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Review of vegetable oils behaviour at high temperature for solar plants: stability, properties and current applications.

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Abstract

With the possible depletion of oil resources and environmental considerations, vegetable oils are considered with great interest in high-temperature applications especially for solar plants. Many parameters affect vegetable oil stability, namely temperature, oxygen, moisture, duration of exposure to heat, etc. Conventional markers such as peroxide or free fatty acids do not always reliably indicate oil quality at high temperature. Evaluating the content of other degradation products such as polymers provides a better estimate. Reducing exposure to oxygen limits oil degradation. Vegetable oils have proven to be a favourable alternative to mineral oils in some applications, and several vegetable oils are commercially available. Their current use in solar cookers gives a good overview of their potential. Several reasons advocate for the use of vegetable oils in concentrating solar power plants: they are renewable resources, environmentally friendly, non-hazardous, highly available and less flammable products. Moreover, their thermophysical properties are similar, if not better, than those of thermal oils commonly used in solar plants. Despite these advantages, vegetable oils face some challenges, as for example their low oxidation stability. If the major challenge of using vegetable oils at high temperatures is their oxidation stability, the numerous environmental, economic and technological advantages make them innovative fluids for high temperature applications, particularly for solar applications.

Key Words: Vegetable oils; Solar plants; Heat transfer fluids; Heat storage materials; Thermal stability; Oxidative stability.

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1 Introduction

Thermal oils are widely used in many non-food applications [1–3]. In solar plants and more generally in solar applications where they are required, heat transfer fluids are heated by sun rays inside a receiver and transmit that heat to a heat engine or to a heat storage material. The thermophysical properties of the heat transfer fluid are determinant for the overall efficiency of the system [4]. Generally, three types of thermal oils are used (Table 1): mineral oils derived from petroleum, synthetic oils made from chemicals and vegetable oils extracted from crops. Mineral oils, despite their excellent performance, availability and low cost are the subject of discussion. On the one hand, because of the possible limitation of oil reserves [5] and, on the other hand, because of their low biodegradability, which is less than 30% [1]. In terms of safety, these mineral oils have a flash point generally between 100 and 170 °C [6]. The presence of polynuclear aromatic hydrocarbons in mineral oils used in electrical transformers for example, has led to the monitoring of transformers present in sensitive areas (schools, rivers, hospitals, etc.) [7], as these toxic compounds for environment and health can be released into the environment in case of explosion or fire in the transformers. Silicon oils and synthetic oils are also used as dielectric and cooling fluids or thermal fluids due to their good properties like high flash points and excellent oxidation resistance [6]. However, they are very expensive and have poor environmental properties [1]. This has led to efforts to develop other transformer insulating oils [8]. The same issues have been considered in many areas such as lubricants [9] and concentrated solar power plants [2,10]. Synthetic esters were developed for their good fire safety and for environmental concerns. They have been used extensively to replace mineral oils in transformers in areas where higher degree of fire safety and environmental protection were required [6]. Synthetic esters derive from chemicals and consist of a polyol molecule bound by saturated carboxylic acids [11]; this gives them great chemical, oxidative and thermal stability. Other fluids, which are the subject of several studies, are vegetable oils, also called natural ester triglycerides, with a view to substituting them for mineral and synthetic oils in various fields [1,2,12]. Indeed, vegetable oils are more than 95 % biodegradable and are renewable [7,13]. In addition, they have low toxicity and high flash points [1] compared to mineral oils. Furthermore, vegetable oils have good fluid properties like high lubricity, high insulating property, low volatility, high viscosity index (the measure of the variation in kinematic viscosity due to changes in the temperature of a fluid between 40 °C and 100 °C) and are highly available [14]. They are used for edible purposes [14–16] but also for non-food applications such as insulating and cooling fluids in transformers [8,11,18,19], heat transfer and thermal storage fluids in concentrating solar applications [2,10] and in many other fields in industry [20].

One of the traditional ways to use vegetable oils at high temperature (above 100 °C) is frying [17,21,22]. But nowadays, vegetable oils are also used as insulating and cooling fluids in distribution and power transformers [6,11] where hot-spot temperatures in oil could rise above 110 °C [23], as lubricants [12,24–26] and as heat transfer fluid in thermal processes [2,10]. Since heat represents three-quarters of

industrial energy demand worldwide and about 52% for low to medium temperature (up to 400 °C) [27], vegetable oils as thermal fluids (renewable resources) could play a major role in CO_2 emission reduction. For these purposes, vegetable oils should challenge conventional fluids mainly concerning oxidation and hydrolysis, which are the main ageing mechanisms [28] but also regarding their thermal stability. If for low temperatures (≤ 100 °C), oxidation is considered as the main path for vegetable oils degradation [29], at high temperature (above 100 °C) hydrolysis seems to be dominant in transformers oils for example [8].

Table 1: Different types of oils and applications

Nature of oil	Source of oils	Type of oils		Applications
Vegetable oils	Natural esters extracted from crops	- Drying - Semi-drying - Non-drying		- Frying - Lubricants - Thermal and insulating fluids - Paints, varnish, etc.
Mineral oils	Hydrocarbon mixture produced from the distillation of crude oil	- Aromatic - Naphthenic - Paraffinic		- Lubricants - Thermal and insulating fluids - Paints, varnish, etc.
Synthetic oils	Synthesised from chemical compounds	Hydrocarbons	- Diphenyl-biphenyl oxide - Alkylated aromatics - Polyalphaolefins, etc.	- Lubricants - Thermal and insulating fluids - Hydraulic fluids, etc.
		Esters	- Polyol esters - Diesters - Phosphate esters	
		Silicones	- Polydimethylsiloxane, etc.	- Thermal and insulating fluids, etc.
		Polyglycols		- Lubricants

This paper gives a comprehensive review of oxidative and thermal stability of vegetable oils, main chemical and thermophysical properties and experimental investigations on vegetable oils use. The aim is to show their great potential as heat transfer or thermal storage material in various application fields above 100 °C and particularly in solar plants.

2 Vegetable oils stability

2.1 Composition of vegetable oils

Vegetable oils are organic fluids that consist of about 95% triglycerides and 5% free fatty acids and minor constituents [2,30]. These triglycerides result from the union of

three fatty acids with glycerol [30,31] (Figure 1). Fatty acids contribute to about 94–96% of the total weight of a triglyceride molecule. The presence of a high number of fatty acids in a vegetable oil [32], as well as multiple possibilities of their combination with glycerol, make vegetable oils very complex mixtures with significantly different structures and properties. It is unusual for natural triglycerides to have only one kind of fatty acid unless a single fatty acid exceeds around 70%. It is the case of olive oil and other high-oleic oils. Usually, two or three different fatty acids are present in triglycerides [20] and their chemical and thermophysical properties depend on fatty acid composition [19,29–34]. However, two vegetable oils containing qualitatively and quantitatively the same fatty acids will have different chemical or physical characteristics if the fatty acids are distributed in different ways in the triglycerides [30]. In fact, each vegetable oil is characterised by its own fatty acid composition [2]. The number of different triglyceride molecules present in oils rises rapidly with the number of fatty acids. With only two fatty acids, such as palmitic and oleic acids, an oil may contain six different triglycerides [20]. This gives an idea of the diversity of vegetable oils composition. Depending on usage, crude vegetable oils may be refined. This involves the removal of undesirable components like phospholipids, free fatty acids, mono- and diglycerides, colour, trace metals, oxidation products, environmental contaminants, etc. from the oil [20] by means of filtration, degumming, neutralisation, bleaching and deodorisation [33].

The fatty acids in vegetable oil triglycerides are all of similar length, between 8 and 24 carbons long, with varying levels of unsaturation [9]. Saturated fatty acids have a carbon chain composed only of simple bonds but unsaturated acids have one or more double bonds in carbon chains. Some of vegetable oils properties such as melting or boiling points depend on the ratio of saturated and unsaturated fatty acids [20,39].

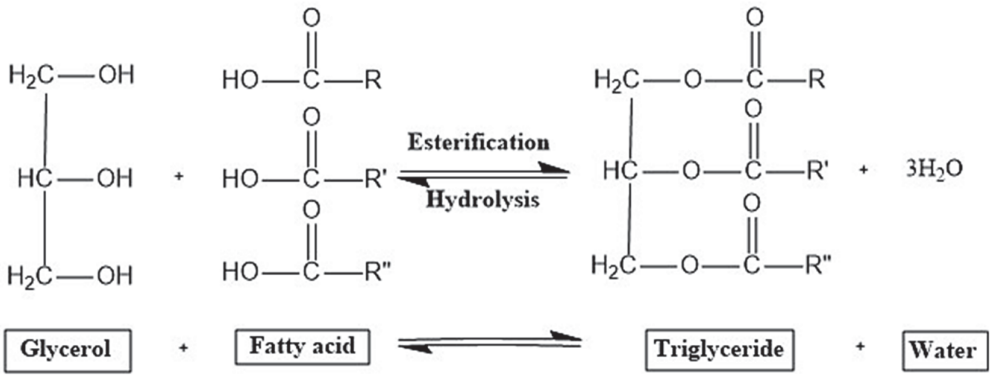

Figure 1 : Triglyceride formation

Generally, the melting point decreases with an increase of the unsaturation degree. Table 2 presents the chemical structure and physical properties of some fatty acids present in vegetable oils.

Table 2: Chemical structures and physical properties of some fatty acids [39]

Fatty acid		Structure	Designation[1]	Melting point (°C)	Boiling point (°C)
Saturated	Caproic	H_3C-$(CH_2)_4$-COOH	C6:0	-3	202
	Caprylic	H_3C-$(CH_2)_6$-COOH	C8:0	16–17	237
	Capric	H_3C-$(CH_2)_8$-COOH	C10:0	31–32	269
	Lauric	H_3C-$(CH_2)_{10}$-COOH	C12:0	44–46	299
	Myristic	H_3C-$(CH_2)_{12}$-COOH	C14:0	58.8	250
	Palmitic	H_3C-$(CH_2)_{14}$-COOH	C16:0	63–64	351
	Heptadecanoic	H_3C-$(CH_2)_{15}$-COOH	C17:0	59–61	227
	Stearic	H_3C-$(CH_2)_{16}$-COOH	C18:0	66–70	365-370
	Arachidic	H_3C-$(CH_2)_{18}$-COOH	C20:0	74–76	328
	Behenic	H_3C-$(CH_2)_{20}$-COOH	C22:0	75–80	306
	Lignoceric	H_3C-$(CH_2)_{22}$-COOH	C24:0	74–78	306
Unsaturated	Palmitoleic	H_3C-$(CH_2)_5$-CH=CH-$(CH_2)_7$-COOH	C16:1	33	162
	Oleic	H_3C-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH	C18:1	13–14	360
	Linoleic	H_3C-$(CH_2)_3$-$(CH_2$-CH=CH$)_2$-$(CH_2)_7$-COOH	C18:2	-5	229
	Linolenic	H_3C-$(CH_2$-CH=CH$)_3$-$(CH_2)_7$-COOH	C18:3	-11	230–232

[1]Ca:x : a = carbon number ; x = double bonds number

The presence of unsaturation in vegetable oils explains their great biodegradability [1,40]. However, it is well established that a high degree of unsaturation causes poor thermal and oxidative stability of vegetable oils [9,26,41,42]. In fact, oxidation is the major cause of oil deterioration [43] by producing low molecular compounds, toxic compounds and oxidised polymers [16]. Another concern is the tendency of vegetable oils to hydrolysis. Indeed, water is a very polar molecule (with regions with different attractions like the poles of a magnet) [6] and the ester linkage in vegetable

oils makes them polar. Water then hydrolyses vegetable oils by attacking ester linkage producing di and mono-glycerides, glycerol and free fatty acids [17]. The consequence of these degradations is that vegetable oil becomes unsafe for human consumption. Therefore, many researchers worked on moisture, oxygen and temperature effects on vegetable oils behaviour [16,43–47] with the aim to improve their stability. The possible positions of vulnerability of vegetable oils are shown in Figure 2.

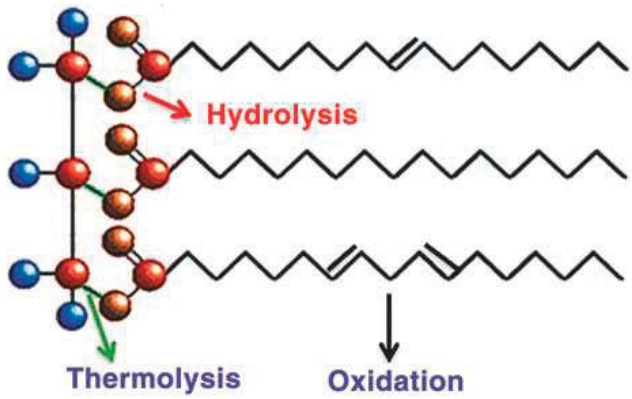

Figure 2: Vulnerability positions of triglycerides [14].

Vegetable oils are oxidised through contact with molecular oxygen in the air during processing and storage [16,39,48]. Autoxidation is an oxidation reaction that occurs without any external influence [29]. Increasing temperature also affects the stability of vegetable oils [17,24,49]. The study of the thermal and oxidative stability of vegetable oils makes it possible to know the evolution of their physical and chemical properties over time, depending on the applications.

2.2 Thermal stability of vegetable oils.

The thermal stability of a vegetable oil could be defined as the ability of the oil to resist to permanent changes due to the effects of heat [50]. Depending on the environment, in the presence or absence of air, thermal oxidative [17] or thermal degradation products [51] may be distinguished. Figure 3 shows physical and chemical changes in vegetable oils during frying due to heat and oxygen [17]. Different types of vegetable oils exhibit significant differences in the composition of the thermally decomposed oil [51]. The main thermal degradation products of vegetable oils are straight chain alkanes and alkenes [52], carboxylic acids, aldehydes, alkenes and alkadienes [53], alcohols and aromatic compounds [51,54].

