

APPLICATION OF COMBINED DENSITY AND VISCOSITY MEASUREMENTS WITH SINGLE SENSOR FOR NEW KINEMATIC VISCOSITY ANALYZER AT REFERENCE TEMPERATURE

Dr. Luc K. Bellière,
Dr. Valerie Lefèvre
Dr. Philippe Burg Corentin Thierry
Sofraser Sofraser USA
Villemandeur, France Houston, TX, USA

KEYWORDS

VISCOSITY, KINEMATIC VISCOSITY, DENSITY, VISCOSITY ANALYZER, VISCOMETER, REFERENCE TEMPERATURE

ABSTRACT

Viscosity is one of the most commonly measured physical properties. It is used more specifically in the refining, polymerization, chemical, food, coating and printing industries. The most common types of viscosity used are dynamic and kinematic viscosity. Kinematic viscosity is measured by taking into account the effect of gravity on a fluid's natural flow. The most common method to do so is to measure dynamic viscosity and density of a fluid using two separate instruments and dividing the first by the later.

In this paper, we will introduce an analyzer capable of measuring continuously with a single sensor kinematic viscosity. The first part of the paper will discuss how the technology of vibration at resonance frequency has been adapted to allow for density measurement. We will then look into how this technology has been adapted into an analyzer to allow for continuous measurement of kinematic viscosity. We will finish by demonstrating how this technique offers improvements on current techniques for viscosity measurement at reference temperature and the ASTM D445 correlation.

INTRODUCTION

Viscosity is a physical property that describes the resistance of fluid to flow under stress. There are many different types of viscosities, e.g.: dynamic viscosity, kinematic viscosity, intrinsic viscosity, inherent viscosity and others. Dynamic and kinematic viscosities are the most common across all industries (intrinsic and inherent viscosities tend to be used more in polymer industries). They both relate to the resistance of a fluid to flow under stress but for dynamic viscosity, the stress can be any force applied to the fluid whereas kinematic viscosity focuses on gravity as the force applied on the fluid.

Practically speaking, kinematic viscosity can be calculated using dynamic viscosity and density, as the ratio of one to the other:

$$\nu = \frac{\eta}{\rho}$$

Where:

ν – Kinematic Viscosity (mm²/s)

η – Dynamic Viscosity (mPa·s)

ρ – Density (g/cm³)

In this paper we will present how a technology used to measure dynamic viscosity was adapted to also measure density and therefore kinematic viscosity. Then we will detail how this technology improvement has been adapted into an analyzer to measure kinematic viscosity at reference temperature. Finally, the last section will present the results of the tests to determine repeatability, accuracy and reproducibility of the new viscosity at reference temperature analyzer.

1. EXISTING TECHNOLOGY FOR KINEMATIC VISCOSITY AT REFERENCE TEMPERATURE MEASUREMENTS

Viscosity measurement at reference temperature is a measurement where the sample is drawn from the process line at process temperature and brought to an analyzer with an internal temperature control system to heat/cool the product to the desired temperature before measuring the viscosity.

There are various ways to make the measurement of kinematic viscosity at reference temperature but we will present here the two most common ways.

The first technique consists of using 2 viscosity sensors to measure the viscosity for 2 temperatures surrounding the reference temperature, one slightly above and the other slightly below. Then, according to the formula given by the ASTM D341 [1], it is possible to

interpolate the viscosity of the sample. It is also worthy to note that this method is commonly used to measure viscosity index. The ASTM D341 requires kinematic viscosity in the calculation. Therefore, combined viscosity and density sensors are most commonly used. The drawbacks of this solution are that, it is not a true viscosity measurement but a calculation as well as the requirement of a series of heat exchanger and controllers to bring the sample near reference temperature which significantly increases the costs.

The second technique for this measurement uses the Hallikainen [2] capillary measurement system combined with an outside densitometer. Its drawbacks include the use of an oil bath and heavy maintenance requirements. The technology used by capillary systems measures the pressure difference between the inlet and the outlet of the capillary to make a direct measurement of viscosity. The capillary is inserted in an oil bath to bring the sample to the required temperature and ensure that the diameter and length of the capillary do not change with temperature. Other systems based on the same capillary technology are available but use an oven instead of an oil bath.

Based on the issues raised for the previous two solutions, we can see there is a need for an instrument with easy maintenance, measuring (by opposition to interpolating) viscosity with a large range of measurement, for more viscous products. We will therefore describe in the next section the equipment that was designed to meet those requirements.

2. DESIGN OF AN ANALYZER TO MEASURE KINEMATIC VISCOSITY AT REFERENCE TEMPERATURE

In this section we will detail the sensor used to measure dynamic viscosity and the advances that were made to the technology, to allow it to measure density. We will then detail how the sensor was adapted as an online analyzer.

