Novel viscosity determination method: Validation and application to fuel flow

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ARTICLE INFO

Article history:
Received 28 July 2011
Received in revised form 10 October 2011
Accepted 11 October 2011

Keywords:
Rheology
Porous media
Fluid flow
Physical properties
Hydrocarbon fuel

ABSTRACT

The kinematic viscosity is a major physical property to be used in numerical, experimental and analytical work in all the related fields of fluid flow research. Its determination can be based on experiments with viscometer and on calculations for single or multi-species components, possibly through the use of mixture law and other intermediate parameters. Its experimental estimation for multi-species and/or supercritical hydrocarbon mixtures under high temperature and pressure remains quite absent. The novel approach proposed in this paper is based on fluid permeation through characterized porous media. The Darcian law or the Darcy–Forchheimer equation are used depending on the flow regime. First tests have been realized with pure gaseous nitrogen at ambient then high temperature (1200 K) for several varying pressures (up to 60 bar). The accuracy of the methods can be as low as 5% by comparison to National Institute of Standards and Technology data. The main source of uncertainty is found to be linked to the characteristics of sensors. The method has been applied to liquid dodecane (from 300 to 700 K and up to 60 bar) with the same order of accuracy before testing it on supercritical n-dodecane (658–700 K up to 60 bar) for which no validation data have been found. By comparisons with computations for multi-species mixture, even multi-phase, a reasonable agreement is found. The novel viscosity determination technique opens a new field of fluid characterization in extreme operating conditions.

1. Introduction

The regenerative cooling technique consists in using hydrocarbon fuel as coolant for the thermal management of hypersonic structures and to take benefits from the endothermicity of its pyrolysis [1,2]. The complex and coupled phenomena need to be studied together to ensure the correct understanding of their relationship [3] even if specific studies dedicated to single phenomena are also required [4]. These latest can be investigated by numerical and experimental work while their entire coupling is preferably studied with numerical simulation [3]. For both approaches, the kinematic viscosity is of importance. It is used indirectly to determine other material properties such as porous media permeability [4] or directly in Computational Fluid Dynamics simulations [3,5]. This fluid property is necessary in almost all the fields related to fluid flow [6]. For this reason, numerous works can be found in open literature on its numerical and experimental determination.

The exploitation of pressure measures, in the case of capillary flow but not only, is known to give access to the dynamic viscosity [7-9]. The experimental methods found for the viscosity determination use rheometers [7], resonating tubes [6], commercial capillary and falling-body viscometers [8–10], and optical methods [11]. They are mainly indirect methods and the kinematic viscosity is often deduced from the dynamic one by using the density [6,9,11]. Nevertheless, most of the studies are related to pure fluid [6], obviously to single phase flow [6,7] and to standard conditions. The temperatures are generally lower than the boiling point and pressure around atmospheric except for petroleum related studies. Indeed, many works focus on viscosity determination of oil and heavy petroleum cuts [7,12-14]. But few results are dedicated to kerosene or hydrocarbon mixtures and only at low temperature conditions [9,15]. The pressure effect is more easily observed although it is of lower importance [16]. The work of Tate et al. must be mentioned for biodiesel [8] because they worked up to 573 K but not more to avoid pyrolysis and boiling. That of Teutenberg et al. [17] is also of interest because they proposed viscosity determination up to 523 K but not for hydrocarbons. Among all of these works, Radovanovic et al. experimentally measured liquid bio-oil viscosity in the case of heating accompanied by gaseous product formation (vaporization and possible pyrolysis) [18]. The temperature was limited (350 K) and they proposed a way to avoid gas perturbation on viscosity determination of the liquid.

Some specific methods are proposed to determine experimentally the viscosity. That of Arzate et al. can be mentioned because it is applied directly onto a process line with online measurement but it is not possible to consider reacting flow [9]. Al-Ghouti et al. [19] propose an interesting technique based on FTIR signal to determine the Viscosity Index (linked to the viscosity variation under thermal conditions) with FTIR spectroscopy.
Fig. 1. Mounting of the sample in the cell (a) and schematic of the permeation cell with sensors (b).

