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RESEARCH ARTICLE

Synthesis of methanol from gaseous products of pyrolysis of sewage sludge

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Abstract

Objectives. To study the influence of compositional variability (different ash and organic matter contents) of sewage sludge on the characteristics of synthesis gas (syngas) and to determine the yield of products in the entire chain of conversion of sewage sludge to methanol through the stage of syngas production by two-stage pyrolysis.

Methods. Syngas was produced by a two-stage pyrolysis method. After heating sewage sludge from 20 to 1000°C in an oxygen-free medium, heterogeneous thermal cracking of the volatile products was carried out in a biochar medium at 1000°C. The syngas was converted to methanol on a CuZnAl catalyst in an isothermal flow heat-pipe reactor at a feedstock feed rate of 600 h^{-1}, an internal reactor pressure of 5 MPa, and temperatures in the catalyst bed of 205, 215, and 225°C. The resultant syngas having a CO_2 content of less than 0.5 vol % and a H_2/CO ratio of 1.8 was used as feedstock for methanol production.

Results. The experimental studies of syngas production from sewage sludge demonstrated the active formation of syngas during two-stage pyrolysis in the temperature range of 140–600°C regardless of the ash content of the sludge. The H_2/CO ratio in the syngas produced by two-stage pyrolysis of sewage sludge was shown to depend on the H/O atomic ratio in the sludge composition. Crude methanol was obtained at maximum yield and purity at a temperature of 225°C in the catalyst bed. The overall conversion of carbon monoxide was 43.6%.

Conclusions. Variability in the composition of sewage sludge significantly influences quantitative parameters to a large extent in terms of the specific volume yield of syngas and insignificantly terms of its composition. No qualitative influence was exerted by the difference in the types of sewage sludge on syngas production. The experimental studies showed that 1 kg of sewage sludge with a relative moisture content up to 5 wt % can produce 1.1 nm^3 of syngas and a further 220 g of pure methanol.

Keywords

sewage sludge, syngas, methanol, two-stage pyrolysis, thermal cracking, catalytic conversion, liquid motor fuels

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НАУЧНАЯ СТАТЬЯ

Синтез метанола из газообразных продуктов пиролиза осадка сточных вод

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Аннотация

Цели. Исследовать влияние непостоянства состава (различное содержание зольности и органической части) осадка сточных вод (ОСВ) на характеристики синтез-газа, определить выход продуктов во всей цепочке превращений осадка сточных вод в метанол через стадию производства синтез-газа методом двухстадийного пиролиза.

Методы. Синтез-газ был получен методом двухстадийного пиролиза, заключающимся в нагреве ОСВ от 20 до 1000°C в бескислородной среде с последующим термическим гетерогенным крекингом летучих продуктов в среде биоугля при температуре 1000°C. Конверсия синтез-газа в метанол проходила на CuZnAl-катализаторе в проточном изотермическом реакторе на тепловых трубах с объемной скоростью подачи сырья 600 $ч^{-1}$, при давлении внутри реактора 5 МПа, температурах в слое катализатора 205, 215 и 225°C. В качестве сырья для производства метанола был использован синтез-газ с содержанием CO_2 менее 0.5 об. % и отношением H_2/CO, равным 1.8.

Результаты. Результаты экспериментальных исследований процесса получения синтез-газа из ОСВ установили, что независимо от величины зольности осадка, активное образование синтез-газа при двухстадийном пиролизе происходило в интервале температур 140–600°C. Отношение H_2/CO в синтез-газе, произведенным методом двухстадийного пиролиза ОСВ, зависело от атомного отношения H/O в составе осадка. Максимальный выход и чистота метанола-сырца были получены при температуре в слое катализатора равной 225°C. Общая конверсия оксида углерода составила 43.6%.

Выводы. Непостоянство состава ОСВ влияло на количественные показатели в значительной степени по удельному объемному выходу синтез-газа и незначительно по его составу. Качественно на протекание процесса получения синтез-газа различие в видах ОСВ влияния не оказывало. Результаты экспериментальных исследований показали, что из 1 кг ОСВ с относительной влажностью до 5 мас. % может быть произведено 1.1 $нм^3$ синтез-газа и далее 220 г чистого метанола.

Ключевые слова

осадок сточных вод, синтез-газ, метанол, двухстадийный пиролиз, термический крекинг, каталитическая конверсия, жидкие моторные топлива

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INTRODUCTION

The 2015 Paris Climate Agreement aims to limit global temperature rise to 1.5–2°C above pre-industrial levels [1]. This is to be achieved primarily by reducing greenhouse gas emissions (CH_4 and CO_2), of which Russia, along with China and the USA, is a leading producer [2, 3]. CO_2 emissions can be reduced by partially replacing fossil fuels with carbon-neutral ones, e.g., biomass [4, 5].

In recent years, Russia has been actively developing a Gas-To-Liquid (GTL) technology for producing synthetic liquid hydrocarbon products. The main stages of this technology are the production of synthesis gas (syngas) and its catalytic conversion to motor fuel components [6]. In the classical process, syngas is formed by steam reforming of natural gas [7]. However, for catalytic conversion to synthetic hydrocarbons, it is of no importance how syngas is produced so long as it meets requirements for composition, impurity levels, etc. In the carbon footprint reduction paradigm, biomass can be used to produce syngas using a two-stage pyrolytic conversion method [8, 9]. An alternative to the conventional Fischer–Tropsch process can be a two-stage catalytic synthesis of liquid hydrocarbons in the first stage of which syngas is catalytically converted to methanol, which is then catalytically converted to components of liquid motor fuels [10].

