

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



**STUDY OF COMBUSTION OF A BIOFUEL INNOVATION IN  
COMBUSTION ENGINES INTERNAL VEHICLES**

***A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT  
OF THE REQUIREMENTS FOR  
THE DEGREE OF HIGHER DIPLOMA IN MECHANICAL &  
CHEMICAL ENGINEERING***

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## Declaration

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# 1 GENERAL INTRODUCTION:

Over the last 20 years we have witnessed significant growth in demand primary energy, which means increased use of fossil fuels. Such evolution has not been possible without posing a number of ecological problems due to intensity of the greenhouse effect, the CO<sub>2</sub> emissions of which originate from the combustion of Hydrocarbons of fossil origin, are the main causes. The Kyoto agreements (1992) clearly demonstrate the desire for change aimed at reducing emissions Greenhouse gas emissions by 5.2% in 2012 compared to 1990 emissions. On 18 November 2005, 156 out of 192 independent countries have ratified, accepted, acceded or approved the protocol[1].

In this context, the search for energy alternatives becomes a major concern on a global scale. Among the solutions in the transport sector, the use of Biofuels derived from biomass and obtained by direct extraction of biomass or by processes of transformation such as pyrolysis, fermentation or gasification. Biofuels are fuels produced from vegetable oils, animal fats and waste. According to the dies, it is sought to produce oil or of alcohol by alcoholic fermentation of sugars or hydrolyzed starch. It also includes sometimes gaseous fuels obtained from plant or animal biomass (dihydrogen or methane) and solid fuels such as charcoal. The ecological balance of these fuels, which is significantly better than petroleum products, could their usage. Indeed, it is a renewable energy that does not emit into the atmosphere than the equivalent of the CO<sub>2</sub> absorbed by plants during their growth, provided that cultures are maintained. They produce six times less carcinogenic particles, half less carbon monoxide, less oxides of nitrogen and no sulfur. In taking account of pollutant emissions from the production chain (seeding land with a tractor, fertilizer pollution, etc.), it is estimated that biofuels reduce greenhouse gas emissions by 80 to 90% compared to petroleum products[2].

Yemen is classified as arid zones, vulnerable to the adverse effects of climate change, thus sensitive to environmental imbalances the global warming that the planet is undergoing.

Among the gas emitting sectors greenhouse gases responsible for this warming, the transport sector, is expanding rapidly in Yemen. The use of renewable energies, including bioenergy as an alternative renewable and less polluting. Bioenergy produced from biomass may represent an alternative to the depletion of fossil fuels and a means of mitigating the adverse effects of global warming by participating in the reduction of greenhouse gas emissions. In the case of Yemen, given that untreated waste represents a significant source of pollution, discharges, industrial waste, etc., the energy recovery of greenhouse gases emitted by such waste, such as methane, is to be considered. It is important to note for the development of the

production of energy and clean fuels in our country, it is not possible to use crops intended for human consumption or animal health. It would be more sensible to turn to second-generation biofuels generation from cellulose, waste or specific crops.

## 1.1 Biomass sources:

**Wood:** wood is the largest source of biomass which is more available in most of the earth areas for example forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste. Lignocellulosic biomass (second-generation biofuels) method is used to harvest energy from wood as fuel, this fuel can be used to derive a proper mechanical machine such as boiler.

**Dedicated Energy Crops:** these kinds of crops are non-food crops, specially grown to supply biomass energy. They are divided into two categories, herbaceous energy crops and Short-rotation woody crops.

**Agricultural Crops and Agricultural Crops residues:** such as cornstarch and corn oil, soybean oil and meal, wheat starch, vegetable oils, corn stover (stalks, leaves, husks, and cobs), wheat straw, and rice straw.

**Aquatic Plants:** such as algae, giant kelp, other seaweed, and marine microflora.

**Biomass Processing Residues:** byproducts and waste streams that yields from biomass processing contains significant amount of energy. The processing of wood for products or pulp produces unused sawdust, bark, branches, and leaves/needles are some examples.

**Municipal Waste:** Any organic matter, including sewage, industrial, and commercial wastes, from municipal waste collection systems.

**Animal Waste:** animal waste contains a complex mixture of organic compounds that can be decomposed into many gases and liquids which are hermitically attack the environment; these waste can be used to produce many gases that is useful as biofuel in many purposes[3].

There are four types of conversion technologies currently available[4], each appropriate for specific biomass types and resulting in specific energy products:

1-**Thermal conversion** is the use of heat, with or without the presence of oxygen, to convert biomass materials or feedstocks into other forms of energy. Thermal conversion technologies include direct combustion, pyrolysis, and torrefaction.

2-**Thermochemical conversion** is the application of heat and chemical processes in the production of energy products from biomass. A key thermochemical conversion process is gasification.

3-**Biochemical conversion** involves use of enzymes, bacteria or other microorganisms to break down biomass into liquid fuels, and includes anaerobic digestion, and fermentation.

4-**Chemical conversion** involves use of chemical agents to convert biomass into liquid fuels.

There are three major types of useful forms for biomass:

1. Biogas: results when animal waste and human swages are processed under a special conditions of treatment, the emitted gases are then cycled in some treatment processes to make it more useful or suitable to store and transport, then these gas can be used as biogas rather than the natural gas in car engines, cooking purposes, electricity generation etc.
2. Biofuel: yield from some kinds of trees or crops, biodiesel and ethanol is the most harvestable fuel as well as most useful form of biofuel.
3. Biorefineries: An emerging concept for the UEMOA to be aware of is biorefineries. A biorefinery involves the co-production of a spectrum of bio-based products (food, feed, materials, chemicals) and energy (fuels, power, heat) from biomass[1].

## **2 BIOFUELS: ELEMENTS BIBLIOGRAPHY**

### **2.1 INTRODUCTION:**

This bibliographic review deals with previous work on the various type of fuels, and their use in diesel engines. Several properties of fuels will be compared to those of conventional diesel fuel.

Finally, the behavior of diesel engines using these fuels will to show their possibilities of use and the consequences that may result. The use of agricultural products as fuels is not an innovation. First diesel engine, developed in 1890[5], was already working with peanut oil [6]. Of many other examples of the use of raw vegetable oils have marked the years of development. The objective was to reduce oil imports to limit the imbalance of the trade balance. These objectives are still but today they are preceded by another concern, rather of an environmental order: the positive impact of biofuels on air pollution with a pollution issue soils become much less acute due to better adapted agricultural practices the production of biomass and the emergence of new types of biofuels[7].

Today, it is essentially the contribution of biofuels to the reduction of gas greenhouse effect which is highlighted in the context of commitments made by various countries within the framework of the Kyoto Protocol and its implications. Road transport does not (25%) of the sources of greenhouse gases, but it is imperative to act on this level, especially as this contribution is expected to increase. Given the ecological context and the likely shortage of fossil fuels in a more or less close to the future , it is particularly crucial to develop transport, oil substitutes with little or no greenhouse gas emissions[8].

The current stakes of biofuels are therefore at the same time of energy and environmental, but also economic. These various issues sometimes have contradictory solutions. Biofuel is therefore the result of a compromise and constitutes an interesting energy transition product.

## **2.2 CLASSIFICATION OF BIOFUELS:**

### **2.2.1 GASEOUS BIOFUELS:**

#### ***2.2.1.1 Hydrogen:***

Hydrogen is currently produced from fossil hydrocarbons. It is used in the chemical industry and in the refining of petroleum products. Hydrogen could however, be used as an energy vector in the transport sector through its transformation of electricity in fuel cells[9].

The production of hydrogen from renewable resources is therefore under study: Bioethanol, syngas resulting from the gasification of biomass, or processes biochemical transformation of biomass, could be sources of hydrogen [9].

#### **A. From bioethanol or syngas:**

Liquid, clean and non-toxic, bioethanol is easily converted to hydrogen with good thermal efficiency (> 80%). Three processes for transforming ethanol in H<sub>2</sub> exist [9]:

- The industrial process commonly used is steam reforming. It consists of one treatment with steam in the presence of a catalyst.
- Another method of hydrogen production is partial oxidation, which consists of reacting a hydrocarbon (in this case ethanol), air and water vapor.
- Finally, the autothermal process, or catalytic partial oxidation, or steam reforming oxidant, appears to lead to better hydrogen yields.

Purification of the H<sub>2</sub> obtained is generally necessary. The choice of process production of H<sub>2</sub> from ethanol will mainly depend on the intended application. The syngas contains H<sub>2</sub>. It can be simply purified where CO can be converted to H<sub>2</sub> according to the so-called gas-to-water or water gas shift reaction:





This exothermic reaction is favored by the presence of water vapor and low temperatures [9].

**B. Through biochemical processes:**

Various biochemical processes make it possible to produce hydrogen [10]:

- Anaerobic fermentation of organic compounds by microorganisms (Heterotrophic production of H<sub>2</sub>).
- Photolysis of water in the presence of light energy (photoautotrophic process).
- Transformation of organic matter in the presence of light energy (process photoheterotrophic).
- The combination of these processes.

Table 1.1 - Average composition of biogas[10]

GAS	%Volume
CH <sub>4</sub>	55-75
CO <sub>2</sub>	25-45
H <sub>2</sub> S	0-1.5
NH <sub>3</sub>	0.05

**2.2.1.2 Biogas:**

Biogas is the product of the methanisation of organic animal vegetable matter rich in sugars by anaerobic methanogenic bacteria (absence of oxygen). Sludge from sewage treatment plants, livestock effluents and agro-food industries and household waste is the main substrate.

Several cultures of bacteria come into action in order to achieve the various methane fermentation steps. This is completed by the production of methane (CH<sub>4</sub>) by the methanogenic bacteria following the reactions:



The calorific value of biogas is a function of its methane content and varies from 20 to 30MJ / kg. To be used as a biofuel or injected into the natural gas methane must be purified of contaminants (for landfill gas), dust and other particles must be removed, dried, and concentrated to more than 95%. Finally, to be used as fuel, the

methane must be compressed between 200 and 250 bar. All types of vehicles, designed to run on natural gas or adapted to run on gas and gasoline, can use biomethane. Heavy vehicles are generally equipped with of the original diesel injection system and a gas ignition system by injection of low amount of diesel fuel. Depending on the mode of production of the electricity used for purification and compression of methane, the use of this gas as a road fuel can reduce CO<sub>2</sub> emissions by 95 to 99% compared to fossil fuels. The emissions of particles and soot, NO<sub>x</sub> and carbohydrates other than methane, are also strongly reduced [11].

## 2.2.2 Liquid biofuels

### 2.2.2.1 Bioethanol:

Bioethanol is obtained by fermentation and then distillation of the sugars contained in such as sugar cane, sugar beet, Jerusalem artichoke. When bioethanol is produced from cereals such as maize or wheat, an intermediate step hydrolysis (generally enzymatic rather than chemical) is necessary to transform the starch contained in the cereal into sugar. Ethanol is blended with gasoline in a proportion of 10% to give an automobile fuel commonly called E 10. This fuel is suitable for all petrol engines. Beyond a concentration of 20%, adaptations to motors are necessary. Recently, researchers have formulated new bioethanol, generation [12][13]. They have the peculiarity of being derived from the lignocellulosic material, abundant and cheap and does not compete with food crops. However, its conversion into fermentable sugars is difficult. The growing interest this arises from the fact that the transformation of the lignocellulosic material biofuel has a very positive environmental impact, that is, the balance sheet energy (energy generated less energy consumed) is higher than manufactured ethanol from grain corn.

In general, any transformation process of lignocellulosic biomass comprises the following steps: pretreatment of the raw material, hydrolysis, ethanol fermentation and separation of ethanol from the fermentation mash (Figure 1.1) [14].



