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Determination of the effective thermal conductivity of solid fuels by the laser flash method

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Abstract In this study, a new laser flash system was proposed for the determination of the thermal conductivity of brown coal, hard coal and anthracite. The main objective of the investigation was to determine the effect of coal rank, composition, physical structure and temperature on thermal conductivity. The solid fuels tested were medium conductors of heat whose determined thermal conductivities were in the range of 0.09 to 0.23 W/(m K) at room temperature. The thermal conductivity of the solid fuels tested typically increased with the rank of coal and the measurement temperature. The results of this study show that the physical structure of solid fuels and temperature have a dominant effect on the fuels' thermal conductivity.

Keywords: Effective thermal conductivity; Effective thermal diffusivity; Specific heat; Laser flash method; Hard coal; Brown coal; Anthracite

Nomenclature

a	–	thermal diffusivity, mm^2/s
c_p	–	specific heat, J/(kg K)
d	–	diameter, m
FC	–	fixed carbon content, wt%
h	–	thickness, m
HHV	–	higher heating value – calorific value, MJ/kg
M	–	moisture content, wt%
m	–	mass, kg

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T – temperature, °C
VM – volatile matter content, wt%

Greek symbols

λ – thermal conductivity, W/(m K)
ρ – density, g/cm^3
σ – standard deviation

1 Introduction

Coal is a complex substance with divergent properties with respect to rank, composition and physical structure. Therefore, it is difficult to characterise and forecast its behaviour during thermal decomposition, combustion, gasification and other utilisation processes [1]. The design of solid fuel combustion and conversion processes requires knowledge of the thermal properties of solid fuels to properly establish the energy balance [2–5]. Thermal conductivity, which represents quantitatively the ability of a solid fuel to conduct heat, is of great significance in heat transfer modelling.

There are a few techniques that can be used to determine thermal conductivity, each of which is suitable for a limited range of materials, depending on the thermal properties and the medium temperature of those materials (Fig. 1). Measurements of the thermal conductivity of solid fuels date back several decades. Early experimental work was primarily performed using the steady-state, guarded hot plate method (e.g., Clendenin *et al.* [6]). Thereafter, transient techniques, such as the hot wire method (Badzioch *et al.* [7], Dindi *et al.* [8]), hot plate method (Dindi *et al.* [8]), heat flow meter method (Singer and Tye [9], Herrin and Deming [10]), plane source method (Suleiman *et al.* [11]), optical scanning method (Popov *et al.* [12]), and numerical CATA (computer aided thermal analysis) technique (Stanger *et al.* [13]) were developed. Measurements of the thermal conductivity of solid fuels are often associated with those of specific heat and are included in the reviews of Clendenin *et al.* [6], Badzioch *et al.* [7], Agroskin *et al.* [14], Eisermann *et al.* [15] and Strezov *et al.* [16].

In the present study, a new laser flash apparatus was proposed for the determination of the thermal conductivity of solid fuels. The flash method is a well-known technique for measuring of the thermophysical properties of solid materials. In 1961, Parker *et al.* [17], for the first time, described a flash method for measuring the thermal diffusivity, heat capacity and thermal conductivity of copper, silver, iron, nickel, aluminium, tin, zinc and some alloys at 22 and 135 °C. The laser flash system allows for the