In this paper, sewage sludge is considered as a feedstock for the production of syngas for the subsequent synthesis of liquid hydrocarbons. Over 100 mln m^3

of sewage sludge with an average moisture content of 96% is generated annually in Russia. After dewatering, sewage sludge is transported from wastewater treatment facilities (WWTFs) to sludge piles. This stage can often mark the end of its useful life since its use as a fertilizer in agriculture is limited by the presence of heavy metal ions in its composition [11, 12]. In European countries, more than 20 sewage sludge processing approaches are used, including landfill, use as fertilizer, incineration, pyrolysis, and others [13]. Despite limitations, the primary use of sewage sludge is in agriculture; of the thermal processing methods, incineration is the most widely used [14]. Incineration can significantly reduce sewage sludge volume while generating thermal energy, but this is accompanied by such significant problems as the formation of sulfur oxides [15]. In addition, thermal energy cannot be transferred over long distances. However, if sewage sludge can be converted to some final or intermediate product that can be used, e.g., in the chemical industry, then it is transformed from a liability into an asset.

The aim of the present study is to investigate the effect of variability in the sewage sludge composition on the yield and properties of syngas, as well as to trace the entire chain of conversion of sewage sludge to methanol, an intermediate product of a two-stage catalytic synthesis of liquid hydrocarbons.

MATERIALS AND METHODS

This study examined sewage sludge samples from three different WWTFs in Russia: (1) *Lyubertsy* WWTF (Moscow oblast); (2) *Togliattikauchuk* WWTF (Samara oblast); (3) *Almetyevsk* WWTF (Republic of Tatarstan). The samples consisted of a gray-brown, loose material containing organic fiber impurities (Fig. 1).

Preliminary preparation of feedstock included drying at a temperature of 105°C to reduce the relative humidity to values not exceeding 3–5 wt %. Technical analysis (determination of ash content *A*, volatile matter *VM*, and fixed carbon *FC*) was performed using a NETZSCH STA 2500 Regulus thermogravimetric analyzer (*NETZSCH Group*, Germany). The heating rate of feedstock was 20°C/min. The elemental composition (C, H, N, S) of the samples was determined using a vario MACRO cube elemental analyzer (*Elementar Analysensysteme GmbH*, Germany). The oxygen content (O) was calculated as a residual. The higher calorific value *HCV* was calculated from the elemental composition data. Table 1 presents the results of the technical analysis and elemental analysis of feedstock samples on a dry basis.

Table 1. Characteristics of sewage sludge samples (dry basis)

Parameter	Unit of measure	Sample		
		1	2	3
C	wt %	27.33	14.88	35.91
H		3.60	3.31	5.15
N		3.59	1.76	6.33
S		1.26	0.78	0.86
O		18.34	28.21	24.03
A		45.88	51.06	27.72
FC		9.74	5.70	13.23
VM		44.38	43.24	59.05
HCV	MJ/kg	11.11	6.21	16.12

Conversion of sewage sludge samples into syngas by two-stage pyrolysis was performed in a laboratory setup described previously [16]. The method involved heating the feedstock (sewage sludge) from room temperature 20°C to 1000°C at a rate of 10 deg/min in an oxygen-free medium (pyrolysis). The formed volatile products passed through a thermal cracking zone filled with biochar, a solid residue from the pyrolysis of the same type of sewage sludge that

(1) (2) (3)

Fig. 1. Sewage sludge samples: (1) *Lyubertsy* WWTF, (2) *Togliattikauchuk* WWTF, and (3) *Almetyevsk* WWTF

was present in the pyrolysis zone. The temperature in the cracking zone was maintained at 1000°C throughout the experiment. The volatile components were decomposed by various chemical reactions to form syngas. Biochar was previously obtained by pyrolysis of sewage sludge to 1000°C. The biochar layer height in the cracking zone was identical for all sewage sludge samples and was 10 cm. The relative moisture content of the feedstock samples did not exceed 1%. The syngas composition was determined using a Vario Plus Industrial flow gas analyzer (*MRU*, Germany) after sampling from a gas holder (*NPF Politekhnika*, Russia) in which the syngas was collected during the experiment. The volume was measured using a Shinagawa WS-1A gas meter (*Shinagawa Corporation*, Japan); the specific volume yield was determined as the ratio of the volume of all syngas released from the sewage sludge to the mass of the sample used in the experimental study. The lower calorific value *LCV* of the syngas was calculated using the volume fractions and the calorific value of the combustible gas components under standard conditions (20°C, 101.325 kPa) using the formula

$$LCV = 10^{-2} \cdot (11.78 \cdot [CO] + \\ + 10.05 \cdot [H_2] + 33.367 \cdot [CH_4]), \quad (1)$$

where [CO], [H_2], and [CH_4] are the contents of the respective gases in the mixture, vol %.

