Compatibility of vegetable oils with solid filler materials for thermocline thermal energy storage systems

J.-F. Hoffmann [a, c, d, e],

T. Fasquelle [a, f], G. Vaitilingom [b], R. Olives [a], X. Py [a], V. Goetz [a*]

[a] PROMES-CNRS UPR-8521 Laboratory, University of Perpignan Via Domitia, Rambla de la Thermodynamique,Tecnosud, 66100 Perpignan, France
[b] CIRAD, unité de recherche BioWooEB, TA B-114/16, 73 rue JF Breton, 34398 Montpellier, France
[c] AQYLON, 46-48 rue Renée Clair, 75892 Paris, France
[d] EDF - R&D, MFEE - Nouvelles Filières de Production et Thermochimie, 6 Quai Waitier, 78401 Chatou, Franc
[e] Current address: Department of Mechanical and Materials Engineering, Masdar Institute, Khalifa University of Science and Technology, Masdar City, P.O. Box 54224, Abu Dhabi, United Arab Emirates
[f] Current address: Palácio do Vimioso, Largo Marquês de Marialva, Apartado 94, 7002-554 Évora,Portugal

* Corresponding author. Tel: (+ 33) 4 68 68 22 36. E-mail address: Vincent.goetz@promes.cnrs.fr

Abstract

Compatibility tests involving four vegetable oils and three different solid materials were performed, with a focus on rapeseed oil and quartzite rock. The objective was to verify the relevance of using vegetable oils as heat transfer fluid in concentrated solar power plants with direct thermocline thermal energy storage. First tests consisted in using small crucibles to put in contact rapeseed oil respectively with quartzite, blast furnace slags and alumina for 2160 hours and at 210 °C. On a chemical point of view, the oil composition was modified by ageing and contact with solids. However, thermal properties that drive heat transfer (density, specific heat, thermal conductivity and dynamic viscosity) were not modified. Thermal stability temperature and flash point decreased and a correlation with the index of acidity of the samples has been found. Second set of tests consisted in putting in contact quartzite with rapeseed, palm, soybean and jatropha oils for 720 hours and at 210 °C. Results confirmed that index of acidity can be a good indicator of the vegetable oil ageing. From the whole study, no incompatibility has been concluded, but one may recommend a limit value of 25 mg KOH.g^{-1} for the index of acidity to consider partial replacement of the vegetable heat transfer.

Keywords

Compatibility tests, Vegetable oils, Heat transfer fluid, Thermal energy storage materials, Concentrated Solar Power (CSP), Organic Rankine Cycle (ORC), Process heating

1. Introduction

Concentrated Solar Power (CSP) with thermal energy storage (TES) has value to stabilize electrical grid and to provide electricity or heat to remote areas. In already developed grids, TES can increase the power plant's incomes by delaying electricity production to high cost periods and it also avoids the use of fossil-fuel-fired power plant during peaks of demand [1]. Current research focuses on increasing efficiency and/or reducing cost of CSP technology. Thus, high concentration and high temperature systems must be developed to reduce energy losses and improve power cycle efficiency [2] while using local and by-product materials to reduce costs [3]. In particular, research on TES materials focuses more and more on natural and local products and/or material from wastes [4].

Thermocline is a technology that gained interest in the past years [5] since it may reduce the cost of TES in CSP plants while being adjustable to available material resources near project sites [6]. Thermocline technology consists in using one single-tank instead of the conventional two-tank system. TES cost is further reduced by replacing a substantial part of the Heat Transfer Fluid (HTF) by cost-effective Thermal Energy Storage Materials (TESM) [7]. However, it causes new issues such as (i) varying outlet temperature [8]; (ii) strong thermo-mechanical stresses [9] and (iii) required compatibility between HTF and TESM [10].

In the present work is investigated the possible use of vegetable oils as HTF in both solar field and TES systems. The approach is to decrease the system cost while using local and environmental friendly materials. However, it constrains the working temperature of the receiver to a lower value (250 °C) than the one that is obtained with conventional thermal oil (400 °C). Therefore, the use of vegetable oil as HTF implies direct heat production or the use of an Organic Rankine Cycle to produce electricity. Vegetable oils could therefore be an alternative to conventional oils if accepting this last drawback and its consequence.

This work was performed simultaneously with a vegetable oil property analysis investigation [11] and a thermal process evaluation of a thermocline tank demonstrator using vegetable oils and solid materials [12, 13]. The oil property study showed that, when compared to the conventional Therminol VP1 synthetic oil, vegetable oils have lower maximum operating temperature but higher volumetric heat capacity and thermal conductivity, along with lower price and lower impact on the environment (Table 1).

Table 1 : Comparison of a synthetic oil (Therminol VP1®) and vegetable oils [11, 14]

Thermal oil		***Therminol VP1***	***Vegetable oils***
Composition	-	73.5% diphenyl oxide / 26.5% diphenyl	Fatty acid
Pour point	*°C*	12	-11 to 20
Temperature limit (maximum operational temperature)	*°C*	400	250
Flash point	*°C*	110	230 – 330
Relative pressure	*kPa*		
@ 100°C		0.5	
@ 200°C		24	0
@ 300°C		239	
Volumetric heat capacity	*MJ m^{-3} K^{-1}*		
@ 100°C		1.77	1.91 – 2.15
@ 200°C		1.87	1.94 – 2.13
Thermal conductivity	*W m^{-1} K^{-1}*		
@ 100°C		0.128	0.148 – 0.155
@ 200°C		0.114	0.130 – 0.144
Dynamic viscosity	*mPa s*		
@ 100°C		0.985	4.6 – 11.9
@ 200°C		0.395	1.2 – 3.5
Chemical compatibility	-	N/A	Good
Cost	*€ kg^{-1}*	5.7	0.4 – 1.2
Availability	-	Low	High
LCA - GHG	*kg CO_2 eq kg^{-1}*	3	0.85 – 1.87
Environmental hazard	-	High	Low

The thermal process study showed that typical thermocline profiles can be obtained with such oil and TESM and some experimental parametric studies were therefore achieved. The present study deals with the compatibility tests that were performed in order to ensure the viability of the joint use of vegetable oils and potential TESM.

Compatibility means the capacity of an element to be well matched with another one. Compatibility tests consist in subjecting HTF and TESM to experimental conditions that will be close to their future use. Often minimized in process systems, physico-chemical compatibility between HTF and its environment is essential and strongly influences efficiency and operational expenditures. Indeed, interactions can occur between HTF and TESM, but also piping, atmosphere, etc., under specific conditions (pressure, temperature…). Last but not least, incompatibility may lead to environment and human hazards. Hence, objective of compatibility tests is to prevent the use of the wrong couple HTF/TESM that would lead to strong evolution of properties of one or both the different materials.

Numerous studies deal with compatibility between molten salts and metal alloys, since TES conventional technology uses two steel tanks full of salts, with no TESM, steel piping and steel heat exchanger. Vignarooban *et al.* [15] in 2015 proposed a quite complete review of heat transfer fluids for CSP that lists most of the compatibility studies between molten salts and steel. The most extensive ones may be those performed by Sandia National Laboratory:

- Goods *et al.* [16] found a corrosion rate of 6-15 µm per year for SS304 and SS316 after a 7000 h immersion into solar salt (60/40% $NaNO_3$/KNO_3) at 570 °C

- Kruizenga *et al.* [17] found corrosion rates of about 15.9 µm and 10.4 µm per year for SS-321 and SS-347 alloys immersed in solar salt at 600 °C during 4000 hours, but these values increased to 460 µm and 447 µm per year when the compatibility test temperature was 680 °C.

Interest for compatibility between heat transfer fluid and potential energy storage materials has grown during the past years. To assess compatibility between a HTF and a TESM, two different methods can be employed [18]:

- Isothermal tests enable to assess the material viability at high temperature. In these tests, TESM and HTF are maintained for a long duration at a fixed temperature and fluid is only moving by natural convection. These tests are easier to perform but have the drawback of not assessing the influence of the displacement of the fluid through the packed bed of materials, as in thermocline TES facilities.

- Thermal cycling tests consist in applying different temperature stages to the materials in order to reproduce actual conditions of a TES system. Cycling experimental setups can be complex and expensive installations, and their results may be underestimated because materials will be at high temperature for a relatively low duration.

One of the reference studies is the one of Brosseau *et al.* [18], in Sandia National Laboratory, in which they found no signification deterioration of quartzite rock after 12-month isothermal tests and 14-month cycling tests in contact with molten salts (Hitec XL and solar salt) up to a temperature of 500 °C. They stated that at least 10,000 cycles are necessary to reproduce an ageing of 30 years (representing one cycle per day during 82% of days).

Several works from PROMES-CNRS and NREL also deal with compatibility between molten salts (solar salts) and solid materials from wastes [19, 20] to be used as TESM. They showed that electrical arc furnace slags do not withstand contact with salts while blast furnace slags and Cofalit (waste from asbestos treatment) ceramics showed good resistance to corrosion.

