

# RELATION BETWEEN HEAT OF COMBUSTION OF WOOD AND ABSORBANCE OF ITS MIR SPECTRUM IN 1515 (1510) $\text{cm}^{-1}$ BAND\*

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SYNOPSIS. The relation between the heat of combustion of wood and the absorbance of its MIR spectrum in the 1515 (1510)  $\text{cm}^{-1}$  band follows a straight line. It was found for both pine and beech wood decomposed by chemical and biotical factors.

KEY WORDS: pine wood, beech wood, heat of combustion, 1515 (1510)  $\text{cm}^{-1}$  band MIR spectrum

## INTRODUCTION

When assessing the quality of wood and its products in production practice, it is wood technical properties, i.e. its mechanical and physical traits, that are taken into consideration. This, by no means, is surprising because, at the present time, advances in analytical methods in wood chemistry involve, primarily, the development of instrumental methods (Analytical methods... 1999). These advances may be achieved, among others, by the substitution of values difficult to measure by easily measurable ones. This will become possible thanks to the knowledge of interrelationships between different physical properties.

The subject of numerous papers included both heat of combustion (HOWARD 1973, DOAT 1977, MURPHEY and MASTERS 1978, DZIURZYŃSKI 1984) and also infrared spectroscopic studies (VODŇANSKÝ at AL. 1963, MARTON and SPARKS 1967, KARKLIN' and ĚRIN'Š 1971, KARKLIN' at AL. 1977, DZIURZYŃSKI at AL. 1988, SUPIŃSKI and DZIURZYŃSKI 1988).

In this context, the relation between the heat of combustion of wood and the absorbance of its middle-infrared (MIR) spectrum in 1515 (1510)  $\text{cm}^{-1}$  band is of particular interest. The existence of such a dependence has been proved beyond any doubt since both the heat of combustion of wood, as well as its absorbance in

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\*To professor Stefan Kinastowski on his 80th birthday.

the 1515 (1510)  $\text{cm}^{-1}$  band, depends on the lignin content (DZIURZYŃSKI 2003). Therefore, the aim of this study was to find the answer to the question how this relationship develops in detail.

## MATERIAL AND METHODS

The investigations made use of the author's earlier papers published in years 1984 and 1988. The object of the experiments was wood of Scots pine (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.) which was subjected to the following processes: pulping in NaOH, hydrolysis in  $\text{H}_2\text{SO}_4$ , decay by the *Coriolus versicolor* fungus and decay by the *Coniophora puteana* fungus (DZIURZYŃSKI 1984). The obtained preparations were used to carry out measurements of the heat of combustion (DZIURZYŃSKI 1984) as well as MIR spectra (DZIURZYŃSKI at AL. 1988, SUPIŃSKI and DZIURZYŃSKI 1988). Variability coefficients for the performed measurements amounted to: 0.3% – for the heat of combustion, and 10% for the absorbance of MIR spectra.

## RESULTS AND DISCUSSION

The absorbance of pine and beech woods decomposed by means of chemical and biotic factors in the 1515 (1510)  $\text{cm}^{-1}$  band of the MIR spectrum as well as their heat of combustion, are presented in Table 1. Methods of absorbance calculation are different for pine and beech wood. However they are best for each of these two wood species (SUPIŃSKI and DZIURZYŃSKI 1988). The obtained relationships are presented in Figures 1 and 2. It is evident from these figures that the experimental points are distributed along a straight line:

for pine wood:

$$Q_{comb} = 5700 \frac{A_{1515}}{A_{1378}} + 15300 \quad (1a)$$

for beech wood:

$$Q_{comb} = 19900 \cdot A_{1510} + 17300 \quad (1b)$$

where:  $Q_{comb}$  – heat of combustion of wood,

$A$  – absorbance of the 1515  $\text{cm}^{-1}$  and 1378  $\text{cm}^{-1}$  bands (pine) or 1510  $\text{cm}^{-1}$  band (beech) of the MIR spectrum.