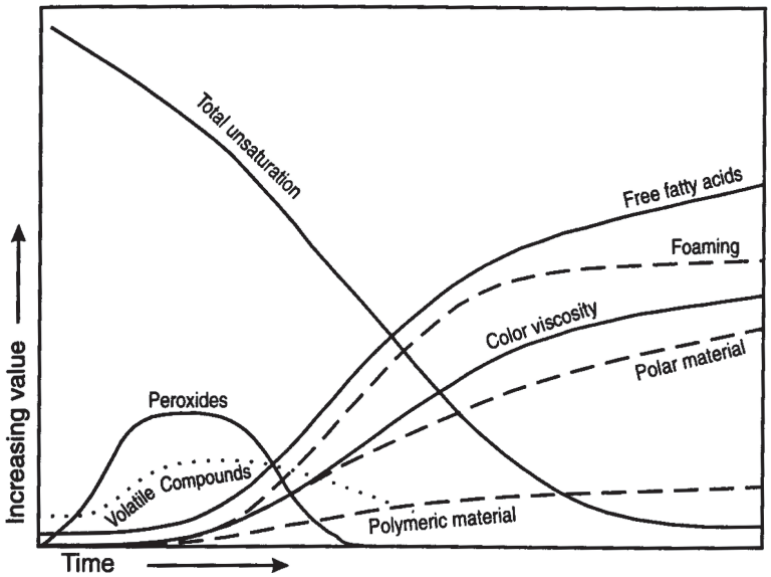

Figure 3: Physical and chemical changes of oil during deep frying [17].

Fortes and Baugh [54] have shown that the temperature, time and type of atmosphere have an influence on degradation products. Mass changes of oils are observed during the formation and breakdown of physical and chemical bonds at high temperatures [16]. Some studies [10,24,50,55,56] have shown thermogravimetric (TG) curves with three stages of degradation for various vegetable oils. The first could correspond to the degradation of polyunsaturated fatty acids, the second and the third respectively to that of the monounsaturated and saturated fatty acids [55,56]. In the case of the use of vegetable oils like thermal oils, since there is no worldwide industry standard test method for measuring thermal stability of organic thermal fluids [57], the standard ASTM D 6743 – 11 has defined a thermal stability test method for a minimum period of 500 hours [58].

2.3 Oxidative stability

Oxidation is the most important reaction of vegetable oils, resulting in chemical and physical properties changes [48]. Oxidative stability is known as the resistance to oxidation under defined conditions and is expressed as the period of time required to reach an end point which can be selected according to different criteria (e.g. development of rancidity) [43]. Oxidative stability depends on the vegetable oil composition and the conditions the sample is subjected to [15].

Saturated compounds are less prone to oxidation than unsaturated compounds [29]. Indeed, the presence of unsaturation in the triglyceride molecule due to C=C bonds from oleic, linoleic and linolenic acid moiety functions as the active sites for various oxidation reactions [48]. The higher the degree of unsaturation (more double bonds), the more sensitive the oil is to oxidation [9,59]. For triglycerides with eighteen carbons (C-18) the relative instability to oxidation is roughly 1:10:100:200 for

saturated, mono-, di-, and tri unsaturated triglycerides [7]. However, the fatty acid composition data of a vegetable oil gives only indicative information about its oxidative stability [60]. It is therefore not a good idea to measure the extent of oxidative degradation in terms of a single parameter, for example polyunsaturation [48].

Epoxidised soya bean oil (ESBO) (70 % palmitic and 30 % stearic acids) was compared to soya bean oil (SBO) and high oleic soya bean oil (HOSBO) for high temperature lubricant applications [26]. ESBO presented oxidative stability higher by a factor of 6 or more than HOSB. At 175 °C, the induction time for insoluble deposit formation of ESBO was roughly twice HOSBO (Figure 4b). This was due to the removal of multiple unsaturations in ESBO fatty acid chains.

According to the application, the use of antioxidants in vegetable oils could lead to different tendencies. The presence of antioxidants such as ascorbic acid 6-palmitate, squalene, oryzanol or phytosterols in refined sunflower and rapeseed oils or the addition of these antioxidants to these oils have shown a strong influence on their oxidative stability at high temperature [60]. If it is proven that antioxidants like caffeic acid, tertiary butyl hydroquinone (TBHQ) or phytosterols improve oxidative stability of frying oils [20,61,62], adding antioxidants may cause darkening of the oil and increases the formation of foam during deep frying [63]. Non-refined crude oils showed remarkably better stability than chemically refined oils at high temperatures [60]. The reason is that during refining of vegetable oils, a considerable amounts of antioxidative components are removed, lowering their natural oxidative stability [64]. Natural antioxidants appear to have stronger oxidation preventive capacity, more thermal stability and more activity after heat treatments in comparison with synthetic ones [65]. Addition of antioxidants like Lubrizol 7652 [26] or dibutyl-p-cresol and alkyldiphenyl amine [12] improves thermal and oxidative stability of vegetable oil base lubricants. However, the use of the latter had some consequences like the reduction of the load-carrying capacity [12].
High oleic (90%) sunflower showed higher resistance to oxidative polymerisation than 100% triolein, soya bean and canola oils during oxidation tests at 150 °C [66] (Figure 4a).

Other works determined the level of unsaturation as the major factor in the degree of oxidative polymerisation. An unsaturation increase in oil leads to polymerisation increase [9].

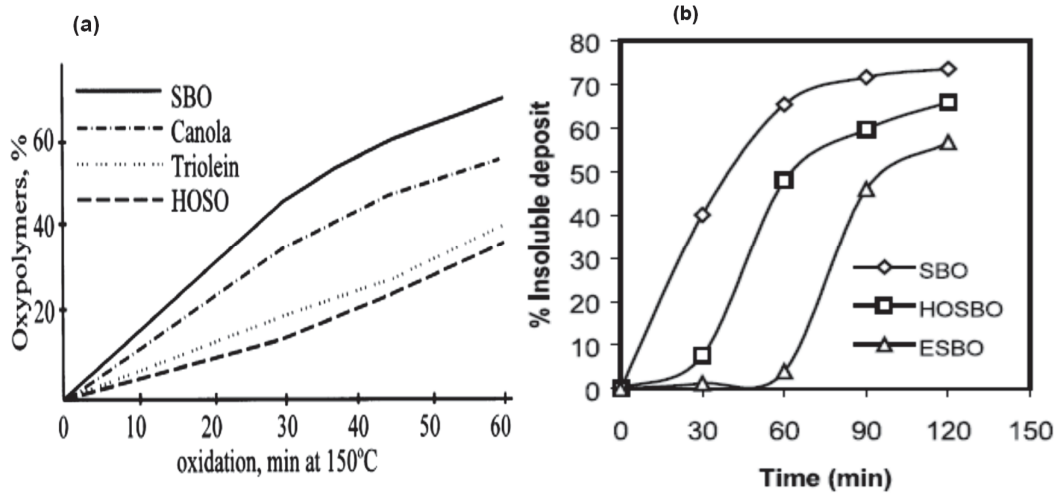

Figure 4: a) Oxy polymerisation tendencies [66] and (b) insoluble deposit [26] of some vegetable oils by thin film micro oxidation test.

2.3.1 Oxidative degradation products

Oil degradation process yields in primary oxidation products also called hydroperoxides [29]. These primary oxidation products degrade to secondary oxidation products: volatiles, non-volatiles, high molecular weight and free fatty acids as shown in Table 3.

Table 3: Oxidative products and analytical methods of identification

Stage	Compounds	Analytical techniques
Primary	Hydroperoxide	Chemiluminescence Electron spin-resonance spectroscopy Infrared Spectroscopy Combined techniques Titration
Secondary	Volatile	Gas chromatography Gas chromatography/mass spectrometry Fourier transform Infrared Spectroscopy
	Non-volatile	Ultra-fast gas chromatography High-performance liquid chromatography/mass spectrometry Atmospheric pressure chemical ionisation/mass spectrometry
	High molecular weight	Gel permeation high-performance liquid chromatography High-performance size-exclusion chromatography
	Free fatty acid	Titration Capillary gas chromatography High-performance liquid chromatography Supercritical fluid chromatography Nuclear magnetic resonance spectroscopy

The formation of oxidation products obeys to a chain mechanism consisting of initiation, propagation, branching and termination steps [17,24,67,68]. Table 4 summarises the oxidation mechanism of vegetable oils. The key event in initiation is the formation of a lipid radical, **R •**. This can occur by thermal or photochemical cleavage of an **R – H** bond or by hydrogen atom abstraction from **R - H** by an initiator free radical [67,69]. Metals can also act as catalysts [69]. Free radicals rapidly react with oxygen to form a peroxy radical **ROO•.** The peroxy radical can then attack another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical **ROOH + R•**, propagating the oxidation process [9]. These hydroperoxides produced are unstable and may degrade to radicals **RO• + •OH** that accelerates propagation of the reactions [24]. The **RO•** radical will react with more oxygen to form new hydroperoxides. However, not all free radicals propagate the oxidation process; some may interact with each other or degrade to give non-radical products [17]. At some point, the collection of hydroperoxides no longer remains stable and decomposes into a myriad of volatile and non-volatile secondary oxidation compounds [8]. Hydroperoxides are also shown to act as pro-oxidants. The oxidised compounds formed by hydroperoxide decomposition lower surface tension in the oil, and increase the introduction of oxygen into the oil to accelerate oil oxidation reactions, leading to deposits [16]. Extended heat treatment at 200–275 °C of unsaturated oils such as sunflower (linoleic-rich) and linseed (linolenic-rich) produces acids with cyclic structures [20]. However, the amounts of cyclic compounds are relatively small compared to non-volatile polar compounds and polymers which are the major decomposition products of frying oils [17]. Roasting of seeds has consequences on oil oxidative stability, antioxidant capacity and composition [62–64]. For Cisneros et al. [72], roasting favoured the oxidative stability of *Sacha-inchi* oil by increasing the antioxidant capacity. Lee et al. [71] found that as roasting temperature increased from 140 °C to 180 °C, the oxidative stability of safflower oil increased while fatty acid compositions remained the same. Yoshida et al. [70] gave for sesame seeds the suggested time and temperature of roasting to have high-quality (flavour and longer storage life) vegetable oil: 25 min at 160 or 180°C, 15 min at 200 °C and 5 min at 220 °C under experimental conditions in their studies.

Table 4: Oxidation mechanism of vegetable oils [9]

Initiation or induction	$RH \rightarrow R\bullet + H\bullet$
Propagation	$R\bullet + O_2 \rightarrow ROO\bullet$ $ROO\bullet + RH \rightarrow ROOH + R\bullet$
Branching	$ROOH \rightarrow RO\bullet + \bullet OH$ $RO\bullet + RH + O_2 \rightarrow ROH + ROO\bullet$ $\bullet OH + RH + O_2 \rightarrow H_2O + ROO\bullet$

Termination	ROO• + ROO• → ROOR + O_2 ROO• + R• → ROOR R• + R• → R-R
Peroxide decomposition	ROOR: various lower molecular weight compounds
Polymerisation	ROOR: various higher molecular weight compounds

2.3.2 Oxidation evaluation methods

There are several procedures for evaluating the oxidation stability of vegetable oils. It is possible to determine either the chemical composition of the oil, the physical properties, quantify the primary or secondary oxidation products or oxygen consumption. Some are called chromatographic methods and other inductive methods.

Most lipid analytical systems are based on the separating ability of a chromatographic procedure. Those of greatest interest are thin layer chromatography (TLC), high performance liquid chromatography (HPLC) and gas chromatography (GC) [20]. Another technique is the two-dimensional comprehensive gas chromatography with enhanced separation power and increased sensitivity that can provide a great advancement of knowledge in qualitative and quantitative components of vegetable oils among others [73]. Ultra-fast gas chromatography coupled with chemometrics is an effective tool used to assess vegetable oils quality during frying [74]. Table 3 presents some analytical methods for different oxidative products.

Inductive methods consist of evaluating the induction period observed before significant production of peroxides or secondary products begins. The induction period is highly dependent on the conditions of the oxidation experiment. These methods include the Schaal oven test, the Swift test or active oxygen method (AOM), and its automated forms such as the Rancimat apparatus or oil stability index (OSI) method. The OSI values are generally well correlated to the corresponding AOM values for peroxide values (PV) greater than 100. The method is automated and thus easier to use than the AOM. However, it is time-consuming and small variations in the airflow rate leads to large errors [75]. Thermoanalytical methods like differential scanning calorimetry and pressurised differential calorimetry (DSC and PDSC) [43,48,76], which are inductive methods, have received considerable attention. These methods present a great advantage because they have higher precision and sensitivity, use smaller amount of samples and the results are obtained faster [41] than with Rancimat method. The PDSC temperature ramping method is used to determine the onset temperature (OT) while oxidation induction time (OIT) is obtained with isothermal PDSC and DSC experiments [42]. OT and OIT are used to evaluate the oxidative stability of various vegetable oils during low temperature

storage. These conventional oxidation evaluation methods are generally carried out from 100 to 130 °C and are useful for determination of oxidative stability of oils during storage. Since frying temperature is in the range of 160 to 200 °C, oxidative stability evaluation by conventional methods can give misleading or poor information [77]. That has led Gertz et al. [77] to propose Oxidative Stability at Elevated Temperature (OSET), a method based on the polymerised triglycerides present in oil used for frying. However, Kowalski et al. [78] suggested that the assessment of vegetable oils stability for high temperature applications (e.g. frying) based on the Rancimat and PDSC methods could give consistent results.

