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VARIOUS
TECHNOLOGICAL PROCESSES

Hydrothermal Treatment of Organic Waste

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Abstract—The yield and properties of solid and liquid products of hydrothermal treatment of organic waste were determined with cheese, meat, and apples as an example. The solid products of hydrothermal treatment of cheese and apples have higher carbon content, lower oxygen content, and, correspondingly, higher heat of combustion compared to the initial biomass, which allows these products to be considered as a promising solid biofuel. The oils obtained in experiments with cheese and meat also have higher carbon content and higher heat of combustion compared to the initial substances, which allows these products to be considered as a promising liquid biofuel.

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Waste is one of the main problems on the pathway of sustainable development of the economy and of the society as a whole. The mankind produces waste in the course of both economic activity and everyday life. About 4 billion tons of various kinds of waste are formed in the world annually, of which 1.6–2 billion tons is solid household waste (SHW) [1]. According to the data of Rosprirodnadzor (Federal Service for Supervision in the Field of Environmental Management of Russia), about 70 million tons of SHW is formed in Russia annually, and this amount increases by 3–4% from year to year.

The world's trend in the field of SHW management is increasing fraction of waste utilized so as to obtain secondary energy resources. Attempts are made to diversify the waste utilization to generate energy (waste-to-energy) by using modern technologies of gasification, pyrolysis, or torrefaction or organic waste [2, 3]. However, implementation of such processes involves problems associated with heterogeneous composition, low density, and high moisture content of SHW.

Food waste, which is also a component of SHW, is commonly considered as a separate kind of waste. The weight fraction of food waste in SHW, as a rule, exceeds that of any other SHW component and varies in different countries from 24 to 67% [4]. In Russia, the weight fraction of food waste in SHW is estimated at 40% [5]. SHW also contains paper, wood, plastic, ferrous and nonferrous metal scrap, glass, textile, and rubber [6].

Food waste is characterized by high moisture content (70–90%), high content of volatiles (80–97%), and carbon to nitrogen weight ratio of 14.7–36.4 [7–9]. Because of high moisture content of food waste, such traditional procedures for processing waste into biofuel as pyrolysis and gasification become inefficient. The moisture content of the biomass delivered to pyrolysis, as a rule, should not exceed 20% [10]. Simple calculation shows that reduction of the moisture content of the waste from 80 to 20% requires about 10 MJ of thermal energy per kilogram of dry waste.

So-called hydrothermal technologies are the best suited for processing moist biomass into biofuel (generally, "hydrothermal process" means any process performed in the presence of water or steam at temperatures higher than 100°C [11–14]). In the case of moist organic waste, technologies of hydrothermal liquefaction and hydrothermal carbonization to obtain liquid [14] or solid [15] biofuel, respectively, are of most interest. One of the main advantages of hydrothermal technologies is that they do not involve preliminary drying of the feed. Waste can be fed into

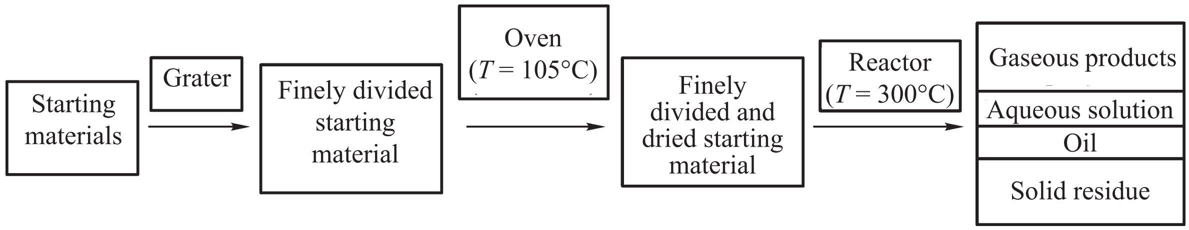

Fig. 1. Scheme of experiments with the substances studied.

a reactor in the moist state, e.g., in the form of an aqueous suspension.

Recent studies [16, 17] were oriented on preparation of solid biofuel by hydrothermal carbonization. The main result of these studies was the determination of the elemental composition and energetic potential of the solid product. On the other hand, insufficient attention was paid to the possibility of producing liquid biofuels from the waste. Determining the chemical composition of liquid products of hydrothermal processing is of separate interest, because this information can be used in analysis of chemical transformations. Knowledge of the chemical composition of the biofuel allows the choice of an optimum processing pathway and optimization of the hydrothermal process itself.

