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Review article

Critical review on sesame seed oil and its methyl ester on cold flow and oxidation stability

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ABSTRACT

The demand for renewable energy is steadily increasing due to rapid population growth and economic development worldwide. An additional reason is that fossil fuel reserves are limited, and this situation results in their non-uniform availability globally. Furthermore, the attitudes of the society, energy policies and technology choices are constantly changing. Thus, renewable energy resources are now considered good alternatives to fossil fuels. In the meantime, liquid energy, such as methyl ester from locally produced vegetable oils, is well accepted by many countries, even though it is currently being blended up to 20% with petroleum fuels. Recently, the industrialisation of biodiesel is a major problem because of its poor cold flow properties and oxidative stability. Vegetable oils are also being blended in an appropriate proportion before transesterification to obtain the desired properties in biodiesel. Similarly, poor cold flow properties and oxidative stability can be improved by choosing suitable vegetable oils for making blends. Amongst all available vegetable oils, sesame seed oil (SSO) has unique cold flow properties and oxidation stability, particularly because of naturally occurring *antioxidants* and *preservatives*, which enhance the stability of oil towards rancidity. Therefore, SSO can be used as a potential feedstock for blending with other vegetable oils to enhance the overall cold flow and oxidation stability properties. This overview summarises sesame cultivation, SSO production, the physicochemical properties of SSO and its potential as an alternative renewable fuel source. In this review, the physicochemical properties of sesame biodiesel are compared with those of biodiesel derived from other vegetable oils. Results show that blending SSO with palm oil before transesterification will successfully improve the cold flow properties and oxidation stability of palm methyl ester (biodiesel).

Contents

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1. Introduction

Rapid population growth has increased energy consumption around the globe. The demand for energy in every sector (e.g. transport, agricultural and domestic) is increasing gradually, and a shortage of fuel will consequently occur due to a gradual decline in fossil fuel reserves (Wakil et al., 2015b). The depletion of fossil fuels poses a serious threat for oil and gas companies to meet the energy demand for all sectors in the future. Oil and gas producers meet energy needs by using available fossil fuel reserves, and this utilisation significantly increases carbon dioxide (CO_2) emissions globally (Absi Halabi et al., 2015). The major concern in replacing fossil fuels with alternative renewable fuels is the eradication of combustion emissions, which are directly linked to climate change, global warming and various diseases (Aransiola et al., 2014). Fossil fuel pollutes the air by releasing toxic gases (i.e. nitrogen oxide (NO_x), unseen particulate matter (PM), carbon monoxide (CO) and unburned hydrocarbons)). A high concentration of PM in the air can cause cancer and respiratory diseases (e.g. asthma and allergies) (Vardoulakis et al., 2015). According to the Global Status Report (2018), the global proportion of energy generated from different sources is as follows: 10.4% (modern sources of renewable energy), 7.8% (traditional biomass), 2.2% (nuclear energy) and 79.5% (fossil fuels). The transport sector represents the bulk of oil consumption. Nearly 50% of total fossil fuel consumption relates to the energy needs of the transport sector. Approximately one-third of the total global energy consumption is attributed to the transport sector. The global energy demand for the transport sector has increased by 39% over the past decade due to the increase in the movement of freight and overall transport demand in emerging countries globally. The transport sector is estimated to contribute up to 50% of the global greenhouse gas emissions by 2030. Renewable and sustainable fuels can overcome the reliance on fossils fuels to comply with the Kyoto Protocol. The share of renewable energy in the transport sector accounts for 3.1% of global energy consumption. A total of 42 countries worldwide have set national targets to increase the share of renewable energy in transport by 20% and 40% by 2020 and 2030, respectively (2018., 2018). The three major categories of biofuels are first-generation (i.e. bioethanol, a biofuel derived from sugar and starch, such as corn and sugar cane), second-generation (i.e. biodiesel, a biofuel derived from oils of vegetables, such as palm, jatropha, neem, rapeseed and sesame) and third-generation (i.e. biofuel that is derived from algae) biofuels (Mat Yasin et al., 2017; Silitonga et al., 2019). Second- and third-generation biofuels can be used to produce biofuels for the transport sector because the use of first-generation biofuels has a serious impact on food supply. The most suitable replacement for fossil fuels is biodiesel because it is quite similar and has better physicochemical properties (e.g. greater lubricity, higher cetane and low sulphur content) than fossil fuel diesel (Patel and Sankhavara, 2017). Biodiesel can be used as an alternative fuel without modifications in an existing diesel engine.

The conversion of vegetable oil into biofuel is not a new idea. In 1900, Rudolph Diesel was the first person to test his new invented diesel engine (i.e. compression-ignition engine) with renewable biofuel extracted from peanut oil instead of petroleum diesel, without any modifications to the engine (Dixit et al., 2012). Biodiesel is safe to use, nontoxic and biodegradable, has high cetane number (CN) and combustion efficiency and provides good lubricity with low sulphur content (Wakil et al., 2015b; Imdadul et al., 2016). Previously, many researchers have studied the production of biodiesel from various feedstocks and the behaviour of biodiesel related to engine emissions and performance. Soybean, palm and rapeseed biodiesels are used in the United States, Asia and Europe, respectively (Silitonga et al., 2013). Currently, the major issue with biodiesel commercialisation and industrialisation is its poor oxidation stability and cold flow characteristics. Synthetic antioxidants are usually used to enhance its oxidation stability, and different additives are utilised to improve its cold flow properties. In the past, some researchers have blended biodiesel obtained from different feedstocks to improve these properties. Researchers today are blending the feedstock oil before transesterification to improve its properties in accordance with standards. For instance, palm oil is predominantly used in Asia, especially in Indonesia and Malaysia. The cold flow properties of palm oil are poor due to the high content of saturated fatty acids (FAs). Various researchers have diagnosed the problems associated with engine operation during low-temperature climate as the result of clogging of filters, incomplete combustion, starting problem and fuel starvation (Dwivedi and Sharma, 2014). A high degree of unsaturation in biodiesel results in poor oxidation stability but good cold flow properties. Conversely, a high percentage of saturated FAs results in good oxidation stability but poor cold flow properties (Lanjekar and Deshmukh, 2016).

The selection of feedstock is therefore critical for blending with palm oil to improve its cold flow properties. Vegetable oils with a high degree of unsaturation can be used for blending with palm oil. However, at the same time, the oxidation stability of palm oil will be decreased. According to literature, sesame seed oil (SSO) can be the most suitable option for blending with palm oil compared with all other feedstock oils. SSO has a high degree of unsaturation (up to 85%) and thus has good cold flow properties. Furthermore, it also exhibits high oxidative stability due to naturally occurring antioxidants (i.e. sesamin sesamol and sesamolin) with tocopherols (i.e. vitamin E) (Pullen and Saeed, 2014).

This review aims to highlight the potential of SSO biodiesel as a green fuel to replace petroleum diesel. This review explains sesame cultivation and SSO production, applications, composition and properties. Moreover, conversion methods, such as transesterification by conventional methods or ultrasound, of SSO to

List of abbreviations

ANN	Artificial neural network
APE	Allylic position equivalent
ASTM	American society for testing and materials
BAPE	Bis-allylic position equivalent
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
Ca	Calcium
CCD	Central composite design
CFPP	Cold filter plugging point
CH_3ONa	Sodium methoxide
CN	Cetane number
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Cloud point
CV	Calorific value
EN	European
EU	European union
FAME	Fatty acid methyl ester
FAO	Food and agricultural organisation
H_2SO_4	Sulphuric acid
HCl	Hydraulic acid
IPGRI	International plant genetic resources institute
K	Potassium
KOH	Potassium hydroxide
KV	Kinematic viscosity
Mg	Magnesium
MPOB	Malaysia palm oil board
MS	Malaysian standard
Na	Sodium
NaOH	Sodium hydroxide
NOx	Nitrogen oxides
OS	Oxidation stability
PDSC	Pressurised differential scanning calorimetry
PG	Propyl gallate
PM	Particular matter
PP	Pour point
PY	Pyrogallol
RIP	Rancimat induction period
RSM	Response surface methodology
SOME	Sesame oil methyl ester
SSO	Sesame seed oil
TBHQ	Tert-butyl hydroxyl quinone
UHC	Unburned hydrocarbons

sesame methyl ester are discussed. Techniques used for optimising the biodiesel yield of SSO are also discussed. Lastly, the physicochemical properties of sesame are discussed in detail. In particular, the stability of biodiesel and cold flow properties of biodiesel and sesame methyl ester are compared with those of other vegetable oil methyl esters to demonstrate that sesame biodiesel is a potential feedstock for the future.