Figure 1.1 - Production process of bioethanol [14].

The fermentation of C<sub>6</sub> sugars and the recovery of ethanol are well controlled industrial steps identical to those used for ethanol production. From sugar and starch plants. The pretreatment and hydrolysis steps subject of in-depth research and development studies adapted to the subject first to be valued. The purpose of pretreatment is to make cellulose accessible to hydrolysis. It may be physical,

physico-chemical or chemical. Avoiding the loss or degradation of sugars and limit the formation of inhibitors and releases, are the main pretreatment constraints. Hydrolysis, on the other hand, may be chemical or enzymatic (biochemical hydrolysis is also called saccharification) and aims at the degradation of cellulose by fermentable sugars (glucose). The glucose resulting from the hydrolysis of the cellulose is fermented in the same manner as that obtained from starch. This fermentation is carried out routinely by the yeast *Saccharomyces cerevisiae* (baker's yeast). Pentoses, mainly derived from hemicelluloses and present in negligible, can be fermented in ethanol but by other microorganisms. The challenge lies in the development of strains of modified tolerant microorganisms to ethanol, capable of fermenting hexoses and pentoses, with good yield and resistant to certain inhibitory molecules resulting from the hydrolysis[14].

#### ***2.2.2.2 Vegetable oils :***

The first use of vegetable oils as fuel was tested by Rudolf Diesel, inventor of the engine that bears his name. The interest in the use of vegetable oils continued to show up in different parts of the world during the Second World War when the war effort created the need for new research sources of energy. But later, the search for alternative diesel fuels was rendered superfluous with the arrival of the peace period and the relative abundance of fossil fuels. However, in the 1970s, rising oil prices 2 to 12 dollars a barrel and the fear of a fuel shortage have rekindled interest in alternative fuels, including vegetable oils as fuels diesel engines[15].

Of the 250,000 known plant species [16], only about 4500 species have been examined and only 100 species are currently known to be plants oleaginous, with an oil content of commercial interest. Among those, only 22 types of vegetable oils are marketed on a large scale today, and 12 of these constitute more than 95% of world production of vegetable oils[15], [16]. The vegetable oils can also be classified according to the oil content of seeds and fruits which produce them (Table 1.2).

Table 1.2 - Oil yield of common oilseeds

Oilseeds	Oil mass / seed mass [%]
Copra	58-65
Babassu	60-65
Sesame Seed	50-55
Fruit of the palm	45-50
Palm tree almond	45-50
Groundnut	45-50
Rape	40-45
Sunflower seed	35-45
Safflower	30-35
Olive	25-30
Cotton seed	18-20

Vegetable oils are fatty substances that are liquid at room temperature, insoluble in water and obtained from oilseeds by pressure, extraction or by comparable procedures [17]. The oil consists mainly of triglycerides. It is a molecule of glycerol connected to 3 molecules of monocarboxylic acids of long chains called "fatty acids" [18], [19]. The latter account for more than 90% of molecular weight of the triglycerides and are extremely numerous, especially in the vegetal. There are two categories of fatty acids [20]:

a. **Saturated acids:** where each carbon atom of the aliphatic chain is bonded to two hydrogen atoms.

b. **Unsaturated acids:** containing more than 10 carbon atoms and one or more carbon-carbon double bonds. Their crude formula is  $C_nH_{2n+1-2d}COOH$  where  $d$  is the number of double bonds.

The various saturated and unsaturated fatty acids that can be found in various vegetable oils are presented in table 1.3 [21], [22]

**Table 1.3 - Fatty acids contained in various edible oils**

Formula	Fatty	Acid
Palmitic	C <sub>16</sub> : 0 CH <sub>3</sub> - (CH <sub>2</sub> ) <sub>14</sub> - COOH	Saturated
Stearic acid	C <sub>18</sub> : 0 CH <sub>3</sub> - (CH <sub>2</sub> ) <sub>16</sub> - COOH	Saturated
Oleic acid	C <sub>18</sub> : 1 CH <sub>3</sub> - (CH <sub>2</sub> ) <sub>4</sub> - CH = CH - (CH <sub>2</sub> ) <sub>7</sub> - COOH	Unsaturated
Linoleic acid	C <sub>18</sub> : 2 CH <sub>3</sub> - (CH <sub>2</sub> ) <sub>7</sub> - CH = CH - CH <sub>2</sub> - CH = CH - CH <sub>2</sub> - COOH	Polyunsaturated
Linolenic acid	C <sub>18</sub> : 3 CH <sub>3</sub> - CH <sub>2</sub> - CH = CH - CH <sub>2</sub> - CH = CH - CH <sub>2</sub> - CH = CH - (CH <sub>2</sub> ) <sub>7</sub> - COOH	Polyunsaturated

Characterizing a vegetable oil by its degree of unsaturation amounts to evaluating its iodine value which is the number of grams of iodine reacting with 100 g of oil; it is an addition reaction of iodine to the unsaturated sites (double bonds) present in the fatty acid chains of oils [23]. The higher the iodine value, the more unsaturated the oil, which it has a high number of double bonds [23]. Schematically, the unsaturated oil is drying, therefore not resistant to oxidation. Table 1.4 shows that when the degree of unsaturation of an oil increases, the rate of oxidation also increases. Saturated, it is resistant to oxidation, but is often solid at room temperature (20 ° C). Table 1.4 gives the melting points of some fatty acids. Solidification points are due to high melting points of saturated fatty acids. Also, more low is the degree of unsaturation, higher will be the point of solidification of the oils.

Fatty acid	Relative oxidation value	Melting point [° C]
Palmitic	-	63.5
Stearic acid	0.6	73.1
Oleic	6	5.5
Linoleic acid	64	-13.1
Linolenic acid	100	-24.2

**Table 1.4 – Fatty acids contained in various edible oils**

Table 1.5 shows the solidification points of some vegetable oils [24]. Vegetable oils consisting predominantly of saturated fatty acids are ambient temperature, which does not allow their use as fuel.

Two other essential characteristics of vegetable oils must be determined: The content of phosphatides and the saponification index [24].

- The content of phosphatides indicates the amount of material forming the gum in oil; It varies according to vegetable oils.

- The saponification index (Is) can be used to calculate the molecular weight average M of the oil using the relationship:

$$M[g] = (56.11 \times 3000)/I_s.$$

Table 1.5 - Solidification point of various edible oils

<b>Oils</b>	<b>Solidification point [° C]</b>
Palme	35 to 42
Groundnuts	2 to 4
Safflower	-13 to -18
Rape	-10
Cotton	+12 to -13
Corn	-10 to -20
Sunflower	-17
Soy	-10 to -16
Lin	-19 to -27

Table 1.6 - Oil properties compared to diesel

Property	Diesel	Soy	Sunflower
Density(kg / m <sup>3</sup> )	830	920	918
Viscosity at 40 ° C (cSt)	2.4	65	58
PCS (MJ / kg)	45.4	39.6	39.5
Acid number (%)	-	0.2	0.15

The cetane number generally expresses the capability of a diesel fuel for auto-inflammation and combustion in a diesel engine. It has direct the cold start capability, the combustion cycle timing, the pressure gradient, maximum pressure and noise. The cetane number of vegetable oils is generally lower than that of conventional gas oil. The difference between the cetane diesel fuel and vegetable oil could be due to their chemical composition and their degree of saturation and refining [25]. The cetane indices of vegetable oils are between 28.3 and 41.5, while the minimum cetane number for gas oils N ° 1-D and No. 2-D is 40 according to ASTM D 975-81[25].

Viscosity (probably the greatest difference between vegetable oils and gas oil) increases with the degree of saturation of the oil. Vegetable oils are generally ten times more viscous than diesel fuel at 40 ° C and thirty times more viscous at 0 ° C. there are many differences between the physico-chemical properties of oils vegetable and diesel fuels. These differences also vary from vegetable oil to other. Table 1.6 shows some properties relative to diesel and other oils Raw Soybean and sunflower seeds [26]. While the gas oil has a viscosity of 2 to 4.5 cSt at 38° C, crude oils have a viscosity of about 25 times greater [27]. Another difference between diesel fuel and vegetable oils is calorific value (PCS), vegetable oils have 5 to 18% less energy than diesel [26], [27].

Because of their chemical composition, vegetable oils have the advantage of being biodegradable and from renewable raw materials. They are as the first possibilities for future motorization. Their use has an impact positive environment for our environment which is becoming increasingly polluted.

However, from a technical point of view, its direct use as fuel is not possible due to the problems which can be caused by its too high viscosity such as deflection of the injection system (injection pump and injectors) of the engine. In order to problems, pre-heating, dilution with an organic solution and transesterification, have been studied by several researchers [28], [29].

### **3 Adaptation of pure vegetable oils**

For pure vegetable oils to be used in a conventional diesel engine unmodified, they must meet certain requirements. The most important those relating to the rheology of oils (viscosity, pour points and cloudiness, mass volumetric, etc.) as well as those relating to their inflammation (cetane number, flash point, etc.). In order for a vegetable oil to be used as a fuel in an engine diesel, it must have a viscosity close to that of diesel, i.e. a maximum of 4.5 mm<sup>2</sup> / s, see a limit of 5 mm<sup>2</sup> / s at 40 ° C.

The continued use of vegetable oils as fuel in diesel engines direct injection causes carbon deposits on cylinder heads, valves, and the nozzles of injectors and the heads of pistons. These deposits are mainly due to spraying during injection, given the high viscosity of vegetable oils[30]–[32].

Vegetable oils are characterized by their high flash points and therefore are more difficult to ignite than diesel. The enormous problem encountered for an engine direct injection with vegetable oil is that the temperature average of the combustion chamber is of the order of 200 to 220 ° C., while the flash point for vegetable oils is between 220 and 350 ° C [31]. Some of the droplets do not vaporize and stick to the cylinder walls causing tarry deposits. These deposits will quickly accumulate on the nose of the disturbing injectors thus the operation of the engine. They will also lodge in the throat of the first segment and modifying its elasticity, which will lead to seizures and rapid this last. On the one hand, there will be loss of compression and cold start on the other hand, deterioration of the efficiency of the engine with an abnormal increase in consumption, an escape of black fumes and a typical odor of oil [31].

The pour point of a fuel is the lowest which the fuel can still flow. This parameter is used to predict conditions of the engine by setting the limits of fuel usage per relatively cold. It is between -10 and -30 ° C for diesel [33] and is higher for vegetable oils with high fractions of saturated fatty acids [34].

Another characteristic to be taken into account for the flow of fuel is the cloud point which indicates the minimum temperature at which fuel begins to crystallize. These crystals can thus obstruct the distribution lines of the fuel. The pour point and the cloud point are intimately linked.

The density of vegetable oils is slightly higher (about 10%) to that of diesel. The calorific value of these oils is, in turn, about 10 to 15% compared to that of diesel. This has the consequence of providing the same power, but for a higher specific fuel consumption. As the density of the oils is greater, it compensates for the low calorific value of the oils, admitting in the cylinder an equivalent amount of fuel, which specific energy consumption.

### **3.1 Preheating**

The oil must undergo preheating to reduce its viscosity, but this process alone, proves insufficient. Among the oil heating systems, the most using a heat exchanger, to recover the internal energy of the engine from the heat of the exhaust gases [33][17]. Studies should be carried out in the direction of fluidization of the oil to overcome its high viscosity without have to heat it, at the risk of appearing phenomena of oxidation and polymerization oil; it must therefore act as a backup.



