Changes of ultimate analysis and properties of solid and gas phases at the heating wood in an inert medium. A new view

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Abstract. A new approach to the study and description of the process of thermal destruction of wood when heated in an inert environment (torrefication and pyrolysis) is presented. Dependencies for determining the sequence of changes in the ultimate analysis of wood at the destruction process are proposed. Dependencies for determining the calorific value and volatile matter for the solid phase as a function of the ultimate analysis, as well as for determining the ultimate analysis and calorific value of volatile matter are proposed. A possibility of extending the method to other fuels of plant origin (straw, peat, coal) is shown. It has been suggested that standard methods do not accurately determine the moisture content of wood.

1. Introduction

Interest in the transformation of wood when heated in an inert medium in the last decade increased due to the widespread use of torrefication in wood pellets production. The torrefication is a moderate (no more than 300 .. 350°C) heating of the crushed wood for a more or less long time in an inert medium. It is believed that in this way it is possible to obtain a mass with a higher calorific value. A considerable experimental data has been accumulated, but a general view of the problem has not been worked out.

The paper proposes to consider the process of torrefication from the point of view, reported by A.B. Levin at the Scientific and Technical Conference of the Moscow State Forestry University in 2012 and published in [1-3]. The discourse in the most general form contains the following positions:

A. Dry ashfree mass of wood can be represented as a certain conventional substance with the chemical formula C₆H₉O₄. It should be noted that the same formula was used in [4].

B. The volatiles yield are 85.5% of dry ash free woody biomass. Accordingly, the relative mass of the carbon residue at the end of the destruction process is 14.5% C. The composition of the dry ash free mass of wood includes only carbon (mass fraction 49.7%) hydrogen (mass fraction 6.2%) and oxygen (mass fraction 44.1%). For untreated wood, the atomic ratio (O/C) = 2/3; atomic ratio (H/C) = 3/2. At the end of the thermal destruction process (O/C) = (H/C) = 0.

D. Wood substance always passes successively through the same states in isobaric heating in an inert medium. Van Krevelen [5] suggested this supposition. Graphically, the well-known Van Krevelen diagram represents it. The function line (H/C) = f (O/C) can be called the curve of the metamorphosis of the wood.
E. The gross calorific value can be calculated for the initial wood, carbon at the end of the thermal destruction process and any intermediate state according to Mendeleev’s equation [6] (kJ/kg):

\[ Q_{s}^{daf} = 339.5C^{daf} + 1256H^{daf} - 108.8O^{daf}, \]  

(1)

F. The efficiency of the process can be characterized by

\[ \eta_{ef} = \eta_g \cdot \eta_q, \]  

(2)

where \( \eta_e \) – the ratio of the mass of the solid residue to the initial mass of dry ashfree wood; mass conversion rate; \( \eta_q \) – the ratio of the gross calorific value of the solid residue to the gross calorific value of initial dry ash free wood, heat conversion rate; \( \eta_{ef} \) – theoretical conversion efficiency coefficient.

2. Results and Discussion

2.1. Changes of ultimate analysis of the solid phase during wood pyrolysis

The graph of the ultimate analysis of woody biomass is based on experimental data [7-9] for isobaric heating in an inert medium (see Figure 1). It can be described by equation with an error not exceeding the error of the initial data

\[ (O/C) = 0.2253(H/C)^2 + 0.125 \cdot (H/C) \]  

(3)

For more than half a century in the Van Krevelen diagram, the values of \( (O/C) \) have been plotted on the abscissa and \( (H/C) \) along the ordinate.

In this case, the equation \( (H/C) = f(O/C) \) should have the form:

\[ (H/C) = \left( -0.125 + \left( 0.125^2 + 4 \cdot 0.225 \cdot (O/H) \right)^{0.5} \right) / (2 \cdot 0.2253) \]  

(4)

A comparison of the calculation according to (3) with the experimental data given in the review [10], which were not used in deriving dependence 3, is presented in Figure 2. The position of the graph of wood metamorphosis on the Van Krevelen diagram is shown in Figure 3. The Van Krevelen diagram graphically represents a change in the ultimate analysis of solid fossil fuels, depending on their "geological age". Peat, lignite, coal and anthracite were formed during the thermal destruction of biomass of ancient forests or seaweeds that covered the surface of the Earth in previous geological epochs and found themselves in the thickness of the earth's crust as the result of global geological processes.

![Figure 1. Approximation of data [7-9].](image-url)
same time, the temperature in these processes is much lower than that at which the termination of thermal destruction of wood biomass is possible. It is interesting that this circumstance is not so clearly manifested in the field of lignite, in Russian-speaking sources commonly called “brown coals”.

Data on the ultimate analysis of stems of herbaceous plants are numerous. Most of the information on the ultimate analysis of thermally non-treated stems of grassy plants (straw) are grouped around a point with coordinates \((O/C) = 2/3\) and \((H/C) = 3/2\). The data on the ultimate analysis of biochars obtained from the straw of various herbaceous plants presented in Figure 4 also agree well with the calculation according to (4).

Experimental data on the ultimate analysis of various types of peat and biochar obtained from it, sometimes called “coke” or “semi-coke” are presented in Figure 5.