2.1 SCIENTIFIC AND TECHNOLOGICAL REQUIREMENTS

In order to design the new analyzer, a set of requirements were established:

- The analyzer is connected to processes so it had to be able to handle process conditions in the sampling loop:
 - o Maximum Temperature: 200 °C
 - o Maximum Pressure: 16 bars
 - o Maximum Flow: 100L/h
- The analyzer will be used for process monitoring and/or control so repeatability is the key to this equipment. A repeatability of 1% of reading was needed for this equipment
- The analyzer will be used with refinery products (amongst others) so it had to have the ability to be correlated to the ASTM D445 [3] : Standard Method of Test for viscosity of transparent and opaque liquids (Kinematic and Dynamic viscosities)

- The analyzer will be operating with hazardous products so it had to have the ability to receive NEC and ATEX certification

2.2 PRESENTATION OF THE VIBRATING TECHNOLOGY USED FOR VISCOSITY MEASUREMENT OF NEWTONIAN AND NON-NEWTONIAN FLUIDS

In 1981, Sofraser created and patented the first vibrating viscometer using the vibrating technology at resonance frequency (Patent N° FR 2 544 496) [4].

The sensor response time is close to zero, and the viscosity information (stability or variation) is available continuously. This allows the control of processes even in the presence of transitory phenomenon or rapid disturbances. The absence of wearable parts guarantees no drift in time and no maintenance.

The vibrating viscometer at resonance frequency is a sensor working at a high shear rate to reduce measurement fluctuations due to fluid speed or flow rate when the product is pseudo-plastic or shear-thinning. This process viscometer is able to measure viscosities over one million centipoises (cP).

The principle of the vibrating viscometer at resonance frequency is simple. The active part of the sensor is a vibrating rod held in oscillation at its resonance frequency. The vibration amplitude of this movement varies according to the viscosity of the product in which the rod is immersed.

The motion of the rod is created by a magnet fixed on the rod and placed in front of a coil driven by an alternating current. Another magnet attached to the rod induces a current in a separate coil which is an image of the motion of the rod (Figure 1). The resulting voltage amplitude is an image of the viscosity.

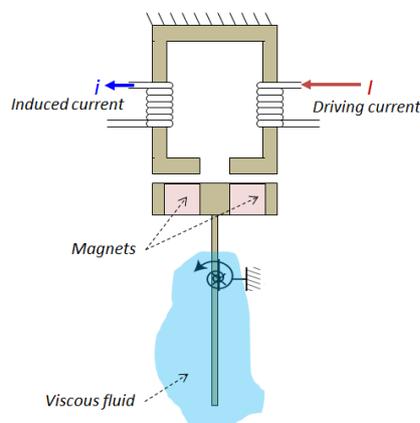


Figure 1. PRINCIPLE OF THE VIBRATING VISCOSITY SENSOR AT RESONANCE FREQUENCY.

During calibration, the amplitude of the vibration is correlated to the viscosity of the product by comparing the vibration in the air (maximum vibration) and in the viscous fluid (Figure. 2), thus providing a reliable, repeatable and continuous viscosity measurement. This principle is described in Patents FR 2 911 188 B1 [5] and FR 2 921 726 B1 [6].

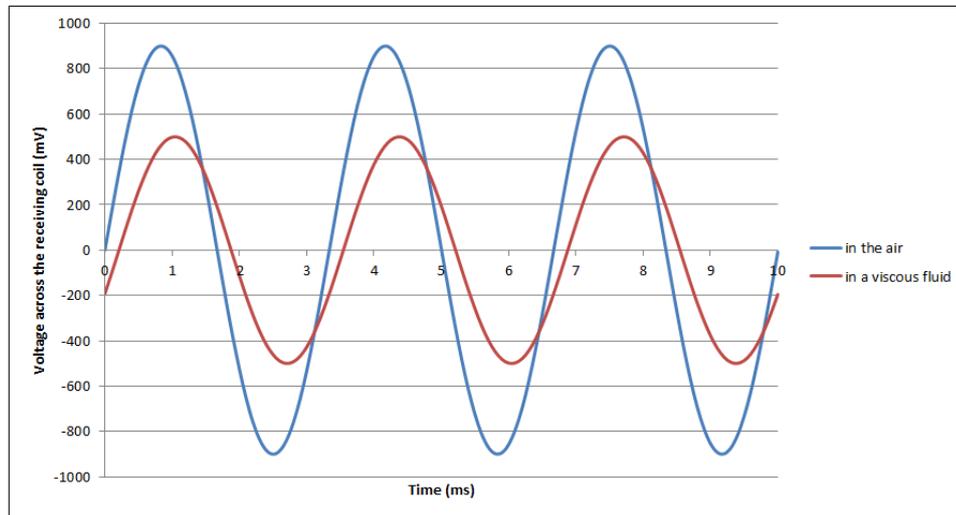


Figure 2. AMPLITUDE DIFFERENCE IN AIR AND IN VISCOUS FLUID.

