

Article

Feasibility of Thermal Utilization of Primary and Secondary Sludge from a Biological Wastewater Treatment Plant in Kaliningrad City

Yuliya Kulikova ^{1,*} , Olga Babich ^{1,*} , Anna Tsybina ², Stanislav Sukhikh ¹, Ivan Mokrushin ³ , Svetlana Noskova ¹ and Nikolaj Orlov ¹

¹ Institute of Living Systems, Immanuel Kant BFU, 236041 Kaliningrad, Russia; stas-asp@mail.ru (S.S.); svykrum@mail.ru (S.N.); 05.01kolya2000@gmail.com (N.O.)

² Environmental Protection Department, Perm National Research Polytechnic University, 614000 Perm, Russia; anna.tsybina@gmail.com

³ Department of Inorganic Chemistry, Chemical Technology and Technosphere Safety of Perm State National Research University, 614990 Perm, Russia; mig@psu.ru

* Correspondence: kulikova.pnpu@gmail.com (Y.K.); olich.43@mail.ru (O.B.); Tel.: +7-912-784-9858 (Y.K.)

Abstract: Hydrothermal liquefaction (HTL) of sewage sludge is considered in the article as an analogue of the natural processes of oil formation (catagenesis). A comparison of the physicochemical composition of primary and secondary sludge with type II kerogen (natural precursor of oil) showed their similarity. Both types of sludge have a slightly higher level of oxygen and nitrogen. The study tested the hypothesis that the elements included in the inorganic part of the oil source rocks can have a catalytic effect on the oil formation processes. For the conducted studies of sludge HTL, the catalysts containing cations and substances found in oil source rocks were chosen: as homogeneous catalysts (KOH, NaOH, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, CoCl_6 , NiSO_4 , CuSO_4 , ZnSO_4 , MoO_3) and as heterogeneous catalysts (MgO , Zeolite, Al_2O_3). The effectiveness of catalysts containing metal ions, zeolite and aluminum oxide has been proven. The highest biocrude yield was achieved in a process with NiSO_4 as the catalyst in a dose 2 g per 10 g of sludge: oil yield increased by 34.9% and 63.4% in the processing of primary and secondary sludge, respectively. The use of catalysts provided an increase in fuel HHV by 10.8–12.5%, which is associated with a decrease in oxygen content (by 10.8–43.2%) with a simultaneous increase in carbon (by 7.9–10.9%) and hydrogen (by 6.5–18.7%) content.

Keywords: secondary sludge; primary sludge; hydrothermal liquefaction; catalyst; carbonization; biocrude; catagenesis



Citation: Kulikova, Y.; Babich, O.; Tsybina, A.; Sukhikh, S.; Mokrushin, I.; Noskova, S.; Orlov, N. Feasibility of Thermal Utilization of Primary and Secondary Sludge from a Biological Wastewater Treatment Plant in Kaliningrad City. *Energies* **2022**, *15*, 5639. <https://doi.org/10.3390/en15155639>

Academic Editors: Abrar Inayat, Abdallah Shanbleh, Mohamed Abdallah and Lisandra Rocha Meneses

Received: 29 June 2022

Accepted: 1 August 2022

Published: 3 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The generation of sewage sludge increases annually as a result of the world's population growth and the development of the centralized sewerage system [1]. The world's volume of sewage sludge generation is about 50–120 million tons (d.m.) per year [2]. In 2019, around 10.6 million tons of sludge was generated in Russia, including 2.5–3 million tons (d.m.) of municipal wastewater treatment sludge [3]. Countries surrounding the Baltic Sea generate approximately 4.0 million tons of sludge per year (d.m.) [4]. Currently, in Russia, only 8% is incinerated or composted and 92% of sludge is disposed on landfills, causing a negative environmental impact [5]. According to cost analysis, sewage sludge management accounts for roughly 50% of the total wastewater treatment plants operating cost in developed countries [6]. Thus, sewage sludge disposal is becoming an urgent global problem, making effective and sustainable sewage sludge management crucial.

Simultaneously, one of the most pressing issues for modern society is the reduction in CO_2 emissions from fossil fuels burnout processes. One of the ways to reduce the climate load is the use of organic waste for direct fuel production.

Technologies for the direct transformation of organic waste into fuel can be roughly divided into two groups: biochemical and thermochemical. The most appropriate treatment method depends on the composition of the sludge, the desired energy results, environmental standards and economic feasibility. Traditional methods of thermal conversion of sewage sludge include combustion, pyrolysis and gasification. A number of authors note that among the thermal methods, only combustion has a positive final energy balance [7]. Traditional pyrolysis and gasification processes are associated with a number of significant limitations, including low energy efficiency (due to the fact that additional drying of sludge is required) and highly complex reactors. The aforementioned difficulties that accompany the use of pyrolysis and gasification for the utilization of sludge are the reason for its limited use; there are only a few examples of their commercial applications worldwide [8,9].

In this regard, hydrothermal methods represent a group of technologies that have shown a high potential for processing wet sewage sludge and, simultaneously, fuels produced in various forms. The moisture in the sludge or biomass is used as the reaction medium during hydrothermal conversion and acts as a solvent and a source of radicals for the treatment of sewage sludge [10]. Hydrothermal processes can be roughly divided into hydrothermal liquefaction, gasification and carbonization. However, the most promising hydrothermal technology is liquefaction. HTL produces oil from sludge with a high moisture content, at 280–350 °C, and a pressure of 4–20 MPa [11,12]. Compared to traditional pyrolysis, which requires biomass drying, processing wet sludge can reduce energy consumption by 30% [13]. The number of studies in this area is growing exponentially. An analysis of the conditions and efficiency of the process (Table 1) allows us to conclude that it is possible to achieve up to 50% yield of oil by HTL sludge processing, even without the use of catalysts and organic solvents [11,14–16].

Table 1. Review of sewage sludge hydrothermal liquefaction conversion practices.