![Figure 2](image2.png)

**Figure 2.** Comparison of data [10] with calculation according to (4) 1 – calculation according to (4); 2 – hexosans, \(n\cdot(C_{6}H_{10}O_{5})\); 3 – pentosans, \(n\cdot(C_{5}H_{8}O_{4})\).

![Figure 3](image3.png)

**Figure 3.** Line of the process of thermal destruction of woody biomass on the Van Krevelen diagram [5]. 1 – calculation according to (4); 2 – \(n\cdot(C_{6}H_{10}O_{5})\); 3 – \(n\cdot(C_{6}H_{10}O_{5})\); 4 – charcoal, \(n\cdot(C_{7}H_{4}O)\); 5 – coke [9].

These data indicate, as well as for grassy plants, that a change in the ultimate analysis during the heating process of peat in an inert environment occurs in the same way, as it occurs at wood heating. However, the ratio \((O/C)\) of different types of natural peat may be in the range of 0.65 .. 0.35. At the same time, the ratio \((H/C)\) of these variables always turns out to be very close to the value calculated according to (4). This means that the transformation of dead plants into peat is accompanied by the changes in the ultimate analysis similar to the changes occurring with the wood when it is heated in an inert environment.
There is not much data on the change in ultimate analysis, when coal is heated in an inert environment. The difference of ultimate analysis of charcoal and coal which is noticeable at (O/C) <0.2 in Figure 3 could be explained by the difference of temperature and pressure of their formation. The value of the ratio (H/C), for coal in its initial state with the same value of the ratio (O/C) is different from the value (H/C)_w calculated from (4) for wood. Let us try to predict the change in ultimate analysis of coal. We introduce the parameter λ equal to the ratio (H/C)_c / (H/C)_w and determine how this parameter changes by heating fossil coal in an inert atmosphere.

Data for various types of coal from the USA, Mongolia, China and the Russian Federation, for which λ values are selected, are presented in Figure 6. The assumption about the constancy of the

Figure 4. The change in the ultimate analysis of solid phase of the herbaceous plant stems during pyrolysis. 1 – calculation according to (4); 2 - 13 – different herbaceous plants [2].

Figure 5. The change in the ultimate analysis of the solid phase of different types of peat during pyrolysis. 1 – calculation according to (4); 2 -9 – different types of peat [2].

Figure 6. The change in the ultimate analysis of solid phase of the different types of coal during pyrolysis. 1 - 8 – various types of coal from the USA, Mongolia, China and the Russian Federation [2].
parameter $\lambda$ is done more or less satisfactorily. You can see that the analogy is more precisely observed, when the carbon content in the original coal is lower.

We have the data for a relatively small number of tested varieties of coal and a small number of points for determining the ultimate analysis for each variety. This makes the picture less expressive, but the tendency appears clearly. Obviously, it can be argued that the lines of thermal metamorphosis of coal are similar, and the values of the ratio $(H/C)_o$ for a given ratio $(O/C)$ can be estimated as the product of the ratio $(H/C)$ was calculated from (3), and the parameter $\lambda$ for this type of coal.

\[ (H/C)_o = \lambda \cdot (H/C)_w. \] (5)

2.2. Changes in the gross calorific value of a dry ash free mass of the solid phase during wood pyrolysis

Experimental data on the gross calorific value were taken from [7, 8, 9, 11, 12], in which samples of woody biomass of various species were studied (a mixture of Canadian conifers, willow, pine, oak, birch, mixtures of species from the USA and mixtures of species from the RF) at different holding times at different temperatures. These data are supplemented by the values of the gross heat value of carbon (the state at the end of the gross calorific value).

![Figure 7](image)

Figure 7. The gross calorific value of dry ash free woody biomass for different degrees of thermal degradation [7, 8, 9, 11, 12].

Dependence on Figure 7 agrees qualitatively with the data of [15]. Accordingly, the thermal conversion coefficient:

\[ \eta_d = -1.67 \cdot (O/C) + 1.71 \] (6)

2.3. The change in the output of volatile matter and mass conversion rate for solid residue during the pyrolysis of wood

There are few experimental data on the yield of volatile species for woody biomass for different values of the ratio $(O/C)$. However, the dependence of the yield of volatiles from the solid residue for intermediate values of the entire range of possible values $0 \leq (O/C) \leq 0.667$ can be obtained with sufficient accuracy from the following more or less obvious considerations.

A. At $(O/C) = 0.667$ (untreated wood biomass) $V_{daf} = 0.855$ and $dV_{daf}/d(O/C) = 0$;
B. At $(O/C) = 0$ (the process of volatilization is complete) $V_{daf} = 0$;
C. The function $V_{daf} = f(O/C)$ is monotonic, continuous, and can be represented by a second degree polynomial.