2. Material and methods

The experimental bench used to determine pressure drop and related mass flow rate through porous media with characterized permeability is presented with the cell containing the porous material (more details in [4]). The test methodology is described and the analytical Darcy’s law used to extract the kinematic viscosity is given.

2.1. Experimental permeation bench

A high pressure and high temperature experimental bench has been set up to enable the study of inert and reactive flows through porous structures. The bench (derived from that of the COMPARER project [29]) is composed of a high pressure pump for liquid fuel injection and of a gas injection for tests with N₂, for example. The reactor is heated by an oven and it is composed of a dedicated permeation cell in which the porous media is inserted. This cell is made of two main parts (High Pressure Chamber – HPC – for the inlet and Low Pressure Chamber – LPC – for the outlet) in order to maintain the porous media in the fluid flow and to avoid leakage (Fig. 1(a)). Despite its small size (external diameter of 40 mm), it enables measurement of the temperature, pressure and mass flow rate on each side of the porous sample (Fig. 1(b)). Over 20 measurements of pressure, mass flow rate and temperature are acquired transiently during the tests. The temperature is even measured inside the media to get the thermal longitudinal distribution. Due to limitations on the pressure sensors notably, pressure drops lower than 20 m bar cannot be measured accurately and this reduces the accuracy of the method. The results to be exploited by means of analytical formulation (next section), are obtained under stationary or transient conditions with spatial isothermal conditions (axial and radial thermal gradients are measured to be lower than 20 K) [4]. The inlet pressure is increased successively up to 60 bar by 2 bar to 10 bar increments for each temperature. The mass flow rate is imposed by the porous media. Some pyrolysis tests have also been performed with fixed hydraulic conditions with temperature increase. The pyrolysis

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
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<tbody>
<tr>
<td>K₀</td>
<td>Darcyian permeability (m²)</td>
</tr>
<tr>
<td>Kₚ</td>
<td>Forchheimer’s permeability (m)</td>
</tr>
<tr>
<td>L</td>
<td>Porous media thickness (m)</td>
</tr>
<tr>
<td>ṗ</td>
<td>Mass flow rate (kg s⁻¹)</td>
</tr>
<tr>
<td>P</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td>r</td>
<td>Constant of real gas (J kg⁻¹ K⁻¹)</td>
</tr>
<tr>
<td>S</td>
<td>Permeation surface (cross-section of fluid flow)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>V</td>
<td>Fluid velocity (m s⁻¹)</td>
</tr>
<tr>
<td>μ</td>
<td>Dynamic viscosity (Pa s)</td>
</tr>
<tr>
<td>ν</td>
<td>Kinematic viscosity (m² s⁻¹)</td>
</tr>
<tr>
<td>ρ</td>
<td>Density (kg m⁻³)</td>
</tr>
<tr>
<td>in</td>
<td>subscript referring to inlet conditions</td>
</tr>
<tr>
<td>mean</td>
<td>subscript for mean value between inlet and outlet conditions</td>
</tr>
<tr>
<td>out</td>
<td>subscript for outlet conditions</td>
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products, if any, are analysed by gas chromatograph coupled to mass spectrometer (GC/MS) and with a Fourier transform infra-red (FTIR) spectrometer NICOLET 6700 [30].

2.2. Analytical formulations for kinematic viscosity determination

The norm ISO4022 (1987 with update in 2006) proposes a method to determine the permeability of porous samples. The Darcy–Forchheimer’s equation (Eq. (1)) is used to link the pressure drop through the porous medium to the fluid velocity. Plotting the term \( \frac{\Delta P}{\mu V} \) as a function of \( \frac{\mu V}{r} \) gives the Darcian term (the origin of the curve). The angle of climb is related to the Forchheimer’s term. The pressure gradient \( \frac{\Delta P}{L} \) is calculated by Eq. (2). With this method, the dynamic viscosity, the density and the fluid velocity (Eqs. (3) and (4)) refer to the mean value computed between the inlet and the outlet of the porous media.

