BIOENERGY

Chapter 1. Photosynthesis. Process description.

Chapter 2. Biomass. Definition, biomass composition, biomass as a carbon dioxide storage, types of biomass.

Chapter 3. Biofuels. Introduction. Definition, classification. World markets, production, basic technologies for biofuel production. Relative production efficiency. Energy balance. Biofuels from the environmental point of view.

Chapter 4. Definition and composition of bioethanol, raw materials, production technologies, industrial processes, applications.

Chapter 5. Biodiesel. Definition, the transesterification process. Raw materials. Industrial production. Uses and applications.

Chapter 6. Definition and composition of biogas. Sources, process of biodegradation, production technologies, applications.

Chapter 7. Thermochemical technologies for solid biomass processing.

Chapter 5. Biodiesel. Definition, the transesterification process. Raw materials. Industrial production. Uses and applications.

1. RAW MATERIALS FOR BIODIESEL PRODUCTION

Raw materials for FIRST generation biodiesel

Oil from oily crops typically used in the food industry

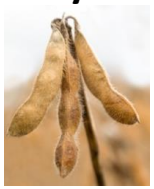
Rapeseed (colza)

Coconut

Sunflower

Palm

Soya



Cooking used oil

Animal fats

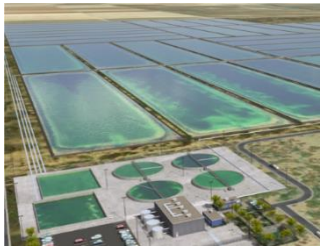
Raw materials for SECOND generation biodiesel Raw materials for THIRD generation biodiesel

Energetic crops

Forestry wastes

Agricultural wastes

Lignocellulosic residues



Algae

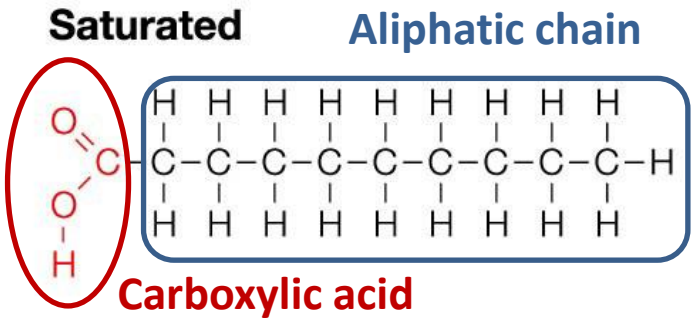
2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

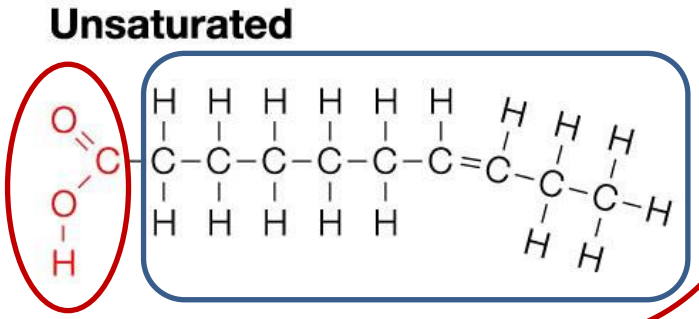
The **oil** obtained from the seeds or fruits of rapeseed, coconut, sunflower, etc. or from animal fat:

- Contains different concentrations of **fatty acids**
- Fatty acid: Molecules formed by aliphatic chains with a **carboxylic acid**

The available fatty acids in vegetable oils are **palmitic** and **stearic**.

- **Fatty acids** can be:
  - **Saturated:** in the aliphatic chain they contain only single bonds between carbon atoms.
  - **Unsaturated:** in the aliphatic chain they contain one or more double or triple bonds between carbon atoms.

