# THERMAL ANALYSIS AND CALORIMETRIC STUDY OF THE COMBUSTION OF HYDROLYTIC WOOD LIGNIN AND PRODUCTS OF ITS PYROLYSIS

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*Thermal decomposition of hydrolyzed lignin is studied in the 300-700єC range in an inert gas atmosphere. The yields of solid, liquid, and gaseous decomposition products are determined. It is demonstrated by combustion calorimetry that the carbonaceous residue of lignin pyrolysis has the highest calorific value. The calorific value of the carbonaceous residue of pyrolysis resin is higher than that of the original lignin. It is shown by thermogravimetry and differential scanning calorimetry with mass spectrometric detection of gases that lignin and its thermal decomposition products could undergo thermolysis with formation of various volatile compounds. Thermal decomposition starts at roughly the same temperature and is 320єC. The loss of sample mass increases in the following sequence: carbonaceous residue < lignin < liquid fraction.*

*Keywords:* *lignin, pyrolysis, combustion calorimetry, thermogravimetry, differential scanning calorimetry, calorific value*

Together with cellulose, lignin is one of the most common natural organic polymers. It consists of phenyl-propane structural units, as well as their methoxyl and hydroxyl derivatives [1]. The lignin content of wood is 20-30 wt. %, which makes it a potential source for obtaining organic compounds. In the world as a whole, roughly 50 million tons of lignin are formed each year in flows of lye at cellulose-paper plants [2]. Of this amount, 98% is simply burned in boilers at cogeneration facilities. It should be mentioned that the advent of biotech methods of converting vegetable matter into biofuels and biopolymers by hydrolysis is also

significantly increasing the volume of lignin wastes [3]. The level of use of lignin to make high-added-value products is currently no higher than 2% [4]. Derivatives of lignin can be used to obtain aromatic hydrocarbons, sorbents, emulsifiers, and additives for road-grade bitumen. They can also be used in machine construction and the production of building materials, synthetic resins, oils, polymers, bioplastics, and biofuels [2].

One nonselective method of recycling lignin wastes into low-molecular-weight substances is thermomechanical conversion - in particular, pyrolysis [2]. Phenolic compounds are the main liquid products from the thermal decomposition of lignin [5]. The thermal decomposition of lignin in a reducing medium can yield up to 5-6 wt. % monophenolic compounds [5], whereas the product yield when phenols are made from coal is just 0.2 wt. % [6].

Thermal decomposition of the polymeric structure of lignin begins at just 200°C. Most of the volatile products are formed at temperatures around 400°C [7]. The thermal breakdown of lignin takes place via two competing reaction paths [8]: intramolecular condensation/polymerization that involves the formation of a carbonaceous residue; thermal depolymerization accompanied by the formation of aromatic hydrocarbons, phenols, guaiacol, and syringol.

Hydrolytic lignin differs significantly from natural and technical lignins obtained in the production of cellulose [5]. It contains appreciably fewer different functional groups apart from the methoxyl groups, which are stable during hydrolysis. Hydrolytic lignin has almost no solubility in alkalis and polar solvents.

To evaluate the thermal properties and calorific value of hydrolytic lignin and the products obtained from its recycling, we studied specimens of lignin obtained from the acidic hydrolysis of softwood at the Kirov Biochemical Plant. The hydrolytic lignin was dried to a constant weight in a drying cabinet at a temperature of 105°C. It was then subjected to mechanical comminution on a mill and separated on screens [9]. The 0.315-0.63 mm fraction was used for the investigation.
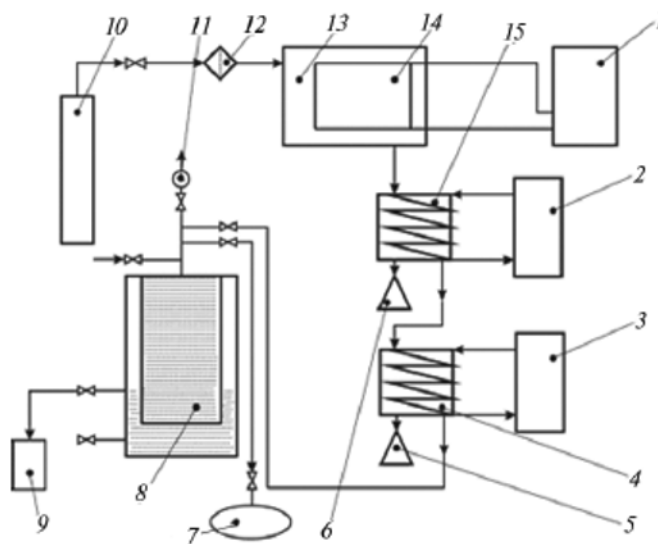


