Research Square

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Hydrolysis Lignin Thermal Treartment in a Laboratory Fixed Bed Reactor

Pavel Alekseev
Federal University named after M. V. Lomonosov
Dmitri Kuchin
Federal University named after M. V. Lomonosov
Mikhail Ivanov
Federal University named after M. V. Lomonosov
Pavel Maryandyshev
p.marjyandishev@narfu.ru
Federal University named after M. V. Lomonosov

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Abstract

This study addresses the need to incorporate hydrolysis industry residues accumulated in Russian Federation and stored for a long time in open dumps into energy and thermochemical conversion processes. Hydrolysis lignin was characterized by proximate and calorimetric analyses of the initial feedstock and solid products, a series of heating experiments in a vertical laboratory glass fixed bed reactor and pyrolytic GC-MS analysis of volatile products. The aim was to establish the relationship between mass loss at 200, 300, 400, 500, and 600°C and the composition of thermal decomposition products determined by GC-MS. Reactor experiments were conducted with sample masses of 5, 10, and 15 g. Target temperature was reached within 20–60 min, and the isothermal residence time was 30 min in all experiments. Average mass loss increased from 11.8% at 200°C to 57.7% at 600°C. The most conversion occurred between 300 and 400°C, when the average mass loss increased from 23.2% to 48.9%. At 400°C, total ion chromatogram (TIC) reached the maximum integrated peak area and the largest number of detected peaks, indicating the highest diversity of volatile products. Fuel characterization revealed a high moisture content of the initial material, a substantial volatile matter content on a dry basis, and an as-received lower heating value of 19.92 MJ/kg. Results identify 400–500°C as the principal temperature range for relating mass loss, solid residue yield and volatile phase composition. For solid residues produced at 200–600°C, residual moisture content decreased to 1.98%, dry-basis ash content increased to 24.58%, and the lower heating value reached 26.54 MJ/kg, indicating deeper thermal conversion and a higher energy density of the product.

1. Introduction

Hydrolysis lignin is a large-volume residue of industrial wood processing. In the Arkhangelsk Region of the Russian Federation, as in several other forest industry regions, accumulation and long-term storage of hydrolysis industry residues remain an important ecological problem. Large quantities of this material were formerly deposited in open dumps, resulting in land occupation and potential adverse effects on environmental components. Nevertheless, hydrolysis lignin should not be regarded solely as a waste because its organic fraction retains considerable potential for energy and thermochemical conversion [1].

Hydrolysis lignin is a technical lignin with a complex and heterogeneous structure. It contains a condensed aromatic matrix, residual polysaccharides, resinous components, and mineral impurities, which proportions depend on the original wood species and the operating conditions of the hydrolysis process [1]. Carbonaceous organic fraction makes this material a potential feedstock for producing a solid carbon product, together with gaseous and condensable thermal decomposition products. This route is consistent with current approaches to lignin valorization for fuel and chemical production [2, 3].

A comprehensive approach is generally used to characterize lignocellulosic feedstocks, with the lignin, carbohydrate, and mineral fractions determined separately and the results reported on a dry basis [4]. This is particularly important for hydrolysis lignin because of its high moisture content, heterogeneity,

and possible presence of residual carbohydrates, which may affect both mass loss and the composition of volatile products.

Selection of a processing temperature cannot be only based on the final mass of the solid residue. Integral mass loss reflects the combined effects of moisture evaporation, volatile release and degradation of the organic matrix, but it does not describe the chemical composition of the evolving vapor phase. Lignin decomposes over a broad temperature range through sequential cleavage of ether and carbon-carbon bonds, producing phenolic compounds, gases, and a carbonaceous residue [5–8]. Therefore, a combined analysis of gravimetric data, volatile product composition, and solid product properties provides a more reliable basis for identifying the main conversion stages.

Pyrolytic gas chromatography with mass spectrometric detection has shown that the product distribution from technical and hydrolysis lignins depends strongly on temperature and feedstock pretreatment. Phenolic compounds constitute the major fraction of organic products from enzymatic hydrolysis lignin, and the chromatograms become most complex around 400°C [9]. Studies of lignin-containing residues from bioethanol production also confirm the formation of guaiacyl, syringyl, and vinylphenolic derivatives during pyrolysis [10]. Mechanistic studies relate phenolic product formation to interunit bond cleavage and hydrogen transfer reactions [11]. In catalytic fast pyrolysis of hydrolysis lignin, the maximum yield of monomeric phenols was reported near 450°C [12], while hydroconversion studies indicate that this type of technical lignin retains high reactivity [13].

Aim of this study was to determine the dependence of hydrolysis lignin mass loss on the heating temperature in a vertical laboratory glass reactor and to compare the observed trends with pyrolytic GC-MS results obtained at 200, 300, 400, 500, and 600°C.

2. Materials and Methods

Hydrolysis lignin originating from hydrolysis industry residues in Arkhangelsk, Russian Federation was used as the investigated material. This material had been stored for an extended period in open dumps; therefore, its high moisture content and heterogeneity were considered during sampling and sample preparation. Ultimate analysis was performed by using an EA3000 analyzer, while mineral elements were quantified by X-ray fluorescence spectroscopy using an EDX 8000 spectrometer. Initial characteristics were selected according to the generally accepted comprehensive analysis scheme for lignocellulosic feedstocks [4]. Total moisture was determined in accordance with ISO 18134-1:2022, water content in the general analysis sample according to ISO 18134-3:2023, and volatile matter according to ISO 18123:2023 [14–16].

Table 1
Fuel and thermal characteristics of the initial hydrolysis lignin

Parameter	Unit	Value
Moisture content, Wa	%	59,557
External moisture	%	12,167
As-received moisture	%	64,477
Ash content on a dry basis, Aa	%	0,346
Ash content on an as-received basis, Ad	%	0,140
Volatile matter on a dry basis, Vd	%	76,048
Volatile matter on a dry ash-free basis, Vdaf	%	76,312
Higher heating value on an as-received basis	kJ/kg	22957,32
Lower heating value on an as-received basis	kJ/kg	19919,20
Lower heating value on a dry basis	kJ/kg	21593,69

Table 2
Elemental composition of the initial hydrolysis lignin

Parameter	Unit	Value
C	%	46,3
O	%	45,7
H	%	5,51
N	%	< 0,1
S	%	1,19
Ca	%	0,853
Si	%	0,265
Al	%	0,153
Fe	%	0,020
K	%	0,012
Mg	%	0,013
Cu	%	0,004
Ti	%	0,004
Mn	%	0,002
Cr	%	0,001
Zn	%	0,001
Sr	%	0,001

