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Co-gasification of Animal Waste, Polyethylene, and Tire-pyrolysis Char in CO₂ Atmosphere: Thermogravimetric Analysis and Synergistic Effects

KEYWORDS

Co-gasification, polyethylene, cattle manure, char, gasification index, thermogravimetric analysis, synergy effects

ABSTRACT

This paper presents the results of research on the gasification of animal biomass waste (cattle manure) with the addition of polyethylene and char obtained from the pyrolysis of waste tires in a carbon dioxide atmosphere. The aim of the study was to determine the influence of fuel composition and component proportions on the gasification behaviour of multicomponent fuel mixtures. Physicochemical characterization of the raw materials and thermogravimetric analysis (TGA) were performed in the temperature range from 25 to 1300 °C. To evaluate fuel reactivity, characteristic parameters such as the initiation and final temperatures of the process and the comprehensive gasification index (S) were determined, allowing a quantitative comparison of the gasification behaviour of individual components and their mixtures. The results indicate that animal biomass promotes earlier process initiation ($T_i \approx 260$ °C), while the addition of polyethylene significantly increases the mass loss rate in the temperature range of 350–500 °C, reaching a maximum of 30.57 %/min for pure PE. It was found that a mixture containing 20% polymer provides more favourable reactivity parameters, reflected in a higher gasification index ($S = 9.42 \times 10$) compared to the mixture with 10% PE ($S = 6.12 \times 10$). The study also revealed the presence of both synergistic and antagonistic effects, depending on temperature and polymer content. Positive deviations from additive behavior were observed in the biomass degradation range (250–350°C), while higher polyethylene content led to temporary inhibition effects during polymer decomposition (430–470 °C). The results contribute to a better understanding of the thermochemical conversion of multicomponent waste fuels.

1. Introduction

Waste biomass originating from animal production, such as cattle, horse, or poultry manure, constitutes a feedstock with significant and still not fully utilized energy potential. In contrast to plant biomass, these raw materials are characterized by constant availability, independent of weather cycles or harvest seasonality, which makes them a stable feedstock for energy installations [1, 2]. Currently, effective utilization pathways for such waste are actively being investigated, among which thermal conversion plays a key role. Although combustion is the most widely applied method, it generates a number of operational problems resulting from the specific properties of this feedstock, particularly high moisture content, high ash content, and a high concentration of fuel nitrogen, which leads to increased nitrogen oxide emissions. Therefore, alternative technologies such as pyrolysis and gasification are gaining increasing attention.

However, even with these technologies, animal biomass remains a challenging feedstock to process due to its low energy density and tendency to form mineral deposits heat-exchange surfaces. Valorization of this waste through blending with other materials may mitigate its physicochemical disadvantages and improve process parameters [3].

One of the key components that can effectively improve the fuel properties of animal biomass is plastic waste, which are synthetic polymers such as polyethylene (PE), polypropylene (PP), or polystyrene (PS) [4]. These materials are characterized by very high calorific value. For example, the calorific value of polyethylene ranges from 40.61 to 46.51 MJ/kg [5]. High calorific value, combined with significant carbon content (approx. 82–85.5%) and hydrogen (approx. 14.0–14.3%), makes them highly efficient energy carriers in thermal processes [6–9]. The literature indicates that co-gasification of biomass with plastics (e.g., poly-

ethylene) may enhance the conversion of fuel mixtures compared with individual components [10]. In practice however, a considerable fraction of plastic waste streams remains difficult to recycle due to contamination, degradation, or complex waste composition. In such cases, thermochemical conversion may constitute an alternative pathway for their utilization. In this context, wastes unsuitable for material recycling may serve as a valuable modifier of alternative fuels, closing the resource loop in the economy [11].

Another important component studied in multicomponent systems is char from thermolysis of waste tires (WC), which represents a product of the management of problematic rubber waste. This material is characterized by a high degree of carbonization and a significant fixed carbon (FC) content in the range of 70–78 wt.% [12]. Introducing char into the fuel mixture enables investigation of its reactivity at high temperatures exceeding 900 °C, where the gasification of carbonaceous residue becomes dominant. At the same time, this material contains relatively high sulfur (4.78 wt.%) and ash (18.9 wt.%), which may constitute a technological challenge during thermochemical conversion. These characteristics require analysis of interactions between mixture components in order to improve the overall conversion behavior of the fuel [12].

