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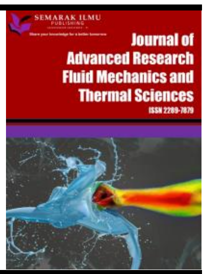

Compatibility Study between Ceramic Balls and Jatropha Curcas Oil Properties under Long Time Heat Treatment: Potentiality for Thermal Energy Storage

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ABSTRACT

Valorisation of local and low-cost eco-materials have become an imperative for the sustainable development of Concentrating Solar Power (CSP) in West Africa. In this study, the compatibility tests were carried out. These involve the application of jatropha curcas oil (JCCO) and ceramic balls, which were developed from clay coal bottom ash and sands with a focus on Burkina dune sand ceramic. The aim was to assess the applicability of using JCCO as heat transfer fluid in CSPs with direct thermocline thermal energy storage. The tests involve the use of a small container to put in contact with Jatropha oil with ceramic balls for 2160 hours and at 210 °C. From the chemical properties' analysis, the peroxide value in the oil decreases with aging time while the acidity increase. However, the acidity remains below the limited value that is 25 mg KOH.g^{-1}. Therefore, thermal properties that drive heat transfer and rheological properties (density, thermal conductivity, kinematic viscosity and so on) were not adjusted significantly at the storage temperature (of about 210°C). Thermal stability temperature decreased to 261.93°C for the oil aged alone as against 263.41 °C for the one that was put in contact with filler material. In the nutshell, there is no incompatibility between JCCO, and the new thermal energy storage material (TESM) developed. These couple of materials could be suitable for thermocline energy storage in CSP plant and for other applications like there use in solar cooker box.

1. Introduction

Energy transition toward renewable solutions, innovative technologies like sustainable thermal energy systems would continue to emerge with their various usage, across different value chain. It includes heat production, electricity generation, chemical manufacturing and other in order to

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enhance possible options in integrating different sectors and technological pathways as discussed in Muritala *et al.,* [1]. Concentrated Solar Power (CSP) technologies like parabolic troughs, power towers, and dish/engines, have the potential to provide the world with clean, renewable, cost-competitive power on a large scale [2]. With thermal energy storage (TES) system, dispatching energy flexibilities, CSP has the possibilities to stabilize electrical grid and to provide electricity and heat to remote locations with solar resource potentials. The TES system can improve energy supply by preventing the delays of electricity generation to high cost supply and importantly avoiding the use of fossil-fuel fired power plants [3]. Nowadays, research is focusing on increasing efficiency and/or reducing the cost of CSP technology. In common CSP plant, two large tanks filled with molten salt are used as thermal energy storage system components [4]. This solution involves relatively high capital expenditure with initial investment of around 20% [5]. This makes the two tanks storage system less attractive to investor and CSP plant unaffordable for developing countries while the potential is significant. In West Africa, the only pilot CSP plant (CSP4AFRICA) is installed at 2ie using two tank of Jatropha curcas oil (low cost material) [6]. To perform this system or technology in the region, several studies were carried out on the thermal stability of JCCO and JCRO in steel reactors for long time [7,8]. To reduce more the initial investment cost, thermocline energy storage tank is required leading to a potential reduction of 35% [9]. Thermocline technology consists in using one single-tank instead of the conventional two-tank system based on temperature gradient. This gives possibility to use natural resources like natural rock, local products and material from wastes as filler materials [8,10-12]. These available materials use as filler materials in a thermocline storage tank, are getting attention of many developers in the past recent years [10,13]. TES cost is further reduced by replacing an important part of the heat transfer fluid (HTF) by low cost TES materials (TESM or filler materials) [14]. However, thermocline energy storage has some issues like outlet temperature variation and filler material size and geometry, strong thermos-mechanical stress and incompatibility between HTF and TESM and [15-19]. Fluid can be used as HTF or thermal energy storage. Thus, water is most popular and already has number of residential and industrial applications. However, it working temperature is limited up to 100°C, at atmosphere pressure and because the vaporization of water requires that expensive pressurizing equipment [20,21]. Therefore, the oil offers the advantage over water in the medium temperature as oil does not vaporize above 100°C [22]. Among these oils, there are minerals and synthetic oils, which are respectively from hydrocarbon mixture produced from the distillation of crude oil and synthesized from chemical compounds [23]. Mineral oils, in addition to sources limitation have several other drawbacks such as, non-biodegradability (not more than 30%), low flash point, non-renewable and could cause a serious problem if there is a spillage [24]. Synthetic oils are also used as thermal oils because of their good properties like high flash point and excellent oxidation resistance, but are expensive [25,26]. To address these issues, vegetable oils have been studied extensively with a view to use them as alternative to minerals or synthetic oils in various applications [25,26]. At high temperature, vegetable oils are known for their use as insulating fluids in transformer industry with reliability and solar oils in solar cookers [23,27]. Therefore, the use of vegetable oils as HTF and TESM in CSP is totally a new field of research. It is important to note that, these vegetable oils may be those that are non-edible in other to avoid competition with food and cooking oil scarcity. This could be referring as a circular approach in putting non-edible oils to good use in energy systems and heat application. Several studies have shown their potentiality in this area. For this propose, thermophysical and rheological properties of seven vegetal oils were investigated in Hoffmann *et al.,* [28]. These thermos-physical properties are on average 13% higher than the one of Therminol VP1® and they were influenced by temperature and fatty acid contents [28]. Jatropha curcas oil is nonedible oil and could be presented as the most suitable HTF and TESM for CSP application in developing countries to avoid any conflict of interest as regard to food shortage and hunger. In this framework, CSP4AFRCA pilot plant was implemented using two tank (expensive configuration) storage system and jatropha curcas oil as HTF and TESM [6]. To this end, the thermal stability of JCCO in steel reactors was investigate in Kenda *et al.,* [8]. JCCO presents good thermal stability up to 210 °C with good energy storage density. However, renewal of oxygen in reactor should be minimize to avoid oil oxidation [8]. In addition, the high present of free acid in JCCO could lead to corrosion of some metals (Zinc, Iron and so on) and accelerate oil oxidation as demonstrated in Kenda *et al.,* [8] and Ferrer *et al.,* [29]. To address these challenges of corrosion and oxidation, the thermal stability of refined Jatropha Curcas oil has been conducted in Gomna *et al.,* [23] for 2160 hours (isothermal test). After 2160 hours, JCRO still had a good specific heat capacity and kinematic viscosity at 100°C, which is confirming jatropha curcas oil stability at 210 °C. However, a drop of flash point to 175°C occurred as noted in the study of Gomna *et al.,* [26]. Table 1 illustrates the properties of some HTF.

Table 1
Thermal properties of mineral, synthetic and vegetal oil as HTF and TESM [23,28,30-32]

Parameter	Mineral oils	Synthetic oils	Silicone oil	Vegetal oils	JCCO
Composition	Complex mixture of hydrocarbons	Pentaerythritol tetra ester	Di-alkyl silicone polymer	Plant-based natural ester	Plant-based natural ester
Flash point	160-193	47-124	>300	220-330	220-240
Fire point	110–185	300–310	340-350	300–360	275°C
Pour point at 1013mbar	-29	-11 to 12	N/A	- 11 to 20	
Total acidity	0.015–1.2	<0.01	N/A	0.015-23.82	11-23.82
υ at 40°C μ at 40°C	3–16	14-29	35–40	16–37	30-35
υ $(mm.s^{-2})$ at 100°C	2–2.5	4-6	15–17	4–8	1.73 at 210°C
μ (m.Pa.s) at 210°C	N/A	0.23-0.55	N/A	1.004-3.155	1.781
$\rho\ at$ 210 °C $(kg.m^{-3})$	736.4	649.8-904	N/A	771.6-805.5	778.2
$\lambda\ at\ 210°C$ $(W.m^{-1}.K^{-1})$	0.13	0.062-0.121	~0.1	0.128-0.143	0.139
C_p $(kJ.kg^{-1}.K^{-1})$ at 210°C	2.643	2.075-2192	N/A	2.440-2.677	2.509
$\rho \times C_p$ $(MJ.m^{-3}.K^{-1})$	1.946	1.433-1.945	N/A	1.95-2.15	1.953
Cost (€.t^{-1})		25000-29000	4580	400-1200	400-1200