\[
\frac{\Delta P}{L \mu V} = \frac{1}{K_D} + \frac{\rho V}{\mu K_F} \tag{1}
\]

\[
\frac{\Delta P}{L} = \frac{P_{\text{in}} - P_{\text{out}}}{L} \tag{2}
\]

\[
\rho_{\text{mean}} = \frac{P_{\text{in}} + P_{\text{out}}}{2 \cdot r \cdot T} \tag{3}
\]

\[
V_{\text{mean}} = \frac{\dot{m}}{\rho_{\text{mean}} \cdot S} \tag{4}
\]

This method is extensively used to determine permeability terms [4] even if other methods are available for such measurement [31]. Nevertheless, for some metallic and composite materials at least, it has been shown that both Darcian and Forchheimer’s permeabilities are constant [4]. As a consequence, if a well characterized material is used, Eq. (1) could be used to determine the kinematic viscosity by assuming the value of permeation terms. In this study, low mass flow rate only will be considered to avoid considering the Forchheimer’s term (the second term of the right side in Eq. (1) is negligible). The Eq. (1) can be rewritten to express the pressure drop through the porous media as a function of kinematic viscosity (Eq. (5)) after rearrangement of terms, notably using the conservation law. The Eq. (5) is known as the Darcy’s law. It can thus be possible to plot the ratio of dynamic viscosity on density as a function of measured pressure drop and mass flow rate notably (Eq. (6)). The geometrical parameters and the Darcy’s term are supposed to be constant. Thus, the kinematic viscosity is obtained as a function of experimental time and even of temperature if it varies because the ratio \( \frac{\Delta P}{V} \) is independent of the thermal effect. This enables conducting stationary and transient studies.

\[
\Delta P = \frac{\mu}{\rho} \times \frac{L \times \dot{m}}{S \times K_D} \tag{5}
\]

\[
\frac{\mu}{\rho} = \frac{SK_D}{L} \times f \left( \frac{\Delta P}{\dot{m}} \right) \tag{6}
\]

The use of hydrocarbon fuel, under high temperature conditions, generally produces pyrolysis [4] and this can be accompanied by coke formation [32] which impacts on the Darcy’s term (clogging of the material porosity). Thus, the results must be carefully analysed and are not valid if any coking activity is detected during the tests. The GC/MS and FTIR apparatus are used in this sense notably [30]. If no carbon deposit is produced but only pyrolysis products, the kinematic viscosity is that of mean composition which can change within the through flow. Indeed, due to the use of a global law instead of a one dimensional equation, the chemical variations cannot be accurately considered and the mean properties between inlet and outlet are the resulting data of this method. This is also the case for pure gas flow of single species such as nitrogen. For this reason, the pressure drop should be limited and the Darcy’s term should be as high as possible (but not too much to ensure the Darcy’s law is still applicable). Furthermore, if the fluid is found under two phases, a single viscosity is not physically justified because the two phases probably filtrate at different speeds notably. This could also be the case with multi-species flow because of differentiated diffusion notably. Nevertheless, the numerical codes which consider such flows may not take explicitly both phases into account. Thus, they use mixture laws which are difficult or impossible to validate [29]. Providing a so called “equivalent kinematic viscosity” presents the major advantage to enable validating both viscosity computation and mixture law efficiency. It can also be noted that the viscosity value of one of the chemical components among others cannot be differentiated and extracted from the measurements, at least by using the proposed approach. This is not seen as a drawback because for a lot of numerical codes, the mean value only is required [33]. By using analytical apparatus for chemical composition, the viscosity values are linked to the fluid composition. The present results could serve later as validation data for numerical methods of viscosity determination.

The utility of the proposed method to determine the fluid property is clearly seen when observing the NIST data (Fig. 2). For dodecane (critical coordinates of 658 K, 18 bar), the results are found up to 700 K and not more due to possible pyrolysis for higher temperature. Furthermore, the supercritical effect is shown to impact the viscosity because no separation between gas and liquid phase appears at 60 bar (Fig. 2). Thus, the range of test conditions proposed in this paper is quite new and of relevance because no data are available in extreme conditions.

3. Results and discussion

Some permeation data are presented for gaseous nitrogen and liquid n-dodecane flow through SS3 porous media (Class 3 Porous Stainless Steel sample [4]) under ambient temperature (Section 3.1) to validate the method of viscosity determination. Then, the latter is applied to the same fluids under high temperature and pressure conditions (Section 3.2). Finally the technique is used on supercritical n-dodecane and multispecies/multiphase flow under pyrolysis (Section 3.3).