2. Overview of sesame seed plantation

2.1. Background history of the sesame plant

Sesame (*Sesamum indicum L.*) belongs to the *Pedaliaceae* family and is widespread in tropical and subtropical regions of Asia, Africa and South America. The word 'sesame' is derived from the Arabic word 'simsim' (Moazzami and Kamal-Eldin, 2009). Globally, it is known as sesame, as til in Asia and as benniseed or simsim in Africa (Amoo et al., 2017). According to prehistory studies, cultivation of sesame was discovered in South Asian wild populations, and cultivation originated in South Asia before 2000 B.C from the time of the Harappan civilisation (Fuller, 2003).

The major crop cultivated in Indus valley civilisation was sesame and later on cultivated in west Mesopotamia (Tunde-AkintundeTY and Akintunde, 2012). SSO was used by Assyrians in medicines, food and salves (ointments).

Sesame is commonly called the 'queen of oilseeds', and SSO was the first oil discovered and consumed by humans; it is also referred to as an 'orphan crop' (Moazzami and Kamal-Eldin, 2009). Sesame has been rarely studied and has not been given a crop mandate by any research institute (Bhat et al., 1999). According to Were et al. sesame is listed amongst neglected and underutilised crop species; however, it has high potential according to International Plant Genetic Resources Institute (Were et al., 2006).

Sesame is the most valued and oldest oilseed crop due to its high-quality seed oil. Sesame is an erect, annual and herbaceous plant that grows 1–2 m tall (Islam et al., 2016). Sesame seeds are flat, pear-shaped, 2–3.5 mg in weight and 2–3 mm in length. Each capsule contains 50–100 seeds (Moazzami and Kamal-Eldin, 2009). Sesame seeds are oval and small, and they come in various colours, such as yellow, dark brown, white, grey, dark grey, black and reddish brown. The number of seeds per capsule, capsule length and seed size significantly vary depending on the cultivar. A total of 1000 sesame seeds weigh approximately 3 grams (Hegde, 2012).

Sesame seeds contain nearly 44%–57% oil, 18%–25% protein and 13%–14% carbohydrates (Borchani et al., 2010). In other literature, sesame seed contains 37%–63% oil depending on the variety, growing season and cultivar (Hegde, 2012). The most prominent feature of SSO is its resistance towards oxidation rancidity during long exposure to air (Islam et al., 2016). The significant resistance to oxidation is due to the naturally occurring endogenous antioxidants in SSO, such as tocopherols and lignins (i.e. sesamin and sesamolin) (Lee et al., 2008). The remaining part of sesame seeds after the extraction of oil (i.e. cake or meal) is rich in protein (45%–50%) and is typically used for animal feed. The cakes of roasted sesame seeds are rich in antioxidant compounds and can therefore be used as a potential source of antioxidants (Moazzami and Kamal-Eldin, 2009).

2.2. SSO capacity

According to statistics by the Food and Agricultural Organisation of the United Nations (FAO), the average global yield of sesame seeds in 2017 was 5.53 million metric tons, which was harvested on 9.98 million hectares. In 2017, major producers of sesame countries included the United Republic of Tanzania, Burma (Myanmar), India, Nigeria, Sudan, China (Mainland China), Ethiopia, South Sudan, Burkina Faso and Chad, as shown in Fig. 1. Sesame seed production shares of Africa, Asia, America and Europe in 2017 were 56.9%, 39.7%, 3.4% and 0%, respectively. Africa, Asia and America produced 3.14 million, 2.19 million and 0.189 million tons of sesame seeds, respectively (FAO, 2018). Amongst all oilseed crops, sesame is ranked at eighth with respect to oil production globally (Mehmood et al., 2018).

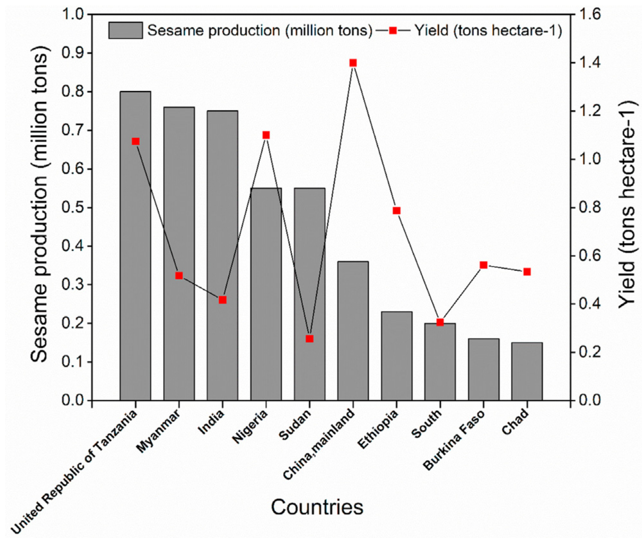


Fig. 1. Top producers of sesame in the world (FAO, 2018).

Table 1
Production of sesame seed and oil in different regions of the world (FAO, 2018).

Region	Sesame seed (tons)	Sesame oil (tons)
Asia	2 195 089	887 199
Africa	3 146 248	683 027
America	189 974	25 138
Europe	0	36 994
Oceania	0	1969

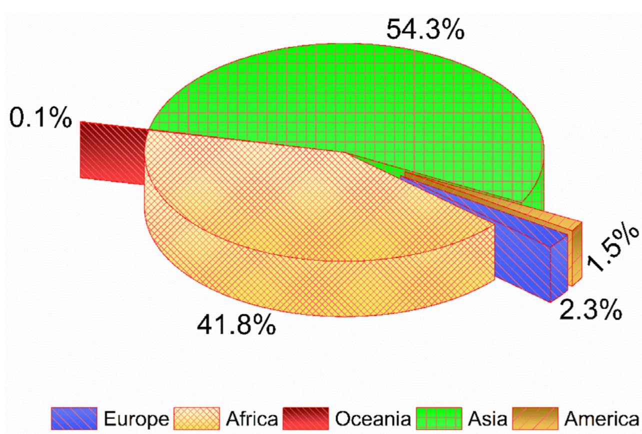


Fig. 2. Production share of sesame oil by region.
Source: FAO (2018).

According to FAO, average global SSO production in 2014 was 1.63 million tons, and major oil-producing countries were the United Republic of Tanzania, Burma (Myanmar), India, Japan, South Sudan, Sudan, Turkey, Republic of Korea and Uganda. Sesame seed production shares of Africa, Asia, America, Europe and Oceania in 2014 were 41.8%, 54.3%, 1.5%, 2.3% and 0.1%, respectively, as shown in Fig. 2 (FAO, 2015) (see Table 1).

The average yield of sesame seeds reported in the FAO report (2018) ranged from 256 kg/ha to 1400 kg/ha. The top three countries in the production of the highest yield were China (Mainland China), Nigeria and United Republic of Tanzania with 1400, 1100 and 1074 kg/ha, respectively, as shown in Fig. 1 (FAO, 2018).

The above-mentioned statistics about sesame seed and oil production should be taken as a rough estimation because most harvested crops are locally consumed and no suitable way to obtain the data for local and domestic production is available. Only several countries properly record data related to sesame seed and oil production and its part in international trade.

2.3. Medicinal, nutritional and industrial applications of SSO

Regarding medical use, sesame seeds oil and paste are applied to the skin for treating wounds and burns (Kiran and Asad, 2008). Around the globe, sesame is used for treatment of anaemia, amenorrhea, dysentery, respiratory infections, cholera, scorpion poison, dysmenorrhea, tinnitus, diarrhoea, dizziness, memory enhancement and bleeding piles (Hegde, 2012; Khan et al., 2014; Kapoor, 2017). SSO is used to treat coughs, burns, migraines, snake bites, tuberculosis, hair loss, eye diseases and demulcent in addition to being used as an antitussive (Hegde, 2012). Low-quality SSO is also used to produce soap, paints and lubricants (Anilakumar et al., 2010). Sesame seeds are used in food, such as buns, chips, crackers, salads, cakes and breads.

SSO has several industrial applications. For instance, sesame is used to prepare perfumes in Africa. Myristic acid made from SSO is used as an ingredient in cosmetics (Anilakumar et al., 2010). Sesamin acts as an antioxidant that can inhibit the absorption of cholesterol and the production of cholesterol in the liver due to its bactericidal and insecticidal effects (Morris, 2002). SSO is used as a solvent for skin softeners and drugs and an ingredient for margarines and soaps (Begum et al., 2000).

