Study on Steam Co-Gasification of Waste Tire Char and Sewage Sludge

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Abstract: The large and growing volume of tire waste and sewage sludge requires disposal, for which thermochemical processes such as gasification can be used. Co-gasification of these two waste products allows the tire char to be used as a charge stabilizer and the sewage sludge to improve reactivity and efficiency. The purpose of this study was to evaluate the effect of the composition of a waste tire char and sewage sludge fuel blend on the gasification process, using steam as the gasification agent. Tests were carried out for tire char, municipal sewage sludge, and blends of the two in ratios of 90:10 and 67:33. An analysis of the materials used was carried out (ultimate and proximate analysis as well as ash composition), and isothermal measurements of steam gasification were taken using the thermal volumetric method for temperatures of 800, 850, and 900 °C at an elevated pressure of 1 MPa. On the basis of the results, the formation curves of the main gasification products (H_2, CO, CO_2, and CH_4) were created, the curves for the degree of carbon conversion were plotted, the reactivity indexes were determined for different degrees of conversion (0.25, 0.5, and 0.75), and the quantity and composition of the resulting gas were analyzed. Using the grain model, the kinetic parameters (activation energy and pre-exponential factor) of the gasification reaction were calculated. The addition of municipal sewage sludge had a positive effect on the reactivity of tire char and increased the efficiency of gasification, because it contained components that act as catalysts in the gasification process. There was a favorable effect from the addition and higher amount of sewage sludge on lowering both the activation energy (49.5 kJ/mol and 89.2 kJ/mol for 90:10 and 67:33 blends, respectively) and the pre-exponential factor. A significant improvement in reactivity, with a high degree of conversion and the best gas composition, was obtained for a 90:10 blend at 900 °C.

Keywords: waste tires; sewage sludge; steam co-gasification; reactivity

1. Introduction

The increasing number of vehicles in use results in an increasing number of vehicle tires and generates a large amount of tire waste: approximately 17 million tons per year, of which only 10% is recycled and 75% becomes landfill [1,2]. In turn, the growing number of industrial and municipal sewage treatment plants generate significant amounts of waste in the form of sewage sludge. Information regarding the amount of sewage sludge produced worldwide is minimal or limited to estimated values. It is estimated that the amount of sewage sludge generated is between 35 and 85 g of sewage sludge dry matter per person per day [3]. From the available statistical data [4], it is estimated that an average of 7.8 million tons of sewage sludge per year (dry basis) is produced in the countries of the European Union in municipal sewage treatment plants alone. Approximately 13.8 million tons (dry basis) of sewage sludge are produced annually in the USA [5]. Both tire and sewage waste should not deposited as landfilled and require alternative disposal, for which

thermochemical processes can be used [6]. In the case of tire waste, pyrolysis is often used for disposal, where in addition to the valuable products (i.e., oil and gas), the by-product char is produced in relatively large quantities (up to 50%) [7,8], requiring further management. The gasification process can be used for this purpose, though tire char has low reactivity due to its high carbon content, unfavorable structure, high ash content, and unfavorable ash composition [9,10]. To improve the efficiency of the process and the quality of the resulting product (syngas), catalysts or additives can be used; these should be inexpensive and readily available [11]. Such a role can be played by sewage sludge, which can be favorable for the gasification process due to its high content of alkali and alkaline earth metals [12,13]. At the same time, waste tire char with a high calorific value will act as a stabilizer of the fuel charge's quality, since sewage sludge is highly variable in its properties. The gas obtained during co-gasification can be used to generate electricity, chemical products, or fuel, or can be a hydrogen-rich gas [14,15].

The gasification of sewage sludge entails a number of difficulties, including the need for drying or pyrolysis before gasification. The intrinsic properties of sewage sludge determine the distribution of main gasification products, the amount of tar formed, and other impurities in the syngas in the form of nitrogen, sulfur, and chlorine compounds, which must be removed from the gas before use [16]. Co-gasification of sewage sludge with another material may be one solution to these problems. To date, research has primarily been conducted on the co-gasification of sewage sludge with various types of biomass, biomass char, and coal [17]. Hu et al. [18] studied co-gasification of wet sewage sludge and pine sawdust; the reaction rate and conversion degree increased with the increasing of pine sawdust content, and the co-gasification behavior had synergistic or coupling effects. In turn, Akkache et al. [19] analyzed the co-gasification of wastewater sludge and different feedstock (waste wood, reeds, olive pomace, solid recovered fuel, paper labels, and plastic labels) in order to combine them in an optimal gasifying blend. In contrast, there are few studies on the co-gasification of sewage sludge and other types of waste, such as tire scraps. Song and Kim [20] gasified tire scrap and sewage sludge in a circulating fluidized bed, and the caloric value of the product gas significantly decreased when wet sludge was added. In the case of gasification of tire scraps or tire char, co-gasification with biomass or the addition of catalysts has so far been mainly used to increase the reactivity of the material and to study the effect on the composition of the gas obtained [21]. Lahijani et al. [22] studied the effect of palm and almond shells as natural catalysts rich in alkali metals to enhance the reactivity of tire char through the co-gasification process, and the activation energy for tire-char gasification was lowered. In turn, co-gasification of waste tire and pine bark in a CO_2 atmosphere was reported by Wang et al. [23], and an increase in the pine bark content enhanced H_2 and CO while lowering hydrocarbon yield. In [24], the authors investigated the co-gasification of tire char and rambutan peel and confirmed the profound effect of biomass in enhancing the reactivity of tire char in reaction with CO_2. Czerski et al. [10] assessed the catalytic effect of various biomass ashes from husks, corn cobs, beet pulp, and beech chips on tire char gasification and reported the positive impact of ashes, depending on their type and quantity. In conclusion, the study of the co-gasification of tire char and sewage sludge requires further research, including determination of the influence of the composition of the blend on the process and the product obtained.