The application of such a three-component mixture may lead to fuels with complementary thermochemical properties. Biomass promotes early process initiation, polyethylene provides a significant fraction of volatile compounds, and char participates in the high-temperature gasification stage.

The main objective of the study was to determine the influence of the addition of plastic waste (polyethylene) and char from elastomer pyrolysis on the gasification behavior of cattle manure. The work aimed to verify how selected proportions of individual components modify the fuel reactivity profile and change characteristic process temperatures in a carbon dioxide atmosphere.

2. Materials and Methods

2.1 Materials

Cattle manure originating from the livestock sector was used as the primary feedstock in the gasification experiments, together with selected industrial wastes. Animal biomass were obtained

from farms located in the Opole region (Poland). The additional materials included polyethylene (PE) and char obtained from pyrolysis of waste car tires (WC). Prior to analysis, all raw materials were subjected to drying and grinding to ensure material homogeneity.

2.2 Experimental methodology

To characterize the fuel properties of the raw materials, proximate and ultimate analyses were carried out in accordance with international standards. Moisture content was determined according to PN-EN ISO 18134, whereas volatile matter and ash content were determined by the gravimetric method in a muffle furnace according to PN-EN ISO 18123 and PN-EN ISO 18122, respectively. Elemental composition (C, H, N, S) was determined using an Elementar Vario Macro Cube analyzer (EN ISO 16948, 16994). The energy potential of the raw materials was evaluated on the basis of the higher heating value (HHV) determined using an IKA C200 calorimeter (PN-EN 18125, ISO 1928).

Thermogravimetric analysis of the gasification process was carried out using a Netzsch STA F449 F3 Jupiter apparatus. Samples of approximately 5 mg were analysed. First, individual raw materials were examined, followed by their mixtures in defined mass proportions (Table 1). Measurements were performed in the temperature range from 25 to 1300 °C with a heating rate of 10 K/min. The test material was placed in an alumina (Al₂O₃) crucible. Experiments were conducted in a reactive carbon dioxide atmosphere under controlled gas flow conditions (50 mL/min carrier gas and 20 mL/min purge gas).

Table 1. Composition of samples for gasification

Sample	Cattle manure (%)	Polyethylene (%)	Tire-pyrolysis char (%)
AM	100	-	-
PE	-	100	-
WC	-	-	100
AM70-PE10-WC20	70	10	20
AM70-PE20-WC10	70	20	10

3. Results

3.1. Physicochemical properties of the studied fuel materials

Table 2 summarizes the proximate and ultimate analysis results of the studied materials, highlighting significant differences in their fuel properties that influence their behavior during thermochemical conversion.

Table 2. Physicochemical properties of the studied fuel materials

wb – as received; db – dry basis; diff – calculated by difference; HHV – higher heating value; O/C, H/C – atomic ratios

Parameter	Unit	Cattle manure (AM)	Polyethylene (PE)	Tire-pyrolysis char (WC)
Moisture content, M_{wb}	%	9.44	-	0.74 ± 0.04
Volatile matter, VM_{db}	%	79.03 ± 0.24	-	2.65 ± 0.06
Fixed carbon, FC_{db}	%	8.15 ± 0.19	-	72.61 ± 0.33
Ash, A_{db}	%	12.82 ± 0.14	-	24.18 ± 0.32
C_{db}	%	46.62 ± 0.41	81.88 ± 0.36	74.62 ± 0.72
H_{db}	%	6.29 ± 0.09	14.29 ± 0.13	0.35 ± 0.09
N_{db}	%	2.61 ± 0.08	0.03 ± 0.06	0.37 ± 0.06
S_{db}	%	0.22 ± 0.03	0.85 ± 0.05	3.34 ± 0.10
O_{db}	%	32.44 ± 0.40	-	-
HHV _{db}	MJ/kg	17.27 ± 0.13	43.64 ± 0.23	26.764 ± 0.213
O/C	-	0.53	-	-
H/C	-	1.67	2.09	-

Cattle manure (AM) used in this study is characterized by a high volatile matter content of 79.03% (db), significantly exceeding the range of 48.01–67.32% (db) typically reported in the literature for similar biomass sources [13–16]. The elemental carbon content (46.62% db) is consistent with values reported by Szymajda et al. [14], while the ash content (12.82% db) is lower than values reported for similar materials in the literature, which may reach up to 37.85% [16]. This combination of high volatile matter content and relatively moderate ash fraction indicates favourable conditions for thermal conversion processes. Furthermore, the relatively high H/C ratio (1.67) and higher heating value (HHV_{db}) of 17.27 MJ/kg indicates that AM as a reactive biomass fuel [13].