For thermocline energy storage development several solid materials have been studied to reduce the quantity of fluid used as TESM. Among them, there are natural rocks, industrials waste or by-products, concretes and ceramics [11,33-35]. In addition, with their good thermal properties, rocks like Dolerite, Rhyolite and quarzitic sandstone have high storage temperature of up to 600°C [33,36]. However, natural rock shape is uncontrollable and big, which can reduce the performance of TES [16]. Concretes can face this issue of size and shape but limited to 400 °C as working point. Waste like steel slag from furnace and asbestos containing waste (glass and ceramic) can handle heating cycle up to 800°C but are not available in developing countries [35]. Kenda *et al.,* [8] developed ceramic from laterite and coal bottom ash (CBA) using solar concentrator at temperature up to 1400 °C. The high melting point (1400°C) of ceramic and CBA could make the manufacturing of the TESM expensive. To reduce the cost and energy consumption of TESM manufacturing, clay and biochar, clay and CBA, clay plus CBA and sand can be used to shape and size ceramic at temperature less than 1100 °C with better thermal properties and stability for thermal energy storage [10,37,38]. Table 2 presents the thermal properties of some filler material.

Table 2
Thermal properties of solid material useful as TESM

Thermal properties	Natural rocks [33]	Concrete [39,40]	Industrial waste (slag cast iron and steel) [40]	Clay, biomass and, waste ceramic [10,37,41]	Ceramic from waste [42,43]
$\rho(kg.m^{-3})$	2640- 3010	N/A	2487-7800	>1500	1.56-3.670
$\lambda(W.m^{-1}.K^{-1})$ $at\ (300°C)$	1.7- 3.8	1-2.5	0.84-40	>0.33	1-2.5
$C_p(kJ.kg^{-1}.K^{-1})$ $at\ (600°C)$	940- 1836	860	0.56-1.11	0.62-1.49	700-1300
$\rho \times C_p$ $(MJ.m^{-3}.K^{-1})$	1.59- 3.41	1.8-2.52	N/A	>1.3	1911–3380
Operating temperature (°C)	>400	>350	>400	N/A	N/A
Cost (€.t^{-1})	<1500		<5000	N/A	N/A

This paper aims to investigate the effect of ceramic balls developed with clay, coal bottom ash (CBA) and sand in Bagre *et al.,* [38] on JCCO different properties.

This approach is to decrease the TES system cost while using local, no conflict interest materials that are environmentally friendly. As a vegetable oil, one of the constraints is the working temperature, which has lower value (250 °C) than the one that that could be obtained with conventional thermal oil (400 °C) [19]. The use of vegetable oil as HTF drives direct heat production or the use of an Organic Rankine Cycle to produce electricity. Jatropha oil could therefore be an alternative to mineral and synthetic oil if improvement could be done on the usability and its consequence [19]. As the HTF could be in contact with TESM during several thermal cycles without been destroyed, it is important to know the compatibility between HTF and the TESM. The most adequate filler materials in contact with molten salt seem to be quartzite and sand [14]. Unlike molten, salt has strong corrosion effect on solid [14,18,42-44]. The few studies carried out show that the oil properties are more affected by the filer material or reactor wall [42,45]. Indeed, the first CSP plant with integrated indirect thermocline storage system to supply the plant auxiliary steam needed worked with coloria-HT-43 oil as HTF in contact with quartzite and sand as filler material. Nevertheless, after three years of operation, the thermocline tank had fire attack at the top due to the significant quantity of water in the oil driving to an over pressurization and the rupture of the tank [46]. In addition, the acidity of oil can increase driving to the flash point and stability temperature decreasing as mentioned by Hoffmann *et al.,* [19]. Few studies have been conducted on oil compatibility with filler material or TES tank wall material to select the best couple (HTF and TESM) for TES. Table 3 presents the effect of solid material on oil properties before and after heat treatment.

Table 3 shows that the main parameters track for thermal oil as HTF or TESM (when being in contact with filler material) are flash point and acid index under heat treatment. The flash point drops with aging time. This drop can depend on the heat treatment method used. Thus, the isothermal test method influences less the flash point than the thermal cycles test due to probably air flow in the reactor during cooling time [7,8]. In addition, the flash point thermal stability of several vegetable oils can be link to acid index according to Hoffmann *et al.,* [19] as follows:

$$T_{flash} = 327.589 - 11.504\ \times IA\ +\ 0.481 \times IA^2 \tag{1}$$

$$T_{stab} = 385.942 - 3.455 \times IA \quad (2)$$

Table 3
The effect of aging time and temperature on oil stability parameters

	New oil					Oil after aging			
PROJECTs	oils	FP (°C)	IA mg.KOH.g^{-1}	W.C (ppm)	υ (mm^2.s^{-1})	FP (°C)	IA mg.KOH.g^{-1}	W.C (ppm)	υ (mm^2.s^{-1})
Aged at 210°C (500h) [8]	JCCO +Iron	236	17.1	508	36	236	18.2	273	39
Vegetable oil aged at 210°C (720 h) [19,47]	Rapeseed +quartzite	285	0.08	N/A	N/A	N/A	10.25	N/A	N/A
	Jatropha+ quartzite	236	23.82	N/A	N/A	N/A	21.82	N/A	N/A
	Palm+ quartzite	280	13.72	N/A	N/A	N/A	25.21	N/A	N/A
	Soybean+ quartzite	330	0.13	N/A	N/A	N/A	12.67	N/A	N/A
Synthetic oil aged at 330°C (500H) [42]	Jarytherm®DBT +CFA	230	0.05	39	N/A	224	<0.01	112	N/A
	Jarytherm®DBT +cofalit	230	0.05	39	N/A	224	<0.01	160	N/A
	Jarytherm®DBT +Alumina	230	0.05	39	N/A	226	<0.01	176	N/A

Synthetic and mineral oil use in CSP plant is more known than vegetable oils. However, due to the low thermal instability and the high environmental hazard, vegetal oil could be an alternative. Several authors such as Gomna *et al.,* [7], Kenda *et al.,* [8], and Hoffmann *et al.,* [19,28], as HTF and TESM, Nébié *et al.,* [27] and Radosevich [46] showed the compatibility of quartzite rocks, steel slags and alumina with vegetable oils. After more than 720 hours of aging time, the team realized that none of oils acidity index reach the required 25 value (mg.KOH.g^{-1}) despite of acidity increasing with aging time. Nevertheless, vegetable oils have usefulness due to food conflict and they used in industry sectors [28]. Some vegetable oil like jatropha curcas oil (JCO) are mostly used in industry sector to produce soap and biofuel, which could be applied in CSP plant. In the framework of CSP4AFRICA, 8 kWh_{th} pilot CSP plant installed at "Institue Internationale d'Ingénierie de l'Eau et de l'Assainisement (2ie) "some studies were conducted on JCO thermal stability. To use JCCO as HTF and TESM, Kenda *et al.,* [8] studied crude oil thermal stability at 210 °C in contact with steel reactors stainless and galvanized one. This study showed that JCCO is more stable in the stainless-steel reactor than the galvanized one due to the migration of iron and zinc element in the oil after 500 hours of heat treatment. Due the high acidity of JCCO, Gomna *et al.,* [7] have done a long time static test on thermal stability of refine JCO at 210 °C in glass containers. A drop to 175 °C of the flash point was observed after 2160 hours versus 220 °C for the reference oil but the thermal properties like specific heat capacity and viscosity were similar to the properties of the new one [7]. As show in Table 3 the acidity of refine jatropha curcas refined oil (JCRO) could decrease with aging time in contact with filler material like quartzite rock [19]. A potential ceramic ball with good volumetric heat capacity have been developed in Bagre *et al.,* [38] using sand, clay and coal bottom as raw materials. The contribution of this work is to do a long-time corrosion test of the new ceramic balls developed in

Bagre *et al.,* [38] in contact with JCCO or assess the compatibility between sand, clay and coal bottom ash ceramic with JCCO. To achieve this objective, the ceramic balls were put in contact with JCCO for 2160 hours. The chemical, physical properties, and thermal stability of JCCO have been measured every 720 hours. The methodology section will provide more details on the compatibility assessment process.