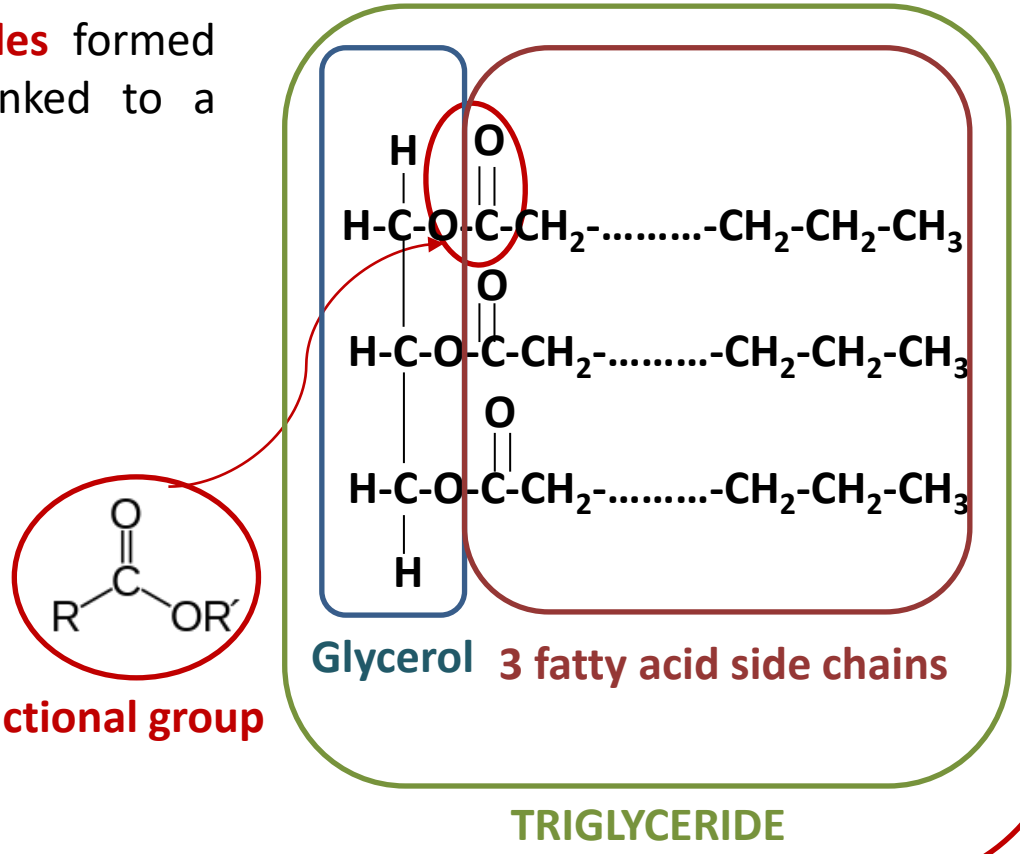




2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

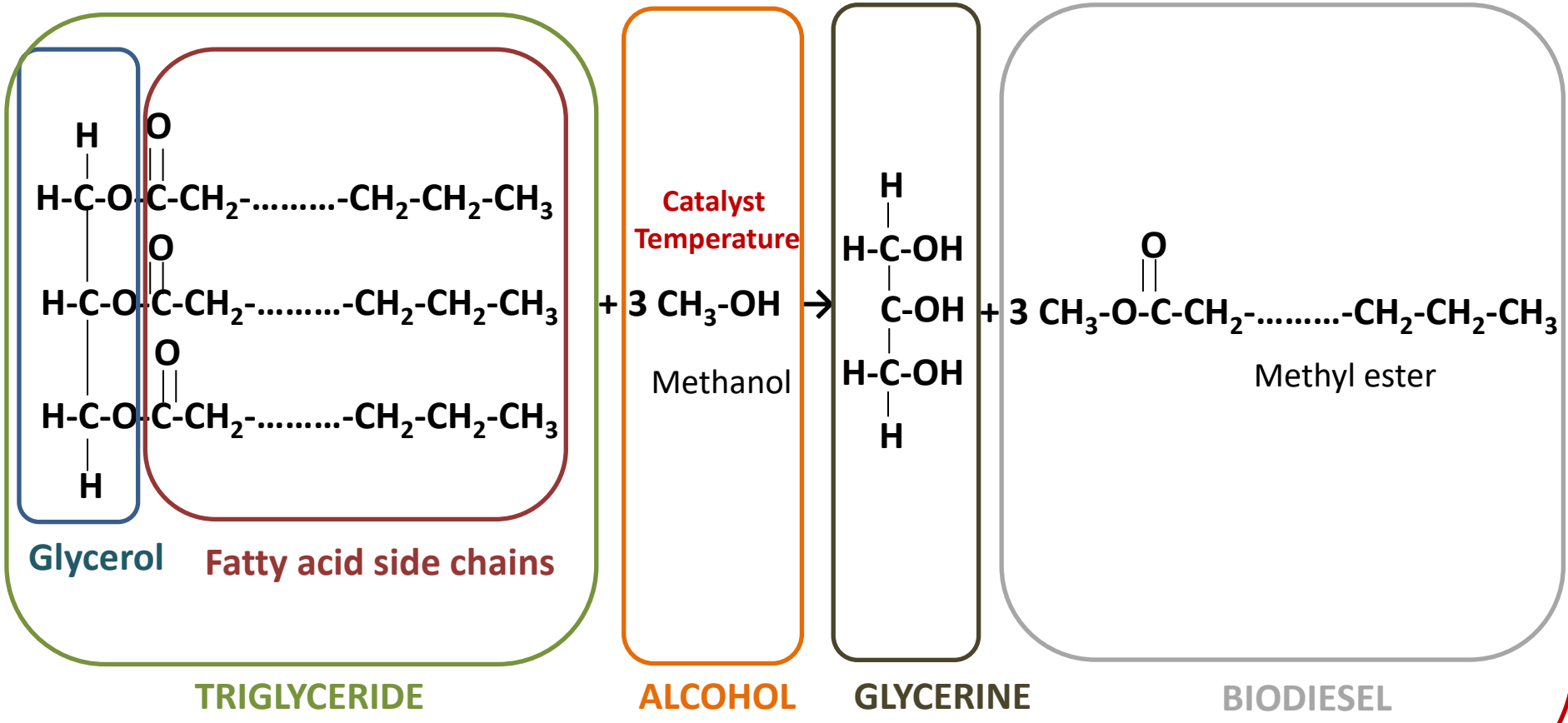
- The **fatty acids** contained in the composition of vegetable oils and animal fats are typically found combined forming **triglycerides.**

- **Triglycerides** are **ester molecules** formed by **3** chains of **fatty acids** linked to a **glycerol** molecule.



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Biodiesel is obtained from **triglycerides** from vegetable oil and/or animal fats when they react with an alcohol in a reaction called **TRANSESTERIFICATION.**



Yields for this reaction are really high: over 95%.

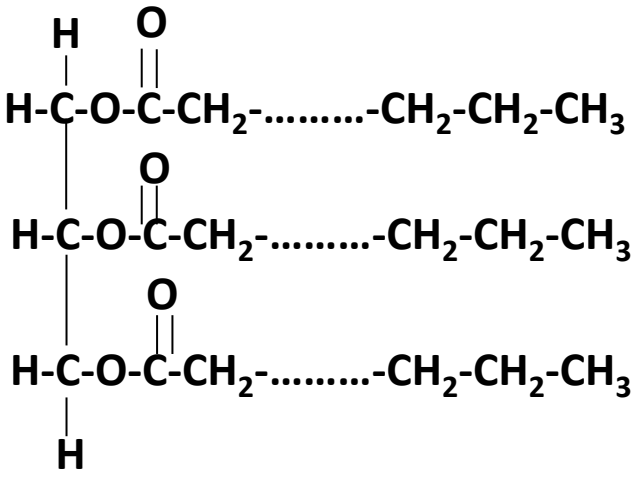
2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Would it be possible to use directly the OIL (triglyceride) as fuel in a diesel engine?

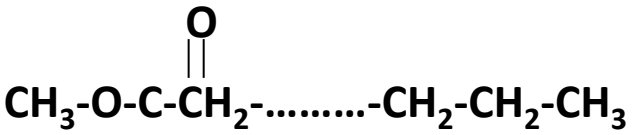
Vegetable oil **cannot** be used directly in diesel engines because of its **higher viscosity** which causes problems, such as poorer atomization of the fuel spray and less accurate operation of the fuel injectors in the engine.

For good performance in the engines it is neccesary to lower the **VISCOSITY**

TRANSESTERIFICATION REACTION GOAL: LOWER THE VISCOSITY OF THE OIL



TRIGLYCERIDE: BIG MOLECULE, HIGH VISCOSITY



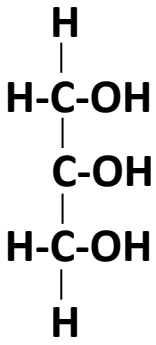
METHYL ESTER : LOWER VISCOSITY

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

PRODUCTS of the reaction:

BIODIESEL (Methyl ester): $CH_3\text{-}O\text{-}C(=O)\text{-}CH_2\text{-}\cdots\cdots\text{-}CH_2\text{-}CH_2\text{-}CH_3$ Reaction **MAIN PRODUCT**

GLYCERINE:



It is the reaction **BYPRODUCT.** It can be used for various purposes after purification.

ALCOHOL: CH_3-OH Even if its a **reactant**, it is used in **EXCESS**, so it's present after reaction.

After reaction a **separation process** is required: alcohol-methylester mix will be separated from the glycerine.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

CATALYST USED IN THE TRANSESTERIFICATION REACTION

They are **essential** because of the **limited solubility of alcohols in oil**.

Catalyst increase the **solubility** allowing the reaction to happen at an **adequate speed**.

TYPES OF CATALYSTS

- **Homogeneous alkalyne** catalysts (KOH, NaOH)

The most used ones
Efficient at short reaction times

- **Homogeneous acid** catalysts (H_2SO_4, HCl, H_3PO_4, RSO_3)

Not used in industry
Require high temperatures and long reaction times.

- **Heterogeneous alkalyne** catalysts (MgO, CaO, Na/NaOH/Al_2O_3)

- **Heterogeneous acid** catalysts (Zeolites, Sulfonic resins, SO_4/ZrO_2, WO_3/ZrO_2)

- **Enzymatic** catalysts (Lipase: Candida, Penicillium, Pseudomona)

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Homogeneous alkalyne catalysts

The most common catalysts are **strong mineral alkalynes, such as sodium or potassium hydroxide (KOH, NaOH).**

After reaction, these catalysts must be neutralised with strong mineral acids, as sulphuric acid (H_2SO_4).