They are still too few studies dealing with the fluid property modifications when put in contact with other materials:

- There are several works dealing with the molten salt modifications due to solid corrosion. For example, McConohy *et al.* [21] put in contact nickel-based metals and molten salts (Solar Salt) during 4000 h and at 680 °C and found that salt endured some decrease of fusion temperature (60 °C) and heat of fusion (30 $kJ.kg^{-1}$). Bonk *et al.* [22] tested compatibility between solar salt and different natural rocks (greywacke, diabase, basalt and quartzite). They concluded that salt properties are not significantly modified (after 5000 hours at 560 °C), but observed presence of some traces of anions species such as sulfates or phosphates that must come from the TESM. They also discriminated diabase because of mechanical instabilities and significant leakage of carbonates into the fluid.

- There are some recent studies dealing with thermal oils, since direct thermocline thermal energy storage with synthetic oil has started to be considered as an interesting option. For example, Fasquelle *et al.* [23] worked on the compatibility between a synthetic oil (Jarysol) with aluminium oxide, Cofalit and coal fly ash bricks (500 h, 330 °C) and stated that oil do not deteriorate solids while presence of TESM increases the oil ageing velocity. It resulted in higher viscosity (up to 41% increase for viscosity at low temperature) and lower flash point (decrease of maximum 34 °C). More recently, Molina *et al.* [24] tested compatibility between the same oil (Jarysol) and different TESM (quartzite, aluminium oxide, steel, concrete, soda lime glass and sand) at 340 °C and during 500 h, with oil composition as main ageing indicator. They confirmed an accelerated ageing due to contact of solid materials, but stated that compatibility was found for glass, steel and alumina. An incompatibility has been found for natural rocks (quartzite) and sand. They observed that presence of iron oxide within the materials could be a catalyst of oil degradation.

There is still some need for such studies in order to assess the impact of a thermocline thermal energy storage on the performance and the operational expenditures of a solar power plant, especially when using oils as heat transfer fluid. There is also a need of standards for such compatibility tests and in order to determine relevant parameters to assess fluid ageing.

In the present study are investigated compatibilities between several vegetable oils (rapeseed, soybean, palm and jatropha) and potential TESMs (quartzite, alumina and blast furnace slag) up to a temperature of 210 °C that has been chosen by the funding project. Chosen parameters of influence are chemical composition, thermal properties and thermal stability of the HTF. TESMs are not expected to be modified by the non-corrosive HTF, neither by the relatively low temperature thermal treatment.

The objective of this work is to answer two main interrogations:

- Is it possible to use vegetable oils as HTF in contact with solid materials such as natural rocks and alumino-silicate ceramics?
- Is there a relevant parameter to easily assess the vegetable oil compatibility and ageing over time?

2. Experimental methodology

In the present study, isothermal tests have been experienced on vegetable oils in contact with TESM, thanks to a dedicated experimental bench and multiple property measurement instruments that equip different laboratories. These evaluations were gathered in three different types of analysis:

- chemical analysis is performed in order to understand to what extent oil has been changed by the tests and to explain why other properties would be modified;
- thermal property analysis is very important in order to assess the fluid capability of being a good HTF;
- thermal stability analysis has to be performed in order to ensure that fluid can still be operated without risks.

Main objective of the whole study is therefore to determine how the fluid degrades, what are the consequences of that degradation, and what is the best indicator of it.

2.1 Experimental setup

The experimental bench that has been developed for these compatibility tests is pictured in Figure 1. Objective is to maintain the materials at 210 °C, which is close to the maximum temperature that vegetable oils can handle (250 °C) and which is the target temperature for a later use in a solar power plant or a thermal energy storage system. Materials are contained in 3.4 L tanks, for around 3 kg of TESM and 1.5 L of HTF. A 0.5 L volume is set free to enable thermal expansion of the oil. TESM materials are crushed rocks with an average diameter varying from 30 mm and 40 mm, for a global void fraction of around 40%. These conditions are the closest to an actual thermocline TES system [12].

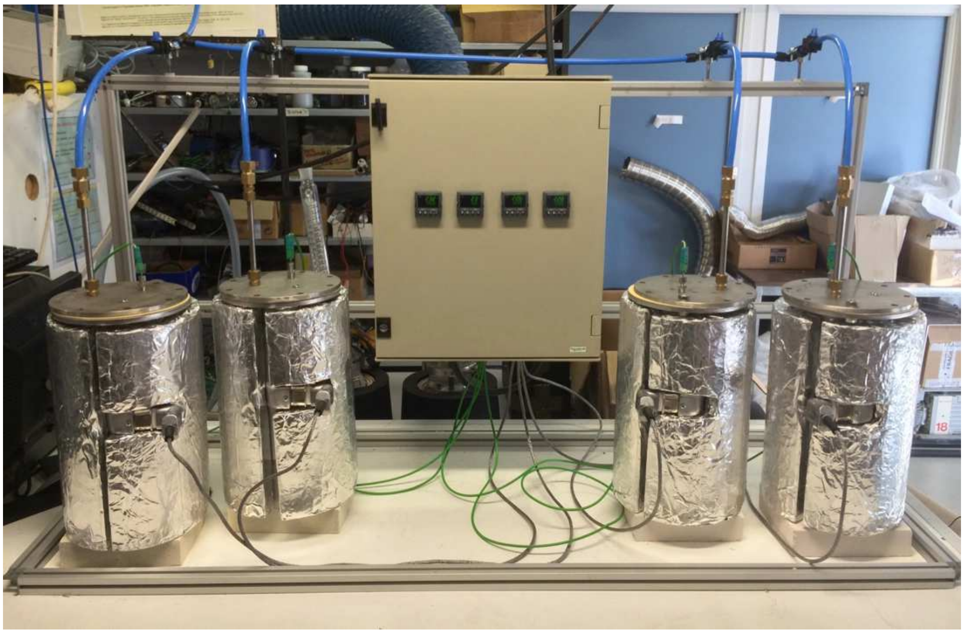


Figure 1 : The experimental bench to perform compatibility tests

To avoid undesirable external effects, tanks are made of stainless steel and a controlled atmosphere of nitrogen is applied. Thus, degradation of the oil thermal properties will be due to TESM contact, temperature and time. A PID controller adjusts the 750 W heating collar power in order to maintain an inside temperature (measured by a type-K thermocouple.) of 210 °C. Material masses were measured before and after experiments and no significant modifications were observed (< 1%).

2.2 Selected vegetable oils

Identification of candidates for these compatibility tests has been performed according to the results of a previous characterization study [11]. Commercial refined oils – rapeseed and soybean – were acquired in French hypermarkets. The more exotic vegetables oils – palm and jatropha – came from agricultural producers in Burkina Faso. Fatty acid compositions of the four selected vegetable oils, determined by gas chromatography at CIRAD - France, are given in Table 2. Depending the origin and the way of production, the fatty acid compositions of the vegetable oil can vary.

Table 2 : Fatty acid compositions of measured vegetable oils.

Carbon number	***Fatty acid name***	***Rapeseed***	***Soybean***	***Palm***	***Jatropha***
C 8 : 0	Caprylic				
C 10 : 0	Capric				
C 12 : 0	Lauric				
C 14 : 0	Myristic				
C 16 : 0	Palmitic	4.78 %	11.32 %	41.73 %	16.01 %
C 18 : 0	Stearic	1.35 %	2.93 %	5.56 %	6.05 %
C 18 : 1	Oleic	60.78 %	23.3 %	42.45 %	41.64 %
C 18 : 2	Linoleic	19.22 %	52.37 %	6.71 %	32.53 %
C 18 : 3	Linolenic	8.92 %	5.84 %		
C 20 : 0	Arachidic				
C 20 : 1	Gadoleic	1.3 %			
Other minor fatty acids compounds		3.65 %	4.24 %	3.55 %	3.77 %
Saturated		6.13 %	14.25 %	47.29 %	22.06 %
Monounsaturated		62.08 %	23.3 %	42.45 %	41.64 %
Polyunsaturated		28.14 %	58.21 %	6.71 %	32.53 %

2.3 Selected thermocline filler materials

Three different potential TESM were tested: quartzite rocks, alumina ceramics and blast furnace slags. Table 3 gives the thermal properties of these different materials.

Table 3 : Thermal properties of the studied TESMs

Material	***T_{max} (°C)***	***ρ ($kg.m^{-3}$)***	***C ($J.kg.m^{-3}$)***	***$\rho \cdot C$ ($MJ.m^{-3}.K^{-1}$)***	***λ ($W.m^{-1}.K^{-1}$)***

Quartzite	600	2500	830	2.08	5.7
Alumina	1200	3670	750-1000	2.75-3.7	14-21
Blast furnace slags	1000	2980	996	2.97	2-3.5

Aluminium oxide, generally called Alumina, is a material that can be obtained from Bauxite sedimentary rocks. It is a reference ceramic material for high temperature thermal energy storage systems, since it proved high thermal and mechanical stability, good compatibility with a lot of materials, high volumetric heat capacity and high thermal conductivity [25, 26].

Quartzite rock is a natural rock that can be found almost worldwide. It is cost-expensive, has a relatively high thermal conductivity in comparison to other rocks and already showed good compatibility with molten salts in the reference thermocline thermal energy storage of Sandia National Laboratory [7, 18].

Blast furnace slags, and more generally slags, are a recently investigated material that could fulfil all the needs for TESM while enhancing circular economy. Indeed, they are wastes from steel industry that can be transformed into high-temperature ceramics by controlling their cooling rate after furnace extraction. An increasing number of research projects are dealing with these materials that are produced in very large quantities [27, 28, 29, 30], as well as other materials from waste such as vitrified asbestos [31].