Therefore, a suitable blend of different types of waste for gasification can be an alternative method for disposal, making use of their specific properties to optimize the process. The purpose of the research was to evaluate the effect of the composition of a waste tire char and sewage sludge fuel blend on the gasification process, using steam as the gasification agent. To the best of the authors' knowledge, there are no reports on steam co-gasification of tire char and sewage sludge mixtures in a fixed bed reactor. A thermal volumetric method was used to analyze the resulting products of gasification; the tests were conducted under isothermal conditions and increased pressure. An analysis was made of the efficiency of the co-gasification process and the composition and quality of the resulting

gas. This made it possible to select the optimal temperature conditions and composition of the fuel blend for the process of steam co-gasification of tire char and sewage sludge.

2. Materials and Methods

2.1. Material Characteristics

The materials analyzed in the study were industrial waste tire char, municipal sewage sludge, and blends of the two prepared in ratios of 90:10 and 67:33. The sewage sludge came from a mechanical/biological sewage treatment plant of a large urban agglomeration (average flow of 160,000 m^3/day). In order to characterize the tested materials, the samples were subjected to proximate analysis (using a TGA Thermostep analyzer by Eltra Hann, Germany, in accordance with standard PN-G-04560:1998 and a Leco AC, Tychy, Poland calorimeter following standard PN-ISO 1928: 2002), ultimate analysis (using a CHS-580 analyzer by Eltra, Hann, Germany in accordance with standards PN-G-04571:1998 and PN-G-04584:2001), and determination of ash composition (using an X-ray fluorescence EDXRF spectrometer, PANalytical, Malvern, United Kingdom). The results characterizing the samples of tire char and sewage sludge are presented in Table 1.

Table 1. Characteristics of the tested materials.

Group of Analysis	Parameter	Tire Char	Sewage Sludge
Ultimate analysis	C^{ad}, %	74.6	11.1
	H^{ad}, %	0.77	3.37
	S^{ad}_t, %	2.87	0.96
Proximate analysis	Moister—W^{ad}, %	1.1	13.4
	Ash—A^{ad}, %	21.3	62.7
	Volatile matter—V^{ad}, %	2.2	19.0
	Fixed carbon—FC^{ad}, %	75.4	4.9
	Higher heating value—HHV^{ad}, kJ/kg	26,211	6410
Ash composition	SiO_2, %	59.90	36.19
	Al_2O_3, %	0.68	4.02
	Fe_2O_3, %	5.73	5.43
	CaO, %	3.54	4.73
	MgO, %	0.74	6.33
	SO_3, %	3.08	-
	ZnO, %	22.97	-
	K_2O, %	1.27	1.01
	P_2O_5, %	1.06	21.65
	TiO_2, %	0.11	0.58
	Co_3O_4, %	0.44	-
	CuO, %	0.14	-
	Na_2O, %	-	0.36
	MnO, %	-	0.09

ad—as determined, t—total.

Tire char has a high carbon content (over 75%), a relatively low hydrogen content, and a high sulfur content (approx. 3%), due to its use in the vulcanization process. As a product of pyrolysis, it contains low amounts of volatile matter, high amounts of fixed carbon, a significant amount of ash, and little moisture. Its calorific value exceeds 26 MJ/kg. With such properties, it can therefore be an attractive raw material for gasification [25].

Sewage sludge has highly variable characteristics, depending on the source of the sewage sludge and the technological processes and drying method used. The main component of the sewage sludge used in the study was ash (over 60%); thus, low carbon and hydrogen content and relatively high sulfur content (approx. 1%) were recorded. This also resulted in a low calorific value (approx. 6.5 MJ/kg). The sewage sludge also consisted of oxygen and nitrogen and much smaller quantities of other elements such as chlorine, fluorine, etc. [26,27]. The low moisture content of sewage sludge was due to the material being dried to an air-dry state; the total moisture content of the sewage sludge before drying was 54.4%. It also had four times the volatile matter of fixed carbon. The high content of non-flammable parts and the relatively low total moisture content is characteristic of sewage sludge that has undergone dewatering and stabilization.

The analysis of the composition of tire char ash showed that it consisted mainly of SiO_2 and ZnO (over 80%), as well as small amounts of compounds that act as catalysts in the gasification process, adversely affecting the reactivity of the material. On the other hand, although the analyzed sewage sludge contained a large amount of SiO_2 and P_2O_5 (the high content of phosphorus compounds may result from commonly used cleaning agents and microorganisms found in the sewage sludge [28]), it also contained oxides of magnesium, calcium, iron, and—to a lesser extent—sodium and potassium, which can favorably affect the efficiency of the gasification process [29,30].

In conclusion, it can be noted that the analyzed materials (i.e., tire char and sewage sludge) differ significantly. Tire char is characterized by a much higher amount of elemental carbon and a much lower content of residual waste components, which translates into a fourfold higher heat of combustion. Sewage sludge, on the other hand, has a higher content of volatile matter than tire char, which leads to higher reactivity. The fixed carbon index is much higher for tire char, so it can be expected that during gasification the contribution of the pyrolysis process will be low and that pyrolysis will be the dominant process for sewage sludge, which has a much lower fixed carbon value. The high value of fixed carbon for tire char may be associated with its lower reactivity, as the energy requirement for endothermic gasification reactions increases with the fixed carbon content [10]. The analysis of the ash composition revealed that the municipal sewage sludge was characterized by a much higher content of catalytically active components, especially alkali metal oxides, which can increase the efficiency of elemental carbon conversion and the selectivity of the formation of individual gas products [31].