The demand for energy is increasing steadily owing to a growth in the global population. The consumption of fuel has increased to meet the needs of the automotive and energy sectors. The rising global energy demand is barely met due to the depletion of fossil fuel resources. In the future, vegetable oils will replace fossil fuels to fulfil energy requirements. Vegetable oil will be converted to diesel via transesterification reaction to produce a product called 'biodiesel'. Issues on the commercialisation of biodiesel produced by vegetable oils have been addressed to facilitate its potential to replace fossil fuels. These issues include high viscosity, deterioration of oil and fouling of engine. B20 (80% crude diesel and 20% biodiesel) can be used in existing diesel burned equipment (e.g. compression ignition engine and boilers) without modifications to the engine (Anilakumar et al., 2010). In the past, some researchers have produced biodiesel from SSO by transesterification using a homogeneous and heterogeneous catalyst in with methanol. Sarve et al. obtained optimised biodiesel from SSO using a catalyst ($Ba(OH)_2$) with methanol, which achieved maximum yield at 98.6% at 31.92 °C. The sesame biodiesel properties include flash point of 180 °C, cloud point (CP) of −5 °C, pour point (PP) of −9 °C, kinematic viscosity (KV) of 40 °C 4.47 and CN of 56.32 (Sarve et al., 2015).

Various researchers have investigated the use of sesame biodiesel in existing diesel engines and found lower emissions than those from crude diesel. B10 sesame biodiesel was tested in a diesel engine in comparison with other feedstock biodiesels, and the sesame infused biodiesel showed better engine performance than other biodiesels (Naik and Balakrishna, 2018). According to Altun et al. and Banapurmath et al. (Altun et al., 2008; Banapurmath et al., 2008) sesame biodiesel reduces the CO and NO_x emissions with a slight increment in the brake specific fuel consumption (BSFC). Different researchers have observed that using SSO methyl ester as a fuel reduces exhaust gas emissions, improves brake thermal efficiency (BTE) and increases BSFC. In accordance with the fuel properties of optimised biodiesel, sesame biodiesel has good cold flow properties and CN, which are favourable for commercialising it for diesel engine fuel blends. SSO is a feasible source of vegetable oil for biodiesel production to replace fossil fuels.

3. Chemical composition of SSO

The chemical composition of SSO contains oil (44%–58%), protein (18%–25%), carbohydrate (∼13.5%) and ash (∼5%) (Elleuch et al., 2007; Sandesh Suresh et al., 2019). The FA composition of SSO varies with geographical region and variety and from feedstock to feedstock. SSO consists of two main FAs: oleic and linoleic acids. The main FAs in SSO are oleic, linoleic, palmitic, stearic and linolenic acids. Table 2 summarises the composition of SSO FAs from different geographical areas (Karmakar et al., 2010; Hassan, 2012; Gharby et al., 2017). SSO contains more than 80% of unsaturated FAs, and the major composition belongs to oleic and linoleic acids. The saturated FAs in SSO represent less than 20% of the total chemical composition of SSO. Stearic and palmitic acids are the most important saturated FAs in SSO.

SSO is considered to be the most resistant towards oxidation rancidity amongst all vegetable oils. The presence of tocopherols (i.e. vitamin E) in SSO exhibits high resistance to autooxidation. SSO contains 0.5%–1.0% sesamin and 0.3%–0.5% sesamolin with few traces of free sesamol. The high resistance of SSO to oxidative rancidity depends on the presence of natural antioxidants (i.e. sesamin, sesamol and sesamolin) and tocopherols (Hegde, 2012).

3.1. Physico-chemical characteristics of SSO

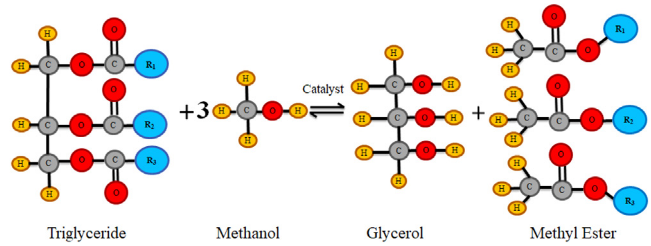
Various researchers have reported the physicochemical characteristics of SSO in the preceding literature. Typical FAs found in SSO are linoleic (C18:2), oleic (C18:1), palmitic (C16:0), stearic (C18:0) and linolenic (C18:3) acids, as shown in Table 2. These properties may vary depending on the extraction method, the geographic location of sesame seeds and analytical methods used for measurement. The physicochemical properties of SSO reported in the literature by various researchers are summarised in Table 3.

4. Transesterification of SSO

SSO can be used directly or mixed with petroleum diesel in a diesel engine. The use of pure SSO and its blends as a fuel in diesel engines is problematic due to its high viscosity, as shown in Table 3. The FA content and high viscosity of SSO lead to several problems in diesel engines, such as fuel lines and filter blockage, poor atomisation of fuel, injector coking and piston ring sticking, gum formation (due to oxidation) during storage and combustion, severe carbon deposition in the engine due to incomplete combustion and degradation and thickening of lubricating oil (Cetin and Yüksel, 2007; Altun et al., 2008). The solution to these problems caused by the high viscosity of virgin oil can be overcome by converting it to viable biodiesel.

Ma and Hanna (1999) reported four possible ways to convert virgin oil to biodiesel as a suitable and viable fuel source for diesel engines, namely, direct use and blends with crude diesel, micro-emulsification, thermal cracking (pyrolysis) and transesterification. The blending of virgin oil with crude diesel and emulsification of virgin oil with solvents (i.e. methanol, ethanol and 1-butanol) reduces the viscosity of virgin oil. Nonetheless, engine performance remains problematic due to carbon deposition and lubricant oil degradation. Thermal cracking or pyrolysis is normally used for producing biogasoline instead of biodiesel. Transesterification is the preferred method for the conversion of virgin oil to biodiesel to improve engine performance.

Transesterification is the chemical reaction of a triglyceride (fat or oil) with an alcohol to produce esters and glycerol, as shown in Eq. (1). The transesterification reaction is the conversion of triglyceride into an FA monoalkyl ester (biodiesel) with alcohol (methanol is used normally due to its lower cost and effectiveness Demirbas, 2005) using a catalyst, and it produces glycerol as a byproduct.



(1)

The presence of a catalyst is important during the transesterification reaction because it enhances the reaction rate and yield, and the selection of a catalyst depends on the free FA content, nature of oil and moisture content (Onoji et al., 2016). The alkali-catalysed transesterification reaction includes sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates and alkoxides of (Na and K), such as sodium methoxide. Acid catalysts include hydrochloric, sulphuric and sulfonic acids. Lipases can also be used as biocatalysts. The alkaline-catalysed transesterification is considerably faster than the acid-catalysed transesterification and is the preferred catalyst in the commercial production of biodiesel (Ma and Hanna, 1999). The conversion of triglycerides into FA mono-alkyl ester and glycerol occurs in three reversible steps (Patel and Sankhavara, 2017), as shown in Eq. (2)(a–c). The equations of a transesterification reaction are given below:

$$\text{Triglyceride} + R'OH \longleftrightarrow \text{Diglyceride} + R'COOR_1 \quad (2a)$$

$$\text{Diglyceride} + R'OH \longleftrightarrow \text{Monoglyceride} + R'COOR2 \quad (2b)$$

$$\text{Monoglyceride} + R'OH \longleftrightarrow \text{Glycerol} + R'COOR3 \quad (2c)$$

Homogeneous alkali base catalysts (NaOH, CH_3ONa and KOH) are the most reactive in the transesterification process for oil with a free FA value less than 1%. Acid catalysts (i.e. H_2SO_4 and HCl) are used for esterification of oil having a free FA value greater than 1% before transesterification reaction. Esterification is necessary to obtain rid of soap formation and a high yield during the transesterification reaction (Onoji et al., 2016). The production methods cited in the literature for the conversion of SSO to sesame methyl ester are conventional and ultrasonic-assisted methods.

The transesterification of SSO is conducted with homogeneous base catalysts (KOH, NaOH, CH_3ONa) using conventional method (Pullen and Saeed, 2014; Dawodu et al., 2014; Betiku and Adepoju, 2013; Karim et al., 2014; Ahmad et al., 2009; Wakil et al., 2014) and has biodiesel yields from 87.80% to 98.36%, as shown in Table 4.

Sarve et al. (2015) produced biodiesel from SSO with a heterogeneous catalyst ($Ba(OH)_2$) by using ultrasound-assisted transesterification at a frequency of 20 kHz, which produced a maximum optimised biodiesel yield of 98.6%. Therefore, ultrasound techniques can minimise the time and temperature to obtain the maximum yield (see Table 5).

4.1. Optimisation of SSO methyl ester

The optimisation of the transesterification process is important to achieve a high yield and ensure the purity of biodiesel. Determining the optimal values for process variables by conventional methods is time consuming because the procedure is costly in terms of labour, money, time consumption and material due to a large number of experiments involved (Ong et al., 2019). During the optimisation, conventional experiments are usually used to

Table 2
Fatty acid composition (%) of Sesame seed oil.

