**THE THERMAL CONDUCTIVITY OF LIGHT HYDROCARBONS**

**IN THE SUPERCRITICAL REGION**

**Bernard Le Neindre1, Yves Garrabos2, Farid Gumerov3**

1 Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux, CNRS, (UPR 3407), F-93430, Villetaneuse, France.

E.mail : bernard.leneindre@lspm.cnrs.fr.

2 ICMCB-CNRS UPR 9048, Université Bordeaux I, 87 Av du Dr A. Schweitzer, F 33608 PESSAC Cedex, France. E.mail :garrabos@icmcb-bordeaux.cnrs.fr

3Kazan National Research Technological University, 68 K. Marx Street, Kazan, 420015 Tatarstan, Russia. E.mail : gum@kstu.ru

# ABSTRACT

The thermal conductivity of propane, pentane and hexane, in the supercritical domain, is measured in a coaxial cylinder cell operating in steady state conditions. A phenomenological equation was used to analyze the critical enhancement of the thermal conductivity of these hydrocarbons, from their critical temperature Tc to a temperature Tf where the density fluctuations are negligible, and in a large range of densities. For these hydrocarbons the estimated deviations between experimental and calculated data are less than ± 5 %. This equation was generalized to calculate the supercritical behavior of the thermal conductivity of other light hydrocarbons.

# INTRODUCTION

Recently there was a renew interest for supercritical fluids in science and industry due to their versatile potential for application. The applications for supercritical fluids range from extraction, particle formation, reactions, cleaning to dyeing. Knowing the thermal conductivity of SCFs is essential in the design of process equipment such as heat exchangers for the recovery of thermal energy in SCF extraction or fractionation processes. Introduced in 1936, a process for the refinement of lubricating oils used propane as solvent of choice. This process was operated in the vicinity of subcritical propane. In 1946, the Solexol process was introduced for the purification of vegetable oil (to produce triglycerides) and fish oil (to produce vitamin A). Supercritical propane was used as solvent. As refining technology in the petrochemical industry, supercritical pentane was used since 1976 in the ROSE process (Residuum Oil Supercritical Extraction) to extract low molecular weight components. The ROSE process is a very efficient solvent-extraction option for recovering higher value products from residuum. ROSE units yield de-asphalted oils that are excellent feed-stocks for fluid catalytic crackers and hydrocrackers, as well as recover resins and asphaltens that have a variety of uses.

# EXPERIMENTAL RESULTS

Several measurements of the thermal conductivity of light hydrocarbons in the supercritical region have been carried out in various laboratories. Some of them are reported in Table 1. NIST Standard Database 23, REFPROP Version 7 was used to calculate the density **(with accuracy of the order of ± 0.2 %) and other thermodynamic properties [11].

**Table 1**. Range of Measurements and Thermodynamic Constants of Hydrocarbons

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Fluids | Temperature range, K | Pressure range, MPa | Tc,K | Pc,MPa | c,kg.m-3 | Authors |
| Methane | 110 - 310 | 0.3 -70 | 190,56 | 4,5992 x 106 | 162,66 | [1] |
| Ethylene | 283 - 581 | 1 - 100 | 282,35 | 5,0418 x 106 | 214,20 | [2] |
| Ethane | 308 - 365 | 1 - 28 | 305,33 | 4,8718 x 106 | 207,00 | [3] |
| Ethane | 305 - 333 | 1.946 - 18.274 |  |  |  | [4] |
| Propane | 85 - 600 | 0.1 - 70 | 369,83 | 4,2477 x 106 | 220,00 | [5] |
| Propane | 370 - 381 | 0.1 - 15 |  |  |  | [6] |
| Butane | 298 - 600 | 0.1 - 70 | 425,13 | 3,7960 x 106 | 228,00 | [7] |
| Isobutane | 300 - 630 | 1 - 100 | 407,81 | 3,6290 x 106 | 225,50 | [8] |
| Pentane | 470 -526 | 0.1 - 30 | 469,70 | 3,3700 x 106 | 232,00 | [9] |
| Hexane | 508 - 595 | * 1. 30
 | 507,82 | 3,0340 x 106 | 233,18 | [10] |

**CORRELATIONS**

We make an analysis of the data based on the residual concept, for which the thermal conductivity is represented as a sum of three contributions

*λ(T,ρ) = λ00(T) + δλ(ρ) + Δλc(T,ρ),* (1)

where *λ00(T )*is the dilute-gas thermal conductivity for the zero density limit, which is dependent only on the temperature, *δλ(ρ)* is the residual thermal conductivity, which is dependent only of the density, and *Δλc(T,ρ)* is the thermal conductivity critical enhancement approaching the liquid-gas critical point, which depends on both density and temperature. This representation allows the theoretically based analysis of each contribution to be considered separately.