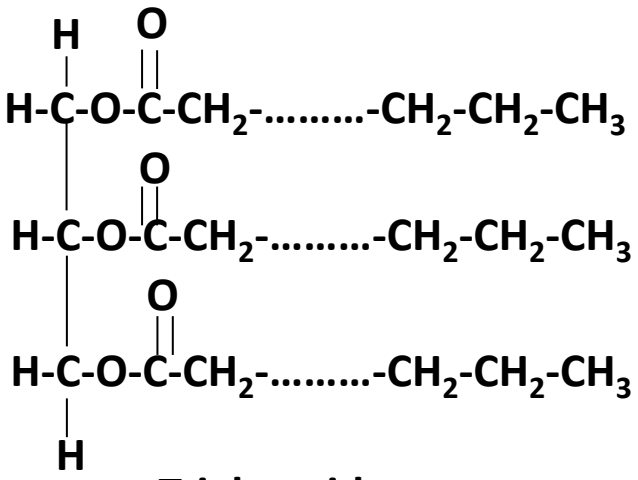
Problem: With homogeneous alkalyne catalysts several undesired secondary reactions may happen: **neutralization and saponification**.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Undesirable Secondary reactions

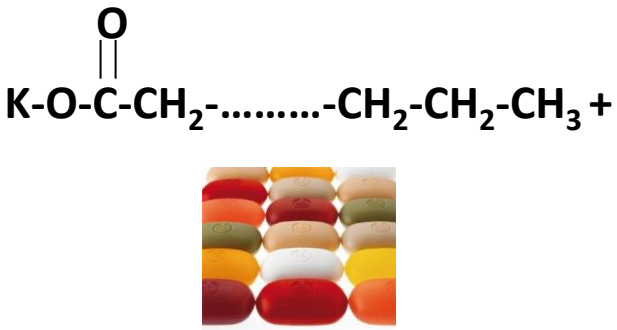
1. Saponification-reaction

If there is **water** in the reaction media, specially at high temperatures, the **triglycerides,** instead of reacting with the **alcohol (CH_3OH)**, they react with the **alkaline catalyst** to form **soap**.



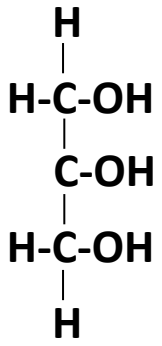
Triglycerides

+ 3 KOH →



Catalyst

Soap



Glycerin

Then, alkaline catalysts use requires that both glycerides and alcohol **must be anhidrous,** (<0,06 % of water) to avoid saponification.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Undesirable Secondary reactions

1, Saponification-reaction

- This reaction is considered **parasitic** because the catalyst DOES NOT make the required mission of accelerating the MAIN reaction and the obtained product is not BIODIESEL but SOAP.

- Soap tends to solidify at room temperature so the product mixture create a mass that is quite difficult to eliminate.

- Foams formation in the reaction media is not desirable as well.

- In addition, **excess soap inhibits** later biodiesel processes, such as separation of ester / glycerol mixture and water/ester mixture after biodiesel washing.

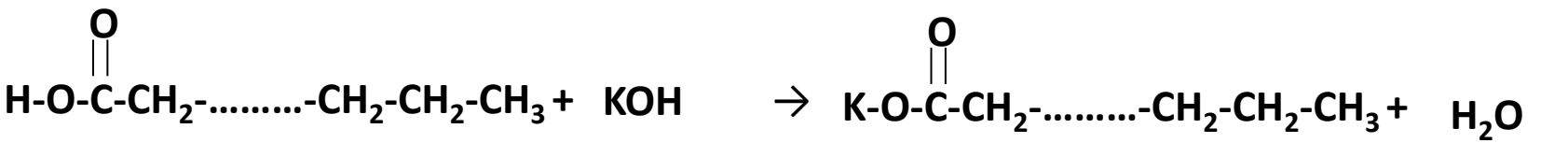
2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Undesirable Secondary reactions

2. Free Fatty Acids neutralization reaction

The vegetable oils and animal fats have a small percentage of fatty acids that are not forming triglycerides. They are called Free Fatty Acids (FFA).

FFAs might react with the ALKALYNE catalyst in the presence of water, producing soap.

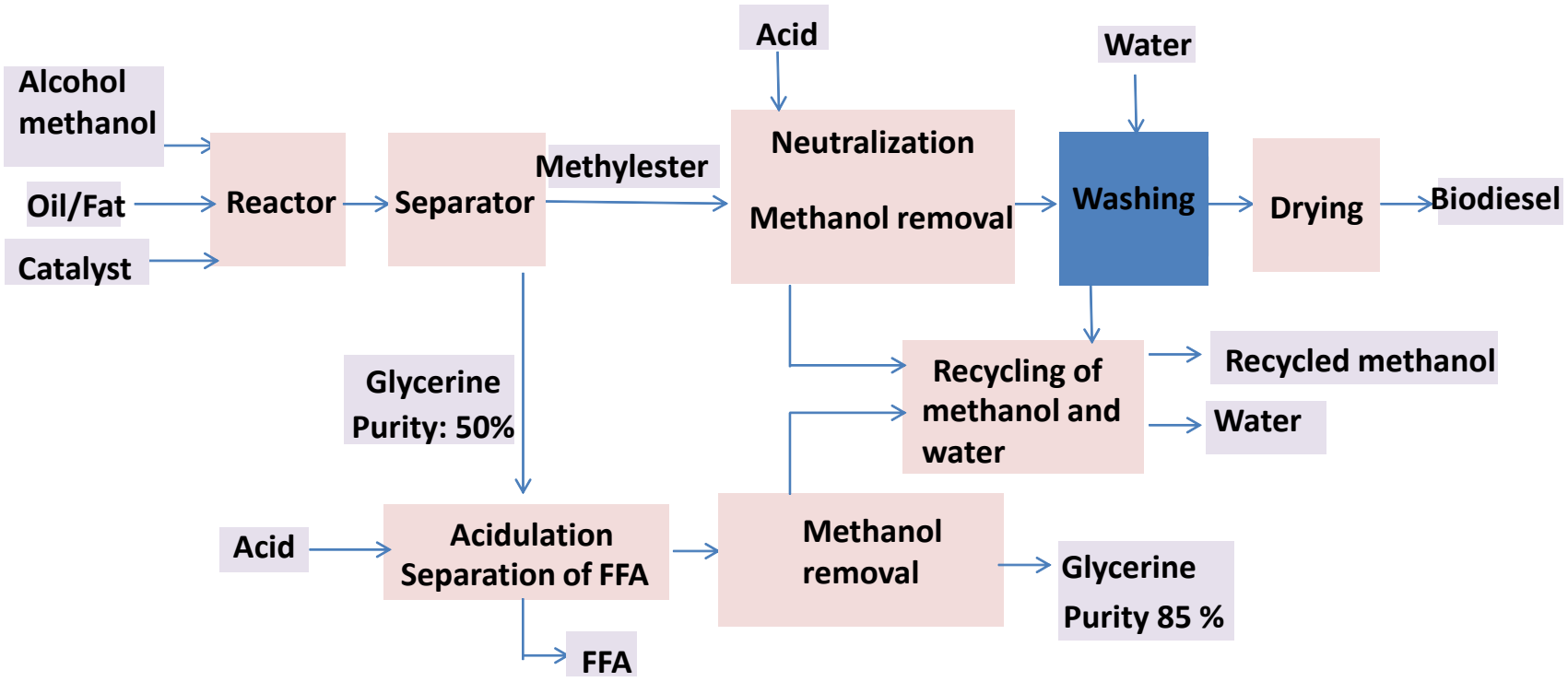


Thus, it is important to:

- **AVOID WATER** in the reaction stage of the first generation biodiesel production process
- It is better to use vegetable oils and fats with low concentrations of **Free Fatty Acids (FFA)**.