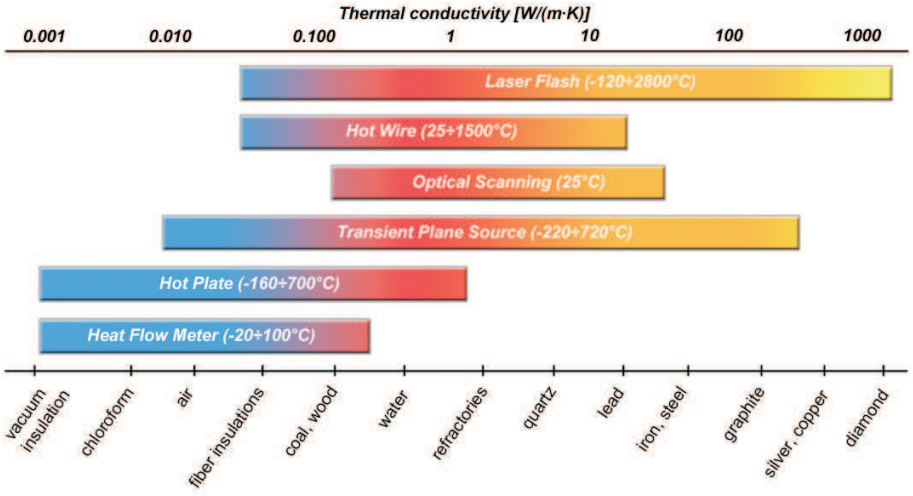


Figure 1: Thermal conductivity determination techniques for various materials.

determination of the thermal conductivity of materials between 0.1 and 2000 W/(m K) over the temperature range of -125 to 1100 °C. Easy sample preparation, short measurement times and high accuracy are only some of the advantages of this noncontact, nondestructive method [18]. Nowadays, the laser flash methods are the most commonly used techniques of thermal diffusivity a measurements of the opaque solids, e.g., [19–21]. However, to date, there are no experimental data available in the open literature regarding the determination of thermal conductivity of solid fuels using this laser flash system.

A variable to be considered in the measurement of the thermal conductivity of a solid piece of coal is the effect of the bedding or laminations in the coal. Singer *et al.* [9] measured the thermal conductivity of coal with the heat flowing perpendicular to the bedding plane in one case and parallel to the bedding in another. They observed that the measured thermal conductivities were higher in the parallel direction. Dindi *et al.* [8] determined the thermal conductivity of coal samples in which the heat flow was oriented parallel and nonparallel to the bedding planes using the transient hot wire and hot plate methods. The authors observed that the thermal conductivities measured with the heat conduction parallel to the bedding planes were approximately 25 to 30% greater than those in the nonparallel configuration. Cercone *et al.* [22] also reported that the thermal conduc-

tivities of their coal samples parallel to the bedding were, on average, 2.4 times higher than the conductivity measured perpendicular to the bedding. Data reported in the literature show that the magnitude of the thermal conductivity of solid fuels depends on the rank of coal, composition, porosity, density and temperature.

In this study, the thermal conductivity of dry brown coal, hard coal and anthracite were determined by using the laser flash technique. The main objective of the study was to determine the effect of coal rank, composition, physical structure and temperature on the thermal conductivity.

2 Experimental

2.1 Laser-flash apparatus

Measurements of the thermal properties of solid fuels were performed using the NETZSCH LFA-457 MicroFlash system shown schematically in Fig. 2. Positioned at the base of the device is the head of a Nd:YAG laser. The laser has a pulse length of 330 μs and a pulse energy output of up to 15 J/pulse. The energy of the laser pulse can be controlled by the accompanying software. The laser pulse is passed through a magnifying optics system that adjusts the beam diameter to the required sample diameter. From the magnifying optics system, the laser pulse is guided via a mirror through a window into the vacuum-tight sample chamber. Inside the sample chamber is an automatic sample changer designed to switch between up to three samples. The samples are positioned in easily user-interchangeable sample holders that can be adjusted to the actual sample dimensions. The entire sample holder system is surrounded by the user-interchangeable furnace. Two furnaces (-125–500 ^{o}C or 25–1100 ^{o}C) can be used in the system. The increase in temperature on the back surface of the sample is measured by employing either an InSb- or an MCT (mercury sadmium telluride) – infrared detector. Data are acquired via a high-speed amplifier and A/D-converter systems with a maximum possible data acquisition rate of 500 kHz [18].

