



Temperature effects on chemical reactions and product yields in the Co-pyrolysis of wood sawdust and waste tires: An experimental investigation

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ABSTRACT

This study investigates the effects of varying temperatures on the co-pyrolysis of wood sawdust (WS) and waste tires (WT) within a stainless steel fixed-bed reactor under a nitrogen atmosphere. The experiments were conducted at three different temperatures: 400 °C, 500 °C, and 600 °C, focusing on the thermal behavior and resultant product yields. At 600 °C, WS produced the highest oil yield (63.6 wt%), suggesting a tendency to generate more aqueous and volatile components. Conversely, WT alone showed an optimal oil yield of 46.4 wt% at 500 °C, while the WS-WT blend achieved 55.6 wt%. Gas chromatography-mass spectrometry (GC-MS) analyses of the pyrolytic oils indicated that WS-heavy mixtures were rich in aliphatic compounds, whereas WT-dominant samples had increased aromatic and phenolic contents, demonstrating the potential for creating valuable chemicals from waste. Additionally, gas analysis highlighted significant variations in syngas composition, with increased methane and decreased CO₂ levels at higher temperatures, emphasizing the role of the water-gas shift reaction. These findings underscore the critical importance of temperature control in optimizing the efficiency and quality of products from co-pyrolysis, presenting a viable method for enhancing the value derived from waste materials.

1. Introduction

The growing concerns over environmental degradation and energy scarcity have intensified the search for alternative energy sources. Solid wastes—including biomass, municipal refuse, tires, and plastics—offer renewable alternatives to the declining fossil fuel reserves. Specifically, biomass and waste tires require environmentally friendly disposal and effective energy utilization strategies. In 2021, Indonesia generated approximately 115.73 million tons of agricultural biomass and 1.1 million tons of waste tires [1,2]. Although advanced combustion techniques have effectively harnessed energy from these sources, they also emit harmful gases such as NO_x and SO_x, leading to inevitable secondary pollution. Consequently, there is a pressing need for clean and efficient recycling methods to transform these wastes into sustainable

energy sources [3,4].

The need to manage waste effectively has led to exploring various technologies, with pyrolysis standing out for its ability to convert waste into energy and valuable chemical products. Research on treating wood sawdust and waste tires through pyrolysis shows that these processes help solve waste disposal problems while producing bio-oil, syngas, and char [5–9]. This study focuses on the environmental benefits of co-pyrolysis of wood sawdust (WS) and waste tires (WT). By converting WS and WT into bio-oil, syngas, and char, this method significantly reduces waste volume and addresses the environmental issues caused by landfilling and incineration. Co-pyrolysis also cuts greenhouse gas emissions by capturing and using the gases produced, reducing CO₂, and increasing cleaner methane [10,11]. The process supports circular economy principles by enhancing resource efficiency and reducing the

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need for new raw materials. Additionally, controlled pyrolysis limits the creation of harmful pollutants, protecting air quality and lowering health risks [12,13]. Recovering energy from co-pyrolysis products offers a sustainable alternative to fossil fuels, improving energy efficiency. Producing stable char from this process lowers the risk of toxic leaching from waste tires, providing a safer waste management solution.

Recent studies have demonstrated that co-pyrolysis of biomass with polymer-based materials can enhance the yield and quality of products through synergistic effects. For example, interactions between volatile compounds from biomass and radical species from polymers can increase the production of aromatic hydrocarbons, which are highly valued in various industrial applications [14]. Furthermore, the role of temperature in pyrolysis is crucial as it influences the kinetics of chemical reactions and the stability of the resulting compounds. Varying temperatures during pyrolysis significantly affect the outcomes. For instance, studies have highlighted the critical role of temperature in determining the yield and composition of bio-oil in the pyrolysis of wood and biomass [15]. The influence of operating temperature on bio-oil yield and composition has been explored in studies involving cellulose, hemicellulose, and lignin, revealing that the design and operating temperature of the reactor significantly impact the overall yield and composition of bio-oil [16]. Additionally, research comparing microwave pyrolysis and conventional pyrolysis indicates that bio-oil yield increases with higher pyrolysis temperatures [17]. Studies on the production of bio-oil from maize straw and other biomass sources have underscored the influence of temperature on the production of bio-oil, char, and syngas [18].