Initial hydrolysis lignin had a moisture mass fraction of 59.56%, an external moisture content of 12.17%, and an as-received moisture content of 64.48%. Ash content was 0.35% on a dry basis and 0.14% on an as-received basis. Volatile matter content was 76.05% on a dry basis and 76.31% on a dry ash-free basis. As-received higher and lower heating values were 22.96 and 19.92 MJ/kg, respectively, while the dry-basis lower heating value was 21.59 MJ/kg. Ultimate analysis comprised 46.3% carbon, 45.7% oxygen, 5.51% hydrogen, 1.19% sulfur, and less than 0.1% nitrogen. Main mineral elements were calcium – 0.85%, silicon – 0.265%, and aluminum – 0.15%; amount of iron, magnesium, potassium, copper, titanium, manganese, chromium, zinc, and strontium did not exceed 0.02% for any individual element.

High moisture content of the initial hydrolysis lignin is an important factor in interpreting the reactor experiments. Technical hydrolysis lignins may contain substantial water content, so the low-temperature heating stage is governed primarily by its removal [1]. Thus the gravimetric results were evaluated

together with the GC-MS data. At low temperatures, main process was contributed to moisture evaporation, whereas at 400–500°C the analysis focused on formation of the organic volatile phase and the main increase in mass loss.

Reactor experiments were performed in a laboratory unit with a vertical tubular reaction zone made of quartz glass and surrounded by an electric heater. Sample was placed in a suspended crucible in the central part of the heated section. Reactor is equipped with upper and lower shutoff valves, a pressure gauge, and an outlet for gaseous products operated under reduced pressure. A schematic diagram of the laboratory reactor and the arrangement of its principal components are shown in Fig. 1. Hydrolysis lignin samples of 5, 10, and 15 g were heated to final temperatures of 200, 300, 400, 500, and 600°C. Time required to reach these temperatures was 20, 30, 40, 50, and 60 min, respectively. Isothermal residence time was 30 min in all experiments. After the cooling the reactor, solid residue mass was determined.

Sample mass loss was calculated as follows:

$$\Delta\,\mathrm{m}\;=\;\frac{\mathrm{m}_1\;-\;\mathrm{m}_2}{\mathrm{m}_1}\;\cdot\;100$$

1

where Δm is the sample mass loss, %; m_1 is the initial sample mass, g; and m_2 is the mass of the solid residue, g.

Solid residue yield was calculated as follows:

$$\mathrm{Ys}\;=\;\frac{\mathrm{m}_2}{\mathrm{m}_1}\;\cdot\;100$$

2

where Y is the solid residue yield, %. Mass ratio is dimensionless.

Pyrolytic GC-MS analysis was performed at 200, 300, 400, 500, and 600°C. Analytical pyrolysis sample mass was 271 μg, and the pyrolysis time was 1 min. Total TIC peak area, number of detected components, and the contributions of water, CO_2, and organic compounds groups were determined from the total ion chromatograms. Py-GC/MS usage to assess temperature-dependent changes in lignin decomposition products is consistent with approaches applied to enzymatic and industrial lignin-containing residues [9, 10]. Analytical results were compared with the integral mass loss measured in the laboratory reactor.

To relate the degree of hydrolysis lignin conversion to the properties of the resulting solid product, residues obtained at 200, 300, 400, 500, and 600°C were analyzed. This temperature series covered

initial low-temperature treatment and subsequent stages of more extensive decomposition of the organic fraction.

Moisture mass fraction, ash content on dry and as-received bases, higher and lower heating values on an as-received basis were determined for the solid residues. These properties were compared with the treatment temperature, mass loss in the reactor experiments, and changes in the volatile phase composition. This presentation makes it possible to assess both the extent of organic matrix decomposition and the evolution of the fuel properties of the carbonaceous products [1, 12].

3. Results and Discussion

For each temperature condition, three samples with masses of 5, 10, and 15 g were analyzed. Heating rate was maintained at 10°C/min. Time required to reach the target temperature increased from 20 min at 200°C to 60 min at 600°C. Isothermal residence time was kept constant at 30 min in all experiments. Temperature-time profiles are presented in Fig. 2. For each sample, initial mass, solid residue mass, mass loss, and solid phase yield were recorded.

Table 3
Heating parameters of hydrolysis lignin in the vertical glass reactor

T, °C	Sample	m1, g	m2, g	Δm, %	Ys, %	τh/τhold, min
200	5 g	5,094	3,796	25,5	74,5	20/30
200	10 g	10,003	9,307	7,0	93,0	20/30
200	15 g	15,094	14,643	3,0	97,0	20/30
300	5 g	5,047	3,524	30,2	69,8	30/30
300	10 g	10,016	7,884	21,3	78,7	30/30
300	15 g	15,057	12,312	18,2	81,8	30/30
400	5 g	5,096	2,619	48,6	51,4	40/30
400	10 g	10,064	5,302	47,3	52,7	40/30
400	15 g	15,041	7,402	50,8	49,2	40/30
500	5 g	5,046	2,334	53,7	46,3	50/30
500	10 g	10,095	4,700	53,4	46,6	50/30
500	15 g	15,014	6,720	55,2	44,8	50/30
600	5 g	5,052	2,236	55,7	44,3	60/30
600	10 g	10,091	4,153	58,8	41,2	60/30
600	15 g	15,047	6,221	58,7	41,3	60/30

As shown in Fig. 3, increasing the final heating temperature progressively increased the mass loss of hydrolysis lignin. Curves also indicate the effect of sample mass on the intensity of thermal decomposition.

Average mass loss was 11.8% at 200°C, 23.2% at 300°C, 48.9% at 400°C, 54.1% at 500°C, and 57.7% at 600°C. Accordingly, average solid residue yield decreased from 88.2% at 200°C to 42.3% at 600°C. The largest increase in mass loss occurred between 300 and 400°C and amounted to 25.7 percentage points. Corresponding increases over 400–500°C and 500–600°C were considerably smaller, at 5.2 and 3.6 percentage points, respectively.

The effect of sample mass was mainly indicated in the 200–300°C range. At 200°C, mass loss of the 5 g sample was 25.5%, whereas the values for the 10 and 15 g samples decreased to 7.0% and 3.0%, respectively. A similar trend was observed at 300°C, with mass losses of 30.2% for 5 g, 21.3% for 10 g, and 18.2% for 15 g. These results indicate that layer thermal inertia and initial moisture content strongly affect the early heating stages. Smaller sample heats more rapidly throughout its volume, resulting in more intensive removal of moisture and light volatile compounds.