2.2. Methodology of Measurements

During the steam gasification process, measurements were taken using the thermo-volumetric laboratory equipment described in Figure 1 under isothermal conditions at temperatures of 800, 850, and 900 °C at an elevated pressure of 1 MPa. The temperature range was chosen to avoid the deactivation of catalytically active compounds. In contrast, measurements under pressure reflect the conditions found in industrial reactors, and higher pressure enhances char gasification kinetics [32]. The equipment was described in detail in [33] and consisted of a high-pressure reactor, a system for feeding the reactor with a gasifying medium and fuel, and a system for collecting and analyzing the resulting gas. After the parameters of the measurements were stabilized (set temperature and pressure; steam flow: 0.3 g/min; argon flow: 2 dm^3/min), a fuel sample with a mass of 0.5 g was introduced onto the grate. The resulting gas was cooled, cleaned, dried, decompressed, and analyzed—the carbon monoxide, carbon dioxide, and methane content was measured continuously using an automatic gas analyzer, whereas the hydrogen content was measured using a gas chromatograph. Every measurement was performed at least twice to ensure the reproducibility of the results.
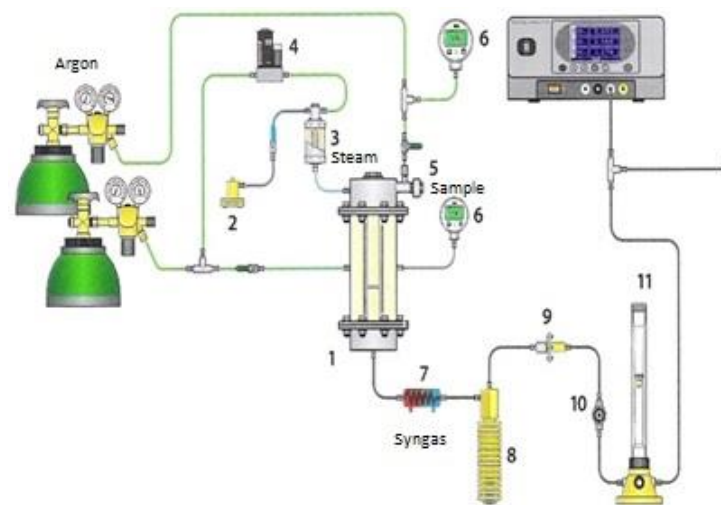
Figure 1. Laboratory equipment for the analysis of gasification: (1) reactor, (2) water pump, (3) steam generator, (4) mass flow meter, (5) fuel feeder, (6) manometer, (7) cooler, (8) condensate tank, (9) filter, (10) pressure regulator, and (11) rotameter.

The measurements of concentrations of gas components were used to determine curves of changes in the formation rates of CO, H_2, CH_4, and CO_2 over time. Based on these curves, changes in the degree of carbon conversion over time $X(t)$ (Equation (1)) and reactivity indexes R_x for degree conversions 0.25, 0.5, and 0.75 (Equation (2)) were determined.

$$X(t) = \frac{\left[V_{CO}(t) + V_{CO_2}(t) + V_{CH_4}(t)\right] \cdot M_C}{V_{mol} \cdot m \cdot C^{daf}} \cdot 100\%$$ (1)

where $V_{CO}(t)$, $V_{CO_2}(t)$, $V_{CH_4}(t)$ is the volume of a given product formed from the beginning of the process to time t (cm³), M_C is the molar mass of carbon $\left(\frac{g}{mol}\right)$, m is the mass of the analyzed sample (g), C^{daf} is the dry and ash-free carbon content (-), and V_{mol} is the molar volume of gas $\left(\frac{cm^3}{mol}\right)$.

$$R_x = \frac{x}{\tau_x}$$ (2)

where x is the assumed conversion degree, and τ_x is the time to achieve a given conversion degree.

After a preliminary analysis of the measurement data, the grain model was selected for the evaluation of kinetic parameters (activation energy E_a and pre-exponential factor A) of the carbon conversion reaction. The grain model assumes that the reaction occurs at the external surface of the char particle, and the surface area decreases nonlinearly with an increase in the reaction degree [34]. The model is given by (Equation (3)), and in an integrated form by (Equation (4)):

$$\frac{dX}{dt} = k_{GM}(1 - X)^{\frac{2}{3}}$$ (3)

$$3\left[1 - (1 - X)^{\frac{1}{3}}\right] = k_{GM}\, t$$ (4)

Knowing the values of reaction rate constant k_{GM} at various temperatures, E_a and A were calculated based on the Arrhenius equation. Experimental data were analyzed for reaction degrees ranging from 0% to 80%.

3. Results and Discussion

In order to evaluate the process of steam gasification of the tested materials and co-gasification of 90:10 and 67:33 blends, curves representing changes in the formation rate of the main gaseous products (CO, CO_2, H_2, and CH_4) were plotted, their yields and proportions of the resulting gas were calculated, the degree of carbon conversion during the

gasification reaction was determined, and the reactivity indexes were analyzed, together with the kinetic parameters.

