

# Progress in Nuclear Energy

## High temperature stability of Terphenyl based thermal oil

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AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE,  
L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

Technology, Facilities and Materials  
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*Head of Advanced Nuclear System Laboratory*

ENEA/FSN FISS SNI

January 14<sup>th</sup>, 2021

Dear Editor,

this is the cover letter accompanying the manuscript “High temperature stability of Terphenyl based thermal oils” that we wish to submit for publication on “Progress in Nuclear Energy”.

The article is concerned with the characterization of a commercial diathermic oil under thermal stress, in order to determine the fluid feasibility in real working operating conditions. In particular, the oil thermophysical features were investigated before and after the thermal treatments, focusing specifically on the chemical stability of the material.

The results showed an increase of the dynamic viscosity, likely due to polymerization phenomena while specific heat was unchanged. The kinetic tests highlighted a first order reaction and the presence of low molecular weight degradation products along with hydrogen and methane.

As a conclusion, the obtained data allow to define a proper working temperatures interval for using this widespread thermal fluid in a safety way.

Moreover, the described experimental procedures represent an innovative approach, especially regarding kinetics tests, suitable for a relative fast evaluation of the operating conditions of thermal oils.

We think that this article can be of interest for Progress in Nuclear Energy, given it is related to cooling systems for nuclear plants, and it might represent a valid contribution for enhancing the knowledge about commercially important thermal fluids and the related analytical techniques.

The presented material has not been published in any other peer reviewed journal and it is not under consideration for publication elsewhere.

With many thanks for your attention and looking forward to hearing from you,

Yours Sincerely

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The present work is concerned with ageing tests on a commercially used thermal oil at temperatures higher than the nominal working ones, including a full post-test characterization.

At this aim, a dedicated experimental set-up was designed and constructed to study the degradation kinetics, and to qualitatively and quantitatively analyze the released gases. As a result, the kinetic parameters were estimated, along with the related changes in the oil thermos-physical properties.

## High temperature stability of Terphenyl based thermal oils

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### Abstract

Thermal oils are nowadays widely used as heat transfer fluids or cooling media in industrial and energy production plants. Currently, very few data are available about their thermal stability in function of the operating temperatures, which is a crucial parameter to estimate oil structural changes and their possible effects the maximum fluids lifetime.

The present work is concerned with ageing tests on a commercially used thermal oil at temperatures higher than the nominal working ones, including a full post-test characterization.

At this aim, a dedicated experimental set-up was designed and constructed to study the degradation kinetics, and to qualitatively and quantitatively analyze the released gases. As a result, the kinetic parameters were estimated, along with the related changes in the oil thermos-physical properties.

### 1. Introduction

Suitable heat transfer fluids are needed for the operation activities of many energy production and industrial plants. The use of thermal oil as cooling fluids started at the end of the 1930s, when organic liquids as heat transfer fluids and moderators in nuclear reactors were at first suggested by Fermi and Szilard in their original patent application for a neutronic reactor in 1944. In particular, they described the use of biphenyl as moderator in a slightly enriched reactor<sup>[1]</sup>. They were selected for their higher heat transfer efficiency and thermal stability plus the possibility to avoid pressurized systems. Since then, significant advancements have been made, and today oils present a lower toxicity and are more thermally stable and able to withstand higher working temperatures at atmospheric pressure than former products. As a result, many companies are investigating the use of these thermal media in heat transfer processes. In particular, sodium cooled (i.e. generation IV nuclear power plants) and liquid lead-bismuth systems need to be equipped with diathermic oils instead of water, mainly to avoid metal-water exothermal reactions, while solar concentrations plants use oils for their higher boiling temperature<sup>[2]-[8]</sup>.

There are several types of heat transfer oils available on the market, such as coolants, chiller fluids, anti-freezes and refrigerants; they are used to provide cooling within machinery, process equipment or combustion engines. Nowadays, they are mainly used in high temperature process applications, in a bulk fluid operating temperature range between approximately 120 °C and 400 °C and, in particular, as heat transfer fluids in solar trough CSP and hybrid nuclear-CSP applications<sup>[9][10]</sup>.

However, one serious drawback to be taken into account is that oils are unstable if temperatures are increased above the rated temperature set-points, causing the oil molecules breakdown and possible oxidation processes.

For these reasons, the diathermic oils need to be characterized against their maximum working temperature, in order to investigate instability effects on their chemical structure and thermophysical features, along with gas formation, amount and nature. These are essential data in order to avoid heat transfer capacity reductions caused by oil degradation and/or circuitry pollution, or any hazards relative to high amounts of reactive gas release.

While these materials were characterized for their stability both under thermal and radiochemical stresses <sup>[11]</sup>  
<sup>[12]</sup><sup>[13]</sup> very few data are present in the scientific literature about only thermal oils stability <sup>[1]</sup><sup>[9]</sup>.

At this purpose, this work is concerned with a preliminary laboratory scale oil stability characterization, with the aim to study the oil behavior under thermal stress. This is a necessary stage to collect data before planning a real cooling loop test.

Therminol 66<sup>®</sup> was selected as cooling material given it presents properties that are feasible for both nuclear (due to its radiochemical inertness) and concentrating solar power applications, and also considering that its chemical structure (aromatic) is representative of many other thermal oils.

## 2. Experimental

### 2.1 Materials

Therminol 66 (Th66), supplied from Tauchemical S.r.l., is a commercial synthetic oil (Table 1), based on terphenyl-derived aromatics, that is, partial hydrogenated terphenyls (74–87%), terphenyl (3–8%) polyphenyls (18%) and quaterphenyl; it shows high-temperature performance and good thermal stability from 0°C to 345°C (boiling point at 359°C) and is pumpable also at low temperatures. Its main characteristics are reported in Table 1<sup>[14]</sup>.