3.1. Validation of the method with N\textsubscript{2}, CH\textsubscript{4} and n-C\textsubscript{12}H\textsubscript{26} at ambient conditions

A 2 mm thick SS3 sample is used for N\textsubscript{2} flow at 294 K with a Darcian term of 1.82 \times 10^{-13} m\textsuperscript{2} to limit the pressure drop inside the porous media (Fig. 3(a)). It reaches a maximum of 4.5 bar for very large mass flow rates (5.5 g s\textsuperscript{-1}) and this is not suitable for the present study because it aims at using the Darcy’s law which is mostly appropriate to low speed flow. When considering the Darcy–Forchheimer’s equation (Eq. (1)), the two terms of the right side have been computed for each acquired data point. Their ratio enables us to observe (Fig. 3(b)) the relative importance of each laminar (Darcy) and turbulent (Forchheimer) term. For a ratio
of 1 around 620 s, both terms are equivalent. This shows that a maximum mass flow rate of 0.5 g s\(^{-1}\) is authorized to ensure that the Forchheimer's term remains "negligible" (about 16% the Darcy's one at a time of 400 s). The corresponding pore Reynolds number is 1.2 for this flow rate. The best option would probably be to use even lower mass flow rate but a minimum value is required to keep a good accuracy on the flow rate and on the pressure drop determinations. As a consequence, the pressure drop is lower than 1.5 bar and it can reasonably be considered that the test is conducted under isobaric conditions. This drop directly impacts the relative accuracy of the pressure to be considered because for pressure around 60 bar, the corresponding error is only of 2.5% while it is of 50% if a 3 bar pressure supply is considered (inlet pressure of 3 bar and outlet one of 1.5 bar for this maximum flow rate). Thus, it is recommended that the lower the pressure of measurement is sought for the viscosity determination, the lower the mass flow rate is authorized. This pilots the choice of experimental sensors and devices to be used.

The kinematic viscosity has been determined by use of Eq. (6) and compared to NIST data for all the ranges of mass flow rate (Fig. 4(a)). The mean pressure (arithmetic one between inlet and outlet pressure) is shown to impact on the viscosity. The error bars correspond to 30% and have been applied on higher pressure values only for a practical view of the plot. This implies that for mass flow rate up to 1 g s\(^{-1}\), the agreement remains excellent (lower than 5%) and that the Forchheimer's effect is no longer negligible above it. It can be noticed that the nitrogen remains gaseous because the critical pressure is not reached (34 bar) although the critical temperature is exceeded (126 K). Another test with much lower flow rate and pressure conditions clearly confirms the good prediction of the method (Fig. 4(b)). Nevertheless, it is given to show the effect of transient flow rate oscillations on the viscosity determination. This is due to the acquisition frequencies of pressure sensors and Coriolis flow meter which are different and not perfectly synchronized. This can introduce uncertainty up to 20%. The present viscosity determination method has been applied to a wide set of porous media [4]. All give similar accuracy as exemplified by data on the SS5 sample (3.88% at 6 bar) with the Darcian term about one order of magnitude higher than of the SS3 sample (Fig. 5).

This test has been done a number of times over several test conditions by varying the porous media notably. The same level of accuracy is always found for nitrogen (Fig. 5). A test with successive methane injections has been done to observe the effect of random chemical composition variation during the test (Fig. 6). The viscosity can change by about 50% for lower pressure (3 bar) but this variation decreases with increase of pressure. Thus, the viscosity determination method is less sensible for high
pressure conditions to chemical composition change than for low pressure ones. Tests with liquid n-dodecane at 298 K enable further validation for the liquid phase after these tests under gas phase. A limitation on mass flow rate is observed (Fig. 7(a)) for lower values due to the lack of sensor accuracy (low pressure losses). The accuracy of the viscosity determination method is much better (Fig. 7(b)) for both high mass flow rate and absolute pressure (3.8% at 12 bar). This was also the case for the gas phase but it is more easily seen on liquids due to the order of magnitude which separates gas from liquid viscosities. The sensors and regulation devices are responsible for this lack of accuracy and not the method itself. The strong oscillations of viscosity observed at low flow rate (50 mg s\(^{-1}\)) in Fig. 7(a) are much lower at 200 mg s\(^{-1}\) (Fig. 7(b)).