In the case of polyethylene (PE), the highest energy potential was recorded, with HHV_{db} of 43.64 MJ/kg. The results of elemental analysis (C = 81.88%, H = 14.29%) show high agreement with

literature data for HDPE-type polymers, where carbon content is approx. 83.3% and hydrogen 13.9% [6]. However, it should be noted that the proximate analysis of PE conducted in this study is incomplete. During the interpretation of the results, difficulties were encountered due to the lack of a clear separation between the volatile release stage (VM_{db}) and the oxidation of fixed carbon (FC_{db}). The specific nature of PE thermal degradation, consisting of almost complete depolymerization in the gas phase, causes the process under the applied measurement conditions to proceed rapidly and almost entirely within the temperature range assigned to the volatile fraction. This prevented the precise experimental determination of residual fixed carbon and ash for this particular sample without a significant risk of measurement error. Therefore, the analytical profile of the material was supplemented using data reported by Sravani et al. [6]. According to their findings, polyethylene is characterized by the absence of moisture (0.0%),

nearly complete volatile matter content (99.9%), and only trace amounts of ash (0.1%).

Char obtained from tire pyrolysis (WC) represents the material with the highest degree of carbonization, as confirmed by the fixed carbon content (FC_{db}) of 72.61%. This value is significantly higher than that reported for raw tires described by Krotz et al. [17], in which volatile matter dominates and the elemental carbon content ranges from 74 to 87%. However, the thermolysis process resulted in the secondary concentration of ash 24.18% (db) and sulfur 3.34% (db) in the solid residue. The sulfur content in WC is clearly higher than in raw rubber and tire samples (0.26–3.15%), which is typical for thermochemical processing of tires. It should be emphasized, however, that HHV_{db} of WC (26.76 MJ/kg) makes it an attractive solid fuel, energetically exceeding the studied biomass.

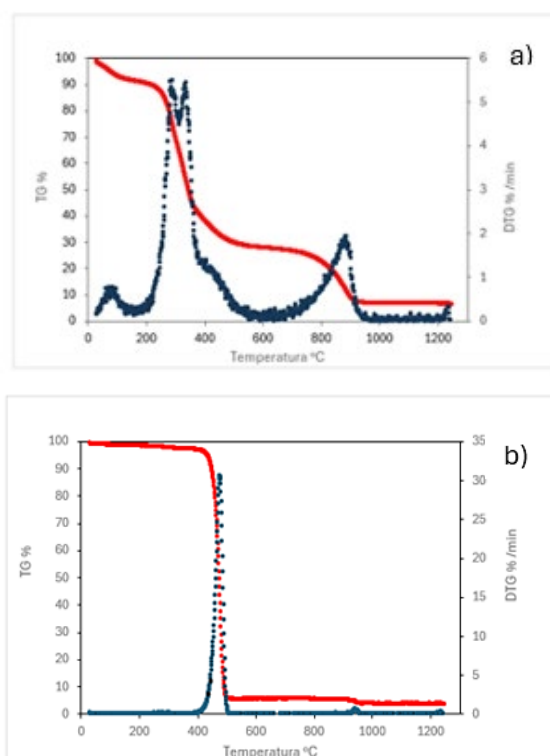
3.2 Analysis of TGA results

Thermal analysis of the reference materials revealed fundamental differences in their stability and thermal degradation. Cattle manure (AM) represents the most complex, multistage thermal profile typical of biopolymer-rich biomass. Unlike studies by Saha et al. [18], where samples were pre-dried, the present analysis showed mass loss already in the range of 0–200°C due to natural moisture presence. The main stage of organic degradation (hemicellulose and cellulose) occurs in the 200–400°C, with maximum decomposition rate at 286°C (5.45%/min), in good agreement with literature data (280°C) - Fig. 1c. However, a significant difference was observed, in total mass conversion, the sample exhibited mass lost up to 90% of its weight, whereas literature [15] indicated values around 65%. Such a high conversion degree, continuing up to 1000°C, indicates high reactivity of the studied biomass and lower content of inert mineral components compared with reference data.