Table 1. Characteristics of Therminol 66 <sup>[14]</sup>

Composition		Hydrogenated terphenyl
Appearance		Clear pale-yellow liquid
Max. bulk temperature		345°C
Max. film temperature		375°C
Kinematic viscosity @ 40°C	DIN 51562 – 1	29.64mm <sup>2</sup> /s (cSt)
Density @ 15°C	DIN 51757	1011 kg/m <sup>3</sup>
Flash point (Closed cup)	DIN EN 22719	170°C
Fire point	ISO 2592	216°C
Auto-ignition temperature	DIN 51794	399°C
Pour point	ISO 3016	-32°C
Boiling point @ 1013mbar		359°C
Coefficient of thermal expansion		0.0009/°C
Moisture content	DIN 51777 - 1	< 150 ppm
Total acidity	DIN 51558 - 1	<0.02 kg KOH/g
Chlorine content	DIN 51577 – 3	< 10ppm
Copper corrosion	EN ISO 2160	<< 1a
Average molecular weight		252

### 2.2 Methods

For all the measurements and the analysis carried out in this work the instrumental precision (Eq.1-3) was calculated as shown below <sup>[15]</sup>, using at least ten independent measurements.

$$X_m = \frac{\sum_{n=1}^{10} X_i}{N} \quad (\text{Eq. 1})$$

$$Err_m = \frac{2 * \sigma}{\sqrt{N}} \quad (\text{Eq. 2})$$

$$Err_{\%} = \frac{Err_m}{X_m} * 100 \quad (\text{Eq. 3})$$

where

$X_m$  = average measured value

$X_i$  = measured values

$N$  = measurements number ( $N \geq 10$ )

$\sigma$  = Standard deviation

$Err_m$  = mean error

$Err\%$  = precision percentage error.

The thermo-gravimetric analysis (TGA) was performed by a Mettler Toledo thermo-balance (TGA/DSC 1), using alumina 70  $\mu$ L crucibles, in a temperature range from 40°C up to 340°C, under 20 ml/min of gas flow (both air and nitrogen) and a temperature rate of 10°C/min. Approximately 20 mg of oil were introduced into a 70  $\mu$ L alumina crucible covered with a lid of the same material. The inaccuracy of the weight data can be considered negligible.

Specific heat was determined by a Mettler Toledo instrument (TGA/DSC), considering a temperature range between 40°C and 160°C under nitrogen atmosphere, in accordance with oil stability as determined by TGA analysis. A DIN 51007<sup>[16]</sup> protocol was employed, where the heat capacity can be evaluated by comparing with a standard of a pure (NIST) sapphire, with an estimated experimental imprecision of around  $\pm 5\%$ , depending on the temperature.

Viscosity measurements were conducted using a TA AR 2000ex Rheometer, equipped with a thermostatic chamber and presenting a rotational type geometry with parallel plates. The method consists in measuring the shear stress as function of a programmed shear rate range (from 100  $s^{-1}$  up to 1000  $s^{-1}$  and back), keeping isothermal conditions at four different temperatures.

Commercial oil 10W40 SAE<sup>[17]</sup> was used as standard material, given its similar viscosity range. The measurements were carried out in air at atmospheric pressure from 40°C up to 100°C according with available standard data. Instrumental precision was around 3%.

Analysis of chemical composition of fresh and aged oil was carried out using an Agilent Gas Chromatograph coupled with a mass spectrometer. The instrument is equipped a capillary column (Alltech Capillary Column Phase: AT-WAX), with a length of 25 meters, external diameter of 0.53mm and film thickness of 1.2 $\mu$ m. A qualitative identification of the species was performed by comparing their MS spectra with the reference patterns present in the NIST library<sup>[18]</sup>.

Each sample (100 ppm) was prepared in cyclohexane, analyzed under 0.7 ml/min of Helium as carrier gas and with a proper temperature program (up to 280°C with a ramp of 10°C/min).

The infra-red spectra were acquired with a Mettler Toledo FTIR probe (React IR 7). FT-IR analysis uses infrared radiation to characterize chemical bonds and identify materials in the wave range of 500 until 4000  $cm^{-1}$ . In this work this analytical technique was used to track the thermal oil behavior by overlapping the spectra obtained from fresh (unheated) and aged (heated) oils

The analysis of the permanent gases produced during the oil stability tests was carried out in real time with an Agilent Micro Gas Chromatograph (Varian Cp 4900 Micro GC)<sup>[19]</sup> placed downstream the experimental set-up shown below (Figure 1). It was equipped with two independent column channels each consisting of an Electronic Gas Control (EGC) injector, a column and a Thermal Conductivity Detector (TCD). The first channel was provided with a molecular sieve capillary column (for low molecular weight species such as hydrogen) while the second one with a *Poraplot* type column (for hydrocarbons, if present). Each GC channel was equipped with a Thermal Conductivity Detector (TCD) that consists of an electrically heated filament in a temperature-controlled cell. The used carrier gas was Argon. An instrumental precision of 0.3 % was estimated on the hydrogen quantification while for accuracy a calibration mixture was used (2% mol hydrogen in Nitrogen metrological mixture ACCREDIA calibrated by an analytical method which provides a percentage error of around 2 %).

### 2.3 Experimental set-up to determine kinetics degradation parameters

A dedicated lab-scale batch with a 1100 ml volume was designed and built up (Figure 1) to evaluate oil stability at high temperatures. At the beginning of the test campaign a fresh oil sample (300 ml) was inserted into the stainless-steel reactor (AISI 304), heated up to a set temperature under nitrogen atmosphere and kept at isothermal conditions for each temperature level. The experimental set-up was kept under nitrogen

pressure to prevent oil evaporation, and the evolution of permanent gases (hydrogen, methane, hydrocarbons) was followed analyzing the tank head space at the end of each test.

To monitor the reaction temperature in real time, two thermocouples were positioned at different heights inside the oil bulk. A tubular furnace with a heating power of 5 kW was regulated by a PID, controlled by a thermocouple positioned on the reactor external side. The wall temperatures reached the set values in around 20 minutes, while the temperature inside the bulk needed around 50-60 minutes to stabilize. Then, the experiments were carried out maintaining the sample at constant temperature for three hours.

At the end of each test, the amount of produced hydrogen was determined discharging the non-condensable gases through a mass flow meter. A downstream, natural convection, air-cooled stainless-steel container collected the reaction condensable products, that were subsequently analyzed by GC-MS.