2.4 Compatibility tests description

Instead of performing compatibility tests for every couple fluid-solid that were investigated, one main vegetable oil and one main TESM have been chosen. From a thorough study of the selected vegetable oil reactions with the four different TESMs and an examination of the chosen TESM effect on the four different HTFs, it will be possible to assess behaviour of the other potential associations of fluids and solids.

Rapeseed oil has been chosen as main candidate for several reasons: (i) It has one of the highest flash point (285 °C), therefore a higher thermal stability and a lower risk of fire and accidents; (ii) It is non-siccative, although close to be semi-siccative, with a iodine index of 105, meaning that no sprinkling should occur on the walls of the compatibility bench; (iii) It shows a high yield of 1 ton per hectare and per year and represents 15% of the global production of oleaginous; (iv) It is available in a lot of different regions of the world and it is relatively cost-effective when compared to other vegetable oils.

Quartzite has been chosen as main TESM candidate because (i) It is one of the most cost-effective; (ii) It has a relatively high thermal conductivity; (iii) It has already been investigated in several studies [7, 10, 32].

Thereby, the different experiments that have been performed with rapeseed oil are listed in Table 4 while tests with quartzite are enumerated in Table 5.

Table 4 : The different compatibility tests performed with rapeseed oil

Vegetable oil	**720 hours (1 month)**	**1440 hours (2 months)**	**2160 hours (3 months)**
Rapeseed	Alone	Alone	Alone
	Quartzite	Quartzite	Quartzite
	Alumina	Alumina	Alumina
	Blast furnace slags	Blast furnace slags	Blast furnace slags

Since oil properties can be modified by both temperature and contact with solid materials, some reference tests with fluid only were performed in the same experimental conditions.

Table 5 : The different compatibility tests performed with quartzite

Vegetable oil	**720 hours (1 month)**
Rapeseed	Alone
	Quartzite
Soybean	Alone
	Quartzite
Palm	Alone
	Quartzite
Jatropha	Alone
	Quartzite

It should be noted that due to project time constraints, every compatibility test has been performed only once.

2.5 Measurements and instrumentation

Oil samples were analysed on a physical and chemical bases with nine different evaluations: (i) Composition in fatty acid; (ii) Index of Acidity (IA); (iii) Oil coloration; (iv) Thermal conductivity; (v) Specific heat, (vi) Viscosity; (vii) Density; (viii) Flash point; (ix) Thermal stability. These evaluations were gathered in three different types of analysis.

In the chemical analysis are gathered the two first evaluations that are described below:

- The fatty acid composition has been measured by gas chromatography (CIRAD, France) which enables to follow the evolution of the different chains of carbon atoms and the presence of simple or double bonds within the samples.

- The IA has been assessed by measuring the needed mass of potassium hydroxide (in mg) to neutralize the free fatty acid that are contained in a gram of oil (CIRAD, France).

Thermal properties of the different oil samples were investigated thanks to the use of different instruments that are detailed in [11]. Main information is given hereunder:

- Density has been assessed by using a pycnometer (PROMES-CNRS, France) that measures the expansion of a sample with temperature, calibrated with Jarysol oil and with an instrumental error of 2.25%.

- Specific heat has been measured by a Setaram® C80 calorimeter (University of Reims, France) with a 3.75% accuracy.

- Thermal conductivity has been measured with the hot wire thermal probe with alternative current excitation and 3ω lock-in detection (University of Reims, France) [33]. The method accuracy is about 2%.

- Dynamic viscosity has been measured using an ARES-G2 rheometer from TA Instrument® (Rheonova, France), with an accuracy of about 10%.

Thermal stability has been assessed by means of two different measurements:

- Flash point has been measured thanks to open Cleveland method (IESPM, France) according to standards ISO 2592, with an accuracy of about 0.1 °C.

- Thermal stability has been assessed by measuring the sample's mass loss with temperature. A thermogravimetric analysis (TGA) has been processed to quantify it, thanks to a Setaram SETSYS Evolution 1750 thermobalance under nitrogen atmosphere (CNRS PROMES, France).

Measurements were performed twice in order to ensure the correctness of the obtained values.

3. Results and discussions

3.1 Rapeseed oil compatibility with different TESMs

3.1.1 Chemical analysis

Chemical analysis enables to assess the fatty acid states of deterioration for the different samples of rapeseed oils that have been aged with or without contact with solid materials. Figure 2 illustrates the evolution of the fatty acid composition of the rapeseed oil alone until test duration of 2160 hours.

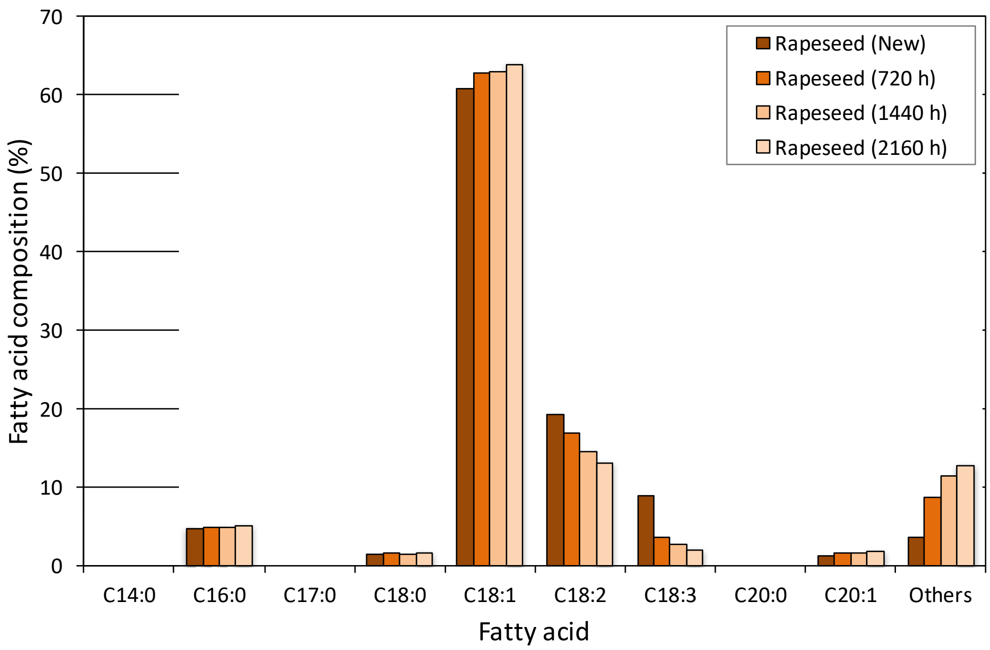


Figure 2 : Evolution of the fatty acid composition of rapeseed oil with thermal ageing (210 °C)

During ageing, unsaturated fatty acids modifications are more important than saturated fatty acids variations. A migration of the polyunsaturated fatty acid (C18:2 and C18:3) to monounsaturated fatty acids (C18:1 and C20:1) can be observed. The field "others" represents observed peaks that have not been identified because they have different number of carbon atoms and bonds.

Figure 3 represents the obtained results with the different tested solid materials, for a total period of 2160 hours. Although modifications are similar, TESM contact seems to accelerate the process of migration of the polyunsaturated fatty acids towards the monounsaturated fatty acids.

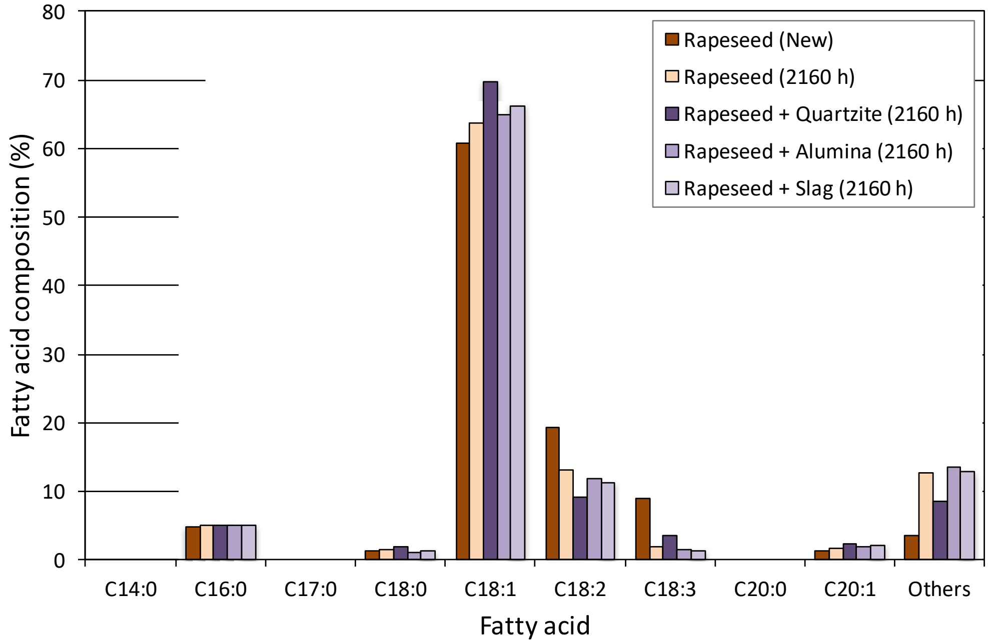


Figure 3 : Effect of the TESMs on the fatty acid composition of rapeseed oil when aged 2160 hours at 210 °C

Quartzite contact leads to slightly different trends, with higher rate of oleic acid (C18:1) and linolenic acid (C18:3) and lower rates of linoleic acid (C18:2)

Table 6 illustrates all the obtained IAs of rapeseed oil samples. New oil has a very low IA but it increases very quickly with ageing and contact with solid materials.