At 400°C, differences among the samples became much smaller. Mass losses were 48.6%, 47.3%, and 50.8% for the 5, 10, and 15 g samples, respectively. This convergence indicates that, once this temperature is reached, the process is governed not only by heating of the material layer but also by active decomposition of the organic matrix. At 500 and 600°C, mass loss values also remained within narrow ranges of 53.4–55.2% and 55.7–58.8%, respectively. Thus, above 400°C, further temperature increases mainly promote decomposition of the remaining components, but do not produce a mass change as pronounced as that observed between 300 and 400°C.

Comparison of average mass loss with the total TIC peak area in Fig. 4 shows that the maximum intensity of detectable volatile product formation does not coincide with the maximum final mass loss. Solid residue mass continued to decrease up to 600°C, whereas the total TIC peak area reached a maximum at 400°C and then declined. This divergence is attributable to the increasing contribution of secondary reactions of volatile compounds and the formation of low-molecular-weight products as the temperature increases [9, 12].

Pyrolytic GC-MS analysis showed that the chromatogram obtained at 200°C consisted almost entirely of water and CO_2. Two peaks were detected, total TIC peak area was 4.60 million arbitrary units, and the relative peak area of water reached 96.26%. This volatile phase composition is consistent with the reactor results and confirms that moisture removal predominates at the lowest temperature. A similar dominance of water under mild thermal treatment was reported for enzymatic hydrolysis lignin analyzed by Py-GC/MS [9].

Table 4
Summary parameters of pyrolytic GC-MS analysis of hydrolysis lignin

T, °C	Sample mass, μg	Pyrolysis time, min	Number of peaks	ΣTIC, million arb. units	CO_2, %	Water, %
200	271	1	2	4,60	3,74	96,26
300	271	1	17	17,03	18,43	54,80
400	271	1	64	143,30	8,31	12,82
500	271	1	22	31,85	4,58	58,88
600	271	1	4	15,09	5,26	92,20

Table 5
Group distribution of products by relative TIC area

T, °C	CO_2	H_2O	Light oxygen-containing compounds	Phenolic and aromatic compounds	Carbohydrate and furan compounds	Hydrocarbons and aromatics
200	3,74	96,26	0,00	0,00	0,00	0,00
300	18,43	54,80	14,29	3,97	3,28	5,23
400	8,31	12,82	20,60	25,26	16,92	16,09
500	4,58	58,88	15,06	22,48	0,00	4,99
600	5,26	92,20	0,00	2,54	0,00	0,00

At 300°C, number of detected peaks increased to 17 and the total TIC peak area to 17.03 million arbitrary units. Relative peak area of water decreased to 54.80%, while the contribution of CO_2 increased to 18.43%. Light oxygenated compounds, phenolic compounds, aromatic compounds, carbohydrate-derived compounds, and furan compounds appeared in the volatile phase. Thus, decomposition of the organic fraction of hydrolysis lignin starts alongside moisture removal. Appearance of several classes of oxygenated compounds in this range agrees with published data on the initial depolymerization of technical lignins [5, 6, 9].

The most complex volatile product composition was obtained at 400°C. At this temperature, number of peaks increased to 64 and the total TIC peak area reached 143.30 million arbitrary units. Simultaneously, relative peak area of water decreased to 12.82%, while the contributions of the organic product groups reached their maximum values. Light oxygenated compounds accounted for 20.60%, phenolic and aromatic oxygenated products for 25.26%, carbohydrate-derived and furan compounds for 16.92%, hydrocarbon and aromatic compounds for 16.09%. The maximum diversity of the volatile phase around 400°C is consistent with Py-GC/MS results for enzymatic hydrolysis lignin, which showed a marked change in the distribution of phenolic products in the same temperature range [9].

At 500°C, average reactor mass loss increased to 54.1%, but the total TIC peak area decreased to 31.85 million arbitrary units and the number of peaks fell to 22. Phenolic and aromatic oxygenated products continued to make a substantial contribution to the volatile phase, while the relative contribution of water increased. Reduction in product diversity after the maximum in the 400–500°C temperature range agrees with literature data showing that further temperature increases promote secondary cracking of primary vapors and reduce the yields of individual monomeric phenols [9, 12].

At 600°C, four peaks were detected, total TIC peak area was 15.09 million arbitrary units, and water dominated the volatile phase with a relative peak area of 92.20%. Average mass loss reached 57.7%. Thus, a high final mass loss was not accompanied by increased diversity of volatile products. This condition corresponds to further decomposition and stabilization of the solid carbonaceous residue. In view of established pyrolysis mechanisms, this behavior may be associated with secondary hydrogen transfer reactions and further degradation of intermediate oxygenated compounds [11].

As shown in Fig. 5, total TIC peak area and the number of detected peaks changed in a consistent manner. Both parameters increased sharply up to 400°C and then decreased at 500–600°C. Between 300 and 400°C, total TIC peak area increased by more than a factor of eight, while the number of peaks increased almost fourfold. At 500°C, TIC area was approximately 4.5 times lower than the maximum, confirming a transition from active formation of organic volatile products to their secondary conversion.

Group distribution of volatile products shown in Fig. 6 reflects a sequential change in the dominant processes. Water prevailed at 200°C. At 300°C, CO_2 contribution of increased and oxygenated organic compounds appeared. At 400°C, composition was the most diverse, corresponding to active degradation of the lignin structure. Phenolic and aromatic oxygenated compounds remained significant at 500°C, whereas the distribution became simpler again at 600°C. Phenolic derivatives predominance during the hydrolysis lignin pyrolysis has also been reported in previous studies [9, 10, 12].

Figure 7 shows changes in the relative peak areas of the principal individual components of the volatile phase. Maximum relative water areas at 200 and 600°C correspond to removal of initial moisture and water formation during secondary high-temperature reactions, respectively. CO_2 maximum at 300°C indicates development of decarboxylation reactions involving oxygenated parts. At 400°C, contributions of levoglucosan, guaiacol, cresol, and methanol increased. Guaiacol and cresol compounds are characteristic products of degradation of the lignin aromatic matrix [9, 10]. It remained detectable at 500°C, although the overall product composition became less diverse.

