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IN-SITU TRANSESTERIFICATION OF *SALICORNIA BIGELOVII* PLANT SEEDS OIL FOR BIODIESEL PRODUCTION VIA ULTRASONIC TECHNIQUE

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ABSTRACT
The research looks at the potential of Salicornia plant oil as a biodiesel source, which is important for lowering harmful and greenhouse gas emissions while also supporting sustainability and biodiversity. The study looks at how different cultivation and fertilisation techniques affect the proportion of seed oil converted into biodiesel through ultrasonic technique. The produced biodiesel samples comprise more than 35% saturated Fatty Acid Methyl Esters (FAME) and more than 50% unsaturated FAME, with a tiny proportion of non-FAME. GC analysis indicated that the seed oil conversion percentage ranged from 55-96%, with good purity and varying levels of alkyl ester content (52-95-5%). The iodine value, saponification value, cetane number, high heating value, density, and kinematic viscosity of the biodiesel samples were also investigated. Sample (16) satisfied the quality standards for good biodiesel fuel, and additional testing verified that it is the best biodiesel. Salicornia Bigelovii biodiesel satisfies the recommendations of American and European biodiesel standards, proving its potential as a diesel substitute for compression-ignition engines.

HIGHLIGHTS

- ***Salicornia bigelovii has great potential as a renewable and sustainable source of biodiesel.***
- ***In-situ transesterification process depends on cultivation and fertilization techniques used.***
- ***Salicornia biodiesel, from irrigated seeds with 25% seawater, met fuel standards.***
- ***Biodiesel had >35% saturated FAME and >50% unsaturated FAME content.***
- ***Optimal biodiesel yield from seeds of nitrogen and phosphorus fertilizers; and highest purity with nitrogen and potassium fertilizers***

Salicornia biodiesel meets quality criteria: high CN, low sulfur, viscosity, pour/cloud points, and HHV.
KEYWORDS: ***Salicornia bigelovii, Biodiesel, Fatty acids, In situ transesterification, Ultrasonication.***

1. INTRODUCTION

Salicornia bigelovii is a salt-tolerant plant that has been identified as one of the most salt-tolerant species among 1560 halophytes. It has been demonstrated that it can sustain normal development even when the soil NaCl concentration surpasses 1.3 M, which is double the salinity of full-strength saltwater (500 mm NaCl) [1,2].

Salicornia bigelovii Torr., a salt-tolerant halophyte, shows significant potential as an oilseed crop in arid coastal regions and wastelands. Its ability to be irrigated with seawater makes it an appealing choice in areas where freshwater resources are limited. Promising results have been obtained from testing Salicornia bigelovii as an oilseed crop along Mexico's arid coast. The Indian Ocean, Gulf of California, Red Sea, and Arabian Gulf coasts have the ability to develop halophytic plant species as oilseed crops. The seeds of this halophyte contain a substantial amount of oil (30%) and a low concentration of salt (less than 3%), making it a highly attractive oilseed halophyte crop for future cultivation. Its oil is of excellent quality, with a high concentration of linoleic acid (75%), an unsaturated fatty acid required for the human diet, and linolenic acid (2%), an omega-3 fatty acid that aids in the prevention of coronary heart disease. Salicornia bigelovii Torr. meal is a good source of protein, having 42-45% protein. This makes it an excellent choice for use as animal feed. Salicornia bigelovii Torr. is a salt-tolerant plant that can be cultivated in dry and coastal environments, making it a viable source of animal feed in these environments. Eritrea and the United States of America have begun. Furthermore, the oil obtained from Salicornia may be used to make biodiesel [3,4]. The experiments discovered that Salicornia may produce substantial biodiesel yields even when cultivated on salty soils. Salicornia is a fast-growing plant that may be picked several times each year. In view of the growing gap between supply and demand for petroleum, as well as expanding environmental laws, the industry is aggressively looking into alternative fuel sources that might improve fuel efficiency. Biofuels are being researched as possible replacements or complements to traditional distilled petroleum fuels. Crops with the ability to generate renewable energy from biological sources are referred to as bioenergy crops. This category encompasses a wide range of perennial and annual crops, including those that produce oil and those that serve as sources of lignocellulose. Significant progress has been achieved in the practical viability of cultivating energy crops since 1978, resulting in the launch of numerous bioenergy projects. Nonetheless, a limitation of conventional biofuel crops is their demand for agricultural land, pastures, and rangelands, which can divert resources from food production to fuel production. Bioenergy crops are a potential source of renewable energy, but they can also compete with food production for land. Saline agriculture is a new approach to growing crops in salty soil, which could help to reduce this competition. By using saline land for agriculture, we can produce food and fuel without taking away from arable land. This is why saline agriculture is a promising new technology [5].

