Title: Intercomparative tests on viscosity measurements of phase change materials

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Keywords: Viscosity, Rheology, Natural convection, Phase Change Materials, Round Robin Test

Highlights

- Advances in intercomparative tests of viscosity of PCMs.
- Three different rheometers/institutions have been involved.
- Viscosity based on temperature of octadecane and RT70 has been determined.
- Results mainly influenced by the true sample temperature.

Abstract

Phase change materials (PCM) are capable of storing thermal energy within a small temperature range due to their high latent heat. When designing a thermal energy storage (TES) system with PCMs, besides the phase change enthalpy, thermal conductivity and density, viscosity based on temperature must be characterized to take into account natural convection. Taking advantage of the facilities of the different research groups working within an international network, a set of intercomparative tests were executed to determine the viscosity based on the temperature of two PCMs: octadecane and the commercial paraffin RT70 HC. Three laboratories have participated, which have used three different rheology equipments: two controlled stress rheometers, AR-G2 from TA Instruments and MCR 502 from Anton Paar and a translational rheometer, IMETER. The intercomparative tests were executed based on a starting methodology approach defined previously by some of the authors. The highest deviations were observed when temperature-controlled geometries or temperature hoods were not used at elevated test temperatures due to the temperature gradients within the sample, as consequence of the heat losses due to the room temperature. Consequently, special attention must be focused on the temperature control, since a uniform temperature throughout the sample should be guaranteed.

Nomenclature

H	Gap (µm)
P	Pressure (kPa)
T	Temperature (ºC)

Greek symbols

$\dot{\gamma}$	Shear rate (s^{-1})
η	Steady shear viscosity (Pa·s)
η*	Complex viscosity (Pa·s)
ω	Angular frequency (rad·s^{-1})

Subscripts

m	Melting

Abbreviation

CR	Cooling rate
CSP	Concentrated Solar Power
ECES	Energy Conservation through Energy Storage
PCM	Phase Change Material
SHC	Solar Heating and Cooling
TES	Thermal Energy Storage

1. Introduction

TES systems with PCM can provide high energy storage densities due to the latent heat associated to the solid-liquid phase change. Natural convection is caused by temperature gradients in the liquid phase, and it strongly influences the heat transfer. Apart from the buoyancy forces, natural convection is mainly influenced by viscous forces. When designing a TES system with PCM for a particular application, analytical or numerical models for an optimized system performance are required. Therefore, the determination of the viscosity property is relevant. Current models that consider natural convection take a constant viscosity value, which could lead to inappropriate TES designs, as shown in the article by Costa et al. [1]. They analysed a TES system where octadecane was confined in a horizontal cylinder. Initially they took a constant viscosity value, but they subsequently observed that changes in the viscosity value caused differences in the melting front.

To date, there are few reported studies about the rheological properties of PCMs. The most recent works are those by Ferrer et al. [2-3], which propose empirical correlations to predict viscosity based on the temperature of paraffins and fatty acids.

More studies can be found related to the viscosity determination of molten salts for their use as heat transfer and thermal storage media in solar power fields, and whose thermophysical and rheological properties directly affect CSP system performance. Its determination is essential to assess the heat transfer process and the pumping energy consumption in these solar power systems. The main obstacles in the determination of the viscosity of molten salts are: the high measurement temperatures, their low viscosity values (close to the detection limit of the equipment) and the corrosive nature of the molten salts [4]. This gives rise to an important scattering of data between different authors for the same salt/mixture [5-6]. Recently, Muñoz-Sánchez et al. [7] have measured solar salt-based nanofluids and two commercial solar salts with different purity grade at different shear rates and temperatures, where two different rheometers with different geometries have been used to analyse among others the influence of the rheometer measuring configuration.

Taking advantage of the various facilities of different research groups working within the framework of the "Joint Task 42 (SHC Programme)-Annex 29 (ECES Programme) of the International Energy Agency: Compact Thermal Energy Storage", a set of intercomparative tests were proposed to determine the viscosity of PCMs: octadecane and the commercial paraffin RT70 HC, taking as a starting point the procedure previously proposed by Delgado et al. [8] to check its reproducibility. The final objective would be to develop standardized methodologies to measure the rheological properties of PCMs reliably and reproducibly.

2. Materials and methods

2.1 Materials

Two organic materials have been characterized: 1) octadecane, specifically the product Parafol 18-97 supplied by the Sasol company having a minimum purity by weight of 97% [9] and 2) the paraffin RT70 HC supplied by Rubitherm [10]. Previous to the measurement of these substances, a general purpose viscosity standard, S3, from Paragon Scientific [11] was measured. This standard oil was chosen because its viscosity is similar to that of both octadecane and RT70 HC in the melted phase. Table 1 describes the main technical specifications of these materials.

Product	Substance	Supplier	T_m (ºC)	Purity	Production process
Parafol 18-97 [9]	Octadecane	Sasol Company	27.85 [11]	>97%*	Fischer-Tropsch process
RT70 HC [10]	Paraffin	Rubitherm	70.00 [9]	-	-
S3 [11]	Viscosity standard oil	Paragon Scientific	-	-	-

Table 1. Materials description

2.2 Apparatus and instrumentation

Three institutions have participated. Two of them used a controlled stress rheometer and the other a translational rheometer. Table 2 shows the technical specifications of these instruments, as well as their features (in particular, geometries and temperature controller used). The measurement methodology is different for the IMETER translational rheometer. A double-walled glass cylinder was filled with the sample. A temperature sensor was submerged inside. This was connected to a thermostatic bath, which controls the sample and the measuring body temperature. The linear displacement is produced by a translational movement of the geometry, different from the angular displacement produced by the rotational movement of the geometries of the controlled stress rheometers.

Institution	Instrument	Methodology	Geometries	Temperature control	Temperature controlled-hood/ heated geometry	Minimun torque (rotational) [µN·m]	Minimun torque (oscillatory) [µN·m]
Fraunhofer ISE	MCR 502, Anton Paar	Controlled stress rheometer	Plate 60 mm	Peltier plate	Yes	0.001	0.0005
			Concentric cylinder	Peltier concentric cylinder	Yes		
University of Zaragoza-I3A	AR-G2, TA Instruments	Controlled stress rheometer	Plate 40 mm made of stainless steel	Peltier plate	No	0.01	0.003
University of Bayreuth	Imeter, Method 5 DiVA	Translational viscometer and rheometer	Concentric cylinder	Temperature chamber	Yes		

Table 2. Technical specifications of the equipment used in the intercomparative tests.

2.3 Method

As mentioned in the introduction, the procedure adopted has taken as a starting point the procedure proposed in a previously published work [8]. This procedure can be followed when working with a controlled stress rheometer.

A Peltier plate as temperature controller and a plate as geometry were selected. The plate geometry, in contrast to the cone geometry, allows modification of the gap during the course of the test in order to absorb the volume change, when viscosity based on temperature is being measured in a dynamic mode. This would not be necessary when working with concentric cylinders.

In practice, due to the availability of geometries and temperature controllers of each institution, the procedure could not be adopted completely. For this reason the measurements were also executed with other geometries in addition to the plate, such as with the concentric cylinder. Plates with different diameters were also used.

