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Processing of excess activated sludge by hydrothermal liquefaction with biofuel production

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Abstract

Currently, there is a shortage of fossil resources in the World, while the problem of climate change is worsening. In this regard, the relevance of obtaining biofuels from organic waste will be improved. In the Kaliningrad region, as in many urbanized territories, there is a problem of finding ways to dispose of excess sludge. The composition of excess activated sludge has been studied and the possibility of obtaining biofuels from sludge by hydrothermal liquefaction has been assessed. Based on the analysis of fuel characteristics and chemical composition of excess sludge, it was found: caloric value 7.6-8.8 J/g a.d.m.; lipid content 2.0-5.2% d.m, protein content 16.6-43.9%, ash content 29.3-44.4%, content heteroatoms in the sludge up to 30% in total. during the HTL experiment of excess sludge, it was found that the time optimum of the process lies in the range of 30-40 minutes. Increase in yield of HTL bio-oil when using acetone averaged was 78.8%, when using alcohol 74.5%.

Keywords: sewage sludge; excess activated sludge; environmental hazard; recycling and recovery; hydrothermal liquefication; biofuel

Introduction

One of the most important challenges facing modern society is to reduce CO_2 emissions from fossil fuel processes in order to mitigate climate change. The only way to reduce greenhouse gas emissions from liquid fuel incineration without major infrastructure changes required to increase the share of renewable resources in fuel production (Ellersdorfer, 2020). One way to reduce the carbon footprint is to use biomass and organic waste for direct fuel production. Excess activated sludge is one of the multi-ton waste generated in all urbanized areas with sewerage and biological treatment of municipal wastewater. The world volume of excess sludge formation is estimated at 1.2 billion tons (Zhang et al., 2017). In Russia, more than 30 million tons of excess sludge is produced annually (Zaitseva and Pyrsikova, 2017), most of which is disposed of in the environment, resulting in the release of a significant amount of greenhouse gases and the migration of accumulated hazardous compounds into the environment. Thus, the selection of an effective technology for the utilization of excess sludge with the production of fuel allows solving three problems at once: achieving a reduction in the volume of organic waste disposed of in the environment, preventing the release of methane into the atmosphere from decomposition processes, and obtaining carbon-neutral fuel.

Technologies of biomass conversion into fuel can be roughly divided into 2 groups: biochemical and thermochemical. The most appropriate treatment method depends on the amount and type of biomass and end-use requirements towards form of energy, environmental standards, and economic feasibility. Traditional thermal methods are known to require pre-drying of the sludge biomass (Kargbo et al., 2021; Marulanda and Gutierrez, 2019), resulting in low energy efficiency of the process. Hydrothermal liquefaction is considered to be the most promising method for the thermal utilization of wet biomass.

Hydrothermal liquefaction (HTL) refers to a thermochemical process in which biomass and organic wastes are decomposed by water in a subcritical state (near the critical point of about 370 °C and 22 MPa pressure, where water acts as a catalyst for numerous reactions, allowing the chemical transformation of almost all types of organic compounds through hydrolysis and ionic reactions (Wądrzyk et al., 2017; Toor et al., 2011).

The process is generally carried out at temperatures of 250 °C to 380 °C and pressures of 4 to 25 MPa in an aqueous environment (Kargbo et al., 2021; Biller et al., 2012; Savage, 2011; Elliott et al., 2015). The typical dry matter content of the input mixture is between 5 and 20% (Ellersdorfer, 2020), so the biomass can be sent for processing without pre-drying.

Like conventional pyrolysis, hydrothermal liquefaction can produce three main products: bio-oil, solid residue and gas phase, and an aqueous phase containing soluble products. The most valuable product is obviously the liquid organic fraction (bio-oil). In this context, the majority of studies are currently devoted to the search for ways to increase the yield of bio-oil, including the use of catalysts (Yang et al., 2019; Koley et al., 2018), the selection of solvents for the extraction of bio-oil from aqueous solution (Xiu et al., 2011; Cheng et al., 2010), and the co-processing of various wastes (Nazari, 2017; Rulkens, 2008).

The composition of excess sludge is rather varying for different biological treatment plants, so that, for example, according to Shchetinin (2010) and Kulikova (2022) the content of organic compounds can vary from 50 to 90%, ash content from 10 to 50 of the total dry matter content, total nitrogen content from 3 to 4%, and phosphorus content from 0.5 to 3%.

The Kaliningrad region occupies a special position, being an enclave, which imposes certain requirements on the organization of technological cycles within the region. One of the key tasks of the region is to find ways of rational waste management that are environmentally friendly and ensure maximum utilization of the resource potential of waste. In this connection, the selection of optimal technological parameters of hydrothermal liquefaction of excess sludge, providing maximum biofuel yield, should be considered as an important practical and knowledge-intensive task. The main objective of this study was to conduct a multifactorial experiment to evaluate the effect of solvents and process time on biofuel yield.