On the basis of these present results at ambient temperature, the technique proposed in this paper is judged to be very promising and it is applied to test temperatures up to 1200 K in the next section.

3.2. Application to \(N_2\) and \(C_{12}H_{26}\) at high temperature

The SS3 sample is still considered for this section and the temperature is increased by successive steps or by regular thermal setup increase. This difference has been verified to not impact on the results and on the accuracy of the method. It is only important for the next section in the case of fuel pyrolysis. Nitrogen has been studied through a wide variety of conditions with mass flow rate and inlet pressure variations. Due to the coupling of both parameters in porous flow, the flow rate variations are seen as pressure variation and the present data should be compared to several NIST data series. For example (Fig. 8(a)), a test up to 25 bar has been done with maximum mass flow rate of 3.5 g s\(^{-1}\). All the values of viscosity are in the range of NIST data but it is difficult to validate each point of measure because the pressure varies too much for each temperature. This is clearly observed on another test (Fig. 8(b)) for which the mass flow rate varies from 80 mg s\(^{-1}\) to 1 g s\(^{-1}\). It can be noticed that a mean slope of viscosity variation may be found lower than for NIST data but this is hazardous due to the pressure variation. The results are judged to be very satisfactory because they are all in the range (up to 12.5 bar for Fig. 8(b)), which is a very significant result. To the author’s knowledge, no measure of viscosity, even for nitrogen, is available up to 1000 K and over. Another test with the SSS sample shows a very good agreement up to 1200 K (Fig. 9). The pressure is given (up to 30 bar) to highlight the better accuracy of the measures for higher pressure due to the sensors’ limitation at lower pressure.

The results for dodecane are presented in three steps. For pure n-dodecane (without pyrolysis), the cases with pressure under 18 bar are related to liquid phase even with temperature increase and can be presented up to 700 K (limit of pyrolysis [4]). For operating pressure over 18 bar and up to 60 bar, the critical temperature of 658 K must be considered to observe the change from liquid phase to supercritical state. Finally, the dodecane pyrolysis is presented in the next section.

The test with dodecane at 15 bar is interesting because it allows a phase change around 654 K as seen in NIST data (Fig. 10(a)). Due to the limitation of pressure sensors, the determination of kinematic viscosity is more difficult when the temperature increases because, contrary to the gas phase, the viscosity decreases and consequently, the accuracy also. One order of magnitude can be found. This is illustrated by successive hydraulic steps (mass flow rate increase) at “constant” temperature. These steps should not impact on the viscosity but, in fact, they are also visible in this property (for temperatures around 350, 415, 580 and 650 K). This is because the related pressure drop is too low and hence not seen by the sensors and this directly impacts the viscosity determination due to Eq. (6). At 60 bar, the thermal increase also decreases the viscosity by a factor of 10 at least but no separation between gas and liquid exists anymore (Fig. 10(b)). The discrepancies between NIST data and this work increase with the temperature rise. The mass flow rate is probably too low but again, this is mainly due to the pressure losses which cannot be measured under 20 m bar due to the sensors. With NIST viscosity, the pressure drop has been computed (Eq. (5)) to be lower than 1 m bar above 400 K. This was anticipated during this work. This is the reason why gas flows have been also studied and why liquid tests at ambient conditions were conducted.

3.3. Application to pure n-dodecane and to related pyrolysis products under single and multi-phase with numerical comparison

The experimental results for dodecane pyrolysis products have been compared with computations of kinematic viscosity (used
in the code RESPIRE [29]). The density is numerically determined as a function of pressure, temperature and mixture composition with the real gas equation of state considering the Lee–Kesler tables and the Pitzer acentric factor through the compressibility factor [29,33]. The dynamic viscosity is obtained [29,33] by the Guo method [35] based on the Peng Robinson equation. Its accuracy is known to be limited but even a factor of 10 on this property is not dramatic for regenerative cooling application [29]. The Chung method notably is known to be better [36]. Several mixture laws are used to give a mean value of multi-phase and/or multi-species fluid [29,33].