Before executing the tests, the following steps were carried out where possible:

1) Calibrating the inertia of the geometry attached to the drive shaft.
2) Performing a standard rotational mapping as a baseline
3) Establishing the zero gap

2.3.1 Procedure adopted to obtain viscosity at a specific temperature

The samples to be measured were placed on the Peltier plate. The amount of sample was controlled in order to have a gap between 500 and 1000 µm. Both rotational and oscillatory mode were used for their characterization. The procedure adopted, to the greatest possible extent bearing in mind that different devices were used, was the following:

Rotational and translational mode

1) Conditioning step

   To keep the sample at the set temperature during 5 minutes. No shearing.

2) Steady state flow

   From 0.001 to 1000 s-1 if possible at the set temperature, measuring 10 points per decade, distributed in logarithm mode.

   Steady flow conditions must be defined or assured in a possible way, for example:

   Tolerance lower than 5% during three consecutive measurements. Maximum time of 1 minute if tolerance is not fulfilled.

Oscillatory mode

1) Conditioning step

   To keep the sample at the set temperature during 5 minutes. No shearing.

2) Frequency sweep step

From 0.01 to 100 Hz measuring 10 points per decade, distributed in logarithm mode, at a stress within the linear viscoelastic region at the set temperature.

Due to the fact that the measurement methodology is different for the IMETER translational rheometer, a procedure as similar as possible was adopted. Prior to the measurements, the minimum and maximum applicable shear rate by the IMETER rheometer was determined, which is restricted through the weighing cell, linear actuator, experimental setup and viscosity of the specimen. Once determined, measurements within this range were executed with at least three successive measurements under the same conditions.

For the sake of clarity, all the procedure details have been compiled in table 3 for the shear sweep tests and in table 4 for the oscillatory tests.

	Shear sweep		
	AR-G2	**MCR 502**	**IMETER**
Geometry	Plate 40 mm	Plate 60 mm, Titanium	Concentric cylinder Outer cylinder 16.005 mm Inner cylinder 14.29 mm
Gap [µm]	500-1000	500-1000	857.5 (at 25 °C, function of the temperature)
Time for thermal stabilization [min]	5	5	5
Shear rate range [s^{-1}]	0.001-1000	0.001-1000	5-300 (octadecane, S3 at 25 °C and 50 °C) 1-800 (RT70 HC, S3 at 60 °C and 80 °C)
Mode	log	log	Equally spaced number of points within shear rate range
Points per decade	10	10	-
Sample period [s]	10	10	Defined by the available stationary movement distance of the cylinder (approx. 25 mm) and the applied shear rate
Definition of steady state	Tolerance<5% during 3 consecutive measurements. Maximum time=1 min	Option not available in MCR502	Constant force acting on the measuring cylinder; no tolerance specified;

Table 3. Details of the procedures adopted by each rheometer for the shear sweep tests.

	Frequency sweep		
	AR-G2	**MCR 502**	**IMETER**
Geometry	Plate	Plate 60 mm, Titanium	-
Gap [µm]	500-1000	500-1000	-
Time for thermal stabilization [min]	5	5	-
Frequency range [Hz]	0.01-100	0.01-100	-
Mode	log	log	-
Points per decade	10	10	-
Oscillation stress [Pa]	1	1	-

Table 4. Details of the procedures adopted by each rheometer for the frequency sweep tests.

2.3.2 Procedure adopted to measure viscosity based on temperature

A second round of tests considered viscosity measurements based on temperature in a dynamic mode. Due to the changes in temperature, changes in the sample volume affect the sample loading when testing with the plate geometry (not with concentric cylinders). The gap could have been modified during the measurement. However, this was not done in this second round, since it was assumed that volume changes were not going to be significant for the result within the temperature range of the tests. The procedure adopted was the following:

Rotational and translational mode:

1) Conditioning step
   To keep the sample at the higher temperature of the temperature range to be measured during 20 minutes. No shearing.
2) Temperature ramp
   At 100 s-1 from the higher temperature of the temperature range to the lower at a cooling rate of 0.5 K/min.

Oscillatory mode:

1) Conditioning step
   To keep the sample at the higher temperature of the temperature range to be measured during 20 minutes. No shearing.
2) Temperature ramp
   At 1 Hz and with a stress of 1 Pa from the higher temperature of the temperature range to the lower at a cooling rate of 0.5 K/min.

For the IMETER translational rheometer, as was mentioned in section 2.3.1, the measurement methodology is different so a procedure as similar as possible was adopted. Namely, the viscosity based on temperature was measured by isothermal steps and at three cooling rates: 0.86, 0.45 and 0.44 K/min.

Again, for the sake of clarity, the procedure is well detailed in table 5 and 6 for the rotational (and translational) and oscillatory mode respectively.

	AR-G2	MCR 502	IMETER
Geometry	Plate 40 mm	Plate 60 mm, Titanium	Concentric cylinder Outer cylinder 16.005 mm Inner cylinder 14.29 mm
Gap [μm]	500-1000	500-1000	857.5 (at 25 °C, function of the temperature)
Time for thermal stabilization [min]	20	20	20
Shear rate [s^{-1}]	100	100	100
Ramp rate [K/min]	0.5	0.5	0.86/0.44/0.45
Sampling time [s]	10	30	Approx. 8 s

Table 5. Details of the procedures adopted by each rheometer for the temperature ramp tests in the rotational and translational mode.

	AR-G2	MCR 502	IMETER
Geometry	Plate 40 mm	Plate 60 mm, Titanium	-
Gap [μm]	500-1000	500-1000	-
Time for thermal stabilization [min]	20	10 (Parafol 18-97) 20 (RT70 HC)	-
Frequency [Hz]	0.048	1	-
Ramp rate [K/min]	0.5	0.5	-
Oscillation stress [Pa]	1	1	-

Table 6. Details of the procedures adopted by each rheometer for the temperature ramp tests in the oscillatory mode.

3. Results and discussion

For a better understanding of the following subsections where the results are discussed, the tests performed by each institution have been compiled in table 7.

Sample	Equipments	Rotational / translational tests						Oscillatory tests					
		Shear sweep	**Gap [µm]**	**P [kPa]**	**Temperature ramp**	**Gap [µm]**	**Pressure [kPa]**	**Freq. sweep**	**Gap [µm]**	**P [kPa]**	**Temperature ramp**	**Gap [µm]**	**P [kPa]**
S3	AR-G2	At 25ºC	555	98.56	-	-	-	At 25ºC	570	99.03	-	-	-
		At 50ºC	620	98.96	-	-	-	At 50ºC	580	99.03	-	-	-
		At 60ºC	645	98.85	-	-	-	At 60ºC	645	98.85	-	-	-
		At 80ºC	645	98.85	-	-	-	At 80ºC	645	98.85	-	-	-
	MCR 502	At 25ºC	600	99.56	-	-	-	At 25ºC	600	99.25	-	-	-
		At 50ºC	700	98.89	-	-	-	At 50ºC	600	99.68	-	-	-
		At 60ºC	732	101.11	-	-	-	At 60ºC	738	101.11	-	-	-
		At 80ºC	702	101.03	-	-	-	At 80ºC	720	101.04	-	-	-
	IMETER	At 25ºC	857.5	97.62	-	-	-	-	-	-	-	-	-
		At 50ºC	855.3	97.18	-	-	-	-	-	-	-	-	-
		At 60ºC	854.4	97.93	-	-	-	-	-	-	-	-	-
		At 80ºC	852.6	97.90	-	-	-	-	-	-	-	-	-
Parafol 18-97	AR-G2	At 35ºC	960	97.87	45-30ºC (0.5 K/min) Isothermal at 30, 35, 40 and 45ºC.	990	98.86	At 35ºC	925	97.30	45-30ºC (0.5 K/min)	765	98.25
	MCR 502	At 35ºC	800	99.03	45-30ºC (0.5 K/min)	820	99.03	At 35ºC	690	99.53	45-30ºC (0.5 K/min)	885	99.91
	IMETER	At 35ºC	856.6	98.63	45-30ºC (0.86 K/min and 0.44 K/min) Isothermal at 30, 35, 40 and 45ºC.	856.6	98.02 (0.86 K/min) 97.99 (0.44 K/min) 98.10 (Isothermal)	-	-	-	-	-	-
RT70 HC	AR-G2	At 80ºC	720	98.63	95-70ºC (0.5 K/min) Isothermal at 80ºC.	720	98.63	At 80ºC	720	98.63	95-70ºC (0.5 K/min) Isothermal at 80ºC.	500	98.63
	MCR 502	At 80ºC	811	101.12	95-70ºC (0.5 K/min)	684	98.84	At 80ºC	811	98.84	95-70ºC (0.5 K/min)	680	98.84
	IMETER	At 80ºC	852.6	98.09	95-70ºC (0.45 K/min) Isothermal at 80 and 95ºC.	852.6	98.05 (0.45 K/min) 98.09 (Isothermal)	-	-	-	-	-	-