2. Materials and methods

2.1. Materials

Ethanol, acetone, dichloromethane were ACS grade of purity and were purchased from Diaem LLC (Moscow, Russia). The water was distilled on an evaporative distiller immediately prior to the HTL process.

2.2. Sampling of excess sludge

Sampling was conducted between January and March 2023. Samples were collected after dewatering from four biological wastewater treatment plants in the Kaliningrad region situated in the following cities: Sovetsk, Kaliningrad, Chernyakhovsk, and Baltiysk. A similar waste water treatment cycle is implemented in all plants, starting with mechanical pre-treatment in sedimentation tanks, followed by aerobic biological treatment in a continuous flow aeration tank, then separation of excess activated sludge in secondary radial flow tanks. At the Kaliningrad and Sovetsk biological treatment plants, dewatering is performed on a drum filter press using a regent based on polyacrylamide and its copolymers as a flocculant. The total capacity of all stations is about 2 million of population equivalent.

Samples were collected in plastic airtight containers of 10 liters each. Samples were stored in a refrigerator (+4 °C) until drying. Upon admission, all samples were dried and stored in plastic containers. A total of 20 liters of sludge with a moisture content of 96-92% was sampled. Dry sample weights ranged from 900 to 1600 grams.

2.3. Design of the hydrothermal liquefaction experiment

The HTL process was conducted in a stainless steel autoclave reactor (300 mL volume) equipped with magnetic stirrer, external electric heating, pressure gauge and thermocouple (Eartha Zhang's, PRC). The average heating rate is 15 degrees per minute. The temperature was varied from 240 to 280 °C. At the end of the process, the reactor was cooled with water to 24°C. Gaseous products were removed by opening the valve. The solid residue was separated from the liquid phase by filtration. The filtered precipitate was dried at 104°C. Extraction of the bio-oil from the liquid phase was performed with dichloromethane followed by separation on a separatory funnel. The diagram of the installation is presented in Figure 1.

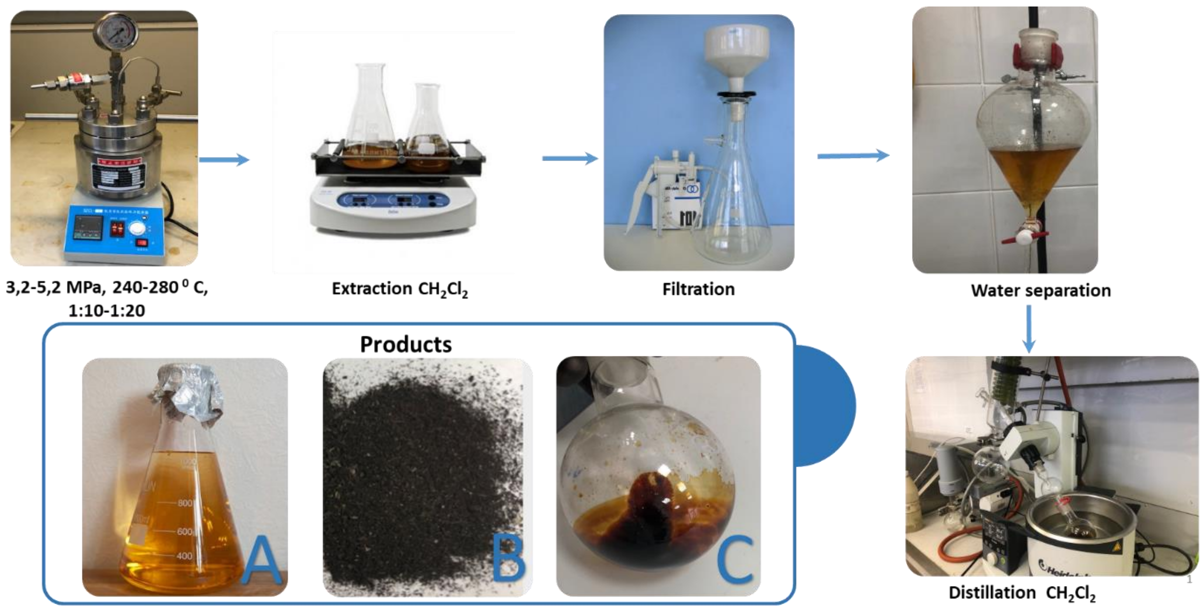


Figure 1. Scheme of the process of hydrothermal liquefaction of excess activated sludge: A – aqueous phase, B – coal residue, C – bio-oil.

