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STUDY OF THERMAL OILS FOR NUCLEAR POWER PLANTS SAFETY SYSTEM APPLICATIONS: THERMAL AGEING AND RADIATION EFFECTS INVESTIGATION

RT/2025/2/ENEA

ENEA
ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES,
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Riassunto

Nel presente rapporto tecnico vengono descritte le attività condotte nell’ambito del progetto ARDECO (ASTRID Research and Development Cooperation). Lo scopo del progetto è stato quello di studiare fluidi di scambio termico per un sistema di mitigazione incidentale per reattori nucleari di IV generazione raffreddati a sodio liquido. Tra diversi tipi di fluidi di scambio termico, gli oli termici rappresentano una valida scelta per diverse ragioni; hanno una buona compatibilità con diversi componenti del sistema, incluso il fluido primario di raffreddamento (sodio liquido), possono essere usati in un ampio range di temperatura e mostrano eccellenti qualità di scambio termico. Per lo studio sono stati selezionati due oli aromatici, commercialmente conosciuti come Therminol 66 e Therminol SP, grazie alla loro stabilità sia allo stress termico che radiolitico. Entrambi sono ampiamente utilizzati sia in campo nucleare che, recentemente, negli impianti solari CSP (Concentrated Solar Power). Per verificarne la stabilità nelle reali condizioni di utilizzo, ne è stato studiato il comportamento in condizioni simulate di invecchiamento termico e radiochimico. Per quanto riguarda i test di invecchiamento termico, ogni campione di olio è stato sottoposto a test di riscaldamento controllato in un range di temperatura superiore a quello di normale utilizzo. Inoltre, per studiare eventuali fenomeni di radiolisi, gli oli sono stati sottoposti a test di invecchiamento nell’impianto di irraggiamento gamma CALLIOPE, dotato di una sorgente di Cobalto 60 (60Co). Gli oli prima e dopo i test di invecchiamento sono stati studiati mediante diverse tecniche analitiche al fine di studiarne gli effetti sulle proprietà chimico-fisiche.

Abstract

The present work describes the activity carried out in the framework of ARDECO (ASTRID Research and Development Cooperation) to study and select suitable Heat Transfer Fluids (HTFs) to be used in safety system heat exchangers for sodium cooled IV generation nuclear power plants. Among several HTFs, thermal oils are a good choice for the under-study application; have good compatibility with other components (such as the primary coolant which is sodium) and can operate in a wide temperature range with remarkable heat transfer properties. Given the studied application, materials with thermal and radiation resistance were selected; two aromatic oils, commercially named Therminol 66 and Therminol SP, widely used for several years both in nuclear and CSP (Concentrating Solar Power plants) were chosen. To study the suitability of selected materials, firstly, extensive thermal ageing laboratory scale tests were performed to undergo oils to controlled heating over working temperature range. Also, radiochemical stability was evaluated; oils samples were tested in the CALLIOPE Gamma Irradiation Facility equipped with a Cobalt 60 (60Co) isotopic source. Different, complementary analytical techniques were used to test oils samples before and after the above reported stress tests; obtained results permit to analyze, separately, thermal and radiochemical effect on the oils chemical structure.

Keywords: *Heat transfer fluids, thermal oils, nuclear power plants, thermal ageing, irradiation tests, chemical-physical characterization.*

Sommario

1. Introduction

Heat transfer fluids are a key component in a wide variety of industrial, civil and technological applications. In the domestic context HTFs are employed in heating and cooling systems such as boilers and heat pumps, while in industry they are indispensable for maintaining temperature control during the production of materials, chemicals and food. In recent years they have found application in data centers and electronic devices cooling systems and to recover the heat waste in cogeneration plants improving the sustainability of the entire process. The selection and appropriate use of these fluids are essential to optimize plant performance, reduce energy consumption and limit environmental impact improving the overall system's energy efficiency.

Heat transfer fluids are also an essential element in the development and implementation of alternative energies. By ensuring efficient heat transfer, they help improve the performance of renewable energy systems, making these technologies more competitive and sustainable. In solar power plants the quality of the fluid is crucial; it must maintain a high thermal capacity to resist freezing in cold weather and tolerate high temperatures without degrading. Efficient heat exchange solutions improve thermal energy storage capacity, making solar thermal a more reliable option, even in regions with variable solar radiation. They also play a critical role both in the operation and safety of nuclear power plants; they are essential for transferring heat generated by nuclear fission into the reactor core to steam generators or turbines and contribute to the reactor's cooling system, ensuring that the core remains at safe operating temperatures to prevent overheating or potential accidents.

Among different kinds of HTFs, thermal oils can operate efficiently at both high and low temperatures without the need for pressurization systems, unlike water or steam. Their excellent heat transfer properties and thermal stability ensure consistent performance even in demanding conditions, while their high boiling points allow for safe operation at elevated temperatures. Additionally, thermal oils are non-corrosive, which extends the lifetime of heat transfer equipment and reduces maintenance costs. These advantages make them an ideal choice for different application areas. Thermal oils are currently largely employed in nuclear and solar power plants. In nuclear power plants they are used in secondary cooling systems to transfer heat from reactors to turbines and to keep the core at a safety temperature. In concentrated solar power (CSP) systems they absorb and transport heat from solar collectors to generate steam for electricity production.

Thermal stability is a critical factor in evaluating the performance of thermal oils as heat transfer fluids. Over time, exposure to high temperatures can cause chemical degradation, leading to a loss of efficiency and the formation of byproducts that may damage the system. Studying thermal stability helps ensure the oil's longevity, safety, and reliability under demanding operating conditions. By understanding how thermal oils behave at elevated temperatures, industries can select the most suitable products, optimize maintenance schedules, and minimize downtime, ultimately improving the efficiency and cost-effectiveness of heat transfer systems.

The present work describes the activity carried out in the ARDECO (ASTRID Research and Development Cooperation) project, a CEA-ENEA joint agreement, with the aim to study thermal oils to be used as coolants for IV generation nuclear power plants safety system.

Although they're largely employed since the 1940s in nuclear applications, very few data are currently available about their stability and possible composition changes under both thermal and radiochemical stress, which are of crucial importance to evaluating the lifetime of these materials in real conditions. Thermal ageing tests were performed with a lab-scale reactor able to undergo oils to controlled heating keeping under control main tests parameters such as pressure, atmosphere (nitrogen or air) and oil temperature. Radiation ageing was performed at the gamma irradiation CALLIOPE Facility (ENEA Casaccia R. C.), a pool type irradiation facility equipped with a ^{60}Co source. Complementary analytical techniques were used to investigate structural and chemical stability under thermal and irradiation stress. Two aromatic based coolants widely used in nuclear and solar applications were selected for the study (Therminol 66 and Therminol SP).

2. Materials

2.1 Therminol 66

The first oil selected for this study is a synthetic oil, based on terphenyl-derived aromatics, commercially marked under Therminol 66. Is a commercial mixture mainly composed of partial hydrogenated terphenyls (74-87%) and terphenyl (3-8%) (Figure 1) with small amount of quaterphenyl and polyphenyls. Different isomers with various degrees of hydrogenation were largely studied as coolant media in nuclear applications since 1950 due to their thermal and radiolytic stability. Nowadays, terphenyl based thermal oils are also employed as heat transfer media in concentrating solar power (CSP). Therminol 66 is synthetic heat transfer fluid that offers high temperature performance from 0°C to 345°C, including excellent thermal stability and low vapor pressure. This oil offers high temperature thermal stability and a wide working temperature range. The technical characteristics of this fluid are shown in Table 1.