3 Physical and chemical properties of vegetable oils

When vegetable oils are exposed to thermal stress with or without oxygen, their physical and chemical properties may change. The fact that vegetable oils are more prone to oxidation than mineral oils [79] leads to investigate their oxidation stability and their thermal ageing performances. The transformer industry has worked extensively on the use of vegetable oils as insulating fluids [6,80]. Vegetable oils have proven to be a favourable alternative to mineral oils and several vegetable oils are commercially available [1]. The popularity of vegetable oils as insulating fluids in distribution and power transformer market increases [6].

Table 5: Overview of electrical transformer insulating oils properties [6,28]

Name	Mineral oils	Silicone fluids	Synthetic esters	Vegetable oils
Type	Refined crude oil based distillate	Synthetic	Synthetic	Refined vegetable oil
Principal components	Complex mixture of hydrocarbons	di-alkyl silicone polymer	Pentaerythritol tetra ester	Plant-based natural ester
Source	Obtained from the distillation of petroleum	Made from chemicals	Made from chemicals	Extracted from crops
Biodegradability	Slow to biodegrade	Very slow to biodegrade	Readily biodegradable	Readily biodegradable
Oxidation stability	Good stability	Excellent stability	Excellent stability	Generally oxidation susceptible
Water saturation at ambient (ppm)	55	220	2600	1100
Dielectric breakdown (kV)	30–85	35–60	45–70	82–97
Total acidity ($mgKOH \cdot g^{-1}$)	0.015–1.2	0.01	0.3	0.015–0.6
Viscosity at 0 °C ($mm^2\ s^{-1}$)	76	81–92	26–50	143–77
at 40 °C	3–16	35–40	14–29	16–37
at 100 °C	2–2.5	15–17	4–6	4–8
Pour point (°C)	-30 to -60	-50 to -60	-40 to -50	-19 to -33

12

Flash point (°C)	100–170	300–310	250–270	275–328
Fire point (°C)	110–185	340–350	300–310	300–360
Density at 20 °C ($kg \cdot dm^3$)	0.83–0.89	0.96–1.10	0.90-1.00	0.87-0.92
Specific heat capacity ($J\ g^{-1}K^{-1}$)	1.6-2.0	1.5	1.8-2.3	1.5-2.1
Thermal conductivity ($W \cdot m^{-1}K^{-1}$)	0.11-0.16	0.15	0.15	0.16-0.17
Expansion coefficient ($10^{-4}\ K^{-1}$)	7-9	10	6.5-10	5.5-5.9

In fact, over 600,000 vegetable oils filled transformers operate worldwide without a reported fire or environmental incident [81]. By monitoring the evolution of some properties, it is possible to determine how vegetable oils are subject to degradations. Some properties like iodine value, peroxide value, total acid number, viscosity, flash point, etc. are commonly used to give an idea of oxidation or thermal degradation of vegetable oils. Table 5 shows some properties of oils used in transformers. Table 6 focuses on vegetable oils properties some of which are of interest for solar applications.

3.1 Iodine Value

The iodine value (IV) is an indicator of the number of unsaturation in the triglyceride. Iodine value represents the number of grams of iodine reacting with 100 g of oil [33] and gives indication of vegetable oil ability to dry in the presence of oxygen in the air.

The drying process is the formation of an elastic film due to oxidation and polymerisation where vegetable oil changes from liquid to solid state [39].

Table 6: Summary of some properties of vegetable oils .

Properties	PFAE oil [82]	Rapeseed oil [28]	Bio Electra [19]	BioTemp [6,7,19,83, 84]	FR3 [6,13,83,8 5]	Bivolt A [83]	Bivolt HW [83]	Palm oil [86]	Sunflower oil [28]	Camellia oil [87]	Coconut oil [86,88]	*Jatropha curcas* oil [83]	Midel eN [13]	High oleic Sunflower oil 90 Plus [13]	Castor oil [28]
Dielectric breakdown (kV)/2.5 mm	81	97.1	65	45-65	48-88	50	50	~33	58.4	-	60 at 100 °C	55	68	76	86.7
Viscosity ($mm^2 s^{-1}$)	5.06	41.1	-	49.81	33-36.7	36.6	40.1	34.5	41.2	39.9	55.8	39.72	37	40	261.5
cSt	-	-	39.2	45	-	-	-	-	-	-	-	-	-	-	-
Flash point (°C)	176	-	330	314-330	314	308	308	~310	-	322	~290	310	-	280	-
Fire point (°C)	-	-	-	347-360	347	342	338	~395	-	-	~320	>340	-	-	-
Pour point (°C)	-32.5	-	-26	-15 to -25	-	-	-	-	-	-	23	4	-	-	-
Density ($g\ cm^{-3}$)	0.86 at 40 °C	-	-	0.91 at 20 °C	-	-	-	-	-	0.90 at 20 °C	-	0.912	-	0.911	-
Total acid value ($mgKOH \cdot g^{-1}$)	0.005	-	-	0.05	0.02	-	-	-	-	0.04	-	0.04	0.06	0.16	-
Moisture content (ppm)	10	-	150	150-163	-	-	-	-	-	-	1	177	-	-	-
Coefficient of expansion ($°C^{-1}$)		-	-	$6.88\ 10^{-4}$	-	-	-	-		-	-	$7\ 10^{-4}$	-	-	-
Specific heat capacity ($J\ g^{-1}\ K^{-1}$)		-	-	1.96	1.88	-	-	-	--	-	-	1.92	-	-	-
Thermal conductivity ($W \cdot m^{-1} K^{-1}$)		-	-	0.17	0.167	-	-	-	-	-	-	-	-	-	-
Basic component	Palm oil		Sunflower oil	Sunflower oil	Soya oil	Corn oil	Sunflower oil	Palm oil	- Sunflower oil	Camellia oil	Coconut oil	Jatropha curcas oil	Rapeseed oil	Sunflower oil	Castor oil

14

Table 7 presents typical values of iodine value for vegetable oils. The more unsaturated is the oil, the higher is the iodine value and the greater is the tendency to dry at ambient temperature due to oxygen in the air. The iodine value accounts for the overall degree of unsaturation of an oil's constituent fatty acids, but does not relate directly to the inherent stability, as the latter is dependent on the fatty acid profile and particularly on the proportion of polyunsaturated fatty acids [33]. Some studies reported a decrease in iodine value during frying or thermal tests related to polyunsaturated fatty acids decrease [2,10,21,89]. The iodine value decrease can be attributed to the destruction of double bonds by oxidation and polymerisation [89]. During frying, the variety of fried items or the adding of new oil makes iodine value better indicator of oil composition rather than oil quality indicators [21].

Table 7: Typical values of iodine value of vegetable oils [90].

Type of vegetable oils	Iodine value ($g(I_2)$)
Non-drying oils	0 to 110
Semi-drying oils	110 to 150
Drying oils	> 150

3.2 Water content

Vegetable oils due to their constitution are hydrophilic because of the presence of ester group –COOR. Indeed, the esters are polar compounds (with regions having different attractions like the poles of a magnet) that tend to form hydrogen bonds with water molecules that are also polar [8]. Figure 5 shows the formation of a hydrogen bond between an ester and a water molecule [6].

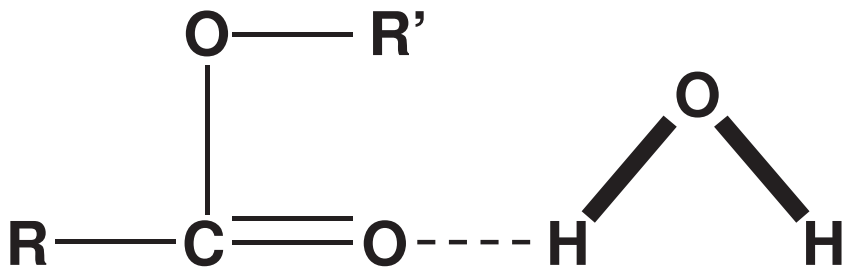

Figure 5: Hydrophilic nature of vegetable oils

This explains why water is 20 times more soluble in vegetable oil than in mineral oil at 23 °C [6] as presented in Table 5.

The main consequence of the presence of water in vegetable oils is the formation of free fatty acids (Figure 1). In transformers, this property of vegetable oils leads to

15

absorb more moisture from the insulating paper and thus to increase its life compared to mineral oils [19,91,92].

Several studies [93–96] have shown that water can have a positive effect on vegetable oils during high temperatures operations. The addition of water in soya bean oil heated at 200 °C and stored at 55 °C for 26 weeks delayed the formation of volatile compounds [93]. Peled et al. [94] observed that 0.7 % of water in cottonseed oil protected the oil from thermal oxidation and hydrolysis similar to the protection achieved by nitrogen atmosphere during frying at 180 °C up to 6 hours. They explained the result by the fact that the water was present in amounts sufficient to generate such a volume of vapours which could act as an inert gas-blanket. However, frying water-saturated cotton balls at 180-190 °C for six hours a day on four consecutive days showed an acceleration of oxidation, hydrolysis and polymerisation of soya bean oil. The degradation has been attributed to the release of free water into the oil [95]. These inconsistent data concerning the effect of water on the quality of the oil during frying led Dana et al. [96] to conduct a study on the role of water injected into the oil at high temperature for an extended period. They simulated frying conditions without food by heating corn and canola oils at 175 °C ± 5 °C up to 22 hours. Distilled water was continuously injected at various flow rates (0.1 to 1.0 $mL \cdot min^{-1}$) using different capillary diameters (0.156 and 0.937 mm) in order to evaluate the influence of the water bubbles size. The acid value increased with the increase in the flow rate and the capillary diameter during the experiment. The injected water had a protective effect on the heated oil samples by comparing the degradation compounds produced to those in the control sample. Furthermore, better oxidation protection was observed when smaller drop size of water was released during the process. The suggested reasons were that the smaller the bubble size, the larger the effective contact area with oil, and the less the agitation of the oil and the formation of an insulating steam blanket over the oil surface.

These results could be relevant for solar processes where nitrogen, which is costly, is generally used as sparging gas to protect heat transfer fluids against oxidation especially in the case of the use of vegetable oils. Kenda et al. [10] studied the suitability of *Jatropha curcas* crude oil, a vegetable oil, as alternative to thermal oils (synthetic or mineral) generally used in concentrating solar plants. The crude oil was aged by through thermal treatments up to 210 °C in galvanised steel and 316 L stainless steel reactors. The water content decreased in all cases and no correlation was made with the acid value, which presented no significant changes.

3.3 Acid value

Acidity is one of the most pertinent properties used for the study of the oxidation stability of mineral oils [5]. The reason is that there is no hydrolysis reaction for mineral oils as with vegetable oils, so the increase in acidity is solely due to oxidation [97]. Higher relative acid value is inherent in natural esters over mineral oils due to

their constitution [98] and, the fact that vegetable oils are sensitive to hydrolysis and oxidation raises the question of the relevance of the use of acid value as a marker of vegetable oils-based thermal fluid degradation. Another concern is the possibility of heat exchangers or pipes metal corrosion due to the acidity increase in case of vegetable use as thermal fluids. Various authors [2,10,85,87] have studied the evolution of acidity in vegetable oils for different ageing periods. After 165 hours of ageing at 120 °C, Perrier et al. [5] found that the acidity of vegetable oils increased more than that of mineral oils and the level of increase could be correlated with the nature of the seeds or vegetable oils improvements. Thermal ageing tests of various vegetable and mineral oils showed that hydrolysis generates more free fatty acids than oxidation [83–85].

Evaluation of free fatty acid content in high-temperature applications does not always reliably indicate vegetable oil quality. Perkins [100] found that a majority of the free fatty acids formed during deep-frying (140 °C–240 °C) are volatilised and removed from the oil by steam generated. Hoffmann [2] measured the acid value of rapeseed oil samples heated at 210 °C and 300 °C in nitrogen atmosphere for respectively 720 hours and 500 hours for their use as heat transfer fluid in concentrating solar applications. Despite ageing more visible by the darkening of the oil (Figure 6a) at 300 °C, the acid values were 0.08; 2.2 and 5.4 $mgKOH \cdot g^{-1}$ respectively for the new oil, the oil aged for 720 hours at 210 °C and for the oil aged for 500 hours at 300 °C. Gas chromatographic analysis of the latter showed the complete disappearance of main fatty acids constituting the oil namely C18:1; C18:2; C18:3; C16:0 and C18:0 as presented in Figure 6b. The oil was thermally polymerised and in this case, acid value did not reflect the degradation rate of oil and could give misleading information on the thermal stability of the fluid [2]. Peled et al. [94] also observed that the presence of carboxylic groups in the polymeric products contribute to raising the acid value of heated oils during frying.