## 3.2 The emulsions

Emulsions can be defined as the mixture of two immiscible substances, forming a microstructure using a mixer (most often the moving mixer axial, where the central axis is provided with blades of various shapes, is used). The additives called emulsifiers (surfactants or surfactants) make it possible to make this mixture stable. In general, these two substances are a fatty substance and an aqueous body. The fatty substance is the continuous phase and the aqueous body is the dispersed phase. Use of surfactants allows the aqueous phase to disperse more easily into the body by reducing the surface tension, thereby stabilizing the mixture.

It is also necessary to specify the speed of rotation of the mixer, since the droplets of the dispersed phase depends on it. Indeed, the higher the speed of rotation large, the smaller the size of the micro-droplets. Micro-emulsions differentiate

Of conventional emulsions by the characteristic size of the dispersed particles (10 to 50 nm in the case of a micro-emulsion, compared with 2 to 50  $\mu\text{m}$  in the case of a conventional emulsion).

Early studies on the use of emulsions in relation to fuels began with the dispersion of water droplets in the gas oil [35]–[37].

The results of tests of these emulsified fuels in compression ignition engines have shown a clear improvement in combustion and a significant reduction in emissions of soot and nitrogen monoxides at the same time, but with regard to emissions of carbon monoxide and hydrocarbon, the results of these studies did not not been all consistent. In 2004, Lin et al. Have conducted investigations into the use of emulsions of alcohol in diesel. They have found that the addition of the alcohols in the emulsions improves combustion and increases the thermal efficiency of the engine. In fact, when the combustion of an emulsion in the engine, the boiling temperature of the droplets water or alcohol is significantly lower than gas oil, which leads to its explosion which causes spraying of the fuel droplets (called the second spray). This second spraying increases combustion efficiency and reduces emissions of pollutants. The latent heat of evaporation of water or alcohol consumes calorific energy, which reduces the maximum temperature of the cycle, responsible for the formation of nitrogen oxides ( $\text{NO}_x$ ). In other works, the emulsion was used to reduce the viscosity of Biofuels such as pyrolysis oils [38], biodiesels [39]and animal fats [28].

Finally, in order not to influence the profitability of this process (i.e. the micro-emulsion), a very fine adjustment of the process is necessary in order to control the size of the micro-droplets, in addition to the high consumption of chemicals and the energy intake.

### 3.3 Mixtures of vegetable oils and diesel oil

The physical properties of vegetable oils can be improved when they are mixed with diesel fuel. Dissolution takes place so that there can be no phase separation.

The properties of mixtures are generally intermediate between those of diesel and vegetable oils (Table 1.7). For some engines that do not accept not crude vegetable oils, some high-diesel mixtures can be used.

Table 1.7 - Properties of vegetable oil mixtures with gas oil

Fuel	Viscosity at 37°C (cSt)	Density at 15°C(kg/m <sup>3</sup> )	Flash point (°C)	Point of Spraying (°C)	Cetane number
Diesel	3.46	865	71	-50	44.3
Peanut					
25%	6.60	879	-	-15	41.8
50%	12.60	892	84	-9	40.5
100%	39.51	918	328	-2	39.0
Corn					
25%	6.85	883	-	-21	42.0
50%	11.37	896	83	-21	40.0
100%	33.46	923	320 4	-19	34.0
Sunflower					
25%	6.40	878	-	-20	42.1
50%	10.75	894	81	-19	40.8
100%	33.46	922	320	-9	33.4
Soy					
25%	6.25	880	-	-25	43.6
50%	11.28	894	82	-19	41.9
100%	32.31	922	314	-9	41.9

### 3.4 Esters of vegetable oils and fats

Another way to change the physical properties of a vegetable oil comparable to a diesel fuel is to change its chemical composition and to transform it into an ester. This reaction called transesterification was studied very largely by several researchers. In the 1940s, more than a dozen patents have been issued to DuPont, Colgate and others for the conversion of vegetable oils into esters. This work very often involves the alcoholysis of triglycerides with an alkaline catalyst, in order to obtain the corresponding alkyl esters [44]. Many authors have contributed to the development of this method [45, 46].

After the Second World War and on the recommendation of the Research Institute for Oils and oilseeds in France (IRHO), ester tests were undertaken at the Bellevue station of the Institute Français du Pétrole (IFP). But it is only in the 1980s that researchers have introduced esters into new direct injection [47].

Purpose of the transesterification reaction

The thermal decomposition of an oil which is a glycerin ester, in the absence of oxygen, leads to the formation of glycerol and a mixture of esters. The objective of such study is the use of esters obtained as diesel fuel. The study same time to:

1. The total removal of glycerin.
2. Reduction of the boiling point of the oil.
3. Reduction of the flash point of the oil.

## 4 Transesterification reaction

The transesterification reaction makes it possible to refine the oil since the greater part phospholipids and free fatty acids will be removed. The free fatty acid disappears completely with the basic catalysts. In acid catalysis, the ester is still acidic, which may cause problems. The iodine value of the methyl esters is practically the same as that of crude oils. The saponification index does not change. The index of peroxide and acidity must be measured again. When the reaction is incomplete, mono and diglycerides may be present in the esters. It is necessary to monoglycerides by filtration or avoid formation.

If the alcohol remains in the esters, some of their characteristics can be (Cold quality, distillation curve, viscosity), but to the detriment of the index cetane and flash point. The manufacture of methyl and ethyl esters from vegetable oils is given by the transesterification reaction in Figure 1.2.

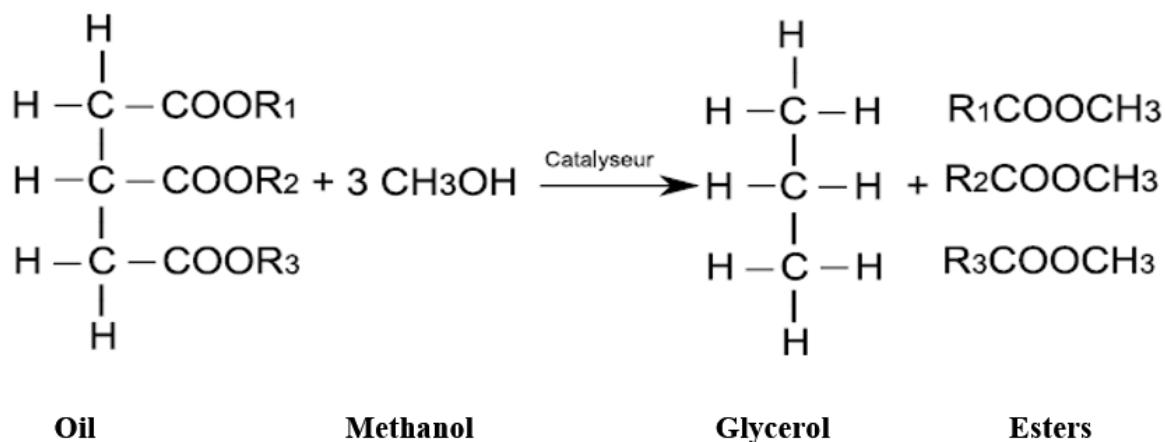


Figure 1.2 - General scheme of the transesterification reaction.

## 4.1 Process for obtaining esters

If the manufacture of the methyl esters from the oils is carried out individually in large units, it generally concerns products intended for chemicals (eg detergents). The use of the esters directly as requires the manufacturer to comply with precise specifications accompanied by specific constraints (compliance with certain standards required for diesel fuel, for example).

The ester must therefore be capable of being manufactured in relatively simple, small scales with common equipment.

A group of researchers [48] subjected to ethanolsis samples of 250 g of rapeseed oil, using 1% of catalyst (NaOH or KOH) or 0.5% of sodium and two types of ethanol: ethanol 190 (95%) and ethanol 200 (100%). At the end of the reaction, the ester obtained after decantation was put in a column and washed by sprinkling therein some water. Emulsions form during washing and 24 to 48 hours are required to observe good phase separation.

For the production of esters on a large scale, the contribution of the Institute Français of Petroleum [29], using two different catalytic systems is very appreciable.

A system of basic catalysis was used when the oil to be esterified is degummed and low acid: Esterfip 1 process (Figure 1.3). The main characteristics of the process Esterfip 1 are illustrated in Table 1.8.

Table 1.8 - Characteristics of the IFP process: Esterfip1 [29]

Raw material	Low acid oil and dry methanol
Conditions	T = 50-70 ° C 15-25% methanol (on the mass of the oil used) 2 basic catalysis 1 treatment
Interest	No filtration No evaporation No washing
Balance sheet	95-97% by weight of esters 97-99% in ester purity Glycerin easy to discolor and purify

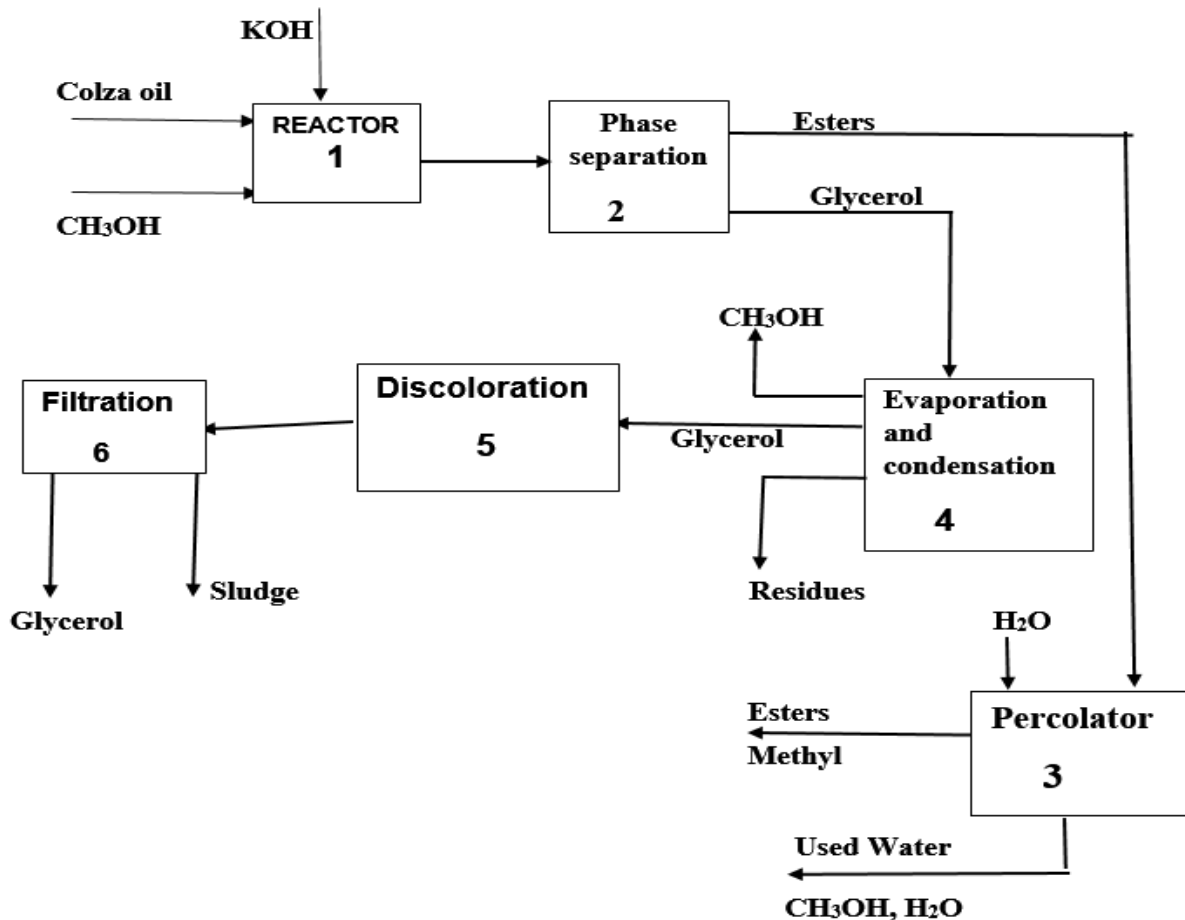


Figure 1.3 - Principle of the complete transesterification process [29, 48].

