**Abstract**

The object of study for this work was the thermal conductivity of gaseous binary systems in several ratio combinations between components, which thermal conductivity was also studied individually. In total, two systems were studied; the first system was composed of nitrogen and isopentane and was completely studied through a set of three different ratios in composition, while the second was composed of isopentane and cyclopentane and was only partially studied with only one ratio of composition studied. The analysis of the results followed two previously developed models in order to further validate and accurate such methods. The model denominated LPUR allows for the prediction of thermal conductivity of pure components and was applied to cyclopentane. The model denominated Extended Wassiljewa Model allows for the estimation of the thermal conductivity in mixtures and was applied to all studied mixtures in the system of nitrogen and isopentane.

**Key words:** Thermal Conductivity; Transient Hot Wire Method; Wassiljewa Model; Nitrogen; Isopentane; Cyclopentane; Binary Mixture, Experimental Data

**1 Introduction**

Rigid polyurethane and polyisocyanurate foams, denominated respectively as PUR and PIR, are applied to a large number of purposes due to their high thermal insulating capacity.

Among those applications are thermal insulation boards to pipe insulation, technical refrigeration processes or industry applications.

These particular kinds of foams are also very common in domestic refrigerators for example, being PUR foam the preferred insulating material, due to several advantages: self-adhesive rigid foam systems enable a weight-saving sandwich construction to be produced in a single operation and the excellent thermal
insulating properties permit a relatively small wall thickness.

Although the heat conduction of the solid material of the foam influences the heat transfer of such a foam, it is in fact the gas or vapour trapped inside the voids of the foam that mainly determine the amount of heat transfer possible. These gases that work as blowing agents account for up to 65 % (and never less than 60 %) of the heat transfer of the foam.

The evaluation of a blowing agent as an insulator is done by the comparison of the thermal conductivity of such an agent in its gaseous form to the thermal conductivity of air that it displaces. In accordance to the reference [2], the normal conductivity of air at 300 K is of 27 mW m\(^{-1}\) K\(^{-1}\).

Until the middle of the decade of 1990 the most used blowing agent was CFC-11 for it presented a value of thermal conductivity of 8,3 mW m\(^{-1}\) K\(^{-1}\) at 300 K (as presented on reference [3]). However, this gas has an elevated Ozone Depletion Potential, which, in virtue of the Montreal Protocol, made it unusable.

Research for the best replacement of CFC-11 was undergone both in Europe and in North-America, resulting in different options.

While in North America the research focused primarily in HCFC’s and, afterwards, due to the implementation of stricter restrictions and regulations, in HFC’s with a null Ozone Depletion Potential; in Europe the research focused in hydrocarbons, mainly cyclopentane and mixtures containing cyclopentane, also possessing a null Ozone Depletion Potential.

Comparing both solutions, HFC’s have the advantages of being non-flammable and a lower gas phase thermal conductivity, and hydrocarbons have a lower Global Warming Potential (the reason why they were chosen in Europe, as can be read in reference [4]) and optimal thermophysical properties for the application to insulation materials.

During the lifetime of a foam, the constitution of the mixture of gases inside the foam pores is not constant, leading to a significant loss of the thermal efficiency. This is due to diffusion processes of both air inwards the foam cells and of the gases outwards the foam cells.

The variation of a PUR foam’s thermal conductivity happens, according to a study carried out at the Oak Ridge National Laboratory, USA [5], in two clearly separated phases. The first is characterized by a rapid increase on the thermal conductivity, which is assumed to be caused by the diffusion of air into the cells; the second is characterized by a slower increase on the thermal conductivity, which is attributed to the diffusion of the original mixture of gases to the exterior of the cells.

Adding to the diffusion effects, also properties of the foam itself – such as the types of isocyanate and polyol used, the cell’s size and openness, the blowing agents used and their initial composition inside the cells – and the interactions between the blowing agents and the external atmospheric gases – defined by
solubility and diffusion coefficients – contribute to the definition of the kinetics of the aging of the foam.