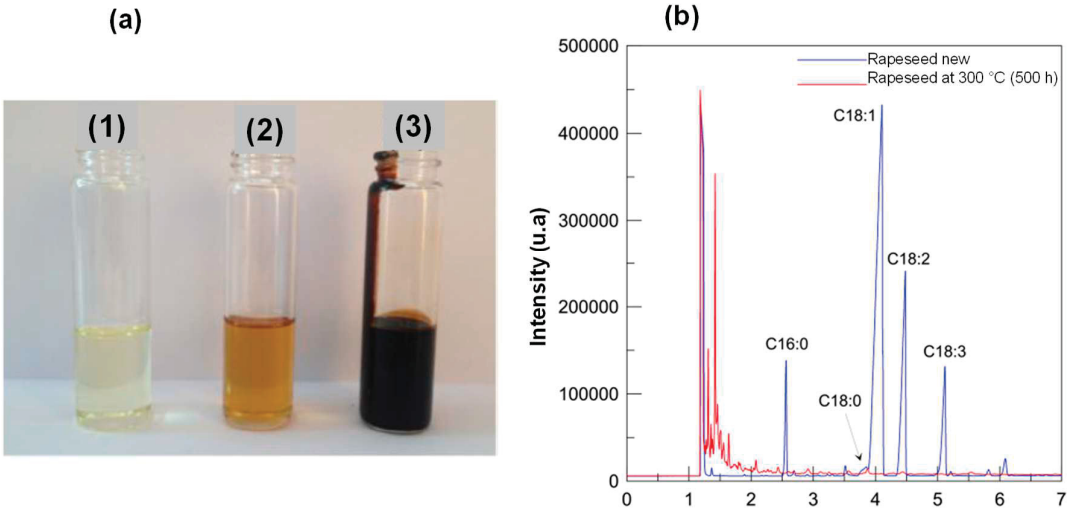

Figure 6:a) Rapeseed oil 1) new, 2) aged at 210 °C, 3) aged at 300 °C and b) fatty acids GC spectra of new and aged oil at 300 °C [2].

Yao et al. [91] thermally aged insulation pressboard samples at 130 °C for 80 days in the presence of either vegetable (FR 3) or mineral (NYMAS Gemini X) insulating oils, with copper wires together in well-sealed stainless vessels. The vessels contained some air in their vacant space at the beginning of the thermal ageing experiments. They observed that, although the acid value of vegetable oil is about 12 times higher than that of mineral oil, the degradation rate of paper insulation during thermal ageing was weaker with vegetable oil.

As a result, acidity, which is used to reflect the performance of mineral oils, may not be suitable for vegetable oils [85,91]. However, a limit value of 2.4 $mgKOH \cdot g^{-1}$ in aged vegetable oil has been suggested as this means that the moisture content in the insulation paper is around 2 % [87].

The maximum limit acid number of new insulating based vegetable oil fluid is 0.06 mg KOH g^{-1} while it is 0.3 mg KOH g^{-1} for the aged ones in service [97]. A recent study on vegetable oils performance in moisture-rich environments [101] found that acidity increase due to hydrolytic degradation is not detrimental to metals. Despite acidity has increased beyond that acceptable limit values (up to 20 times higher than the standard limit after 1984 h of ageing), copper conductors and steel sample holders used in the study have not shown any sign of corrosion. The suggested reason was that hydrolysis of vegetable oils mainly yield long-chain fatty acids which do not cause extra corrosion of copper and steel. Adversely to the short chain acids resulting to the breakdown of mineral oil during oxidation which are more corrosive [98]. Therefore, it has been suggested to measure both low molecular acids (responsible for corrosion) and total acid content for vegetable oils insulating fluid diagnostics [101].

The fact that short-chain carboxylic acids (C7:0 and C8:0) dissociated into H+ ions explained their corrosiveness with copper and steel since the H+ ions govern corrosion mechanism [101]. Short-chain fatty acids could be therefore used as markers to give an early indication of oil quality.

3.4 Peroxide value

As already said, vegetable oils tend to oxidise when exposed to heat and oxygen. This oxygen combines with the double bonds of fatty acids to form hydroperoxides [33]. Temperature increase favours the oxidation of vegetable oils and then the peroxide value [102]. The peroxide value tends to increase during the first 20 hours of deep-frying and then decreases [21]. Furthermore, peroxides generally decompose at about 150 °C and hence at temperatures above no accumulation of peroxides occurs [17,102,103]. Peroxide value provides an indication of nutritional quality of vegetable oils. The fact that peroxides decompose faster as the temperature rises and give rise to secondary products, makes this parameter not the best to assess the decomposition status of oils at high temperature [21].

3.5 Flash, fire and smoke points

The flash point is the temperature at which sufficient oil volatile is generated to support ignition but not a flame. The fire point is the temperature at which an oil generates volatile enough to support a flame. The smoke point is the temperature at which a continuous smoke begins to form and can be seen as bluish smoke. These temperatures are lower for oils with a higher free fatty acid content or with short-chain acids. The reason is that free fatty acids have a higher vapour pressure than triglycerides [33].

The required smoke point temperature for vegetable oils used for frying is at least 200 °C [17]. During deep-fat frying, accumulation of decomposition products like free fatty acids and glycerol results in a decrease of the smoke point temperature [63]. The smoke is an indication of chemical breakdown of the oil to glycerol and free fatty acids [104]. The use of oils in temperature above their smoke point result in high emissions of volatile compounds including potential toxic compounds such as acrolein (cancerigenic aldehyde) [104].

Compared to some industrial fluids generally used, vegetable oils have higher flash and fire points (Table 8) [2,12,74–76]. These properties are suitable both for frying and for high temperature lubricants or thermal fluids where fire retardant played a great role.

Table 8: Flash and fire points of some thermal and insulating oils

Oil	Therminol VP-1 [10]	Syltherm XL T [10]	Xceltherm 600 [10]	NYTRO Gemini X [105].	Soya bean [2]	*Jatropha curcas* crude oil [2,10]	MIDEL 7131 [106]	ProEco TR 3746
Composi-tion	Diphenyl oxide / biphenyl	Polysiloxane	Paraffinic	Mineral oil	Triglycerides	Triglycerides	Synthetic ester	Synthetic ester
	synthetic oil	synthetic oil	mineral oil		Natural ester (edible)	Natural ester (non-edible)		
Flash point (°C)	124	47	193	> 140	330	220-240	275	> 280
Fire point (°C)	127	54	216		363	254-275	322	

Hydrolysis and oxidation breakdown triglycerides, producing free fatty acids and the laters lower the flash and fire points. It is therefore important to evaluate flash and fire points evolution during oxidation and thermal tests. Divakaran et al. [86] compared flash and fire points of a mineral oil with those of two vegetable oils (coconut oil and palm oil) for 30 days at 150 °C, using copper as a catalyst. Despite the fact that fire and flash points of the oils decreased with ageing time and conditions, vegetable oils had much higher values than the mineral oil. That means vegetable oils are less flammable than mineral oils [7] and thus expected to provide a smooth operation at higher thermal condition, high-loading condition and in high voltage transformers [86].

19

Hoffmann [2] studied thermal stability of rapeseed oil at 210 °C by measuring the flash point during isothermal tests of 720 hours and 2160 hours with various thermal energy storage materials. The flash point evolution was correlated to acid value (IA) by Equation (1).

$$T_{flash\,point} = 327.589 - 11.504\,IA + 0.481\,IA^2 \quad (1)$$

Where IA is acid value in mg KOH g^{-1} and *T* the temperature in degree Celcius. The flash point decreases with acid value increase. For the colza aged alone a decrease of 9% was registered for IA of around 4 mg KOH g^{-1}. Moreover, storage materials insert in oil samples reduced the flash point compared to oil samples aged alone as presented in Figure 7a.

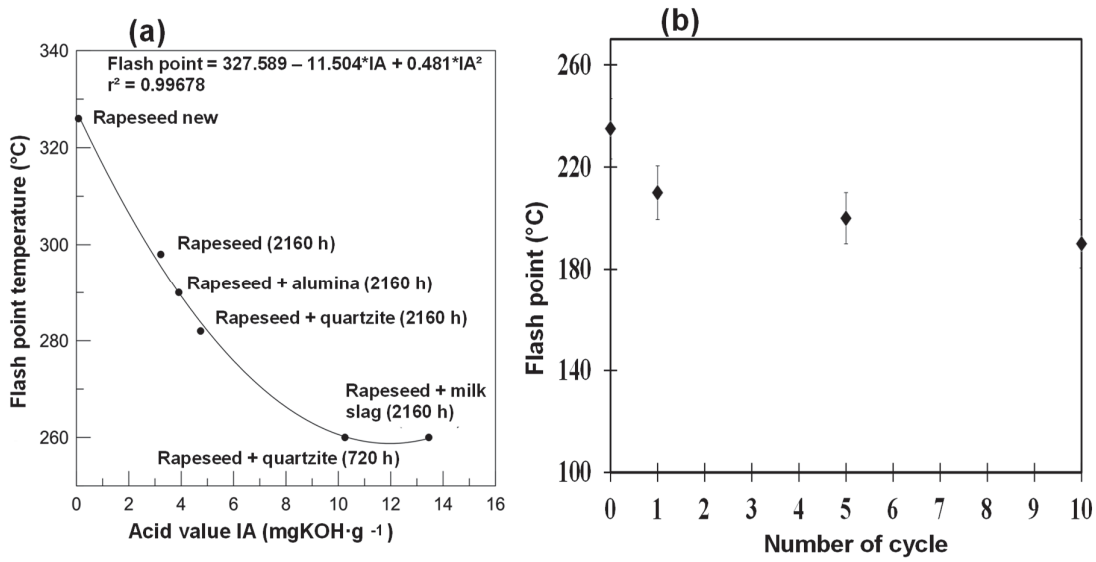

Figure 7: a) Flash points of new and aged rapeseed oil as the function of acid value [2] and b) Flash point of JaCCO as the function of cycles during pseudo-static tests [10].

Kenda et al. [10] measured the flash point of *Jatropha curcas* crude oil (JaCCO) during thermal ageing tests using galvanised steel and 316L stainless steel reactors under steady state and dynamic conditions up to 210 °C. The flash point remained constant at 235 °C after an isothermal test of 500 hours. However, irrespective of the type of reactor, a drop in the flash point was observed during the intermittent heating tests as presented in Figure 7b. The suggested reason for this decrease was the fact that the reactor's repeated openings for sampling renewed the oxygen and accelerated the oxidation reaction.

3.6 Specific heat capacity

The specific heat capacity is the energy required to raise the temperature of the unit mass of a given substance by 1 K. Specific heat capacity (Cp) values of vegetable oils are very important for industrials to optimise processes and energy inputs.

Different calorimetric techniques with various degrees of accuracy and precision have been developed to determine specific heat of vegetable oils: differential scanning calorimetry (DSC), adiabatic scanning calorimetry (ASC), modulated differential scanning calorimetry (MDSC) etc. Among them, DSC is the most widely used thermal analysis technique [8,78–81]. The combination of DSC and MDSC provides complementary results that can be used in further quality assessment of vegetable oils submitted to thermal stress [110]. Hoffmann et al. [4] used a calorimeter for the measurement of specific heat capacity of seven vegetable oils from ambient to 240 °C. The equipment was theoretically more accurate than DSC depending on its low temperature ramp (1 °C min^{-1} against 5 °C min^{-1} for DSC), the larger quantity of samples and a more accurate heat flow-metre.

Several correlations presented in Table 9 were proposed for specific heat determination of various vegetable oils: The specific heat capacity of vegetable oils has often been observed to increase with temperature [4,113].

In 2000, Morad et al. [114] presented a mathematical model to estimate the specific heat of liquid triglycerides based on their fatty acid composition and molecular weight in temperature range of 60 to 180 °C. The estimated specific heat capacity was compared to experimental results obtained by DSC analysis and the uncertainty was within ± 5%. The mathematical model was presented as applicable to all types of vegetable oils provided the fatty acid composition is known. However, it was observed in some cases an increase of deviation between estimated and experimental values of specific heat capacity with temperature increase (Figure 8); the reason is the fact that specific heat capacity depends not only on molecular weight but also on degree of unsaturation and temperature [114].

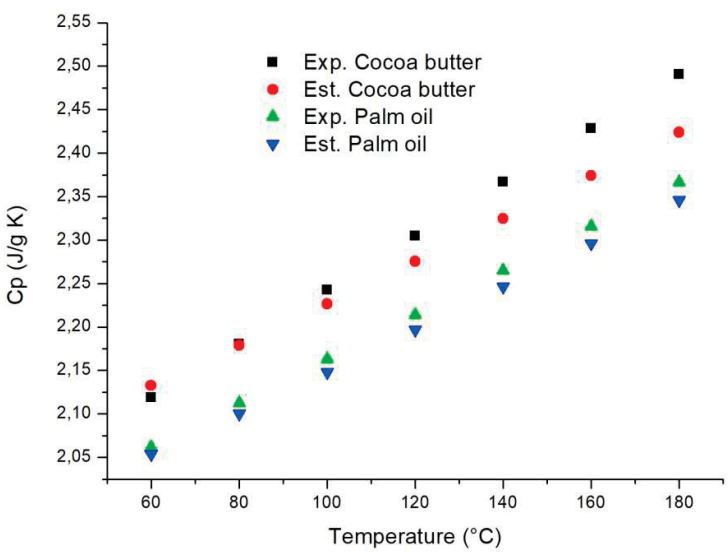

Figure 8: Comparison of estimated and experimental specific heat values of cocoa butter and palm oil [114]

21

Wang and Briggs [111] used the mathematical model developed by Morad et al. [114] as presented in Table 9. From the results, specific heat increased with the increase in chain length and degree of saturation of vegetable oils. Experimental values of specific heat were not given for comparison with these estimated values.

The specific heat capacity of twelve vegetable oils of varied chemical composition was experimentally determined as a function of temperature from 35 °C to 180 °C [112] by DSC as presented in Table 9. About 8 mg to 10 mg of oil samples was placed in hermetically sealed aluminium pans and the scan rate was 20 °C min^{-1}. Olive oil had the lowest values and almond oil the highest values respectively 1.746 $kJ \cdot kg^{-1} \cdot K^{-1}$ to 1.787 $kJ \cdot kg^{-1} \cdot K^{-1}$ and 2.354 $kJ \cdot kg^{-1} \cdot K^{-1}$ to 2.823 $kJ \cdot kg^{-1} \cdot K^{-1}$. The specific heat capacity of the oils samples increased with temperature and the percent increase was about 17 % for all the twelve oils in the temperature range.