Oilseed halophytes are gaining popularity as bioenergy crops for the generation of liquid biofuels in the burgeoning field of saline agriculture. The potential environmental advantages and the fact that energy crops are a renewable source of energy are driving the attention. Biofuels from halophyte crops are a potential option since they may be grown on ground that is unsuitable for regular agriculture. Many technologies for converting vegetable oil into a form appropriate for use as fuel have recently been developed as a consequence of recent efforts. Furthermore, oil-producing crop plants are a significant component of agricultural economic growth. Because of their potential use as biofuels, oilseeds containing atypical fatty acids are industrially significant [6]. One promising approach to developing biofuels from halophytes is to produce multiple products from a single species or farming operation. For example, the oil from Salicornia bigelovii can be used to produce biodiesel or Bio-SPK (Bio-Synthetic Paraffinic Kerosene). Studies have also shown that the seed meal from *S. bigelovii* and *S. brachiata* plants can be used as a source of animal feed [7, 8, 9, 10]. Oils obtained from halophytic plants, such as Salicornia bigelovii, have been studied as a replacement for diesel fuel in compression ignition engines. Salicornia bigelovii seeds are a feedstock for biofuel production, however, the energy demand and amount of biomass available for conversion must be taken into account [11,12,13]. The oil content of Salicornia seeds was found to be rather high, often surpassing 30% of the seed biomass. This is consistent with earlier observations on the oil content of Salicornia europaea and other species such as Salicornia bigelovii, although it is about double the value reported in other studies for S. europaea. Surprisingly, the oil content of the seeds increased in response to greater saline levels. While the greatest oil values were reported in our study when the seeds were watered with brackish water, previous research has revealed that optimum oil content in seeds may be attained at salinity levels of about 600 mM NaCl, which is equal to values observed in saltwater [14,15,16]. Biodiesel is generated through a transesterification process that combines vegetable oil, animal fat, or waste cooking oil with alcohol and a catalyst [17]. Ultrasound is utilized in this process to enhance the reaction by facilitating improved agitation between the immiscible reactants. By generating microbubbles near the boundary between the alcohol and oil phases, ultrasound promotes the formation of micro-turbulence and disrupts the phase boundary, resulting in the emulsification process [18, 19, 20]. Employing ultrasound in the transesterification process enhances the interfacial area and mass transfer between the alcohol and oil phases, thereby accelerating the reaction kinetics [21, 22]. Furthermore, ultrasonography may be used to boost the standard mechanical extraction technique for extracting oil from seeds [23, 24]. The extraction efficiency is affected by the sonication settings as well as the paste's physicochemical qualities. Several investigations have indicated that sonication is a more efficient approach than mechanical stirring for the alkaline transesterification of soybean oil. Sonication results in better biodiesel yields with quicker reaction times. Other research has demonstrated that both mechanical stirring and sonication may produce the same biodiesel yields, although sonication needs far shorter response times [25, 26]. In-situ transesterification refers to conducting the transesterification reaction directly within the same reaction vessel as the raw materials, eliminating the need for an intermediate separation step. In contrast, conventional transesterification involves a two-step process where triglycerides are first extracted from the raw material and then reacted with alcohol and a catalyst to produce esters. The choice between in-situ and conventional transesterification depends on various factors, including the type of feedstock, reaction conditions, and the intended application of the final product. For instance, in-situ transesterification may be more suitable for feedstocks that are challenging to separate, such as waste cooking oil. It can also be preferable for reactions requiring precise control of reaction conditions, particularly for the production of high-quality biodiesel [25].

The main objective of the present work was to apply modern technology for biodiesel production via in-situ transesterification using an ultrasonic technique. Consequently, investigate the effect of different cultivation and fertilization treatments on the percentage of seed oil conversion into biodiesel, its purity % and the percentage of alkyl ester content. Some of the physical and chemical properties of producing biodiesel will be examined to evaluate the quality and performance of the resulting biodiesel.

2. MATERIALS AND METHODS

2.1. Salicornia Plant Characteristics

Field studies were carried out in the King Marriott neighbourhood of Alexandria, Egypt, throughout the 2018/2019 season on homogenous chosen plots (1 m2 / plot) of naturally growing Salicornia bigelovii plants. The research sought to identify the best irrigation and fertilisation practices for generating high-quality seeds and oil appropriate for biofuel production. Sixteen different combined irrigation and fertilization treatments were tested, including four irrigation treatments using diluted seawater (100% well water, 100% seawater, 50% sea and 50% well water, and 25% seawater + 75% well water) and four fertilization treatments using NPK (20-20-20), NPK + Micronutrients (3% of each of Fe, Mn, Zn, and 0.5% Cu in chelated form), Algae Amphora extract (20% amino acids, macro- and micronutrients, and some growth regulators) as a

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biofertilizer, and NPK + Micro + Algae as an integrated fertilizer. A control sample was also included, which was left untreated without irrigation or fertilization. High-purity analytical-grade chemicals were used for all laboratory tests. Following the treatments, seeds were harvested from the *Salicornia bigelovii* plants, and the oil percentages were recorded for all samples (1-17) under different cultivation conditions in a previous study [27]. The humidity percentage will be calculated for each sample by weight W_0 g. of *S. bigelovii* seeds and dry at 85 °C until constant weight W_0. After cooling, the percentage of humidity is calculated by the following equation.

Humidity % = $(W_0 - W_1) / 100$………………... (1)

Where: W_0 is the initial weight and W_1 is the final weight.

