

Green valorization of waste date seed oil for biodiesel production

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Abstract

During recent decades, focus has increased on biodiesel production from wastes or other nonedible resources. The high expense of the manufacturing process is one of the major obstacles it faces. So, continuous research for cheaper and safer resources is more important. Seed oil from various vegetables and fruit species has garnered a lot of attention recently in the production of biodiesel, such as date palm. The date palm is one of the most popular fruits in the Middle East. Egypt has recorded now as the highest countries production of dates. The oil of date seeds (DSO) has high concentrations of fatty acids and minerals. In biodiesel production, lipid extraction is an important step. But the advanced extraction techniques are preferred to protect human health and the environment. Therefore, the demand for innovative and environmentally friendly products is now necessary. Transesterification is the process in which oils (mostly triglycerides) bond with alcohol in the existence of a catalyst to form an alkyl ester. Synthesizing the green catalyst and utilizing it in the manufacture of biodiesel have a great added value. The high yield of biodiesel supports the catalyst suitability for the transesterification reaction. Immobilized lipase, moreover, plays a critical function in the transesterification process, that it is more effective and safer. DSO is being studied to see if its fatty acid profile or physicochemical properties suggest it could be a suitable biodiesel source.

1. Introduction

Energy consumption has increased, particularly during pandemics such as Covid19. Researchers and policymakers should do a study on circular bio economic methods. Waste biomass conversion to sustainable fuel via an up-cycling process provides an appropriate path for economic growth. Biodiesel is widely regarded as one of the most well-known alternative vehicle energizers for diesel engines with comparable actual properties, and it is utilized in diesel engines without or with minor changes (Balat et al. 2010; Demirbas 2009; Singh and Sharma et al 2009; Kalam; Masjuki 2002)

Biodiesel is a trans fatty methyl ester derived from plant oils including rapeseed, jatropha, sunflower, cottonseed, corn, palm, and soybean oil, as animal fats, waste cooking oil, and microalgal oils (Lee et al 2014). Transesterification of fatty compounds or esterification of free unsaturated fatty compounds can be used to produce biodiesel. Biodiesel differs from fossil-based diesel in terms of biodegradability and toxicity, as evidenced by lower sulphur content and an increase in the flash point of additional diesel fuel (Yee et al 2009.) It is critical to recognize that there are three techniques of mitigating environmental change, with renewable energy being one of the most frequent (Carmo et al 2009). Biodiesel produced from non-edible vegetable oil is a viable answer because it does not compete with human food. Date processors commonly discard date seeds. Except for small amount used for animal feed such as chicken, camel, sheep, and cows, date seeds remain a weight as large trash. Date seeds may be collected in large quantities from date processing factories and companies using either fast or irregular methods. The Phoenix *Dactylifera* (date palm) is the main tree in Middle Eastern nations, for all intents and purposes in the Gulf participation chamber nations (Mekhilef et al 2011). In certain nations, the date palm is the most important crop, accounting for more than half of total farmed area. Dates are a staple part of many people's diets, and they can be consumed raw or in many processed forms. The date palm is one of the most genetically diverse plants on the planet. Date yield increases seasonally, while harvesting losses increase. Because of its high content of free unsaturated lipids, date seed oil cannot be easily converted to biodiesel. As a result, the preparation of date seed oil must be more complicated. Cleansers are described as a side effect that occurs when a large homogenous catalyst is utilized for the transesterification of oil feed with FFAs, resulting in a decrease in the provided biodiesel yield owing to saponification. At the Tamar stage, once they are ready for harvesting, date varieties can be classified according to a variety of characteristics. Dates are generally elongated, oblong, or oval in shape, however some varieties, such as Algeria's Tinteboucht, are somewhat spherical. Their length varies between 1.5-7 or 8 cm, and their weight varies between 2–15 g. They are available in a range of hues, ranging from yellowish white to extremely dark brown, almost black, as well as amber, red, and brown (Lobo et al 2014; Soliman et al 2015). The fruit of the date palm is good enough as a dependable supper. It is composed of a fleshy seed coat and a seed, as seen in Fig. 1. Dates' chemical composition varies depending on cultivar, soil conditions, agronomic practices, and ripening stage. Dates mature in stages, which are generally described by changes in color, texture, and flavor (Nehdi et al 2018; Sirisena et al 2016).

The optimization of biodiesel production based on date seeds as a cheap environment source was achieved by employing the response surface approach (RSM) in conjunction with central composition design (CCD) (Khalil et al 2017; Atabani et al 2012).

The Life cycle assessment (LCA) can be applied to show the environmental impacts from life cycle for biodiesel made from seed palm. This review will focus upon date seeds biomass, collection, and characterization, date seeds oil extraction, chemical catalysis for oil transesterification, Biocatalysts for transesterification process, biodiesel characterization and evaluation, life cycle assessment, economic impact (visibility study), or cost analysis.

2. Date Seeds Biomass, Collection & characterization

Since diesel fossil fuel supplies are diminishing and will eventually run out (Jimmy 2015) a fossil-fuel replacement must be developed to meet predicted energy demands (Hariram, and Bharathwaaj 2015; Rajagopal et al. 2015b; Daryono 2015). The world's attention is directed towards the use of biofuels instead of fossil fuels for several reasons, the most important of which is that it is considered a source of renewable and clean energy, unlike fossil fuels such as petroleum, which is believed to be depleted within the next ten years (Kamil et al. 2019). Biofuels, including biodiesel Seed oil from various vegetable and fruits species; has lately attracted much interest in the production of biodiesel such as date palm seeds oil, soybean oil, castor oil, Parkia biglobosa oil, Jatropha curcas oil, sunflower oil, coconut oil, rapeseed oil, safflower oil, groundnut oil, neem oil, peanut oil, and cottonseed oil (Aransiola et al. 2012; Berchmans; Hirata 2008). The date palm, also known as Phoenix dactylifera, is a well-known fruit in the Middle East (Al-Farsi and Lee 2011). Al-Farsi and Lee (2011) reported that the date palm is the main crop in some countries, accounting for over half of the total agricultural zone, and the date palm's large residue is the seeds, which account for nearly 10–15% of the overall residue and are therefore inedible. According to Al-Abdulkader et al. (2016) Egypt is considered one of the first countries in the production of dates of all kinds and varieties, followed by the state of Iran and Saudi Arabia and as a result of that, there are huge quantities of date waste Fig. 2.

Therefore, unused dates are considered one of the most important resources for alternative energy, which scientists are now turning to use as an alternative to biofuels. Where there are now strategies to get rid of agricultural waste in a new and innovative way instead of throwing it in a landfill.

2.1. Date Seeds Biomass, Collection

Date seeds are available near to where dates are packed or processed. The high-quality date seeds are collected from several different sources, then they were hand- isolated and soaked in a large basin filled with water, where they were washed several times to take off any lasting date flesh and then left to dry in the sun for a period of 3 to 7 days, then they were sited in the oven at a temperature of 60°C overnight (Jamil et al. 2016). The date seed was then mashed using a mortar and pestle before being crushed with a heavy-duty crusher and passing through a 0.6 mm screen filter (Al-Farsi et al. 2007). Figure 3 illustrates the process of collection.

2.2. Chemical Composition of Date Seeds

There's been a lot of research done on the constitution of date seeds from all over the globe. Table 1 summarizes the contents of various date kinds of seeds based on several publications. The variations might be attributed to the diversity of cultivars examined as well as meteorological circumstances (Golshan Tafti et al. 2017; Saafi et al. 2008). The fat content of date seeds varies depending on variety, provenance, harvesting season, and fertilizer (Abdul Afiq et al. 2013). Saafi et al. (2008) found 6.88: % moisture, 8.12: % total sugars, 6.63: % reducing sugars, 1.49: % sucrose, 5.31: % protein, and 8.33: % fat in the seeds of a combination of developed traditional date arrays called "Khalti." Protein 5.56; and 5.17; % fat 10.19 and 12.67; %, ash 1.15; and 1.12; %, and total carbohydrate 83.1; and 81.0; % were also attained for Deglet Nour and Allig cultivars, one-to-one. The seeds of Kabkab and Shahani date varieties from Bushehr, Iran, enclosed 10.50% moisture 5.56% protein 12.59% lipid, 62.18% soluble fiber in acidic solutions, and finally 1.35 percent ash, accordingg; to Amir Azodi et al. (2014). Date seeds, on the other hand, are primarily composed of carbohydrates and fat. Also, seeds from three different date diversities (Fard, Khalas, and Lulu) in the United Arab Emirates contain from;7–10; % moisture, 9; -13.5; % protien, 1-1.8; % ash. The date seed, according to Amany et al. (2012), contains 3.10; -7.10% moisture 2.30; -6.40% protein, 5; -13.20% fat, 0.9; -1.80% ash, and 22.50; -80.20% dietary fiber. In contrast to date fruit, date seeds have a relatively high protein and fat content (1.5; -3% protein and 0.1; -1.4% have fat) (Al; -Farsi and Lee 2011). Date fruit proteins contain the bulk of necessary amino acids (Al-Farsi and Lee 2014) and have a greater concentration of sulphur amino acids (methionine, cystine) than some other seed proteins (soybeans, peanuts, cottonseed).

Glutamic acid, aspartic acid, and arginine account for almost half of the amino acids recovered from the seeds of the Ruzeiz and Sifri date types. Tryptophan is the first preventative amino acid found in date seed proteins. Abdul Afiq et al. (2013) found that date seeds have higher lysine content. Date seeds contain soluble proteins such as (albumin, globulin, and glutelin). Date seeds have high fiber content, with 77.8; – 80.2 g/100 g fresh weight (Al-Farsi et al. 2007) or 64.5; -80.15 g/100 g fresh weight (Al-Farsi and Lee 2011). Some date seeds contain 58%total dietary fiber, with 53 percent% of that being insoluble dietary fiber (hemicellulose, cellulose, and lignin). Dietary fiber variations are linked to the maturation stage and variety (Abdul Afiq et al. 2013).

The seeds of three date varieties (Fard, Khalas, and Lulu) in the United Arab Emirates produced 51% acid cleansing agent fiber and 65–69% neutral cleansing agent fiber, suggesting a high lignin level and resistant starch (Ibrahim et al. 2021). Date seeds contain many dietary minerals, including Na, K, Mg, Ca, P, Fe, Mn, Zn, Cu, Ni, Co, Cr, Pb, and Cd; (Abdillah and Andriani 2012; Abdul Afiq et al. 2013). Date seeds have higher concentration of P, Mg, K, Ca, and Na (Demirbas 2017). In some data among the microelements, Fe, Mg, Zn, and Cu are also present in higher concentrations. Phosphorus was discovered in trace amounts in the seeds of different date cultivars in Saudi Arabia's Qassim region (0.19–0.26 percent). Another mineral found in date seeds is selenium. The selenium content of ten date varieties grown in Saudi Arabia ranged from 1.48 to 2.96 mg/g. Some date varieties have a high selenium concentration, which may be associated with the earth's selenium content (Al-Farsi and Lee 2011). Table 2 lists most of the components found in various date seed types. According to some authors when methanol–water, acetone–water, ethanol–water, and water alone were used as solvents for extraction at temperatures of 22, 45, and 60° C, the polyphenol content of date seeds ranged from 21 to 62 mg gallic acid equivalents/g date seed (Guizani et al. 2014).