Equations 1a and 1b are straight lines going through points designating *in situ* lignin and *in situ* holocellulose (DZIURZYŃSKI 2003) as illustrated by the directional coefficients of the 1a and 1b straight line:

for pine wood

$$5700 = \frac{q_l - q_h}{\left(\frac{A_{1515}}{A_{1378}}\right)_l - \left(\frac{A_{1515}}{A_{1378}}\right)_h}$$

Table 1. Absorbances of MIR spectra bands 1515 (1510)  $\text{cm}^{-1}$  and heat of combustion of pine and beech wood decomposed by chemical and biotical factors

Kind of decomposition	Pine				Beech			
	time of decomposition	yield [%]	absorbance $A_{1515}/A_{1378}$	heat of combustion $\text{kJ/kg}^{-1}$	time of decomposition	yield [%]	absorbance $A_{1510}$	heat of combustion $\text{kJ/kg}^{-1}$
Holocellulose	–	67.4	0.326	17 790	–	69.5	0.000	17 780
Lignin	–	27.6	2.058	28 200	–	23.5	0.433	26 820
Original wood	–	100	0.795	20 120	–	100	0.117	19 920
1.2 m NaOH 165°C	1 min	79.0	0.871	20 200	1 min	74.5	0.142	20 010
	2 h	66.7	0.710	19 460	2 h	48.0	0.038	18 260
	6 h	52.2	0.517	18 230	6 h	41.3	0.028	17 630
6 m H <sub>2</sub> SO <sub>4</sub> 100°C	20 min	89.8	0.820	20 410	20 min	86.2	0.150	20 100
	6 h	77.4	0.970	20 750	1 h	76.0	0.148	20 290
	30 h	68.4	1.030	21 210	30 h	57.3	0.200	20 770
<i>Coriolus versicolor</i> 22°C	30 days	94.0	0.719	19 580	10 days	97.0	0.099	19 860
	70 days	86.0	0.725	19 550	30 days	76.0	0.121	19 960
	300 days	71.3	0.775	19 700	50 days	67.0	0.110	19 800
					120 days	37.0	0.115	19 570
<i>Coniophora puteana</i> 22°C	10 days	88.0	0.863	20 030	10 days	97.5	0.125	19 930
	30 days	77.0	0.930	20 210	30 days	84.0	0.130	19 890
	90 days	62.0	1.026	20 670	50 days	77.0	0.170	20 060
	220 days	37.0	1.563	23 050	120 days	64.0	0.176	20 110
					250 days	43.0	0.252	21 590

Numerical data in the table come from papers (DZIURZYŃSKI 1984, SUPIŃSKI and DZIURZYŃSKI 1988).

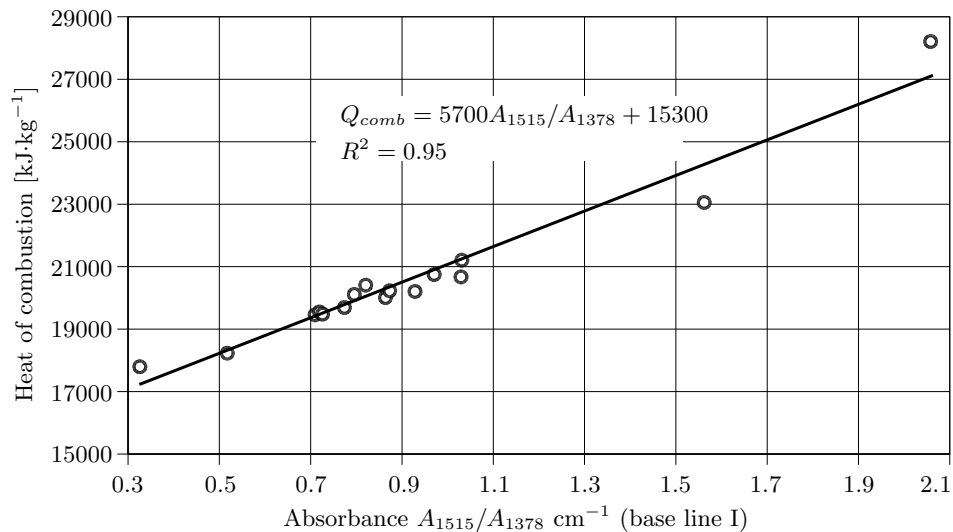


Fig. 1. Relation between the absorbance of MIR spectra band 1515/1378 cm<sup>-1</sup> of pine wood decomposed by chemical and biotical factors and its combustion heat

