

Review

The Use of Artificial Neural Networks for Identifying Sustainable Biodiesel Feedstocks

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Abstract: Over the past few decades, biodiesel produced from oilseed crops and animal fat is receiving much attention as a renewable and sustainable alternative for automobile engine fuels, and particularly petroleum diesel. However, current biodiesel production is heavily dependent on edible oil feedstocks which are unlikely to be sustainable in the longer term due to the rising food prices and the concerns about automobile engine durability. Therefore, there is an urgent need for researchers to identify and develop sustainable biodiesel feedstocks which overcome the disadvantages of current ones. On the other hand, artificial neural network (ANN) modeling has been successfully used in recent years to gain new knowledge in various disciplines. The main goal of this article is to review recent literatures and assess the state of the art on the use of ANN as a modeling tool for future generation biodiesel feedstocks. Biodiesel feedstocks, production processes, chemical compositions, standards, physio-chemical properties and in-use performance are discussed. Limitations of current biodiesel feedstocks over future generation biodiesel feedstock have been identified. The application of ANN in modeling key biodiesel quality parameters and combustion performance in automobile engines is also discussed. This review has determined that ANN modeling has a high potential to contribute to the development of renewable energy systems by accelerating biodiesel research.

Keywords: renewable energy; biodiesel; Artificial Neural Networks (ANN); second generation feedstock

Nomenclature and Abbreviations:

<i>AFR</i>	air-fuel ratio	<i>IV</i>	iodine value
<i>ANN</i>	artificial neural network	<i>L</i>	load
<i>ANOVA</i>	analysis of variance	<i>Lb</i>	lubricity
<i>BMEP</i>	brake mean effective pressure	<i>LHV</i>	lower heating value
<i>BSFC</i>	brake-specific fuel consumption	<i>LPG</i>	liquid petroleum gas
<i>BTE</i>	brake thermal efficiency	<i>MLR</i>	multiple linear regression
<i>C</i>	cylinder	<i>MRE</i>	mean relative error
<i>CB</i>	cylinder bore	<i>MSE</i>	mean square error
<i>CFPP</i>	cold-filter plugging point	<i>N₂</i>	nitrogen
<i>CI</i>	compression ignition	<i>NA</i>	naturally aspirated
<i>CME</i>	coconut methyl ester	<i>NO_x</i>	nitrogen oxides
<i>CN</i>	cetane number	<i>O₂</i>	oxygen
<i>CNG</i>	compressed natural gas	<i>OS</i>	oxidation stability
<i>CO</i>	carbon monoxide	<i>P</i>	power
<i>CO₂</i>	carbon dioxide	<i>PCA</i>	principle component analysis
<i>CP</i>	cloud point	<i>PCR</i>	principle component regression
<i>DU</i>	degree of unsaturation	<i>PLS</i>	partial least square regression
<i>ECP</i>	Engine cylinder pressure	<i>PM</i>	particulate matter
<i>CPO</i>	crude palm oil	<i>PME</i>	palm oil methyl ester
<i>CR</i>	compression ratio	<i>PP</i>	pour point
<i>EGR</i>	exhaust gas recirculation	<i>R²</i>	regression coefficient
<i>ES</i>	engine stock	<i>RME</i>	rapeseed methyl ester
<i>ET</i>	engine temperature	<i>RPM</i>	rotation per minute
<i>FAME</i>	fatty acid methyl ester	<i>S</i>	sulphur
<i>FAEE</i>	fatty acid ethyle ester	<i>SI</i>	spark ignition
<i>FDR</i>	fuels blend ratio	<i>SME</i>	soybean methyl ester
<i>FFA</i>	free fatty acid	<i>SO_x</i>	sulphur oxides
<i>FFR</i>	fuel flow rate	<i>T</i>	torque
<i>GHG</i>	greenhouse gas	<i>TC</i>	turbocharged
<i>H₂</i>	hydrogen	<i>Texh</i>	exhaust gas temperature
<i>HC</i>	hydrocarbon	<i>TP</i>	throttle position
<i>HV</i>	heating value	<i>UHC</i>	unburned hydrocarbons
<i>HHV</i>	higher heating value	<i>VT</i>	valve timing
<i>ICE</i>	internal combustion engines	<i>WCO</i>	waste cooking oil
<i>IP</i>	injection pressure	<i>ρ</i>	density
<i>IT</i>	injection timing	<i>ν</i>	kinematic viscosity

1. Introduction

Since the beginning of the Industrial Revolution in the late 18th and early 19th century, energy has become an indispensable tool for mankind, contributing to economic growth and increased standards of living. World primary energy demand is expected to grow by 1.6% *per annum* over the period 2010 to 2030, which will require 39% additional energy by 2030 [1]. There are many potential energy sources around us from which energy can be converted for use and stored. These sources can be classified as fossil, fissile and renewable. Fossil energy sources were formed thousands of years ago, and are not renewable in a short time horizon. They include liquid crude oil, coal, natural gas and tar sands. The major fissile energy sources are uranium and thorium that are fissionable by neutrons with zero kinetic energy. Renewable energy is generated from natural sources such as biomass, solar, wind and geothermal resources.

Most of the primary energy used today comes from fossil-based resources, predominantly crude oil (35%), coal (29%) and natural gas (24%), while nuclear and renewable resources account for 7% and 5% of global energy consumption, respectively [1]. Fossil-based resources are therefore the single largest source of energy, representing 88% of the total World consumption. However, fossil resources are being consumed rapidly. Based on current production scenarios, it is expected that a peak of global oil production will occur between 2015 and 2030 [2]. Therefore, fossil resources have practical limitations in their capacity to supply future global energy requirements in which there are currently few large scale alternatives available. Moreover, combustion of fossil fuels results in greenhouse gas emissions and contributes to anthropogenic climate change. Despite global measures such as the Kyoto Protocol and scientific innovation, atmospheric CO₂ concentration continues to increase and is exceeding benchmark levels much earlier than had previously been predicted [3].

The transportation sector globally is the third largest energy consumer after the industry and the building sectors which is the fastest growing sector. By 2030, the energy consumption and CO₂ emissions from this sector are predicted to be 80% above the levels of today [4]. The transportation sector is also the sector most reliant upon petroleum fuels (primarily through the crude oil-derived liquid products gasoline and diesel). The sector currently consumes 30% of crude oil globally and this is predicted to increase to 60% by 2030 [5]. Furthermore, the availability of conventional crude oil is geographically restricted impacting on the security and cost of supply.

These issues have forced researchers to seek alternative carbon neutral transport fuels which promote sustainable development, energy efficiency and environmental preservation [6]. As of yet, few large scale commercially viable options exist for the transportation sector. Moreover, cars with no tailpipe greenhouse gas emissions (e.g., electric, solar, hydrogen) are a long way from being viable across the sector. Therefore, the development of sustainable long-term solutions using alternative fuels is essential [6,7].

As a consequence, biodiesel produced from oil crops and animal fats, is receiving much attention as an alternative to conventional petroleum fuels. In particular, fuels produced from biomass feedstocks have emerged as one of the more promising and environmentally sustainable renewable energy options. Fuels produced from these technologies are referred to as biofuels. Biofuels offer many benefits over conventional petroleum fuels, including the wide regional distribution of biomass feedstocks, high greenhouse gas reduction potential, biodegradability and their contribution to sustainability [8].

Biofuels produced by conventional technologies (ethanol and biodiesel) typically contain oxygen levels of 10%–45% by mass, while petroleum fuels (gasoline and diesel) contain very low oxygen levels. This makes the chemical properties of biofuels more favorable for complete combustion, although it reduces energy density. In addition, biofuels typically have very low sulphur contents and often low nitrogen contents reducing the production of potentially harmful emissions. Biomass resources can be used to produce a variety of biofuels. This includes liquid fuels such as biodiesel ethanol, methanol, and Fisher-Tropsch diesel; and gaseous fuels such as hydrogen, syngas and methane. Liquid biofuels are primarily used in vehicles, but can also be used in stationary engines or fuel cells for electricity generation. Biodiesel is widely used as an alternative fuel for diesel engines, whereas ethanol is used as a substitute for automotive gasoline [2].

Biodiesel is currently produced in commercial quantities from edible oil feedstocks such as soybean oil, palm oil, and canola oil. Biodiesels produced from these feedstocks are generally referred to as first generation biodiesels. Although biodiesels from these feedstocks offer reductions in greenhouse gas emissions (GHG) and improves domestic energy security, first generation biodiesels are unlikely to be sustainable in the longer term due to land use impacts and the price and social impacts associated with using food-based feedstocks. Second generation biodiesels produced from non-edible feedstocks have the potential to overcome the disadvantages associated with first generation feedstocks while addressing many of the challenges of climate change and energy availability.

However, the majority of current vehicle engines are not optimized for the use of biodiesel. When using biodiesel as a fuel, unoptimized engines may show increased problems with carbon deposition, corrosion, lubricating oil contamination, poor low temperature performance, and heavy gum and wax formation compared to petroleum diesel [9]. The differences in performance between petroleum diesel and biodiesel may be attributed to the variation between their physical properties and their chemical compositions. Petroleum diesel is composed of hundreds of compounds boiling at different temperatures (determined by the petroleum refining process and crude oil raw material), whereas biodiesel contains primarily 6–24 carbon chain length alkyl esters (determined entirely by the feedstock) [10]. In addition to these alkyl esters, biodiesel may also contain minor amounts of mono-, di- and tri-glycerides resulting from incomplete transesterification, methanol, free fatty acids, chlorophyll (in the case of algae) and sterols [11].

As engines are currently manufactured to be optimized for petroleum fuels, Original Equipment Manufacturers (OEMs) and industry associations have shown a cautious response in their acceptance of biodiesel, especially from new feedstocks or processes [12]. Engine manufacturers and users may be reluctant to realize the potential of using second biodiesel in engines (especially from new feedstocks) because its suitability as an automobile engine fuel may not be readily verified. As a consequence, the potential of second generation biodiesel is still largely unexplored and is yet develop as a mainstream transportation fuel. This is in spite of the fact that there are many such potential biodiesel feedstocks that have already been identified including oilseed plants [13–15] and marine algae [16,17]. The slow uptake of biofuels can be associated with the challenges of ensuring a consistent supply of feedstock, feedstock cost, and the lack of experimental data to prove the quality of the fuel (resulting in limited acceptance by consumers who are concerned about engine warranties and performance) [18]. Undertaking experiments with automotive engines and measuring multiple fuel quality parameters requires considerable quantities of fuel, which can be a challenge from new sources. Fuel testing

requires sophisticated equipment and expert personnel which can be costly. These concerns potentially restrict the progress of scientific research to establish widely acceptable second generation biodiesels.

In recent years, ANN modelling techniques have gained in popularity due to their ability to accurately predict from small data sets (examples) rather than from larger data sets requiring costly and time-consuming studies and experiments. ANN has been successfully applied in various disciplines, including neuroscience [19], mathematical and computational analysis [20], learning systems [21], engineering design and application [22–24] and chemical and environmental engineering [25–28]. In this paper, the potential of ANN modelling techniques in identifying sustainable future generation biodiesel feedstock are identified based on the most recent literature. Current biodiesel technology (feedstocks, properties, production processes, chemical compositions and factors contributing to fuel quality and its applicability as an alternative fuel) and the application of ANN in fuel technology and the potential second generation biodiesel feedstock is also discussed. Findings from this literature review contain valuable information to assist biodiesel manufacturers and researchers to make important decisions to accelerate the technological development of biofuels.

2. Biodiesel

Fatty acid methyl or ethyl esters, commonly referred to as “biodiesel”, are a liquid fuel alternative to diesel. They are made from agricultural products, forest organic matter and animal fat feedstocks. Biodiesel is the only currently available alternative transport fuel made from oilseed crops and animal fat which can be used directly in conventional unmodified diesel engines. Biodiesel is safer to handle, store and transport compared to petroleum diesel because it is biodegradable, non-toxic and has a higher flash point than diesel. One of the major advantages of biodiesel is that it has potential to reduce dependency on imported petroleum through the use of domestic feedstocks for production [29,30].

In fuel property terms, biodiesel has a higher cetane rating than petroleum diesel which improves engine performance. In addition, it has better lubricant properties than petroleum diesel which can extend engine life [12]. The use of biodiesel reduces particulate emissions by up to 75% when compared with conventional diesel fuel. Biodiesel also substantially reduces unburned hydrocarbons, carbon monoxides and particulate matters, including elimination of sulphur dioxide in exhaust emissions. The exhaust emissions of particulate matter from biodiesel have been found to be 30% lower than overall particulate matter emissions from fossil diesel. The exhaust emissions of total hydrocarbons are up to 93% lower for biodiesel than diesel fuel [31].

As a fuel, there are currently several disadvantages to using biodiesel in diesel engine applications. These differences mainly result from the difference in chemical compositions between petroleum diesel and biodiesel. These major disadvantages are: lower energy density, higher viscosity, higher copper strip corrosion and issues with the degradation of fuel in storage for prolonged periods. Biodiesel also has a higher cold-filter plugging point temperature than fossil diesel which means it will crystallise into a gel at lower temperatures when used in its pure form. Biodiesel can also cause dilution of engine lubricant oil, requiring more frequent oil changes than when using petroleum diesel fuels in conventional diesel engines. This increase in dilution and polymerisation of engine sump oil is due to the higher viscosity at lower temperatures of biodiesel compared to petroleum diesel [9].

2.1. Biodiesel Feedstock

Feedstocks for biodiesel production can be classified into four groups. These are: (1) virgin vegetable oil feedstocks such as rapeseed, soybean, sunflower, palm oil; (2) waste vegetable oils; (3) animal fats including beef tallow, lard and yellow grease; and (4) non-edible oils such as jatropha, neem oil, castor oil and the prevalence of these feedstocks varies around the World (Figure 1). The regional availability of feedstocks for biodiesel production depends greatly on climate, soil conditions and options for alternate land use. Consequently, different regions are focusing their efforts on different feedstocks [32]. As an example, the widespread use of soybeans in the USA as a food product has led to the emergence of soybean biodiesel in that country. In Europe, rapeseed is the most common source of biodiesel production. In India and Southeast Asia, the jatropha tree is used in biodiesel production, and in Malaysia and Indonesia, palm oil is used as a significant biodiesel source.

Figure 1. Biodiesel feedstocks around the world.

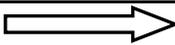


2.2. First and Second Generation Biodiesel

Many potential feedstocks for biodiesel production have been investigated including soybean oil [33], sunflower oil, corn oil, used fried oil, olive oil [34], rapeseed oil [35], castor oil, lesquerella oil, milkweed (*Asclepias*) seed oil [36], *Jatropha curcas*, *Pongamia glabra* (karanja), *Madhuca indica* (mahua) and *Salvadora oleoides* (Pilu) [37], palm oil [38] and linseed oil [39]. Most of those are produced from edible oil feedstock and known as first generation biodiesels [40]. Although the range of biodiesels available reveals the flexibility and potential of the biodiesel industry, this potential is challenged by social and economic concerns. The most contentious issue affecting the production of first generation biodiesel is the use of agricultural land for biodiesel production. This issue is commonly referred to as the “Food versus Fuel” debate, whereby the main two issues are the use of edible crops for biodiesel production, and the land space devoted to the growing of inedible crops. First generation biodiesels are primarily made from edible vegetable oils, therefore crop space used for biodiesel production limits the crop space available for food production. Farmers of these crops now have the choice to sell to the biodiesel production market or the food market. Farmers must find ways

to retain their viability, and if a higher price is offered by the biodiesel production market, this will more often than not be the option they will choose. This is of particular concern in disadvantaged countries where crops used for biodiesel production displace the production of food crops, causing shortages. Supply and demand dictates that a shortage will cause a price rise, where countries such as Malaysia are currently experiencing [41]. This issue became a global debate due to the 2007–2008 world food price crisis. Differing arguments exist for the cause of this crisis, however there has been widespread speculation that the increasing consumption of biodiesel contributed to the food shortage and subsequent price increases [42]. Although there is a global demand for biodiesel due to its proven benefits and its potential to decrease dependence on fossil fuels, this should not lead to of people suffering from hunger. As a result, first generation biodiesels are unlikely to be sustainable in the longer term, having limitations in their ability to contribute to socio-economic growth [43]. Therefore, an alternative must be considered which eliminates the downfalls of first generation biodiesels. Research is currently underway in second and third generation biodiesels which are targeted at addressing the “Food versus Fuel” debate [44]. A comparison of first and second generation biodiesel in terms of feedstock, advantages and associated problems are shown in Table 1.

Table 1. Advances in biodiesel technology.