2. Methodology

2.1 Materials

2.1.1 Jatropha curcas oil (JCCO) as HTF and TESM

Jatropha curcas L. (Jatropha) is known as a physic nut. It is a large shrub or small tree that belongs to the genus Euphorbiaceous, which produces oil-containing seeds. This species is native to North and Central America and is now widespread all over the tropical and subtropical regions of the world, such as Africa, India, Southeast Asia, and China. Jatropha species are well adapted to extreme drought and soil conditions, and are thus able to grow well in semi-arid and arid regions, with high temperatures and a low soil moisture [48]. It is a friendly eco-material known for its multiples used like biodiesel and soap manufacturing [49,50]. Jatropha curcas oil can also use as HTF and TESM for heat application [8,23]. The jatropha curcas crude oil (JCCO) supplied by the Belwet Company in Burkina Faso was used in the present study. The extraction of the crude oil is done in an AISO bar press and after direct filtration with an adapted AISO plate filter. Without any addition processing the JCCO oil is cheaper than the refined where the process of neutralization of the free fatty acid could increase the cost of oil. The extraction methods are available in Riayatsyah *et al.,* [51]. The main composition of JCCO is fatty acid like acid oleic (41.64%), linoleic (32.53%), Stearic (6.05%) and palmitic (16.01%) [28]. The initial characteristics of the oil were determined at the beginning of each test because the physical and chemical properties of the oil may be impacted by the quality of the feedstock, the processing production and storage conditions.

2.1.2 Ceramic balls used as TESM and their properties

The different ceramic balls were obtained using dune, mining and natural sand, clay and coal bottom ash [38]. Table 4 illustrates the thermal properties at room temperature of the different ceramic balls.

Table 4
Thermal properties of the ceramic balls [38]

Ceramic balls	$\boldsymbol{\lambda}$ (W.m^{-1}. °C^{-1})	$\boldsymbol{\rho c_p}$ (MJ.m^{-3}°C^{-1})	D (mm^{2}s^{-1})
Sand clay +CBA	0.331-1.014	2.4075-3.426	0.123-0.177

2.1.3 Corrosion test processing on the materials

A stainless-steel rectangular box was used for the corrosion test and experiment. Twelve (12) different pellets developed with dune sand from Burkina Faso and Niger, Mining sand from Burkina Faso and Natural sand from Niger. The mean diameter of each ceramic ball developed is around 2.88 cm with average weight of around 23 g [38]. For the corrosion tests processing:

i. Fifteen (15) waterproof glass containers of 100ml were used as reactors. One sheet of ball was put in a container filled with JCCO and closed with glass cover avoiding any contact between air and oil;
ii. Twelve (12) reactors with balls and three (3) without pellet were prepared and which ad-up to a total of fifteen (15);
iii. For comparative analysis between JCCO and JCRO two additional reactors with ceramic ball were prepared with JCRO.

The fifteen containers were put in stainless steel box and the box is kept in an oven as presented in Figure 1. The objective is to study pellet corrosion maintaining the materials at 210 °C in JCCO oil during 2160h. Every month each type of sample was removed. The ceramic balls were observed, and oil samples analysed. The same method was used for refined oil. The static aging method used in this study (similar to the used in Kenda *et al.,* [8] and Gomna *et al.,* [26]) consists to accelerate the storage materials degradation involve in the storage systems to come out with the best indicators for the storage system maintenance or to choose the material for thermal energy storage or CSP plant.

Fig. 1. Materials corrosion and heat treatment test process.

2.1.4 Measurement and instrumentation

To study the effect of ceramic balls on JCO properties and thermal stability, physical and chemical properties of oil samples were analysed on a bases with eight different evaluations:

i. Index of Acidity (IA);
ii. Oil coloration;
iii. Peroxide value;
iv. Thermal conductivity;
v. Kinematic viscosity;
vi. Density;
vii. Flash point; and;
viii. Thermal stability.

For chemical analysis, two evaluations that are described below were conducted:

i. The Index of Acidity has been assessed using potentiometric titration according to the ASTM D974 standard method. This consists of to measure the need of potassium hydroxide (in mg) mass to neutralize the free fatty acid that are contained in a gram of oil. As oil acid value increase with time and temperature, tracking the acidity during aging time because an elevate acid value can affect the TES vessel (tank and pipe) due to corrosion [52].

ii. The peroxide value (PV) of sample was assessed by the potentiometric titration method according to the NFT 60–220 standard methods. This parameter, which increases with oil oxidation could eventually increase acid value.

Thermal properties of the different oil samples were investigated thanks to the use of different instruments. Main information is given hereunder:

i. Density has been assessed at room temperature by using an analytical balance of 0.1mg of accuracy and a flask of 10ml. The density has been computed as follows:

$$\rho = \frac{m}{v} \tag{3}$$

With m oil sample mass in g, v the flask volume in ml or cm^3 and ρ the density in g.cm^{-3}.

ii. Flash point was measured with an open-cup Seta flash 3'Plus'model 33000–0 analyser from STANHOPE-SETA according to the ASTM D93A standard method. The flash point is a key parameter to check whether to replace the oil or not. It provides information on thermal stability of oil.

iii. The thermal conductivity has been measured by using a KD2PRO at room temperature [53]. The small single needle KS-1 sensor (6 cm long, 1.3 mm diameter) was used to measure the thermal conductivity as recommended for liquid samples and insulating materials by the constructor. Before starting any measurement, the device was calibrated using the calibration oil (glycerin). Measure the oil thermal conductivity of oil with aging time will provide information on the vulnerability of oil thermal properties to heat treatment being in contact with the ceramic balls.

iv. The kinematic viscosity was measured at 40°C and 100°C with a viscometer. The kinematic viscosity was then predicted at any temperature ranging from 40°C to 210°C using the power function correlation given in (4):

$$\upsilon = AT^B \tag{4}$$

With T temperature in °C, A and B constants determine with data obtained at 40°C and 100°C.

v. To confirm the thermal stability of the different samples, after the measurement of the flash point, 7 samples were chosen for thermogravimetric analysis (TGA) according to the facilities available in the ground. The reference oil, three sample aged alone and three put in contact with the pellet developed with dune sand from Burkina Faso. Thermogravimetric analysis and differential thermal analysis of oil samples was investigated by thermogravimetric analyzer (SETSYS Evolution 1750, Setaram Instrumentation) under inert environment. The samples were analyzed under nitrogen (50 ml min−1) using aluminum pans with heating rate of 10°C per min in the 24–1000°C temperature range.

3. Results

3.1 Effect of Ceramic Ball on JCCO Chemical Properties

3.1.1 Acid value results of JACCO

Potentiometric titration analysis enables to assess the acid index with uncertainties of 5.03%. The Figure 2 presents the different results of acid value. An increase of the acid value is observed with aging time for oils in contact or not with ceramic balls. The total acid value increases respectively 54.38%, 39.68%, 41.72%, 40.73%, 40.42% for the oil aged alone, the one put in contact with dune and mining sand from Burkina and dune and natural sand from Niger after the third month compared to the reference oil (CO0). The acid value of oil put in contact with ceramic ball is less than the one aged alone. The results obtained should be the consequence of the combined action of peroxide thermal decomposition, hydrolysis reactions and thermal oxidation as mentioned also in Gomna *et al.,* [7] and Yaakob *et al.,* [52]. The peroxide degradation during heat treatment is illustrated in Table 5. It is observed that, the decomposition rate is different from a sample to another. The highest rate of degradation is obtained with the oil aged alone and the lowest with the oil in contact with ceramic developed with dune sand from Burkina Faso (CODB2). The ceramic balls reduce the destruction of peroxide. As the ceramic is porous, air in the pores of ceramic could contribute more to the oxidation of oils. The difference in porosity of the specimens could explain the difference in peroxide decomposition of oil in contact of ceramic balls because more the ceramic is porous, more it will contain air [38]. This confirms that peroxides were producing during heat treatment, but the degradation was more important.