Hydrogen production can be followed determining its concentration by gas chromatography and calculating the produced moles using the equation below (Eq. 4):

$$n_{H_2} = \frac{\chi_{H_2} * P_{TOT} * V_{hs}}{RT} \quad \text{Eq. 4}$$

where:

$V_{hs}$  = Reactor head space volume [l] (practically constant over the reaction time)

$\chi_{H_2}$  = hydrogen molar fraction, measured by GC analysis

$n_{H_2}$  = moles of hydrogen produced [mol]

$P_{TOT}$  = total reactor pressure [atm]

$R=0.00821$  [atm\*l/mol\*K]

At the end of each analysis the oil sample was cooled down, the gas line purged with Nitrogen and the procedure was then repeated with another test. In particular, four different temperatures were tested with the first oil sample (Test I) and three with the second one (Test II).

Another experimental campaign was performed (Test III) trying the duration of the isothermal tests for 1, 2 and 3 hours, with the same procedures described for Test I and Test II was used.

Finally, a separate experiment was carried out to check the thermo-physical properties of the thermally stressed oil; in this case the sample was kept at 430 °C for three hours and subsequently analyzed as a characteristic example of aged specimen.

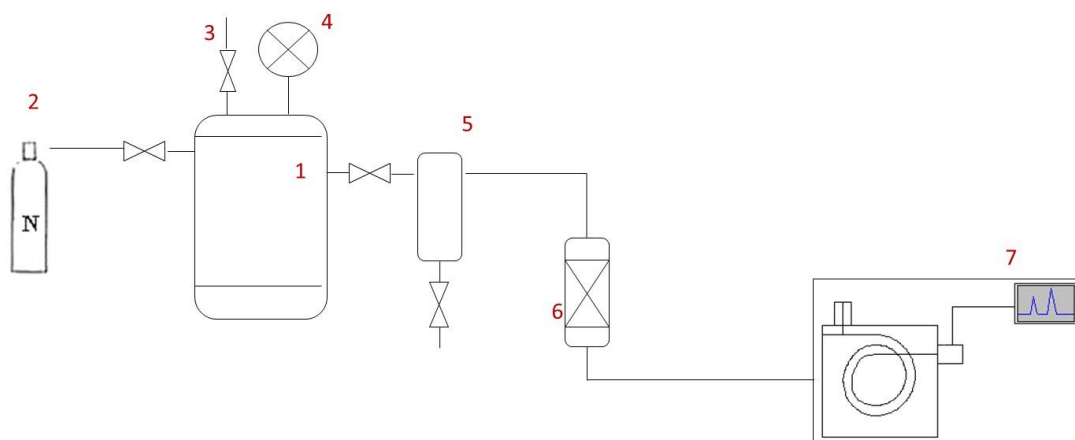


Figure 1 - Schematic representation of the experimental set-up: electrically heated reactor (1), nitrogen tank (2), oil inlet (3), manometer for reactor pressure measurement (4), trap for collecting condensable products (5), silica trap for humidity (6) Micro GC with upstream flow controller (7).



## 4. Results and discussion

### 4.1 Kinetics degradation analysis

To estimate the degradation kinetics rate some assumptions were necessary. Given hydrogen is the main product at the investigated temperatures [1] its formation was used as indicator of oil degradation, considering only qualitatively other possible reactions, such as methane production. According to the scientific literature [1], hydrogen is produced by hydrogenated terphenyl following a first order kinetic law. From the supplier technical data sheet hydrogenated terphenyl represents the 80wt% of the mixture [14], and it can be considered as the less stable component and therefore as the main Hydrogen source.

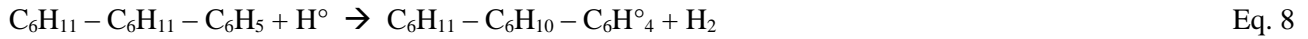
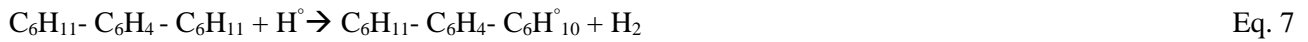
The global equilibrium reaction can be assumed to be:



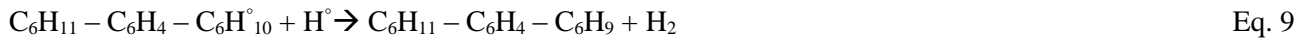
in accordance with the reaction mechanism proposed by Schneider and Morgan [9],[13], where the first step consists of a hydrogen atom elimination from a cyclohexyl ring:



Then, a second hydrogen atom could be extracted from another cyclohexyl or from a benzene ring:



Afterwards, the cyclohexyl ring radical (-C<sub>6</sub>H<sub>10</sub>) may undergo the following reaction (Eq. 8):



Under the above considered hypothesis, the total reaction is expected to be quite endothermic. Considering the reaction stoichiometry (Eq 5), where one mole of hydrogen is formed from one mole of hydrogenated terphenyl, and integrating the mass balance of a batch system, it is possible to assume a first order equation with respect to the hydrogenated terphenyl (HT) concentration. Given the short reaction time it is realistic to suppose that thermodynamic equilibrium was not achieved and, consequently, it is also possible to neglect the effect of the back reaction. According to the manufacturer declared maximum working temperature [14], kinetic tests started from 340°C onward. The obtained results are summarized in Table 2.

Table 2 – Hydrogen concentration for Test I, II and III at different temperatures and isotherm values.

Test I (3 h)		Test II (3 h)		Test III			
Toil	[H <sub>2</sub> ]	Toil	[H <sub>2</sub> ]	Toil	1h - [H <sub>2</sub> ]	2h- [H <sub>2</sub> ]	3h- [H <sub>2</sub> ]
°C	μmol	°C	μmol	°C	μmol	μmol	μmol
339.6	2275	331.5	1140	354	503.8	1453.7	1865.1
360.7	3093	369.5	9196	373	2292.3	2740.1	3467.6
385.4	6666	398.0	41325	388	4890.4	7561.3	7867.7
401.8	43625						

The values of hydrogen production moles, determined after three hours for the three tests, are reported together in Figure 2. The results showed a good agreement between the results of different test series and a clear trend, represented by a regular increase with temperature, from 330 °C to about 390 °C followed by a sharp increment at 400 °C, that can be explained by a change in the degradation mechanism accompanied by methane formation, as illustrated in Figure 3.