The thermal diffusivity, a, and specific heat, c_p, can be ascertained using the signal measured by an infrared detector. System control and evaluation of the measurement results were carried out using the accompanying software, which allows for fully automatic tests and provides state-of-the-art analysis routines to apply to the processed data. For example, the software package includes nonlinear regression routines to consider for radial and

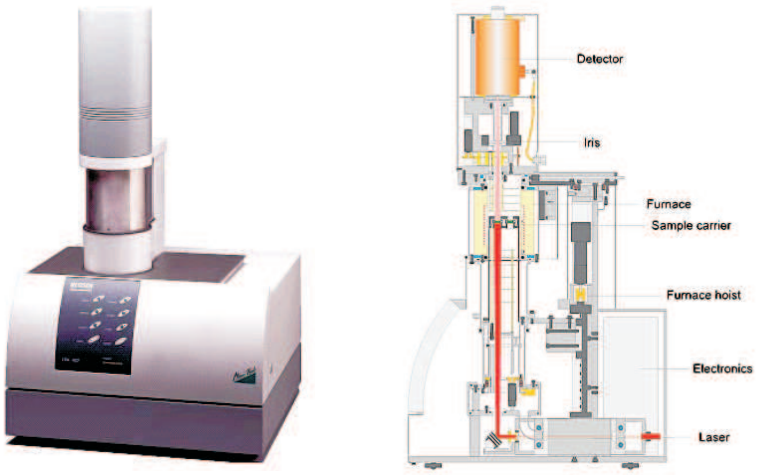


Figure 2: The NETZSCH LFA 457 *MicroFlash* apparatus.

facial heat losses, finite-pulse effects, and internal radiative heat transfer applying different analytical solutions. If the bulk density of the material, ρ, is known, the thermal conductivity can be directly determined according to the following relation:

$$\lambda(T) = a(T)c_p(T)\rho(T) \; . \tag{1}$$

Tests on standard materials such as NIST (National Institute of Standards and Technology) – certified reference materials or pure metals have demonstrated that the system has an accuracy better than 3%.

2.2 Solid fuels tested

Polish brown and hard coals as well as Russian anthracite were used in this study. The results of the proximate analyses (on air-dried basis), ultimate analyses (on dry, ash-free basis) and mercury porosimetry (on air-dried basis) of the tested solid fuels are presented in Tab. 1.

2.3 Sample preparation

Solid fuels were cut by a diamond saw into thin ($\sim$ 2 mm thick), flat pieces and then round samples ablated by a pin-cutting drill with the inner diameter of 10 mm. Water was applied as a coolant during cutting and drilling. The samples, which occurred as randomly oriented aggregates, with the best

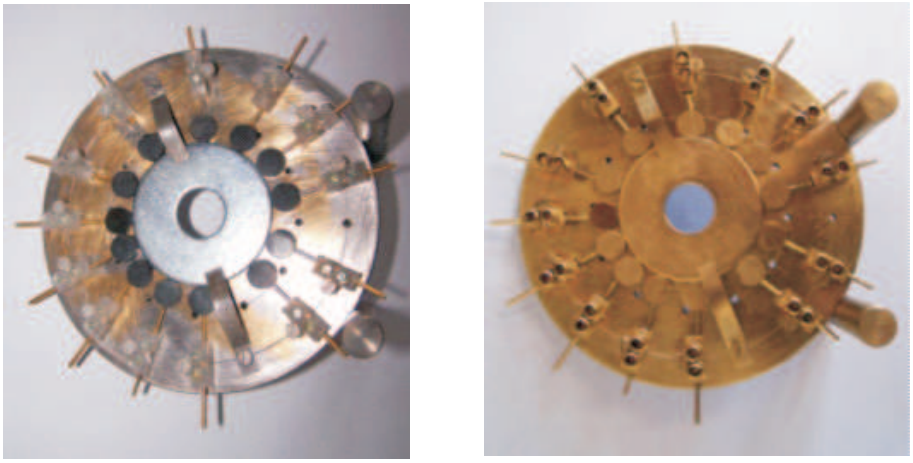
Table 1: Proximate and ultimate analyses, and mercury porosimetry of the tested solid fuels.