3.1. Gasification Product Formation Curves

Figure 2 shows a comparison of the formation curves for the main gasification products of the analyzed materials at an sample temperature of 850 °C. Due to the large difference in the rate of formation of gaseous products for tire char and sewage sludge and in order to make the charts more legible, a different maximum value on the y-axis (dV/dt) was used for sewage sludge. The results for all temperatures are not presented because the effect of this parameter on the gasification process is well understood, and the authors' focus is on the differences between the materials under analysis.
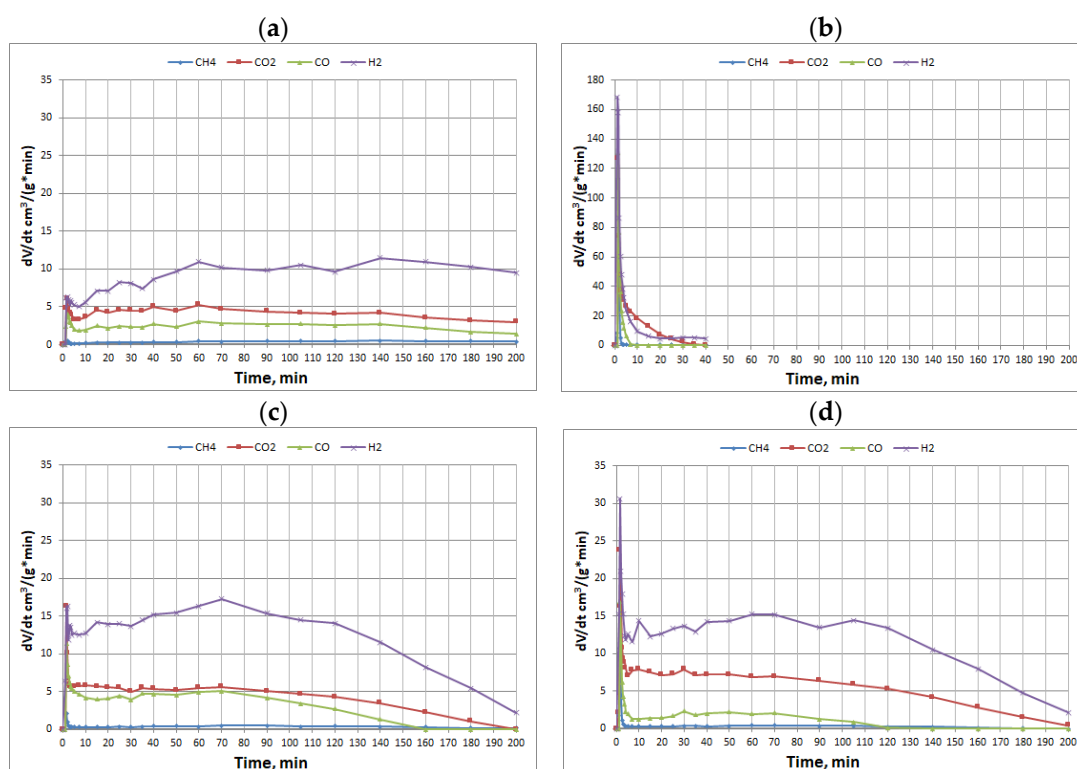
Figure 2. Changes in the formation rates of H_2, CO, CO_2, and CH_4 during steam gasification at 850 °C of (**a**) tire char, (**b**) sewage sludge, (**c**) a 90:10 blend, and (**d**) a 67:33 blend.

The observable differences in the curves between tire char and sewage sludge are due to the different nature of these materials. In the case of tire char, pyrolysis is negligible and steam gasification reactions dominate, while the rates of formation of individual products are slow and remain at a similar level, with a decreasing trend after reaching the maximum value. The low reactivity of tire char is mainly due to the high carbon content, the low fixed carbon content, and the unfavorable composition of ash, with components that inhibit gasification reactions. In contrast, in the case of sewage sludge, high rates of formation of gaseous products were observed, which were generated initially in the intensive pyrolysis process and then during slower gasification reactions. The contribution of pyrolysis was dominant throughout the process, which is due to the characteristics of the sewage sludge (see Table 1 for the proportions of volatile matter and fixed carbon). On the other hand, the rate of gasification reactions was limited by the very high ash content, which can block reactants from accessing active sites on the surface of the sewage sludge char, while some of the ash components can catalyze these reactions. The process took much less time for sewage sludge (for temperatures of 800 and 900 °C, it was 40–60 min and 160–240 min, respectively), which, together with significantly higher rates of gas product formation,

indicates that its reactivity is much higher. In the case of tire char, hydrogen was formed at the highest rate, followed by CO_2 and CO at comparable rates and methane at a minimal rate. For sewage sludge, the highest rates accompanied the pyrolysis process, where all gas components are generated, while during the steam gasification of the resulting sewage sludge char, the highest rate was recorded for CO_2, followed by hydrogen, and was much lower for CO. Methane was not generated during this process.

In the co-gasification of tire char and sewage sludge blends, with tire char as the reference material, the higher proportion of sewage sludge increased the formation rate of all components during pyrolysis. In addition, an improvement in the rate of formation of gaseous products was observed during the gasification stage, with the exception of methane, which was only generated during pyrolysis. This positive effect is probably related to the development of a porous structure, a larger surface area available to the gasification agent, and the presence of sewage sludge ash components acting as catalysts in the gasification process. In both blends, the highest formation rates were observed for hydrogen. Increasing the proportion of sewage sludge (67:33 blend) resulted in a higher rate of CO_2 formation, with a slight reduction in the rate of hydrogen formation and a significant reduction in CO generation. This unfavorable effect may be due to the fact that more sewage sludge in the blend results in a higher content of ash, which—especially at higher temperatures—can agglomerate, melt, and limit the access of the gasification agent to the surface of the reacting material [35]. The formation of the products is also influenced by the C:H:O ratio in the blends; with addition of sewage sludge, the increase in O and H share improved formation rates, but reduction of C share decreased the product yields containing carbon.

Similar relationships were observed for the entire temperature range under analysis (800–900 °C), except that as the temperature increased, higher formation rates of individual products resulting from the endothermic nature of the gasification reaction were recorded, resulting in a shorter duration of the entire process.