Table 7. Details of the tests performed by each institution.

Standard uncertainties: AR-G2: $u_r(P)$=1%; $u_r(\dot{\gamma})$=0.86%; $u_r(H)$=0.7%; u(T)=0.1 K; MCR 502: $u_r(P)$=1%; $u_r(\dot{\gamma})$=0.42% u(H)=0.65 µm; u(T)=0.03 K;

IMETER: u(P)=0.005 kPa; $u_r(\dot{\gamma})$=0.13%; u(H)=15 µm at 25ºC; u(T)=0.03 K

3.1 Standard oil S3

On the one hand, the standard oil S3 was measured at 25ºC and 50ºC, to verify the accuracy of the instruments when measuring octadecane in the melted phase, and at 60 and 80ºC when measuring the RT70 HC.

3.1.1 Results according to procedure 2.3.1

Results in rotational mode

Values with a deviation from the certified value below 10% were obtained at 25ºC with the different instruments and geometries used for the viscosity characterization from a shear rate value of approximately 10 s^{-1}, with the exception of the MCR 502 rheometer when using the concentric cylinder. Figure 1 shows a high deviation at high shear rates, probably due to secondary flows found with high-speed testing of low viscosity liquids with this type of geometry.

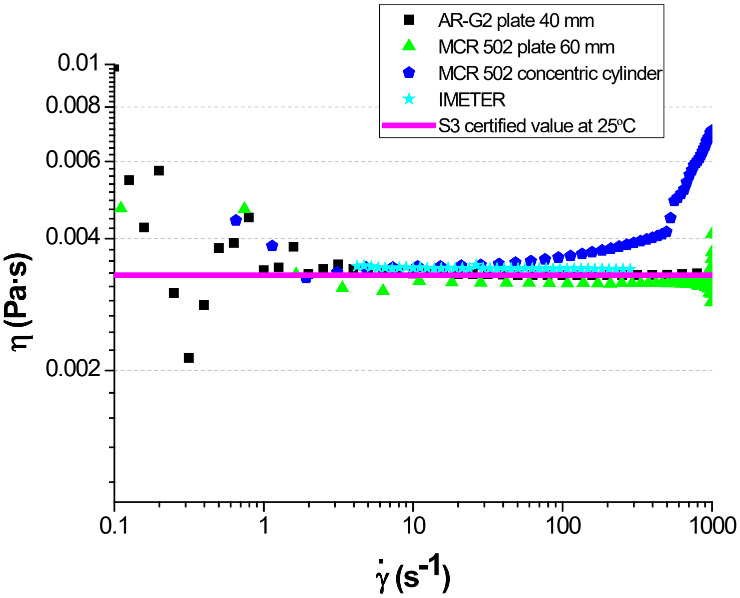

Figure 1. Comparison of the viscosity values of the standard oil S3 at 25ºC obtained in rotational and translational mode.

Dispersion of the results was also observed when testing at low shear rates. Due to the low viscosity of the standard oil, when low shear rates are used, the torque to be applied by the rheometer should be very low, below the minimum torque of the rheometer, leading to erroneous results. Viscosity values with the IMETER translational rheometer at low shear rates were not measured, since the shear rate range where accurate measurements could be obtained was determined previously. For this reason, viscosity was measured from 5 s^{-1} instead of from 0.001 s^{-1}.

This pattern was also observed when the standard oil S3 was measured at 50, 60 and 80ºC. Figure 2 shows the results obtained focusing on the shear rate range of 10-1000 s^{-1}. At first sight, it is observed that a larger deviation was obtained when the standard oil was characterized with the AR-G2 at 80ºC, probably due to temperature gradients inside the sample, since the geometry used was not an upper heated plate for Peltier plate (see table 1). As mentioned in Laun et al. [12], a quantitative mismatch of viscosities measured by different rheometers or laboratories for identical samples is often due to errors in determining the true sample temperature. Possible reasons for errors are: 1) an offset between set and actual sample temperature, 2) radial or axial temperature gradients within the sample or 3) a lag of sample temperature behind the set heating and cooling rate. In this case, as deviations are not observed at low temperature, being an isothermal measurement, it could be thought that temperature gradients within the sample at 80ºC are taking place, since a non-heated geometry is being used. Barker and Ian Wilson [13], aware of this problem, analysed both experimentally and numerically the temperature profile within a sample contained between the upper and the lower disks of a rotational rheometer fitted with a temperature-controlled lower plate, and the effect of temperature gradients within the system.

Table 8 compiles the shear rate range where the deviation from the certified viscosity values is lower than 10%, together with the average deviation and the relative standard uncertainty. For the AR-G2 rheometer, a higher test temperature means a higher deviation, due to the problem already mentioned, which could be solved by means of upper heated geometries. It can be stated that all the instruments obtain precise and accurate results within those shear rate ranges with the exception of the AR-G2 at 80ºC. Even so, an average deviation of 8.05% is achieved. It should be pointed out that the deviation observed for the MCR 502 rheometer is higher at 25ºC and 50ºC than at 60ºC and 80ºC because the experiments at 25ºC and 50ºC were carried out without the temperature hood. The technicians underestimated the influence of the heat loss on the measurement results due to the room temperature of the laboratory (30ºC) during the tests performed. It is clearly observed for the AR-G2 rheometer, that the experimental window (or shear rate range) becomes narrower as a consequence of the viscosity decrease, when increasing the temperature.