2.3 ADAPTATION OF THE VIBRATING ROD TECHNOLOGY TO MEASURE DENSITY

In the previous section we demonstrated how the vibrating rod technology can be used to measure viscosity. In this section we will focus on the work accomplished to allow the measurement of density using a single sensor based on vibration at resonance frequency.

2.3.1 SCIENTIFIC & TECHNOLOGIC REQUIREMENTS

The following requirements were considered for the development of the density measurement:

- Simultaneous measurement of dynamic viscosity and density
- Continuous density measurement
- Density measurement range of 0.6 g/cm^3 to 1.6 g/cm^3
- Maximum viscosity for density measurement: 1,000 cP
- Repeatability of $\pm 0.005 \text{ g/cm}^3$
- Accuracy of $\pm 0.01 \text{ g/cm}^3$

The final requirement was on the sensor. The development of density measurement was to be adapted to the sensor in order to benefit from the available options and designs.

2.3.2 PRINCIPLE

When a rod immersed in a fluid is held in vibration at resonance frequency, the vibration changes and evolves depending on the fluid. A variation of the amplitude can be seen (ΔA) but also of the resonant frequency (Δf). Figure 3, shows the amplitude and frequency shift from air when immersing the vibrating rod in a liquid product.

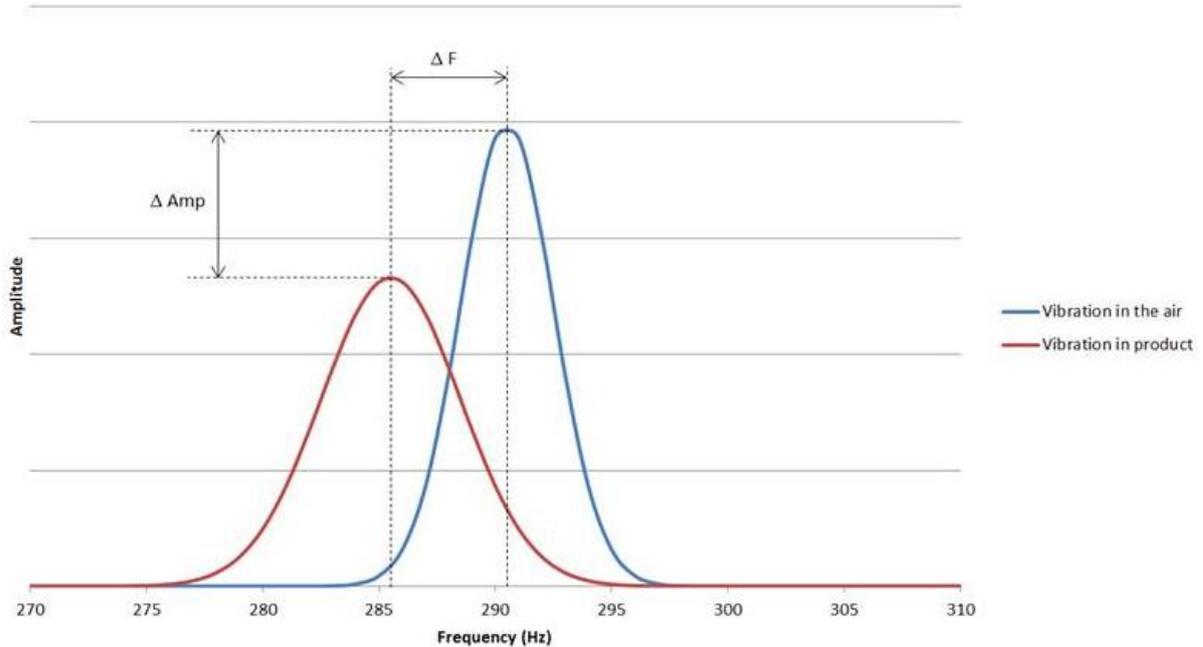


FIGURE 3. FREQUENCY AND AMPLITUDE SHIFT BETWEEN AIR AND LIQUID PRODUCT

As explained in the previous section, the amplitude variations correlate to the dynamic viscosity of the fluid. A relationship $\Delta A = f(\eta)$ was established in the past which allows for the measurement of dynamic viscosity of fluids.

The variation of frequency is made possible by the resonant state at which the viscometer operates, as opposed to other types of sensor using a known set frequency to operate. The resonant frequency depends upon the characteristics of the oscillator but also, on the medium in which the rod vibrates. The medium acts as a buffer dampening the motion of the rod (and hence, its frequency).

