



## Waste To Wonder: Production Of Bio-Diesel From Agri-Waste- A Comprehensive Review

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<i>Article History</i>	<i>Abstract</i>
Received: 30/09/2023 Revised: 15/10/2023 Accepted:30/10/2023	In the contemporary era, the world is grappling with the challenges posed by the excessive consumption of fossil fuels and the degradation of the environment. The quest for an alternative fuel source that aligns harmoniously with sustainable development, energy preservation, efficiency, and environmental protection has gained paramount importance. This issue is particularly salient in our modern lives. The physical and chemical attributes of vegetable oil closely resemble those of mineral diesel. Consequently, vegetable oil has emerged as a viable substitute for diesel. However, it's worth noting that unrestricted utilization of vegetable oils can lead to a range of engine-related complications. To address this, the process of trans-esterification has demonstrated its efficacy as a productive method to refine vegetable oil for use as fuel. This study focuses on conducting a comprehensive review of existing literature to assess the viability of pumpkin seed oil and its biodiesel as a feasible alternative to traditional diesel.
CC License CC-BY-NC-SA 4.0	<b>Keywords:</b> <i>Bio-diesel, Agri-waste, vegetable oil, trans-esterification, pumpkin-seed</i>

### Introduction:

Diesel fuel, being highly versatile and adaptable in various sectors such as construction, industry, agriculture, and transportation, is continuously extracted from the Earth's crust. However, the reserves of diesel fuel are finite and expected to be depleted within the next 35 to 45 years. Additionally, diesel engines release greenhouse gases, which have detrimental effects on plant and animal life. (Ahtesham *et al.*, 2020)

Biodiesel is composed of mono-alkyl esters of fatty acids and is produced from sources such as vegetable oils, used cooking oils, and animal fats. The majority of commercially-driven biodiesel production involves a trans-esterification process where triglycerides found in vegetable oils and animal fats react with mono-alkyl alcohols, typically facilitated by homogeneous base or acid catalysts. Selecting the appropriate fat or oil for biodiesel production is a decision influenced by both chemical and economic factors. In terms of chemical

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considerations, the primary distinction among various fat and oil options lies in the quantity of Free Fatty Acids (FFAs) present within the triglycerides. Another crucial parameter linked to the choice of oil is the iodine value. (Schinas *et al.*, 2009).

Vegetable oils and animal fats primarily consist of triglyceride molecules, where three fatty acid groups are bonded to a single glycerol molecule. Biodiesel can be produced from these triglycerides through the process of trans-esterification.

Biodiesel is a liquid biofuel produced through chemical reactions involving vegetable oils or animal fats and alcohol. It is suitable for use in diesel engines either on its own or in combination with regular diesel fuel. Biodiesel primarily comprises mixtures of alkyl esters and holds promise as a viable liquid alternative to conventional petroleum-based diesel fuel, primarily due to its similar fuel properties. (Ossai, 2011)

Biodiesel offers several advantages, including minimal sulfur and aromatic content, a higher flash point, improved lubricity, and a higher Cetane number. However, it also comes with some disadvantages, including higher viscosity, a lower calorific value, and lower volatility.

On a global scale, a 20% biodiesel blend with regular diesel fuel, known as B20, is widely accepted and recognized as a suitable compromise. When using B20, emissions of hydrocarbons (HC) and carbon monoxide (CO) are reduced compared to using pure diesel fuel. However, it's important to note that nitrogen oxides (NO<sub>x</sub>) emissions tend to be higher with B20 than with pure diesel. (Shaikh *et al.*, 2020)

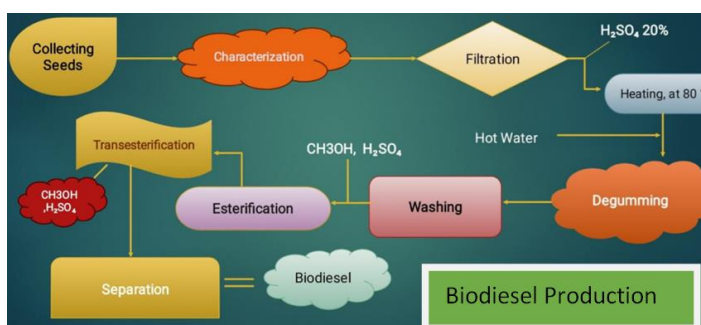
Pumpkin seeds, derived from the Cucurbita species, have typically been regarded as agricultural byproducts and often go unused. While in some regions of the world, these seeds are consumed in various forms like raw, roasted, or cooked, it has primarily been at the household level. Recently, Greece has witnessed a growing acceptance of FAME (biodiesel) as a substitute for petroleum diesel. In Greece, the primary raw materials for biodiesel production include traditional seed oils such as cottonseed oil, sunflower oil, soybean oil, and rapeseed oil, as well as used frying oils.