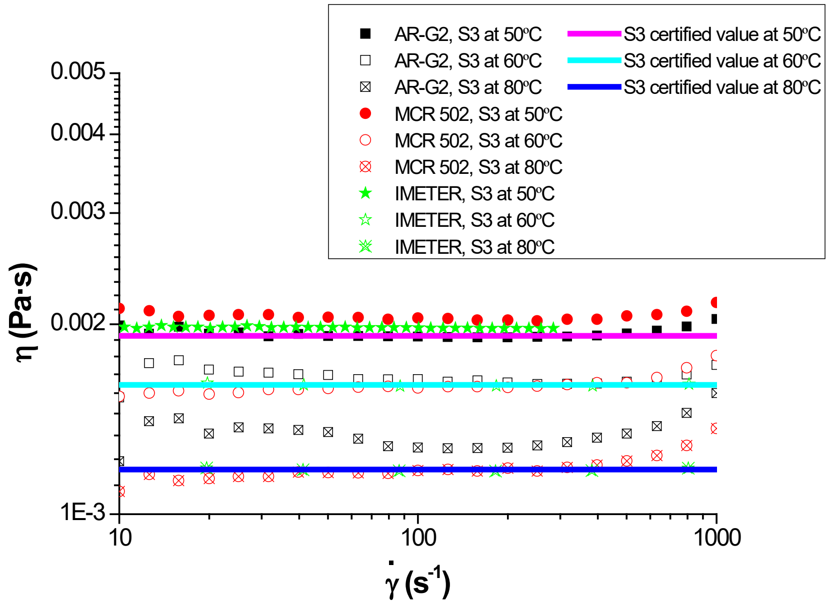

Figure 2. Comparison of the viscosity values of the standard oil S3 at 50, 60 and 80ºC obtained in rotational and translational mode.

	Shear rate range (s^{-1})	**Average deviation (%)**	**Relative standard uncertainty (%)**
	25ºC		
AR-G2	2-1000	1.00	0.26
MCR 502	1.65-982	-3.77	0.34
IMETER	4.22-283.10	2.03	0.08
	50ºC		
AR-G2	6.31-1000	1.20	0.39
MCR 502	12.60-794	7.18	0.24
IMETER	7.13-284.18	1.33	0.06
	60ºC		
AR-G2	10-1000	3.12	0.66
MCR 502	5.01-794	-0.92	0.50
IMETER	2.10-808.70	0.85	0.54
	80ºC		
AR-G2	79.43-251.20	8.05	0.17
MCR 502	5.01-794	-1.10	0.75
IMETER	2.10-803.6	1.43	0.87

Table 8. S3 measurements in rotational and translational mode at 25, 50, 60 and 80ºC. Shear rate range where deviation observed is lower than 10% together with the average deviation and relative standard uncertainty.

Results in oscillatory mode

Both the AR-G2 and MCR 502 rheometers (both controlled stress rheometers) allow measurements in oscillatory mode. Figure 3 shows the results obtained by these two rheometers working in oscillatory mode together with the viscosity certified values. It is observed that in contrast to the rotational mode, reliable results at low and medium angular frequency values were obtained. At the same angular frequency range (0.06-0.10 rad/s), the MCR 502 rheometer obtained higher deviations. From 1 rad/s the deviation observed in the measurements executed by the AR-G2 rheometer increased abruptly, while the MCR 502 rheometer even decreased this deviation (see table 3). This could be due to a higher inertia of the motor and geometry, since a stainless steel geometry was attached to the AR-G2 shaft, which is quite massive. It is also clearly observed that for the MCR 502, the deviation begins to rise at lower angular frequencies for higher temperatures, an indicator of the sample inertia. Secondary flows increase the measured torque and therefore incorrectly increase the apparent viscosity. It must also be pointed out that in contrast to the results in rotational mode for the MCR 502, which showed a negative deviation (except at 50ºC because the measurement was executed without the temperature-controlled hood), this deviation was positive when measured in oscillatory mode.

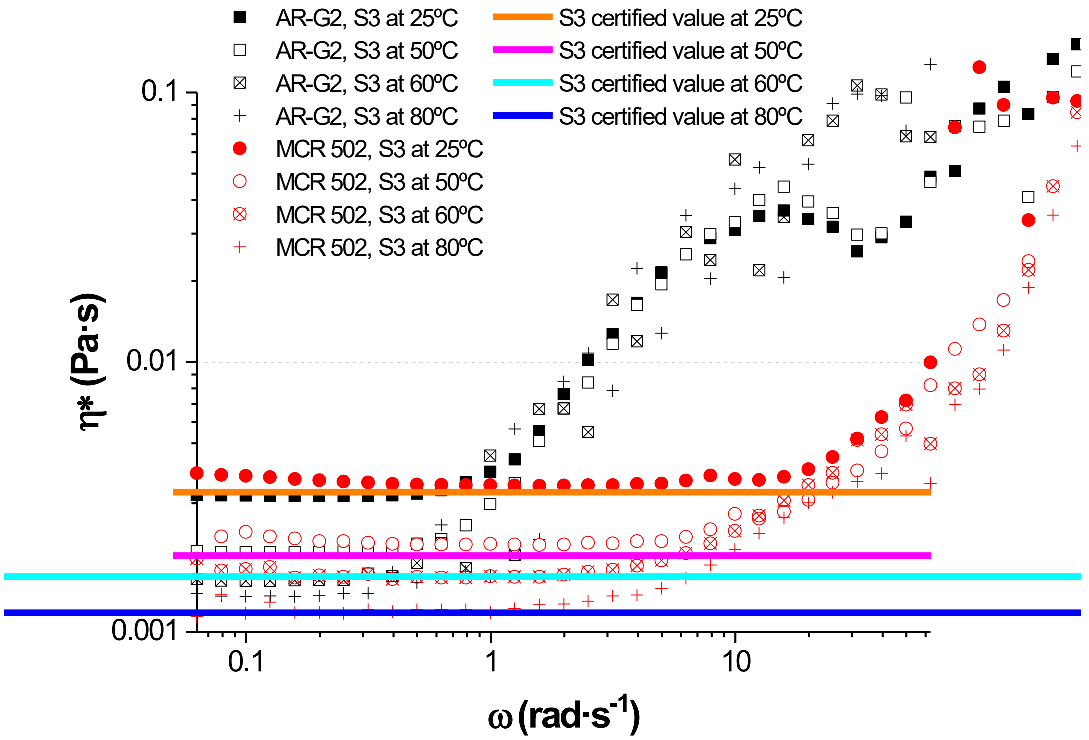

Figure 3. Comparison of the viscosity values of the standard oil S3 at 25, 50, 60 and 80ºC obtained in oscillatory mode.

Table 9 compiles, as with the rotational tests, the angular frequency range where the deviation from the certified viscosity values is lower than 10%, as well as the average deviation in that range and the relative standard uncertainty. As in the rotational mode, the AR-G2 at 80ºC provides elevated deviations due to possible temperature gradients inside the sample, and maybe as a result of secondary flows due to the lower viscosity at higher temperatures. In this case, the deviation is even higher than 10%, in particular a deviation between 14-17% for the angular frequency range of 0.06-0.31 rad/s has been estimated. As in the case of the rotational experiments, tests at 25 and 50ºC executed by the MCR 502 rheometer show higher deviations than at higher temperatures (60 and 80ºC), since the Peltier hood was only used for the latter RT70 measurements, as well as for the standard oil measurements in relation to this substance, that is to say at 60 and 80ºC (second round of tests), due to the experience gained in the first round of tests. Therefore, the higher deviation observed at 25 and 50ºC can be attributed to temperature gradients inside the sample. The AR-G2 obtained accurate results at lower angular frequency values than the MCR 502 rheometer, which would mean longer characterization tests. This could be improved by using less massive geometries to diminish inertia problems when the frequency increases. It can be stated that accurate and precise results can also be obtained in oscillatory mode.