However, these actions on JCOO under heat treatment could be low in presence of ceramic balls. Compare to the results found by Hoffmann [47]. Acid value increase quickly with the other vegetable oils in contact with filler material than refine jatropha curcas oil [45,47]. It was even decreasing. In the present study a slight increase has been observed with JCCO.

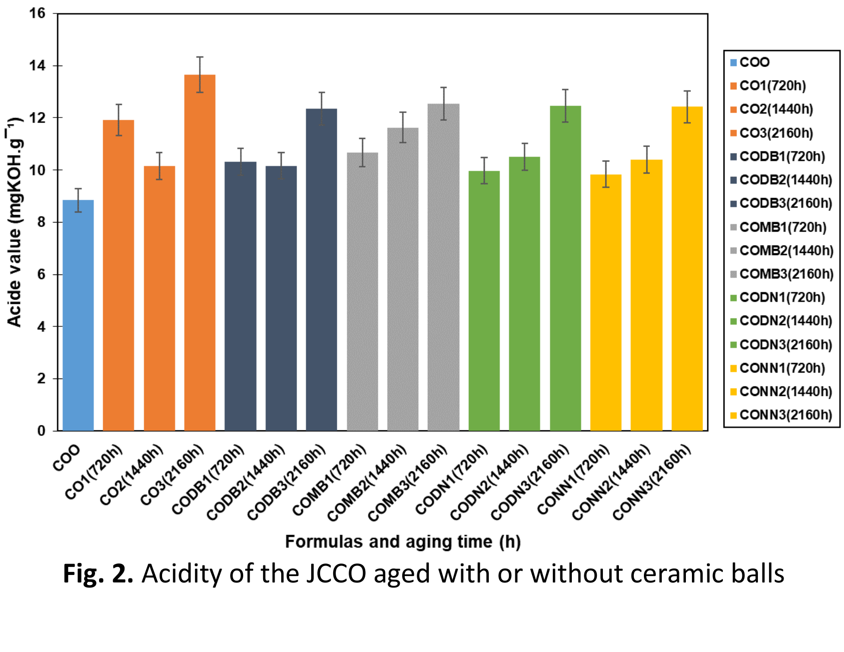

Fig. 2. Acidity of the JCCO aged with or without ceramic balls

Table 5
Effect of heat treatment on peroxide degradation

Aged Oil and aging time(h)	Peroxide value (mgE.O_2/g $\pm 5\%$)
COO	27.60
CO1(720h)	8.436
CO2 (1440h)	2.591
CODB1(720h)	13.177
CODB2(1440h)	6.677
COMB1(720h)	9.705
COMB2(1440h)	3.635
CODN1(720h)	13.115
CODN2(1440h)	3.024
CONN1(720h)	9.255
CONN2(1440h)	3.687

3.1.2 Oil sample and solid materials analysis

The different oils samples and ceramic balls were photographed and present in Figure 3. Regarding the oil samples, there is colour degradation turning to black after the third month. This colour change may be explained by the long-time heat treatment at 210 °C driving to the decomposition of peroxide (Table 5). The residues resulting from these decompositions have settled to the bottom of class centenaries and could they be polymers. However, the change in colour should not affect the HTF quality [46,54]. It can be concluded that the PV and the colour could not be an indicator for the compatibility analysis between both oil and ceramic ball.

For the ceramic balls, there structure did not change anymore after the three months according to macroscopically observation as illustrated in Figure 3. Also, the balls have not softened or crushed. This well holding of the ceramic can be explained by their porosity, oil leaked into the pellets, but this did not seem to affect them [14]. Apart from oil residues, there were not production of any other fine particles of material from ceramic pellets.

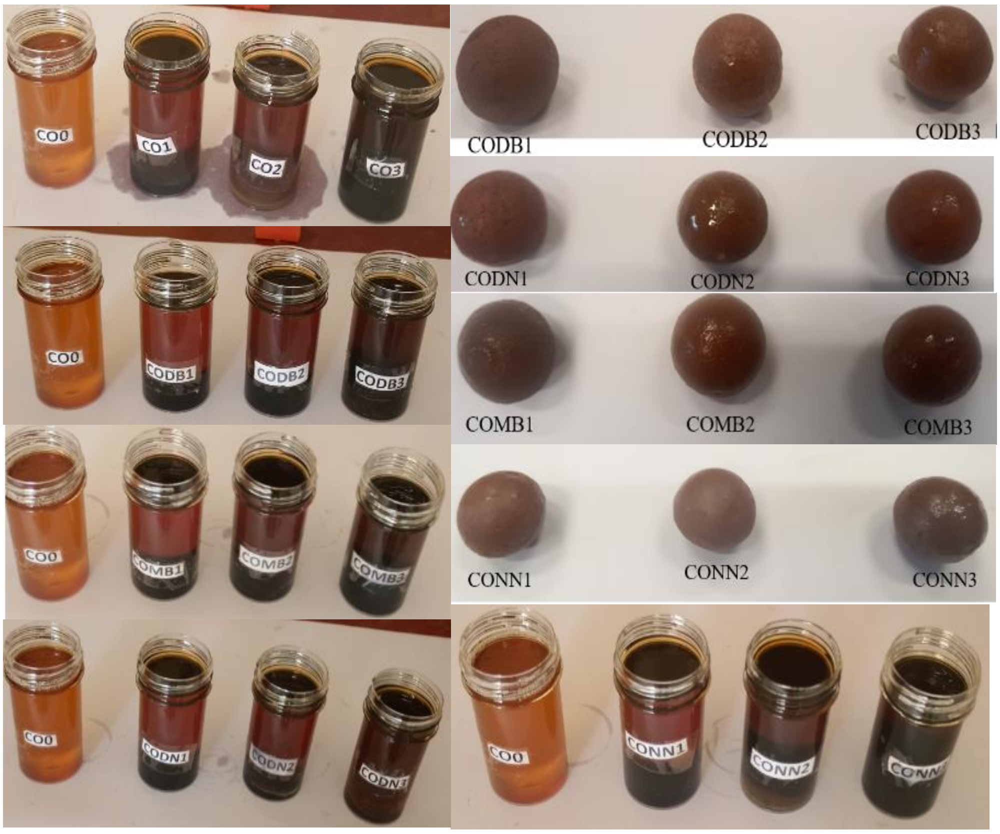

Fig. 3. Oil and ceramic balls before or after heat treatment with different sample comparison

3.2 Thermal Properties Result of JCCO
3.2.1 Density

Density influences heat transfer and energy storage capacity of the oil. A decrease of density is prejudicial to the plant performance. The density of the different aging oils measured at room temperature is plotted and presented in Figure 4. The density values of the different samples measured range from 901.23 $kg.m^{-3}$ to 905.4 $kg.m^{-3}$. The density variation is low and shows a slightly lower density of 0.3%, 0.2% and 0.33% than new oil respectively for the oil aged alone and the one put in contact with Niger dune and natural sand ceramic balls. However, after 740 hours a slightly higher density of 0.17% and 0.14% than the one-month aged oil was observed for the oil put in contact respectively with Burkina dune and mining sand ceramic balls after decreasing of 0.23% and 0.022% respectively. Therefore, from the second month the dune and mining sand ceramic balls could release deposited solid particles in the fluid. However, taking into count the measuring error (2.25%) and the accuracy of the device (10%), no sensible modification of density with ageing or contact with TESM at 210 °C and for 2160 hours could be confirmed.