3.2. Carbon Conversion and Reactivity Indexes

In order to evaluate the efficiency of the gasification process of tire char, municipal sewage sludge, and blends of the two, as well as the reactivity of the materials, the curves of changes in the degree of carbon conversion were plotted (presented in Figure 3).

It can be noted that low degrees of conversion were obtained for tire char (especially at 800 °C). This material is characterized by low reactivity, and it is advisable to support it during gasification by adding substances to catalyze the process [10]. On the other hand, high degrees of conversion were obtained for sewage sludge and in a much shorter time, confirming the high reactivity of this material, comparable to highly reactive lignite [36]. It is therefore justified to use it as an additive to facilitate tire char gasification. The degree and gradient of the conversion curves (indicative of the speed of the process) of tire char significantly improve with temperature. On the other hand, in the case of sewage sludge, the curve changes favorably at 850 °C, while at 900 °C it has a very similar curve. This may indicate that the high ash content, combined with its characteristics (Table 1), resulted in partial melting of the ash and deactivation of potential catalysts and in restriction of the flow of reactants to the surface of the sewage sludge char.

For both blends of tire char and sewage sludge, more favorable elemental carbon conversion curves were obtained than for tire char alone. At lower temperatures, the impact of adding sewage sludge was greater. For 800 °C, a greater positive effect was obtained for the 67:33 blend, at 850 °C the effect of the two was similar, and at 900 °C it was more favorable to use a 90:10 blend, with a lower sewage sludge content. This is due to the aforementioned negative effect of high temperature on sewage sludge ash and the possibility of its melting.
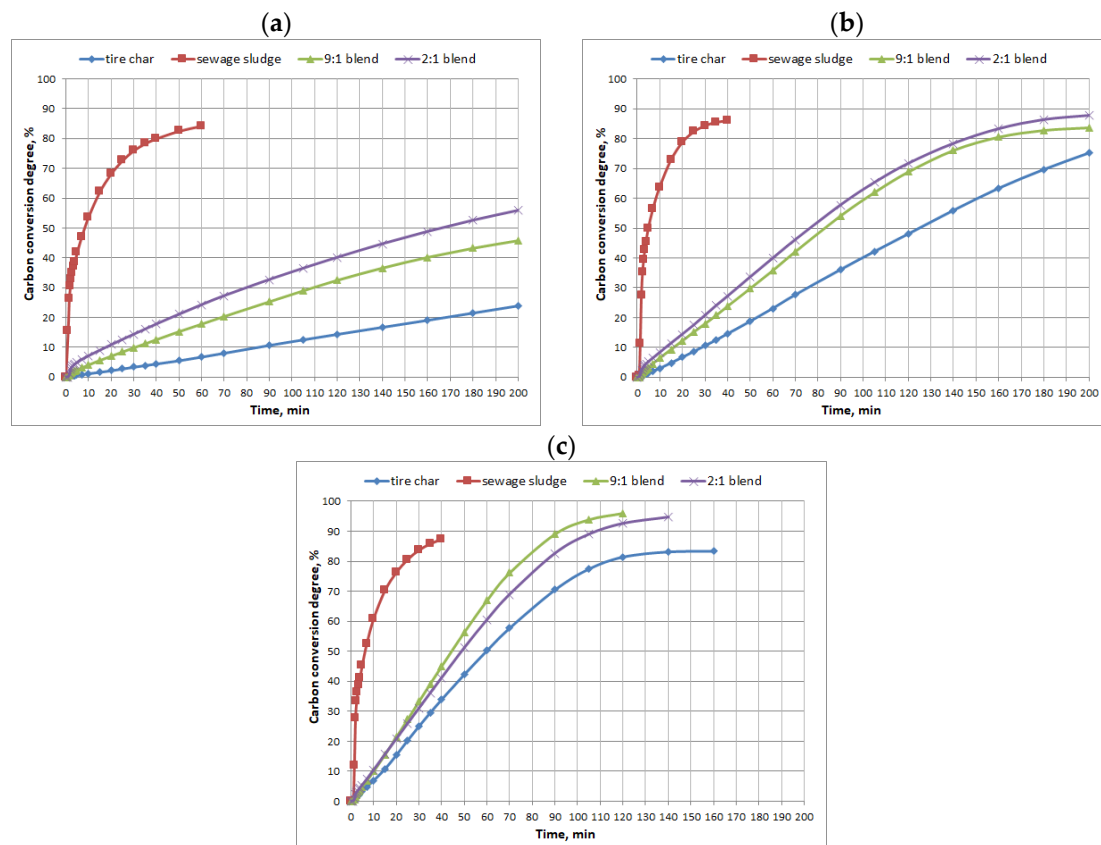
Figure 3. Changes in carbon conversion during steam gasification at (**a**) 800 °C, (**b**) 850 °C, and (**c**) 900 °C.

In order to quantify the reactivity of the tested materials, Table 2 summarizes the reactivity indexes R_x for the specified degrees of conversion of 0.25, 0.5, and 0.75.

Table 2. Reactivity indexes R_x during steam gasification.