The work that has been carried and is presented here is inserted in a larger project that focuses on the thermal conductivity of the gas phase inside the foam cells at the same time as it focuses on the research of a blowing agent that conjugates good thermophysical properties as well as a stability of such properties throughout the lifetime of the foam. To that purpose it’s particularly useful to study mixtures that include nitrogen, for being that the most abundant gas in the atmosphere; such mixtures will give a precise idea of the behaviour of the diffusion-aged foams.

The project also intends to establish a systematic prediction method for the thermal conductivity of gas mixtures, either by proving pure theoretical modelling methods, or through the development of a semi-empirical method. More specifically, in the study carried out in performing this thesis, the objective on this matter was to further aggregate data to a previously [1] presented model, validating it, if possible.

In this work, the thermal conductivity of pure cyclopentane and mixtures of isopentane, nitrogen and cyclopentane was measured sing the trasient hot-wire method, which is the IUPAC standard method for the determination of thermal conductivities [6]. The measurements were performed at temperatures between 303 K and 395 K and at pressures up to 1.0 MPa.

The obtained results were correlated with the Wassiljewa mixing rule modified by Mason and Saxena. A study of how the parameter $\varepsilon$ changes with temperature, pressure and composition of the mixtures was performed, culminating in the development of a mathematical model which allows the calculation of values for this parameter for any given conditions. Another model is also presented for the calculation of $\lambda$ values for any given pressure and temperature, for pure compounds.

Thermal Conductivity

In any material, solid, liquid or gas, a heat flux occurs whenever a temperature gradient is applied. This heat flux starts in the high temperature region towards the part of the material with the lower temperature.

If the energy is transferred by conduction, the heat flux per unit area is proportional to the temperature gradient:

$$Q = -\lambda \frac{\partial T}{\partial x}$$

where $Q$ is the heat flux per unit area and $\frac{\partial T}{\partial x}$ is the temperature gradient in the direction of heat flux. The proportionality constant $\lambda$ is the thermal conductivity. The numerical value of the thermal conductivity indicates the velocity of the heat transference when the material is perturbed from an equilibrium state by a temperature gradient. The negative signal is required by the second law of thermodynamics, since $\frac{\partial T}{\partial x}$ is negative (the temperature decreases in the direction of the heat flux).

The physical mechanism of thermal conduction of gases at low pressures is
simple. The gas molecules are in a continuous and random movement, colliding with each other, exchanging energy and movement. When a molecule goes from a high-temperature region to a low-temperature region, it transports kinetic energy to this last region increasing the kinetic energy in the low-temperature region, consequently the temperature increases.

The Method

The measurements of thermal conductivity in this work were performed in an apparatus based on the transient hot wire method, the standard method adopted by IUPAC to evaluate thermal conductivity. The theoretical bases of this method, as well as its equations and assumptions, have been described intensively by a good number of authors [6-10] and for that reason only a short note on the subject will be presented here.

The method consists in the application of a time dependent perturbation – a heat flux, in this case – to a fluid initially in equilibrium, using a very thin platinum wire for the purpose. According to equation 2, where \( a \) stands for the thermal diffusivity and \( C = \exp (\gamma) \), \( \gamma \) being Euler’s constant (\( \gamma = 0.57721… \)), the evolution of the temperature gradient registered in function of time will allow the calculation of the thermal conductivity of the fluid

\[
\Delta T = \frac{q}{4\pi\lambda} \ln \left( \frac{4at}{r_o^2 C} \right) \tag{2}
\]

This equation corresponds to an ideal model in which a number of considerations and approximations are made. In reality, several correction factors have to be applied for the correct calculation of \( \lambda \) from the raw data. Some approximations however were already accounted for during the design and careful dimensioning of the apparatus, making the correspondent corrections negligible.

Concerning the platinum wire, the ideal model makes the following considerations:
- Infinitely long heat source
- Linear, vertical and with infinitesimal diameter
- Zero heat capacity and infinite thermal conductivity
- Heat dissipation constant and radial

Concerning the fluid, the model stands that:
- Isotropic and infinite fluid
- Physical properties independent of the temperature

In addition, the model also considers that the heat transfer occurs exclusively by conduction, without any occurrence of convection or radiation.

Reports from previous works carried out with this same apparatus also contain information about the theory behind the method, together with the description of the apparatus [10-12].

