

A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation

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ABSTRACT

In the present work, a detailed statistical investigation is conducted in order to a) assess the average values of all properties (incl. fatty acid composition) of the most investigated biodiesels and b) quantify the effects of feedstock unsaturation on the physical and chemical properties of the derived methyl ester. To this aim, the available literature on biodiesel properties and fatty acid composition was gathered (more than 750 papers published in international Journals and Conferences), and the reported measurements are statistically analyzed with respect to the feedstock and its chemical composition and structure; in total, 26 different biodiesel feedstocks are studied, comprising of twenty-two edible and non-edible vegetable oils and four animal fats. From the analysis, collective results and statistical data are derived for each property that are then compared with the European and American specifications. The effects of unsaturation are investigated with separate best-fit linear curves provided for each interesting property with respect to the average number of double bonds. The various trends observed are discussed and explained based on fundamental aspects of fuel chemistry and on the consequences they have on real engine operation.

Keywords: Biodiesel; Fatty acid composition; Degree of unsaturation; Statistical analysis; Properties

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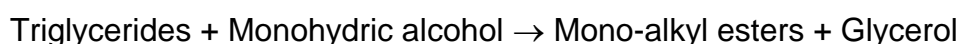
1. Introduction

Biofuels made from agricultural products reduce the dependence on oil imports and support local agricultural industries, while offering serious benefits in terms of sustainability, reduced pollutant and greenhouse gas emissions, and increased energy diversity and economic security [1]. Among the biofuels currently in use or under consideration, biodiesel (methyl or ethyl ester) is considered as a very promising fuel for the transportation sector since it possesses similar properties with diesel fuel, it can be blended with diesel practically at any proportion and can be used without changes in the existing distribution infrastructure.

The major biodiesel advantage relative to diesel fuel is its renewability. Life-cycle analyses have shown that the source-to-wheel CO₂ emissions from neat biodiesel combustion account for at least 60% savings with respect to petroleum diesel fuel, whereas for the most popular B20 blend it is of the order of 15–20% [2,3]. To this aim, the European Parliament has passed Directive 2009/28/EC [4] on the promotion of the use of energy from renewable sources that contains a specific mandate for Member States to include 10% (by energy content) of renewable fuel in the transport sector by 2020. In parallel in the US, the Energy Independence and Security Act of 2007 (EISA) increased four-fold the volume of renewable fuel required to be blended into transportation fuel, from 34 billion liters in 2008 to 136 billion liters by 2022.

Nonetheless, although the renewability of biodiesel is an extremely hopeful fact in view of the increasing global warming contribution from the transportation sector, other issues should not be ignored such as food prices and biodiversity. Not surprisingly, concerns over the latter issues have sparked the research on second-generation biodiesels (and biofuels in general) from non-edible sources such as jatropha, castor or microalgae [5–7].

Biodiesel is produced by transesterification of vegetable oils, animal fats or recycled cooking oils, and consists of long-chain alkyl esters, which contain two oxygen atoms per molecule [8–11]. The reversible reaction proceeds with a catalyst (usually KOH or NaOH) or even without catalyst by using primary or secondary monohydric aliphatic alcohols; the glycerol-based tri-esters that make up the fats and oils are converted into mono-esters yielding free glycerol as a byproduct:



The more widely used biodiesels are rapeseed methyl ester (RME) in Europe and soybean methyl ester or methyl soyate (SME) in the US, but there are many other popular feedstocks such as palm (PME, particularly in Asia), sunflower, cottonseed, yellow grease and tallow methyl esters. These are collectively known as fatty acid methyl esters (FAME), since methanol is primarily employed in the transesterification process due to its low cost compared with the other alcohols. It is well established today that biodiesel-blended fuels succeed to a large extent in reducing the amount of emitted PM or the smokiness from diesel engines. In general, similar positive effects have been noticed as regards HC and CO emissions (although contradicting results have been reported too, particularly if measurements after the diesel oxidation catalyst are considered), whereas a usually moderately negative impact is experienced with regard to NO_x [2,8,12]. Other notable advantages of FAMEs over their mineral diesel counterpart are their biodegradability, safer storage due to higher flash point, better lubricity and low toxicity.

One of the peculiarities of biodiesel with respect to other biofuels is the fact that it can be produced from a variety of feedstocks. Since each originating oil or fat is characterized by different (fatty acid) composition, it is not surprising that the properties of the final ester will differ substantially from place to place, based largely on the feedstock used but also on the alcohol employed in the esterification and the exact chemical process followed [13]. To this aim, both the European Union (EU) and the US have issued specifications that should be met by the methyl esters intended for use in compression ignition engines; Table 1 summarizes these acceptable limits in comparison to their conventional diesel oil ones. With respect to these specifications, the major technical problems associated with the use of biodiesel as a fuel for diesel engines, apart for the higher production cost (largely owing to the high cost of the feedstock), are its susceptibility to oxidation as well as its poor low-temperature properties, requiring additives in the form of anti-oxidants and cold-flow improvers.

Past research, either in the form of experimental/simulation [e.g. 14–18], or statistical [19] investigations, has highlighted some important aspects regarding the inter-dependence between biodiesel composition and (some of) its physical and chemical properties. The target of the present work is to expand on these analyses as regards a) the sample of biodiesel feedstocks taken under consideration, b) the number of the investigated methyl ester properties, and c) the amount of studies reviewed. To this aim our intent was to gather the biodiesel physical and chemical properties and the respective

feedstocks' fatty acid compositions from the largest amount of studies possible and for the widest range of feedstocks so far, and to analyze them statistically in order to:

- Assess the average fatty acid composition of each originating biodiesel feedstock,
- Evaluate the basic statistical values of each property, and compare these values to the European and US specifications for each methyl ester, and
- Correlate the most important methyl ester properties with the degree of unsaturation of the feedstocks in order to provide possible best-fit relations useful for simulations by researchers and long-term planning by administrations and international institutions.

2. Methodology

In order to analyze statistically the physical and chemical properties of biodiesel from various feedstocks, a huge amount of data was carefully collected from papers published in international Journals, Conferences and reports issued by renowned research centers. Practically, the whole electronic databases of Elsevier, American Chemical Society, SAGE Publishing, Taylor and Francis, Wiley International, IEEE and Springer were 'scanned' for interesting papers, with a noteworthy amount of datasets contributed from papers presented in SAE International, ASABE and various other indexed Conferences around the world. All in all, the total number of collected papers used in the statistical investigation was more than 750, all published during the last three decades, (mostly during the last decade), and comprising more than 30 different biodiesel feedstocks.

Fig. 1 demonstrates the absolute number (upper sub-diagram) and the percentage (lower sub-diagram) of the various biodiesel datasets included in the current analysis classified with respect to the originating feedstock. In the end, 26 feedstocks were chosen for the statistical investigation, namely four animal fats (beef tallow, chicken, lard and fish), twenty-one oils derived from various plants (canola, castor, coconut, corn (maize), cottonseed, croton, hazelnut, karanja (honge), jatropha, linseed (flax), mahua, neem, olive, palm, peanut, rapeseed, rice bran, rubber seed, safflower, soybean and sunflower), as well as waste cooking oil. These 26 feedstocks eventually provided 945 different data series of biodiesel properties and 700 data series of fatty acid compositions. On the

whole, the dataset contains a good mix of American, European and Asian animal or vegetable feedstocks, with both edible and non-edible oils included.

From Fig. 1 it is made obvious that the most popular feedstock is soy, which comprises almost one fifth (18.1%) of the investigations worldwide. This is most probably due to its relatively low cost, since the corresponding yield falls short (sometimes by a lot) to other feedstocks such as palm, coconut, jatropha or castor [20]. It is also interesting that SME has been investigated practically worldwide (although the majority of the research has been conducted in America) and with a continuous interest over the last three decades. Rapeseed and the closely related canola (10.4+3.1=13.5%) are the next most common feedstocks, with a considerable interest also found in palm (7.8%), the non-edible jatropha (6.9%; mainly during the last years in India), waste cooking (9.5%) and sunflower (5.6%). On the other hand, the cumulative percentage of all animal fats (including fish) is of the order of 8.1%, with the majority of the research (50%) focused on beef tallow. The non-edible karanja with 3.8% (primarily during the last few years), cottonseed with 3.1% (more popular in the Mediterranean countries), as well as castor (3.3%), rice bran (2.5%), coconut (2.4%), corn (used for ethanol production too – 2.0%), linseed (1.9%), safflower (1.8%) and mahua and neem (each 1.5%) comprise smaller but still important shares of the worldwide biodiesel research. Various other feedstocks such as polanga (*calophyllum inophyllum*), grape seed, tobacco seed, jojoba (*simmondsia chinensis*), chinese pistache (*pistachio chinensis*), hemp (*cannabis sativa*), babassu (*orbignya oleifera*), sesame (*sesamum indicum*) and mustard, classified as 'other' in Fig. 1, were not included in the statistical analysis that follows since it was not possible to gather at least five different data series of their respective biodiesel properties.

During the data collection, particular effort was paid to avoid duplicate entries, and in general, to only include data from those researchers who actually measured themselves the values reported, following the internationally accepted experimental standards. Although the initial intent was to include all property values found, it was inevitable that some markedly 'extreme' data should ultimately be excluded from the database. For example, if the majority of the researchers had measured the density of a specific FAME to range from 860 to 880 kg/m³ and one particular researcher had reported a value of 840 or 910 kg/m³, then this value was excluded from the database. If, however, more than 2 different researchers confirmed such extreme values, then these were retained in the database, and this is ultimately reflected in the corresponding high values of the derived

standard deviations. Moreover, and this is primarily valid for density and viscosity, some researchers did not provide data for these two properties at the universally requested temperatures of 15 and 40°C respectively; these values too were excluded from the analysis. Since many of the biodiesel properties depend apart from the originating oil, also on the alcohol used in the transesterification process (e.g. the iodine value, with ethyl esters having lower iodine values than methyl esters of the same fat or oil), only methyl ester (and not ethyl ester) property values are included in the analysis that follows.

In total, 39 different biodiesel properties were registered during the data collection process, namely kinematic viscosity; density; cetane number; lower and higher heating values; iodine number; flash point; cold flow properties (pour, cloud and CFP point); weight percentage and number of atoms of carbon, hydrogen and oxygen; acid value; oxidation stability; weight content of sulfur, carbon residue, ash, water, methanol, ester; distillation temperatures (initial, 10%, 50%, 90% and final); molecular weight; stoichiometric air-fuel ratio; boiling point; surface tension; heat of evaporation; amount of mono-, di-, tri-glycerides; free and total glycerol. The most investigated properties were found to be: viscosity (680 observations), density (663), cetane number (474), flash point (445), cloud point (315), sulfur content (294), higher heating value (291), acid value (275), pour point (265), lower heating value (257), iodine number (195) and cold filter plugging point (188).

3. Results and discussion

3.1. Overall results

The chemical composition of biodiesel is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. With few exceptions (e.g. fish oil), the carboxylic (fatty) acids are all straight-chain compounds ranging in size from 8–20 carbons. Acids may be saturated (cannot chemically add hydrogen), which means that they contain only single bonds, or unsaturated (can be hydrogenated), which means that they contain at least one double bond. For each double bond, one hydrogen molecule can be added per fatty acid [3,8]. Tables 2a and 2b summarize the average values and standard deviations of the fatty acid composition from all analyzed vegetable oils (Table 2a) and animal fats

(Table 2b); the number of observations used are also provided in the last column. Further, Figs 2 and 3 graphically illustrate the most important values from Table 2.

The most obvious comment regarding Tables 2a and 2b is the high standard deviation observed for almost all the fatty acids that are found in the waste cooking oil. This is not surprising since used cooking oil may originate from a large variety of vegetable oils depending on the specific region of the research. Equally high are the standard deviations noticed in fish oil, again owing to the variety of the originating feedstock (salmon, mackerel, sardines etc). Similar observations were true for the initially employed category 'ground-animal fat', which was then split into three sub-categories, beef tallow, chicken fat and lard. Some researchers did not specify the exact origin of the animal fat used; these cases, although registered in the database, were not included in the feedstock-based analysis that follows; for what is worth, the line 'animal fat' in Table 2b includes all derived entries, i.e. beef tallow, chicken, lard and undefined. Despite this stricter classification, tallow fat (popular in many countries worldwide) still exhibits rather high variation in its fatty acid composition, indicative of the different animal breeding and nutrition habits employed. Not surprisingly, the fatty acid composition of all three examined ground-animal fats present similarities (in palmitic, oleic and linolenic acid composition), with the one derived from chicken being richer in the unsaturated palmitoleic and linoleic acids, and tallow richer in the saturated stearic acid. As regards the vegetable oils, it is the sunflower that seems to be prone to variation in its composition (sunflower has been the subject of research in many countries worldwide, hence the disparity in its oil composition mirrors different soils, cultivations and growth conditions). On the other hand, the three most intensely investigated feedstocks soybean, rapeseed and palm oil present the highest cohesion in their fatty acid composition.

Although for the majority of the examined feedstocks the primary unsaturated acids are oleic, linoleic and linolenic (Fig. 3), there are some noteworthy exceptions. For example, castor is rich in the mono-unsaturated ricinoleic acid (contains hydroxyl), which is responsible for the FAME's high viscosity and density. Fish, on the other hand, is rich in poly-unsaturated acids of longer than 18 carbon atoms chain, comprising up to 6 double bonds (Table 2b). Apart from castor, another feedstock that is well known to differentiate as regards its composition (and some of the corresponding biodiesel properties as will be discussed later in the text) is coconut. The lower sub-diagram of Fig. 2 that illustrates the weight percentage of the saturated fatty acids, reveals that coconut is almost 90%

saturated. The next highest values come from palm (49%), beef tallow (48%), mahua (46%) and lard (41%). Interestingly, all three ground-animal fats have a degree of saturation that is higher than the overall average value. On the other hand, the highest percentages of mono-unsaturated fatty acids are noticed in castor (91%), hazelnut (80%), olive oil (76%), rapeseed/canola (63–64%) and karanja (55%), whereas the highest percentages of poly-unsaturated fatty acids are to be found in croton (83%), safflower (75%), linseed (71%), sunflower (68%), soybean (60%), corn (58%), rubber seed (56%) and cottonseed (55%). An even more detailed picture of the most important fatty acids weight percentage in the 26 studied feedstocks (and mainly of the unsaturated ones) is further demonstrated in Fig. 3. It can be observed that croton, corn, cottonseed, safflower, soybean and sunflower are primarily rich in linoleic (18:2) acid, whereas linseed and rubber seed, and to a lesser extent rapeseed and canola, in linolenic (18:3). Consistent with the remarks made earlier, fish oil is the only one of the 26 studied feedstocks that is rich in poly-unsaturated acids of 20, 21 and 22 carbon atoms chains.

Finally, Table 3 summarizes, and Fig. 4 graphically illustrates, the most important physical and chemical properties of all biodiesels investigated. As mentioned earlier, 39 properties were registered in total. Since many of them, however, depend on the transesterification reaction rather than the feedstock itself (e.g. amount of mono-, di-, tri-glycerides, free and total glycerol, carbon content, moisture, ash content, ester content etc), only the most important feedstock-related ones, for which a relatively large number of entries was available are summarized in Table 3 and depicted in Fig. 4. Standard deviations are also designated graphically in Fig. 4 highlighting the high, in some cases, disparity in the reported results owing to differentiations in the composition of the parent oil, the purity of the final ester and sometimes also in the measuring procedure. These properties will be discussed in more detail in the next section with respect to the unsaturation level of the originating feedstock. In Fig. 4, the respective European and US specification limits are also provided in order to initially assess those feedstocks that seem to fall outside the acceptable range.

3.2. *Unsaturation effects*

A very influencing parameter of biodiesel (feedstock) is its degree of unsaturation, with a usual measure being the iodine number. Table 4 elaborates on the degree of

unsaturation based on the values provided in Table 2. In the literature, there are three approaches that are mostly used to evaluate the degree of unsaturation. The first (1st column in Table 4) simply counts the saturated and unsaturated percentage weights without any distinction between mono-unsaturated and poly-unsaturated fatty acids (termed here ‘unweighted’ degree of unsaturation). In the second approach (2nd column in Table 3), all fatty acids with 3 or more double bonds are assumed to weigh equally as the ones with 2 double bonds (termed ‘partially weighted’ degree of unsaturation) [15]. In the third and more accurate approach (3rd column in Table 3), each unsaturated fatty acid weighs according to the number of double bonds in its molecule (‘fully weighted’ degree of unsaturation); the later degree of unsaturation also corresponds to the average number of double bonds. Lastly, Table 4 also documents the average chain length of each feedstock; with the clear exception of coconut, all the other oils range from 17 to 18 carbon atoms on average.

For those feedstocks with small amount of linoleic and linolenic acids (e.g. coconut) the ‘un-weighted’ and the ‘partially’ or even ‘fully weighted’ degrees of unsaturation are comparable. Likewise, for those feedstocks where the majority of unsaturated fatty acids are 18:1 oleic and 18:2 linoleic (e.g. animal fats, castor, corn, cottonseed, hazelnut, jatropha, mahua, neem, palm, peanut, safflower, sunflower etc – see also Fig. 3), the ‘partially weighted’ and the ‘fully weighted’ degrees of unsaturation are close or even equal. The existence of fatty acids with three (e.g. linolenic) or more double bonds is reflected in the differences between the ‘partially’ and the ‘fully weighted’ degrees of unsaturation in Table 4. The most obvious cases where the ‘partially’ and the ‘fully weighted’ unsaturation degrees differ by a lot are those feedstocks that are rich in linolenic (primarily linseed, and to a lesser extent rubber seed, and rapeseed/canola) or even more highly unsaturated acids (fish).

For what is worth, Table 4 also provides the average values of unsaturation from all feedstocks, and, most importantly, the correlations between the various degrees of unsaturation with the iodine number of the final methyl ester. It is the ‘fully-weighted’ degree of unsaturation, or otherwise known as the average number of double bonds, that exhibits the strongest correlation with the respective FAME iodine number (see next paragraph). The latter unsaturation degree will thus be used in the following sub-sections for the investigation and the corresponding graphical depiction of the various correlations established between the physical and chemical properties of the 26 biodiesels analyzed.

To this aim, the results presented in Table 5 will also contribute; in this table, the Pearson correlation coefficients are demonstrated that were found to be valid for the inter-dependence between the various examined properties.

3.2.1. *Iodine value*

The iodine number (IN, or iodine value IV) is a parameter used to determine the degree of unsaturation in a vegetable oil or animal fat. This number indicates the mass of iodine (I_2) in grams that is necessary to completely saturate, by means of a stoichiometric reaction, the molecules of 100g of a given oil [21]. The (average) iodine values of the examined feedstocks range from 7.8 (for the most saturated ME, coconut) to 184.5 (for the most unsaturated one, linseed), with an overall average value of 98.4. There is no specification in the US for the IN, but European specifications require that biodiesels used in compression ignition engines have a (rather low) maximum value of IN of the order of 120. The idea behind this specification is that high fuel iodine values indicate propensity for polymerization resulting in deposit formation [8]. This means that many of the investigated FAMES have to be excluded from use in pure form in Europe, namely croton, fish, linseed, rubber seed and safflower, whereas corn, soybean and sunflower are only marginally accepted (see Fig. 4); moreover, the most popular in Europe rapeseed ME, having an average IV of 112, is actually quite close to the specification limit.

