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Comparison and storage stability of biodiesels from expired oils

Farklı depolama koşulları altında biyodizellerin üretimi, karşılaştırılması ve depolama kararlılığı

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Comparison and Storage Stability of Biodiesels From Expired Oils

Highlights

- *This study had been relied on expired oils, which are a new and important source of biodiesel,not being sufficiently studied.*
- *the effect of pumpkin seeds on biodiesel productivity was studied, which showed significant.*
- *the degradation of the obtained samples were studied, to estimate the effect of light/dark conditions and temperature on the quality of the studied biodiesel compounds.*

Graphical Abstract

The addition of pumpkin seed has a positive effect on improving the yield of biodiesel samples by 0.97%, and 4%.

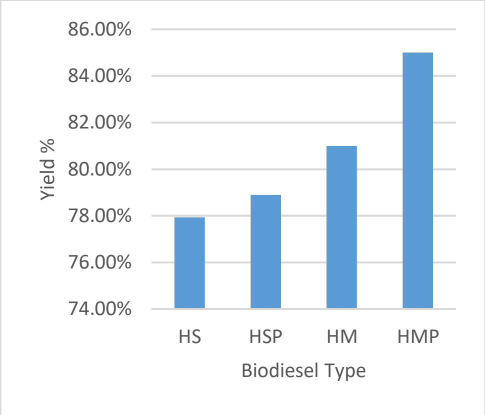

Figure. Effect of pumpkin seed oil on biodiesel yield

Aim

The aim of this study is the comparison bitween 4 types of biodiesel blends produced from 4 type of vegetable oils and the study of the effect of different storage conditions on the quality of biodiesel in comparison with fossil fuels.

Design & Methodology

The production of biodiesel by transesterification of vegetable oils, by the presence of 1% of KOH and an alcohol/oil molar ratio of 6:1; in a reaction time equal to 4 hours.

Originality

The transesterification is the normal boiling temperature of the alcohol (65 ° C), makes it possible to obtain the methly esters of vegetable oils or ethyl esters according to whether the alcohol used.

Findings

The yield of the studied biodiesel blendes increases by 0.97% and 4%. The results also showed that under real conditions of high temperature and lighting exposure: The acid value of biodiesel (HM) is rapidly increasing at a rate of 0.91 mg KOH per Week compared to diesel 1.39 mg KOH/g per Week.

Conclusion

The pumpkin seed have a positive effect on increasing the yield of biodiesel. As it found that The high temperature combined with the lighting strongly enhances the degradation phenomenon. but In comparison with Diesel, Diesel degrades strongly and rapidly from a biodiesel in terms of Acid Value, pH and Density.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Comparison and Storage Stability of Biodiesels from Expired oils

Araştırma Makalesi /Research Article

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ABSTRACT

Transesterification of expired vegetable oils is possible by heating them with a significant amount of methanol and an acidic or basic catalyst to improve the reaction rate and yield. In this study 4 samples have been selected, including 4 types of vegetable oils, namely: soybean, sunflower, rapeseed, pumpkin seed. The operative conditions of the reaction were reaction time (4 h), catalyst concentration (1 w/wt %), and oil-to-methanol molar ratio (6:1). The parameters studied to compare the quality of biodiesel obtained by each type of compound are: yield, pH, density, acid value. The results shows that The pumpkin seed have a positive effect on increasing the yield of Soybean biodiesels as well as biodiesel blends based on Soybean, Sunflower and rapeseed. This paper examines also the degradation of several biofuels in comparison with fossil fuels (Diesel and gasoline) with different storage conditions over 9 Weeks period. The Results indicated that: High temperature combined with the lighting strongly enhances the degradation phenomenon. The acid value of biodiesel (HM) is rapidly increasing at a rate of 0.91 mg KOH/g /Week. The pH of diesel has experienced a strong decrease of 66%. In comparison with Diesel, Diesel degrades strongly and rapidly from a biodiesel in terms of Acid Value, pH and Density.

Keywords: Biodiesel, pumpkin, degradation, valorization, methyl esters.

Farklı Depolama Koşulları Altında Biyodizellerin Üretimi, Karşılaştırılması ve Depolama Kararlılığı

ÖZ

Son kullanma tarihi geçmiş bitkisel yağlar, reaksiyon hızını ve verimini artırmak için büyük miktarda susuz metanol ve asidik veya bazik bir katalizör ile ısıtılarak transesterifiye edilebilir. Bu çalışmada soya fasulyesi, ayçiçeği, kolza tohumu ve kabak çekirdeği olmak üzere 4 çeşit bitkisel yağ içeren 4 örnek seçilmiştir. Reaksiyonun çalışma koşulları reaksiyon süresi (4 saat), katalizör konsantrasyonu (ağırlıkça %1) ve yağ-metanol molar oranı (6:1) idi. Her bir bileşik türünden elde edilen biyodizelin kalitesini karşılaştırmak için incelenen parametreler şunlardır: verim, pH, yoğunluk, asit değeri. Sonuçlar, kabak çekirdeğinin soya fasulyesi biyodizellerinin yanı sıra soya fasulyesi, ayçiçeği ve kolza tohumu bazlı biyodizel karışımlarının verimini artırmada olumlu bir etkiye sahip olduğunu göstermektedir. Bu makale aynı zamanda çeşitli biyoyakıtların 9 hafta boyunca farklı depolama koşullarında fosil yakıtlarla (Dizel ve benzin) karşılaştırmalı olarak bozulmasını da incelemektedir. Sonuçlar şunu göstermiştir: Aydınlatma ile birlikte yüksek sıcaklık bozunma olayını güçlü bir şekilde arttırmaktadır. Biyodizelin (HM) asit değeri 0.91 mg KOH/g /Hafta oranında hızla artmaktadır. Dizelin pH değerinde %66'lık güçlü bir düşüş yaşanmıştır. Dizel ile karşılaştırıldığında, Dizel Asit Değeri, pH ve Yoğunluk açısından bir biyodizelden güçlü ve hızlı bir şekilde ayrışmaktadır.

Anahtar Kelimeler: Biyodizel, kabak, bozunma, değerleme, metil esterler

1. INTRODUCTION

1.1. Biodiesel

Biofuels are fluids produced from non-fossil organic materials and derived from biomass or feedstock considered to be the biodegradable fraction of products, wastes and residues from agriculture, forestry and their related industries, as well as the biodegradable fraction of industrial and municipal waste.

The term biofuel is generic and includes bioethanol, biodiesel, bio-oil, biogas, Fischer-Tropsch liquids and bio-hydrogen.