Crude methanol was synthesized from syngas in an isothermal catalytic heat-pipe reactor (R-1) [17]. Syngas was fed into the flow-through methanol synthesis reactor at a flow rate of 60 L/h from a cylinder in which a mixture of the desired composition had been previously prepared (Table 2). The volumetric syngas feed rate was 600 h^{-1}. The content of CH_3OH and H_2O in the raw methanol was determined chromatographically using the NetChrom hardware and software system (*NPF META-KHROM*, Russia); the content of dimethyl ether (DME) was measured using a Model 3700 chromatograph (*KHROMATOGRAF*, Russia); the content of trace impurities in methanol was determined chromatographically using a Khromos GKh-1000 chromatograph (at the laboratory of *Khromos*, Dzerzhinsk, Nizhny Novgorod oblast, Russia). The volumetric composition of the syngas at the outlet of the R-1 reactor was measured using an MRU Vario Plus Industrial gas analyzer.

To evaluate the methanol synthesis efficiency, the following metrics were calculated.

1. Overall CO conversion K_1, %:

$$K_1 = \frac{[CO]_{react} \cdot 100}{G \cdot [CO]_{in} \cdot \frac{28}{24.04}} \cdot 100\%, \quad (2)$$

where $[CO]_{react}$ is the mass flow rate of reacted CO, g/h; $[CO]_{in}$ is the CO content of the feedstock, vol %; 28 is the molar mass of CO, g/mol; 24.04 is the molar volume of CO at a temperature of 20°C, L/mol; and G is the volume flow rate of syngas, L/h.

2. Carbon efficiency of CO conversion to methanol, K_2, %:

$$K_2 = \frac{[CH_3OH]_{form} \cdot \frac{12}{32}}{[CO]_{in,m} \cdot \frac{12}{28}} \cdot 100\%, \quad (3)$$

where $[CH_3OH]_{form}$ is the mass of methanol formed, g; $[CO]_{in,m}$ is the mass of the initial carbon monoxide, g; 12 is the molar mass of carbon, g/mol; and 32 is the molar mass of methanol, g/mol.

3. Carbon efficiency of CO conversion to DME, K_3, %:

$$K_3 = \frac{[C_2H_6O]_{form} \cdot \frac{12}{46}}{[CO]_{in,m} \cdot \frac{12}{28}} \cdot 100\%, \quad (4)$$

where $[C_2H_6O]_{form}$ is the mass of DME formed, g.

4. Carbon efficiency of CO conversion to CO_2, K_4, %:

$$K_4 = \frac{[CO_2]_{form} \cdot \frac{12}{44}}{[CO]_{in,m} \cdot \frac{12}{28}} \cdot 100\%, \quad (5)$$

where $[CO_2]_{form}$ is the mass of carbon dioxide formed, g.

Table 2. Composition of syngas fed to methanol production reactor, vol %

CO	H_2	CO_2	N_2	CH_4	Total
34.30	61.95	0.40	2.70	0.65	100

Table 3. Conditions of experimental studies of the synthesis of components of liquid motor fuels from syngas

Parameter	Unit of measure	Reactor R-1
Temperature inside reactor	°C	205, 215, 225
Pressure inside reactor	MPa	5
Volumetric feedstock feed rate	h^{-1}	600
Feedstock	–	Syngas
Catalyst	–	CuO–ZnO/Al_2O_3 metal oxide catalyst (GL-7, *Süd-Chemie*, Germany)
Catalyst properties	–	Loading 100 cm^3, fraction 1.5–2 mL
Catalyst bed height	mm	221

Table 3 presents conditions of experimental studies of the synthesis of methanol from syngas.

RESULTS AND DISCUSSION

Feedstock properties

As a secondary biomass, sewage sludge has characteristics related to its origin. For all types of sewage sludge, the ash content varies from 28 to 57 wt %, the volatile matter content is 38–60 wt %, and the fixed carbon content is 3–11 wt % [15]. The total carbon content of sewage sludge, recalculated on an ash-free basis, is on average approximately 50%, which is comparable to the carbon content of sawdust (53 wt % [18]), and slightly lower than that of lignite (65–70 wt % [18, 19]). This fact allows for a higher calorific value of sewage sludge (on a dry basis) of 22 MJ/kg. In comparison, the corresponding parameter for wood sawdust is in the range of 18–20 MJ/kg; that of rice husks, 15–16 MJ/kg; lignite, 11.8–21.9 MJ/kg [15].

The samples taken for analysis in this study were typical representatives of sewage sludge. Sample 3 stood out from the previously presented ranges in terms of its ash, volatile matter, and fixed carbon contents. In particular, its fixed carbon content *FC* was 2.2% higher than the typical range (Table 1). Among the samples, were included a high-ash sample (51.06 wt %, sample 2) and a sample with an ash content close to the lower limit of the typical range (27.72 wt %, sample 3), indicating different organic matter contents in the samples.

Based on the composition of the syngas, the main elements determining its H_2 and CO contents were carbon, oxygen, and hydrogen. Sample 3 had the highest volatile carbon content (the difference between total *C* and *FC*) at 22.68 wt %, as well as the highest contents of volatile components and hydrogen, the lowest ash content, and a slightly lower oxygen content as compared with sample 2 (Table 1). Therefore, under identical experimental conditions, this sample was expected to produce the maximum syngas volume. In comparison with sample 1, sample 2 contained less volatile carbon (9.18 *vs* 17.59 wt %), but more oxygen (28.21 *vs* 18.34 wt %). Since the contents of volatile components and hydrogen for these two samples were very close (Table 1), at that stage, it was impossible to predict which of samples 1 and 2 would give a higher syngas yield.