As it is illustrated in Fig. 5, there exists a very strong correlation between IN and unsaturation degree, confirming the results of previous research on smaller samples [14,15,19]; in fact, it is the 3 'extreme' feedstocks (the most saturated, coconut, and the most unsaturated, fish and linseed) that only differentiate from the almost perfect linear relationship between average number of double bonds and IN. The respective linear best-fit relation is also provided inside this figure. High INs have been also linked with storage stability problems [16], a fact however, that could not be confirmed by the present statistical investigation, at least partly owing to the great disparity of the reported oxidation stability values between the various researchers (Table 3 and Section 3.2.10).

3.2.2. *Cetane number*

One of the most influential properties of the diesel fuel is the dimensionless cetane number (CN), which represents the ignitability of the fuel, particularly critical during cold starting conditions. Low cetane numbers lead to long ignition delay, i.e. long time between fuel injection and start of combustion. Consequently, the lower the CN the more abrupt the

premixed combustion phase, leading also to higher combustion noise radiation [22]. On the other hand, higher cetane numbers promote faster auto-ignition of the fuel, and often lead to lower NO_x emissions [23,24] (although no unambiguous trend has been established), particularly during low-load (i.e. premixed-controlled) engine operation [2,25]. A lot of researchers prefer to provide the cetane index instead of (or combined with) the cetane number; the cetane index is calculated based on the fuel's density and distillation curve.

The cetane number of biodiesel (unlike what is valid for the originating vegetable oils or animal fats) is usually higher, sometimes by a lot, than that of the conventional diesel fuel. Excluding castor, the (average) cetane numbers of the 25 feedstocks range from 50.4 for rubber seed methyl ester to 61.2 for PME, with the mean value from all feedstocks being 54.8; that is 8–10% higher than that of petrodiesel. Castor biodiesel, on the other hand, differentiates considerably, with an average CN=42.1, but also a high standard deviation of 6.83. Graboski and McCormick [8] argued that the broad range of observed biodiesel CNs may be caused by a) differences in the fractional conversion of triglycerides to ester, and b) by presence of residual methanol and glycerol in the final fuel; the second argument, however, has not been confirmed by the present statistical analysis, which included methanol and (free and total) glycerol effects. It has also been argued that the effect of blending biodiesel on the CN is approximately linear for mixtures of esters with diesel fuel [8].

European specifications dictate a cetane number of (bio)diesel fuel of at least 51, which means that some of the investigated feedstocks, namely castor, croton and rubber seed lie outside the acceptable limits in pure form (Fig. 4), whereas other common feedstocks, such as safflower, sunflower, fish, linseed and the very popular in America soybean are only marginally accepted. On the contrary, in the US the minimum CN limit is much lower (47), a fact that practically renders all analyzed feedstocks acceptable, except for B100 castor.

As is made obvious in Fig. 6 that illustrates the inter-dependence between cetane number and the degree of unsaturation, a significant correlation ($R^2=0.77$) between CN and the number of double bonds is established. Cetane number decreases as the number of double bonds (or the unsaturation) increases, i.e. as the composition becomes richer in linoleic and/or linolenic acids. In contrast, highly saturated esters such as those derived from coconut, palm and tallow exhibit the highest values of CN. From the analysis it can

be extrapolated that FAMEs with more than 1.84 double bonds in their molecule (corresponds to $IN=148$) do not meet the minimum European specification of $CN=51$. On the other hand, no clear correlation could be established between the FAME's cetane number and the average chain length. In the literature [8,13,26] it has been shown that CN increases as the chain length increases or branching decreases. A notable example for the latter dependence is the existence of the branched γ -OH radical in the ricinoleic acid of castor oil that most probably explains the latter FAME's low CN compared with other equally mono-unsaturated oils. As regards the inter-dependence between CN and chain length, this argument holds true vis-a-vis pure fatty acid esters (e.g. (18:0) stearic acid ME has a higher CN value than (16:0) palmitic acid ME, which in turn has higher CN than (14:0) myristic acid ME etc). Since biodiesels are mixtures of a variety of pure fatty acids esters, the above correlation with chain length weakens considerably in the final FAMEs, which, as documented in Table 4, with the exception of coconut, demonstrate very close values of chain length.

Lastly, Table 5 documents that there exists a noteworthy correlation between CN and other FAME properties, namely density (see also next section), LHV, viscosity, cloud and pour point, oxygen content, T_{90} distillation temperature and stoichiometric air-fuel ratio.

3.2.3. Density

The density of a material or liquid is defined as its mass per unit volume. Many researchers prefer the dimensionless term specific gravity, which is defined as the ratio of the density of a substance to the density of a reference substance (usually water). Biodiesel fuels are, in general, characterized by higher density than conventional petroleum diesel, which means that volumetrically-operating fuel pumps will inject greater mass of biodiesel than conventional diesel fuel. This in turn will affect the air-fuel ratio hence the local gas temperatures and NO_x emissions, as long as the engine retains its diesel-fuel calibration. Actually, it has been argued that there exists a correlation between density and NO_x emissions, with lower densities favoring lower NO_x [24], although other researchers have not confirmed such an unequivocal trend.

The (average) densities of the 25 investigated methyl esters, again excluding castor, range from 870.8 to 891.5 kg/m^3 , with the overall average value being 880.2 kg/m^3 (i.e. almost 5% higher than the corresponding petrodiesel value). It is again the castor

biodiesel that differentiates considerably from the other feedstocks, with an average density of the order of 917.6 kg/m³. In the US, there is no specification for biodiesel density; in the EU on the other hand, the acceptable range is quite wide (860–900 kg/m³), and this is met by all examined methyl esters except for the pure castor biodiesel.

Fig. 7 demonstrates the strong correlation between density and the degree of unsaturation, with a clearly high coefficient of determination ($R^2=0.86$). Density increases with the increase in the number of double bonds, which means that the more unsaturated the originating oil, the higher the density of the derived methyl ester, and the greater the fuel mass that will be injected if a diesel-tuned engine is run on biodiesel. This strong correlation is maintained to a large extent ($R^2=0.58$) even if we move from the average values (Fig. 7) to the individual ones (Fig. 8) from all available pairs of density-IN in the database (158 observations from 25 feedstocks). As was also the case with cetane number, no correlation could be established between density and the FAME's average chain length, even if the 'extreme' values of coconut and castor are excluded [19]. The correlation, however, between density and cetane number ($R^2=0.57$) from all investigated feedstocks is presented in Fig. 9, with higher densities imparting lower cetane numbers.

Moreover, and according to Table 5, a significant correlation is valid between density and both heating values, viscosity, cloud and pour point, carbon content, T_{90} distillation temperature and stoichiometric air-fuel ratio.

3.2.4. Heating value

The lower (LHV) and the higher (HHV) heating values are measures of a fuel's heat of combustion, with the difference between them being the water's heat of vaporization. Biodiesel contains on average 10–12% w/w oxygen, which leads to proportionally lower energy density and heating value, thus more fuel needs to be injected in order to achieve the same engine power output. It is rather well established today from the extensive experimentation that the decrease in PM/smoke emissions with the use of biodiesel (or from other biofuels such as alcohols) derives from the higher oxygen content of the biofuel-diesel fuel blend that enhances the in-cylinder soot oxidation rate. The higher the oxygen content, hence the lower the heating value, the higher the potential for PM reduction [1–3]. On the other hand, the fact that greater mass of biodiesel needs to be injected in order to achieve the same engine power as with conventional diesel fuel is responsible for an increase in NO_x emissions in EGR equipped engines/vehicles; the latter

engines rely on the mass flow signal in order to determine the appropriate EGR valve position [27].

Previous research has shown that the energy content of fatty acid methyl esters is directly proportional to chain length (again for pure fatty acids) [28], whereas FAME with similar C:O but lower C:H ratios (i.e. more hydrogen) exhibit greater LHV. As a result, lower energy content is obtained from progressively greater levels of unsaturation for methyl esters of similar chain length [29].

There is no specification as regards the biodiesel heating value, neither in the EU nor in the US. According to the values presented in Table 3 and Fig. 4, the 26 studied methyl esters exhibit LHV from 35,990 (for the most saturated biodiesel, coconut ME) to 38,800 kJ/kg (for one of the most unsaturated FAMEs, fish), with an average value of 37,610 kJ/kg; this is 10–11% lower than the corresponding mineral diesel fuel's LHV (practically the same percentage as the typical biodiesel oxygen content). For the HHV, accordingly, it is 38,980 (coconut)–40,550 kJ/kg (fish), and the overall average value is 40,100 kJ/kg. Fig. 10 illustrates the effect of unsaturation on the heating values and shows that increasing the unsaturation or the number of double bonds, results in a moderate increase in the FAME heating value [23]; the relationship is more important for the LHV although not very strong. Moreover according to Table 5 (Pearson correlation coefficients), both heating values correlate rather well with the oxygen content, whereas LHV seems to have a noteworthy inter-dependence with viscosity and cloud point. It should be mentioned however, that a) linseed, castor (HHV only) and coconut exhibit high disparity (Table 3a) due to very few values available; b) oddly, karanja seems to differentiate by a lot from the other values as regards the LHV, with more than one different researchers having measured low surprisingly LHV values. In any case, both the reading of the values in Table 3 and the graphical illustration of the results in Fig. 10 should be made with great caution, because many researchers did not actually clarify which heating value (lower or higher) they measured.

3.2.5. Kinematic viscosity

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear or tensile stress. For the case of liquid fuels, the less viscous the fluid is, the greater its ease of movement (fluidity). In a diesel engine, higher viscosity leads to less accurate operation of the fuel injectors, and to poorer atomization of the fuel spray, increase in the

Sauter mean diameter of the fuel droplets and of the jet break-up time; these inefficiencies are exaggerated during cold starting. Moreover, the reduced fuel leakage losses in the (mechanical) fuel pump owing to higher kinematic viscosity lead also to higher injection pressures and, hence, mass of injected fuel [11].

Vegetable oils have high viscosity (one order of magnitude higher than the acceptable diesel fuel values), which means that they cannot be used safely as fuels in a compression ignition engine, at least not without prior heating (viscosity decreases exponentially with increasing temperature), and only for relatively small blending ratios. The transesterification process, on the other hand, reduces considerably the viscosity of the FAME to levels comparable to (but still higher than) that of petrodiesel.

The (average) viscosity values of the 25 examined feedstocks, excluding castor, range from 2.78 mm²/s (for the most saturated coconut ME; actually, this is the only one of the investigated methyl esters with a kinematic viscosity very close to that of the mineral diesel fuel) to 5.06 mm²/s (for mahua ME), with the mean value from all feedstocks being 4.55 mm²/s. European specifications dictate an acceptable biodiesel viscosity range between 3.5 and 5 mm²/s, which means that it is the above mentioned two extremes (but also marginally olive and karanja) that should be excluded in B100 form. In the US on the contrary, the specified range is much wider (1.9–6 mm²/s), a fact that renders all 25 analyzed feedstocks acceptable. Apart from coconut, another ME whose viscosity differentiates by a lot from the other feedstocks is castor. Castor biodiesel is rich in ricinoleic acid (contains OH) that significantly increases the viscosity of the final ester. For castor ME, the average kinematic viscosity from the reviewed studies was found to be 14.5 mm²/s, i.e. almost three times higher than that of the majority of the MEs reported in Table 3 and Fig. 4.

As is made clear in Fig. 11 that illustrates the inter-dependence between kinematic viscosity and the degree of unsaturation, a correlation exists (although not as strong as those observed for CN or density) between kinematic viscosity and the average number of double bonds. It should be pointed out that for the results depicted in Fig. 11, 24 methyl esters have been taken under consideration (coconut and castor were excluded since their values fall way beyond the ones from the other feedstocks). Confirming the results of previous research [30], the higher the saturation of the FAME, the higher the corresponding kinematic viscosity. If the feedstocks that present the highest disparity (mahua, safflower, olive, karanja, rubber seed) are excluded, then for the remaining 19

feedstocks, a promising correlation exists too between viscosity and density (Fig. 12), at least equally strong as the one between viscosity and unsaturation. Although the existence of double bonds reduces viscosity, it has been argued that it is actually the *cis* double bonds that are more responsible for lower viscosities than their *trans* counterparts (the latter are usually found in used cooking oils) [31].

Viscosity is also known to increase with increasing chain length [18,32], whereas branching seems to play a secondary role [31]. Although, the majority of the examined MEs have a chain length between 17 and 18 carbon atoms (and they actually have comparable viscosities as is illustrated in Fig. 11), coconut ME, which is the only biodiesel that drastically differentiates as regards the number of carbon atoms (13.12), unsurprisingly exhibits also the lowest viscosity.

Lastly, Table 5 documents that apart from IN and density, there exists a noteworthy correlation between viscosity and CN, density, LHV, carbon content, T_{90} distillation temperature and stoichiometric air-fuel ratio.

3.2.6. Flash point

The flash point (FP) is a measure of the temperature to which a fuel must be heated such that the mixture of vapor and air above the fuel can be ignited; FP varies inversely with the fuel's volatility. As is documented in the values presented in Table 3 and Fig. 4, storage of neat biodiesel is thus much safer than diesel in this regard. Specifically, the (average) values of flash point for all 26 examined feedstocks in the present work range from 127.7°C (for the most saturated FAME, coconut) to 174.5°C (peanut ME), with the mean value from all feedstocks being 163.3°C. European specifications require biodiesel fuels to have at least 101°C flash point, whereas in the US the minimum required level is lower (93°C); both are meant to determine a lower limit of purity in the final FAME, and are easily met by all studied biodiesel feedstocks. It should be noted that some researchers have reported very low values of flash point, i.e. lower than 80°C; these were not included in the database, since they were usually indicative of increased residual methanol, in other words, decreased purity of the final ester.

Although flash point depends, in general, on the originating oil, it is not directly linked to the fatty acid composition [33], and this is documented in Fig. 13 that illustrates the (rather weak) correlation between flash point and degree of unsaturation (coconut ME is excluded), although a slight increasing trend is noticed as the number of double bonds

increases. Apart from coconut, it is the values from mahua, peanut and croton that primarily seem to differentiate by a lot from the general trend. Closer examination of the flash point standard deviations in Table 3 reveals that the disparity in the reported FP values is high for the majority of the methyl esters studied (most probably owing to varying methanol fluctuation in the final ester), and this seems to explain the weak correlation demonstrated in Fig. 13. Moreover as is documented in Table 5, FP was not found to correlate well with any other property.

3.2.7. Low-temperature flow properties

The key flow properties for winter fuel specification are cloud and pour point. Cloud point (CP) is the temperature at which wax form a cloudy appearance. It is measured as the temperature of first formation of wax as the fuel is cooled. Pour point (PP) is the lowest temperature at which the fuel becomes semi solid and loses its flow characteristics being no longer pumpable; hence it is a measure of the fuel gelling point. The pour point is always lower than the cloud point. The cloud point is not generally affected by additives called flow improvers. However, flow-improver additives can decrease the size, or inhibit the formation, of the wax crystallites formed upon cooling the fuel, and thus lower the temperature at which wax plugging becomes a problem [8]. Poor cold flow properties may result in fuel line and pump blockage, ultimately leading to fuel starvation. These problems are particularly enhanced during cold starting particularly at low ambient temperatures. The two cold flow properties are highly inter-dependent, as is demonstrated in Fig. 14 that depicts all 170 available pairs of CP and PP values in the database; if only the average CP and PP values from the 26 biodiesels are taken under consideration, the correlation is even higher ($R^2=0.90$; Pearson correlation coefficient 0.92).

There are no European or US specifications for low temperature properties (each country is free to determine its own limits according to local weather conditions), but it is well known that biodiesel fuels suffer from cold flow properties way more (i.e. they are higher) than mineral diesel fuel. The (average) values of CP for the 26 examined feedstocks in the present work confirm this fact; they range from -15.1°C (castor ME; however with 12.5°C standard deviation, which indicates contradicting results) to 13.8°C (tallow ME), with the mean value from all feedstocks being 2.1°C (almost 20°C higher than for conventional diesel fuel). For PP, it is -23.4°C (again castor ME; standard deviation 3.9°C) up to 11.8°C (palm ME), with an overall mean value of -2°C (more than 30°C

higher than conventional diesel fuel). Apart from tallow and palm, other MEs with bad cold flow properties are rice bran, karanja, chicken, lard (i.e. all ground-animal-fat derived), mahua and neem, whereas the best biodiesels in this respect are castor, canola/rapeseed, safflower, croton, linseed, corn and olive.

In general, saturated acids exhibit higher freezing points than unsaturated ones. For example, stearic acid is solid at 70°C, while oleic acid melts at 16°C. The only chemical difference between them is the existence of a double bond in the structure of oleic acid. Hence it seems that for freezing points, the chemical structure is very influential [8]. Figs 15 and 16 illustrate the correlation between CP (Fig. 15) and PP (Fig. 16) with the degree of unsaturation for overall 23 feedstocks (castor, coconut and hazelnut MEs are excluded), and confirm the above findings; similar trends exist for the cold filter plugging point (CFPP). Although the respective values of R^2 are not very high (0.62 for CP and 0.54 for PP, even lower for CFPP), it is obvious that the lower the saturation the lower the cloud and pour points, with highly saturated MEs, such as palm and tallow, exhibiting very high values (of the order of >10°C) [29]. In fact, Imahara et al. [34] developing a prediction model to estimate CP of biodiesel from various fats/oils, argued that CP is determined mainly by the amount of saturated esters, and does not depend on the composition of unsaturated ones.

Particularly as regards the cloud point, the castor, croton, fish, mahua and neem MEs differentiate by a lot from the other values; it is the same MEs that also present the highest standard deviation in Table 3, which means that more CP and PP values are required for a more accurate representation. As was also the case with the previously examined properties, no correlation could be established with the average chain length, although it is known that for pure esters, reducing the chain length improves the cold flow properties [8,35]. On the other hand, both PP and CP correlate well with CFPP, density and cetane number, but also with the FAME carbon content and the molecular weight (Table 5).

In order to enhance the poor cold flow properties of biodiesel, various measures have been suggested, such as the use of cold-flow improvers [36], ethyl or iso-propyl esterification (of higher cost than the use of methanol), removal of those components that have high melting points (e.g. stearic and palmitic), or even modification of the fatty acid composition of the originating oil in order to produce an ester with optimum characteristics (concerns arise in this case over genetic modification issues) [13,28,35].

3.2.8. Carbon content and stoichiometric air-fuel ratio

Fig. 17 demonstrates the correlation between FAME carbon content and number of carbon atoms with the respective degree of unsaturation (coefficient of determination $R^2=0.79$ and 0.69 respectively). Since not many researchers provide values for these two 'properties' (particularly for the number of carbon atoms), the corresponding sample is narrower compared with the previous properties. It seems that the higher the unsaturation of the originating feedstock, the higher the carbon content although the absolute differences are small. Nonetheless, no such correlation could be established for the hydrogen content. Apart from the degree of unsaturation, Table 5 shows that the FAME carbon content correlates rather well with the CN, density, viscosity and all cold flow temperatures (corresponding R^2 values higher than 0.50).

