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Measurement of thermal diffusivity for carbon dioxide (CO_2) at T = 293.15–406.15 K and pressures up to 11 MPa by dynamic light scattering (DLS)

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A B S T R A C T

The sharply increasing use of carbon dioxide (CO_2) in area of the trans-critical and supercritical technology urgently requires the study of thermophysical properties of CO_2 near the critical point where the lack of the accuracy experimental data is very obvious. The thermal diffusivities of CO_2 along six isobaric lines (p = 7.0, 7.5, 8.0 9.0 10.0 and 11.0 MPa) and in the temperatures from 293.15 to 406.15 K were measured around the critical point of CO_2. The relative combined standard uncertainty in thermal diffusivity is estimated to be less than 0.01 over the whole examined p–T region. Moreover, the comparison between the experimental data and the calculated results from REFPROP 9.1 were made. The absolute average of relative deviation (AARD) between the experimental data and the calculated results is 3.51% in the investigated region of $0.980 < T/T_C < 1.013$ and $0.949 < p/p_C < 1.503$.

1. Introduction

Carbon dioxide (CO_2) is one of the most widely used industrial fluids in the area of supercritical technologies. In recent years, the supercritical CO_2 (S-CO_2) Brayton cycle has been of considerable primary interest for application to some medium and low-temperature heat sources, such as coal fired units, solar energy, waste heat from gas turbine or fuel cells, and geothermal energy [1–4]. Currently, the S-CO_2 Brayton cycle has been considered as one of the most potential alternatives in gen-IV nuclear energy system to potentially provide higher thermodynamic efficiency. For the S-CO_2 Brayton cycle, the significant improvement of the thermodynamic efficiency results from the reduction of compressor work by performing the compression process close to the critical point of CO_2, which comes from the low compressibility of CO_2 near the critical point [5]. It is, therefore, essential to have available accurate experimental data and prediction models for the thermodynamic and transport properties of CO_2, especially for that of CO_2 near the critical point. Thermal diffusivity is a fundamental transport property for the investigation of heat transfer and designing of heat exchanger. To describe the operational state of the S-CO_2 Brayton cycle, the thermal diffusivities of CO_2 must be known first, especially their bizarre change regulation in the vicinity of critical point.

The thermal diffusivity measurement of CO_2 is very scant. Available experimental data were presented in Fig. 1. Becker et al. [6] measured the thermal diffusivity of CO_2 along four isothermal lines (T = 298.15, 304.35, 305.25 and 307.95 K) and in the pressures from 3.110 to 48.704 MPa. Swinney et al. [7] measured the thermal diffusivity of CO_2 along the critical isochore line at temperatures ranging from 304.248 to 309.453 K and the pressures from 7.400 to 8.291 MPa. Both of the two previous research reports were mainly about the near-critical region of CO_2. In addition, the experimental thermal conductivities of CO_2 were collected, which are relatively abundant and listed in Table 1. The temperatures range from 277 K to 1373 K and the pressure up to 210 MPa.

Dynamic light scattering (DLS) method is an effective method for measuring thermal diffusivity. In this paper, the thermal diffusivities of CO_2 were measured using DLS method in the near-critical region above the critical point to supplement the thermophysical property data of CO_2.

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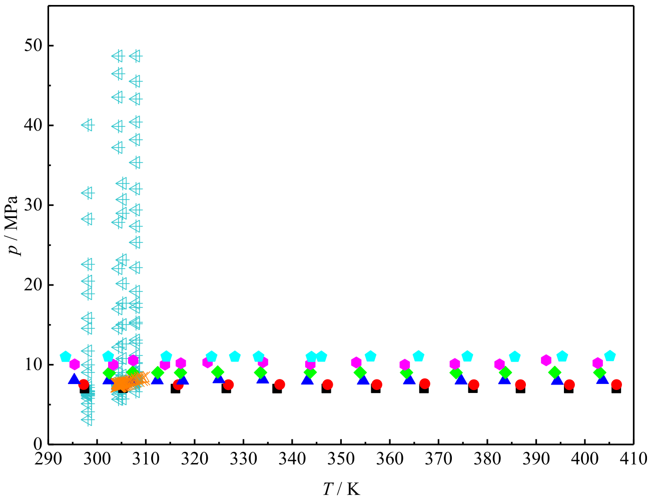

Fig. 1. The p–T region of the measurements for thermal diffusivity in CO_2, (⨯) Swinney et al.; (◁) Becker et al.; (■) This work 7.0 MPa; (●) This work 7.5 MPa; (▲) This work 8.0 MPa; (◆) This work 9.0 MPa; (⬢) This work 10.0 MPa; (⬟) This work 11.0 MPa.

