as saponifiable substances.

Neutralization vs saponification

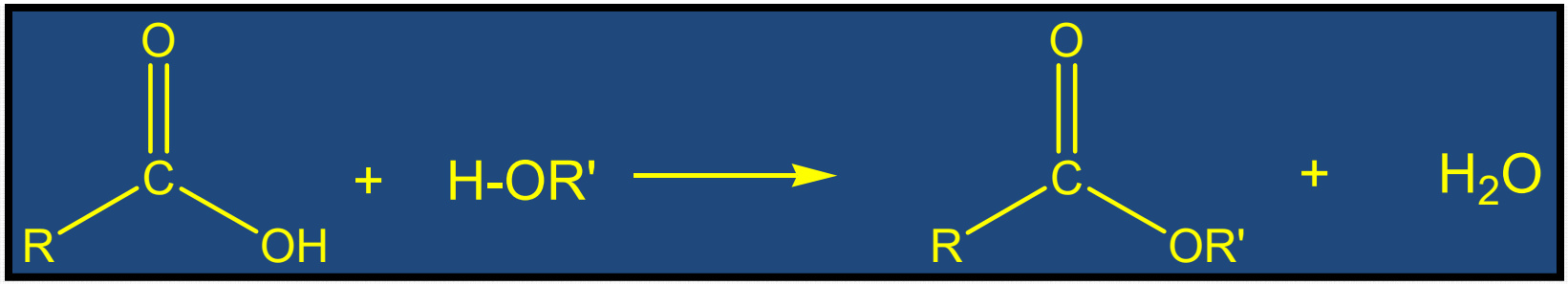
- Neutralization process- fatty acids
- Saponification process -triglycerides
- The advantages of neutralization process:-

a. Simpler and faster

b. Simple procedure. No washing required to remove glycerol

c. Quality of soap

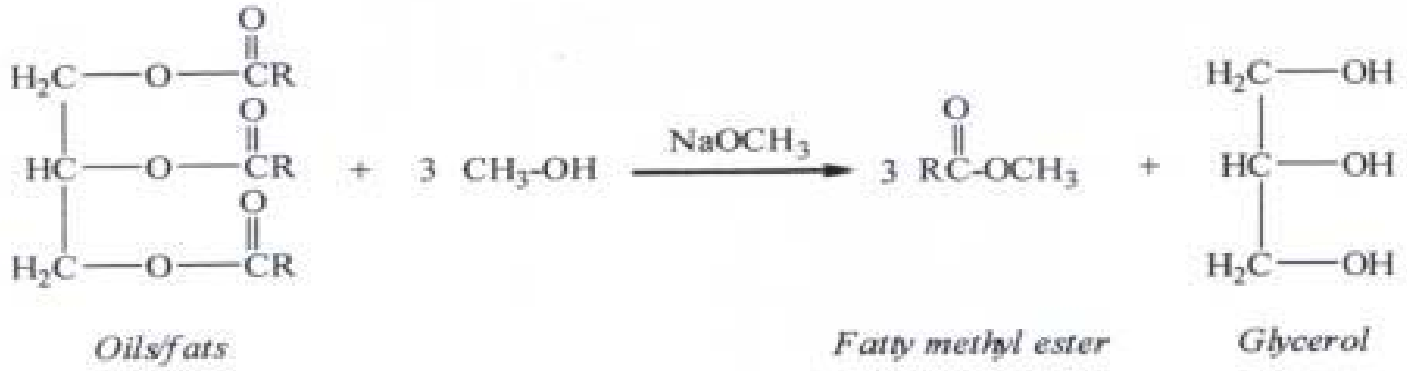
Esterification of Fatty Acids



Catalyst: 1-3 % sulfuric acid/hydrogen chloride

Alcohol: monohydric/polyhydric

Fatty Methyl Esters Production Routes from TAG



Transeterification

Hydrogenation of fatty acid to produce fatty alcohol

Esterification Reaction

Fatty Acids Methanol Methyl Esters

Hydrogenation Reaction

Methyl Ester Fatty Alcohol

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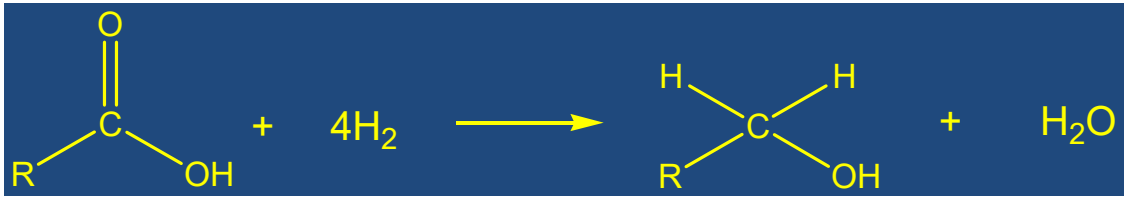
Hydrogenolysis of Fatty Acids

Product: fatty alcohol

Fatty alcohol : $C_6 – C_{10}$ plasticizer

$C_{12} – C_{18}$ industrial detergent

Reaction:



Operational Parameters:

T = 300°C ; P = 30 - 80 bar

Catayst: copper chromite

Industrial Consumption of Fatty Acids

Tire Industry
Shoes
PVC
Cosmetic
Softener
Fatty alcohol
Soap
Pharmaceuticals
ETC.