Further, Fig. 18 demonstrates the inter-dependence between the stoichiometric air-fuel ratio and the level of unsaturation, with highly unsaturated feedstocks leading to lower AF_{st} values, although, again, the absolute differences are relatively small, as is also the corresponding feedstock sample. As was also the case with the carbon content, the FAME AF_{st} correlates well with the CN, density, viscosity, HHV and, interestingly, oxidation stability (Table 5). In general, the stoichiometric air–fuel ratio is of the order of 12.5 for the neat biodiesel, whereas it is approximately 15 for the neat diesel fuel. This means that the air–biodiesel mixtures can reach the stoichiometric conditions nearly 15% faster than their air–diesel counterparts. It is expected that this difference in the air–fuel ratio, caused by the presence of bound oxygen in the biodiesel, must influence combustion. More specifically, if the combustion process is mixing controlled, the use of biodiesel injection has a beneficial effect, while if the combustion process is evaporation controlled, the effect is adverse [11].

3.2.9. Distillation temperature

Distillation is a method of separating mixtures based on differences in volatilities of components in a boiling liquid mixture. While petrodiesel contains hundreds of different compounds (resulting in highly variable distillation curves), in Table 2 it was demonstrated that most biodiesels generally contain a few number of major fatty acid compounds; these boil at roughly the same temperature (approximately $330\text{--}357^\circ\text{C}$ at atmospheric pressure). The distillation temperature specification has been incorporated to ensure that fuels have not been contaminated with high boiling materials such as used motor oil. Hence, the

distillation of biodiesel fuel is a method that actually provides a demonstration of the FAME's quality [37]. In fact, in cases where unusually low distillation temperatures were reported, these were actually combined with low CN and flash point, indicative of high residual amounts of methanol and/or glycerol content.

The values measured/reported in the literature correspond to initial, 10%, 50%, 90% (T_{90}) and final distillation temperature. Only the (most common) T_{90} will be considered here, for which a relatively large amount of reported values is available from 18 out of the 26 methyl esters (in general, distillation temperature has not received great attention in the literature). There are no European specifications for biodiesel distillation, whereas in the US an upper limit of 360°C is dictated for T_{90} .

The (average) values for T_{90} in the database range from 333.5°C (mahua ME) to 361°C (linseed and fish), with the mean value from all feedstocks being 347.7°C; near the high end of the range reported for diesel. Consequently, only linseed and fish MEs could be marginally rejected based on the US specifications. Fig. 19 demonstrates the correlation between T_{90} and the degree of unsaturation for 18 MEs. In the literature it has been argued that boiling temperatures are in general dependent on chain length but with minor dependence on unsaturation [8,33]. The data illustrated in Fig. 19 from the statistical investigation, however, indicate that increasing the number of double bonds increases also the distillation temperature, with highly unsaturated feedstocks, such as linseed and fish (rich in tri- and higher unsaturated acids) exhibiting the highest values of T_{90} . In support to this argument, Fig. 20 demonstrates the whole distillation curves for some biodiesels for which an adequate amount of data was available for all distillation temperatures. Other notable correlations exist between T_{90} and CN, density, viscosity, cloud point and carbon and oxygen content of the FAME (Table 5).

3.2.10. Oxidative stability

One of the major issues that limit the use of biodiesel as a fuel in compression ignition engines is its poor oxidative stability. A brief inspection of Table 3 reveals that only a few of the investigated biodiesels fulfill the European specification of 6h oxidation stability using the Rancimat method (EN 14112). The US specifications are also in this case more lenient, hence biodiesel produced from feedstocks such as corn, coconut, fish, jatropha and karanja could be approved. In any case, as was mentioned earlier, the results of Table 3 and Fig. 4 regarding the oxidative stability index (OSI) should be

interpreted carefully since many researchers used additives or did not apply the same esterification clean-up or storage conditions, all of which influence considerably the oxidation values.

In general, it is the poly-unsaturated methyl esters such as croton, safflower, soybean, linseed, and sunflower, rich in linoleic and linolenic acids, that are prone to oxidative degradation [13,35,38]. On the contrary saturated fatty acids such as coconut, palm and animal fat are oxidatively more stable. The oxidation process is further enhanced by factors such as presence of air and/or metals, and high storage temperatures. The auto-oxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds. The CH₂ positions allylic to double bonds in the fatty acid chains are those susceptible to oxidation. The bis-allylic positions in poly-unsaturated fatty acids, such as linoleic acid (double bonds at C-9 and C-12, giving one bis-allylic position at C-11) and linolenic acid (double bonds at C-9, C-12, and C-15, giving two bis-allylic positions at C-11 and C-14), are even more prone to autoxidation than allylic positions [35]. Relative rates of oxidation have been reported to be 1 for oleates, 41 for linoleates, and 98 for linolenates [39]. However, the unsaturation degree is not the only variable affecting the oxidation stability. The presence of water and other compounds derived either from external contamination or from thermal degradation (the last two being more likely in the case of oils that have been used for cooking) may also promote oxidation. Also the reduction in the natural anti-oxidants when the oil is subjected to a frying process contributes to the lower oxidation stability of waste cooking oils esters documented in Table 3 [40].

A rather promising in terms of oxidation stability feedstock seems to be castor, which has been measured by many researchers to exhibit high OSI values (even of the order of tens of hours). This is most probably associated with the fact that cold-extracted castor oil has relatively high content of natural anti-oxidants [33]. Another promising alternative has been proposed by Sarin et al. [41], who found that the oxidation stability of jatropha ME can be improved through blending with the more oxidatively stable palm ME.

4. Summary and conclusion

A huge amount of data published in International Journals, Conferences and from renowned research centers was gathered and analyzed as regards the biodiesel physical

and chemical properties and the respective fatty acid composition. Overall, 26 biodiesel feedstocks were investigated from data reported in more than 750 paper/reports published during the last 3 decades. From the data gathered, average values and standard deviations were provided for all interesting oil/fats fatty acid compositions and for the respective biodiesels' physical and chemical properties with reference to the specifications valid in the EU and the US. The most important (feedstock-related) properties of biodiesel were discussed with respect to the real engine operation and the possible inefficiencies they may induce. Moreover, they were correlated with the degree of unsaturation of the parent oil/fat, providing also linear best-fit curves that are believed to prove useful in future simulation studies as well as long-term planning by institutions and administrations. The degree of unsaturation (average number of double bonds) was found to correlate excellently with the iodine number; a high statistical correlation ($R^2 > 0.60$) was also established for cetane number, density, pour point, carbon content, number of carbon atoms, stoichiometric air-fuel ratio and T_{90} distillate temperature. Smaller but still significant correlations were established between unsaturation and kinematic viscosity, lower and higher heating values, cloud point and flash point.

Since the composition of the parent oil/fat was found to affect the final ester's properties decisively, a question arises as to which is the biodiesel feedstock with the best properties, or whether it is more preferable to use saturated or unsaturated oils for the production of methyl esters. Although production cost, apart from the chemical properties, plays a pivotal role here, it is not easy to answer this question in a single and irrevocable manner. Saturated feedstocks (such as those derived from coconut, palm and tallow) excel in cetane number and oxidation stability (and usually lower NO_x emissions), while exhibiting poor cold flow properties, higher kinematic viscosity, lower (but still high enough) flash point and lower heating value. In contrast, increasing the unsaturation decreases the kinematic viscosity, improves the cold flow properties (additives are most probably still required) and increases moderately the heating value, but also lowers the CN and deteriorates the oxidation stability. Interestingly, it is the most unsaturated feedstocks that are susceptible to rejection based on the existing specification limits. Specifically, and based on the linear best-fit curves derived, feedstocks with more than 1.47 double bonds in their molecule (corn, croton, fish, linseed, rubber seed, safflower, sunflower, soybean) have to be excluded in Europe in pure form on the grounds of IN higher than 120. Further, if the number of double bonds is higher than 1.84 (corresponds

to $IN > 148$), then the minimum European limit of $CN = 51$ is not probably met, whereas for more than 2.15 double bonds ($IN > 171$; linseed only) it seems that the American upper limit of T_{90} might not be met too.

There are two feedstocks that differentiate by a lot from the others, i.e. coconut and castor. Coconut ME is the most saturated biodiesel, and is characterized by low viscosity and high cetane number. Castor, on the other hand, although exhibiting excellent oxidation stability and at the same time has very good cold flow properties, fails to fulfill three major fuel specifications namely, cetane number, viscosity and density. Interestingly, the most popular ME worldwide, SME, should be rejected in pure form in Europe since it does not meet the (rather strict) IN , the oxidation stability and usually the CN specification. Other feedstocks that do not (or only marginally) fulfill at least two specifications in the EU or the US are the most unsaturated ones, namely linseed, fish, safflower, sunflower rubber seed and croton. In any case, the use of the more realistic smaller biodiesel ratios, e.g. up to 20% v/v in the fuel blend, tends to reduce considerably the differences between the various feedstocks, and renders practically all biodiesel blends acceptable, with the possible exception of castor.

References

- [1] Hansen AC, Kyritsis DC, Lee CF. Characteristics of biofuels and renewable fuel standards. In: Vertes AA, Qureshi N, Blaschek HP, Yukawa H, editors. Biomass to biofuels - Strategies for global industries. Oxford: Blackwell Publishing; 2009.
- [2] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends”, *Progr Energy Combust Sci* 2012 (doi:10.1016/j.pecs.2012.05.002).
- [3] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels in internal combustion engines. *Progr Energy Combust Sci* 2007;32:233–71.
- [4] Directive 2009/28/EC of the European Parliament and of the Council on the promotion of the use of energy from renewable sources, 2009.
- [5] Komninos NP, Rakopoulos CD. Modeling HCCI combustion of biofuels: A review. *Renew Sustain Energy Rev* 2012;16:1588–610.
- [6] Gallagher BJ. The economics of producing biodiesel from algae. *Renew Energy* 2011;36:158–62.
- [7] Pinzi S, Garcia IL, Lopez-Gimenez FJ, Luque de Castro MD, Dorado G, Dorado MP. The ideal vegetable oil-based biodiesel composition: A review of social, economic and technical implications. *Energy Fuels* 2009;23:2325–41.
- [8] Graboski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. *Progr Energy Combust Sci* 1998;24:125–64.
- [9] Demirbas A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progr Energy Combust Sci* 2005;31:466–87.
- [10] Gog A, Roman M, Toca M, Paizs C, Irimie FD. Biodiesel production using enzymatic transesterification – Current state and perspectives. *Renew Energy* 2012;39:10–16.
- [11] Rakopoulos CD, Antonopoulos KA, Rakopoulos DC, Hountalas DT, Giakoumis EG. Comparative performance and emissions study of a direct injection diesel engine using blends of diesel fuel with vegetable oils or biodiesels of various origins. *Energy Convers Manage* 2006;47:3272–87.
- [12] US Environmental Protection Agency. A comprehensive analysis of biodiesel impacts on exhaust emissions. Draft Technical Report. EPA 420-P-02-001, US, EPA, Washington DC, USA 2002.
- [13] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process Technol* 2005;86:1059–70.

- [14] Gopinath A, Puhan S, Nagarajan G. Theoretical modeling of iodine value and saponification value of biodiesel fuels from their fatty acid composition. *Renew Energy* 2009;34:1806–11.
- [15] Ramos MJ, Fernandez CM, Casas A, Rodriguez L, Perez A. Influence of fatty acid composition of raw materials on biodiesel properties. *Biores Technol* 2009;100:261–8.
- [16] Pinzi S, Leiva D, Arzamendi G, Gandia LM, Dorado MP. Multiple response optimization of vegetable oils fatty acid composition to improve biodiesel physical properties. *Biores Technol* 2011;102:7280–8.
- [17] Demirbas A. Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel* 2008;87:1743–8.
- [18] Ramirez-Verduzco LF, Rodriguez- Rodriguez JE, Jaramillo-Jacob ADR. Prediction of cetane number, kinematic viscosity, density, and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel* 2012;91:102–11.
- [19] Hoekman SK, Broch A, Robbins C, Cenicerros E, Natarajan M. Review of biodiesel composition, properties and specifications. *Renew Sustain Enege Rev* 2012;16:143–69.
- [20] Gui MM, Li KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy* 2008;33:1646–53.
- [21] Lapuerta M, Rodriguez-Fernandez J, de Mora EF. Correlation for the estimation of the cetane number of biodiesel fuels and implications on the iodine number. *Energy Policy* 2009;37:4337–44.
- [22] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Combustion noise radiation during acceleration of a turbocharged diesel engine operating with biodiesel or n-butanol diesel fuel blends. *IMEchE* 2012;226 (Part D);226:971–86.
- [23] Peterson CL, Taberski JS, Thompson JC, Chase CL. The effects of biodiesel feedstock on regulated emissions in chassis dynamometer tests of a pickup truck. *Trans ASABE* 2000;43:1371–81.
- [24] McCormick RL, Graboski MS, Alleman TL, Herring AM. Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. *Environ Sci Technol* 2001;35:1742–7.
- [25] Zhang Y, Boehman AL. Impact of biodiesel on NO_x emissions in a common rail direct injection diesel engine. *Energy Fuels* 2007;21:2003–12.
- [26] Klopfenstein WE. Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels. *J Am Oil Chem Soc* 1985;62:1029–31.
- [27] Rakopoulos CD, Giakoumis EG. Diesel engine transient operation. London: Springer; 2009.

- [28] Knothe G. "Designer" biodiesel: optimizing fatty ester composition to improve fuel properties. *Energy Fuels* 2008;22:1358–64.
- [29] Moser BR, Williams A, Haas MJ, McCormick RL. Exhaust emissions and fuel properties of partially hydrogenated soybean oil methyl esters blended with ultra low sulfur diesel fuel. *Fuel Process Technol* 2009;9:1122–8.
- [30] Allen CAW, Watts KC, Ackman RG, Pegg MJ. Predicting the viscosity of biodiesel fuels from their fatty acid ester composition. *Fuel* 1999;78:1319–26.
- [31] Knothe G, Steidler KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. *Fuel* 2005;84:1059–65.
- [32] Rodrigues JA, Cardoso FP, Lachter ER, Estevao LRM, Lima E, Nascimento RSV. Correlating chemical structure and physical properties of vegetable oil esters. *J Am Oil Chem Soc* 2006;83:353–7.
- [33] Berman P, Nizri S, Wiesman Z. Castor oil biodiesel and its blends as alternative fuel. *Biomass Bioenergy* 2011;35:2861–6.
- [34] Imahara H, Minami E, Saka S. Thermodynamic study on cloud point of biodiesel with its fatty acid composition. *Fuel* 2006;85:1666–70.
- [35] Knothe G. Improving biodiesel fuel properties by modifying fatty ester composition. *Energy Environ Sci* 2009;2:759–66.
- [36] Bhale PV, Deshpande NV, Thombre SB. Improving the low temperature properties of biodiesel fuel. *Renew Energy* 2009;34:794–800.
- [37] Smith BL, Ott LS, Bruno TJ. Composition-explicit distillation curves of commercial biodiesel fuels: comparison of petroleum-derived fuel with B20 and B100. *Ind Eng Chem Res* 2008;47:5832–40.
- [38] Moser BR. Comparative oxidative stability of fatty acid alkyl esters by accelerated methods. *J Am Oil Chem Soc* 2009;86:699–706.
- [39] Holman RA, Elmer OC. The rates of oxidation of unsaturated fatty acids and esters. *J Am Oil Chem Soc* 1947;24:127–9.
- [40] Lapuerta M, Rodriguez-Fernandez J, Ramos A, Alvarez B. Effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels. *Fuel* 2012;93:391–6.
- [41] Sarin R, Sharma M, Sinharay S, Malhotra RK. Jatropha-palm biodiesel blends: An optimum mix for Asia. *Fuel* 2007;86:1365–71.

Nomenclature

Abbreviations

AF _{st}	stoichiometric air-fuel ratio
CFPP	cold filter plugging point (°C)
CP	cloud point (°C)
EGR	exhaust gas recirculation
EU	European Union
FAME	fatty acid methyl ester
FP	flash point (°C)
HHV	higher heating value (kJ/kg)
IN/IV	iodine number/value
LHV	lower heating number (kJ/kg)
ME	methyl ester
MW	molecular weight
OSI	oxidation stability index
PM	particulate matter
PME	palm methyl ester
PP	pour point (°C)
R ²	coefficient of determination
RME	rapeseed methyl ester
SME	soybean methyl ester
T ₉₀	90% distillation temperature (°C)
v/v	% vol.
w/w	% mass

Table Captions

Table 1. European (EN 14214:2008) and US (ASTM D6751) specifications for biodiesel in comparison with conventional diesel fuel (test method in parentheses).

Table 2a. Fatty acid weight percentage in all analyzed vegetable oils (standard deviation in parentheses; absence of standard deviation indicates only one available value; only fatty acids with at least 0.05 percentage weight are referenced).

Table 2b. Fatty acid weight percentage in all analyzed animal fats (standard deviation in parentheses; only fatty acids with at least 0.05 percentage weight are referenced).

Table 3. Summarization of various biodiesel physical and chemical properties for all analyzed feedstocks (standard deviation in parentheses).

Table 4. Degree of unsaturation of the fatty acid oils considered, as well as its correlation with the FAME iodine number.

Table 5. Pearson coefficients for the correlations between the various FAME physical and chemical properties (light blue highlighted values have a coefficient higher than 0.80, and light green highlighted values have a coefficient between 0.60 and 0.79).

Figure Captions

Fig. 1. Number of observations (upper diagram) and percentage (lower diagram) of biodiesel datasets analyzed in the current study.

Fig. 2. Comparative illustration of saturated, mono- and poly-unsaturated percentage weights in all analyzed feedstocks (solid line corresponds to average values).

Fig. 3. Comparative illustration of specific fatty acids percentage weight in all analyzed feedstocks (solid line corresponds to average values).

Fig. 4. Comparative illustration of various biodiesel properties average values and corresponding standard deviations for all analyzed feedstocks; biodiesels are presented in order of increasing unsaturation.

Fig. 5. Correlation between oil/fat unsaturation level and FAME average iodine number from all 26 investigated feedstocks.

Fig. 6. Correlation between oil/fat unsaturation level and FAME average cetane number from 25 investigated feedstocks (castor excluded).

Fig. 7. Correlation between oil/fat unsaturation level and FAME average density from 25 investigated feedstocks (castor excluded).

Fig. 8. Correlation between FAME iodine number and density from 25 investigated feedstocks (158 observations excluding castor).

Fig. 9. Correlation between FAME average density and cetane number from 25 investigated feedstocks (castor excluded).

Fig. 10. Correlation between oil/fat unsaturation level and FAME average lower/higher heating values from all 26 investigated feedstocks.

Fig. 11. Correlation between oil/fat unsaturation level and FAME average kinematic viscosity from 24 investigated feedstocks (castor and coconut excluded).

Fig. 12. Correlation between FAME average density and kinematic viscosity from 19 investigated feedstocks.

Fig. 13. Correlation between oil/fat unsaturation level and FAME average flash point from all 26 investigated feedstocks.

Fig. 14. Correlation between FAME pour and cloud point from all 26 investigated feedstocks (170 observations).

Fig. 15. Correlation between oil/fat unsaturation level and FAME average cloud point from 23 investigated feedstocks (castor, coconut and hazelnut excluded).

Fig. 16. Correlation between oil/fat unsaturation level and FAME average pour point from 23 investigated feedstocks (castor, coconut and hazelnut values).