## **4.2 Characteristics and kinetics of the reaction:**

### **4.2.1 Effect of stoichiometry:**

One of the most important variables that affects the formation of esters is the ratio molar ratio of alcohol to vegetable oil. The stoichiometry of the reaction requires 3 moles of alcohol for 1 mole of oil [molar ratio 3-4 to obtain 3 moles of acid esters fat and 1 mole of glycerol. To obtain 90 and 97% conversion to esters [49], ratios molar ratio of 4: 1 (33% excess methanol) and 6: 1 (100% excess methanol) are necessary. For a theoretical ratio of 3: 1 and below the percentage of ester decreases rapidly with corresponding growth in mono, di and triglycerides. This means that the conversion is not complete. Figure 1.5 shows the composition of the products of the transesterification of sunflower oil into sunflower oil methyl esters (E.M.T.) by considering the effect of stoichiometry. The increase in this ratio to more than 100% excess does not increase yield (which is already close to 98-99%) and complicates recovery of glycerol. It also entails additional costs for recovery alcohol. Figure 1.5 shows the yield of methyl esters of peanut oil, soya, cotton and sunflower seeds. It should be noted, however, that these oils are edible and have refined, bleached, filtered and deodorized prior to use.

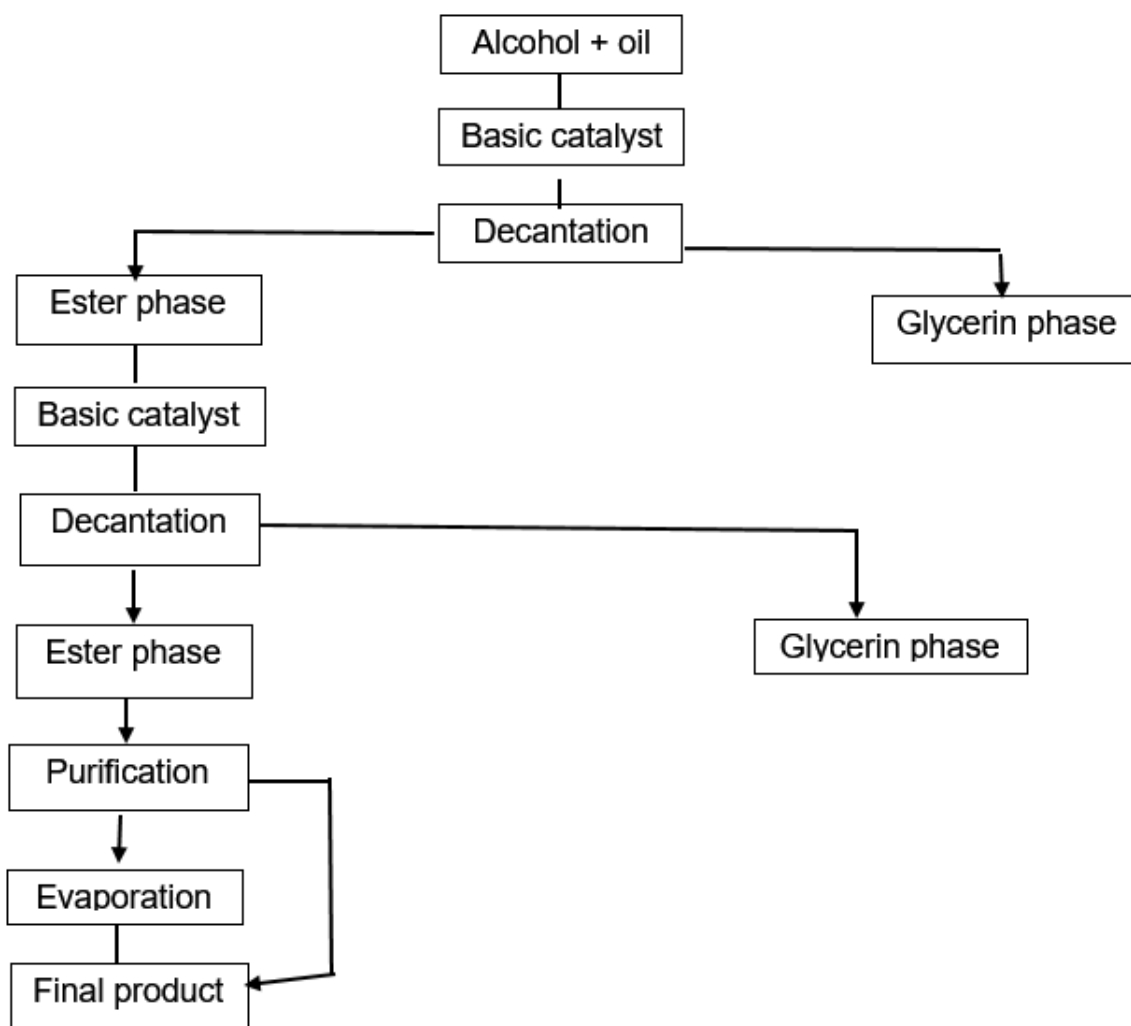


Figure 1.4 - Principle of the IFP process: Esterfip 1 [70].

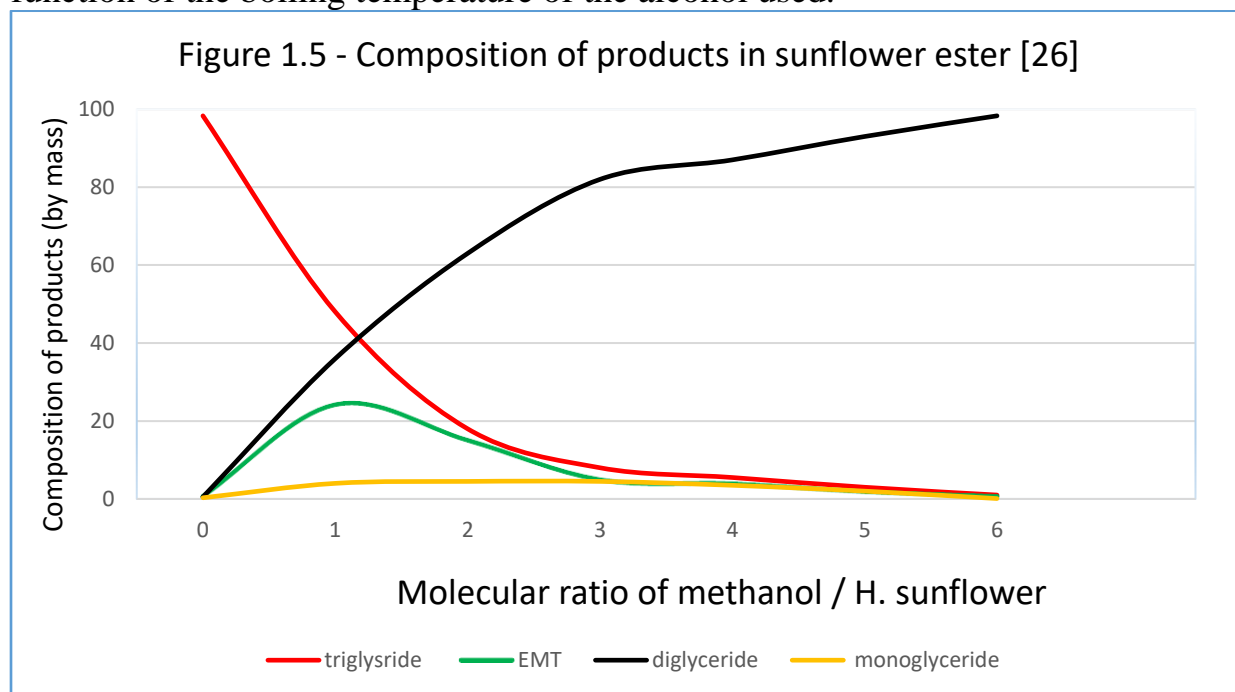
#### 4.2.2 Effect of reaction time on alkaline alcohol:

During the transesterification of the peanut oil, 80% of the ester obtained after 2 hours of reaction was formed in 5 minutes [50]. Similarly, the alcoholysis of menhaden oil has led to conversion rates of 80-99% using several varieties of alcohols, temperatures of 60-100 ° C for a reaction time between 2-60 minutes. The methanolysis of refined peanut, soybean, cotton and sunflower oils has been reported by Freedman [46]. Figure 1.7 shows the effect of the reaction time on the percentage conversion when 100% excess methanol, i.e. a 6: 1 molar ratio was used. Whereas

in the first minute, almost 80% of soya and sunflower oil, the conversion rate for cottonseed and groundnut oils hardly exceeds 55%. However, after 60 minutes of reaction, the conversion (except for cottonseed oil) reaches 95%.

### 4.2.3 Effect of the nature of the alcohol:

Figure 1.8 illustrates the degree of conversion in the transesterification reaction of sunflower oil with methanol, ethanol and butanol. Whatever the molar ratio alcohol / oil used (3: 1 or 6: 1), the conversion is higher with butanol than with ethanol or methanol. This is due to the reaction temperature which must be increased as a function of the boiling temperature of the alcohol used.