Syngas production

Figure 2 shows the dependence of the specific volume yield of syngas and its formation rate (the temperature derivative of the specific volume yield of syngas) on the temperature in the pyrolysis zone for three sewage sludge samples. Syngas production began at a temperature of 140–160°C, which was due to the release of physical moisture from the samples and the subsequent formation of syngas in the cracking zone filled with biochar according to the reaction

$$H_2O + C = H_2 + CO. \quad (6)$$

The intense release of syngas from sample 1 was in the temperature range of 160–600°C; from sample 2 at 150–600°C; from sample 3 at 140–600°C. Since sample 3 had the maximum content of organic matter among the considered sewage sludge, the earlier (lower-temperature) release of syngas from this sample may be associated with the presence of lighter compounds—for example, methanol—in the volatile products [20]. For sample 1, the peak rate of syngas formation was observed at a temperature of 375°C; for sample 2 at 345°C; for sample 3 at 347°C. Thus, regardless of the mineral

matter content of the sewage sludge, the maximum rate of syngas release was in the temperature range of 340–380°C; by the time a temperature of 600°C was reached, the intense release of syngas had ended. It was shown in [21] that, in the composition of the volatile products of pyrolysis of sewage sludge, the mass of pyrolysis liquid consisting of water and organic matter in the temperature range of 200–600°C is four times larger than the mass of the formed incondensable gases. For this reason, the main feedstocks for syngas from the composition of the volatile products of pyrolysis are tars and water. The maximum rates of formation of tars and water are in the temperature ranges of 300–350 and 290–380°C, respectively [21]. Pyrolysis tars contain oxygen-containing compounds (the main ones are acids, ketones, phenols, alcohols, saccharides), aromatic and aliphatic hydrocarbons, and nitrogen-containing compounds (nitriles, pyridines, pyrroles, amines, amides) [22]. All of these are converted to syngas during thermal cracking. The higher the organic matter content of sewage sludge, the higher the mass yields of water and tars, and the higher the specific volume yield of syngas. Sample 3 had the maximum organic matter content, which favored the maximum specific volume yield of syngas among the samples studied. Sample 2 had the maximum ash content, which affected the quantitative characteristics of the syngas (Fig. 2).

Figure 3 shows the results of thermogravimetric analysis (TGA) of sewage sludge samples 1–3 in an inert medium in the temperature range of 150–900°C. The intense release of volatile products from these samples began at 200°C. The end of the range of active mass loss of the samples was at 550 ± 5°C. The two peaks in the rate of mass loss occurring at 290 and 340°C within this temperature range for sample 3 were associated with the decomposition of hemicellulose and cellulose components in the sewage sludge [23]. For sample 1, in the temperature range of hemicellulose decomposition, a shoulder was observed in the range of 294–314°C. This was a combination of several peaks responsible for the decomposition of complex organic compounds with different temperatures of the onset of destruction. The second peak was observed at 344°C, which is within the temperature range of cellulose decomposition [23]. For sample 2, the first peak was observed at 299°C with a shoulder in the range of 329–340°C instead of the second peak. For samples 1 and 2, in the temperature ranges of 394–464°C and 399–419°C, respectively, a shoulder-like structure was also observed on the mass loss rate curve. Due to the overlapping peaks of several reactions, the peak for sample 3 had a shoulder structure over a wide temperature range. Lignin, which is also present in the sludge, is known to actively decompose in this temperature range [24, 25]. Sewage sludge samples were studied by thermogravimetric analysis at different heating rates [26]. According to the presented data, the presence of shoulders on the mass loss rate curve of sewage sludge samples is a typical pattern.

The presence of peaks in the temperature range of 715–750°C for samples 1–3 (Fig. 3) may be due to the decomposition of inorganic carbonates, which are actively formed at temperatures up to 700°C by the interaction of CO_2 from volatile pyrolysis products with CaO from the sewage sludge ash [27, 28]. At temperatures above 700°C, the reverse reaction of $CaCO_3$ decomposition to form CO_2 occurs [29]. Sample 2, which had the maximum ash content, had the highest peak of the mass loss rate in this temperature range.

The TGA results for the sewage sludge samples under study (Fig. 3) correlated well with the results of measurements of specific volume yields and calculations of syngas formation rates for these samples (Fig. 2). The highest syngas formation rate among the studied samples was obtained for sample 3, which exhibited the highest

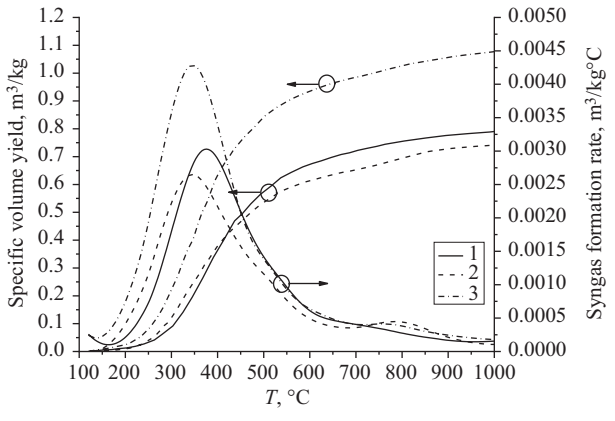

Fig. 2. Specific volume yield and formation rate of syngas from sewage sludge samples 1–3 *vs* temperature in the pyrolysis zone