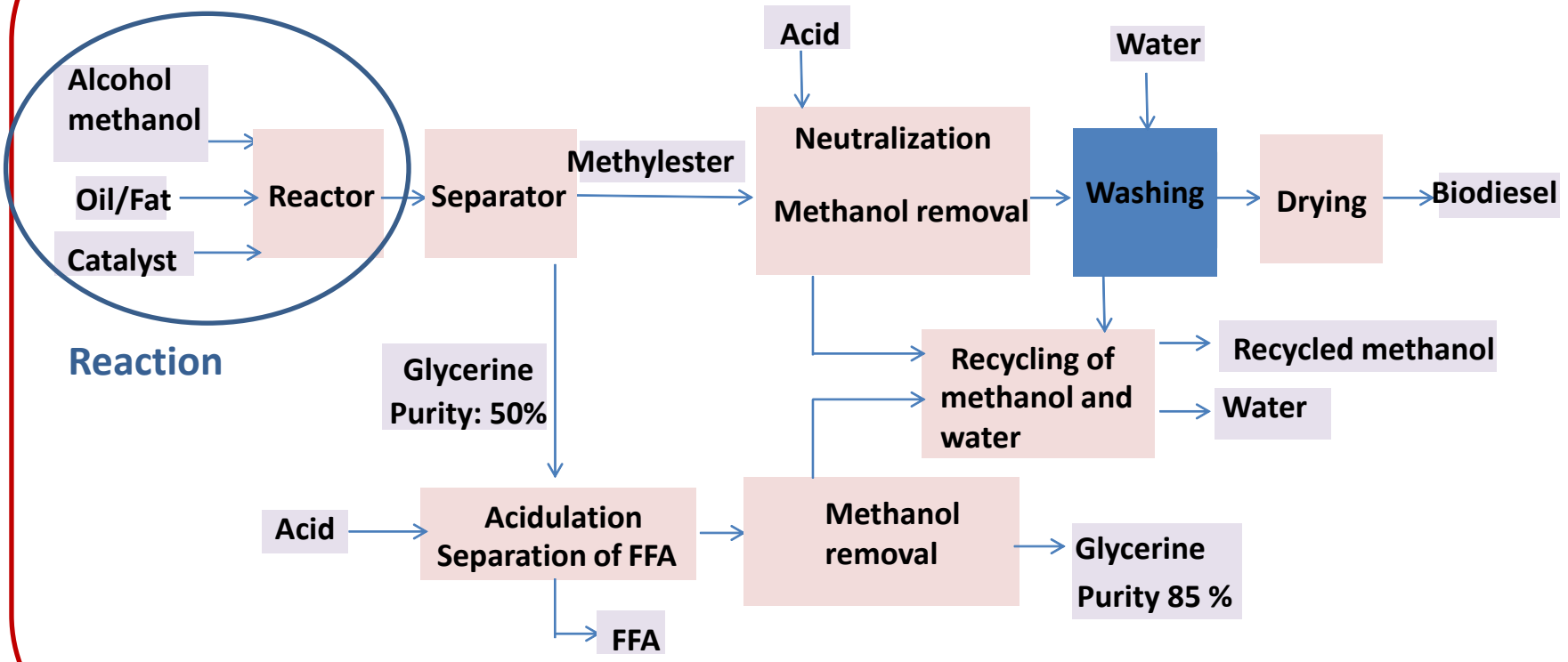
2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step

- **TRANSESTERIFICATION REACTION**

- Methanol and the catalyst are pre-mixed and loaded into the oil containing reactor.

- The mixture is kept for **1h** at **65 °C**.

- **Excess of methanol** is added to ensure a total conversion of the oil into methyl ester.

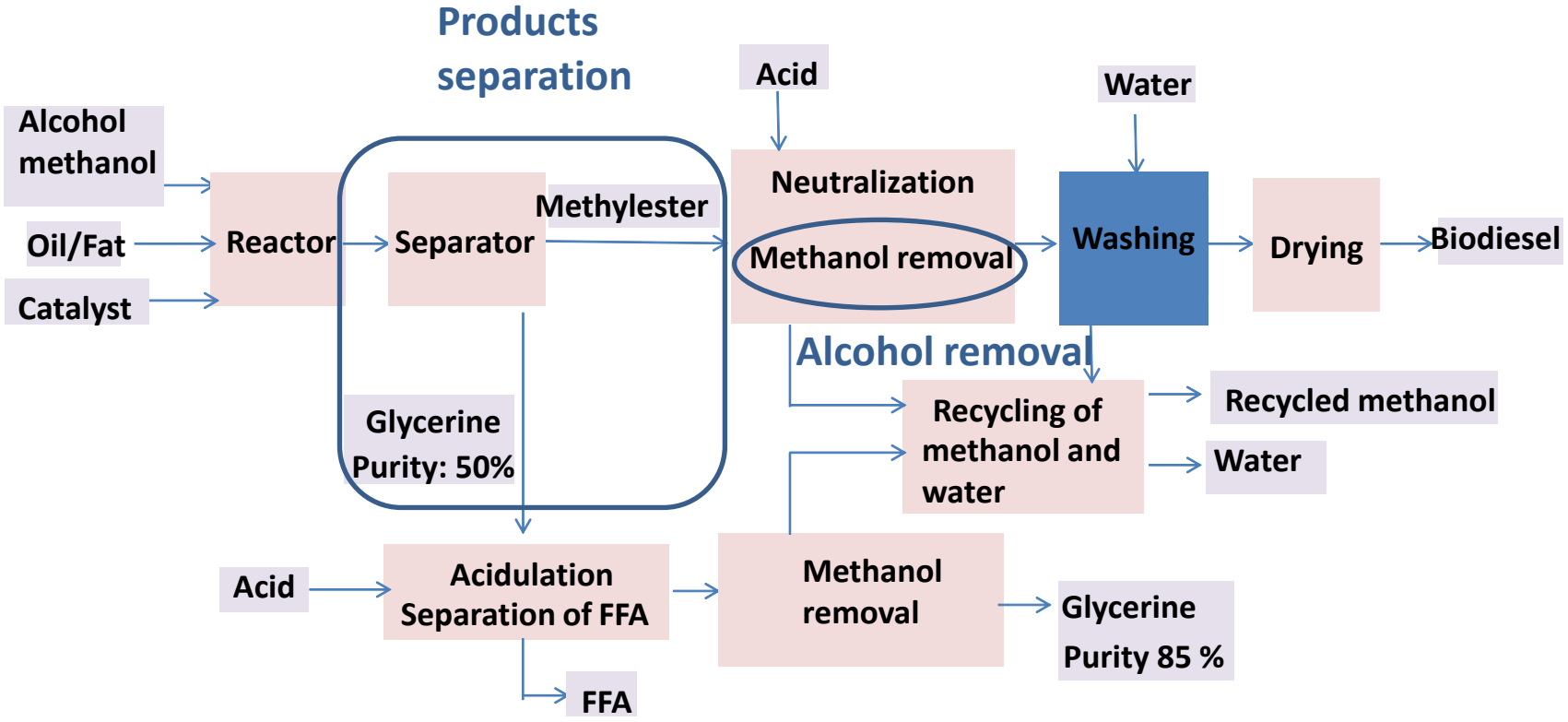
- The **catalyst** (typically NaOH or KOH) will **react first** with any **FFA** in the oil to form **soap**, so there must be enough catalyst to catalize the main reaction and to react with the FFA.

- If the level of FFA is too high (0,5% to 1%) or, if there is water present, the soap formed will generate emulsions with the oil and the methanol hindering the main reaction (undesired reactions).

-Because of this, oil will be usually treated to remove FFAs and will make sure all feedlines are water-free.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step

- **Separation**

- Once the reaction is completed, **two main products are obtained: methyl ester and glycerine.**

- Because of their density difference:
  - Density of esters: 880 kg/m^3
  - Density of glycerol: min. 1.050kg/m^3, depending on the used alcohol, the presence of water and catalyst contents)
  - They can be separated by gravity or centrifugation.

Industrial centrifugue

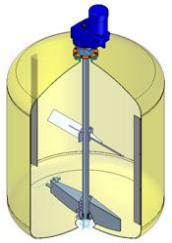
2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step

Factors that influence the separation process

1. Stirring of the mixture

- It is necessary, at least, at the begining of the reaction.
- If stirring continues during reaction, glycerol droplets might disperse inside the mixture slowering the separation process.
- For this reason, it is recommended to slow down stirring as reaction progresses to facilitate phase-separation.