	Sudan (El Khier et al., 2008)	Congo (Nzikou et al., 2009)	Turkey (Ünal and Yalçın, 2008)	Egypt (Hassan, 2012)	Morocco (Gharby et al., 2017)	Karmakar et al. (2010)	Pullen and Saeed (2014)
Myristic acid	–	–	0.02	–	0.1	–	0.1
Palmitic acid	12.9	8.66	8.9	8.47	11.3	7–9	10.1
Stearic acid	3	5.45	5.43	5.53	4.9	4–5	4.0
Oleic acid	47.5	38.86	41.5	41.6	41.9	40–50	37.8
Linoleic acid	36.4	46.2	42.7	42.77	42.1	35–45	45.1
Linolenic acid	–	–	0.3	0.3	0.2	0.4–1	0.7
Saturated fatty acids	15.9 ± 0.2	14.85	14.3 ± 0.2	14	16.3 ± 0.2	12.5	15.8
Unsaturated fatty acids	83.9 ± 0.2	85.15	84.5 ± 0.2	84.37	84.3 ± 0.2	85.7	84.2

Table 3
Physico-chemical properties of sesame seed oil.

Parameters	Units	Sarve et al. (2015)	Kaniz et al. (Ferdous et al., 2012)	Dawodu et al. (2014)	Betiku and Adepoju (2013)	Karim et al. (Karim et al., 2014)	(Saydut et al., 2008)	Singh and Singh (2010)	Borchani et al. (2010)
Kinematic viscosity at 40 °C,	mm^2/s	31.51	52.5	22.63	31.39	33.61	25.78	35.5	
Density	g/cm^3	0.9	0.88	0.8525	0.833	0.936	0.899	0.913	
Acid value	mg KOH/g oil	0.42		3.15	0.50	0.443			1.64
Iodine value	g I_2/100 g		75.3	86.15	108		82.45		113
FFA	%		6.1	1.58					0.82
Moisture content	%	0.03	0.08		0.09	0.00			
Saponification value	mg KOH/g oil		213	142.2					186
Cetane no.		48.57			50.73			40.2	
Flash point	°C	240				312	245	260	
Pour point	°C	−6				−3	−10	−9.4	
Calorific value	MJ/kg	38.9			40.20		39.5	39.3	
Cloud point	°C	1				3	1	−3.9	

Table 4
Optimum conditions for transesterification of sesame oil.

Catalyst type	Production technique	Operating parameters				Biodiesel yield (%)	References
		Methanol/oil ratio	Catalyst weight	Temp (°C)	Time mins		
CH_3ONa	Conventional with CCD	6:1	0.75%	50	30	87.80	Dawodu et al. (2014)
NaOH	Conventional with RSM	6.24:1	1.04%	63	51.09	98.36	Betiku and Adepoju (2013)
KOH	Conventional	6:1	1.5%	60	120	96	Karim et al. (2014)
NaOH	Conventional	6:1	0.5%	60	120	74	Saydut et al. (2008)
$Ba(OH)_2$	Ultrasonic with 20 kHz RSM + ANN	6.69:1	1.79%	31.92	40.30	98.6	Sarve et al. (2015)
CH_3ONa	Conventional	10:1	–	60	–	92	Ahmad et al. (2009)
KOH	Conventional	25% (V/V)	1%	60	120	–	Wakil et al. (2014)
NaOH	Conventional	6:1	1%	60	60	96.8	Pullen and Saeed (2014)

Table 5
Fuel properties of sesame oil methyl ester.

Parameters	Units	SOME (Betiku and Adepoju, 2013)	SOME (Karim et al., 2014)	SOME (Saydut et al., 2008)	SOME (Sarve et al., 2015)	SOME (Ahmad et al., 2009)	SOME (Wakil et al., 2014)
Density	g/cm^3	0.833	0.8972	0.8672	0.867	0.871	0.884
Kinematic viscosity at 40 °C,	mm^2/s	4.03	4.58	4.2	4.47	5.77	4.3989
Acid value	mg KOH/g oil	0.25	0.32	–	0.12	–	–
Iodine value	g I_2/100 g	86.72	–	80.32	–	–	–
FFA	%	–	–	–	–	–	–
Moisture content	%	0.014	0	–	0.017	–	–
Saponification value	mg KOH/g oil	–	–	–	–	–	–
Cetane no.		59.80	69.3	50.48	56.32	53	–
Flash point	°C	180	155	170	180	110	208.5
Pour point	°C	6	−5	−14	−9	−18	1
Calorific value HHV	MJ/kg	41.35	–	40.4	40.1	–	39.996
Cloud point	°C	18	1	−6	−5	−6.3	1
CFFP							−1

determine the optimum values for process variables by trial and error.

Response surface methodology (RSM) software is used for process optimisation. It is widely used for optimising and examining the effect of input variables on output variables (operational variables) (Maran et al., 2013b,c). RSM is typically used to optimise the responses or select the best-operating conditions for achieving maximum output result (Maran et al., 2017). The central composite design (CCD), which is also called the Box–Wilson design, is an experimental design to obtain maximum information about a process from a small number of experiments (Prakash Maran et al., 2017). In CCD, the experimental design is used to analyse the behaviour of input variables or parameters on output response. From previous literature or preliminary experiments, process input variables and ranges are normally determined. After the input variables and their ranges are selected, experiments are designed with various factors at three levels, and each input variable is coded between −1, 0 and +1 (Maran et al., 2013a). RSM is used to optimise the response variable (output) depending on various independent variables (input). RSM is the best option with minimal process data; thus, it saves experimental cost and precious time (Shanmugaprakash and Sivakumar, 2013).

Artificial neural network (ANN) is a prominent technique for optimising the process in biodiesel research (Gul et al., 2019) because it can model using the mathematical background of the problem and for studying the linear and nonlinear relationships directly from the set of variables (Maran et al., 2013d; Sarve et al., 2015). ANN is considered a superior alternative technique to conventional modelling techniques due to its nonlinearity and complexity (Aghbashlo et al., 2015). A well-trained neural network is a fast, reliable and easy to use tool for solving and optimising engineering problems (Kurtgoz et al., 2017).

Sarve et al. (2015) compared both modelling techniques (i.e. ANN and RSM) to predict the yield of SSO methyl ester obtained from ultrasonic-assisted transesterification. ANN is more reliable than RSM in optimising the biodiesel yield. Ultrasound-assisted transesterification is feasible in producing biodiesel whilst using heterogenous catalyst (Tan et al., 2019).

Dawodu et al. (2014) used CCD for transesterification of sesame (*Sesamum indicum* L.) oil to optimise the process variables. The maximum yield of SSO methyl ester was predicted to be 87.80% when the reaction temperature, reaction time, sodium methoxide (CH_3ONa) as a catalyst and amount of methanol/oil ratio were 50 °C, 30 min, 0.75% and 6:1, respectively. Betiku and Adepoju (2013) used a CCD-based RSM technique to optimise the reaction temperature, the molar ratio (methanol: oil), reaction time and amount of catalyst of the transesterification process to optimise the yield of biodiesel. The biodiesel yield was optimised to 98.36% under the following conditions: (1) molar ratio (methanol to oil): 6.24:1, (2) reaction time: 2 h, (3) sodium hydroxide (catalyst) concentration: 1.04% and (4) reaction temperature: 63 °C.

Sarve et al. (2015) compared RSM and ANN to optimise the reaction temperature, catalyst concentration, reaction time and molar ratio of methanol to oil to increase the yield of biodiesel. The optimised yield conversion was 98.6% under these process conditions: (1) methanol to oil molar ratio: 6.69:1, (2) barium hydroxide ($Ba(OH)_2$) heterogeneous catalyst concentration: 1.79%, (3) reaction time: 40.30 min and (4) reaction temperature: 31.92 °C. The sensitivity analysis was used to analyse the effect of each independent variable on the response to the output variables. Sensitivity analysis showed that the catalyst concentration was the main affecting factor of the FA methyl ester content. The results showed that the lower values of correlation of coefficient, root mean square error, standard error of prediction and relative percent deviation for ANN than RSM verified that ANN was a superior prediction model for FA methyl ester (FAME) content.

5. Biodiesel standards

Biodiesel is considered an alternative fuel to crude diesel for diesel engines. Biodiesel is produced from edible and non-edible vegetable oils by transesterification following ASTM D6751 and EN 14214 standards.