Santos et al. [108] measured the specific heat capacity of eight vegetable oils including sunflower, olive and soya bean from 40 to 190 °C by DSC. 22.0 mg ± 0.5 mg of vegetable oil samples were placed in aluminium crucibles, scan rate of 5 °C min^{-1} up to 30 °C and were kept for 5 min then heated at 10 °C min^{-1} up to 200 °C, under a dynamic atmosphere of nitrogen (50 mL min^{-1}). The specific heat capacity of olive oil and for mixtures containing olive oil was higher than those of other oils. The difference was attributed to the higher concentration of monounsaturated fatty acids present in olive oil (71.3 %) compared to other oils (65.0, 23.0, 33.5, 24.3, 40.8, 29.2 and 41.3 % respectively for rapeseed, sunflower, corn, soya bean, rice bran, soya bean/olive mixture and sunflower/olive mixture oils). However, rapeseed oil with one of the highest values of monounsaturated fatty acid percentage (65.0 %) had one of the lowest specific heat values for the temperature range (40 °C-190 °C). This implies that it is not simply the monounsaturation percentage that defines the specific heat capacity value. Indeed, Contreras-Gallegos et al. [109] showed that if the monounsaturated acids increase the specific heat capacity value, the presence of polyunsaturated acids in vegetable oils reduces it.

Hoffmann et al. [4], found (Table 9) a specific heat capacity correlation for seven vegetable oils from 25 °C to 240 °C. The specific heat increased for all the tested oils with temperature increase except in certain intervals where large variations (decreasing) were visible. Kowalski [113] measured specific heat capacity of some edible oils and fats by DSC from 343 K to 413 K. At temperature above 380 K, sunflower oil (89 % unsaturated) presented exothermal effect attributed to autoxidation in air atmosphere. However, in nitrogen atmosphere, despite the fact that the exothermal was shifted toward higher temperatures, it was not completely suppressed. For Kowalski [113], it is the proof that there are thermal events other than oxidation in vegetable oils heated samples.

22

Table 9: Temperature dependence of specific heat capacity correlations

References	Generalised expression of specific heat capacity: $Cp\ (T) = aT^4 + bT^3 + cT^2 + dT + e$				
	Correlation: polynomial	$Cp = cT^2 + dT + e$ (T in K)			
	Oil samples:	Soya bean	Rapeseed	Sunflower	Corn
Kowalski, 1988 [113]	c (× 10^{-4} kJ kg^{-1} K^{-3})	0.1681	-0.03122	-0.1021	-0.2078
	d (× 10^{-3} kJ kg^{-1} K^{-2})	14.64	-0.8973	9.492	16.83
	e (× kJ kg^{-1} K^{-1})	-1.1356	1.8928	-0.6634	-1.2917
	Temperature range (K)	343–413	*343–408*	343–398	343–398

	Correlation: linear	$Cp = dT + e$ (T in K)				
Wang and Briggs, 2002 [111]	Oil samples: soya bean	Commodity	High oleic	Lipoxygenase-free	Low-linolenic	Low-saturated
	d(kJ kg^{-1} K^{-2})	0.0024	0.0024	0.0024	0.0024	0.0024
	e (kJ kg^{-1} K^{-1})	1.8146	1.8583	1.8210	1.8178	1.7992
	Temperature range (°C)	25–300	25–300	25–300	25–300	25–300

	Correlation: linear	$Cp = dT + e$ (T in K)											
	Oil samples	Almond	Canola	Corn	Grape seed	Hazelnut	Olive	Peanut	Saf-flower	Sesame	Soya bean	Sun-flower	Walnut
Fasina and Colley, 2008 [112]	d (× 10^3 kJ kg^{-1} K^{-2})	3.314	3.003	3.162	2.920	2.492	1.715	3.677	2.832	3.043	2.792	3.477	2.835
	e (× kJ kg^{-1} K^{-1})	2.143	2.086	1.963	2.037	1.807	2.025	2.449	2.181	2.446	1.956	2.566	2.165
	R^2	0.996	0.998	0.997	0.993	0.996	0.998	0.985	0.998	0.997	0.996	0.998	0.962
	Temperature range (°C)	35–180	35–180	35–180	35–180	35–180	35–180	35–180	35–180	35–180	35–180	35–180	35–180

	Correlation: polynomial	$Cp = aT^4 + bT^3 + cT^2 + dT + e$ (T in °C)						
Hoffmann et al., 2015 [4]	Oil samples	Copra	Cotton	Jatropha	Palm	Rape-seed	Soya bean	Sunflower
	a (× 10^{-9} kJ kg^{-1} K^{-5})	–0.830	1.373	2.262	2.782	1.621	0.807	0.760
	b (× 10^{-7} kJ kg^{-1} K^{-4})	4.647	–7.924	–10.423	–16.443	–8.735	–3.705	–3.310
	c (× 10^{-5} kJ kg^{-1} K^{-3})	–8.632	14.060	12.947	30.534	14.933	5.491	4.147
	d (× 10^{-3} kJ kg^{-1} K^{-2})	8.856	–5.443	0.441	–16.320	–5.976	–0.409	1.200
	e (kJ kg^{-1} K^{-1})	1.8447	2.1186	1.9608	2.4558	2.0985	1.9664	1.9506
	R^2	0.99932	0.98861	0.98443	0.99582	0.99016	0.99508	0.99356
	Temperature range (°C)	25–240	25–240	25–240	40–240	25–240	25–240	25–240

23

The specific heat of vegetable oils depends on some factors (chain length, degree of saturation, temperature etc.). If for unused vegetable oils the specific heat capacity value increases with temperature, it is important to know how it behaves after thermal ageing.

Numerous studies reported changes in thermal characteristics of vegetable oils [41,90–92] after being used for frying. Gloria and Aguilera [116] heated 200 g of three vegetable oils (sunflower, colza and groundnut) at 180 °C without food in open glass beakers (250 mL) for 10 hours. Enthalpy of oils decreased from 46.8 $J \cdot g^{-1}$ to 4.5 $J \cdot g^{-1}$ for sunflower oil, 49.0 $J \cdot g^{-1}$ to 5.7 $J \cdot g^{-1}$ for colza oil and 29.0 $J \cdot g^{-1}$ to 2.3 $J \cdot g^{-1}$ for groundnut oil. The decrease was attributed to the disappearance of triglycerides and degradation products formed. Tan and Man [117] obtained similar results after heating of various vegetable oils in open fryers at 180 °C for 12 hours. Paul and Mittal [22] collected 38 samples of canola oil at the end of each day from a North American fast food chain. Oils were heated about 160 °C up to 9 days but authors were not precise on whether the fryers were open or not. Decomposition products mostly consisted of free fatty acids about 49 % to 69 % in highly degraded oil. A significant decrease in specific heat (14.1 %) was observed with higher levels of canola oil degradation in 7 days at around 160 °C. Another study [115] looked on the recovery of used sunflower oil utilised in repeated deep frying process (170 °C, 50 consecutive deep frying). The adsorbent (mixture of 2 % pekmez earth, 3 % bentonite, and 3 % magnesium silicate) used for that purpose was developed elsewhere [118]. The free fatty acids content of oil increased during the frying from 0.17 % to 0.29% and the use of adsorbents reduced that value to 0.13 %. If the adsorbent reduced peroxide value of oil, it increased the amount of aldehydes (secondary oxidation products). As presented in Figure 9a. Specific heat of treated oil was lower than that of untreated one except for the first frying.

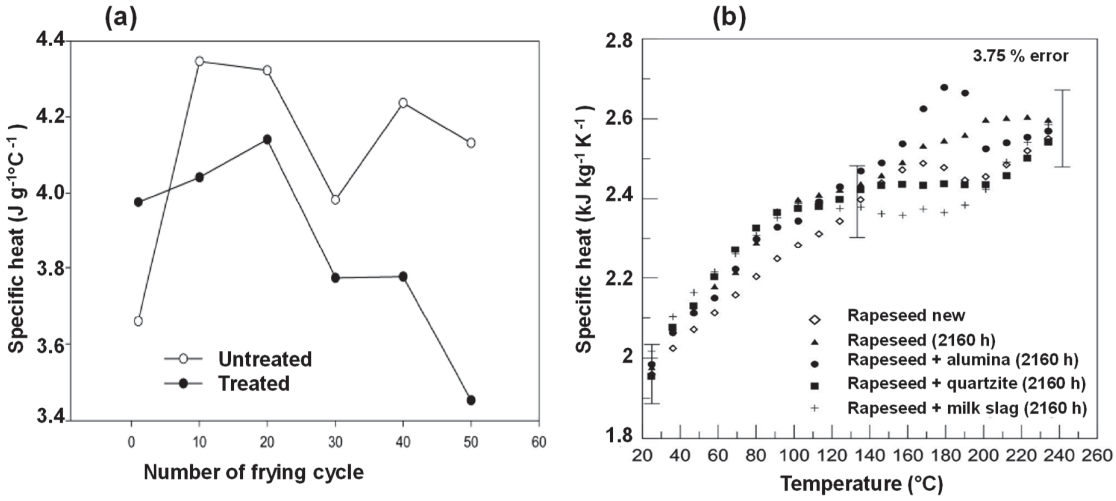

Figure 9: a) Specific heat capacity values of used sunflower oil [115] and b) rapeseed oil thermally aged [2].

24

The specific heat capacity of new rapeseed oil and rapeseed oil heated alone and coupled with some storage materials for 2160 hours isothermal test at 210 °C was determined from ambient to 240 °C [2]. Stainless steel reactors and nitrogen atmosphere were used to limit external interactions. All specific heat values increased with temperature increase except in certain intervals. Despite variations between 150 °C and 210 °C, values were quite similar around 240 °C (Figure 9b).

3.7 Thermal conductivity

Thermal conductivity measures the ability of a material to conduct heat [119] or the rate of heat transfer through a unit thickness of the material per unit area and per unit temperature difference [120]. Thermal conductivity of vegetable oils generally decrease with temperature increase [37,119,121,122]. There are several methods for measuring thermal conductivity of fluids: transient hot wire (THW) [37], photo acoustic techniques [123], temperature oscillation technique [124], 3 omega-hot wire method [121], etc. Most of them were used to measure the thermal conductivity of vegetable oils [37,123,125,126] below 100 °C. Nevertheless, some authors have studied the temperature dependence of thermal conductivity of vegetable oils [121,127].

Spieß et al. [127] reported the results of thermal conductivity measurement of some foods including olive oil from 50 to 135 °C. A collaborative study was organised in some laboratories and for olive oil a very pronounced scatter of experimental values was observed. For one group of results, an increase of thermal conductivity with temperature increase was obtained while for another one it was the opposite behaviour. The measuring procedures were incriminated due to the variability in contact between heat source and test material or contact between test material and thermal sensors.

Hoffmann et al. [121] studied thermal conductivity of seven vegetable oils from 20 °C to 230 °C for use as heat transfer fluids in concentrated solar power plants. The method used was 3 omega-hot wire with low relative error (1.2 %) and an absolute accuracy of 2 %. The method allows continuously, independently and real-time measuring of thermophysical properties of oils for thermal applications. For all the investigated oil samples, the thermal conductivity decreased with temperature increase. Three different behaviours were observed depending on fatty acid composition: Saturated oils (copra oil with 93.12 % saturated fatty acids) had stronger decrease than unsaturated oils (rapeseed oil with 90.22 % unsaturated fatty acids). For vegetable oils with approximately the same amount of unsaturated fatty acids, the absolute values of thermal conductivity and temperature dependencies were similar (Figure 10). Moreover, thermal conductivity of some vegetable oils is nearly similar if not higher than those of well-established thermal oils at 210 °C [10,121].

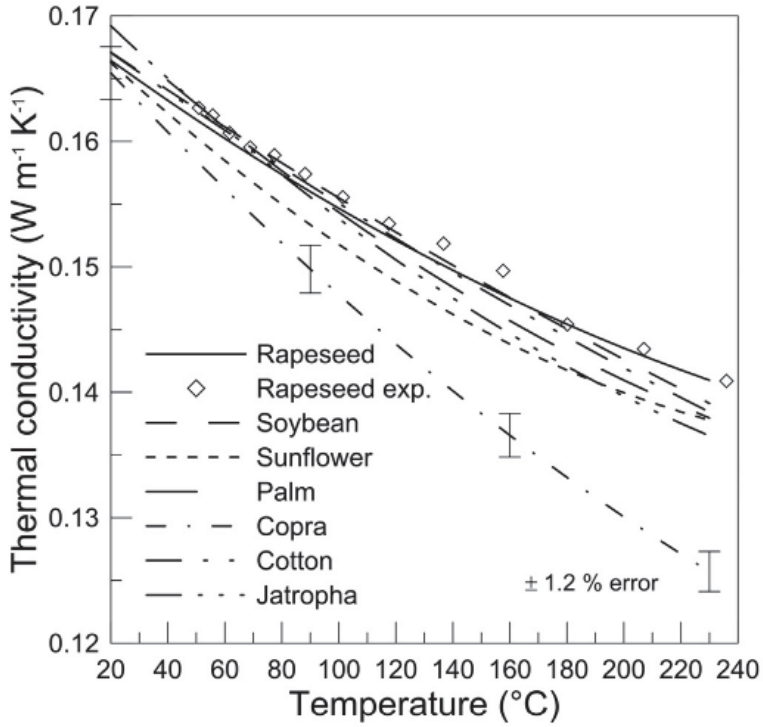

Figure 10: Temperature dependence of thermal conductivity for some vegetable oils [4].