Fig. 1. Diagram of the experimental stand for studying the pyrolysis of lignin: 1) power supply; 2) thermostat; 3) container for coolant; 4) heat exchanger; 5, 6) vessels for collecting the condensate; 7) gas sampler; 8) gas holder; 9) measurement vessel; 10) cylinder with inert gas; 11) bleed valve; 12) filter; 13) pyrolysis chamber; 14) heating element; 15) condenser.

The hydrolytic lignin underwent pyrolysis on an experimental unit (Fig. 1) [10] that includes a reactor with a mesh heater, a condensation system, and a gas holder. The pyrolysis was done in a stream of nitrogen within the temperature range 300-600°C. The average heating rate was 28 deg/sec and the final temperature during the pyrolysis operation was 700°C. Condensation of the vapor-gas mixture took place in a surface-type heat exchanger with a coolant temperature of 15°C. The lignin specimens were placed on a reticular heating element and hermetized in the pyrolysis chamber by using a cover. The reaction chamber was then heated to 150°C. After inert gas was injected into the chamber, the power supply was connected and the pyrolysis operation was executed. Measurements were then made to determine the weights of the pyrolysis products: liquid products, carbon, and gas.

The heat of combustion of lignin and the products of its thermal decomposition were determined on a 6000-series IKA calorimeter. The measurement was performed on a 0.5-g sample in the isoperibolic regime with excess oxygen and a temperature of 25°C. The operations of filling with oxygen, thermal stabilization, ignition, and discharge of the gases that remained after ignition were done automatically. Several experiments were performed for each product.

Table 1

| Product | Yield, wt. % |
|---|---|
| Coal | 45.7 |
| Gas | 15.6 |
| Liquid products, including | 38.6 |
|    aqueous phase | 15.4 |
|    organic phase (resin) | 23.2 |

Table 2

| No. of specimen | Higher heat of combustion, MJ/kg | Average value, MJ/kg |
|---|---|---|
| *Lignin* | | |
| 1 | 24660 | |
| 2 | 24922 | |
| 3 | 24570 | |
| 4 | 24833 | |
| 5 | 24777 | |
| 6 | 24921 | 24781±111 |
| *Coal* | | |
| 1 | 30369 | |
| 2 | 30770 | |
| 3 | 30395 | |
| 4 | 30591 | |
| 5 | 30755 | |
| 6 | 30333 | 30536±170 |
| *Resin* | | |
| 1 | 28428 | |
| 2 | 27340 | |
| 3 | 27573 | |
| 4 | 28035 | 27884±584 |

Lignin and its pyrolysis products were subjected to thermal analysis on modern thermal analyzer STA 449 C Jupiter (Netzsch, Germany) used together with quadrupole mass spectrometer QMS 403 C Aeolos (Netzsch) to analyze the gaseous decomposition products (TA/DSC/Ms). The measurements were made within the temperature range 30-600°C in a dynamic argon atmosphere (gas flow rate 75 ml/min). Heating rate was 10 deg/min. The analysis was described in detail in [11, 12].