Raw Material	Conditions	Products	Yield	Reference
Primary sludge	Sludge:water ratio = 1:2, t = 250–400 °C, time 60 min	Oil	Max yield 52% at 350 °C	[14]
Primary sludge	Sludge:water ratio = 3:20, t = 300–350 °C, time 0–60 min, microwave pretreatment	Oil with HHV 26.3 MJ/kg	Max yield 35.4% at 350 °C	[15]
Primary sludge	Sludge:water ratio = 13:100, t = 300–400 °C and 12–14 MPa time 30–120 min	Oil	Max yield 34% at 325 °C, 30 min	[16]
Secondary sludge	Sludge:water ratio = 1:10, t = 260–350 °C time 10 min	Oil	Max yield 22.9% at 340 °C, 10 min	[11]
Secondary sludge	Sludge:water ratio = 1:10, t = 310 °C time 10 min, catalyst: KOH 0.13%; solvent: 15% ethanol	Oil	30%	[17]
Secondary sludge	Sludge:water ratio = 1:10, t = 310 °C time 10 min, catalyst: KOH 0.5%	Oil	23.1%	[18]
Primary and secondary sludge	Sludge:water ratio = 7:25, t = 350 °C time 15 min, catalyst: K ₂ CO ₃ 2.5%	Oil	28% (+12%)	[19]
Primary and secondary sludge	Sludge:water ratio = 7:25, t = 350 °C time 15 min, catalyst: CH ₃ COOH 2.5%	Oil	26% (+8.3%)	[19]
Primary and secondary sludge	Sludge:water ratio = 1:5, t = 300 °C time 40 min, catalyst: FeSO ₄ 5%		46% (+15%)	[20]
Primary sludge	Sludge:water ratio = 1:4, t = 300 °C, catalyst: K ₂ CO ₃ 2.5%		48% (+140%)	[12]

At the same time, the use of homogeneous alkaline catalysis and metal-containing heterogeneous catalysts can increase fuel yield by 8–140%. According to Basar et al. [12], bio-oil obtained from primary and secondary sludge is characterized by high energy content (HHV at the level of 22–48 MJ/kg), low content of nitrogen (3–7%) and oxygen (10–17%), but rather high sulfur content (0.5–2%).

There is a point of view that the hydrothermal liquefaction of biomass mimics the natural geological process of oil formation in an accelerated manner. Looking at the problem from this angle and attempting to develop a nature-like method of oil production, the question of considering the patterns of natural oil genesis and the composition of natural oil precursors becomes important. In view of the foregoing, this paper compares the physicochemical composition of sewage sludge with kerogen (oil natural precursor) for the first time.

Selecting catalytic systems for the HTL of sludge in most studies is based on empirical experience gained in the practice of oil cracking and thermal conversion. Considering HTL in terms of approaching the oil formation natural process is the advanced hypothesis that there is an influence of the mineral phase composition of source rocks on the processes of catagenesis. Thus, a promising strategy of effective catalysts choosing for HTL is their selection from chemical elements and compounds which are included in oil source rocks. The paper presents novel results by evaluating the effectiveness of catalysts for the HTL of sewage sludge.

This study aimed to assess the resource potential of primary and secondary sludge from the biological treatment plant in Kaliningrad in terms of its use for fuel production in catalytic HTL. In addition, the goal was to evaluate the effectiveness of the maximum approximation of the HTL process compared to the natural conditions of catagenesis.

2. Materials and Methods

2.1. Materials

Samples of dried sludge were received in April, 2022 from a biological wastewater treatment plant (Kaliningrad, Russia). The design capacity of the treatment facilities is 150,000 m³ per day. The treatment plant under discussion takes wastewater from households, partly storm water, and wastewater from industrial enterprises (mainly food industry). The plant implements a traditional biological treatment process, which includes mechanical treatment with grids, sand traps and radial primary clarifiers. The sludge from the primary clarifiers is discharged by airlift pumps to the dewatering station equipped with a belt filter press. Furthermore, wastewater treated in aeration tanks with active sludge.

The samples were dried at 60 °C and crushed in a knife crusher and sieved in order to achieve a fraction size of 2–4 mm. Then, the resulting fraction was dried to a constant weight (for 12–18 h) in an oven at 104 °C.

Catalysts were purchased from Russian suppliers (OOO “LenReaktiv”, Saint Petersburg, Russia).

2.2. Sludge Characterization Methods

Water content of sludge was determined gravimetrically by drying at 104 °C to a constant weight. Ash content was also measured gravimetrically by ignition at a temperature of 550 °C in accordance with ASTM-E1755-01R20 [21].

For the elemental analysis of sludge, the elemental analyzer Vario EL Cube (Hanau, Germany) CHNS model was used. The content of elements was determined based on the area of the chromatographic peaks of N₂, CO₂, H₂O, and SO₂, using a calibration straight line constructed from standard compounds [22]. Each sample was analyzed in three independent parallels and the mean values are presented.

The protein content was determined using the Kjeldahl method [23], which consists of mineralizing organic matter with sulfuric acid in the presence of a catalyst, forming ammonium sulfate, destroying ammonium sulfate with alkali, releasing ammonia and

removing ammonia with water vapor into a solution of boric acid. Mineralization of the sample was carried out in a digester at a temperature of 360 °C for 120 min.

Total lipid content was determined in accordance with Russian standards gravimetrically by extraction of crude fat from a sample with diethyl ether in a Soxhlet apparatus, removing the solvent and weighing the defatted residue [24].

Carbohydrate content was calculated using the following equation:

$$\text{Carbohydrate content (\%)} = 100\% - \text{lipid content (\%d.m.)} - \text{protein content (\%d.m.)} - \text{ash content (\%d.m.)}, \quad (1)$$

Simultaneous thermal analysis was used for the evaluation of calorific value and the thermal properties of sludge samples. For these purposes, a NETZSCH STA 449C Jupiter synchronous thermal analysis instrument (NETZSCH-Gerätebau GmbH, Selb, Germany) was used. Tests were conducted in an oxidizing (air) environment with a heating rate of 20 degrees/minute and a furnace gas flow rate of 40 mL/min, and the PtRh20 85 µL crucible was used.