Most researchers have concluded that biodiesel is fire resistant due to the its higher flash point than that of diesel. Amber-yellowish coloured biodiesel has viscosity comparable to that of crude diesel (Al-Dawody and Bhatti, 2013; Mat Yasin et al., 2017). Biodiesel producers should follow the fuel standard requirements set by two reputable biodiesel standards that are used for testing fuels. The standards used to ensure the biodiesel quality are EN 14214 for European Union and ASTM D6751 for American biodiesel standard (Atabani et al., 2012). The significant affecting factors of the quality of biodiesel include the technique used to produce biodiesel, the FA composition of vegetable oil, feedstock quality, animal fats and waste oil, the refining process and post-production parameters (Gautam and Agarwal, 2015; Mat Yasin et al., 2017). The low fraction variants of biodiesel, such as B7 or B10, are being utilised in many countries, such as Malaysia. In 2019, Malaysia started utilising B10 biodiesel, which is produced from palm oil, for the automotive industry. Malaysia is the second-largest global producer of palm oil after Indonesia. Malaysia has established its own biodiesel testing standards for palm oil methyl ester. The standard values are mostly taken from ASTM D6751 and EN 14214 standards. According to ASTM D6751 standard, each property of pure biodiesel must be in the range (set by standards) before being utilised neat or blended with diesel in diesel engines. According to EN 14214 European standard, minimum and maximum values of various parameters are defined to ensure the quality of biodiesel. Before the commercialisation of biodiesel as a pure biofuel or blending stock for diesel fuel, it should fulfil the minimum or maximum limits set by the standard. EN 14214 standard specifies the maximum allowable concentration of different parameters within biodiesel to ensure the quality of biodiesel. To facilitate the local implementation of palm oil methyl ester in Malaysia, Malaysia Palm Oil Board played a key role in the publication of Malaysian biodiesel standard (MS 2008:2008) in October 2008 for palm oil methyl ester (Goosen et al., 2007; Lam et al., 2009) (see Table 6).

6. Physicochemical properties of sesame oil biodiesel

6.1. Density

The density of biofuel is a key parameter for calculating the precise volume of fuel for adequate combustion (Ramírez Verduzco, 2013). In diesel engines, air to fuel mixing mostly depends on the density of the fuel. The fuel–air mixture is conducted at a pressure range of 15–50 MPa and a temperature range of 300 K–350 K in the combustion chamber (Sajjadi et al., 2016). Density directly affects the injection process and efficiency of fuel atomisation because the quantity of fuel injected through injector nozzle in the combustion chamber is assessed by its volume (Kaya et al., 2009). Density is also considered an important property of biodiesel that links with viscosity, CN and heating value (Hoekman et al., 2012). ASTM D6751 standard does not specify the density of a biofuel. EN 14214 standard specifies that a biodiesel's density should be in the range of 860–900 kg/m^3. Compared with petroleum diesel's density (850 kg/m^3), the density of biodiesel (880 kg/m^3) is slightly higher; such density can be overcome by increasing the percentage of biodiesel in blends (Silitonga et al., 2013; Wakil et al., 2015b). Sesame, palm, coconut and pequi derived FA methyl esters have the lowest density amongst vegetable oil methyl esters (Sajjadi et al., 2016). Biodiesel (higher unsaturated) with more than two double bonds exhibits a relatively high

Table 6
ASTM D6751, EN14214 and Malaysian fuel standard MS 2008:2008 for biodiesel (Mat Yasin et al., 2017; Sarve et al., 2015; Betiku and Adepoju, 2013; Ahmad et al., 2011; Pullen and Saeed, 2012).

Properties	Unit	ASTM D6751		EN14214		Malaysian standard MS 2008:2008	
		Limit	Method	Limit	Method	Limit	Method
Density at 15 °C	kg/m^3	870–890	ASTM D4052–91	860–900	EN ISO 3675	860–900	ASTM D4052
Kinematic viscosity at 40 °C	mm^2/s	1.9–6.0	D445	3.5–5.0	EN ISO 3104	3.5–5.0	MS 1831
Flash point	°C	130 min	D93	>101	EN CD 3679e	120	ASTM D5453
Cetane number	–	47 min	D613	51.0	EN ISO 5165	51.0	MS 1895
Acid value	mg KOH/g	< 0.50	D664	0.50	EN 14104	0.50	MS 2011
Oxidation stability	h	> 3	EN 14112	6	EN 14112k	6	EN 14112
FAME content	% (m/m)	–	–	95.5	EN14103	–	–
Water content	mg/kg	500 max	D2709	500 max	EN ISO 12937	500	ASTM E 203
Iodine value	% (m/m)	–	–	120 max	EN 14111	110	EN 14111
Sulphur content	mg/kg	< 15	D5453	10 max	–	10	–
Sulphated ash content	% (m/m)	0.02 max	D874	0.03 max	ISO 3987	0.02	ISO 3987
Methanol content	% (m/m)	–	–	0.2 max	EN 141101	0.2	EN 14110
Monoglyceride content	% (m/m)	–	–	0.8 max	EN14105m	0.8 max	ASTM S 6584
Diglyceride content	% (m/m)	–	–	0.2 max	EN14105m	0.2 max	ASTM S 6584
Triglyceride content	% (m/m)	–	–	0.2 max	EN14105m	0.2 max	ASTM S 6584
Free glycerine	% (m/m)	0.020 max	D6584	0.02 max	EN14105m/EN14106	0.02 max	ASTM S 6584
Total glycerine	% (m/m)	0.240 max	D6594	0.25 max	EN14105m	0.25 max	ASTM S 6584
Total contamination	mg/kg	–	–	24 max	EN 12662	24 max	ASTM D 5452
Phosphorus content	mg/kg	10 max	D4951	4 max	EN14107p	10 max	ASTM D 4951
CFPP	°C	–	–	max + 5	EN 116	15	EN 116
Pour point	°C	−15 to 16	D 97	–	–	–	–
Group I metal (Na + K)	mg/kg	< 5	EN14538	< 5 max	EN14108	5.0	EN 14108
Group II metal (Ca + Mg)	mg/kg	< 5	EN14538	< 5 max	EN14538	5.0	EN 14109
Carbon residue	% (m/m)	< 0.05	D 4530	< 0.3	EN ISO 10370	–	–

density (Karmakar et al., 2010). According to Wakil et al. (2015b), sesame biodiesel has the trend of increasing density (0.849, 0.853, 0.857 and 0.86 at 50%, 60%, 70% and 80% blend percentage). In Fig. 3, the densities of all the feedstock are greater than those of petroleum diesel (839 kg/m^3), and the density (867 kg/m^3) of sesame biodiesel is within the range of EN 14214 standard.

6.2. Kinematic viscosity

Kinematic viscosity (KV) is the measurement of inherent resistance to liquid flow. The thickness of oil is estimated by the time at 40 °C for a volume of liquid to flow through a calibrated liquid in glass in viscometer (Sajjadi et al., 2016; Silitonga et al., 2013). The KB of vegetable oil is usually 10 times higher than that of crude diesel, as shown in Table 3 in the case of SSO. According to Sajjadi et al. (2016), vegetable oils are more viscous at 9 to 17 times and 1.6 times than biodiesel and petroleum diesel, respectively. High viscosity fuels form large droplets during injection and cause problems, such as carbon deposits on engine parts and formation of soot due to poor atomisation during combustion (Silitonga et al., 2013; Wakil et al., 2015b; Sajjadi et al., 2016). During the winter season or in cold weather, high viscosity fuel mixes with air slowly, and this condition leads to weak combustion and increased exhaust emissions. Fuel with low viscosity cannot provide sufficient lubrication during fuel injection and thus results in wear and leakage (Freitas et al., 2010). According to biodiesel standards EN 14214 and ASTM D6571, the limits of biodiesel viscosity are 3.5–5.0 and 1.9–6.0 mm^2/s, respectively. Engine operation at low speed causes high injection volumes and pressure due to the high viscosity of fuel; as a result, clogging of fuel lines and poor atomisation and carbon deposits occur (Masjuki et al., 2004). Sarve et al. (2015) observed that the viscosity of SSO was 31.51 mm^2/s. After the transesterification, the high viscosity of SSO is significantly decreased to 4.47 mm^2/s for SSO methyl ester and thus meets the required limits set by biodiesel standards. The transesterification aims to reduce the viscosity of oil for meeting the limits of biodiesel standards. As shown in Fig. 3, the KV (4.47 mm^2/s) of SOME is within the range of EN 14214 standard and is greater than those of crude diesel (2.9 mm^2/s), linseed (3.95 mm^2/s) and corn (4.363 mm^2/s) but is less than those of palm (4.63 mm^2/s), jatropha (4.73 mm^2/s), soybean (5.429 mm^2/s) and sunflower (4.719 mm^2/s).

6.3. Calorific value

Calorific value (CV) is also considered to be the most important parameter in the selection of fuel. It is the amount of heat released during the combustion of a specified amount of fuel to produce CO_2 and H_2O at its initial temperature. It has no standard value in American (ASTM D6751) and European (EN 14214) standards, but the minimum value of 35 MJ/kg is given in EN 14213 standard (Silitonga et al., 2013). The calorific value for biodiesel is more influenced by high unsaturation than by the length of the carbon chain. The calorific value of biodiesel declines up to 0.21 MJ/kg by an increase in each percentage of unsaturation of FA methyl ester (Ramírez-Verduzco et al., 2012). The heating value of biodiesel (39.57–41.33 MJ/kg) is 12% lower than petroleum diesel (∼46 MJ/kg) due to its higher oxygen content (Sajjadi et al., 2016). As shown in Fig. 3, SOME heating value (40.1 MJ/kg) is the highest of all feedstocks.