Empirical studies have allowed us to establish a relationship between the resonance frequency of the motion and the characteristics (namely dynamic viscosity and density) of the fluid in which the rod is immersed. The relationship appears as follows:

$$\Delta f = f(\rho, \rho \cdot \eta)$$

Below is a 3D model (Figure. 4) of the frequency shift in hertz against viscosity and density for a variety of liquid products. Each point represents a Cannon standard oil (N.4, N1, N2,

S3, S6, N10, and S20) or a reference product used for calibration and verification: Pentane, Hexane, Propanol, Trichloroethylene (C_2HCl_3) and Tetrachloroethylene (C_2Cl_4).

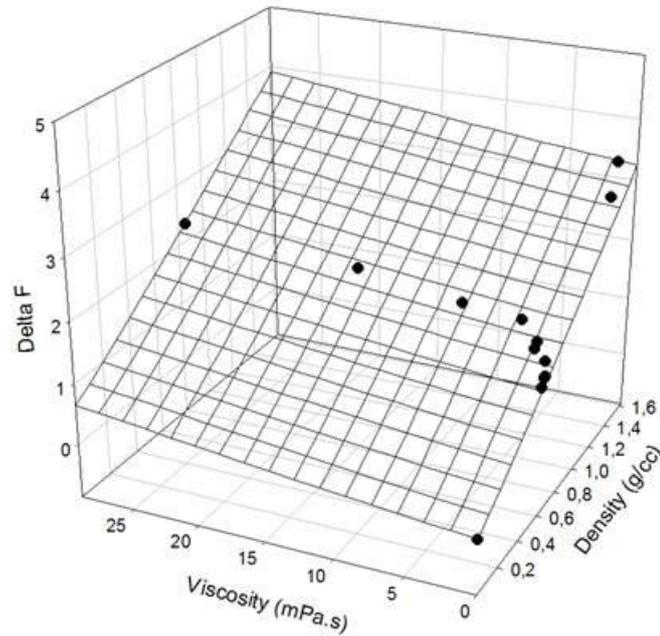


FIGURE 4. FREQUENCY SHIFT AGAINST VISCOSITY AND DENSITY OF VARIOUS PRODUCTS.

Mechanical characteristics of the oscillator such as Young's modulus all vary with temperature, therefore, the frequency of the vibration also varies with temperature. In order to have proper frequency measurement and thus density measurement, a temperature probe must be used in order to monitor the temperature of the medium. The temperature is used to account for the thermal drift of frequency in the density calculation. The model used to perform the tests incorporated a Pt100 probe in a thermowell to allow direct measurement of fluid temperature.

2.3.3 TESTS AND RESULTS

This section will present the results of density measurement on various products based on the calibration shown in the previous section.

After calibration, the sensor was used to measure the density of reference products to evaluate the accuracy of density measurement. Every test was made using the same sensor: MIVI 9701 (Serial Number: ESS 1759) with an incorporated Pt100.

The results are summarized in Table I. The experiments showed an average relative standard deviation of 0.64% and an average absolute standard deviation of 0.005 g/cm^3 . Based on those results, the accuracy of the density measurement was established to be of $\pm 0.01 \text{ g/cm}^3$.

TABLE I. MEASUREMENT RESULTS ON VARIOUS PRODUCTS

Product	Temperature (°C)	Viscosity (mPa.s)	Theoretical Density (g/cc)	Frequency (Hz)	Δf (Hz)	Measured Density (g/cc)	Standard deviation (g/cc)	Standard deviation (%)	
AIR	22.40	0.000	0.000	285.591	0.000	0.000	0.000	0.00%	
Cannon Standards	N.4	21.9	0.323	0.673	284.316	1.275	0.668	-0.004	-0.62%
	N1	21.75	0.890	0.729	284.191	1.400	0.726	-0.002	-0.30%
	N2	21.99	2.125	0.760	284.091	1.500	0.768	0.008	1.04%
	S3	21.94	3.773	0.864	283.866	1.725	0.867	0.003	0.35%
	S6	22.10	8.734	0.873	283.791	1.800	0.880	0.007	0.76%
	N10	21.77	17.722	0.876	283.741	1.850	0.872	-0.004	-0.43%
	S20	21.77	33.853	0.859	283.666	1.925	0.865	0.006	0.69%
Reference products	Pentane	22.14	0.223	0.624	284.416	1.175	0.620	-0.004	-0.56%
	Hexane	22.30	0.305	0.657	284.326	1.265	0.664	0.007	1.01%
	Propanol	21.98	2.091	0.802	284.031	1.560	0.796	-0.006	-0.78%
	C ₂ HCl ₃	22.32	0.570	1.456	282.666	2.925	1.455	-0.001	-0.09%
	C ₂ Cl ₄	22.48	0.862	1.622	282.316	3.275	1.620	-0.002	-0.14%

2.4 NEW ANALYZER DESIGN AND ADAPTATION OF THE VIBRATING TECHNOLOGY TO THE ANALYZER

The sensor technology previously described was adapted into an online analyzer at reference temperature over 10 years ago with numerous successes for the measurement of dynamic viscosity, at reference temperature [7]. Figure 5 shows a schematic of this analyzer