Proximate analysis of Solid Residues Obtained at Different Treatment Temperatures

Solid products obtained at 200, 300, 400, 500, and 600°C were analyzed. Properties compared included the as-received moisture content W□, dry-basis and as-received ash contents A□ and A□, and the as-received higher and lower heating values Q□□ and Q_i□. 200 and 300°C conditions represent low-temperature treatment close to torrefaction, whereas decomposition of the organic matrix and carbonization of the solid product became increasingly important at 400–600°C [1, 5, 6].

Table 6
Fuel and thermal characteristics of hydrolysis lignin solid residues

Temperature, °C	Wr, %	Ad, %	Ar, %	Qsr, MJ/kg	Qir, MJ/kg	Qsr, kcal/kg	Qir, kcal/kg
200	4,770	2,550	2,428	21,992	20,786	5252,699	4964,651
300	4,716	3,190	3,040	23,776	22,571	5678,800	5390,991
400	4,661	6,064	5,781	25,560	24,355	6104,901	5817,092
500	3,323	13,250	12,810	26,634	25,447	6361,422	6077,912
600	1,985	24,580	24,092	27,707	26,538	6617,703	6338,492

Residual moisture content of the solid product generally decreased with the temperature increase. The value of W□ was 4.77% at 200°C, decreased to 3.32% at 500°C, and reached a minimum of 1.98% at 600°C. Over the 200–600°C range, moisture mass fraction decreased by 58.4% relative to the value at 200°C.

Removal of moisture and organic components was accompanied by relative enrichment of the mineral fraction in the solid residue. Dry-basis ash content A□ increased from 2.55% at 200°C to 6.06% at 400°C, 13.25% at 500°C and 24.58% at 600°C. A similar trend was observed for A□, which increased from 2.43% to 24.09%. Thus, over the investigated range, A□ and A□ increased by factors of 9.6 and 9.9, respectively. The most rapid increase in the ash fraction occurred above 400°C, where the reduction in organic matter became the principal factor controlling solid product composition. Such relative mineral enrichment characterizes the extensive thermal conversion of lignin [1, 12].

Heating values increased regularly, as shown in Fig. 8. As-received higher heating value rose from 21.99 MJ/kg at 200°C to 25.56 MJ/kg at 400°C and 27.71 MJ/kg at 600°C. Across the investigated range, Q□□ increased by 5.72 MJ/kg, or 26.0%. Lower heating value increased from 20.79 to 26.54 MJ/kg, corresponding to an increase of 5.75 MJ/kg, or 27.7%. Increase in specific heating value is associated with moisture removal and a higher degree of carbonization. However, simultaneous increase in ash content limits evaluation of product quality based solely on heating value and requires consideration of the solid phase yield [1, 12, 13].

Combining laboratory reactor and pyrolytic GC-MS data makes it possible to divide the investigated temperature range into several stages. 200–300°C range corresponds mainly to moisture evaporation, CO_2 release, and initial formation of low-molecular-weight oxygenated compounds. In this temperature range, average mass loss remained below 25%, and the effect of sample mass was mainly presented. This behavior is consistent with general features of the initial thermal degradation of lignin and lignocellulosic components [5–9].

Temperature of 400°C is decisive for interpreting the conversion process. Average reactor mass loss reached 48.9%, while the GC-MS analysis gave the maximum total TIC peak area and 64 detected peaks.

A similar temperature maximum in volatile product diversity has been reported for enzymatic hydrolysis lignin, for which the ratio of guaiacyl and syringyl derivatives changed at 400°C [9]. Therefore, this region is characterized by the most intensive degradation of the organic matrix and formation of a broad spectrum of volatile compounds.

At 500–600°C, additional mass loss was less than between 300 and 400°C. At the same time, total TIC peak area and number of peaks decreased, and volatile phase composition became simpler. Results from catalytic fast pyrolysis of hydrolysis lignin likewise show that, after the temperature corresponding to the maximum monomeric phenol yield has been exceeded, further heating intensifies secondary cracking [12]. At the molecular level, these changes may be promoted by hydrogen transfer reactions and sequential cleavage of C–O and C–C bonds [11].

The detected guaiacol, cresol, and other phenolic compounds confirm that lignin-derived products constitute the major part of the organic volatile fraction. Similar compounds are regarded as characteristic products of pyrolysis of enzymatic and industrial lignin residues [9, 10]. Direct quantitative comparison with published data is nevertheless limited by differences in feedstock origin, heating rate, vapor residence time, sample mass and catalyst presence.

Fuel properties of the initial material and solid residues provide additional information for interpreting the reactor experiments. Initial hydrolysis lignin had a high water content. The moisture mass fraction was 59.56%, while the as-received value including external moisture reached 64.48%. Dry-basis volatile matter content was 76.05%, and as-received lower heating value was 19.92 MJ/kg. These values reflect a well-known characteristic of hydrolysis lignins, which high moisture content is one of the principal limitations to direct energy utilization [1].

Solid residue properties changed systematically with increasing temperature. Moisture content decreased from 4.77% at 200°C to 1.985% at 600°C. Dry-basis ash content increased from 2.55% to 24.58% because of the reduction in the organic fraction and the corresponding concentration of mineral components. At the same time, lower heating value increased from 20.79 to 26.54 MJ/kg. Formation of a more carbon-rich product at higher temperatures agrees with studies of thermochemical and catalytic processing of hydrolysis lignin [1, 12, 13].

Comparison of fuel properties with mass loss shows that the 300–400°C interval is transitional not only in decomposition intensity but also in formation of solid product properties. At 300°C, lower heating value was 22.57 MJ/kg at an average solid residue yield of 76.8%, whereas at 400°C it increased to 24.36 MJ/kg and residue yield decreased to 51.1%. Further heating to 500–600°C increased the lower heating value to 25.45–26.54 MJ/kg but produced a comparatively small additional mass reduction. Consequently, preferred operating condition depends on the intended product. 300–400°C range is preferable when a higher solid yield must be retained, whereas 500–600°C provides more extensive carbonization.

Conclusions

Thermal decomposition of hydrolysis lignin sampled from hydrolysis industry residues in Arkhangelsk was investigated in a vertical laboratory glass fixed bed reactor and using pyrolytic GC-MS at 200, 300, 400, 500, and 600°C. Average mass loss increased from 11.8% at 200°C to 57.7% at 600°C, while the average solid residue yield decreased from 88.2% to 42.3%.

The most pronounced process change occurred between 300 and 400°C. At 400°C, increase in mass loss was accompanied by the maximum total TIC peak area and the largest number of detected peaks. 400–500°C range is therefore the key region for relating decomposition extent, volatile phase composition, and development of the solid residue properties.