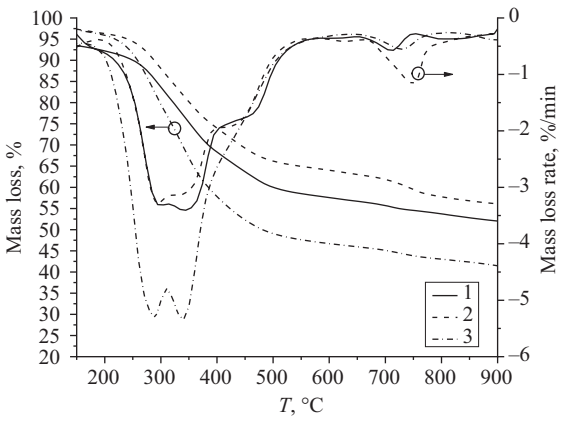

Fig. 3. Results of thermogravimetric analysis of sewage sludge samples 1–3: mass loss (left) and mass loss rate (right)

mass loss rate during thermogravimetric analysis. The data for samples 1 and 2 similarly agreed. The temperature range of intense syngas production for all three samples was 140–600°C, while the range of intense mass loss during thermogravimetric analysis was determined to be 200–550°C. The difference in the earlier onset and later end of the syngas release in comparison with the TGA data was explained by the difference in the masses of the samples used for the two types of analysis (10–20 mg for TGA *vs* 10–15 g for experimental studies), as well as by a small time delay in the determination of the volume yield of syngas in the gas meter in comparison with the measurement of the temperature inside the pyrolysis zone during the experimental study. It is worth noting the increase in the syngas formation rate for samples 2 and 3 at temperatures of 789 and 761°C, respectively (Fig. 2). A fourth peak of the mass loss rate observed in the temperature range of 670–800°C was associated with the formation of CO_2 by the decomposition of inorganic carbonates. During thermal cracking in the presence of carbon, CO_2 was actively converted to CO. It has been shown that H_2 formation actively increases at a sewage sludge pyrolysis temperature above 550°C with the peak occurring at 680°C [21]. Furthermore, throughout the heating of the sewage sludge sample in an oxygen-free medium, the volatile products contained water with one of the peaks of its formation rate at a temperature of 710°C. According to reaction (6), water is converted to syngas by thermal cracking in a charcoal medium. All these circumstances led to the increase in the syngas formation rate for samples 2 and 3 in the temperature range of 760–790°C.

Production of syngas from sewage sludge with an ash content of 22.7% by two-stage pyrolysis was studied [30]. The results were identical to those obtained in the present study: the intense release of syngas continued up to 570°C. The two-stage pyrolysis method was applied to plant biomass [31]. The results showed that the temperature range of intense release of syngas from plant biomass was 200–480°C.

Table 4 presents the main characteristics of the syngas obtained from three types of sewage sludge. The key parameters of the syngas that must be taken into account for its further conversion to liquid products are the H_2/CO ratio and the specific volume yield. For all three sewage sludge samples, the H_2 and CO contents were in the ranges of 57–60 and 37–41 vol %; this indicates the sufficient homogeneity of the syngas composition regardless of the different origin of the sewage sludge and the organic matter content. In addition, the syngas from all three sludge samples had a lower calorific value of 12 MJ/nm^3, a CO_2 content less than 0.5 vol %, and a CH_4 content less than 1 vol %. The organic matter content of sewage sludge determines the specific volume yield of syngas: for sample 3, this metric was maximum, while for sample 2, it was minimum, which correlates with the mineral matter contents of these samples.

Table 4. Characteristics of syngas obtained by two-stage pyrolysis of sewage sludge

Parameter	Unit of measure	Sample		
		1	2	3
Specific volume yield	m^3/kg	0.8	0.7	1.1
H_2	vol %	59.6	57.2	60.9
CO		39.2	41.6	37.9
CO_2		0.4	0.5	0.2
CH_4		0.8	0.7	1.0
H_2/CO ratio	–	1.5	1.4	1.6
LCV	MJ/m^3	11	11	11

The H_2/CO ratio was in the range of 1.4–1.6. The maximum H_2/CO ratio, as well as the maximum H_2 content, was obtained for sample 3. It was assumed and experimentally proven [32] that the H_2/CO ratio in the composition of syngas obtained by two-stage pyrolysis depends on the H/O atomic ratio in the original biomass: the higher the latter ratio, the higher the former. For the sewage sludge samples used in this study, the H/O atomic ratios were 3.1, 1.9, and 3.4, respectively (Table 1). The data in Table 3 show that the H_2/CO ratio was maximum for sample 3 and minimum for sample 2. Based on the obtained experimental data, it can be stated that the assumption [32] is also valid for the sewage sludge studied.

The total content of hydrogen and carbon monoxide in the resulting syngas, as well as their ratio, depends on the type of biomass processed. Two-stage pyrolysis of various samples of primary and secondary biomass was previously studied (Table 5) [30, 32]. Syngas produced from wood biomass (sawdust, not bark) had an H_2/CO ratio close to 1. Syngas obtained by the thermochemical conversion of birch and aspen bark had an H_2/CO ratio of more than 2. The behavior of secondary biomass (chicken litter and sewage sludge) differs during two-stage pyrolysis. Chicken litter has a specific volume yield of syngas and an H_2/CO ratio similar to those of plant biomass (except for bark samples), whereas sewage sludge has a lower specific yield, but a higher H_2/CO ratio (Table 4).