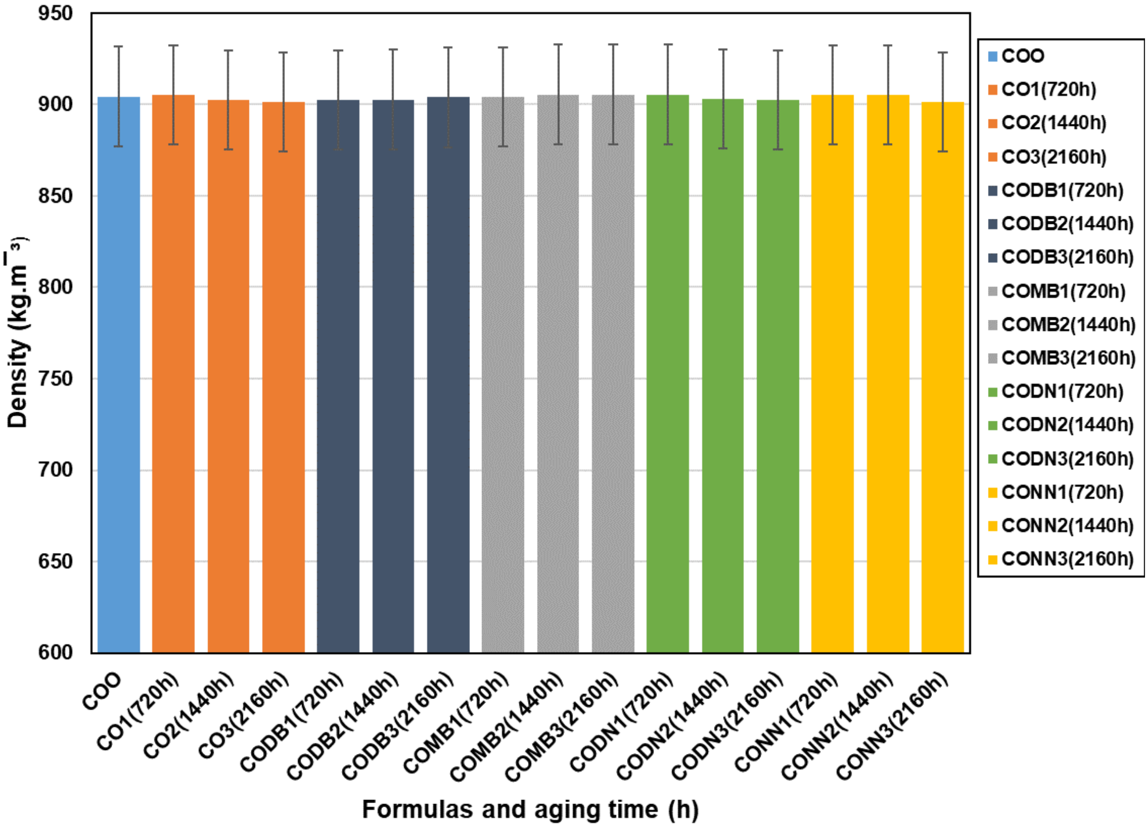

Fig. 4. Density of JCOO aged with or without ceramic balls

3.2.2 Thermal conductivity

Thermal conductivity acts in heat transfer of oil with its environment. Higher is the thermal conductivity, better is the heat transfers. Figure 5 presents the evolution with aging time of the thermal conductivity of the JCCO samples that have been aged with or without ceramic balls. A slight increase of the JCCO thermal conductivity is observed with the oil samples aged alone and the one put in contact with balls. JCCO sees its thermal conductivity increase to 0.8% and 3.125%, 1.875% respectively for the one aged alone and the one put in contact with mining sand and natural sand ceramic balls after 2160h. The inverse is observed with decreasing of 1.25% for the JCCO put in contact with Niger sand ceramic ball. Considering the measuring error (1%) and the accuracy of the device (10%), the oil deterioration does not significantly affect oil thermal conductivity in contact with the ceramic balls TESM at 210 °C and for 2160 hours.

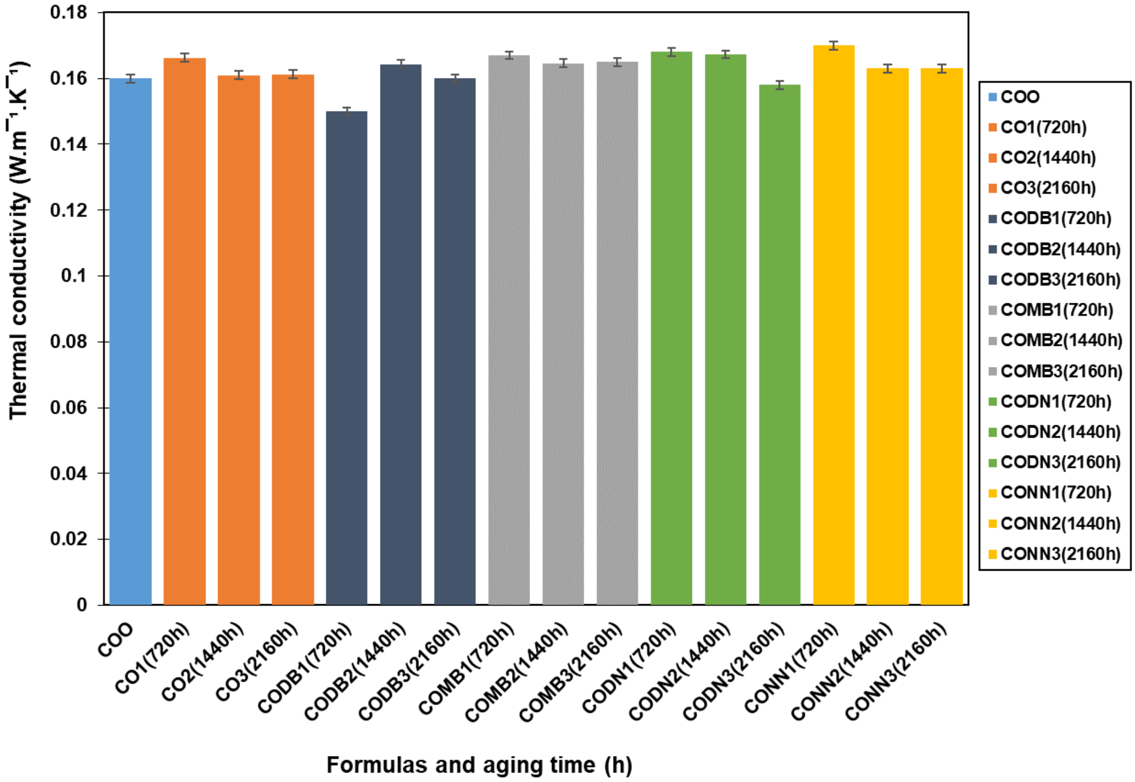

Fig. 5. Thermal conductivity of JCCO aged with or without ceramic balls

3.2.3 Kinematic viscosity

Table 6 illustrates the kinematic viscosity results of JCCO of the different oil samples at 40°C and 100°C. As this parameter depend on temperature, the constant A and B were computed and used to predict the kinematic viscosity based on Eq. (4). The profiles of the overall oil samples as a function of temperature are presented in Figure 6. The viscosity remained stable after 2160 hours of thermal treatment at 210 °C. After three months, the maximal kinematic viscosity is 2.83mm^2/s which is closed to the one of reference oil (mm^2/s) at the working temperature (210°C). However, an increase of 54.4% ,50.8%, 48.35%, 47%, 47, 34% respectively for the oil aged alone or aged with Burkina dune and mining sand ceramic balls, Niger dune and natural sand ceramic balls was observed. The viscosity of the oil aged alone is higher than the one put in contact with filler materials (ceramic balls) after 2160 hours. This increase is the consequence of vegetable oil polymerization by thermal oxidation due to peroxide degradation leading to polymeric material (faster peroxide degradation for the oil age alone than the one in contact with oil, illustration in Table 5) [7]. The presence of ceramic ball mitigates the increase of the viscosity making it more stable than the viscosity of the one aged alone.