Table 1:The chemical composition of some date seeds varieties

| Date varieties | Moisture | Fat | Protein | Ash | Total carbohydrate | References |
|---------------------------|-----------------|------------|----------------|------------|---------------------------|------------------------|
| Khalti | 6.88 | 8.33 | 5.31 | - | - | Saafi et al. 2008 |
| Allig | - | 12.67 | 5.17 | 1.12 | 81 | Al-Zahrani et al. 2022 |
| Deglet Nour | - | 10.19 | 5.56 | 1.15 | 83 | Al-Zahrani et al. 2022 |
| Kabkab and Shahani | 10.5 | 12.5 | 5.5 | 1.35 | 8.65 | Amir Azodi et al. 2014 |
| Fard (UAE) | 10.3 | 9.9 | 5.7 | 1.4 | - | Ibrahim et al. 2021 |
| Khalas(UAE) | 7.1 | 13.2 | 6 | 1.8 | - | Ibrahim et al. 2021 |
| LuLu (UAE) | 9.9 | 10.5 | 5.2 | 1.0 | - | Ibrahim et al. 2021 |

Table 2
The minerals contained in different date seeds

| Date varieties | Na mg/100g seeds | P mg/100g seeds | Ca mg/100g seeds | Fe mg/100g seeds | Cu mg/100g seeds | Mg mg/100g seeds | Mn mg/100g seeds | Z mg/100g seeds | References |
|----------------|------------------|-----------------|------------------|------------------|------------------|------------------|------------------|-----------------|------------------------|
| Allig | 10.35 | 293 | 28.90 | 2.2 | - | 58.40 | - | - | Al-Zahrani et al. 2022 |
| Deglet Nour | 10.40 | 229 | 38.80 | 2.30 | - | 51.70 | - | - | Al-Zahrani et al. 2022 |
| Kabkab | 160 | 2489.3 | 189.3 | 19.2 | 5 | 811.3 | 7.12 | 1.6 | Amir Azodi et al. 2014 |

2.3. Date Seeds Biomass Characterization

Characterization of dry date seeds should be occurred by using proximate and ultimate analysis to determine physicochemical properties. As part of the proximate analysis, the humidity, ash content, volatile matter composition, and fixed carbon content are all assessed. The moisture content can be determined for 24 h at 150°C by evaluating the mass consumption (Robles-Medina et al. 2009). Volatile matter content was evaluated at 350°C for 3 h by putting the dry biomass sample inside (Lenton furnace) to measure the mass consumption due to volatile substance (Saafi-Ben Salah et al. 2012). The fixed carbon content of the biomass was determined using the residue left after the volatile matter was ejected, which included both mineral matter and non-volatile carbon, using ASTM Standard Method Number E1755-01, which involved burning the biomass at 650°C for 6 hours in open crucibles on a dry weight basis. The bulk density was determined by filling a 10-ml tube with dry adsorbent. The tubes were sealed, and then tapped on a table to ensure a constant capacity before being weighed. Particle density was determined using a volume displacement technique (Khanmohammadi et al. 2015) that employed water instead of kerosene. After mixing 1 g of powdered biomass with 20 mL deionized water (1:20) and heating to 90°C with continual stirring for 20 minutes, the pH of the biomass was measured using a pH meter (Ahmad et al. 2010; Demirbas 2017). The ultimate analysis is an elemental analysis that employs a Stable Isotope Analyzer (SIA) to determine the carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) content (Eurovector EA 3000 elemental analyzer). All measurements were made in triplicate at room temperature (23°C). The moisture content and ash content of date seed are (5–10% & 1–2%), respectively, (Bouchelta et al. 2008; El May 2012) as well as the volatile content, fixed carbon, and bulk density (74%, 17.5% & 656). Based on these data, we may deduce that the date seed biomass had a high volatile content, low moisture content, and a high bulk density. The biomass included little ash (inorganic compounds) and had a pH of 4.8, suggesting that it was acidic.

Date seeds are more appropriate as a biodiesel feedstock if they have a greater volatile content, fixed carbon, bulk density, and lower ash level, according to previous studies.

3. Extraction Of Date Seed Oil: Traditional And Innovative Methods

A few recent studies suggested that date seed oil (DSO) may be utilized as a biodiesel feedstock. However, they only looked at the manufacturing processes and how various factors impact oil extraction and biodiesel yield (Al-Zuhair et al. 2017). Furthermore, because only a few DSO biodiesel characteristics have been measured against industry standards, it is uncertain if the final fatty acid methyl ester (FAME) product fulfills biodiesel criteria (Azeem et al. 2016; Jamil et al. 2016). With a content of 5–13 percent, the date seed oil is high in phenolic compounds, tocopherols, and phytosterols (Nehdi et al. 2010). Other authors have researched date seed oil, and its high concentration of ν fatty acids and minerals sorts it useful in food products (Habib et al. 2013). Cold extraction and traditional Soxhlet extraction are the most frequent procedures for extracting oil from a solid plant matrix. Both are simple to operate and effective in extracting all types of lipids, but they are sluggish and create a lot of chemical compounds that are exhaled. As a result, health and environmental issues such as emissions and toxicity limit their ability to operate. Alternative new technologies such as microwave, ultrasonication, supercritical fluid extraction (SC), and solvents have been introduced in recent years and are based on a range of concepts. These technologies provide a more environmentally friendly (green technology) alternative that makes use of less hazardous chemicals including ethanol, isopropanol, butanol,

acetic esters, and combinations of these compounds. When compared to solvent extraction techniques, these methods have some benefits (significantly reduced solvent quantity, temperature, and extraction time) (Chen et al. 2020).

3.1. Conventional extraction techniques

Lipid extraction is a crucial stage in of the manufacture biodiesel. Lipids are chemical substances that decompose in organic solvents not even in polar solvents. These compounds include fatty acids, phospholipids, acylglycerols, phytosterols, fat-soluble supplements, and carotenoids (McClements et al. 2009).

3.1.1. Oil extraction using different chemical solvents

The most prevalent technique for extracting oil is organic solvent extraction. Although there have been minor improvements over the years, the Folch and Bligh and Dyer methods are the oldest techniques for total lipid extraction. Both processes are very similar. However, the solvent-to-solvent and solvent-to-tissue ratios differ (Ranjith Kumar et al. 2015). The Folch technique removes lipid from homogenized cells using a chloroform-methanol (2:1 v/v) solution (Folch et al. 1957; Cheirsilp and Torpee 2012). The lipids settled in the upper phase of the resulting mixture, which was allowed to split into two layers. The ability to process a large number of samples quickly and easily is a significant benefit of this technique. However, when compared to other recent processes, it is less delicate (Ranjith Kumar et al. 2015). The Bligh and Dyer technique extracts lipids using a chloroform; -methanol (1:2 v/v) solution (Bligh and Dyer 1959). These solvents have properties like high solvent–solute ratio, oil viscosity, polarity, and easygoing to remove from extracts by evaporation (Takadas and Doker 2017). The capability of the solvent to drive the extraction process and achieve total value determines the type of solvent used. The date seed is washed, dried, then pulverized in an organic solvent process to break the oily cells and make the oil available to the solvent. The mobility of the solvents to the oil-containing cells determines the extraction yield. Soxhlet extraction is perhaps the most widely used process for oilseed extraction, and it is widely accepted as a standard. During solvent extraction, the primary process at work is diffusion. Whenever the seed comes into contact with the solvent, the solvent spreads throughout the seed mass, extracting the oil from the fissures in the fat cells. Rota vapor is then used to separate the oil from the solvents (Thyagarajan 2012). Hexane has been used as an extraction solvent by many researchers and industrialists because of its availability, high oil extractability (98%), and ease of use. Although Soxhlet extraction yields a higher oil extraction yield, it produces much more complicated extracts and has certain disadvantages that are particularly harmful to the therapeutic and oil trades just like lengthy running, extraordinary solvent ingestion, and in addition to the existence of solvent residual in the end result, a large quantity of organic solvents is discharged into the atmosphere.

3.2. Advanced Extraction Techniques

The extraction of bioactive substances using organic solvents is becoming increasingly limited, to protect human health and environmental protection (De Melo et al. 2014). The demand for innovative and environmentally friendly products is now necessary. These systems have many benefits, including lower costs and shorter processing times (as little minutes), as well as increased oil quality. Advanced extraction techniques, on the other hand, to improve extraction performance, they've been utilized to augment traditional extraction procedures.

3.2.1. Ultrasonic-Assisted Extraction (UAE)

Sonication-assisted or ultrasonic-assisted extraction (UAE) is a new and emerging method for extracting vegetable oils from a variety of seeds. It reduces extraction time, reduces solvent consumption, is simple to usage and energy effective (Gordon et al. 2018; Rajha et al. 2019) and can also be scaled up to an industrial level (Rajha et al. 2019). Because of its role in sustainable development, its debut as a unique green technology had gotten a lot of attention. UAE is an advanced approach that uses high-intensity, high-frequency ultrasonic sound waves to improve the physicochemical properties of plant tissues, as well as to increase vibration (plant cell wall breakdown), enabling for improved interaction between the solvent and the plant measurable and the relief of recoverable components (Chen et al. 2020). Cavitation occurs when ultrasound is passed through a liquid, which causes cell disruption. Sound wave propagation and interaction modify materials' physicochemical properties, triggering a sequence of pressure variations in the solvent and the formation of microbubbles in the liquid. That marvel is termed "acoustic cavitation" and generates annihilation of the cell wall. UAE improves the accessibility of the solvent into plant cells as a result of

several physical effects: on seed surfaces, cavitation, and the creation of cracks and microfractures (Jadhav et al. 2016). The use of UAE is a unique approach for enhancing oil recovery while increasing the efficiency of bioactive chemical extraction from plants and seeds. The United Arab Emirates is noted for reducing extraction times and enhancing production efficiency. The productivity of UAE seed oil extraction was comparable to or better than traditional extraction (Soxhlet), but with a significant reduction in extraction time. (Elcioglu and Murshed 2021). This has also been verified when it comes to extracting oil from date seeds (Jadhav et al. 2016), with the result that the UAE method lowers extraction time (by 75% compared to the Soxhlet scheme), which assembly a more operative process because of its minimal energy usage (76.64 percent below Soxhlet). When dealing with papaya seeds, it took just 30 minutes to obtain a 76.1 percent oil production, compared to 12 hours for Soxhlet (Samaram et al. 2013). The UAE, on the other hand, has a drawback. The medium's high energy level promotes free radical production, decreasing the oil's oxidation stability when used for oil extraction (Samaram et al. 2015). The oxidation chain events that give oxidized oils their unique taste is started by free radicals. The seed/solvent ratio during extraction appears to be directly related to this sonication side effect. When this ratio is greater than 10, oxidative stability suffers a significant decrease, promoting the strategy of using the least amount of solvent to be possible (Böger et al. 2018).

3.2.2. Supercritical Fluid Extraction (SFE)

To extract bioactive compounds, the SFE approach uses CO₂ at a temperature above critical 31°C and pressure at 7.38 MPa. Currently, there are no liquid or gas types that prevail, although physicochemical features that are comparable to those of a gas and a liquid can be observed. This method can be used to dissolve chemicals in gas or liquid phases that are just partly or not at all soluble. Because they have gas-like properties such as low viscosity and great diffusivity, supercritical fluids are ideal for penetrating cell-matrix and dissolving compounds of interest (Azmir et al. 2013). Because of its numerous benefits over conventional extraction, SFE is being studied as a safe alternative to solvent extraction (King 2014). As a result, supercritical fluid extraction has turned into popular besides, recently has been used in the pharmaceutical and food industries to extract useful compounds from solid substrates. Because it uses supercritical carbon dioxide (SC-CO₂) as a lubricant, SFE had considered a green and environmentally friendly approach. It is biologically secure and doesn't leave any solvent residue in the finished product, making it ideal for sensitive sectors such as pharmaceuticals, cosmetics, and food. As a result, SC-CO₂ might be a promising strategy for extracting crop matrix oils without degradation (Canabarro et al. 2020). Due to its great diffusion capability with an extraordinary solvent influence of CO₂, SC-CO₂ has reflected the greatest effective way to remove mixtures from plant patterns besides the utmost regularly solvent castoff in SFE (Mrabet et al. 2020). Additionally, control parameters such as pressure and temperature can affect CO₂ solubility discrepancies. Aris et al., have characterized stress to enhance solution solubility as the dominant factor, leading to increased extraction of date seed oil. Increased pressure improves CO₂ density, which increases extraction output (Al-Rawi et al. 2013). Moreover, Takadas and Doker (2017) discovered that as the temperature rises, the vapor pressure rises too, resulting in a decrease in CO₂ density and thus a decrease in oil yields. The effects of a variety of variables (pressure, temperature, and particle size) on the extraction revenue and fatty acid profile of Algerian date seed oil extracted via the SC-CO₂ technique were studied by Louaer et al. (2019). The findings showed that pressure, as well as the relationship of temperature and pressure has a major confident impact on date seed oil extraction revenue. About 7.55% polyunsaturated, 42.75% monounsaturated, and 49.85% saturated fatty acids were found in the fatty acid profile obtained by Soxhlet extraction. As a result, SC-CO₂ extraction is seen as a talented way for extracting date seed oil and adding significance to this by-product. It's a harmless way to get eatable oils without polluting them with organic solvents, and the incomes are comparable to Soxhlet extraction. The major drawback of SC extraction is the high cost of the equipment, which makes it costly more than conventional extraction.