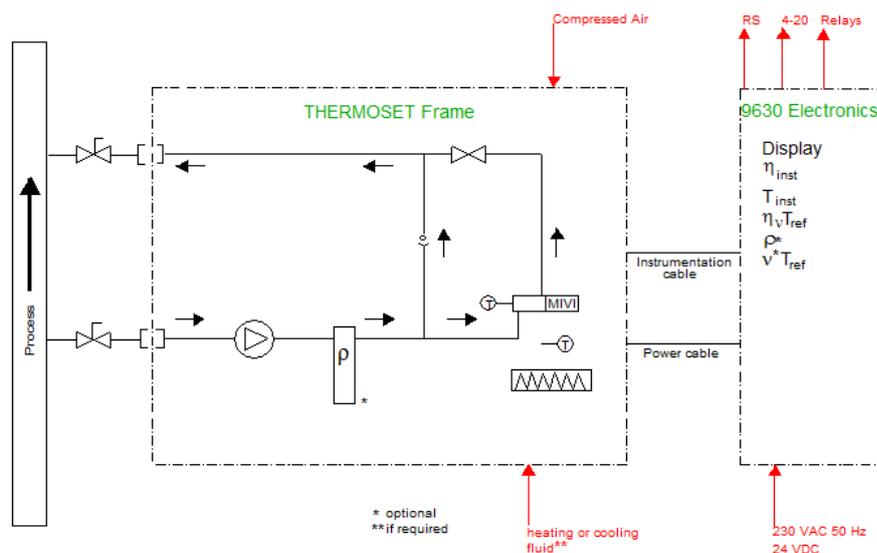


FIGURE 5. SCHEMCATICS OF THE ORIGINAL ANALYZER.

This analyzer has recently been adapted into an enclosure to reduce cost and increase flexibility. This second analyzer was also described in previous papers [6] and was used in order to design the kinematic viscosity analyzer.

With the recent advances of density measurement, the sensor was mounted in the same enclosure to see if it would be possible to obtain a kinematic viscosity measurement at reference temperature.

The analyzer is based on cyclical measurements during which the product is cooled/heated to the reference temperature. At first, the product enters at high temperature into the analyzer, filling up a flow-cell. Once the flow cell is full, the line is closed so that the product can cool/heat to the desired reference temperature. In the meantime, a bypass loop opens to allow the product to keep on flowing through the analyzer.

In light of the previous section where we explained that density measurement was sensitive to temperature variations (more so with large and rapid temperature changes), the design of the analyzer had to be modified to limit temperature variations to allow stable and repeatable density measurement, needed to measure kinematic viscosity.

In order to stabilize the temperature of both product and sensor, the analyzer design was slightly changed to insert a first heat exchanger before the product inlet (Figure 6). This first heat exchanger allows bringing the temperature of the product within a few degrees of the reference temperature. The coolant used in the first heat exchanger is supplied by a water chiller to allow controlling the coolant temperature to a few degrees above reference temperature.

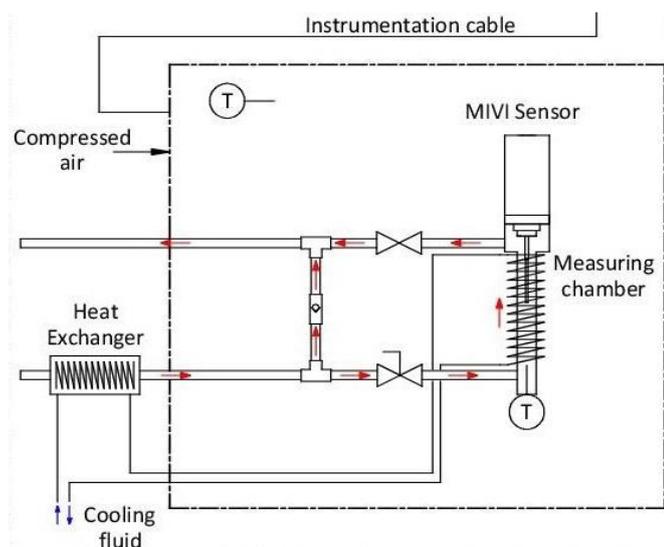


FIGURE 6. NEW ANALYZER SCHEMATIC.

Once the product exits the first heat exchanger, its temperature is a few degrees above reference temperature. The temperature of the product is monitored continuously as it exits the heat exchanger. If the temperature of the product is the same as reference temperature (within an acceptable limit) and it reaches the sensor, the product flows through the flow-cell and the kinematic viscosity measurement at reference temperature is made continuously.

If product temperature is too high with regards to the reference temperature, the product is locked into the flow-cell (on a bypass loop) and is allowed to cool to the reference temperature. As the product is only a few degrees above reference temperature, the cooling cycle is short. Hence, the name mini-cycle.