6.4. Cetane number

Cetane number (CN) is a key parameter of the quality of diesel fuel. CN indicates the ignition delay time within the combustion chamber upon injection. High CN takes short ignition delay time to ignite, and this condition results in low idling noise and good cold startup. By contrast, low CN takes long ignition delay time to ignite, and this condition results in power output reduction, an increase in engine noise, incomplete combustion and inefficiency in fuel conversion (Mat Yasin et al., 2017). Biodiesel easily fulfils the ASTM D6751 minimum specification of 47 for CN, but European standard EN 14214 is more rigorous and is similar to the minimum specification of 51. As shown in Fig. 3, palm oil methyl ester exhibits the highest CN (59.5), followed by SSO methyl ester (56.35) and soybean methyl ester (53.8). The CN of biodiesel produced from linseed oil methyl ester (48) is on borderline. According to previous literature, adding alcohol-based additives, such as methanol, diethyl ether and ethanol, in small proportions can improve the CN significantly for biodiesel and blended fuel of diesel (Ali et al., 2016, 2015; Yasin et al., 2014).

6.5. Cold flow properties

The cold flow properties of biodiesel are considered a major barrier in widespread utilisation (Sajjadi et al., 2016). CP, cold filter plugging point (CFPP) and PP is considered the cold flow properties. These properties are crucial in the utilisation of biodiesel under cold weather conditions (Wakil et al., 2015b). CP is the temperature at which cloudy appearance can be visualised due to the wax formation. The fuel filter, injectors and lines of diesel engines are clogged due to the presence of wax in biodiesel. PP is the lowest temperature at which biodiesel changes its phase from liquid to semi-solid and loses its flow characteristics. Biodiesel is not pumpable when it reaches a semi-solid phase. CFPP is the lowest temperature at which a given volume (20 ml) of diesel type fuel passes through a standardised filter within a specified time (60 s) during cooling under certain conditions. A high value of CFPP will clog the diesel engine (Dwivedi and Sharma, 2014; Sajjadi et al., 2016). The freezing point of biodiesel decreases with double bonds and increases with an increase in carbon atoms in its chemical structure (Atabani et al., 2012). The low-temperature properties of biodiesel are strongly dependent on the degree of unsaturation FA chains. A high degree of unsaturation leads to an enhanced low-temperature performance of biodiesel (Hoekman et al., 2012). A high percentage of saturated FAs, such as palmitic acid (C16:0) and stearic acid (C18:0), in fuel decreases the low-temperature performance of fuel and increases the values of cold flow properties; thus, the engine of the vehicle easily clogs (Sajjadi et al., 2016). High-saturated esters have a higher melting point and poorer cold flow properties than unsaturated esters. Saturated FA (stearic acid) is solid at 39 °C, whilst unsaturated FAs (methyl oleate) melt at −19 °C and methyl linoleate melts at −35 °C (Lanjekar and Deshmukh, 2016). Ramos et al. (2009) reported a relationship ($R^2 = 0.96$) of the CFPP with a long chain of saturated FA methyl ester content of different feedstocks. The biodiesel having the highest content of saturation showed the worst CFPP. To overcome this problem in cold countries, various options, such as the following, can be utilised: blending with fossil diesel fuel, blending with different vegetable oil methyl esters having good low-temperature performance, use of additives and blending of feedstock oils to obtain good cold flow properties (Echim et al., 2012).

SSO contains (80%–85%) unsaturated FAs. The high degree of unsaturation in SSO methyl ester improves its cold flow characteristics compared with other vegetable oils FA methyl esters. The cold flow properties (i.e. CP and PP) of SSO methyl ester have been studied in various literature, and different researchers have reported values for PP (°C) (−5, −14, −9, −18 and 1) and CP (°C) (1, −6, −5, −6.3 and 1) (Karim et al., 2014; Saydut et al., 2008; Sarve et al., 2015; Ahmad et al., 2009; Wakil et al., 2014). Wakil et al. (2014) reported the value of CFPP (−1 °C) for SSO methyl ester. SSO methyl ester or SSO can be blended with other methyl esters or feedstocks to improve cold flow properties. SSO methyl ester has more favourable cold flow properties than other feedstock oils, as shown in Table 7.

Linseed oil methyl ester has more than 90% unsaturation, which is favourable for cold flow properties, but has very poor oxidation stability (1.5 h), as shown in Table 7. In comparison, SSO methyl ester has good cold flow characteristics and oxidation stability. Palm oil methyl ester has higher saturation than other feedstock and thus has very poor cold flow properties, namely, CP (10 °C) and PP (11 °C). SSO methyl ester exhibits very the best cold flow properties, namely, CP (−6 °C) and PP (−9 °C), amongst all feedstock due to its high unsaturation, as shown in Fig. 3.

6.6. Oxidation stability

Oxidation stability is an important biodiesel fuel quality parameter (Sendzikiene et al., 2005). Biodiesel is more vulnerable to oxidation than other diesels, and its properties deteriorate rapidly during long-term storage due to its chemical composition (presence of double bonds) and high unsaturated FAs (Patel and Sankhavara, 2017; Silitonga et al., 2020). The commercialisation of biodiesel is a major problem due to its degradability and susceptibility towards oxidation during storage (Kumar, 2017). The major influential factors associated with biodiesel stability are FA composition (presence of double bonds), presence of light, heat, air, a trace of metals, elevated temperature, antioxidants and peroxides (Wakil et al., 2015b; Silitonga et al., 2013). These factors act as a catalyst during the start of the oxidation process to remove the hydrogen bond from the backbone of the biodiesel (Kumar, 2017). The poor stability of biodiesel is associated with the auto-oxidation rate, which depends on the number and position of the double bond in its chemical composition (Atabani et al., 2012; Hoekman et al., 2012). The reactivity of biodiesel with oxygen increases in exposure to direct sunlight, air and water due to double bonds in its chemical structure (Wakil et al., 2015b). During long-term storage, biodiesel degradation due to oxidation leads to the following: an increase in viscosity, acid value and peroxide value; formation of gums; sedimentation; clogging of the fuel filter; rough engine operation; and fuel thickening (Patel and Sankhavara, 2017). The biodegradability of biodiesel due to oxidation alters its important physicochemical and tribological properties during storage, such as peroxide value, density, polymer content, iodine value, acid value and KV, and reduces its applicability as an alternative fuel for CI engines (Kumar, 2017). Biodiesel oxidation usually occurs in two stages, namely, primary and secondary. In the primary stage of the oxidation process, peroxides and hydroperoxides are formed. In the secondary stage, aldehydes and ketones are formed, and resins, sludges or gums form later on during the polymerisation process (Dixit et al., 2012; Kumar, 2017). During the primary stage of oxidation, the antioxidants present within fuel deplete, and the quality of fuel remains the same. During the secondary (polymerisation) phase, the rapid formation of products, such as acid resins, gums and sludge, severely deteriorate the fuel quality. These degradable products will create problems, such as clogging of filters and injectors (Christensen and McCormick, 2014; Strömberg et al., 2013; Kumar, 2017). Biodiesel fuel exposure to a high temperature (250 °C–300 °C or above) can also be the other reason for oxidation (Thermal polymerisation) of fuel (Yamane et al., 2007). Moser (2009) concluded that the oxidation stability of alkyl esters increases with decrease in double bonds by utilising pressurised differential scanning calorimetry (PDSC) and rancimat method (EN 14112).

The relative oxidation rates for oleates, linoleates and linolenates are 1, 41 and 98, respectively (Holman and Elmer, 1947). The rate of oxidation depends on number of double bonds and the position of double bond, such as linoleic (with two double bonds and one bis-allylic position at C-11) and linolenic (with three double bonds and two bis-allylic positions at C-11 and C-14); thus, hydrogen radical can be easily extracted from these bis-allylic sites during the initial stage of oxidation; accordingly, linolenic acid is more prone to oxidation than linoleic acid (Kumar, 2017). Biodiesel oxidation stability can be improved by transforming cis FA methyl ester to trans FA methyl ester because trans FAs have better oxidation stability and lower reactivity than cis FAs (Liu et al., 2019). The contents of unsaturated FAs (e.g. linoleic and linolenic acids) play a significant role in the oxidation stability of biodiesel fuel (Park et al., 2008). Two important structure indices are allylic position equivalent (APE) and bis-allylic position equivalent (BAPE) related to oxidation stability of biodiesel (Knothe and Dunn, 2003). Oxidation stability can be increased by reducing APE and BAPE (Yang et al., 2013).