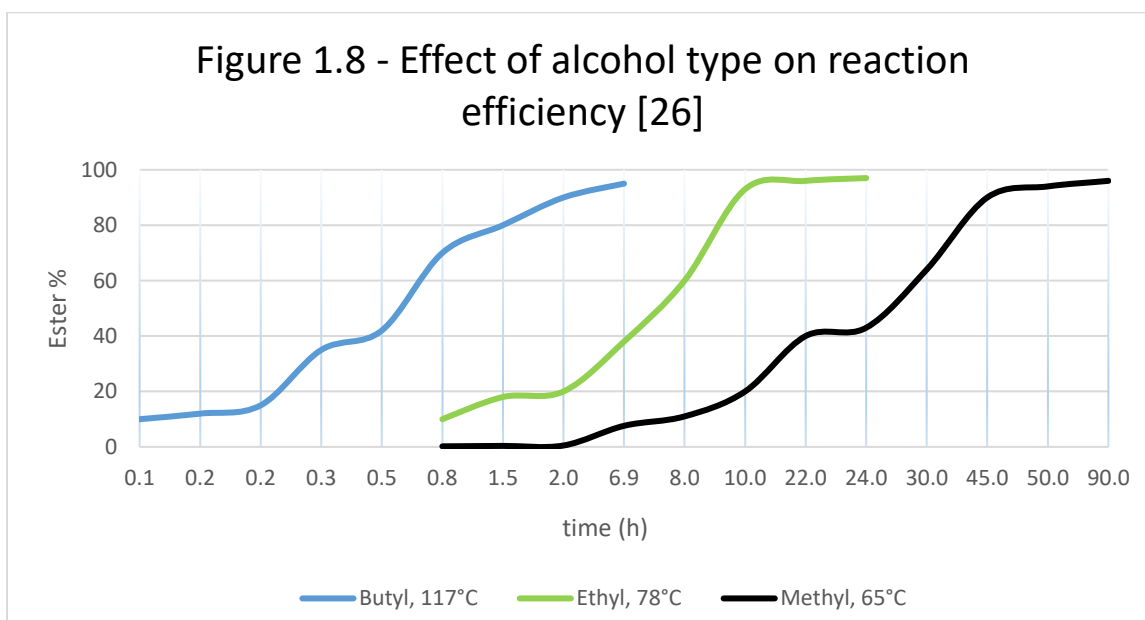
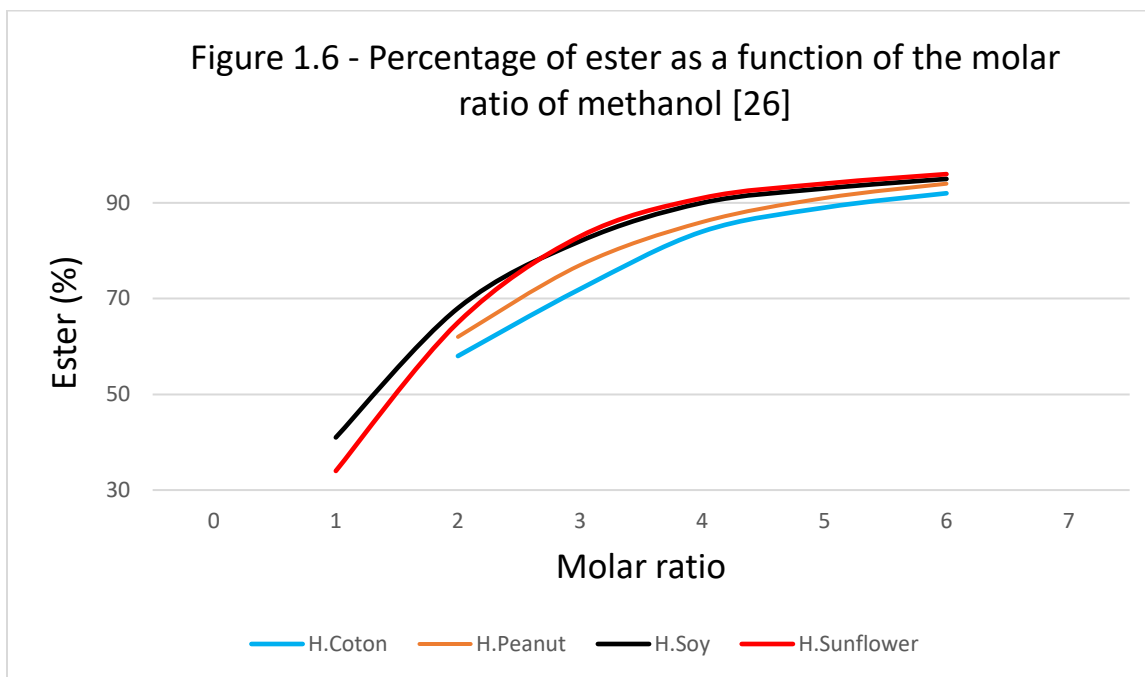
### 4.2.4 Effect of temperature:

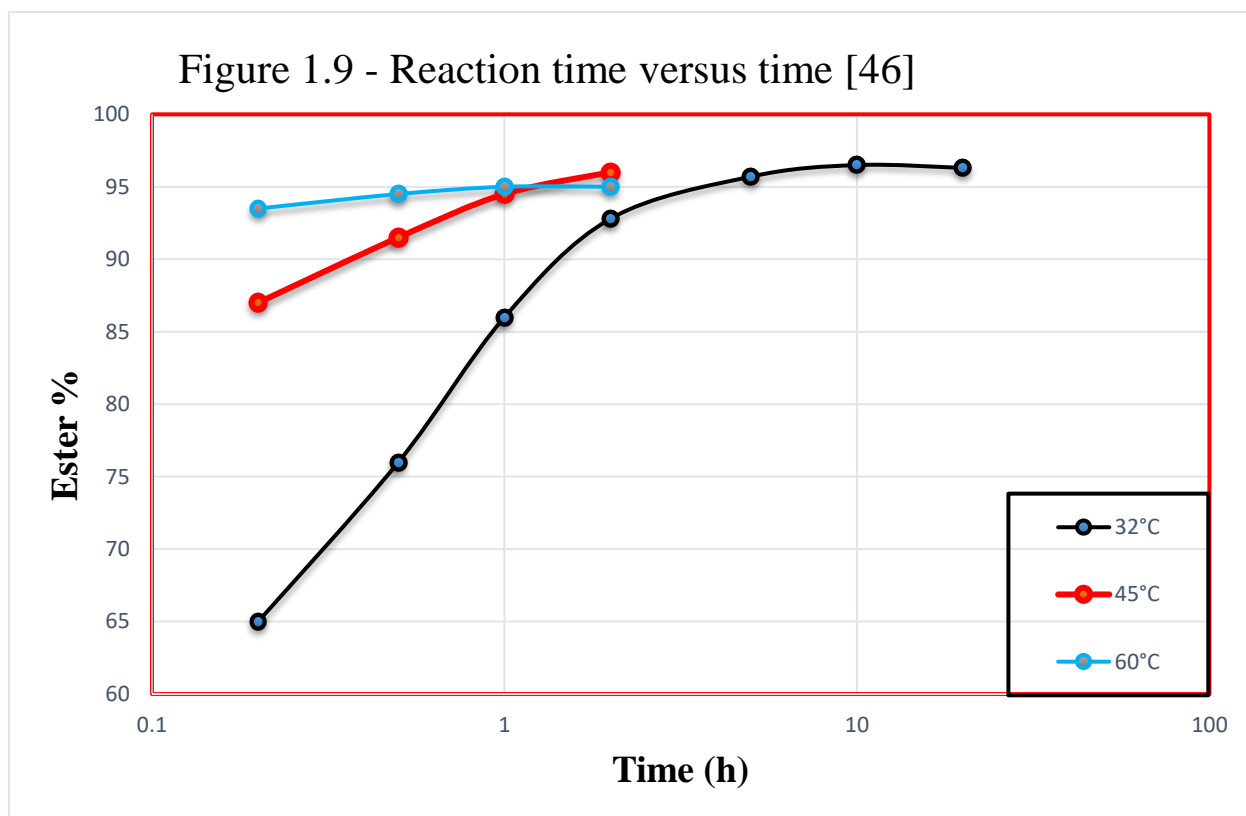
The alkaline alcoholysis of vegetable oils is normally carried out in the vicinity of point boiling of the alcohol used. However, researchers have reported that the reaction may take place at room temperature.

Freedman [46] studied the methanolysis of refined soybean oil at 60, 45 and 32 ° C, using the conditions of Figure 1.9. Because of the exothermicity of the reaction, when the catalyst is added to the reaction mixture at room temperature of 28 ° C, the



temperature rises to 32 ° C. in the mixture. After 5 minutes of reaction, the esters present in the reactions at 60, 45 ° C and 32 ° C respectively represent 94, 87 and 64% of the mass of oil used. After 1 hour of reaction, the conversion rate is identical (96%) for reactions at 60 ° and 45 ° C. and slightly lower (92%) for that at 32 ° C. After 4 reaction time the conversion rate of the reaction at 32 ° C slightly exceeds those of other cases (45 and 60 ° C).





#### 4.2.5 Effect of catalyst

One of the most important characteristics of the transesterification reaction is nature and quality of the catalyst. The literature reports a broad vision of the various catalysts used in this reaction. The catalysis may be alkaline or acidic according to the types of oils used and particularly according to their acidities.

##### A) Alkaline Catalysis (basic)

The basic catalysts used are generally grouped into two groups: natural catalysts and industrial catalysts. Several researchers have worked satisfactory results have been found both with the former and with the latter [35].

##### A-1) Alkaline Catalysis and Natural Catalysts

The natural catalysts consist of ash and carbonization residues. Among the many alcoholysis catalysts, natural mineral catalysts, i.e. compounds which can be readily available, are preferable: clays of calcium carbonate (limestone sediments), lime, magnesia (dolomitic sediments), zeolites (volcanic sites). However, catalysts such as faugeasites, montmorillonite, sieves 4A and magnesia are inactive under certain conditions of reactions. Other catalysts such as lime give low ester yields and a formation of soaps follows. These soaps are secondary products hydrolysis of the ester functions with a higher percentage of ethanol. When using methanol, the percent conversion is lower.

The ratio of alcoholate and hydroxide ions depends, on the one hand, on the nature of the alcohol (methanol, ethanol) and, on the other hand, the water content of the medium. The same proportion of water favors the formation of hydroxide ions in ethanol than in the methanol. With ethanol 96 (ethanol-water azeotrope) and potassium hydroxide as catalyst, under the experimental conditions of Graille et al. [1985], the yields in esters do not exceed 80%. The increase in the proportion of catalyst has the effect of increase the proportion of soaps that can reach 30%.

#### A-2) Alkaline Catalysis and Industrial Catalysts

The catalysts most commonly used for a transesterification reaction are potassium and sodium hydroxides. These catalysts (easily handled) were used in the majority of alcoholysis work with an amount of 0.6% in mass relative to the mass of the rapeseed oil used [47], when absolute methanol is used.

One of the important points to consider during the basic catalysis of vegetable oils is the rate at which the reaction occurs in the presence of sodium methoxide.

Kinetic studies show that the butyl, methyl and ethyl esters of sunflower are formed in a proportion of 88, 80 and 76% (based on the weight of oil) respectively after 1 hour [55]. After 1 hour of reaction, the percentages of the esters methyl, ethyl and butyl are 98, 96 and 96%, respectively. In catalysis basic, where 100% excess methanol is used, the transesterification is complete in 1 hour. The reaction mixture should be anhydrous (less than 0.3% moisture) and vegetable oil must have a free acidity of less than 0.2%. Water and acidity destroy the catalyst. Figure 1.10 illustrates the ester conversion of a vegetable oil, using 1.0, 1.2 and 1.3% KOH as catalyst. With various concentrations of hydroxide of potassium, Peterson et al. [52] carried out these tests illustrating the effect of increasing the amount of catalyst from a certain value (1.3% by weight of oil). So if

The percentage of catalyst is quite high, its use will only serve to complicate the reaction (increase the rate of saponification for example).