Technology	First generation biodiesel 	Second generation biodiesel
Feedstock	Edible vegetable oil and animal fat	Non-edible feedstock Cheap and abundant biomass
Advantage	Commercially available Renewable Environmentally friendly Economic	Renewable Not competing with food Environmentally friendly More sustainable Social security
Problems	Limited feedstock Competing with food Engine durability Not likely to be sustainable	In development stage Unreliable sources of feedstock High production cost

2.3. Potential Second-Generation Biodiesel Feedstocks

Non-edible oils, which are considered as second-generation biodiesel feedstock, currently contribute less than 5% of total global biodiesel production [13]. Therefore, second-generation biodiesels are yet to make a significant impact on the mainstream alternative energy system. One of the main reasons for this is the lack of reliable and commercially viable feedstock sources. The feedstocks most often used in second-generation biodiesel production are jatropha, cottonseed, karanja, mahua, castor and waste cooking oils. A considerable amount of research has been carried out in an effort to determine alternative feedstocks for biodiesel production over the last few years. A large number of non-edible oilseed plants and algae species have been identified around the world which could be a valuable source for future generation biodiesel. For example, Ashwath [15] investigated the biodiesel potential of more than 200 Australian native plants species, based on their ability to produce abundant quantities of seeds in their natural environment in Queensland. Among those, 20 species have been identified as containing more

than 20% of non-edible oil in their seed. This study has concluded that Australia has potential to be a major source of next-generation biodiesel feedstock, having vast areas of grazing (cleared) and degraded (mined) land on which biodiesel crops could successfully be established.

In Thailand, 27 types of plants have been found to contain more than 25% (w/w) of non-edible oil in the seed [45]. Mohibbe Azam *et al.* [46] identified 75 different non-edible plant seed oils produced from plant species growing naturally in India, and containing more than 30% of oil in their seeds or kernels. Kumar and Sharma [47] presented a brief description of the biology, distribution and chemistry of fifteen potential non-edible oilseed plants from India. Moreover, in a critical review, Balat and Balat [48] reported that there are more than 350 potential oilseed crops for biodiesel production which have been identified, with most of them being non-edible, yet useful as alternative fuel sources for diesel engines.

Besides non-edible oilseed plants, researchers worldwide are giving more attention to algae species as a promising source of second-generation biodiesel feedstocks. Algae are usually found in seas, rivers, lakes, soils, walls, in plants and animals—almost anywhere that there is light for photosynthesis. While growing, they convert sun energy into chemical energy through photosynthesis and complete an entire growth cycle every few days [49]. Their growth and bio-oil production rates can be accelerated by the addition of specific nutrients and sufficient aeration [49]. Therefore, it is possible to find species best suited to local environments or which have specific growth characteristics, which is not possible with current first-generation biodiesel feedstocks (e.g., soybean, rapeseed, sunflower and palm oil) [16]. Moreover, the oil productivity of many algae greatly exceeds the oil productivity of even the best producing oil crops [50]. For example, some algae species are able to produce bio-oil at a rate approximately 200 times higher than that of soybean plants over an acre of land area [51].

Algae also offers some significant advantages in the production of second generation biodiesel including: (1) providing a reliable and continuous supply for naturally growing oil all year round; (2) can be harvested batch-wise nearly all year round; (3) higher photon conversion efficiency (as evidenced by increased biomass yields per hectare); (4) utilising salt and waste water streams, thereby greatly reducing freshwater use; (5) possibility of combining CO₂-neutral fuel production with CO₂ sequestration; and (6) producing non-toxic and highly biodegradable biofuels [52]. Furthermore, algae species are very diverse in nature with a diversity much greater than that of land plants. Hu *et al.* [53] reported that over 40,000 species have already been identified, with potentially many more. These species are commonly classified into multiple major groups which include: cyanobacteria (Cyanophyceae), green algae (Chlorophyceae), diatoms (Bacillariophyceae), yellow-green algae (Xanthophyceae), golden algae (Chrysophyceae), red algae (Rhodophyceae), brown algae (Phaeophyceae), dinoflagellates (Dinophyceae) and “pico-plankton” (Prasinophyceae and Eustigmatophyceae). Several additional divisions and classes of unicellular algae have been described, and details of their structure and biology are available [54,55].

The concept of using diverse non-edible oils produced from oilseed plants and algae species has been explored in depth over the past few decades. At the same time, a large number of new feedstocks have been identified, based on oil content. Table 2 summarises the potential oilseed plants and algae species feedstock for future generation biodiesel production, focusing on feedstocks containing at least 40% non-edible oil by dry weight as reported in some recent studies. The chemical compositions of

most of the oil produced from the feedstock listed in the Table 2 have also been analysed [56]. However, the production of those oils is primarily confined to high-value specialty oils with nutritional value, rather than commodity oils for biofuel, and scalable, commercially viable systems have yet to emerge. In considering any new oil as a candidate for large-scale production in order to use as a biodiesel fuel source, several other issues should be considered which include the economic necessities revolving around the production of biodiesel and its suitability for use as fuel in combustion engines.

Table 2. Second-generation biodiesel feedstock containing at least 40% oil by dry weight [13–16,53,56–58].

Non-edible oilseed plants		Microalgae	
Feedstock	Oil content (% dry wet)	Feedstock	Oil content (% dry wet)
<i>Aleurites moluccana</i>	42	<i>Botryococcus braunii</i>	25–75
<i>Argemone mexicana</i>	38–54	<i>Chaetoceros calcitrans</i>	40
<i>Atalaya hemiglauca</i>	18–43	<i>Chlorella emersonii</i>	25–63
<i>Azadirachta indica</i>	45–61	<i>Chlorella minutissima</i>	57
<i>Brachychiton acerifolius</i>	45–50	<i>Chlorella protothecoides</i>	14.6–57.8
<i>Brachychiton bidwillii</i>	19–55	<i>Chlorella vulgaris</i>	5–58
<i>Calophyllum inophyllum</i>	42–65	<i>Cryptocodinium cohnii</i>	20.0–51.1
<i>Cerbera odollam</i>	54	<i>Cylindrotheca</i> sp.	16–40
<i>Cocos nucifera</i>	49–52	<i>Dunaliella tertiolecta</i>	16.7–71.0
<i>Jatropha curcas</i>	20–60	<i>Isochrysis galbana</i>	7–40
<i>Euphorbia lathyris</i>	48	<i>Nannochloris</i> sp.	20–56
<i>Garcinia indica</i>	45.5	<i>Nannochloropsis</i> sp.	31–68
<i>Hevea brasiliensis</i>	40–60	<i>Neochloris oleoabundans</i>	29–65
<i>Linum usitatissimum</i>	35–45	<i>Nitzschia</i> sp.	16–47
<i>Madhuca indica</i>	35–50	<i>Phaeodactylum tricorntutum</i>	18–57
<i>Melia azedarach</i>	19–45	<i>Porphyridium cruentum</i>	9.0–60.7
<i>Michelia chaampaca</i>	45	<i>Scenedesmus dimorphus</i>	16–40
<i>Nicotiana tabacum</i>	36–41	<i>Scenedesmus obliquus</i>	11–55
<i>Pongamia pinnata</i>	21–50	<i>Schizochytrium</i> sp.	50–77
<i>Putranjiva roxburghii</i>	42	<i>Skeletonema costatum</i>	13.5–51.3
<i>Raphanus sativus</i>	40–54		
<i>Ricinus communis</i>	20–50		
<i>Salvadora oleoides</i>	45		
<i>Simmondsia chinensis</i>	45–55		
<i>Syagrus romanzoffiana</i>	38–44		

However, major technical and economic hurdles are still to be overcome before they can be widely deployed on a fully commercial scale, and unfortunately, the progress of research to address these issues is not progressing strongly. The quality and suitability of biodiesel produced from a large number of non-edible oil-bearing feedstocks as the alternative to petroleum fuel for automobile engine application is still uncertain. Therefore, many potential non-edible feedstocks are yet emerging to mainstream biodiesel production, and it appears that its contribution to the global energy system is a long way off [59]. In order to accelerate the progress of second-generation biodiesel as an alternative

automobile fuel, more detailed research is still needed to ensure that second-generation biofuels will provide economic benefits whilst fulfilling quality standards and combustion performance in automobile engines. Such research requires pilot scale biodiesel production plants, specialised equipment and a skilled workforce—all of which involve high-level research investment and considerable economic risk. Therefore, it has become challenging for many countries (especially developing or underdeveloped countries) to take the initiative to establish their own biodiesel manufacture from locally grown non-edible feedstock.

2.4. Production of Biodiesel

More than 100 years ago, Rudolph Diesel demonstrated the operation of a diesel engine using vegetable oil as a fuel, hence the potential of using these feedstocks has been long recognised. However, vegetable oils are extremely viscous, with viscosity ranging from 10 to 17 times higher than that of petroleum diesel. This makes vegetable oil unsuitable to use as a direct fuel in the modern diesel engine. As a consequence, researchers and scientists have developed various methods to reduce the viscosity of bio-oils to make them suitable for diesel engine use. Some of these methods include dilution with other fuels, esterification, microemulsification, pyrolysis and catalytic cracking. Of these techniques, esterification is the most promising and widely used solution due to its high conversion efficiency, simplicity, low conversion cost and the fuel qualities of the product. Transesterification of bio-oils with alcohols to produce esters is a widely used technique for commercial biodiesel production [32].

Transesterification is a chemical reaction in which oils (tri-glycerides) are converted into esters as shown in Figure 2. Triglycerides react with alcohols (e.g., methanol, ethanol) under acid or base catalysed conditions, producing fatty acid alkyl esters and glycerol. A catalyst is used to improve the reaction rate and yield. Because the transesterification reaction is reversible, excess alcohol is used to shift the equilibrium to favour production of the ester. After the reaction is complete, glycerol is removed as a by-product. The biodiesel produced may be denominated by the feedstock used and the ester formed including Fatty Acid Methyl Ester (FAME), Fatty Acid Ethyl Ester (FAEE), Soybean Methyl Ester (SME) and Rapeseed Methyl Ester (RME). The total ester content in biodiesel is the measure of the completeness of the transesterification reaction [60].

The yield of biodiesel in transesterification is affected by several process parameters. These parameters include the reaction temperature, the molar ratio of alcohol to oil, the type and concentration of catalyst and the reaction time [61,62]. While conducting experiments to optimise the transesterification reaction conditions of two feedstock oils (including waste cooking oil and canola oil), Leung and Guo [63,64] determined that the optimal values of these parameters for achieving maximum conversion of triglycerides to esters depended on the chemical and physical properties of the feedstock oils. Other research has also determined varying optimum process conditions for different oil feedstocks as shown in Table 3.

Alkali-catalysed transesterification cannot be directly used to produce high quality biodiesel from feedstocks containing high levels of free fatty acids (FFA). This is because FFAs react with the catalyst to form soap (Figure 3), resulting in emulsification and separation problems. To overcome this problem, a pre-esterification process may be used to reduce the content of FFAs in the feedstock. A typical pre-esterification processes uses homogeneous acid catalysts, such as sulphuric acid,

phosphorous acid combined with sulphonic acid, or heterogenous “solid-acid” catalysts, to esterify the free fatty acids [64] as shown in Figure 4.

Figure 2. Transesterification reaction [60].

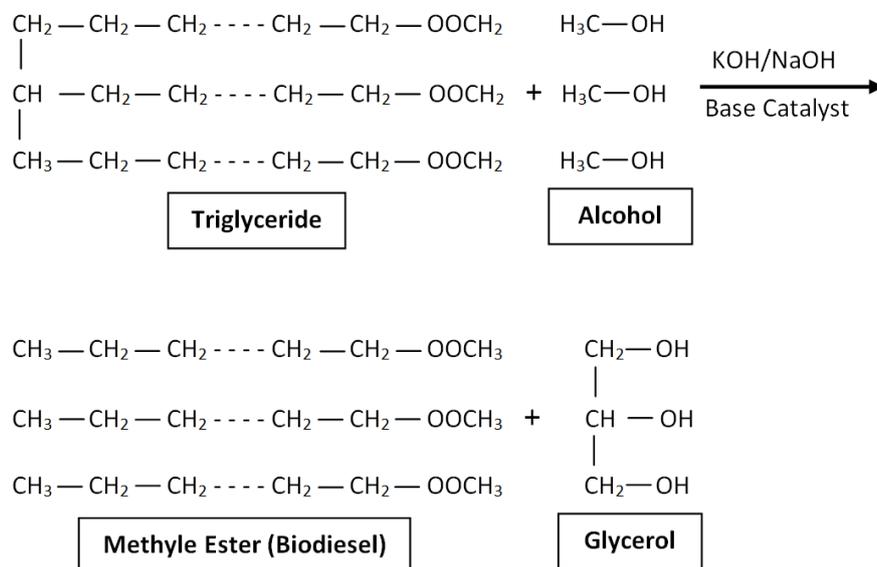


Table 3. Reported optimum conditions for transesterification of oils for biodiesel production.

Feedstock	Reaction parameters				Ester (wt.%)	References
	Temp (°C)	Alcohol: Oil (mol:mol)	Catalyst (wt.%)	Time (min)		
Palm	38.44	6.44:1	1.25	26	98.02	Worapun <i>et al.</i> [65]
	65	6:1	1.0	60	82	Darnoko and Cheryan [66]
Cottonseed	60	6:1	0.3	60	96	Hoda [67]
	60	12:1	2	480	90	He <i>et al.</i> [68]
Rapeseed	65	6:1	1.0	120	96	Rashid and Anwar [40]
Sunflower	60	6:1	1.0	120	97.1	Rashid <i>et al.</i> [69]
	70	3:1	0.28	60	96	Antolin <i>et al.</i> [70]
Jatropha	60	6:1	1.0	40	98.6	Nakpong and Wootthikanokkhan [71]
Canola	45	6:1	1.0	60	98	Leung and Guo [63]
Waste cooking	60	7:1	1.1	20	94.6	Leung and Guo [63]
Soybean	70	9:1	0.5	180	99	De <i>et al.</i> [72]

Figure 3. Soap formation [60].

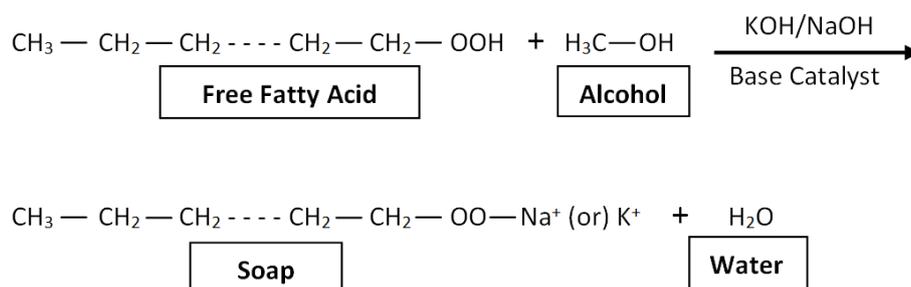
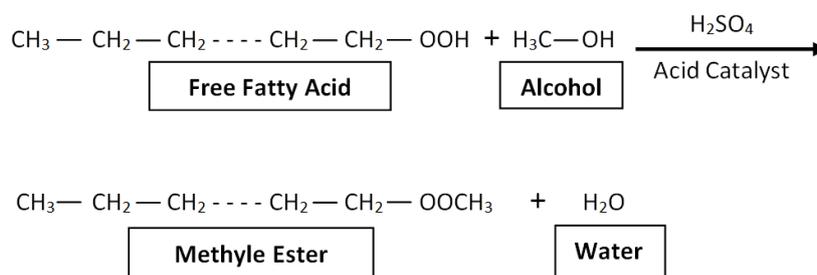


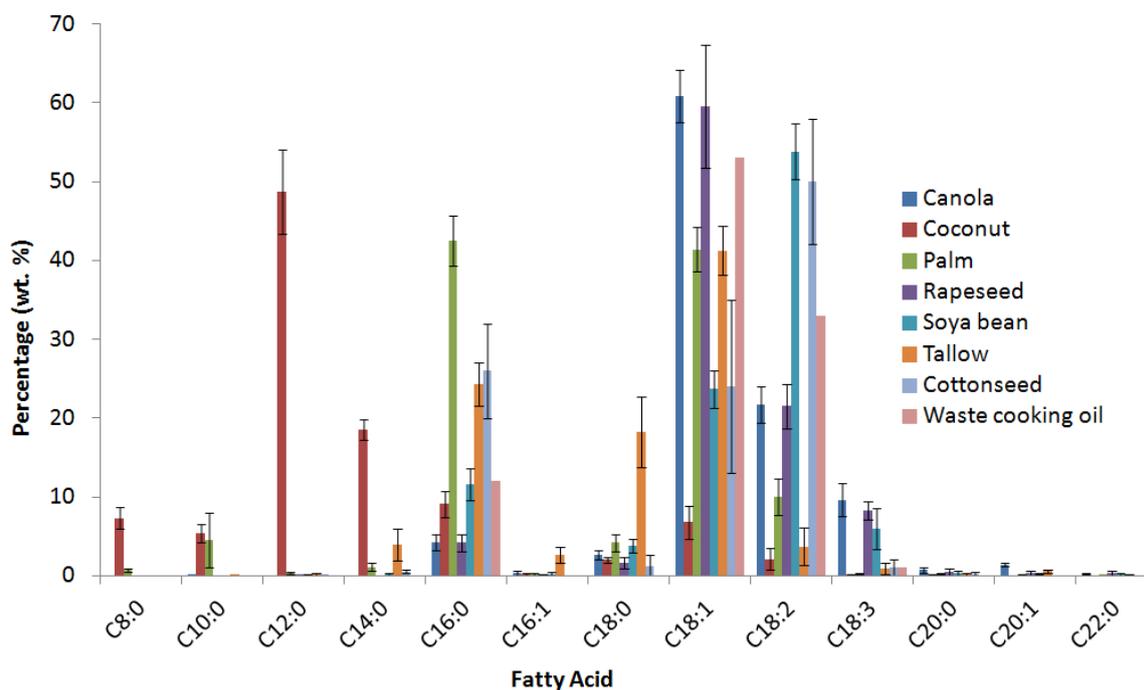
Figure 4. Acid pre-esterification [60].