2.4. Methods of biomass composition control

Humidity was determined gravimetrically by drying at 104 °C to constant weight. Ash content was also determined gravimetrically by calcination at 550 °C in accordance with ASTM-E1755-01R20.

Elemental analysis of algal biomass was performed using a CHNS elemental analyzer Elementar Analysensysteme (Germany) model Vario EL Cube.

Synchronized thermal analysis in oxidizing (air) and inert (argon) environments was used to evaluate caloric and thermal properties. The analyses were performed on a NETZSCH STA 449C Jupiter synchronous thermal analysis instrument (NETZSCH-Gerätebau GmbH, Germany).

Protein content was determined according to the Kjeldahl method (Hwang, 2020). Total fat content was estimated in accordance with the Russian standard gravimetrically by extraction of crude fat from the sample with diethyl ether in a Soxhlet apparatus with subsequent distillation of the solvent (Thiex, 2003).

2.4. Statistical analysis

Each sample was examined in 3 independent parallels, and the mean values are presented. Results were presented as mean ± standard deviation. Standard statistical methods were used to process the obtained data. Data were subjected to analysis of variance using Statistica 10.0 software (StatSoft Inc., 2007, USA).

3. Results and discussion

3.1. Assessment of excess sludge composition from different biological treatment plants

During the study of the composition of the excess sludge sampled from different typical municipal wastewater treatment plants in Kaliningrad region (4 plants in total), it was found that the excess sludge has the following characteristics: carbon content 23-38.2%, nitrogen 2.65-7.02%, oxygen 18.53-25.69%, and sulfur 0.67-0.91% (Table 1, Figure 2). In terms of elemental composition, the closest to type 2 kerogen, which is a precursor of oil in the natural genesis of oil, can be considered the excess sludge of Kaliningrad, because it is this sludge that is characterized by high carbon content and minimum content of heteroatoms at the level of 26.33%. Such a comparison was not accidental. As it is known, the natural processes of oil genesis are similar to those that occur during hydrothermal vivification, namely the presence of high pressure, humid environment and elevated temperatures (Kulikova et al., 2022).

Table 1. Elemental composition and ash content of studied sewage treatment sludge

Waste type	Content of the main elements						Ash content, %
	C	H	N	S	O	Total content of hetero-atoms	
Excess sludge from the Sovetsk wastewater treatment plant	31.68±1.23	5.88±0.29	5.89±0.18	0.83±0.03	21.28±0.98	28.0±2.71	34.5±4.4
Excess sludge from the Baltiysk wastewater treatment plant	37.09±1.07	6.08±0.11	5.90±0.13	0.91±0.04	20.12±1.14	29.9±2.49	29.9±2.9
Excess sludge from the Chernrnyakhovsk wastewater treatment plant	23.01±0.97	3.58±0.20	2.65±0.07	0.67±0.02	25.69±0.78	29.01±2.04	44.4±3.1
Excess sludge from the Kaliningrad wastewater treatment plant	38.24±1.01	6.13±0.08	7.02±0.25	0.78±0.03	18.53±0.65	26.33±2.02	29.3±1.6
Type II kerogen [Tissot, 1984]	70-73	70-73	1-2	0.78-1.27	9-11	10.78-14.27	-

The main difference between sewage sludge and type II kerogen should be considered a higher oxygen content, which is due to the presence of a significant amount of carbohydrates.