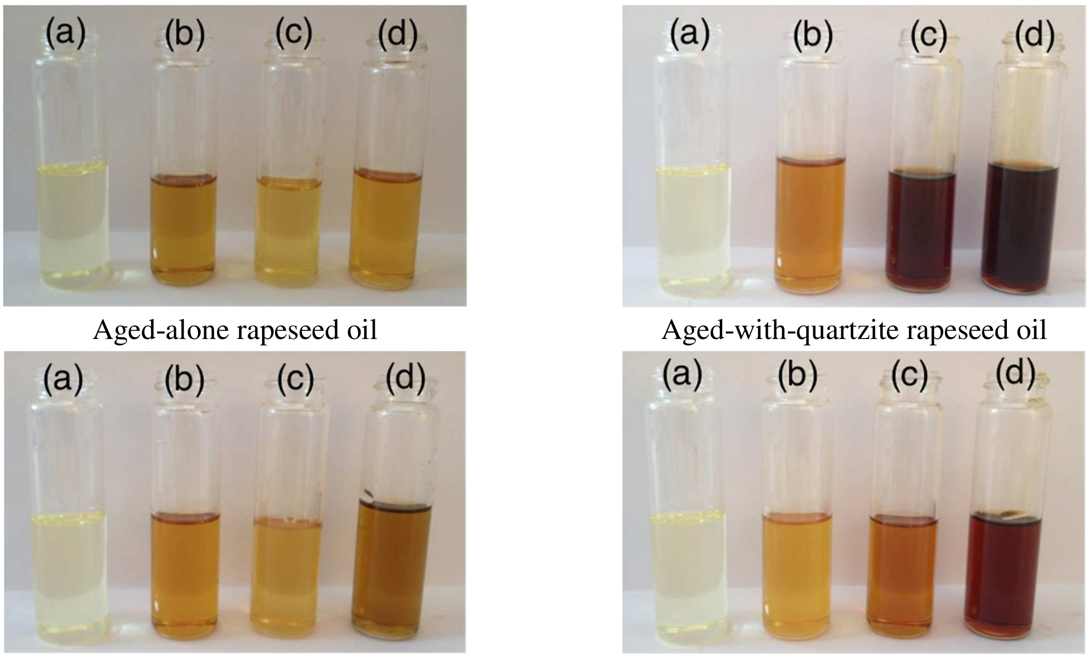
Table 6 : Index of Acidity of differently aged rapeseed oil samples

	Oil Sample	**IA (mgKOH g^{-1})**
Rapeseed	Alone (New)	0.08
	Alone (720 h)	2.20
	Alone (1440 h)	2.39
	Alone (2160 h)	3.22
	Quartzite (720 h)	10.25

Quartzite (1440 h)	6.12
Quartzite (2160 h)	4.74
Alumina (720 h)	3.65
Alumina (1440 h)	2.75
Alumina (2160 h)	3.91
Slag (720 h)	3.96
Slag (1440 h)	6.71
Slag (2160 h)	13.45

For example, slag contact for 2160 hours at 210 °C leads to an IA three times more important that for the other TESMs. The IA evolution itself is not identical for all materials: quartzite contact first leads to a quick IA increase and then a slow decrease. Understanding these evolutions would necessitate a simultaneous study of all the property evolution during ageing.

Coloration of the oil with ageing may only be a qualitative parameter of the oil deterioration state. The change of colour could even be only due to metallic oxides migrating from TESM to HTF. However, even though it is not relevant to assess fluid degradation, it is interesting information that is related to the experiment condition and duration. Figure 4 therefore illustrates the colour modification of the rapeseed oil samples: from a light-yellow, samples get darker and darker with ageing, especially in contact with solids.



Aged-alone rapeseed oil

Aged-with-quartzite rapeseed oil

Aged-with-alumina rapeseed oil

Aged-with-slag rapeseed oil

Figure 4: Pictures of the different rapeseed oil samples: (a) new, (b) 720 h, (c) 1440 h and (d) 2160 h

3.1.2 Heat transfer parameters analysis

Heat transfers are influenced by the thermal characteristics of the HTF. Using a vegetable oil as HTF demands a high stability of these parameters with ageing and contact with TESM. A strong modification of these properties may lead to a need for HTF replacement, leading to extra expenditures. This is why the evolution with ageing and solid contact of rapeseed oil thermal properties, i.e. density, specific heat, thermal conductivity and dynamic viscosity has been investigated.

Density influences heat transfer and energy storage capacity. A decrease of density is prejudicial to the plant performance. Figure 5 shows the evolution of density of the different rapeseed oil samples with temperature.

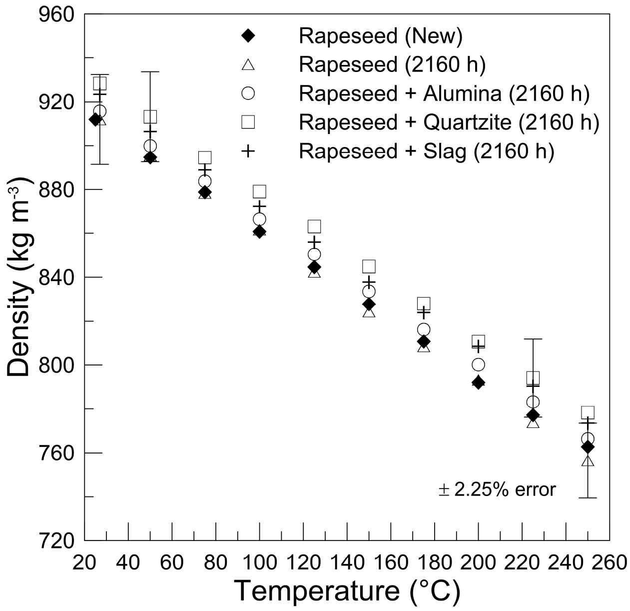


Figure 5 : Comparative density measurement for different rapeseed oils: aged with different solid materials, aged alone and new oil. Instrument error is ± 2.25% of the read value and has been represented with error bars for the two extreme values of reference sample.

For every sample, the dilatation coefficient, represented by the slope of the fitted lines, seem to be identical. However, density absolute values are more important for samples that have been in contact with TESM. Solid materials may have introduced suspended solid particles in the fluid, especially for the case of quartzite. Aged-alone rapeseed oil shows a slightly lower density (0.2%) than new oil. However, knowing the measuring instrument error (2.25%), no sensible modification of density with ageing or contact with TESM at 210 °C and during 2160 hours can be concluded.

Specific heat influences heat transfer and storable energy. It must not decrease with ageing; otherwise it would decrease the plant performance. Specific heat evolution with temperature for all the tested samples is illustrated in Figure 6.

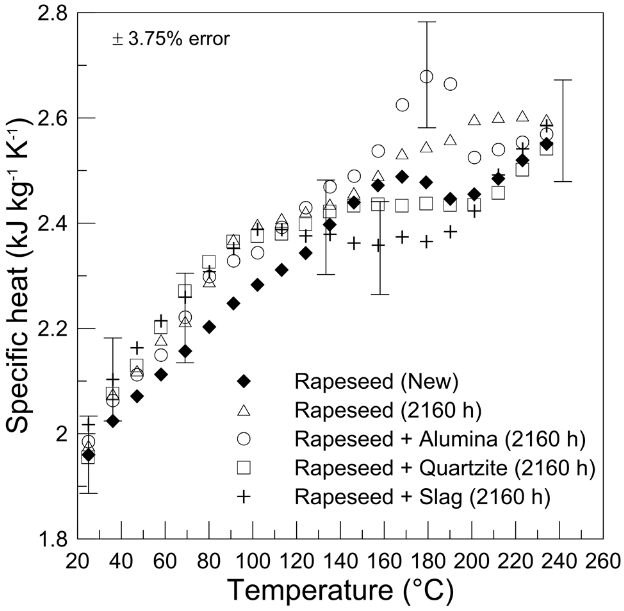
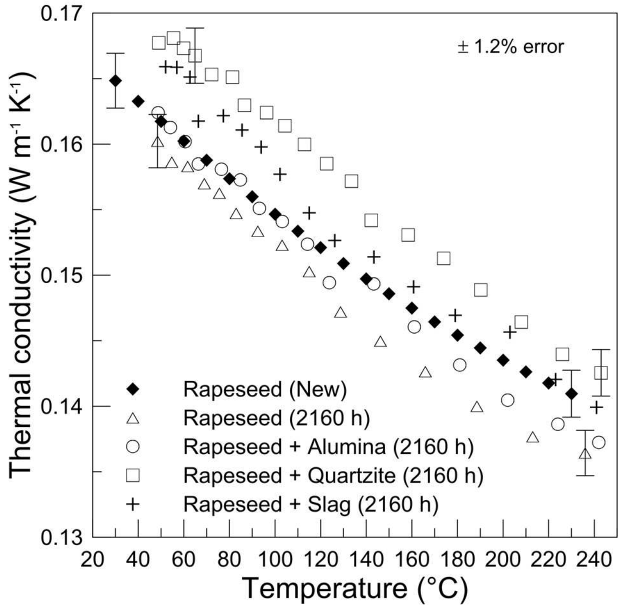


Figure 6 : Comparative specific heat measurement for different rapeseed oils: aged with different solid materials, aged alone and new oil. Instrument error is ± 3.75% of the read value and has been represented with error bars for the two extreme values of reference sample.