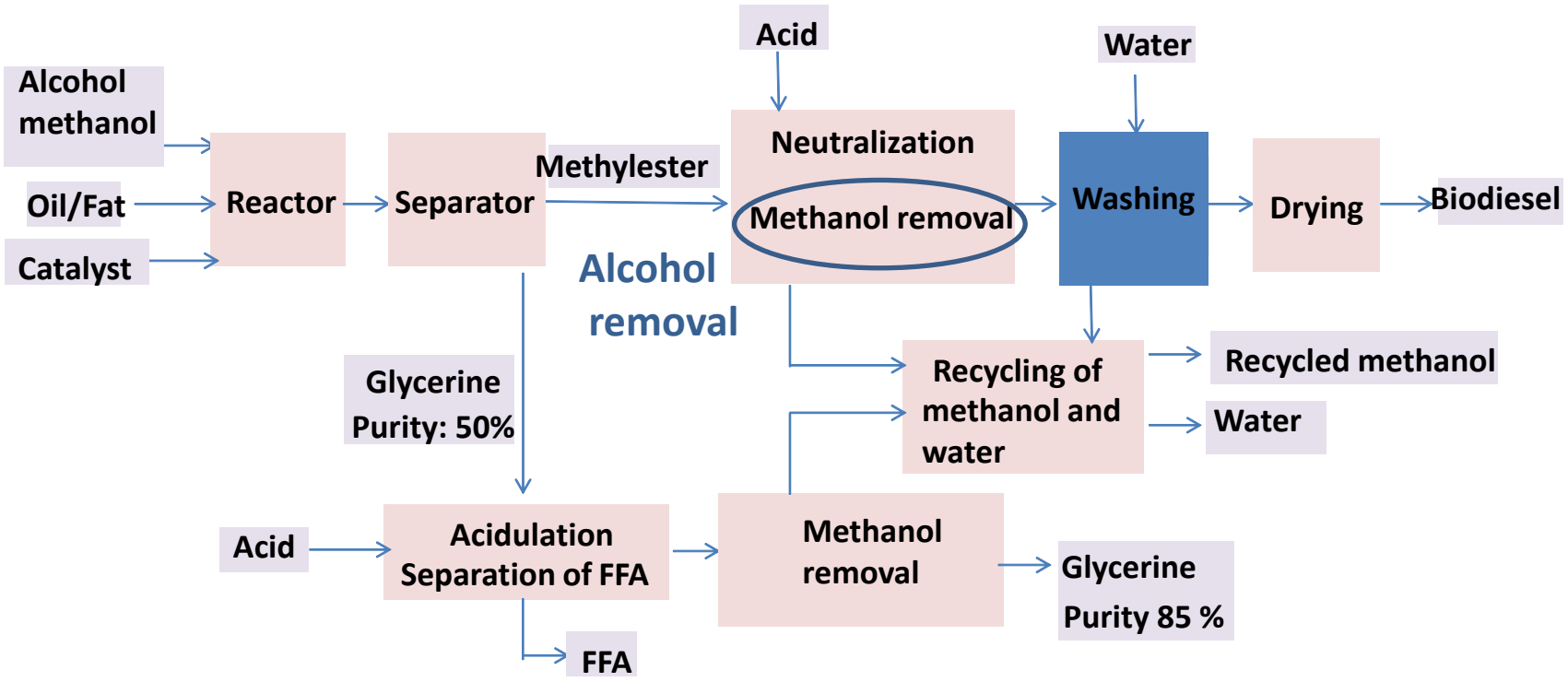
2. pH: the nearer the pH to neutral (7), the faster will the glycerol form a single phase. This is one of the reasons to mimimize the addition of the catalyst.

3. Formation of high amounts of mono-, di- and triglycerides in the final mix:

They might create an intermediate phase. This would cause that the biodiesel obatined would not comply with use especifications and would have to be processed again.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step

- **Alcohol removal**

- As the alcohol (methanol) is added to the reaction in excess, the non reacted part remains in the media and needs to be recovered and reused.

- The presence of methanol helps during phase separation and, above all, stops the reversal of the transesterification reaction.

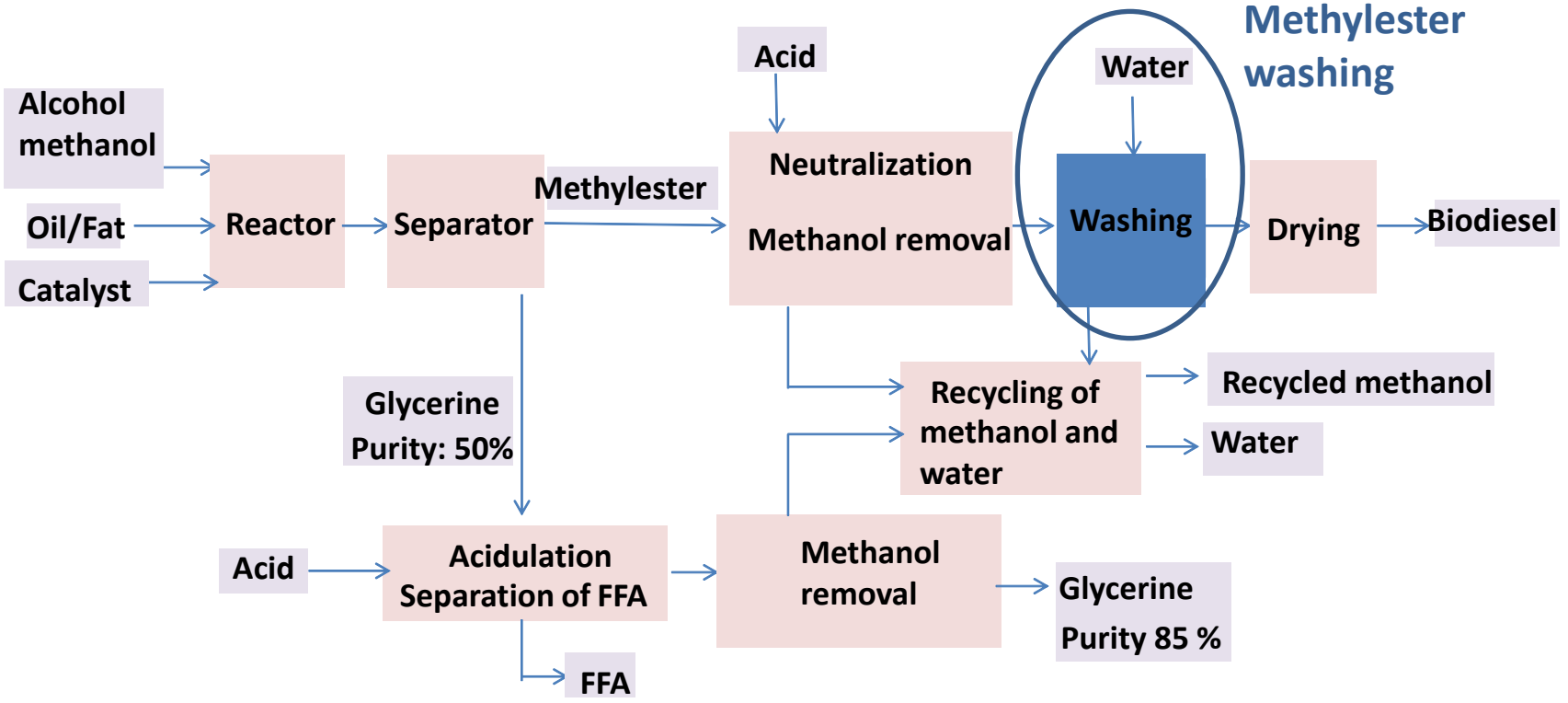
- Excess methanol is removed by distillation **ONLY ONCE glycerine and methylester have been separated**.