Then:

\[ V_{daf} = -1.933 \cdot (O/C)^2 + 2.571 \cdot (O/C) \] (7)

The available experimental data agree with the dependence (6), as can be seen in Figure 8.
Now it is possible to find the mass conversion rate for any intermediate state of woody biomass as:

\[ \eta_g = \frac{0.145}{\left(1 - (-1.933 \cdot (O/C)^2 + 2.571 \cdot (O/C))\right)} \]  

(8)

**Figure 8.** Comparison of the experimental data with the calculation according to (6). 1 – calculation according to (6); 2 – data [7, 13]; 3 – data [14], quoted by [13]; 4 – data [9].

2.4. **Changes of the conversion efficiency coefficient during wood pyrolysis**

Calculating the effective conversion coefficient \( \eta_{ef} = \eta_q \cdot \eta_g \) for various values of \( (O/C) \) in the range from zero to 0.667, we obtain as the graph of the dependence of the conversion efficiency factor from the atomic ratio \( (O/C) \), which is shown in Figure 9. It can be seen that the value of \( \eta_{ef} \) remains about 1.0 at the values \( (O/C) \) from 0.667 to 0.58, and at \( (O/C) = 0.62 \) is 1.02. With a further decrease of the ratio \( (O/C) \), the \( \eta_{ef} \) falls to 0.248 at \( (O/C) = 0 \). The effect is associated with the removal of that part of the moisture that remains in the wood after the drying is completed by determination the moisture content with a standard weight method, i.e., holding the sample in a drying oven at a temperature of 103 ± 2 °C until the sample mass became constant.

**Figure 9.** Dependence of conversion efficiency factor from the ultimate analysis of woody biomass.

According to modern concepts, the equilibrium absolute humidity of wood under these conditions is at least 1%. This systematic error entails inaccuracies in determining the yield of volatiles – this moisture is included in their volume. Also, the moisture of the supposedly “absolutely dry” wood is included in the mass of water vapor formed when the hydrogen of the fuel is oxidized in the process of determining the ultimate analysis. There is also an inaccuracy in calculating the gross calorific value with the use of calorific value according to the calorimetric bomb and the moisture content of the analytical mass of wood fuel. An accurate assessment of these errors and methods for their elimination require special investigations.

The increasing of the calorific value of the torrefied wood obtained from 1 kg of dry ash-free wood is not sufficient itself, in order to approve the costs of the process of torrefication. However, the
interest to torrefication still does not diminished; on the contrary, it increases. This interest is caused by the fact that pellets are sold and bought at prices proportional to the net calorific value, not to the gross one. The net calorific value can be calculated as [6] (kJ/kg):

\[ Q_{daf} = Q_{daf} \cdot (100 - A_r - W_r)/100 - 25.2 \cdot (9 \cdot H_r) \]  

(9)

Let us compare this indicator to "white" pellets with \((O/C) = 0.667\) and moisture content \(W_r = 8\%) and pellets from the optimally torreficated wood biomass with \((O/C) = 0.62\) and humidity \(W_r = 1\%) with the same ash content \(A_r = 1\%\).

From the results of calculation it follows, that the net calorific value of the torreficated wood is 15\% higher than that of untreated wood. Therefore, the gain in the bulk energy density can so much reduce the costs of transportation of a unit of energy, that it may justify the cost of the process of torrefication.

2.5. Changes in the composition and properties of the gas phase during wood pyrolysis

The above-stated approach has been applied to the study of changes in the elemental composition of the gas phase [3]. This study suggested that standard methods for determining humidity and volatile matter yield do not allow us to establish their real values. It is considered that the final removal of a certain amount of moisture, which is not taken into account by standard methods, proceeds in the temperature range from 100°C to the starting temperature of the noticeable formation of gaseous decomposition products of the actual wood substance at about 160°C.

Figure 10. Changes of ultimate analysis of gas phase \((O/C)1\) and \((H/C)1 = W = 0.0025; (O/C)2\) and \((H/C)2 = W = 0.01\).

Figure 10 shows the change in the ultimate analysis of volatile matter as a function of the relative mass loss, for two values not determined by standard methods of determination of residual moisture \(W = 0.01\) and \(W = 0.0025\). Probably, in the initial stage of the pyrolysis, volatiles consist exclusively or predominantly of water vapor, therefore, \((O/C) \rightarrow \infty\) and \((H/C) \rightarrow \infty\). Reliable data on the composition of volatile substances in the initial phase of pyrolysis or on the amount of undetectable moisture of the wood could not be found. It is necessary to fulfill a special careful research of changes in mass, the composition of volatile and thermal effects in an area of temperature 100… 160 °C.

3. Conclusions

A new approach to the study and description of the process of wood pyrolysis is proposed, which allows to associate the change in the thermophysical properties of wood with the relative change of mass. Relationships have been obtained for calculating the conversion efficiency ratio, and opportunities for optimizing the torrefication process have been opened.

This approach has also been applied to investigate changes in the elemental composition of the gas phase [3]. This study suggested that standard methods for determining moisture and volatile matter do not allow us to establish their true values. In the temperature range from 100 °C to the temperature
of the starting of the noticeable formation of gaseous decomposition products of the actual wood matter (it is considered to be about 160 ° C), a final removal of a certain amount of moisture, not taken into account by standard methods, occurs. Special careful studies are needed in this range of temperature changes in mass composition of volatiles and in thermal effects as well.

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