2.2. In-Situ Transesterification Using Ultrasonic Probe:

For the transesterification reaction, methanol was used in a ratio of 6:1 v/w of alcohol to oil, based on the amount of oil in each sample from a previous study [27]. The catalyst used was KOH, in a ratio of 1% w/w of catalyst to oil, which was dissolved in a calculated amount of methanol before adding to the reaction mixture. Dried seeds (10g), methanol (6:1 v/w of oil) , and KOH solution (1% w/w) were combined in a glass reactor and subjected to an ultrasonic generator probe (Model Sollics Vibra Cell V500) at room temperature for 15 minutes, with a pulse of 45 seconds on and 30 seconds off. At the end of the reaction time, the catalyst was neutralized using glacial acetic acid to stop the reaction. The reaction mixture was then filtered, and excess methanol was removed by evaporation using a rotary evaporator. The resulting filtrate was transferred into a separating funnel by adding a small amount of n-hexane to separate the two layers, with the upper layer containing the fatty acid methyl ester dissolved in n-hexane and the lower layer containing glycerol and unreacted catalyst Figure (1). After settling for 6-8 hours, the layers were separated. All experiments were conducted in duplicate. The conversion percentage to biodiesel was calculated according to the total weight of oil in the seeds [28] from the following equation:

Conversion % = $(Mass\ of ester\ layer / Mass\ of\ reactant\ oil) \times 100$……………. (2)

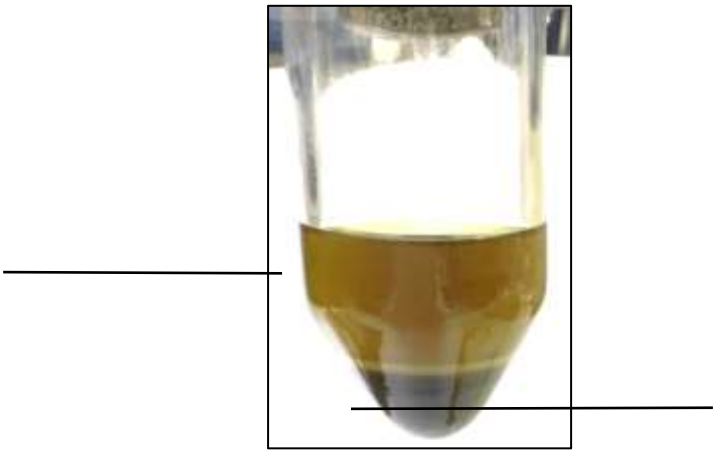

Fig. (1): Filtrate Sparation Layrs.

2.3. EVALUATION OF THE FUEL PROPERTIES

2.3.1. Fatty Acid Profile of Produced Biodiesel

The qualitative analysis of Fatty Acid Methyl Ester (FAME) was performed using a Hewlett-Packard Model 6890 Chromatograph (United States). The analysis utilized a flame ionization detector with a split automatic injector and a silica capillary column (DB-5) measuring 30 m × 0.25 mm × 0.25 µm. Helium was used as a carrier gas at a flow rate of 1 mL/min. The column was maintained at 150°C for 1 minute and then ramped to 240°C at a rate of 30°C/min, where it was held for 30 minutes. The FAsME were identified by comparison of the retention time of the sample with that of a standard (FAME mix Supelco-37, Supelco United States).

The purity is a fraction of esters in the biodiesel layer obtained by GC analysis according to the method SRPS EN 14103. The condition of GC analysis was as mentioned above. Methyl heptadecanoate (above 99%, Fluka) was used as an internal standard (IS) for quantification of the content of the individual fatty acid [29]. The percentage of purity of biodiesel was determined from the following equation:

$$Purity\ \% = \frac{\text{Total peak areas of FAME} - \text{Peak area of IS}}{\text{Total peak areas of FAME}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots.. (3)$$

The Alkyl ester percentage is calculated according to the following equation:

Alkyl ester % = $(Mass\ of ester\ layer\ / Total\ mass\ of\ reactants) \times Purity$ ……... (4)

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2.3.2 The Saponification Value (SV):
As the saponification is a chemical reaction that converts an ester into a salt of a fatty acid Figure (2), the saponification value is a useful tool for assessing the quality of fats and oils. It can be used to determine the purity of a fat or oil and to assess its suitability for different applications.

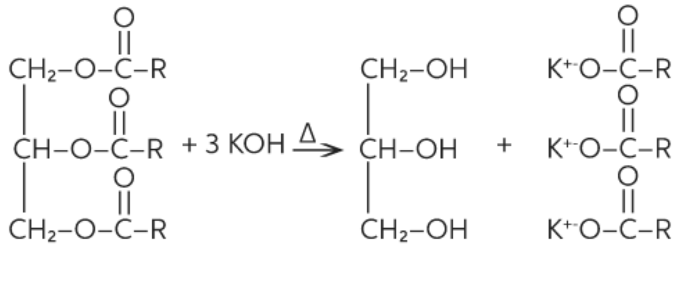

Fig. (2): Saponification Reaction Mechanism

Saponification value (SV) represents the number of milligrams of hydroxide required to saponify one gram of fat. As the saponification value increases, the average molecular weight of triglycerides decreases. The saponification value of pure fatty acid methyl ester mixture of biodiesel can be calculated according to the following equation [30,31]

$$\text{Saponification value (SV)} = \sum \frac{560 \times Ai}{MWi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (5)$$

Where Ai is the mass fraction percentage of a methyl ester and MWi is the molecular weight of a methyl ester.

2.3.3. Iodine Value (IV)
It is referred to the degree of unsaturation of biodiesel fatty acid methyl ester, which has effects on the oxidation stability of the fuel. It can be calculated from the following equation: [30]

$$\text{Iodine value (IV)} = \sum \frac{(254 \times D \times Ai)}{MWi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (6)$$

Where D is the number of double bonds in a methyl ester, Ai is the mass fraction percentage of a methyl and MWi is the molecular weight of a methyl ester.

2.3.4. The Cetane Number (CN)
It specifies the fuel ignition quality related to the ignition delay time. Cetane numbers are calculated using the following equation [32]:

$$\mathbf{CN = \Sigma\, X_{ME}\, (wt.\ \%)\, CN_{ME}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (7)$$

Where CN, is the cetane number of the biodiesel, X_{ME} is the mass fraction of a methyl ester, and CN_{ME} is a cetane number of individual methyl esters.