Polyethylene (PE) exhibits a completely different thermal profile (Fig. 1b). This material, due to its synthetic nature and high energy value, shows no detectable moisture in the initial heating phase. Thermal decomposition of PE is rapid and almost complete; initiation occurs at 452°C and the process ends at 514°C. The key parameter here is the extremely high maximum decomposition rate of 30.57%/min at 476.2°C. These results correlate with observations by Janajreh et al. [19], confirm-

ing that aliphatic polymers undergo depolymerization within a narrow temperature window. The absence of solid residue after the process (100% conversion) makes PE an ideal fuel component with minimal ash content.

The highest resistance to thermal degradation was observed for WC, whose mass remained stable at low temperature. Its low moisture content (0.74%) and volatile matter (2.65%) indicate a strong resistance to thermal decomposition and a predominantly high-temperature reactivity. The primary degradation of this sample begins only at 947°C (Fig. 1a), reaching a maximum rate of 5.60%/min at 1041.9°C. Compared to the findings of Kandasamy et al. [20], who reported a maximum tire decomposition rate at 950°C, the present results suggest greater structural stability of the studied char. This is further supported by its lower overall mass conversion (85% versus 99%), indicating the presence of more developed carbon structures or a higher mineral content in the sample.



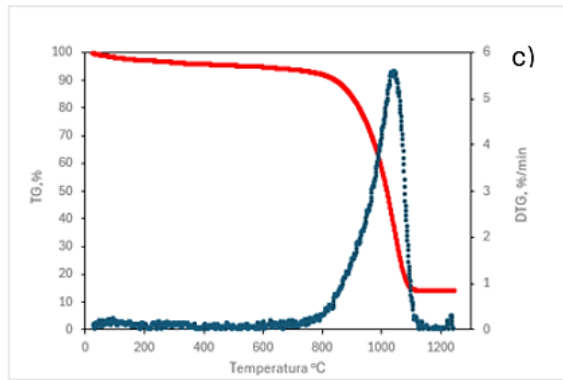


Figure 1. TGA-DTG results for reference samples:
a) AM, b) PE, c) WC

Thermogravimetric analysis of the AM-PE-WC mixtures shows that the degradation profile of the system results from the superposition of characteristic decomposition stages of individual components, while the intensity of particular stages depends on the proportion of each fraction.

The mixture containing 70% AM, 20% WC and 10% PE (sample AM70-PE10-WC20, Fig. 2a) exhibits a typical three-stage degradation pattern. In the low-temperature range (up to 200°C), an initial mass loss associated with evaporation of residual moisture was observed, characteristic of raw biomass. The main stage of organic degradation occurs in the 200–400°C range, where hemicellulose and cellulose fractions originating from AM decompose. The presence of 10% PE manifests as a distinct narrow peak on the DTG curve in the 450–500°C interval. Despite the relatively low polymer share, its rapid decomposition significantly affects the instantaneous mass-loss rate of the entire system. The final stage, occurring above 800°C, is dominated by WC (20%). The high share of this fraction prolongs gasification of the carbonaceous residue, shifting final mass stabilization toward higher temperatures.

Increasing the PE share to 20% at the expense of WC (sample AM70-PE20-WC10, Fig. 2b) shifts the main thermal activity toward the medium-temperature range. This results in the dominance of the DTG peak around 475°C. The intensity of this signal is almost twice as high compared with the first mixture, directly translating into higher decomposition intensity at this stage. At the same time, reducing WC content to 10% caused a clear decrease in high-temperature decomposition intensity (above 800°C). Conversion of the residual carbon structure is completed faster, resulting in earlier stabilization of the TG curve.

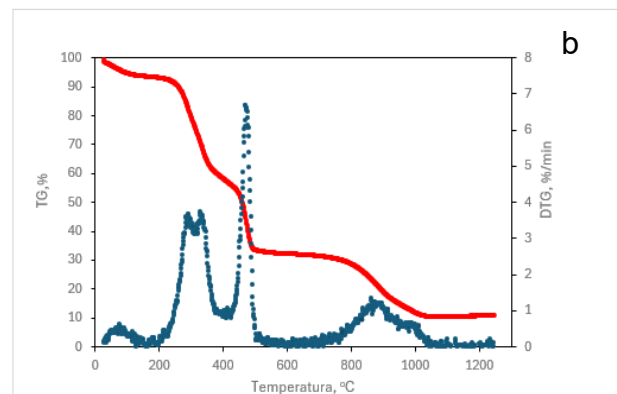
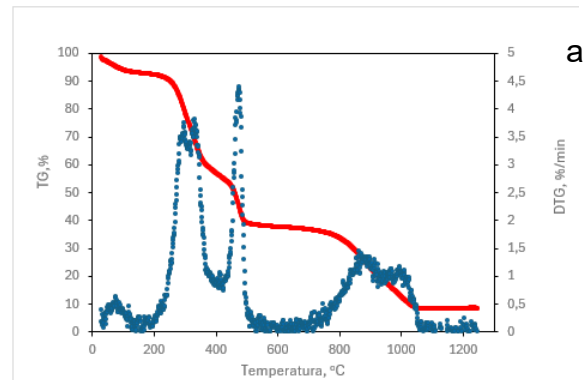