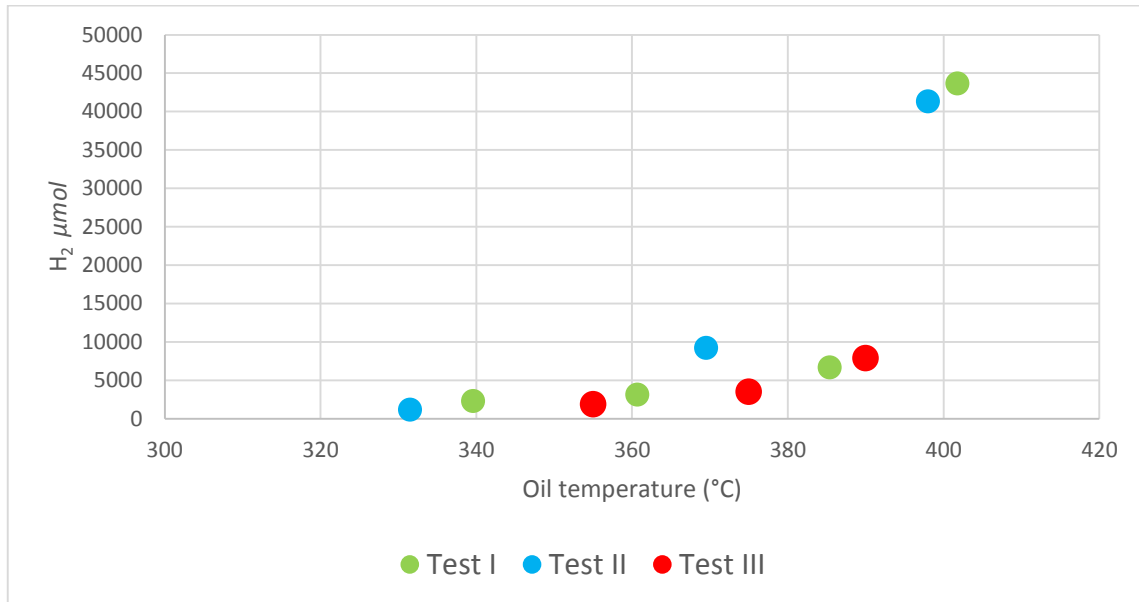


Figure 2. Amount of produced hydrogen in function of reaction time

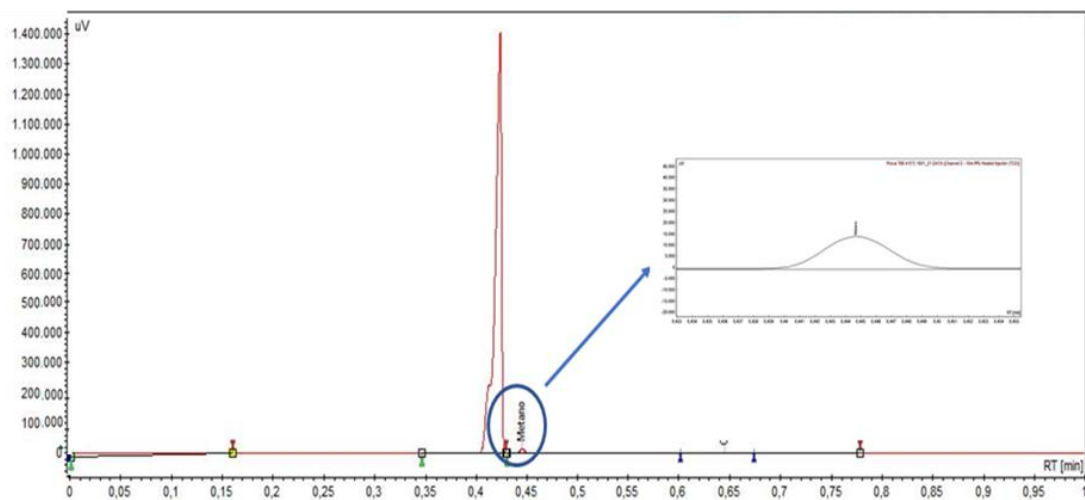


Figure 3. Chromatogram acquired at 402°C; a weak methane peak at 0.42 min is visible in the second column (poraplot).

The analysis of the results obtained in Test III showed that a significant amount of hydrogen is produced during the heating phase, at least when the oil is heated at temperature higher than 350°C. Until about 385°C hydrogen production in function of time is well approximated by a linear trend, leading to a constant formation velocity. Consequently, it is possible to estimate the kinetic constants by dividing the hydrogen production rate with hydrogenated terphenyl moles, which remain practically constant due to the very small degradation extension. The results are shown in Table 3, while in Figure 4 the kinetic parameters are plotted on logarithmic scale against the inverse of reaction temperature and fitted with a least square curve, obtaining a value of 12090K for  $\frac{E_A}{R}$ , that corresponds to an activation energy value of 100 KJ/mol, slightly less than the only currently available literature data<sup>[1]</sup>.

Table 3- Test III: Hydrogen production rate and kinetic parameters

T (°C)	μmol /min	k (min <sup>-1</sup> )
354	10.7	13.6 · 10 <sup>-6</sup>
373	12.1	15.4 · 10 <sup>-6</sup>
388	24.8	31.6 · 10 <sup>-6</sup>