3.2.3. Enzyme assisted extraction (EAE)

EAE has lately been used to extract several compounds in the food industry. It's seen as an environmentally friendly, effective, and gentle extraction method, as well as a prospective replacement for present extraction methods (Nadar et al. 2018; Zhu et al. 2018). To effectively use enzymes for EAE, you must first understand their catalytic specificity and mode of action, as well as investigate the optimum conditions and which enzymes or enzyme combinations are suitable for the raw materials. Before selecting a suitable enzyme or enzyme combination, it is also preferable to determine the sample matrix's cell wall composition

(Nadar et al. 2018). Many key factors, such as enzyme composition and concentration, extraction solvent type, solid/liquid, enzyme/substrate ratios, pH, extraction temperature, and time, can influence the effect of enzymes on cell wall degradation and disruption, as well as the release of bioactive components that have been targeted (King 2014). Apart from particular parameters for enzymatic reactions, common extraction processing parameters such as particle size, other important impacting variables are the extraction solvent type and the solvent/matrix ratio. Bioactive compounds have been extracted from a variety of plant sources using EAE., for instance, oil from grape seed, flavonoid (naringin) extraction from the citrus peel (Puri et al. 2012), and pomegranate peel total phenolics (Nag and Sit 2018). The EAE of oil from seeds is depicted in Fig. 4 as a series of stages. EAE seems to have some benefits in aspects of bioactive compound extraction, nevertheless, it also has potential Technical and financial burdens. For starters, currently, available enzyme preparations are unable to efficiently hydrolyze matrix cell walls, resulting in lower yields of phyto-bioactive chemical extraction (Marić et al. 2018).

Second, enzymes having a high enzyme/substrate ratio may be economically unfeasible in large-scale or industrial-scale production. Third, because enzymes behave differently depending on their surroundings (temperature and pH), and because temperature and pH might change inside an industrial-sized impeller, EAE can be difficult to scale up in the industry (Puri et al. 2012). If the flaws described above can be fixed, EAE might provide a way to not only boost extraction yields and shorten extraction times, but also improve extract quality by using softer extraction conditions (like lower extraction temperatures). Novel extraction techniques would give rise to higher extraction yields in a shorter period of time, improved quality of the product and less climate change. In research, employing these novel extraction technologies in combination is becoming increasingly common. It appears that complementary approaches provide greater advantages, as well as a more promising extraction potential. Nonetheless, these novel extraction processes would require careful planning to create the best conditions for scaling, they may be a significant step toward the long-term production and utilization of bioactive compounds derived from natural sources in everyday life (Marić et al. 2018). The following Fig. 5 concludes the advantages and disadvantages of almost all strategies used in oil extraction.

4. Chemical Catalysis For Oil Transesterification

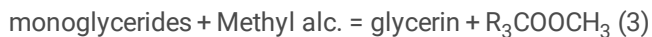
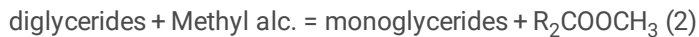
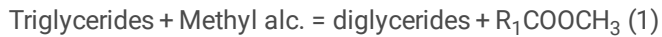
Biodiesel was made by reacting vegetable oil methyl esters (mostly triglycerides) with short-chain alcohols in a chemical reaction (methanol and ethanol). In biodiesel manufacture, the methyl esters mechanism is carrying out in the presence of different catalysts (Gebremariam and Marchetti 2017). Base catalysts (KOH and NaOH) (Al-Hamamre and Yamin 2014) acid catalysts (H_2SO_4 , HCl), and enzymes can be used all in the esterification process (Patil et al. 2012). Amongst, the time and cost of the alkaline and acid catalyst esterification reaction, for instance, take less time and cost than the enzyme catalyst. Several studies have shown that the same parameters, like the catalyst kind and quantity, temperature and time of the reaction, and the methanol / oil ratio, influence the biodiesel processing process (Kılıç et al. 2013).

Biodiesel is seen to be a viable alternative to conventional diesel. Biodiesel is made from vegetable oil, and it has a variety of chemical and physical benefits over diesel, such as biodegradability, non-toxicity, renewability, better gas release, and reduced particle, smoke, and carbon monoxide emissions (Sousa et al. 2010). Biodiesel is made by reacting oil with an alcohol such as methanol to produce methyl ester, which is subsequently transformed into biodiesel. The amount of free fatty acids in the oil used to make biodiesel is an essential cost-cutting factor. Recent research found that oil with a high proportion of free fatty acids required an extra catalyst (potassium hydroxide (KOH) or sodium hydroxide (NaOH) to maintain its acidity (Qiu et al. 2011). The date seed oil provides a low percentage of free fatty acids, ranging from 0.53–1.05%, which is advantageous (Nehdi et al. 2010; Jain and Sharma 2010). However, no study has been done on the production of biodiesel or date seed oil from the sector. Because date seed oil is generated from a waste product, it may be inexpensive (date seed). Another rationale for the commercialization of date seed oil might be the expected output of more than 1 million tons of date seed, which can be extracted using the same oil extraction process as palm kernel oil (Abdul Afiq et al. 2013). Transesterification of the extracted date seed oils employing a Methanol/KOH combination resulted in the formation of fatty acid methyl esters (biodiesel).

Transesterification, the process of converting vegetable oils into molecules with more technically acceptable fuel properties, has received a lot of attention in recent years. Because it decreases the viscosity of the feedstock/vegetable oils to that of typical fossil-based diesel oil, transesterification is an important stage in the biodiesel manufacturing process (Mumtaz et al. 2017). The

word "transesterification" refers to a chemical process in which the alkoxy group of one ester is exchanged for that of another. The reactants are mixed to establish equilibrium in the transesterification process. The equilibrium can be hastened and controlled if a catalyst (acid or base) is present, allowing for a greater ester yield; however, the alcohol must be utilized excessively. The complete procedure consists of three reversible processes that produce di- and monoglycerides as intermediates. The stoichiometric process requires 3 mol of alcohol and 1 mol of triglycerides. To enhance alkyl ester production and facilitate physical separation from the glycerol generated, a significant quantity of alcohol is employed. Throughout the biodiesel production process, the methyl esters procedure takes place in the presence of several catalysts. Alcoholysis of triglycerides with methanol in the presence of a strong acid or basic catalyst gives fatty acid methyl ester (FAME) as shown in the chemical reaction below (Eqs. 1, 2, and 3). Triglyceride transesterification is accomplished in three stages, using monoglyceride and diglyceride as intermediates (Jothiramalingam and Wang 2009).

The transesterification reactions are performed in the following order:



The kind of catalyst (alkaline or acid), the alcohol/vegetable oil molar ratio, temperature, the purity of the reactants (mainly water content), and the concentration of free fatty acids are all the factors that affect the transesterification process.

Transesterification with methanol is more practical than ethanol, according to published studies Methanol is selected due to its low cost as its physical and chemical properties. Another benefit of using methanol is that it can be used to separate glycerin, which can be obtained with easy decantation (Nagi et al. 2008).

4.1. Homogeneous catalyst

In the transesterification process, for example, there are two types of homogeneous catalysts:

4.1.1. Base catalyst

Because of their low cost and availability, homogeneous base catalysts are the most widely researched in the transesterification of vegetable oil to fatty acid methyl ester (FAME). For the synthesis of FAME, a variety of homogeneous base catalysts have been used, including KOH, NaOH, and NaOCH₃. The use of KOH and NaOH as catalysts resulted in exceptional catalytic activity for biodiesel synthesis, including a fast reaction time and large biodiesel production, all at room temperature and pressure. Since alkaline catalysts are less corrosive than acid catalysts, alkaline-catalyzed transesterification is usually favored at an industrial scale. However, there are certain limits to this process, such as the creation of water as a byproduct, which reduces biodiesel output. Because no water is produced throughout the process, sodium methoxide and potassium methoxide, in addition to KOH and NaOH, create superior biodiesel. An alkaline catalyst cannot be used to transesterify high-free-fatty-acid-content vegetable oils (> 2 wt. %). However, it is acceptable for FFA-free processed vegetable oils (ranging from less than 0.5 wt. percent to less than 2 wt. %). A few tests were carried out using a homogeneous KOH catalyst to explore the feasibility of date seed oil as a biodiesel feedstock (Amani et al. 2013; Jamil et al. 2016; Azeem et al. 2016). Using a standard base catalyst, Jamil et al. (2016) improved oil extraction and biodiesel production from Date pits. The optimum yield of production oil was 16.5 weight % when the process temperature was 70°C, the solvent-to-seed ratio was 4:1, and the extraction time was 7 hours. Based on its physicochemical characteristics, Azeem et al. (2016) researched the possibility of manufacturing biodiesel from Date pits and identified high-quality biodiesel oil. As a result, date pit oil was selected as the best non-edible option for biodiesel production. Al-Zuhair et al. (2017) examined the yields of two different catalysts (NaOH and Novozym®435) and observed that they were comparable. However, as compared to other acids, NaOH shown considerable selectivity for transesterifying trans-9-elaidic acids, whereas Novozym®435 transesterified the majority of acids in the oil sample evenly. Samad Akbarzadehd, Foroutan et al. (2015), produces biodiesel from a 1:1 mixture of sunflower and date seed oils, KOH and NaOH as catalysts, and methanol. The study

discovered that combining date seed oil and sunflower oil to make biodiesel is more effective than using one of them alone. Finally, ASTM-D6751 and EN14214 biodiesel analysis can be used as desired.

4.1.2. Acid catalyst

Base catalysts are favored because they are more reactive and less expensive than acid catalysts. Base catalysts, on the other hand, could have an impact on the FFA in the feedstock throughout transesterification, producing saponification and destroying the catalyst and decreasing its resonance. For the time being, because an acidic catalyst is FFA-neutral, it functions well in the transesterification or esterification of high FFA vegetable oils or fats (2 wt. percent). By esterifying the cation before transesterification with a base catalyst, acid catalysts are frequently used to decrease the FFA level of WCO and animal fats (Kulkarni et al. 2006). The transesterification of vegetable oils was mainly done with acids like H_3PO_4 , HCl, H_2SO_4 and sulfonated acids (Atadashi et al. 2013). Acid-catalyzed biodiesel processing there are several disadvantages to this method, including a sluggish reaction rate (4000 times slower than base-catalyzed transesterification) and a high alcohol/oil molar ratio. It also has environmental and corrosion issues (Jacobson et al. 2008). Owing to these limitations, acid-catalyzed biodiesel synthesis is not very popular or investigated. M.W. Azeem et al. (2016) used acids like HCl, base as KOH, immobilized enzyme (lipase), immobilized enzyme-to-acid (lipase/HCl), and immobilized enzyme-to-base (lipase/KOH) catalyzed procedures to produce biodiesel from the oils derived from Zahidi's waste, which accessible in Basra, and date seeds of Khazravi. In addition to acid or base catalysis, mixed catalysis (immobilized enzyme acid or immobilized enzyme base) yielded higher yields.