In the pursuit of new, cost-effective alternative sources for biodiesel production, researchers at the National Technical University of Athens in Greece have conducted a study focused on the evaluation of pumpkin (Cucurbita pepo Linn.) seed oil. Based on existing literature, pumpkin seeds are recognized as a valuable biodiesel source in Ethiopia, where they are readily available as a local raw material for biodiesel production. However, it's worth noting that there is currently no commercial application of pumpkin seed for biodiesel in Greece. (Ossai *et al.*, 2011).

Therefore, this research delved into the characterization of pumpkin seed oil and examined its conversion into FAME (fatty acid methyl esters) through a base-catalyzed trans-esterification process.

### Methods for production of bio-diesel :

**Sample Treatment and Sampling:** Mature seeds of pumpkin, locally known as "Kabushi" in the Hausa language of the area, were gathered at the Kasuwar Daji markets near the city of Sokoto. Before the initial processing, these collected seed samples were kept inside a bag made of polyethylene in a lab environment. The seeds were carefully dehulled to retrieve their seed kernels, that were then ground into a powder in the laboratory atmosphere utilizing a pestle along with mortar. The resulting oil was then physically extracted using a steamy water stirring technique from the crushed seed samples.



**Fig 1:** Different Steps of biodiesel production

**Transesterification:** Using a base-catalyzed procedure, the extracted oil's transesterification was completed. Typically, vegetable oils have a low free fatty acid content. Therefore, a homogeneous transesterification process was employed, using a procedure outlined by Demirbas *et al.* (2005). In a nutshell, 1 gram of potassium hydroxide (KOH) dissolved in methanol (75 cm<sup>3</sup>) was combined with C (100 grams). Pepo oil was placed in a corked, 500 cm<sup>3</sup> round-bottom flask. A magnetic stirrer was used to agitate the liquid for 5 minutes. The mixture was then cooked for an hour at 60°C on a water bath. It was then moved into a separation funnel and left to stand the following day. This led to the development of two separate layers: an upper, yellowish layer (biodiesel) and a thick, brown level at the bottom (glycerol). The remaining methanol was removed from the biodiesel layer by heating it at 90°C in an evaporating dish over a water bath. After that, the methyl esters were rinsed with 5 cm<sup>3</sup> of 0.1 M phosphoric acid and 1:5 cm<sup>3</sup> of water till the wash water's pH reached 7.0. Heating the methyl ester using hot anhydrous sodium sulphate (1000 °C) eliminated the remaining water.

**GC-MS Analysis:** A QP-2010 type GC-MS equipment was used to characterize the biodiesel. A 2µl specimen from the biodiesel was put through the gas chromatograph during the examination. With an ignition rate of 50°C per minute with a holding duration, the temperature of the oven program had a range of 60 °C to 2800 °C. Helium gas was used as the carrier gas while a column was used to separate the injected sample within the gas chromatograph. The study was carried out using a mass sensitive detector in scan mode. Software was used to identify components by contrasting their mass spectrum to reference mass spectrum. To calculate the components' weight ratios, the respective peak regions of each component were employed. Equations 1 and 2 were used to calculate the biodiesel's saponification and iodine values, respectively (Mohibbe *et al.*, 2005).

$$IV = \sum \frac{(254 \times D \times A_i)}{MW_i} \quad (1)$$

$$SV = \sum \frac{(560 \times A_i)}{MW_i} \quad (2)$$

In the provided equation: **IV** represents the **value of Iodine**, **SV** represents the **value of saponification**, **D** represents double bond number, **A<sub>i</sub>** represents the % breakdown of a certain ester, **MW<sub>i</sub>** represents a certain ester's molecular weight.

Equation 3 was used to determine the cetane number, according to Mohibbe *et al.* (2005), as a measure of the ignition quality of the biodiesel. Additionally, the Equation 4 was used to evaluate the biodiesel's high heating value to determine its energy content or calorific value. These calculations are essential for evaluating biodiesel product's the performance and energy characteristics.

$$CN = 46.3 + \frac{5458}{SV} - 0.225 \times Iv \quad (3)$$

$$HHV(MJ / kg) = 49.43 - 0.041(Sv) - 0.015 (Iv) \quad (4)$$

$$DU = (\text{monosaturated Cn: 1 wt \%}) + 2 (\text{Polyunsaturated Cn: 2, 3 wt \%}) \quad (5)$$

Equation 5 was used to calculate the degree of unsaturation (DU), as explained by Mohibbe *et al.* (2005). This equation relies on the percentages of monounsaturated and polyunsaturated FAMES (Fatty Acid Methyl Esters) in the produced biodiesel to determine the level of unsaturation present in the fuel. The DU value provides important information about the biodiesel's chemical composition and properties related to its combustion and stability.