In the present work, bare platinum wires were used as well as the same equation and approximations considered by Santos and Oliveira [13, 14] and Fonseca [1].
2 Results and Discussion

Thermal Conductivity of mixtures

Several models have been proposed to explain and define the thermal conductivity of mixtures from the values of thermal conductivity of the pure components, one of the most significant being developed by Wassiljewa [14]. A number of changes to the initial model have been proposed along the time by different authors. The solution presented by Maxon and Saxena [19] is one of the most widely used since it allows good results and it is relatively simple, and it will be used in this work. More information about this subject can be found in literature [18-21] and in the reports of previous workers [11-13].

According to Wassiljewa, the thermal conductivity of a mixture can be calculated from the corresponding values for the pure components through the equation 3, where $y$ represents the mole fraction of the component and $A_{ij}$ is the Wassiljewa function for the binary mixture between components $i$ and $j$.

$$\lambda = \sum_{i=1}^{n} y_i A_i = \sum_{i=1}^{n} \frac{n}{\sum_{j=1}^{n} y_j A_{ij}}$$  \hspace{1cm} (3)

Maxon and Saxena [19] stated that the function $A_{ij}$ can be calculated by equation 4, where $M$ stands for the molar mass and $\varepsilon$ is a numerical constant close to unit.

$$A_{ij} = \frac{\varepsilon \left[1 + \left(\frac{\lambda_{wz}}{\lambda_{wj}}\right)^{0.5} \left(\frac{M_i}{M_j}\right)^{0.25}\right]^2}{8 \times \left(1 + \frac{M_i}{M_j}\right)}$$  \hspace{1cm} (4)

For a long time, and in the work of several authors, $\varepsilon$ was considered to assume a constant value for each mixture, regardless of the temperature and pressure values. In the present work, following the first attempts from Fonseca [1], there is an attempt to go further and evaluate how the value of $\varepsilon$ can be influenced by both these parameters. This became possible with the increase in both the precision and accuracy of the apparatus, result of the several improvements performed, not only in this work but in the previous ones as well.

Nitrogen and isopentane system

![Figure 1: Extrapolation of the data obtained for the system N₂ + i-C₅ for a pressure of 1 bar](image)

In the present case, the thermal conductivity seems to evolve linearly with the progression of temperature, though in different extension for the different compositions of the mixture, being stronger for the greater compositions of nitrogen and less accentuated for greater compositions of isopentane. Analysing the
slopes, it is possible to conclude that at a temperature above 400 K there would be a point at which nitrogen and isopentane would have the same value of thermal conductivity. That would happen at 481 K for the pressure of 1 bar. This temperature is much greater then the top limit studied in this work and it is not certain that the apparatus could withstand such conditions. However, this linear change happens with different extension for each concentration, which makes it impossible to determine a mathematical expression that relates the thermal conductivity with both temperature and concentration of the components simultaneously.

It is also noticeable that at a given pressure the increase of thermal conductivity is not regular as well. It is evident that the increase from pure isopentane to a mixture with a composition of 25 % of isopentane is much smaller than the increase from the mixture with a 75 %composition in isopentane to pure nitrogen.

That can be further seen in figure 2 where $\lambda$ is represented as a function of the composition of the mixtures for each temperature. The lines refer to the Wassiljewa method, with the Maxon and Saxena modifications. The parameter $\varepsilon$ was fitted individually for each temperature from the experimental data. The deviations between the experimental points and the Wassiljewa model are presented in figure 3.

The agreement between the method and the experimental data is within an acceptable limit, not overcoming 1,2 % and with an average deviation of 0,6 %.

The values originated by the independent fitting of the values of $\varepsilon$ with the Wassiljewa model for each combination of temperature and pressure are presented on Table 1.
Table 1: Values obtained for the fitting of $\varepsilon$ for different pressures and temperatures.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>1 bar</th>
<th>5 bar</th>
<th>10 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (333,15 K)</td>
<td>0,93602</td>
<td>0,90759</td>
<td>0,87478</td>
</tr>
<tr>
<td>$\varepsilon$ (353,15 K)</td>
<td>0,93475</td>
<td>0,91414</td>
<td>0,89049</td>
</tr>
<tr>
<td>$\varepsilon$ (373,15 K)</td>
<td>0,93360</td>
<td>0,91992</td>
<td>0,90440</td>
</tr>
<tr>
<td>$\varepsilon$ (393,15 K)</td>
<td>0,93263</td>
<td>0,92503</td>
<td>0,91678</td>
</tr>
<tr>
<td>$\varepsilon$ (413,15 K)</td>
<td>0,93180</td>
<td>0,92957</td>
<td>0,92783</td>
</tr>
</tbody>
</table>