Figure 2. TGA-DTG results for mixtures: a) AM70-PE10-WC20, b) AM70-PE20-WC10

3.3. Analysis of synergistic effects during co-gasification

To evaluate non-additive interactions between the components of the studied mixtures, the experimental mass-loss rate profiles were compared with theoretical curves calculated according to the additivity rule [21]. The theoretical mass-loss rate of the mixture was calculated as the weighted sum of the DTG curves of the individual components:

$$DTG_{calc}(T) = \sum_{i=1}^n x_i \cdot DTG_i(T) \quad (1)$$

where:

$DTG_{calc}(T)$ – theoretical mass-loss rate of the mixture at temperature T ,

x_i – mass fraction of component i in the mixture, $DTG_i(T)$ – mass-loss rate of component i at temperature T .

Synergistic effects were evaluated based on the difference between experimental and calculated curves:

$$\Delta DTG(T) = DTG_{exp}(T) - DTG_{calc}(T) \quad (2)$$

Positive values of ΔDTG indicate an acceleration of the process relative to the additive behaviour, while negative values indicate a local inhibition of the process.

Fig. 3 presents the ΔDTG profiles for the mixtures AM70-PE10-WC20 and AM70-PE20-WC10. The analysis indicates a clear dependence of the interaction effects on both the temperature range and the polyethylene content in the mixture. In the temperature range of 250–350°C, positive values of ΔDTG are present, particularly evident for the mixture containing 10% PE, indicating that the degradation of the biomass fraction proceeds faster than predicted by the additive model. In the 430–470°C range, a distinct negative deviation of ΔDTG is observed, especially for the system containing 20% PE. This effect can be attributed to the presence of a molten polymer phase formed during polyethylene depolymerization [22]. Liquid intermediates may temporarily coat the surface of biomass particles and carbonaceous residues, limiting access of the gasifying agent to reactive sites. An increase in polyethylene content from 10 to 20% changes the nature of the interactions within the mixture from a synergistic effect observed at lower polymer content to a local antagonistic effect in the temperature range corresponding to polyethylene decomposition. In the 600–800°C temperature range, the ΔDTG values remain close to zero, indicating the absence of significant interactions between the mixture components in this region.

At temperatures above 850°C an increase in ΔDTG is observed, suggesting an acceleration of the gasification of the carbonaceous residue relative to the additive behaviour. This effect may be associated with the presence of mineral species originating from biomass [23], which can act as catalysts in the gasification reactions occurring in a CO₂ atmosphere.

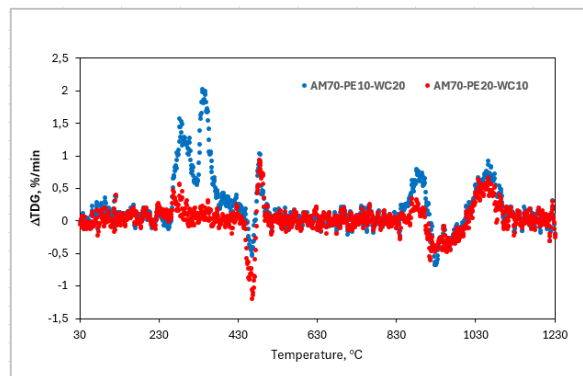


Figure 3. Synergy effects for mixtures AM70-PE10-WC20 and AM70-PE20-WC10

3.4. Quantitative evaluation of the comprehensive Gasification Index S

To evaluate the overall reactivity of the studied fuels during gasification, the comprehensive gasification index S was used. It combines mass-loss dynamics (DTG_{max} , DTG_{mean}) with the process temperature range (T_i , T_f). Calculations were performed using Equation 3:

$$S = \frac{\left(\frac{da}{dt}\right)_{max} \cdot \left(\frac{da}{dt}\right)_{Avg.}}{T_i^2 \cdot T_f} \quad (3)$$

where:

T_i – initiation temperature,

T_f – final temperature,

DTG_{max} – derivative at maximum decomposition point,

DTG_{mean} – average mass-loss derivative calculated from mean decomposition results between initial and final temperatures.