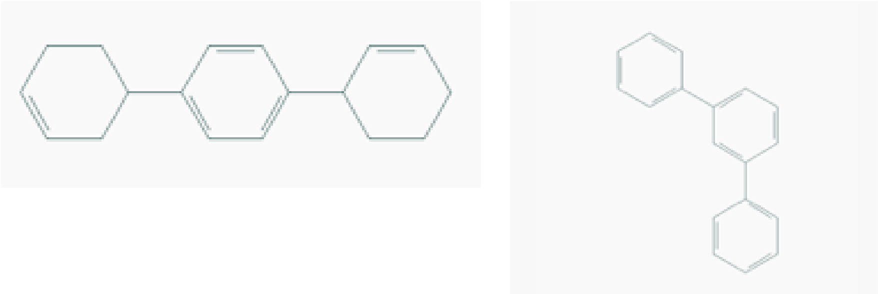

Figure 1. Hydrogenated terphenyls (left) and Terphenyl (1,3-Diphenylbenzene) (right).

Table 1 Characteristics of Therminol 66

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	29.64 mm^2/s (cSt)
Density @ 15°C	DIN 51757	1011 kg/m^3
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

Figure 2 and Figure 3 show, respectively, thermophysical properties and physical-flow characteristics as function of temperature taken from the technical data sheet. Therminol 66 has a freezing point at around 0°C as it is clearly visible in the dynamic viscosity graph (Figure 2).

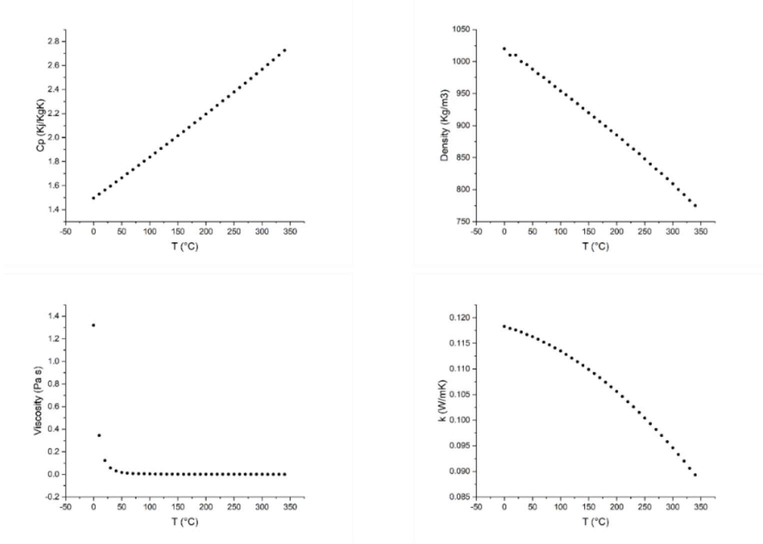

Figure 2. Therminol 66 physical properties from data sheet.

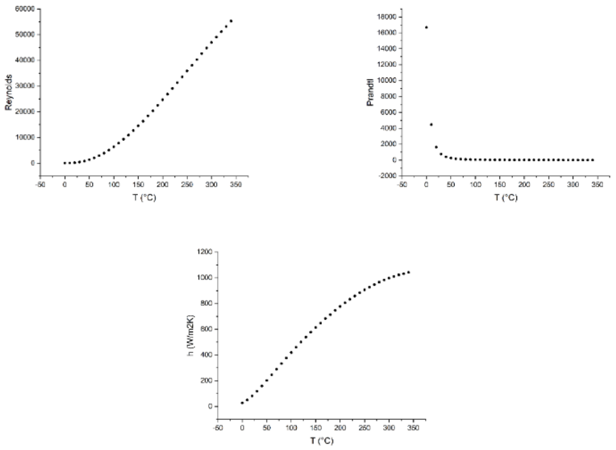

Figure 3. Therminol 66 physical-flow properties from data sheet.

2.2 Therminol SP

The second oil is a commercial mixture of C13-C20 alkyl substituted benzene (Figure 4) commercially known as Therminol SP. This oil was studied as a candidate material to be used as heat transfer media in CSP power plants. Therminol SP is a synthetic heat transfer medium with a recommended working range from -10°C to 315°C, the low freezing point makes this fluid well pumpable also at lower temperature in comparison with other thermal oils. The technical characteristics of this fluid are shown in Table 2 .

Figure 4. C13-C20 alkyl benzene.

Table 2 Characteristics of Therminol SP

Composition		*Mixture of synthetic hydrocarbons*
Appearance		Clear yellow liquid
Max. bulk temperature		315°C
Max. film temperature		335°C
Kinematic viscosity @ 40°C	DIN 51562 – 1	19.0 mm2 /s (cSt)
Density @ 15°C	DIN 51757	875 Kg/m^3
Flash point	DIN EN 22719	166°C
	DIN 51376	177°C
Fire point	ISO 2592	218°C
Auto-ignition temperature	DIN 51794	366°C
Pour point	ISO 3016	-40°C
Boiling point @ 1013mbar		351°C
Coefficient of thermal expansion		0,00096/°C
Moisture content	DIN 51777 – 1	< 150 ppm
Total acidity	DIN 51558 – 1	< 0,2 mg KOH/g
Chlorine content	DIN 51577 – 3	< 10 ppm
Copper corrosion	EN ISO 2160	<< 1 a
Average molecular weight		320

Thermophysical properties and physical-flow characteristics as function of temperature from the technical data sheet are reported in, respectively, Figure 5 and Figure 6.

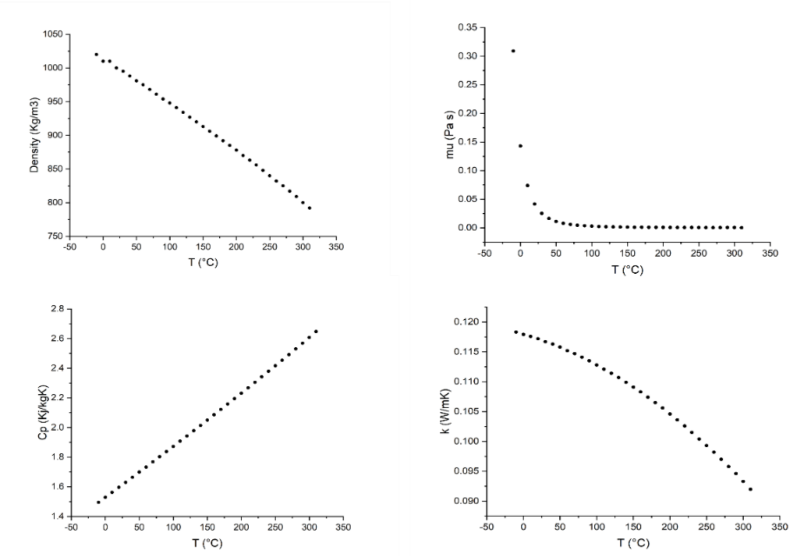

Figure 5. Therminol SP physical characteristics from data sheet.