Table 6
Kinematic viscosity if the different JCCO and the constant A and B values to predict kinematic viscosity

Oil samples	40°C	100°C	constant B	constant A
CO0(reference oil)	33.94	7.574	-1.63689632	14227.15123
CO1(720)	44.44	8.898	-1.75524359	28825.68116
CO2 (1440)	42.23	8.778	-1.71439285	23560.32479
CO3(2160h)	52.4	10.34	-1.77114825	36042.67618
CODB1(720h)	45.28	9.009	-1.76214961	30128.38191
CODB2(1440h)	46.75	8.898	-1.81054731	37186.64769
CODB3(2160h)	51.18	10.34	-1.74543833	32018.22055
COMB1(720h)	41.39	8.135	-1.7754884	28929.06228
COMB2(1440h)	44.61	8.824	-1.76852467	30388.89062
COMB3(2160)	50.35	9.783	-1.78802685	36857.49026
CODN1(720h)	40.89	8.41	-1.72594135	23805.57581
CODN2(1440)	43.82	8.896	-1.74015576	26884.76831
CODN3(2160h)	49.89	9.966	-1.7577841	32665.48332
CONN1(720h)	39	7.983	-1.73116164	23146.71732
CONN2(1440h)	44.24	8.775	-1.76551233	29803.81036
CONN3(2160h)	50.01	9.97	-1.75996804	33008.91383

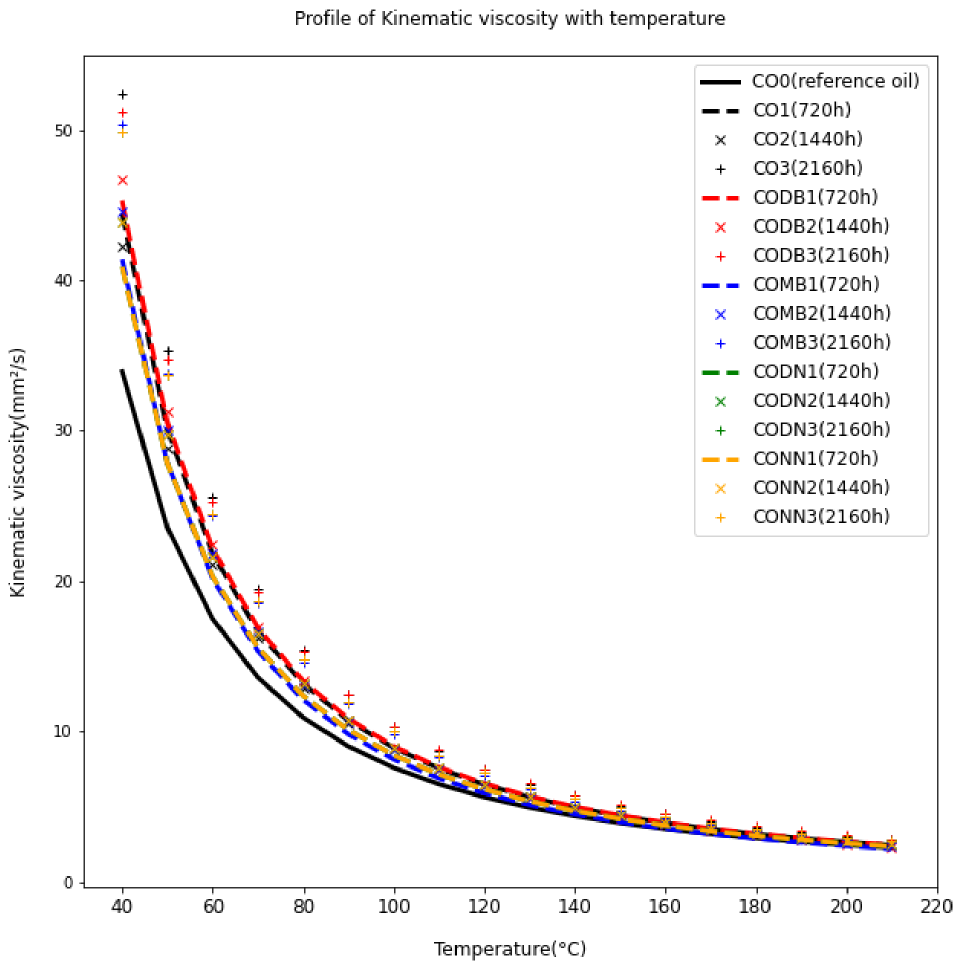

Fig. 6. Kinematic viscosity of the oil aged with or without ceramic balls

Regarding the flash point results of JCCO, after the 2160h of heat treatment the oil aged with or without ceramic balls remain stable and higher than 220°C, highlighting that there is no degradation at this temperature level. Using the same method (static method) of heat treatment, similar results was found in Kenda *et al.,* [8]. To confirm the stability of all oil samples, the oil aged when in contact with Burkina dune sand ceramic, which had the highest kinematic viscosity after three months thermogravimetric analysis (TGA) was conducted.

3.3 Static Thermal Stability Analysis of JCCO Aged Alone or with TESM

The thermal stability temperature explains the sample mass loss with temperature. A material with high thermal stability shows a high resistance to thermal decomposition as show in this work. Figure 7 and Figure 8 show the non-isothermal thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis of JCCO aged with or without TESM under nitrogen (N2) environment up to 500°C. A significant degradation peak is observed between 421.36°C and 427.61°C on the DTG curve (Figure 7) depending on the oil. In the same range of temperature, the TGA (Figure 8) curve shows a mass loss of around 70% for the overall sample. This can be attributed to the thermal decomposition fatty acid (up to 90%) in JCCO which could occurred from 280°C [55]. However, the curves show a thermal stability of JCCO up to a temperature of 287.1 °C, 263.41°C and 261.93°C respectively for the reference oil and the one aged with or without ceramic ball for three months. After three months CO3 has a thermal stability temperature of 261.93 °C against 263.41°C for CODB3 at 3% of oil mass loss. As demonstrated previously the ceramic ball mitigates the degradation of JCCO thermal stability. As the ceramic ball is made from sand, this ball could release some fine particle in the oil which could improve the thermal stability of JCCO as demonstrated in AlQaydi *et al.,* [56] where 2wt% of sand increases the thermal stability temperature of molten salt from 682 °C to 694 °C.