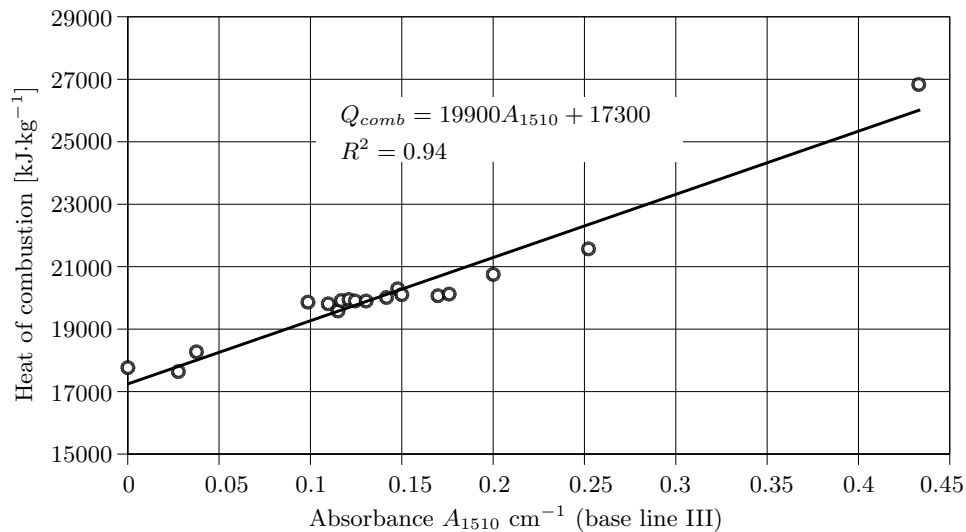


Fig. 2. Relation between the absorbance of MIR spectra band 1510 cm<sup>-1</sup> of beech wood decomposed by chemical and biotical factors and its combustion heat

for beech wood

$$19900 = \frac{q_l - q_h}{(A_{1510})_l - (A_{1510})_h}$$

where:  $q_l$ ,  $q_h$  – heat of combustion of lignin and holocellulose *in situ*,

$$\left(\frac{A_{1515}}{A_{1378}}\right)_l, \left(\frac{A_{1515}}{A_{1378}}\right)_h, (A_{1510})_l, (A_{1510})_h \text{ the absorbance of: 1515, 1378,}$$

and 1510  $\text{cm}^{-1}$  bands of lignin and holocellulose *in situ*.

Generally speaking, the deviations from straight lines visible in Figures 1 and 2 fall within limits of measurements repeatability. Greater deviations were observed in the case of holocellulose and lignin preparations (extreme points) and in the case of wood samples most degraded by the *C. puteana* fungus. Holocellulose preparations show elevated heat of combustion. This could have been caused by residue lignin. On the other hand, lignin preparations are characterised by depressed absorbance of the 1515 (1510)  $\text{cm}^{-1}$  band. This resulted from the presence of furfural polymers in them (DZIURZYŃSKI 2003). In the case of wood samples most degraded by the *C. puteana* fungus, the deviations from the straight line, representing reduction of the heat of combustion, amounted to about 1150 kJ/kg (5%) in pine and to about 700 kJ/kg (3%) in beech. This can be explained by the hydrolysis and oxydation reactions of wood – both of its carbohydrate and lignin constituents.

In the course of hydrolysis of carbohydrates and lignin, their heat of combustion decreases. It is worth mentioning here that the heat of combustion of glucose is by 10% smaller than the heat of combustion of cellulose. The depolymerisation and, hence, the hydrolysis of the wood decomposed by the *C. puteana* fungus has been confirmed by the increased content of substances soluble in 0.1 m NaOH. This increase was found to be 10.1-fold for the pine wood (yield = 37%) and 5.8-fold for the beech wood (yield = 43%) (DZIURZYŃSKI 1984).

Wood oxidation reactions also contribute to a decline in its heat of combustion because, similarly to water, oxygen is energetic ballast. The oxidation of wood strongest degraded by the *C. puteana* fungus is corroborated by the absorbance of its C=O bonds of carboxyl and carbonyl groups in the 1743  $\text{cm}^{-1}$  band of the MIR spectra. In comparison with the original wood, this absorbance increased by 2.3 times for the degraded pine wood (yield = 37%) and by 1.4 times in the case of the degraded beech wood (yield = 43%) (DZIURZYŃSKI at AL. 1988).

## CONCLUSIONS

1. The relationship between the heat combustion of wood and the absorbance of its infrared spectrum in the 1515 (1510)  $\text{cm}^{-1}$  band follows a straight line.
2. In the case of wood strongly degraded by the *C. puteana* fungus, the deviation from the straight line resulting from the decreased heat of combustion amounted to: about 5% (pine) and about 3% (beech). This decrease could have been caused by the hydrolysis and oxidation reactions of wood degraded by the above-mentioned fungus.

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