	Angular velocity range (rad·s^{-1})	**Average deviation (%)**	**Relative standard uncertainty (%)**
	25ºC		
AR-G2	0.06-0.79	-1.59	1.04
MCR 502	0.25-4.99	6.73	0.28
	50ºC		
AR-G2	0.06-0.40	3.86	0.42
MCR 502	1.58*	9.54	-
	60ºC		
AR-G2	0.06-0.40	-1.80	0.76
MCR 502	0.08-3.15	2.02	0.75
	80ºC		
AR-G2	Deviation higher than 10%		
MCR 502	0.10-1.99	2.60	0.84

Table 9. S3 measurements in oscillatory mode at 25, 50, 60 and 80ºC. Angular velocity range where deviation observed is lower than 10%, together with the average deviation and relative standard uncertainty.*Only one angular velocity value meets the deviation criterion

3.2 Octadecane

Octadecane was measured at 35ºC and the results were compared to other measurements found in the literature [14-17]. Where known, the methodology adopted in each one of these works is shown in table 10.

Ref	Equipment	Data provided by authors about methodology
[14]	Brookfield DV-II + Pro viscometer with UL Adapter (rotational viscometer)	Rotating cylindrical spindle. Temperature controller: thermostatic bath. Measurements under steady state conditions. Measuring time: 10 min for each measurement. Estimated accuracy with a viscosity standard fluid of ±1%.
[15]	Brookfield DV-II + Pro (rotational viscometer)	Standard deviation of less than ±1%.
[16]	-	-
[17]	Calibrated glass capillary viscometer	Measurement of the time for a volume of liquid to flow under gravity.

Table 10. Data about the viscosity measurements of octadecane found in the literature.

3.2.1 Results according to procedure 2.3.1

Results in rotational mode

Figure 4 shows the measurements obtained and their comparison to the literature values. It can be observed that they are within the range of values taken from the literature. It must be pointed out that the IMETER rheometer obtained lower values in contrast to its results with the standard oil, and that the MCR 502 rheometer, just as with the standard oil S3, showed a higher deviation when measuring at high shear rates with the concentric cylinder geometry.

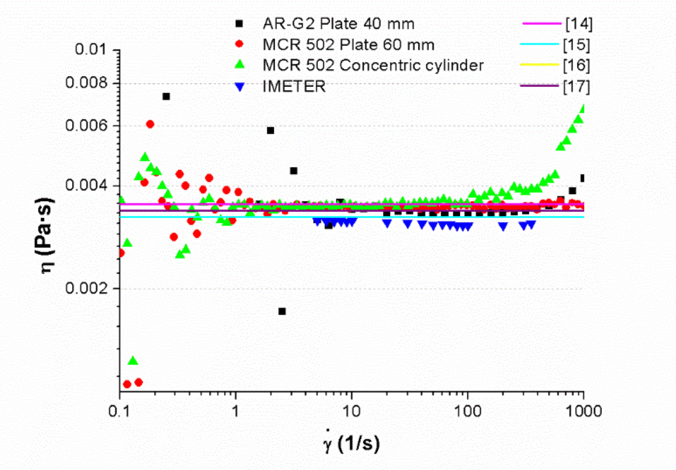

Figure 4. Comparison of the viscosity values of octadecane at 35ºC (melted phase) in rotational and translational mode. *Data from [16] hidden by data from [17] as they are identical values.

Results in oscillatory mode

Figure 5 shows the results in oscillatory mode. The MCR 502 rheometer was able to obtain accurate results in oscillatory mode in a wider angular frequency range compared to the AR-G2. The AR-G2 rheometer was able to obtain lower deviations when measuring at low frequencies, while the MCR 502 rheometer did so when measuring at high frequencies, probably due to the massive geometry used by the AR-G2. In the medium range, both instruments achieved accurate and precise results. Table 11 compiles the average viscosity value, the deviation from the average literature value (3.4 mPa·s) and the relative standard uncertainty within the shear rate and angular frequency range defined by the previous measurements of the standard oil S3 at temperatures of 25 and 50ºC, considering the most restrictive range. The data tabulated of these measurements are compiled in table 12 and 13.

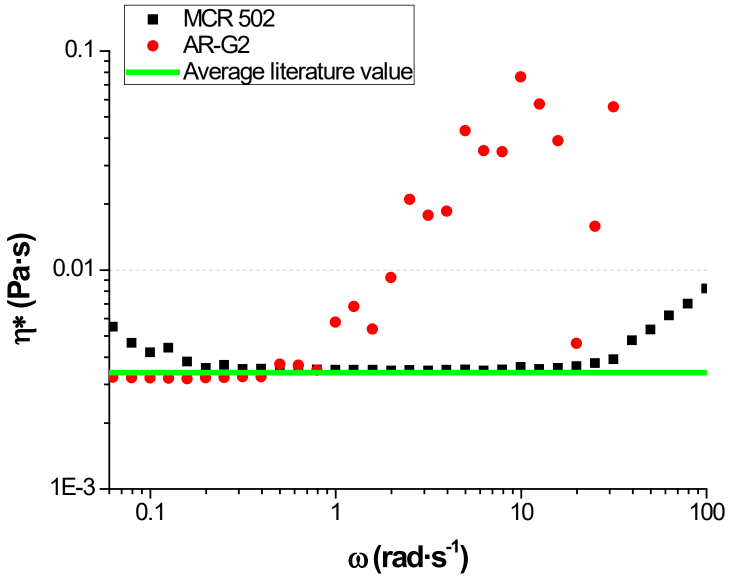

Figure 5. Comparison of the viscosity values of octadecane at 35ºC in oscillatory mode.

	Rotational			Oscillatory		
	Average viscosity value (mPa·s)	Average deviation (%)	Relative standard uncertainty (%)	Average complex viscosity value (mPa·s)	Average deviation (%)	Relative standard uncertainty (%)
AR-G2	3.444	1.29	1.36	3.222	-5.23	0.24
MCR 502	3.486	2.53	0.22	3.500	2,94	-
IMETER	3.112	-8.47	0.32	-		-

Table 11. Average viscosity value for octadecane measured at 35ºC. Average literature value: 3.400 mPa·s.

AR-G2		MCR 502		IMETER	
Shear rate (s-1)	Viscosity (mPa·s)	Shear rate (s-1)	Viscosity (mPa·s)	Shear rate (s-1)	Viscosity (mPa·s)
2.51	1.718	1.67	3.517	5.00	3.174
3.16	4.424	1.87	3.484	6.00	3.165
3.98	3.525	2.10	3.406	7.00	3.158
5.01	3.191	2.36	3.536	8.00	3.165
6.31	3.068	2.66	3.472	9.00	3.153
7.94	3.576	2.98	3.467	10.00	3.164
10.00	3.414	3.35	3.503	20.00	3.135
12.59	3.43	3.76	3.451	30.00	3.120
15.85	3492	4.23	3.502	40.00	3.106
19.95	3.344	4.75	3.480	50.00	3.089
25.12	3.369	5.34	3.489	60.00	3.100
31.62	3.391	5.99	3.518	70.00	3.094
39.81	3.345	6.73	3.482	80.00	3.074
50.12	3.343	7.56	3.502	90.00	3.069
63.10	3.333	8.5.	3.542	100.00	3.066
79.43	3.332	9.55	3.531	200.00	3.069
100.00	3.327	10.7	3.494	300.00	3.085
125.90	3.336	12.00	3.466	350.00	3.108
158.50	3.337	13.50	3.471		
199.50	3.344	15.20	3.475		
251.20	3.361	17.10	3.502		
316.20	3.389	19.20	3.570		
398.10	3.432	21.50	3.561		
501.20	3.510	24.20	3.479		
631.00	3.645	27.20	3.592		
794.30	3.872	30.50	3.500		
1000.00	4.217	34.30	3.551		
		38.50	3.582		
		43.30	3.577		
		48.60	3.567		
		54.60	3.602		
		61.40	3.654		
		68.90	3.598		
		77.40	3.534		
		87.00	3.571		
		97.70	3.547		
		110.00	3.789		
		123.00	3.647		
		138.00	3.737		
		156.00	3.833		
		175.00	3.656		
		196.00	3.824		
		221.00	3.732		
		248.00	3.967		
		278.00	3.927		
		313.00	3.850		
		351.00	3.916		
		394.00	3.917		

443.00	4.087
498.00	4.177
559.00	4.321
628.00	5.204
706.00	5.422
792.00	5.854
890.00	6.257

Table 12. Octadecane viscosity at 35ºC obtained in rotational and translational mode.