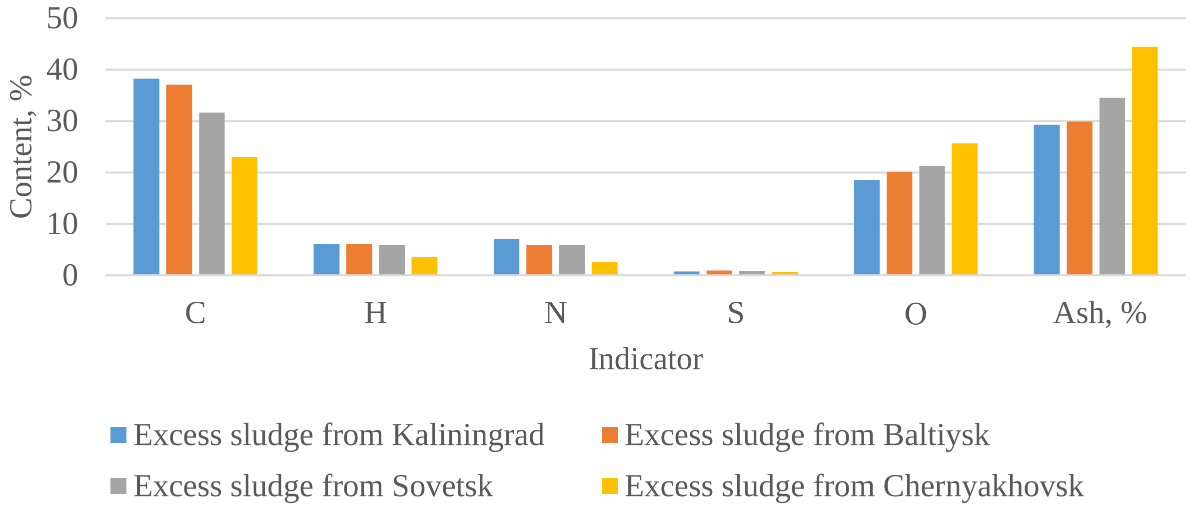


Figure 2. Elemental composition and ash content of the studied excess sludge from different biological treatment plants

The results of evaluating the content of the main groups are presented in Table 2 and Figure 3.

Table 2. Content of main groups of substances in sewage sludge

Waste type	Fats	Proteins	Carbohydrates
	% a.d.m.		
Excess sludge from the Sovetsk wastewater treatment plant	4.4±0.3	36.8±1.0	24.4±1.2
Excess sludge from the Baltiysk waste water treatment plant	4.8±0.2	35.9±1.9	28.4±0.9
Excess sludge from the Chernrnyakhovsk wastewater treatment plant	2.0±0.1	16.6±0.6	37.0±2.2
Excess sludge from the Kaliningrad wastewater treatment plant	5.2±0.3	43.9±1.7	21.6±1.1

The main organic compounds of the excess sludge are proteins, whose content varies from 16 to 44%, which makes them a good raw material for hydrothermal liquefaction processes, because according to the Maillard reaction proteins with carbohydrates can form melanoidins (Basar, 2021), which are part of the synthetic oil produced (Table 2).

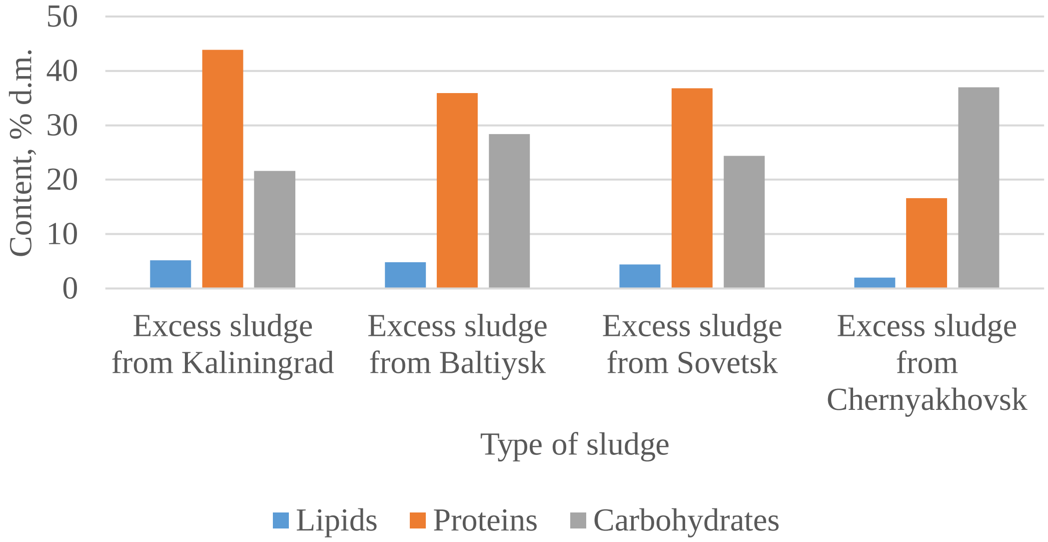


Figure 3. Content of main groups of substances in excess sludge from different biological treatment plants

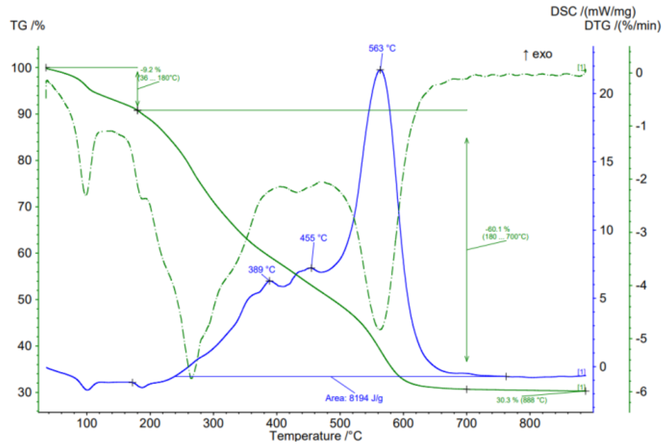
The lipid content as one of the main components of bio-oil varies from 2 to 5.2%. Excessive activated sludge from Chernyakhovsk should be considered the least attractive feedstock for bio-oil production, as its main component was carbohydrates, and the total content of proteins and fats did not exceed 19%, which is 2-2.5 times less than that of other sludges. This fact is related to the fact that at the time of sampling, the treatment facilities were not yet fully operational, and the sampled sludge underwent partial mineralization as a result of long-term storage and aeration in the excess sludge regenerator.