2.5. Chemical Composition of Biodiesel

Petroleum diesel fuels are saturated straight chain hydrocarbons with carbon chain lengths of 12–18, whereas vegetable oils and animal fats consist of 90%–98% triglycerides, small amounts of mono and diglycerides and free fatty acids. The fatty acid compositions of triglycerides differ in relation to the chain length, degree of unsaturation and the presence of other functional groups. The fatty acid compositions are feedstock dependent and are affected by factors such as climatic conditions, soil type, plant health, and plant maturity upon harvest. Using the carboxyl reference system, fatty acids are designated by two numbers: the first number denotes the total number of carbon atoms in the fatty acid and the second is the number of double bonds indicating the degree of unsaturation. For example, 18:1 designates oleic acid which has 18 carbon atoms and one C=C double bond. The most common fatty acids found in biodiesels and their structures are listed in Table 4. However, biodiesels from differing feedstock and origins have variations in the fatty acid in their molecules, as shown in Figure 5.

Table 4. Chemical structure of common fatty acid in biodiesels [31,73–75].

Fatty acid	Chemical structure
Caprilic (8:0)	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
Capric (10:0)	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
Lauric (12:0)	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic (14:0)	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Myristoleic (14:1)	$\text{CH}_3(\text{CH}_2)_5 \text{CH}=\text{CH} (\text{CH}_2)_5 \text{COOH}$
Pentadecenoic (15:0)	$\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$
Palmitic (16:0)	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Palmitoic (16:1)	$\text{CH}_3(\text{CH}_2)_6 \text{CH}=\text{CH} (\text{CH}_2)_6 \text{COOH}$
Meptadecenoic (17:0)	$\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$
Stearic (18:0)	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Oleic (18:1)	$\text{CH}_3(\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Linoleic (18:2)	$\text{CH}_3(\text{CH}_2)_4 \text{CH}=\text{CHCH}_2\text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Linolenic (18:3)	$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7 \text{COOH}$
Arachidic (20:0)	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
Behenic (22:0)	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$
Erucic (22:1)	$\text{CH}_3(\text{CH}_2)_9 \text{CH}=\text{CH} (\text{CH}_2)_9 \text{COOH}$
Lignoceric (24:0)	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$

Figure 5. Fatty acid profile of various biodiesel fuels [31,73,74,76–79].

2.6. Biodiesel Standards

Quality standards are crucial for the commercial use of any fuel product. They serve as guidelines for production, assure customers that they are buying high-quality fuels, and to provide authorities with approved tools for a common approach to transport, storage and handling. Modern diesel engines using common rail fuel injection systems are more sensitive to fuel quality. Therefore, engine and automotive manufacturers rely on fuel standards in determining consumer warranties. However, the chemical compositions of biodiesel and petroleum diesel are very different, and these differences result in varying physio-chemical properties. In order to improve the viability of biodiesel for as a commercial fuel for direct replacement of petroleum diesel, the properties of biodiesel need to reflect functional equivalence with diesel.

Biodiesel can be used as a pure fuel (B100) or blended with petroleum diesel in varying concentrations. For B100, the most internationally recognized standards are EN14214 (Europe) and ASTM D-6751 (USA). Both standards are similar in content, with only minor differences in some parameters [31]. Many other countries have defined their own standards, which are frequently derived from either EN14214 or ASTM D-6751 [31]. As a part of the *Fuel Quality Standards Act 2000*, the Australian government released a biodiesel fuel standard, “Fuel Standard (Biodiesel) Determination 2003”. A summary of the major fuel quality parameters in these standards is detailed in Table 5.

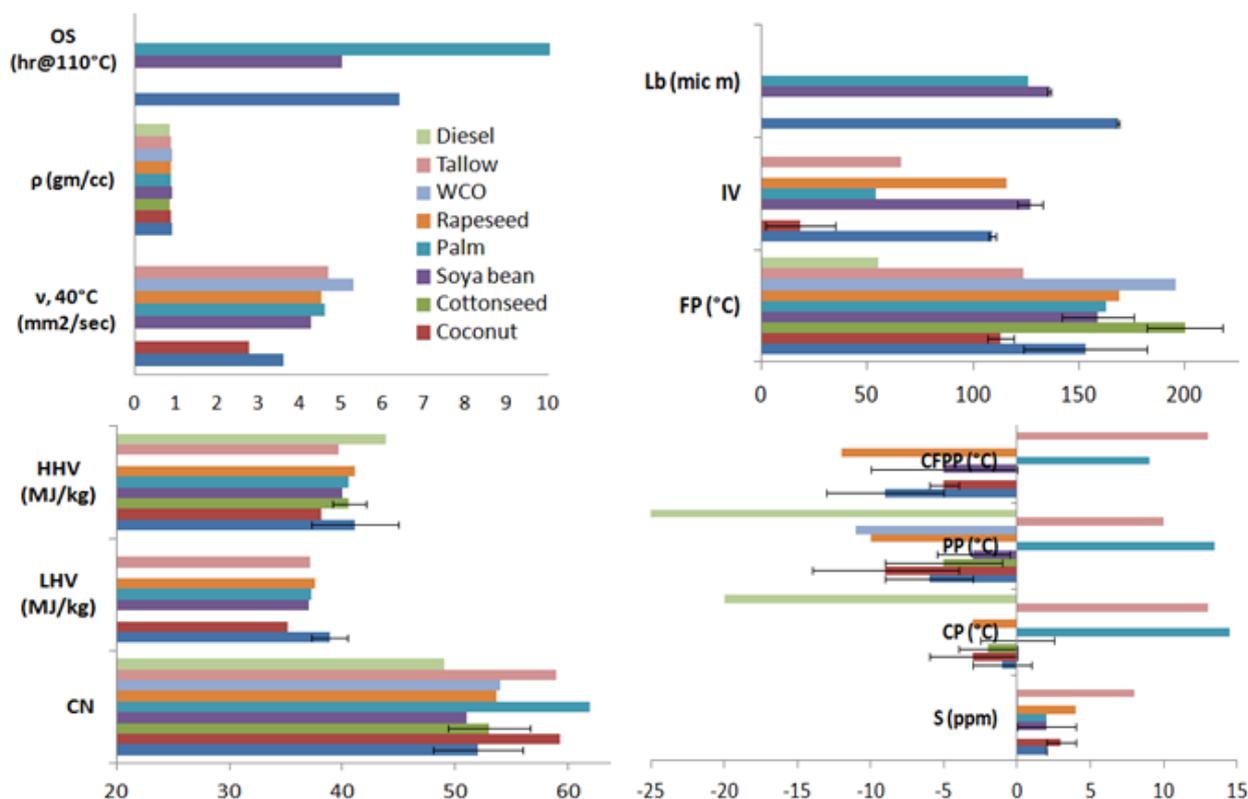
Table 5. International biodiesel standards [74,80].

Properties	Units	USA ASTM D-6751	Europe EN 14214	Australia
Viscosity, 40 °C	mm ² /sec	1.9–6.0	3.5–5.0	3.5–5.0
Density	gm/m ³	n/a	0.860–0.900	0.860–0.900
Cetane number	-	47 min	51 min	51 min
Flash point	°C	130 min	120 min	120 min
Cloud point	°C	report	report	report
Acid number	mg KOH/g	0.80 max	0.5 max	0.8 max
Free glycerine	wt.%	0.02 max	0.02 max	0.02 max
Total glycerine	wt.%	0.24 max	0.25 max	0.25 max
Iodine number	-	-	120 max	n/a
Oxidation stability	h	-	6 min	n/a
Monoglyceride	Mass (%)	-	0.8 max	n/a
Diglyceride	Mass (%)	-	0.2max	n/a
Triglyceride	Mass (%)	-	0.2 max	n/a
CFPP	°C	-	-	-4

2.7. Fuel Properties

Biodiesel fuel properties vary significantly between feedstocks due to their differing chemical compositions. Figure 6 summarises the key fuel properties of various biodiesels reported in the more recent literature. The factors that influence biodiesel fuel properties are discussed below.

Figure 6. Variation in fuel properties of various biodiesel [75,76,79,81–86].



2.7.1. Kinematic Viscosity

Viscosity is defined as the resistance to shear or flow; it is highly dependent on temperature and it describes the behavior of a liquid in motion near a solid boundary such as the walls of a pipe. The presence of strong or weak interactions at the molecular level can greatly affect the way the molecules of an oil or fat interact, therefore affecting their resistance to flow. Viscosity is one of the most critical features of a fuel. It plays a dominant role in fuel spray, fuel-air mixture formation and the combustion process. In a diesel engine, the liquid fuel is sprayed into compressed air and atomised into small droplets near the nozzle exit. In the combustion chamber, fuel forms a cone-shaped spray at the nozzle exit which effects the viscosity affects the atomisation quality, penetration and size of the fuel droplet [85]. Higher viscosities result in higher drag in the fuel line and injection pump, higher engine deposits, higher fuel pump duties and increased wear in the fuel pump elements and injectors. Moreover, the mean diameter of the fuel droplets from the injector and their penetration increases with an increase in fuel viscosity [87]. Higher pressure in the fuel line can cause early injection, moving the combustion of the fuel closer to top dead centre, increasing the maximum pressure and temperature in the combustion chamber [87–89]. Therefore, fuel viscosity significantly influences engine combustion, performance and emissions, especially carbon monoxide (CO) and unburnt hydrocarbon (UHC) [90].

To estimate the influence of biodiesel viscosity on diesel engine exhaust emission, Ng *et al.* [91] conducted experiments on a light-duty diesel engine using coconut methyl ester (CME), palm methyl ester (PME), soybean methyl ester (SME) and blends with petroleum diesel. This study found that an increase in kinematic viscosity by 1 mm²/s has the potential to raise the emitted CO concentration by 0.02 vol%. UHC was increased by 1 ppm vol. for every 1 mm²/s rise in kinematic viscosity. Problems with high viscosity in the fuel became more severe in cold weather as viscosity of biodiesel increases with decreasing temperature [92]. However, very low fuel viscosity is not desirable because the fuel then doesn't provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Therefore, all biodiesel standards define the upper and lower limits of biodiesel shown in Table 4.

The viscosity of biodiesel is dependent on its fatty acid composition. A recent study showed that viscosity increases with increasing length of both the fatty acid chain and alcohol group [93]. As the lengths of the acid and alcohol segments in the ester molecules increased, so did the degree of random intermolecular interactions and consequently viscosity. The effect becomes more evident at lower temperatures, where molecular movements are more restricted [94,95]. However, Refaat [96] reported that shorter fatty acid chains with longer alcohol moieties display lower viscosity than ester with longer fatty acid chains and shorter alcohol moieties. Other factors that influence biodiesel viscosity include: number and position of double bonds [97], degree of saturation [98], molecular weight [99], branching [100] hydroxyl groups and the amount of impurities, such as unreacted glycerides or glycerol [90,99].

2.7.2. Density

Density is an important fuel property that influences the amount of fuel injected into the engine cylinder. This is because in a diesel engine fuel injection system, pumps and injectors must deliver a

precise amount of fuel to provide proper combustion [101,102]. However, fuel injection pumps meter fuel by volume and not by mass, leading to denser fuel which contains a greater mass for the same volume. Thus, changes in the fuel density will influence engine output power due to the different mass of the fuel injected, and this directly affects engine performance characteristics [85]. Moreover, density increases the diameter of the fuel droplets in the combustion chamber. Since the inertia of the bigger droplets is relatively large, their penetration in the combustion chamber will be higher as well [87]. When a fuel with lower density and viscosity is injected, improved atomisation and mixture formation can be attained which consequently affects exhaust emissions. Szybist *et al.* [103] found that fuel density correlated with particulate matter (PM) and NO_x emissions, with higher densities generally causing an increase in PM and NO_x emission in diesel engines. However, while investigating the biodiesel fuel properties on exhaust emission in a light-duty diesel engine, Ng *et al.* [91] found that fuel properties moderately affect CO emissions but have no significant impact on NO_x, UHC and smoke opacity levels. Density is also a key factor in the design of reactors, separation processes and storage tanks in biodiesel production [104].

Density of biodiesel is closely related to the fatty acid composition and the purity of a biodiesel. Studies have shown that density increases with decreasing chain length and an increasing degree of unsaturation [105,106].

2.7.3. Cetane Number (CN)

Cetane number (CN) is a widely used diesel fuel quality parameter, and is a measurement of the combustion quality of diesel fuels during compression ignition. It is related to the ignition delay (ID) time, that is, the time that passes between injection of the fuel into the cylinder and the onset of ignition. A shorter ID time results in a higher CN which provides better ignition properties [107]. A high CN will help to ensure good cold start properties and will minimise the formation of white smoke. On the other hand, lower CN may result in diesel knocking and an increase in exhaust emissions.

Standards have been established worldwide for CN determination. It is measured by comparing blends of two reference fuels. A long straight-chain hydrocarbon, hexadecane (C₁₆H₃₄; trivial name “cetane”, giving the cetane scale its name) is the high quality standard on the cetane scale with an assigned CN of 100. A highly branched compound, 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also C₁₆H₃₄), a compound with poor ignition quality, is the low-quality standard and has an assigned CN of 15. Both the Australian biodiesel standard and the European petroleum diesel standard EN 590 limit the cetane number to a minimum value of 51, as shown in Table 4.

CN is dependent on the fatty acid composition of a biodiesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number [108,109]. The most significant factor in lowering CN is the degree of unsaturation. Geller and Goodrum [93] observed that a low CN was associated with highly unsaturated compounds such esters of linoleic (C18:2) and linolenic (C18:3) acids, whereas high CNs were observed for esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids. Similar results have been reported by Knothe *et al.* [110]. Bangboye and Hansen [111] observed that a feedstock that is high in saturated fatty esters has a high CN, while a feedstock with predominantly unsaturated fatty acids has lower CN values.

2.7.4. Heating (Calorific) Value

Heating value is a significant fuel property which influences the suitability of biodiesel as an engine fuel, as it indicates the energy content in the fuel. Due to the high oxygen content of biodiesel, it is generally accepted that biodiesels are about 10% less energy dense as compared with petroleum diesel. The heating value of biodiesel is related to its fatty acid profile. Heating value increases with increasing carbon number in fuel molecules due to mass fraction decreases [112]. Studies have also found that unsaturated esters have lower mass energy content (MJ/kg). Demirbas [29] studied the correlation between viscosity and higher heating value (HHV) by performing a linear least square regression analysis. This study found that there is a high correlation between the heating value and the viscosity of vegetable oils and their methyl esters and that the heating value of vegetable oils and biodiesels increases with viscosity.

2.7.5. Flash Point

Flash point is often used as a descriptive characteristic of liquid fuel and is defined as the lowest temperature at which the fuel will start to vapourise to form an ignitable mixture when it comes to contact with air [113]. Hence, flash point is an important parameter for assessing fire hazards during fuel transport and storage. This is reflected by the respective limits within Australian standards (≥ 120 °C) and the European fossil diesel standard, EN 590 (> 55 °C). However, the flash point of biodiesel is approximately double that of petroleum diesel, which makes biodiesel a more acceptable engine fuel in relation to concerns about safety. It is also an important parameter in engine combustion performance. Canakci and Sanli [93] found that with a high flash point, NO_x emission decreased due to low combustion pressure and temperature. Moreover, high flash point is also important in niche applications such as underground mining. On the other hand, studies show that a high flash point can cause cold engine startup problems, misfiring and ignition delay, which increases carbon deposition in the combustion chamber [113].

Biodiesels from animal fat generally have higher flash points than those from vegetable oils. This is the result of the highly saturated fatty acid compounds in biodiesels from animal fats increasing the flash point temperature. Alcohol residue in biodiesel significantly decreases flash point [80].

2.7.6. Oxidation Stability

Oxidation stability is an important fuel property which reflects the resistance to oxidation during long-term storage. Usually biodiesels are more sensitive to oxidative degradation than petroleum diesel due to their chemical composition. Fuel quality declines due to gum formation during the oxidation process. This gum does not combust completely resulting in poor combustion, carbon deposits in the combustion chamber and lubrication oil thickening [114]. Monyem *et al.* [115] observed that oxidised biodiesel starts to burn earlier than unoxidised, increasing NO_x emissions due to the associated increase in viscosity and cetane number.

The chemical structure of biodiesel is an important factor in the oxidation reaction. Oxidation is influenced by the presence of double bonds in the chains, that is, feedstocks rich in polyunsaturated fatty acids are much more susceptible to oxidation than the feedstocks rich in saturated or

monounsaturated fatty acids [10]. However, our understanding of oxidation is complicated by the fact that fatty acids usually occur in complex mixtures, with minor components in these mixtures catalysing or inhibiting oxidation. In addition, the rates of the oxidation of different unsaturated fatty acids or esters can vary considerably. The other factors that affect the oxidation stability of biodiesel include double bond configuration, temperature, air, light and storage tank materials [48].