AR-G2		MCR 502	
Angular velocity (rad·s-1)	Complex viscosity (mPa·s)	Angular velocity (rad·s-1)	Complex viscosity (mPa·s)
0.06	3.238	0.25	3.680
0.08	3.220	0.31	3.530
0.1	3.208	0.40	3.540
0.13	3.201	0.50	3.490
0.16	3.184	0.63	3.490
0.20	3.220	0.79	3.510
0.25	3.225	1.00	3.500
0.31	3.253	1.25	3.500
0.40	3.252	1.58	3.500
0.50	3.715	1.99	3.470
0.63	3.672	2.50	3.490
0.79	3.480	3.15	3.470
		3.96	3.500
		4.99	3.510

Table 13. Octadecane viscosity at 35ºC obtained in oscillatory mode.

3.2.2 Results according to procedure 2.3.2

Results in rotational mode

Figure 6 shows the results obtained in rotational mode for a temperature ramp from 45 to 20ºC. It was observed that the IMETER rheometer started the measurement at 45ºC with a lower viscosity value, maybe because the sample had not reached thermal equilibrium. The values obtained by the IMETER rheometer with the continuous ramp and by isothermal steps fitted each other. The MCR 502 measurements fitted with the literature values, while the AR-G2 showed a slightly higher deviation. Both the IMETER and the MCR 502 rheometers obtained similar values to the literature values.

The lower slope of the measurements from the AR-G2 rheometer could be due to a lack of temperature equilibrium in the sample. To check this possible problem, isothermal measurements were executed from 45 to 30ºC. The temperature step was 5 K, and was decreased in a period of time of 20 minutes. Isothermal measurements were also executed from 30 to 45ºC to analyze possible differences, since the heating/cooling is not symmetrical. Then the viscosity was measured every 10 seconds during 5 minutes, obtaining the average values for each temperature, represented also in figure 6. During the 5 minutes of measurement, deviations in the results were not observed, so it could be confirmed that the sample was in thermal equilibrium. The values obtained in isothermal mode were similar to the values obtained by the temperature ramp. The higher deviation from the average literature value [14-17] was at 30ºC, with a deviation of 7%. Additionally, the viscosity-temperature values were compared to the values obtained after applying the model proposed by Ferrer et al. [2] for predicting viscosity values for the paraffin family, showing a higher deviation. This model, a third degree polynomial, was obtained from the viscosity of three paraffins, RT21, RT27 and RT55. A correction parameter must be applied, which takes into account the material melting point. In this case, the melting temperature used was that provided by NIST [20]. Deviations could come from the model itself or from the uncertainty in the estimation of the melting temperature.

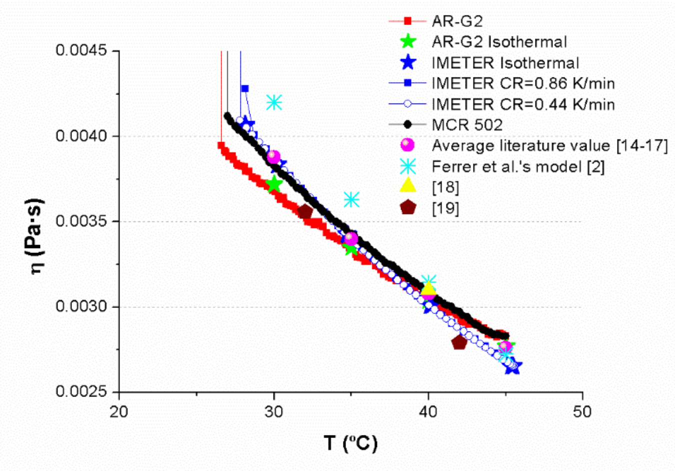

Figure 6. Comparison of the viscosity-temperature curves of octadecane measured in rotational and translational mode at 100 s^{-1}.

The gap in these experiments was between 500 and 1000 µm following the procedure described in section 2.3.1. In the previous work [8], the influence of the gap chosen was studied, as well as the heating and cooling rate. These factors must be taken into account in relation to the temperature gradients inside the sample, especially when working with PCMs due to their low thermal conductivity. This effect could be more significant in cooling experiments, since in non-heated geometries, natural convection is not promoted. An equivalent approach to that proposed by Lázaro et al. [21] should be carried out to find the appropriate rate to ensure thermal equilibrium.

Results in oscillatory mode

Both controlled stress rheometers measured the viscosity based on temperature curves in oscillatory mode, obtaining the results plotted in figure 7. The same behaviour as in rotational mode was observed in the AR-G2 measurements, both in isothermal steps and by the temperature ramp. In these tests, the University of Zaragoza chose a lower frequency than that recommended in the procedure, since the inertia phenomenon was observed when testing with a frequency of 1 Hz, as can be seen in figure 5. A frequency of 0.048 Hz was chosen. Since the equipment needs at least one period of time to measure (the inverse of frequency), it is of interest to have as high a frequency as possible, to avoid a very significant temperature variation during the dynamic measurement (temperature ramp of 0.5 K/min). In this case the viscosity values from the MCR 502 rheometer were higher than the literature values. This deviation is more significant at higher temperatures, that is to say at the beginning of the test. In these experiments, as mentioned previously, the Peltier hood was not used, so the measurements could be affected by the temperature gradients in the sample due to the heat loss. These results are in accordance with the oscillatory results for the standard oil, which also showed a positive deviation (see table 3). What is curious is that these deviations were not observed in the temperature ramps in rotational mode. Additional isothermal measurements should be carried out.

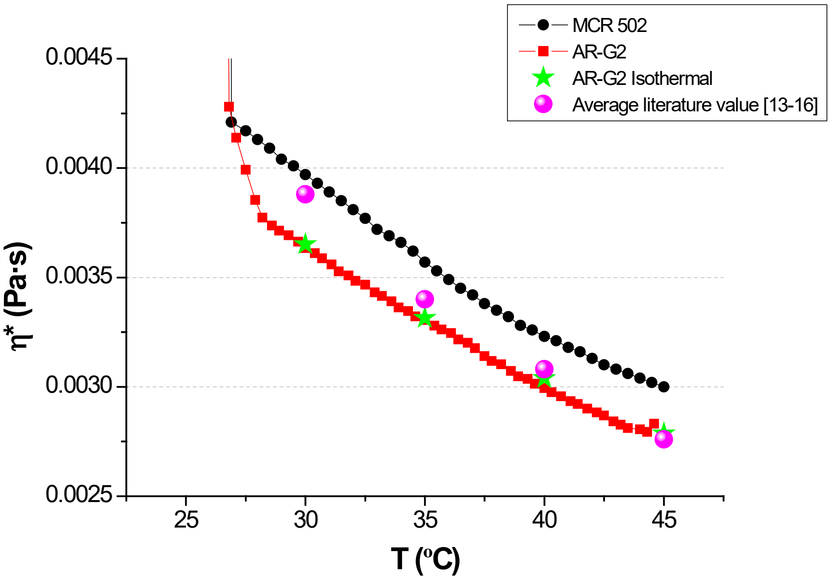

Figure 7. Comparison of the viscosity-temperature curves of octadecane measured in oscillatory mode.