The high moisture content of the excess sludge (up to 98%) and the high ash content (30-44%) render it an unpromising feedstock for conventional thermal conversion processes, such as pyrolysis and combustion. Table 3 presents a comparison of the thermal properties of different excess sludges.

The thermograms obtained during the synchronous thermal analysis of all sludges exhibited a high degree of similarity (figure 4). The process of thermal decomposition in air can be divided into three stages: the evaporation of moisture (up to approximately 150°C), the decomposition of organic compounds (up to 500°C), and their subsequent mineralization (at temperatures exceeding 550°C) (Hernández et al., 2017; Oladejo, 2017).

Table 3: Thermal properties of sludge and excess activated sludge (on the example of waste from Kaliningrad wastewater treatment plants)

Parameters	Excess activated sludge				Sawdust [Hernández, 2017 and Oladejo, 2017]
	Kalinin-grad	Chernrya khovsk	Sovetsk	Baltiysk	
Fire point, °C	280	240	240	210	308
Temperature of max. degradation rate, °C	549	472	563	537	443
Ashing temperature (T_b), °C	600	720	600	720	490
Solid residue, %	29.8	50.7	30.3	41.4	11.95
HCV, MJ/kg (d.m.)	8.76	7.595	8.194	7.835	15.86



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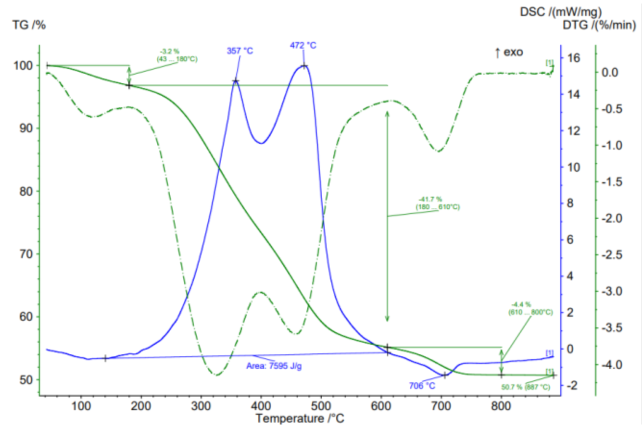

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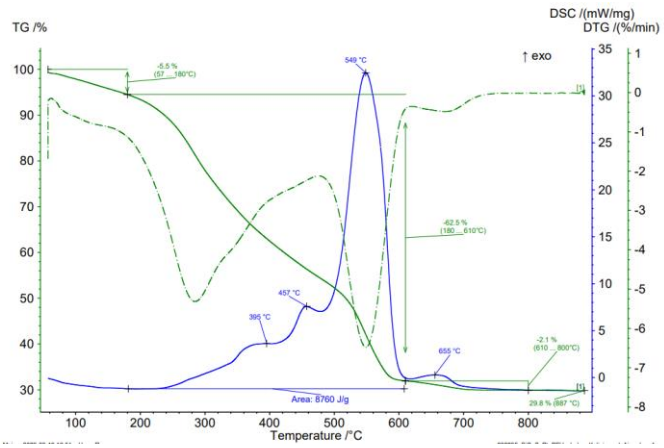

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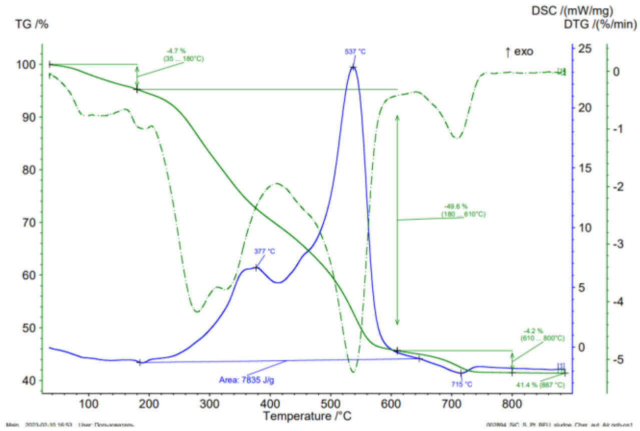


d)

Figure 4. Thermograms of excess sludge from city plants: a-Sovetsk, b-Cherniakhovsk, c-Kaliningrad, d-Baltiysk.