## Discussion:

Methyl tetradecanoate (C<sub>15</sub>H<sub>30</sub>O<sub>2</sub>) is present in the biodiesel made from C. pepo oil at an amount of 0.4% by weight, according to the composition of the methyl ester. (Ahtesham *et al.*, 2020). This article focuses on one of the distinctive ingredients present in biodiesel generated from C. pepo oil.

Methyl (12E)-octadecenoate (C<sub>19</sub>H<sub>36</sub>O<sub>2</sub>) and methyl hexadecanoate (C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>), each making up 9.63% and 82.90% of the content, were also found in the biodiesel. methyl docosanoate (C<sub>23</sub>H<sub>46</sub>O<sub>2</sub>), Methyl eicosanoate

( $C_{21}H_{42}O_2$ ) and methyl tetracosanoate ( $C_{25}H_{50}O_2$ ), having relative percentages of 2.48%, 0.97%, and 0.47%, were also revealed to be esters in the biodiesel. Notably, the profile revealed that the major molecule in the mixture, accounting for the largest percentage at 82.90%, was methyl (12E)-octadecenoate ( $C_{19}H_{36}O_2$ ).

According to Knothe (2009), one of the most important factors in assessing whether a feedstock is suitable for the synthesis of biodiesel is its fatty acid methyl ester (FAME) profile. Monounsaturated methyl (12E) octadecenoate is the most prevalent ester in *C. pepo* biodiesel. (Ahtesham, *et al.*, 2020) This is a positive feature for the biodiesel's stability because a higher degree of unsaturation in FAMEs can lead to polymerization and peroxidation issues, especially at elevated temperatures encountered in combustion engines, resulting in the formation of gum-like polymerized fatty methyl esters (Gaby and Peter, 1997).

Feedstocks with a high percentage of polyunsaturated fatty acids are generally unsuitable for biodiesel production. However, since the dominant FAMEs in *C. pepo* biodiesel, namely they are monounsaturated, methyl hexadecanoate and methyl (12E) octadecenoate are less susceptible to fast peroxidation. and may exhibit better stability. These dominant FAMEs share similarities with the major FAMEs found in *Jatropha curcas*, which has percentages of 14.3% and 51.7% for these esters, respectively. Additionally, olive oil and palm methyl esters, known for being good biodiesel feedstocks (Andrew *et al.*, 2009), also feature methyl hexadecanoate and methyl (12E) octadecenoate as dominant esters, comparable to those in *C. pepo* biodiesel. Furthermore, in rape seed methyl esters, methyl hexadecanoate and methyl (12E) octadecenoate had component percentages of the most prevalent esters, which were 3.86% and 77.9%, respectively (Bangboye and Hansen, 2008). Similar findings were reported for *Annona reticulata* and *Rhus succulanea* Linn, as indicated by Harrington (1986), Therefore, One can assume that *C. pepo* FAMEs exhibit characteristics that make them a potentially suitable material for biodiesel production, given their monounsaturated composition and resemblance to FAME profiles in other successful biodiesel feed stocks production.

The Cetane number (CN) serves as a critical parameter in assessing the quality of diesel fuel, as it is linked to both the ignition delay time and combustion characteristics. A higher cetane number indicates superior ignition properties, as noted by Meher *et al.* (2006), and indicates that the methyl ester is of a higher quality to be used as diesel fuel. For an engine to work at its best, the cetane number must be sufficient. High cetane ratings improve cold starting abilities and reduce the amount of white smoke produced during combustion. Typically, the cetane number is determined by comparing the fuel's behavior with that of a reference fuel, often n-cetane.

In this study, cetane numbers for biodiesel are estimated using Equation (Ahtesham,*et al.*, 2020), providing a valuable insight into the fuel's ignition characteristics and quality for diesel engine use.

In the case of biodiesel derived from *C. pepo* seeds oil, the dominant ester features a longer carbon chain and low unsaturation, indicating an expectedly high cetane number of 60.01. This suggests that biodiesel made using *C. pepo* seed oil has excellent ignition quality.

Standards such as UNE-EN 14214 (2003) specify a at least cetane number of 51 for biodiesel, while ASTM D6751-02 sets the at least cetane number at 47. According to these standards, *C. pepo* biodiesel exceeds the minimum requirements, indicating good ignition properties.

Low cetane numbers have been associated with highly unsaturated components like esters of linoleic (C18:2) and linolenic (C18:3) acids, which were not detected in *C. pepo* biodiesel. This aligns with findings by Van Gerpen (1996) and Knothe (2003), who discovered that methyl palmitate had high cetane levels ( $C_{16}:0$ ) and stearate ( $C_{18}:0$ ), while methyl lenolenate had a very low cetane number.