Fig. 17. Correlation between oil/fat unsaturation level and FAME average carbon content and number of carbon atoms.

Fig. 18. Correlation between oil/fat unsaturation level and FAME average stoichiometric air-fuel ratio from 7 investigated feedstocks.

Fig. 19. Correlation between oil/fat unsaturation level and FAME average T_{90} distillation temperature from 18 investigated feedstocks.

Fig. 20. Distillation curves for six biodiesels (sunflower SuME; corn CRME; rapeseed RME; soybean SME; beef tallow BTME, and palm PME).

Table 1. European (EN 14214:2008) and US (ASTM D6751) specifications for biodiesel in comparison with conventional diesel fuel (test method in parentheses).

PROPERTY	BIODIESEL		ULTRA LOW SULFUR DIESEL
	Europe EN 14214:2008	USA ASTM D6751	Europe EN 590
Density (kg/m ³ @ 15°C)	860–900 (EN 12185)	–	820–845
Viscosity (mm ² /s @ 40°C)	3.5–5.0 (EN 3104)	1.9–6.0 (D445)	2.0–4.5
Distillation (°C)	–	<360 @ 90% (D1160)	350 @ 85% ÷ 360 @ 95%
Flash point (°C)	>101 (EN 3679)	>93 (D93)	>55
Cold filter plugging point (°C)	country specific (EN 116)	–	country specific
Cloud point (°C)	country specific	– (D2500)	–
Sulfur content (mg/kg)	<10 (EN 20884)	<15 (D5453)	<10
Carbon residue (% w/w)	<0.30 (10% dist. residue) (EN 10370)	<0.05 (100% dist. residue) (D4530)	<0.30 (10% dist. residue)
Sulfated ash (% w/w)	<0.02 (EN 3987)	<0.02 (D874)	<0.01
Water (mg/kg)	<500 (EN 12937)	<500 (D2709)	<200
Contamination (mg/kg)	<24 (EN 12662)	–	<24
Copper strip corrosion (3h @ 50°C)	Class 1 (EN 2160)	Class 3 (D130)	Class 1
Oxidation stability (h @ 110°C)	>6h (EN 14112)	>3h (EN 14112)	(25 g/m ³)
Cetane number (-)	>51 (EN 5165)	>47 (D613)	>51
Acid value (mg KOH/g)	<0.5 (EN 14104)	<0.5 (D664)	–
Methanol (% w/w)	<0.20 (EN 14110)		–
Ester content (% w/w)	>96.5 (EN 14103)	–	–
Monoglyceride (% w/w)	<0.80 (EN 14105)	–	–
Diglyceride (% w/w)	<0.20 (EN 14105)	–	–
Triglyceride (% w/w)	<0.20 (EN 14105)	–	–
Free glycerol (% w/w)	<0.02 (EN 14105)	<0.02 (D6584)	–
Total glycerol (% w/w)	<0.25 (EN 14105)	<0.24 (D6584)	–
Iodine value (-)	<120 (EN 14111)	–	–
Linolenic acid ME (% w/w)	<12 (EN 14103)	–	–
Poly-unsaturated acid MEs (% w/w)	<1 (EN 14103)	–	–
Phosphorus (mg/kg)	<4 (EN 14107)	<10 (D4951)	–
Gp I metals (Na, K) (mg/kg)	<5 (EN 14538)		–
Gp II metals (Ca, Mg) (mg/kg)			–
PAHs (% w/w)	–	–	<11
Lubricity/wear (µm @ 60°C)	–	–	<460

	8:0 C ₈ H ₁₆ O ₂	10:0 C ₁₀ H ₂₀ O ₂	12:0 C ₁₂ H ₂₄ O ₂	14:0 C ₁₄ H ₂₈ O ₂	16:0 C ₁₆ H ₃₂ O ₂	16:1 C ₁₆ H ₃₀ O ₂	17:0 C ₁₇ H ₃₄ O ₂	18:0 C ₁₈ H ₃₆ O ₂	18:1 C ₁₈ H ₃₄ O ₂	18:1 OH C ₁₈ H ₃₄ O ₃	18:2 C ₁₈ H ₃₂ O ₂	18:3 C ₁₈ H ₃₀ O ₂	20:0 C ₂₀ H ₄₀ O ₂	20:1 C ₂₀ H ₃₈ O ₂	22:0 C ₂₂ H ₄₄ O ₂	22:1 C ₂₂ H ₄₂ O ₂	24:0 C ₂₄ H ₄₈ O ₂	Count
Mol. weight (kg/kmol)	144.21	172.26	200.32	228.37	256.42	254.41	270.45	284.48	282.46	298.46	280.45	278.43	312.53	310.51	340.58	338.57	368.63	
Formal (common) name	Octanoic (Caprylic)	Decanoic (Capric)	Dodecanoic (Lauric)	Tetradecanoic (Myristic)	Hexadecanoic (Palmitic)	cis-9 Hexadecenoic (Palmitoleic)	Heptadecanoic (Margaric)	Octadecanoic (Stearic)	cis-9 Octadecenoic (Oleic)	12-hydroxy, cis-9 Octadecenoic (Ricinoleic)	cis-9, cis-12 Octadecadienoic (Linoleic)	cis-9, cis-12, cis-15 Octadecatrienoic (Linolenic)	Eicosanoic (Arachidic)	cis-11 Eicosenoic (Gondoic)	Docosanoic (Behenic)	cis-13 Docosenoic (Erucic)	Tetra- cosanoic (Lignoceric)	
Animal Fat or Vegetable Oil																		
Canola	-	-	-	-	4.51 (0.82)	0.36 (0.34)	0.14 (0.71)	2.00 (0.63)	60.33 (2.05)	-	21.24 (1.55)	9.49 (1.60)	0.62 (0.37)	1.49 (0.83)	0.35 (0.10)	0.42 (0.29)	0.16 (0.11)	28
Castor (<i>ricinus communis</i>)	-	-	-	-	1.38 (0.50)	-	-	1.11 (0.42)	3.35 (0.70)	88.07 (1.85)	4.84 (0.76)	0.56 (0.34)	0.25 (0.08)	0.42 (0.14)	-	-	-	17
Coconut (<i>cocos nucifera</i>)	6.46 (2.11)	5.62 (1.34)	46.91 (5.45)	18.74 (1.34)	9.69 (1.52)	0.11 (0.10)	-	2.83 (0.58)	6.83 (1.71)	-	2.21 (1.30)	-	0.10 (0.06)	-	-	-	-	29
Corn (<i>zea mays</i>)	-	-	-	-	11.81 (1.07)	0.12 (0.20)	-	2.13 (0.45)	27.35 (2.84)	-	57.74 (3.88)	0.63 (0.40)	0.34 (0.29)	0.33 (0.51)	-	-	0.14 (0.05)	32
Cottonseed (<i>gossypium</i>)	-	-	-	0.72 (0.49)	25.93 (2.64)	0.36 (0.36)	-	1.74 (0.87)	15.98 (2.63)	-	55.12 (2.97)	0.16 (0.18)	0.22 (0.45)	0.07	0.11 (0.16)	-	-	24
<i>Croton (codiaeum variegatum)</i>				0.10	7.25 (2.81)	0.10	0.10	3.43 (0.95)	10.80 (1.56)	-	77.25 (6.85)	5.40 (2.12)		0.10				4
Hazelnut (<i>hazel corylus</i>)					6.32 (1.97)	0.30 (0.09)		3.71 (1.95)	79.17 (2.14)	-	10.67 (4.30)	0.15 (0.13)	0.10 (0.10)	0.10 (0.17)				5
Jatropha (<i>jatropha curcas</i>)	-	-	-	0.15 (0.29)	14.42 (1.94)	0.69 (0.36)	0.08 (0.06)	5.82 (1.77)	42.81 (3.50)	-	35.38 (4.87)	0.23 (0.26)	0.09 (0.09)	0.10 (0.09)	0.14 (0.23)	-	1.47 (2.28)	40
Karanja (<i>pongamia pinnata</i>)	-	-	-	-	10.89 (1.59)	-	-	7.89 (1.78)	53.56 (3.59)	-	21.34 (4.13)	2.09 (1.71)	1.82 (1.22)	1.15 (0.99)	4.11 (1.23)	-	1.33 (1.17)	13
Linseed (<i>linum usitatissimum</i>)	-	-	-	-	5.18 (0.88)	0.10 (0.11)	-	3.26 (1.11)	19.04 (2.23)	-	16.12 (1.72)	54.54 (5.93)	0.09 (0.10)	0.07 (0.10)	0.10 (0.06)	0.20 (0.40)	-	19
Mahua (<i>madhuca indica</i>)	-	-	-	0.15 (0.10)	22.23 (2.40)	-	-	22.49 (3.65)	39.01 (4.11)	-	14.87 (2.11)	0.10 (0.17)	1.01 (0.55)	-	-	-	-	10
Neem (<i>azadirachta indica</i>)			0.40 (0.57)	0.18 (0.28)	17.57 (1.14)			16.60 (1.92)	45.83 (5.16)	-	17.79 (3.70)	0.72 (0.69)	1.18		0.15 (0.21)			10
Olive (<i>olea europaea</i>)	-	-	-	0.05 (0.07)	11.47 (2.33)	0.90 (0.49)	0.07 (0.05)	2.83 (0.75)	74.52 (3.58)	-	9.54 (3.07)	0.51 (0.29)	0.49 (0.15)	0.29 (0.25)	0.16 (0.07)	-	0.17 (0.17)	31
Palm (<i>arecaceae</i>)	0.08 (0.05)	0.06 (0.05)	0.37 (0.28)	1.13 (0.96)	42.39 (2.81)	0.17 (0.12)	0.06 (0.06)	4.20 (0.86)	40.91 (2.97)	-	9.97 (1.54)	0.29 (0.20)	0.29 (0.13)	0.16 (0.06)	-	-	0.05 (0.05)	51
Peanut (<i>arachis hypogaea</i>)	-	-	-	-	10.33 (2.41)	-	-	2.79 (0.58)	47.63 (4.77)	-	31.52 (2.99)	0.64 (0.58)	1.07 (0.41)	1.48 (0.91)	2.86 (0.78)	0.10 (0.11)	1.30 (0.69)	16
Rapeseed (<i>brassica napus</i>)	-	-	-	0.04 (0.04)	4.07 (0.82)	0.23 (0.11)	0.07 (0.12)	1.55 (0.48)	62.24 (2.28)	-	20.61 (1.63)	8.72 (1.42)	0.87 (0.79)	1.09 (0.74)	0.27 (0.26)	0.71 (0.90)	-	47
Rice bran (<i>oryza sativa</i>)	-	-	0.08 (0.09)	0.45 (0.38)	18.12 (3.30)	0.20 (0.09)	-	2.17 (0.99)	42.35 (6.02)	-	34.84 (2.72)	0.93 (0.62)	0.45 (0.26)	0.22 (0.16)	0.21 (0.09)	-	0.16 (0.30)	19
Rubberseed (<i>hevea brasiliensis</i>)				0.51 (0.95)	9.39 (1.13)	0.13 (0.12)		9.41 (1.13)	24.22 (2.12)	-	38.12 (2.38)	17.54 (3.27)	0.28 (0.29)	0.12 (0.10)	0.08 (0.08)			7
Safflower (<i>carthamus tinctorius</i>)	-	-	-	0.08 (0.10)	7.42 (1.34)	0.05 (0.06)	-	2.38 (0.55)	14.41 (2.59)	-	75.31 (3.44)	0.09 (0.09)	-	-	-	-	-	22
Soybean (<i>glycine max</i>)	-	-	0.08 (0.14)	0.12 (0.20)	11.44 (1.80)	0.16 (0.25)	-	4.14 (0.75)	23.47 (1.85)	-	53.46 (2.31)	6.64 (2.03)	0.33 (0.25)	0.22 (0.24)	0.27 (0.22)	0.07	0.13 (0.13)	91
Sunflower (<i>helianthus annuus</i>)	-	-	-	0.04 (0.05)	6.26 (1.83)	0.06 (0.07)	-	3.93 (1.18)	20.77 (5.93)	-	67.75 (6.63)	0.15 (0.35)	0.23 (0.17)	0.13 (0.11)	0.70 (0.31)	-	0.26 (0.09)	42
Waste cooking	-	-	0.20 (0.42)	0.67 (0.59)	15.69 (8.55)	0.73 (0.68)	0.20 (0.13)	6.14 (3.55)	42.84 (10.42)	-	29.36 (14.78)	2.03 (2.40)	0.39 (0.23)	0.56 (0.27)	0.44 (0.31)	0.15 (0.12)	0.30 (0.18)	56

Table 2a. Fatty acid weight percentage in all analyzed vegetable oils (standard deviation in parentheses; absence of standard deviation indicates only one available value; only fatty acids with at least 0.05 percentage weight are referenced).

	8:0 C ₈ H ₁₆ O ₂	10:0 C ₁₀ H ₂₀ O ₂	12:0 C ₁₂ H ₂₄ O ₂	14:0 C ₁₄ H ₂₈ O ₂	16:0 C ₁₆ H ₃₂ O ₂	16:1 C ₁₆ H ₃₀ O ₂	17:0 C ₁₇ H ₃₄ O ₂	18:0 C ₁₈ H ₃₆ O ₂	18:1 C ₁₈ H ₃₄ O ₂	18:1 OH C ₁₈ H ₃₄ O ₃	18:2 C ₁₈ H ₃₂ O ₂	18:3 C ₁₈ H ₃₀ O ₂	20:0 C ₂₀ H ₄₀ O ₂	20:1 C ₂₀ H ₃₈ O ₂	22:0 C ₂₂ H ₄₄ O ₂	22:1 C ₂₂ H ₄₂ O ₂	24:0 C ₂₄ H ₄₈ O ₂	Count
Mol. weight (kg/kmol)	144.21	172.26	200.32	228.37	256.42	254.41	270.45	284.48	282.46	298.46	280.45	278.43	312.53	310.51	340.58	338.57	368.63	
Formal (common) name	Octanoic (Caprylic)	Decanoic (Capric)	Dodecanoic (Lauric)	Tetradecanoic (Myristic)	Hexadecanoic (Palmitic)	cis-9 Hexadecenoic (Palmitoleic)	Heptadecanoic (Margaric)	Octadecanoic (Stearic)	cis-9 Octadecenoic (Oleic)	12-hydroxy, cis-9 octadecenoic (Ricinoleic)	cis-9, cis-12 Octadecadienoic (Linoleic)	cis-9, cis-12, cis-15 Octadecatrienoic (Linolenic)	Eicosanoic (Arachidic)	cis-11 Eicosenoic (Gondoic)	Docosanoic (Behenic)	cis-13 Docosenoic (Erucic)	Tetra-cosanoic (Lignoceric)	
Animal Fat																		
Beef tallow	–	0.06 (0.05)	0.15 (0.18)	2.41 (0.82)	24.39 (3.07)	2.66 (1.24)	0.90 (0.48)	19.08 (6.23)	41.65 (4.37)	–	5.91 (7.23)	0.72 (1.04)	0.41 (0.71)	0.47 (0.37)	0.03	0.06 (0.13)	0.27 (0.25)	29
Chicken	–		0.10	0.73 (0.20)	24.06 (2.53)	5.65 (1.89)	0.20 (0.17)	6.42 (1.20)	41.43 (2.97)	–	18.83 (4.56)	1.06 (0.66)	0.05 (0.06)	0.41 (0.09)	0.30	0.40	0.25 (0.21)	24
Lard	–	0.05 (0.07)	0.25 (0.37)	1.62 (0.45)	25.10 (1.85)	2.68 (0.67)	0.41 (0.35)	13.23 (1.67)	44.36 (1.93)	–	12.06 (3.27)	1.18 (0.70)	0.18 (0.13)	0.93 (0.21)		0.13 (0.23)		19
ANIMAL FAT (cumulative)		0.06 (0.05)	0.18 (0.23)	1.69 (0.91)	24.27 (2.99)	3.68 (1.93)	0.59 (0.46)	13.40 (6.83)	42.22 (4.48)	–	11.44 (8.09)	0.98 (0.86)	0.30 (0.58)	0.57 (0.34)	0.05 (0.10)	0.10 (0.17)	0.19 (0.21)	77
Fish																		
	8:0 C ₈ H ₁₆ O ₂	10:0 C ₁₀ H ₂₀ O ₂	12:0 C ₁₂ H ₂₄ O ₂	14:0 C ₁₄ H ₂₈ O ₂	16:0 C ₁₆ H ₃₂ O ₂	16:1 C ₁₆ H ₃₀ O ₂	16:2 C ₈ H ₂₈ O ₂	16:3 C ₈ H ₂₆ O ₂	16:4 C ₈ H ₂₄ O ₂	17:0 C ₁₇ H ₃₄ O ₂	17:1 C ₁₇ H ₃₂ O ₂	18:0 C ₁₈ H ₃₆ O ₂	18:1 C ₁₈ H ₃₄ O ₂	18:2 C ₁₈ H ₃₂ O ₂	18:3 C ₁₈ H ₃₀ O ₂	18:4 C ₁₈ H ₂₈ O ₂		17
	–	–	0.15 (0.02)	5.57 (1.52)	16.29 (5.66)	–	0.79 (0.35)	(0.19)	0.70	0.82 (0.48)	0.62 (0.24)	4.57 (3.73)	22.59 (8.46)	5.93 (4.13)	4.67 (4.32)	2.90 (0.95)		
	20:0 C ₂₀ H ₄₀ O ₂	20:1 C ₂₀ H ₃₈ O ₂	20:2 C ₂₀ H ₃₆ O ₂	20:3 C ₂₀ H ₃₄ O ₂	20:4 C ₂₀ H ₃₂ O ₂	20:5 C ₂₀ H ₃₀ O ₂	21:5 C ₂₁ H ₃₂ O ₂	22:0 C ₂₂ H ₄₄ O ₂	22:1 C ₂₂ H ₄₂ O ₂	22:2 C ₂₂ H ₄₀ O ₂	22:3 C ₂₂ H ₃₈ O ₂	22:4 C ₂₂ H ₃₆ O ₂	22:5 C ₂₂ H ₃₄ O ₂	22:6 C ₂₂ H ₃₂ O ₂	24:0 C ₂₄ H ₄₈ O ₂	24:1 C ₂₄ H ₄₆ O ₂		
	0.62 (0.59)	2.47 (1.35)	0.33 (0.04)	0.69 (0.84)	2.27 (1.17)	8.48 (5.30)	0.54	0.27 (0.37)	2.35 (1.14)	0.15 (0.06)	0.25 (0.11)	0.23 (0.24)	3.21 (1.20)	11.66 (3.21)	–	0.53 (0.20)		

Table 2b. Fatty acid weight percentage in all analyzed animal fats (standard deviation in parentheses; only fatty acids with at least 0.05 percentage weight are referenced).