Table 5. Characteristics of syngas obtained by two-stage pyrolysis of various types of biomass

Material	Specific volume yield, m^3/kg	H_2/CO	Reference
Wood sawdust	1.3*	1.1	[32]
Birch bark	1.3*	3.0	[32]
Aspen bark	1.3*	2.1	[32]
Chicken litter	1.2	1.2	[30]

* Specific volume data are presented on a dry ash-free basis.

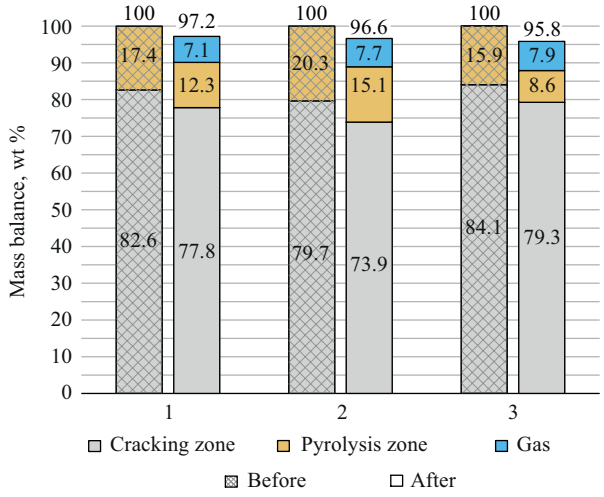

Fig. 4. Mass balance of two-stage pyrolysis of sewage sludge samples 1–3

Figure 4 illustrates the mass balance of two-stage pyrolysis of samples 1–3. For each of the samples, the left column represents the sum of the mass of the test material in the pyrolysis zone and the mass of charcoal in the cracking zone before the experiment. The right column shows the mass distribution of the two-stage pyrolysis products relative to the total mass of the materials before the experiment. The discrepancy in the mass balance is due to the error of the measuring instruments (scales, gas meter, flow gas analyzer), as well as the unaccounted-for mass of pyrolytic carbon deposited on the inner surface of the reactor during the homogeneous cracking of volatile products, which occurs simultaneously with the heterogeneous cracking in the biochar medium in the high-temperature region. However, this discrepancy does not exceed 4.2%. In addition, during the thermal cracking of the volatile products of sewage sludge pyrolysis, nitrogen- and sulfur-containing components are present in the syngas [33]. While this study did not determine nitrogen and sulfur dioxide impurities in the syngas, these factors could also have contributed to the mass balance discrepancy. The resulting syngas contained no liquid fraction, indicating complete conversion of all volatile pyrolysis products to syngas. Thus, unlike conventional methods of syngas tar removal (using cyclones, filters, and scrubbers), two-stage pyrolysis technology preserves the chemical energy contained in the tars, converting it to the calorific value of the syngas.

Methanol synthesis

The error in the volume content of components during the preparation of the gas mixture in the cylinder is 15%. Syngas obtained from sample 3 was used for the preparation of the mixture. Taking into account the error in the component contents, the H_2/CO ratio in the syngas mixture from the cylinder used for methanol synthesis was overestimated at 1.8.

Figure 5 presents the composition of the methanol synthesis products. The mass yield of crude methanol was 9.6, 10.3, and 12.3 g/h at catalyst bed temperatures of 205, 215, and 225°C, respectively.

The syngas leaving the methanol synthesis reactor had lower contents of carbon monoxide and hydrogen,

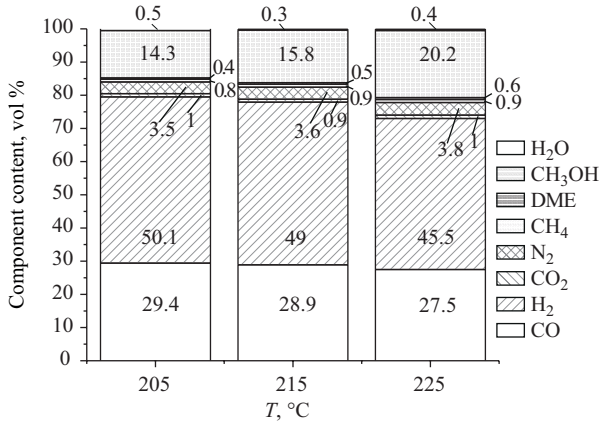

Fig. 5. Composition of methanol synthesis products

which were consumed in the main reaction of methanol synthesis:

$$CO + 2H_2 \rightarrow CH_3OH. \quad (7)$$

The H_2/CO ratios in the gas mixtures also decreased to 1.71, 1.69, and 1.61, respectively, at different catalyst bed temperatures. The carbon dioxide content increased in comparison with that in the feed gas due to the water-gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (8)$$

Nitrogen and methane were ballast gases and did not participate in the chemical reactions. Therefore, their volume flow rates remained unchanged, but their contents in the effluent increased due to some of the syngas being converted to methanol. This led to an overall decrease in the volume of reaction products. In this case, DME was a byproduct formed by the methanol dehydration reaction

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O, \quad (9)$$

which reduced the methanol yield. With increasing temperature inside the catalyst bed, the contents of unreacted CO and H_2 decreased and the DME content increased. At the same time, the methanol yield increased. The maximum methanol yield (38.2% of the mass of the synthesis products) was observed at a temperature inside the catalyst bed of 225°C (Fig. 6a). At temperatures of 215 and 225°C, the crude methanol consisted of more than 98.9% pure methanol (Fig. 6b).