The cetane values obtained in this study are in agreement with those reported for soybean oils (ranging from 45 to 60) and rapeseed biodiesel (ranging from 48 to 61.2) in the study by Bangboye and Hansen (2008).

Kinematic viscosity ( $\nu$ ) is a measure of a fluid's resistance to flow under the influence of gravity. In the context of fuel, viscosity plays a significant role in the functioning of engine fuel injection and atomization systems. It can also impact engine wear and the tendency of fuel injectors to become fouled.

The structural makeup of the crude or virgin oil utilized in the manufacturing of biodiesel has an impact on its viscosity. According to research by Knothe (2008) and, viscosity generally tends to rise with the quantity of  $CH_2$  molecules (methylene groups) within the fatty ester chain and fall with increasing unsaturation. This indicates that biodiesel has a reduced viscosity because of the many double bonds (unsaturation) present in the chemical structure. Because of the degree of unsaturation throughout the main constituents of the ester, the created biodiesel mentioned in your earlier communications may have a somewhat high viscosity. It is crucial to comprehend biodiesel viscosity because it affects engine maintenance and performance. Iodine value: The amount of overall unsaturation in a combination of fatty acids is measured by the iodine value. The quantity

of iodine needed to iodize each the double bonds that are in the biodiesel is referred to as the iodine requirement. The measurement is in grams of iodine per 100 grams. According the requirements of the European biodiesel standard (UNE-EN 14214, 2003), the iodine value is restricted to 120 g I<sub>2</sub>/100 g. Due to the substantial amount of unsaturated fats in most vegetable oils, the European Biodiesel Standard's requirement of 120 g I<sub>2</sub>/100 g precludes several viable oil sources (Mittelbach and Remschmidt, 2004). With an iodine value that is in line with EN 14214 criteria, biodiesel made from *C. pepo* seeds oil has a moderate level of unsaturation. This further confirmed its usefulness for the production of biodiesel.

kinematic viscosity and its significance in the context of fuel, particularly biodiesel, very important. Indeed, The parent oil's structural makeup, which is utilized to create biodiesel, significantly affects the viscosity of the fuel. A higher amount of CH<sub>2</sub> groups in the chain of fatty ester tends to increase viscosity, while greater unsaturation, characterized by multiple double bonds, leads to lower viscosity. This understanding is crucial, as biodiesel viscosity can influence engine performance, fuel injection, and injector maintenance, making it an important consideration in the evaluation of biodiesel quality and suitability for use in engines.

When evaluating fuel consumption, the heat of combustion becomes a key factor. According to Knothe *et al.* (2008), reduced fuel consumption is indicated by an increased temperature of combustion. A European standard for utilizing biodiesel as heating oil, EN 14213, provides a minimal heating value requirement of 35 MJ/kg but biodiesel standards like ASTM D6751 and EN14214 do not.

Longer carbon chains have a tendency to produce more heat of combustion, while more instauration results in less heat of combustion. The fact that the diesel made from *C. pepo* exceeds the minimal heating value needed for heating oil suggests that it has the potential to be an important addition to petroleum diesel. This implies as *C. pepo* biodiesel may function well as a substitute in a variety of fuel applications.

### **Conclusion:**

The source material, sometimes referred to as the feedstock, has a considerable impact on several final biodiesel product qualities because it is mainly utilized as a fuel. Cetane number, cold flow characteristics, and stability are only a few examples of these qualities. The findings of the analysis showed that methyl oleate is the main ingredient in the biodiesel made from *C. pepo* seed oil, and polyunsaturated methyl esters were not found in the sample. The biodiesel thus shows no instability susceptibility. The produced biodiesel's cetane number also complies with ASTM requirements, and its heating properties are comparable to those found in other biodiesel products on the market. Consequently, it is advised to utilize biodiesel made from *C. pepo* seed oil for an effective substitute for diesel fuel.

### **Future scope:**

Over the last thirty years, there has been notable progress in the advancement of biodiesel as a renewable energy source. While embracing biodiesel presents both opportunities and challenges, it is imperative to substitute a portion of our prevailing conventional fossil fuel energy sources. This becomes especially significant given that food waste can contribute to environmental issues such as greenhouse gas emissions, presenting a significant obstacle to attaining sustainable development. We anticipate witnessing its widespread integration within the automotive sector and the emergence of new innovations in the coming years.

### **Authors' contribution**

Dr. Rupali Dhara Mitra conceptualized the topic. Priya Rani Ghosh and Debaksi Saha done all the necessities to execute the review paper. Soumyaduti Chowdhury prepared all the figures and tables in the manuscript. Dr. Rupali Dhara Mitra provided comprehensive editing and a final revision for the entire manuscript.

### **Conflict of Interest**

Authors declare no conflict of interest.

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