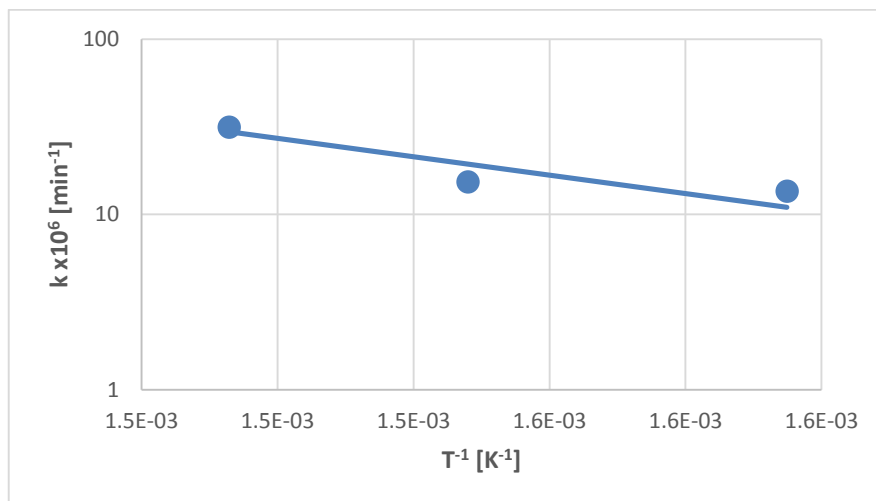


Figure 4. Arrhenius plot of the kinetic constants with the least square curve fitting

#### 4.2 Condensed products analysis

The condensable products formed at high temperature (3 hours at 430°C) were analyzed by gas chromatography with mass spectroscopy detection. Figure 5 and Figure 6 report the chromatograms for the sample diluted in cyclohexane, considering, respectively, low and high molecular weight zone, which corresponds to short and long elution times.

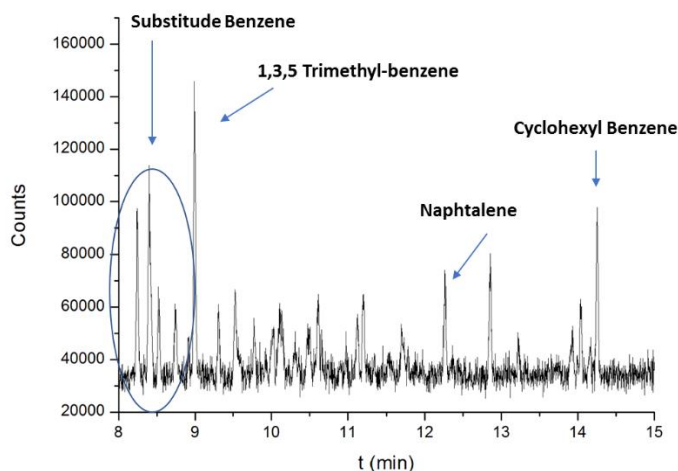


Figure 5. Low molecular weight zone chromatogram; the main identifiable peaks, by comparison with the NIST library, are marked

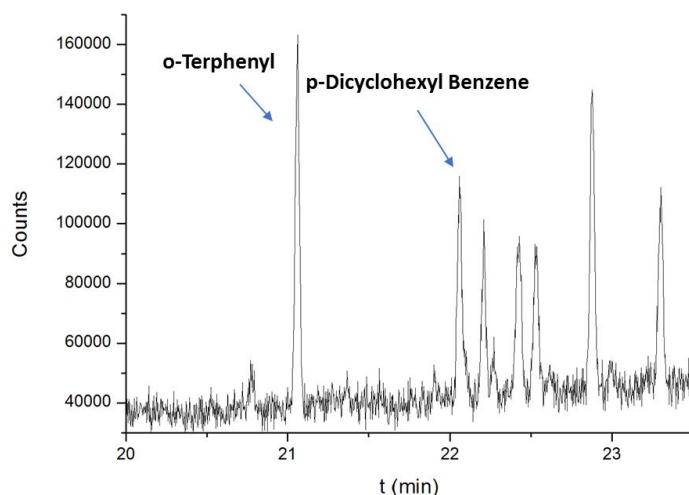


Figure 6. High molecular weight zone chromatogram; the main identifiable peaks, by comparison with the NIST library, are marked

The formation of the detected aromatic and hydrogenated aromatic compounds can be due to the cracking of one terphenyl ring, although no data were found in the scientific literature about this mechanism, and only a generic degradation into “light” molecular weight species is reported [1], [9], [13] (where “light” stands for compounds between diphenyl (excluded) and benzene (included)), especially above 350°C, with a degradation path that could be either parallel or consecutive to the one of hydrogen formation [13].

## 5. Comparison between aged and fresh oil

### 5.1 Preliminary thermogravimetric Analysis (TGA)

Oil thermal stability and volatility were tested by a thermogravimetric analysis. The weight loss was about 3% at around 215 °C both under nitrogen and air, showing oil stability in that temperature range even in presence of oxygen (Figure 7).

At higher temperatures the weight loss is connected with strong evaporation of the sample, and, therefore, this test was propaedeutic to set a proper measurement temperature range for specific heat and viscosity determination.

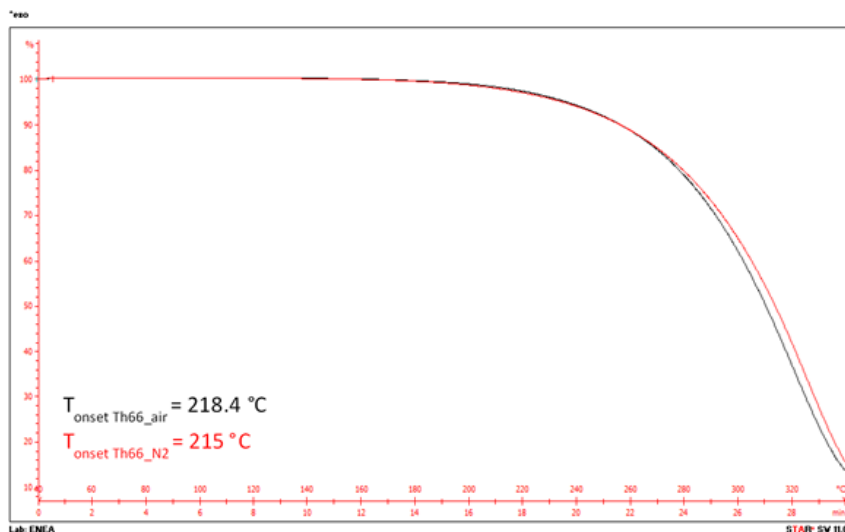


Figure 7. TGA of fresh Therminol 66 both under nitrogen (red) and under air (black). The onset temperatures represent the temperature at which samples lose 3% of their initial weight

The TGA analysis was repeated with the aged sample under nitrogen. As illustrated in Figure 8, the oil volatility decreases for the aged oil and the weight loss onset temperature shifts from 215°C to 222.6 °C, likely pointing out a partial increase in the average oil molecular weight.