	Cetane number	Density (kg/m ³)	LHV (kJ/kg)	HHV (kJ/kg)	Viscosity (mm ² /s)	Flash point (°C)	Pour point (°C)	Cloud point (°C)	CFP point (°C)	Iodine number	Oxidation stability (h)	Acid number (mg KOH/g)	Sulfur content (ppm)	Distillation temp. 50% vol. (°C)	Distillation temp. 90% vol. (°C)	C (% w/w)	H (% w/w)	O (% w/w)	Molecular weight (kg/kmol)
Beef tallow	60.9 (5.55)	874.3 (3.82)	37,220 (274)	40,040 (216)	4.83 (0.50)	157.2 (8.6)	10.0 (2.0)	13.8 (1.8)	12.2 (2.3)	54.5 (10.3)	0.45 (0)	0.30 (0.18)	14.3 (5.5)	329.2 (3.5)	344.2 (6.6)	76.09 (0.69)	12.60 (0.81)	11.35 (0.39)	–
Canola	54.8 (3.37)	881.6 (3.51)	37,980 (860)	39,975 (150)	4.40 (0.25)	159.0 (14.0)	-8.0 (2.6)	-1.8 (1.4)	-8.8 (3.3)	104.0 (4.6)	11.0 (0.95)	0.22 (0.14)	2.2 (1.2)	352.0 (1.7)	354.3 (4.9)	–	12.84	11.04	–
Castor	42.1 (6.83)	917.6 (6.98)	37,630 (243)	39,900 (1926)	14.52 (1.78)	160.9 (37.5)	-23.4 (4.0)	-15.1 (12.5)	5.9 (18.5)	85.2 (3.3)	12.9 (6.1)	0.39 (0.18)	0.5 (0.45)	327 (8.5)	381.6 (23.4)	–	–	–	270
Chicken fat	57 (5.66)	876.3 (6.37)	37,610	39,890 (405)	4.81 (0.50)	162.2 (9.8)	4.40 (1.8)	7.5 (1.3)	2.7 (0.6)	78.7 (1.30)	8.7 (3.21)	0.32 (0.15)	–	–	–	–	–	–	–
Coconut	61 (6.46)	870.8 (4.71)	35,985 (921)	38,985 (1369)	2.78 (0.26)	127.7 (29.1)	-3.8 (1.2)	-1.2 (3.9)	-4.7 (0.6)	7.8 (2.5)	11.0 (5.64)	0.16 (0.11)	3.3 (1.3)	–	–	72.75 (0.07)	11.65 (0.50)		–
Corn	52.5 (2.64)	882.2 (4.71)	38,600 (69)	40,190 (826)	4.32 (0.37)	165.7 (5.9)	-5.1 (2.5)	-3.0 (1.6)	-7.5 (3.2)	120 (16.9)	3.0 (1.34)	0.19 (0.06)	3 (2.1)		345.8 (7.0)	76.71 (0.56)	11.52 (0.54)	10.98 (0.03)	–
Cottonseed	53.3 (2.75)	879.0 (5.49)	38,175 (1135)	40,480 (435)	4.70 (0.88)	165.4 (14.0)	-0.2 (4.1)	1.2 (4.4)	4.8 (2.5)	105.7	1.8	0.29 (0.18)	5.3 (4.2)	–	349.5 (9.1)	76.86 (0.77)	11.89 (0.16)	11.21 (0.62)	–
Croton	50.6 (5.66)	883.2 (4.95)	37,825 (1578)	40,280	4.48 (0.28)	174.5 (20.5)	-6.3 (4.6)	-4.0	11.0	142	4.0	0.31 (0.26)	–	352	358	77.83	11.97	10.20	–
Fish	51 (1.52)	887.3 (7.15)	38,800 (1131)	40,550 (955)	4.30 (0.33)	162.6 (8.8)	-4.0 (0)	-0.3 (2.41)	-3.0 (3.7)	142.6 (13.81)	8.2 (3.46)	0.39 (0.35)	5.7 (4.2)	339	360.2 (18.9)	77.40	11.85	–	–
Hazelnut	53.8 (1.70)	877.9 (15.2)	37,230	39,800 (469)	4.55 (0.91)	163.5 (30.8)	-14.0 (1.4)	-12 (3.8)	-10.2 (5.4)	92.5 (2.1)	7.6	0.22	–	–	–	76.57	11.94	–	–
Jatropha	55.7 (2.84)	878.7 (6.52)	38,050 (956)	40,380 (1259)	4.72 (0.56)	158.5 (19.5)	-0.9 (4.7)	5.7 (4.3)	-1.2 (3.9)	99.0 (5.4)	5.0 (1.88)	0.34 (0.12)	12.9 (15.4)	333.3 (0.6)	341.2 (12.1)	76.57 (0.37)	12.21 (0.28)	11.32 (0.66)	–
Karanja	55.4 (2.49)	882.9 (5.50)	36,490 (426)	40,275 (671)	5.04 (0.60)	163.6 (14.7)	2.5 (3.4)	7.6 (4.3)	-7.0	85.5 (2.2)	4.1 (2.44)	0.44 (0.05)	13.5 (9.2)	334	345.4 (11.1)	76.35 (1.51)	11.95 (0.70)	11.51 (0.96)	–
Lard	–	873.0 (2.25)	36,910	39,950 (212)	4.89 (0.11)	153.5 (9.2)	11.0	15	9.0 (4.2)	64.5 (11.4)	–	0.36 (0.26)	–	329	337	76.01	12.11	11.71	–
Linseed	51.3 (4.24)	891.5 (3.61)	37,830 (1713)	40,410 (676)	4.06 (0.20)	170.3 (5.6)	-8.0 (4.2)	-1.7 (2.0)	-7.7 (1.7)	184.5 (17.9)	0.40 (0.25)	0.29 (0.15)	8.2 (8.5)	338	361	77.75 (0.37)		11.29 (0.31)	290.07 (3.49)
Mahua	56.9 (6.07)	874.5 (7.54)	36,880 (53)	40,180 (879)	5.06 (0.54)	150.6 (24.1)	4.0 (2.2)	4.0 (1.0)	–	70.8 (13.1)	2.1	0.41 (0.09)	–	–	–	–	–	–	294.4
Neem	54.2 (3.61)	876.2 (6.03)	37,155	39,960 (642)	4.72 (0.42)	162.5 (14.4)	6.1 (3.5)	11.6 (1.8)	–	86.3 (11.0)	–	0.26 (0.10)	–	–	–	76.7	12.10	10.72	–
Olive	58.9 (2.00)	881.2 (1.56)	37,290	40,280 (1048)	5.05 (0.39)	171 (6.5)	-5.0 (1.7)	-2.0 (0)	-5.3 (3.8)	80.3 (3.2)	1.7 (2.33)	0.37 (0.33)	7.8 (3.1)	–	–	–	–	–	–
Palm	61.2 (4.90)	874.7 (4.01)	37,080 (855)	39,985 (688)	4.61 (0.61)	161.9 (17.3)	11.8 (2.4)	13.3 (2.3)	11.4 (4.7)	52.7 (5.6)	11.4 (2.38)	0.27 (0.11)	3.1 (2.7)	327.7 (4.0)	339.3 (6.7)	76.09 (0.37)	12.44 (0.50)	11.27 (0.43)	284.12 (0.14)
Peanut	54.9 (2.78)	882.9 (2.62)	38,050	39,930 (205)	4.77 (0.26)	174.5 (5.9)	-2.7 (8.4)	4.3 (3.8)	16.3 (0.6)	80.5 (15.1)	–	0.19 (0.13)	5.9 (7.8)	–	–	–	–	–	–
Rapeseed	54.1 (3.32)	882.2 (4.06)	37,625 (663)	40,335 (743)	4.63 (0.37)	164.4 (15.5)	-9.7 (3.4)	-3.3 (2.4)	-11.3 (5.9)	111.7 (7.4)	7.4 (1.81)	0.24 (0.11)	4.6 (3.6)	340.7 (10.1)	344.3 (4.6)	77.07 (0.49)	11.84 (0.46)	10.93 (0.48)	294.80
Rice bran	56.3 (5.49)	880.9 (5.71)	38,045 (1335)	40,475 (1201)	4.70 (0.44)	157.8 (23.3)	-0.9 (2.7)	5.0 (4.8)	0.3 (2.4)	91.8 (13.0)	–	0.28 (0.18)	5.3 (4.7)	336.0	346.0 (1.7)	76.22	12.38	11.26	–
Rubber seed	50.4 (1.14)	882.3 (4.37)	37,820 (807)	40,350 (1018)	4.79 (0.63)	158.3 (24.8)	-7.0 (1.3)	3.6 (1.5)	-1.0	139.7 (6.2)	7.2 (0.93)	0.22 (0.10)	–	–	–	–	–	–	–
Safflower	51.8 (2.53)	883.8 (5.21)	38,145 (862)	40,155 (644)	4.10 (0.12)	169.9 (17.6)	-8.1 (2.9)	-4.9 (1.7)	-8.3 (2.1)	136.7 (5.7)	–	0.32 (0.05)	–	–	–	–	–	–	–

	Cetane number	Density (kg/m ³)	LHV (kJ/kg)	HHV (kJ/kg)	Viscosity (mm ² /s)	Flash point (°C)	Pour point (°C)	Cloud point (°C)	CFP point (°C)	Iodine number	Oxidation stability (h)	Acid number (mg KOH/g)	Sulfur content (ppm)	Distillation temp. 50% vol. (°C)	Distillation temp. 90% vol. (°C)	C (% w/w)	H (% w/w)	O (% w/w)	Molecular weight (kg/kmol)
Soybean	51.8 (3.93)	882.8 (5.12)	37,750 (944)	40,020 (671)	4.29 (0.37)	158.8 (19.5)	-3.0 (2.7)	0.1 (2.0)	-3.6 (3.4)	126.0 (6.9)	5.0 (2.59)	0.32 (0.28)	2.7 (3.8)	336.3 (6.1)	345.0 (6.6)	77.03 (0.50)	11.90 (0.31)	10.95 (0.52)	290.83 (2.17)
Sunflower	51.9 (4.73)	882.9 (4.70)	37,800 (895)	40,000 (647)	4.53 (0.51)	172.0 (7.9)	-3.8 (2.3)	0.9 (2.4)	-3.5 (2.0)	128.6 (2.1)	1.3 (0.42)	0.32 (0.14)		355.7 (7.2)	356.5 (2.1)	76.90 (0.37)	11.84 (0.29)	10.98 (0.15)	294.05 (0.50)
Waste cooking	56.2 (3.91)	880.6 (6.04)	37,880 (1088)	39,805 (607)	4.75 (0.46)	161.7 (19.0)	-0.3 (5.5)	5.3 (5.1)	-2.8 (3.3)	85.1 (17.1)	5.0 (3.28)	0.41 (0.14)	8.6 (14.6)	340.4 (6.7)	350.3 (8.6)	76.90 (0.55)	12.02 (0.44)	10.77 (0.47)	289.31 (3.86)

Table 3. Summarization of various biodiesel physical and chemical properties for all analyzed feedstocks (standard deviation in parentheses).

Table 4. Degree of unsaturation of the fatty acid oils considered, and its correlation with the FAME iodine number.

Animal fat or vegetable oil	'Unweighted' degree of unsaturation (%) *	'Partially weighted' degree of unsaturation **	'Fully weighted' degree of unsatura- tion (average number of double bonds) ***	Chain length	FAME iodine number
Beef tallow	0.52	0.58	0.59	17.37	54.5
Chicken fat	0.68	0.88	0.89	17.42	78.7
Canola	0.92	1.24	1.33	17.99	104
Castor	0.97	1.03	1.03	17.99	85.2
Coconut	0.09	0.12	0.12	13.12	7.8
Corn	0.86	1.45	1.45	17.79	120.3
Cottonseed	0.71	1.27	1.27	17.46	105.7
Croton	0.90	1.76	1.74	17.86	142
Fish	0.96	1.15	2.10	16.72	142.6
Hazelnut	0.90	1.01	1.01	17.87	92.5
Jatropha	0.78	1.15	1.15	17.79	99
Karanja	0.75	1.02	1.04	18.08	85.2
Lard	0.60	0.74	0.74	17.40	64.5
Linseed	0.91	1.61	2.15	17.91	184.5
Mahua	0.54	0.69	0.69	17.57	70.8
Neem	0.64	0.83	0.83	17.66	86.3
Olive	0.85	0.96	0.97	17.79	80.3
Palm	0.51	0.62	0.62	17.08	53.1
Peanut	0.82	1.16	1.16	18.04	80.5
Rapeseed	0.93	1.24	1.32	18.08	111.7
Rice bran	0.78	1.14	1.15	17.64	93.2
Rubber seed	0.80	1.36	1.54	17.80	139.7
Safflower	0.90	1.65	1.65	17.85	136.7
Soybean	0.84	1.44	1.51	17.79	126.2
Sunflower	0.89	1.57	1.57	17.92	128.6
Waste cooking	0.76	1.07	1.09	17.69	85.2
<i>Ground-animal fat (cumulative)</i>	<i>0.60</i>	<i>0.73</i>	<i>0.74</i>	<i>17.40</i>	<i>65.9</i>
<i>Vegetable oil (cumulative)</i>	<i>0.78</i>	<i>1.16</i>	<i>1.20</i>	<i>17.58</i>	<i>101.6</i>
<i>Overall average values</i>	<i>0.76</i>	<i>1.10</i>	<i>1.18</i>	<i>17.53</i>	<i>98.4</i>
Correlation with iodine number	R ² =0.612	R ² =0.836	R ² =0.942	R ² =0.295	–

* All unsaturated fatty acids assumed to have the same percentage weight

** All unsaturated XX:y (y≥2) fatty acids have a percentage weight of 2

*** XX:2 fatty acids have a weight percentage of 2, XX:3 fatty acids a weight percentage of 3 etc

	Unsat.	CN	Density	LHV	HHV	Visc.	FP	IN	CP	PP	CFPP	C	H	O	Sulfur	OSI	Acidity	T ₉₀	AF _{st}	MW
Unsat.	1																			
CN	-0.88	1																		
Density	0.93	-0.76	1																	
LHV	0.77	-0.63	0.65	1																
HHV	0.65	-0.49	0.60	0.60	1															
Visc.	-0.76	0.60	-0.63	-0.63	-0.13	1														
FP	0.49	-0.35	0.58	0.32	0.08	-0.35	1													
IN	0.98	-0.91	0.90	0.71	0.66	-0.74	0.49	1												
CP	-0.79	0.73	-0.82	-0.62	-0.42	0.53	-0.51	-0.80	1											
PP	-0.74	0.67	-0.69	-0.55	-0.37	0.54	-0.45	-0.72	0.92	1										
CFPP	-0.36	0.33	-0.53	-0.18	-0.07	0.34	-0.25	-0.35	0.74	0.60	1									
C	0.89	-0.81	0.85	0.56	0.36	-0.75	0.64	0.91	-0.81	-0.75	-0.68	1								
H	-0.22	0.42	-0.22	-0.04	0.09	0.22	-0.51	-0.22	0.35	0.47	0.35	-0.70	1							
O	-0.70	0.61	-0.59	-0.73	-0.77	0.44	-0.32	-0.68	0.38	0.35	-0.07	-0.55	-0.14	1						
Sulfur	-0.07	0.20	0.0	-0.18	0.28	0.53	-0.05	-0.04	0.38	0.51	0.10	-0.27	0.20	-0.09	1					
OSI	-0.26	0.20	-0.30	-0.12	-0.46	-0.14	-0.28	-0.33	0.01	0.11	0.04	-0.19	0.19	0.27	-0.65	1				
Acidity	0.01	0.08	0.07	-0.06	0.28	0.35	-0.35	-0.04	0.32	0.19	0.01	0.02	0.05	-0.37	0.43	-0.21	1			
T ₉₀	0.49	-0.64	0.83	0.38	-0.04	-0.69	0.49	0.43	-0.63	-0.54	-0.04	0.82	-0.18	-0.63	-0.38	0.33	0.04	1		
AF _{st}	-0.87	0.63	-0.89	-0.36	-0.68	0.96	-0.48	-0.90	0.48	0.49	0.38	-0.78	0.50	-0.57	-0.30	0.69	0.21	-0.69	1	
MW	0.26	-0.57	0.16	-0.02	0.46	0.24	0.07	0.30	-0.63	-0.76	-0.71	0.54	-0.96	-0.50	0.62	-0.77	-0.27	-0.73	-0.10	1

Table 5. Pearson coefficients for the correlations between the various FAME physical and chemical properties (light blue highlighted values have a coefficient of at least 0.80, and light green highlighted values have a coefficient between 0.60 and 0.79).

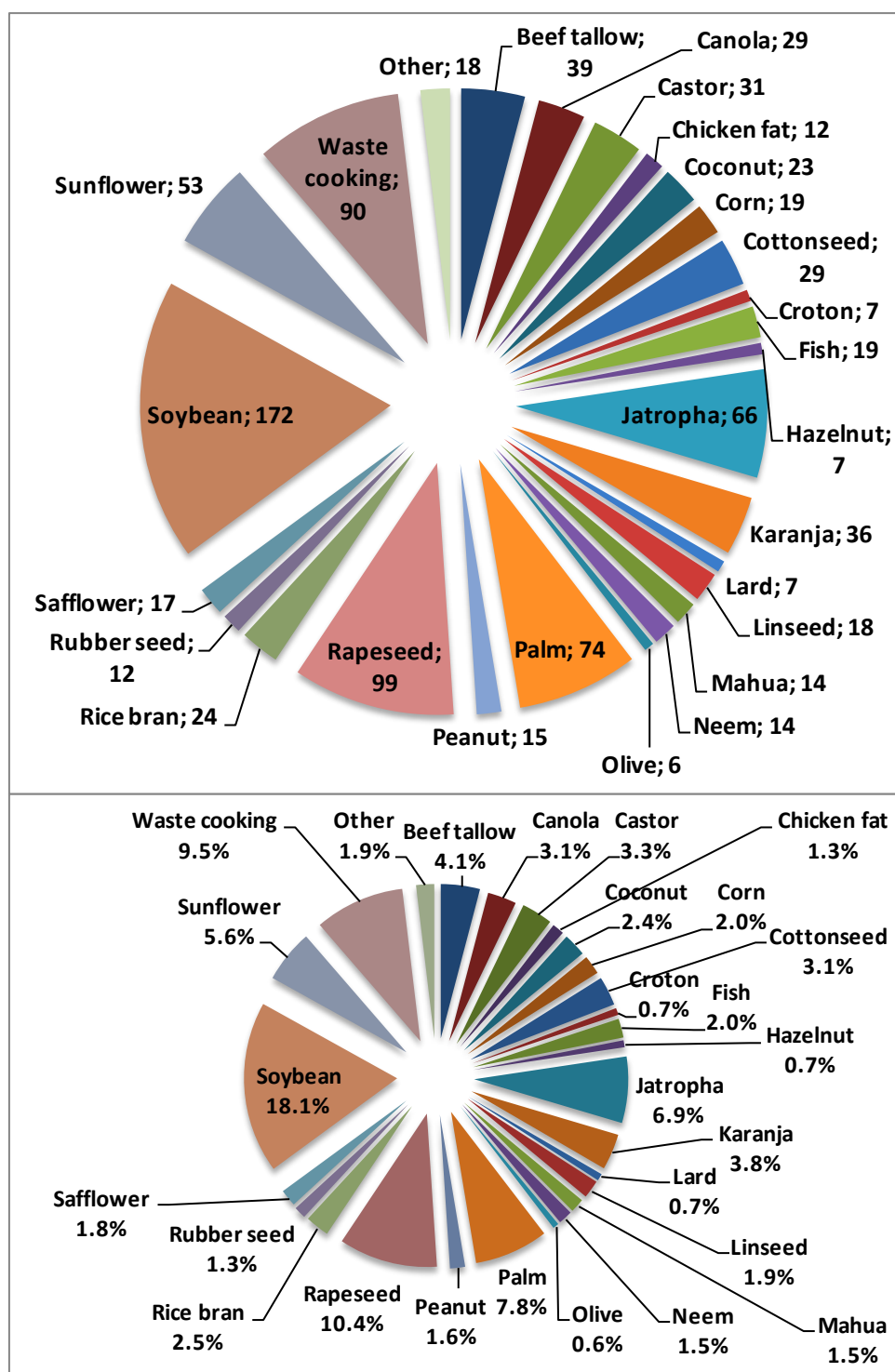


Fig. 1. Number of observations (upper diagram) and percentage (lower diagram) of biodiesel datasets analyzed in the current study.