2.3. Hydrothermal Liquefaction Procedure

The HTL process was carried out in a stainless-steel autoclave reactor (volume 300 mL) equipped with a magnetic stirrer, external electric heating, manometer and thermocouple (Eartha Zhang's, PRC). The average heating rate is 10 deg/minute. The sealing reactor was purged with N₂ beforehand. Temperature was in all experiments 260 °C, retention time 20 min, pressure 4.4 MPa and sludge dose 10 g (d.m.) per 100 mL distilled water. Dose for all catalysts was 2 g per 10 g of sludge (d.m.).

Upon completion of the process, the reactor was cooled with water to 24 °C. Gas products were vented. At this stage of the study, the composition of the gas phase was not analyzed. A periodic assessment of gases volume showed that their quantity did not exceed 200 mL (atm).

Solid residue was separated from the liquid phase by filtration. The filtered cake was dried at 104 °C in an oven to a constant weight. The oil fraction was extracted from the remaining liquid phase with dichloromethane and separated from the aqueous phase using a funnel. The distillation of the solvent was carried out using a rotary vacuum evaporator at 40 °C and vacuum 0.780 bar. The scheme of the experiment is shown in Figure 1.

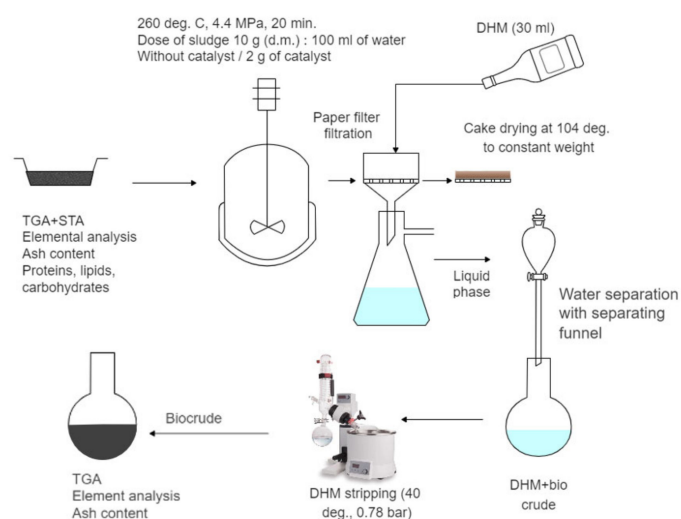


Figure 1. Research scheme.

2.4. Products Characterization Methods

Thermogravimetric analysis in argon atmosphere of biocrude was performed with a NETZSCH STA 449C Jupiter synchronous thermal analysis instrument (NETZSCH-

Gerätebau GmbH, Selb, Germany). The heating rate was 20 degrees/minute, the furnace gas flow rate was 40 mL/min, and PtRh20 85 μ L was used. TGA was used as the analog of oil distillation. Three volatile fractions were calculated: with boiling temperature 42–150 °C—gasoline; 150–360 °C—kerosene and diesel; 360–500 °C—heavy fuel oil. The elemental composition of C, H, N and S was assessed using the elemental analyzer Vario EL Cube (Hanau, Germany) CHNS model.

3. Results and Discussion

3.1. Primary and Secondary Sludge Characterization

Active sludge is a complex heterogeneous mixture of organic compounds (content 50–90% d.m.) and mineral components (content 10–50% d.m.), including total nitrogen (content 3.4–4.0% d.m.), and phosphorus (content 0.5–2.5% d.m.) [4,25]. The composition of sludge from biological treatment plants is not constant and varies depending on the stage of culture growth and the composition of the utilized substrate. The content of key biogenic elements C, H, N, S, and O in the biomass is an important parameter, since it allows predicting potential calorific value and fuel quality, as well as the viability of using one or the other methods of sludge processing. Table 2 presents the results of the elemental composition analysis of primary and secondary sludge.

Shchetinin [26] propose the following typical empirical formula for excess secondary sludge $C_5H_7O_2N$. In our case, this ratio was slightly different, so the formula for the studied sludge was $C_5H_{12}O_2N$, which indicates a higher content of fats and carbohydrates and a lower content of proteins in the sludge biomass. This was further confirmed by the analysis of the main groups of organic substances (Table 2). Therefore, it was found that lipids content in the secondary sludge is 10.2% d.m. or 14.8% of volatile solids, which is slightly higher than that reported in the literature (8–12%) [12]. The content of proteins was 29.6% of volatile solids; according to the literature data, this parameter varies from 48 to 52% [27]

The elemental composition of sludge from the primary clarifiers varies over a very wide range depending on the type of sewage system of the served area, type of subscribers, season, times of day, etc. In our case, the composition of primary sludge is fairly similar to that of active sludge. The difference is in the higher content of nitrogen, as primary sludge is rich in proteins and heterocyclic nitrogen-containing chemicals (for example, indoles) [28]. The molecular formula for the investigated primary sludge is the following: $C_{15}H_{27}O_5N$.

The content of proteins, as expected, was 2 times lower (13.7% of volatile solids) than in secondary sludge. This led to a similar decrease in the nitrogen content in biomass: from 10.2% in secondary sludge to 4.2% in primary sludge.

As noted earlier, an attempt to draw a parallel between HTL and natural processes of oil formation was made in this study. A common oil formation hypothesis is the biogenic one, which outlines three steps in the process of organic matter transformation [29]: diagenesis; catagenesis and metagenesis. The first stage involves normal sedimentation of organic matter of phyto- and zooplankton and phytobenthos biomass and its biological transformation due to anaerobic/anoxic degradation, which eliminates oxygen-containing groups. The product obtained at the first stage of transformation is usually called kerogen [29]; it has a higher content of carbon and a lower content of oxygen in comparison with raw biomass. All kerogen varieties can be categorized into three types, according to B. Tissot [29]. The biomass of algae, phytoplankton, and zooplankton in seas and oceans form type II kerogen, which is chemically closest to primary and secondary sludge. It should be emphasized that type II kerogen is a typical precursor to liquid hydrocarbons. The hypothesis that the production of liquid hydrocarbons is possible only in an aquatic environment is now widely accepted. Additionally, the transformation of terrestrial vegetation leads to the formation of coal and gaseous hydrocarbons [29]. In this study, the composition of sewage sludge is compared with type 2 kerogen (Table 2).

Table 2. Comparison of kerogen and sewage sludge composition.