The rancimat method is a commonly used accelerated method to determine the oxidation stability of oils and biodiesels. It is mentioned in biodiesel standards EN 14214 and ASTM D6751. As per the biodiesel European standard 14214 and ASTM D6751, the minimum induction periods at 110 °C are 6 and 3 h, respectively, for oxidation stability. In vegetable oils and their FA methyl esters, antioxidants can be present naturally or can be added intentionally to improve the oxidation stability of the fuel. Natural antioxidants, such as tocopherols (i.e. vitamin E), which are present as an additive, ensure the stability of fuels (Pullen and Saeed, 2012). The oxidation stability of methyl ester is improved by adding different synthetic antioxidants, such as propyl gallate, butylated hydroxytoluene, pyrogallol, butylated hydroxy anisole and tert-butyl hydroxyl quinone (Patel and Sankhavara, 2017).

SSO is the least prone to oxidative rancidity amongst all other commonly used vegetable oils (Budowski, 1950). The high stability of SSO is due to the presence of a large proportion of unsaponifiable matters, such as sesamin and γ-tocopherol (i.e. vitamin E), compared with α- and δ-tocopherol, and their concentration is influenced by geographical, genetic and environmental factors (Hegde, 2012). SSO contains 0.5%–1.0% sesamin and 0.3%–0.5% sesamolin with a trace amount of free sesamol (Budowski, 1950). SSO is less susceptible to oxidative rancidity due to natural antioxidants (i.e. sesamin, sesamolin and sesamol) with tocopherols (i.e. vitamin E) present in oil (Gharby et al., 2017). According to Gharby et al. (2017), SSO contains 446 mg/kg tocopherols. The majority of tocopherol is γ-tocopherol (90.5%), followed by δ-tocopherol (7.3%) and α-tocopherol (2.2%). Fatnassi et al. (Saloua et al., 2009) concluded that α-tocopherol had lower antioxidant capacity than γ-tocopherol. Gharby et al. (2017) measured the oxidation stability of SSO at 110 °C with a Rancimat 743 (Metrohm Co., Basel) under an airflow rate of 20 L/h with a sample of 3 g oil. The induction time examined for SSO by Rancimat method was 28.5 ± 1 h at 110 °C. FA composition of SSO revealed high unsaturation (around 86%) and showed 7.32 h induction period due to the presence of natural antioxidants (Conceição et al., 2019).

Pullen and Saeed (2014) prepared more than 12 biodiesel samples from different oils (e.g. sesame, olive, sunflower, jatropha, rapeseed, soybean, cold-pressed rapeseed (CPR), corn, palm, used cooking oil, groundnut and grapeseed) and two FAME from animal fats (e.g. tallow and lard). Four commercially prepared FAME samples, namely, jatropha, palm, soybean and coconut, were used for comparison. A total of 18 biodiesel samples were used to measure the oxidation stability using the Rancimat method 873 Biodiesel Rancimat instrument under specific operating conditions. For instance, biodiesel sample (3 g) was heated to 110 °C under a steady flow rate (10 l/h) of air. The Rancimat induction period (RIP) results varied significantly amongst all samples. Only sesame (6.25 h) fulfilled the EN 14214 minimum set requirement ($\geq$ 6 h). Most biodiesel samples showed low RIP ($<$1 h). The SSO contained natural antioxidants, such as tocopherol (i.e. vitamin E) and preservatives, sesamin and sesamol. As a result, it is more stable towards oxidative rancidity than other vegetable oil and fats.

Two biodiesel samples, namely, sesame and CPR oil (300 g each), were stored in an airtight glass jar and immersed in a water bath (constant temperature of 40 °C) for 100 days to estimate the storage life. During the storage, KV (at 40 °C) and acid value were measured periodically (after every 10 days) for the prediction of oxidation. In the case of rapeseed, an increase was noticed in KV and acid value around 500 h. However, sesame showed good resistance towards change in values until 2000 h. In Fig. 3, SSO methyl ester had 6.25 h oxidation stability instead of having more than 84% unsaturation. The major reason for the high oxidation stability of SSO methyl ester is due to naturally occurring antioxidants and preservatives, such as tocopherol (i.e. vitamin E), sesamol and sesamin.

7. Engine performance and emission characteristics of SSO methyl ester and its blends

Most researchers have found a decrease in hydrocarbons (HC), CO and smoke opacity emissions by substituting diesel fuel with biodiesel, as shown in Table 8. Biodiesel contains more than 11% oxygen, which improves the combustion quality (complete combustion) by assisted conversion of CO to CO_2 (Habibullah et al., 2014). Complete combustion of fuel results in low CO and particulate emissions. SSO methyl ester exhibits lower HC, NO_x and smoke emissions and higher CO emissions than crude diesel. The formation of NO_x mainly depends on in-cylinder combustion temperature, residence time of reaction and concentration of oxygen (Sharon et al., 2013). Sesame biodiesel reduces the NO_x emissions amongst all other biodiesels, as presented in Table 8. Low CN of sesame biodiesel reduces the in-cylinder combustion temperature, and this condition results in low NO_x emissions. The BSFC of all biodiesel-diesel blends are higher than that of crude diesel, except linseed and jatropha methyl ester blends. High density and viscosity of biodiesel inject large amount of fuel during combustion, which results in increments in BSFC. BTE is inversely proportional to BSFC. Sesame and corn biodiesel reduce the NO_x amongst the other biodiesel-diesel blends. Engine performance and emission characteristics of sesame biodiesel have been rarely researched (Wakil et al., 2015a; Banapurmath et al., 2008). Sesame biodiesel is a potentially viable source to eradicate the NO_x emissions by blending with another potential feedstock.

8. Cost analysis of SSO

Process description of sesame cultivation, harvesting, oil extraction and production of biodiesel, along with cost analysis, is exhibited in Fig. 4. Sesame crop is mainly cultivated in Africa and Asia. Acid-free, light sandy and medium loam soils are preferable for the cultivation of sesame. Sesame crop is preferably cultivated in July of every year in Asia. The average yield of sesame seeds is 1400 kg/ha in the United Republic of Tanzania (FAO, 2018). Sesame crop matured in 100–120 days, and 75% of the mature crop can also be harvested (Chapke et al., 2018). Sesame seeds are segregated on seed quality. High-quality seeds are utilised for the food industry, and few seeds are used for SSO production. High-quality SSO is used for salad and meal garnishing. SSO is not recommended for frying the food. The high-quality sesame seed's price in Pakistan is 0.85 $/kg, and that of SSO is 1.7 $/L. Low-quality sesame seeds utilised for extraction of SSO are used for animal feeding in the winter season. Cake of sesame seeds is also utilised as a food for animals. SSO has the potential to be utilised as an emerging feedstock for biofuel production due to its unique characteristics. The low-quality sesame seed price in Pakistan is 0.64 $/kg, and that of SSO is 1.28 $/L. The production cost of biodiesel is 0.66 $/L (Felix et al., 2010). SSO price is relatively expensive due to the weak demand in the market. SSO price will be decreased in the future by increasing the overall production of sesame seeds worldwide. The production rate of sesame seeds can also be increased by suggesting new alternative ways of utilisation, such as biodiesel production. SSO can also be blended with other feedstocks to improve their cold flow and oxidation stability characteristics and reduce NO_x emissions. Sesame biodiesel can be used in the future as a viable alternative feedstock for biodiesel production due to its unique physicochemical properties.