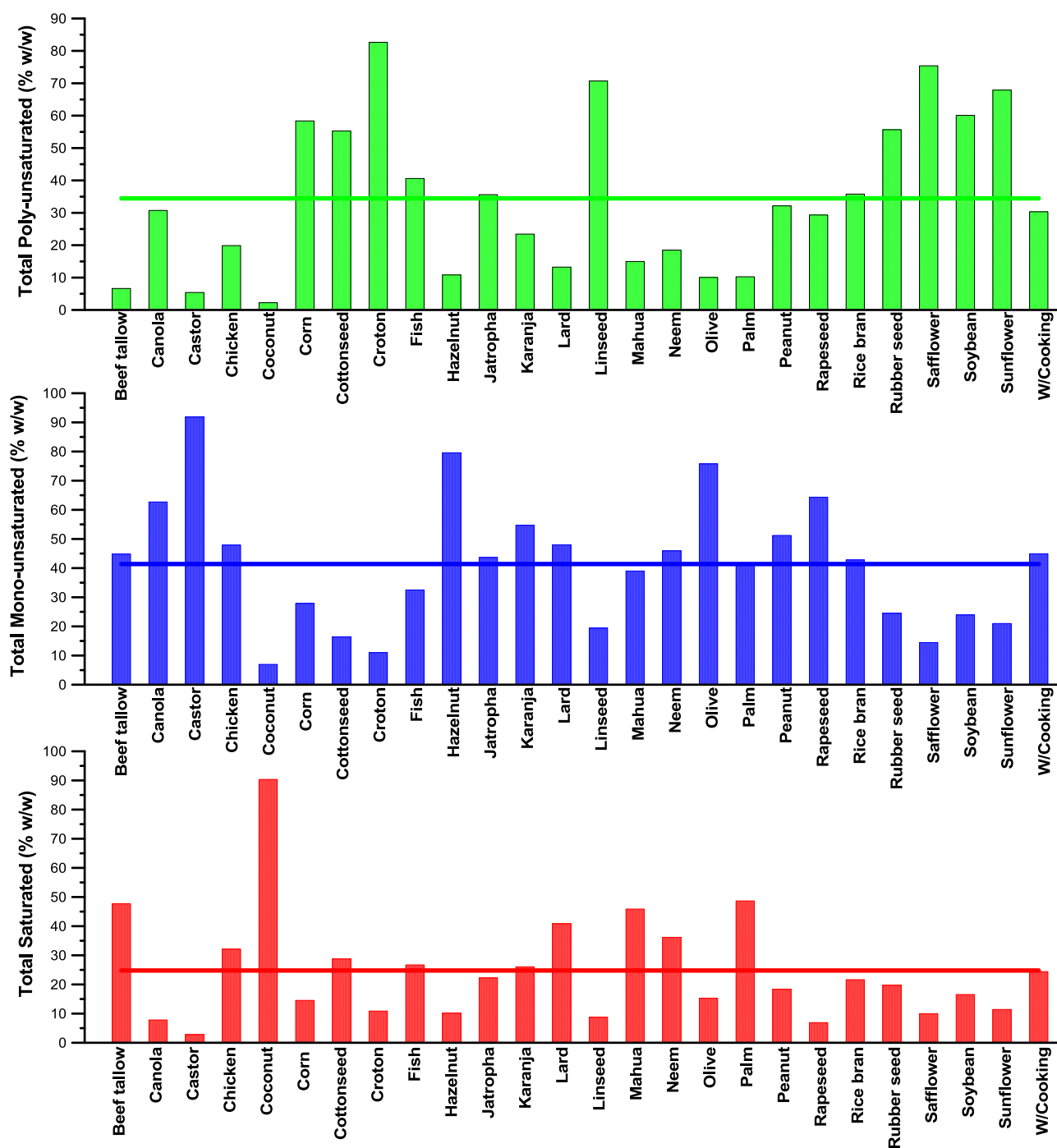


Fig. 2. Comparative illustration of saturated, mono- and poly-unsaturated percentage weights in all analyzed feedstocks (horizontal line corresponds to average values).

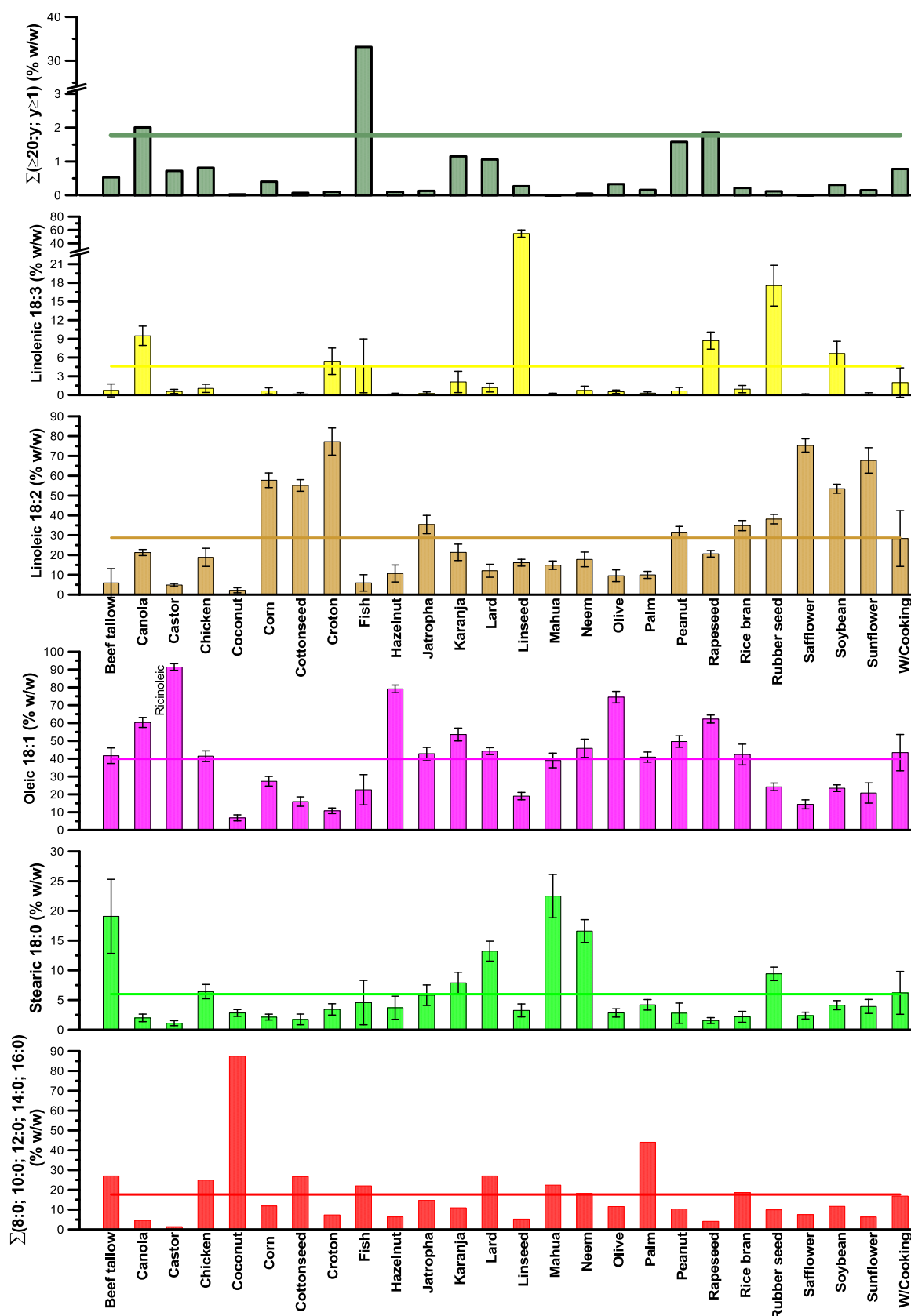


Fig. 3. Comparative illustration of specific fatty acids percentage weight in all analyzed feedstocks (horizontal line corresponds to average values).

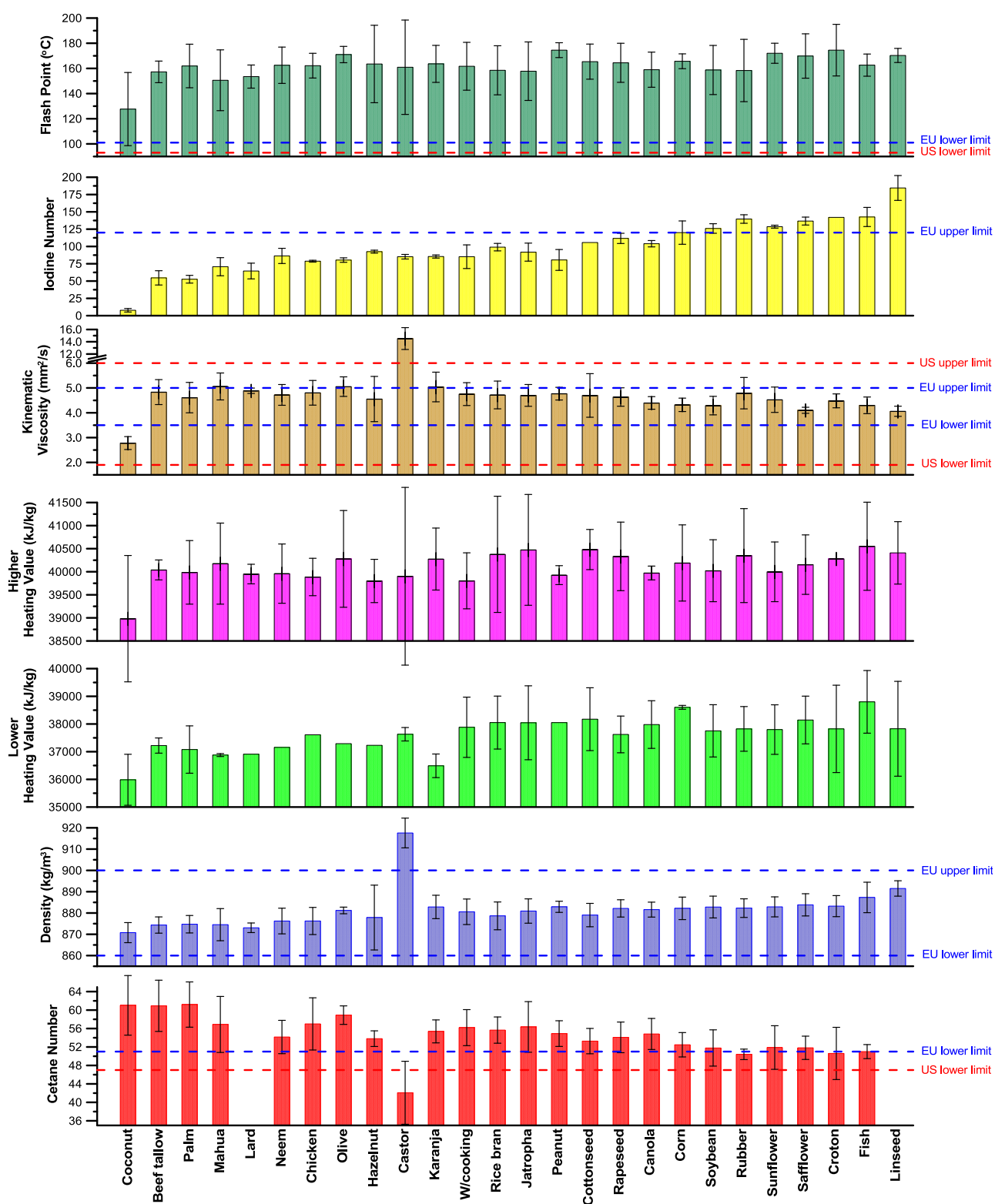


Fig. 4. Comparative illustration of various biodiesel properties average values and corresponding standard deviations for all analyzed feedstocks; biodiesels are presented in order of increasing unsaturation.

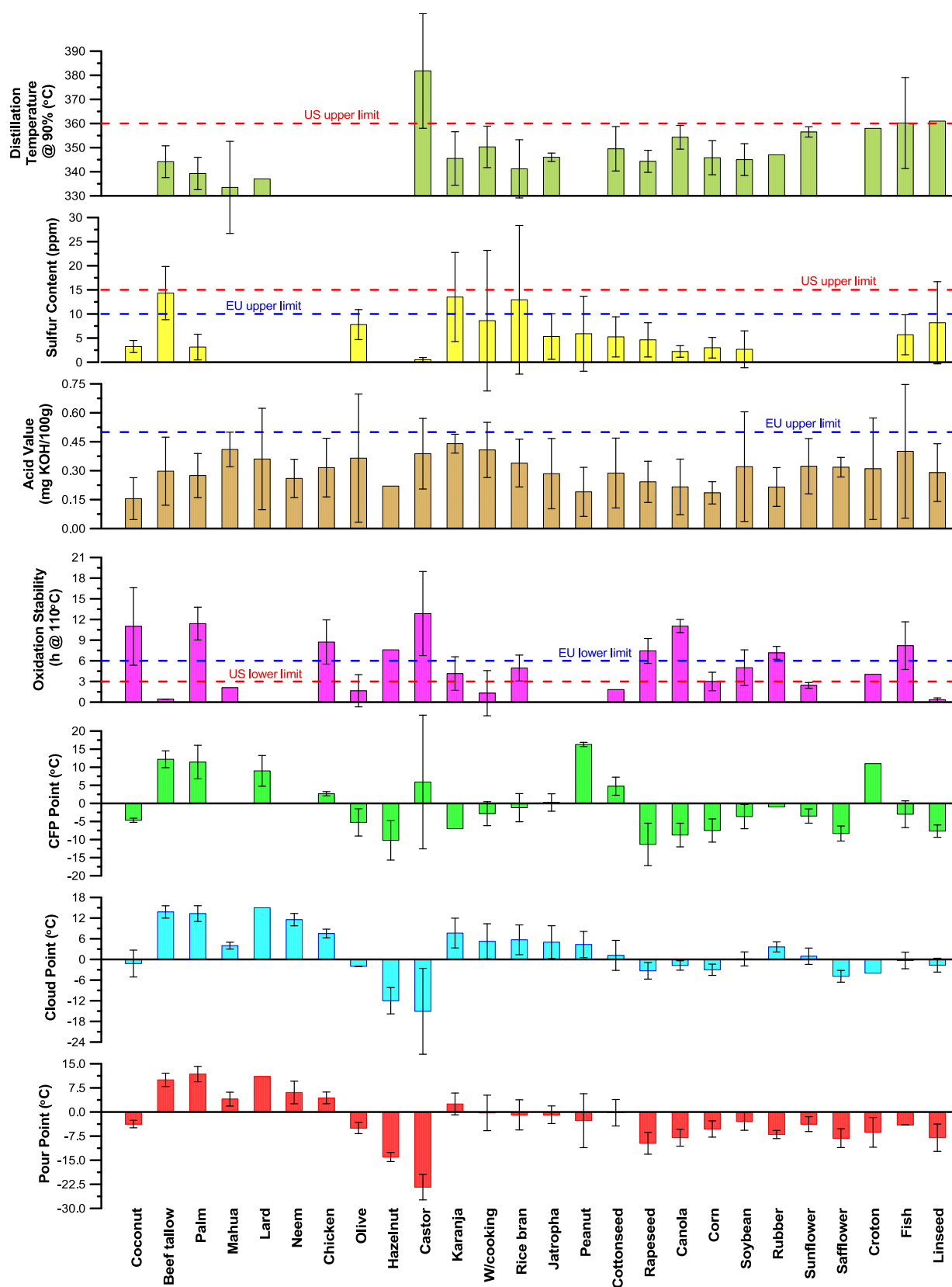


Fig. 4 (continued). Comparative illustration of various biodiesel properties average values and corresponding standard deviations for all analyzed feedstocks; biodiesels are presented in order of increasing unsaturation.

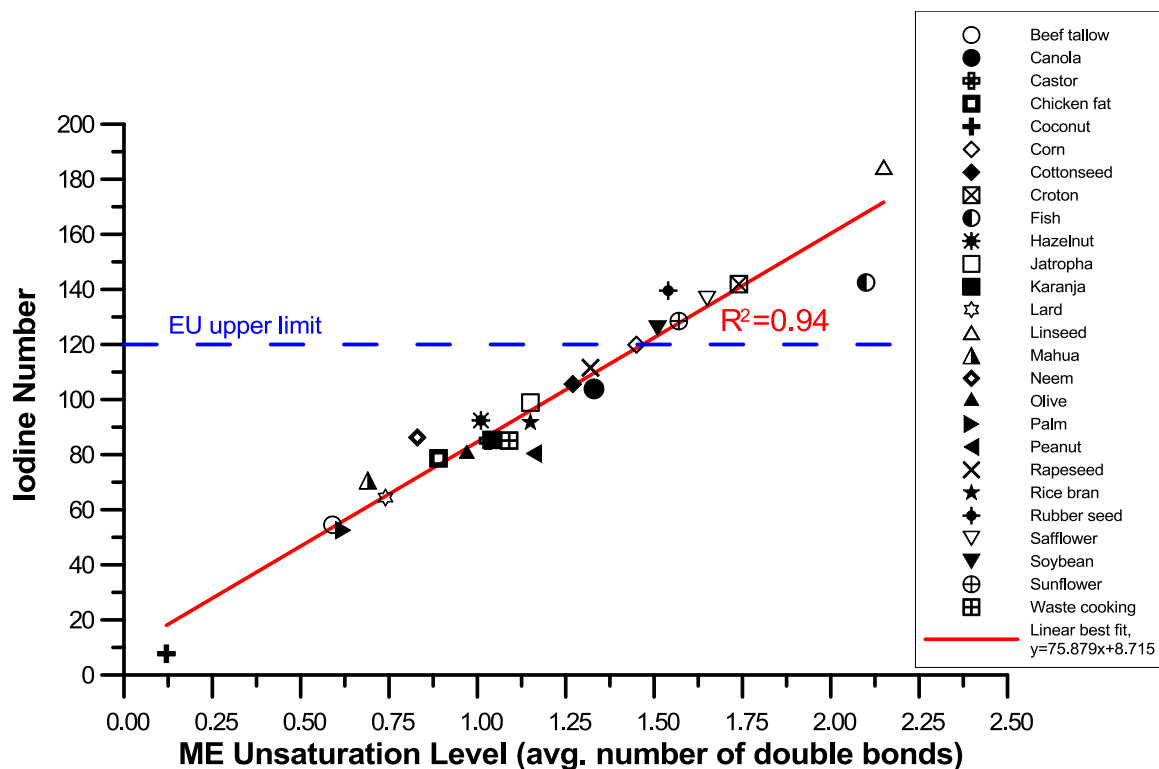


Fig. 5. Correlation between oil/fat unsaturation level and FAME average iodine number from all 26 investigated feedstocks.