Ahmed Abu-Jrai et al. (2017) used a carbon-based catalyst to convert date seed oil into biodiesel. According to the scientists, using a 9:1 methanol to oil ratio and a reaction time of 1 hour at 65°C, the selected catalyst produced 91.6% biodiesel with a catalyst loading of 6 wt. % and reusability of up to three runs. According to the literature, there is still a great potential for developing a powerful catalyst for date seed oil transesterification to create a cost-effective and environmentally friendly biodiesel operation. Thrown-away eggshells were successfully employed to construct affordable pricing. environmentally safe, and powerful catalyst for the development of biodiesel from date seed oil (Farooq et al. 2018). The catalyst produced at 900°C displayed remarkable transesterification activity and provided a maximum yield of fatty acid methyl esters of up to 93.5% when used under optimal reaction conditions, which included a 1.5-hour reaction time, a 12:1 methanol–oil molar ratio, and a 5% catalyst. Throughout the biodiesel conversion process, the catalyst also demonstrated good stability and reusability.

4.2. Heterogeneous catalysts

While the homogeneous catalyst has some advantages, including high reactivity and low cost, it also has several disadvantages when used in biodiesel production. The low quality of glycerol produced, the inability to replenish the catalyst, and the lengthy biodiesel purification process are only a few disadvantages. As a result, the whole procedure is labor-intensive and inefficient. As a result, throughout the previous few years, the heterogeneous catalyst has gotten a plenty of focus for biodiesel processing, since it can be tuned to individual needs and quickly recycled and reusable for several catalytic reaction cycles, possibly decreasing labor and biodiesel costs. Heterogeneous catalysts, unlike homogeneous catalysts, are often solid; as a result, the catalyst and the reaction mixture are in different stages. The catalyst surface is the primary reaction site in heterogeneously catalyzed processes (Dalvand et al. 2018). The following benefits of using a solid catalyst in transesterification help to make the process more environmentally friendly: The catalyst could be recycled, very little wastewaters across the process, separating glycerol from the final mixture (glycerol, biodiesel, and catalyst) is significantly easier, and high-quality glycerol is obtained. Heterogeneous catalysts provide numerous benefits over homogeneous catalysts, such as ease of separation, recyclability, and reuse. Solid catalysts are also less harmful to the environment, less corrosive, and use fewer resources. As a result, solid catalysts make biodiesel processing more competitive and cost-effective (Leung et al. 2010; Ma et al. 2017; Farooq et al. 2013). Recently, several heterogeneous catalysts have been designed that may boost both esterification and transesterification processes in the same reaction vessel (one-pot). These catalysts are commonly used to produce biodiesel from vegetable oils or animal fats that contain a considerable quantity of FFA without the need for a separate pretreatment step to lower the FFA concentration (Farooq et al. 2013).

4.2.1. Basic catalysts

Basic heterogeneous catalysts have gotten a lot of attention in recent years because of their ability to transcend the limitations of homogeneous basic catalysts while also demonstrating outstanding catalytic performance below moderate conditions of the reaction. These catalysts, On the other hand, these catalysts are only effective for biodiesel feedstocks with a low FFA percentage; furthermore, catalysts would react with the FFA and cause the saponification reaction to produce soap. This increases the time it takes to separate biodiesel from glycerol, reducing biodiesel output. For biodiesel synthesis, various simple oxides of the metals forms catalysts have been documented in the literature. Here's a look at some of the high-performance catalyst compositions and how they're used in biodiesel synthesis. A detailed investigation on the added value of discarded date pits was conducted by synthesizing the green carbon catalyst and using it to produce biodiesel from date pit oil (Al-Muhtaseb et al. 2018). The properties of a carbon catalyst modified with CaO were found to be ideal for transesterification of date pits crude. C₂ (4 wt. % CaO@ Carbon) is the most appropriate catalyst, with a pore diameter of 7.19 nm, which makes for fast triglyceride molecule diffusion and pore channeling to convert into biodiesel. The high yield of biodiesel (98.2 wt. %) supports the catalyst's suitability for the transesterification reaction.

However, the homogeneous catalyst used in biodiesel processing has some disadvantages, concerns issues with fuel separation, soap creation, and the final combination's corrosiveness. This research (Nguyen et al. 2021) investigated using a heterogeneous catalyst based on locally sourced raw materials (kaolin and eggshell) to prepare biodiesel from desert date seed oil. The kaolin from Bauchi's Alkali Mining Site was calcined for three hours in an oven at 800°C. Following that, chemically, the calcined kaolin was activated. The eggshell-based catalyst was also made from raw eggshells after being washed, dried, ground, sieved using a 0.3 mm sieve scale, and calcined for 3 hours at 900°C. Furthermore, employing solvent extraction, the oil content of a desert date seed obtained from a local market in Bauchi was removed in a laboratory, yielding 42%. The biodiesel was then made by heating the oil, methanol, and catalyst for a set time in a flask with a flat bottom. To get the best yield, the concentration of the catalyst, methanol / oil ratio, and time of the reaction were all modified. The results showed that an optimum yield of 29% could be obtained using 1.5 gm of eggshell-based catalyst, a 6:1 methanol / oil ratio, and a reaction time of 60 min, while an optimum yield of 22% could be obtained using 0.6 gm of kaolin-based catalyst, a 60-min reaction time, and a 4:1 methanol / oil ratio. It is suggested that further research be done to increase biodiesel yield produced with heterogeneous catalysts. A chemical precipitation process was used to prepare a heterogeneous base nano catalyst of CaO-Fe₃O₄ with a Fe₃O₄ magnetic core (Ali et al. 2017). CaO and Fe₃O₄ with CaFe₂O₄ have been discovered to be the catalyst. This catalyst is a composite that was utilized in the catalytic transesterification of palm seed oil. Maximum biodiesel yields of 69.7% for palm seed oil were achieved under the following conditions (300 min reaction time, 20 methanol-to-oil molar ratio, 65°C reaction temperature, and 10% CaO/Fe₃O₄ catalyst loading). It was discovered that catalyst volume and time had the greatest impact on biodiesel yields, although reaction temperature had little effect at low catalyst amounts. The CaO/Fe₃O₄ nanomagnetic solid base catalyst used in biodiesel production showed promise for future growth and use. Significant features of date seed biodiesel are its high cetane number, low flashpoint, and low viscosity. In contrast to other biodiesel fuels, these factors may raise engine performance while lowering emissions. According to the present research, date seed oil's methyl ester might be utilized as biodiesel in internal combustion engines. The catalyst was generated by controlled physical stimulation of Mahogany fruit shells (Dass et al. 2018). Biodiesel oil was produced from non-edible desert date (*Balanites scoparia*) plant seeds using heterogeneous catalysis. FTIR and GC MS spectroscopic techniques were used to identify the catalyst as well as the biodiesel oil. Biodiesel oil yield from *Balanites aegyptiaca* seeds is 49.9%. The catalyst made from Mahogany fruit shells, on the other hand, yielded an 80.0% yield of biodiesel oil. As a result, waste *Balanites aegyptiaca* seed oil and a catalyst made from Mahogany fruit shells are used to make biodiesel oil, a green energy source.

4.2.2. Acidic solid catalysts

Heterogeneous acid catalysts are easier to separate and reuse since they do not dissolve in the alcohol or feedstock. Because they are effective for both the esterification of FFA and triglycerides, such catalysts are widely used. Date seed oil was recently transesterified into biodiesel using a bimetallic Mn-(MgO-ZrO₂) catalyst, yielding 96.4% biodiesel in a 4-hour process at 90°C reaction temperature, 3% catalyst heating, and methanol to oil ratio of 15. It is also possible to reuse the catalyst for up to six cycles (Al-Muhtaseb et al. 2017).

4.2.3. Waste-derived Natural heterogeneous catalyst

Using a heterogeneous catalyst can be beneficial to lower biodiesel's current high production cost, allowing it to compete with petro-diesel fuels. As a result, research has to be focused on creating a cost-effective and environmentally friendly heterogeneous catalyst for biodiesel processing (Yasar et al. 2019).

MgO, CaO, and SrO are alkaline earth metal oxides with elevated activity for use in traditional processes that take place at low temperatures and ambient pressure. CaO is similar to the environmental substance of the alkaline earth metal oxides. Typically, the basic material utilized to create CaO catalysts is usually Ca(OH)₂, CaCO₃, or Ca(NO₃)₂ (Talha et al. 2016). Several natural calcium sources from wastes, such as eggshells, mollusk shells, and bone, can be used instead of making CaO catalysts. Not only will waste disposal expenses for the biodiesel industry be reduced, but high-cost efficacy catalysts will also be available. Oyster shells and chicken eggs have been discovered to be effective catalysts for the conversion of vegetable oil to methyl ester (Cho et al. 2009). In a 5-hour reaction cycle, researchers discovered that with 25% wt. % thermally activated (at 700°C) oyster shell and a 6:1 methanol: oil molar ratio, the yield of biodiesel synthesis is over 70% with a purity of 98.4% (Boey et al. 2011). On the cost of a higher catalyst and a longer reaction time, a conversion at a reasonable (6 methanol: 1 oil) ratio was achieved. With molar ratio (9 methanol: 1 oil) and a reaction temperature of 65°C, soybean oil was transesterified at 100°C using a 3 wt.% calcined eggshell to generate a yield of over 95% in 3 hours (Nakatani et al. 2009). Furthermore, the catalyst of the waste might be used up to 13 times without losing any functionality, according to research.

Calcined eggshell yielded a very active, reusable solid catalyst. Calcined eggshells have to be very effective in the biodiesel transesterification of vegetable oil using methanol. Making catalysts from eggshell waste has the potential to minimize pollutants, lower catalyst costs, and make catalysts more environmentally friendly.

In reality, this low-cost, high-efficiency eggshell catalyst has the potential to make biodiesel manufacturing both cost-effective and sustainable. The environmentally sustainable and cost-effective method could effectively lower biodiesel production costs, bringing it compatible with petroleum diesel (Wei et al. 2009). In a large-scale biodiesel production site, a low-cost catalyst may be employed, making the process both cost-effective and environmentally friendly. Aside from biodiesel, processing, such environmentally acceptable eggshell-derived catalysts may be used in a number of other base-catalyzed important organic processes.

These catalysts have a lot of economic promise, especially in the biodiesel industry, because they can be manufactured inexpensively from waste materials, cutting the cost of biodiesel production and making it competitive with petroleum fuel. According to Sanjay et al. (2013), ease of availability, biodegradability, and environmental acceptability are three factors that favor catalysts. Because they are reusable for several reaction cycles, their large-scale use will not pose a disposal issue. Because these catalysts are made from renewable biomass, they are environmentally friendly, and biodiesel production is also a potential green technology. Carbon generated by carbonization and impregnation with Pt and Pd metals is used to create active catalysts from waste date pits. The hydrodeoxygenation of date pits oil for the development of second-generation biofuels such as jet fuel and green diesel fractions was used to test the catalysts' functionality. The synthesized catalysts are shown to be particularly active in the hydrodeoxygenation of date pit oil. The degree of deoxygenation (DOD) of commodity oil for the Pd/C and Pt/C catalysts, according to elemental analysis, was 97.5% and 89.4%, respectively. The high DOD was confirmed through product testing, which includes paraffinic hydrocarbons. The results also revealed that Pd/C had a higher hydrodeoxygenation activity than the other two catalysts, which attributed to the high DOD of the resulting oil due to hydrocarbon formation. The highest proportions of hydrocarbons created with Pd/C and Pt/C catalysts were 72.03% and 72.78% green diesel, and 30.39% and 28.25% jet fuel, respectively, based on the kind of components in the product oil. According to the research, waste date seeds are a suitable platform for the creation of catalysts and biofuels.