Table 1 shows the material balance in the high-speed pyrolysis of lignin. After being allowed to settle, the liquid products of the pyrolysis operation were separated into two phases: water and resin (the water is above the resin). It can be seen that a significant portion of the hydrolytic lignin is left as a
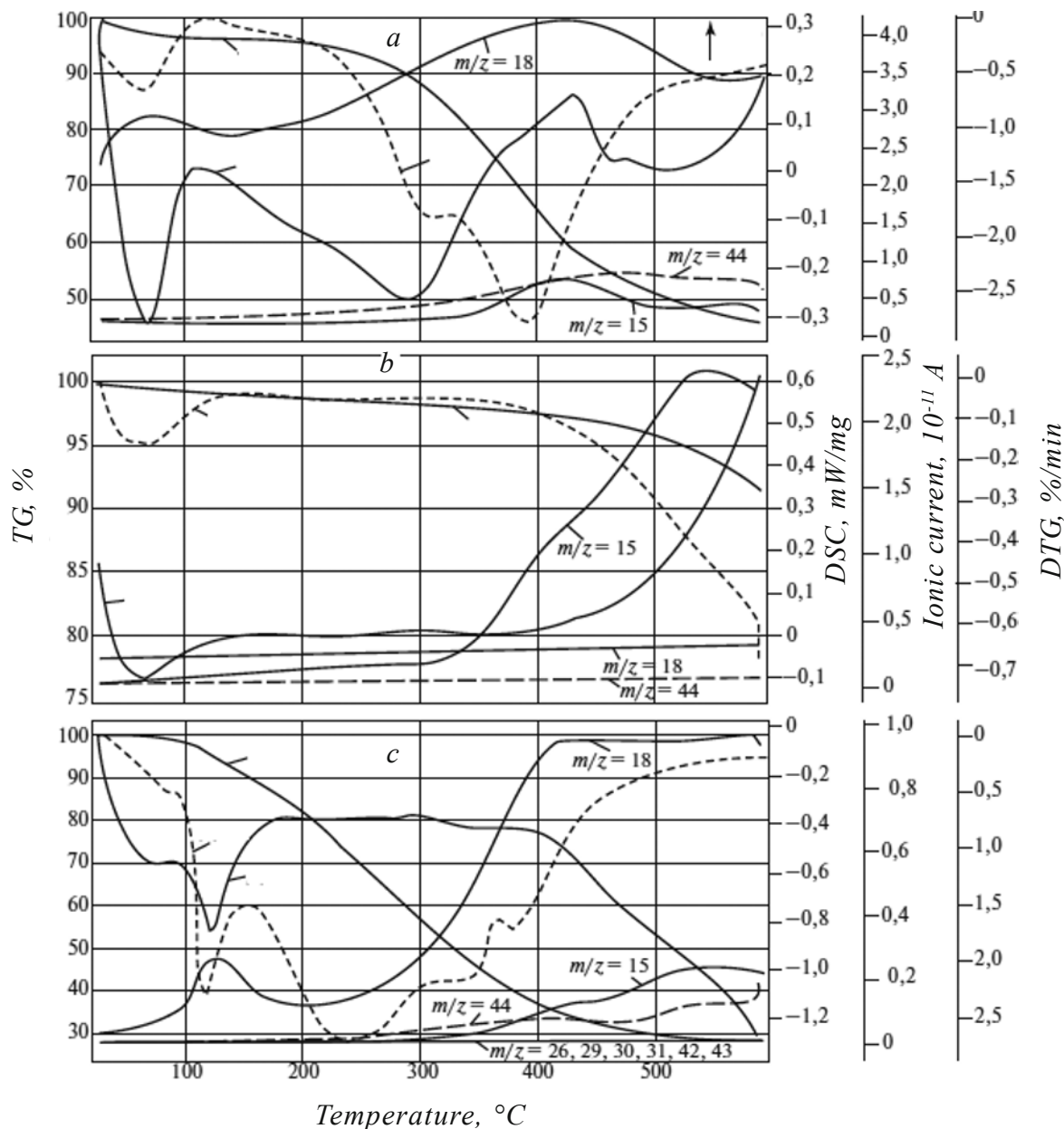


Fig. 2. Results obtained from the TG/DSC/MS analysis: a) lignin; b) carbonaceous residue; c) resins.

carbonaceous residue after thermal decomposition. The lignin particles are sintered into an agglomerate during pyrolysis, which is indicative of the lignin's plasticization and the interaction of the particles with each other during decomposition. Several studies, such as [13], have examined the formation of aggregates and the complexity of recycling technical lignin in fluidized-bed reactors.

Table 2 shows data on the heat of combustion of lignin and the products of its pyrolysis. It can be seen that different specimens of a single product have similar values for heat of combustion despite the inhomogeneity of the lignin and coal specimens. This confirms the reliability of the experimental data. Substantial differences are seen only in the case of the resins, which is due to the high viscosity and the consequent nonuniformity of their composition. The data which is obtained might also be affected by differences in the water content of different resin specimens. The highest-energy product of lignin's thermal decomposition is the carbonaceous residue, which can be attributed to its high carbon content. The heat of combustion of the resins is also greater than that of lignin. If we compare the high heat of combustion of lignin against the heat of combustion of other materials used as alternative fuels, we find that lignin is more efficient than fuel briquettes (19.5 MJ/kg), brown coal (15 MJ/kg) and hard coal (22 MJ/kg) [14].