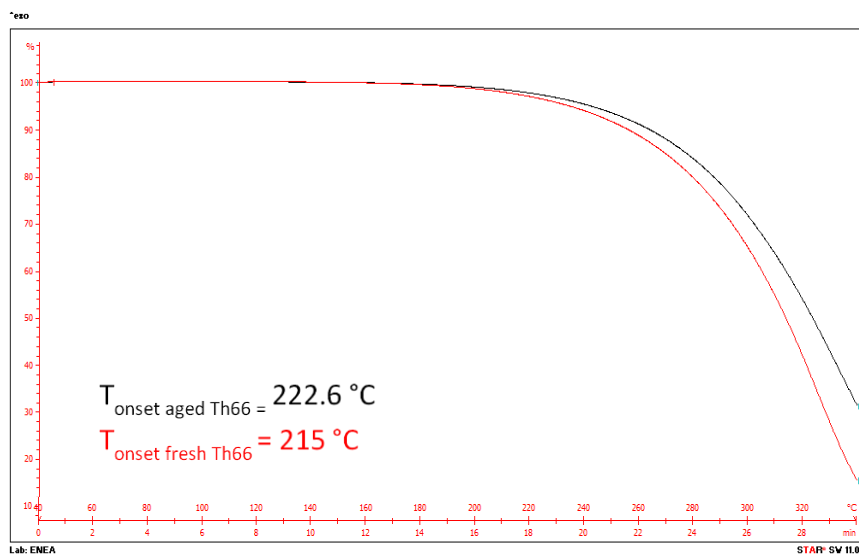


Figure 8. Fresh (red line) and aged (black line) Therminol 66 thermogravimetric curves under nitrogen. The onset temperatures represent the temperature at which samples lose 3% of their initial weight

## 5.2 Infrared spectroscopy

Fourier transformed infrared spectroscopy FT-IR coupled to Attenuated Total Reflectance (ATR) was used in the wave number range between 500 and 4000  $\text{cm}^{-1}$ . In Figure 9 the FT-IR spectra of pure and aged Therminol 66 are shown.

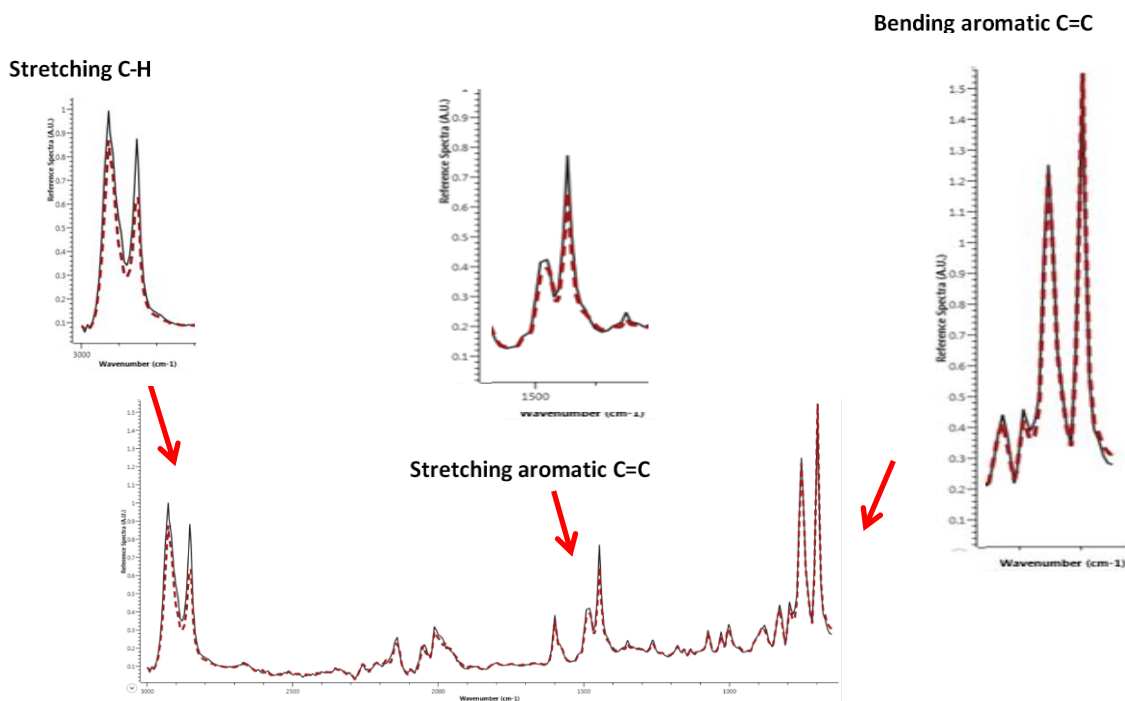


Figure 9. FT-IR Therminol 66. The black line stands for the unheated and the red line for the heated sample

The aged samples needed a previous decantation process in order to let the solid impurities accumulated

during the heating process precipitate. The only detectable difference that can be spotted between the two spectra is in the Stretching C-H zone, confirming both the release of hydrogen and polymerization processes. During these reactions the C-H bonds are broken while the C-C bonds are formed. The used analytical method is more sensitive for C-H bonds than C-C, given a general higher absorption coefficient for the former, and therefore no significant differences were detectable in spectral zones related to the latter chromophore.

### 5.3 Gas chromatography coupled with mass spectrometry (GC-MS)

Acquired chromatograms of fresh and aged Therminol 66 are shown overlaid in Figure 10. The main characteristic peaks of the oil, identified with the NIST library by a match greater than 90%, are marked.