In this study, separate ingredients of moist organic waste, namely, meat, cheese, and applies, were subjected to hydrothermal treatment in an autoclave at 300°C. The elemental composition and energetic potential of the solid and liquid products of hydrothermal treatment were determined. Super-high-resolution Fourier transform ion cyclotron resonance mass spectrometry [18–23] was also used for studying the liquid products of hydrothermal processing. This method allows detection of tens of thousands of compounds in one spectrum without fractionation and determination of the empirical formulas of the identified molecules.

EXPERIMENTAL

The starting materials (cheese, meet, and apples) were purchased in the nearest supermarket. Distilled water was used in the experiments. The scheme of the experiments with the substances is shown in Fig. 1. Figure 2 shows the photographs of the starting materials and products of their processing.

Hydrothermal treatment experiments were performed in a laboratory installation schematically shown in Fig. 3. We used a 0.5-L pressure vessel operating at pressures of up to 25 MPa and temperatures of up to 400°C with external ohmic heating. The heating process (heating rate, maximal temperature, time of keeping at the maximal temperature) was controlled by a computer operator using an automatic control system. The temperature inside the reactor was measured with a temperature sensor, which was arranged in a special tube (socket) inserted into the reactor.

The reactor was charged with 150 g of distilled water and 30 g of the starting material in the dried state. The starting material was preliminarily dried in a Binder VD53 oven at 105°C. Prior to the experiment, the reactor was sealed and purged with nitrogen. Then, the reactor was heated to 300°C over a period of approximately 120 min and kept at 300°C for 60 min. Figure 4 shows a typical temperature–time plot for hydrothermal treatment of the starting material (cheese, meat, or apples). The final pressure in the reactor was close to the saturated water vapor pressure at 300°C. After the process completion, the reactor heater was switched off, and the reactor was allowed to cool to room temperature over a period of approximately 5 h. Then, the reactor was opened, and the contents (generally, a mixture of aqueous solution of organic compounds, undissolved oil, and solid residue) were taken off and transferred into a glass beaker.

Then, the solid and liquid products of hydrothermal liquefaction were left for 72 h for phase separation depending on the density of the phases. In the experiments with cheese and meat, the hydrothermal liquefaction product (after settling in the beaker) consisted of a solid residue, an aqueous solution of organic substances, and an undissolved oil whose density was lower than that of the aqueous solution, so that it floated up. In the experiment with apples, the hydrothermal liquefaction product (after settling in the beaker) consisted of a solid residue and an aqueous solution of organic substances; in con-