A temperature dependence of thermal conductivity correlation was determined for each vegetable oil studied as presented in Table 10.

During isothermal tests of 2160 hours at 210 °C, rapeseed oil showed a slight decrease in average thermal conductivity of 2 %. The introduction in oil of thermal energy storage materials (alumina, basalt, milk slag and quartzite) had an incidence on thermal conductivity values. For rapeseed oil with alumina, a drop of 0.7 % compared to the reference oil was observed while and increase of 1.9 % and 3.8 % was noted with milk slag and quartzite respectively [2].

Table 10: Temperature dependence of thermal conductivity correlations for some vegetable oils [4]

Correlation: polynomial	$\lambda(T) = fT^2 + gT + h$ (T in °C)						
Oil samples	Copra	Cotton	Jatropha	Palm	Rapeseed	Soya bean	Sunflower
f ($\times 10^{-7}$ W m^{-1} K^{-3})	2.44	1.06	2.80	2.58	2.00	0.92	3.50
g ($\times 10^{-4}$ W m^{-1} K^{-2})	-2.503	-1.629	-2.258	-2.113	-1.714	-1.563	-2.232
h (W m^{-1} K^{-1})	0.1703	0.1702	0.1736	0.1729	0.1698	0.1702	0.1706
R^2	0.99567	0.99214	0.99222	0.99382	0.99214	0.99486	0.99214
Temperature range (°C)	25–230	25–230	25–230	40–230	25–230	25–230	25–230

26

3.8 Viscosity

Viscosity is an important property in fluid flow, heat transfer unit operation, etc. It could be defined as the resistance of oil to flow [33]. Vegetable oils viscosity increases with chain lengths of triglyceride fatty acids and decreases with unsaturation [128,129]. Monounsaturated (C18:1) and polyunsaturated (C18:2) acids make a great contribution to flow behaviours of vegetable oils. Viscosity decrease was observed with an increasing portion of C18:2 and a decreasing portion of C18:1 [130]. Viscosity is better related to polyunsaturated than to monounsaturated fatty acids [128]. Toscano et al. [131] confirmed the important role played by unsaturation and molecular size of triglycerides on viscosity. Unsaturation and chain length were described by the effective carbon number (ECN) and correlated with activation energy (E_a) (Equation 2) and viscosity for soya bean oils of different fatty acids compositions [111]. The relationship was linear and showed that the longer the chain of the fatty acyl group, the more viscous the oil, the greater the E_a and the more rapid decrease of viscosity with temperature increase.

The effect of the temperature on viscosity of vegetable oils has been extensively studied [9,24,83,86,87,108–110] and several correlations summarised in four equations were used to model it [135,136] as presented in Table 11. The decrease of vegetable oils viscosity when temperature increases is due to the decrease of intermolecular forces (attraction between the polar molecules) in oil and thermal energies increase [137]. Fasina and Colley [112] experimentally determined viscosity of twelve vegetable oils from 35 to 180 °C and three models: two exponential models (Arrhenius and modified Williams-Landel-Ferry WLF) and one power law model were used to describe temperature effect on viscosity. All the models had correlation coefficient greater than 0.99 but modified WLF equation was the most suitable model with the lowest values of standard errors of estimate and Arrhenius, the worst of all the oils in the temperature range. Noureddini et al. [136] correlated the temperature dependence of viscosity from 23 °C to 110 °C of various oils and fatty acids using Equation 2. Coefficients were found in the temperature range for each vegetable oil and fatty acids with a mean deviation less than 2.0 %. Hoffmann et al. [4] experimentally obtained the viscosity evolution of seven vegetable oils in temperature range of 50 °C to 300 °C. The power law (Equation 4) was used and coefficients were given for each of the oils with correlation coefficients greater than 0.98.

Vegetable oils viscosity is generally higher than that of mineral oils used as thermal oils (Table 5). Many studies reported the viscosity increase with thermal ageing [2,5,10,83,85,128]. The main reason for that increase is oxidation or thermal degradation of oils leading to polymerisation [17,85,128].

In the case of polymerisation, the viscosity increase is an irreversible phenomenon different to thickening observed when vegetable oils are exposed to cold temperatures [138]. Viscosity should be taken into account to assess the vegetable oils ageing because higher viscosity would affect the ability to transfer heat and result

in hot-spots. It is therefore of great interest to study that property to confirm the possible replacement of mineral oils by vegetable oils.

Table 11: Temperature dependence of viscosity correlations

Exponential [112,135,136]		Power law [4]	Polynomial [135]
$\eta = \eta_0 + Ae^{(B+\frac{C}{T+E}+\frac{D}{TZ})}$	$\eta = B + \left[\frac{(A-B)}{\left(1+e^{\frac{T-T_0}{dT}}\right)}\right]$	$\eta = AT^n$	$\eta = A + BT + CT^2 + DT^3$
Equation 2:	*Equation 3:*	*Equation 4:*	*Equation 5:*

A,B,C,D,E and Z are constant, T is absolute temperature (K), E_a is activation energy (J/mol), T_0 is absolute temperature for dynamic viscosity 50 Pa s, dT is width and η is dynamic viscosity (Pa s).

Vegetable oils presented good potential as high temperature lubricant [26,44] due to their structure and properties. The triglyceride structure of vegetable oils provides desirable qualities in a lubricant. Long polar fatty acid chains provide high strength lubricant films that interact strongly with metallic surfaces, reducing both friction and wear [9,26]. Vegetable oils make the best lubricants when they have high levels of oleic acid and low levels of both saturated and polyunsaturated fatty acids [20]. High saturated fatty acids content leads to low cold flow behaviour of vegetable oils while high content of polyunsaturated fatty acids like linoleic and linolenic are undesirable because they reduce oxidative stability [20,41]. The more resistant a lubricant is to oxidation, the less is the tendency it has to form deposits, sludge, corrosive by-products and it is more resistant to undesirable viscosity increases [41]. Rapeseed oil based hydraulic fluid was used, often at temperatures above 100 °C, in agricultural machinery for more than 35,000 hours and 21,000 km [25]. No damage was observed in the machines and levels of biodegradability and ecotoxicity remained constant. On average, 60 % of the machines' oil reserve was replaced during the 6 years field experiments. This has shown the possible application of rapeseed oil in agricultural machinery. Asadauskas et al. [44] showed the potential of high oleic vegetable oils as a lubricant.

Murakami and Sakamoto [12] studied the lubricating properties of three vegetable oils of different composition and paraffinic oil (mineral oil) containing unsaturated fatty acids under high-contact-pressure conditions up to 200 °C. They found that the types of fatty acids composing the triglycerides and the concentration of dissolved oxygen appeared mainly to control the lubricating performance. Castor oil (85–90 % ricinoleic acid) showed lower friction over the full temperature range. Olive oil (86 % oleic and 11 % palmitic acids) gave low friction at low temperature but the friction increased at high temperature while rapeseed (many unsaturated acids) presented the opposite behaviour. Increasing dissolved oxygen concentration produced stable low friction and increased load-carrying capacity in rape seed oil at high temperature. The

addition of linolenic acid to paraffinic oil with high oxygen content enhanced the load-carrying capacity and maintained low friction even under high-loading conditions [12]. This may be explained by the formation of a friction polymer that produced low friction and low wear [12,26]. It was uncertain, however, as to which aspect led to the improved performance: increased viscosity, free acids or polymerisation [9].

It is well known that have catalytic effect on oxidative stability of vegetable oils [6,85,139]. Copper is usually used as a catalyst to analyse oxidative stability of thermal oils used in transformers at high temperatures [5,91]. Kenda et al. [10] found that galvanised steel affected more the viscosity of *Jatropha curcas* crude oil than 316 L stainless steel at 210 °C during various thermal treatments.

Heating vegetable oils in the presence of air makes viscosity increases with ageing duration more than in sealed conditions [5,85,87,91,99]. Since viscosity affects heat transfer, vegetable oils are therefore recommended for hermetically sealed transformers [85,91].

However, the fact that viscosity decreases with temperature increase is a good thing for high temperature applications. Dynamic viscosity of several vegetable oils becomes closer at 250 °C, despite a great difference at ambient temperature (Figure 11a).

Hoffmann [2] thermally aged in stainless steel reactors rapeseed oil with some thermal energy storage material at 210 °C up to 2160 hours in controlled nitrogen atmosphere. Except with the case of quartzite, all samples had lower viscosity than reference rapeseed new oil in experimental conditions (Figure 11b). Wilhelm et al. [99] observed that the increase of the water content in insulating papers does not affect the viscosity of vegetable oils during ageing tests without oxygen.

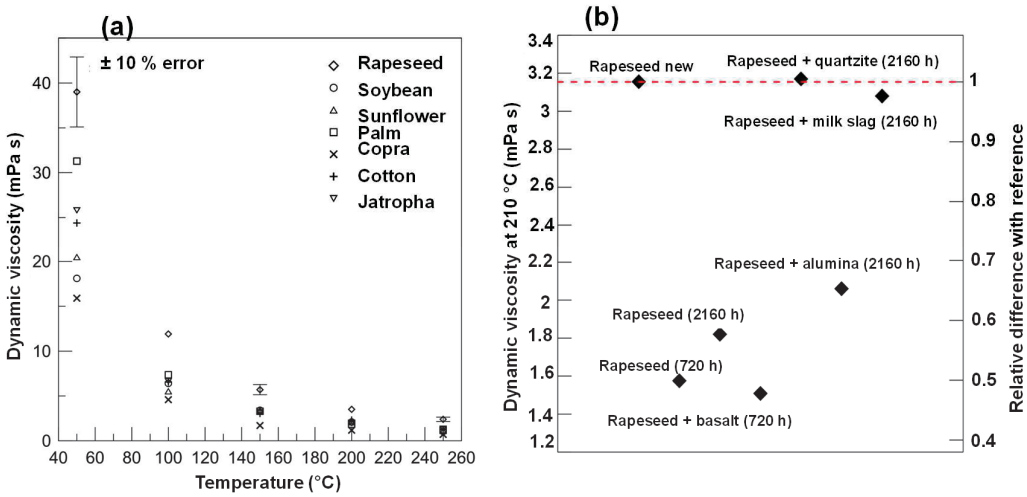

Figure 11. a) Effect of temperature and b) ageing with storage materials on dynamic viscosity of vegetable oils [2].

29

3.9 Gassing tendency

After accelerated ageing by cycling tests (30 °C to 120 °C up to 93 cycles) of vegetable oil and thermal oil in transformers functioning conditions, Jeong et al. [140] found that the amount of dissolved carbon monoxide (CO) and carbon dioxide (CO_2) is greater for vegetable oil than mineral oil [140]. The reason is that for mineral oils, CO and CO_2 are mainly produced by insulation paper decomposition [8,141] while for vegetable oils in addition to that there is also the breakdown of carbonyl group –COO [7]. After 64 hours at 120 °C, vegetable oils produced more gases than other various insulating oils (Figure 12 a) especially hydrogen and ethane [5]. Biotemp® (transformer vegetable oil based fluid) produced more hydrogen (about 30 µL L^{-1}) than mineral Nynas Nytro 11 EN oil (<5 µL L^{-1}) below 110 °C but, from 180 to 190 °C the concentration of both fluids increased over 200 µL L^{-1}. The main gases produced under electrical stress are hydrogen, acetylene, methane, ethane, carbon dioxide and carbon monoxide [1,5]. The total amount of gas produced from arcing of Biotemp® (4.2 mL) was one-fourth of that produced by mineral oil (18.2 mL) [142]. This showed the high arc-quenching ability of that vegetable oil [7].

Figure 12b shows the high gas absorbing ability of vegetable oils [5,6] compared to synthetic ester and mineral oils. This tendency is good for applications in sealed systems [5].

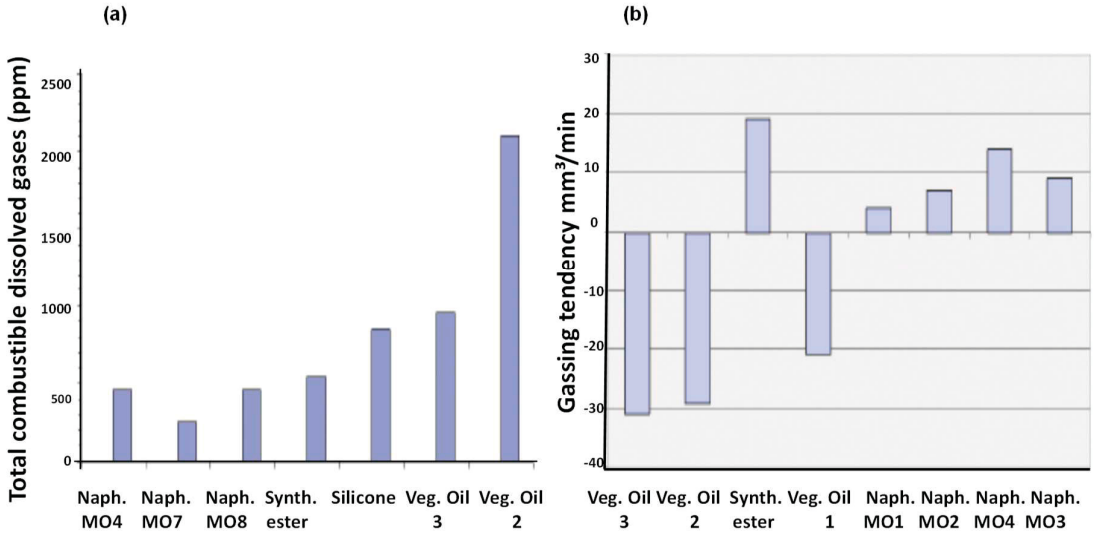

Figure 12: (a) Dissolved gases and (b) gassing tendency of different insulating fluids [5]

30

4 Heat transfer and thermal storage fluids in solar thermal applications

4.1 Introduction

Usually, high temperature heat generation from the sun is made via concentrating solar processes. Figure 13 shows the basic principle of heat and/or power generation from concentrating solar processes. These processes use reflectors to concentrate the direct solar irradiation into a location, called the receiver, where the temperature increases. The heat at high temperature is recovered, generally using a heat transfer fluid, to supply various thermal processes such as power blocks for power generation or solar cooking, etc.