- In order to meet economic criteria, the excess of methanol must be recovered by distillation. The methanol boiling point is (64,7°C), so it is easily separated from the mixture by **flash evaporation and recondensation**.

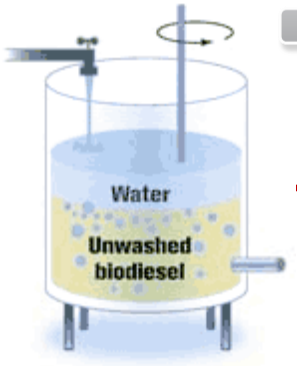
Furthermore, as this compound is toxic, it cannot be emmited to the atmosphere.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS



Process of transesterification with basic catalyst step-by-step

- **Washing of the Methylester**

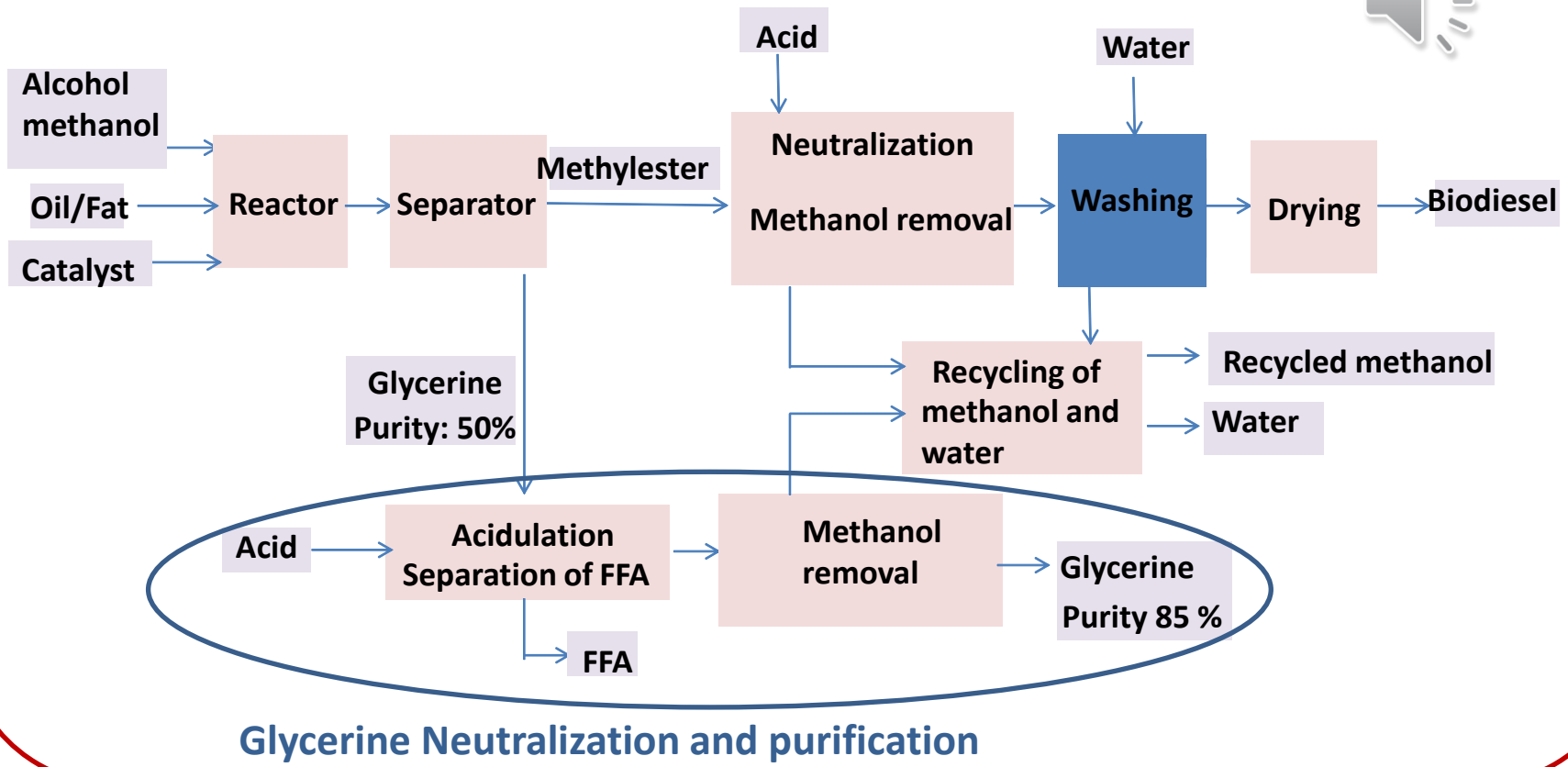
- Washing the methylester with water will remove **remaining catalysts, soap, salts, methanol or glycerol.** The neutralisation step, previous to washing, lessens the amounts of water needed and avoids possible emulsion formation.

- **Warm Water usage (50-60°C)** prevents precipitation of saturated fatty acid esters and delays formation of emulsions.
- **"Softened" Water (slightly acid)** eliminares contamination by Ca and Mg and neutralizes the remaining basic catalyst. The elimination of Fe and Cu ions, catalysts, favors fuel stability. This type of washing prevents emulsion formation and favors a fast and complete phase separation.

- The separation of water and ester phases is, generally, very clean and complete.
- Nevertheless, solubility of water in ester in equilibrium exceeds the water content specifications for B100. Thus, **vacuum drying** is used to eliminate water. The system works at very low pressures and is able to evaporate water at lower temperatures.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step



Glycerine Neutralization and purification

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with basic catalyst step-by-step

- **Glycerine neutralization and purification**

- The glycerine, as obtained, is mixed with unused catalyst, methanol and soap from FFAs. This mixture is neutralized with an acid and then treated with steam to remove the remaining methanol.

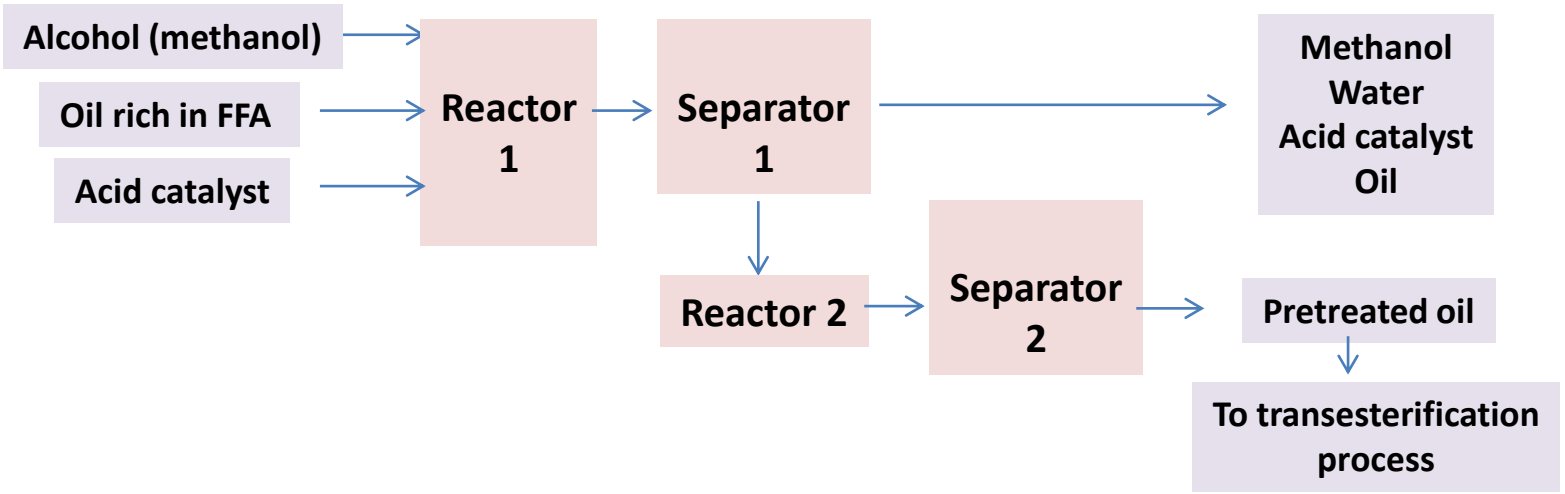
- After this processes, the purified product will have a concentration between 80 and 88 %.