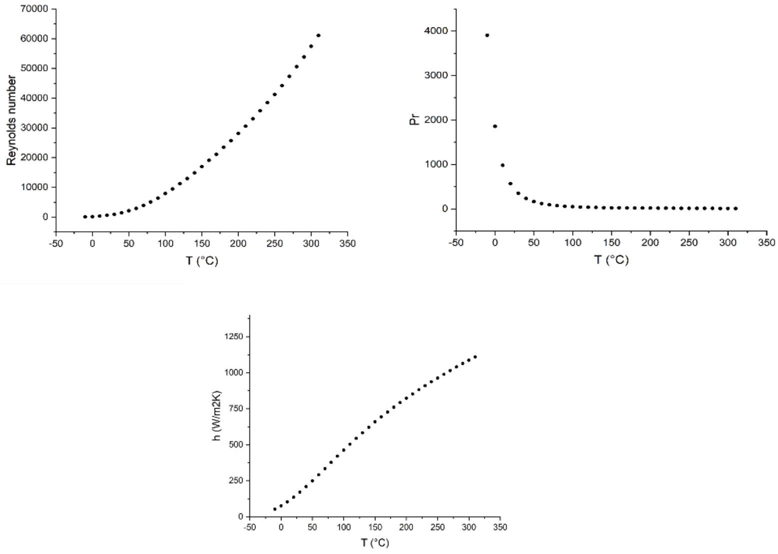

Figure 6. Therminol SP physical-flow characteristics from data sheet.

3. Thermal stability Experimental Set-Up

To study the degradation processes involved in the oils thermal ageing, a batch lab-scale experimental set-up was utilized. A schematic representation of the experimental system is reported in Figure 7. It consists of a stainless-steel reactor with a total volume of around 1.1 l, electrically heated by a tubular furnace with a power of 5 kW, in which the temperature is regulated by a PID (Proportional Integral Derivative) with a thermocouple positioned on the outer surface of the reactor and controlled by two thermocouples positioned at different heights of the reactor. A manometer placed at the top of the reactor measures eventually pressure variation during the tests.

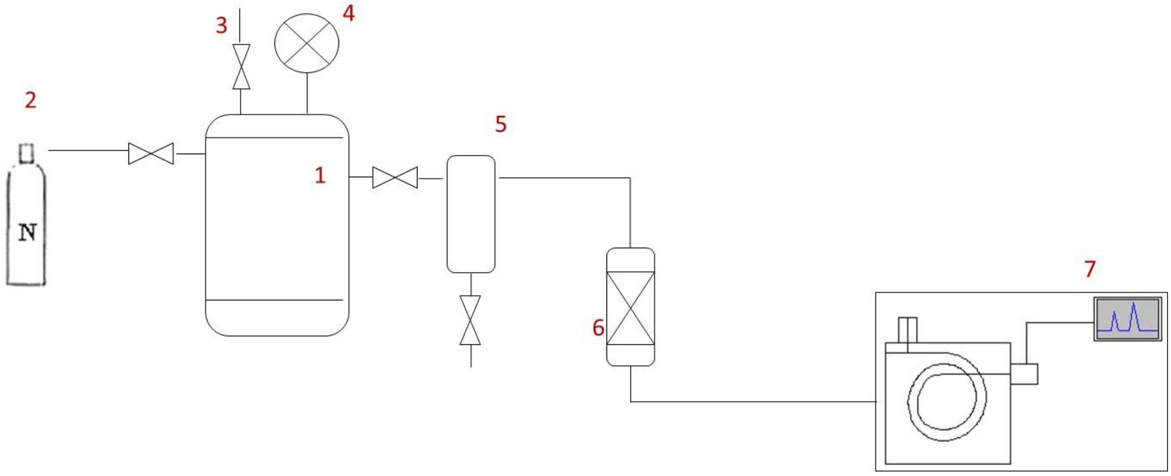

Figure 7. Schematic representation of the experimental set-up. In the picture are reported the electrically heated reactor (1), nitrogen tank (2), oil inlet (3), manometer for the pressure measurement (4), condensation trap for the condensable products collection (5), silica trap (6) and the Micro GC with flow controller (7).

With the described experimental system, the oils samples (300 ml) were undergoing to a controlled heating under nitrogen atmosphere; each oil sample was kept under isothermal condition for a set time (1-3 hours), and then the main decomposition products analyzed. The more thermally stressed oil sample was taken as reference of "aged material" and compared with fresh (unheated) oils samples.

To collect and analyze the degradation products in gaseous and vapor phase, downstream the reactor are placed; a mass flowmeter and a micro-GC, able to detect and quantify online the permanent gases produced in the reactor head space, and an air-cooled stainless-steel container, to collect the reaction products condensable at local conditions to be analyzed offline with a gas chromatograph coupled with mass spectrometry (GC-MS) instrument. The liquid fraction was observed to check eventually solid phase presence and then analyzed to perform a comparison between fresh and thermally aged oils samples. Used Instrument are described in the following sections.

By the knowledge of the thermal degradation compounds together with the oils chemical structure and thermo-physical properties changes with temperature, overall thermal ageing processes can be studied.

4. Instrumental equipment

4.1 Gas Chromatograph– Thermal Conductivity Detector (GC-TCD)

In this work, a Varian Cp 4900 Micro Gas Chromatograph (GC) was used to detect and quantify online the permanent gases produced during the thermal ageing tests; a picture and a schematic representation of the used device are shown in Figure 8. The instrument has two columns working in parallel: a molecular sieve capillary column, for low molecular weight permanent gases identification, and a Poraplot like column that provides the separation of methane from the composite air peak and separate carbon dioxide from methane and C2 hydrocarbons. Each GC channel is equipped with a Thermal Conductivity Detector (TCD) which uses a thermal wire sensor to detect the temperature variation due to the difference in thermal conductivity of the sample. Micro GC is connected to a carrier gas line, the instrument used in this work is configured to use Argon. To quantify the main gases, the instrument was calibrated with a certified gas mixture of Hydrogen (2%), Carbon dioxide (2%) and Methane (2%) diluted in Nitrogen.

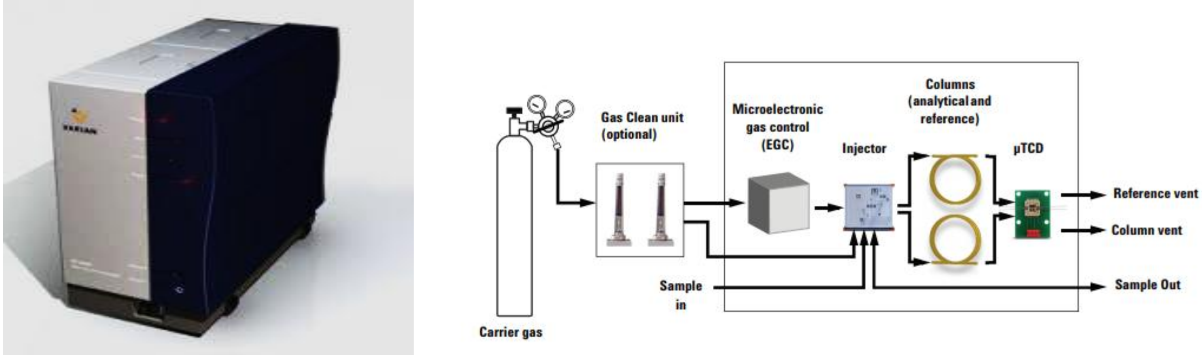

Figure 8. Varian Cp 4900 Micro GC (left) and its schematic representation (right).

4.2 Gas Chromatograph coupled with Mass Spectrometry (GC-MS)

Gas chromatograph coupled to a mass spectrometer (GC-MS), is an analytical technique which allows to separate and identify compounds by complex mixtures of chemicals. The instrument used in this work is an Agilent GC-MS (Figure 9) equipped with a capillary column (Alltech Capillary Column Phase: AT-WAX), with length of 25 meters, external diameter of 0,53mm and film thickness of 1,2µm.