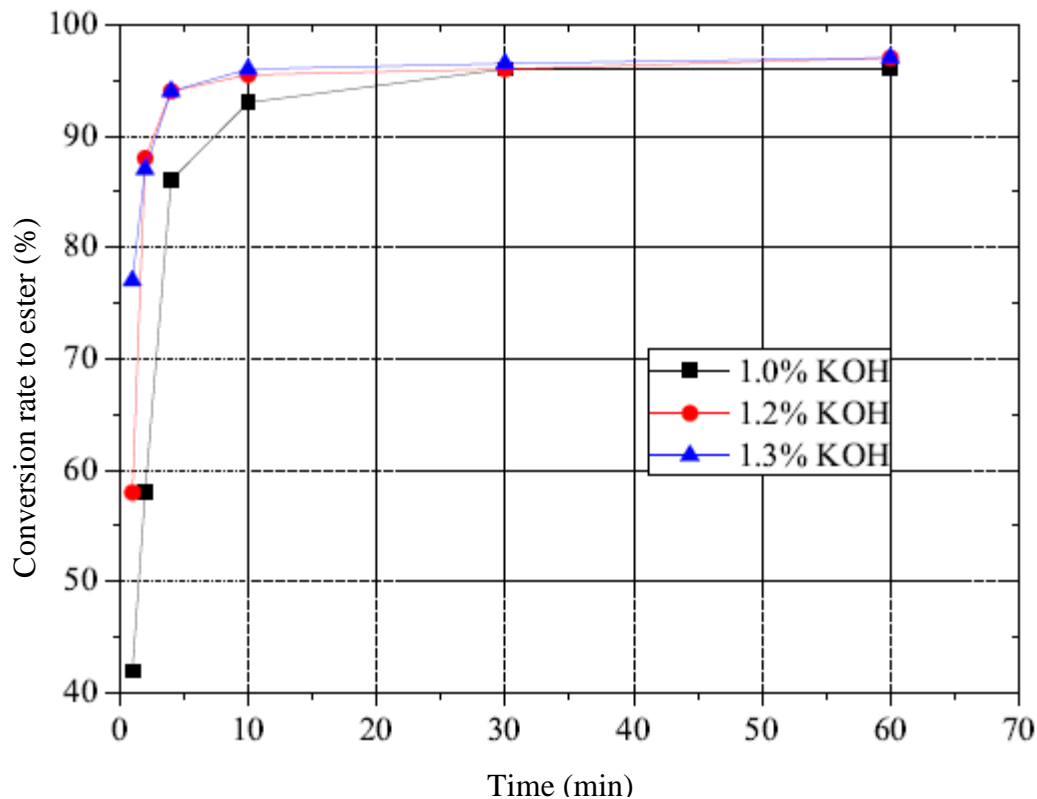


Figure 1.10 - Conversion rates for 3 different concentrations of KOH

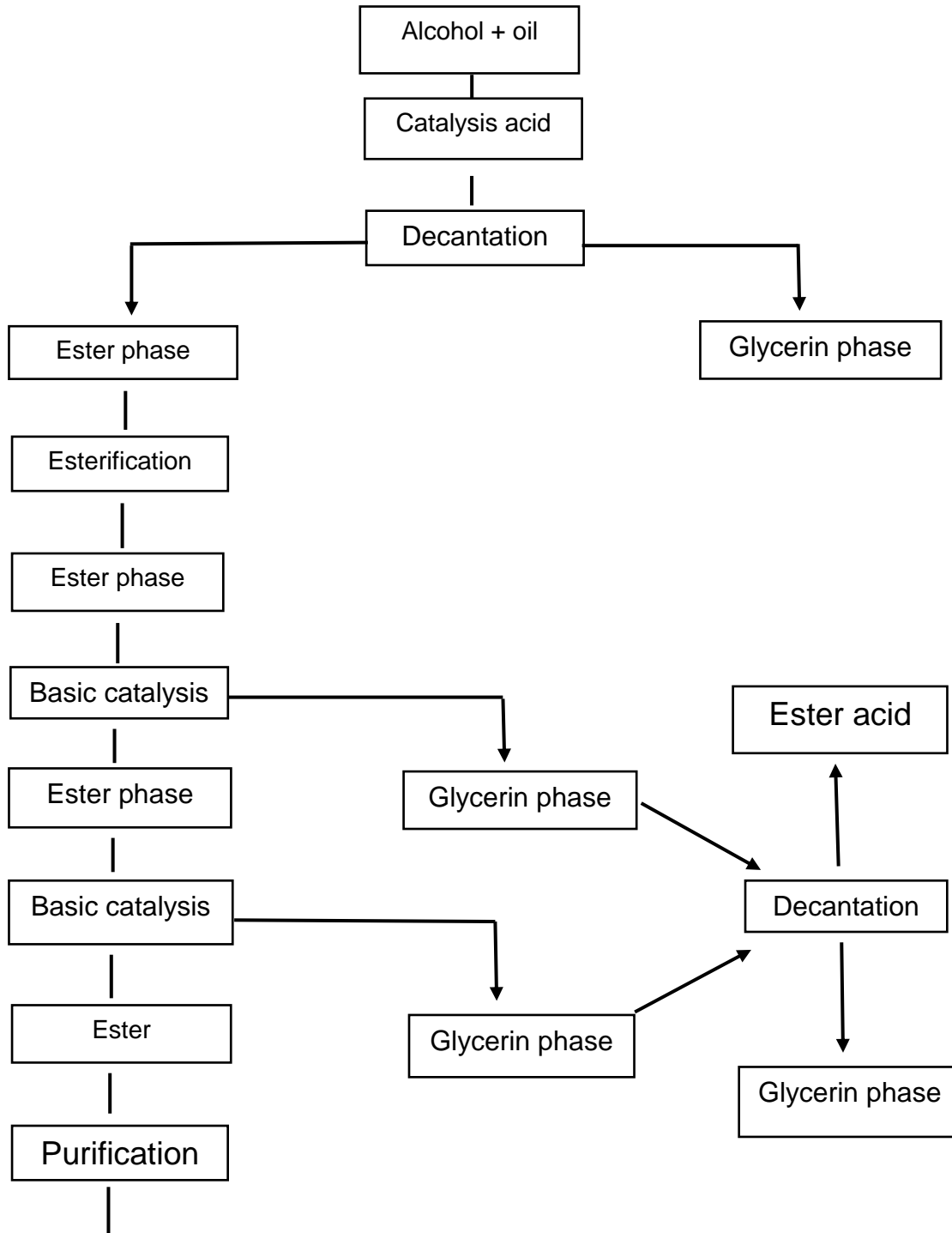
## B) Acid Catalyst

The acid catalysis reaction is used when the oils used are low in acid fat, high acidity or contain water. Fatty acids could deactivate the alkaline catalyst and then render it inactive. It is known that alkaline catalysis is much faster than acid catalysis [35]. While at room temperature, reaction in basic catalysis proceeds rapidly, the reaction in acid catalysis requires a temperature above 100 ° C. The reaction time can vary from 3 to 48 hours (Except when the reaction occurs at high temperature and at high pressure).

Pryde and Al. [55] report that only traces of esters are formed with 1% of sulfuric acid after 1 hour of reaction. A 30: 1 molar ratio of methanol / oil of soybean and 44 hours of heating of the reaction mixture are required for catalysis acid. However, in 4 hours' time, when butyl alcohol is used, a conversion percentage of 98% is observed with 1% sulfuric acid. This top the conversion rate is certainly due to the high temperature, equal to 114 ° C at which the reaction proceeds, as compared to 60 ° C when the methanol is used as the alcohol.

In order to maintain the use of ethanol 96, the use of acid catalysts such as sulfuric and hydrochloric acids is recommended [35]. One obtains interesting results with refined palm oil and sulfuric acid (4% in oil) when using excess ethanol 96 (10 stoichiometric equivalents).

The yield of ethyl esters is 97% after 10 hours of reaction. For identical experimental conditions, but with a high acidity oil (38%), yields of ethyl esters with ethanol 100 and ethanol 96, are respectively 95 and 90% using hydrochloric acid as catalyst. As for the Esterfip process 2 [70], it allows the conversion of vegetable oils with an approaching yield 100%. The main characteristics of the Esterfip 2 process are illustrated in Figure 1.11.



Final ester

Figure 1.11 - Schematic diagram of the IFP process: Esterfip 2.

## 5 Tests of biofuels in diesel engines

Two major periods marked the revival of research on alternative fuels in diesel engines: before 1950, when the war effort created the need for research into new sources of energy, then the first oil crisis in 1973. The price of crude oil has been increased from \$ 2 to \$ 12 / bbl.

In this section, some differentiation will be made between the various fuels used by the various engines: pure (or unmodified) vegetable oil, vegetable oil esters and fuel mixtures. Modern diesel engines are built to operate with standard diesel fuel. In order to function with vegetable oils it is necessary not only to change the physicochemical properties of the oils in order to make them comparable to gas oil, but also to redesign certain geometrical characteristics of the engines.

### 5.1 Unmodified plant fuels.

#### 5.1.1 Performance testing.

The performance tests are carried out on a test bench on which certain conventional parameters (power, efficiency, consumption, emission of pollutants, exhaust temperature, etc.) are detected. All possible conditions of regime and load are to be considered and the experiment is supplemented by finer measurements such as injection conditions and cycle timing.

Some researchers [38] mention a certain decrease in potency with vegetable oils, others have shown the opposite [57]. The maximum reduction in power during operation with vegetable oils according to Kaufman et al. [38] was 9%, while the maximum increase in power reported by Quick [57] was 7%. However, with equal fuel consumption, a lower power with vegetable oils is expected compared to diesel [44].

Specific consumption is higher for vegetable oils than for diesel, with a few exceptions. A high specific consumption is observed because vegetable oils have a lower calorific value than gas oil [9].

Performance testing of a Hatz E89 pre-combustion engine with diesel and then with oil, have shown that at some loads specific consumptions can approach, but in general they are higher at full load when the crude oil is used. The only case of specific decline in consumption (2.9% compared to diesel) occurs when 100% sunflower oil was used in a direct injection turbo-diesel engine (Bruwer et al., [12]). The comparison of fuels with different calorific values can also be done on the basis of the thermal efficiency which is a measure of the capacity of an engine to convert the energy of a fuel into useful work. The results presented by Bruwer [12] were typically in the scale of the observed efficacy divergences, which ranged from a 3.9% decrease to a 9.9% increase in thermal efficiency for sunflower oil Compared to diesel. Cruz et al. [17] found that vegetable oils give low efficiencies compared to diesel when a direct injection diesel engine is used but lead to better efficiency with indirect injection engines.

Researchers have reported a reduction in black smoke during the use of vegetable oils. Quick [57] reported a 50% smoke drop to the exhaust. Results at both extremes were found by Bruwer et al. [12]. During these tests, five engines gave a smoke reduction above 71% for vegetable oils, but four other engines gave an increase (in smoke) of more than 27%.

It has been reported that vegetable oils cause hard carbon deposits on cylinder heads, valves, injector nozzles and piston heads. These deposits are mainly due to poor spraying (due to the high viscosity of vegetable oils) during injection. This situation can be improved by reducing the viscosity of vegetable oils by heating and / or dilution. As reported by Bruwer et al. [12], the accumulation of carbon around the orifices of the injector nose causes an increase in exhaust fumes.

Difficulties in starting a cold engine with vegetable oil at room temperature are also reported. A diesel starter system is recommended under these conditions, and then by means of a "by-pass" valve, the vegetable oil line is opened [35]. Cold start tests of a Hatz E89 engine with junk oil have revealed that after 70 hrs, the engine is no longer able to start easily. The injector nose and the head of the pregauge spark plug were dirty. The calibration of the injector showed that even the diesel could no longer be sprayed; It drips at the set pressure of 150 bars. After cleaning the injector, the engine was able to restart easily. When the engine is warm (or even lukewarm), starting with vegetable oil is as easy as with diesel [35].

### **5.1.2 Endurance tests.**

The short-term performance of unmodified diesel engines with the use of vegetable oils may be satisfactory, but researchers have encountered problems during long-term testing [30]. Fouling of the injector nozzles can degrade the atomization of the

fuel and lead to problems of coke formation, gumming and blocking of the segments, dilution of the crankcase oil and subsequent polymerization of the lubricating oil.

## **5.2 Modified vegetable oils.**

### **5.2.1 Esters.**

Test reports on sunflower oil esters were carried out by Bruwer et al. [12]. The engine operated a dynamometer at 80% of its maximum load for 100 hours. The results showed that vegetable oil ester fuels cause less coking, produce less exhaust fumes and increase the thermal efficiency of the engine compared to the use of diesel fuel.

### **A-Engine Performance Testing.**

Performance tests using the methyl and ethyl esters of various vegetable oils have been carried out by some researchers. Baiju et al. [7] studied the performance and emissions of a 4-stroke direct-injection single-cylinder diesel engine when it was fed with diesel oil blends with the methyl and ethyl esters of Karanja vegetable oil. They concluded that the performance of the engine in the use of the different mixtures was similar to that of the pure gas oil. Soot opacity and CO concentration decreased with biodiesel, and this decrease was greater with increasing proportions of biodiesel in blends. NO<sub>x</sub> was increased as the amount of biodiesel in the mixture increased.