Research by Rejeb et al. [19], highlights that optimal temperature ranges are essential for maximizing the yields of specific valuable chemicals while minimizing the formation of undesired byproducts, underscoring the need for detailed research on temperature-dependent behaviors during the co-pyrolysis of heterogeneous waste materials such as wood sawdust and waste tires. The primary challenge in the co-pyrolysis of these materials lies in understanding and optimizing the interactions between these dissimilar materials under various thermal conditions, which significantly affect the efficiency of the process and the quality of the outputs. While the individual pyrolysis processes are well-understood, co-pyrolysis involves complex chemical reactions influenced by temperature, the proportions of the feedstock materials, and their properties. Addressing this challenge requires a systematic study of the temperature-dependent chemical reactions and the corresponding yields of different products, which can facilitate the development of optimized pyrolysis protocols that are economically viable and environmentally beneficial. Research into the co-pyrolysis of biomass and rubber-based materials has unveiled several strategies to enhance both reaction outcomes and product yields. Notably, pre-treatment techniques such as torrefaction have been effective in homogenizing and stabilizing the feedstock, thus enhancing the consistency of product yields across different temperature regimes [20]. Moreover, the application of catalysts like zeolite has proven instrumental in steering pyrolysis reactions toward the production of desired products, significantly modifying the pathways of thermal decomposition and curtailing the generation of gases and char [21]. Additionally, computational modeling has become an essential tool for anticipating the results of co-pyrolysis reactions. This technique enables researchers to simulate various temperature and feedstock scenarios prior to practical application, identifying optimal conditions for specific chemical yields and thereby reducing both experimental costs and time. Collectively, these techniques constitute an advanced methodological framework that substantially refines the co-pyrolysis process, thereby enhancing economic efficiency and environmental sustainability [22].

Despite extensive research on pyrolysis, the interactions and optimal conditions for the co-pyrolysis of wood sawdust and waste tires, particularly in relation to temperature, have not been thoroughly explored. The study aims to address the existing knowledge gap by systematically examining how temperature variations impact chemical

reactions and product yields during the co-pyrolysis process. It explores the synergistic effects of combining two different waste materials at various temperatures, an area that has not been comprehensively studied before. Additionally, the research aims to optimize process parameters to maximize the yield of high-value products while minimizing environmental impacts. This effort significantly contributes to the development of sustainable waste management strategies. The findings of this study enhance the understanding of co-pyrolysis mechanisms and introduce innovative methods to increase the efficiency and sustainability of converting waste materials into valuable chemicals and energy.

2. Materials and methods

2.1. Materials and chemicals

The primary raw materials used in this study were wood sawdust (WS) and waste tires (WT), which were sourced from local vendors in West Java Province, Indonesia. The wood sawdust was derived from pinewood, while the waste tires were of various origins, collected to ensure a representative sample. Both materials were selected for their abundance and potential for co-pyrolysis. The chemicals used for analyses, including nitrogen gas (N_2) for creating an inert atmosphere, and solvents for GC-MS analysis, were of analytical grade and procured from reliable suppliers.

2.2. Apparatus and instruments

The co-pyrolysis experiments were conducted using a stainless steel (SS304) tubular fixed-bed batch reactor. The reactor had an inner diameter of 5 cm, an outer diameter of 5.6 cm, and a length of 40 cm. Key instruments included: GC-MS Analyzer: Shimadzu GC-MS QP2010 SE equipped with an Rtx®-5MS capillary column, used for characterizing pyrolytic oils. Thermogravimetric Analyzer (TGA): PerkinElmer TGA 4000, employed for thermal degradation analysis. Gas Analyzer: Gasboard 3100P, used to measure non-condensable gases. Calorimeter: LECO AC500 Isoperibol Calorimeter, used to determine the higher heating value (HHV) of the feedstocks and pyrolytic oil. Elemental Analyzer: LECO CHNS 932, used for ultimate analysis of carbon, hydrogen, nitrogen, and sulfur content.

2.3. Experimental methods

2.3.1. Feedstock preparation, proximate and element analysis

This experiment utilized pinewood sawdust (WS) and waste tires (WT) as primary raw materials. Both feedstocks underwent initial milling and were subsequently screened through a 40-mesh sieve to achieve a uniform and fine particle size. This size standardization is crucial for ensuring consistent heating rates and chemical reaction interfaces during the co-pyrolysis process. Following size reduction, the feedstocks were dried in a furnace at 110 °C for 4 h to eliminate moisture, which is essential to prevent any steam reactions during pyrolysis that could affect the yield and quality of the final products.