When the sample solution is injected into the GC inlet, it is vaporized and swept into a chromatographic column by the carrier gas (helium). The sample flows through the column and the compounds of interest are separated as a function of their relative interaction with the coating of the column (stationary phase) and the carrier gas (mobile phase). A heated transfer line converts the compounds eluting from the column to ions species; when the resulting peak from this ion is seen in a mass spectrum it gives the molecular weight of the compound. Energy provided to ions are high enough to fragment it and produce smaller ions with characteristic relative abundances which provide a 'fingerprint' for a molecular structure; ions are separated by a mass analyzer (quadrupoles) in function of their mass to charge ratio and then they enter a detector the output from which is amplified to boost the signal.

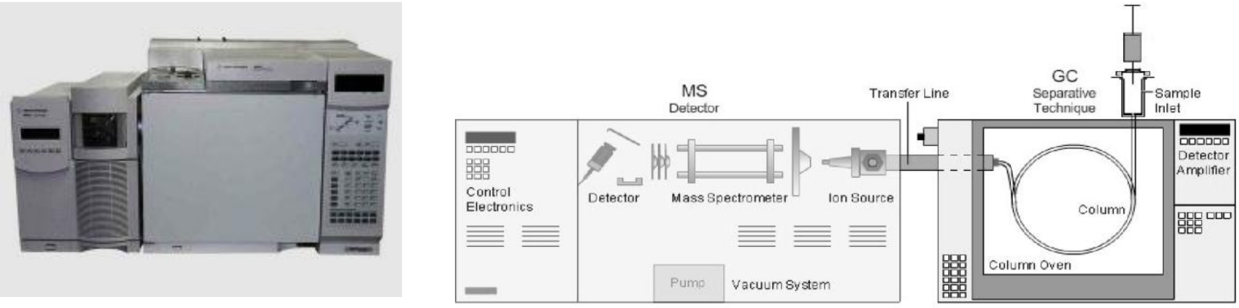

Figure 9. GC-MS used instrument on the left and schematic representation on the right.

The GC-MS instrument was used to compare the fresh and aged oil chemical composition and for the condensable products analysis. Samples (100 ppm) were prepared in cyclohexane and 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). Obtained results were matched with mass spectra enclosure in NIST library to identify the main compounds present in the analyzed samples.

4.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis permits to measure the amount of weight change of a material as a function of time and temperature in a controlled atmosphere. Measurements were carried out using a Mettler Toledo thermogravimetric analyzer (TGA 1, Figure 10) both under nitrogen and air atmosphere. Instrument consists of a precision balance with a sample holder located in a furnace, the oven is able to work with programmable temperature control up to 1100°C. During the analysis the sample weight is constantly measured and recorded. Around 30-40 µl of sample are placed in a 70 µl alumina crucible and positioned into the furnace. In our case, thermogravimetric analysis was performed to evaluate the volatility; the TGA output curves were analyzed considering the onset degradation temperature i.e. the temperature at which the oil loses about 3% of its initial weight.

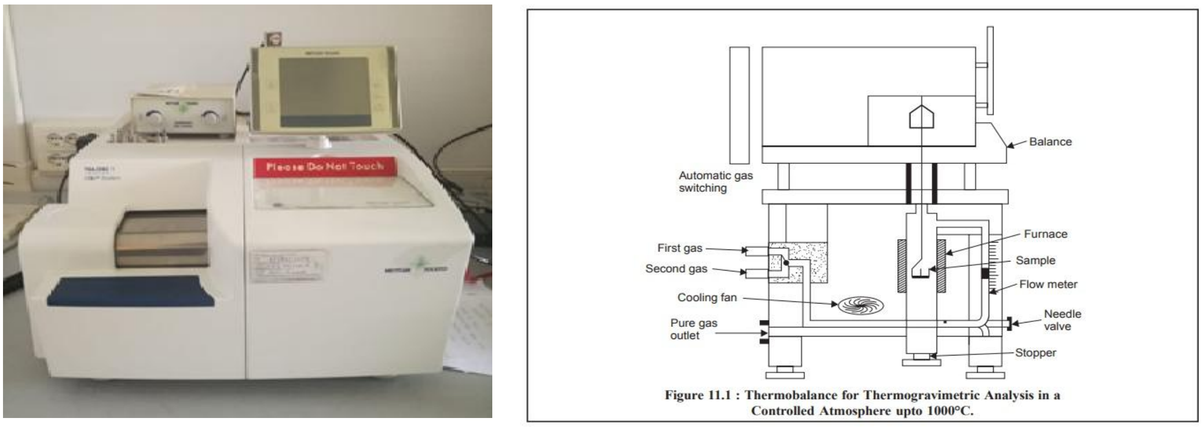

Figure 10. Thermogravimetric balance (left) with the schematic representation (right).

4.4 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) technique is one of the most commonly used techniques for thermal analysis. It permits to obtain information about material behavior, while it is subjected to controlled heating/cooling cycles, by monitoring the difference in thermal flow between the sample and a reference material. This technique can be used to measure specific heat (Cp), alias the heat that must be absorbed by a substance of unit mass, at the temperature, in order to raise its temperature by

1 ° K. Specific heat versus temperature can be measured using as reference pure sapphire (NIST certificated) to compare the DSC curves and calculate the sample specific heat as shown below.

The instrument used in this work is a Mettler Toledo calorimeter (DSC 1), reported in Figure 11. It is equipped with two identical pans; one of the two pans will remain empty because it will serve as a reference for differential measurement. The DSC software allows to set the temperature program and the flow of the carrier gas (N2, air). The heat transferred from the furnace heats both the sample and the reference in the same way; a control circuit compares the mean value between the temperatures detected on the sample and on the reference with the one selected by the temperature controller. Any temperature variation is due to phenomena that arise in the material being analyzed: an exothermic reaction will raise the temperature of the sample while an endothermic will do the opposite. During the experiments a system of 28x2 thermocouples collects the temperature data and sends it to specific software, which generates the DC output. The differential heat flow is directly proportional to the temperature difference between the output signals from the thermocouples.

Figure 11 used instrument, TGA/DSC Mettler Toledo module.

The measurements were carried out according to the DIN 51007 protocol, as a comparison with a substance whose specific heat values are exactly known at each temperature, a sapphire standard was used in this work.

Instrumental precision was evaluated by comparing measured and literature values for fresh oil. To evaluate the instrumental precision ten different measurements were carried out for each sample and error was estimated as shown in the equations below:

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

$$Err_m = \frac{2 * \sigma}{\sqrt{N}} \qquad \text{Eq. 2}$$

$$Err_{\%} = {}^{Err_m}/_{X_m} * 100 \qquad \text{Eq. 3}$$

where

X_m = average measured value [j / g*K]

X_i = measured values [j / g*K]

N = measurements number

σ = Standard deviation

Err_m = mean error

Err % = precision percentage error

Since sample weight needs to remain constant for a proper specific heat evaluation, tested oils specific heat was measured according to volatility as provided by TGA analysis. Therminol 66 specific heat was measured in the temperature range 40-160°C while Therminol SP up to 190°C. Measurements were performed under a constant air and nitrogen flow (20Nml/min).

4.5 Viscosity measurements – Rheometer

Viscosity was determined using a rotational type with parallel plates rheometer (AR2000 ex, Figure 12). The instrument is equipped with an oven and a thermostatic chamber allowing viscosity measurements from room temperature up to 1000°C. The rotating spindle is moved by a motor and angular inclination controlled by an optical reader. During the measurement the sample is positioned inside a stainless-steel plate mounted on a fixed base, another plate transfers to the sample the rotational motion of the spindle. Daily calibration of the instrument must be performed, to set rheometer inertia, rotational mapping and the zero gap (distance equal to zero between the two plates).

Figure 12 AR2000 ex rheometric system used and sample positioning for viscosity measurements.