Group of Analysis	Temperature, °C	Reactivity Indexes, 1/min		
		$R_{0.25}$	$R_{0.5}$	$R_{0.75}$
Tire char	800	1.09×10^{-3}	-	-
	850	3.90×10^{-3}	4.00×10^{-3}	3.76×10^{-3}
	900	8.34×10^{-3}	8.38×10^{-3}	7.52×10^{-3}
Sewage sludge	800	1.33×10^{-1}	6.01×10^{-2}	8.77×10^{-3}
	850	1.30×10^{-1}	9.86×10^{-2}	1.49×10^{-2}
	900	1.31×10^{-1}	7.95×10^{-2}	1.31×10^{-2}
90:10 blend	800	2.82×10^{-3}	-	-
	850	5.94×10^{-3}	6.01×10^{-3}	5.48×10^{-3}
	900	1.08×10^{-2}	1.13×10^{-2}	1.09×10^{-2}
67:33 blend	800	4.01×10^{-3}	3.01×10^{-3}	-
	850	6.85×10^{-3}	6.52×10^{-3}	5.77×10^{-3}
	900	1.04×10^{-2}	1.02×10^{-2}	9.52×10^{-3}

The results presented in Table 2 confirm previous observations from the analysis of gas product formation curves and the degree of conversion of elemental carbon. Tire char displays low R_x indexes. At 800 °C, a very low degree of conversion was achieved, making

it impossible to determine $R_{0.5}$ and $R_{0.75}$ indexes and confirming its low reactivity [37]. Higher temperatures in the tested range resulted in a significant improvement in reactivity indexes. As the gasification reaction progresses, the values of reactivity indexes initially increase slightly and then decrease for 75% degree of conversion, but the change is small. A similar relationship during the progress of tire char gasification was noted in [38]. In contrast, much higher reactivity rates were obtained for sewage sludge, and their variability according to the progress of the reaction is of a completely different nature. Namely, the highest R_x values were recorded for a degree of conversion of 0.25, which is due to the fact that intense pyrolysis reactions take place in the initial phase. As the gasification process progresses, the reactivity rates decrease significantly, due to the increasing amount of ash in the sewage sludge char (initially approx. 63%), which limits the surface area available to the gasification agent. It can be observed that the reactivity index of $R_{0.25}$ remains constant regardless of the temperature, which confirms that pyrolysis occurs in the initial phase, which is less dependent on this parameter. For degrees of conversion of 0.5 and 0.75, where gasification reactions are already occurring, a temperature increase from 800 to 850 °C results in higher values of reactivity indexes. Significantly, for a temperature of 900 °C, instead of an increase, a slight decrease in these indicators can be observed, which is probably due to the melting of some of the ash and less interaction between the components that catalyze gasification reactions.

These observations are reflected in the reactivity index measurements of the blends under study. For the gasification of both blends, better reactivity indexes were obtained compared to tire char alone. In the temperature range of 800–850 °C, better results were recorded for the 67:33 blend; at 900 °C, slightly higher R_x values were obtained for the 90:10 blend. This is due to the previously described adverse effect of the high ash content in sewage sludge and its properties, in particular at high temperatures. It was also observed that a higher amount of sewage sludge in the blend resulted in a larger contribution of pyrolysis and a different relationship of reactivity indexes as the gasification process progressed.

3.3. Yields and Composition of Gasification Products

The next step was to analyze the yields of the individual gas components (Figure 4) and the composition of the gas (Table 3). In the case of tire char, by far the highest yields were obtained for hydrogen, followed by much lower yields for CO_2, then CO and relatively low yields for methane, which was only generated during pyrolysis. Temperature significantly affected the production of the main components of the synthesis gas, i.e., hydrogen and especially carbon monoxide, which is due to the endothermic nature of the water–gas reaction. In addition, the fact that the amount of CO significantly increased with temperature may be due to the Boudouard –Bell reaction occurring in the presence of CO_2. There is an optimum temperature for which the maximum hydrogen yield can be achieved, but for CO an increase in temperature generates a higher yield. Okati et al. [39] showed that further increases in temperature above 1000 °C result in decreased hydrogen molar fractions, but carbon monoxide production increases with temperature up to 2000 °C. Similar results and relationships to those shown in Figure 4 were obtained by Hasanzadeh et al. [40] and Mojaver et al. [41], i.e., hydrogen yield firstly improved, and then, mitigated by increasing gasification temperature, carbon monoxide yield was increased and carbon dioxide yield was reduced by increasing gasification temperature. They also justified these observations using the Boudouard and the water–gas endothermic reactions, which are shifted to the right side with the rise of the gasification temperature. In addition carbon dioxide is consumed and converted to carbon monoxide by increasing gasification temperature based on the Boudouard reaction.
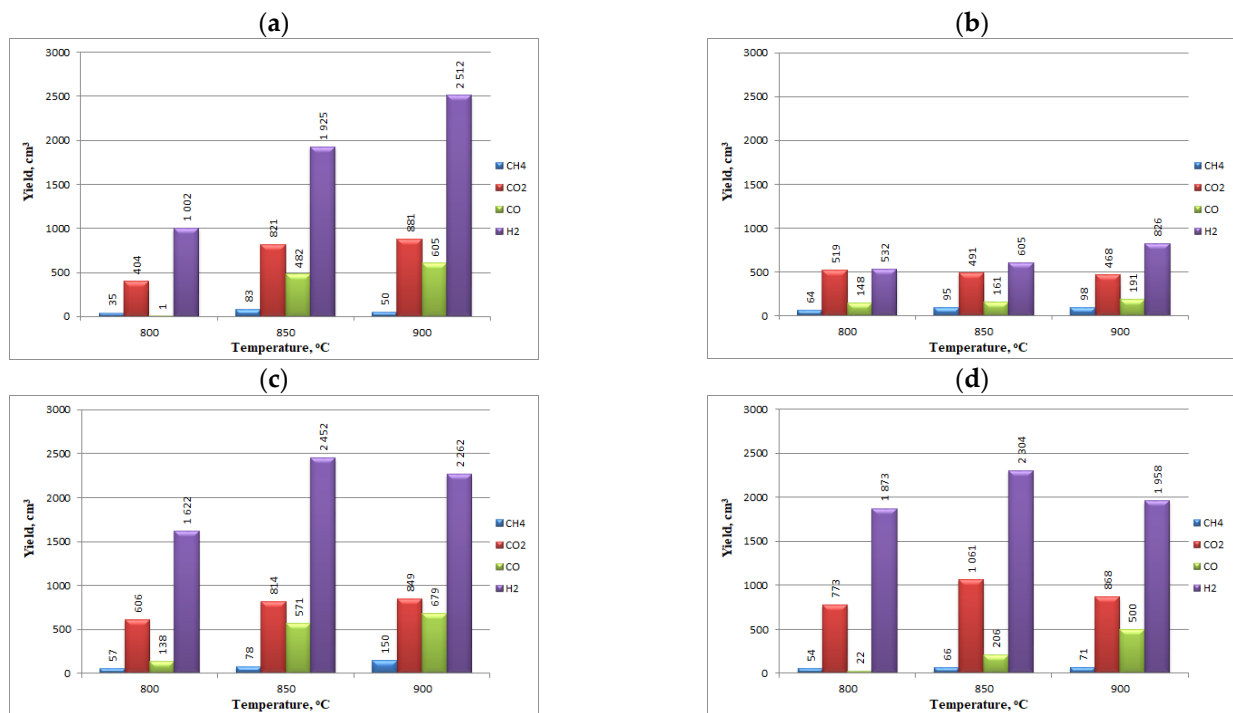
Figure 4. Yields of H_2, CO, CO_2, and CH_4 during the steam gasification of (**a**) tire char, (**b**) sewage sludge, (**c**) a 90:10 blend, and (**d**) a 67:33 blend.