Fuel characterization showed that the initial material had a high moisture content, a substantial volatile matter content, and an as-received lower heating value of 19.92 MJ/kg. Considering that this feedstock had been stored in hydrolysis industry dumps, obtained results can support selection of conditions for preliminary drying, heating, and subsequent analysis of the solid residue and volatile products.

Properties of solid residues confirmed the progressive conversion of hydrolysis lignin. Between 200 and 600°C, lower heating value increased from 20.79 to 26.54 MJ/kg and dry-basis ash content from 2.55% to 24.58%. The most substantial changes in mass yield and volatile phase composition occurred between 300 and 400°C. Further heating to 600°C continued the carbonization process and increased the specific heating value of the solid residue.

Defined relationships indicate that hydrolysis lignin can be used as a feedstock for producing a solid carbonaceous product with adjustable fuel properties. Treatment at 300–400°C initiates intensive degradation of the organic matrix and produces a marked increase in the heating value, whereas treatment at 500–600°C results in more extensive carbonization, a further increase in heating value, and higher ash content.

Declarations

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Author Contribution

Pavel Alekseev, Dmitri Kuchin, Mikhail Ivanov - experimental part, prepared the main manuscript, prepared the figures and tables.Pavel Maryandyshev - overall supervision, idea and task setting, reviewed and corrected the manuscript