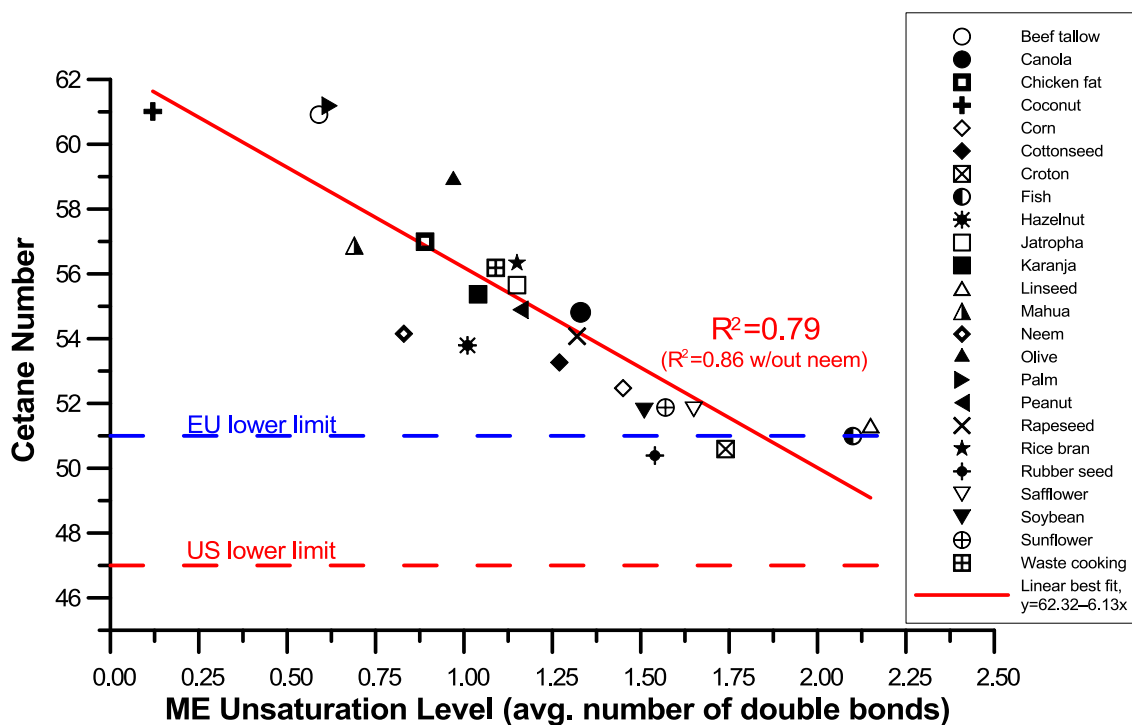


Fig. 6. Correlation between oil/fat unsaturation level and FAME average cetane number from 25 investigated feedstocks (castor excluded).

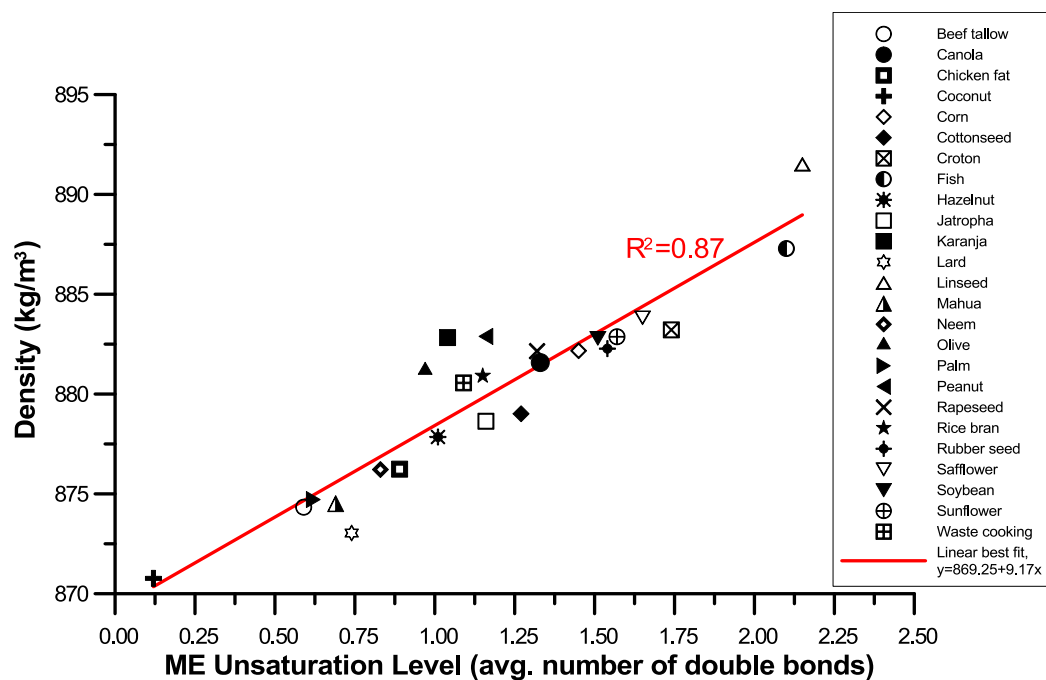


Fig. 7. Correlation between oil/fat unsaturation level and FAME average density from 25 investigated feedstocks (castor excluded).

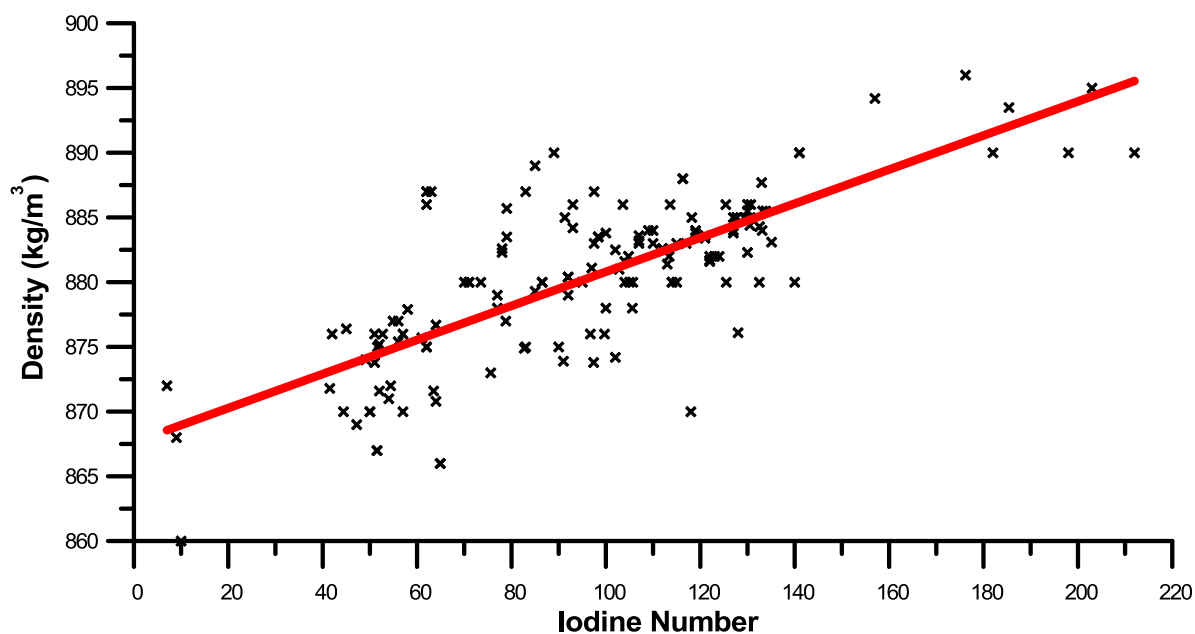


Fig. 8. Correlation between FAME iodine number and density from 25 investigated feedstocks (158 observations excluding castor).

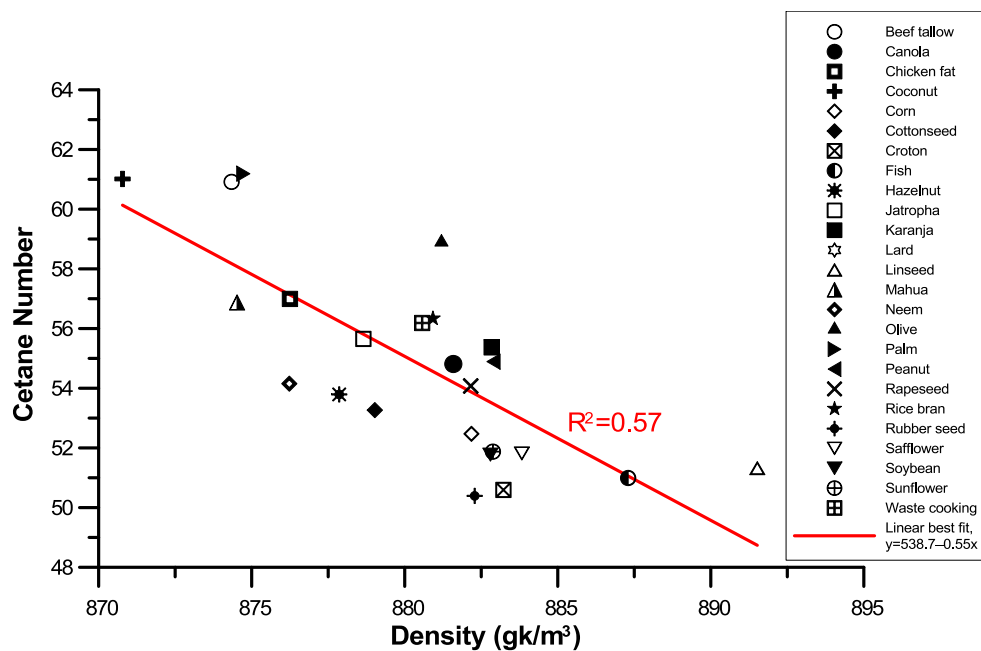


Fig. 9. Correlation between FAME average density and cetane number from 25 investigated feedstocks (castor excluded).

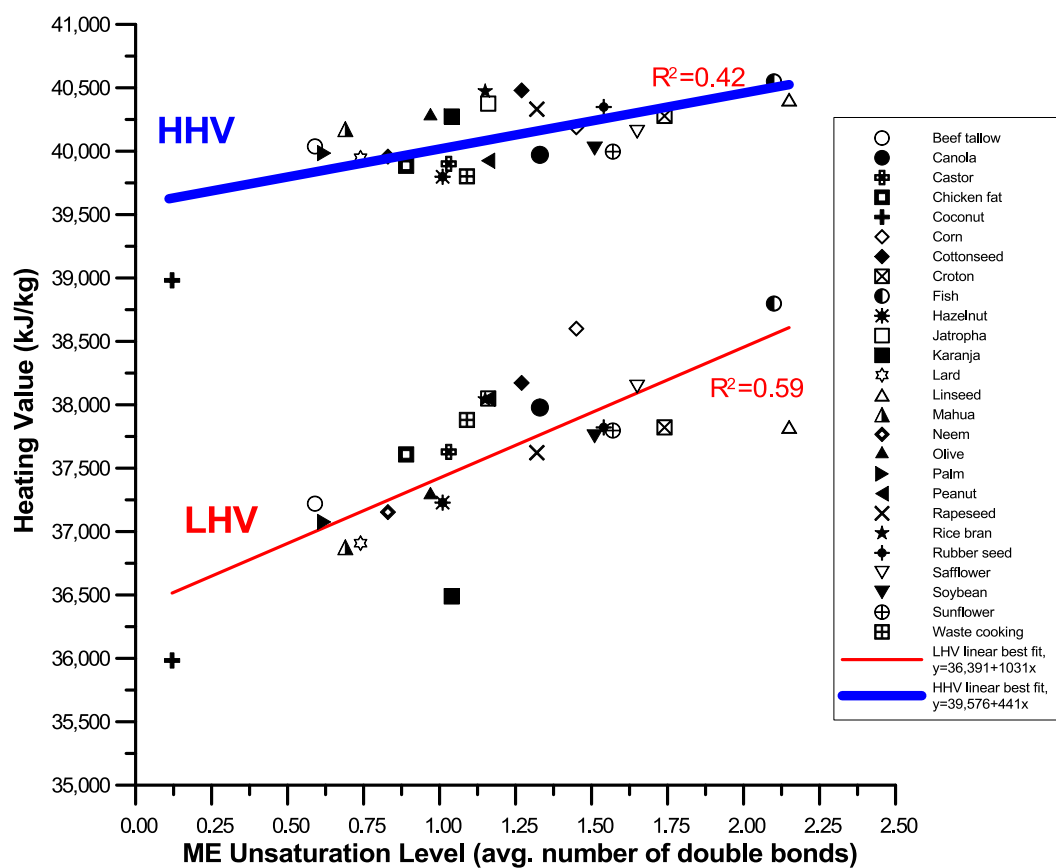


Fig. 10. Correlation between oil/fat unsaturation level and FAME average lower/higher heating values from all 26 investigated feedstocks.

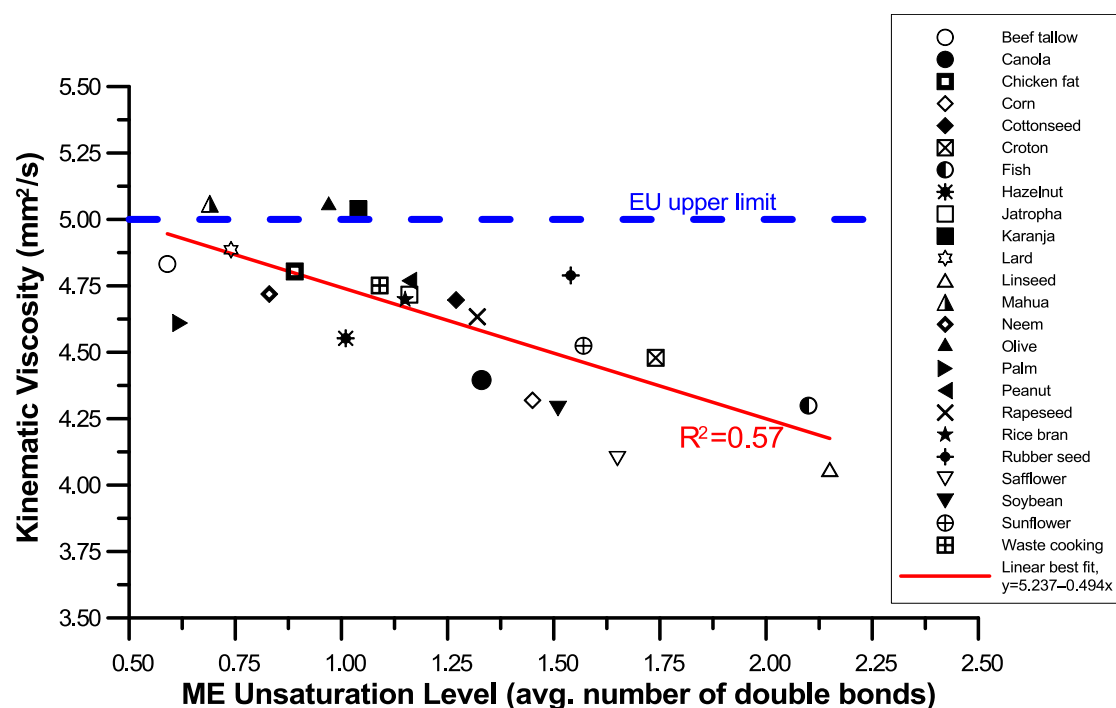


Fig. 11. Correlation between oil/fat unsaturation level and FAME average kinematic viscosity from 24 investigated feedstocks (castor and coconut excluded).

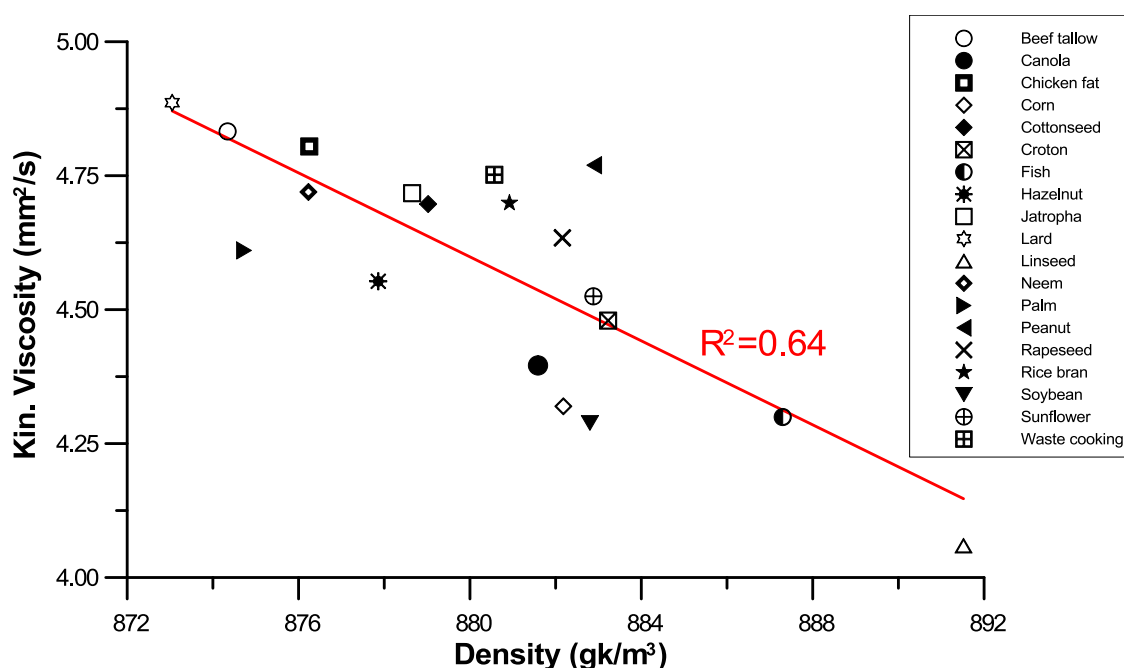


Fig. 12. Correlation between FAME average density and kinematic viscosity from 19 investigated feedstocks.