2.7.7. Cold Temperature Properties

One of the major problems associated with the use of biodiesel in countries with a cold climate include the poor cold flow properties when compared with petroleum diesel fuels. The parameters generally used to determine cold flow properties are cloud point (CP), pour point (PP) and cold-filter plugging point (CFPP). CP is the temperature at which a material becomes cloudy due to the formation of crystals and solidification of saturates, with PP being the lowest temperature at which the fuel can be pumped [100]. In general, the CP occurs at a higher temperature than the PP, with the CFPP defined as the lowest temperature at which a fuel portion will pass through a standardised filtering device in a specified time. Studies have found that biodiesel from all feedstock has a relatively high CP, PP and CFPP when compared with petroleum diesel [116]. Moreover, biodiesel contains relatively few components compared to petroleum diesel, and each component has its own solidification temperature. Therefore, the solidification of biodiesel is more rapid and difficult to control as one or two components can tend to dominate. At low temperatures, solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems.

The fatty acid composition of biodiesel greatly influences its cold-flow properties. Biodiesels made from feedstocks containing higher concentrations of high-melting point saturated long-chain fatty acids tends to have relatively poor cold flow properties [117]. Studies found that the freezing point of a biodiesel fuel increases with increasing numbers of carbon atoms in the carbon chain, and decreases with increasing double bonds [10,98,112]. Therefore, saturated components have poor cold flow properties over unsaturated components. Moreover, the double bond position also affects the cold flow properties. Rodrigues [95] reports that a double bond position near the end of the carbon chain results in poor cold flow properties as compared with a double bond found in the middle of the molecules. While conducting studies on the effects of chemical structure on the crystallisation temperature using a series of branched alcohol esters, Nascimento *et al.* [118] observed in the studies that branching in the carbon chain reduces the crystallisation of esters.

2.7.8. Lubricity

Lubricity is defined as the ability of fuel to provide hydrodynamic and/or boundary lubrication to prevent wear between engine moving parts. It is an important parameter for diesel engine operation, because poor lubrication leads to the failure of engine parts, such as fuel injectors and pumps as they are directly lubricated by the fuel itself [119]. Increasingly strict regulations on the sulphur content of commercial petroleum fuel have resulted in a decrease in fuel lubricity over time. Therefore, the issue of lubricity in fuel is becoming increasingly important with respect to diesel engine operation. Biodiesels typically have superior lubrication properties when compared with petroleum diesel [120]. Studies show that biodiesel derived from vegetable oils can significantly increase diesel fuel lubricity

at blend concentrations of less than 1%. Therefore, biodiesel can be used as an additive to improve the lubricity of petroleum fuel [33,34,121,122].

Knothe and Steidley [90] examined the lubricity of biodiesel and petroleum diesel components. They found better lubricity in fatty acid compounds than hydrocarbons in petroleum diesel. This study also reported that pure free fatty acids, monoacylglycerols, and glycerol possess better lubricity than pure esters. The main components responsible for biodiesel lubricity are FAMES, hydroxyl groups and monoacylglycerols followed by free fatty acids (FFAs) and diacylglycerols, whereas triglycerols do not have any significant effect on the lubricity of biodiesel [93,120]. On the other hand, the structures of fatty acids have an impact on biodiesel lubricity. Increasing saturation leads to a stronger lubrication layer as molecules can align themselves more easily in straight chains and when they are packed closely on the surface [123]. However different results have been reported by Knothe [98], Anastopoulos *et al.* [121] and Bhuyan *et al.* [124] who found that lubricity increases with the increase in length of fatty acid chains, while Geller *et al.* [93] showed that there is no consistent trend relating chain length to lubricity enhancement.

2.7.9. Iodine Value

Iodine value (IV) is a common method used to determine the degree of unsaturation in a mixture of fatty materials regardless of their relative share of mono-, di- and polyunsaturated compounds [125]. When iodine is added to the fat or oil, the amount of iodine in grams absorbed per 100 mL of oil is reported as the IV. As it is a measure of total unsaturation, several studies found a linear correlation between the degree of unsaturation (DU) and the IV: the more unsaturation in the oil, the higher the iodine value [126,127]. Methyl esters show an almost identical IV to that of corresponding vegetable oils or animal fats [98].

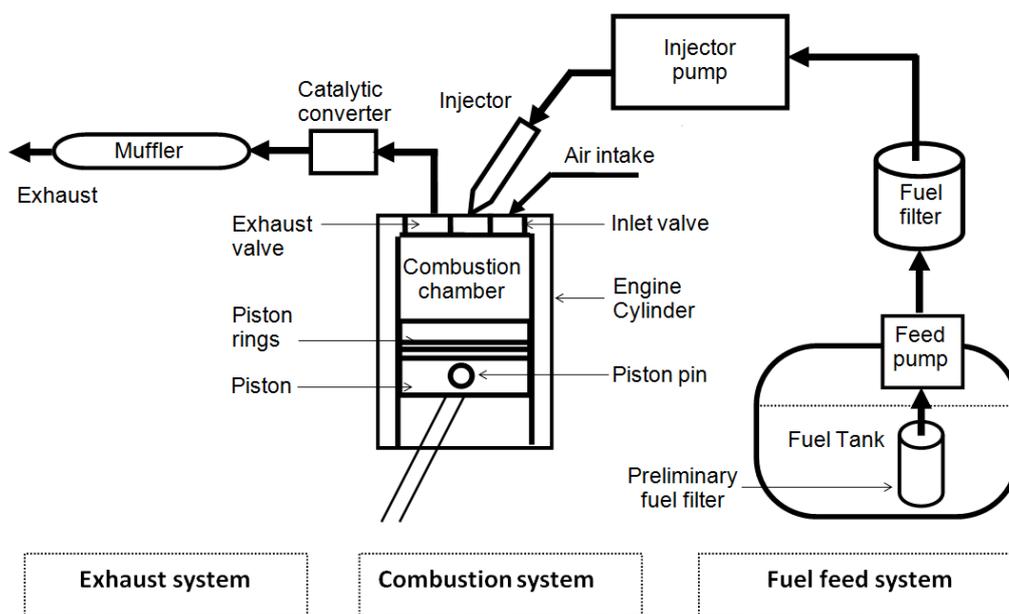
Iodine value is an important parameter in regard to fuel quality because higher IV biodiesel leads to a higher rate of polymerisation of glyceride, which increases rapidly with temperature. This results in increasing fuel viscosity, adversely affecting the fuel's ease of flow, and causing the formation of engine deposits, thus adversely affecting fuel injector spray patterns. This will ultimately lead to poor combustion, high emissions and, consequently, engine failure [98].

3. Biodiesel as a Diesel Engine Fuel

Diesel engines produce mechanical power from conversion of the chemical energy contained in the fuel. Energy is released by the combustion and oxidation of the fuel inside the engine. The fuel-air mixture prior to combustion and the products from combustion are the working fluids. The boundary work which provides the desired power output occurs directly between these working fluids and the mechanical components of the engine [128].

Since the advent of the diesel-powered engine, compression ignition engine technology has been under continuous development. However, the basic components of the engine (Figure 7) have been unchanged, with the main difference between a modern day engine and its predecessor being its combustion performance [129].

Figure 7. Schematic diagram of a typical diesel engine fuel system [12].



Biodiesel can be used in modern diesel engines in its pure form (B100), or blended with petroleum diesel in any ratio [130]. There is an increasing body of literature reporting on research into diesel engine performance and engine emissions when fuelled with biodiesel. Some of these studies are summarised in Table 6.

Table 6. Performance and emission of diesel engines with biodiesel.

Fuel type	Engine	Test condition	Increase/decrease vs. diesel								References		
			Power	Torque	BSFC	BTE	T _{exh}	CO	CO ₂	NO _x		PM	HC
Soybean	1C	1400–2000 rpm	↓	↓	↑			↓		↓			[131]
Cottonseed	1C	850 rpm			↑	↓		↓		↑	↓		[132]
Sunflower	1C	1000–3000 rpm	↓	↓	↑	↓		↓	↓	↓			[133]
Waste cooking	4C	1750–4400 rpm	↓	↓	↑		↓	↓	↓	↓			[134]
Cottonseed	4C	1500 rpm	↓	↓	↑	↓		↓		↑	↓		[135]
Sunflower oil	4C	1100–2800 rpm	↓	↓	↑	↓	↑				↓		[136]
Soybean	4C	1400 rpm	↓	↓	↑	↓	↓	↓	↓	↑	↓	↓	[137]
Waste cooking	4C	800–1400 rpm	↓	↓	↑	↑	↓		↓	↑			[138]
Waste cooking	4C	1400–200 rpm	↓	↓	↑	↓	↓		↓	↑			[138]
Mahua	1C	1600 rpm	↓	↓	↑	↓	↑		↓	↑			[139]
Tobacco seed	4C	1500–300 rpm	↑	↑	↓	↑	↓	↓		↑			[140]
Rapeseed oil	4C	1200–2400 rpm	↑	↑	↓			↓		↑			[141]
Cottonseed	1C	1200–2500 rpm	↑	↑	↓	↑	↓	↓		↑			[142]

3.1. Engine Performance

Diesel engine performance parameters evaluated with biodiesel fuels in literature typically includes engine power, torque, brake specific fuel consumption (BSFC), thermal efficiency, and exhaust gas temperature (Table 5). While illustrating the effect of biodiesel on engine power and/or torque, it is commonly argued that biodiesel drops engine power and torque. This is mainly due to the lower heating value of biodiesel compared with petroleum diesel. Utlu and Kocak [134] ran a four-cylinder diesel engine with waste frying oil methyl ester (WFOME), varying the engine speed from 1750 to 4400 rpm. They found on average a 4.5% and 4.3% reduction in power and torque respectively. Similar results have been reported in many other studies, with some fluctuations in the reduction percentage. Studies found that the loss of power was 7.14% for biodiesel when compared to diesel on a three-cylinder, naturally aspirated (NA) submarine diesel engine at full load, yet the loss of heating value of biodiesel was about 13.5% when compared to diesel [141,143,144]. Hansen *et al.* [143] observed that the brake torque loss was 9.1% in biodiesel at 1900 rpm as the results of variation in heating value (13.3%), density and viscosity. Findings from these studies confirm that the lower heating value of biodiesel is not the only factor which influences engine power and torque. Other biodiesel fuel properties including viscosity, density and lubricity have significant effects on engine output power and torque.

For instance, higher viscosity of biodiesel improves air-fuel mixing by enhancing spray penetration, and thus recovery in power and torque when compared to diesel [145,146]. Higher viscosity can also reduce engine power by decreasing combustion efficiency due to poor fuel injection atomisation [142]. On the other hand, the higher density of biodiesel improves engine power and torque. Moreover the high lubricity in biodiesel may result in reduced friction power loss, and this will subsequently recover engine output power and torque [147]. Therefore, it is not surprising that some studies have reported increased power and torque from engines when running on biodiesel.

For an example, Song and Zhang [148] showed power and torque increased with an increase in biodiesel percentage in blends while running an engine with soybean oil methyl ester. Usta [140] also found similar results when using tobacco seed oil in a four-cylinder turbo-charged diesel engine. Furthermore, negligible variation in engine power and torque between biodiesel and petroleum diesel has also been found [5,149]. More interesting results have been reported by Haşimoğın *et al.* [136] while using waste cooking oil biodiesel in a four-cylinder turbo-charged diesel engine operating between 1100 and 2800 rpm. This study found lower engine torque and power at lower engine speeds (1100 to 1600 rpm) while power and torque increased at medium and high engine speeds. However, Carraretto *et al.* [150] has overcome the power loss of biodiesel engine by optimising biodiesel combustion through reducing the injection advance. It is therefore evident that power and torque developed in biodiesel engines is not only dependent on feedstock and fuel properties, but also on the engine type and operating conditions, such as engine speed, load, injection timing and injection pressure. Similar correlations have been found in the literature for other performance parameters such as brake specific fuel consumption, thermal efficiency, exhaust gas temperature and combustion characteristics [32,139,142,144].

3.2. Exhaust Emissions

Combustion chemistry in internal combustion engines (ICE) is very complex and depends on fuel types and operating conditions. In the combustion chamber, hydrocarbon reactions are generally grouped into three distinct steps. The first step is the breakdown of hydrocarbons; the second step is the oxidation of hydrocarbons and hydrogen; the third step is the oxidation of combustion reaction products. The exhaust gas from diesel engines contains many components including carbon dioxide (CO₂), carbon monoxide (CO), hydrogen (H₂), oxygen (O₂), sulphur oxides (SO_x), unburned hydrocarbons (HC), particulate matter (PM), and nitrogen oxides (NO_x). These pollutants have various potential adverse health and environmental effects.

Numerous studies have been conducted to investigate the effect of biodiesel on exhaust emissions in diesel engine applications. The emission parameters investigated include carbon dioxide (CO₂), carbon monoxide (CO), hydrocarbon (HC), nitrogen oxides (NO_x), sulphur oxides (SO_x) smoke, particulate matter (PM). Table 5 shows that most of the studies found a sharp reduction in all exhaust emissions when biodiesel was used was compared with petroleum diesel fuel (except NO_x). However, a reduction in NO_x in biodiesel use has also reported in some other literature.

In general, biodiesel contains about 10% oxygen by mass, while diesel has little to no oxygen. Biodiesel fuels result in more complete combustion and thereby reduces exhaust emission, and various researchers have postulated reasons for this outcome. The percentage change in emissions varies amongst these studies. The variety of results reported can be attributed to variations in the fuel properties and chemical structure of the biodiesels used, varying feedstocks and due to the variety of engines used in tests. For example, Lin *et al.* [138] conducted an experiment with biodiesel from eight different feedstocks and found a significant reduction in PM emissions (50%–73%). While conducting experiments with coconut, jatropha and rapeseed oil biodiesel, Lance *et al.* [151] showed that rapeseed oil biodiesel tended to give amongst the highest NO_x emissions. Similarly, variations in emissions from biodiesels using different feedstocks have been reported in many other recent studies [152–155]. Monyem and Gerpen [115] found that oxidised biodiesel can significantly reduce emissions while investigating the effect of biodiesel oxidation on diesel engine emissions. This study found that oxidised biodiesel resulted in approximately 15% less CO emissions and 21% less HC emission when compared with unoxidised biodiesel.

The vast majority of the literature reports that NO_x emissions are the only parameter that increases while operating diesel engines on biodiesel as compared to petroleum diesel. Therefore, NO_x emission may be the single most critical parameter for biodiesel application. Many studies have suggested that properties of biodiesel such as cetane number, oxygen content, biodiesel feedstock, advance in fuel injection, engine type and operating conditions have an important effect on the formation of NO_x [156,157]. It is commonly argued that high cetane numbers improve combustion, therefore the temperature in the combustion chamber is expected to be higher which leads to the formation of more NO_x emissions in higher oxygen content fuel. Another common argument is that a high cetane number reduces ignition delay which can cause higher NO_x emission. However, some authors oppose this argument. NO_x usually forms in the combustion phase and a high cetane number not only reduces ignition delay, but also leads to lowering of the premixed combustion phase, which eventually reduces the formation of NO_x. Therefore, it is not surprising that some literature reports show a reduction of

NO_x emission with biodiesel [131,134,141]. Moreover, the different chemical structure of biodiesels influences the formation of NO_x emissions and most of the authors agreed that shorter chain lengths and more saturated biodiesels were preferable to reduce NO_x emission. Knothe *et al.* [9] tested NO_x in a six-cylinder diesel engine with conventional diesel fuel and three different fatty acid methyl esters including oleic (C18:1), palmitic (C16:0) and lauric (C12:0). They found a 4% and 5% reduction in NO_x emissions for the saturated palmitic and lauric esters, respectively, and a 6% increase for the oleic ester. While blending short chain methyl esters such as caprylic (C8:0) and capric (C10:0) with soybean oil biodiesel, Chapman and Boehman, [158] also found a significant reduction in NO_x emission.

Particulate matter is another important factor which needs to be considered while using biodiesel as an engine fuel. Particulate matter emitted by petroleum diesel engines consists of black carbon (soot), hydrocarbons, sulphates and metallic ashes [159]. Most studies found in the literature indicate that biodiesel reduces diesel engine particulate emissions on a mass basis. However, adverse health effects from exposure to particulates may increase with a decreasing in particle size, even though the particles are composed of toxicologically inert materials. For example, fine particles with aerodynamic diameters lower than 2.5 µm (PM_{2.5}) appear to have considerably enhanced toxicity per unit mass compared to coarse particles with aerodynamic diameters lower than 10 µm (PM₁₀). Particles deposit in different parts of the lung according to their aerodynamic diameter, and smaller particles are able to penetrate deeper into the human lung. Furthermore, smaller particles tend to stay in the atmosphere for longer periods of time, which means that there is a higher probability that they will be inhaled and lead to respiratory diseases, inflammation and damage to the lungs [160]. By considering these adverse effects of ultrafine particles, an emission standard based on a solid particle number has already been implemented by the European Union (EU) for its member states. Particle number and size distribution is therefore a more appropriate parameter of DPM when placing regulatory controls on the use of fuels, rather than relying on PM mass alone [161].