Rahimi et al. [58] also studied the eff and the use of mixtures of diesel, sunflower biodiesel and ethanol on a diesel engine. They noted similar performances between pure gas oil, diesel-biodiesel mixtures and gas-biodiesel-alcohol mixtures. On the other hand, emissions of unburnt hydrocarbons and the lowest carbon dioxide were recorded with diesel-biodiesel-alcohol mixtures, followed by diesel-biodiesel blends and then diesel fuel.

### **B-Endurance testing of engines.**

The similar performance of biodiesel and diesel, as well as the reduction of pollutant emissions, are biodiesel's assets, but they are not sufficient to adopt it as an alternative fuel on diesel engines. These results must be combined with endurance studies on engines.

Endurance tests were performed on a direct injection diesel engine (Caterpillar 3306) equipped with a turbo-compressor using rapeseed oil methyl esters [45]. After 150 hours of testing, the pistons were kept clean. The injectors were slightly fouled but no wear was observed.

Wer Grabowski and McCormic [30] highlighted problems related to the long-term use of biodiesel in diesel engines, such as carbon deposits on valves and low-load injectors due to the presence of mono, di or triglycerides and Glycerine and the poor



viscosity and volatility of the fuel. The high boiling point of the biodiesel does not allow the part which escapes to the lubricating oil to evaporate leading to the dilution of the latter. The lubricity of biodiesel is not a problem because it is better than that of diesel fuel.

On the other hand, other studies have shown good endurance of engines with biodiesel. Cetinkaya et al. [13] tested the eff and the use of biodiesel from used frying oil on a Renault Megane 4-cylinder 75 kW on an urban road of 7500 km. The test period was divided into two parts, half the journey was made in winter and the other half was done in the spring. After using diesel fuel on the car, the engine was disassembled and inspected as well as after each part of the tests. Performance and emissions are also compared with diesel. The performance of the engine decreased slightly when biodiesel was used but the specific fuel consumption was similar to that of gas oil and the opacity of the smoke was reduced by 60%. After the winter test period, the engine was disassembled and the injectors, pistons, cylinders and catalytic converter were inspected. The injectors were carbonized because of the low viscosity and poor combustion and the catalytic converter was clogged. On the other hand, the surfaces of the pistons and cylinders had no deposits. During the second test period, additives which lower the viscosity and the cloud point were added. At the end of this period, the inspection showed that the injectors and the catalytic converter had no problem.

## **6 Production of biodiesel in the world:**

Today, Europe's diesel consumption accounts for 60% of global fuel demand. Since 1992, biodiesel production has increased remarkably, with almost 35% annual average growth rate in the European Union.

Germany is the leading producer and consumer of biodiesel in Europe. Since 1991, production and sale of biodiesel has increased from 200 t to 800 000 t in 2003. Pure oil from rapeseed is used without transformation to supply directly to vehicles with dedicated engines. In 2003, 5000 t of pure rapeseed oil was used in 4000 vehicles, mainly agricultural. Biodiesel is used in its pure form, ie without being mixed (B100) in Germany and Austria in engines of cars, buses, trucks, tractors and other agricultural machinery. This path has great potential for CO<sub>2</sub> savings. Emissions reductions are proportional to the rate of incorporation of biodiesel.

In France, biodiesel bears the registered trademark of Diester. An incorporation rate of 5% diester in diesel is homologated by the French authorities and is distributed to

the pump while a diester with 30% incorporation is currently reserved for captive flies. In the same country, the production of biodiesel is accompanied by co-production of oilcakes which replace imports of soybean meal. In 2002, the Price Water House Coopers carried out a study estimating over € 151 million per year, the positive impact of the biodiesel fuel on France's balance of trade.

Brazil has large arable land with 90 Mha of agricultural land and is second only to 26% of world soybean production. In 2003-2004, it produced 52 Mt of soybean, yielding 9.4 Mt of oil. Other transesterified oils are used such as sunflower, cotton and castor. The synthesized esters are largely ethyl esters, taking into account the availability of ethyl alcohol, whereas methanol is mainly imported.

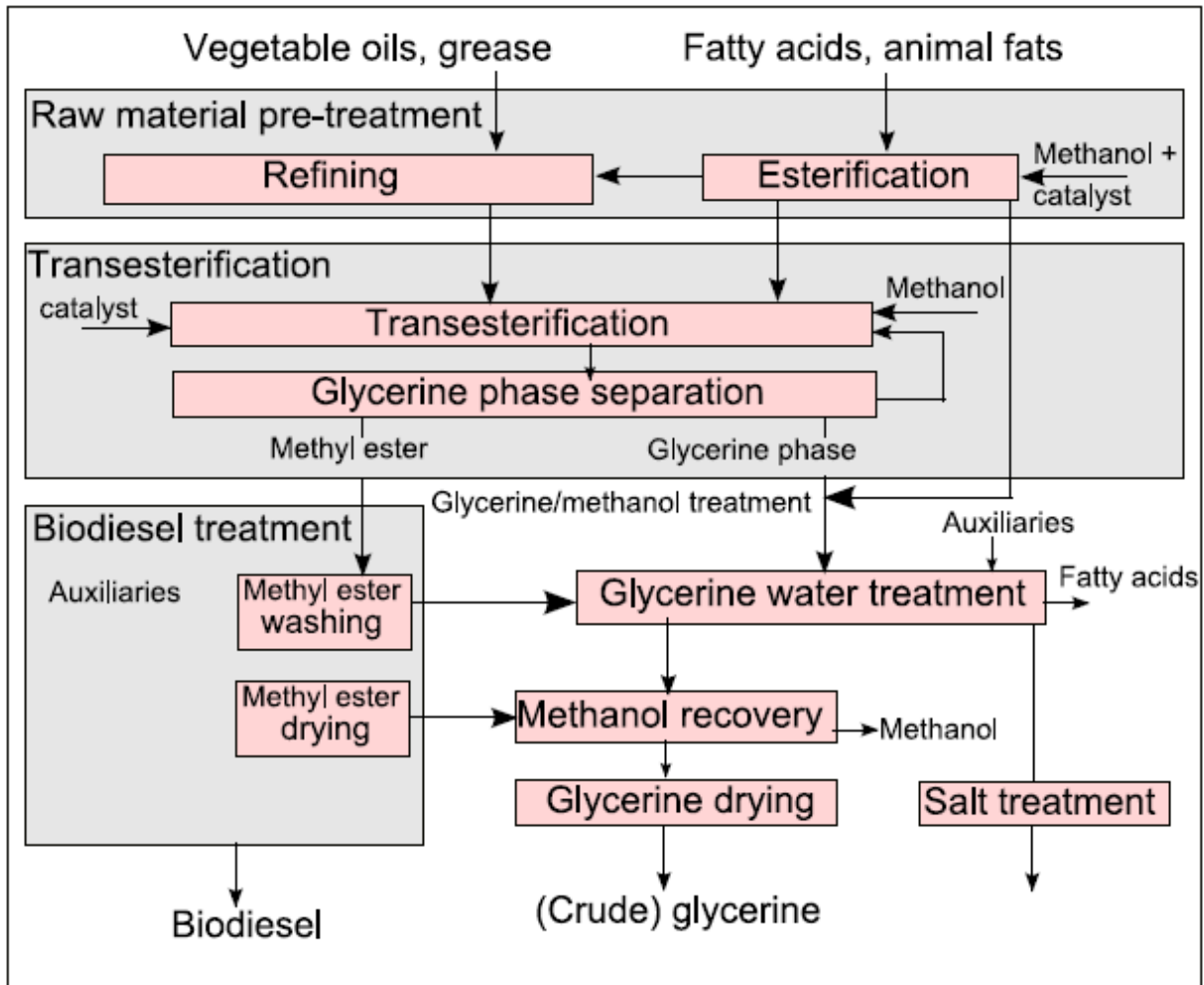
In the United States, biodiesel production is close to 200,000 t / yr, divided into 25 units. Biodiesel is synthesized from virgin and used soybean oil and animal fat, with mixing rates of 2 and 20% in diesel.

In Yemen, renewable energies are currently at the heart of concerns. Aware of their growing interest and stake, Yemen has integrated the development of renewable energies into its energy policy by adopting a legal framework favorable to the development of these energies. The realization of important infrastructures in this field and the planning of important projects is the perfect illustration of this. Biodiesel is a promising avenue for reducing diesel imports and contributing to the reduction of greenhouse gas and greenhouse gas emissions and combating desertification.

## **7 Cost of production of biodiesel**

Several factors influence the cost price of biodiesel production: the raw material (vegetable oil, animal fat, etc.), other reagents (alcohol and catalyst), and the nature of the purification, the production capacity and its storage. The price of biodiesel depends mainly on the price of the raw material used to produce it [23]. For example, biodiesel produced from animal fat and used cooking oil is cheaper than that produced from vegetable oils such as oilseed rape, palm oil, soybeans and the like. As a matter of fact, the cost of raw materials accounts for the large share of biodiesel production expenditures, roughly 65-80% of the total cost [5], and reaches 88% in the Haas study [34] who worked with 'Soya oil. As animal fat and spent cooking oil are classified as waste, their cost will therefore be lower in comparison to vegetable oils, so that the cost of biodiesel obtained from these materials will also be lower [78]. The cost of production follows the same trends as the cost of raw materials. Figure 1.12 shows the general pattern of production of biodiesel from vegetable oils and animal fats by transesterification. This diagram makes it possible to understand the production process in order to better inventory the elements to be taken into

account when estimating the cost of production. The scheme shows that some of the excess methanol in the reaction can be recovered, this will lead to a reduction in the proportion of the cost due to methanol and thus to the reduction of the total cost of production of the esters. This reduction in the cost of ethanol, coupled with the recovery (by the soap and cosmetics industry) of the aqueous glycerine phase, will decrease the production cost of biodiesel by approximately 6 to 10%.



**Figure 1.12 - Biodiesel production plan (Amigun and Al., 2008).**

The cost of producing biodiesel produced from hazelnut oil was assessed by Gumus [33] in the period 1997-2007 in Turkey. As shown in Figure (1.13), production of biodiesel is much more expensive than that of diesel oil, mainly because of very low oil prices in this period. In 2003, average diesel prices rose, unlike biodiesel prices, which reached their lowest levels. Beyond this year, the gap between the price of diesel and that of biodiesel is becoming more and more important. The price of diesel fuel is still used as a benchmark and determines the price at which biofuel production

becomes profitable. It is the starting point, also called break-even point or equilibrium point, of the economic study of the production of biofuels. Thus, the high cost of biodiesel remains the main obstacle to its commercialization.

## 7.1 Methodology for estimating the cost of production

The process for the production of biodiesel by transesterification is technically controlled. According to Santana et al. [66], the total investment cost ( $I_{tot}$ ) includes fixed capital (direct and indirect investments) for the acquisition of equipment and the fund for its operation.

Figure 1.13 - Biodiesel cost of hazelnut oil compared to diesel (Gumus 2008)

Within the direct investment class, there are resources allocated to the acquisition, transport and installation of equipment directly involved in the production process (IDI) and other resources allocated to equipment Outside the circuit and / or the production area (IDII). The cost of IDII investment is estimated at 45% of the cost of IDI investments. Indirect investments include all other costs and are estimated at 25% of direct investment.

Total investment can be estimated as a function of IDI investment. It is given by the relation (1.4):

$$I_{tot} = 1.81 \times IDI \quad \dots \dots \dots (1.4)$$

The cost of producing biodiesel is calculated using equation (1.5):

$$CP = \frac{CAE + C_{Exp} - C_{Glyc}}{PAB} \quad (1.5)$$

Where CAE is the equivalent annual cost,  $C_{Exp}$ , annual operating cost,  $C_{Glyc}$  is the share of revenue corresponding to the sale of the entire amount of glycerin produced, PAB is the annual production of biodiesel.