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Figures

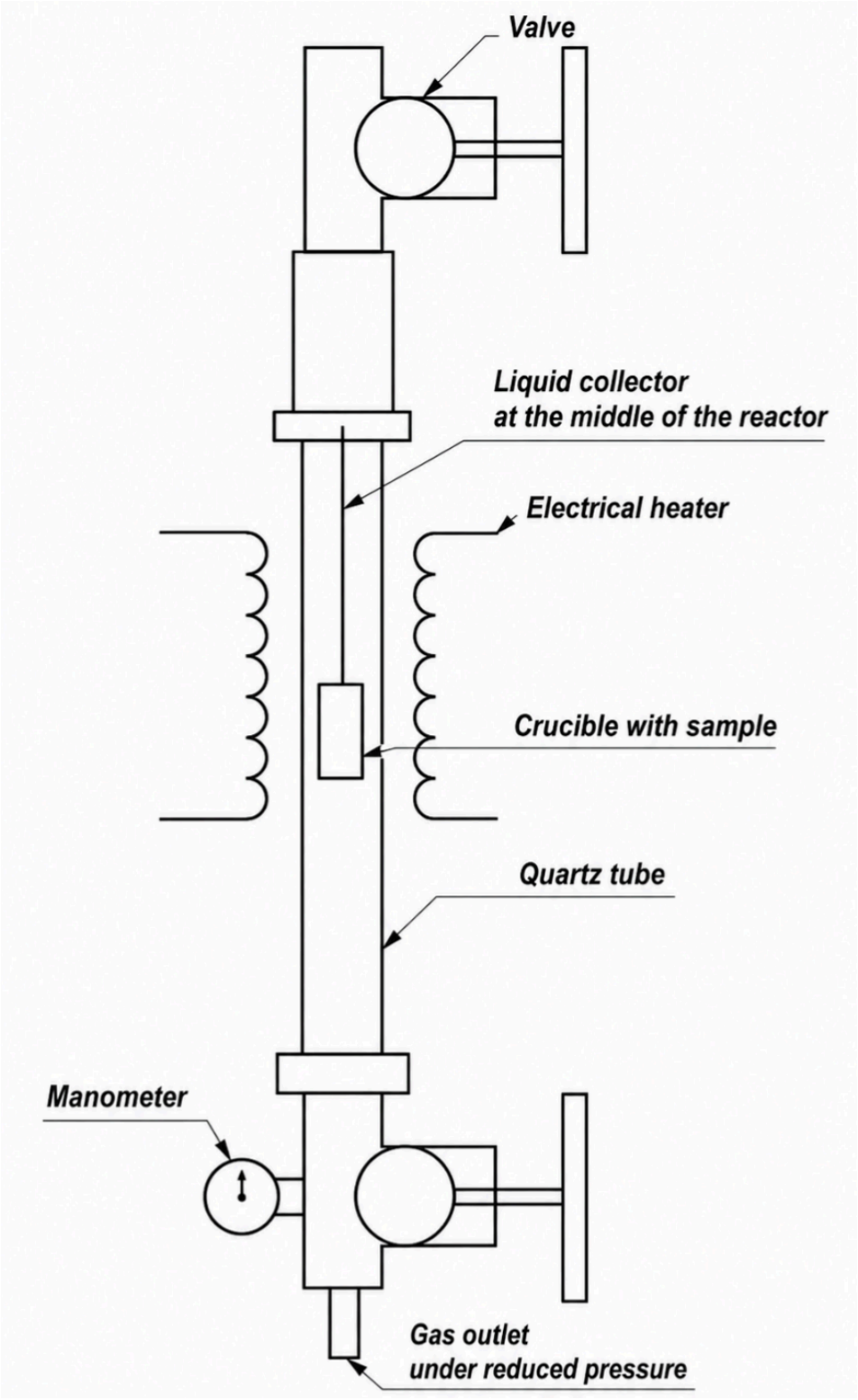


Figure 1

Schematic diagram of the laboratory tubular reactor

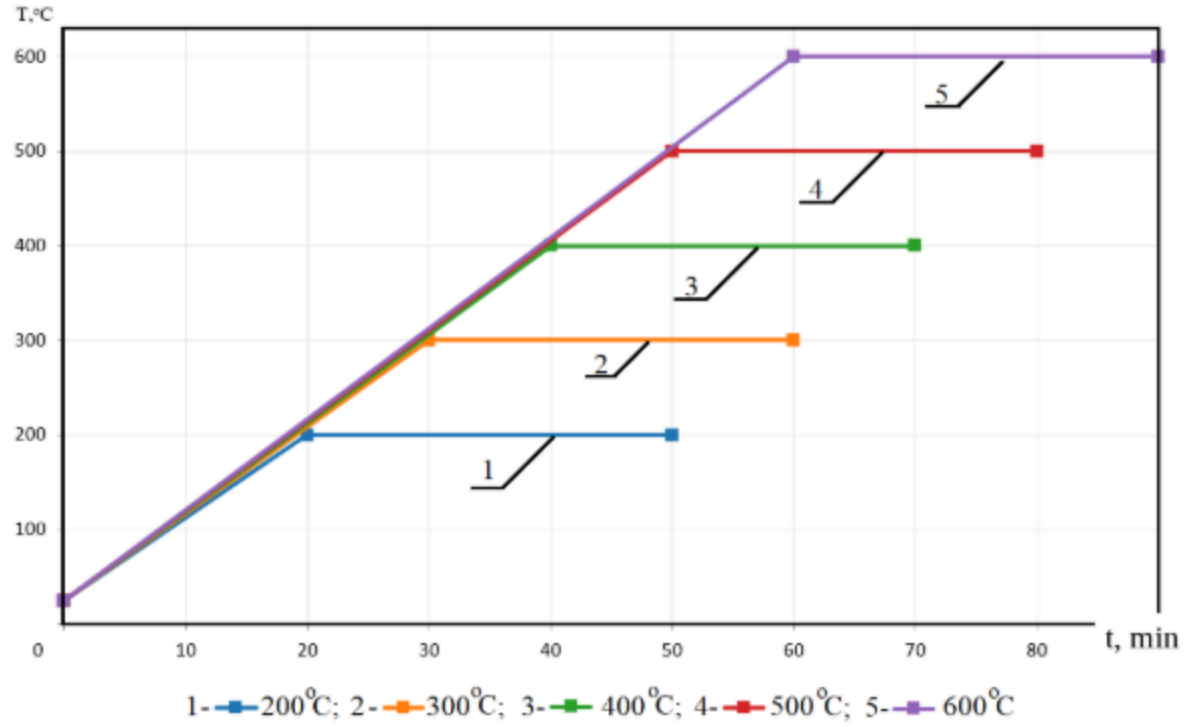


Figure 2

Temperature-time heating profiles of hydrolysis lignin in the glass tubular reactor