Making use of the equation 5 proposed by Fonseca [1] for the prediction of values of $\varepsilon$, it was possible to arrive at the values for the parameters that are present in table 2

$$\varepsilon = A_1 \cdot e^{A_2 P} \cdot T^{A_3 P + A_4}$$

(5)

Table 2: Values obtained for the parameters in equation 5, fitting the experimental values of $\varepsilon$.

<table>
<thead>
<tr>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,28384</td>
<td>-0,19737</td>
<td>0,03273</td>
<td>-0,05340</td>
</tr>
</tbody>
</table>

Figure 4 shows for various values of pressure how $\varepsilon$ changes with the temperature. The lines refer to calculations performed with equation 5. In Figure 5 are represented the deviations of the experimental points relatively to the values given by the equation 5.

In order to further verify the usefulness and good capacity of the LPUR equation proposed by Fonseca, the data for pure cyclopentane was modelled through equation 6 presented below.

$$\lambda = A + B T + C P + D T P$$

(6)

This could be done for, as Fonseca also noticed for his own data on thermal conductivity for pure compounds, $\lambda$ presents a linear dependence to both temperature and pressure.
Table 3: Values obtained for the parameters in equation 6, for cyclopentane.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-23.45460</td>
<td>0.11309</td>
<td>-0.95632</td>
<td>0.00241</td>
</tr>
</tbody>
</table>

Verification of LPUR eq. for cyclo-pentane

Isopentane and Cyclopentane system

Since only one composition of mixture for this system was studied, any results presented here would be nothing more than demonstrative and, therefore, meaningless.

It was decided to simply leave the data prepared for future treatment when more data is made available.

3 General Conclusions

Accomplished in this work

One pure component was studied in this work, producing good quality results that went to further prove the good applicability of the previously proposed LPUR model. The applicability of the model was proven for cyclopentane, therefore adding one more component to the list of the hydrocarbons for which the model has proven valid.

Also two binary systems were studied in this work with satisfactory results.

One of these systems showed a behaviour that could be predicted correctly by the previously proposed Extended Wassiljewa Method, this way contributing with further proof of the validation of this particular model.

The other system was very limitedly studied due to a lack of time – derived of apparatus related difficulties – and it was impossible to take any conclusions from it at this point.

Recommendations for future work

First and foremost, the studies of the isopentane and cyclopentane system should be continued in order to obtain a full set of raw data that will allow proceeding with the modelling of the system with the previously proposed equations. In fact, seeing that the results for this mixture had to be reduced to such a short and, therefore, inaccurate ensemble, these experiments should be redone.

Second, the results obtained with the system consisting of nitrogen and isopentane could be further improved with the measuring of some points at low temperatures. Since this system has a low amount of different pressure points for he lower isotherms, if they could be improved it would be greatly benefit, for the results and the conclusions concerning this system.
Third, the future work could focus on three component systems, consisting of nitrogen and any two components combination between isopentane, cyclopentane and n-pentane. This would be easy to implement because when supplying nitrogen to the measuring cell, the pressure vessels are not needed, which would allow to maintain prepare a three component mixture in the cell by maintaining two hydrocarbons in the pressure vessels. The experimental procedure for the preparation of this suggested mixture would not be complicated neither rather different from the one that is in use at this point, being that the only precaution would be to always establish a mixture that involves nitrogen for only two pressure vessels are available, and that the nitrogen is added as the final component. A new model would have to be defined for these systems and, in the future, a third pressure vessel could be added to the apparatus in order to achieve new systems – a desired example would be the combination of isopentane, cyclopentane and n-pentane.

4 References


[18] – A. Wassiljewa, Phys. Z., 1904, 5, 737 (cited in [20]).