Table 3. Calculated gasification index S values for analysed samples

Sample	DTG_{max} (%/min)	DTG_{mean} (%/min)	T_i (°C)	T_f (°C)	S (-)
AM 100%	5.52	1.16	258	974	9.88E-08
PE 100%	30.57	13.46	452	514	3.92E-06
WC 100%	5.6	3.27	947	1130	1.81E-08
AM70-PE10-WC20	4.39	1.03	263	1069	6,12E-08
AM70-PE20-WC10	6.73	1.02	261	1070	9.42E-08

The highest S value (3.92×10^{-6}) was recorded for pure PE, resulting from its rapid decomposition within a narrow temperature window (452–514°C) at a record rate of 30.57%/min.

In contrast, pure char showed the lowest reactivity ($S = 1.81 \times 10^{-8}$), determined by a very high decomposition initiation temperature (947°C). Although the average mass-loss rate for char (3.27%/min) was higher than for cattle manure (1.16%/min),

biomass, due to its low process initiation temperature (258 °C), achieved a higher overall gasification index ($S = 9.88 \times 10^{-8}$). This result highlights the strong influence of the process initiation temperature on the overall value of the gasification index.

Analysis of multicomponent systems showed that changing proportions between char and polyethylene directly affects mixture gasification efficiency. The mixture containing 20% PE achieved a higher index ($S = 9.42 \times 10^{-8}$) compared with the mixture with 10% polymer ($S = 6.12 \times 10^{-8}$). This increase results from raising the maximum decomposition rate from 4.39%/min to 6.73%/min. Importantly, both mixtures exhibited similar initiation ($T_i \approx 260^\circ\text{C}$) and final temperatures ($T_f \approx 1070^\circ\text{C}$), suggesting that biomass determines the initiation temperature of the process, while polyethylene intensifies its intermediate stage. The presence of biomass also reduced the final process temperature by about 60°C compared with pure char, indicating a beneficial effect of released volatiles on conversion of the carbonaceous residue.

Combined with the ΔDTG results, these results demonstrate that increasing polyethylene content modifies both the interaction mechanisms during thermal decomposition and the overall reactivity of the system, reflected in the value of the gasification index S .

4. Conclusions

The results showed that cattle manure (AM) plays a key role in determining the initiation of the conversion process in multicomponent fuel systems. Due to its relatively low decomposition onset temperature, the presence of AM promotes the initiation of thermal conversion, lowering the initiation temperature of the studied mixtures to approximately 260°C.

The addition of polyethylene modifies the reactivity of the system and affects the course of the conversion process. Increasing the polyethylene content from 10 to 20% in the three-component mixtures enhanced the reactivity of the system, which was reflected in the increase of the gasification index S from 6.12×10^{-8} to 9.42×10^{-8} and an increase in the maximum mass loss rate from 4.39%/min to 6.73%/min. The ΔDTG analysis revealed that polyethylene influences the interaction mechanisms within the mixture. At lower polymer content, a synergistic effect was observed in the temperature range associated with biomass degradation, whereas higher polyethylene content leads

to a local antagonistic effect in the temperature range corresponding to polymer decomposition.

Tire-derived char (WC), characterized by high structural stability and a high decomposition initiation temperature (947°C), showed the lowest reactivity ($S = 1.81 \times 10^{-8}$) among the components studied. However, the presence of biomass facilitated the high-temperature conversion of the carbonaceous residue, lowering the final conversion temperature of char by about 60°C compared with the pure WC sample.

Co-gasification of AM, PE and WC represents a promising approach of a multicomponent fuel system, as it combines early process initiation provided by biomass, enhanced system reactivity due to the presence of polyethylene, and utilization of the high-temperature potential of tire-derived char. At the same time, the results indicate that a mixture with 20% PE content achieves the best balance between reactivity and stability, although carefully balanced proportions are required to avoid local antagonistic effects in the temperature range corresponding to polymer decomposition.

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