Parameter	Type II Kerogen [29]	Sludge from the Primary Clarifiers	Excess Secondary Sludge
C content, %	70–73	54.58 ± 2.33	56.66 ± 0.31
H content, %	8–9	8.20 ± 0.28	8.93 ± 0.11
O content, %	9–11	25.30 ± 0.96	20.74 ± 0.18
N content, %	1–2	4.22 ± 0.25	10.22 ± 0.12
S content, %	0.78–1.27	n/a	n/a
H/C ratio (atomic)	0.5–1.25	1.8	1.89
O/C ratio (atomic)	0.1–0.3	0.35	0.27
Ash content (% d.m.)	-	26.93 ± 0.23	31.3 ± 0.13
Total lipid content (%)	-	5.2 ± 0.5	10.2 ± 0.7
Total protein content (%)	-	9.98 ± 0.21	20.32 ± 0.21
Total carbohydrates content (% calc.)	-	57.89 ± 0.26	38.179 ± 0.25

Comparisons of the elemental composition of sludge with type II kerogen (Table 3) have shown that both types of sludge contain nearly the same amount of hydrogen and carbon, but a significantly larger amount of oxygen, which is associated with the presence of a considerable number of hydrocarbons. At the same time, the nitrogen content in the secondary sludge is almost 10 times and in primary 4 times higher than in type II kerogen. Therefore, it is necessary to pretreat the biomass using catalytic or biochemical methods, which ensures the destruction of some organic substances and removes oxygen and nitrogen from the biomass in order to obtain high quality bio-oil. The second scenario for solving this problem is condition-produced fuel, which undoubtedly will have a higher content of oxygen and nitrogen.

The dynamics of the thermal destruction of secondary and primary sludge was evaluated at the second stage of the research using synchronous thermal analysis (STA) and thermogravimetric analysis (TG). The research results are presented in Figures 2 and 3.

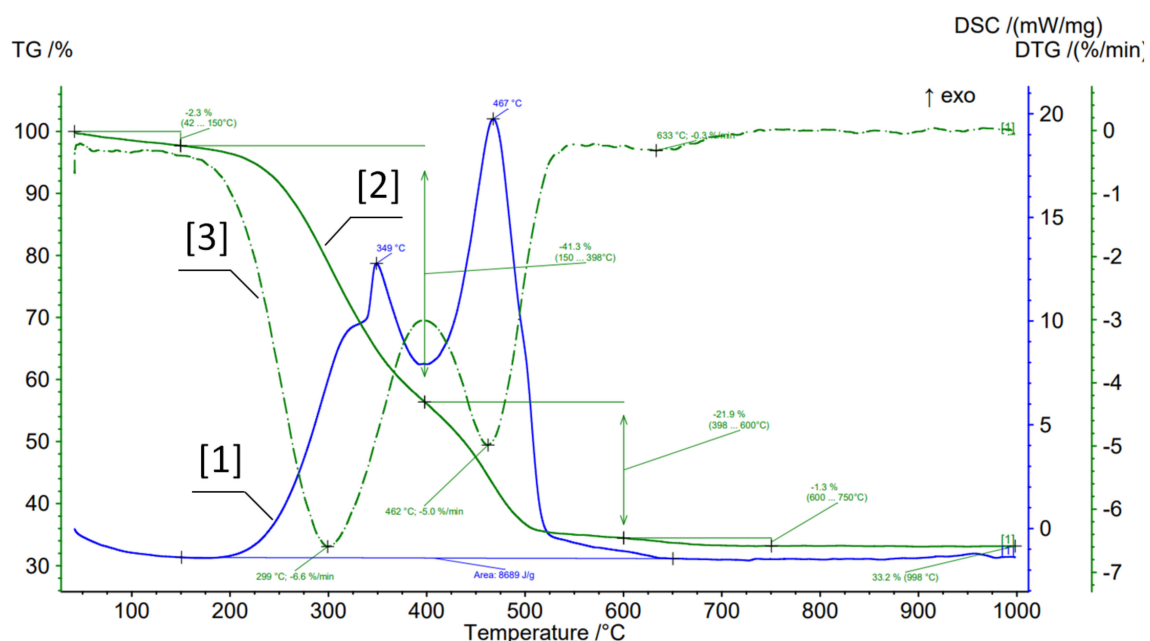


Figure 2. Results of simultaneous Thermal Analysis in the air atmosphere of active sludge: 1—DSC curve, 2—mass loss curve, 3—mass loss rate.

Table 3. Main thermal characteristics of primary and secondary sludge.

Parameter	Secondary Sludge	Primary Sludge	Sawdust [32]
Ignition temperature (T_i), °C	220	200	308
Maximum mass loss rate temperature (T_{max}), °C	299	508	443
Ashing temperature (T_b), °C	520	550	490
Maximum mass loss rate (R_{max}), %/min	6.6	8.5	39
Average mass loss rate ($R_{average}$), %/min	4.2	3.8	5.2
Combustion index (S), $\times 10^{-6}$	1.1	1.5	4.36
Ash content, %	24.9	33.2	11.95
HHV, MJ/kg (d.m.)	8.69	7.41	15.86
Initial water content, %	92–98	92–95	

It was found that secondary sludge is characterized by a higher total calorie content, which is associated with a higher portion of organic compounds, in comparison with primary sludge, which is characterized by a higher portion of mineral components (ash content of primary sludge is 33% higher than secondary sludge). A calculation of the true calorific value (calorific value of only volatile organic compounds) showed that HHV (v.m.) of secondary sludge is 13.47 MJ/kg and of primary sludge this value is 10.55 MJ/kg.

The comparison of the combustion indices of primary and secondary sludge indicates low combustion dynamics, even in comparison with sawdust. As is well known, fuels with a low burnout rate are prone to incomplete burnout and agglomeration. This factor with sludge high moisture content limits its direct combustion. Thus, taking the high initial water content of sludge into account, HTL should be considered as the more promising technology studied in this work. The results of the HTL process studies are presented below.