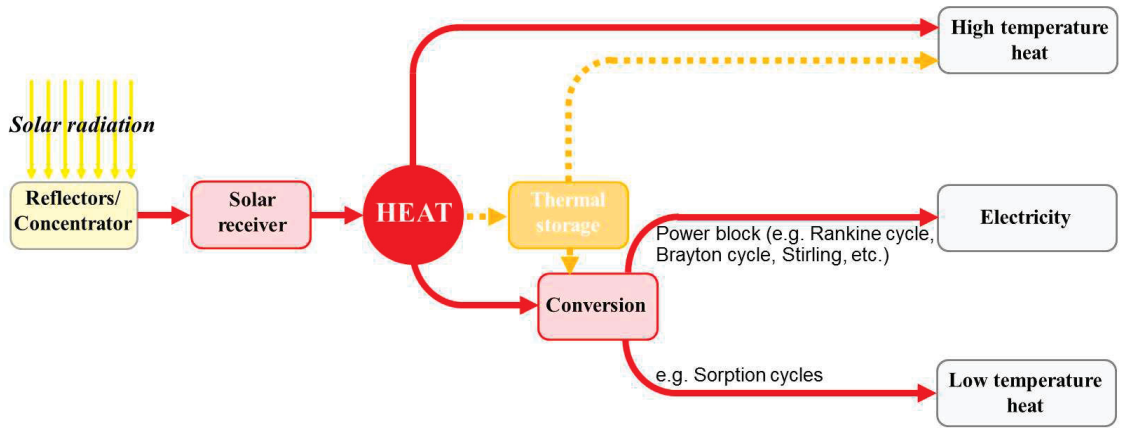

Figure 13: Heat and/or power generation from concentrating solar plants.

In order to reduce, avoid or eliminate the effect of the intermittence of the solar resource (at night-time for instance), a heat storage unit may be introduced in the system (Figure 13). Heat storage is seen as the most significant advantage of concentrating solar power (CSP) over other renewable energy technologies since heat storage is up to date much cheaper and more efficient than electricity storage [143]. A CSP plant then generates electricity with the same principle as a conventional gas, coal or nuclear power plants. The major difference is that the heat used here is from the sun, not from the combustion of gas, coal, or other fuel or uranium from the high temperature heat. The four main CSP technologies currently available are presented in Figure 14.

31

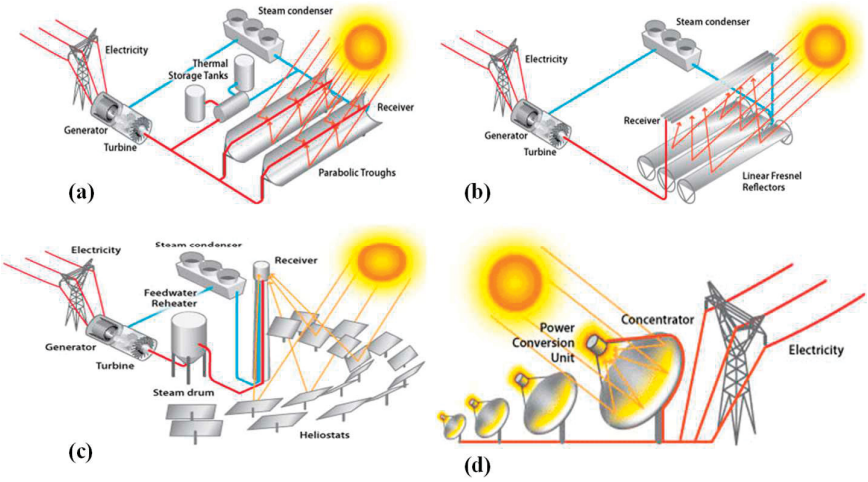

Figure 14: Overview of the four CSP technologies a) Parabolic trough b) Linear Fresnel c) Central receiver system and d) Parabolic dish [144]

4.2 Selection criteria for thermal fluids

The selection of a thermal fluid (HTF) is critical for industrial processes. In fact, thermophysical and chemical properties of fluids will influence heat exchanger sizes, pumping consumption, vessels pressure rating [145] or pipes and storage tank materials [10].

The commonly used heat transfer fluids are water, mineral oils, silicon fluids, inhibited glycol-based fluids, paraffinic oils or molten salts [146]. Thermal oils represent around 92 % of HTF used in CSP plants followed by salts 5 % and water/steam/air 3 % [147]. Many studies are considering the use of vegetable oils as heat transfer fluids or thermal storage materials [2,9,94,134–137] in concentrating solar power and solar cooking applications. For that purpose, vegetable oils should meet criteria, some of which are listed below [146,152]:

- Low lower temperature limitation (solidification temperature).
- High upper temperature limitation (evaporation temperature and/or thermal stability limit) at low pressures.
- High thermal conductivity : receiver temperature close to HTF temperature.
- Low viscosity : lower pumping power requirements.
- High density and heat capacity : enable use as storage medium.
- Possibility of usage as working fluid.
- Chemical compatibility (low corrosiveness) with contact materials.
- Low cost, high availability.
- Low toxicity, flammability, explosiveness and environmental hazards.

First of all, the thermal fluid should be stable within the operating temperature range of the system [153]. As seen previously, this thermal stability is a function of the fluid's chemistry, the temperature to which it is exposed, and the duration of the exposure [145]. At the current level of research, the temperature limit for thermal

fluids based vegetable oils is set to 250 °C [4], which is relevant for cooking, domestic heating, industrial heating processes or micro-concentrating solar plants and cooling systems.

Furthermore, as presented in section 3, vegetable oils exhibit good thermophysical properties namely, thermal conductivity, specific heat capacity, flash point, density. The viscosity decrease tendency with temperature is also of great interest regarding pumps electrical consumption and heat transfer. Moreover, one of the reasons why vegetable oils are really interesting is their good environmental properties and high availability. Compared to diphenyl oxide/biphenyl (the generic name of the products known as Dowtherm A or Therminol VP-1), which is the most popular thermal oil used in CSP plants [4], vegetable oils have lower green gas emissions, lower environmental hazards, lower costs and higher availability (Table 12).

Table 12: Comparison of typical values of Therminol VP1 ® (synthetic oil) and vegetable oils [4,10].

Thermal oil	Therminol VP-1	Vegetable oils
Composition	73.5% diphenyl oxide / 26.5% biphenyl	Fatty acids
Pour point (°C)	12	–11 to 20
Atmospheric boiling point (°C)	257	295
Temperature limit for use (°C)	400	250
Flash point (°C)	110	230–330
Relative pressure (kPa)		
at 100 °C	0.5	0
at 200 °C	24	
at 300 °C	239	
Volumetric heat capacity ($MJ \cdot m^{-3} \cdot K^{-1}$)		
at 100 °C	1.77	1.91–2.15
at 200 °C	1.87	1.94–2.13
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)		
at 100 °C	0.128	0.148–0.155
at 200 °C	0.114	0.130–0.144
Dynamic viscosity (mPa·s)		
at 100 °C	0.985	4.6–11.9
at 200 °C	0.395	1.2–3.5
Chemical compatibility	N/A	Good
Cost (€ kg–1)	5.7[a]–25[b]	0.4–1.2
Availability (–)	Low	High
Life cycle assessment–Greenhouse gas ($kg \cdot CO_2 \cdot eq\ kg^{-1}$)	3	0.85–1.87
Environmental hazard –	High	Low

[a] [4] [b] [10] These prices are different maybe depending on the provider.

33

4.3 Vegetable oils in solar thermal applications

As mentioned previously, many studies are considering the use of vegetable oils as heat transfer and thermal storage fluids in solar applications. If Hoffmann et al. [4] presented a good temperature dependency of thermophysical properties of vegetable oils up to 250 °C, all these studies target operative temperature up to 210 °C (Table 13).

Pikra et al. [149] studied the development of a small scale concentrated power plant of 10 kW_{el} using parabolic trough as solar absorber and palm oil as the heat transfer and thermal storage fluid. They chose palm oil instead of mineral oil because of availability, low cost and similar physical properties with the later. The thermal storage capacity of the small plant is 107 kW for 6 hours operations time with palm oil temperatures of 150 °C and 200 °C respectively, for the low and high operating temperature.

Table 13: Some vegetable oils projected or used as heat transfer or thermal storage fluid in solar applications.

Designation	Fluid used	Function	Temperature range (down and up)	Status	References.
Design of small scale concentrated power plants of 10 kW_{el}.	Palm oil	Heat transfer and thermal storage fluid	150 °C to 200 °C	Projected	[149]
Innotherm III project: solar cooling (heat discharging rate from the storage: 138 kW_{th})	Rapeseed oil	Heat transfer fluid	175 °C to 210 °C	Projected	[2]
CSP4Africa project: small scale concentrated power plants of 10 $kW_{el.}$	*Jatropha curcas* oil	Heat transfer and thermal storage fluid	150 °C to 200 °C	Assembled, under testing	[10,148]
Thermal energy storage oils for solar cookers during charging	Sunflower oil	Thermal storage oil	Ambient to 180 °C	In use	[151]

Natural convection flat-plate collector cooker	Coconut, peanut and sunflower oils	Heat transfer and thermal storage fluid	Ambient to 220 °C	in use	[150,154]

Hoffmann [2] studied the suitability of seven vegetable oils like heat transfer fluids in concentrating solar applications. The case study was a solar cooling system of 100 kW in the frame of the Innotherm III project. The low and high operating temperature were respectively 175 °C and 210 °C. To fill the lack of thermophysical data of vegetable oils at high temperature, measurement was made with non-used oils from ambient to 250 °C. The main thermophysical properties presented were thermal conductivity, dynamic viscosity, specific heat and density. Correlations were given for each property in the considered temperature range. All the seven vegetable oils studied had nearly similar thermophysical properties.

In the framework of the concentrating solar plant for Africa (CSP4Africa) project a pilot of micro-central tower plant of 10 kW_{el} was built in Burkina Faso [148]. *Jatropha curcas* crude oil (JaCCO), a local available non-edible vegetable oil, was envisaged as heat transfer and thermal storage fluid. Preliminary comparison of JaCCO with well-established thermal oils (Therminol VP-1 and Syltherm XLT) commonly used in concentrating solar power plant was done by Kenda et al. [10]. JaCCO presented lowest energy storage material acquisition costs compared to Therminol VP-1 and Syltherm XLT of 12, 464 and 573 € kWh^{-1} respectively, for a temperature change of 100 °C.

For solar cookers with sensible thermal storage units, oils are widely used as thermal fluids [155]. Thermal oils commonly used are mineral oils [151,156,157], synthetic oils [158] or vegetable oils [150,154]. Cookers with vegetable oils as heat transfer and thermal storage fluid are commercially available [159]. Coconut oil was used as heat transfer fluid in a double-glassed flat plate collector solar cooker [150]. Temperatures of approximately 150 °C were achieved between 10:00 h and 14:00 h. The vegetable oil presented many advantages like high boiling point, availability and non-toxicity. At 120 °C, the heat storage capacity of 21 L of oil was evaluated to be 5 MJ. The viscosity of coconut was reduced to around 90 % at 100 °C enabling easier thermosyphon circulation.

Schwarzer et al. [154] developed and installed about 250 solar cooking systems of various sizes and for different applications in many countries of the world. Vegetable oils were usually used as working fluids. The oil was heated up in the collectors and moved by natural flow to the cooking unit, where it transferred part of its sensible energy to the cooking goods in double-walled pots. The thermal sensible efficiency of solar cooking systems using vegetable oils varied from 30 % to 34 %. That value was lower than that of a unit using a synthetic oil (38 %) [158].

For Silva et al. [158] the difference can be associated to the different nature of oils used in that experiment. Furthermore, they used synthetic oil instead of vegetable oil due to instability of the latter at temperature around 200 °C.

Mawire et al. [151] evaluated during charging experiments three solar thermal oils for a domestic heat storage application. The three thermal oils were sunflower oil, shell Thermia C and Shell Thermia B and the energy and exergy-based thermal parameters were evaluated. The vegetable oil (sunflower oil) performs better than the two mineral oils (Shell Thermia C and Shell Thermia B) under high power charging at a low flow-rate. The suggested reason was the higher specific heat capacity and density of sunflower oil compared to the mineral oils.

Based on studies on vegetable oils as thermal fluids results, we can see that vegetable oils have high energy density, high flash point, better thermal conductivity compared to common thermal fluids used in CSP at 210 °C as presented in Table 14.

Thus, vegetable oils with low costs, high availability, great ecobalance are presented as an innovative heat transfer fluids [4,10].

Table 14 : Thermophysical properties of some thermal oils at 210 °C [2,10].