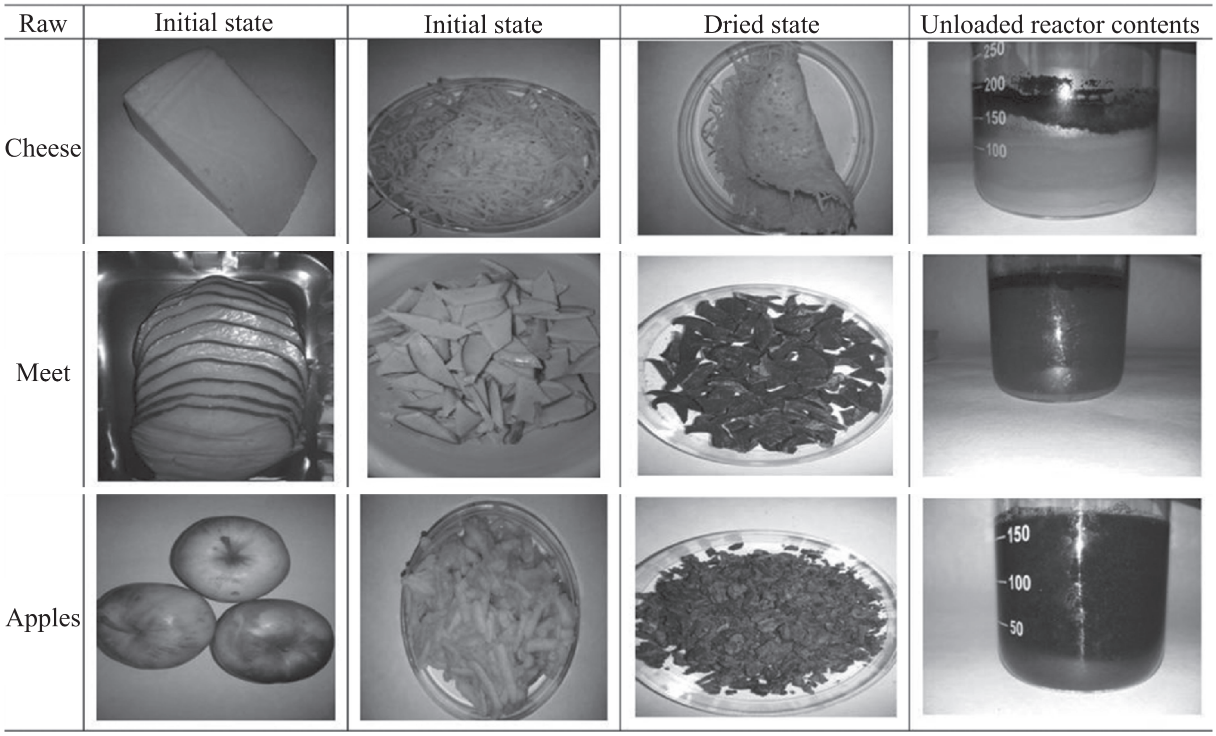

Fig. 2. Photographs of the starting materials and products of their processing.

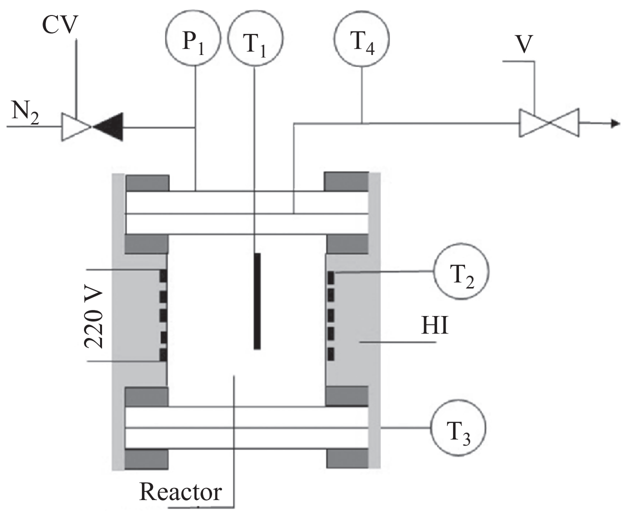

Fig. 3. Scheme of the laboratory installation with a pressure vessel. (CV) Check valve, (HI) heat insulation, (V) valve, (P) pressure gage, and (T) thermocouples.

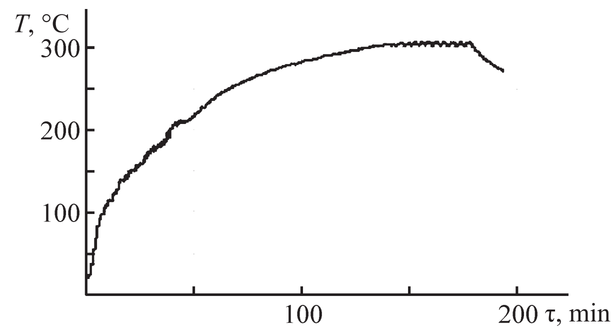

Fig. 4. Variation of the temperature T with time τ in hydrothermal treatment experiments.

trast to the experiments with cheese and meat, no oil was obtained.

The oil film was removed from the beaker with a laboratory spatula, placed in a Petri dish, and dried in an oven at 75°C to constant weight. The solid residue was separated from the aqueous solution by filtration using a Büchner funnel, a Bunsen flask, and a vacuum pump. Then, the solid residue was dried at 105°C to constant weight.

To determine the concentration of organic compounds in the aqueous solution, five 1 cm^3 samples of this solution (to estimate the random error) were taken with a syringe and transferred into five test tubes. The tubes were placed in an oven at 75°C for water evaporation. The tubes were kept in the oven until their weight became constant (no changes in 2 h). The product yield was determined from the weight of the residue. The sample weights were measured with a Sartorius Cubis MSA324S analytical balance.