Since this new kinematic viscosity analyzer is based on the same design as the dynamic viscosity analyzer in an enclosure, they share many common advantages including low pricing compared to competing technologies due to shared development cost and shared components.

3. RESULTS

In this section we will details the tests that were performed on the analyzer to evaluate stability and analytical performance, namely: accuracy, repeatability and reproducibility.

3.1 TEST CONDITIONS

All tests were made using the Cannon standard mineral oil S200. Below (Table II) are the manufacturer's certified properties for the lot used during testing [9]:

TABLE II. S200 MINERAL OIL PROPERTIES

<i>Temperature</i> (°C)	Kinematic Viscosity mm ² /s (cSt)	Dynamic Viscosity mPa.s (cP)	Density g/cm ³
20.00	542.7	455.7	0.8397
25.00	402.2	336.5	0.8366
37.78	203.3	168.5	0.8290
40.00	182.6	151.1	0.8276
50.00	115.9	95.26	0.8216
80.00	38.95	31.30	0.8036
98.89	23.00	18.22	0.7923
100.0	22.34	17.68	0.7916

The product entering the analyzer was at a temperature of 100°C much higher than the reference temperature of 40°C. After the heat exchanger, the temperature of the product was slightly above reference temperature at 44°C \pm 1°C. The temperature of the cooling fluid

(44°C) was chosen to maintain the internal temperature of the analyzer to 40°C. Ambient temperature was varying between 10°C and 20°C. Flow rate of the product was set to 60 L/h.

3.2 RESULTS ON REFERENCE PRODUCT

This section will focus specifically on the results obtained from the tests described in the previous section.

3.2.1 DISCUSSION

As it has been previously shown, the technology at resonance frequency offers a relative measurement of viscosity. Secondary measurements rely on the calibration of an analyzer with standards in order to guarantee performance. One approach to evaluate the quality of a calibration is to look at the “scale ratio” between the physical quantity measured and the desired physical quantity [10]. The typical parameters used to evaluate an analyzer are repeatability, reproducibility and accuracy [11].

Repeatability is an indication of how close one measurement is from another under the same experimental conditions. In order to calculate the repeatability of an analyzer, the same measurement is made repeatedly under the same conditions. Practically, observers will run the analyzer under the same conditions and compare one measurement with the other, the closer the measurements, the more repeatable the analyzer. These experiments allow the determination of a “scale ratio”, then, the dispersion of measurements gives the overall repeatability of the analyzer.

Reproducibility is an indication of how an analyzer performs when the experimental conditions change from one measurement to the other. When evaluating the reproducibility of an analyzer, various experiments are run with different operating parameters. Similarly to repeatability, the differences between “scale ratio” variations are used to calculate the reproducibility. For each of the experiments, the difference between the model and actual value is calculated and the overall differences between all the experiments give the reproducibility of the analyzer.

Finally, accuracy is the indication of how close from the reference value a measurement is. Accuracy is a measurement of how consistent the “scale ratio” is between every measurement. Practically, this means that the observers calculate the difference between the value predicted by the model and the value of the standard.

After correction of any bias by the adjustment of the “scale ratio”, the accuracy of the equipment is then included in the reproducibility limit, which is “the lowest or equal value to which the absolute difference between two test results obtained under reproducibility conditions may be expected to have a probability of 95%” [11].

As a matter of fact, these corrections have to be made in all measurements, whether absolute or relative, as it has been explained in the ASTM standards [12, 13] and demonstrated by Barbosa et al. [14].

In the scope of this article, due to the method used to quantify accuracy, repeatability and reproducibility, the accuracy performance of the analyzer can be extracted from the reproducibility tests. We consider that, by knowing the error on the “scale ratio” from the reproducibility data, then a proper rescaling of the correlation allows reducing the error and therefore increasing accuracy.

Finally, one must consider how other technologies used to measure kinematic viscosity evaluate the repeatability and accuracy. Most technologies rely on 2 separate analysis, one for dynamic viscosity and one for density. This means that the repeatability of the analyzer needs to take into account the error on both measurements. Most manufacturers publish the repeatability and accuracy data for dynamic viscosity only, as the error on density is considered low. For the purpose of this study, it was decided to publish directly the performance obtained for kinematic viscosity.

3.2.2 RESULTS

In order to evaluate repeatability, the analyzer ran for 24 consecutive hours. Figure 7 and 8 below show the recorded density and dynamic viscosity along with the statistical distribution of the measurement. It can be seen that the analyzer provides good stability and low results dispersion.