Temperature, shear rate, shear stress, pressure, time and the history of the sample can influence measurements; to define how the viscosity changes as a function of these parameters, it is necessary that others are kept strictly constant. Both oils tested were analyzed keeping isothermal conditions at four different temperatures from 40°C to 100°C, at each isothermal point shear stress was measured over a programmed shear rate range (from 100 s^{-1} up to 1000 s^{-1} and vice versa).

The instrumental precision was evaluated by comparing measured and literature values for fresh oil. In particular, ten different measurements were carried out for each sample and error was estimated as seen above for the specific heat.

Instrumental accuracy was measured according with 4, using as standard materials Therminol 66 and Therminol SP theoretical data, which are certified by the supplier.

$$Err_{\%} = \frac{(|X_{Th} - X_m|)}{X_{Th}} * 100 \qquad \text{Eq. 4}$$

where

X_m = average measured value [Pa s]

X_{Th} = value from technical data sheet[Pa s]

4.6 Fourier-transform infrared spectroscopy (FT-IR)

Infrared (IR) spectroscopy exploits the interaction of the latter with the light in the infrared region of the electromagnetic spectrum to study and identify chemical substances or functional groups in solid, liquid, or gaseous samples. Molecules absorb specific frequencies that are characteristic of their structure; the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-IR (14000-4000 cm^{-1}), mid-IR (4000-400 cm^{-1}) and far-IR (400-10 cm^{-1}) in relationship of the visible spectrum.

The used instrument is a Perkin Elmer spectrometer (spectrum 100, Figure 13) with an operative wavenumber range of 7800-350 cm-1. The device is equipped with an ATR (attenuated total reflection) module able to perform direct analysis on liquid and solid samples. An infrared beam is passed through a zinc selenide (ZnSe) crystal, the IR radiation travels through the crystal and interacts with the sample on the surface in contact with the ATR crystal. Because of the differences in refractive indices of both materials, total internal reflection occurs. This reflection forms the so-called "evanescent wave" which extends into the sample. Based on the sample's composition, a small part of the infrared light is absorbed when the evanescent wave interacts with the sample, resulting in a slightly attenuated total reflection. Total internal reflection does not explain the interaction of the IR beam and sample because the IR beam never leaves the ATR crystal. Instead, the interaction of the IR beam and sample occurs through an evanescent field, often called "evanescent wave".

Figure 13. Infrared Spectra instrument.

Oil samples were measured in the 4000-500 cm^{-1} wavenumber range, IR analysis was used to track eventually changes in chemical structure due to the ageing tests by overlapping the spectra obtained from fresh and both thermally and irradiated oils.

5. Irradiation facility

Radiochemical stability of tested oil was studied analyzing the effect of gamma radiation on fresh and thermally aged oils samples at CALLIOPE facility. The CALLIOPE irradiation facility, located at ENEA-CASACCIA research center, is a pool type facility equipped with a Cobalt 60 (^{60}Co) source with a mean emitted energy of around 1.25 MeV. The radio-isotopic source consists of 25 ^{60}Co rods placed in a linear rack and stored in a 8 m deep pool (Figure 14).

Figure 14. Pool view of CALLIOPE 60Co rack sources

With an irradiation cell of 7.0 X 6.0 X 3.9 m3, CALLIOPE allows testing materials in a wide range of dose rate by placing samples in specific position with respect to the radiation source. Also, thanks to a steel platform with a proper aperture for the source passage, dose rate value up to 10.8 kGy/h can be reached. Dose rate, together with exposure time, allows to evaluate the sample absorbed dose (energy deposited per unit mass).

Dosimetric systems are used to ensure that the samples are exposed to the desired dose rate value. Different kinds of dosimetry are available depending on the dose range; from mGy of Thermo Luminescent Dosimetry (TLD) to Mgy of Red Perspex. Dosimeters are made by a substance which undergoes to a measurable change when exposed to ionizing radiations; depending on the type of dosimeter used, a suitable measuring instrument will therefore be required to determine the absorbed dose. The CALLIOPE facility laboratory is equipped with several instruments able to measure different kinds of dosimeters and also to perform analysis on materials before and after radiation tests to study the radiation induced damage.

Tested oils were tested under a dose rate of 1 kGy/h for 100 hours with an absorbed dose of 100 kGy, eventually changes in the oils structure were evaluated.

6. Results

Thermal stability tests were performed with the showed experimental set-up. In each test pressure increasing, due to heating and gas evolution processes, was monitored and a maximum-security threshold of 10 bar was considered. Consequently, the experimental conditions for the two oils were set according both the maximum oil operating temperature and volatility. For tested oils, two different independent tests were carried out (Test I and Test II) keeping the oil samples at isothermal conditions for a given reaction time at three different temperatures. At the end of test campaigns, oils were overheated and considered as a benchmark representative of a thermally stressed sample, to be used for confrontations with fresh oil specimens (Figure 15).

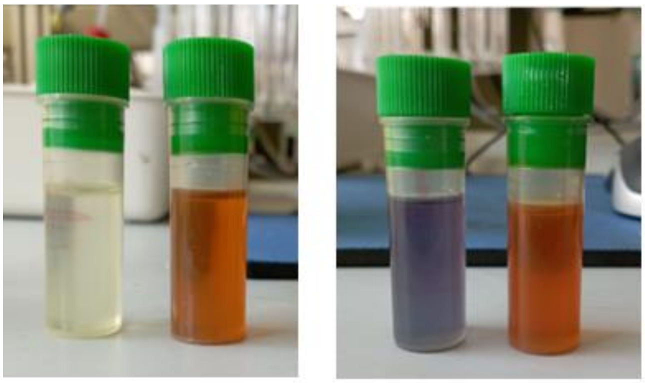

Figure 15. Fresh (left) and thermally aged (right) Therminol 66 on the left and Fresh (left) and thermally aged (right) Therminol SP on the right.

Table 3 reports the tested temperature range for both oils studied together with the amount of condesables collected and quantified permanent gases. According to maximum operating temperature, tests start from 350°C onward for both Therminol 66 and Therminol SP. The upper limit, as discussed above, is mainly due to the pressure values reached inside the reactor during the tests. Given the Therminol SP higher volatility, with a partial pressure of 11 bar reached inside the reactor after 1 hour at 405°C, it was tested for 3 hours at a nominal temperature of 350°C, 2 hours at 375°C and just 1 hour at 390 °C. While Therminol 66 reaction time was 3 hours for each temperature tested.

Table 3. Summary of thermal stability tests

Tested oil	*Temperature range tested*	*Overheating temperature*	*Reaction time*	*Partial pressure reached*	*Amount of condensable production*	*Gaseous products*
	°C	°C	h	bar	ml	
Therminol66	350-415	430	3	9	35	H_2
Therminol SP	350-390	405	3,2,1	12	25	H_2

The obtained GC results allow to quantitatively measure the amount of hydrogen produced during the thermal ageing tests. The hydrogen production (n_{H_2},mol) was calculated by the GC experimental parameters following the equation below (Eq. 5):

$$n_{H_2} = \frac{\chi_{H_2} * P_{TOT} * V_{hs}}{RT}$$ Eq. 5

where:

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

χ_{H_2}= hydrogen molar fraction (measured by GC analysis)

Vhs = Reactor head space volume [l] (constant over the reaction time)

P_{TOT}= total reactor pressure [atm]

R=0.00821 [atm l/mol K-1] (gas constant)

Considering the two performed test series, the results are in good agreement to each other. Table 4 reports the obtained results for Test I and Test II as a function of temperature. Hydrogen production rate rise with temperature and a sharp increase was observed for both oils at the higher temperatures.