Table 1. Residue after evaporating 1 cm^3 of aqueous solution of organic compounds at 75°C

Test tube no.	Residue amount, g		
	cheese	meat	apples
1	0.0845	0.1022	0.0216
2	0.0807	0.1015	0.0168
3	0.0837	0.1067	0.0171
4	0.084	0.1059	0.0163
5	0.0839	0.1004	0.0192
Average	0.0834	0.1033	0.0182

For the starting substances in the finely divided and dried state and for the dried solid product of hydrothermal treatment, we determined the elemental composition and energetic potential.

For the liquid products of hydrothermal treatment, we determined the elemental composition, energetic potential, and accurate chemical composition (by super-high-resolution mass spectrometry).

The elemental analysis (for C, H, N, O, and S) of the samples was performed with a Thermo Scientific Flash 2000 HT analyzer. The oxygen content was determined by subtraction.

The specific heat of combustion was determined with an IKA C6000 calorimeter. Benzoic acid was used for the device calibration.

The chemical composition was studied with an LTQFTUltra high-resolution mass spectrometer (Thermo Electron, Bremen, Germany) equipped with a superconducting magnet (7 T). The samples for mass-spectrometric analysis were dissolved in methanol to obtain 1 g L^{-1} solutions. Single-use electrospray emitters were used for decreasing the contamination. Ions were generated in the positive and negative electrospray modes. The desolvating capillary temperature was set at 300°C. The sample was introduced at a rate of 1 μL min^{-1}. The electrospray needle voltage was 3 kV. The resolution of 400 000 was reached. Each spectrum was averaged over 100 scans. To analyze the samples, the LTQFTUltra device was calibrated with a Thermo standard calibrant.

RESULTS AND DISCUSSION

The weights of the residues obtained after evaporating 1 cm^3 of aqueous solutions at 75°C are given in Table 1. The largest amount of the dissolved organic substance in the aqueous solution after the hydrothermal treatment was obtained in the experiment with meat, and the smallest amount, in the experiment with apples.

The results of determining the yield of the products of hydrothermal liquefaction of cheese, meat, and apples are given in Table 2. The highest yield of the liquid biofuel (oil + organic substance dissolved in aqueous solution) upon hydrothermal liquefaction was obtained in the experiment with cheese, 75.8% (relative to the weight of the dried starting material). In the experiment with meat, the yield was slightly smaller, 60.5%. In the

Table 2. Results of determining the product yields in hydrothermal liquefaction of cheese, meat, and apples

Parameter	Cheese	Meat	Apples
Moisture content of starting material, %	20.75	69.7	87.9
Amount of dried starting material loaded into reactor, g	30	30	30
Total amount of starting material and water loaded into reactor, g	180	180	180
Amount of condensed product in reactor after opening, g	172.44	167	167.2
Solid residue weight, g	4.94	1.17	11.95
Oil weight, g	5.02	1.57	–
Aqueous solution weight, g	162.48	164.26	152.27
Weight of organic substances dissolved in aqueous solution, g	17.71	16.59	2.98
Total weight of oil and organic substances dissolved in aqueous solution, g	22.73	18.16	2.98
Yield of liquid biofuel (oil and organic substances dissolved in aqueous solution), %	75.8	60.5	9.9

experiment with apples, the yield of the liquefied product was as low as 9.9%, whereas the yield of the solid product (coke residue) was almost 40%. The smallest yield of the solid residue was obtained in the experiment with meat (3.9%), and in the experiment with cheese it was 16.5%. Figure 5 shows the distribution of the yields of the hydrothermal treatment products (solid residue, organic substance dissolved in aqueous solution, oil, and gaseous products) for cheese, meat, and apples.

The elemental compositions and heats of combustion of the starting materials and products of their hydrothermal treatment are given in Table 3. The solid products of the hydrothermal treatment of cheese and apples have higher carbon content, lower oxygen content, and, correspondingly, higher heat of combustion compared to the initial biomass. The heat of combustion of the hydrothermal treatment product obtained from apples was 27.84 MJ kg^{-1}, which is comparable with the heat of combustion of energetic coal. The organic substances dissolved in water are similar in the composition and heat of combustion to the starting substances. The oil obtained in the experiments with cheese and meat also has higher carbon content, lower oxygen content, and, correspondingly, higher heat of combustion compared to the starting material. This effect is more pronounced for cheese.