4. Artificial Neural Networks

The foundation of artificial neural networks (ANN) in a scientific sense begins with a biological neuron as shown in Figure 8. In the brain, there is a flow of coded information (using electrochemical media, the so-called neurotransmitters) from the synapses towards the axon. The axon of each neuron transmits information to a number of other neurons. Groups of neurons are organised into sub-systems and the integration of these sub-systems forms the brain. On the other hand, an ANN is composed of a large number of simple processing units called neurons which are fully connected to each other through adoptable synaptic weight (Figure 9). This resembles a brain in two aspects. Knowledge can be acquired through training and knowledge can be stored. In the training process, weights are adjusted to minimise the error between actual output and desired output.

The most important feature of artificial neural networks is their ability to solve problems through learning by example, rather than by fully understanding the detailed characteristics of the systems. This feature makes it very useful because it works like a “black box” model, and does not require detail or complete information about the problem, and can be utilised when all that is available are sets of data inputs and outputs of the system. It has a natural propensity to store experiential knowledge and

to make it available for use (Figure 10). Therefore, this nonlinear computer algorithm can model large and complex systems with many interrelated parameters.

Figure 8. Biological neuron [162].

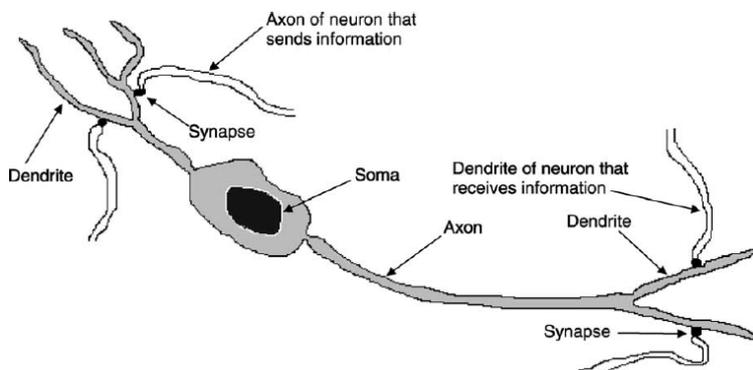


Figure 9. Multi-layer ANN model.

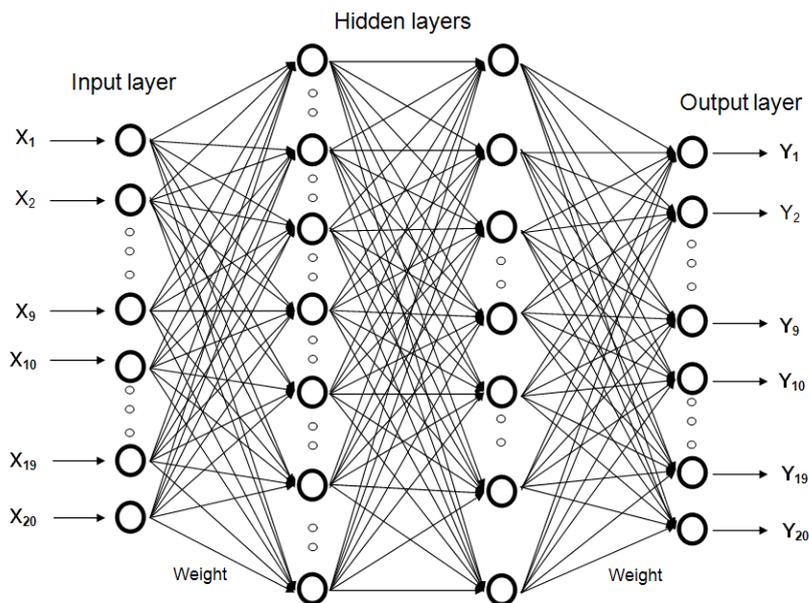
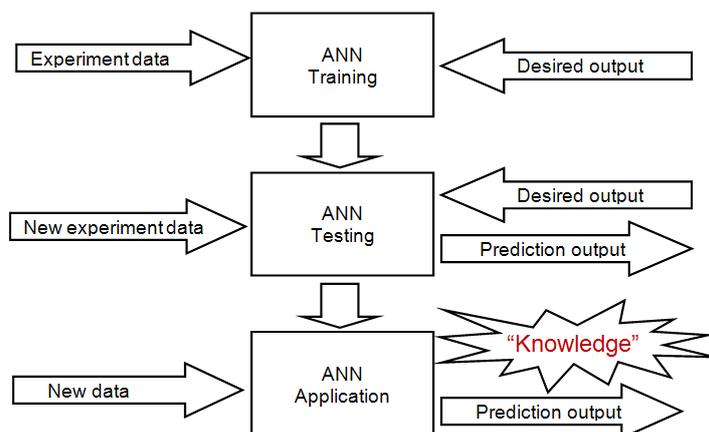
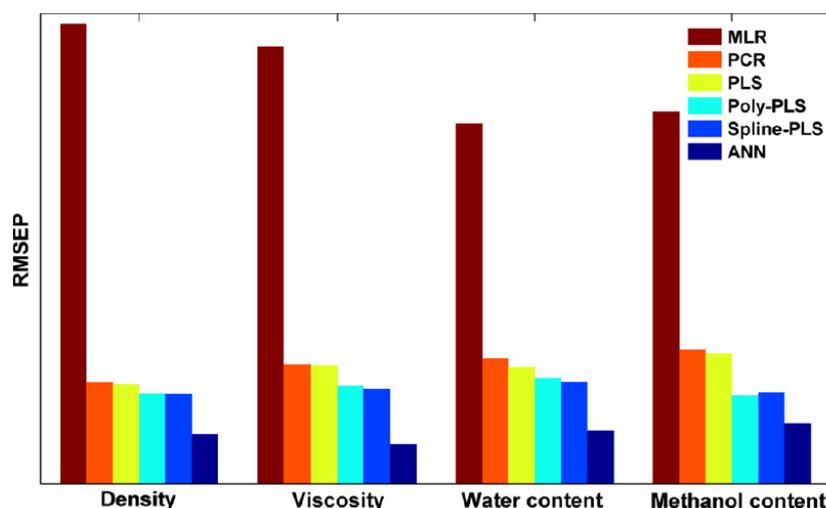


Figure 10. Working principle of ANN.



Since the development of high speed digital computers, the application of the ANN approach has progressed at a very rapid rate. In recent years, this method has been applied to various disciplines including automotive engineering, and in the forecasting of fuel properties and engine thermal characteristics for various working conditions [163]. Prediction accuracy of the ANN approach was found to be superior when compared with other linear and non-linear statistical techniques. Balabin *et al.* [164] compared the prediction performance of artificial neural networks (ANN), multiple linear regression (MLR), principal component regression (PCR), polynomial and Spline-PLS versions, and partial least squares regression (PLS) for prediction of biodiesel properties from near infrared (NIR) spectra. The model was created for four biodiesel properties density (at 15 °C), kinematic viscosity (at 40 °C), water (H₂O) content and methanol content. This study reported the lowest root mean square errors of prediction (RMSEP) for ANN when compared to other techniques as shown in Figure 11. Agarwal *et al.* [165] compared the linear regression and ANN techniques in predicting biodiesel properties. Results of this study indicated that ANNs were able to predict the properties of biodiesel better than a linear regression model. Similarly Cheenkachorn [97] predicted biodiesel properties such as viscosity, high-heating value, and cetane number using the fatty acid compositions of various vegetable oils by statistical methods and ANN. It was observed that ANN was able to predict more accurately than statistical methods.

Figure 11. Comparison of the performance of between ANN and various linear and non-linear prediction techniques [164].



On the other hand, ANN is not without having limitations. The main disadvantage of an ANN model is due to the “black box” approach; it is difficult to gain insight in to a problem without extra effort. Statistical techniques allow the user to determine the most significant parameters among the important variables, hence, eliminating the variables that do not fit the model which is not standby available with ANN. However, this limitation can be overcome where necessary by combining the ANN with multivariate data analysis, such as PCA or ANOVA. Moreover the requirements of computational resources and standard software for ANN modeling may also be considered as drawbacks over statistical techniques [166].

4.1. ANN in Predicting Engine Emission and Performance

One of the most important factors that affect the viability of an automobile fuel is its suitability in terms of engine performance and exhaust emissions as discussed in the previous section. However, conducting actual experiments with automobile engines not only requires considerable amounts of fuel, heavy equipment and skilled personnel, but it is also very time consuming and costly. Therefore, the use of ANN modeling techniques in predicting performance parameters of internal combustion engines has gained in popularity over the last few decades. Combustion related performance using various types of fuels including diesel, gasoline, natural gas, ethanol and biodiesel have successfully been modeled using ANN. Cay *et al.* [166] developed an ANN model to predict the brake specific fuel consumption, effective power and average effective pressure and exhaust gas temperature of the methanol engine. A four-cylinder, four-stroke test engine was operated at different engine speeds and torques to obtain model training and testing data. After training, this study found an ANN prediction accuracy with R^2 values close to 1 for both training and testing data. RMS values less than 0.015 and mean errors less than 3.8% for the testing data were reported. This study concluded that the ANN model is a powerful technique for predicting performance parameters of internal combustion engines.

Similarly, while predicting engine performance emissions with ANN, Sayin *et al.* [167] found prediction performance with correlation coefficients in the range of 0.983–0.996, mean relative errors in the range of 1.41%–6.66%, and very small root mean square (RMS) values, and concluded that ANN was an alternative to classical modelling techniques. Arcaklioğlu and Çelikten [168] conducted experiments with petroleum diesel in a turbo-charged four-cylinder diesel engine. Using experimental data, the ANN model was developed to predict engine torque, power, brake mean effective pressure, specific fuel consumption, fuel flow, and exhaust emissions such as SO₂, CO₂, NO_x and smoke level based on injection pressure, engine speed and throttle position. The study found the precise prediction ability of the ANN in diesel engine performance and emission parameters provided a good correlation between experiment and predicted values. The overall mean square errors in their study were less than 0.03% and R^2 values were close to 1.

Yap and Karri [169] conducted experiments on a single-cylinder, spark ignition engine using various engine speeds and throttle positions. They have developed an ANN model for the prediction of engine power, CO, CO₂, HC and O₂ emissions. Parlak *et al.* [170] also successfully used ANN to predict diesel engine brake specific fuel consumption and NO_x emission for a Ricardo E6 type, single-cylinder diesel engine considering engine speed, brake mean effective pressure and fuel injection timing as input variables.

ANN modelling techniques have also been utilised for predicting engine performance and emissions based on the physical properties of various fuels. Canakci *et al.* [171] used ANN model in predicting fuel flow rates, maximum injection pressure, thermal efficiency, load, maximum cylinder pressure and exhaust emission (CO, NO_x, HC) of a diesel engine based on fuel density, kinetic viscosity and lower heating value. Similarly, Karonis *et al.* [172] were successful in predicting exhaust emissions (CO, NO_x, HC and PM) of a single-cylinder diesel engine using fuel cetane number, density and kinetic viscosity.

ANN has also been used to predict diesel engine emissions from in-cylinder pressure along with engine operating parameters [173,174] investigated the effectiveness of various biodiesel fuel

properties and engine operating conditions on diesel engine combustion towards the formation of exhaust emissions using ANN. They conducted experiments on a single-cylinder direct injection (DI) diesel engine using blends of biodiesel from pongamia, jatropha and neem oils. This study found good predictability of ANN modelling techniques in predicting brake power, brake thermal efficiency, brake specific fuel consumption, volumetric efficiency, and exhaust gas temperature regulated exhaust emissions (CO, HC, NO_x) based on diesel-biodiesel blend percentage, fuel properties and various engine operating conditions. Similarly, different types of engines have been successfully modeled using ANN techniques in a wide range of operating conditions, performance parameters and fuels which are summarised in Table 7. All of these studies demonstrated the suitability of ANN modeling techniques in internal combustion engine application.

4.2. ANN in Predicting Fuel Properties

The properties of fuel need to be estimated before their application to particular combustion systems as these will significantly influence the end use performance of such systems, as shown in previous sections. Modern official standards list more than 20 parameters that must be determined to certify any fuel's quality before its use as automobile engine fuel. However, testing of these properties requires considerable amounts of fuel sample, standardised testing equipment, expert technicians and also carries a significant cost [164]. Therefore it is a worthwhile option to consider a prediction model to estimate the properties of any new fuel prior to beginning large-scale production. As a consequence, a number of models have been developed to predict the important fuel properties of diesel and biodiesel using conventional linear regression and ANN techniques. Most of these are based on fuel types, diesel-biodiesel blend ratios, chemical composition, production methods *etc.*, Agarwal *et al.* [165] developed linear regression and an ANN model to predict several fuel properties of biodiesel including heating value, density, viscosity, pour point, flash point, iodine value and saponification value based on fatty acid composition. Experiments were conducted using biodiesel produced from various edible and non-edible vegetable oils. This study found a good correlation between the properties of biodiesel and its chemical composition, with the ANN demonstrating a higher prediction ability than linear regression techniques in predicting all the fuel properties.

A similar study has been conducted by Cheenkachorn focused on determining biodiesel fuel properties based on fatty acid profile only [97]. However, these studies did not consider other chemical compositions contained in biodiesel through the model input, including the amount of free glycerol, free fatty acid, methanol and impurities which may have an impact on the physical properties of the biodiesel. Kumar and Bansal [175] compared the applicability of the traditional statistical technique of linear regression (principle of least squares) and ANN techniques in estimating the flash point, fire point, density and viscosity of diesel and biodiesel mixtures. They have optimised the network with three training algorithms, along with ten different sets of weight and biases. Results of this study show that neural network is the better choice over principle of least squares to predict the fuel properties of various mixtures of diesel and biodiesel. However, the performance of a neural network can further be improved by adjusting the other training parameters like goal, epochs, learning rate, magnitude of the gradient, *etc.*

Table 7. ANN used in automobile engine application.

References	Model Input	Model Target	Engine	Prediction accuracy	Fuel used
Arcaklioğlu and Çelikten, [168]	IP, RPM, TH	T, P, BMEP, BSFC, FFR, SO ₂ , CO ₂ , NO _x , S	4S, 4C, TC	R^2 : 0.9999; MSE: 8.5%	Diesel
Yap and Karri, [169]	RPM, AFR, TH	P, CO, CO ₂ , HC, O ₂	2S, 1C, SI	MSE: 2.27%–4.74%	Gasoline
Parlak <i>et al.</i> [170]	RPM, BMEP, IT	BSFC, T _{exh}	4S; 1C, NS, CI	MSE: 1.93%–2.36%	Diesel
Choi and Chen, [176]	CR, FFR, AFR, IT, EGR	Start-of-combustion	4S, 1C, HCCI	-	Methane/ <i>n</i> -heptane
Karonis <i>et al.</i> [172]	CN, ρ , v , Distillation curve	CO, HC, NO _x , PM	4S, 1C, CI	R^2 : 0.937–0.99	Diesel
Çelik and Arcaklioğlu, [177]	RPM, P, Cooling water temperature	BSFC, T _{exh} , AFR	4S, 8C, CI	R^2 : 0.99, MRE: 5.5%	Diesel
Deh Kiani <i>et al.</i> [178]	RPM, L, FBR	P, T, CO, CO ₂ , NO _x , HC	4S, 4C, SI	R^2 : 0.71–0.91	Gasoline, Ethanol
Renald <i>et al.</i> [179]	L, FDR, Cylinder head geometry	T _{exh} , CO, CO ₂ , O ₂ , HC, NO _x , ET	1C, 4S, SI	-	Gasolin, LPG
Yusaf <i>et al.</i> [180]	RPM, FBR	P, T, BTE, BSFC, T _{exh} , NO _x , CO, CO ₂	4S, 1C, CI	R^2 : 0.95707–0.9934	Diesel, CNG
Yusaf <i>et al.</i> [181]	RPM, FBR	P, T, BTE, BSFC, T _{exh} , NO _x , CO, CO ₂	4S, 1C, CI	MSE: 0.0004	Diesel, CPO
Obodeh and Ajuwa, [182]	L, RPM	NO _x	4S, 4C, CI	MRE: 0.68%–3.34%	Diesel
Shivakumar <i>et al.</i> [183]	L, IT, CR, FBR	BTE, BSEC, T _{exh} , NO _x , HC	4S, 1C, CI	MRE: 1.778%–5.889%	Diesel, WCO biodiesel
Tasdemir, [184]	RPM, Intake valve opening advance	P, T, BSFC, HC	4S, 1C, SI	-	Gasoline
Sayin <i>et al.</i> [167]	T, RPM, HV, Air inlet temperature	BSFC, BTE, T _{exh} , CO, HC	4S, 4C, SI	R^2 : 0.983–0.996	Gasoline
Kesgin, [173]	ECP, CT, FAR, RPM, ES, CB, VT	P, BTE, NO _x , Heat Transfer	TC, SI	-	Natural gas
Canakci <i>et al.</i> [171]	RPM, HV, ρ , v , Environmental conditions	FFR, BTE, CO, NO _x , HC, L, IP, ECP	4S, 4C, NA, CI	R^2 : 0.99	WCO, Diesel
Shanmugam <i>et al.</i> [185]	L, FBR	BTE, CO, HC, CO ₂ , NO _x , S	4S, 1C, NA, CI	R^2 : 0.975–0.999	Diesel, Bioethanol, Cottonseed biodiesel
Sharon <i>et al.</i> [186]	P, FBR	BSFC, BTE, NO _x , HC, CO, S	4S, 1C, NS	R^2 : 0.9989–0.999	Diesel, WCO biodiesel
Manjunatha <i>et al.</i> [174]	L, HV, CN, ρ , FBR	P, BTE, BSFC, T _{exh} , CO, HC, NO _x	4S, 1C, CI	R^2 : 0.95–0.99	Diesel, pongamia, jatropha, neem oils biodiesel

Satyanarayana and Muraleedharan [187] developed the ANN model to analyse the relation of esterification methods with fuel properties for biodiesel produced from rubber seed. They used transesterification reaction parameters such as the methanol-oil ratio, catalyst concentration, reaction time, and reaction temperature in the input layer and acid value of biodiesel in output layer while constricting the ANN model. Although a good prediction was obtained, this study did not consider the initial acid value of the vegetable oil, which may have an impact on the final acid value of the biodiesel. This issue has been addressed by Rajendra *et al.* [68] while using ANN techniques to predict the acid value of sunflower oil biodiesel, including its initial acid value as well as transesterification reaction parameters. Liu *et al.* [188] compared the reputability of standard fuel property testing methods with ANN while developing a model to predict density, flash point, freezing point, aniline point and net heat of combustion of 80 different jet fuels. This study found that the repeatability of neural network models for measuring density and flash point were lower than the ASTM test methods. However, for the freezing point, aniline point and net heat of combustion, the repeatabilities of the ANN methods are equal to the ASTM methods. Therefore it can be said that not only the prediction accuracy but also the ANN approaches are comparable to the repeatability values of the standard ASTM methods, which are used for the experimental determination of the properties.