Fatty acid methyl ester (FAME)

- Fatty acid was the gateway to oleochemicals, however it been replaced by fatty acid methyl ester (FAME)
- FAME: Milder operating condition that lower the production cost.
- End products are better quality
- Lesser acidic that make this compound lesser corrosive
- Production of FAME through transesterification of TAG or esterification of fatty acids with methanol.

Uses of Fatty Esters

- Ester from monohydric alcohol is normally used in the cosmetics and plasticizer industries.
- Meanwhile, ester from polyhydric alcohol:
    i. glycol diester → vinyl plasticizer
    ii. monoester → surface-active agent
    iii. glyceride → surface-active agent
    iv. triolein → plasticizer
    v. and others

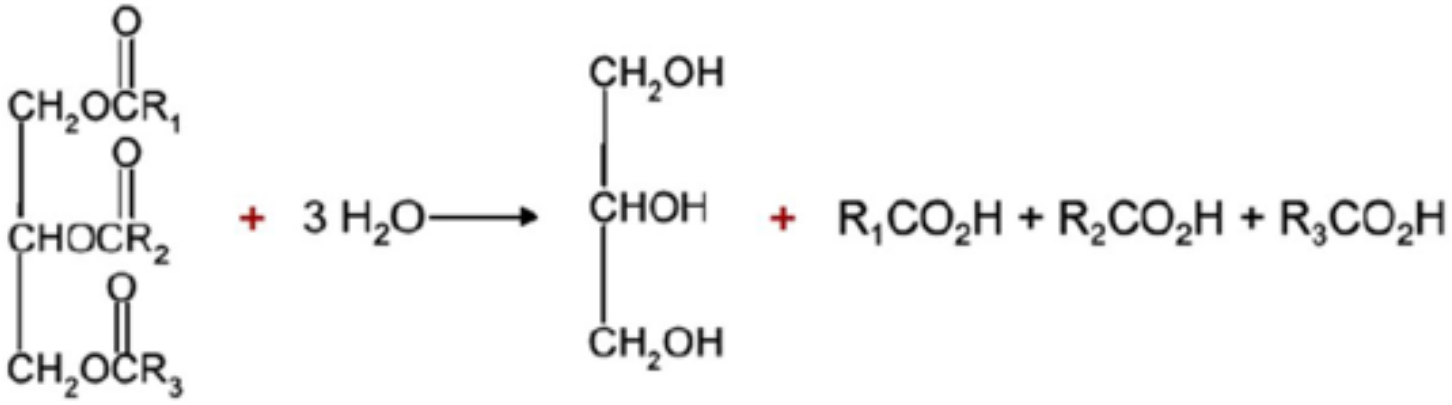
Examples:

Esterification with polyols : high temperature (230 – 235^{o}C)

Catalyst : $ZnCl_2$ / $PbCl_4$

Products : mono, di & triglyceride + water

Hydrolysis reaction



Palm Kernel Oil Glycerin Fatty Acids

Type of crude glycerin

Types	Description
Hydrolyzer crude	From sweetwater of fat hydrolysis. Contains 88-91% glycerol.
Ester crude	From transesterification of vegetable oil. Contains ~90% glycerol.
Soap lye crude	Spent lye from soap production. Typically contains 80% glycerol.