2. FIRST GENERATION BIODIESEL PRODUCTION PROCESS

Process of transesterification with ACID catalyst

- Even if it is possible to use acid catalysts for transesterification reactions, **these reactions are too slow for industrial production of biodiesel.**

- The **main use** for the **acid catalyst reaction** is as a **pretreatment stage** for vegetable oils or fats that contain high amounts of FFAs. This way, the present FFA are transformed into triglycerides.



3. SECOND GENERATION BIODIESEL

Fischer Trops synthesis (FTS)

FTS is based on the conversion of a mixture o carbon monoxyde (CO) and hydrogen (H_2) into liquid hydrocarbons.

$$n\,CO + 2n\,H_2 \rightarrow nCH_2 + nH_2O$$

LIGNOCELLULOSIC BIOMASS

Gasification

RAW SYNGAS
H_2/C ratio =1.5

Syn Gas Cleaning

PURE SYNGAS
H_2/C ratio = 2

Fischer Tropsch synthesis

FTS wax

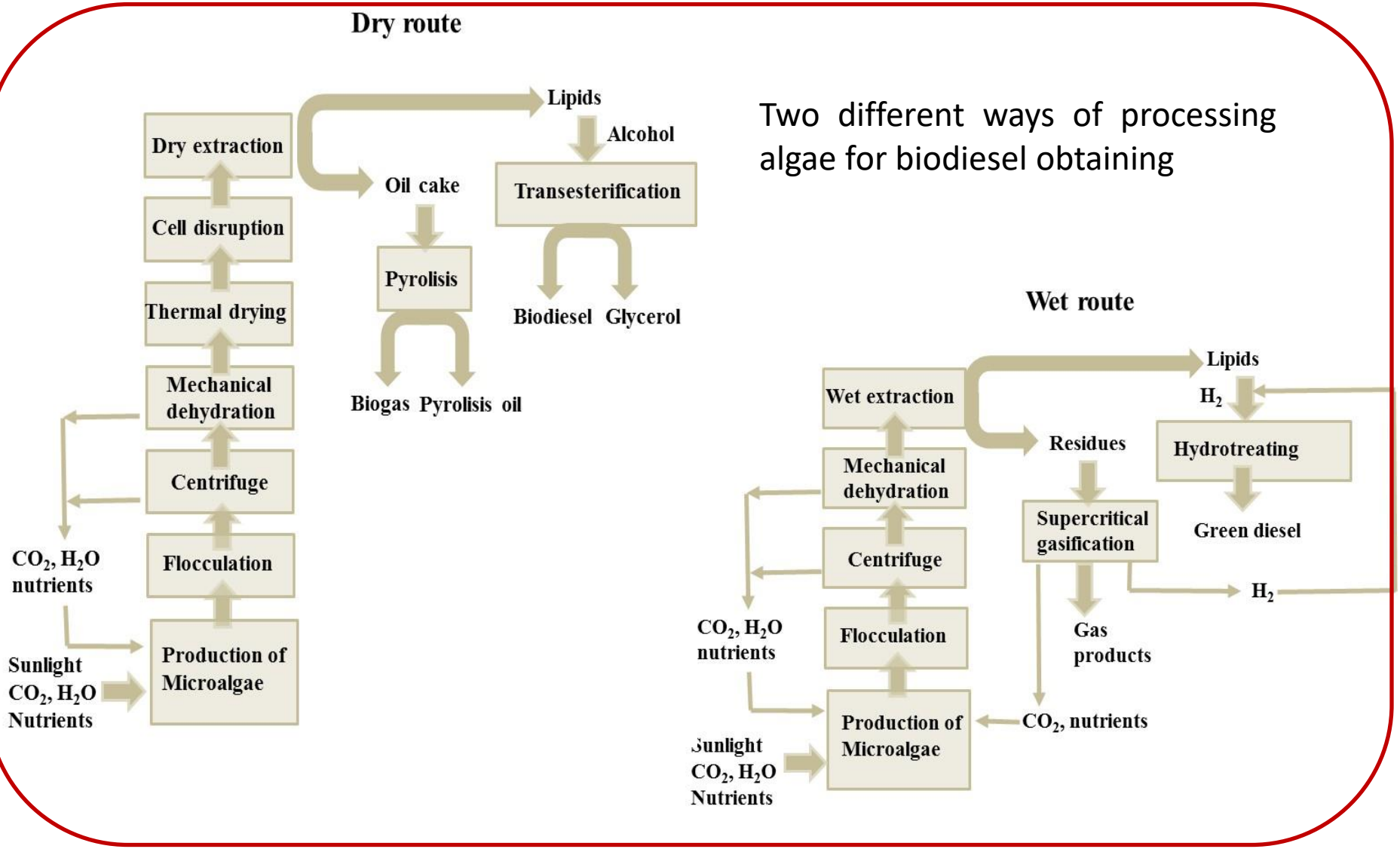
C_xH_y liquids

Wax hydrocracking

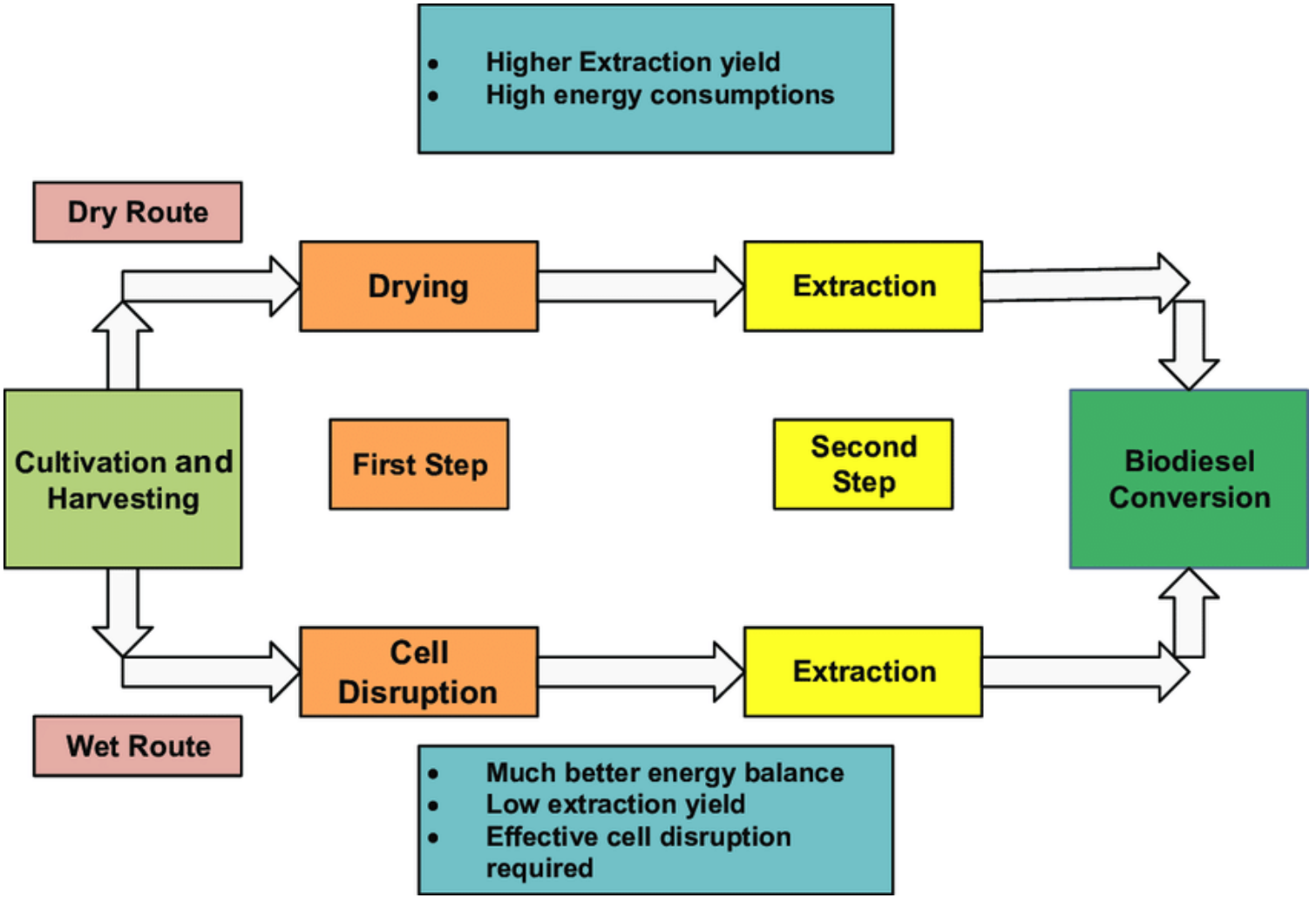
STEAM

Gaseous fuels
dimethylether, methanol, ethanol
Liquid fuels
Naphta, diesel

4. THIRD GENERATION BIODIESEL



4. THIRD GENERATION BIODIESEL



Fazal, T., Renewable and Sustainable Energy Reviews (2017), https://doi.org/10.1016/j.rser.2017.10.029

5. INDUSTRIAL PRODUCTION

The industrial processes for biodiesel production can be:

- Discontinuous
- Continuous

Discontinuous: It is the simplest way to produce biodiesel. It gives versatility, allowing production of biodiesel from different sources of varying quality. They use “batch” reactors.

Continuous: they are prepared for plants with high productions, that justifies a larger amount of workforce and requires uniformity of the feedstock.

-The choice of the technology will be made depending of the desired production capacity, the feedstock quality and recovery capacity.

5. INDUSTRIAL PRODUCTION

5.1. Discontinuous process

-**Typical operational conditions**

- **Ratio alcohol:triglyceride**: 4:1-20:1 (mol:mol), **6:1** the most typical one.
- **Temperature**: 40- 85 ^{o}C, **65^{o}C** the most used one.
- **Catalyst**: NaOH or KOH in percentages: **0,3% - 1,5% in weight**.

It is neccesary to have a **good stirring system** to obtain a good oil-alcohol mixture at the beginning of the reaction.

When **the reaction** is almost finished, the stirring needs to be stopped to allow the separation of the glycerine and ester.

Reaction yields: **85% to 99%.**

5. INDUSTRIAL PRODUCTION

5.2. Continuous process

- It can be performed in **a series of stirred-tank continuous reactors** of different volumes.

- After separating the primary glicerol, a second reaction is performed in a second reactor. This reaction is much faster and it is responsable of about a 98% of the total reaction product.

- It is very important to have a constant concentration in the reactors, so a good mixture level is required and stirring is used.

- Other technology that is used is the **Plug Flow Reactor**. In this case the reactor is a tube, not a stirred tank, where the reaction mixture moves in the axial direction. The residence times are shorter and temperatures and pressure elevated.

6. BIODIESEL PROPERTIES AND QUALITY

Factors influencing biodiesel properties

1. The type of **fatty acids** in the composition of the vegetable oil or fat

   - **The length of the aliphatic chain** (properties enhance with increasing chain length).