Table 6 presents the contents of impurities in the composition of methanol.

Table 6. Microimpurities in methanol, wt %

Component	Temperature in catalyst bed		
	T_1 = 205°C	T_1 = 215°C	T_1 = 225°C
Acetaldehyde	0.20997	0.00457	0.03351
Formic acid	0.04779	0.01956	0.04226
Acetone	0.00073	0.00020	0.00176
Methyl acetate	0.00387	0.00145	0.00120
Ethanol	0.15065	0.08668	0.04937
Propan-1-ol	0.03830	0.02716	0.01452
n-Butanol	0.00583	0.00415	0.00175
Butan-1-ol	0.03662	0.01756	0.01321
Acetic acid	0.00457	0	0
Total	0.50	0.16	0.16

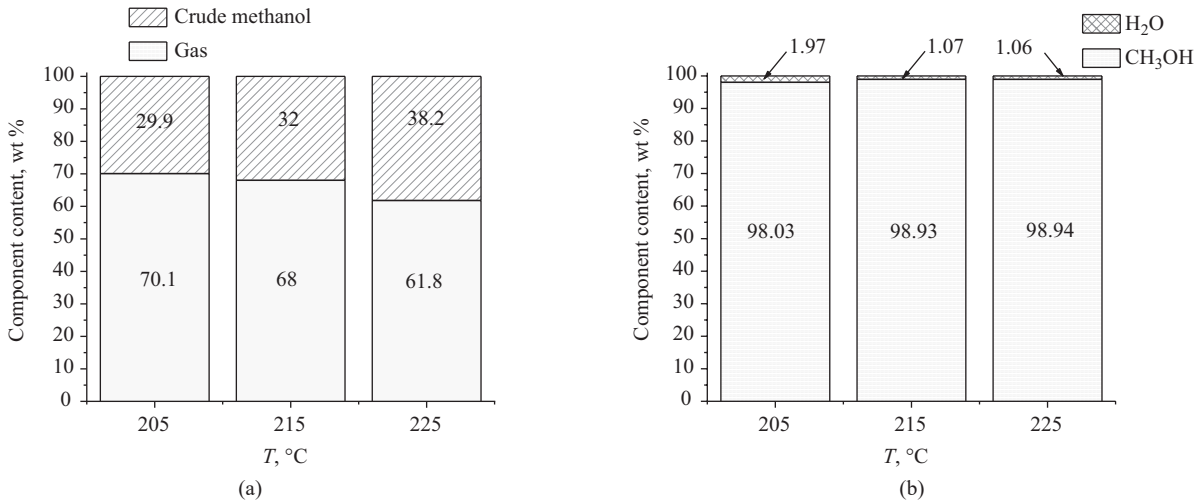

Fig. 6. (a) Mass balance of methanol synthesis and (b) the composition of crude methanol at various temperatures in the catalyst bed

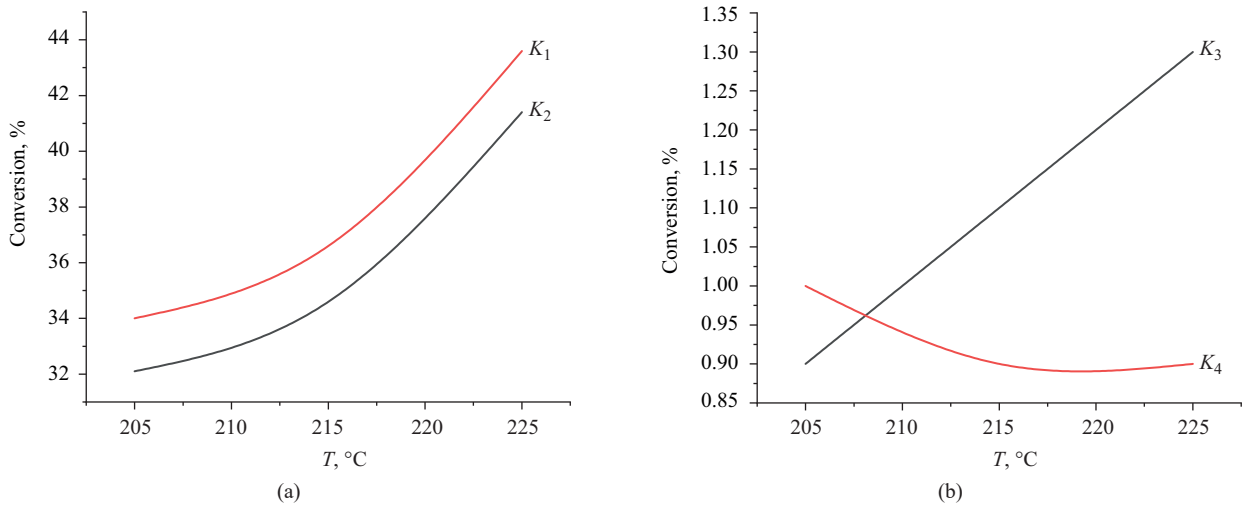

Fig. 7. Dependence of CO conversion on the temperature inside the catalyst bed: (a) K_1 and K_2; (b) K_3 and K_4

The impurity content of methanol decreased with increasing catalyst bed temperature. The water, acetone, formic acid, and ethanol contents of technical methanol were monitored. After reducing the water, formic acid, and ethanol contents, the resulting methanol can be classified as technical grade B methanol in accordance with GOST 2222-95[1].