Table 3. Composition of the gas during steam gasification.

Group of Analysis	Temperature, °C	Gas Component, %			
		H_2	CO_2	CO	CH_4
Tire char	800	69.4	28.0	0.1	2.5
	850	58.1	24.8	14.6	2.5
	900	62.0	21.8	15.0	1.2
Sewage sludge	800	42.7	40.4	11.8	5.1
	850	44.8	36.3	11.9	7.0
	900	52.1	29.6	12.1	6.2
90:10 blend	800	66.9	25.0	5.7	2.4
	850	62.7	20.7	14.6	2.0
	900	57.4	21.6	17.2	3.8
67:33 blend	800	68.8	28.4	0.8	2.0
	850	63.3	29.2	5.7	1.8
	900	57.6	25.6	14.7	2.1

As with tire char, sewage sludge gasification yielded the largest volumes of hydrogen, although CO_2 was generated in similar amounts. Significantly lower amounts of CO and methane were obtained. It should be borne in mind that pyrolysis plays a much larger role in the gasification of sewage sludge and significantly affects the resulting gas. In addition, the amount of hydrogen and CO increased with temperature at the expense of carbon dioxide, which is due to the endothermic reactions mentioned above (water–gas and Boudouard–Bell). Comparing the yields from the gasification process of the materials under analysis, tire char yielded significantly higher amounts of gaseous products (i.e., hydrogen, CO, and CO_2). In the case of sewage sludge, higher volumes were recorded only

for methane, which was formed solely by pyrolysis, much more intensely during sewage sludge gasification.

As in the case of individual materials, in the co-gasification of tire char and sewage sludge—regardless of the blend ratio—the highest yield was obtained for hydrogen, followed by CO_2, then CO, and the lowest for methane. Higher temperatures promoted a significant increase in CO and, to a lesser extent, methane, while for CO_2 this increase was observed only with the 90:10 blend. In the cases of hydrogen in both blends and CO_2 in the 67:33 blend, the yields of these gases increased at 850 °C, after which a decrease was observed. The decrease in hydrogen and increase in CO may be due to a change in the equilibrium of the water–gas shift reaction. From the 90:10 blend, the yields obtained for the two main products, hydrogen and carbon monoxide, were higher than from tire char alone, which is probably due to the larger proportion of components catalyzing the gasification process in the blend. The use of a 67:33 blend generated more hydrogen at lower temperatures (800 and 850 °C), with lower CO yields throughout the temperature range. Therefore, it can be concluded that the best quality gas was obtained for a 90:10 blend and that the catalytic effect associated with the addition of sewage sludge was particularly evident at lower temperatures.

For each of the analyzed cases, the primary component of the resulting gas was hydrogen, though increasing the temperature in the blends with tire char resulted in a smaller share resulting from the formation of other gas products—particularly CO—in greater quantities. The co-gasification of tire char and sewage sludge blends thus makes it possible to produce hydrogen-rich gas. The strong dependence between the amount of CO generated and the temperature also resulted in a higher proportion of this gas. The gasification of sewage sludge and the blend with a high sewage sludge content yielded a gas with an unfavorably high amount of carbon dioxide. The results indicate that the optimal condition for syngas production (maximum yield and proportion of H_2 + CO) is co-gasification of a 90:10 blend at 850 °C. The gas formed in this process could be successfully used to produce hydrogen, chemicals, or energy [14].

3.4. Kinetic Parameters

In order to determine the effect of adding sewage sludge on the kinetics of the steam gasification process of tire char, the activation energy (E_a) and the pre-exponential factor (A) of the carbon conversion reaction were calculated with use of the grain model. The results are summarized in Table 4. Additionally, together with the values of the determination coefficient R^2 in Table 4, Figure 5 presents the fit of experimental data for co-gasification of the selected blends to the curves for the degree of carbon conversion developed with use of the grain model.

Table 4. Kinetic parameters of steam gasification.