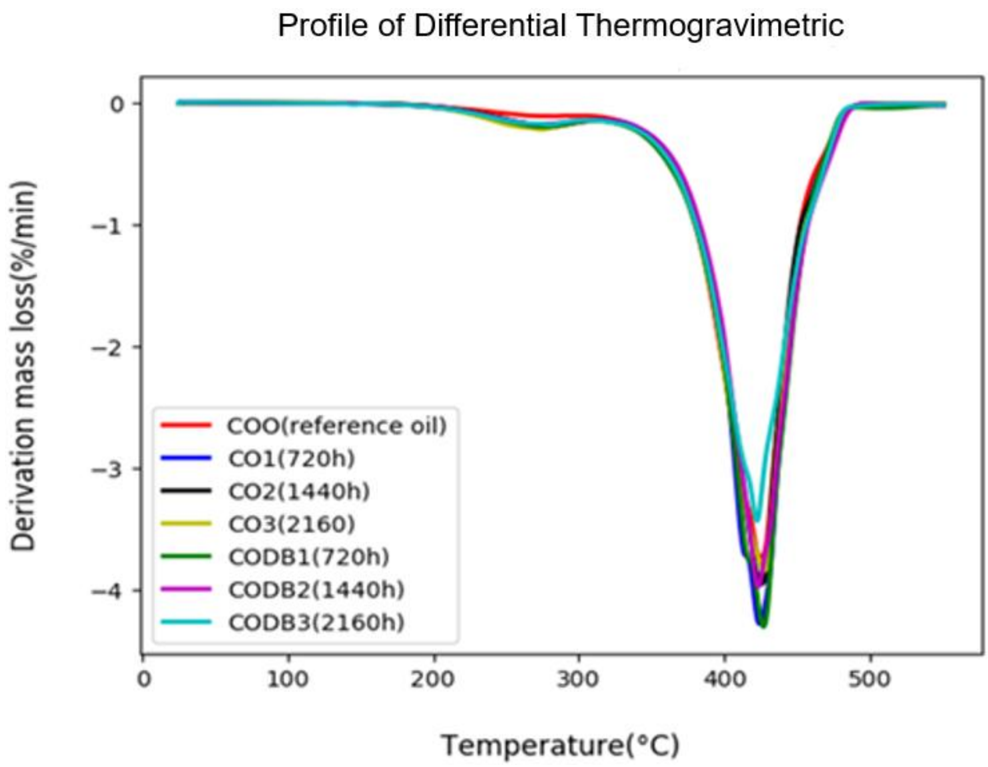

Fig. 7. DTA profile of the different JCCO aged with or without Ceramic balls

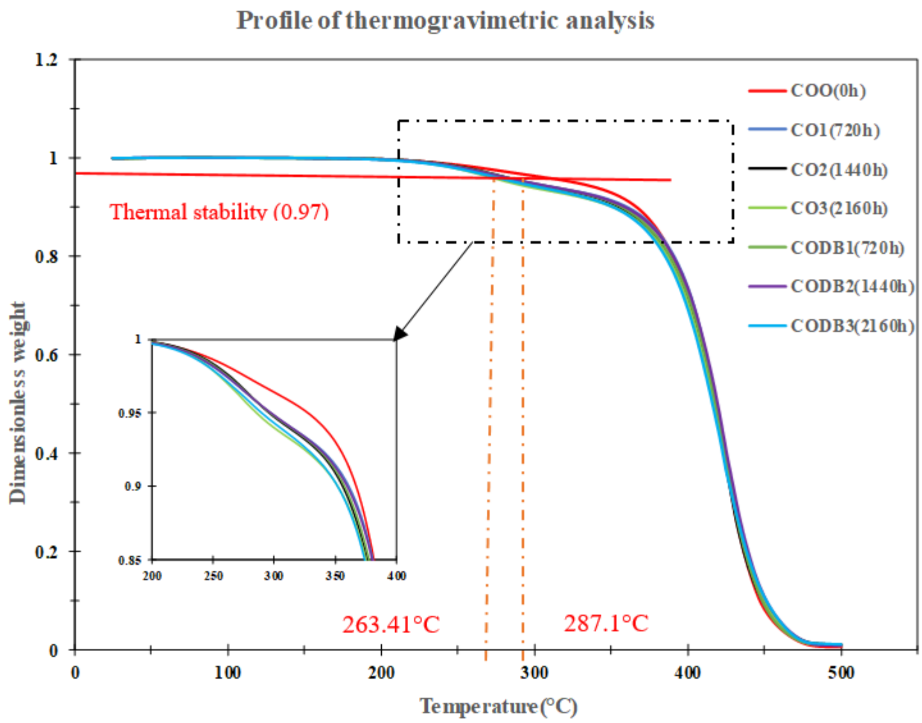

Fig. 8. TGA profile of the different JCCO aged with or without Ceramic balls

3.4 Comparative Thermal Stability Study of Jatropha Curcas Crude Oil (JCCO) and Jatropha Curcas Refine Oil (JCRO) In Contact with the Ceramic Balls.

Figure 9 illustrates the profile of TGA and DTG of JCCO and JCRO in contact with ceramic balls for 2 months (1440h). The results show that for the new oils the JCCO has thermal stability temperature of 281.1°C against 261.1°C for JCRO. The low thermal stability of refine oil is explained by the refined process. During the refined process vegetal oil is put under heat treatment. To eliminate the free fatty acid the first process after extraction is the degumming process, which consists of to remove the phosphorus-based compounds, mainly lecithin and cephalin from the fresh oil before converting it into biodiesel. The removed substance is called “gums.”. Throughout this process the oil is heated to 55-60 °C after adding a de-ionized water. The second step is neutralization process, which consists of two mix the degummed oil with potassium hydroxide (KOH) aqueous solution to eliminate the free fatty acid. After neutralization the neutralized oil is washed with the de-ionized water. To separate oil and water, decantation can be used at small scall, otherwise centrifuge is requested. The last step of oil refining is to remove waxes to avoid cloud forming. During this process 5% of NaOH and 5% of deionized water have to be mixed with the neutralized oil and placed in a chiller setting at 5ºC during 4 hours [57]. All these processes have low effect on thermophysical properties but could impact highly the melting point as discussed in Onyema and Ibe [58]. As the melting point decreasing during refining process, it may also decrease the thermal stability temperature as observed in this study. In contact with ceramic ball a continuous decreasing has been observed with JCCO during the two months (Figure 11), while for the JCRO the thermal stability temperature become better than the reference oil after being dropped to 253.45°C, it has increase to 262.39°C. Similar behaviour was observed in contact with quarzitic in Hoffmann *et al.,* [45]. As observed for JCCO, JCRO could be more mitigated by the ceramic balls. After 720h in contact with ceramic a drop of 18°C and 7.65 °C of the thermal stability is observed respectively for the JCCO and JCRO. And depend highly on the oils acid value as illustrated by Eq. (6), Figure 10 and Figure 11. The increasing of JCRO thermal stability temperature is a result of the decreasing of its acidity (Figure 10 and Figure 11) after the second month. Thus, higher is the acidy low is the thermal stability and vis versa. The thermal stability as function of acid index can be written as follows:

$$T_{stability} = 1.918AI^2 - 18AI + 302.58 \quad (6)$$

However, after 1440 h the drop of thermal stability temperature was very low for JCCO, but always higher than the one of JCRO even if its thermal stability temperature has increased to 262.39°C.

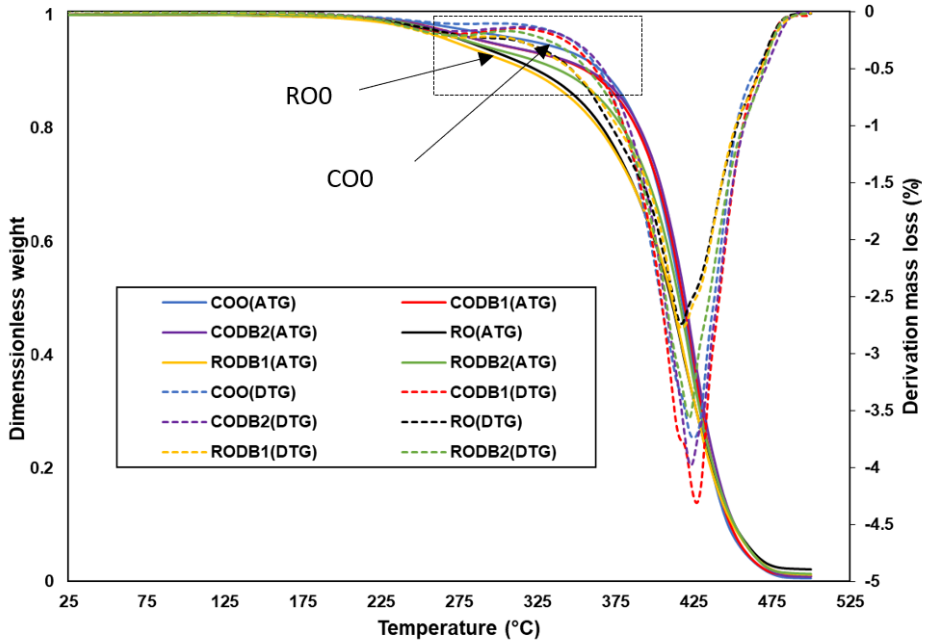

Fig. 9. ATG and DTG profile of JCCO and JCRO in contact with ceramic ball during 1440h