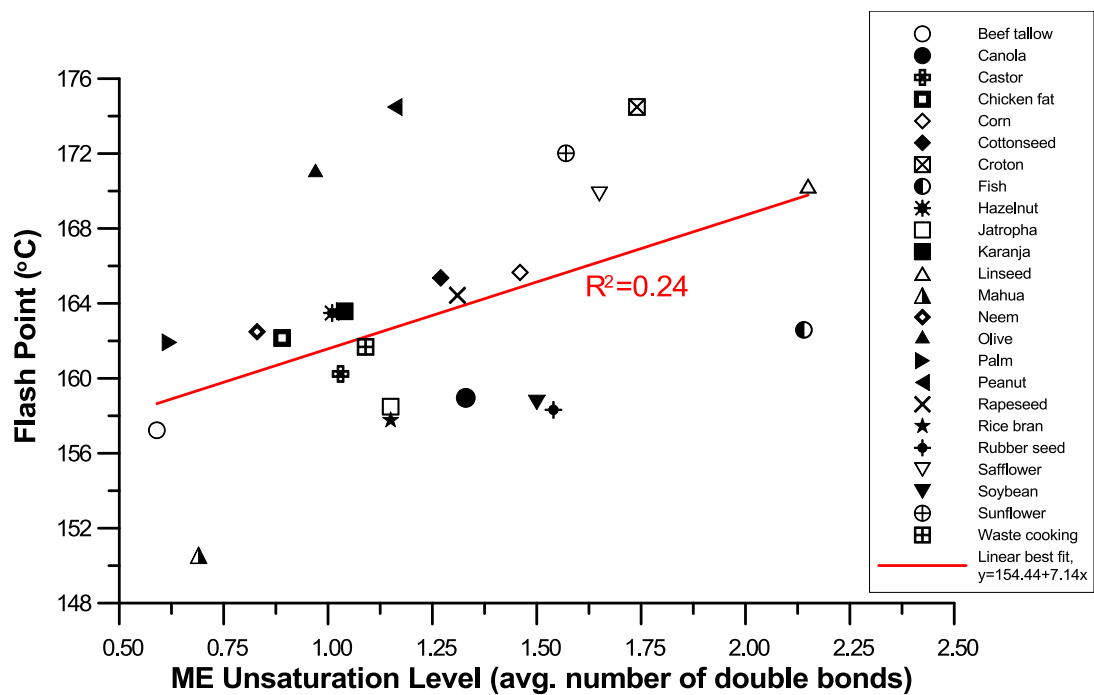


Fig. 13. Correlation between oil/fat unsaturation level and FAME average flash point from all 26 investigated feedstocks.

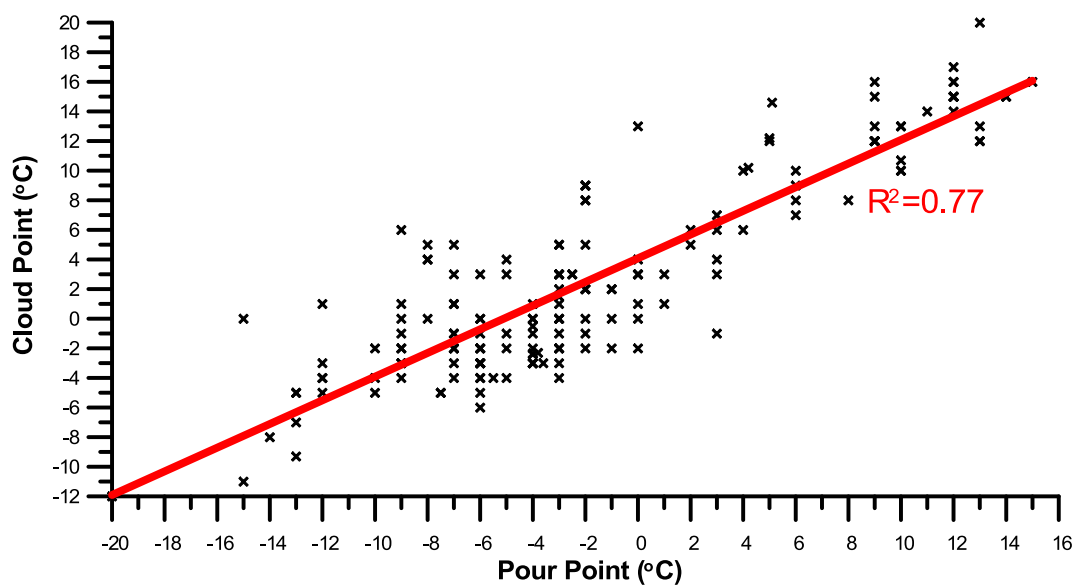


Fig. 14. Correlation between FAME pour and cloud point from all 26 investigated feedstocks (170 observations).

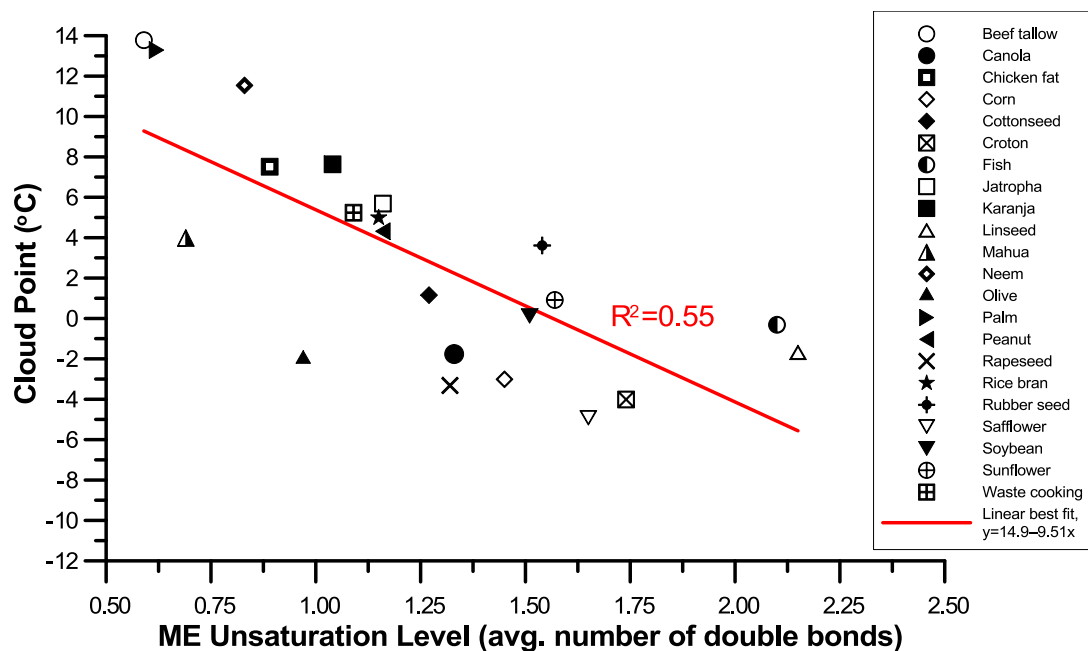


Fig. 15. Correlation between oil/fat unsaturation level and FAME average cloud point from 23 investigated feedstocks (castor, coconut and hazelnut excluded).

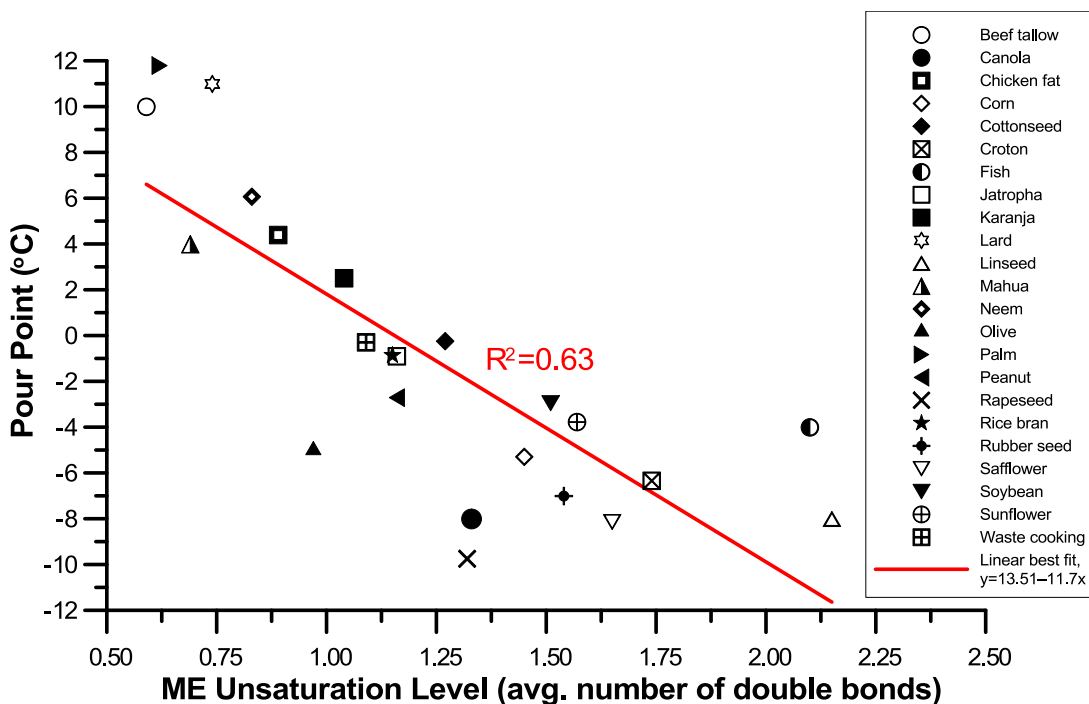


Fig. 16. Correlation between oil/fat unsaturation level and FAME average pour point from 23 investigated feedstocks (castor, coconut and hazelnut values).

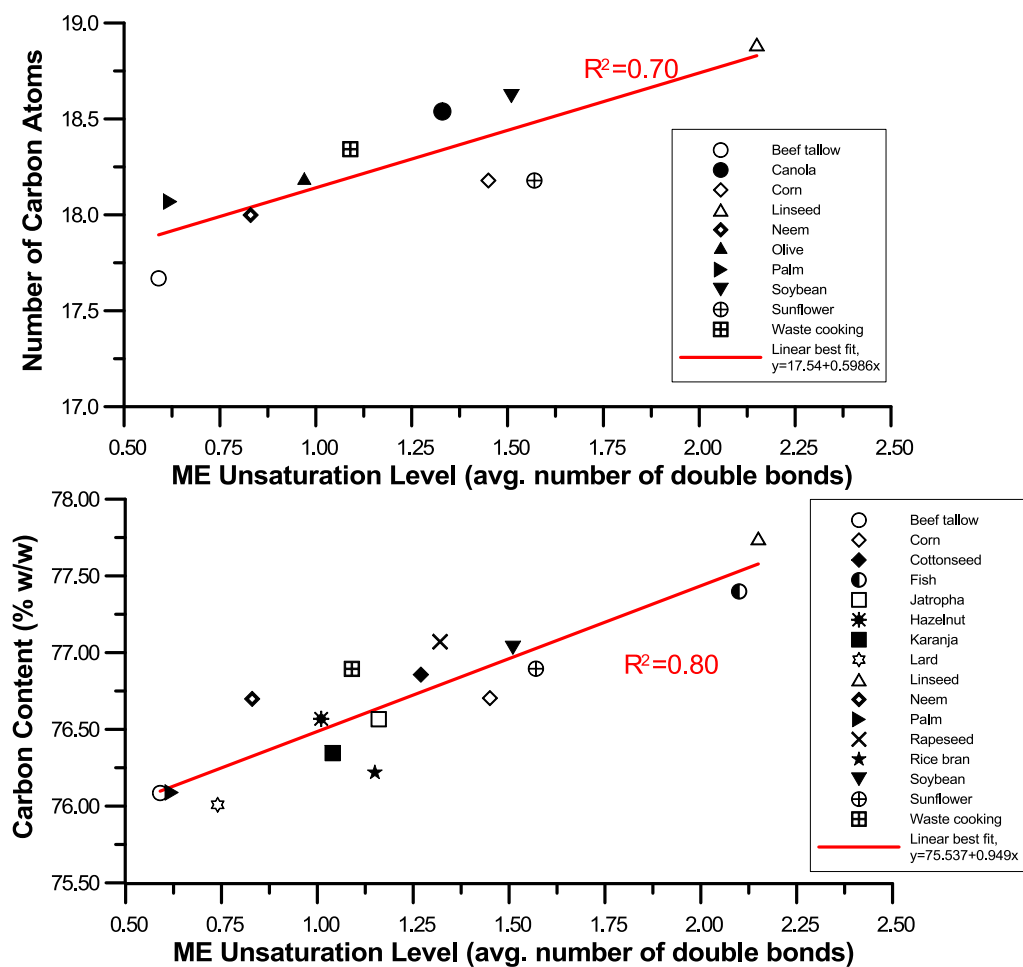


Fig. 17. Correlation between oil/fat unsaturation level and FAME average carbon content and number of carbon atoms.

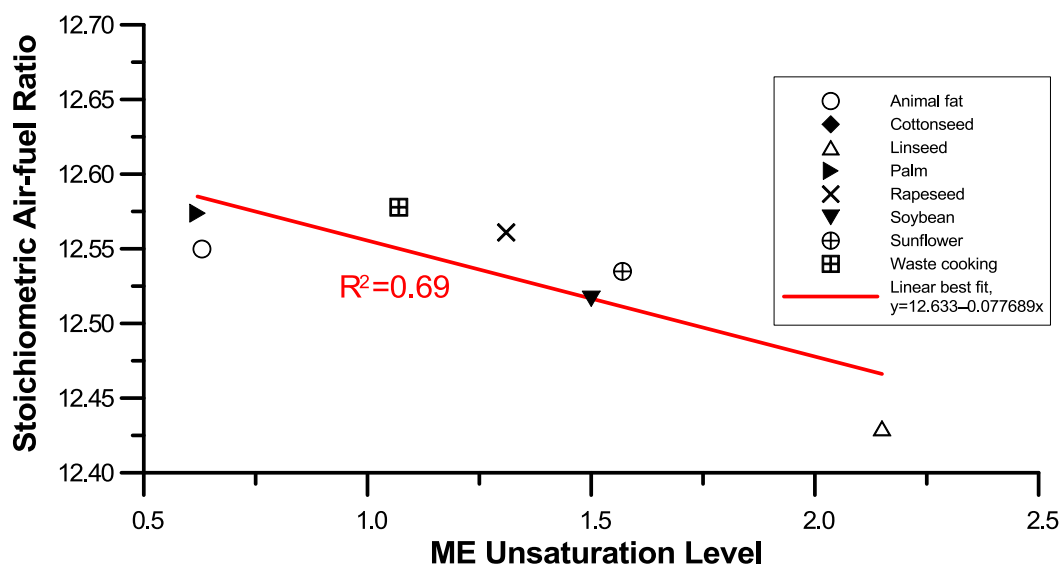


Fig. 18. Correlation between oil/fat unsaturation level and FAME average stoichiometric air-fuel ratio from 7 investigated feedstocks.

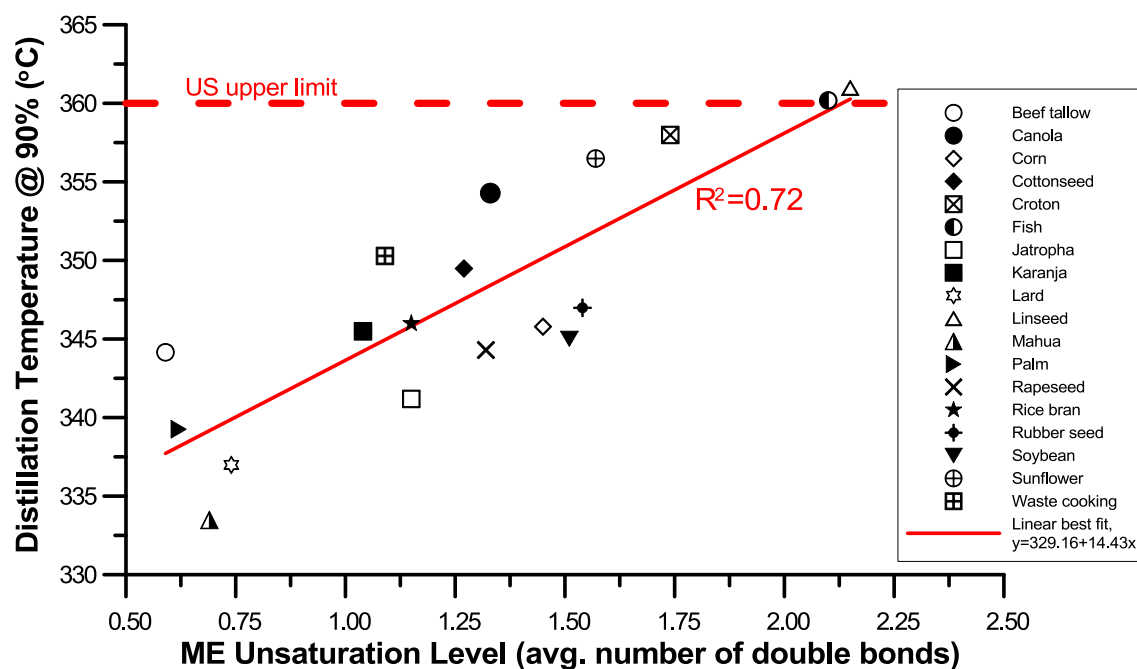


Fig. 19. Correlation between oil/fat unsaturation level and FAME average T_{90} distillation temperature from 18 investigated feedstocks.

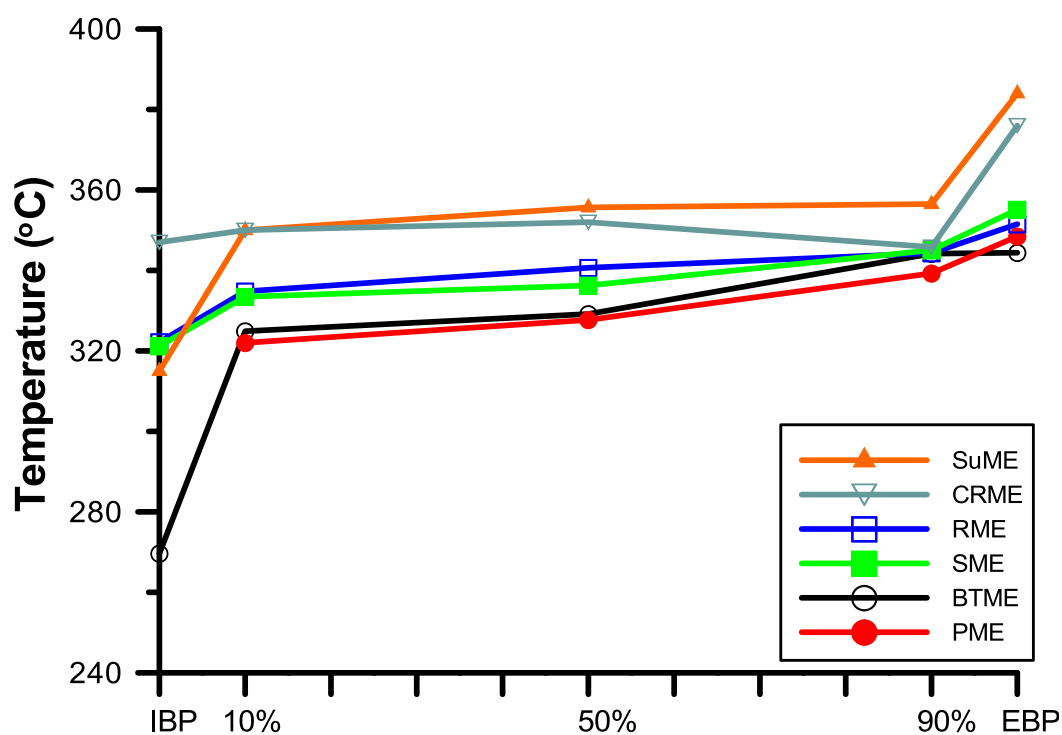


Fig. 20. Distillation curves for six methyl esters (sunflower; corn; rapeseed; soybean; beef tallow and palm).