2. Experimental section

2.1. Material

CO_2 was supplied by Jinan Deyang Special Gas Co. Ltd. and had nominal mass fraction of > 0.99999 (Gas Chromatography). The samples were not further purified. The sample specifications were listed in Table 2.

2.2. Measurement principle and apparatus

The thermal diffusivities of CO_2 were measured by Dynamic light scattering (DLS) method. The significant advantage of DLS is that it can be used to determine the thermal diffusivity within macroscopic thermodynamic equilibrium [25–27], so it has a good adaptability to measure fluids' thermal diffusivity in the near-critical region.

DLS method was developed based on the analysis of the scattered light characteristics. For pure fluid, the microscopic temperature fluctuation at constant pressure induces the scattered light. In time domain, the thermal diffusivity of sample is related to the decay time. The decay time can be obtained according to the time correlation function of the photocurrent, which can be expressed as an exponential decay function as:

$$G(\tau) = A + B\exp(-\tau/\tau_R) \quad (1)$$

where τ_R is the decay time constant and A and B are the fitted constants. As shown in Fig. 2, the discrete data points were collected by the correlator and used to obtain the photon auto-correlation function $G(\tau)$ by the nonlinear least-squares fitting (NLSF). Then the decay time constant τ_R can be determined. The sample's thermal diffusivity as function of the decay time constant was expressed as

$$a = 1\Big/\left(q^2\tau_R\right)(\text{where: } q = 2\pi \sin\Theta_{EX}/\lambda_0) \quad (2)$$

where a is the thermal diffusivity and q is the scattering vector modulus. The scattering vector can be expressed as function of the laser wavelength in vacuum (λ_0) and the incident angle (Θ_{EX}). The thermal diffusivity of the sample can be determined by Eq. (2). Here, the measuring principle and working equations of DLS were introduced briefly. The detailed descriptions of the DLS fundamental principles can be found in some specialized literature [28–30].

The detailed introduction of the experiment setup can be found in our previous paper [31]. Here only the main instruments are listed. A laser (Cobolt Samba™) is employed as the light source. A

Table 2
Specifications of CO_2.

Material	Carbon dioxide
CAS number	124–38–9
Molecular formula	CO_2
Molecular weight	44.0095
Critical temperature/K	304.18 ± 0. 02 [6]
Critical pressure/MPa	7.38 ± 0.01 [6]
Critical density/kg·m^{-3}	468 ± 1 [6]
Supplier	Jinan Deyang Special Gas Co. Ltd
Mass purity	>0.99999[a]

[a] The mass fraction was supplied by the supplier.

Table 1
Summary of CO_2 thermal conductivity data used in current study.

Corresponding author	Year of publication	T (K)	p (MPa)	No. of data	Technique employed[a]	Uncertainty (%)
Pátek et al. [8]	2005	298–428	0.5–15	77	THW	1.2
Heinemann et al. [9]	2000	323–420	0.1	3	THW	5
Dohrn et al. [10]	1999	323–420	0.1	7	THW	5
Chen et al. [11]	1999	304–316	1.5–13	21	TM	2
Wakeham et al. [12]	1987	305–425	0.68–6.7	91	THW	1
Wakeham et al. [13]	1984	300–301	0.62–3.9	23	THW	0.5
Masuoka et al. [14]	1984	298	0.1–5.4	13	CC	3
Clifford et al. [15]	1983	301–349	0.3–24.6	92	THW	1
Wakeham et al. [16]	1979	301–304	0.6–5.9	22	THW	0.5
Leneindre et al. [17]	1973	293–961	0.1–128	529	CC	2–5
P.Gupta et al. [18]	1970	373–1348	0.07	11	HW	5
Roenbaum et al. [19]	1969	335–434	3–69	47	CC	3
Michels et al. [20]	1962	295–350	1–210	77	CC	1
Guildner et al. [21]	1962	277–348	0.21–30	27	CC	5
Guildner et al. [22]	1958	304–348	0.2–30.4	14	CC	5
Rothman et al. [23]	1955	651–1073	0.1–0.4	11	CC	1
Rothman et al. [24]	1954	631–1047	0.1	23	CC	3
Overall	/	277–1373	0.07–210	1293	/	0.5–5

[a] CC, Coaxial cylinder; THW, Transient hot wire; TM, Thermoelectric method; HolInt, Heated plate observed by holographic interferometry.