Types of refined glycerin grade

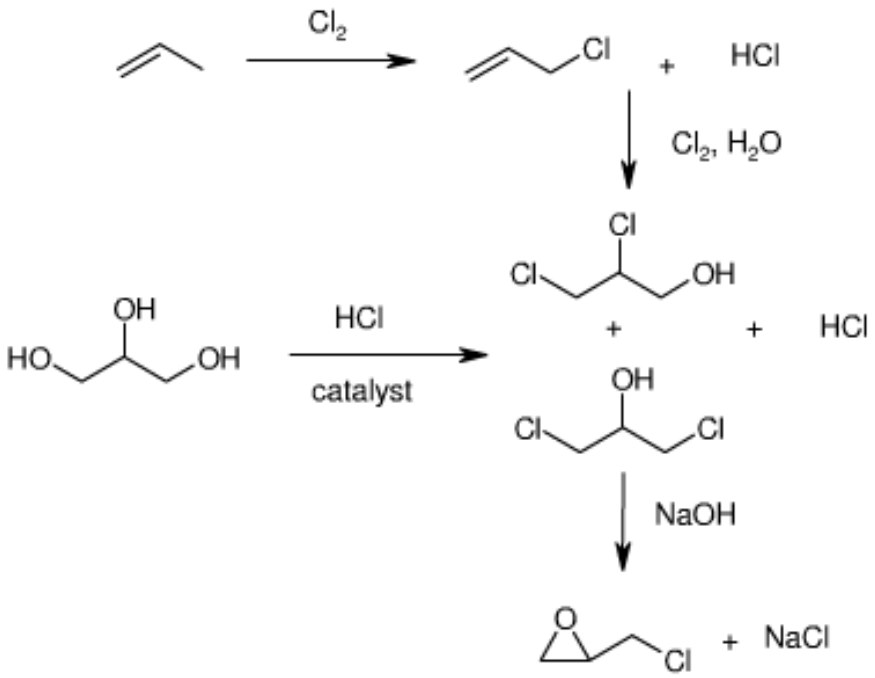
Types	Description
US Pharmacopoeia (USP) (PH.Eur.)	96-99.9% glycerol. Used in cosmetics, pharmaceutical and foods.
Chemically Pure (CP)	Min. 99% glycerol. Close to USP grade.
High Gravity	99% pure glycerol. Conforms to ASTM. Primarily used in industrial applications.
Dynamite	99% glycerol. Specs. Similar to High Gravity except colour. Must meet standards set by US Federal Color Std.
Kosher	Meets all USP requirements. Must be from vegetable oil sources.
Synthetic	Grade meets all USP specifications.

Properties of refined glycerin produced in Malaysia

Parameters/Grades	99.5%	Refined	Pharma-ceutical
Glycerol (wt.%)	99.5	99.8	99.7
R.density (20/20C) g/ml	1.2621	1.2628	1.2625
Ref. Index 20C	1.4731	1.4735	1.4740
Colour (APHA)	5.9	2.3	6.9
Water (wt%)	0.26	0.29	0.16
Ash (wt%)	0.002	0.002	0.0007
Sulphated ash (mg/kg)	9.1	4.3	10.0
Acidity (meq/100g)	0.05	0.05	0.05
Ester equivalent (meq/100g)	0.31	0.05	0.10
Choride (mg/kg)	3.3	3.5	2.8
Halogenated comp. (mg/kg)	<35	<35	<35
Arsenic (mg/kg)	<0.2	<0.2	<0.2
Heavy metals (mg/kg)	<1	<1	<1

Glycerol reactions

Epichlorohydrin from glycerol



- Solvay Epicerol® process
- Demonstration - Tavaux, France

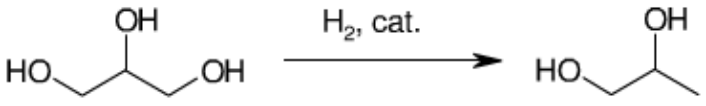
- Commercial
- Plant location - Map Ta Phut
- Capacity 100,000 tonnes
- Glycerine demand – 120,000 tonnes
- Start Up - Q1 2012

Propylene glycol

- $C_3H_8O_2$
- **HO –CH_2-CHOH –CH_3**
- **Ethylene glycol**, is commonly used in acrylic paints, brake fluid, antifreeze, tile grout, primer, sealant paste, floor polish,

Glycerol reactions

Propylene glycol from glycerol



- ADM – Propylene glycol
- Plant location – Decatur US
- Capacity 100,000 tons

DOW Chemical Company - Status unknown
Huntsman Corporation – Status unknown
Cargil/Ashland – Capacity 65,000 tonnes, location Europe

Acrolein

- Used in reparation of polyester resin, polyurethane and acrylic acid.
- Glycerol decomposes into acrolein after being heated to 280°C.
- Properties: Colorless to yellow liquid. Irritating odor

Glycerol Applications

- Glycerol can be used as the substrate to growth microorganism and also can be used to produce ethanol
- In foods sector, glycerol also can be used as a humectant, solvent, and sweetener, and believe can be used to preserve foods.
- It is also used as a thickening agent in some liqueurs.
- Glycerol is also used to produce mono- and di-glycerides
- **Glycerol** is a simple polyol compound (3 –OH in one glycerol compound) that make it very soluble in water.
- Physical properties: It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations.

Conclusion

- Oleochemical derivatives mostly are from the fatty acids and glycerol
- All the oleochemical derivatives have been used in various applications

Chapter description

All pictures/photographs/diagrams/figures used in this chapter is subjected to common creative that for education purposes