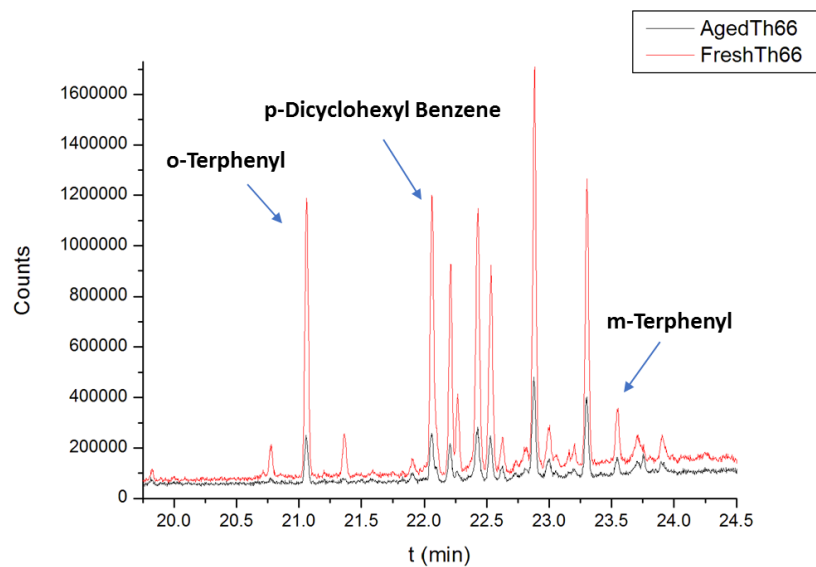


Figure 10. Therminol 66: Overlaid chromatograms for fresh (black) and aged (blue)

### 5.4 Dynamic viscosity

Dynamic viscosity measurements were carried out in air at atmospheric pressure from 40°C up to 100°C, as described above. Figure 11 shows the comparison between fresh and aged Therminol 66 at 40°C and 100°C, where shear stress is plotted versus shear rate. It is possible to note that both samples present a Newtonian behavior, as marked by linear least square fittings passing through the origin.

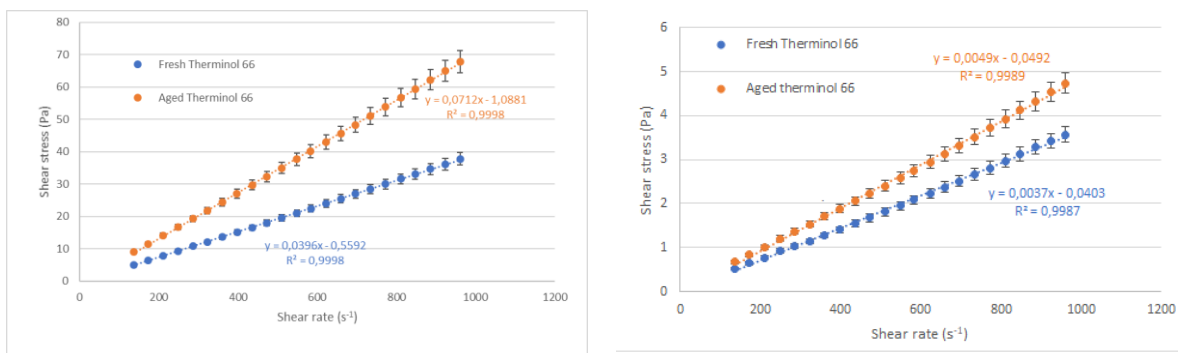


Figure 11. Shear stress Vs Shear rate for fresh (blue) and aged (orange) Therminol 66 at 40°C on the left and at 100 °C on the right

Viscosity as a function of temperature is reported in Table 4 for both aged and fresh oils samples, and the data can be fitted according to the Andrade's viscosity equation [20]. The resulting equations are reported

below (Eq. 10 and 11):

$$\ln \mu_{Fresh} = 16.35 + 3986 * T^{-1} \quad (\text{Eq. 10})$$

$$\ln \mu_{Aged} = 18.08 + 4697 * T^{-1} \quad (\text{Eq. 11})$$

where

$\mu_{Fresh}$  = measured values on the fresh oil (Pa s)

$\mu_{Aged}$  = measured values on the aged oil (Pa s)

T = tested temperatures (K)

Table 4 - Rheometric comparison between aged and fresh T66.

T (°C)	FreshTh66	AgedTh66	Diff %
40	2.94E-02	5.19E-02	76.8
60	1.12E-02	1.66E-02	48.5
80	5.87E-03	7.78E-03	32.5
100	3.80E-03	4.66E-03	22.5

The obtained curves are shown in Figure 12, on a logarithmic scale as a function of the inverse of the temperature. The results demonstrated that during the thermal ageing the oil underwent to a significant viscosity increase, in particular at lower temperatures. Moreover, aged samples presented a markedly higher viscosity dependence from temperature, as illustrated by the coefficients in equations 10 and 11.

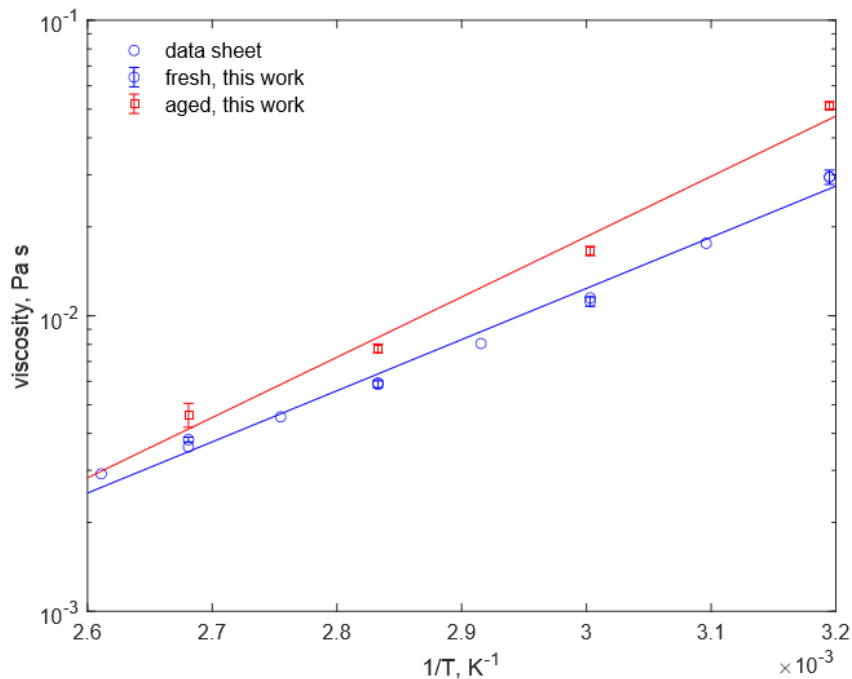
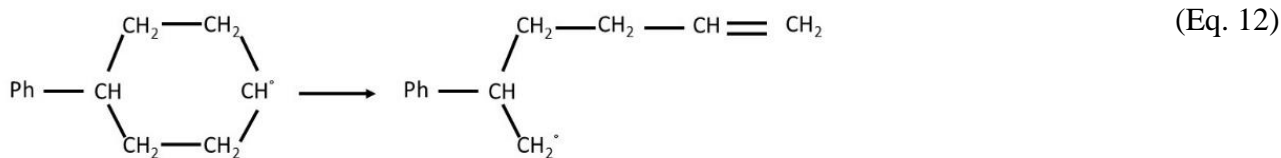