2.3.2. Pyrolysis experiments and product analysis

Pyrolysis experiments were conducted using a stainless steel (SS304) tubular fixed-bed batch reactor under atmospheric pressure (Fig. 1).

Prior to each experiment, the reactor was thoroughly flushed with nitrogen (N_2) to establish an inert atmosphere and prevent oxygen contamination. A 25 g sample, placed in an aluminum container, was then positioned at the center of the reactor. After sealing, the reactor was purged with N_2 for an additional 15 min to ensure the complete elimination of any residual oxygen. Following the cooling period, the products were carefully collected for analysis. Pyrolytic oil and solid char were extracted and weighed to determine their respective yields. The pyrolytic oil was characterized using a GCMS QP2010 SE, a Shimadzu,

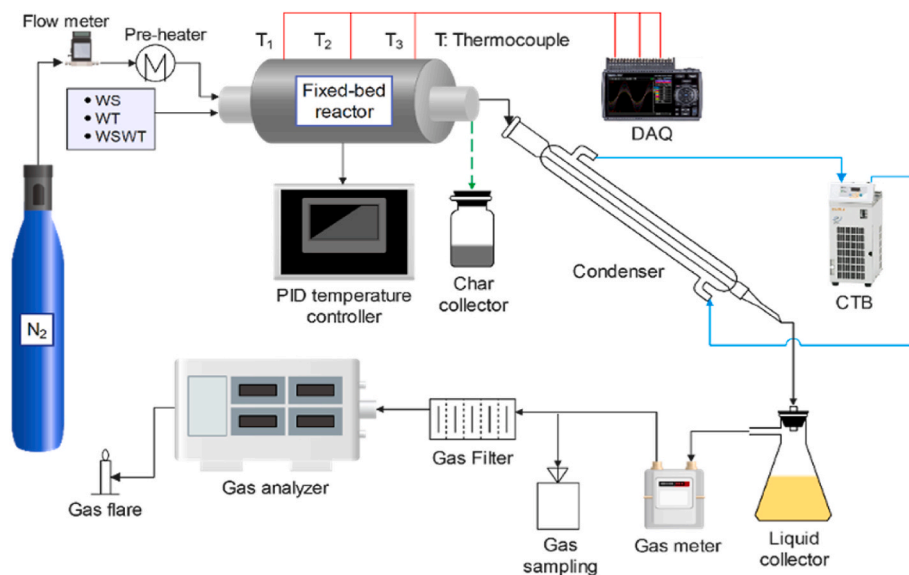


Fig. 1. Experimental apparatus for co-pyrolysis of WS and WT.

Japan-based instrument equipped with an Rtx®-5MS capillary column. The thermal degradation analysis for char production was performed using a thermogravimetric analyzer (TGA 4000 PerkinElmer). Non-condensable gases were measured using a gas meter, filtered, and analyzed using an inline portable gas analyzer (Gasboard 3100P, EU Authorization No.: EP2796856) before being vented to prevent back-flow. The yield of gaseous products was calculated using specified formulas that account for the volume of gas produced and the conditions under which pyrolysis was conducted. This systematic approach ensures precise quantification of all pyrolysis outputs, which is crucial for evaluating the efficiency and effectiveness of the process.

$$\text{Oil yield (\%)} = \frac{\text{mass of oil obtained}}{\text{total mass of feed input}} \times 100 \quad (1)$$

$$\text{Char yield (\%)} = \frac{\text{mass of char obtained}}{\text{total mass of feed input}} \times 100 \quad (2)$$

$$\text{Gas yield (\%)} = 100 - (\text{oil yield} + \text{char yield}) \quad (3)$$

2.3.3. Physicochemical characterization of feedstock

This study involved the ultimate analysis, measurement of moisture content and bulk density, and determination of the heating value. The moisture content was assessed using the ASTM D3173 method. The ultimate analysis, which included measurements of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in each feedstock, was conducted using a LECO CHNS 932 analyzer according to ASTM D5291-96. The higher heating values (HHV) of the raw materials (dry basis) and pyrolytic oil were determined using a LECO AC500 Isoperibol Calorimeter. All experiments were conducted in triplicate, and the average results are presented in Table 1.