It is important to note that the heat of combustion was determined on a dry mass basis for the excess sludge. Taking into account that the natural moisture content of sludge is 96-98%, the energy attractiveness of the bottom type of organic waste decreases sharply. Thus, conventional thermal methods without pre-drying of the sludge are not applicable. In the current situation, hydrothermal liquefaction should be considered as a more promising technology.

Higher heat of combustion ranges from 7.595 to 8.76 MJ/kg, which is about 2 times lower than that of sawdust. The most caloric sludge from the Kaliningrad wastewater treatment plant was found to be the most caloric. It can be reasonably deduced that the absence of mixing between the primary clarifier sludge and excess sludge, coupled with the high degree of maturity and heterotrophic dominance of the sludge, including multicellular microorganisms (rotifers, nematodes, etc.), is the probable cause.

3.2. Evaluation of the effect of process time on biofuel yields

The effect of process time on fuel yield was analyzed on 3 types of sludge at two temperatures: 240 and 260 °C. The results are presented in Figure 5.

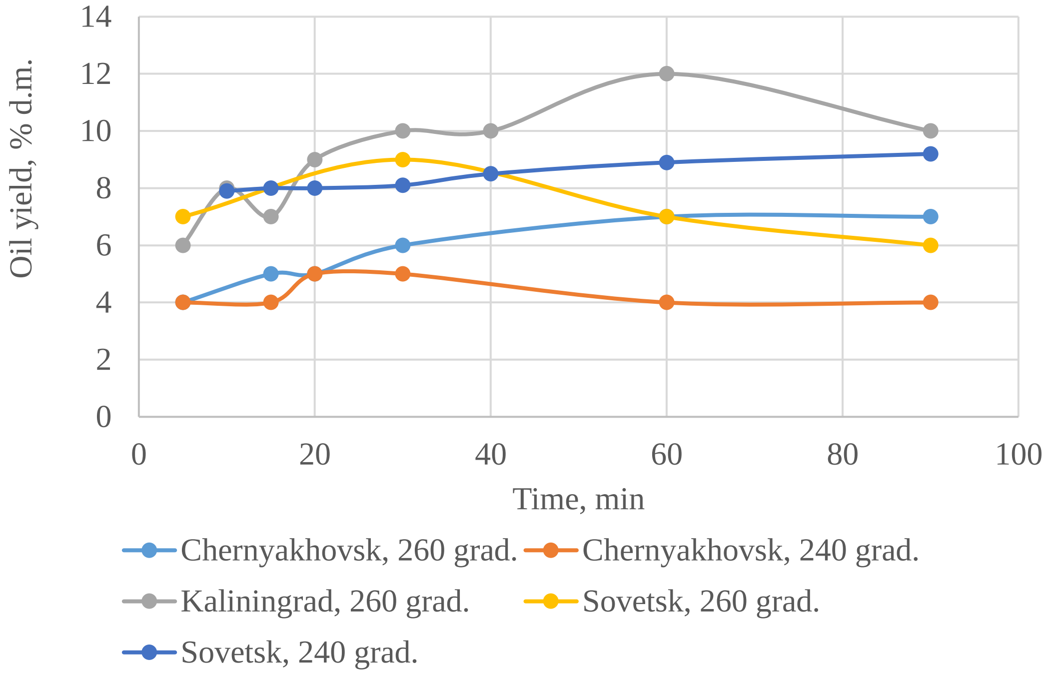


Figure 5. Effect of process time on fuel yield

As we can see, the fuel yield was much higher when processing excess sludge from the wastewater treatment plants in Kaliningrad and Sovetsk, which was predicted based on the analysis of thermal and physicochemical properties of the sludge.

At lower temperatures, the influence of time is less noticeable than at higher temperatures. Thus, when increasing HTL retention time of sludge from treatment plant Sovetsk from 5 to 30 minutes we observe an increase in fuel yield by 25% at a temperature of 240 °C and by 50% at a temperature of 260 °C.

At the same time, we observe a general trend for all excess sludge, so that when increasing the time up to 40 minutes, there is a stable increase in fuel yield, while when increasing the time up to 60 minutes, there are variations of experience, when a slight decrease in yield is observed. Further increase of time up to 90 min does not bring significant change of liquid fuel yield or the yield decreases. This phenomenon is most likely caused by condensation and solid residue formation starting to occur in the reacting mass.