Similar conclusions have been made by Pasadakis *et al.* [189,190] while predicting pour point (CP), cloud point (CP) of diesel and octane number of gasoline based on the chemical composition of the respective fuels. Several other studies which were also successful in utilising ANN to estimate the properties of various fuels, which are summarised in Table 8. The success of those studies proved that ANN has the ability to accurately estimate the fuel properties instead of having costly and time consuming experimental measurements.

Table 8. ANN in predicting fuel properties.

References	Use of ANN model
Baroutian <i>et al.</i> [102]	Density prediction in different temperatures for palm oil biodiesel
Ramadhas <i>et al.</i> [163]	Cetane number prediction based on the fatty acid profile of biodiesel
Balabin <i>et al.</i> [165]	Density, kinetic viscosity, water and methanol content prediction for various biodiesels
Kumar <i>et al.</i> [191]	Flash point, fire point, density and viscosity prediction based on diesel-biodiesel blend ratio
Liu <i>et al.</i> [188]	Density, flash point, freezing point, aniline point and net heat of combustion prediction for various jet fuels based on their chemical composition
Korres <i>et al.</i> [192]	Lubricity prediction from physical properties of diesel
Marinovic <i>et al.</i> [193]	Prediction of diesel cold temperature properties based on density, kinetic viscosity, conductivity, sulphur content and 90% distillation point
Pasadakis <i>et al.</i> [189]	Octane number prediction from chemical composition of gasoline
Pasadakis <i>et al.</i> [190]	Cold temperature properties and distillation curve prediction from the chemical composition of diesel
Wu <i>et al.</i> [194]	Prediction of cold filter plugging point of diesel from physical properties
Yang <i>et al.</i> [195]	Cetane number and density prediction using chemical composition of diesel
Cheenkachorn [97]	Viscosity, cetane number and heat of combustion prediction from fatty acid composition of various biodiesel feedstocks

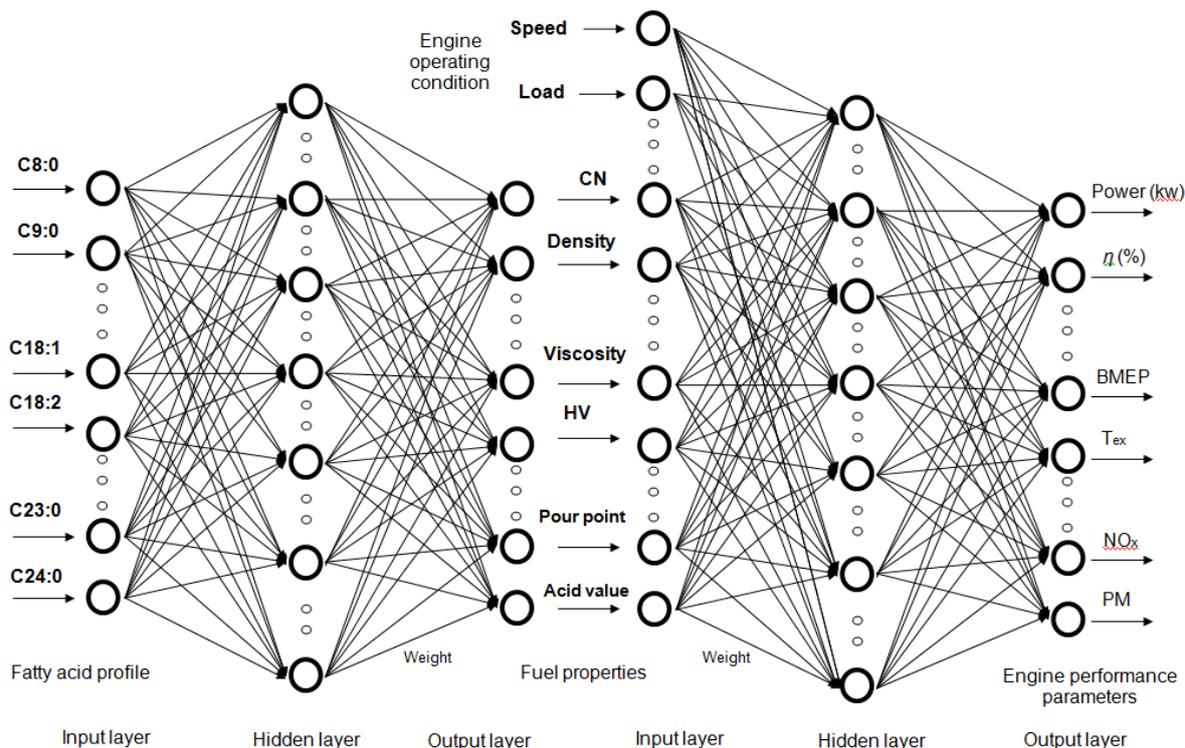
Table 8. Cont.

References	Use of ANN Model
Agarwal <i>et al.</i> [164]	Heating value, density, viscosity, pour point, flash point, iodine value and saponification value prediction based on fatty acid profile of biodiesel
Kumar and Bansal [186]	Flash point, fire point, density and viscosity prediction for diesel and biodiesel blends
Satyanarayana and Muraleedharan [187]	Acid value prediction in various combinations of transesterification reaction parameters for rubber seed oil

5. ANN Modeling of Second Generation Biodiesel

Although numerous feedstocks including oilseed crops and algae species have been identified as being suitable for producing second-generation biodiesel, these types of biodiesel have not yet been established, due to the unavailability of feedstock supply, high production costs and a lack of knowledge about the fuel's quality. Moreover, by producing fuels from new feedstock, optimising production processes, ensuring fuel quality through measuring a number of physical and chemical properties, and evaluating the end-use performance in automobile engines is costly, time-consuming and requires a wide variety of specialised equipment and skilled workers. These concerns have restricted the progress of second-generation biodiesel technology, making it still unacceptable to both automobile engine manufacturers and customers, which is yet to begin industrial-scale production. In order to address this issue, the ANN modelling technique could be a very useful tool in predicting fuel quality and engine combustion-related parameters when considering the chemical composition of new biodiesel feedstocks. It would require laboratory scale biodiesel production and basic chemical testing equipment, which will significantly reduce the research cost, and hence accelerate the investigation of future generation biodiesel. However, researchers should move to develop a universal ANN prediction model for second-generation biodiesel, and this will enable the instigation of a wide range of biodiesel feedstock and automobile engine systems. While training the network, they need to consider all possible parameters in feedstock that affect the production process, the quality and the combustion performance of biodiesel in automobile engine applications. A two-stage artificial neural network (ANN) prediction model can be proposed for this purpose. At the 1st stage of the model, chemical composition of biodiesel in terms of fatty acid profile can be used as input parameters and fuel properties can be used as output or target variable. In the 2nd stage of the model, fuel properties alone with engine specification and operating condition can be used as input layer, whereas, engine performance, emission and combustion parameters can be used as the target vector of output layer. The structure of such a two-stage ANN model as proposed is shown in Figure 12. It can be expected that such an approach will generate new knowledge, based upon which, second-generation biodiesel will be more sustainable, commercially available and a key contributor to the mainstream global energy system.

Figure 12. Proposed structure of ANN model.



6. Conclusions

Biodiesel, produced from renewable feedstocks represents a more sustainable source of energy and will therefore play a significant role in providing the energy requirements for transportation in the near future. However, first-generation biodiesels used around the World today are unlikely to be sustainable in the long term as a result of being produced from edible oil feedstock. Second-generation biodiesels produced from non-edible feedstocks have the potential to overcome this challenge, and to serve as a more sustainable energy source in the near future.

Chemically, all biodiesels are fatty acid methyl esters (FAME), produced from raw vegetable oil. Numerous fatty acids, ranging in chain length from 6 to 24, have been found in various biodiesels, which are identical to their respective feedstock. However, clear differences in chemical structure are apparent from one feedstock to the next in terms of chain length, degree of unsaturation, number of double bonds and double bond configuration—which all determine the important fuel properties of biodiesel. This includes kinetic viscosity, density, cetane number, calorific value, flash point, oxidation stability, cold temperature properties and iodine value. Therefore, different levels of combustion performance and emission levels have been observed in the literature when using different types of biodiesel as diesel engine fuel. While considering production optimization and engine durability issues, similar trends have been observed. The literature reviewed in this study has assured that the suitability of any biodiesel as automobile engine fuel can be explained largely through the chemical composition of its respective feedstock.

ANN is a powerful computational modeling tool which has the ability to identify complex relationships from input-output data. It can result in a higher level of accuracy in its prediction ability when compared with other statistical methods. Therefore, ANN has emerged and has found extensive

acceptance in many disciplines for modeling complex real world situations. However, most of the literatures compared the prediction accuracy of ANNs and statistical methods based on MSE or RMS which may not much appropriate. It is recommended to consider some other error measurement technique including residual plots, the maximum error percentage, minimum error percentage *etc.*

Recent literature shows that the complex relationship between biodiesel chemical composition, fuel properties and diesel engine combustion performance can be established at different operating condition conation by using ANNs. Several ANN models have been developed to estimate the combustion-related performance of various fuels in automobile engine applications with a high prediction accuracy, as shown in Table 6. However, applicability of these models is limited to a specific engine and to fuel types that have been used to collect the experimental data upon which the network has been trained. These models also have serious limitations, considering the limited number of engine operating parameters used in the experiments. The automobile engine is a complex system, with a large number of parameters directly influencing its combustion performance. Moreover, no study has considered the physical and chemical properties of fuel while developing the ANN model for predicting combustion performance, in spite of there being a strong correlation between these parameters. Therefore, it would be worthwhile for researchers to develop a universal ANN model which will be able to predict the combustion performance of versatile automobile engines and fuel types. To ensure the most robust ANN model, data should be used which cover as much a range as possible. This model will able to access the sustainability of the wide ranges of biodiesel feedstock collecting from different origin.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. *Energy Outlook 2030*; BP: London, UK, 2012. Available online: <http://www.bp.com> (accessed on 15 March 2012).
2. Demirbas, A. Progress and recent trends in biofuels. *Prog. Energy Combust.* **2007**, *331*, 1–18.
3. Weitzman, M.L. A review of the stern review on the economics of climate change. *J. Econ. Lit.* **2007**, *45*, 703–724.
4. Metz, B.; Davidson, O.; Bosch, P.; Dave, R.; Meyer, L. *Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: New York, NY, USA, 2007.

5. Luque, R.; Herrero-Davila, L.; Campelo, J.M.; Clark, J.H.; Hidalgo, J.M.; Luna, D.; Marinasa, J.M.; Romero, A.A. Biofuels: A technological perspective. *Energy Environ. Sci.* **2008**, *1*, 513–596.
6. Jahirul, M.I.; Masjuki, H.H.; Saidur, R.; Kalam, M.A.; Jayed, M.H.; Wazed, M.A. Comparative engine performance and emission analysis of CNG and gasoline in a retrofitted car engine. *Appl. Therm. Eng.* **2010**, *30*, 2219–2226.
7. Lapuerta, M.; Herreros, J.M.; Lyons, L.L.; Garcia-Contreras, R.; Brice, Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. *Fuel* **2008**, *87*, 3161–3169.
8. Rajindars, L. Conditions for the sustainability of biomass based fuel use. *Energy Policy* **2006**, *34*, 863–876.
9. Jayed, M.H.; Masjuki, H.H.; Saidur, R.; Kalam, M.A.; Jahirul, M.I. Environmental aspects and challenges of oilseed produced biodiesel in southeast Asia. *Renew. Sustain. Energy Rev.* **2009**, *13*, 2452–2462.
10. Graboski, M.S.; McCormick, R.L. Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog. Energy Combust. Sci.* **1998**, *24*, 125–164.
11. Knothe, G. “Designer” biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy Fuels* **2008**, *22*, 1358–1364.
12. Haseeb, A.S.M.A.; Fazal, M.A.; Jahirul, M.I.; Masjuki, H.H. Compatibility of automotive materials in biodiesel: A review. *Fuel* **2011**, *90*, 922–931.
13. Banković-Ilić, I.B.; Stamenković, O.S.; Veljković, V.B. Biodiesel production from non-edible plant oils. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3621–3647.
14. Ahmad, A.L.; Yasin, N.H.M.; Derek, C.J.C.; Lim, J.K. Microalgae as a sustainable energy source for biodiesel production: A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 584–593.
15. Ashwath, N. Evaluating Biodiesel Potential of Australian Native and Naturalised Plant Species. Available online: <https://rirdcinfoservicescomau/downloads/10-216> (accessed on 24 August 2012).
16. Mata, T.M.; Martins, A.A.; Caetano, N.S. Microalgae for biodiesel production and other applications: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 217–232.
17. Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* **2007**, *25*, 294–306.
18. Asia Pacific (APAC). *Biofuel Consultants. Australian Biofuels*; EnergyQuest and Ecco Consulting: Canberra, Australia, 2009.
19. Alkim, E.; Gürbüz, E.; Kılıç, E. A fast and adaptive automated disease diagnosis method with an innovative neural network model. *Neural Netw.* **2012**, *33*, 88–96.
20. Costa, M.A.; Braga, A.P.; Menezes, B.R. Convergence analysis of sliding mode trajectories in multi-objective neural networks learning. *Neural Netw.* **2012**, *33*, 21–31.
21. Carrillo, S.; Harkin, J.; McDaid, L.; Pande, S.; Cawley, S.; McGinley, B.; Morgan, F. Advancing interconnect density for spiking neural network hardware implementations using traffic-aware adaptive network-on-chip routers. *Neural Netw.* **2012**, *33*, 42–57.
22. Samura, T.; Hayashi, H. Directional spike propagation in a recurrent network: Dynamical firewall as anisotropic recurrent inhibition. *Neural Netw.* **2012**, *33*, 236–246.
23. Gao, D.; Yang, Z.; Cai, C.; Liu, F. Performance evaluation of multilayer perceptrons for discriminating and quantifying multiple kinds of odors with an electronic nose. *Neural Netw.* **2012**, *33*, 204–215.