# CRITICAL ENHANCEMENT

The analysis of the thermal conductivity hydrocarbons in the critical region was carried out in terms of the effective values of the critical exponents, using a similar approach of the crossover modelling initially proposed by Luettmer-Strathmann and Sengers12 to describe the singular behaviour of the thermal diffusivity, where *Cp* is the isobaric specific heat The above separation of the thermal conductivity into critical and background contributions implies a corresponding separation of the thermal diffusivity *DT* into a background contribution and a critical contribution

, (2)

The mode coupling of critical dynamics theory predicts that *ΔDc* of a critical pure fluid in the hydrodynamic limit can be written asymptotically near its critical point as

, (3)

where*η* is the shear viscosity, *ξ* is the long range correlation length of the density fluctuations, and *RD* ≈ 1.05 is a universal amplitude combination [13], [14]

# CRITICAL ENHANCEMENT ALONG THE CRITICAL ISOCHORE

Along the critical isochore, *Δλc(T,ρc),*can be also rewritten following the approximated form [15].

 , (4)

where  (5)

On the other hand, it was found along the critical isochore over an extended temperature range of any pure fluid [16], that the rescaled isothermal compressibility  , lies on a single curve when it is plotted as a function of the rescaled temperature , where ;;; and is the slope of the vapour pressure curve at the critical point. is the usual reduced form of the isothermal compressibility. A similar analysis [16] has also shown that the rescaled correlation length, where  is a single function of *τ*. Consequently, he rescaled quantity should be also a single function of *τ*

The fit of the complete data set by an effective pure power law with adjustable exponent and adjustable amplitude gives for propane; for pentane ; for hexane .

An alternative empirical approach consists to explicit directly the effective pure power laws that are only valid in this restricted temperature range. We have thus rewritten eq.4 as follows

 (6)

In eq. 6 we have introduced an effective amplitude term *RD,eff* to account for the effective values of the exponents that describe the observed temperature behaviour of and **along the critical isochore. The quantities *, Cp-CV*, are calculated from NIST tables, and the correlation length by the leading Ising power law. The prefactor term *RD,eff* was represented by a power law, and we calculate for propane ; for pentane ; for hexane . Introducing all these previous singular behaviors in eq. 6, the phenomenological power law equation of the critical enhancement of the thermal conductivity can be recalculated along the critical isochore.

# CRITICAL ENHANCEMENT IN THE SUPERCRITICAL DOMAIN

In order to calculate Δλc outside the critical isochore, we have then generalized eq.6as  (7)

where the temperature and density dependences of the correlation length and the amplitude term , are accounted for introducing the reduced quantity *t* of eq. 6 and the reduced density . The values of, andare calculated from the NIST tabulated data. The value of the correlation length is adjusted to the theoretical value.The functional form of  was written as the product of two main contributions, separating then the respective temperature and density contributions.

**ESTIMATION OF THE THERMAL CONDUCTIVITY**

We used the theoretical valueto estimate the thermal conductivity along the critical isochore, and in order to check the validity and the accuracy of the estimation, the calculated values are compared to the experimental data reported in the literature. In the whole supercritical domain the thermal conductivity is calculated using the prefactoras an empirical function in order to characterize the extend density range measured . The term  is assumed to be a constant.

**REFERENCES**

[1] H. M. Roder. *Int. J. Thermophys*.**6** (1985) 119.

[2] B. Le Neindre et al. (under press)

[3] P. Desmaret, R. Tufeu. *Int. J Thermophys*.,**8** (1987) 293

[4] R. Mostert. PhD Thesis, University of Amsterdam (1991)

[5] K. N. Marsh, R. A; Perkins, M. L. V. Ramires.*J.Chem. Eng. Data*, **47** (2002)932.

[6] B. Le Neindre, Y. Garrabos, M. Nikravech. Accepted in *J Chem. Eng. Data* (2014)

[7] C. A. Nieto de Castro, R. Tufeu, B. Le Neindre, *Int. J Thermophys*. **4** (1983) 1.

[8] J. C. Nieuwoudt, B. Le Neindre, R. Tufeu, J.V. Sengers, *J Chem. Eng. Data*, **32** (1987) 1

[9] B. Le Neindre, Y. Garrabos, F. Volve, F. Gumerov. To be publish in *Fluid Phase Equilibria.*

[10] B. Le Neindre, Y. Garrabos, F. Volve, F. Gumerov To be publish in *J. Chem. Eng. Data.*

[11] M. O McLinden, S. A. Klein, E. W. Lemmon, A. W. Peskin. NIST Standard Database 23, REFPROP Version 7, Nat. Inst. Stand. Technol., Boulder, Colorado 2004.

(12) J. Luettmer-Strathmann, J. V. Sengers. *High Temp. High Press.***26** (1994) 673.

(13) P. C. Hohenberg, B. I. Halperin. *Rev. Mod. Phys.***49** (1977**)**, 435.

(14) J. V. Sengers, R. A. Perkins, M. L. Huber, B. Le Neindre, *Int. J. Thermophys.* **30** (2009) 1463.

(15) H.J.M. Hanley, J. V. Sengers, J. F. Ely. On Estimating Thermal Conductivity Coefficients in the Critical Region of Gases, in "*Thermal Conductivity 14*», Eds. Klemens P. G.; Chu T. K., Plenum Press, N.Y. pp. 383-407, 1976.

(16) B. Le Neindre, Y. Garrabos, R.Tufeu. *Int. J. Thermophys*. **12** (1991) 307.