Table 4 Hydrogen production obtained with three different tests (Test I, II and III) at different bulk temperatures and setup-operating isotherm periods

Therminol 66				**Therminol SP**			
Test I		Test II		Test I		Test II	
T_{oil}	*H_2*	T_{oil}	*H_2*	T_{oil}	*H_2*	T_{oil}	*H_2*
°C	*µmol*	°C	*µmol*	°C	*µmol*	°C	*µmol*
339.6	2275	331.5	1140	340	755	338.4	918
360.7	3093	369.5	9196	362.4	2749	362.8	3154
401.8	43625	398.0	41325	375.2	5576	372.4	6626

The trapped condensable products were analysed by GC-MS and the experimental results are shown in Figure 16 and Figure 17 for Therminol 66 and Therminol SP respectively. The compounds identify with NIST library are marked; the most intense peaks in the lower molecular weight zone are corresponded to produced degradation products while, at higher elution time, oils characteristic peaks were identified. For both oils under study thermal degradation products in condensable phase are mainly composed by different kind of substitute benzene. Regarding Therminol SP, also decane was detected indicating that the thermal degradation involves alkyl chain fragmentation.

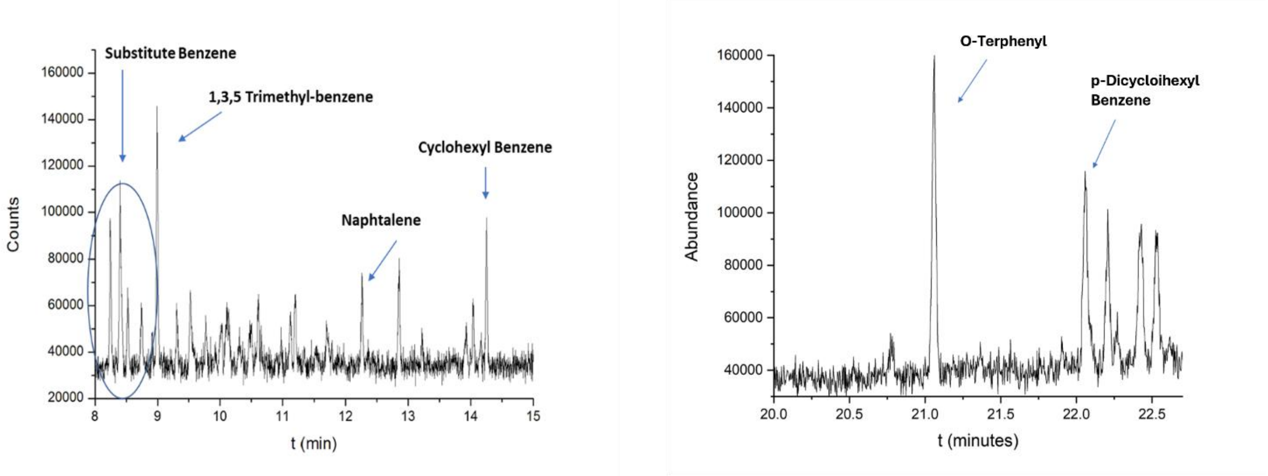

Figure 16 Low (left) and high (right) molecular weight zone chromatogram of Therminol 66 condensable degradation products. Main identifiable peaks, determined by comparison with the NIST library, are marked.

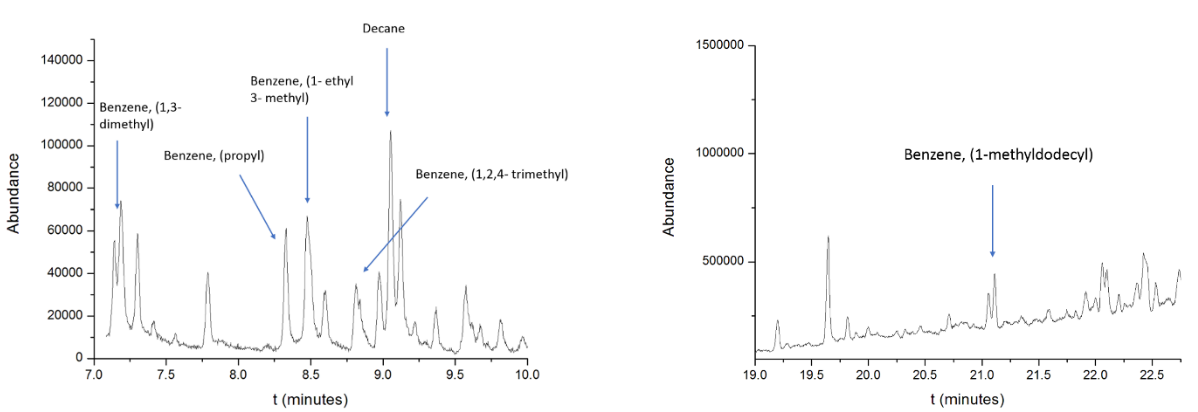

Figure 17 Low (left) and high (right) molecular weight zone chromatogram of Therminol SP condensable degradation products. Main identifiable peaks, determined by comparison with the NIST library, are marked.

The aged samples were used as reference material in order to perform a comparative analysis with fresh oils.

Fresh oils volatility were determined by thermogravimetric analysis up to 350 °C both under nitrogen and air atmosphere and compared with curves acquired on aged samples under nitrogen atmosphere. As onset temperature value was taken the temperature that corresponds to a weight loss of about 3% of the sample initial value. This test was also propaedeutic to set a proper measurements range for specific heat and viscosity determination for which a constant weight is needed. Measured onset temperatures are reported in Table 5.

Therminol 66 presents a weight loss of about 3% at around 215°C, both under nitrogen and air, while oil volatility slightly increases in the heated oil (onset: 222.6°C). The onset for fresh Therminol SP sample was at around 244°C under nitrogen and 231 °C under air, showing some decrease of oil stability in presence of oxygen, on the other hand, a strong increase in volatility was observed in the aged sample.

Table 5. Therminol 66 and Therminol SP onset temperatures for fresh and aged oils samples

Tested oil	*Fresh oil onset temperature (°C)*		*Aged oil onset temperature (°C)*	
	N_2	Air	N_2	Air
Therminol 66	215	218.4	222.6	-
Therminol SP	243.7	231.2	177.2	-

DSC temperature ranges were set in accordance with the TGA results. A DIN 51007 method was utilized, where sapphire is considered as benchmark to ensure measurement accuracy. The method precision was evaluated by a statistical analysis on ten independent measurements, and the result showed a relative error below 5%. Figure 18 report the comparison between fresh and thermally stressed oils long with a confrontation with together literature data. Reported error bars are in agreement with the measured instrumental precision. In both cases, considering the experimental error, specific heat does not change during the ageing process; variation of molecule bonds structure and strength is limited, and does not affect significantly the global heat capacity properties.