24. Minnett, R.C.J.; Smith, A.T.; Lennon, W.C., Jr.; Hecht-Nielsen, R. Neural network tomography: Network replication from output surface geometry. *Neural Netw.* **2011**, *245*, 484–492.
25. Zendehboudi, S.; Ahmadi, M.A.; James, L.; Chatzis, I. Prediction of condensate-to-gas ratio for retrograde gas condensate reservoirs using artificial neural network with particle swarm optimization. *Energy Fuels* **2012**, *26*, 3432–3447.
26. Roosta, A.K.; Setoodeh, P.; Jahanmiri, A.H. Artificial neural network modeling of surface tension for pure organic compounds. *Ind. Eng. Chem. Res.* **2012**, *51*, 561–566.
27. Kumar, V.K. Neural network prediction of interfacial tension at crystal/solution interface. *Ind. Eng. Chem. Res.* **2009**, *48*, 4160–4164.
28. Ahmadi, M.A.; Zendehboudi, S.; Lohi, A.; Elkamel, A.; Chatzis, I. Application of hybrid genetic algorithm with particle swarm optimization and neural network for reservoir permeability prediction. *J. Geophys. Prospect.* **2013**, *61*, 582–598.
29. Demirbas, A. Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel* **2008**, *87*, 1743–1748.
30. Fernando, S.; Karra, P.; Hernande, R.; Kumar, J.S. Effect of incompletely converted soybean oil on biodiesel quality. *Energy* **2007**, *32*, 844–851.
31. Hoekman, S.K.; Broch, A.; Robbins, C.; Cenicerros, E.; Natarajan, M. Review of biodiesel composition, properties, and specifications. *Renew. Sustain. Energy Rev.* **2012**, *161*, 143–169.
32. Lin, L.; Cunshan, Z.; Vittayapadung, S.; Xiangqian, S.; Mingdong, D. Opportunities and challenges for biodiesel fuel. *Appl. Energy* **2011**, *884*, 1020–1031.
33. Goodrum, J.W.; Geller, D.P. Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. *Bioresour. Technol.* **2005**, *96*, 851–855.
34. Anastopoulos, G.; Lois, E.; Karonis, D.; Kalligeros, S.; Zannikos, F. Impact of oxygen and nitrogen compounds on the lubrication properties of low sulfur diesel fuels. *Energy* **2005**, *30*, 415–426.
35. Terry, B. *Impact of Biodiesel on Fuel System Component Durability*; The Associated Octel Company Limited: London, UK, 2005.
36. Holser, R.A.; Harry-O’kuru, R. Transesterified milkweed *Asclepias* seed oil as a biodiesel fuel. *Fuel* **2006**, *85*, 2106–2110.
37. Kaul, S.; Saxena, R.C.; Kumar, A.; Negi, M.S.; Bhatnagar, A.K.; Goyal, H.B.; Gupta, A.K. Corrosion behavior of biodiesel from seed oils of Indian origin on diesel engine parts. *Fuel Process. Technol.* **2007**, *88*, 303–307.
38. Raadnui, S.; Meenak, A. Effect of refined palm oil RPO fuel on wear of diesel engine components. *Wear* **2003**, *254*, 1281–1288.
39. Agarwal, A.K. Performance Evaluation and Tribological Studies on a Biodiesel Fuelled Compression Ignition Engine. Ph.D. Thesis, Indian Institute of Technology, Delhi, India, 1999.
40. Rashid, U.; Anwar, F. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel* **2008**, *873*, 265–273.
41. Bradsher, K. The Other Oil Shock: Vegetable Oil Prices Soar The New York Times, World Business. Available online: <http://www.nytimes.com/2008/01/19/business/worldbusiness/19ihtpalmoil19339824html> (accessed on 18 June 2012).

42. Kingsbury, K. After the Oil Crisis, a Food Crisis. Available online: <http://www.time.com/time/business/article/0,8599,1684910,00html?iid=sphere-inline-sidebar> (accessed on 20 April 2012).
43. IEA Bioenergy. From 1st to 2nd Generation Biofuel Technologies. Available online: <http://www.iea.org> (accessed on 10 April 2012).
44. Posten, C.; Schaub, G. Microalgae and industrial biomass as a source for fuel—A process view. *J. Biotechnol.* **2009**, *142*, 64–69.
45. Winayanuwattikun, P.; Kaewpiboon, C.; Piriayakananon, K.; Tantong, S.; Thakernkarnkit, W.; Chulalaksananukul, W.; Yongvanich, T. Potential plant oil feedstock for lipase-catalyzed biodiesel production in Thailand. *Biomass Bioenergy* **2008**, *3212*, 1279–1286.
46. Mohibbe Azam, M.; Waris, A.; Nahar, N.M. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass Bioenergy* **2005**, *294*, 293–302.
47. Kumar, A.; Sharma, S. Potential non-edible oil resources as biodiesel feedstock: An Indian perspective. *Renew. Sustain. Energy Rev.* **2011**, *154*, 1791–1800.
48. Balat, M.; Balat, H. A critical review of bio-diesel as a vehicular fuel. *Energy Convers. Manag.* **2008**, *4910*, 2727–2741.
49. Khan, S.A.; Rashmi Hussain, M.Z.; Prasad, S.; Banerjee, U.C. Prospects of biodiesel production from microalgae in India. *Renew. Sustain. Energy Rev.* **2009**, *139*, 2361–2372.
50. Karmakar, A.; Karmakar, S.; Mukherjee, S. Properties of various plants and animals feedstocks for biodiesel production. *Bioresour. Technol.* **2010**, *101*, 7201–7210.
51. Hossain, A.B.M.S.; Salleh, A.; Boyce, A.N.; Chowdhury, P.; Naquiuddin, M. Biodiesel fuel production from algae as renewable energy American. *J. Biochem. Biotechnol.* **2008**, *4*, 250–254.
52. Schenk, P.M.; Thomas-Hall, S.R.; Stephens, E.; Marx, U.C.; Mussgnug, J.H.; Posten, C.; Kruse, O.; Hankamer, B. Second generation biofuels: High-efficiency microalgae for biodiesel production. *Bioenergy Res.* **2008**, *1*, 20–43.
53. Hu, Q.; Sommerfeld, M.; Jarvis, E.; Ghirardi, M.; Posewitz, M.; Seibert, M.; Darzins, A. Microalgal triacylglycerols as feedstocks for biofuel production: Perspectives and advances. *Plant J.* **2008**, *544*, 621–639.
54. Demirbas, A.; Fatih Demirbas, M. Importance of algae oil as a source of biodiesel. *Energy Convers. Manag.* **2011**, *521*, 163–170.
55. Scott, S.A.; Davey, M.P.; Dennis, J.S.; Horst, I.; Howe, C.J.; Lea-Smith, D.J.; Smith, A.G. Biodiesel from algae: Challenges and prospects. *Curr. Opin. Biotechnol.* **2010**, *213*, 277–286.
56. Gouveia, L.; Oliveira, A. Microalgae as a raw material for biofuels production. *J. Ind. Microbiol. Biotechnol.* **2009**, *362*, 269–274.
57. No, S.Y. Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: A review. *Renew. Sustain. Energy Rev.* **2011**, *151*, 131–149.
58. Amaro, H.M.; Guedes, A.C.; Malcata, F.X. Advances and perspectives in using microalgae to produce biodiesel. *Appl. Energy* **2011**, *8810*, 3402–3410.
59. Sims, R.E.H.; Mabee, W.; Saddler, J.N.; Taylor, M. An overview of second generation biofuel technologies. *Bioresour. Technol.* **2010**, *1016*, 1570–1580.
60. Rajendra, M.; Jena, P.C.; Raheman, H. Prediction of optimized pretreatment process parameters for biodiesel production using ANN and GA. *Fuel* **2009**, *885*, 868–875.

61. Balat, M.; Balat, H. Progress in biodiesel processing. *Appl. Energy* **2010**, *87*, 1815–1835.
62. Demirbas, A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Convers. Manag.* **2008**, *49*, 125–30.
63. Leung, D.Y.C.; Guo, Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process. Technol.* **2006**, *87*, 883–890.
64. Zhang, J.; Jiang, L. Acid-catalyzed esterification of *Zanthoxylum bungeanum* seed oil with high free fatty acids for biodiesel production. *Bioresour. Technol.* **2008**, *99*, 8995–8998.
65. Worapun, I.; Pianthong, K.; Thaiyasuit, P. Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 189–197.
66. Darnoko, D.; Cheryan, M. Kinetics of palm oil transesterification in a batch reactor. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1263–1267.
67. Hoda, N. Optimization of biodiesel production from cottonseed oil by transesterification using NaOH and methanol. *Energy Sources A* **2009**, *325*, 434–441.
68. He, C.; Baoxiang, P.; Dezheng, W.; Jinfu, W. Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts. *Front. Chem. Eng. China* **2007**, *1*, 11–15.
69. Rashid, U.; Anwar, F.; Moser, B.R.; Ashraf, S. Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass Bioenergy* **2008**, *32*, 1202–1205.
70. Antolin, G.; Tinaut, F.V.; Briceno, Y.; Castano, V.; Perez, C.; Ramirez, A.I. Optimisation of biodiesel production by sunflower oil Transesterification. *Bioresour. Technol.* **2002**, *83*, 111–114.
71. Nakpong, P.; Wootthikanokkhan, S. Optimization of biodiesel production from *Jatropha curcas* L oil via alkali-catalyzed methanolysis. *J. Sustain. Energy Environ.* **2010**, *1*, 105–109.
72. De Oliveira, D.D.; di Luccio, M.; Faccio, C.; Dalla Rosa, C.; Bender, J.; Lipke, N. Optimization of alkaline transesterification of soybean oil and castor oil for biodiesel production. *Appl. Biochem. Biotechnol.* **2005**, *122*, 553–560.
73. Kapdan, I.K.; Kargi, F. Bio-hydrogen production from waste materials. *Enzym. Microb. Technol.* **2006**, *38*, 569–582.
74. Singh, S.P.; Singh, D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 200–216.
75. Ramos, M.J.; Fernández, C.M.; Casas, A.; Rodríguez, L.; Pérez, A. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresour. Technol.* **2009**, *100*, 261–268.
76. Taravus, S.; Temur, H.; Yartasi, A. Alkali-catalyzed biodiesel production from mixtures of sunflower oil and beef tallow. *Energy Fuels* **2009**, *23*, 4112–4115.
77. Chuck, C.J.; Bannister, C.D.; Hawley, J.G.; Davidson, M.G.; La Bruna, I.; Paine, A. Predictive model to assess the molecular structure of biodiesel fuel. *Energy Fuels* **2009**, *23*, 2290–2294.
78. Kinoshita, E.; Myo, T.; Hamasaki, K.; Nishi, S. *Combustion Characteristics of Diesel Engine with Coconut Oil Ethyl Ester*; SAE Technical Paper No. 2007-01-2021; SAE International: Washington, DC, USA, 2007; doi:10.4271/2007-01-2021.
79. Kocak, M.S.; Ileri, E.; Utlu, Z. Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils. *Energy Fuels* **2007**, *21*, 3622–3626.

80. Canakci, M.; Sanli, H. Biodiesel production from various feedstocks and their effects on the fuel properties. *J. Ind. Microbiol. Biotechnol.* **2009**, *35*, 431–441.
81. Benjumea, P.; Agudelo, J.R.; Agudelo, A.S.F. Effect of the degree of unsaturation of biodiesel fuels on engine performance, combustion characteristics, and emissions. *Energy Fuels* **2010**, *251*, 77–85.
82. Sanford, S.D. Feedstock and Biodiesel Characteristics Report Renewable Energy Group. Available online: <http://www.regfuel.com> (accessed on 10 March 2012).
83. Canakci, M.; Sanli, H. An assessment about the reasons of NO_x rise in biodiesel's exhaust emissions. *J. Naval Sci. Eng.* **2005**, *3*, 81–92.
84. Barnwal, B.K.; Sharma, M.P. Prospects of biodiesel production from vegetable oils in India. *Renew. Sustain. Energy Rev.* **2005**, *9*, 363–378.
85. Alptekin, E.; Canakci, M. Determination of the density and the viscosities of biodiesel-diesel fuel blends. *Renew. Energy* **2008**, *33*, 2623–2630.
86. Kinast, J.A. *Production of Biodiesel from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends*; Report No NREL/SR-510-31460; National Renewable Energy Laboratory: Golden, CO, USA, 2003.
87. Choi, C.Y.; Reitz, R.D. A numerical analysis of the emissions characteristics of biodiesel blended fuels. *J. Eng. Gas Turbines Power* **1999**, *121*, 31–37.
88. Lee, S.; Tanaka, D.; Kusaka, J.; Daisho, Y. Effects of diesel fuel characteristics on spray and combustion in a diesel engine. *JSAE Rev.* **2002**, *23*, 407–414.
89. Tat, M.E.; Gerpen, J.V. Biodiesel blend detection with a fuel composition sensor. *Am. Soc. Agric. Biol. Eng.* **2002**, *19*, 30–36.
90. Knothe, G.; Steidle, K.R. Kinematic viscosity of biodiesel fuel components and related compounds Influence of compound structure and comparison to petrodiesel fuel components. *Fuel* **2005**, *84*, 1059–1065.
91. Ng, J.H.; Ng, H.K.; Gan, S. Development of emissions predictor equations for a light-duty diesel engine using biodiesel fuel properties. *Fuel* **2012**, *95*, 544–552.
92. Joshi, R.M.; Pegg, M.J. Flow properties of biodiesel fuel blends at low temperature. *Fuel* **2007**, *86*, 143–151.
93. Geller, D.P.; Goodrum, J.W. Effects of specific fatty acid methyl esters on diesel fuel lubricity. *Fuel* **2004**, *83*, 2351–2356.
94. Knothe, G.; Steidley, K.R. Kinematic viscosity of biodiesel components fatty acid alkyl esters and related compounds at low temperatures. *Fuel* **2007**, *86*, 2560–2567.
95. Rodrigues, J.A.; Cardoso, F.P.; Lachter, E.R.; Estevao, L.R.M.; Lima, E.; Nascimento, R.S.V. Correlating chemical structure and physical properties of vegetable oil esters. *J. Am. Oil Chem. Soc.* **2006**, *83*, 353–357.
96. Refaat, A.A. Correlation between the chemical structure of biodiesel and its physical properties. *Int. J. Environ. Sci. Technol.* **2009**, *6*, 677–694.
97. Cheenkachorn, K. Predicting Properties of Biodiesels Using Statistical Models and Artificial Neural Networks. In Proceedings of the Joint International Conference on Sustainable Energy and Environment, Hua Hin, Thailand, 1–3 December 2004.

98. Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol.* **2005**, *86*, 1059–1070.
99. Gunstone, F.D. *Vegetable Oils in food Technology: Composition, Properties and Uses*; Blackwell Publishing Ltd: Oxford, UK, 2002.
100. Lee, I.; Johnson, L.A.; Hammond, E.G. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1155–1160.
101. Boudy, F.; Seers, P. Impact of physical properties of biodiesel on the injection process in a common-rail direct injection system. *Energy Convers. Manag.* **2009**, *50*(12), 2905–2912.
102. Baroutian, S.; Aroua, M.K. Estimation of vegetable oil-based ethyl esters biodiesel densities using artificial neural networks. *J. Appl. Sci.* **2008**, *8*, 3005–3011.
103. Szybist, J.P.; Song, J.; Alam, M.; Boehma, A.L. Biodiesel combustion, emissions and emission control. *Fuel Process. Technol.* **2007**, *88*, 679–691.
104. Veny, H.; Baroutian, S.; Aroua, M.; Hasan, M.; Raman, A.; Sulaiman, N. Density of *Jatropha curcas* seed oil and its methyl esters: Measurement and estimations. *Int. J. Thermophys.* **2009**, *30*, 529–541.
105. Blangino, E.; Riveros, A.F.; Romano, S.D. Numerical expressions for viscosity, surface tension and density of biodiesel: Analysis and experimental validation. *Phys. Chem. Liq.* **2008**, *46*, 527–547.
106. Lang, X.; Dalai, A.K.; Bakshi, N.N.; Reaney, M.J.; Hertz, P.B. Preparation and characterization of bio-diesels from various bio-oils. *Bioresour. Technol.* **2001**, *80*, 53–62.
107. Meher, L.C.; Vidya Sagar, D.; Naik, S.N. Technical aspects of biodiesel production by transesterification—A review. *Renew. Sustain. Energy Rev.* **2006**, *10*, 248–268.
108. Bajpai, D.; Tyagi, V.K. Biodiesel: Source, production, composition, properties and its benefits. *J. Oleo Sci.* **2006**, *55*, 487–502.
109. Demirbas, A. Biodiesel production from vegetable oils via catalytic and noncatalytic supercritical methanol transesterification methods. *Prog. Energy Combust.* **2005**, *31*, 466–487.
110. Knothe, G.; Matheaus, A.C.; Ryan, T.W. Cetane numbers of branched and straight chain fatty esters determined in an ignition quality tester. *Fuel* **2003**, *82*, 971–975.
111. Bangboye, A.I.; Hansen, A.C. Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester FAME composition. *Int. Agrophys.* **2008**, *22*(1), 21–29.
112. Demirbas, A. Chemical and fuel properties of seventeen vegetable oils. *Energy Sources* **2003**, *25*, 721–728.
113. Ali, Y.; Hanna, M.A.; Cuppett, S.L. Fuel properties of tallow and soybean oil esters. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1557–1564.
114. Ma, F.; Hanna, M.A. Biodiesel production: A review. *Bioresour. Technol.* **1999**, *70*, 1–15.
115. Monyem, A.; Gerpen, J.V. The effect of biodiesel oxidation on engine performance and emissions. *Biomass Bioenergy* **2001**, *20*, 317–325.
116. Durrett, T.P.; Benning, C.; Ohlrogge, J. Plant triacylglycerols as feedstocks for the production of biofuels. *Plant J.* **2008**, *54*, 593–607.
117. Dunn, R.O. Cold Weather Properties and Performance of Biodiesel. In *The Biodiesel Handbook*; Agriculture Research Service (AOCS) Press: Champaign, IL, USA, 2005; Chapter 63, pp. 405–438.