Solid fuel	Brown coal Turów Mine	Hard coal Ziemowit Mine	Anthracite Russia
Proximate analysis *(air-dried basis)*			
Moisture (M), %	13.3	8.7	2.2
Ash (A), %	22.4	18.9	8.0
Volatile matter (VM), %	39.1	26.8	1.8
Fixed carbon (FC), %	25.2	45.6	88.0
Calorific value (HHV), MJ/kg	17.33	21.69	30.77
Ultimate analysis *(dry, ash-free basis)*			
Carbon (C), %	64.4	73.3	95.7
Sulphur (S), %	1.5	2.3	1.1
Hydrogen (H), %	4.6	4.3	1.7
Nitrogen (N), %	0.9	1.1	0.9
Oxygen (O), % (by difference)	28.6	19.0	0.6
Mercury porosimetry *(air-dried basis)*			
Total porosity, %	21.48	10.46	4.12
Total specific pore volume, mm^3/g	210.92	90.53	29.29
Bulk density, g/cm^3	0.95	1.29	1.47
Apparent density, g/cm^3	1.29	1.48	1.62

mechanical properties were selected (with small amounts of visible cracks and pores) for further investigations. The selected samples were dried in air at 120 °C for 12 h in a compartment dryer, and after cooling, the dimensions of the samples were measured with an accuracy of 0.01 mm (diameter d, thickness h,) and weighed (mass m) with the accuracy of 0.0001 g (Sartorius balance). The bulk densities of the materials, ρ, were calculated from the average geometrical parameters and masses of samples.

Samples were coated on both sides with a thin layer of gold (1 to 2 μm) by the magnetron sputtering technique (Fig. 3). A thin layer of Au hinders the decomposition of materials during thermal conductivity measurements. Next, the samples were spray-coated with a thin layer of graphite to improve the absorption of the laser light. The same procedure was applied to the reference graphite sample (Poco graphite). The samples were placed in a furnace and annealed at a given temperature for 12 h. After annealing, the preparation procedure was repeated for the next measurement at the next temperature. Measurements were performed under the flow of argon (20 cm^3/min). Three laser shots with a pulse length of 0.5 ms were applied to each sample at a given temperature. The final result for each parameter is presented as the average value of three partial measurements.

The measured signal was fitted with the heat radiation model including laser pulse correction. The heat radiation model is used for porous materials, for which heat transfer by radiation cannot be neglected.



a) b)

Figure 3: Coal samples for determination of thermal properties by laser flash method before coating (a), and after coating with Au (b).

3 Results and discussion

The aim of this investigation was to determine the effective thermal conductivity, λ, of solid fuels using the laser flash method. Tables 2–4 show the results of measurements performed for brown coal, hard coal and anthracite samples over the temperature range from 25 to 1000 °C. The arithmetic mean values of the thermal conductivity as well as their standard deviations were calculated from the sets of three partial measurements. The extent to which the sample temperature deviated was ±1 °C. The measured thermal diffusivity, a, and specific heat, c_p, of the solid fuels will be analysed in detail in future studies.

The first stage of investigation was the determination of the thermal properties of the solid fuels at room temperature (25 °C). The magnitude of the thermal conductivity of solid fuels depends on the rank of coal, composition, physical structure and temperature.

Table 2: Results of measurements for brown coal.

Temperature	Mass	Bulk density	Thermal diffusivity	σ_a	Specific heat	σ_{cp}	Thermal conductivity	σ_λ
T, °C	m, g	ρ, g/cm^3	a, mm^2/s	mm^2/s	c_p, J/(g K)	J/(g K)	λ, W/(m K)	W/(m K)
25	0.1286	0.91	0.072	0.008	1.347	0.004	0.088	0.009
300	0.1200	0.88	0.113	0.002	1.345	0.006	0.134	0.003
500	0.1115	0.84	0.315	0.013	1.501	0.035	0.399	0.027
700	0.0898	0.81	0.605	0.003	1.706	0.021	0.837	0.004
900	0.0820	0.77	1.005	0.008	1.777	0.026	1.373	0.013
1000	0.0800	0.76	1.250	0.008	1.865	0.034	1.772	0.016

Table 3: Results of measurements for hard coal.