3.2. Catalytic Sludge Hydrothermal Liquefaction

According to Tissot, the formation of oil from kerogen proceeds at the stage of catagenesis at a temperature of 50–150 °C and pressure of 30–150 MPa. The choice of optimal process conditions was based on the successful practice described in the literature. Based on the analysis, it was decided to increase the reaction temperature to 260 °C and reduce the pressure to 4–7 MPa (concerning the natural conditions of catagenesis).

In order to bring the conditions of the HTL process as close as possible to the natural ones, the search for catalytic systems was carried out from elements included in the oil source rocks.

As is well known, oil source rocks are most often black mudstone, which are dark-colored sedimentary rocks rich in organic matter (5% or more carbon content). The inorganic base of black mudstone is represented by clay minerals and quartz grains. In terms of chemical composition, the main components are aluminum oxide, silicon oxide, calcium, potassium, sodium and magnesium oxides, iron sulfides and oxides, phosphorus as part of mineral complexes and certain trace elements (U, V, Cu, Ni, Mn, Ti, Co, Zn) [27].

At this stage of the research, we chose as homogenous catalysts: KOH, NaOH, $H_4Fe(SO_4)_2$, $CoCl_6$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, MoO_3 . Catalysts cations included in the listed salts and alkalis were considered as the target active components. For heterogeneous catalysis, we chose MgO, Zeolite and Al_2O_3 as the main compounds of black mudstone. The results of the experiments are presented in Table 4 and Figure 4.

Table 4. Results of HTL experiments.

Substrate	Catalyst	Oil Yield, % (Oil Yield Increase, %)	Solid Residue Yield, %	Water Soluble Phase Yield, %
Secondary sludge	None	29.75 ± 2.2 (0)	62.1 ± 4.5	8.2 ± 0.8
Primary sludge	None	30.7 ± 2.2 (0)	42.8 ± 3.5	26.6 ± 1.5
Primary+Secondary sludge 1:1	None	35.3 ± 2.8 (+18.6%)	46.6 ± 3.2	18.1 ± 1.1
Homogeneous catalysis				
Secondary sludge	KOH	21.6 ± 1.7 (−27.5%)	32.5 ± 2.8	45.9 ± 3.3
Secondary sludge	NaOH	10.9 ± 1.7 (−63.4%)	14.8 ± 0.9	74.3 ± 5.7
Secondary sludge	NH ₄ Fe(SO ₄) ₂	42.8 ± 4.3 (+43.6%)	50.8 ± 4.1	6.4 ± 0.4
Primary sludge	NH ₄ Fe(SO ₄) ₂	36.6 ± 2.7 (+19.2%)	47.1 ± 3.5	16.3 ± 0.9
Secondary sludge	CoCl ₆	44.5 ± 3.6 (+49.3%)	42.7 ± 3.3	12.8 ± 0.3
Primary sludge	CoCl ₆	28.8 ± 1.6 (−6.2%)	43.4 ± 2.8	27.8 ± 2.2
Secondary sludge	NiSO ₄	48.7 ± 2.5 (+63.4%)	47.6 ± 2.8	3.7 ± 0.2
Primary sludge	NiSO ₄	41.4 ± 3.6 (+34.9%)	44.0 ± 2.3	14.6 ± 0.9
Secondary sludge	CuSO ₄	35.5 ± 2.2 (+19.1%)	57.8 ± 1.9	6.7 ± 0.3
Secondary sludge	ZnSO ₄	42.0 ± 3.8 (+40.9%)	51.9 ± 3.1	6.1 ± 0.4
Secondary sludge	MoO ₃	32.6 ± 1.9 (+9.4%)	37.0 ± 2.4	30.4 ± 1.6
Primary sludge	MoO ₃	23.8 ± 1.7 (−22.5%)	53.0 ± 4.2	23.2 ± 1.7
Heterogeneous catalysis				
Secondary sludge	MgO	27.4 ± 2.4 (−8.1%)	47.1 ± 3.6	25.5 ± 1.7
Secondary sludge	Zeolite	35.0 ± 2.6 (+17.4%)	39.8 ± 2.7	25.2 ± 1.6
Primary sludge	Zeolite	33.3 ± 2.8 (+8.5%)	37.4 ± 1.6	29.3 ± 1.4
Secondary sludge	Al ₂ O ₃	37.1 ± 2.1 (+24.5%)	48.4 ± 2.5	14.5 ± 1.4
Primary sludge	Al ₂ O ₃	39.1 ± 3.1 (+27.4%)	31.9 ± 4.4	29.0 ± 1.6

The results of the catalytic HTL of sludge showed that the alkaline catalysis does not have a positive effect on bio-oil yield, although some researchers achieved a positive effect [17,18]. It is difficult to find an explanation for this fact. This experiment was repeated many times with different doses of alkalis, but none of them gave a positive effect.

The best catalytic effect for secondary sludge HTL was achieved in the presence of catalysts of NiSO₄ (increase of oil yield by 63.4%), NH₄Fe(SO₄)₂ (increase of oil yield by 43.6%) and CoCl₆ (increase of oil yield by 49.3%). At the same time, no similar catalytic effect was observed when using the same catalysts for the conversion of primary sludge; moreover, with CoCl₆, the fuel yield decreased by 6%. This phenomenon is related to the fact that sludge has a different chemical composition.

Catalysts that have shown maximum efficiency in the process of secondary sludge conversion most likely catalyze proteins and fats destruction, of which the content in secondary sludge is higher than in primary. At the same time, all used catalytic systems turned out to be less efficient in the processes of primary sludge conversion. The maximum increase in bio-oil yield (by 34.9%) was achieved during primary sludge conversion with NiSO₄ as the catalyst.