5. Biocatalysts For Transesterification Process

Biocatalysts are defined as biological catalysts. They are natural substances, such as enzymes from biological sources or whole cells that are used to accelerate chemical reactions. Enzymes play a critical role in hundreds of reactions, including the production of alcohols. Biocatalysts have become increasingly important in discussions about biodiesel production and, more recently, in most biodiesel manufacturing processes. Again, homogeneous biocatalysts face the same issues as chemical

homogeneous catalysts, including reuses, separation, and process cost-effectiveness. Biocatalysts are naturally occurring lipases that were demonstrated to perform the transesterification processes required for production of biodiesel. *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Rhizomucor miehei*, *Rhizopus oryzae*, *Candida rugosa*, *Thermomyces lanuginosus*, and *Candida antarctica* have all been found to produce lipases. Lipase can be immobilized using various techniques such as adsorption, covalent bonding, entrapment, encapsulation, and cross-linking. As a result, immobilized or encapsulated biocatalysts play a key role in catalytic reactions. Recent years have seen these immobilization strategies used to improve lipase stability for biodiesel production. Adsorption is still the most common way to keep lipase immobilized. To convert triacylglycerols to their corresponding fatty acid methyl esters, at least stoichiometric amounts of methanol are required (Mamat et al. 2017). For renewable synthesis technologies, biocatalysis has been seen as a trend because of the catalyst's biologic base, selectivity, and potential to recycle agro-industrial wastes for biocatalyst manufacture (Teixeira et al. 2014). Enzymatic catalysis has been utilized to make biodiesel, which is presently being manufactured on a large scale in China (Tan et al. 2010). However, certain considerations affect the conversion of an enzymatic transesterification reaction, such as water content of the reaction medium, solvent type, substrate alcohol type, temperature of the reaction, kind of immobilization, and lipase concentration. In the studies, various lipases have been used to produce biodiesel; nonetheless it's difficult for drawing general conclusions regarding the best conditions of the reaction. This is due to the fact that lipases of different origins respond toward variations in the reaction medium in different ways (Bajaj et al. 2010; Antczak et al. 2009; Abdulla et al. 2013; Ondul et al. 2012). Chemical biodiesel processing costs have remained smaller than those of enzymatic processes; but, when environmental degradation is taken into account, these costs are equivalent. The high enzyme cost has a direct effect on the process viability in enzyme-catalyzed biodiesel processing.

For many reasons, biocatalysts outperform chemical catalysts. Chemical catalysts have a number of drawbacks, in the production of soap in base-catalyzed transesterification, difficulties purifying glycerol, and alkali-catalyzed transesterification involving a lot of energy within downstream biodiesel processing (Madras et al. 2004). When sulfuric acid (H_2SO_4) is used as a catalyst, the reactor corrodes and a significant amount of wastewater is produced during the neutralization of mineral acid and a large amount of catalyst is required in the base-catalyzed transesterification reaction. Transesterification using an acidic catalyst increases the molar ratio of alcohol and oil (Musa et al. 2016). Chemically catalyzed biodiesel demands a high reaction temperature, and while alkali catalysts (NaOH and KOH) are inexpensive and widely, their operating temperature used is lower (Demirbas et al. 2008). Without a catalyst, the transesterification process can be carried out at a higher temperature, but the biodiesel yield at temperatures below 350°C is undesirable. At temperatures below 400°C, however, thermal degradation occurs (Demirbas et al. 2007). Alcohols in their supercritical state have also been shown to contain higher methyl ester yields of fatty acids (FAME) (Demirbas et al. 2008). Alkali and acid catalysts, as well as enzymatic (lipase) biocatalysts, are required to speed up the process, to minimize energy expenditure. Transesterification with an alkali catalyst is more common in industry than acid-catalyzed transesterification because it is. If the oil contains a large amount of free fatty acids and water (FFA), acid-catalyzed transesterification is a better option because FFA and water obstruct the reaction. While chemical-catalyzed transesterification provides suitable conversion speeds in short reaction cycles, it has many disadvantages, including being energy intensive, difficult to recover glycerol, requires the acidic or alkaline catalyst to be removed from the substance, requiring water treatment, and being affected by FFAs and water. Enzyme-mediated (biocatalysts) transesterification can solve problems that arise during chemical catalysis, and they are becoming most important in biodiesel synthesis as a result of their capacity to replace chemical catalysts. Because of their properties and advantages, enzymes have been identified as possible biocatalysts for biodiesel processing (Fukuda et al. 2001). For example, using an enzyme catalyst throughout the biodiesel synthesis process is a greener choice than processing renewable fuel. Enzymatic catalysts are biologically derived, and utilizing them consumes less energy due to their gentler operating conditions than chemical catalysts (Sendzikiene et al. 2015). As compared to chemical catalysts, enzyme catalysts have many advantages, including being environmentally efficient, having a very rapid reaction, requiring less energy and temperature, no soap is making, and requiring less water for cleaning. Enzymatic methanolysis using lipases as biocatalysts has become more interesting for biodiesel processing because it can overcome several limitations

5. 1. Bio catalysis classification

Lipases have recently been investigated as whole-cell immobilized lipases for biodiesel output. When it comes to lowering the biocatalyst's contribution to the final cost of biodiesel, each kind of biocatalyst has its own set of advantages and

disadvantages. Recent research has focused on enhancing the enzyme's catalysis efficiency and stability to save money of lipase in the biodiesel conversion method (Teixeira et al. 2014).

5.1.1. Free biocatalysts

Microbial lipases have grown in importance in industry, accounting for around 5 percent of the enzymes in the world demand afterward carbohydrates and proteases. Plant and animal lipases are less stable than lipases and can be purchased in large quantities at a reduced rate than lipases from other sources. When compared to bacterial lipases, yeast lipases are easier to manage and expand. *Candida rugosa* is a yeast lipase that has grown in commercial importance. Lipases generated by microbes which formed from a variety of yeast, fungal and bacterial organisms, to produce biodiesel in the presence of biocatalyst are the most widely (Christopher et al. 2014). Immobilized lipases are much more expensive than free enzymes. It can be obtained in an aqueous solution consisting of a solution of enzyme in the presence of a preservative to avoid the growth of microbes such as, benzoate and a stabilizing agent to prevent the enzyme denaturation (for example, glycerin or sorbitol) (Nielsen et al. 2008).

5.1.2. Immobilized biocatalysts

Entrapment, physical adsorption, ion exchange, and crosslinking are all methods used to immobilize lipases. Cellulosic nanofibers, silica, sea beads, and polyurethane foam are examples of carriers for lipase immobilization. According to the requirements for selecting the immobilization system and carrier, the system of reactions (aqueous, organic solution, or two-phase system) and bioreactor type (batch, stirred tank, membrane reactor, column, and plug-flow) can be established depending on lipase's source. Depending on the lipase source, the reaction method (aqueous, organic solution, or two-phase system) and bioreactor form (batch, stirred tank, membrane reactor, panel, and plug-flow) can be adjusted based on the requirements for selecting the immobilization technique and carrier. Lipase-producing bacteria, enzyme immobilization methods, and physical carriers are all mentioned in the literature. The challenges in finding a carrier and immobilization method which allowed for the most lipase operation is stabilization, and stabilization on the oil substrate. The most basic and extensively used method for lipase immobilization is adsorption. The adsorption process involves weak forces as van der Waals or hydrophobic interactions to bind the lipase to the immobilization support board. Due to the low binding strength between the enzyme and the support, the fundamental disadvantage of this technique is enzyme desorption from the support. (Christopher et al. 2014).

5.1.3. Whole-cell biocatalysts

Whole-cell immobilized lipases have been studied for biodiesel synthesis in recent years. This process is less expensive because it avoids the need for the purification of enzymes and the separation of fermentation broth. The transesterification method's performance may be improved with whole-cell biocatalysts made from microbial cells that contain intracellular lipase (Christopher et al. 2014). Filamentous fungi have been discovered must be effective biodiesel processing whole-cell biocatalysts, with *Rhizopus* and *Aspergillus* being the greatest commonly used (Gog et al. 2012). Several recent studies have reported the use of yeast, fungi, and bacteria as whole-cell biocatalysts in the biodiesel method (Teixeira et al. 2014).

5.2. Role of Lipase in the transesterification

Long chains of triacylglycerols are hydrolyzed by the lipase enzyme, which serves as a catalyst. The transesterification reaction is catalyzed by lipase in two steps: (a) hydrolyzes fatty acid ester bonds, converting triglycerides to diglycerides. (b) Alcohol serves as an acyl acceptor, resulting in the formation of an ester. The next transesterification reaction is carried out by free lipase (Jegannathan et al. 2008). The presence of water affects lipase production as well. It keeps lipase active by creating an oil-water interface with water, which aids in enzyme activation and active site reconstruction by conformational change. In aqueous conditions, the three-dimensional structure of the lipase enzyme that comprises polar and nonpolar groups, making it distinctive and active. Lipase enzymes, like other enzymes, undergo lipolytic reactions, and Lipolytic processes are complicated by the insolubility of lipids in water (Manurung et al. 2016). Interface characteristics, interfacial nature, and interfacial region can all affect lipase's catalytic activities. The lipase enzyme is activated by an adsorption process and the interface aids in the lipase's catalytic active site is open. As a result, lipases are being used as biocatalysts for biodiesel production has gotten a lot of attention in the last ten years (Fukuda et al. 2008). Many attempts have been made to create an enzymatic pathway using lipase as a biocatalyst, either extracellular or intracellular. Triacylglycerol lipase (also known as Triglyceride lipase) EC 3.1.1.3, is an

enzyme that hydrolyzes triglyceride ester linkages) glycerol and free fatty acids (FFAs) produced. Serine, aspartic (or glutamic) acid, and histidine amino acid groups make up the active sites of lipases. Generally, lipases have a unique feature called interfacial activation for their usage in the transesterification of fats and oils, which happens when a lipase active site structure and a substrate are both present. Lipases are being used in a range of fields due to their capability to use mono, di, and triglycerides and FFA, low material inhibition, high activity and produce in non-aqueous media, low reaction time, temp, and alcohol resistance. However, their high cost continues to be a barrier to their industry applications. The enzyme may be immobilized on the appropriate carrier and repeated several times to reduce the cost of the operation. For the immobilization of lipases to manufacture biodiesel, a variety of methods and carriers have been used so far. They've been immobilized on porous kaolinite particles, silica, celite, macroporous resin, biomass support particles, gel-entrapped, and Eupergit C250L (Ondul et al. 2015). Lipases have grown in importance in the enzyme biotechnology world as results of their catalytic reactions are generally chemo-selective and regio-selective, allowing them to be versatile in hydrolysis and synthesis, or enantioselective. Lipases are used in a variety of industries, including food, pharmaceuticals, fine chemicals, oil chemicals, biodiesel, and commercial detergents. Lipases are enzymes that catalyze the hydrolysis of ester carboxylate bonds at the organic-aqueous interface, resulting in the release of fatty acids and organic alcohols. In water-limited conditions, however, the reverse process (esterification) or even alternate transesterification processes can occur, as Pottevin demonstrated for the first time in 1906. Lipases can be of vegetable, fungal, animal (pancreatic, hepatic, and gastric) or microbial (bacterial and yeast) origin, and they have a wide range of catalytic properties. Microbial lipases have been the subject of the most research so far. Microbial lipases account for roughly 58% of all lipase publications, plant lipases for 42%, and latex lipases for only 11%. Despite the wide variety of microbial lipases, industrial usage of these enzymes is currently restricted due to high processing costs, thus other sources of these enzymes are preferred (Mazou et al. 2016).

5.3 Use of immobilized lipase in biodiesel production

In the field of biotechnology, the use of immobilized enzymes is important. Biocatalyst will isolate from the reaction product due to lipase immobilization, and it can be used in the transesterification reaction to increase yield and lower the cost of the operation. An enzyme that has been immobilized has been bound to inert and insoluble substances. Methods for immobilizing lipases enzymes include entrapment, covalent linkage, encapsulation, adsorption, cross-linking, and others (Budzaki et al. 2019; Juna et al. 2019).