Temperature	Mass	Bulk density	Thermal diffusivity	σ_a	Specific heat	σ_{cp}	Thermal conductivity	σ_λ
T, °C	m, g	ρ, g/cm^3	a, mm^2/s	mm^2/s	c_p, J/(g K)	J/(g K)	λ, W/(m K)	W/(m K)
25	0.1485	1.16	0.107	0.010	1.270	0.006	0.157	0.011
300	0.1412	1.12	0.125	0.003	1.508	0.003	0.210	0.006
500	0.1199	1.04	0.296	0.011	1.604	0.042	0.492	0.018
700	0.1081	1.02	0.549	0.001	1.985	0.012	1.107	0.001
900	0.0750	0.90	0.869	0.008	2.280	0.002	1.779	0.062
1000	0.0716	0.88	1.114	0.001	2.543	0.008	2.507	0.004

Table 4: Results of measurements for anthracite.

Temperature	Mass	Bulk density	Thermal diffusivity	σ_a	Specific heat	σ_{cp}	Thermal conductivity	σ_λ
T, °C	m, g	ρ, g/cm^3	a, mm^2/s	mm^2/s	c_p, J/(g K)	J/(g K)	λ, W/(m K)	W/(m K)
25	0.2300	1.53	0.201	0.001	0.907	0.013	0.228	0.002
300	0.2200	1.47	0.157	0.007	1.398	0.020	0.280	0.013
500	0.2200	1.47	0.139	0.056	1.711	0.082	0.640	0.010
700	0.2100	1.41	0.395	0.008	1.843	0.039	1.191	0.021
900	0.2000	1.36	0.832	0.003	1.975	0.016	2.080	0.009
1000	0.2000	1.36	0.822	0.021	2.017	0.032	2.694	0.036

3.1 Effect of coal rank

The degree of metamorphism that occurs as a coal matures from brown coal to anthracite is referred to as the rank of the coal. Brown coal is the lowest rank of coal because it has a low carbon content and high volatile matter contents (see Tab. 1). The highest rank of coal is anthracite, which has the

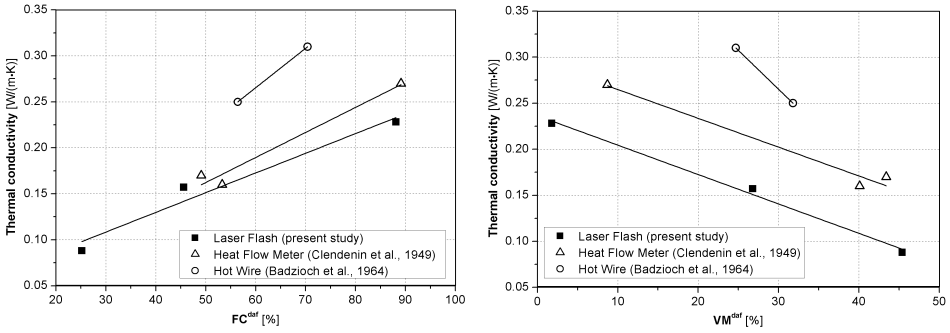
highest fixed-carbon content and the lowest moisture and volatile matter contents. The arithmetic means of the effective thermal conductivities of brown coal, hard coal and anthracite were determined to be 0.09 W/(m K), 0.16 W/(m K) and 0.23 W/(m K), respectively. Thus, it can be observed that the solid fuels are moderate conductors of heat. The thermal conductivity of solid fuels increases with the rank of coal. Herrin and Deming [10] measured the matrix thermal conductivities of 6 lignites, 10 subbituminous coals, 36 bituminous coals, and 3 anthracites from the United States and observed a mean value of 0.33 W/(m K) for the values ranging from 0.22 to 0.55 W/(m K) at 22 °C. The authors concluded that rank by itself is not a sufficient predictor of thermal conductivity.

3.2 Effect of composition

The effects of parameters such as fixed carbon and volatile matter contents were also investigated. Figure 4a shows the effect of fixed carbon on the thermal conductivity of the solid fuels tested. The thermal conductivity increased with fixed carbon (FC) content. The relationship between the volatile matter (VM) content and thermal conductivity of the solid fuels indicates the opposite trend (Fig. 4b). The experimental data reported by Clendenin *et al.* [6] and Badzioch *et al.* [7] also confirm that thermal conductivity depends on the fixed carbon and volatile matter contents of coal. It can be noted that the thermal conductivity of solid fuels measured by the laser flash technique is significantly lower than the thermal conductivities measured by the heat flow meter and hot wire methods. This discrepancy may be associated with differences in the measurement techniques and sample preparation procedures as well as the moisture content in the solid fuels tested. Dindi *et al.* [8] determined the thermal conductivity of wet and dry coal samples using the transient hot wire and hot plate methods. The authors observed that at ambient temperature the thermal conductivity decreased from 0.4 to 0.2 W/(m K) as a result of drying. This finding was most likely obtained because the thermal conductivity of water is approximately three times higher than that of dry coal.

3.3 Effect of physical structure

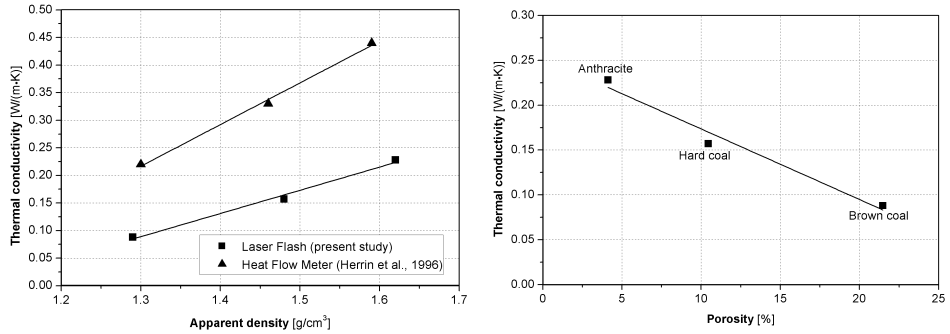
Figure 5 shows the relationship between the apparent density and porosity (obtained in mercury porosimetry, see Tab. 1) and the thermal conductivity of the solid fuels. The thermal conductivity of the solid fuels increases with



a) b)

Figure 4: Effect of fixed carbon content (a) and volatile matter content (b) on thermal conductivity of solid fuels at room temperature.

apparent density. Herrin and Deming [10] also observed that the thermal conductivity of solid fuels tested is controlled by the apparent density. However, the thermal conductivity quickly decreases with the increase in porosity. This finding is primarily a result of the fact that the conductivity of the solid framework is many times greater than that of the gaseous medium in pores. Low-rank coals typically have a lower apparent density and greater total porosity than high-rank coals. Coal porosity is distributed among



a) b)

Figure 5: Relationship of thermal conductivity to apparent density (a) and porosity (b) of solid fuels at room temperature.

macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm), with low-rank coals containing a large proportion of macropores and high-rank coals containing a large proportion of micropores. This finding is consistent with a decrease in the porosity of coal as its rank increases.

3.4 Effect of temperature

The second stage of this study involved determination of the effect of temperature on thermal conductivity. In the literature, few studies have considered the temperature dependence of the thermal conductivity of coal. For example, Badzioch *et al.* [7] measured the thermal conductivity of 12 types of coal by the hot wire method from the room temperature to 900 °C. The authors observed that the thermal conductivity increased with increasing temperature for all tested coals. Dindi *et al.* [8] also measured the thermal conductivity of coal by the hot wire method at temperatures up to 420 °C. Furthermore, Singer *et al.* [9] demonstrated a variation in conductivity data gathered by the hot plate method at test temperatures up to 800 °C. Stanger *et al.* [13] determined the thermal conductivity of maceral concentrates from a coal using the numerical computer aided thermal analysis technique. Figure 6 shows the effect of temperature on the thermal

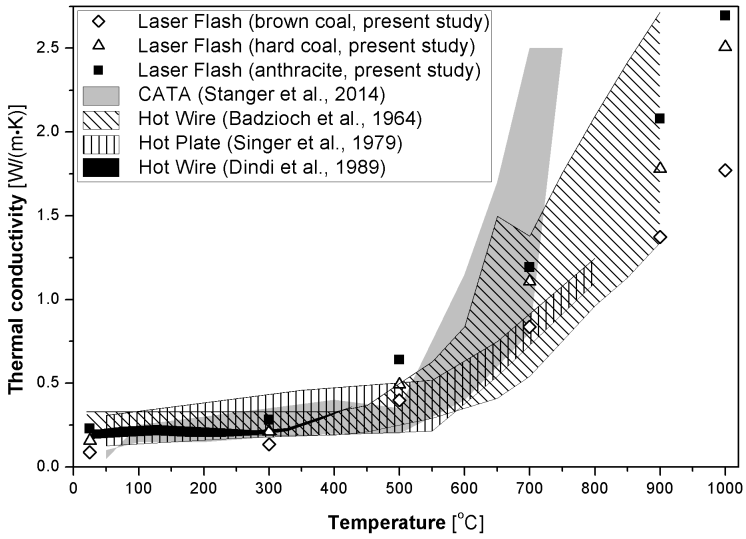


Figure 6: Influence of temperature on thermal conductivity of solid fuel determined by various techniques.

conductivity of the solid fuels determined by various techniques. Comparison with the data reported by other investigators generally indicated a good agreement with respect to the trends and values observed. The present study and the studies reported by Badzioch *et al.* [7], Singer *et al.* [9], Dindi *et al.* [8], and Stanger *et al.* [13] show an increase in thermal conductivity

values with temperature. In all of the data, a rapid rise in thermal conductivity above 600 °C can be observed. This rapid increase in thermal conductivity is due to massive devolatilisation and the combustion of char. The increase is also attributed to radiant heat transfer across pores and cracks, which is well known to occur in all porous materials, and changes in the conductivity of the material structures during carbonisation. The effective thermal conductivities of brown coal, hard coal and anthracite at the temperature of 1000 °C increased to: 1.77 W/(m K), 2.51 W/(m K) and 2.69 W/(m K), respectively.

4 Conclusions

The general conclusions drawn from the correlation of published data on the thermal conductivity of solid fuels are summarised as follows:

1. The laser flash technique is appropriate for determination the thermal conductivity of solid fuels.
2. The solid fuels tested in this investigation are moderate conductors of heat as indicated by their determined effective thermal conductivities, which ranged from 0.09 to 0.23 W/(m K) at room temperature.
3. The thermal conductivity of solid fuels usually increases with the rank of coal. The thermal conductivity of brown coal is approximately 0.09 W/(m K) at 25 °C, whereas the thermal conductivity of anthracite is approximately 0.23 W/(m K).
4. Thermal conductivity usually decreases with volatile matter content, whereas it increases with the fixed carbon content.
5. The magnitude of the thermal conductivity of solid fuels increases with apparent density and decreases with the porosity of coal. These trends are primarily a result of the fact that the conductivity of the solid framework of the fuels is many times greater than that of the gaseous medium in the materials' pores.
6. The thermal conductivities of the solid fuels tested were generally observed to increase with temperature. The effective thermal conductivities of brown coal, hard coal and anthracite at the temperature of 1000 °C increased to 1.77 W/(m K), 2.51 W/(m K) and 2.69 W/(m K), respectively.

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References

[1] Kosowska-Golachowska M.: *Coal Combustion*. Handbook of Combustion, Vol. 4: *Solid Fuels*, (M. Lackner, F. Winter and A.K. Agarwa, Eds.), 171–215. Wiley-VCH, Weinheim 2010.