As example of numerical computation, two cases under sub- and supercritical pressure (Fig. 11) are given with the mass fraction of dodecane to observe the viscosity change as a function of temperature and of chemical composition. These calculations correspond to the COMPARER configuration (open SS tubular reactor) and not to the permeation test but they are at least of qualitative interest. The first value of viscosity is given around 620 K (Fig. 11(a)). It decreases when pure dodecane is heated before increasing during the pyrolysis (from 800 to 1000 K). Some of the species are liquid and others are gaseous. A numerical mean viscosity is considered even if not physical but this is compulsory for 1-D simulations. For pressure around 60 bar, all the possible pyrolysis products are supercritical when the temperature of dodecane decomposition is reached [29]. The viscosity is found to increase with the temperature but the chemical composition also impacts its value because its variation is not regular (Fig. 11(b)).

Comparing these numerical results to experimentally determine kinematic viscosity gives very interesting results. The values are of the same order and a maximum of 50% is found among the results (Fig. 12). All the curves present a slight decrease and then increase in the range 680–880 K. Due to the difficulty to get such results and because of their novelty, the agreement is judged to be satisfactory. The determination of the kinematic viscosity under pyrolysis (if no coking activity is detected) is demonstrated to be possible with adapted pressure sensors and with specific experimental methodology (constant flow rate and thermal increase would be better).

4. Conclusions

The determination of kinematic viscosity has been proposed with a newly developed method based on the Darcy’s law which provides a relationship between the pressure drop through a porous media and the related mass flow rate. This formulation can be rearranged to express the viscosity as a function of the ratio of both measures. A specific test bench developed for porous media characterization enabled over hundred tests to be performed with nitrogen, hydrogen, methane, water, dodecane and some of their mixtures for temperature up to 1200 K and pressure up to 60 bar. Single and multi–species flows have been observed under single or multi–phase and even at supercritical state. On the basis of these results, a validation of the method has been proposed with pure nitrogen and dodecane flow due to the lack of data for other test conditions. The technique has been applied to dodecane under pyrolysis. Some comparisons to numerical simulation have been provided. For all the cases, the viscosity is at least determined with the same order of magnitude even if its validation is not possible due to unavailable validation data. The method is judged to be promising and its accuracy, when possible with other experimental results, is estimated around 5% with best stabilized and controlled conditions. Up to 16% of error can be encountered due to the omission of Forchheimer’s term over 0.5 g s⁻¹ and this would require treating the flow with Darcy–Forchheimer’s equation instead of the Darcian law for high speed flow. Up to 20% of uncertainty may be observed in the case of transient oscillations in the process because of the steady-state validity of these equations.

As perspectives, the experimental conditions are planned to be better controlled and new sensors should be used in a future work particularly to enable better precision for high temperature tests with dodecane. It is the only method to the authors’ knowledge to furnish a single value of kinematic viscosity for multi-component mixtures and to be applicable to high temperature and pressure conditions (even at supercritical state) in comparison to common viscometers. It presents reliable viscosity values under controlled...
Fig. 10. Effect of sensors’ inadequate range for dodecane viscosity determination at 15 bar (a) and 60 bar (b).

Fig. 11. Kinematic viscosity computed by the RESPIRE code at 15 bar (a) and 60 bar (b) for dodecane under heating and pyrolysis.

Fig. 12. Numerical and “corrected” experimental data of kinematic viscosity at 15 and 60 bar for dodecane pyrolysis products.

isothermal and isobaric conditions for monitored chemical fluid composition. The viscosity is also given in case of multi-phase flow despite its limitation of physical meaning. This result is particularly interesting to validate the numerical method of viscosity determination and mixture laws but also to propose for example data tables to be used in numerical codes.

Acknowledgments

This work was supported by the ESA-ESTEC, Contract no.: 3-12861/09/NL/PA. The authors would like to sincerely thank J. Bioud from PRISME, J. Steelant from ESA and M. Bouchez and B. Le Naour from MBDA-France for their help involving this project. The highly valuable work of D. Blanc and D. Courillault involving the measurement cell has been greatly appreciated.

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