Figure 12. Comparison between the viscosities of fresh and aged Therminol 66. Literature data<sup>[14]</sup> are also reported.

Also considering the thermogravimetric analysis discussed in a previous paragraph, the increase in dynamic viscosity and decrease in volatility of the thermally stressed oil can be explained considering a partial polymerization of the T66 components, actually already reported in the scientific literature <sup>[9], [21]</sup>. In fact, if a hydrogen atom is removed from the second or third aromatic position, the resulting cyclohexyl radical ring (-C6-H10) may open forming a double C-C bond <sup>[9]</sup> (Eq. 12) that can be the precursor of polymerization processes.



The ring opening would leave the double bond at the end of the chain; this could lead to a longer polymeric chain.

### 5.5 Specific heat

Figure 13 compares the specific heat values for fresh and aged oils. According to the results of thermogravimetric analysis, the tests were carried out under nitrogen and up to 160°C.

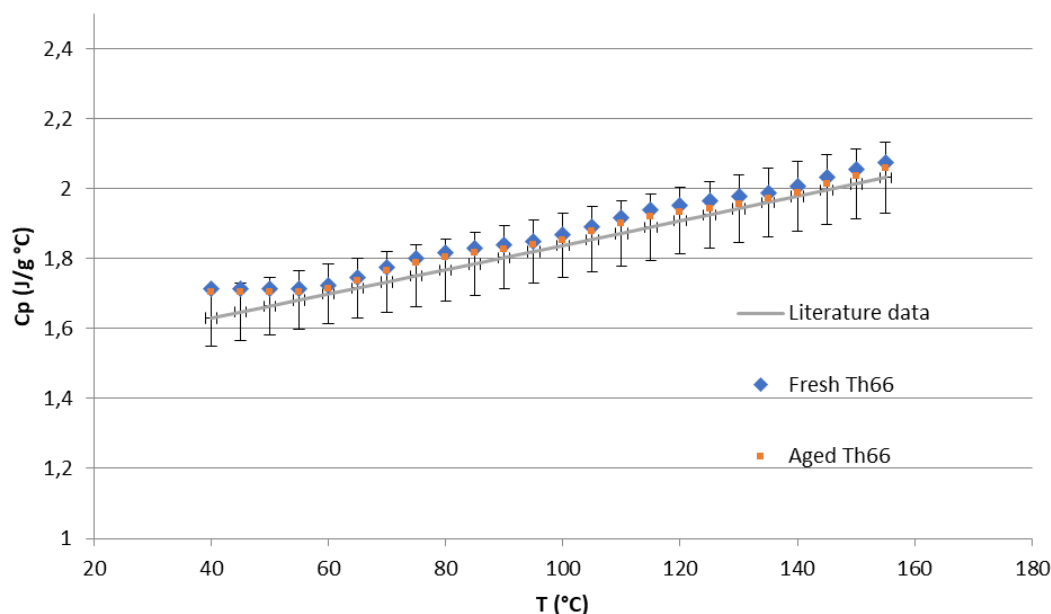


Figure 13. Comparison between fresh, aged and literature data <sup>[14]</sup> for Therminol 66 specific heat

No significant differences can be detected for this parameter. This could mean that the number of C-H bonds broken, and C-C bonds formed is not relevant for significantly changing the vibrational levels distribution.

### 5.5 Final remarks

Overall, it clearly results that polymerization processes are only detectable by viscosity and IR measurements, given their formation do not affect neither the thermal stability properties (TGA) nor the heat capacity (DSC). Moreover, the polymerization products are expectably not volatile and therefore undetectable by GC-MS technique. Nevertheless, the presence of these types of reactions can be positively inferred considering the first above mentioned techniques and the available literature data, and this aspect can be considered as a very unfavorable by products of hydrogen evolution.



## 6. CONCLUSIONS

1  
2 A dedicated experimental campaign was carried out on a widely used thermal oil Therminol 66 under  
3 conditions on which there are very few literature data.  
4

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6 By employing time saving methods, the Arrhenius parameters for hydrogen production (the main oil  
7 decomposition compound) were determined, making it possible to estimate the chemical behavior and the  
8 maximum allowable lifetime of the fluid in contact with hot spots inside a heat exchanger. Overall, it can be  
9 stated that at and above 400°C the thermal oil becomes quite thermally unstable. Actually, also small  
10 quantities of methane are produced above 390°C, probably due to a parallel degradation path; above this  
11 temperature, significant amounts of low molecular weight aromatics are as well produced.  
12

13  
14 The comparison between fresh and thermally stressed oil highlighted a partial polymerization of the  
15 compounds in the aged material, with a significant increase of dynamic viscosity, especially near room  
16 temperature, while oil specific heat and volatility remain practically unmodified.  
17

18  
19 The methodology described in this work can be readily employed to characterize any other kind of  
20 diathermic oil, and, in general, represents a rapid and low-cost criterion for a preliminary screening for heat  
21 exchange fluids, before their performance tests in pilot scale setups.  
22  
23

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24  
25  
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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: