Changes in thermal conductivity of wood during its thermochemical conversion

I G Donskoy, D A Svischtev and V A Shamanskiy
1Melentiev Energy Systems Institute of SB RAS, 130 Lermontova st., Irkutsk, Russia
E-mail: donskoy.chem@mail.ru

Abstract. Plant biomass is a fuel with better environmental characteristics than fossil fuels. The paper considers the effect of wood fuel conversion on its thermophysical properties. The measurements made allow us to establish a relationship between the degree of conversion and the coefficient of thermal conductivity. Thermal conductivity increases linearly with increasing density of samples and decreases as the pyrolysis proceeds, which is associated with a change in the porous structure and chemical composition of the material. The data obtained are used in a mathematical model of the pyrolysis of a wood particle. The influence of the anisotropy of the thermal conductivity coefficient on the characteristic drying and pyrolysis times is estimated.

1. Introduction
Reactivity of wood strongly depends on particle size. During thermochemical conversion wood particles are heated non-uniformly: at the same time, the particle contains areas with varying degrees of conversion. Since chemical changes in wood occur under the influence of temperature, the heating rate is important factors in combustion and gasification of wood waste. There are several types of mathematical models of wood particles heating and pyrolysis: phase transition approximation [1]; brutto-reactions approximation [2]; detailed kinetic models [3]. It is usually assumed that the particle has spherical of cylindrical symmetry so it could be described in a one-dimensional approximation, although such a simplification is not always applicable (for example, due to the inherent anisotropy of wood [4]). Conditions of reducing wood particle pyrolysis problem to one-dimensional formulation are considered in [5]. Moving front approximation was used in [6] to describe wood particle decomposition during fixed-bed combustion.

Authors of [7, 8] carried out a theoretical analysis of the chemical transformation process with a neutral-/endothermic effect, highlighted the criteria for the pyrolysis process in the kinetic mode and heat transfer mode (convective or conductive) without taking into account anisotropy. In [9], anisotropic thermal conductivity of wood was considered in the two-phase approximation. When considering the decomposition of high-moisture fuels, it is necessary to take into account the structure of the material and its change in the process [10, 11]. During the pyrolysis and combustion of wood, its porosity and chemical composition changes significantly, which leads to a significant change in the transfer coefficients [12]. Additive approximation is widely used to describe decaying material [13, 14], but its applicability cannot always be substantiated.

To enhance the reliability of mathematical models, instrumental determination and analysis of the thermophysical properties of wood at different stages of conversion is necessary. These studies,
however, are a non-trivial task, primarily due to the fact that when the temperature rises to 200-300°C, the pyrolytic decomposition of wood organic mass begins. In addition, the chemical composition of the fuel continuously changes during thermal transformation, and its thermal effects prevent the correct measurement of the sample properties. Therefore, to obtain reliable data, stabilization of the composition at the experimental temperature is required so that the sample can be considered as inert for the temperature range from room temperature to the heating temperature. A set of dependences for samples obtained at different holding temperatures can give a more complete picture of the changes in the biomass fuel properties in the process of its conversion.

2. Experimental section

Samples of raw and heat-treated fuel were prepared according to the following procedure. To produce the required sample volume, 2-3 samples of dry pine sawdust (100-125 g) were subjected to heating. Two values of the final temperature were chosen: 300 and 400°C. During torrefaction (pyrolysis at 300°C), wood fuel loses 27% of its initial weight. The main mass loss is mainly associated with the decomposition of hemicellulose. The conversion of fuel carbonized at 400°C is 63%, and the weight loss is mainly due to the decomposition of hemicellulose and cellulose. The thermal conductivity of the samples was determined according to GOST 30256-94 by the method of a cylindrical probe. The samples intended for the study were pressed in paper holders. To measure thermal conductivity, the following sample density values were chosen: bulk density; increased two and four times relative to bulk density; maximum density achieved by pressing a sample with a force of 10 tons.

At low density (< 200-300 kg/m³), the thermal conductivity of heat-treated fuel is comparable to the original wood. It is likely that in this density range, the thermal conductivity of the material mainly depends not on the properties of material, but on its porosity. When density of torrefied and carbonized samples increases, the fraction of large pores decreases and the microstructure of the substance becomes significant. Presumably, the porosity of the torrified fuel is low and the decrease in thermal conductivity is caused, first of all, by the processes of depolymerization and decomposition of hemicellulose [15]. Carbonated fuel has a high porosity, providing its relatively low thermal conductivity.

It is also worth noting that the torrified sawdust is characterized by good compressibility and form a mechanically strong pellet with a density of 910 kg/m³ when pressed with a force of 10 tons. Carbonized fuel is characterized by poor compressibility. After removing the load, the punch pushes out the expanding mass of charcoal from the matrix. Pellets from such fuel refuse to be fragile, and easily crumble under mechanical stress.

The results of measuring the thermal conductivity of pellets and a comparison with the data of other authors are presented in Fig. 1. Variations in the coefficient of thermal conductivity may depend both on the origin of the wood and on other factors, for example, moisture content and fiber orientation. Experimental data on thermal conductivity of wood by other authors are presented at Table 1.

Table 1. Equations for thermal conductivity of wood material.

| Source          | Equation                                      |
|-----------------|-----------------------------------------------|
| Mason [16]      | $\lambda = 1.3 \times 10^{-4} \rho + 0.037$ |
| TenWolde [17]   | $\lambda = 2.14 \times 10^{-4} \rho + 0.0186$ |
| McLean [18]     | $\lambda = 2.01 \times 10^{-4} \rho + 0.024$ |
| Harada [20]     | $\lambda = 2.49 \times 10^{-3} + 1.45 \times 10^{-4} \rho + 1.84 \times 10^{-4} (T - 273)$ |
| 20°C            | $\lambda = 3.06 \times 10^{-4} \rho - 0.0048$ |
| 300°C           | $\lambda = 1.99 \times 10^{-4} \rho + 0.0284$ |
| 400°C           | $\lambda = 6.72 \times 10^{-5} \rho + 0.0358$ |
3. Numerical model

The obtained data on thermal conductivity were used to estimate the heating rate of a single lignocellulosic particle (chips, pellets). At this stage, the change in component composition is not taken into account. The mathematical model of the pyrolysis of a cylindrical wood particle includes the equations of heat transfer and brutto-kinetics and is written as follows:

\[ c_p \rho \frac{dT}{dt} = \frac{1}{r} \frac{\partial}{\partial r} \left( \lambda_r r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda_z \frac{\partial T}{\partial z} \right) - c_p \rho_g u_r \frac{\partial T}{\partial r} - c_p \rho_g u_z \frac{\partial T}{\partial z} - Q_{dry} \rho_0 \frac{W}{100} \frac{dX_w}{dt} - Q_{pyr} \rho_0 \frac{V}{100} \frac{dX_v}{dt} \]

\[ u_r = -\frac{k_P}{\mu} \frac{\partial P}{\partial r}; \quad u_z = -\frac{k_P}{\mu} \frac{\partial P}{\partial z} \]

\[
\begin{align*}
    \frac{dX_w}{dt} &= \begin{cases} 0, & T \leq 373 \\
                       \frac{100 c_p \rho}{Q_{dry} \rho_0 W} \frac{\partial T}{\partial t}, & T > 373 
                \end{cases} \\
    \frac{dX_v}{dt} &= -k_{pyr} \exp \left( -\frac{E_{pyr}}{RT} \right) X_v \\
    \rho &= \rho_0 \left( 1 - \frac{W}{100} X_w - \frac{V}{100} X_v \right)
\end{align*}
\]

Here \( T \) is temperature, \( \lambda \) – thermal conductivity, \( r \) – radius, \( z \) – length. Boundary conditions at inner surface \( \Omega \) and at centerline \( (r = 0) \) are as follows:

\[ T(\Omega) = T_{out}, \quad \frac{\partial T}{\partial r} \bigg|_{r=0} = 0 \]

\[ P(\Omega) = P_0, \quad \frac{\partial P}{\partial r} \bigg|_{r=0} = 0. \]
Particle size: diameter 5 mm, length 20 mm; wood properties: initial density is 900 kg/m$^3$; initial moisture content is 5%; volatiles content is 85%. Environment temperature $T_{\text{out}}$ is 700-900 K, the pressure is atmospheric. Kinetic coefficients of pyrolysis rate are taken as follows: $k_{\text{pyr}} = 9.82 \times 10^3$ s$^{-1}$; $E_{\text{pyr}} = 77.07$ kJ/mol, $Q_{\text{pyr}} = -100$ kJ/kg. Shrinking is not taken into account. The system of equations is solved on a uniform spatial grid by the implicit method. The numerical algorithm is described in [21, 22]. Calculations are carried out until the end of the pyrolysis process (residual volatile mass is less than 0.1% of the initial one).

The thermal conductivity coefficients $\lambda_1$ and $\lambda_2$ are different, and depending on the conditions of the formation of chips/pellets. In order to take into account the effect of anisotropy, we use the relation:

$$\lambda_\perp = a\lambda_1$$

Here $a$ is a constant coefficient that does not change during the conversion process. Then, if table 1 gives the average value of the coefficient of thermal conductivity, it is possible to determine the coefficient of thermal conductivity in the longitudinal and transverse directions as follows:

$$\lambda_\perp = \lambda_1 \frac{2a}{1 + a}; \quad \lambda_\parallel = \lambda_1 \frac{2}{1 + a}$$

In our calculations value of $a$ is 3/5 [23], therefore there are three possible ratios of thermal conductivity coefficients: $\lambda_1/\lambda_2 = 3/5$ (fibers are directed along $z$ coordinate); $\lambda_1/\lambda_2 = 5/3$ (fibers are directed along radius $r$); and $\lambda_1/\lambda_2 = 1$ (fibers are directed in random order). Dependence of thermal conductivity on conversion degree is given by linear interpolation.

4. Modeling results

The thermal conductivity data obtained in this work and the Harada data recommended in [20] are used. The change in particle mass during heating is shown in Fig. 2. As expected, pyrolysis occurs faster if the fibers are directed across the particle: the heat spreads faster and the pyrolysis ends earlier. Particles with uniform thermal conductivity (such as pellets) heat up and lose volatiles faster than particles whose fibers are directed along the central axis.

![Figure 2. Calculated change in particle mass over time with different data on the thermal conductivity of wood ($T_{\text{out}} = 700$ K).](image-url)
Figure 3 shows the characteristic reaction times of a wood particle: drying time and devolatilization time. As can be seen from the presented results, notable sensitivity to the value of the coefficient of thermal conductivity is observed for the drying process: the variance of drying time values is up to 50% of the average value. An increase in the heating temperature by 200 K affects the drying rate less than a change in the thermal conductivity coefficients in the mentioned ranges.

![Figure 3](image_url)

**Figure 3.** Characteristic times of pyrolysis (a) and drying (b) at temperatures of 700–900 K obtained using different equations for the thermal conductivity coefficients.

The devolatilization time is determined by the heating temperature to a greater extent than the value of the thermal conductivity, due to the strong dependence of the decomposition rate kinetic coefficient on temperature. However, the same dependencies are observed. One of the features of the process, as mentioned above, is the formation of carbonized surface layer: the outer part of the particle transform into char with lower thermal conductivity, while the inner regions of the particle can preserve the original wood material [24]. In this case, the surface layer can act as an active reagent for releasing volatiles and moisture [25]. The data obtained will make it possible to more accurately assess the conditions for the formation of this layer and its effect on the combustion and gasification of the particle.

**Conclusions**

Using a mechanical press, pellets were obtained from crushed wood samples prepared at temperatures of 300 and 400°C. The values of thermal conductivity coefficients of pellets with different densities were measured, and the obtained dependences were used to model the pyrolysis of a single particle. The influence of the anisotropy of the material on the drying rate and the yield of volatiles is estimated. The results obtained are compared with the published data on the thermal conductivity of wood materials.

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