Figure 6 shows the mass spectra of samples obtained from the tested materials: oil and organics dissolved in water. As can be seen, the spectra are very complex and strongly differ from each other.

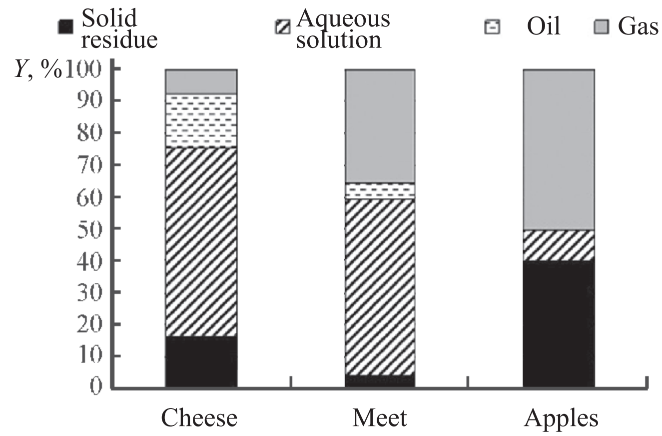

Fig. 5. Yield Y (based on the weight of the dried starting material) of the solid residue, aqueous solution of organic substances, oil, and gaseous products upon hydrothermal treatment (300°C) of cheese, meat, and apples.

As can be seen, the spectrum of crude oil, taken for comparison, is the most complex. For all the five samples obtained by hydrothermal treatment, the majority of peaks are located in the interval up to m/z = 500, whereas the mass spectrum of traditional crude oil contains strong peaks of heavier ions in the range m/z = 500–800. The water-soluble organic substances derived

Table 3. Elemental composition (dry ashless state) and heat of combustion of the dried starting materials and of products of their hydrothermal treatment

Sample	Content of indicated element, wt %					Heat of combustion, mJ kg^{-1}
	N	C	H	S	O	
Starting material:						
cheese	5.16	47.58	8.61	0.56	38.09	18.83
meat	11.91	44.98	6.87	1.39	34.86	16.11
apples	0.36	36.31	6.78	0.15	56.40	12.67
Solid residue:						
from cheese	4.89	61.51	8.02	0.88	24.70	22.19
from meat	6.22	43.61	6.83	0.81	42.54	16.76
from apples	1.09	71.58	5.52	0.00	21.81	27.84
Organic substances dissolved in water:						
from cheese	8.37	39.34	7.65	0.89	43.75	16.91
from meat	9.71	42.99	7.79	0.88	38.63	16.86
from apples	0.99	38.01	6.08	0.40	54.52	12.74