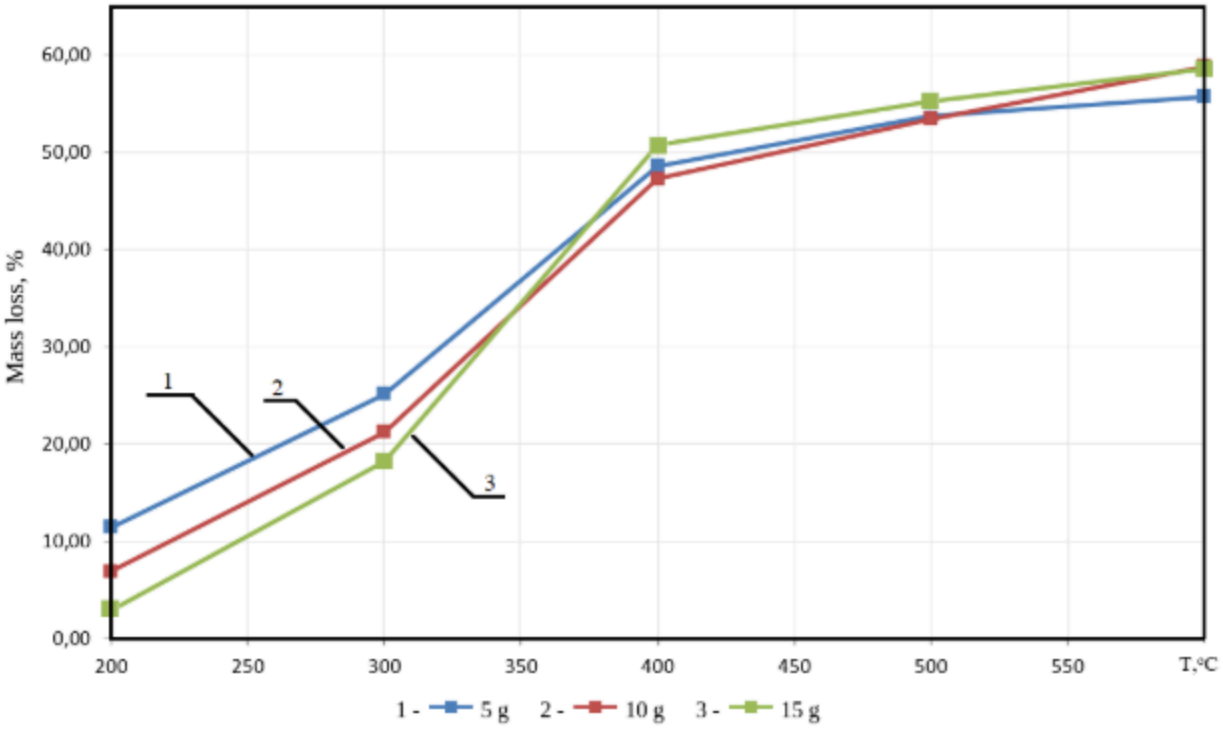


Figure 3

Dependence of hydrolysis lignin mass loss on temperature and sample mass

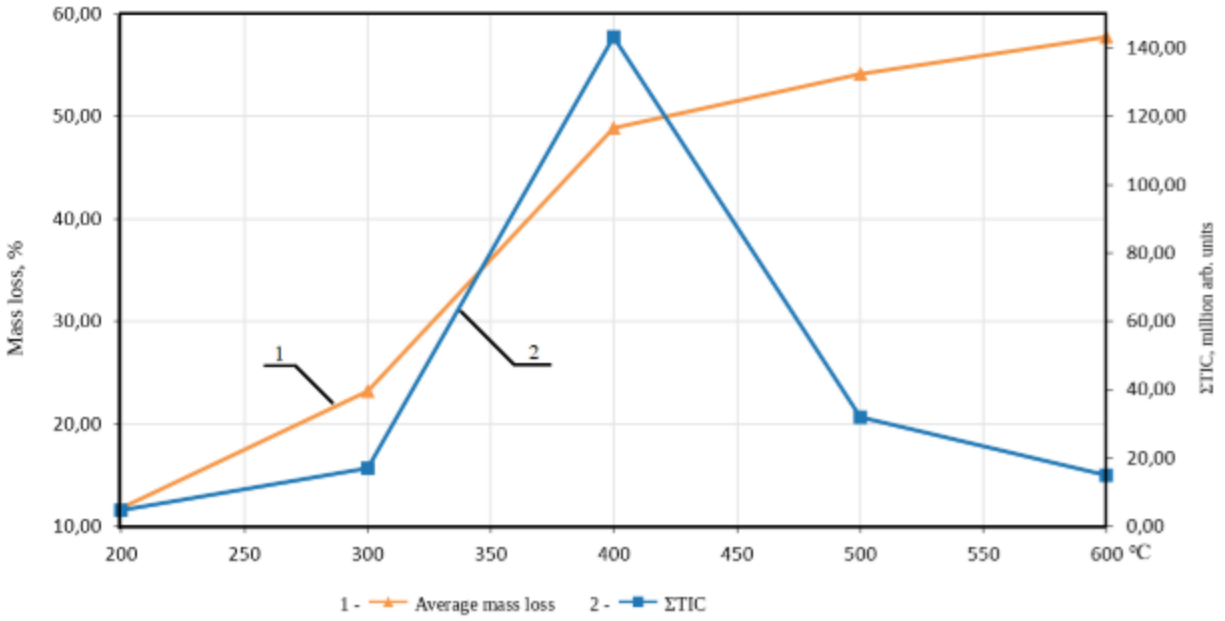


Figure 4

Comparison of the average mass loss and the total TIC area

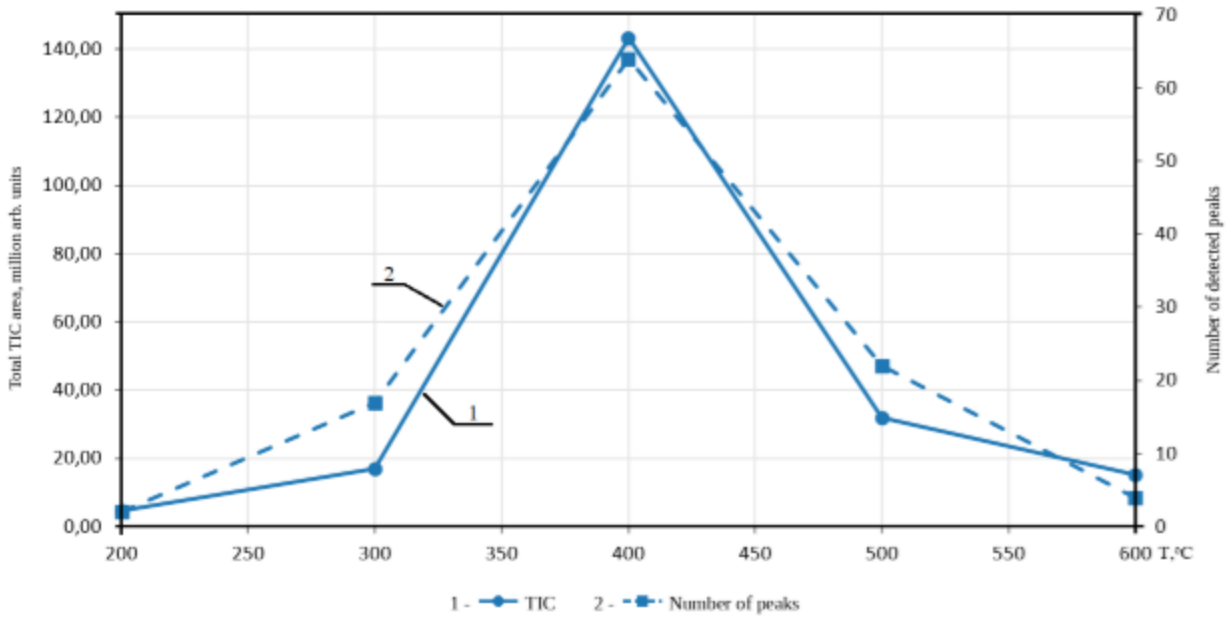


Figure 5

Variation in the total TIC area and the number of peaks during hydrolysis lignin pyrolysis