Figure 7 shows the dependence of the CO conversion on the catalyst bed temperature. With increasing temperature inside the catalyst bed, the conversion of CO to CO_2 decreased, and the conversion of CO to DME and methanol increased. The maximum overall carbon monoxide conversion was 43.6% at a catalyst bed temperature of 225°C. Currently, under industrial conditions, the conversion of syngas to methanol in a single pass does not exceed 20% [34].

The syngas from the cylinder that was used for experimental methanol production studies had a higher H_2/CO ratio than that obtained experimentally from sewage sludge (Tables 2 and 4, respectively). A decrease in the H_2/CO ratio in the syngas led to a decrease in the CO conversion and, consequently, to a decrease in the mass yield of methanol and to an increase in the content of organic impurities [35].

The studies showed that, at a volumetric syngas feed rate of 600 h^{-1}, the maximum methanol yield and maximum CO conversion to methanol were achieved at a catalyst bed temperature of 225°C.

Currently, research is actively being conducted worldwide into methods for producing methanol as an intermediate product for the further synthesis of motor fuels. However, in the context of decarbonization policies, the focus of research has shifted toward the production of biomethanol [36]. Depending on the equipment design, all processes are divided into three groups: high-pressure synthesis on Zn/Cr catalysts (370–420°C, 20–35 MPa), low-pressure synthesis on Zn/Cu/Cr or Zn/Cu/Al catalysts (210–270°C, 5–10 MPa), and synthesis in a gas–liquid–solid three-phase system [34]. In addition, not only experimental studies but also process simulation using various software packages are actively conducted. For example [37], the Aspen Plus software was used to simulate the catalytic conversion of syngas to methanol in a continuous stirred-tank reactor at a temperature of 270°C and a pressure of 40 bar. The simulation results showed that hydrogen recycle to the system provided an increase in methanol production by 50.4% in comparison with the results of the process without H_2 recycle. The conversion of CO, CO_2, and H_2 was 50.4, 99.8, and 100%, respectively. One of the feedstock options for methanol production is syngas mixed from separately produced hydrogen and CO_2 captured from locally available point sources. In this regard, studies are being conducted to assess the role of CO and CO_2 in the methanol synthesis reaction catalyzed by Cu. It has been shown [38] that the rate of methanol synthesis from CO_2 is more than an order of magnitude higher than the rate of synthesis from CO, which helps to substantiate that CO_2 is a direct source of carbon for methanol on a Cu-containing catalyst. The role of CO is to bind water formed during methanol synthesis to form CO_2 via the water-gas shift reaction. Typically, to initiate the reaction of methanol production from syngas, the CO_2 content in the gas mixture must be at least 5 vol %. A method for increasing methanol yield

[1] GOST 2222-95. Interstate Standard. Technical methanol. Specifications. Moscow: Izdatelstvo standartov; 2000, 19 p. (In Russ.).

by creating a cascade of three flow-through catalytic reactors was presented [39]. Syngas unreacted in the first reactor is fed to the second, then to the third. At each stage, crude methanol is collected.

In the present study, the results of which are presented above, the syngas used for conversion to methanol had a CO_2 content of 0.4 vol % (Table 2). The novelty of the obtained results is determined by the apparent lack of publicly available publications on methanol synthesis from syngas at a low CO_2 content (less than 0.5 vol %). The use of sewage sludge as a feedstock for methanol production further underlines the relevance of the research.

CONCLUSIONS

The results of the experimental studies presented in this study confirm that sewage sludge is a suitable feedstock for methanol synthesis. Regardless of the ash content of the sewage sludge, intense syngas production by two-stage pyrolysis began at 140°C and continued until 600°C. The pattern of syngas formation from the sewage sludge samples under study correlated well with the results of their thermogravimetric analysis. With increasing ash content of the samples, the specific volume yield of syngas decreased. The H_2/CO ratio in the syngas obtained by two-stage pyrolysis from the sewage sludge, as well as that obtained from plant biomass, depended on the H_2/O atomic ratio in the sludge. The sample with the lowest H_2/CO atomic ratio yielded syngas with the lowest H_2/CO ratio. The same analogy was observed for the sample with the highest H_2/O atomic ratio. Thus, the heterogeneity of the composition of sewage sludge when processed by two-stage pyrolysis affects only the quantitative characteristics of the syngas and does not influence the actual process.

The maximum yield and purity of crude methanol were achieved at a catalyst bed temperature of 225°C. At this temperature, an overall CO conversion of 43.6% was achieved. After reducing the water, formic acid, and ethanol contents, the resulting methanol can be classified as technical grade B methanol.

Considering the entire chain of conversion of sewage sludge to methanol, 1 kg of sewage sludge can yield 1.1 nm^3 of syngas and then 220 g of pure methanol. The yield of methanol can be increased by creating a cascade of three flow-through catalytic methanol synthesis reactors.

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Authors' contributions

O.M. Larina—processing and analysis of experimental research results on obtaining syngas and its further synthesis into methanol, writing the text of the article.

I.I. Lishchiner—conducting experimental research on converting syngas into methanol, analysis of results.

O.V. Malova—conducting experimental research on converting syngas into methanol, analysis of results.

Yu.M. Faleeva—conducting experimental research on obtaining syngas from sewage sludge.

The authors declare no conflicts of interest.

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