[2] Atkinson B., Merrick D.: *Mathematical models of the thermal decomposition of coal. 4. Heat transfer and temperature profiles in a coke-oven charge*. Fuel **62**(1983), 553–561.

[3] Gajewski W., Kosowska-Golachowska M.: *The thermal fragmentation of coal in a bubbling fluidized bed*. Arch. Thermodyn. **28**(2007), 2, 85–96.

[4] Gajewski W., Kijo-Kleczkowska A., Leszczyński J.: *Analysis of cyclic combustion of solid fuels*. Fuel **88**(2009), 221–234.

[5] Pełka P.: *Modeling of mass loss of char particle during combustion on flow of inert material*. Fuel **90**(2011), 904–932.

[6] Clendenin J.D., Wright C.C.: *Thermal and electrical properties of anthracite and bituminous coals*. In: Transactions of the Seventh Annual Anthracite Conference of Lehigh University, 1949.

[7] Badzioch S., Gregory D.R., Field M.A.: *Investigation of the temperature variation of the thermal conductivity and thermal diffusivity of coal*. Fuel **43**(1964), 267–280.

[8] Dindi H., Bai X., Krantz W.B.: *Thermal and electrical property measurements for coal*. Fuel **68**(1989), 185–192.

[9] Singer J.M., Tye, R.P.: *Thermal, mechanical and physical properties of selected bituminous coal and cokes*. Bureau of Mines Report of Investigations 8364 (1979).

[10] Herrin J.M., Deming D.: *Thermal conductivity of U.S. coals*. J. Geophys. Res. **101**(1996), 25, 381–386.

[11] Suleiman B.M., Larfeldt J., Leckner B., Gustavsson M.: *Thermal conductivity and diffusivity of wood*. Wood Sci. Technol. **33**(1999), 465–473.

[12] Popov Y.A., Pribnow D.F.C., Sass J.H., Williams C.F., Burkhardt H.: *Characterization of rock thermal conductivity by high resolution optical scanning*. Geothermics **28**(1999), 253–276.

[13] Stanger R., Xie W., Wall T., Lucas J., Mahoney M.: *Dynamic measurement of coal thermal properties and elemental composition of volatile matter during coal pyrolysis*. J. Mater. Res. Technol. **3**(2014), 1, 2–8.

[14] Agroskin A.A., Goncharo E., Gryaznov N.S.: *Thermal properties of coals in plastic state*. Coke Chem. USSR **9**(1972), 3–5.

[15] Eisermann W., Johnson P., Conger W.L.: *Estimating thermodynamic properties of coal, char, tar and ash*. Fuel Process. Technol. **3**(1980), 39–53.

[16] Strezov V., Lucas J.A., Evans T.J., Strezov L.: *Effect of heating rate on the thermal properties and devolatilization of coal*. J. Therm. Anal. Calorim. **78**(2004), 385–397.

[17] Parker W.J., Jenkins R.J., Butler C.P., Abbott G.L.: *Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity*. J. Appl. Phys. **32**(1961), 1679.

[18] Min S., Blumm J., Lindemann A.: *A new laser flash system for measurement of the thermophysical properties*. Thermochim. Acta **455**(2007), 1, 46–49.

[19] Terpiłowski J.: *A pulse method for determination of specific heat and thermal diffusivity of plastics*. Arch. Thermodyn. **29** (2008), 2, 61–72.

[20] Terpiłowski J., Szczepaniak R., Woroniak G., Rudzki R.: *Adaptation of the modified pulse method for determination of thermal diffusivity of solids in the vicinity of the second-order phase transition points*. Arch. Thermodyn. **34** (2013), 2, 73–92.

[21] Panas A. J., Cudziło S., Terpiłowski J.: *Investigation of thermophysical properties of metal- polytetrafluoroethylene pyrotechnic compositions*. High Temp.–High Press. **34**(2003), 691–698.

[22] Cercone K.R., Deming D., Pollack N.: *Insulating effect of coals and black shales in the Appalachian Basin, Western Pennsylvania*. Org. Geochem. **24**(1996), 2, 243–249.