Even when it is blended, utilizing biodiesel has several benefits, however some environmental ones rely on how the fuel is made. One advantage is just the fact that biofuel originates from a resource that is universally available, renewable, and sustainable, which lessens our reliance on foreign oil. Additionally, the amount of air toxics emitted into the atmosphere is decreased by using biodiesel. EPA (Environmental Protection Agency) research Research shows that compared to diesel, biodiesel produces 11% fewer CO_2 and 10% fewer particulates. In contrast to diesel, which contains benzene and sulfur, a research by Energy and gricultural Department indicated that the use of biodiesel reduced CO_2 emissions by 78 percent.

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1.1. Properties of Biodiesel

1.1.1. Density

Density is a crucial factor, especially for biofuels, as it determines the design and technological biofuels, as it influences the technology and detail design specifics of the injectors and pumps. Moreover, on an installed system, using biofuels with widely differing densities would lead to changes in combustion settings with repercussions on maximum power, efficiency and pollutant emissions. The values of the density according to the European standards vary between 0.86 and 0.9 g/cm³ [1]

1.1.2. Acid Value (AV)

Also called acid number, it is the mass in mg of KOH necessary to neutralize the free fatty acids contained in 1g of lipid at room temperature.

1.2. Biodiesel Produced From Plants

Vegetable oils are obtained from various plants through their fruits or seeds. they are composed mainly of triglycerides also called triacylglycerol (TAG) to 90-98% [2]; [3], whose molecular weight is high (600 to 900 g/mol) [4]. TAGs, are glycerol triesters, which consist of a glycerol backbone with three fatty acids grafted onto it with the same or different chemical structure. The linear chains of fatty acids typically include an even-numbered carbon atoms ranging from 8 to 22.

The group of lipids is formed by the vegetable oils along with fats and essential oils. They are compounds made up essentially of carbon, hydrogen and oxygen, and possibly nitrogen and phosphorus.

1.2.2. Sunflower oil

Sunflower oil is an oil produced from sunflower seeds. With an excellent ecobalance, very light, this oil is widely used as biofuel but it has the particularity of containing more gum than rapeseed oil, for example. Its average yield is 662 liters of oil per hectare per year.

1.2.3. Soybean oil

Soybean oil is fluid and of a more or less dark yellow color depending on the nature of the seeds and the extraction process. When fresh, it has a pronounced bean flavor that gradually fades. [6] It is rich in polyunsaturated fatty acids and in particular in alpha-linoleic essential fatty acid. It is recommended for seasoning.

1.2.4. Pumpkin seed oil

Pumpkin seed oil is a vegetable oil extracted by cold pressing of roasted pumpkin seeds. It is characterized by a density of 0.884, a kinematic viscosity that equals 4.41 mm^2/s at 40°C.

Numerous studies on pumpkin seeds failed to examine the oils' viability for biodiesel use or other industrial uses. [7] the amount of fats in the seeds was 13.15%, composed mainly of polyunsaturated fatty acids. The iodine number was 115.6, showing a semi-drying oil. [8]. The capacity to absorb ambient oxygen is a characteristic of these groups of oils with an iodine number between 100 - 150, but it is insufficient to classify them under drying oils because they thicken and keep sticky, without forming a dry and hard film. The findings show that the oil had larger levels of low molecular weight fatty acids, and the acid values show that the oil may be kept in storage for a long period without significantly degrading. The acid value was 1.7 percent, indicating that the oil is not rancid. The obtained peroxide value (POV) was 2.26, the relative density and the Index of Refraction (at 250 °C) were 0.92 and 1.46, respectively. [8].

Table 1. Comparative physical properties ooils, their corresponding esters and diesel

Oil or ester	Density (g/mL)	Viscosity at 37.8°C (mm^2/s)	Index of Cetane	Point trouble (°C)	Flash point (°C)
Diesel reference	0.832	1.6-6.0	45.0	- 17.8	46
Oil peanut	0.921	41.2	41.5	+ 3	237
Peanut methyl ester	0.883	4.9	54.0	+ 5	176
Soya oil	0.923	36.8	38.5	- 4	219
Soybean methyl ester	0.885	4.5	45.0	+ 1	178
Sunflower oil	0.924	37.1	35.5	- 5	232
Sunflower methyl ester	0.880	4.6	49.0	+ 1	183
Colza oil	0.92	30.2 at 40°C	35		> 320
Rapeseed methyl ester	0.88 - 0.885	4.5 at 40°C	51	170 - 180	
Palm oil	0.918	39.6	42.0	+ 31	267
Palm methyl ester	0.880	5.7	62.0	+ 13	164

Note: Adapted from “Transestérification des huiles végétales par l’éthanol en conditions douces par catalyses hétérogènes acide et basique’’ by B. Hamad, 2012, Copyright 2012 by Berna Hamad

1.2.1. Rapeseed oil

Rapeseeds are crushed to produce rapeseed oil, also known as canola oil in Canada. It is an oil very low in saturated fatty acids.

It is easily used as a biofuel and is inexpensive. The average yield of rapeseed is 572 liters of oil per hectare per year. [5]

1.3. Diesel's physical and chemical properties

The table below compares some physical properties of diesel with those of oils and their oils and their esters [9].

It is noted that the properties of the ester from the oil vary according to the nature of the oil used, especially the cetane number, cloud point and flash point, as these physical properties change enormously when passing from the oil to its corresponding ester. However, the properties of esters are close to those of diesel, which is the objective of the transesterification process. There are European [1] and American [10] standards to control these chemical and physical properties.

1.2. Lipid Transesterification processes

In general, biodiesel is produced by transesterification, with or without catalyst, by enzymatic interesterification, by microemulsification or by pyrolysis. Transesterification (with acid, basic catalysts or enzymatic catalysts, homogeneous or heterogeneous type) is the most used reaction [11].

1.2.1. Transesterification by Basic Catalysis

The basic catalysis by homogeneous or heterogeneous way is the most used process for biodiesel production. Homogeneous catalysis is preferable to heterogeneous catalysis because of the cost of the catalyst and the shorter reaction time. The main advantage of basic transesterification compared to acid or enzymatic catalysis is the reaction time, basic transesterification being a fast reaction (0.5h to 9h). Generally, the temperature of basic transesterification is the normal boiling temperature of the alcohol (65°C for MeOH). The yield of alkyl esters during basic transesterification is better (generally higher than 85%).

The main drawback of basic transesterification is the formation of soap. In the basic transesterification reaction, the amount of soap varies depending on the FFA content of the oil, the type of catalyst and the reaction temperature. For example, NaOH tends to induce a higher soap formation than that obtained with KOH. Thus, if the oil has a FFA content higher than 0.5 mgKOH/g oil, it should be pretreated before basic transesterification. The soap formed during the basic transesterification (formation of an emulsion during biodiesel water washing) consumes the catalyst and prevents the separation of the alkyl esters and glycerol (by-product of the transesterification of the oils). After the basic transesterification reaction, it is necessary to cool the reaction mixture in order to separate the glycerol from the biodiesel [12]. The alkyl esters of vegetable oils.