Biodiesel has been generated using a variety of immobilized lipases including *C. rugosa* lipase on Fe_3O_4 nanocomposite, Lipase from *B. cepacia* on magnetic nanoparticles, *R. oryzae* lipase on magnetic graphene oxide, *P. fluorescence* lipase immobilized on carbon nanomaterials, *C. antarctica* and *R. miehei* lipase on silica, *C. antarctica* lipase on magnetic nanoparticles, *Fusarium heterosporum* lipase and *P. cepacia* lipase on bio-support beads (Bhan et al. 2020). Immobilized lipase was used to synthesize biodiesel on a variety of components, including organic polymers, carbon nanotubes, silica nanoparticles, and magnetic nanoparticles, according to Zhong et al. (2020). However, using immobilized lipase in transesterification has the downside of increasing the price of processing. When opposed to chemically catalyzed transesterification, lipase-catalyzed biodiesel processing is considered an environmentally sustainable solution since it takes input with less energy and requires washing in less water. According to Avhad and Marchetti (2019), 2.5 kg of Lipozyme RMIM can convert about 1000 kg of oil to biodiesel, and the enzyme that has been immobilized can be reused. for around 50 cycles. In comparison to traditional acid/alkali catalysis for biodiesel processing, transesterification using enzymes as biocatalysts (Amini et al. 2017) is a relatively new technique. Biocatalysts are enzymes produced naturally by the fermentation of biobased materials. Lipolytic enzymes are essential for convert and lipids, a key element of the earth's biomass, are mobilized from one creature to another. Biosurfactants are lipid solubilizers produced by microorganisms such as bacteria and fungus. Additionally, using enzymes as biocatalysts during algal oil transesterification results in cleaner, more ecologically friendly alternatives, includes a benefit for microalgal biofuels of the third generation. Lipase (triacylglycerol acyl hydrolases, EC3.1.1.3) and esterase (EC 3.1.1.1) are the two primary kinds of lipid hydrolytic enzymes that are being explored as commercial biocatalysts (Jia et al. 2019). Shorter-chain fatty acid esters (C8) are hydrolyzed by the esterase enzyme (Ramnath et al. 2017). Lipases are divided into three groups depending on the substrates they work with: (i) lipases with regio- or positional specific lipolytic activity, (ii) lipases specific for fatty acids, and (iii) lipases that are very specific to just certain acylglycerols found in oils (Teo et al. 2014). Dairy, fruit, detergents, fats and oils, organic synthesis, biodiesel, agro-chemicals, novel polymeric textiles, paper and pulp, leather, fine chemicals, cosmetics, and medicines

are just a few examples. These lipolytic enzymes are in high demand as potential industrial biocatalysts, with applications ranging from soil bioremediation to the biodegradation of environmentally harmful substances such as phenolic chemicals and endocrine disruptors. Although lipases can be found in practically all microorganisms, plants, and humans, microbial lipases generated from bacteria and fungus are the most commonly used lipase sources. (Sreelatha et al. 2017). Microbial lipases have many benefits over other extraction sources, including a shorter cycle time, lower cost, and the ability to expand and immobilize on any inexpensive solid media (substrates). They also produce higher yields and are often convenient for genetic modification. Enzyme catalysts, in comparison to chemical catalyzed reactions, require milder atmospheric conditions for the successful activity, resulting in a significant reduction in energy consumption and hence operating costs. Enzymatic reactions also have high substrate selectivity and can esterify triglycerides and free fatty acids in a single step, resulting in a high-quality byproduct (glycerol) with no waste or recovery expenses. Enzymes are very specific to their substrates, so there are no unintended side reactions and no requirement for post-reaction byproducts. Enzymes are highly specific to substrates, eliminating the need to isolate the byproduct after reaction and unwanted side reactions. Enzymatic reactions are also environmentally safe, presenting no risks during disposal. Over the last decade, immense efforts have been made to focus on lipase enzyme synthesis and characterization for a variety of applications. Lipase as a biocatalyst in biodiesel processing is a relatively new field of research, with specific applications for first- and second-generation biodiesel feedstocks including sunflower oil, Jatropha oil, soybean oil, and palm oil (Saranya et al. 2020). Enzymatic catalysts can be useful in the synthesis of ethyl esters, but the reaction conditions must be optimized (temperature, molar ratio, pH, amount of catalyst). By using a co-solvent or longer reaction durations, ester yields can surpass 80% (Brunschiwig et al. 2012). Because oil extraction and transesterification occur concurrently, the enzymatic in situ approach takes longer than standard oil transesterification. The optimal length of the biotechnological phase has been determined to be 19–24 hours (Makareviciene et al. 2020; Gumbyte et al. 2018). The production of biodiesel using an alternative feedstock, date pit oils, has been investigated. These oils provide the same advantages as pure oils. But they are derived from a waste substance. Biodiesel was produced by transesterifying the extracted oils with methanol in the presence of Novozym®435 or Eversa® Transform. Because methanol suppresses lipase activity, the oil and enzyme are introduced first, then the methanol (Al-Zuhair et al. 2017). New enzyme-based catalysts (biocatalysts) have been created in recent years to avoid some problems such as excessive usage of energy, material corrosion, and the difficulty of transesterifying triglycerides as well as post-reaction techniques such as catalyst recovery (Bautista et al. 2015), resulting in improved specificity and selectivity. Transesterification and esterification reactions can be carried out at lower temperatures with immobilized lipases and with less energy, making the catalyst recovery and glycerol purification easier (Guldhe et al. 2015). However, water in the reaction medium which may allow esters to hydrolyze is the major issue with biocatalysts. Furthermore, the usage of some solvents, like methanol, can cause the catalyst to become inactive (Navarro et al. 2016). For the whole procedure to be commercially feasible, heterogeneous biocatalysts must be used. So, they can be reused, owing to the high price of enzymes. Furthermore, immobilizing solid-state enzymes improves thermal and chemical stability while also protecting the denaturation of enzyme molecules. Enzymatic immobilization can be accomplished in a variety of ways, including attachment to a support, cross-linking and containment or encapsulation, and. The most popular method is to covalently or ionically link the enzyme to the support or to use physical adsorption. Materials as carbon nanotubes or mesoporous silicas (FDU-12, MCM-41, SBA-15, SBA-16,) (Rios et al. 2016; Zniszezol et al. 2016) have been used to achieve this immobilization. The enzymes can be housed in huge pores or cavities in the materials mentioned above. However, to obtain improved anchorage, it is normally important to functionalize the support surface with phenol groups, sulfur, chloride, or amine (Da Silva et al. 2018). Lipases' catalytic activity is highly dependent on the source organism that produces the enzyme due to their high specificity for various substrates. Lipases from *Thermomyces lanuginosus*, *Candida rugosa*, *Pseudomonas cepacia*, *Candida antarctica* and *P. fluorescens*, have been used to make the majority of biodiesel from microalgal oil. *C. antarctica* is commonly in the form of Novozym 4356, a commercial catalyst. Although the majority of studies used single lipases, a few writers found that using a combination of lipases increased Fatty Acid Ethyl Ester (FAEE) yield. To enhance biodiesel processing methods, the principle of combi-lipase biocatalysts was recently introduced (Sánchez-Bayo et al. 2019). Because of the simplicity for separation the product and their reusability in subsequent processes, the use of immobilized enzymes will greatly increase fine and specialty chemical production. Biocatalysts have been immobilized on a wide range of surfaces, including alumina, silica composites, silica, alginates, polymers, resins, glass beads, and others. The use of carbonaceous supports in the immobilization of biocatalysts has been reported before, but it has not been fully exploited. The higher cost of biocatalysts, supports production from waste biomass, such as carbon material, is always chosen over the other supports mentioned previously (Dhawane et al. 2019).

5.4. Application of Lipase for processing of biodiesel from a number of sources

Immobilized lipase plays a critical function in the transesterification process. Lipase enzymes are effective catalysts, so their synthesis and usage may be a safer choice than chemical catalysts. Lipase enzyme is primarily generated by microbes in the atmosphere. A number of natural foods produce the lipase enzyme (animals and plants). Maize seeds, developing barley seeds, papaya, babaco latex, and other sources all contain lipase. Lipase enzymes were isolated and immobilized on polypropylene support from *P. fluorescens*, *P. cepacia*, and *Mucor* sp. In the production of biodiesel, lipase produced from fungus, primarily yeast and filamentous mushrooms, is often employed. Lipase from yeasts like *Candida rugosa*, *Candida antarctica*, and others is used to make biodiesel in China. Lipase from *Aspergillus niger*, *Thermomyces lanuginosus*, *Rhizomucor miehei*, *Rhizopus oryzae*, and *Penicillium expansum* is also used to make biodiesel (Bhan et al. 2020). Kareem et al. (2017) used a solid-state fermentation procedure to manufacture lipase enzyme from *A. niger*.

Several experiments have established that plant-derived lipase enzymes can also be used to make biodiesel (alkyl ester). Lipase has been tested as a catalyst potential for biodiesel processing using extracts from a variety of plants and their components. Plant lipase, on the other hand, has received less attention for biodiesel production than microbial lipase. Plant parts used to create crude lipase include black cumin seeds, seeds of castor bean, rapeseed, rice bran, lipase of wheat, seed of barley, linseed, and maize seed powder. Lipase, like Babaco and papaya latex, is utilized in oil transesterification. Suwanno et al. (2017), examples, employed palm oil as a substrate and isolated crude lipase from palm fruit. The use of enzyme catalysts will reduce the need for chemical catalysts, making the process more environmentally sustainable. The lack of a large volume of feedstock and the lipase enzyme are the two biggest obstacles to commercial biodiesel processing.

6. Characterization Of Date Seed Oil And Its Biodiesel

Marketing of biodiesel can be authorized by ASTM D6751 and ISO EN14214 which it related to DSO.

6.1. Fatty acids profile of date seeds oil

The most of seed oil is made up of triacylglycerides (TG) and other minor components like phytosterols, phenols, carotenoids, tocopherols, and phospholipids (Gunstone et al. 2013). The seed oil has a higher proportion of fatty acids. The fatty acid (FA) composition of the oil samples was investigated using a Gas Chromatography facility. To get the oil's fatty acid composition, TG must be converted to fatty acid methyl ester (FAME), which lowers the boiling point. Biodiesel contains five fatty acids lauric acid, myristic acid, linoleic acid, palmitic acid, linoleic acid, and oleic acid with varying quantities characterizes the fatty acid of many date seed oils, and account for more than 90% of total fatty acid content (Nehdi et al. 2018). Some fatty acids, like linolenic, gadoleic and palmitoleic acids, were observed in lower concentrations. Date seed oil's fatty acid makeup varies according to the varietal, stage of fruit production, and extraction procedure. Fifty percentage saturated fatty acids show seed oil content, 43% percent monounsaturated and 8% percent polyunsaturated fatty acids (Bouallegue et al. 2019). In the Deglet Nour cultivar, oleic acid has been the most abundant unsaturated fatty acid (41–48%), lauric (17.8%) was the most prevalent saturated fatty acid, and linoleic acid was the most abundant saturated fatty acid in the Allig cultivar (15%). Furthermore, date seed oils have a lower degree of unsaturation than common olive oils. As a result, the date seed oil is high in oleic acid and has a considerable fatty acid concentration comparable to that of rice bran oil. Because of their excellent durability and nutritional value, oils having a high oleic acid concentration are quite interesting. Owing to its health benefits against a variety of heart and circulatory disorders, low saturation, potential for decreasing blood cholesterol, and high oxidative stability, oleic acid is among the most essential unsaturated fatty acids in human food (Mrabet et al. 2020).