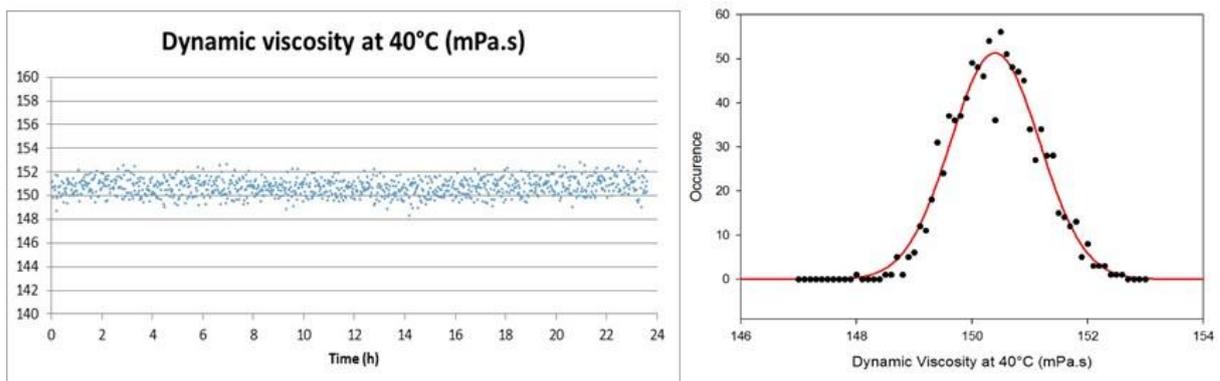


FIGURE 7. RECORDING OF DYNAMIC VISCOSITY OVER 24H ALONG WITH STATISTICAL DISTRIBUTION.

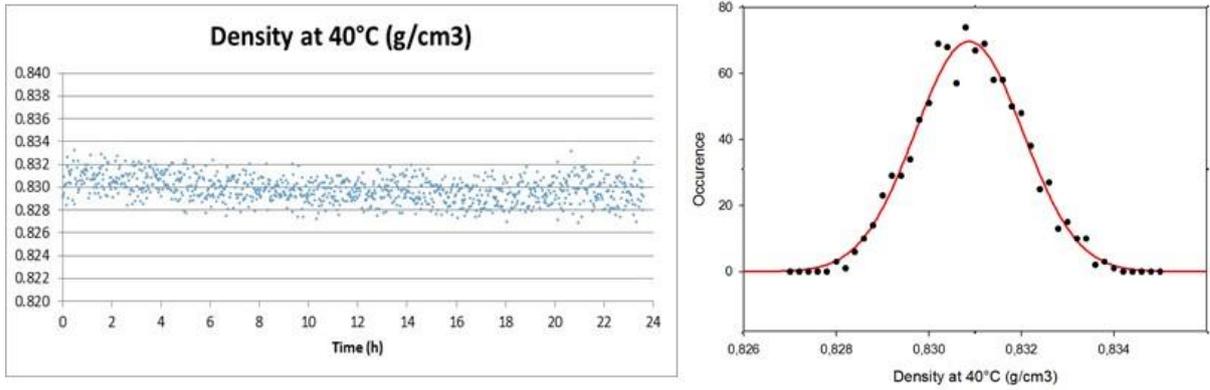


FIGURE 8. RECORDING OF DENSITY OVER 24H ALONG WITH STATISTICAL DISTRIBUTION.

Using both dynamic viscosity and density, the analyzer calculated real-time kinematic viscosity (using equation (1) presented in the introduction). Figure 9 below presents the recording over 24h for kinematic viscosity using the new analyzer along with the statistical distribution.

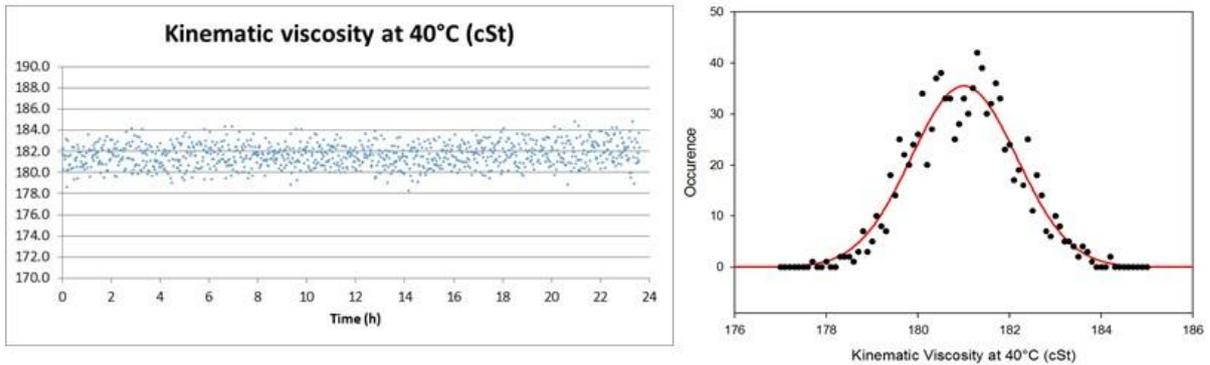


FIGURE 9. RECORDING OF KINEMATIC VISCOSITY OVER 24H ALONG WITH STATISTICAL DISTRIBUTION.