118. Nascimento, R.S.V.; Soares, V.L.P.; Albinante, S.; Barreto, L.R. Effect of ester-additives on the crystallization temperature of methyl hexadecanoate. *J. Therm. Anal. Calorim.* **2005**, *79*, 249–254.
119. Lacey, P.I.; Lestz, S.J. *Effect of Low Lubricity Fuels on Diesel Injection Pumps Part I: Field Performance*; SAE Technical Paper No. 920823; SAE International: Washington, DC, USA, 1992; doi:10.4271/920823.
120. Hu, J.; Du, Z.; Li, C.; Min, E. Study on the lubrication properties of biodiesel as fuel lubricity enhancers. *Fuel* **2005**, *84*, 1601–1606.
121. Anastopoulos, E.L.; Zannikos, F.; Kalligeros, S.; Teas, C. Influence of aceto acetic esters and di-carboxylic acid esters on diesel fuel lubricity. *Tribol. Int.* **2001**, *34*, 749–755.
122. Van Gerpen, J.H.; Soyulu, S.; Mustafa, E.T. *Evaluation of the Lubricity of Soybean Oil-Based Additives in Diesel Fuel*; ASAE Paper No 996134; American Society of Agricultural Engineers: St. Joseph, MI, USA, 1999.
123. Wadumesthrige, K.; Ara, M.; Salley, S.O.; Simon Ng, K.Y. Investigation of lubricity characteristics of biodiesel in petroleum and synthetic fuel. *Energy Fuels* **2009**, *23*, 2229–2234.
124. Bhuyan, S.; Sundararajan, S.; Yao, L.; Hammond, E.G.; Wang, T. Boundary lubrication properties of lipid-based compounds evaluated using microtribological methods. *Tribol. Lett.* **2006**, *22*, 167–172.
125. Knothe, G.; Dunn, R.O. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *J. Am. Oil Chem. Soc.* **2003**, *80*, 1021–1026.
126. Lin, C.Y.; Lin, H.A.; Hung, L.B. Fuel structure and properties of biodiesel produced by the peroxidation process. *Fuel* **2006**, *85*, 1743–1749.
127. Kyriakidis, N.B.; Katsiloulis, T. Calculation of iodine value from measurements of fatty acid methyl esters of some oils: Comparison with the relevant American oil chemists society method. *J. Am. Chem. Soc.* **2007**, *7*, 1235–1238.
128. Heywood, J.B. *Internal Combustion Engines Fundamentals*; McGrawHill: New York, NY, USA, 1988.
129. Ferguson, C.R.; Kirkpatrick, A.T. *Internal Combustion Engine*, 2nd ed.; John Wiley Sons: New York, NY, USA, 2001.
130. Lebedevas, S.; Vaicekauskas, A. Research into the application of biodiesel in the transport sector of Lithuania transport. *Transport* **2006**, *21*, 80–87.
131. Qi, D.H.; Geng, L.M.; Chen, H.; Bian, Y.Z.H.; Liu, J.; Ren, X.C.H. Combustion and performance evaluation of a diesel engine fueled with biodiesel produced from soybean crude oil. *Renew. Energy* **2009**, *34*, 2706–2713.
132. Nabi, M.N.; Rahman, M.M.; Akhter, M.S. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. *Appl. Therm. Eng.* **2009**, *2911*, 2265–2270.
133. İlkılıç, C.; Aydın, S.; Behcet, R.; Aydın, H. Biodiesel from safflower oil and its application in a diesel engine. *Fuel Process. Technol.* **2011**, *923*, 356–362.
134. Utlu, Z.; Koçak, M.S. The effect of biodiesel fuel obtained from waste frying oil on direct injection diesel engine performance and exhaust emissions. *Renew. Energy* **2008**, *33*, 1936–1941.
135. Kumar, A.S.; Maheswar, D.; Reddy, K.V.K. Comparison of diesel engine performance and emission from neat and transesterified cotton seed oil. *Jordan J. Mech. Ind. Eng.* **2009**, *3*, 190–197.

136. Haşimoğlu, C.; Ciniviz, M.; Özsert, İ.; İcingür, Y.; Parlak, A.; Sahir Salman, M. Performance characteristics of a low heat rejection diesel engine operating with biodiesel. *Renew. Energy* **2008**, *337*, 1709–1715.
137. Mustafa, C. Combustion characteristics of a turbocharged DI compression ignition engine fueled with petroleum diesel fuels and biodiesel. *Bioresour. Technol.* **2007**, *986*, 1167–1175.
138. Lin, C.Y.; Li, R.J. Engine performance and emission characteristics of marine fish-oil biodiesel produced from the discarded parts of marine fish. *Fuel Process. Technol.* **2009**, *907*, 883–888.
139. Raheman, H.; Ghadge, S.V. Performance of compression ignition engine with mahua *Madhuca indica* biodiesel. *Fuel* **2007**, *8616*, 2568–2573.
140. Usta, N. An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Convers. Manag.* **2005**, *4615*, 2373–2386.
141. Karabektas, M. The effects of turbocharger on the performance and exhaust emissions of a diesel engine fuelled with biodiesel. *Renew. Energy* **2009**, *34*, 989–993.
142. Aydin, H.; Bayindir, H. Performance and emission analysis of cottonseed oil methyl ester in a diesel engine. *Renew. Energy* **2010**, *35*, 588–592.
143. Hansen, A.C.; Gratton, M.R.; Yuan, W. Diesel engine performance and NO_x emissions from oxygenated biofuels and blends with diesel fuel. *Trans. Am. Soc. Agric. Biol. Eng.* **2006**, *49*, 589–595.
144. Murillo, S.; Miguez, J.L.; Porteiro, J.; Granada, E.; Moran, J.C. Performance and exhaust emissions in the use of biodiesel in outboard diesel engines. *Fuel* **2007**, *86*, 1765–1771.
145. Oner, C.; Altun, S. Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. *Appl. Energy* **2009**, *86*, 2114–2120.
146. Monyem, A.; van Gerpen, J.H.; Canakci, M. The effect of timing and oxidation on emissions from biodiesel-fueled engines. *Trans. Am. Soc. Automob. Eng.* **2001**, *44*, 35–42.
147. Ramadhas, A.S.; Muraleedharan, C.; Jayaraj, S. Performance and emission evaluation of diesel engine fueled with methyl esters of rubber seed oil. *Renew. Energy* **2005**, *30*, 1789–1800.
148. Song, J.T.; Zhang, C.H. An experimental study on the performance and exhaust emissions of a diesel engine fuelled with soybean oil methyl ester. *Proc. Inst. Mech. Eng. D* **2008**, *222*, 2487–2496.
149. Pal, A.; Verma, A.; Kachhwaha, S.S.; Maji, S. Biodiesel production through hydrodynamic cavitations and performance testing. *Renew. Energy* **2010**, *35*, 619–624.
150. Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A.; Tonon, S. Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy* **2004**, *29*, 2195–2211.
151. Lance, D.L.; Goodfellow, C.L.; Williams, J.; Bunting, W.; Sakata, I.; Yoshida, K.; Taniguchi, S.; Kitano, K. *The Impact of Diesel and Biodiesel Fuel Composition on a Euro V HSDI Engine with Advanced DPNR Emissions Control*; SAE Technical Paper No. 2009-01-190; SAE International: Washington, DC, USA, 2009.
152. Wu, F.; Wang, J.; Chen, W.; Shuai, S. A study on emission performance of a diesel engine fueled with five typical methyl ester biodiesels. *Atmos. Environ.* **2009**, *437*, 1481–1485.

153. Sahoo, P.K.; Das, L.M.; Babu, M.K.G.; Arora, P.; Singh, V.P.; Kumar, N.R. Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine. *Fuel* **2009**, *889*, 1698–1707.
154. Ozsezen, A.N.; Canakci, M.; Turkcan, A.; Sayin, C. Performance and combustion characteristics of a DI diesel engine fueled with waste palm oil and canola oil methyl esters. *Fuel* **2009**, *884*, 629–636.
155. Banapurmath, N.R.; Tewari, P.G.; Hosmath, R.S. Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters. *Renew. Energy* **2008**, *339*, 1982–1988.
156. Xue, J.; Grift, T.E.; Hansen, A.C. Effect of biodiesel on engine performances and emissions. *Renew. Sustain. Energy Rev.* **2011**, *152*, 1098–1116.
157. Fazal, M.A.; Haseeb, A.S.M.A.; Masjuki, H.H. Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renew. Sustain. Energy Rev.* **2011**, *152*, 1314–1324.
158. Chapman, E.; Boehman, A.L. Emissions Characteristics of a Light Duty Diesel Engine Fuelled with a Hydrogenated Biodiesel Fuel. In Proceedings of the 231st National Meeting of the American Chemical Society, Atlanta, GA, USA, 26–30 March 2006.
159. Majewski, W.A. Diesel Exhaust Particle Size. In *Dieselnet Technology Guide*; Ecopoint Inc.: Mississauga, ON, Canada, 2002. Available online: http://www.dieselnet.com/tech/dpm_sizehtml (accessed on 25 March 2012).
160. Garshick, E.; Laden, F.; Hart, J.E.; Rosner, B.; Smith, T.J. Lung cancer in railroad workers exposed to diesel exhaust. *Environ. Health Perspect.* **2004**, *112*, 1539–1543.
161. Surawski, N.C.; Miljevic, B.; Roberts, B.A.; Modini, R.L.; Situ, R.; Brown, R.J.; Bottle, S.; Ristovski, Z.D. Particle emissions, volatility, and toxicity from an ethanol fumigated compression ignition engine. *Environ. Sci. Technol.* **2009**, *441*, 229–235.
162. Kalogirou, S.A. Artificial intelligence for the modeling and control of combustion processes: A review. *Prog. Energy Combust. Sci.* **2003**, *29*, 515–566.
163. Ramadhas, A.S.; Jayaraj, S.; Muraleedharan, C.; Padmakumari, K. Artificial Neural Networks used for the prediction of the cetane number of biodiesel. *Renew. Energy* **2006**, *3115*, 2524–2533.
164. Balabin, R.M.; Lomakina, E.I.; Safieva, R.Z. Neural network ANN approach to biodiesel analysis: Analysis of biodiesel density, kinematic viscosity, methanol and water contents using near infrared NIR spectroscopy. *Fuel* **2011**, *905*, 2007–2015.
165. Agarwal, M.; Singh, K.; Chaurasia, S.P. Prediction of biodiesel properties from fatty acid composition using linear regression and ANN techniques. *Indian Chem. Eng.* **2010**, *524*, 347–361.
166. Çay, Y.; Çiçek, A.; Kara, F.; Sağıroğlu, S. Prediction of engine performance for an alternative fuel using artificial neural network. *Appl. Therm. Eng.* **2012**, *370*, 217–225.
167. Sayin, C.; Metin Erturk, H.; Hosoz, M.; Kilicaslan, I.; Canakci, M. Performance and exhaust emissions of gasoline engine using artificial neural networks. *Appl. Therm. Eng.* **2007**, *27*, 46–54.
168. Arcaklioğlu, E.; Çelikten, I. A diesel engine's performance and exhaust emissions. *Appl. Energy* **2005**, *801*, 11–22.
169. Yap, W.K.; Karri, V. Emissions predictive modelling by investigating various neural network models. *Expert Syst. Appl.* **2012**, *393*, 2421–2426.

170. Parlak, A.; Islamoglu, Y.; Yasar, H.; Egrisogut, A. Application of artificial neural network to predict specific fuel consumption and exhaust temperature for a diesel engine. *Appl. Therm. Eng.* **2006**, *268*, 824–828.
171. Canakci, M.; Ozsezen, A.N.; Arcaklioglu, E.; Erdil, A. Prediction of performance and exhaust emissions of a diesel engine fueled with biodiesel produced from waste frying palm oil. *Expert Syst. Appl.* **2009**, *365*, 9268–9280.
172. Karonis, D.; Lois, E.; Zannikos, F.; Alexandridis, A.; Sarimveis, H. A neural network approach for the correlation of exhaust emissions from a diesel engine with diesel fuel properties. *Energy Fuels* **2003**, *175*, 1259–1265.
173. Kesgin, U. Genetic algorithm and artificial neural network for engine optimisation of efficiency and NO_x emission. *Fuel* **2004**, *837*, 885–895.
174. Manjunatha, R.; Badari Narayana, P.; Hema Chandra Reddy, K. Application of Artificial Neural Networks for emission modelling of biodiesels for a CI engine under varying operating conditions. *Mod. Appl. Sci.* **2010**, *4*, 77–89.
175. Kumar, J.; Bansal, A. Application of artificial neural network to predict properties of diesel—Biodiesel blends. *Kathmandu Univ. J. Sci. Eng. Technol.* **2010**, *62*, 98–103.
176. Choi, Y.; Chen, J.Y. Fast prediction of start-of-combustion in HCCI with combined Artificial Neural Networks and ignition delay model *Proc. Combust. Inst.* **2005**, *302*, 2711–2718.
177. Çelik, V.; Arcaklioglu, E. Performance maps of a diesel engine. *Appl. Energy* **2005**, *813*, 247–259.
178. Deh Kiani, M.K.; Ghobadian, B.; Tavakoli, T.; Nikbakht, A.M.; Najafi, G. Application of Artificial Neural Networks for the prediction of performance and exhaust emissions in SI engine using ethanol-gasoline blends. *Energy* **2010**, *351*, 65–69.
179. Renald, C.J.T.; Somasundaram, P. Experimental investigation on attenuation of emission with optimized LPG jet induction in a dual fuel diesel engine and prediction by ANN model. *Energy Procedia* **2012**, *140*, 1427–1438.
180. Yusaf, T.F.; Buttsworth, D.R.; Saleh, K.H.; Yousif, B.F. CNG-diesel engine performance and exhaust emission analysis with the aid of artificial neural network. *Appl. Energy* **2010**, *875*, 1661–1669.
181. Yusaf, T.F.; Yousif, B.F.; Elawad, M.M. Crude palm oil fuel for diesel-engines: Experimental and ANN simulation approaches. *Energy* **2011**, *368*, 4871–4878.
182. Obodeh, O.; Ajuwa, C.I. Evaluation of artificial neural network performance in predicting diesel engine No_x emissions. *Res. J. Appl. Sci. Eng. Technol.* **2009**, *13*, 125–131.
183. Shivakumar, P.; Srinivasa Pai, P.; Shrinivasa Rao, B.R. Artificial Neural Network based prediction of performance and emission characteristics of a variable compression ratio CI engine using WCO as a biodiesel at different injection timings. *Appl. Energy* **2011**, *887*, 2344–2354.
184. Tasdemir, S.; Saritas, I.; Ciniviz, M.; Allahverdi, N. Artificial neural network and fuzzy expert system comparison for prediction of performance and emission parameters on a gasoline engine. *Expert Syst. Appl.* **2011**, *3811*, 13912–13923.
185. Shanmugam, P.; Sivakumar, V.; Murugesan, A.; Ilangkumaran, M. Performance and exhaust emissions of a diesel engine using hybrid fuel with an artificial neural network. *Energy Sources A* **2011**, *33*, 1440–1450.

186. Sharon, H.; Jayaprakash, R.; Karthigai Selvan, M.; Soban Kumar, D.R.; Sundaresan, A.; Karuppasamy, K. Biodiesel production and prediction of engine performance using SIMULINK model of trained neural network. *Fuel* **2012**, *990*, 197–203.
187. Satyanarayana, M.; Muraleedharan, C. Prediction of acid values of vegetable oils having high free fatty acids using artificial neural networks. *Energy Sources A* **2013**, *216*, 1479–1489.
188. Liu, G.; Wang, L.Q.H.; Shen, H.; Zhang, X.; Zhang, S.; Mi, Z. Artificial neural network approaches on composition—Property relationships of jet fuels based on GC–MS. *Fuel* **2007**, *8616*, 2551–2559.
189. Pasadakis, N.; Gaganis, V.; Foteinopoulos, C. Octane number prediction for gasoline blends. *Fuel Process. Technol.* **2006**, *876*, 505–509.
190. Pasadakis, N.; Sourligas, S.; Foteinopoulos, C. Prediction of the distillation profile and cold properties of diesel fuels using mid-IR spectroscopy and neural networks. *Fuel* **2006**, *857*, 1131–1137.
191. Kumar, J.; Bansal, A.; Jha, M.K. Comparison of Statistical and Neural Network Techniques in Predicting Physical Properties of Various Mixtures of Diesel and Biodiesel. In Proceedings of the World Congress on Engineering and Computer Science, San Francisco, CA, USA, 24–26 October 2007.
192. Korres, D.M.; Anastopoulos, G.; Lois, E.; Alexandridis, A.; Sarimveis, H.; Bafas, G. A neural network approach to the prediction of diesel fuel lubricity. *Fuel* **2002**, *8110*, 1243–1250.
193. Marinovic, S.; Bolanca, T.; Ukcic, S.; Rukavina, V.; Jukic, A. Prediction of diesel fuel cold properties using artificial neural networks. *Chem. Technol. Fuels Oils* **2012**, *481*, 67–74.
194. Wu, C.; Zhang, J.; Li, W.; Wang, Y.; Cao, H. Artificial neural network model to predict cold filter plugging point of blended diesel fuels. *Fuel Process. Technol.* **2006**, *877*, 585–590.
195. Yang, H.; Ring, Z.; Briker, Y.; McLean, N.; Friesen, W.; Fairbridge, C. Neural network prediction of cetane number and density of diesel fuel from its chemical composition determined by LC and GC–MS. *Fuel* **2002**, *811*, 65–74.