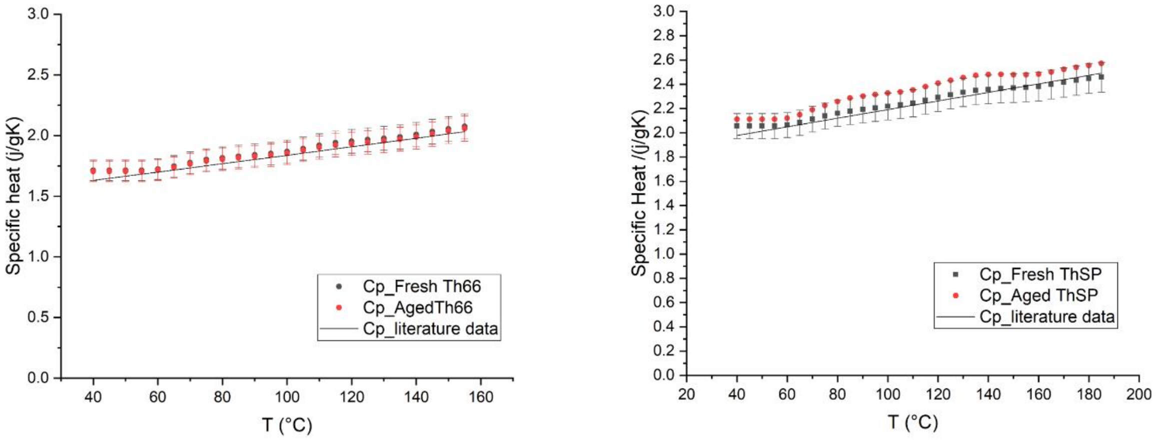

Figure 18. Therminol 66 (left) and Therminol SP (right) measured specific heat: comparison between fresh sample, aged sample and literature data.

Similarly to the procedure for specific heat, rheometer instrumental precision was evaluated over ten independent measurements, and it was estimated that in the tested temperature range (40-100°C) the methodology relative error was around 10%. Figure 19 shows the plot of Therminol 66 and Therminol SP viscosity as a function of temperature, including the measured values for fresh and aged samples together with literature data.

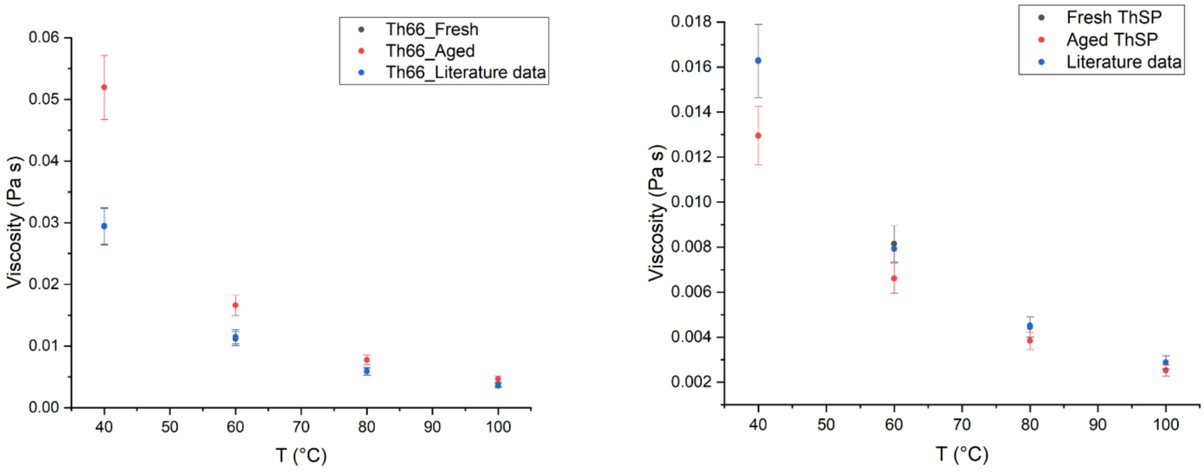

Figure 19. Comparison between the Therminol 66 (left) and Therminol SP (right) viscosity of fresh, aged and literature data.

The results clearly show that Therminol 66 viscosity increase significantly with thermal ageing, and that this difference is particularly marked at lower temperatures. This behaviour can be explained considering a partial polymerization of the oil components according to the TGA results. Regarding Therminol SP, the aged oil presented a slight, but still detectable, viscosity decrease. Considering also the results of the thermogravimetric analysis, this behaviour could be explaining hypnotizing molecular cracking processes, which led to a diminution of the components average molecular weight.

Since Therminol 66 and Therminol SP are a mixture of different compounds, GC-MS is a suitable technique to obtain a qualitative analysis of the oils chemical compositions and to detect how it changes with thermal treatments. The acquired chromatograms of fresh and aged oils samples are reported in Figure 20 and the most characteristic peaks, identified by NIST library considering a match greater than 90%, are marked.

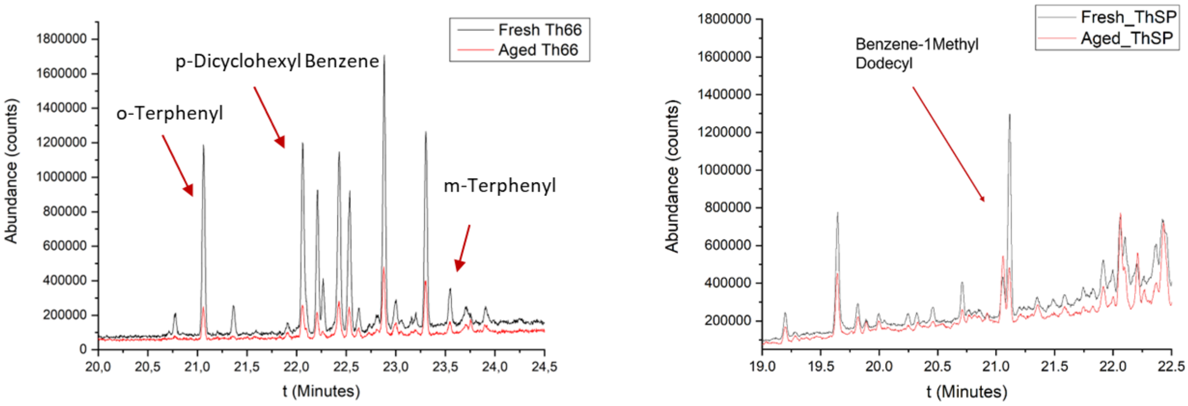

Figure 20. Overlaid chromatograms for fresh (black) and aged (blue) Therminol 66 and Therminol SP.

The strong decrease of terphenyl compounds in Therminol 66 aged sample is probably due to polymerization and production of low molecular weight aromatic components, as shown by the analysis of the condensed products presented above. Also for Therminol SP, the strong decrease of the Methyl Dodecyl Benzene peak in the aged sample could be explained considering the molecular cracking and low boiling compounds production occurring with thermal ageing.

Fourier transformed infrared spectroscopy (FT-IR) was used in the wave number range between 500 and 4000 cm^{-1} to perform a comparative analysis regarding changes in chemical structure and/or the formation of new compounds. Both thermally stressed and irradiated samples were analysed in the 4000-650 cm^{-1} wavenumber range and compared with results obtained on the respective fresh oil samples.

Figure 21 shows the comparison between acquired IR spectra on fresh (untreated) Therminol 66 samples with the respective stressed samples after thermal (Figure 22.a), radiation (Figure 22.b) and both thermal and radiation (Figure 22.c) ageing tests. Therminol 66 IR spectra show the terphenyl characteristic peaks; a C-H stretching band (*3000-2800 cm*$^{-1}$), C=C aromatic stretching and bending absorption bands at respectively 1500 *cm*$^{-1}$ and 750 *cm*$^{-1}$ respectively. By comparison of IR spectra acquired on fresh and thermally Therminol 66 samples some differences are detectable in the Stretching C-H zone and in the aromatic C-C double bond; resulting in agree with the hydrogen release together with the polymerization processes, where C-H bonds are broken and C-C bonds are formed. Regarding irradiation test, both fresh and thermally aged oil seems to be stable up to 100 kGy with no significant changes detected; the Therminol 66 overall chemical structure doesn't change if exposed to gamma radiation in the studied experimental conditions. It is also important to note that also the thermally stressed samples are no effected to gamma radiation highlighting the Therminol 66 high radiation stability.