The specific heat increase with temperature is not linear for every oil sample; however the obtained plateaus could be due to some instrument limitations. Indeed, although the instrument obtained values are relevant, they show a plateau for all the samples that are studied (vegetable oil or synthetic oil [23]). Nonetheless, comparison between the different curves shows that specific heat values, between 20 °C and 150 °C, are increased by ageing. For higher temperatures, values are more close to the others. As for density, it can therefore be concluded that oil deterioration due to TESM contact does not degrade the oils specific heat for tests at 210 °C and during 2160 hours.

Thermal conductivity takes action in heat transfer of oil with its environment: the higher the thermal conductivity the better the heat transfers. Figure 7 represents the evolution with temperature of the thermal conductivity of the rapeseed oil samples that have been aged with or without solid materials.



339 *Figure 7 : Comparative thermal conductivity measurement for different rapeseed oils: aged with different solid materials, aged alone and new oil. Instrument error is ± 1.2% of the read value and has been represented with error bars for the two extreme values of reference sample.*

Rapeseed oil that has been aged alone sees its thermal conductivity decrease by around 2%. Contact with solid materials seems to inverse the trend, leading to a 0.7% decrease with alumina and even 1.9% and 3.8% increase with slags and quartzite, respectively. From these results and knowing the instrumental error (1.2%), it seems that the oil deterioration does not significantly affect its thermal conductivity for compatibility tests with the chosen TESM at 210 °C and during 2160 hours.

Oil viscosity is a very important parameter. A viscosity increase will lower heat exchange and increase pumping consumption. Measured dynamic viscosity values for the different rapeseed samples in log-log representation depending on temperature are shown in Figure 8.

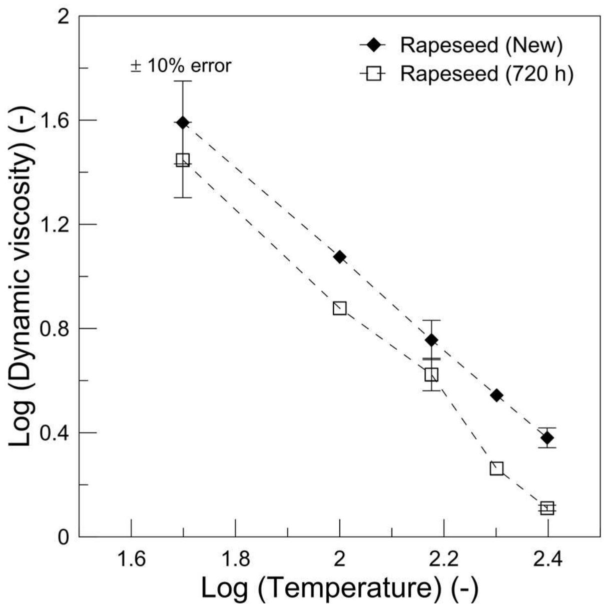


Figure 8 : Comparative dynamic viscosity measurement for different rapeseed oils: aged with different solid materials, aged alone and new oil. Instrument error is ± 10% of the read value and has been represented with error bars for the two extreme values of reference sample.

Although the share of oleic acid has increased with ageing, dynamic viscosity has surprisingly decreased for all the samples when compared to the reference (new rapeseed oil). Contact with TESM does not seem to have an influence on this property. Since variations at high temperature are not easy to assess, Figure 9 compares the dynamic viscosity at 210 °C of the different samples.

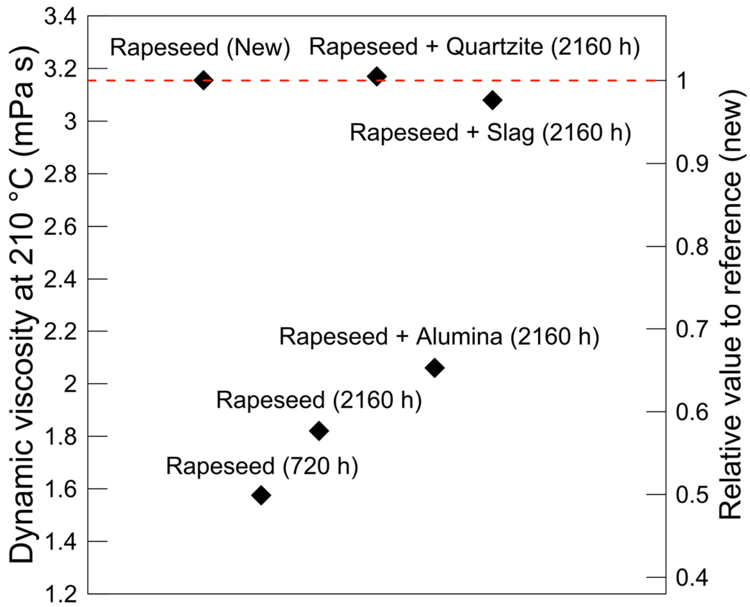


Figure 9 : Dynamic viscosity at 210 °C of the different rapeseed oil samples

For the oil sample that has been aged alone, dynamic viscosity decreased a lot during the first 720 hours, then slightly increased until 2160 hours of thermal treatment. All the samples that have been aged with TESMs show a dynamic viscosity lower than the new oil but higher than the aged-alone oil. As a conclusion, contact with TESM has an influence on the oil viscosity, however it does not deteriorate the plant performance when compared to new oil samples. Once again, for a use at 210 °C and during 2160 hours, no incompatibility can be concluded from these measurements.

3.1.3 Thermal stability analysis

During ageing, oils are subjected to decomposition or denaturation. These modifications can lead to some hazard that has to be avoided. That is why studying flash point and thermal stability temperature is essential.

Flash point is the minimum temperature for the oil to emit a sufficient amount of inflammable vapour to be ignited by a flame. Decrease of the flash point is symptomatic of the oil degradation. It has been observed that flash point decrease can be correlated to the increase of the index of acidity. Figure 10 illustrates this decrease for the different characterized samples, with respect to their IA.

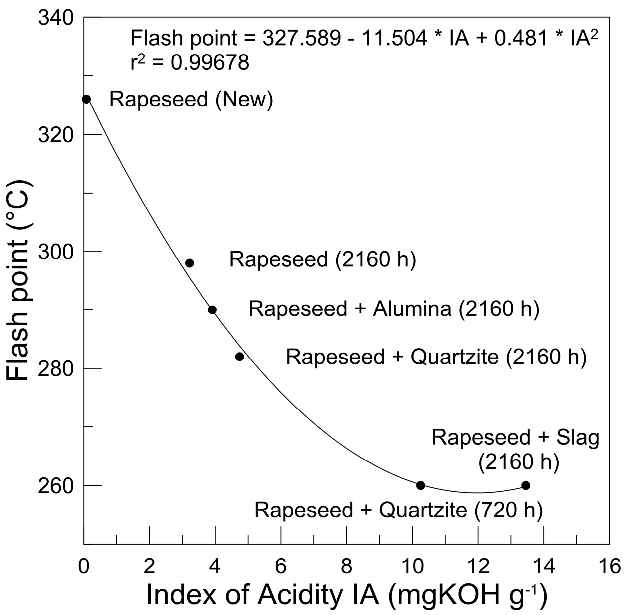


Figure 10 : Flash point of the different rapeseed oil samples (new, aged-alone and aged with TESMs) with respect to the IA.

Linking oil degradation, more specifically here flash point decrease, with the oil index of acidity, is a novelty that was not encountered in previous works. Here, a relatively simple correlation has been found between the residual IA and the flash point of an aged oil sample. Further results could be necessary to refine this model, but a first interpretation with a second degree equation can be used ***(1)***.

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

with IA the index of acidity in mg $KOH.g^{-1}$ and T_{flash} the oil flash point in centigrade.

New rapeseed oil has a flashpoint of 326.0 ± 0.1 °C, which is higher than what was expected according to literature [34]. After ageing at 210 °C during 2160 °C, the flash point decreased to 298.0 ± 0.1 °C. Because of the contact with TESMs, the value further decreased down to 260.0 ± 0.1 °C. This decrease is not linear; a first phase shows a strong decrease with IA, then a second phase shows a slower one after 10 mg $KOH.g^{-1}$.

Although flash point significantly decreased, its lowest value (260.0 ± 0.1 °C) is 50 °C higher than the wanted utilization temperature (210 °C), preventing discrimination of one of the TESM for a use in a thermocline storage up to 210 °C.

The thermal stability temperature qualifies the sample loss of mass with temperature. A material with a high thermal stability shows a high resistance to thermal decomposition. The thermal stability temperature obviously necessitates being above the process temperature in order to avoid fast degradation and hazard. For the present measurement, a 70 mg mass of oil has been heated in a platinum crucible up to a temperature of 500 °C, under nitrogen atmosphere with a thermal ramp of $10°C.min^{-1}$. Based on the results the water removal from the thermal oil was completed at 300°C, hence first part of the x-axis has been cut. This temperature was used to define the anhydrous weight of the samples. The maximum working temperature was taken as temperature at which the oil sample has lost 3% of its anhydrous weight, known as the T3 method [35]. Figure 11 illustrates the non-dimensional mass evolution of the rapeseed sample with temperature. T3 was used for a comparative ranking of the heat transfer fluid candidate and Figure 12 correlates it to the IA.

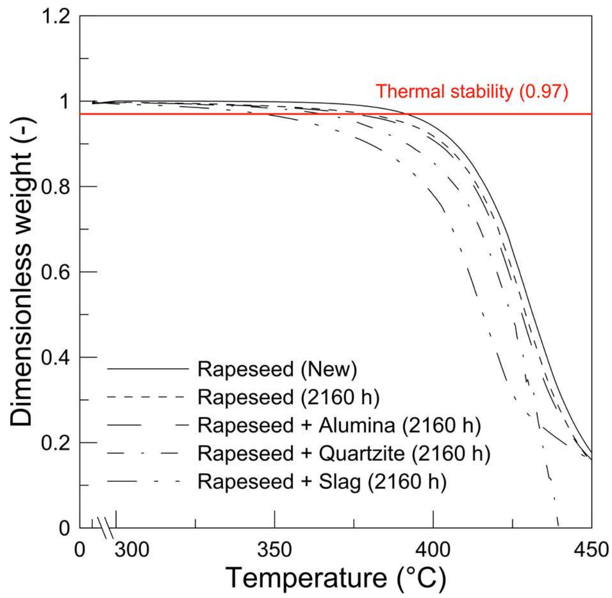


Figure 11 : Dimensionless weight evolution with temperature of the different rapeseed oil samples (new, aged-alone and aged with TESMs).

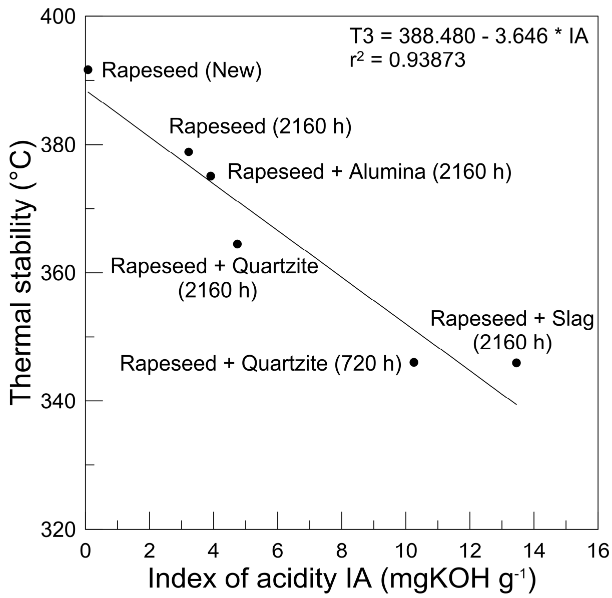


Figure 12 : Thermal stability of the different rapeseed oil samples (new, aged-alone and aged with TESMs) with respect to the IA.

The following correlation between thermal stability temperature and index of acidity is finally obtained (2).

$$T_{st} = 388.480 - 3.646 \cdot IA \tag{2}$$

The new rapeseed oil showed a thermal stability of 391.7 °C, while it decreases with both ageing and contact with TESM. Figure 12 also shows that the compatibility test duration did not necessarily impacted the thermal stability: the oil sample that has been aged during 720 hours has a lower thermal stability temperature than others that have been aged during longer periods. Finally, the influence of the type of TESM on the thermal stability seems to be the same than the influence on the flash point.

Despite the thermal stability deterioration with ageing, the most deteriorated oil has a T_{st} of 346.4 °C, which is still higher than the utilization value (210 °C). This difference is sufficiently important to avoid oil deterioration and compatibility can again be assessed regarding this parameter.

3.1.4 Filler material analysis

At 210 °C, the tested solid materials do not endure modifications. Moreover, the tested oils are not corrosive. As a consequence, only the oil impregnation has been verified within the TESM samples. Oil impregnation can be quantified thanks to Scanning Electron Microscopy (SEM) imaging. Figure 13 illustrates the secondary electrons emitted by atoms after electron beam excitement of a quartzite sample (cut into small disk from pieces that were in contact with oil) after thermal ageing with rapeseed oil at 210 °C and during 2160 hours.

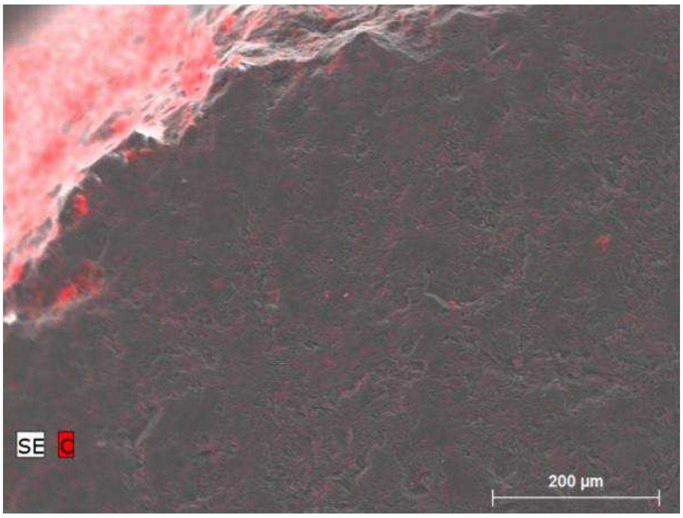


Figure 13 : Oil impregnation of a quartzite sample with SEM imaging (carbon atom in red).

A carbon atom map has been highlighted in red. For every analysed sample, no oil impregnation was visible inside the material; only sample surfaces presented some traces of oil. Since impregnations were very low, no further analysis has been performed.

In addition, mass evolution of the different samples has been examined. A maximum increase of 0.8% has been observed. This increase must come from some residual oil on the sample surfaces and in the surface porosities. It can therefore be concluded that rapeseed oil does not impregnate the tested TESM after compatibility test at 210 °C and during 2160 hours. The TESM's thermal and mechanical properties are considered stable and no extra cost due to oil refilling should be anticipated for a use in a storage system.

3.2 Quartzite compatibility with 4 different vegetable oils

The quartzite compatibility with 4 different vegetable oils (rapeseed, soybean, palm and jatropha) has been investigated. Tests consisted in putting the materials together in the experimental bench for 720 hours at 210 °C. The chosen vegetable oils have been selected because they are relatively cost-effective and their production is handled. In addition, their geographical repartition enables to choose a local solution for every project involved in a developing country.

Soybean oil has the highest flash point (330 °C) and represents 27% of the global production of vegetable oils. Palm oil is the most produced vegetable oil, with a 35% share, and has the highest energy storage capacity (2.07 $MJ.m^{-3}.K^{-1}$). Jatropha oil is the last selected one because it is a non dietary oil and would enable to avoid a conflict between CSP and agriculture.

For this study, only the oil properties that were modified during the compatibility tests are treated; Not mentioned values, for example those of heat transfer properties, did not show significant modfications.

Figure 14 shows the fatty acid composition of the different samples before and after the compatibility tests with quartzite.

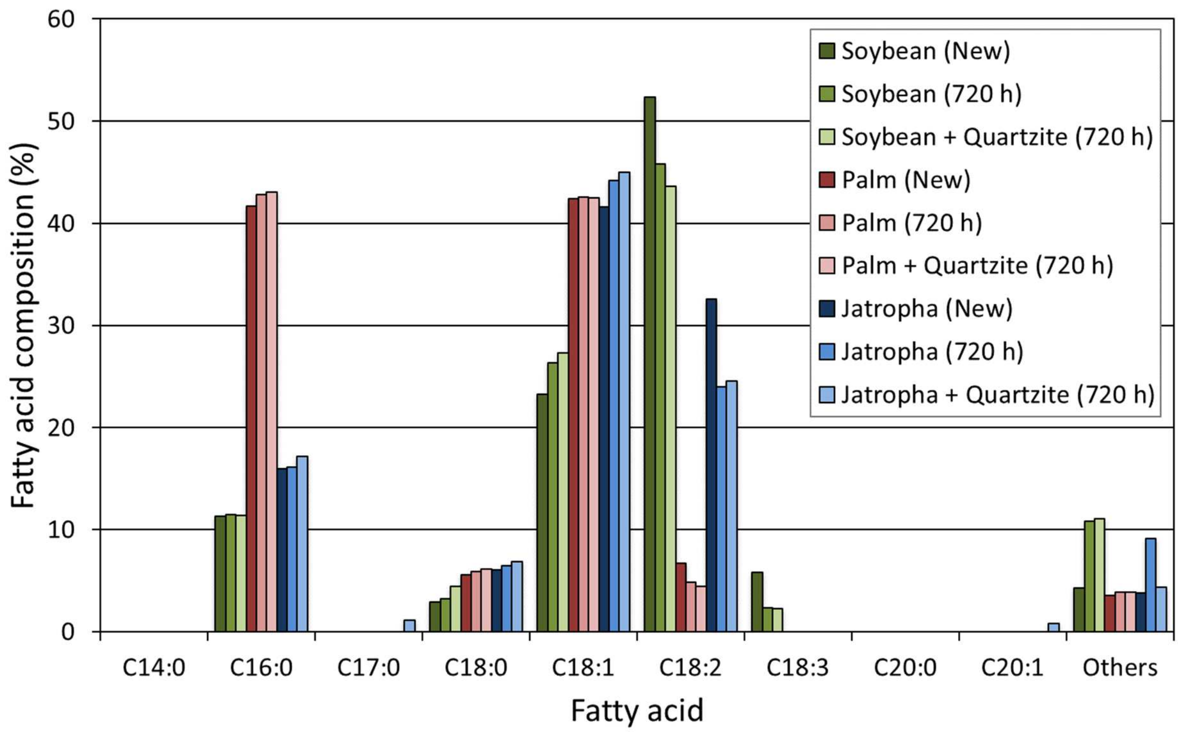


Figure 14 : Fatty acid composition of the different oils before and after ageing with quartzite.

Soybean and jatropha oils have similar reactions as rapeseed. During ageing, polyinsatured fatty acids (C18:2 for jatropha oil and C18:2 and C18:3 for soybean oil) are transformed into oleic mono-insaturated fatty acids (C18:1). For these two oils, a slight increase of the stearic acid share is also visible (C18:0). Palm oil has a different behaviour: its polyinsaturated fatty acid decrease produces an increase of its saturated acid amount (C16:0 and C18:0). Moreover, contrary to all the other studied oils, no perceptible modification of its oleic acid has been observed.

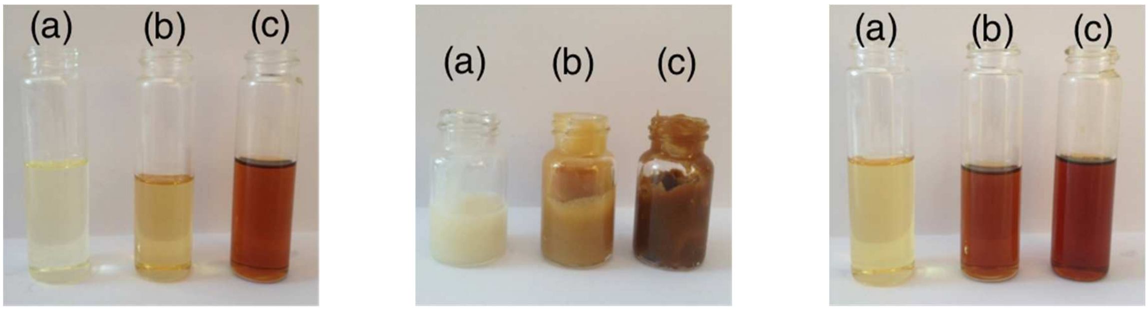
Modification endured by soybean, palm and jatropha oils are slighlty accentuated by the presence of the solid material. A small variation of their thermal properties should therefore be expected, but not on a scale that would be prejudiciable for a use as HTF.

Table 7 gathers all the results regarding the IA. For refined oils such as rapeseed and soja, the IA of the new oil is very low, then it increases with ageing. For jatropha and palm oils, the IA is initially higher than those of the most aged samples of rapesseed, however their behaviour with ageing is different. Palm oil sees its IA increasing with ageing and with the presence of TESM. Jatropha oil’s IA decreases with ageing but this behaviour is slower when TESMs are aged with the fluid.

Table 7 : Index of acidity of the different oil samples that have been aged in the presence of quartzite

Tested vegetable oil	**Index of acidity (mgKOH g^{-1})**
Rapeseed (New)	0.08
Rapeseed (720 h)	2.20
Rapeseed + Quartzite (720 h)	10.25
Soybean (New)	0.13
Soybean (720 h)	2.43
Soybean + Quartzite (720 h)	12.67
Palm (New)	13.72
Palm (720 h)	20.24
Palm + Quartzite (720 h)	25.21
Jatropha (New)	23.82
Jatropha (720 h)	19.28
Jatropha + Quartzite (720 h)	21.47

Regarding coloration, the same conclusions than with rapeseed can be obtained: oils are browner and browner with ageing and TESM contact (Figure 15).



Soybean Palm Jatropha

Figure 15 : Pictures of the aged oils : (a) new, (b) aged-alone (c) aged with quartzite.

Once again, thermal stability temperature for all the samples can be linked with the index of acidity IA. Figure 16 represents the drop of thermal stability for all the samples with respect to their IA.

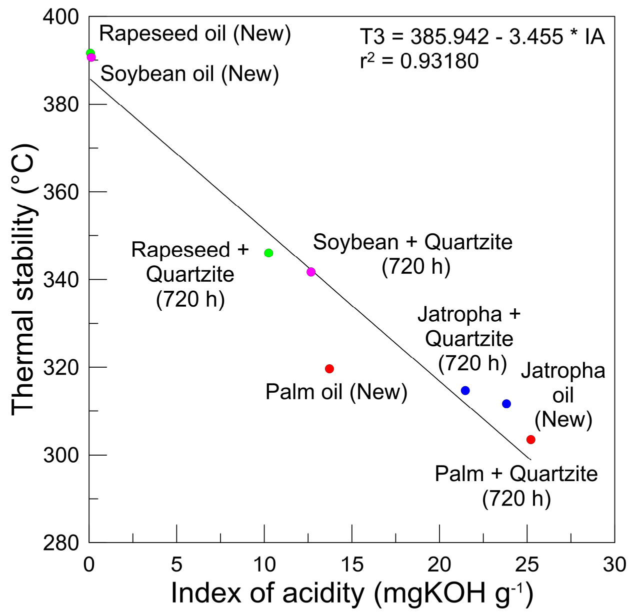


Figure 16 : Thermal stability temperature of the different oil samples that have been aged with quartzite

The presence of TESM induced a drop of the thermal stability temperature for the rapeseed, the soybean and the palm oils compared to the new vegetable oils. For jatropha oil, as it would have been possible to predict knowing the IA increase, the thermal stability has slighlty increased.

Another empirrical correlation for several vegetable oils *(3)* can be obtained in order to extend Equation ***(1)***.

$$T_{stab} = 385.942 - 3.455 \cdot IA \tag{3}$$

It can also be observed that above an IA of 25 mg KOH.g^{-1}, the thermal stability of the vegetable oil is under 300 °C, giving less than 50 °C safety margin between operating temperature (250 °C) and oil degradation. As a consequence, it may be recommended to partially change the oil in an installation when such value of IA is reached.

This complementary study enables to enlarge the scope of possible candidated as HTF for thermocline storage in CSP plants. It shows that evolution of their chemical characteristics is acceptable when aged with quartzite rocks. As a consequence, thermocline thermal energy storage with vegetable oil and quartzite rock seems to be a relevant solution.

4. Conclusions

The present compatibility study evaluates the behaviour of several vegetable oils with temperature and contact with potential solid filler materials. A particular focus has been set on rapeseed oil because of its high thermal stability, its good physico-chemical properties and because of its ease of production.

Rapeseed oil has been aged up to a period of 2160 h and at 210 °C in contact with various solid materials (natural rocks, metallic industry co-product and ceramics). From the compatibility study between the oil and quartzite rocks, steel slags and alumina, 4 conclusions can be drawn:

- Because of thermal ageing of the oil, polyunsaturated fatty acids are transformed in monounsaturated fatty acids. Presence of solid materials slightly accelerates the chemical transformation.
- The thermal properties (density, specific heat, thermal conductivity and dynamic viscosity) of the oil are not significantly modified by ageing and contact with solids.
- The oil flash point and the oil thermal stability temperature decrease with ageing and contact with filler materials, although no solid has been discriminated for the testing period.
- Deterioration rate of oil can be assessed by measuring its index of acidity. From this measurement, flash point and thermal stability of the aged oil can be estimated. This main result may help to evaluate the quality of the heat transfer fluid when used in a concentrated solar power plant. Measurement of the index of acidity informs about the possible partial replacement of the oil to avoid any risk. An index of acidity higher than 25 mg $KOH.g^{-1}$ corresponds to a thermal stability lower than 300 °C. Therefore, it seems to be a reasonable limit value.

A complementary study has been performed with quartzite and various vegetable oils. Quartzite has been chosen because of its already proven compatibility with molten salts and its worldwide availability. Two conclusions came out of the compatibility tests between quartzite and rapeseed, soybean, palm and jatropha vegetable oils at 210 °C and during 720 hours:

- It has been confirmed that index of acidity is a relevant indicator of the ageing state of the vegetable oil.
- The four tested vegetable oils are relevant solution for a use in a thermocline thermal energy storage system with quartzite as filler materials. Thus, local and cost-effective resource can be used to provide an environmental-friendly heat transfer fluid to a concentrated solar power plant working up to a temperature of 210 °C.

Numerous solutions are available worldwide to provide an efficient, cost-effective and environmental-friendly thermal energy storage system. This study confirms that natural products, industry by-products and wastes are underestimated resource for the future of energy. However, there is still a need for several material and process investigations about this topic.