Transesterification allows to obtain the alkyl esters of vegetable oils, preferably methyl (MEHV: Methyl Esters of Vegetable Oils) or ethyl (EEVO: Ethyl Esters of Vegetable Oils) depending on whether the alcohol used during its production is methanol or ethanol respectively [13].

1.2.2. Vegetable Oil Methyl Esters (VOME)

Many current processes for the synthesis of alkyl esters use methanol as alcohol in the transesterification reaction of triglycerides. The conversion rates as well as the yields are very satisfactory with this alcohol, which is explained by its solvent power, its small steric bulk and its higher acidic character compared to other linear or branched alcohols. However, methanol is nowadays mainly produced from fossil resources. Indeed, industrially, methanol is obtained from a synthesis gas containing carbon monoxide (CO), dihydrogen (H_2) and small quantities of carbon dioxide (CO_2). This methanol, derived mainly from fossil resources, is therefore widely used for the production of vegetable oil methyl esters, which are defined as bioproducts [12].

1.3. Degradation of Biodiesel

Biodiesel is more convenient than petrodiesel, in terms of storage, since its flash point is higher. HoweverIt needs to be kept in a mild stainless steel, aluminum, or Teflon tank under appropriate temperature and humidity. For example, the temperature should be below 30 °C for biodiesel from sunflower oil. It should be noted that in general, methyl esters are more stable than ethyl esters [14, 15, 16, 17]; During storage, biodiesel undergoes degradation occasioned primarily by hydrolysis and oxidation reactions [18, 19]. Factors influencing the stability of biodiesel include the presence of air, antioxidants or impurities (such as free fatty acid residues), catalysts, metals and peroxides, heat (which can, among other things, facilitate the isomerization of molecules), light and even the molecular structure of the biofuel. Indeed, the more double bonds there are, the more unstable the fuel is, i.e. likely to oxidize and thus to degrade. The origin of the biodiesel, i.e. the type of feedstock from which it is produced, therefore influences its storage capacity [20, 21, 18, 22].

Microorganisms can easily grow in biodiesel. This phenomenon becomes more pronounced when the water content of the biodiesel increases. This can lead to significant sediment formation resulting in rapid clogging of engine filters or accumulation in tanks [23]. Microbial growth must therefore be controlled, preferably with biocides [16].

Increased UV absorption and/or acid and peroxide concentration is an indicator of biodiesel degradation [24, 25]. This acid concentration must be monitored since corrosion may result (especially in the presence of water) [19]. When biodiesel is exposed to air (wet or not), biodegradation is low as long as the temperature remains below 20°C, while at a temperature of 40°C and above, biodiesel purity can decrease by 40% in less than 1 year [18]. On a commercial scale, several distributors recommend a storage period of less than 6 months [26].

Finally, Despite all the advantages of biodiesels already mentioned, these studies remain limited in terms of environmental impact, considering that the main objective of the biodiesel industry is to revalue the wastes, preserve the environment and reduce the dependence on primary natural resources, while reducing the cost of production, which leads to the adoption of biodiesel instead of diesel. This can only be achieved by focusing on a consumed or non-usable source.

all of those fuels fulfill the ASTM Standard.

Pure (virgin) soybean cooking oil (PSCO) was purchased from local UOA shopping Mall, Kuala Lumpur, Malaysia

Table 2. The physical and chemical properties of the fuels

	Diesel	Gasoline	Test Method	Limits
PHa	7.4	7.4	ASTM D6423	6.5-9.0
Density b	0.83	0.72	ASTM D4052	Diesel: 820-860 Kg/m^3 Gasoline: 710-770 kg/m^3
Acid Value c	0.2	0.25	ASTM D664	Max 0.5

Note. [a.] The data for PH is from "ASTM D6423" by ASTM, 2020, Copyright 2020 by ASTM International. [b.] The data for Density is from "ASTM D4052" by ASTM, 2019, Copyright 2019 by ASTM International. [c.] The data for Acid Value is from "ASTM D664" by ASTM, 2019, Copyright 2019 by ASTM International.

Our current research had been relied on expired oils, which are a new and important source of biodiesel, not being sufficiently studied.

In addition, this study was based on a blend of vegetable oils in order to study the effect of pumpkin seeds on biodiesel productivity, which showed significant results in terms of yield.

In order to make the study more thorough, the degradation of the obtained samples were studied for a period of 9 weeks, to estimate the effect of light/dark conditions and temperature on the quality of the studied biodiesel compounds.

2. MATERIALS AND METHODS

The raw materials used for the realization of this work represent four types of expired oils: Pure Soybean oil (HS), Soybean and pumpkin seed oil (HSP), consisting of 80% soybean oil and 20% pumpkin seed, Mixed oil (HM) consisting of 33% Rapeseed, 33% Soybean and 33%Tounesol and Mixed oil and pumpkin seed (HMP) consisting of 25% Rapeseed, 25% Soybean, 25% Tournesol and 25% pumpkin seed.

Pure soybean oil (virgin) was bought from Savola Group. Pure (virgin) Sunflower cooking oil was purchased from the Lesieur company. Pure (virgin) Rapeseed cooking oil was purchased from the Lesieur company. Pure (virgin) Pumpkin seed oil was purchased from Nature Soin. Two samples of fuels were selected for comparison in this study: the gasoline samples were purchased from Afriquia gas station, Akwa Group. The diesel samples were purchased from Afriquia gas station, Akwa Group.

2.1. Reagents

The different reagents used for our experiments are: Potassium hydroxide (KOH) and methanol (C_2H_5OH).

2.2. Physico-Chemical Characteristics of Fossil Fuels and Vegetable Oils

The initial physical and chemical properties of the fuels are shown in Table 2.

In order to determine the physico-chemical characteristics of the different oils used in this study. It's based on the methods given by the French Association of Standardization, European Standards and International organization for standardization.

In our study, the following parameters are determined: the density [27], Acid Value [28] pH [29].

2.3. Transesterification Method

In this part of our work, the production of biodiesel was carried out by transesterification of vegetable oils (expired) by methanol.

The operative conditions of the reaction were established following a preliminary study.

In this part, It's considered useful to study the influence of the nature of the oil used on the yield and quality of biodiesel. The transesterification reaction of the oils was carried out with methanol in presence of a basic catalyst at a temperature of 60°C. This synthesis was carried out with an alcohol/oil molar ratio of 6:1 and KOH of 1% (by mass) compared to the oil. . The duration of the reaction is 4 hours at the considered temperature. The yield of the reaction is calculated according to the following formula:

$R (\%) = mb/mh \times 100$ [30]

with: mb: mass of biodiesel; mh : mass of oil.

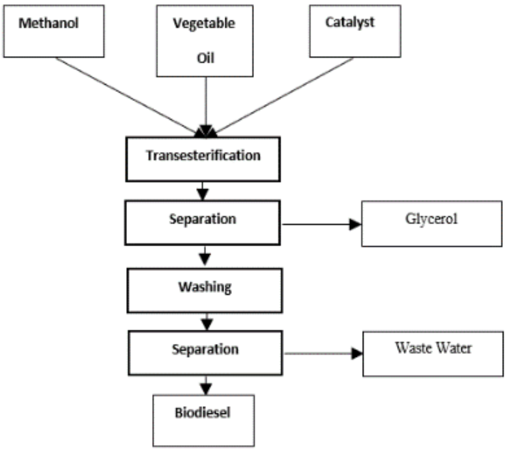

Figure 1. The main stages of biodiesel production [31].

2.3.1. Transesterification reaction

- The oil is heated to 60°C then 100g of this oil is mesured.
- 21.66 grams of methanol is poured into a glass container.
- Adding 1 gram of potassium hydroxide (1% solution) to the container containing the methanol and leaving it to dissolve the catalyst completely in the methanol.
- Adding the catalyst/methanol mixture.
- Stirring the mixture for 30 min at a stirring speed of 200 rpm.

2.3.2. Separation step

The elements are let to be settled for 4 hours in the separating funnel. During the reaction, two products are formed: biodiesel and glycerol. The biodiesel being less dense, it forms the top layer.

Figure 2. The mixture after 4 hours of decanting

Finally, the glycerol is drained from the bottom of the separating funnel into a bottle. Taking into account that no glycerol remains in the biodiesel.

Figure 3. The quantities of glycerine obtained after Separation of (HMP-HSP-HM-HS) successively

2.3.3. Washing

After the transesterification of the old oils and the decantation of the reaction mixture, the product obtained must be washed. For each wash, 84 ml of distilled water were used. This process is stopped when the washing water becomes pure and clear. Purification with distilled water has the role of eliminating all traces of catalyst, soap, salts, etc. methanol and residual glycerin remaining in the biodiesel. Because of how delicate this process is, it must be performed with the least amount of agitation feasible to prevent the creation of an emulsion, which lowers the synthesis's yield.

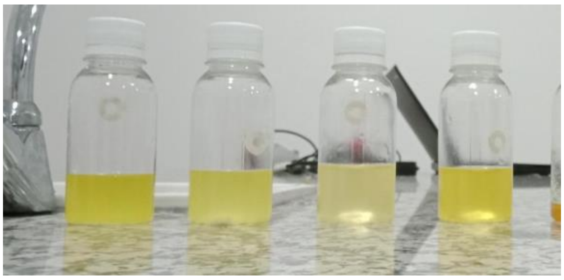

Figure 4. The biodiesels obtained after washing HMP-HSP-HM-HS successively

2.4. Storage Tests Procedure

Every sample was split into two separate, 250 mL samples. Additionally, these 12 samples were split into two groups. in both temperature and lighting different conditions (20 °C and 37 °C). Each group was made up of 6 samples:

- The first samples were stored under real conditions, the tracking was carried out in Beni Mellal Moroccan city during the two months of July and August, under lighting exposer conditions at an average temperature of 37 °C. [32, 33].

- The second samples were maintained in a dark room at ambient temperature of 20 °C.

- All the samples were maintained in glass bottles to simulate the real storage conditions.

3. RESULTS AND DISCUSSIONS

In this part, It's considered useful to study the influence of the choice of raw material and the nature of the oil used on the yield and quality of the biodiesel. For this, a comparative study is done between the biodiesel synthesized from an expired oil (soybean): HS. and the biodiesel synthesized from a mixture of expired oils (soybean + rapeseed + sunflower):HM, in the absence and presence of a pumpkin seed oil.

In a second part, the influence of storage circumstances (Darkness and light) on the quality of the biodiesel samples is studied in comparison with fossil fuels.

3.1. Comparison of the Yield of Different Oil Types

From the results obtained, it is noted that :

The biodiesel obtained from pure Soybean has a yield of 77.93%, this value is close to that found by [34], which are found a maximum yield of 80.2% under the same operating conditions.

Table 3. Biodiesel Yield in function of oil types

Biodiesel	HS	HSP	HM	HMP
Yield	77.93 %	78.9%	81%	85%

The addition of pumpkin seed has a positive effect on improving the yield of soybean oil biodiesel by 0.97%.

The yield of mixed soybean, rapeseed and sunflower (HM) is higher than the yield of pure soybean (HS), this is because of high yield of sunflower and rapessed [34].

For Sunflower, A maximum yield of 83.3% was found by [34]with constant parameters (concentration of (KOH) 1%, temperature of reaction 65ºC, time of reaction 3 hours).

In the same sense [35] achieved a maximum yield of 80% with constant parameters (catalyst concentration (NaOH) 1.0%, temperature of reaction 60ºC, time of reaction 3 hours).

For Rapeseed a yield of 96.5%-99% was achieved with an optimum ratio of 6:1 (alcohol: oil), concentration of (KOH) 1%, temperature of reaction 65ºC, time of reaction 2 hours. Mixing is important because of the lack of mutual solubility of the substrates [36].

The addition of pumpkin seed has a positive effect on improving the yield of biodiesel from blended oil by 4%.

At a reaction temperature of 55 °C, pumpkin seed oil demonstrated the greatest average percentage optimum yield of biodiesel (97%),using NaOH as a catalyst, and a ratio of 6:1 alcohol to oil. The chosen feedstocks was effectively converted into a variety of biodiesel fuels and blends with attributes that are quite similar to those of conventional vehicle gas oil under the provided circumstances [37].

3.2. Effect of Oil Composition on Acid Number

Acid value is determined by a simple acid-base assay, using phenolphthalein as a color indicator, then performed by adding a volume VKOH of a caustic potash solution.

Table 4. Acid number of selected samples

Biodiesel	HS	HSP	HM	HMP
Acid Value (mg KOH/g)	0.14	0.14	0.22	0.21

Acid value was calculated using the following equation: $AV(mg\ KOH/g) = \frac{M\ N\ V}{w}$ [38]

M: Molar mass of KOH=56.1

N: Normality of KOH

V: Oil sample's consumption of titrant (in ml) at the stoichiometric point.

W: Wight of sample

The values obtained for the acidity index of the synthesized biodiesels are relatively low (less than 1%), It was in conformity with both the American (under 0.8 mg KOH/g) and European (under 0.5 mg KOH/g) standards.

For soybean oil biodiesel, this value is being less than find by other researches: (0.41 mg of KOH/g) [39].

On hand, after examining biodiesel produced under optimal conditions, which included a volumetric oil-to-methanol ratio of 1:6, 1% KOH, and a reaction temperature of 40 °C. [40] showed that compared to biodiesel formed of pure soybean cooking oil (0.43 mg KOH/g), biodiesel formed of waste soybean cooking oil. had a greater acid value (0.46 mg KOH/g). On the other hand, the Use of natural antioxidants in oxidative stability of soybean biodiesel led to a similar result of our work (0.15 mg KOH/g oil) [41].

What concerns the biodiesel mixture obtained from Soybean, Rapeseed and sunflower, it is noticed that the values are a little bit high compared to the values obtained from pure Soybean, this may be due to the high acid value of rapeseed, values of 0.48 mg KOH/g found by [42] Using Ultrasonic power.

It's observed also that the presence of pumpkin seed oil does not affect the Acid value of biodiesel. Indeed, research carried out on pumpkin seeds shows that the results obtained fell below the recommended 3.0% FFA contents for biodiesel feedstocks [37], and 5.0% FFA for non-rancid oils [43].

3.3. Effect of Oil Composition on Biodiesel Density

The values of density are in the range of 0.83 to 0.88 g/ cm^3 for the different types of biodiesel.

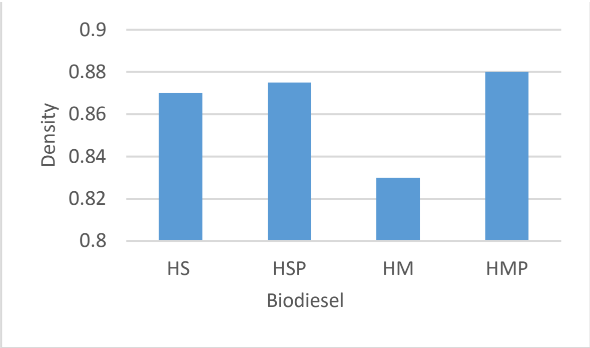

Figure 5. Density of biodiesel samples

These values are almost identical to those of the European standards, whose value varies between 0.86 to 0.9g/cm. If the biodiesel has a higher density, it will be necessary to inject a little higher mass of fuel because the fuel injection system employs a metric flow device. When the density is too low, material is lost, which lowers the power.

In this study, the density of all biodiesel complies with the standards and is equivalent to that of diesel [1].

3.4. Variation of pH as a Function of the Number of Washes

After transesterification of the expired oils and decantation of the reaction mixture to remove the aqueous phase as well as the glycerol, the resulting product must be washed. The washing can be done using distilled water or acid, which serves to remove glycerol and neutralize the alkaline medium [44]. As a result, this washing causes a decrease in pH.

3.4.1. HS

at the beginning of washing (from the 1st washing to the 6th washing), It's noticed that there is a strong decrease of pH. This is due to the easy removal of glycerol and impurities during the first washing phases.

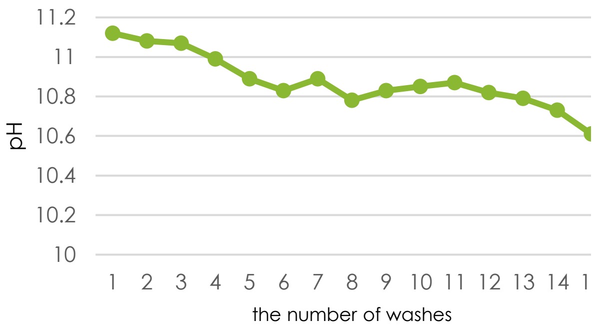

Figure 6. pH variation of (HS) as a function of the number of washes

After the 6th washing, the pH values decrease slightly until stabilization in the 15th washing at pH=10.61, due to the elimination of all traces of glycerol and impurities.

3.4.2. HSP

At the beginning of washing (from the 1st washing to the 5th washing), It's noticed that there is a strong decrease of pH. This is due to the easy removal of glycerol and impurities during the first washing phases.

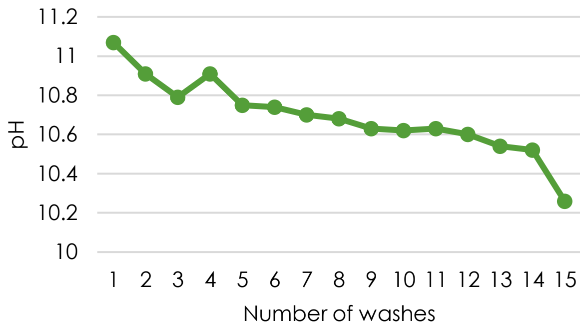

Figure 7. pH variation of (HSP) as a function of the number of washes

After the 7th washing, the pH values decrease slightly until stabilization in the 15th washing at pH=10.26, due to the elimination of all traces of glycerol and impurities.

3.4.3. HM

At the beginning of washing (from the 1st washing to the 3rd washing), It's noticed that there is a strong decrease of pH. This is due to the easy removal of glycerol and impurities during the first washing phases.

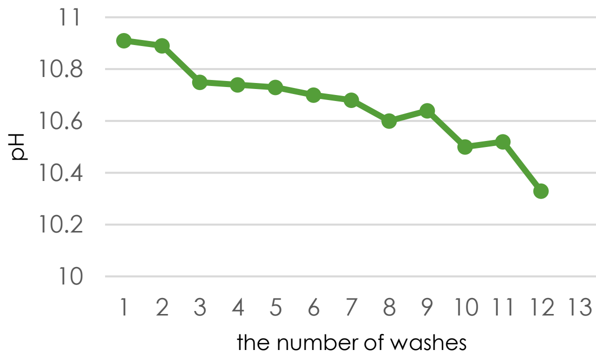

Figure 8. pH variation of (HM) as a function of the number of washes

After the 4th washing, the pH values decrease slightly until stabilization in the 13th washing at pH=10.33, due to the elimination of all traces of glycerol and impurities.

3.4.4. HMP

At the beginning of washing (from the 1st washing to the 9th washing), It's noticed that there is a strong decrease of pH. This is due to the easy removal of glycerol and impurities during the first washing phases.

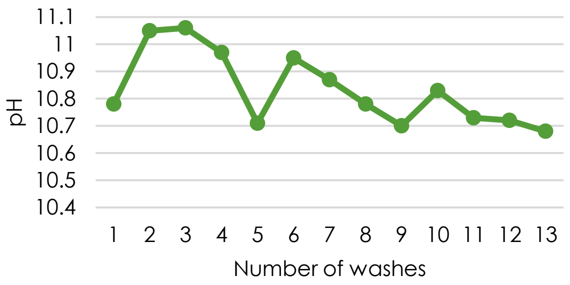

Figure 9. pH variation of (HMP) as a function of the number of washes

After the 10th washing, the pH values decrease slightly until stabilization in the 13th washing at pH=10.68, due to the elimination of all traces of glycerol and impurities

The final pH values obtained are close to 10.6 for HS, 10.26 for HSP, 10.33 for HM and 10.68 for HSP. These high values of PH are due to the operation of transesterification which is based on the use of two types of alcohol (KOH and CH_3OH).

Successive washing and high agitation can produce soap with all three types by preventing separation of the ester from the water phase. Biodiesel obtained from expired oil has an additional difficulty. If soap has been generated, it will form an emulsion with the water and biodiesel, making washdowns long and difficult. For this biodiesel, it is recommended to use vinegar rather than water. The soap in acidic solution becomes a free fatty acid again, which will be easier to remove.

3.5. Degradation Study

The study of biodiesel degradation under different environmental conditions is a very important element to know and control parameters influencing this degradation.

Several studies have been done for biodiesel concerning the influence of various elements on the characteristics and properties of biodiesel.

The study done by [24] showed that temperature and air exposure have a great effect on purity, acid value of biodiesel.

In this section the effect of storage conditions (temperature and light) will be discussed on the degradation of the properties of 4 types of biodiesel (pH, density, acid value) in comparison with fossil diesel.

3.5.1. Effect of high temperature and light exposure

3.5.1.1 pH variation

The deterioration of numerous substances, including lubricants, diesel fuel, and foods with organic components, is influenced by a number of critical variables, including temperature and lighting.

The quality of biodiesel is anticipated to be impacted by temperature as well.

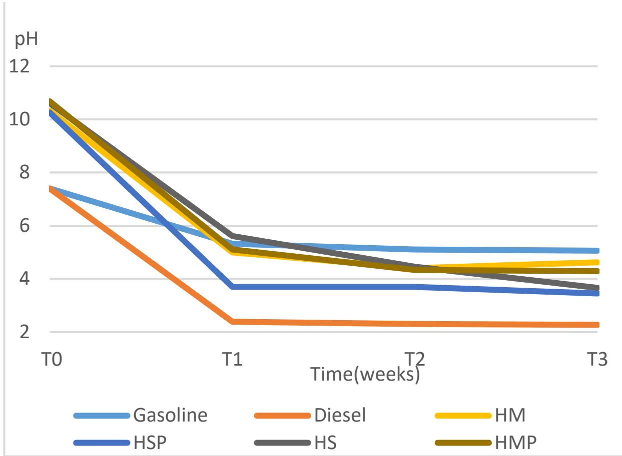

Figure 10. pH of biodiesel degradation for different samples in function of time

Figure 10 show the degradation of different samples in function of time under high Temperature and lighting exposure conditions.

Based on the graphics, it can be inferred that the biodiesel's pH has decreased, which represents the process of degradation. Figure 10 illustrates how the rate of biodiesel degradation rises over time.

Those samples exposed to a high temperature of 37 °C, have the lowest Ph just after the third week (T1). a strong decrease in pH rematched to the HSP sample, a pH drop rate equal to 64% is found.

At the 6th week (T2), It's noticed that the pH has decreased moderately; There is no appreciable differences in the rate of degradation from the 6th week

At the 9th week (T3), a slight drop was noticed for the samples of gasoline and HS.

The figure 11 shows that the pH levels decrease to between 31.62 % and 69.32% after 9 weeks of storage, their rate of pH decrease rank in descending order is Diesel (69.32%)> HSP (66.37%)> HS (65.50 %) > HMP (59.83%)> HM (55.28%) > Gasoline (31.62 %).

The results indicated that high temperature, together with Lighting exposure, play a significant role in decreasing Ph of biodiesel samples.

Diesel's normal pH ranges from 5 to 8, these values are an indicator there could be a problem. Because a lower pH, is a meaning of high risk of major corrosive damage to the system's metal parts.

The problem is often that specific bacteria and microorganisms consume the trace methanol contamination in biodiesel and turn it into acidic acid.

In this case, results mean that high temperatures with lighting exposure increase the potential of bacterial contamination that contribute to fuel pH instability.

3.5.1.2 Density variation

Several studies show that there is a strong correlation between density and certain variables, especially temperature; the study conducted by [45] has successfully defined models that can help to determine the density of diesel-biodiesel-bioethanol blends precisely for temperatures between 15 °C and 75 °C.

In this work, It have been tried to demonstrate the effect of both high temperature and lighting exposure on Density, by studying the variation of density as a function of time.

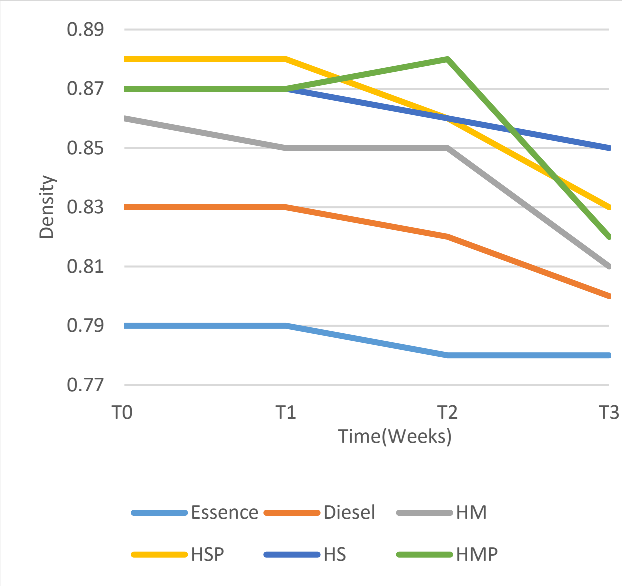

Figure 11. Density variation in high Temperature and in lighting exposure

The results obtained showed that there is an effect on the density as a function of time in the condition of high temperatures and lighting exposure.

Those samples exposed to a high temperature of 37 °C, have the highest density decrease just after the third week (T1). a decrease in density rematched to the HM sample, a density drop 0.01kg/l is found.

At the 6^{th} week (T2), It's noticed that the density has decreased moderately, the rate of drop continues to decrease from the 6^{th} week.

At the 9^{th} week (T3), a slight drop of rate was noticed for all the samples.

In general, the density of biodiesel is between 0.86g/cm^3 and 0.90g/cm^3 , the density of biodiesel produced at the beginning is between these values. (HM) has the lowest density among biodiesels and the densities of the others are close to each other, as presented in After 9 weeks of stockage, the biodiesel samples become unconfirmed to ASTM biodiesel standards.

It's noticed also that biodiesel fuels have higher density than diesel fuels. Although the density of biodiesel is higher, the energy content of biodiesel is lower, either by mass or by volume, compared to diesel fuel [46]. This implies that more fuel must be fed into the combustor in order to get the same engine output [47].

This aspect will result in an increase in fuel usage. On the other hand, the composition of fatty acids and their purity influences the densities of biodiesels [48].

3.5.1.3 Acid value variation

Figure 12 compare the Acid Value of the different samples of biodiesel and fossil diesel of for different samples under high Temperature and lighting exposure conditions. The degradation is represented by an increase of AV (Acid Value) of biodiesel and diesel samples as determined from the Graphics.

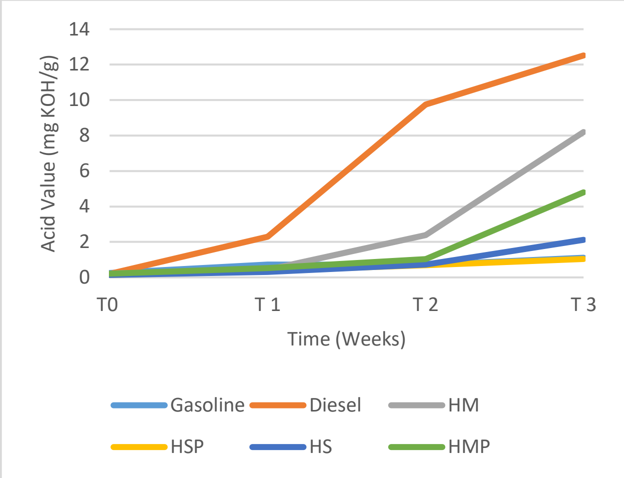

Figure 12. Acid Value variation in high Temperature and in lighting exposure

As shown in the Figure 12, there is an increase in biodiesel degradation in function of time:

In the first week (T1), a strong increase from 0.25 mg KOH/g to 0.72 mg KOH/g Value is found in the Diesel sample.

At the 6^{th} week(T2), It's also noticed that the Acid value of diesel sample has strongly increased to a value of 9.75 mg KOH/g the rate of drop continues to increase from the 6^{th} week.

At the end of the test (i.e., T3(week 9)), a remarkable increase also noticed for the Acid Value to a value of 12.52 mg KOH/g for diesel sample, a dramatic increase noticed also for all the samples. HM has reached the value of 8.2 mg KOH/g, Followed by HMP (4.8 mg KOH/g), HS (2.12 mg KOH/g), Gasoline (1.11 mg KOH/g), HSP coming he last with an AV of 1.04 mg KOH/g.

this agrees with the PH and density test result shown in Figure 12

Based on the aforementioned findings, the pH and density of the samples have a direct correlation with the acid number.

The acid number will increase as the sample deteriorates further.

3.5.2. Effect of ambient temperature and dark storage conditions on pH variation

3.5.2.1. Ph variation

Figure 13 Show the degradation for different samples in function of time under ambient Temperature and dark stockage conditions. Based on the graphics, it can be inferred that the biodiesel's pH has decreased, which represents the process of degradation.

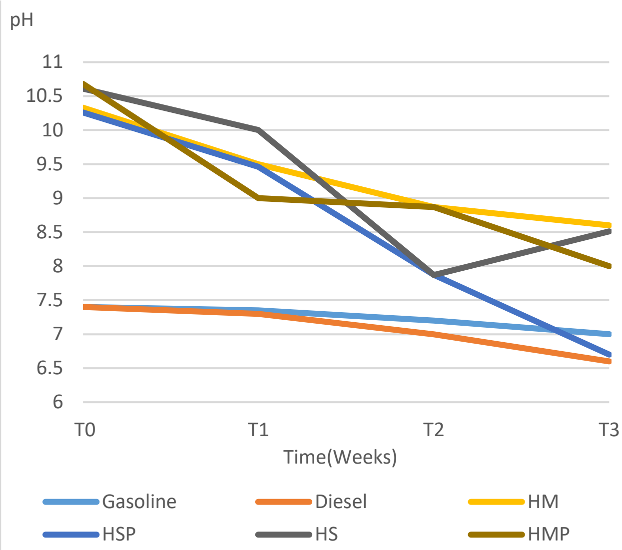

Figure 13. pH variation in function of time at ambient Temperature in dark storage conditions

The figure 13 shows the comparisons of biodiesel pH under dark stockage conditions at 20 °C degree. When the samples were stored at 20 °C Their pH levels decrease to between 5.41% and 34.70% (refer to figure) after 9 weeks of storage and their rate of pH decrease rank in descending order is HSP (34.70%)> HMP (25.09%)> HS (19.79%) > HM (16.75%)> Diesel (10.81%) > Gasoline (5.41%).

Under these two storage conditions, neither the impacts of ambient temperature nor the effects of darkness on biodiesel pH degradation were particularly pronounced. However, those factors have a noticeable impact on the pH degradation of diesel.

It's also noticed that these values are less than others noticed for high temperature and lighting exposure conditions.

The results indicated that high temperature, together with Lighting exposure, play a significant role in decreasing Ph of biodiesel and diesel samples.

The normal pH for diesel is between 5 and 8, these values are conformed to the norms [29].

3.5.2.2. Density variation

The results obtained showed that there is an effect on the density as a function of time in the condition of ambient temperature and dark stockage conditions.

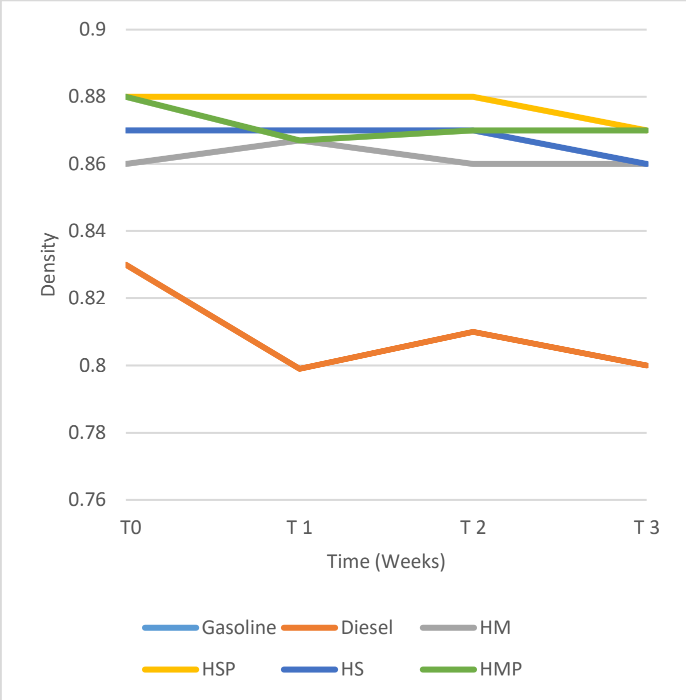

Figure 14. Density variation in ambient Temperature and in dark stockage conditions

In general, the density of biodiesel is between 0.86g/ cm^3 and 0.90g/cm^3 [1], the density of biodiesel is between these values. The density of (HM) is still the same without variation after 9 weeks. The samples (HS, HSP, HMP) decreased by a value of 0.1g/cm^3 after 9 weeks of stockage.

In general, the density of diesel is between 0.82g /cm^3 and 0.86g /cm^3 and between 0.71 g / cm^3 and 0.77g /cm^3 for Gasoline [9]. The density of fossil fuels after 9 weeks is between these values For gasoline (0.78 g/cm^3) and under the requirements for diesel (0.80 g/cm^3).Diesel has the highest density rate decrease by 0.3 g/cm^3. The density rate decrease of Gasoline is 0.1g/cm^3.

It's also noticed that for the fossil fuel samples, the rate of decreasing is the same in both conditions. either in High Temperature and lighting exposure, or in ambient temperature and dark stockage conditions.

For the biodiesel samples, It's noticed that the results are different in the two conditions. The lowering is in the order of 0.1 g/cm^3 in these conditions. It varies between 0.2 g/cm^3 and 0.5 g/cm^3 at high temperature and lighting exposure.

3.5.2.3. Acid value variation

The results obtained support the results obtained by [47], which shows that the acid numbers of samples stored at 20 °C increased less than samples maintained at 40 °C.

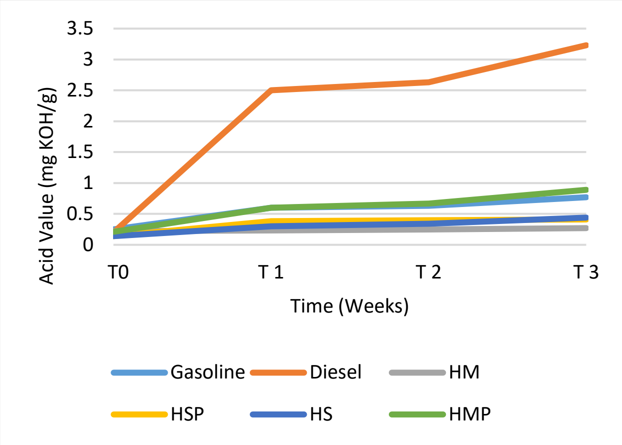

Figure 15. Acid Value variation in ambient Temperature and in dark stockage conditions

Figure 15 compare the Acid Value of the different samples of biodiesel and fossil diesels for different samples under ambient Temperature and dark stockage conditions. The degradation is represented by an increase of AV (Acid Value) of the biodiesel and diesel sample as determined from the Graphics.

As shown in the figure 15 There is an increase in biodiesel and diesel degradation in function of time:

In the the first week (T1), a sharp increase from 0.21 mg KOH/g to 0.60 mg KOH/g is found in the HMP sample in comparison with 0.20 mg KOH/g to 2.50 mg KOH/g Value is found in the Diesel sample.

At the 6th week (T2), It's noticed that the Acid value of all the samples has moderately

The rate of drop continues to increase
from the 6th week. Between the 6th week and the 9th week. a remarkable increase of Acid Value equal to 22.81% is noticed for diesel sample and a dramatic increase noticed also for all the samples. HMP has reached the value of 0.89 mg KOH/g, followed by gasoline (0.77 mg KOH/g), HS (0.44 mg KOH/g), HSP (0.41 mg KOH/g), Hm coming the last with an AV of 0.27 mg KOH/g.

This agrees with the PH and density tests results shown in Figure 13 and figure 14.

From the above observations, the acid value has a direct correlation with the pH and acid Value of the samples. The acid value will increase as the sample deteriorates.

4. CONCLUSION

From the results obtained from the transesterification of the different types of biodiesels, It's concluded that:

- The addition of pumpkin seed has a positive effect on the yield increase of biodiesel from Soybean as well as biodiesel blends based on Soybean, Sunflower and rapeseed: HMP (85%) > HM (81%) > HSP (78.9%) > HP (77.93%)
- The high temperature combined with the lighting strongly enhances the degradation phenomenon.

The results showed that under real conditions of high temperature and lighting exposure:

- The density of biodiesel degrades rapidly at a rate of 0.0066 g/cm^3 /Week Compared to diesel 0.001 g/cm^3/Week.
- The acid value of biodiesel (HM) is rapidly increasing at a rate of 0.91 mg KOH/g /Week compared to diesel 1.39 mg KOH/g/Week.
- The pH of diesel has experienced a strong decrease of 66% compared to diesel 69.32%.
- The samples' pH and acid value are directly correlated with the acid value.
- Diesel degrades strongly and rapidly from a biodiesel in terms of Acid Value, pH and Density.
- Biodiesel loses its stability in terms of pH rapidly, this is due to various microorganisms consuming the trace methanol and biodiesel and converting it to acetic acid.

As a perspective, further studies can be done on the influence of pumpkin seed mixed with another biodiesel source like palm oil.

NOMENCLATURE

HS: Biodiesel obtained from Soybean oil.

HM: Biodiesel obtained from a mixture of oils: Soybean, Sunflower and Rapeseed.

HSP: Biodiesel obtained from a mixture of oils: Soybean and Rapeseed

HMP: Biodiesel obtained from a mixture of oils: Soybean, Sunflower, Rapeseed and Pumpkin.

T: Time in weeks

POV: peroxide value

ASTM: American Society for Testing and Materials

MEHV: Methyl Esters of Vegetable Oils

EEVO: Ethyl Esters of Vegetable Oils

AGO: Automotive Gas Oil

FFA: Free Fatty Acids

AV: Acid Value

EPA: Environmental Protection Agency

TAG: Triacylglycerol

DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Soufiane GHANIMI: Performed the experiments and analyse the results and wrote the manuscript.

Badreddine ELMEJHED: Performed the experiments.

Wafa TEROUZI: Provided consultancy, check all data and helped writing manuscript.

Fouzia KZAIBER: Provided consultancy, check all data and helped writing manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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