Group of Analysis	Temperature, °C	k_{GM}, 1/min	R^2, -	A, 1/min	E_a, kJ/mol
Tire char	800	0.00128	0.9984	1.76×10^8	227.8
	850	0.00544	0.9922		
	900	0.01121	0.9961		
Sewage sludge	800	0.02846	0.9498	1.10×10^5	135.3
	850	0.05593	0.8678		
	900	0.05281	0.8865		
90:10 blend	800	0.00285	0.9983	1.44×10^6	178.3
	850	0.00798	0.9922		
	900	0.01563	0.9886		
67:33 blend	800	0.00357	0.9951	2.13×10^4	138.6
	850	0.00842	0.9968		
	900	0.01336	0.9941		
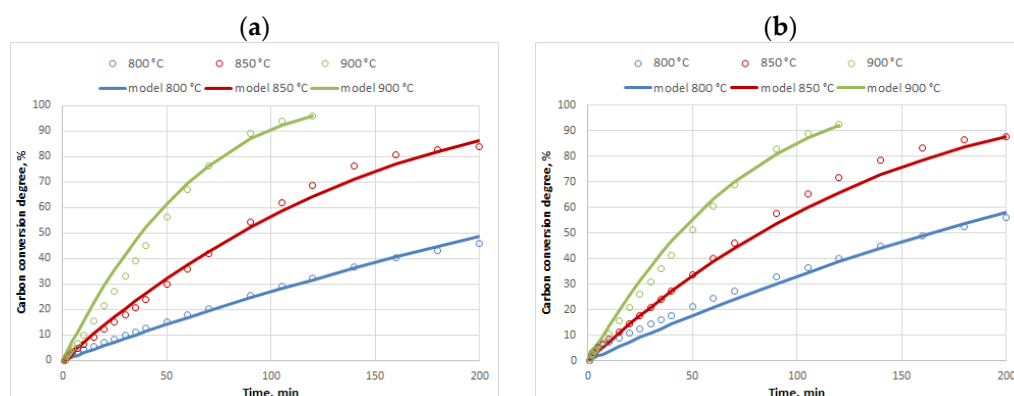
Figure 5. Experimental and model results for degree of carbon conversion at time $X(t)$ for (**a**) the 90:10 blend and (**b**) the 67:33 blend.

The values of the reaction rate constant k_{GM} confirm previous observations regarding the positive effect of adding sewage sludge and the varying impact of temperature (a more favorable effect of the 67:33 blend at 800–850 °C and of the 90:10 blend at 900 °C) on the rate of reactions occurring during the steam gasification of tire char. Since a lower reaction rate was recorded for pure sewage sludge at 900 °C than at 850 °C, the kinetic parameters A and Ea were determined for this material based on measurements in the temperature range of 800–850 °C. Significantly higher values of both activation energy and pre-exponential factor were obtained for tire char than for sewage sludge, confirming the low reactivity of the former. Thus, a favorable effect of the addition and amount of sewage sludge on lowering both the activation energy (by 49.5 kJ/mol and 89.2 kJ/mol for 90:10 and 67:33 blends, respectively) and the pre-exponential factor (by two and four orders of magnitude, respectively) was noted during co-gasification of the selected blends. This effect is due to a change in the reaction pathway and a greater number of active sites [42].

Moreover, for samples containing tire char, the values of the coefficient of determination R^2 were very high (no lower than 0.985); the use of the grain model for their analysis is therefore justified. In the case of pure sewage sludge, the R^2 values were lower, which is due to the different characteristics of this material and, most significantly, the action of intensive pyrolysis reactions in the process. The analysis comparing the model curves to the measured data for the blends under study warrants the conclusion that the fit of the model is good enough.

4. Conclusions

In this study, the process of co-gasified tire char and sewage sludge was evaluated, and the main conclusions are as follows:

- Tire char and municipal sewage sludge are materials of very different natures (in terms of elemental carbon content, fixed carbon and residual waste components, calorific value, and the content of elements catalyzing the process in the ash), which affects the course of the gasification process, the reactivity of the materials, and the amount and composition of the resulting gas.
- During the gasification of sewage sludge, pyrolysis plays an important role, while for tire char it is marginal.
- The use of sewage sludge in the blend increased the rate of formation of all gas components (H_2, CO, CO_2, and CH_4) during pyrolysis, while methane was not affected during gasification. Increasing the proportion of sewage sludge in the blend resulted in a higher rate of CO_2 formation, with a slight reduction in the rate of hydrogen formation and significant CO generation.
- Compared to the gasification of tire char alone, a more favorable course of carbon conversion curves and higher values of reactivity indexes were obtained for blends of tire char and sewage sludge.

- The positive effect of adding sewage sludge decreased with temperature. The blend with a higher amount of sewage sludge was favorable in the temperature range of 800–850 °C, while slightly better results were obtained at 900 °C for the 90:10 blend. This is due to the negative effects of such high temperatures on sewage sludge ash, which can potentially melt, and the deactivation of catalytically active components during the gasification reactions.
- Increasing the amount of sewage sludge and introducing more ash into the blend also resulted in lower reactivity rates as the process progressed.
- Regardless of the blend ratio of tire char and sewage sludge the highest yield was obtained for hydrogen, followed by CO_2, then CO, and the lowest was recorded for methane. Higher temperatures promoted the formation of more CO and, to a lesser extent, methane, while for hydrogen, the highest volumes were obtained at 850 °C.
- The addition of sewage sludge to tire char and increasing the amount of sewage sludge significantly reduced the kinetic parameters of steam gasification (activation energy and pre-exponential factor).

In summary, the addition of municipal sewage sludge containing components that act as catalysts in the gasification process has a positive effect on the reactivity of tire char and increases the efficiency of the gasification process. A significant improvement in reactivity, with a high degree of conversion and the best gas composition, was obtained with the 90:10 blend at 900 °C. The testing regarding the gasification and co-gasification of tire char and sewage sludge enabled the determination of the impact that individual components, blend composition, and temperature conditions had on the gasification process and the quality of the resulting gas. These results allow the process to be optimized, for example, for producing hydrogen-rich gas.

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