Acknowledgments

This project was supported financially by ANRT, a PhD grant through a CIFRE program n°2012/1516, AQYLON and EDF R&D Company and the Program "Investissements d'avenir" (Investment for the Future) of the Agence Nationale de la Recherche (National Agency for Research) of the French State under award number ANR-10-LABX-22-01-SOLSTICE. The authors thank the University of Reims (J.-F. Henry, M. Chirtoc and D. Caron) for their scientific support. The authors also thank Jeremy Valette (CIRAD) for the many characterizations carried out.

[1] P. Denholm, Y.-H. Wan, M. Hummon and M. Mehos, "An analysis of concentrating solar power with thermal energy storage in a California 33% renewable scenario," Technical Report NREL/TP-6A20-58186, Golden, USA, 2013.

[2] P. Dutta, "High temperature solar receiver and thermal storage systems," *Applied thermal engineering,* vol. 124, pp. 624-632, 2017.

[3] X. Py, Y. Azoumah and R. Olives, "Concentrated solar power: Current technologies, major innovative issues and applicability to West African countries," *Renewable and Sustainable Energy Reviews,* vol. 18, pp. 306-315, 2013.

[4] Y. Grosu, I. Ortega-Fernandez, L. Gonzales-Fernandez, U. Nithiyanantham, Y. F. Baba, A. A. Mers and A. Faik, "Natural and by-product materials for thermocline-based thermal energy storage system at CSP plant: Structural and thermophysical properties," *Applied Thermal Engineering,* vol. 136, pp. 185-193, 2018.

[5] T. Esence, A. Bruch, S. Molina, B. Stutz and H.-F. Fourmigué, "A review on experience feedback and numerical modeling of packed-bed thermal energy storage systems," *Solar Energy,* vol. 153, pp. 628-654, 2017.

[6] H. Grirate, H. Agalit, N. Zari, A. Elmchaouri, S. Molina and R. Couturier, "Experimental and numerical investigation of potential filler materials for thermal oil thermocline storage," *Solar Energy,* vol. 131, pp. 260-274, 2016.

[7] J. E. Pacheco, S. K. Showalter and W. J. Kolb, "Development of a Molten-Salt Thermocline Thermal Storage System for Parabolic Trough Plants," *Journal of Solar Energy Engineering,* vol. 124, pp. 153-159, 2002.

[8] T. Fasquelle, Q. Falcoz, P. Neveu and J.-F. Hoffmann, "A temperature threshold evaluation for thermocline thermal energy storage in concentrated solar power plants," *Applied Energy,* vol. 212, pp. 1153-1164, 2018.

[9] N. Sassine, F.-V. Donzé, B. Harthong and A. Bruch, "Thermal stress numerical study in granular packed bed storage tank," *Granular Matter,* vol. 44, pp. 20-34, 2018.

[10] C. Martin, A. Bonk, M. Braun, C. Odenthal and T. Bauer, "Investigation of the long-term stability of quartzite and basalt for a potential use as filler materials for a molten-salt based thermocline storage concept," *Solar Energy,* vol. 171, pp. 827-840, 2018.

[11] J.-F. Hoffmann, G. Vaitilingom, J.-F. Henry, M. Chirtoc, R. Olives, V. Goetz and X. Py, "Temperature dependence of thermophysical and rheological properties of seven vegetable oils in view of their use as heat transfer fluids in concentrated solar plants,"

Solar Energy Materials and Solar Cells, vol. 178, pp. 129-138, 2018.

[12] J.-F. Hoffmann, T. Fasquelle, V. Goetz and X. Py, “A thermocline thermal energy storage system with filler materials for concentrated solar power plants: Experimental data and numerical model sensitivity to different experimental tank scales,” *Applied Thermal Engineering,* vol. 100, p. 753–761, 2016.

[13] J.-F. Hoffmann, T. Fasquelle, V. Goetz and X. Py, “Experimental and numerical investigation of a thermocline thermal energy storage tank,” *Applied Thermal Engineering,* vol. 114, p. 896–904, 2017.

[14] Solutia, “Therminol VP1,” [Online]. Available: http://twt.mpei.ac.ru/tthb/hedh/htf-vp1.pdf. [Accessed 05 04 2019].

[15] K. Vignarooban, X. Xu, A. Arvay, K. Hsu and A. Kannan, “Heat transfer fluids for concentrating solar power systems - A review,” *Applied Energy,* vol. 146, pp. 383-396, 2015.

[16] S. Goods and R. Bradshaw, “Corrosion of stainless steels and carbon steel by molten mixtures of commercial nitrate salts,” *Journal of Materials Engineering and Performance,* vol. 13, no. 1, pp. 78-87, 2004.

[17] A. M. Kruizenga, “Corrosion mechanisms in chloride and carbonate salts,” Sandia National Laboratory Reports, 2012.

[18] D. Brosseau, P. Hlava and M. Kelly, “Testing thermocline filler materials and molten-salt heat transfer fluids for thermal energy storage systems used in parabolic trough solar power plants,” Sandia National Laboratory Reports, 2004.

[19] N. Calvet, J. Gomez, A. Faik, V. R. A. Meffre, G. Glatzmaier, S. Doppiu and X. Py, “Compatibility of a post-industrial ceramic with nitrate molten salts for use as filler material in thermocline storage system,” *Applied Energy,* vol. 109, pp. 387-393, 2013.

[20] F. Motte, Q. Falcoz, E. Veron and X. Py, “Compatibility tests between solar salt and thermal storage ceramics from inorganic industrial wastes,” *Applied Energy,* vol. 155, pp. 14-22, 2015.

[21] G. McConohy and A. Kruizenga, “Molten Nitrate Salts at 600 and 680 °C: Thermophysical property changes and corrosion of high-temperature nickel alloys,” *Solar Energy,* vol. 103, pp. 242-252, 2014.

[22] A. Bonk, C. Martin, M. Braun and T. Bauer, “Material investigations on the thermal stability of solar salt and potential filler materials for molten salt storage,” in *SolarPACES2016*, Abu Dhabi, 2016.

[23] T. Fasquelle, Q. Falcoz, P. Neveu and J. W. G. Flamant, “Compatibility study between synthetic oil and vitrified wastes for direct thermal energy storage,” *Waste and Biomass Valorization,* vol. 8, no. 3, pp. 624-631, 2017.

[24] S. Molina, D. Haillot, A. Deydier and J.-P. Bedecarrats, “Material screening and compatibility for thermocline storage systems using thermal oil,” *Applied Thermal Engineering,* vol. 146, pp. 252-259, 2019.

[25] R. Anderson, S. Shiri, H. Bindra and J. Morris, “Experimental results and modeling of energy storage and recovery in a packed bed of alumina particles,” *Applied Energy,* vol. 119, pp. 521-529, 2014.

[26] J. Felinks, S. Richter, B. Lachmann, S. Brendelberger, M. Roeb, C. Sattler and R. Pitz-Paal, “Particle-Particle heat transfer coefficient in a binary packed bed of alumina and zirconia-ceria particles,” *Applied Thermal Engineering,* vol. 101, pp. 101-111, 2016.

[27] N. Calvet, G. Dejean, L. Unamunzagua and X. Py, "Waste from metallurgic industry: A sustainable high-temperature thermal energy storage material for concentrated solar power," in *ASME 7th International Conference on Energy Sustainability*, 2013.

[28] K. A. Naimi, T. Delclos and N. Calvet, “Industrial waste produced in the UAE, Valuable high temperature materials for thermal energy storage applications,” *Energy Procedia,* vol. 75, pp. 2087-2092, 2015.

[29] I. Ortega-Fernandez, Y. Wang, M. Duran, E. Garitaonandia, L. Unamunzaga, D. Bielsa and E. Palomo, “Experimental validation of steel slag as thermal energy storage material in a 400 kWht prototype,” in *SolarPACES*, Casablanca, 2018.

[30] J. Haunstetter, M. Krüger and S. Zunft, “Slag as an inventory material for heat storage in a concentrated solar tower power plant: experimental studies on design and performance of the thermal energy storage,” in *SolarPACES*, Casablanca, 2018.

[31] X. Py, N. Calvet, R. Olives, P. Echegut, C. Bessada and F. Jay, “Low-cost recycled material for thermal storage applied to solar power plants,” in *SolarPACES*, Berlin, 2009.

[32] H. Grirate, N. Zari, I. Elamrani, R. Couturier, A. Elmchaouri, S. Belcadi and P. Tochon, “Characterization of several Moroccan rocks used as filler material for thermal energy storage in CSP plants,” in *SolarPACES*, Las Vegas, 2013.

[33] J.-F. Hoffmann, J.-F. Henry, G. Vaitilingom, R. Olives, M. Chirtoc, D. Caron and X. Py, “Temperature dependence of thermal conductivity of vegetable oils for use in concentrated solar power plants, measured by 3omega hot wire method,” *International journal of thermal sciences,* vol. 107, pp. 105-110, 2016.

[34] G. Vaitilingom, *Qualité combustible des biocarburants : influences des caractéristiques particulières des huiles végétales terrestres et marines sur leur comportement en tant que remplaçant des produits pétroliers,* 2013.

[35] J. C. Gomez, N. Calvet ,"Ca(NO3)2-NaNO3-KNO3 Molten Salt Mixtures for Direct Thermal Energy Storage Systems in Parabolic Trough Plants," *Journal of Solar Energy Engineering*, vol. 135, pp. 1-8, 2013.