3.3 RT70 HC

3.3.1 Results according to procedure 2.3.1

The viscosity of RT70 HC was measured at 80ºC, in its melted phase. Viscosity data for this product have not been found in the literature.

Results in rotational mode

It can be observed in figure 8 that the three rheometers obtained very similar values if the attention is focused on the shear rate range from 10 to 1000 s-1. As predicted with the characterization of the standard oil S3 at 80ºC by the AR-G2, higher viscosity values were obtained due to the temperature gradients, since a non-heated geometry is used. These viscosity values were not compared to the values calculated by Ferrer et al.'s model [2], because their proposed model has been built from paraffins with lower phase change temperatures.

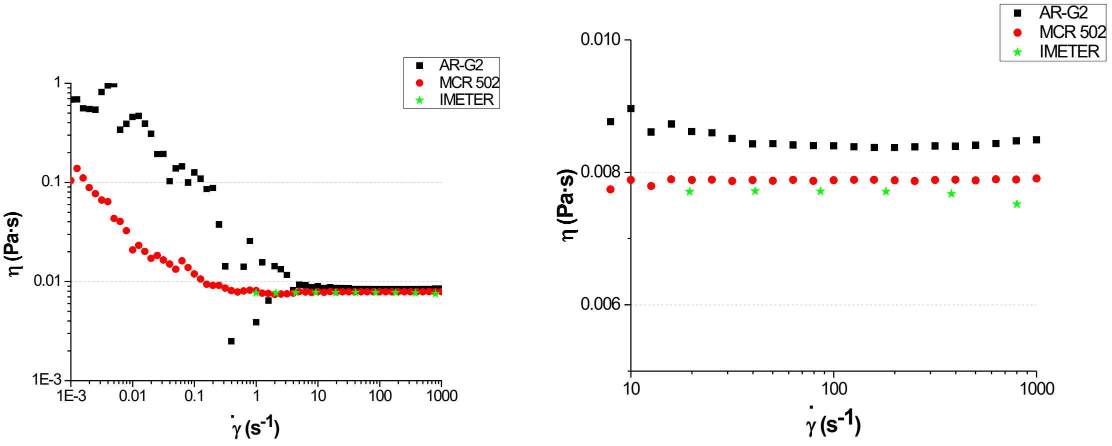

Figure 8. Comparison of the viscosity values of RT70 HC at 80ºC (melted phase) in rotational and translational mode.

Results in oscillatory mode

In oscillatory mode, similar values to those obtained in rotational mode have been measured, as can be observed in figure 9. Once again, the influence of non-uniform temperature in the sample in the AR-G2 rheometer gives rise to higher viscosity values in comparison to the values measured by the MCR 502 rheometer. In the same manner, the MCR 502 can measure over a wider range of angular frequency values. Table 14 compiles the average viscosity value and the relative standard uncertainty within the shear rate and angular frequency range defined by the previous measurements of the standard oil S3 at temperatures of 60 and 80ºC, having considered the most restrictive range. Table 15 and 16 shows the data tabulated.

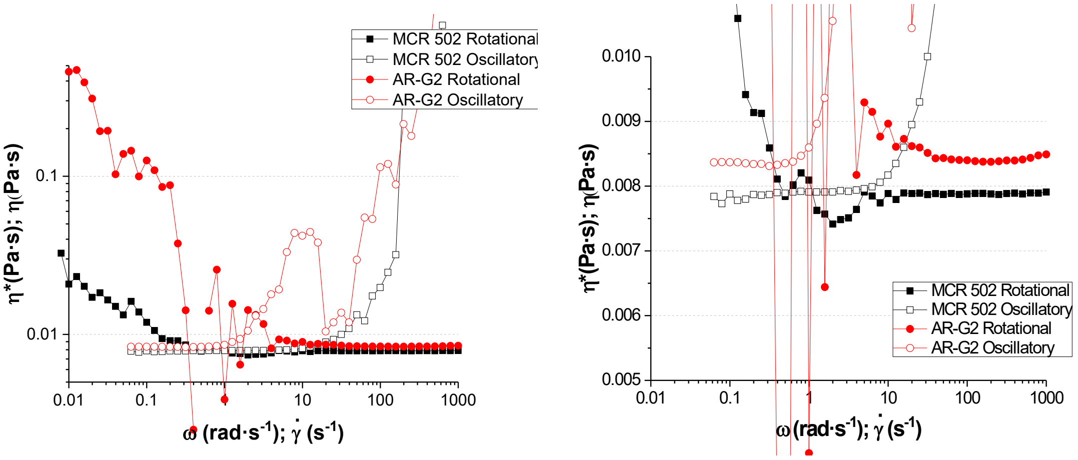

Figure 9. Comparison of the viscosity values of RT70 HC at 80ºC (melted phase) in oscillatory mode. Comparison with the results of rotational mode.

	Rotational		Oscillatory	
	Average viscosity value (mPa·s)	Relative standard uncertainty (%)	Average complex viscosity value (mPa·s)	Relative standard uncertainty (%)
AR-G2	8.388	0.05	8.350	0.09
MCR 502	7.873	0.10	7.880	0.14
IMETER	7.682	0.28	-	-

Table 14. Average viscosity value for RT70 HC measured at 80ºC.

	MCR 502		IMETER	
Viscosity (mPa·s)	Shear rate (s-1)	Viscosity (mPa·s)	Shear rate (s-1)	Viscosity (mPa·s)
8.403	5.01	7.710	2.10	7.657
8.399	6.31	7.865	4.41	7.693
8.385	7.94	7.909	9.28	7.737
8.377	10.00	7.808	19.51	7.710
8.375	12.60	7.926	41.02	7.717
8.384	15.80	7.875	86.16	7.714
	20.00	7.862	181.07	7.712
	25.10	7.88	380.62	7.677
	31.60	7.917	800.19	7.52
	39.80	7.900		
	50.10	7.912		
	63.10	7.910		
	79.40	7.922		
	100.00	7.909		
	126.00	7.915		
	158.00	7.911		
	200.00	7.908		
	251.00	7.923		
	316.00	7.906		
	398.00	7.918		
	501.00	7.915		
	631.00	7.908		
	794.00	7.932		

Table 15. RT70 HC viscosity at 80ºC obtained in rotational and translational mode.

AR-G2		MCR 502	
Angular velocity (rad·s-1)	Viscosity (mPa·s)	Angular velocity (rad·s-1)	Viscosity (mPa·s)
0.06	8.370	0.10	7.880
0.08	8.370	0.12	7.780
0.10	8.370	0.16	7.800
0.12	8.370	0.20	7.870

0.16	8.350	0.25	7.860
0.20	8.340	0.31	7.870
0.25	8.340	0.40	7.900
0.31	8.310	0.50	7.890
0.40	8.330	0.63	7.910
		0.79	7.920
		1.00	7.910
		1.25	7.910
		1.58	7.910
		1.99	7.910

Table 16. RT70 HC viscosity at 80ºC obtained in oscillatory mode.