Thermophysical properties at 210 °C	Rapeseed oil	Soya bean oil	Sun-flower oil	Palm oil	Copra oil	Cotton oil	*Jatropha curcas oil*	Therminol VP-1	*Xceltherm 600*	*Syltherm XLT (220 °C)*
Flash point °C	285	330	316	280	230	243	220-240	124	193	47
Thermal conductivity (λ) W m^{-1} K^{-1}	0.143	0.141	0.139	0.140	0.128	0.141	0.139	0.112	0.121	0.062
Dynamic viscosity (μ) mPa s	3.155	1.722	1.695	1.674	1.004	1.800	1.781	0.368	0.559	0.22
Specific heat capacity (Cp) kJ kg^{-1} K^{-1}	2.492	2.440	2.444	2.677	2.587	2.508	2.509	2.075	2.643	2.192
Density (**ρ**) kg m^{-3}	787.7	805.5	798.3	774.1	771.6	787.6	778.2	904	736.4	649.8
Thermal energy storage capacity (ρ Cp) MJ m^{-3} K^{-1}	1.963	1.965	1.951	2.072	1.996	1.975	1.953	1.876	1.946	1.424

4.4 Vegetable oils compatibility with contact materials

Vegetable oils have relative poor oxidative stability due to unsaturations in their structure. And it is well known that the presence of metals in oils catalyse oxidation reactions leading to oil degradation [16]. In solar applications, the receiver, pipes, heat exchangers and storage tanks are generally metals made (copper, carbon steel, stainless steel, aluminium etc.). In some cases, thermocline storage tanks are filled with thermal storage solid materials (to reduce the thermal energy storage cost) [160]

which will be in contact with the vegetable oil heat transfer fluid. To be considered as good solar oils, vegetable oils have to achieve a good compatibility with these materials. The objective of compatibility study is to prevent changes over time of the thermal oil and the contact materials.

Ferrer et al. [161] studied the compatibility between container materials (aluminium, copper, carbon steel, stainless steel 304 and stainless steel 316), generally used in solar energy storage units for residential heating and four different phase change materials (PCM). Two of the four PCM were fatty acid eutectic consisted of 73.5 % capric acid·+·26.5 % myristic acid and 75.2 % capric·acid·+·24.8 %·palmitic acid. Metals specimens were immersed in glass test tubes containing the PCM and placed in a stove at 38 °C for different periods up to 12 weeks. The test tubes were covered by a plastic lid to avoid contact with environmental agents. Despite the corrosion rate quite high of copper (6–10 $mg \cdot cm^{-2} \cdot yr^{-1}$) compared to other metals (0–1 $mg \cdot cm^{-2} \cdot yr^{-1}$ for stainless steels), according to the guide for corrosion weight loss used in the industry [162], all these metal containers are recommended for long-term service with the two fatty acid eutectic. This result is interesting when we know that these fatty acids are generally found as free fatty acids in vegetable oils used as thermal oils.

Kenda et al. [10] heated *Jatropha curcas* crude oil (JaCCO) in two reactors: one made in stainless steel 316 L and the other made in galvanised steel. The oil (projected to be used as heat transfer and thermal storage fluid in CSP4Africa project) was heated up to 210 °C and then cooled down to ambient temperature during up to 10 cycles. Thermophysical properties and metal content of oil were evaluated at the end of each cycle for both the reactors. It was noticed an increase of iron (3.33 ppm·to·63.59 ppm) and zinc (0 ppm to 6 ppm) contents in JaCCO contained in galvanised steel reactor. However, in stainless steel 316 L the metal content of oil remained constant (≈ 3.7 ppm). The suggested reason of the iron content increase was that the zinc coating layer in galvanised steel reactor started to fail and degraded during tests by corrosion, due to high acidity levels of the oil (17.1 $mg \cdot KOH \cdot g^{-1}$). Moreover, oil in galvanised reactor was darker and contained more peroxides than that in stainless steel 316 L. Based on these results, it was concluded that JaCCO had better compatibility with 316 L stainless steel material than galvanised steel.

Hoffmann [2] studied physicochemical compatibility between four vegetable oils (rapeseed, soya bean, palm and jatropha) and various thermal energy storage materials (TESM) up to 2160 hours (Figure 15a and Figure 15b). The TESM and vegetable oils were put inside stainless steel reactors and heated at 210 °C for the test period in permanent presence of nitrogen atmosphere in order to protect the system against oxidation. The thermal stability is the first requirement for a thermal fluid and is depend on the chemistry of the fluid. Since the upper operative temperature in Innotherm III project is 210 °C, Hoffmann studied the impact of the acidity on the thermal stability of rapeseed aged with quartzite, basalt, alumina and

37

milk slag. As presented in Figure 15a, milk slag had the most drastic effect on rapeseed acid value after 2160 hours of tests while alumina had the least. Furthermore, the acid value after 720 hours was bigger than that of 2160 hours for rapeseed aged with quartzite.

This result tends to confirm the fact that evaluation of vegetable oils quality based on acid value could lead to misleading information. However, despite the acidity increase, up to 2160 hours, the thermal stability temperature remained above 340 °C. Regarding the dynamic viscosity evolution at 210 °C presented in Figure 11b, TESM increased the viscosity value after 2160 hours compared to oil aged alone. However, the viscosity value was similar to that of the new oil for the worst (quartzite). A decrease of the flash point was also observed from 326 °C for the new oil to 260 °C for oil aged with alumina during 2160 hours.

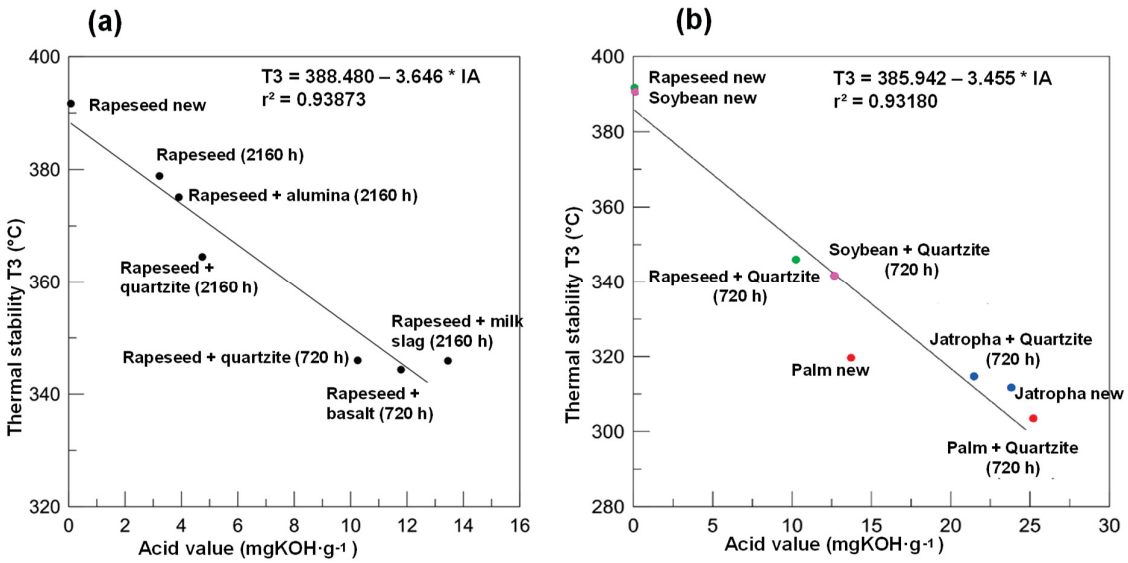

Figure 15: Effect of acid value on thermal stability of a) rapeseed with TESM and b) some vegetable oils with quartzite [2].

When rapeseed, jatropha, palm and soya bean oils were thermally aged with quartzite up to 720 hours (Figure 15b) at 210 °C, an acid value increase was noted for all the oil samples excepted for jatropha oil. Despite the observed decrease of acid value, the thermal stability temperature was above 300 °C after 720 Hours of test. The colour of thermally aged oils was compared, it was found that all the oil samples aged with quartzite were browner than those aged alone. It could be important to take this into account when visual evaluations of the solar oil quality would be done.

Concerning the thermal conductivity of rapeseed oil, a decrease of 2 % was observed for the oil thermally aged alone while an increase was noted with TESM introduction as presented in Figure 16a. Regarding the uncertainty (1.2 %) of the measuring instrument used and the different results, it was concluded that the deterioration of

38

the vegetable oil does not significantly affect the thermal conductivity. No drastic decrease was noted in specific heat capacity value up to 2160 hours for oils aged with the different TESM. The specific heat capacity value was around 2.6 $kJ \cdot kg^{-1} \cdot K^{-1}$ at 240 °C for all the samples tested (Figure 16b).

No degradations were observed on TESM with scanning electron microscope (SEM) after 2160 hours of compatibility tests. The conclusion was that rapeseed oil had good compatibility with basalt, alumina, quartzite and milk slage in the case of its use as solar oil.

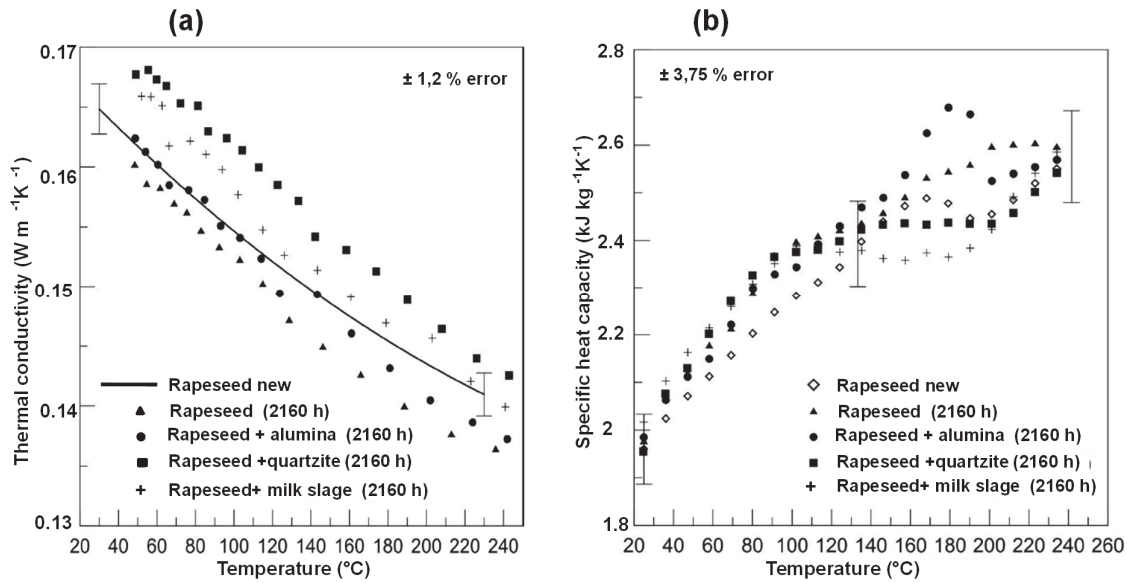

Figure 16: a) Thermal conductivity and b) specific heat capacity of rapeseed oil thermally aged alone and with various TESM [2].

In the light of these results Hoffmann [2] thought that the modification of the thermophysical properties of these vegetable oils because of the quartzite immersion was insignificant. He therefore concluded that the compatibility was good and these vegetable oils could be used with quartzite in solar processes.

5 Conclusion

In this study, a comprehensive review of the available literature on vegetable oils behaviour as thermal oils for concentrating solar applications is presented. The review presents the vegetable oils oxidative and thermal stability, evaluation methods of oxidation, main chemical and physical properties of vegetable oils when used at a temperature above 100 °C. The use of vegetable oils as solar oils is a relatively new topic. However, applications such as frying or the electrical transformer industry provide valuable information for this purpose. In frying, where vegetable oils are widely used, several criteria are available to access oil stability. Since some degradation products in frying oils are potentially carcinogenic to humans, the main reasons why frying oils are rejected concern mainly health. It is not the same

39

reflexion concerning their use as insulating or thermal fluids. The overview of vegetable oils used in high-temperature applications show that a lot of work has been done by the transformer industry where commercial fluids are already available. Insulating based vegetable oils fluids are now used in various scale transformer units and data collected show their reliability. As thermal solar oils, vegetable oils are widely used in solar cookers and some studies have presented their great potential in concentrating solar power plants. Vegetable oils are low cost and widely available, present similar if not better thermophysical properties compared to thermal oils generally used in CSP plants. Regarding environmental concerns, vegetable oils are fully biodegradable and have low greenhouse gas emissions. These advantages advocate for the use of vegetable oils in CSP plants where new clean heat transfer and heat storage fluids are required. However, despite their good performances, vegetable oils are at an early stage of use and their main weakness is their tendency to oxidate, though they are reported as highly stable in well-sealed equipment. More studies are therefore required to improve their oxidation stability, provide sufficient feedback on their use over time for their application, thus promoting their acceptance by users. Moreover, the diversity of vegetable oils makes it essential to adopt standards for characterisation of vegetable oil-based heat transfer and heat storage fluids.

Regarding the thermal stability of vegetable oils, specific findings highlighted in the review are as follows:

- The level of unsaturation is the major factor in the degree of oxidative polymerisation of vegetable oils [9].
- The intermittent heating and cooling of vegetable oils causes higher deterioration than continuous heating [163].
- Viscosity should be taken into account to assess the vegetable oils ageing because higher viscosity would affect the ability to transfer heat and result in higher hot-spots.
- Sufficient amount of water in oil at high temperature generates a steam blanket which could protect the oil from thermal oxidation and hydrolysis similar to the protection achieved by nitrogen atmosphere [94].
- Ageing markers, which are well established for conventional thermal oils, do not seem to be useful parameters in monitoring vegetable oil-based thermal fluid performance [85].
- Vegetable oils are highly stable in well-sealed equipment [91].
- Acidity due to hydrolysis has limited impact on metal corrosion contrary to acidity caused by oxidation [101].

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Declaration of interest

None.

41

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48

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52