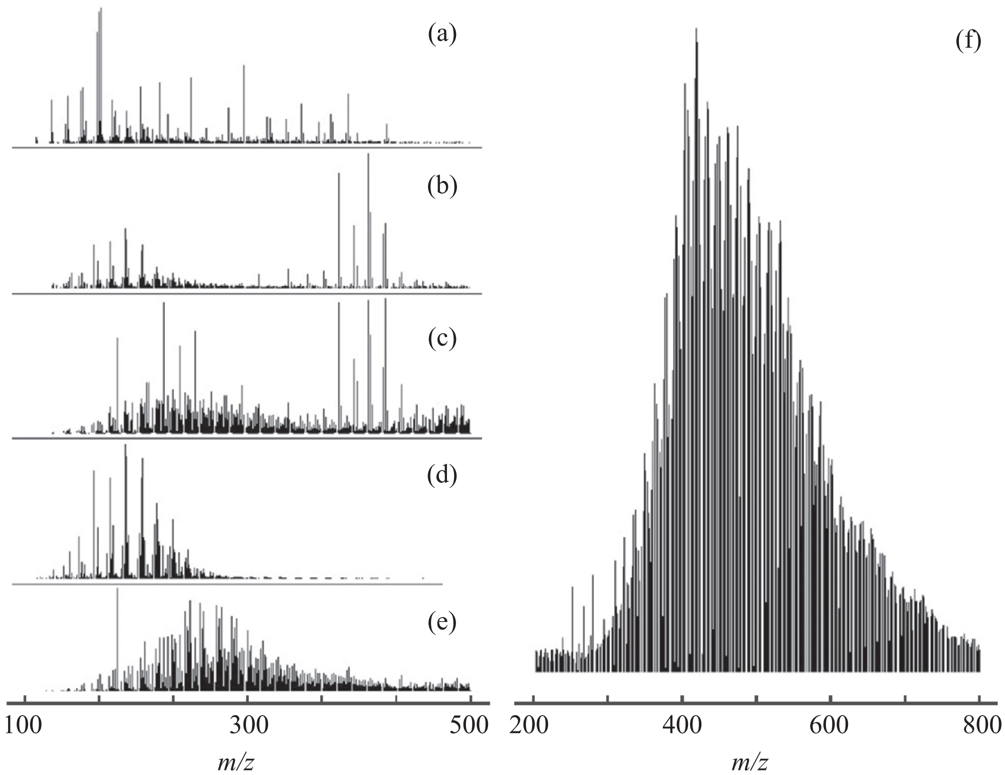

Fig. 6. Mass spectra of the samples: (a) water-soluble organics from apples, (b) water-soluble organics from cheese, (c) oil from cheese, (d) water-soluble organics from meat, (e) oil from meat, and (f) crude oil (Russkoe deposit).

from meat are the lightest, with ions at *m*/*z* > 300 detected in trace amounts.

The compositions of oils obtained from cheese and meat are more complex than the compositions of the water-soluble organic substances obtained from the same materials. As seen from Table 4, 4344 substances with different empirical formulas were identified in the oil from cheese, and only 3088 substances, in the water-soluble fraction obtained from cheese. Still more substances (4711) were identified in the oil from meat, whereas only 2182 substances were identified in the corresponding water-soluble fraction.

Table 4. Number of substances identified in the samples. Numerals in crossings of columns and rows indicate the numbers of coinciding substances in the corresponding samples

Sample	Total number of identified molecular formulas	Number of common molecular fragments in samples					
		organic substances dissolved in water			oil		Traditional crude oil (Russkoe deposit)
		from cheese	from meat	from apples	from cheese	from meat	
Organic substances dissolved in water:							
from cheese	3088		839	275	1112	1182	212
from meat	2182	839		235	637	635	123
from apples	3383	275	235		209	222	148
Oil:							
from cheese	4344	1112	637	209		1587	288
from meat	4711	1182	635	222	1587		376
Traditional crude oil (Russkoe deposit)	4336	212	123	148	288	376	

The numbers of substances with common empirical formulas in the samples of oil, of organics dissolved in water, and of traditional crude oil (Russkoe deposit) are given in Table 4. The samples tested (water-soluble organics from meat and cheese, oil from meet and cheese) are more similar to each other than to traditional crude oil (Russkoe deposit). The oil sample from meat is characterized by the largest number of substances (376) with the same empirical formula as in the crude oil sample (the total number of identified substances in crude oil is 4336).

The water-soluble organics from cheese and meet are also largely similar in the composition (about 30% of the identified substances coincide), whereas much fewer substances coincide with the water-soluble organics from apples. On the other hand, the mass spectra of the water-soluble organics from meat and cheese (Fig. 6) differ significantly: For cheese, there are strong peaks in the region of $m/z = 400$, whereas for meat the corresponding substances are detected only in trace amounts.

Similar pattern is observed for the oils. For cheese and meat, 1587 substances (i.e., also about 30% of substances) coincide, but the mass spectra differ significantly.

CONCLUSIONS

(1) The yield and properties of solid and liquid products of hydrothermal treatment of food waste were determined for cheese, meat, and apples as examples. The highest yield of liquid products (oil + organic substances dissolved in water) was reached with cheese; slightly lower yield (60.5%), with meat; and the lowest yield (9.9%), with apples. In the latter case, the highest yield of the solid product, about 40%, was reached.

(2) Solid products of hydrothermal treatment of cheese and apples have higher carbon content, lower oxygen content, and, correspondingly, higher heat of combustion compared to the initial biomass, which allows these products to be considered as a promising solid biofuel. The oils obtained in the experiments with cheese and meat have also higher carbon content and higher heat of combustion compared to the initial substances, which allows these products to be considered as a promising liquid biofuel.

(3) Comparison of the high-resolution mass spectra of the obtained liquid products of hydrothermal liquefaction with that of a sample of traditional crude oil shows that more than 30% of substances are common for the samples from meat and cheese, but these samples virtually do not coincide in the composition with the sample obtained from apples and with the crude oil sample. The sample from apples and the crude oil sample virtually do not coincide with each other.

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