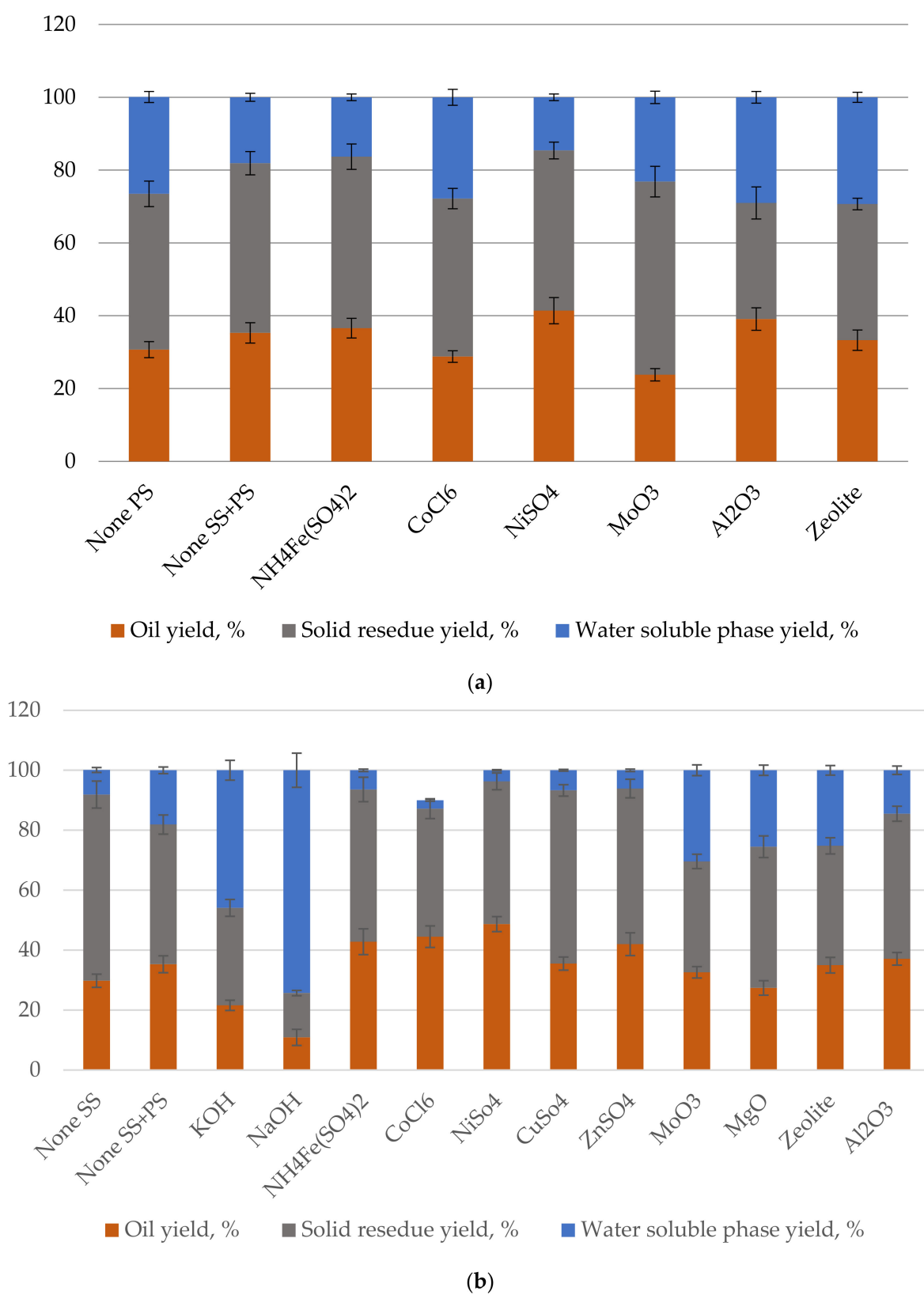


Figure 4. Effect of homogeneous and erogenous catalysis on product yield: (a)—primary sludge, (b)—secondary sludge; “none”—experiment without catalyst, red line—oil yield in experiment without catalyst.

Thus, homogeneous catalysis $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and NiSO_4 showed a stable positive result for primary and secondary sludge, and can be recommended for further extended studies in order to assess the effect of HTL process parameters and catalyst concentration on oil yield.

The heterogeneous catalysis had modest results in oil yield promotion. Usage of zeolite as catalysts for primary and secondary sludge allows an increase in oil yield by 8.5% and 17.4%, respectively, with the usage of Al_2O_3 oil yield growth by 27.4% and 24.5%. Aluminum oxide can be recommended for further consideration in extended experiments.

3.3. Bio-Oil Characterization

As mentioned above, TGA of oil was carried out in this study to assess the composition of substances by boiling points. The TGA of oil was carried out in four experiments: two experiments without catalytic systems and two experiments with a catalyst. Since the best result was obtained using nickel sulfate, the bio-oil from this experiment was subjected to analysis (Table 5).

Table 5. Boiling point distribution of biocrude substances.

Type of Bio-Oil	Boiling Point Temperature Range			
	42–150 °C	150–360 °C	360–600 °C	Rest
Bio-oil from HTL of primary sludge without catalyst, 4.4 MPa, 260 °C	1.8	56.7	24.6	16.8
Bio-oil from HTL of secondary sludge without catalyst, 4.4 MPa, 260 °C	1.7	54.4	34.3	9.6
Bio-oil from HTL of primary sludge, cat. 2 g NiSO_4 , 4.4 MPa, 260 °C	2.4	56.6	26.6	12.4
Bio-oil from HTL of secondary sludge cat. 2 g NiSO_4 , 4.4 MPa, 260 °C	2.7	65.32	26.9	5.0

Distribution of bio-oil substances by boiling temperatures showed that the content of residue (ash and char) in the oil from secondary sludge is much lower than from primary sludge, which is associated with a lower mineralization of the initial biomass. However, at the same time, the share of light and medium-boiling products in the composition of oil from the primary sludge is 58.5% and from the secondary 56.1%. The use of a catalyst significantly affected the share of non-combustible residue: the decrease in its share during the processing of primary and secondary sludge was by 26.2% and 47.9%, respectively. The share of fractions with a boiling point up to 360 °C during the processing of primary sludge with the catalyst remained effectively unchanged, while during the processing of secondary sludge the share of this fraction increased by 17.5%.

An analysis of the elemental composition of oil is presented in Table 6. High heating value (d.m.) was calculated using Equation (3) (proposed for HHV calculation by Channiwala [33]) and the results of the elemental composition of bio-oil.

$$\text{HHV} = 0.3491 \cdot \text{C} + 1.1783 \cdot \text{H} - 0.0151 \cdot \text{N} + 0.1005 \cdot \text{S} - 0.1034 \cdot \text{O} - 0.0211 \cdot \text{A} \quad (3)$$

where C, H, N, S, O—element content, % d.m.; A—ash content, % d.m.