Figure 2 shows the results obtained from thermal analysis of the lignin specimens. Several stages of mass loss can be seen on the thermogravimetric curve (TG) for the decomposition of lignin (Fig. 2a). The specimens undergo dehydration in the range 30-200°C, as indicated by the presence of a signal from the mass spectrometer for $m/z = 18$. The mass loss corresponding to this process is 4.2%. At temperatures above 250°C, lignin undergoes thermal decomposition and water, carbon dioxide ($m/z = 44$), and methane ($m/z = 15$) are formed as the main products. Within the temperature range from 200 to 320°C, carbohydrate residues – most likely, pentose and cellulose residues – may also decompose. The mass loss seen from lignin specimens in the range 200-320°C – the same range in which carbohydrate residues might decompose – is 15.5%. In accordance with the curve obtained from differential thermogravimetry (DTG), the maximum cracking rate is reached at temperatures of 380-400°C.

Several phenomena are seen on the DSC curves obtained for the decomposition of lignin. The endothermic effect which is seen with a peak at 69.6°C is connected with the evaporation of water. Thermal degradation of lignin at temperatures above 250°C is accompanied by an endothermic effect with a peak at 292.7°C. This effect smoothly transforms into an exothermic effect with a peak at 429.8°C. The presence of the exothermic effect might be an indication of the secondary interaction (recombination) of the primary pyrolysis products. The presence of methane in the gases formed during decomposition reflects the decomposition of lignin's functional groups at temperatures above 350°C. The main stage of the pyrolysis of lignin occurs in the range 320-500°C.

Compared to lignin, the amount of mass lost with the solid carbonaceous residue is considerably smaller within the given temperature range (Fig. 2b). The mass loss connected with the evaporation of water is 1.4% in that range and is no greater than 7% in the range 250-600°C. The change in the mass of the carbonaceous residue after lignin's pyrolysis takes place within a wider temperature range compared to lignin and is not fully completed even at 600°C. This is evident from the curves that show the release of methane ($m/z = 15$) and from the DSC results. The exothermic effect that is readily seen at temperatures above 380°C is almost certainly related to recombination, condensation, and consolidation of the more stable aromatic fragments.

The thermal decomposition of resin presents a more complex pattern (Fig. 2c) compared to lignin. Sorbed water is more strongly retained by the resin than by lignin or coal. Evaporation of the water takes place at temperatures above 100°C and continues to 200°C. The resin undergoes thermal decomposition

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above 200°C, as is indicated by the release of $CO_2$. Thermal decomposition of the resin above 320°C is accompanied by the release of different products with $m/z$ = 15, 18, 26, 29, 30, 31, 42, 43, and 44. The existence of these fragments might be related to the decomposition of hydroxyl-bearing, methoxyl-bearing, and hydrocarbon fragments ($m/z$ = 26, 29, 30, 32, 42, and 43). Total mass loss within the investigated temperature range is 71.9%. It can be concluded from this that the resin has a higher content of low-molecular-weight substances. The composition of those substances will be studied in greater detail in future investigations. Lignin and the products of its pyrolysis begin to thermally decompose at roughly the same temperature, which is 320°C. Here, methane is released within a narrow range of temperatures in the case of lignin, while the thermal decomposition of the resin is accompanied by the formation of a large number of products.

Comparison of the material balance of lignin pyrolysis with a heating rate of 1500 deg/min (see Table 1) and the results of the TG analysis of lignin with a heating rate of 10 deg/min (see Fig. 2a) shows that the yield of the carbonaceous residue changes little as heating rate changes (45.7 and 48.4 wt. %, respectively). Thus, the material balance of the process of lignin pyrolysis is most affected by macrokinetic effects. An increase in the size of the particles of the feedstock is accompanied by more rapid secondary decomposition of the components of the vapor-gas mixture and an increase in the yield of solid products. Thus, in making practical use of lignin pyrolysis technology, it is necessary to pay special attention to the quality of the feedstock's preliminary comminution and to make use of mechanical activation.

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