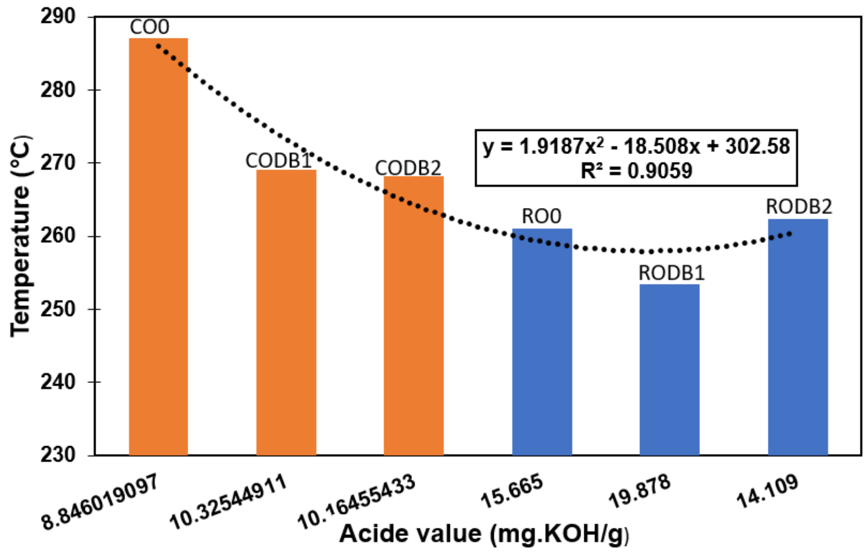

Fig. 10. Thermal stability temperature (°C) of JCCO and JCRO under heat treatment in contact with ceramic balls

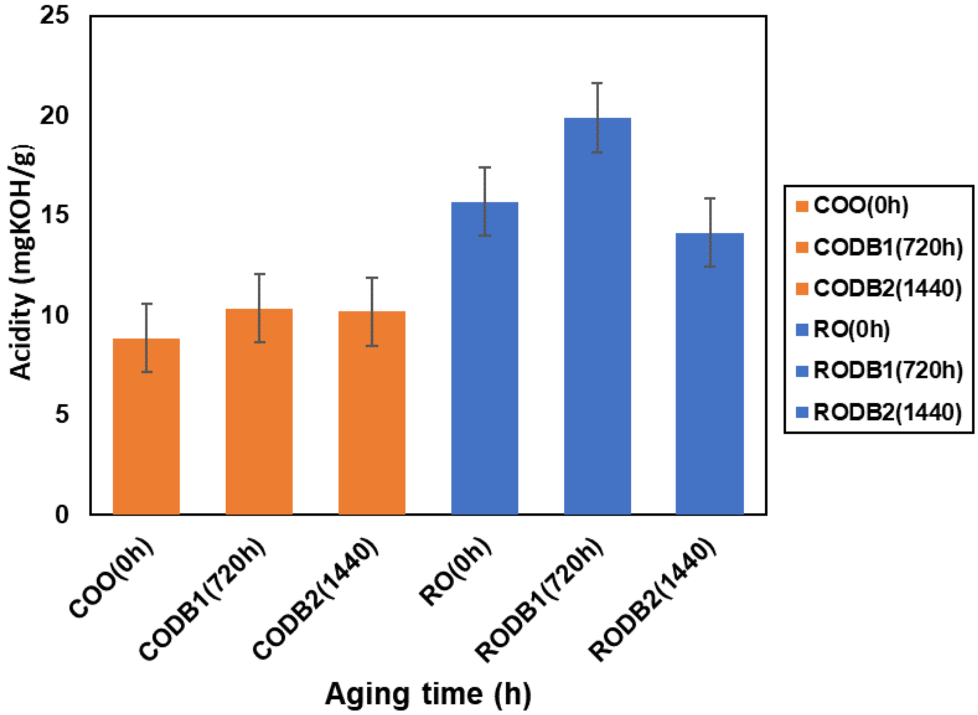

Fig. 11. Effect of heat treatment on JaCCO and JCRO in contact with ceramic balls

This study showed that JCCO have better thermal stability and cost effectiveness than JCRO. However, the refining process provides a clean oil which could reduce the corrosion effect on filler material as illustrated on Figure 12.

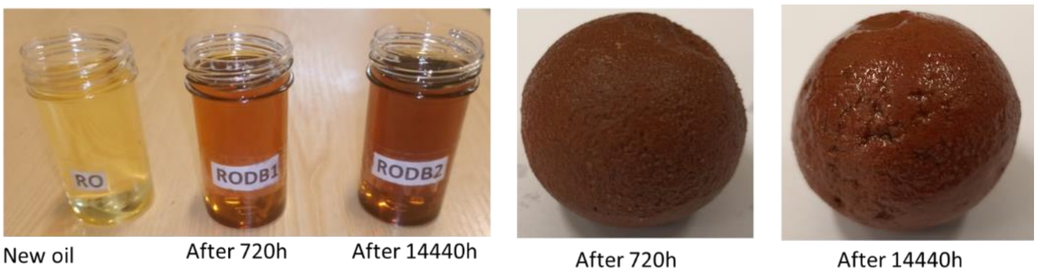

Fig. 12. Aspect of JCRO and ceramic ball before or after heat treatment

4. Conclusion

The present study evaluates the behaviour of several JCCO samples with temperature and put in contact with potential solid filler materials [38]. Jatropha curcas crude oil could age up during a period of 2160 hours and at 210 °C when in contact with ceramic balls made with clay coal bottom ash and various sand. The study is based on local materials and waste valorisation approach for clean energy production. From these studies three conclusion can be drawn regarding the ceramic balls effect on JCCO:

i. The thermal properties (density, thermal conductivity, and Kinematic viscosity) of the oil are not significantly modified by ageing and contact with solid materials.
ii. The oil flash point remains higher than 220 °C. but thermal stability drops with ageing time (less with filler materials contact). In addition, no solid has been crushed for the testing period.

iii. Deterioration rate of oil can be assessed by measuring the index of acidity. From this measurement the thermal stability of the aged oil can be estimated. Therefore, index of acid can be the best indicator to evaluate the quality of the heat transfer fluid when using it as HTF in CSP as well as in thermal energy storage systems. Measurement of the index of acidity informs the possible partial replacement of the oil to avoid any risk of fire, because oil with index of acidity higher than 25 mg $KOH.g^{-1}$ have to be avoided [19]. In this work, during the studying period the maximum acid value was 13.657 mg $KOH.g^{-1}$ and 12.355mg $KOH.g^{-1}$ respectively for the oils aged alone and the one in contact with the filler material. Compared to the limit value, there is no risk to continue using the oil after 6 years. In a nutshell, the couple JCCO-ceramic ball has a potential to be used for sensible heat storage in CSP plant.
iv. The comparative study between JCCO and JCRO in contact with ceramic balls show that JCCO have better thermal stability than JCRO. But the JCRO can be more stable and mitigate in contact with ceramic balls compare to JCCO. In term of cost effectiveness, the refining process cost increase the jatropha curcas oil price making the crude oil cost effective. Therefore, the JCCO needs refinement when it contains sufficient residues, high acid value and moisture. This refinement helps to reduce polymerization of oil which could lead to oil movement in the storage system or plant vessels.

Numerous innovative solutions are available worldwide to provide more efficient, cost-effective, and environmental-friendly thermal energy storage system. This study confirms that natural products and industry wastes could be valuable resource materials that could be applied for sustainable energy systems in realm of waste-to-energy and circularity. This work provides some justification for the utilization of non-edible oil from the abundant bioresources available across different regions of the globe and particularly in West Africa. Non-edible oils also have the advantages of being renewable, liquid, having a higher heat content, having a lower sulphury level, being biodegradable, having a lower aromatic content, and being readily available.

Furthermore, compared to the thermal oils that are frequently used in solar plants, their thermophysical characteristics are comparable, if not superior. Process analysis and intensification would provide more insights into the thermocline units for thermal energy storage application. Especially, unit component designs and material selection (structure and chemical composition analysis of ceramic balls) to have a complete solution that are ready for deployment and industrial implementation. In addition, further performance studies for heating and cooling (that is thermal cycles) behaviour assessment of the complete thermocline could be investigated extensively in future works.

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