The results of the calculations showed that the calorific value of the fuel with the use of catalysts increased significantly by 10.8–12.5%, which is associated with a decrease in the proportion of oxygen in the fuel and its ash content. Through the use of catalysts, the content of carbon increases by 7.9–10.9% and hydrogen by 6.5–18.7%. At the same time, the content of nitrogen and sulfur in the fuel remains practically unchanged.

Table 6. Results of element analysis.

Parameter	Boiling Range			
	Primary Sludge Without Catalyst	Secondary Sludge Without Catalyst	Primary Sludge Cat. 2 g NiSO ₄	Secondary Sludge Cat. 2 g NiSO ₄
Elemental composition (% d.m.)				
C	63.63 ± 2.15	67.22 ± 0.62	70.56 ± 0.84	72.97 ± 0.34
H	10.20 ± 0.23	9.17 ± 0.14	10.86 ± 0.11	11.21 ± 0.16
N	1.77 ± 0.15	6.85 ± 0.04	1.51 ± 0.03	4.29 ± 0.14
S	0.75 ± 0.09	1.06 ± 0.04	0.78 ± 0.04	1.05 ± 0.09
O (calculated)	6.85	6.10	3.89	5.44
HHV, (MJ/kg, d.m.)	33.22	33.45	36.82	38.06

4. Conclusions

Samples of primary and secondary sludge contain a complex of organic substances with energy potential. On the basis of synchronous thermal and thermogravimetric analysis, low combustion dynamics of the dry matter of studied primary and secondary sludge was proved; so, for PS and SS, the combustion index was 1.1×10^{-6} and 1.5×10^{-6} , respectively, which is 4 times lower than that of sawdust. The high ash content of secondary sludge (33.2%) and primary sewage sludge (24.9%), their HHV (d.m.) of 8.69 MJ/kg and 7.41 MJ/kg, respectively, as well as the high initial humidity (approximately 92–98%), led to the conclusion that use of traditional thermal conversion methods for their disposal (pyrolysis, gasification, and incineration), which require preliminary drying of the waste, is infeasible.

Hydrothermal liquefaction is a nature-like technology because it replicates the processes of kerogen transformation in the catagenesis. The properties of type II kerogen (the closest analogue) and primary and secondary sludge were compared, and it was discovered that sludge is similar to the natural oil precursor and can be successfully used for biofuel production. At the same time, the samples of sludge contained a higher amount of oxygen and nitrogen, which, in natural conditions of oil formation, decreases at the stage of diagenesis through destruction under anoxic/anaerobic conditions.

This study has shown the effectiveness of catalysts searching for HTL among the cations and substances included in the oil source rocks. The best results have been obtained with NiSO₄ as the catalyst, the use of which provided oil yield increased by 34.9–63.4%. Among the heterogeneous catalysts, aluminum oxide showed the maximum efficiency: oil yield growth was 24.5–27.4%. The use of catalysts provided an increase in fuel HHV by 10.8–12.5%. Along with this was observed a decrease in oxygen content and an increase in carbon and hydrogen content. In the future, it is crucially important to continue research on the search for effective catalysts, as well as to run expanded studies with catalysts selected based on the results of this investigation.