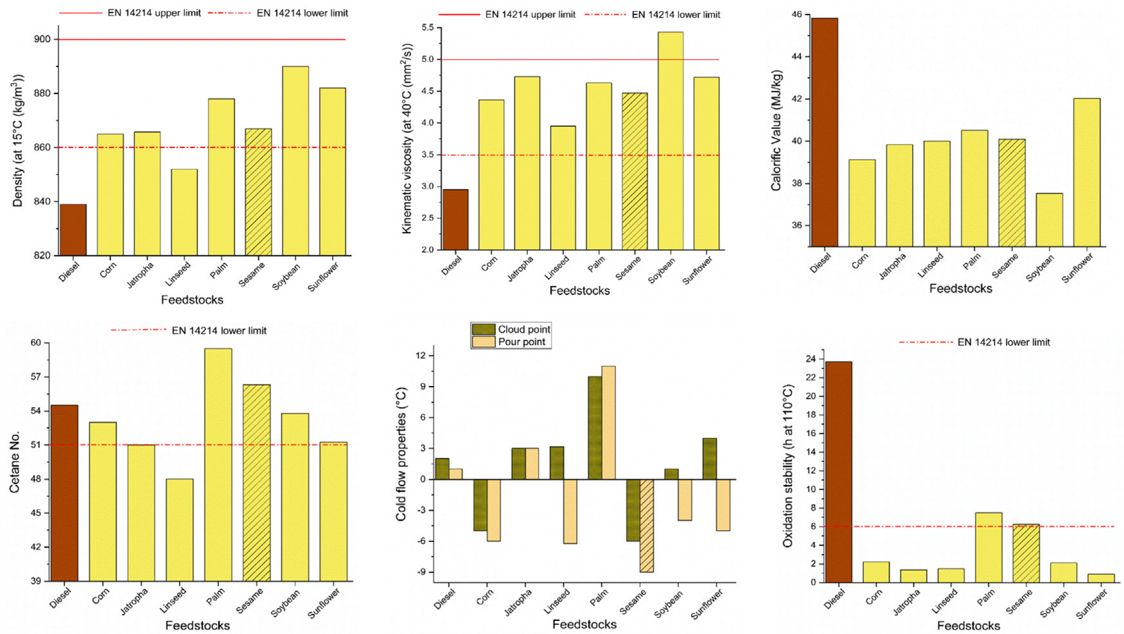


Fig. 3. Physicochemical properties of various bio-based fatty acid methyl esters (biodiesel).

Table 7
Physico-chemical properties of fatty acid methyl esters from various vegetable oils (Pullen and Saeed, 2014; Karmakar et al., 2010; Sandesh Suresh et al., 2019).

Vegetable oil methyl esters ↓	Fatty acid composition		Cold flow properties		Oxidation stability (OS) (h) at 110 °C	Cetane no.	Density (kg/m^3) at 15 °C	Kinematic viscosity at 40 °C (mm^2/s)	Flash point °C	Heating value (MJ/kg)	References
	Sat %	Un-sat %	CP °C	PP °C							
			± 0.1 °C	± 0.1 °C	± 0.01 h		± 0.1 kg m^{-3}	± 0.35%	± 0.1 °C	± 0.1%	← Equipment accuracy (Wakil et al., 2014)
Palm	44.6	55.4	10	11	7.50	59.5	878	4.63	182.5	40.51	Rashed et al. (2016), Silitonga et al. (2013)
Linseed	8.3	91.7	3.17	−6.25	1.5	48	852	3.95	151	40	Kumar et al. (2013), Dixit et al. (2012)
Sesame	16	84	−6	−9	6.25	56.32	867	4.47	180	40.1	Sarve et al. (2015)
Corn	14.4	85.6	−5	−6	2.2	53	865	4.363	170	39.12	Nagaraja et al. (2016)
Jatropha	22.6	77.4	3	3	1.37	51	865.7	4.73	184.5	39.83	Rashed et al. (2016)
Sunflower	10.5	89.5	4.0	−5	0.9	51.25	882	4.719	183	42.02	Naureen et al. (2015) and Saydut et al. (2016)
Soybean	15.6	84.4	1	−4	2.1	53.80	890	5.429	148	37.52	Can et al. (2016)
Diesel	–	–	2	1	23.70	54.5	839	2.95	71.5	45.825	Silitonga et al. (2013) and Mat Yasin et al. (2017)

9. Conclusion

In recent decades, biodiesel has been considered a potential candidate to overcome the dominance of petroleum diesel and mitigate environmental pollution. Biodiesel is used in the existing diesel engine without any modification. Many researchers have studied ways to find different potential feedstocks for the production of biodiesel, some of which are in commercialising biodiesel. The major problem associated with biodiesel industrialisation is its poor cold flow and oxidation stability properties. This study highlights the potential and suitability of sesame (*Sesamum indicum* L.) oil for the production of biodiesel. The blend of SSO with other vegetable oils is used for biodiesel production to enhance the cold flow and oxidation stability properties of the final product. SSO is a viable feedstock for biodiesel production due to its unique physicochemical properties compared with other feedstocks. The physicochemical properties of SSO methyl ester comply with US (ASTM D6751), Malaysian (MS 2008:2008) and European (EN 14214) standards. SOME has good *cold flow properties* (i.e. CP, PP and CFPP) due to the high unsaturated FA carbon chain. SOME exhibits good *stability* towards rancidity. The oxidation stability of SSO should be low due to high unsaturation. However, the presence of *natural antioxidants*, such as tocopherols (i.e. vitamin E), and *naturally occurring preservatives* (i.e. sesamol, sesamolin and sesamin) restrict to rancidity. Poor cold flow and

Table 8
Comparison of engine performance and emission characteristics of various biodiesel-diesel blends with diesel.

Biodiesel	Biodiesel blend	References	Engine performance		Engine emissions			
			BTE	BSFC	CO	HC	NOx	Smoke
Linseed	B10	Akram et al. (2019)	↑	↓	↓	↓	↑	↑
Sesame	B20	Wakil et al. (2015a)	↓	↑	↑	↓	↓	↓
Palm	B20	Gad et al. (2018)	↓	↑	↓	↓	↑	–
Soybean	B20	Özener et al. (2014)	–	↑	↓	↓	↑	↓
Jatropha	B20	Ong et al. (2014)	↑	↓	↓	↓	↑	↓
Sunflower	B10	Dueso et al. (2018)	↓	↑	↓	↓	↑	↓
Corn	B20	Balamurugan et al. (2018)	↓	↑	↑	↑	↓	↑

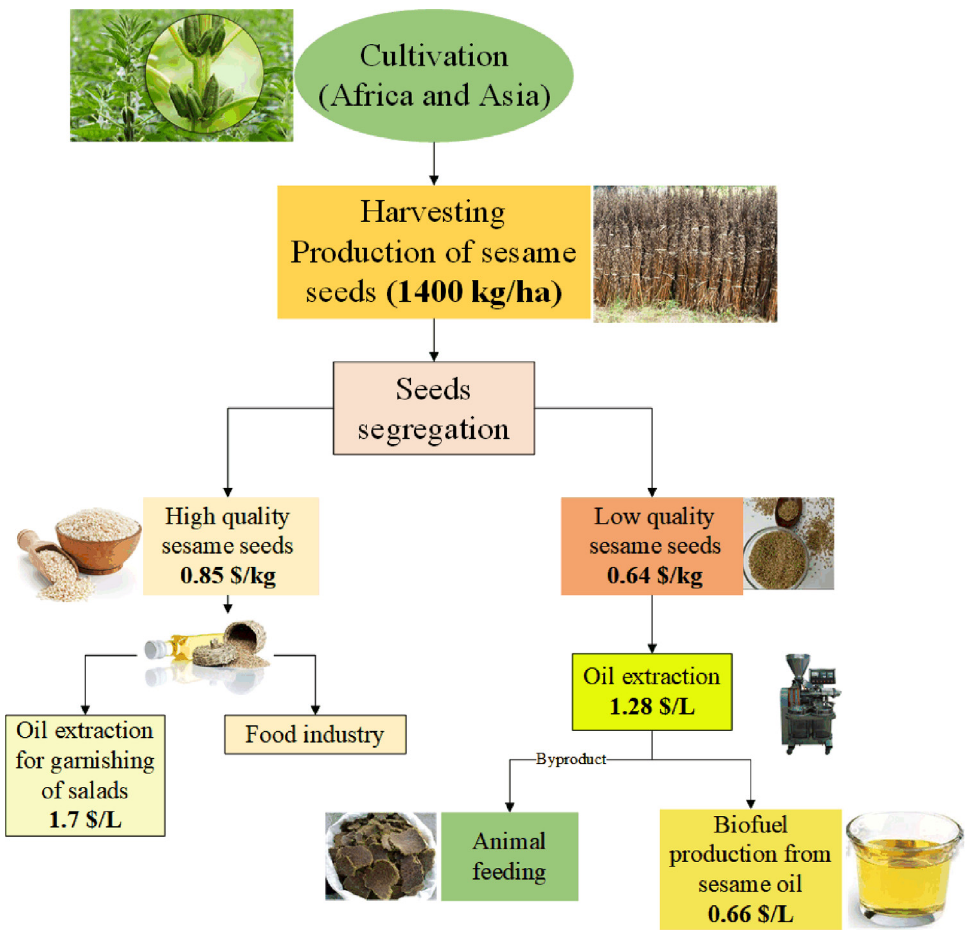


Fig. 4. Cost analysis of sesame crop to sesame oil for biofuel production.

oxidative stability properties of other vegetable oils (e.g. palm oil) can be improved successfully by blending them with SSO in an appropriate proportion before the transesterification process.

An in-depth study is required to analyse the behaviour of SSO methyl ester in a diesel engine for optimising the engine operation. Engine performance and emission characteristics of sesame methyl ester should be investigated. Lubricity characteristics and tribological behaviour of sesame methyl ester should be analysed as well.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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