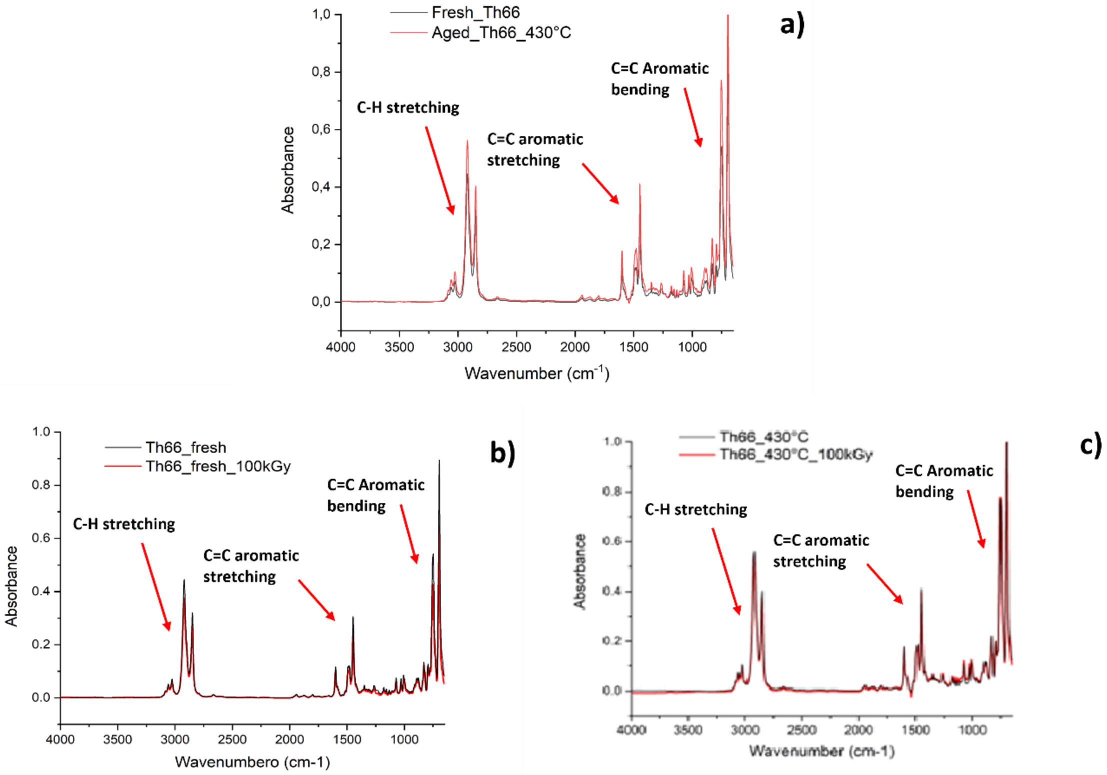

Figure 21. FT-IR curves: comparison between fresh and thermally aged (a), fresh and irradiated (b), thermally and both thermally and radiated (c) aged Therminol 66 samples

Similarly to Therminol 66, fresh Therminol SP IR spectra was compared with the relative thermal (Figure 23.a), irradiated (Figure 23.b) and both thermally and radiated stressed samples (Figure 23.c). As for Therminol 66, a C-H stretching band (*3000-2800 cm*$^{-1}$) and the benzene ring absorption bands at 1500 cm-1 (C=C aromatic stretching) and 750 cm^{-1}(C=C aromatic bending) were found. For Therminol SP is also of interest the absorption related to C-H aromatic bending at *1150-900* cm^{-1}that change with both thermal and gamma radiation ageing. Obtained results confirms the occurrence of molecular cracking reactions involving C-H breakages and new C-C bonds production as seen with other analytical techniques.

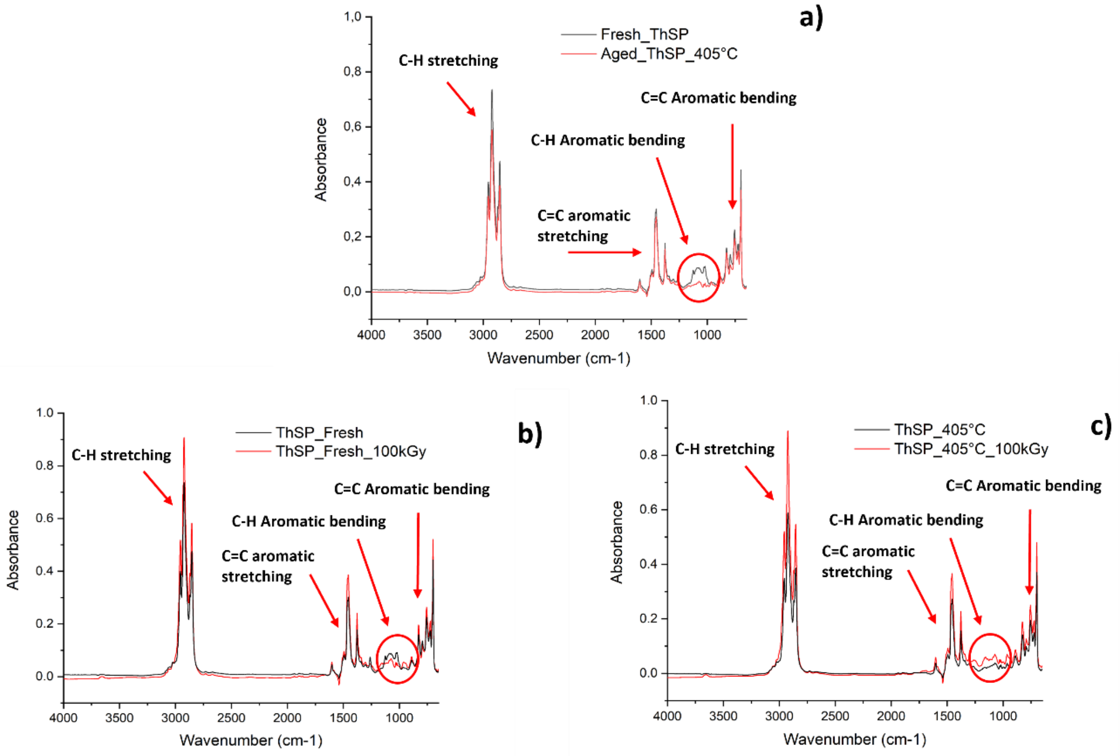

Figure 22. FT-IR curves: comparison between fresh and thermally aged (a), fresh and irradiated (b), thermally and both thermally and radiated (c) aged Therminol SP samples

7. Conclusions

Selected oils were studied to test their suitability to the concerned application and to have a better understanding of their thermal and radiolytic degradation processes. Therminol 66 and Therminol SP thermal ageing was performed by testing them within a temperature range from the maximum operating temperature up to the temperature at which a pressure of 10 bar is reached. A comparison between fresh and thermally aged oils, together with degradation products analysis have permitted to understand the main thermal degradation processes. According to their chemical structures, Therminol 66 ageing processes mainly involve polymerization as shown by thermogravimetric analysis and viscosity measurements while Therminol SP undergoes a molecular cracking process at different positions of the alkyl chain. Regarding irradiation tests, both fresh and aged oils showed excellent stability under gamma radiation with small changes produced in the global oil structure at 100 kGy as shown by infrared analysis. Overall, both oils tested seem to be suitable for the under-study application; Therminol 66 and Therminol SP have shown good thermal and radiochemical resistance in the studied experimental conditions.

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