2.3.5. Density
The performance of the engine is fuel density affected and can be estimated through the equation [33]:

$$\boldsymbol{\rho = \sum Ai\ \ \rho i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where, **ρ** is the density of the fuel, Ai is the mass fraction percentage of a methyl ester and, **ρi** is the density of a methyl ester.

2.3.6. High Heating Value (HHV)
It is the number of heat units (MJ OR KJ) for the complete combustion of 1Kg fuel.
The relation between **(IV), (SV),** and (HHV) was proven by Demibras [34]. So, the HHV can be calculated by equation (8)

$$\text{HHV (MJ/Kg)} = 49.43 - 0.041\ (SV) - 0.015(IV) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (8)$$

2.3.7. Kinematic Viscosity
The capillary viscometer (manufactured by Cannon Company, USA) equipped with a refrigerated/heated circulating bath (RW-0540G, Jeio Tech, South Korea) was used to measure the kinematic viscosity of *S. bigelovii* biodiesel. The measurements were taken at a temperature of 40 ◦C [35].

***2.3.8.* Pour Point**
The pour point is an indication of the lowest temperature at which a liquid can be pumped. Sample vol. of 40 ml was tested in SETA apparatus, according to ASTM D97 standards where the temperature at which the biodiesel becomes semi-solid was noted as the pour point of biodiesel [36].

2.3.9. Cloud Point
The cloud point, determined by the ASTM D6751 standard using the SETA apparatus, indicates the temperature at which wax crystals form and can potentially clog engine filters. It is the temperature at which the biodiesel starts solidifying and becomes cloudy.

2.3.10. Flash point
The flash point of biodiesel was determined according to ASTM D6751-2 standard. This standard specifies the procedure for determining the flash point of liquids using the Pensky-Martens closed cup apparatus. The standard also specifies the minimum flash point for biodiesel, which is 64°C (147.2°F). The flash point of biodiesel is an important property that should be considered when using or storing this fuel [36].

3. RESULTS AND DISCUSSION

3.1. Biodiesel Fatty Acids Compositions
The corresponding data of gas chromatography spectra of pure *S. bigelovii* biodiesel samples are shown in Table (1), as fatty acids profile. The biodiesel samples are composed of 5 -6 different FAME with more than 35 wt. % of saturated and more than 50wt %of unsaturated FAME. They contained a small percentage of non-FAME. In general, there is a balanced mixture of saturated and unsaturated fatty acid methyl ester which is necessary for high-quality biodiesel. Saturated FA is provided stability and resistance to oxidation while unsaturated fatty acids provide better cold flow properties and improved fluidity according to the American Society for Testing and Materials (ASTM) [36-37].

Table (1): Fatty Acids Profile of S. Bigelovii Biodiesel

Sample / Fatty A.	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}
Myristic C14	0.5	1.3	2.0	1.4	1.3		1.9	1.6	1.4	0.8		1.3	1.5	1.2	1.1	1.2	1.2
Palmitic C16	17.2	22.9	25	15.8	23.1	23.9	19.1	15.9	23.6	23.3	13.6	20.7	24.1	23.5	19	21.0	22.9
Steric C18	20.5	19.0	18	19.2	19.1	21.4	18.4	19.1	19.3	15.7	23.3	20.6	17.9	20.1	20.4	13.1	21.8
SFAME	38.2	43.2	43	36.4	43.5	45.3	39.4	36.6	44.3	39.8	36.9	42.6	43.5	44.8	40.5	35.3	43.9
Oleic C18-1	47.3	35.3	35	32.0	29.5	43.4	33.7	26.7	29.6	31	41.2	30.5	30.7	30.7	31.1	50.9	35.5
Linoleic C18-2	9.0	19.1	20.6	22.6	22.5	11.3	24	33	22.1	31.0	18.3	21.5	21.8	20.2	25.6	13.8	13.3
Linolenic C18-3	1.6	-	-	2.5	-	-	-	-	1.5	1.2	-	1.6	-	2.4	2.3	-	1.9
USFAME	57.9	54.4	55.6	57.1	52.0	54.7	57.7	59.7	53.2	63.2	59.5	53.6	52.5	53.3	59.0	65.7	52.7
TFA	96.1	97.6	98.6	93.5	95.5	100	97.1	96.3	97.5	100	96.4	86.2	95.0	98.1	99.5	100	95.6

- S_n: Sample number
- SFAME: Saturated Free Fatty Acid
- USFAME: Unsaturated Free Fatty Acid

3.2. The Percentage of Conversion, Purity, And Alkyl Ester
The percentage of S. Bigelovii samples oil conversion through the in-situ transesterification process is calculated by Equation (2). Samples 14&16 have a higher conversion percentage (92.3,96.0 respectively), these samples differed in fertilization with the same irrigation treatments. Sample 2&4 had the lower conversion (< 60%). The conversion of other samples ranged between 75-90%, as shown in Figure (3). The purity % of obtained biodiesel was calculated by equation (3), these results

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were represented in Figure (3) where the purity percentage of all samples was higher than 90% except sample no. 3 its purity was 84.8%, its fertilization of algae with irrigation 100% well water may be decreased its purity more than the other samples. The biodiesel samples have different percentages of alkyl ester.

As shown in Figure (3) and calculated by Equation (4), the biodiesel samples (14) & (16) has alkyl ester content higher than 90%. These samples were subject to the same condition of irrigation and differed in fertilization. The alkyl ester content of samples 8,10 &13 which differ in their irrigation and fertilization treatments, were higher than 85%, while samples 7,9&12 were more than 70%. The other samples have alkyl ester less than 70% excluding 2,4&15 samples lower than 60%.

The high value of conversion with high purity and high alkyl ester content refers to the high efficiency of the produced biodiesel [37], characteristic of the sample (16) which was irrigated by 25% seawater + 75% well water, fertilized by NPK and microalgae.

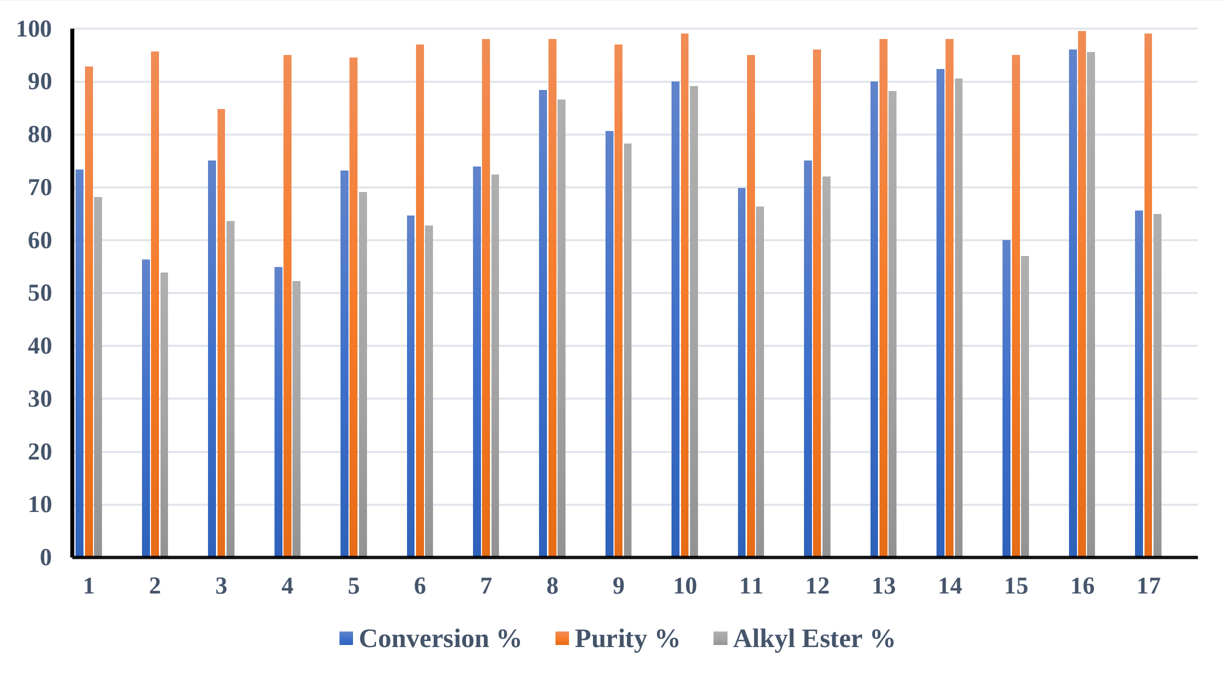

Fig. (3): The Percentage of Conversion, Purity, and Alkyl Ester Content.

3.3. 0 The Saponification Value

The saponification value range of biodiesel can vary depending on the specific feedstock and production process used. However, in general, the saponification value range of biodiesel is typically between 170 and 200 KOH/g (potassium hydroxide per gram of biodiesel) [6]. The saponification value is a measure of the amount of potassium hydroxide required to saponify a specific amount of the fuel and is related to the fuel's fatty acid profile and molecular weight.

It is an important parameter for assessing the quality and performance of biodiesel, as it can provide information about the fuel's purity, composition, and potential for use in various applications. The results showed that the saponification values of the samples ranged between 163 to 183 KOH/g as illustrated in Figure (3), which are considered in the acceptable range [7]. Accurate testing using appropriate standards and protocols is necessary to determine the specific saponification value of a biodiesel sample, and to evaluate its suitability for different applications.

3.4. The Iodine Value

The iodine value (IV) of biodiesel varies depending on the type of feedstock used to produce the biodiesel. It is a measure of the degree of unsaturation and is just one of many properties used to characterize biodiesel, and it doesn't necessarily indicate the quality or performance of the fuel.

There is no specific iodine value range that defines high-quality biodiesel. However, a lower iodine value generally indicates a higher quality biodiesel.

Biodiesel with an iodine value below 120 is considered to have good oxidative stability and low susceptibility to polymerization, which can lead to deposits and filter plugging in the fuel system [7]. However, biodiesel with higher iodine values can still be of good quality if it meets other performance criteria. The iodine value of all samples that were subjected to different treatments of irrigation and fertilization ranged between 47.5 to 77.7, using equation 7 and represented in Figure (4). Biodiesel which was produced from these samples has a high efficiency.

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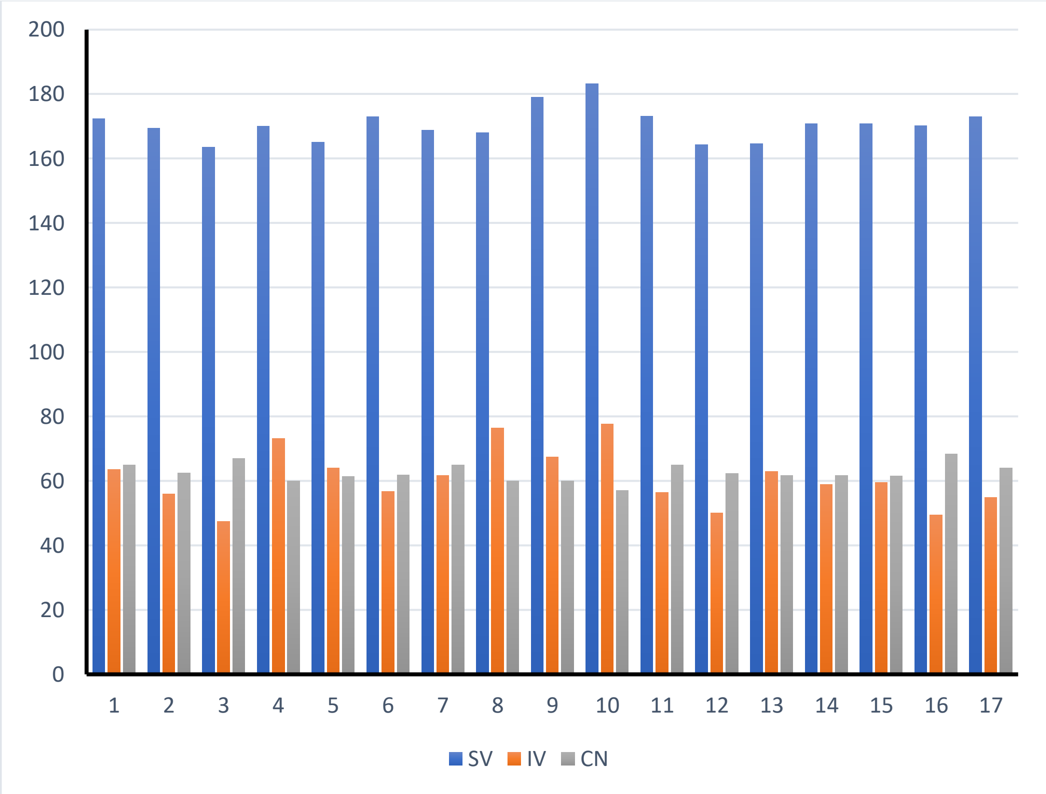

Fig. (4): The Saponification Value, Iodine Value And, Cetane Number.

3.5. The Cetane Number (CN):

Biodiesel is typically characterized by its cetane number, which is a measure of its ignition quality. The accepted minimum cetane number value of biodiesel according to ASTM D6751 and EN 14214 standards is typically between 49 and 55 [7]. However, some biodiesel producers strive to produce biodiesel with a cetane number higher than 55, as a higher cetane number can improve combustion efficiency and reduce emissions. Biodiesel with a higher cetane number can result in improved engine performance, such as reduced engine noise, faster cold starts, and lower emissions. This is because a higher cetane number means that the fuel ignites more quickly and completely, leading to a more efficient combustion process [38] while a higher cetane number can be beneficial for biodiesel efficiency, it is just one of several factors that contribute to the fuel's performance in a diesel engine [39]. CN was calculated by equation 8 and as shown in Figure (4), All samples of biodiesel produced showed a high value of CN > 55 which suggests the high quality of the biodiesel formed.

3.6. Density

The density of biodiesel can vary depending on the feedstock and the production process, but it typically ranges between 0.86 and 0.90 (g/mL) at 15°C. For comparison, the density of petroleum diesel is around 0.83 to 0.87 g/mL at the same temperature. Lower density biodiesel may also have different properties that could affect its performance, such as flash point, pour point, and cetane number. The results showed that there were samples 1,2,6,9,10,14,15,16, and 17 had acceptable density values within the typical range for biodiesel density values, while the rest of the samples had low values of density < 0.86 g/ML, Figure (5).

It's important to note that the density of biodiesel can affect its properties and performance, such as its energy content and viscosity. Therefore, it's necessary to consider the density when formulating and using biodiesel as a fuel. If the biodiesel meets the relevant specifications and requirements for its application, including density, then it could be considered acceptable [40].