3. Results and discussion

3.1. TGA analysis

Fig. 2(a) show the thermal decomposition profiles of wood sawdust (WS), waste tire (WT), and their mixture (WSWT) have been studied, revealing distinct behaviors during drying, devolatilization, and char formation. WT exhibited the highest resistance to thermal degradation, retaining 40.33 % of its mass as charcoal, while WS retained 24.80 %, and the mixture (WSWT) retained 31.41 %. These findings are supported by Ref. [23], which focused on the reduction of sulfur oxides and fly ash

Table 1

Physicochemical characterization of feedstocks.

	WS	WT	WSWT (50:50 wt %)
Ultimate analysis (wt.%) rowhead			
C (carbon)	49.73 ± 1.2	78.48 ± 1.5	64.11 ± 1.3
H (hydrogen)	6.40 ± 0.5	7.29 ± 0.6	6.85 ± 0.5
N (nitrogen)	0.00 ± 0.0	0.27 ± 0.1	0.13 ± 0.1
S (sulfur)	0.29 ± 0.1	1.88 ± 0.2	1.08 ± 0.2
O (oxygen)	43.58 ± 1.0	12.08 ± 0.9	27.83 ± 1.2
Moisture content (wt. %)	2.3 ± 0.2170 ± 0.5	170 ± 0.5	19.83 ± 1.1
Bulk density (kg/m ³)	0.5	385 ± 1.0	277.5 ± 1.5
HHVdb (MJ/kg)	19.83 ± 1.1	38.90 ± 1.5	40.03 ± 0.2
		1.5	

emissions during co-combustion, indicating interactions during thermal decomposition that lead to the formation of specific compounds in the ash. Additionally, P. Osorio-Vargas et al. [21] studied the dynamic pyrolysis characteristics of waste tire catalytic pyrolysis, providing insights into the devolatilization behavior of waste tire materials. Furthermore, Abdul Jameel et al. [24] investigated the pyrolysis of waste tire oil and observed distinct stages in the pyrolysis process that aligned with the observed resistance of waste tires to thermal degradation. The decomposition rate for those raw are shown in Fig. 2(b).

Fig. 2(b) show most pronounced changes occur in the devolatilization zone, where there is a sharp increase in decomposition rate. Here, WSWT reaches its peak decomposition rate at the lowest temperature of 382.15 °C, suggesting an earlier breakdown compared to WT, which peaks at 383.76 °C, and WS, which peaks at 398.99 °C. The rate of decomposition then markedly decreases in the char formation zone, reflecting the transition to primarily char residue, signifying the stabilization of the material after the release of volatiles. This thermal decomposition behavior aligns with the findings of Fazli et al. [25], who highlighted significant mass losses in waste tires between 300 °C and 500 °C through thermogravimetric analysis (TGA), suggesting a similar active decomposition phase. Similarly, Mendes et al. [26] explored the thermal conversion of pine wood sawdust under specific gas conditions, providing insights that reinforce the observed pyrolysis behavior of sawdust materials, such as WS. Allen and Downie [27] discussed how different constituent fractions in biomass affect thermal stability, which correlates with the variable decomposition rates and temperatures