These tests show that under repeatability conditions, the standard deviation of the measurements made by the analyzer is 0.6% of reading, (for an expected viscosity of 182.6 cSt, the standard deviation is 1.09 cSt). The repeatability limit (i.e. The value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95 %) is equal to 1.2 % of the reading (twice the standard deviation).

The heat exchanger at the inlet of the analyzer ensures that the measurement is made under repeatability conditions at all times. This means that, for this specific measurement,

repeatability and reproducibility can be considered as the same value. Hence, the reproducibility of the analyzer is set to be at 1.2% of reading.

The analyzer is designed to operate around a specific operating point (One target viscosity at a specific reference temperature). The analyzer is therefore calibrated in order to ensure that at the operating point, the measurement is as close to the viscosity of the reference product as possible. Based on this, the reproducibility limit and accuracy are considered to be identical, which gives an accuracy of 1.2% for the measurement. Table III below summarizes the results of the tests.

TABLE III. SUMMARY OF TEST RESULTS

	Density at 40°C (g/cm ³)	Dynamic Viscosity at 40°C (mPa.s)	Kinematic Viscosity at 40°C (cSt)
<i>Reference value</i>	0.8276	151.1	182.6
<i>Mean Value</i>	0.8297	150.64	181.55
<i>Mean error</i>	0.0021	0.46	1.05
<i>Mean error (%)</i>	0.3%	0.3%	0.6%
<i>Standard Deviation</i>	0.0011	0.73	1.09
<i>Standard Deviation (%)</i>	0.1%	0.5%	0.6%

CONCLUSIONS

At the beginning of this article, we explained the problems with online, real-time measurement of kinematic viscosity. We then presented the existing technologies and their weaknesses.

In order to solve the issues raised in the previous sections, we presented how a technology used to measure dynamic viscosity was adapted, to also measure density and therefore kinematic viscosity. We then detailed how this technology was adapted into a new analyzer to measure kinematic viscosity at reference temperature.

Finally, we demonstrated that the performance of this new analyzer, can be correlated to the ASTM D445 which corresponds to the needs of most customers. This new analyzer therefore brings a new solution to customers to do a kinematic viscosity measurement of the same sample for both dynamic viscosity and density.

REFERENCES

- [1] ASTM D341-09 (2015) : “Standard practice for viscosity – Temperature charts for liquid petroleum products”
- [2] Hallikainen. K.E., “Viscosmetry”, Instruments and Control System, November 1972
- [3] ASTM D445-15a (2005): Standard test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity)
- [4] FR2 911 188, Sofraser, “Procédé et système mettant en oeuvre un élément oscillant pour déterminer les caractéristiques physiques d’un produit”, 1985
- [5] FR2 921 826, Sofraser, “Method and system for determining the viscosity of a product”, 1992
- [6] FR 13 62 507, Sofraser, “Système et procédé de mesure en ligne de la viscosité d’un produit”, 1986
- [7] Belliere, L.K., et al., “On-line viscosity measurement at reference temperature and viscosity index calculation”, ISA 57th Analysis Division, Anaheim, CA, USA, 2012.
- [8] Belliere, L.K., et al., “New Analyzer for viscosity measurement at reference temperature”, ISA 60th Analysis Division, Session 02-3, Galveston, TX, USA, 2015.
- [9] The kinematic viscosities were determined by the Master Viscometer technique reported in the journal of Research of the National Bureau of Standards (Vol.52, N°3, March 1954, Research Paper 2479), ASTM methods D2162, D445, D446, D2161, ISO 3104, 3105. Density were determined using ASTM methods D4052, D1480 and D1217. Dynamic viscosity were determined using ASTM methods D2171.
- [10] Saaty, T.L., “What is relative measurement? The ratio scale phantom”, Mathl. Comput. Modelling, Vol 17, No. 4/5, pp. 1-12, 1993.
- [11] ISO 5725-1 :1994, “Accuracy (Trueness and precision) of measurement methods and results – Part 1 General principles and definitions”, International Organization for Standardization, Geneva, Switzerland, 1994.
- [12] ASTM D3764-09, “Standard practice for validation of process stream analyzer systems”, ASTM International, West Conshohocken, PA, USA, 2009.

[13] ASTM D6708-08, “Standard practice for statistical assessment and improvement of expected agreement between two test method that purport to measure the same property of a material”, ASTM International, West Conshohocken, PA, USA, 2008.

[14] Barbosa, E., “Case study – Validation and assessment of the correlation according to ASTM D3764”, ISA 57th Analysis Division, Session 08-2, Anaheim, CA, USA, 2012.