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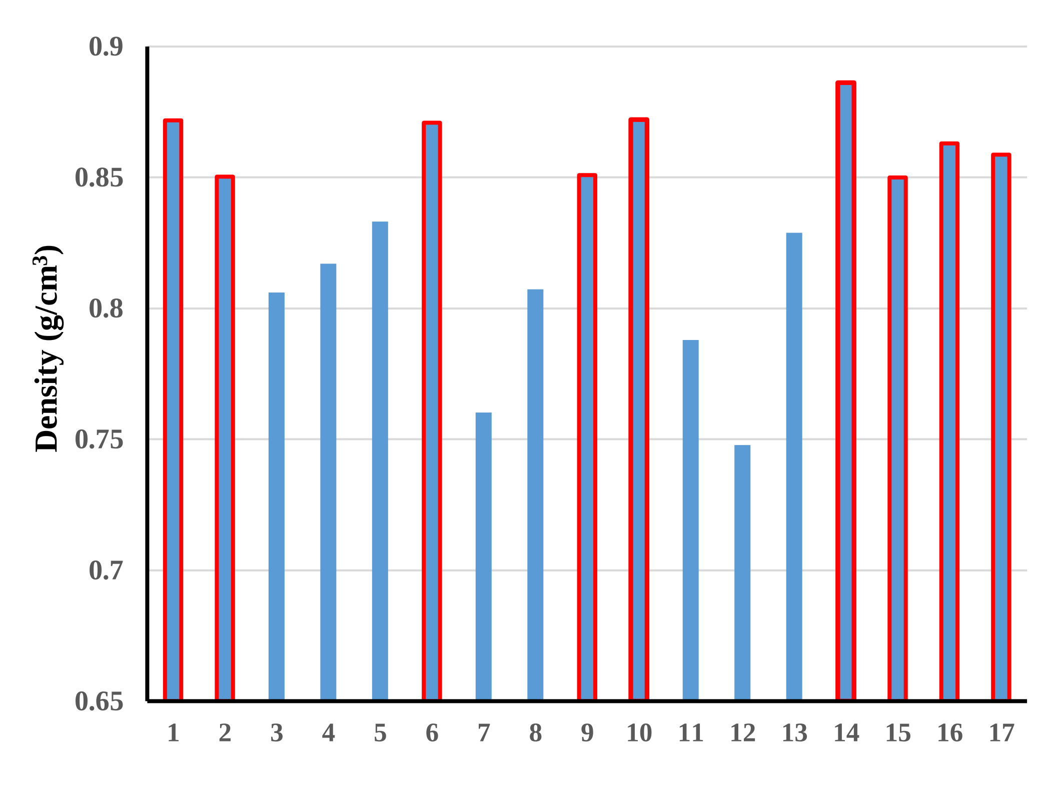

Fig. (5): The Density Values

3.7. High Heating Value (HHV):

The high heating value (HHV) of biodiesel represents the maximum amount of energy that can be released from the fuel, and it includes the energy contained in the fuel itself as well as the energy released from the combustion process. It's worth noting that the HHV of biodiesel can be affected by various factors, such as the feedstock used to produce the fuel, the production process employed, and the presence of impurities. For example, biodiesel produced from feedstocks with a higher lipid content can have a higher HHV than biodiesel produced from feedstocks with a lower lipid content. Additionally, impurities such as water and free fatty acids can lower the HHV of biodiesel. The HHVs of biodiesel (39 to 43.33 MJ/kg) are slightly lower than that of diesel (49.65 MJ/kg) due to its lower energy density, which is related to its lower carbon-to-hydrogen ratio and higher oxygen content [41]. However, biodiesel can still provide a significant amount of energy per unit volume, and it can be used as a viable alternative to petroleum diesel in many applications.

Figure (6) demonstrates that all samples evaluated for HHV had a value exceeding 40 MJ/Kg, with samples 7 and 16 having the highest HHV values of 43.6 MJ/Kg each.

The HHV of biodiesel is an important consideration in its use as a fuel, as it can affect the fuel's performance and efficiency. In general, higher heating values can result in better fuel efficiency and improved performance in engines. Therefore, it's necessary to consider the HHV when formulating and using biodiesel as a fuel.

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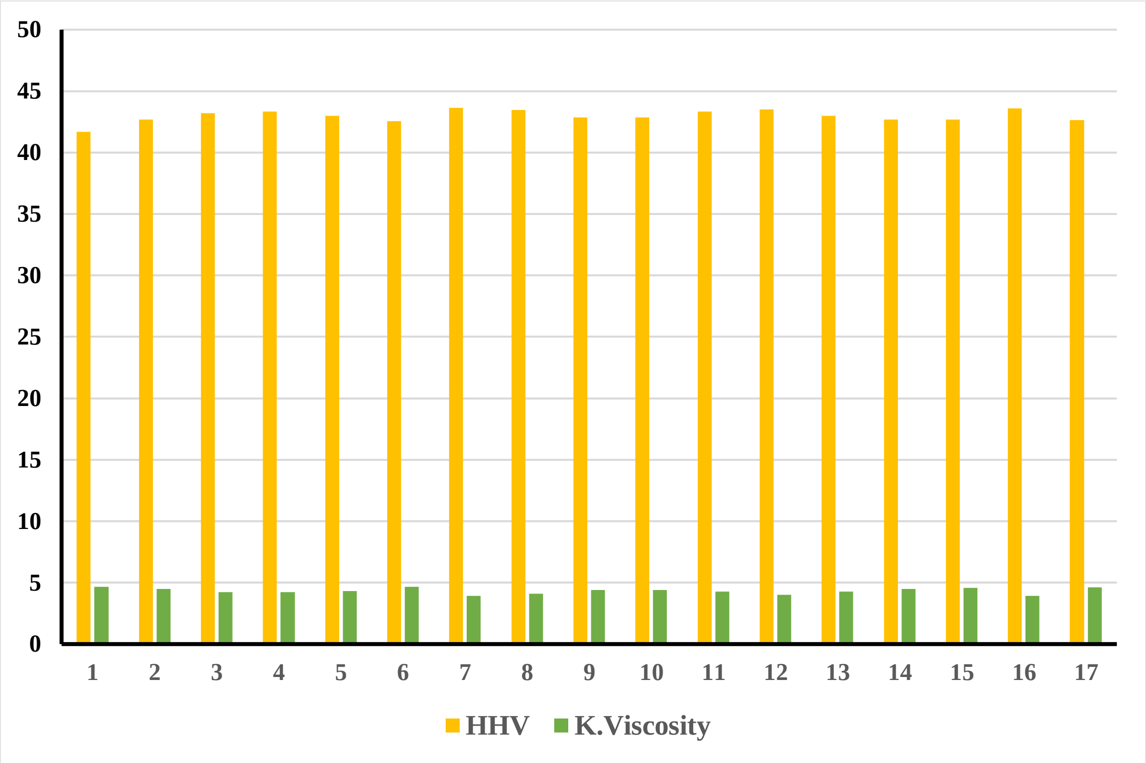

Fig. (6): The High Hating Value, and Kinematic Viscosity

3.8. Kinematic Viscosity

The kinematic viscosity KVI of biodiesel is a measure of its resistance to flow, and it can vary depending on factors such as the feedstock used, the production process employed, and the temperature at which it is measured. In general, biodiesel has a higher viscosity than petroleum diesel, which can impact its performance in engines.