A comparable outcome was observed by Ma et al. (2020), who discovered that prolonging the hydrothermal liquefaction of Ulva *prolifera* macroalgae beyond 40 minutes resulted in a reduction in the liquid fraction yield and an increase in the char yield. Santhosh and Periyasamy (2023) proved that optimum time for HTL of *Kappaphucus alverizii* (red macroalgae) is 35 minutes. Thus, a process time of 20-40 minutes should be considered optimal.

3.3. Effect of temperature on fuel yield

In evaluating the effect of temperature (Figure 6), certain difficulties were encountered due to the peculiarities of the operation of the available hydrothermal liquefaction reactor.

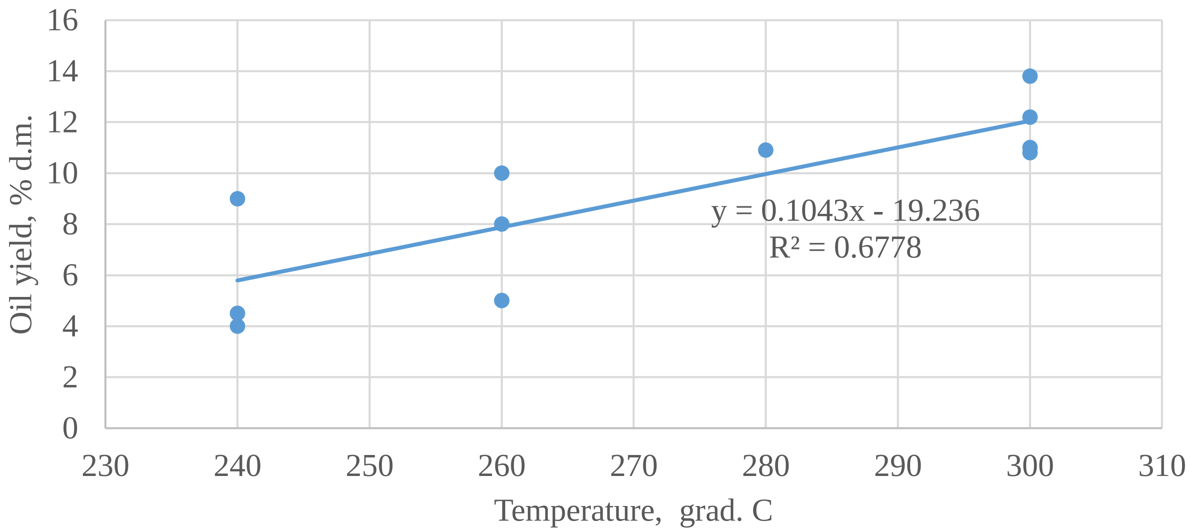


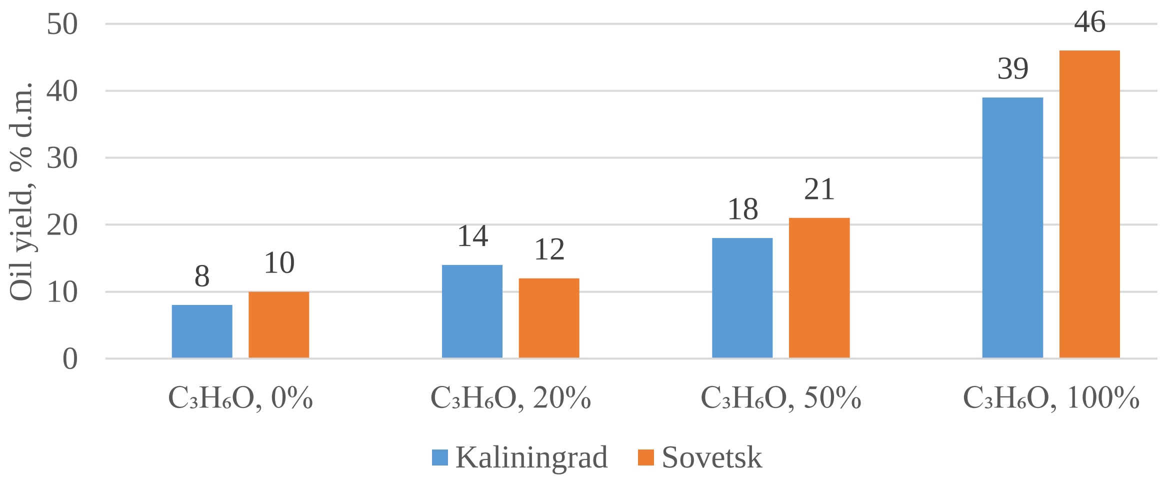
Figure 6. Effect of temperature on fuel yield.