   - The **number of unsaturations** (properties reduce with increasing number of unsaturations).

2. The used **alcohol** in the transesterification reaction

These factors affect the cetane number, which is connected to combustion, emissions, coldflow, oxidative stability, viscosity, lubricity, etc.

6. BIODIESEL PROPERTIES AND QUALITY

Key fuel properties of biodiesel

- **Density, viscosity, flash point, calorific value, cloud point, oxidation stability and cetane number.**

- The density and viscosity of biodiesel are similar to the ones of gasoil.

- The **flash point** of a volatile material is the lowest temperature at which its vapors ignite if given an ignition source (but, if the source disappears, the ignition stops).
  Video of flash point https://www.youtube.com/watch?v=w_nVhkvPEpI

- Usually, **biodiesel** has a **lower calorific value** than **diesel**

- **Cloud point** refers to the temperature below which wax in in biodiesels forms a cloudy appearance. The presence of solidified waxes thickens the oil and clogs **fuel** filters and injectors in engines. The lower the **cloud point**, the better the performance in cold weather.

- **Cetane number** is an indicator of the combustion speed of diesel fuel and compression needed for ignition. A high **cetane number** (75-85 CT) ensures clean and efficient combustion.

6. BIODIESEL PROPERTIES AND QUALITY

Key fuel properties of biodiesel

Specifications/ranges	Biodiesel (FAME)	Diesel
Density (15 °C) (kg/m^3)	865	825
Viscosity (40 °C) (cSt)	4.7	2.5
Cetane number	55	50
Cold filter plugging point (°C)	−3	−12
Gross heating value (MJ/kg) (measured)	40.3	46.1
Lower heating value (MJ/kg) (calculated)	37.7	43.3
Water content (mg/kg)	330	—
Acid number (mg KOH/g)	0.16	—
Sulfur content (ppm)		50
Iodine number g iodine/100g	117	—

FAME: fatty acid methyl ester.

International Journal of Engine Research, 2014, 15(4):406-420

7. APPLICATIONS FOR BIODIESEL

B5, B30

- Can be used safely in any diesel (compression-ignition) engine:
  - Diesel cars, trucks, tractors, boats and electrical generators

- Biodiesel mixes with gasoil up to **B5**, 5% (v/v) are considered gasoil (UNE EN 590).

- Nevertheless, the car guarranty is not kept if biodiesel mixes in percentages higher than **B5** are used (UNE EN 590). This regulation is being revised in order to increase this figure up to B10.

- Biodiesel mixes with gasoil up to **B30** as well have been succesufully used in vehicles without any modifications.

B100

- Can be used in any diesel (compression-ignition) engine:
  - <1994 engines need updating in the fuel lines and frequent fuel filter changes
  - >1994 engines only need filter changes

7. APPLICATIONS FOR BIODIESEL

Biodiesel for cogeneration and thermal use

- Biodiesel can be used in boilers **in a thermal use or in cogeneration devices.**

- In Spain it is not usual to have biodiesel as a substitute of gasoil in burners even if it is perfectly suitable.

Why?

- The taxes that are paid in Spain for the gasoil of thermal uses (gasoil C) are lower than the ones of gasoil A (used in transport). This fact makes that this use may not be economically interesting.

- In **Italy**, both taxes are the same and the use of biodiesel for thermal purposes is very commun.

- In **Germany**, they have the National Parlament or Reichstag, that uses biodiesel to supply the 40% of the thermal demand.