3.3.2 Results according to procedure 2.3.2

The influence of a non-uniform temperature was also observed in the results of the dynamic cooling and by isothermal steps, as shown in figures 10 and 11.

Results in rotational mode

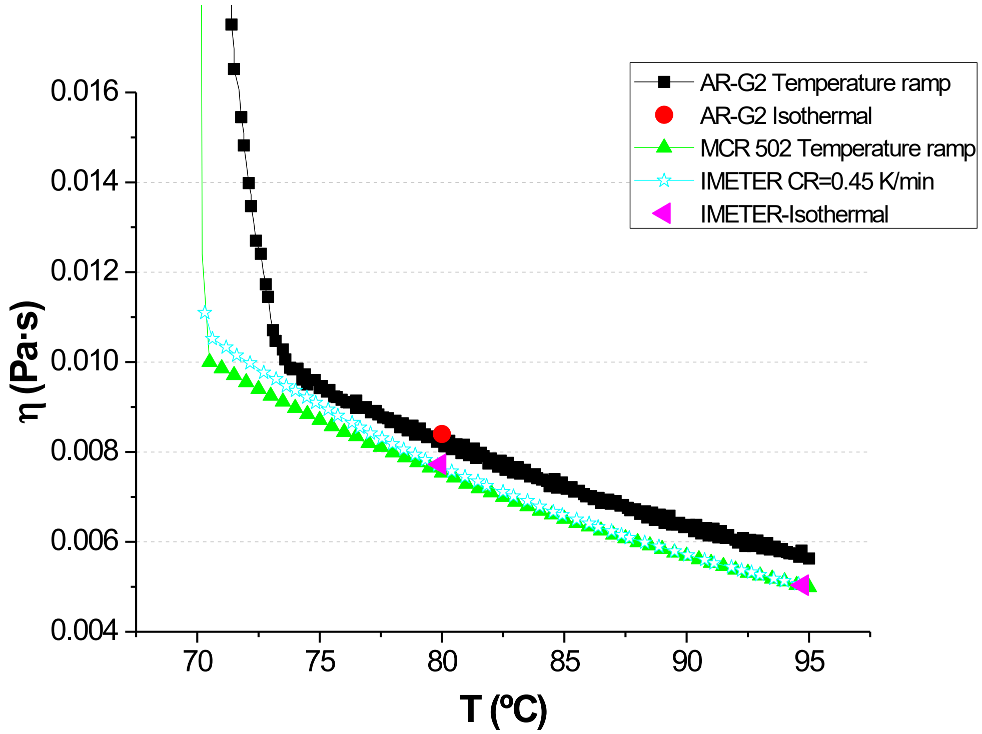

Figure 10. Comparison of the viscosity-temperature curves of RT70 HC measured in rotational and translational mode at 100 s^{-1}.

As a result of the ambient temperature influence, the abrupt increase in viscosity due to the solidification is seen for the AR-G2 at a higher temperature, as the true sample temperature is not that provided by the Peltier plate.

Results in oscillatory mode

Similar results were obtained in both oscillatory and rotational mode.

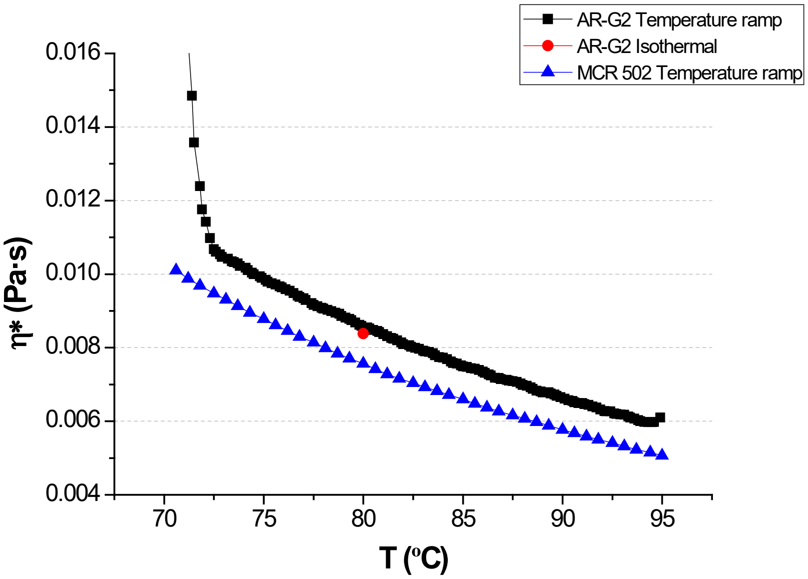

Figure 11. Comparison of the complex viscosity-temperature curves of RT70 measured in oscillatory mode at frequencies of 0.048 and 1 Hz for AR-G2 and MCR 502, respectively.

4. Conclusions

According to the results of the intercomparative tests, there is a good agreement between the viscosities measured with the different rheometer types and between the certified values for standard oil S3 and the values reported in the literature for octadecane.

The characterization of RT70 HC has shown a positive deviation of the AR-G2 measurements in comparison with the IMETER and MCR 502 characterization, due to the non-heated geometry used. This deviation was also observed when measuring the standard oil S3 at 80ºC. This demonstrates the importance of the requirement of temperature-controlled geometry or a temperature-controlled hood when samples are tested at elevated temperatures.

The procedures in both rotational and in oscillatory mode turn out to be appropriate to accurately measure viscosity. Although the choice of the measurement type, rotational or oscillatory, makes little difference, it is important to establish an experimental window with limitations at high shear rates or frequencies due to instrument and sample inertia, as well as a limitation at low shear rates due to the torque limit.

The average deviations observed when measuring the standard oil S3 were the following:

- Below 7.18 % in rotational mode for the two controlled stress rheometers (Temperature range: 25-80ºC) if AR-G2 values at 80ºC are omitted as a non-heated geometry was not used. Even if these are considered, the average deviation is lower than 8.05%.
- Below 3.86% in oscillatory mode for the AR-G2 rheometer (Temperature range: 25-60ºC)
- Below 6.73% in oscillatory mode for the MCR 502 rheometer (Temperature range: 25-80ºC) if values at 50ºC are omitted as the Peltier hood was not used.
- Below 2.03% for the translational rheometer IMETER (Temperature range: 25-80ºC)

Next steps:

- In future tests, before executing viscosity based on temperature measurements in a dynamic mode, the cooling rate at which the thermal equilibrium can be guaranteed should be determined.
- The exact reason for the deviations observed at elevated temperatures for the AR-G2 rheometer should be evaluated.
- Measurement of PCMs at higher temperatures.

Acknowledgements

I3A-University of Zaragoza would like to thank the Spanish Government for funding this work within the framework of the research projects (MICINN-FEDER): ENE2014-57262-R and ENE2017-87711-R. Fraunhofer ISE is grateful to the German Federal Ministry for Economic Affairs and Energy for funding the work of this project (03ESP357B) and the Project Management Jülich for the administrative support. The University of Bayreuth sincerely thanks the German Federal Ministry for Economic Affairs and Energy (BMWi) for research funding and support within the project with contract number 03ESP227B.

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