6.2. Date Seed Oil's Physicochemical Characteristics

Date seed oil content varied according to date variability, location of harvest, particle size, and extraction method. Degla-Baidha and Tafezouine are two Algerian cultivars., for example, have 5.6 and 5.4 percent oil, respectively (Boukouada et al. 2014), Sudanese cultivars (Albarakavi, Alqundeila) had 10.5 and 7.8 percent (Abdalla et al. 2012), and three types of Iranian dates (Shekar, Kabkab, Shahabi) had 8.2, 8.3, and 8.4 percent, respectively (Akbari et al. 2012). These values show that in comparison to other seed oils, seed oil has a significant number of dates, like corn (3.0–6.5%). Date seed oil possesses physicochemical

qualities such as being liquid at ambient temperature, having a yellowish colour, and a nice odor. The purity of plant oils is determined by several factors:

Iodine value (IV), however, does not identify a particular composition of fatty acids, which is a desirable character for the evaluation of unsaturation and stability of oils in industrial applications. High IV of oils shows the occurrence of numerous unsaturated bonds and extra unsaturated fatty acids (Comelio-Santiago et al. 2021). Oil IV is also well-known to forecast the drying properties of oil and to represent them. Dry oils are approximately 190 in IV, 130 semi-drying, and 100 non-drying. Thus, date seed oil is categorized as non-drying with an IV lower than 100.

Acidity is an additional feature attribute and it's also the amount of KOH required to neutralize the free acids in one gramme of sample. The acidity of biodiesel is a factor to consider when storing and transporting it, as it can cause engine part corrosion and deposits to accumulate. The mass (mg) of base KOH required to neutralize 1 g of methyl ester is defined as the acid number (AN) of a fuel (Gonzaga et al. 2021). Due to the fact of strong mineral acids have a greater effect on FFAs than weak carboxylic acids, AN is an excellent indicator of FFA in biodiesel. In the methyl ester, AN is already a measure of water content or oxidation susceptibility. The DSO biodiesel had an AN of 0.29 mg KOH/g, that was far lower than the ASTM D 664 requirement of 0.5 mg KOH/g.

The saponification value (SV) is a metric for calculating the molecular weight of fatty acids. It is based on their average molecular weight and offers information on several kinds of fatty acids. Low molecular weight fatty acids have SVs in excess of or equivalent to 180 mg KOH/g, and inversely. It's often used to find out what kinds of triacylglycerols are present in the oil. Date seed oil's high SV implies a high proportion of triacylglycerols with low molecular weight, according to Nehadi et al. (2012). This is a beneficial feature for using date seed oil as biodiesel and in the production of melting soaps and shampoos (Reddy et al. 2017). Date seed oil has an SV of 198 to 228 mg KOH/g oil on average (Herch et al. 2014). Useful oils such like oil of palm (196–205 mg KOH/g), corn oil (187–196 mg KOH/g), and oil of palm kernel (247 mg KOH/g) all had similar results. The date seed oil has physicochemical features that suggest it could be valuable as an oil source, despite its lower extraction yield than other oilseeds. This oil could be used in cooking or industry, but it could also be utilized as functional oil due to its phytochemical makeup.

Stability, Biodiesel stability refers to the ability of biodiesel to withstand chemical reactions or changes at high temperatures (thermal stability) while also long-term storage conditions at near-ambient temperatures (storage or oxidation stability). Owing to the existence of unsaturated molecules, biodiesel is more susceptible to oxidative deterioration than petrol diesel (with double bonding). Linoleic acid (C18:2) (fraction in DSO: 9.95 percent) and linolenic acid (C18:3) are the FAs with the highest oxidation ability (fraction in DSO: 0.11 percent). Uniform trace amounts of unsaturated fatty acids can cause significant oxidation. High-temperature air, metal pollutants, and the existence of light can affect biodiesel oxidation, that it may enhance oxidation by 30,000 times (producing "photo-oxidation"). Under the right conditions, biodiesel oxidation produces hydroperoxides, which polymerize and cause increases in acidity and viscosity. Indeed, tocopherols and tocotrienols, antioxidants found obviously in seeds of date, can inhibit the oxidation of DSO biodiesel (51.5 mg of total tocopherols have been discovered per 100 g of date seed oil) (Al-Hartomy et al. 2021). Although the widespread establishment of the biodiesel oxidation issue, there is no commonly recognized method for evaluating biodiesel stability has been developed.

Flash Point (FP), definite as the lowest temperature where the fuel discharges sufficient gas to generate a combustible combination, is a security standard that governs fuel shipping and preservation (Fu 2019). The DSO biodiesel's FP was 164°C, nearly triple that of diesel fuel that was commonly used (55–66°C) and significantly higher than the requirements (min. 130°C in ASTM D6751 and min. 120°C in EN 14214). As a result, the DSO biodiesel's high FP is an appealing feature since the fuel is extremely safe. The methyl ester's FP is determined by its ingredients of the vapour pressure. As a consequence of the drastic drop in biodiesel FP caused by the presence of methanol residual (FP 10°C), the ASTM D6751 standard requires that the methanol content be less than 0.2 vol. percent, which the DSO biodiesel was able to achieve after purification (do Nascimento et al. 2020).

Composition of Chemical Elements

Sulfur, calcium, magnesium, arsenic, sodium, and potassium are not found in biodiesel (ester) molecules, but they can be found in the feedstock or occur during the manufacturing process. By clogging the particulate set-up or the consume catalytic converter, such components poison the emission control after-treatment system (Ahmadi et al. 2019). Furthermore, these components result in increased noxious releases. The concentrations of S, Na, and K in DSO biodiesel were within acceptable limits. Acceptable levels of Mg, Ca, and P were also attained after a phosphoric acid handling to lower the ranks of these elements.

Cetane Number (CN), the DSO biodiesel had a CN of 62, which was significantly higher than the standards for petrol diesel (43 in the US and 50 in the EU). This high value is attributed to the DSO feedstock's high saturated fat content (44.55 wt.%). Because DSO biodiesel has a higher CN, it has a faster ignition time, which improves combustion. Too much fuel is supplied before ignition if the ignition delay is too long, resulting in quick burning, rapid pressure ascendance, and the possibility of cracking (Ahmadi et al. 2019).

Cloud Point (CP), is defined as the measure of cold weather where below this degree of temperature the wax crystals appeared. The ASTM D6751 and EN 14214 standards do not define a CP boundary; nevertheless, they do demand that the CP of fuel be stated so that customers can create educated decisions. Because it is made from saturated fats with significant molecular weights, the DSO's CP was comparatively high (9.4° C). In cold weather, a higher CP funds denser fuel and the possibility for fuel injectors and filters to become clogged. DSO biodiesel had the sixth-highest CP out of 35 biodiesels tested from a variety of feedstocks (Sajjadi et al. 2016). Several therapies or alterations to reduce the impacts of high CP in fuel have been proposed. For fixed diesel vehicles in unheated locations, fuel lines and filters can be protected, or fuel tanks and lines can be installed with heaters. Another option is to use winterization, which involves cooling the methyl ester and then filtering and separating the high-melting components. However, owing to the extraordinary percentage of biodiesel misplaced during the progression (up to 25%), this is not a favorite option. Another possibility is to use branched-chain alcohols (like isopropyl and 2-butyl) in place of classic alcohols (as methanol), which will lower the CP by 7–14° C (Mishra et al. 2021). Transesterification reaction and the high cost of branched-chain alcohols rather than methanol are the classic challenges.

A big successful solution is to mix high and low-CP biodiesel (Moser 2008). Cold flow improvers (additives) such as polymethacrylate and Malan-styrene ester reduce the CP by altering the shape and size of the potential crystals, which is arguably the most practical approach (Bahale et al. 2009). Some other evaluation tests such as Distillation, Sulfated Ash, and Engine Performance are still required to complete the assessment of the produced biodiesel. The following Table 3 shows DSO biodiesel characterization concerning American and European standards (ASTM and EN).

Table 3
Properties of DSO biodiesel and it's related to American and European standards

| Character | Units | Standard | DSO Biodiesel | References | |
|----------------------------|---------------------------------|--------------|---------------|-------------------|--------|
| Density @ 40 ° C | kg/m ³ | ASTM D 93 | 897.4 | Kamil et al. 2019 | |
| Viscosity | mm ² /s | ASTM D 445 | 4.38 | | |
| Cloud point | ° C | ASTM D 2500 | + 9.4 | | |
| Acid Value | Mg KOH g-1 | ASTM D 664 | 0.29 | | |
| Chemical Element Content | Sulfur | ppm (µg/g-1) | ASTM D 5453 | | 0.93 |
| | Calcium & Magnesium Combined | mg/kg | EN 14538 | | 3.27 |
| | Phosphorous content | % Mass | ASTM D 4951 | | 0.0002 |
| | Sodium & potassium Combined | ppm (µg/g-1) | EN 14538 | | 3.2 |
| | Flash Point | ° C | ASTM D 93 | | 164 |
| Water & sediment | (vol. %) | ASTM D 2709 | 0.019 | | |
| Sulphated ash | % Mass | ASTM D 874 | < 0.02 | | |
| Oxidation stability | Hr @ 110 ° C | EN 15751 | 7.4 | | |
| Carbon residue | % Weight | ASTM D 4530 | 0.023 | | |
| Cetane number | %/ vol | ASTM D 613 | 62 | | |
| Higher heating value (HHV) | MJ/kg | ASTM D6751 | 32.63 | Fadhil et al.2017 | |
| Saponification Value | mg KOH/g | ASTM D6721 | 201 | | |

7. Techno-economic Feasibility Of The Biodiesel Production

For commercial-scale biodiesel production from non-edible oil feedstock, a techno-economic feasibility analysis is critical. Techno-economic feasibility assessments are influenced by commercially successful transesterification methods, feedstock cost, biodiesel sale price, and numerous by-products produced throughout biodiesel production (Rinc'on et al, 2014). When estimating the biodiesel production value, operational expenses (feedstock price, chemicals, employees, and utility), fixed charges (tax), and general costs (research, advancement, and financial) were all considered (Rezania et al 2019). Furthermore, the feedstock price is the most important issue in biodiesel manufacturing, accounting for around 80% of the entire cost. In addition, the cost of catalyst has an impact on biodiesel generation. On the other hand, using low-cost components like biomass waste-derived catalysts would minimize biodiesel production. Biodiesel conversion technology, employment costs of harvesting non-edible crops, and transportation costs of non-edible crops from the plantation to the biodiesel production plant all must be put into consideration throughout technoeconomic feasibility valuation for producing biodiesel from non-edible oil.

8. Non-edible Oil As Both A Feedstock For Biodiesel: Potential And Challenges

Thanks to rising modern technology, non-edible feedstock can be a cost-effective and efficient resource for prospective biofuel development. It's a clean energy source made from domestic and renewable energy that may be blended with diesel to make biodiesel (Atabani et al 2013). The usage of non-edible crops, (especially their wastes) as a feedstock would put an end to the dispute over food vs. biodiesel. Biodiesel derived from non-edible crops also offers unique properties such biodegradability, renewability, ease of availability, reduced sulphur content, and higher heat content, making it an effective biodiesel feedstock

alternative. The emergence of non-edible crops as a potential biodiesel feedstock, according to the review of the literature, represents a hazard to energy security. This is due to the fact that: (i) forests are the source of non-edible crops, making harvesting, gathering, and transportation difficult. (ii) the main disadvantages of establishing biodiesel producing industries include worse fuel efficiency, non-edible crops are only available during certain seasons, and marketing avenues are useless. (iii) the existence of high FFAs and moisture content needs a pre-treatment to decrease FFAs and water content in the oil prior to the transesterification method. On the other side, new technology, especially waterless extraction processes like supercritical fluids, could prevent it. (iv) Non-edible crops' oil quality is harmed by a lack of post-harvest technologies. (v) Existing extraction of oil and biodiesel conversion technologies are inefficient because they necessitate several purifying and separation processes. As a result, via non-edible oil as a feedstock for biodiesel presents both obstacles and opportunities for use as a petro-diesel alternative fuel with environmental and economic benefits. This calls for more research into non-edible crops or crop waste production and cost-effective biodiesel conversion technology. These will make the most of the restricted amount of crop-growing land accessible