Varying the temperature was only possible within fairly narrow limits. It was reliably found that temperatures below 260 °C were not sufficient to achieve effective degradation. This conclusion correlates quite well with the data obtained by other researchers studying the hydrothermal liquefaction of different types of biomass: microalgae (Chen et al., 2014; Song et al., 2019; Cheng et al, 2017; Zhang et al., 2022), macroalgae (Biswas et al., 2018; Yan et al., 2019) excess sludge (Badrolnizam et al., 2019; Xu et al., 2018; Chen et al., 2020; Mishra and Mohanty, 2020), plants (Madsen and Glasius, 2019; Zhang, 2020).

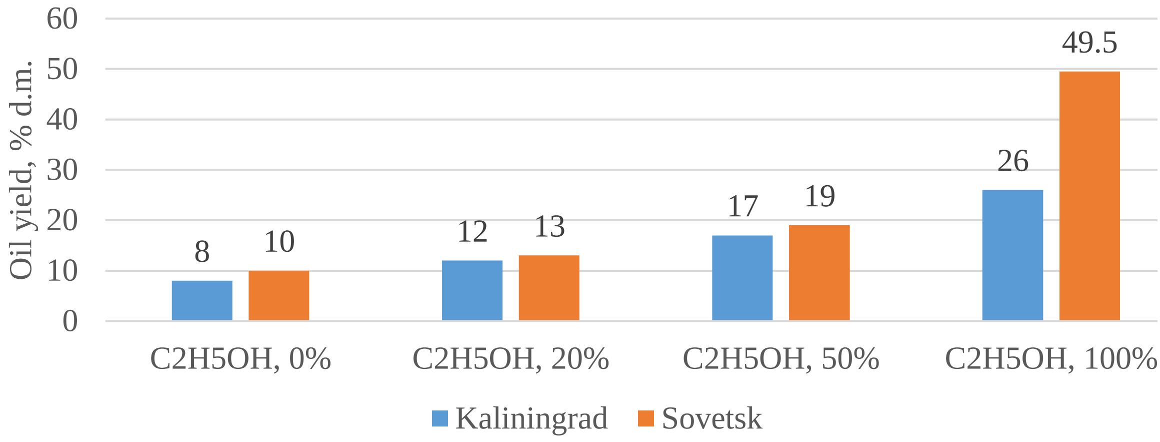
Further study of the effect of temperature should be continued in the second stage, as an autoclave reactor with a wider operating temperature range will be purchased.

3.3. Evaluation of the effect of different types of solvents on fuel yields

Experiments to evaluate the effect of solvents on fuel yield were conducted using two of the most common, available, and inexpensive hydrophilic solvents: ethyl alcohol and acetone. The concentration was varied from zero to 100%. As we can see (Figure 7), the fuel yield increased when both solvents were used. So the increase in yield when using acetone averaged 78.8%, when using alcohol 74.5%.



A)



B)

Figure 7. Evaluation of the effect of solvents on fuel yield: A) acetone, B) alcohol.

This increase in yield is due to the fact that these solvents have a lower critical temperature and pressure, i.e. for ethanol the critical state is reached at a temperature of 240ºC and a pressure of 6.3 MPa, for acetone this point is reached at a temperature of 235ºC and a pressure of 4.76 MPa. So in our case, the solvents were in a syncretic and critical state. In such a state, as is known, the number of radicals in the reaction medium increases sharply, which triggers the processes of breaking the carbon chain of large organic macromolecules, which ultimately leads to an increase in fuel yield.

Conclusion

Based on the analysis of fuel characteristics and chemical composition of excess sludge, it was found that it has the potential to be used for biofuel production by hydrothermal liquefaction. Sludge that has not been stabilized in aerators and composting sites has a higher caloric value (8.2-8.8 J/g a.d.m.). But given the high natural moisture content of the sludge, they are unsuitable for direct thermal conversion by conventional methods.

In addition, the presence of a significant number of heteroatoms in the sludge composition (up to 30% in total) is likely to result in poor quality of the resulting fuel.

Analysis of the influence of temperature showed that the temperature optimum of the process is above 260 °C when water is used as the solvent. It was decided to continue the research on the establishment of the temperature optimum at the next stage of research.

When evaluating the influence of process time, it was found that the optimum process time is 20-40 minutes, because further increase of time leads to partial recombination of substances and increase of coke residue yield. Less time is insufficient for the realization of carbon chain breaking processes.

Experimental studies to evaluate the effect of acetone and alcohol on yield have shown that the use of acetone increases fuel yield by an average of 78.8%, while the use of ethanol increases fuel yield by 74.5%.

The results of the research can be successfully used for the development of a technological scheme of utilization of excess sludge with obtaining of carbon-neutral fuel. In the future, the effect of different conditions of fuel production by HTL method on the quality of the produced fuel should be evaluated.

Acknowledgements:

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