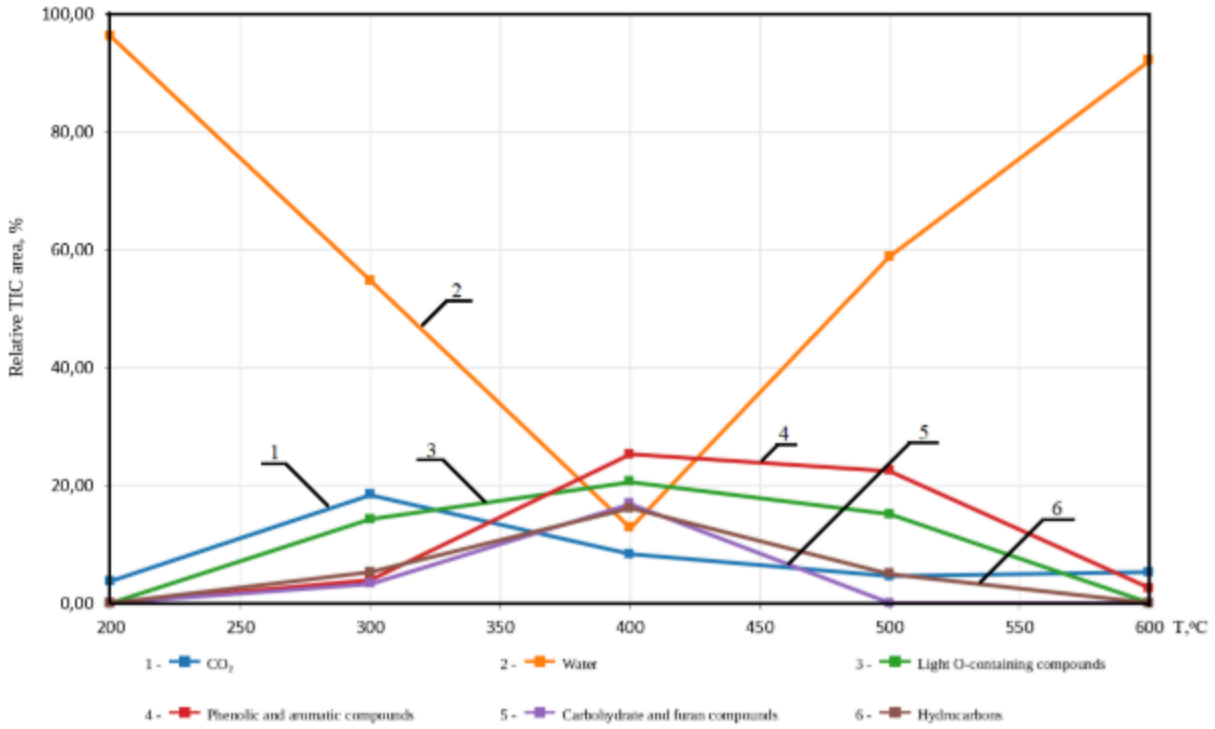


Figure 6

Group distribution of volatile products according to GC-MS data

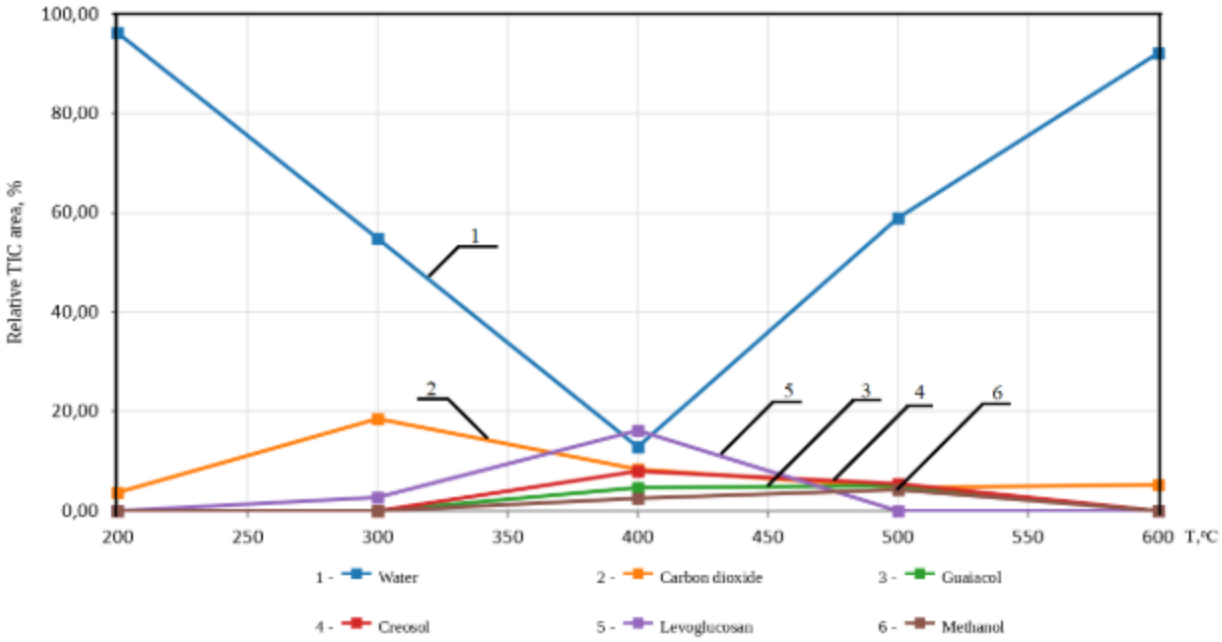


Figure 7

Variation in the relative area of the main products

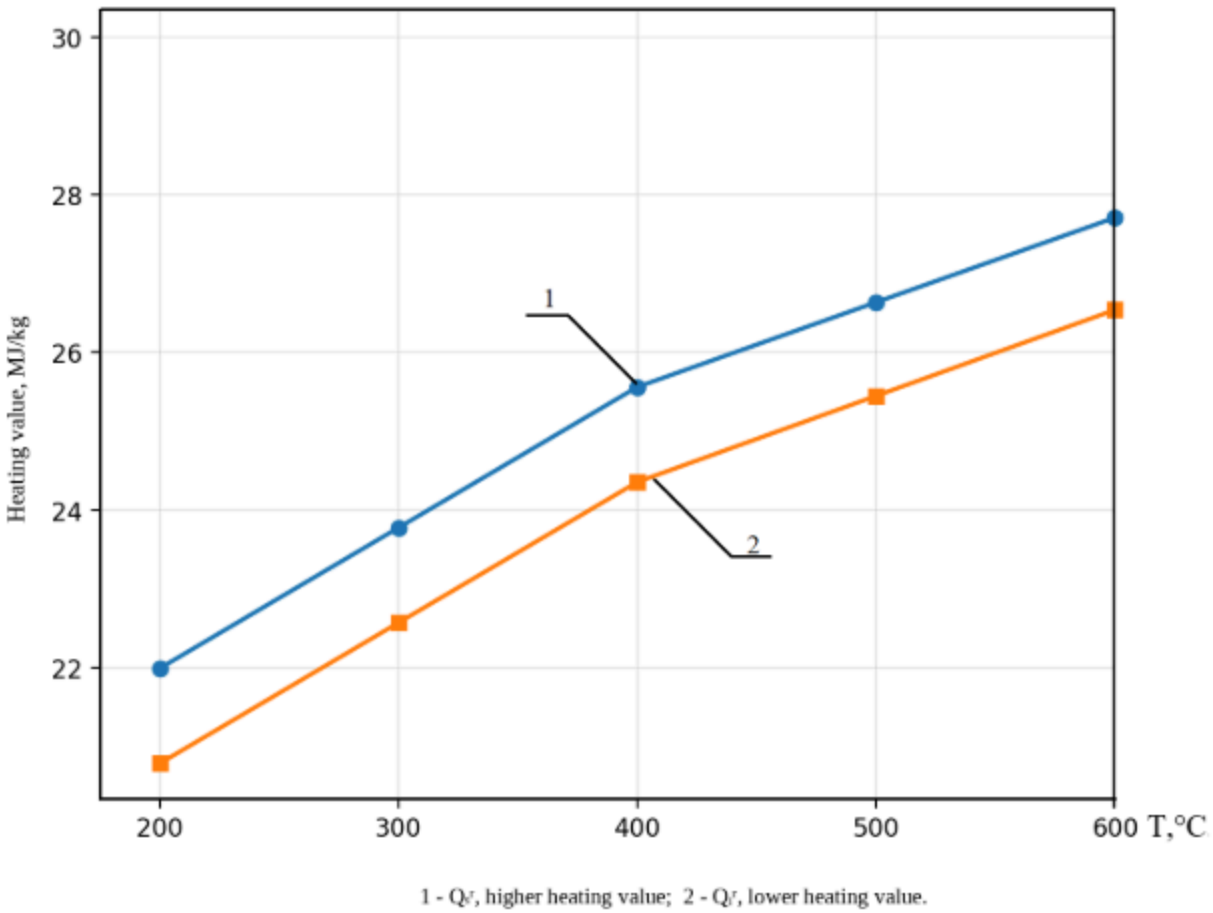


Figure 8

Dependence of the higher and lower heating values of solid residues on treatment temperature

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