The equivalent annual cost of the initial investment is calculated from the annualization of the total investment. The ACE is calculated using the equation:

$$CAE = I_{tot} \left[ \frac{j(1+j)^t}{(1+j)^t - 1} \right] \quad (1.6)$$

Where  $j$  is the annual interest rate on financial markets (often fixed at 15% [66]),  $t$  is the lifetime required to analyze project viability (often fixed at 10 years).

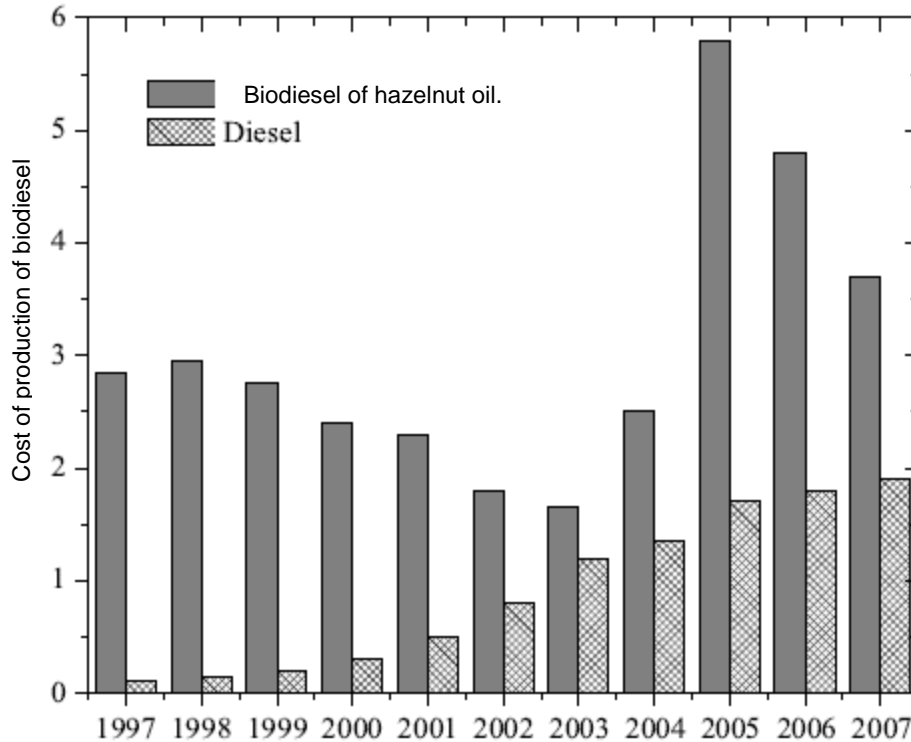


Figure 1.13 - Biodiesel cost of hazelnut oil compared to diesel (Gumus 2008)

In this model, the  $C_{Exp}$  operating costs include the costs of raw materials, services, repairs and maintenance and operators. In addition to operating costs, depreciation of equipment must be taken into account. The depreciation rate is often set at 10% [49]. Revenue from the sale of glycerin produced drops the biodiesel production price by about 6-10%.

In their model of the cost of production of biodiesel, Deshpande [21] uses the same parameters. Their respective costs are evaluated over a period of one year (as in the case of Santana et al. [66]). The term "operating costs" is more complex and includes other independent terms such as raw material costs and service costs. This cost of production (CP) is estimated using the following general equation:

$$CP = 0.2536CFI + 2.2835C_{Exp} + 1.0309(C_{Ser} + C_{DC} + CMP) \quad (1.7)$$

Where CFI represents fixed investment capital,  $C_{Exp}$ , operating costs,  $C_{Ser}$ , cost of services,  $C_{DC}$ , cost for waste treatment, CMP, cost of raw materials  
 Fixed capital investments take into account the acquisition costs of all equipment directly related to production, their installation and instrumentation costs, and indirect costs such as transportation, engineering costs, General expenses, insurance,

etc. Operating costs include the costs of personnel involved in the installation. Raw materials include different oils and the alcohol used.

## 7.2 Factors to reduce the cost of production

### 7.2.1 Raw material

Amigun and Al. [5] analyzed the cost of production for an industrial plant capable of processing various raw materials (animal fat, rapeseed oil). The comparison is made from the distribution of the costs of the different terms of the relation (1.6). In the case of rapeseed oil, the cost of raw materials is 72%, the operating cost is 21% and the share of capital is 7%. In the case of grease, the cost of raw materials is 66%, operating cost 21% and capital, 13%. The cost of pretreatment increases the share of capital in the case of fats. The differential between the cost of fat and rapeseed oil (between fats, waste oils and pure vegetable oils) influences the total cost of biodiesel.

The capital invested may be extremely large, but the impact on the final cost of biodiesel remains minimal. They account for about 10-15% of the total biodiesel production cost [78]. Amigun and Al. Have shown that for a plant with a capacity of 100,000 tons / year, a 10% increase in the cost of investments leads to an increase in the cost of biodiesel from 0.730 to 0.731 euro / liter.

Table 1.9 - Comparison of Biodiesel Production Costs for Options A and B

Option	Production capacity (l / d)	Production costs (USD / yr)	Net cost (USD / l)
9175		3322708	4.09
56000		16817463	3.33
9175		3342872	4.26
56000		16919737	3.47

Changes in technical and economic performance in the production of biofuels are mainly due to differences in the assumptions made regarding the different costs (raw material costs, labor costs, interest rates, co-product costs), The economic lifetime of the installation, the type of technology and the size of the installation.

### **7.2.2 Production process and capacity**

Deshpande et al. [21] proposed and designed an integrated technology for the production of biodiesel by transesterification of various vegetable oils and animal fats with methanol / supercritical ethanol and cogeneration as compared to the conventional catalytic process. The energy required for the reaction can be supplied by a generator integrated in the system (Option A) or by a burner (Option B) in the case of installations with large production capacities. The generator and burner use a small fraction of the biodiesel produced. For example, calculating the cost of producing biodiesel gives the system a break-even point at around 0.07 and 0.09 euro / liter of biodiesel produced, with the integrated generator or with the burner respectively, for a facility with daily capacity Of about 56000 l. In both cases, this threshold is always below the threshold of 0.13 euro / liter of biodiesel produced by the usual catalytic transesterification process.

Table 1.9 compares the production costs of biodiesel in cases where the energy required for the biodiesel production process is supplied by a generator (Option A) or a burner (Option B). It also gives the revenue from the sale of part of the electricity produced and the profitability thresholds of the installation. In this table, it is noted that the cost of producing biodiesel for a unit (Option A) with a daily capacity of 9175 liters / day is USD 3322708 / year for a break-even point of USD 4.09 / l of biodiesel product. Thus, if the capacity increases to approximately 56,000 liters / day, the break-even point becomes 0.88 euro / l. In the case of option B, the break-even point is 1.13 and 0.91 euro / l and the conversion cost of 0.29 and 0.08 euro / l for the unit of 9175 and 56000 liters / Day respectively. Option A (with built-in generator) therefore appears to be advantageous as option B (with burner).

## **8 Synthesis of the review of the literature**

The transesterification reaction makes it possible to refine the vegetable oils to bring their characteristics closer to those of a conventional gas oil. It eliminates the free acidity of oils which can thus adapt to engines without serious consequences, especially when basic catalysis has been used. In acid catalysis, the ester is still acidic, which is likely to cause problems. The iodine value of the methyl esters is practically the same as that of crude oils. The saponification index does not change. The peroxide value and acidity must be measured again.

When the reaction is incomplete, mono and diglycerides may be present in the esters. Monoglycerides should be eliminated by nitration or should not be formed. If the

alcohol remains in the esters, the cold quality, the distillation curve and the viscosity can be improved, in contrast to the cetane number and the flash point.

The short-term performance tests of a diesel engine with unmodified vegetable oils and vegetable oil esters appear to be satisfactory. Differences in the physical and chemical properties of vegetable oils, esters and diesel have different effects on the performance of diesel engines.

Endurance testing of engines with unmodified vegetable oils shows some problems in use. The most important are the coking of the nozzle nose, which can prevent the spraying of the fuel, the scrubbing of the pistons, the dilution of the lubricating oil and, consequently, its polymerization and gelling. As for the esters they are to date, the best alternative fuels in direct injection diesel engines. The problems of operation of the engines encountered are less severe with esters and mixtures of oils than with unmodified vegetable oils.

## **9 General conclusion**

Technically, any vegetable oil can be used as a fuel prices, crop yields and environmental number of candidates such as olive oil characterized by an exorbitant cost price.

Our choice was based on human and climatic considerations, as eucalyptus is non-food plant species, which can not in any way compete with foodstuffs intended for human or animal consumption. Eucalyptus oil is classified in the second generation of biofuels. The use of eucalyptus oil as fuel for compression-ignition engines is not new, but its physico-chemical properties make the oil delicate to use. Indeed, its use in a motor causes carbon deposits to form in the cylinder up to the obstruction of the injectors.

The transesterification reaction can give good yields of conversion, both in basic catalysis and in acid catalysis. However, catalysis acid, it consumes a lot of alcohol even though it gives high conversion rates for strongly acid oils. Therefore, it is preferable to use basic catalysis for the transesterification of free acid oils of 15-20%, using a high alcohol boiling point (butanol, for example).

The physical and chemical characteristics of the eucalyptus oil were determined to highlight those that had to be adapted for this oil to be used as fuel in the engine. The physical and chemical properties of eucalyptus oil (Calorific value, cetane number, density) are very close to those of the gas oil, but its viscosity is about 30



cST at 40 ° C. Eucalyptus oil includes about 7% palmitic acid (saturated fatty acid) and about 90% oleic acid (acid unsaturated fatty acid), the other acids being quantitatively less important. The large fraction of unsaturated fatty acids causes the oil not to be solid at room temperature and the weak fractions, in terms of saturated and polyunsaturated fatty acid, tend to give a biodiesel, with good oxidation stability. Once the physical and chemical characteristics of the fuel have been verified and validated.

The use of pure or mixed biodiesel in engine performance testing diesels with direct injection (Lister Petter ID) is very satisfactory.

A slight decrease in power is (1.3-6%) compared to the power of the engine when operating at diesel. At equal power, the actual specific consumption increases slightly, which is due to the difference in calorific values of the various fuels tested. The clearance for all fuels was almost identical to that of diesel, with the same intensity. Self-ignition times for biofuels were slightly shorter compared to those of diesel owing to their higher cetane number. Biodiesel and its mixtures have a longer burning time than diesel. In fact the power calorific lower than that of gas oil has led to higher consumption of biodiesel in order to maintain the same effective power, so the amount of fuel injected into the cylinder is larger and takes longer to burn.

Emissions of nitrogen monoxide increase in the case of combustion of biodiesel but, at high engine loads, emissions of NO<sub>x</sub> decreases considerably in the case of pure biodiesel.

Currently, the use of biodiesel as fuel for diesel engines is very possible without any modification of the engine, but their exorbitant price requires to find solutions to reduce production costs so that they can credible alternative to diesel fuel. The cost of producing biodiesel depends on the production capacity. A study must be carried out for an installation to reduce these production costs. As the large units are energy-intensive, it would require a large generator, which is not always easy to set up.

A low / medium size plant appears to be the right choice for remote and available but located close to the source of the raw materials.

The use of vegetable oils, which are not intended for human or animal consumption, as fuel for diesel engines seems to be an interesting solution to undertake the fossil fuels depletion and the global warming caused by the greenhouse gases emissions. The physicochemical characterization of the pure eucalyptus oil shows that it cannot fueling directly the diesel engine due to its high viscosity and poor volatility.

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