The kinematic viscosity of biodiesel is typically measured in centistokes (cSt) at a specific temperature, such as 40°C or 60°C. The KVI value of biodiesel is typically lower than that of petroleum diesel, indicating that biodiesel is less sensitive to changes in temperature. The typical values for the kinematic viscosity of biodiesel at 40°Care in the range of 3.2-5.0 centistokes (cSt), while values for petroleum diesel are in the range of 2.0-4.5 cSt at the same temperature [42]. The kinematic viscosity of biodiesel can be affected by various factors, such as the degree of unsaturation of the fatty acids in the fuel, the presence of impurities, and the specific production process used. For example, biodiesel produced from feedstocks with a higher degree of unsaturation can have a higher viscosity than biodiesel produced from feedstocks with a lower degree of unsaturation. The viscosity of biodiesel can impact its performance in engines, particularly in terms of fuel flow and atomization. Biodiesel with higher viscosity can have reduced fuel flow rates and may require modifications to the fuel system to ensure proper performance. Additionally, biodiesel with a higher viscosity may have reduced fuel atomization, which can lead to incomplete combustion and increased emissions.

The results show that the viscosity values for all samples were within the range of biodiesel, where the values range between 3.93 and 4.66 cSt**,** Figure (6).

The results of iodine value, saponification value, cetane number, high heating value, density, and kinematic viscosity showed that sample 16 is the most one that met the quality criteria as good biodiesel fuel. The criteria were as follows:
1. The iodine value was within acceptable limits (49.4 g iodine /100g) of biodiesel, indicating low unsaturation and good oxidative stability.
2. The saponification value was 170.7 mg of KOH/g of biodiesel, which means it is within the acceptable limits, indicating the appropriate ester content and low free fatty acid content.
3. Cetane number (68.4) within acceptable limits, which indicates good ignition quality and engine performance.
4. The high heating value was 43.6 MJ/kg (> 36 MJ/kg), which ensures good energy content and efficient fuel use.
5. The density was 0.863, ensuring proper fuel flow and accurate volume measurements.
6. The value of the kinematic viscosity was 3.91cSt, which indicates the appropriate flow of fuel and its atomization in the engine.

To ensure the safe and efficient operation of engines, biodiesel samples must meet the quality criteria outlined above.

To further assess the quality and performance of sample (16), which was deemed to be the most favourable sample, we conducted additional biodiesel tests. These tests involved examining the fuel's flash point, pour point, and cloud point, as listed in Table (2). The results of these tests can offer valuable insights into the fuel's characteristics and its appropriateness as biodiesel.

Table (2): Physical Properties of The Best Sample (Sample 16):

Property	Result Value	Limits
Flash Point (ºC)	123	100-170 [42]
Pour Point (ºC)	-9	-15 – 16 [42]
Cloud Point (ºC)	3	0-10 [42]
Saponification Value (KOH/g)	160.2	170-200 [6]
Iodine Value (g I_2 /100g)	49.4	< 120 [7]
Cetane Number (MJ/Kg)	68.4	49-55 [37]
Density (g/mL^3) at 15°C	0.863	0.86 - 0.90 [38]
High Heating Value (MJ/kg)	43.6	39 - 43.33 [39]
Kinematic Viscosity (cSt)	3.91	3.2-5.0 [40]

4. CONCLUSION

Salicornia bigelovii has great potential as a renewable and sustainable source of biodiesel. The in-situ transesterification process of *Salicornia bigelovii* depends on the specific cultivation and fertilization techniques employed. The biodiesel produced from *Salicornia bigelovii* seeds irrigated with a mixture of 25% seawater and 75% well water and fertilized with nitrogen and microalgae exhibited excellent fuel properties, meeting the recommendations of US and European biodiesel standards. The produced biodiesel contained more than 35 wt. % of saturated fatty acid methyl ester (FAME) and over 50 wt. % of unsaturated FAME. Overall, the study demonstrates the potential of Salicornia plant oil as a vital source of renewable and clean energy that can help reduce toxic gas emissions and greenhouse gas emissions, enhance sustainability and biodiversity, and act as a diesel alternative to compression ignition engines. More research is needed to improve the cultivation and fertilization methods of Salicornia to increase oil yield and improve biodiesel production efficiency.

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Data Availability

The data supporting the findings of this study are available upon request.

Author Contributions

-All authors contributed to the study's conception and design.
-Material preparation, data collection, and analysis were performed by R. El-Araby, S.A. Abo El-Enin, A. I. Rezk, A. B. El-Nasharty and O. A. Nofal.
-The first draft of the manuscript was written by R. El-Araby, S.A. Abo El-Enin- and all authors commented on previous versions of the manuscript.
-All authors read and approved the final manuscript.

Plant Guidelines

The use of plants in the present study complies with international, national, and institutional guidelines.
Permissions to collect the plants: Not applicable.