Author Contributions: Formal analysis, O.B.; Funding acquisition, S.S.; Investigation, Y.K. and I.M.; Methodology, O.B. and I.M.; Resources, S.S.; Validation, S.N.; Visualization, S.S. and N.O.; Writing—original draft, Y.K. and A.T.; Writing—review and editing, O.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Higher Education of the Russian Federation, project number FZWM-2021–0016.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Christodoulou, A.; Stamatelatos, K. Overview of legislation on sewage sludge management in developed countries worldwide. *Water Sci. Technol.* **2015**, *73*, 453–462. [CrossRef] [PubMed]
- Zhang, Q.; Hu, J.; Lee, D.-J.; Chang, Y.; Lee, Y.J. Sludge treatment: Current research trends. *Bioresour. Technol.* **2017**, *243*, 1159–1172. [CrossRef] [PubMed]
- Zaitseva, N.A.; Pyrsikova, A.N. Ispol'zovanie osadkov stochnykh vod v kachestve udobrenii [The use of sewage sludge as fertilizers]. *Int. Res. J.* **2015**, *3*, 104–107.
- Kacprzak, M.; Neczaj, E.; Fijałkowski, K.; Grobelak, A.; Grosser, A.; Worwag, M.; Singh, B.R. Sewage sludge disposal strategies for sustainable development. *Environ. Res.* **2017**, *156*, 39–46. [CrossRef]
- Dyakov, M.S. Strategy for the management of solid waste from municipal wastewater treatment plants. *Bull. PNRPU Appl. Ecol. Urban. Dev.* **2019**, *2*, 35–48. [CrossRef]
- Bajbekov, R.F.; Merzlaya, G.E.; Vlasova, O.A. Organic waste utilization for the agroecosystem fertilization. *Crop Husb.* **2015**, *2*, 34–36.
- Oladejo, J.; Shi, K.; Luo, X.; Yang, G.; Wu, T. A Review of Sludge-to-Energy Recovery Methods. *Energies* **2019**, *12*, 60. [CrossRef]
- Jiang, G.; Xu, D.; Hao, B.; Liu, L.; Wang, S.; Wu, Z. Thermochemical methods for the treatment of municipal sludge. *J. Clean. Prod.* **2021**, *311*, 127811. [CrossRef]
- Samolada, M.C.; Zabanitoutou, A.A. Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. *Waste Manag.* **2014**, *34*, 411–420. [CrossRef]
- Kulikova, Y.; Sukhikh, S.; Ivanova, S.; Babich, O.; Sliusar, N. Review of Studies on Joint Recovery of Macroalgae and Marine Debris by Hydrothermal Liquefaction. *Appl. Sci.* **2022**, *12*, 569. [CrossRef]
- Xu, D.; Lin, G.; Liu, L.; Wang, Y.; Jing, Z.; Wang, S. Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures. *Energy* **2018**, *159*, 686–695. [CrossRef]
- Basar, I.A.; Liu, H.; Carrere, H.; Trabaly, E.; Eskicioglu, C. A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications. *Green Chem.* **2021**, *23*, 1404. [CrossRef]
- Yang, T.; Liu, X.; Li, R.; Li, B.; Kai, X. Hydrothermal liquefaction of sewage sludge to produce bio-oil: Effect of co-pretreatment with subcritical water and mixed surfactants. *J. Supercrit. Fluids* **2019**, *144*, 28–38. [CrossRef]
- Badrolnizam, R.; Elham, O.; Hadzifah, S.; Husain, M.; Hidayu, A.; Mohammad, N.; Mohamad Daud, A. Sewage sludge conversion via hydrothermal liquefaction (HTL)—A preliminary study. *J. Phys. Conf. Ser.* **2019**, *1349*, 012108. [CrossRef]
- Chen, G.; Hu, M.; Du, G.; Tian, S.; He, Z.; Liu, B.; Ma, W. Hydrothermal Liquefaction of Sewage Sludge by Microwave Pretreatment. *Energy Fuels* **2019**, *34*, 1145–1152. [CrossRef]
- Mujahid, R.; Riaz, A.; Insyani, R.; Kim, J. A centrifugation-first approach for recovering high-yield bio-oil with high calorific values in biomass liquefaction: A case study of sewage sludge. *Fuel* **2020**, *262*, 116628. [CrossRef]
- Lin, Y.; Ma, X.; Peng, X.; Yu, Z.; Fang, S.; Lin, Y.; Fan, Y. Combustion, pyrolysis and char CO₂-gasification characteristics of hydrothermal carbonization solid fuel from municipal solid wastes. *Fuel* **2016**, *181*, 905–915. [CrossRef]
- Nazari, L. Hydrothermal Liquefaction of High-Water Content Biomass and Waste Materials for the Production of Biogas and Bio-Crude Oil. Electronic Thesis and Dissertation Repository. 2016. Available online: <https://ir.lib.uwo.ca/etd/4069> (accessed on 7 May 2022).
- Shah, A.A.; Toor, S.S.; Seehar, T.H.; Nielsen, R.S.; Nielsen, A.H.; Pedersen, T.H.; Rosendahl, L.A. Bio-Crude Production through Aqueous Phase Recycling of Hydrothermal Liquefaction of Sewage Sludge. *Energies* **2020**, *13*, 493. [CrossRef]
- Malins, K.; Kampars, V.; Brinks, J.; Neibolte, I.; Murnieks, R.; Kampare, R. Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge. *Bioresour. Technol.* **2015**, *187*, 23–29. [CrossRef]
- ASTM-D7348; Standard Test Method for Ash in Biomass. ASTM: West Conshohocken, PA, USA, 2020; pp. 1–3.
- Kulikova, Y.; Sukhikh, S.; Babich, O.; Yuliya, M.; Krasnovskikh, M.; Noskova, S. Feasibility of Old Bark and Wood Waste Recycling. *Plants* **2022**, *11*, 1549. [CrossRef]
- Hwang, S.H.; Koo, M.; Jo, S.; Cho, Y.S. A comparison study of crude protein contents obtained utilizing the kjeldahl method and dumas combustion method in foods. *J. Anal. Sci. Technol.* **2020**, *33*, 143–150. [CrossRef]
- Thiex, N.; Anderson, S.; Gildemeister, B.; Adcock, W.; Boedigheimer, J.; Bogren, E.; Coffin, R.; Conway, K.; DeBaker, A.; Frankenius, E.; et al. Crude Fat, Diethyl Ether Extraction, in Feed, Cereal Grain, and Forage (Randall/Soxtec/Submersion Method): Collaborative Study. *J. AOAC Int.* **2003**, *86*, 888–898. [CrossRef]
- Rulkens, W.H. Sewage sludge as a biomass resource for the production of energy: Overview and assessment of the various options. *Energy Fuels* **2008**, *22*, 9–15. [CrossRef]
- Shchetinin, A.I. Elemental composition of activated sludge. *Water Supply Sanit. Eng.* **2010**, *11*, 49–54. (In Russian)
- Manara, P.; Zabanitoutou, A. Towards sewage sludge based biofuels via thermochemical conversion: A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2566–2582. [CrossRef]

28. Whitehead, T.; Price, N.; Drake, H.; Cotta, M. Catabolic Pathway for the Production of Skatole and Indoleacetic Acid by the Acetogen *Clostridium drakei*, *Clostridium scatologenes*, and Swine Manure. *Appl. Environ. Microbio.* **2008**, *74*, 1950–1953. [[CrossRef](#)] [[PubMed](#)]
29. Tissot, B.; Welte, D. The Fate of Organic Matter in Sedimentary Basins: Generation of Oil and Gas. In *Petroleum Formation and Occurrence*, 2nd ed.; Springer: Berlin/Heidelberg, Germany; New York, NY, USA; Tokyo, Japan, 1984; pp. 69–130.
30. Hernández, A.B.; Okonta, F.; Freeman, N. Thermal decomposition of sewage sludge under N₂, CO₂ and air: Gas characterization and kinetic analysis. *J. Environ. Manag.* **2017**, *196*, 560–568. [[CrossRef](#)] [[PubMed](#)]
31. Oladejo, J.M.; Adegbite, S.; Pang, C.H.; Liu, H.; Parvez, A.M.; Wu, T. A novel index for the study of synergistic effects during the co-processing of coal and biomass. *Appl. Energy* **2017**, *188*, 215. [[CrossRef](#)]
32. Guida, M.Y.; Lanaya, S.; Rbihi, Z.; Hannioui, A. Thermal degradation behaviors of sawdust wood waste: Pyrolysis kinetic and mechanism. *J. Mater. Environ. Sci.* **2019**, *10*, 742–755.
33. Channiwala, S.; Parikh, P.P. A Unified Correlation for Estimating HHV of Solid, Liquid and Gaseous Fuels. *Fuel* **2002**, *81*, 1051–1063. [[CrossRef](#)]