9. Future Perspectives

Biodiesel production is rapidly increasing around the world based on energy security and other environmental concerns. The governments of industrialized countries are under enormous pressure to enact mandatory rules requiring a mixture of biodiesel and traditional fossil fuels. Government controls to switch to renewable energy, increasing petroleum prices and emerging pollution concerns will all drive up demand for biofuels in the coming years. Despite the numerous advantages of biodiesel, there are still hurdles that must be addressed in order to create biodiesel on a commercial basis. It's worth noting that feedstock oil makes up the lion's share of the production costs. As a result, the most important criterion in cost-effective biodiesel manufacturing is optimal feedstock oil selection. As a result, some waste oils (such as date seed oil) may provide a long-term solution for biodiesel synthesis, although this requires a well-developed feedstock collection management system. Non-edible plants with high yields should be the focus of future study. Instead of their homogeneous counterparts, the most promising catalysts for biodiesel generation are heterogeneous and enzymatic catalysts. Heterogeneous catalysts are simple to separate, recover, and reuse from reaction mixtures, leading in higher efficiency and cheaper production costs. Enzymatic catalysts offer similar advantages, but the reaction can be done out under milder working conditions even with low-cost high FFA oil. Accordingly, the biodiesel technologies of the future seem to be heterogeneous and enzymatic catalysts. In recent years, various excellent and innovative biodiesel enhancement approaches have been introduced. Heating of microwave, ultrasonic irradiation, reactors of membrane, stationary mixers, reactive distillation, and other intensification techniques are only a few of the methods for reducing energy use while improving reaction rate and biodiesel production. Most of these technologies, however, will require more research, particularly through optimization studies and mathematical modelling, in order to obtain a better knowledge of reaction kinetics, develop efficient reactors, estimate costs, and scale up from the current laboratory-scale stage. Aside from the aforementioned challenges, social acceptance of biodiesel is a major issue relating to public trust. It is not possible to force society to embrace it. Rather, those working in this field, as well as authorities, must make a real effort. To summarize the preceding discussion, biodiesel's prospects include the following challenges:

- To develop new and abundant biodiesel feed stocks from cost-effective sources that do not conflict with sources of food.
- To develop heterogeneous catalysts and a lipase immobilization method that are less expensive, easier to use, and take less time.
- To improve the present biodiesel production method by employing process intensification techniques that is appropriate feedstock and catalyst at a cheap cost
- Persuade people that biodiesel is a suitable substitute for petroleum-based diesel.

Conclusion

The current review article aimed to contribute to solving the global energy crisis. Palm date seeds could be regarded as a rich and attractive waste that has a valuable content of very efficient oil as a source of biodiesel. Several techniques were used for the extraction of oil from date seeds. But new and advanced methods should be used to increase the extraction efficiency. The DSO

converted to methyl ester via the process of trans esterification in the presence of an economic and viable catalyst. The biodiesel produced for marketing should be authorized by ASTM D6751 and ISO EN14214. So, some evaluation tests should be performed to confirm the assessment of the produced biodiesel. The effects of biodiesel produced from the date seed oil on the environment and human health were evaluated through the life cycle assessment. Finally, we could conclude that the date seeds would be progressed from just a waste to a very important feedstock for biodiesel production and that would support the economic and public development of date producer areas.

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Figures

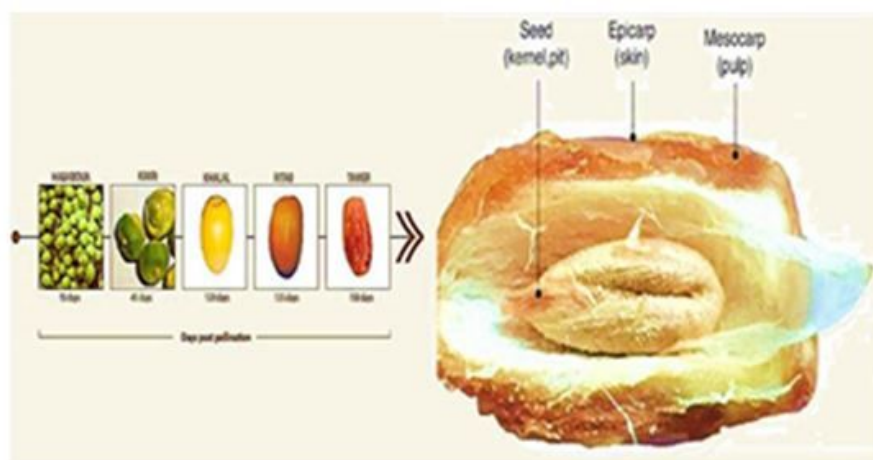


Figure 1

A. Development of date fruit over time (Ghnimi et al 2017) B. The anatomy of the Tamar stage of the date fruit (Khalil et al 2017)

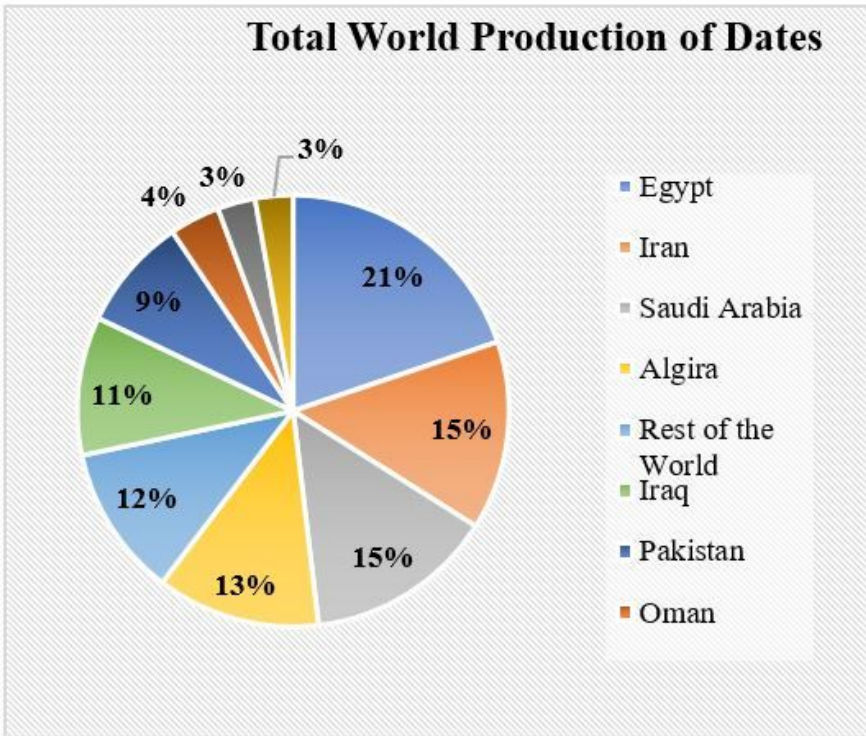


Figure 2

World production of dates to A1-abdulkader et. al.(2016).



Figure 3

Collection of date seeds process

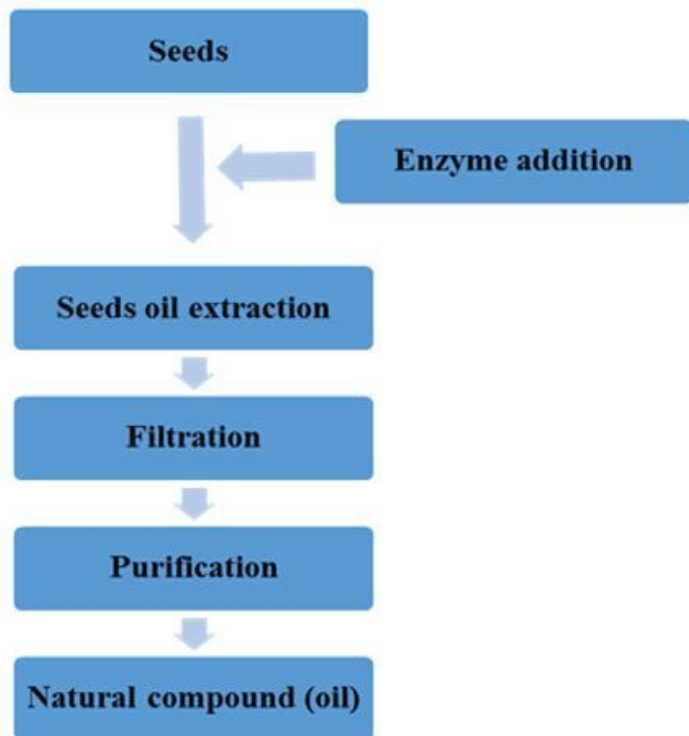


Figure 4

the steps of seeds oil extraction with Enzyme addition

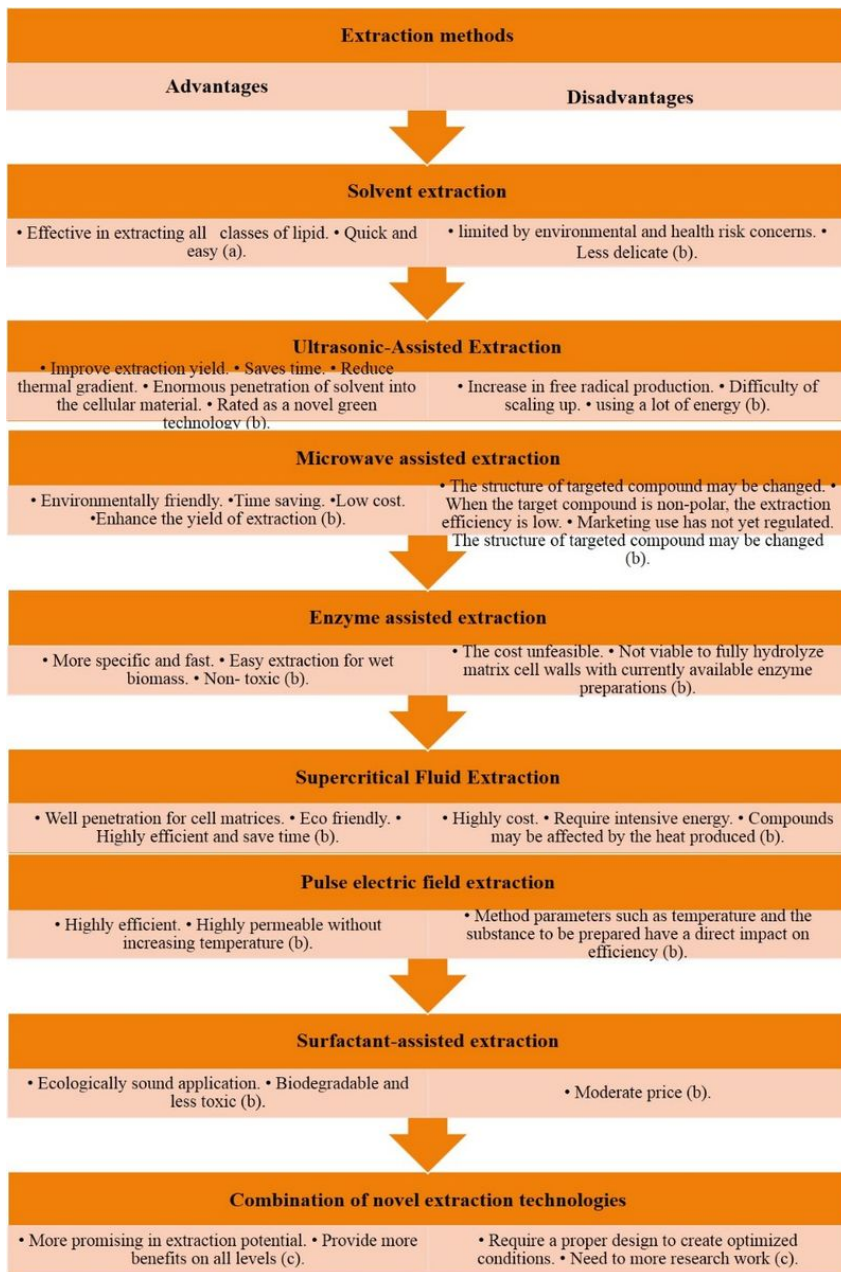


Figure 5

Advantages and disadvantages of almost all techniques used in oil extraction (a) Ranjith Kumar et al. 2015, (b) Okolie et al. 2019, (c) Wen et al. 2020.