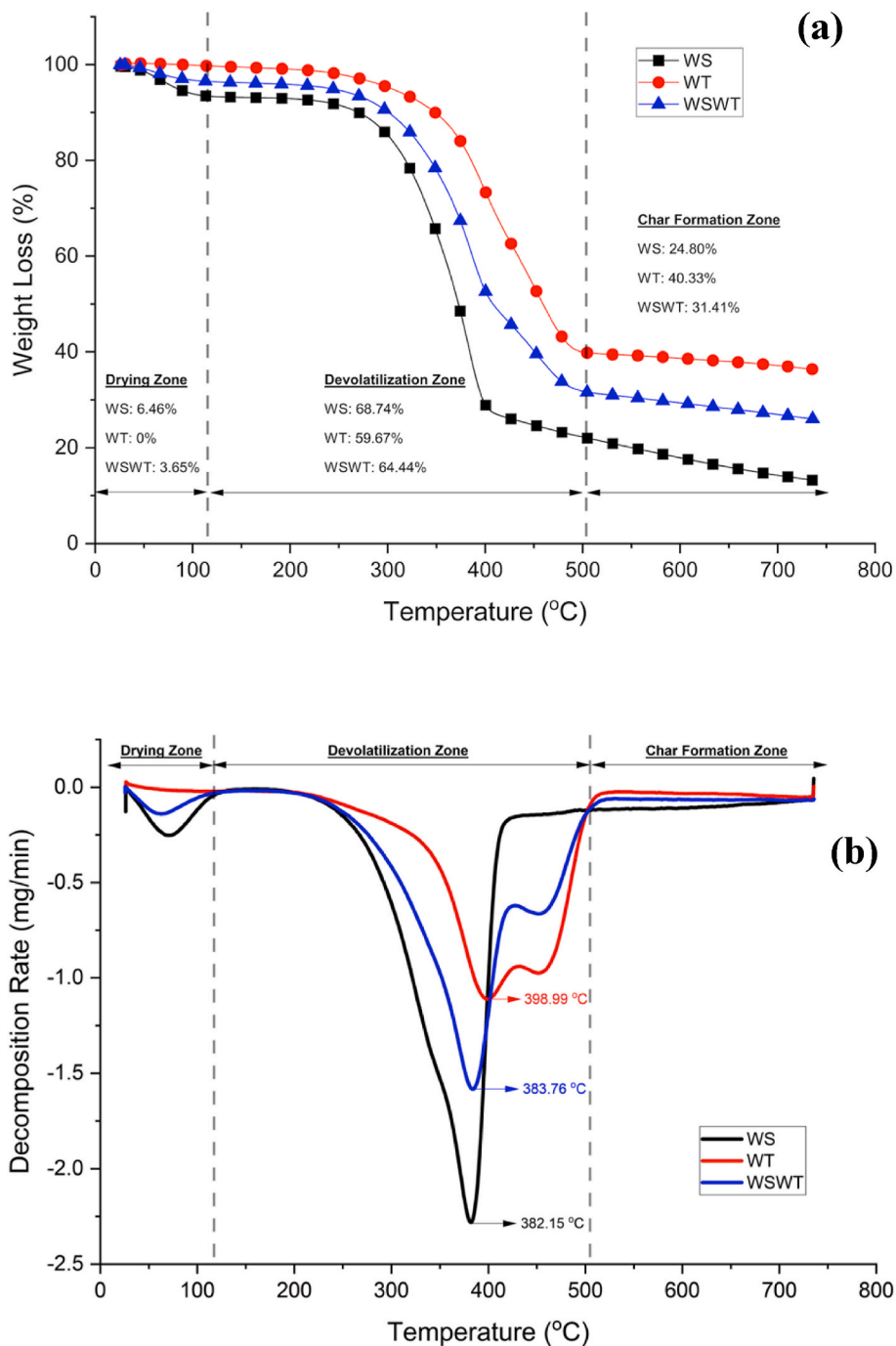


Fig. 2. (a) TG curves of WS, WT, and WSWT (50:50 wt%); (b) DTG curve of SW, WT, and WSWT (50:50 wt%).

observed among WS, WT, and WSWT, indicating that the physical and chemical compositions of these materials significantly affect their thermal degradation patterns.

3.2. Effect of pyrolysis temperature on product distribution

Fig. 3 illustrates the distribution of solid, liquid, and non-condensable gas products from the pyrolysis of WS, WT, and their mixture WSWT (50:50 wt%) at various temperatures. The most notable observation is the exceptionally high liquid oil yield from WS at 600 °C, which reaches 63.6 wt% and includes a significant proportion of pyrolytic water. This indicates that WS, under high-temperature conditions, tends to produce more aqueous and volatile components [28]. In

contrast, the pyrolysis of WT and WSWT achieves optimal oil yields at a lower temperature of 500 °C, yielding 46.4 wt% and 55.6 wt% respectively.

This suggests that WT and WSWT have different thermal behaviors compared to WS, possibly due to variations in their material compositions or the presence of additives that affect their degradation pathways [29]. The optimal mixing ratio for co-pyrolysis of WS and WT was found to be 50:50 by weight, as this ratio provided the best balance in terms of product yield and quality. Specifically, at 500 °C, the co-pyrolysis of WS and WT at a 50:50 ratio achieved a liquid yield of 55.6 wt%, which is higher than the yields from WS (52.4 wt%) and WT (46.4 wt%) under similar conditions. This enhancement can be attributed to the interactions between the biomass and rubber components that facilitate

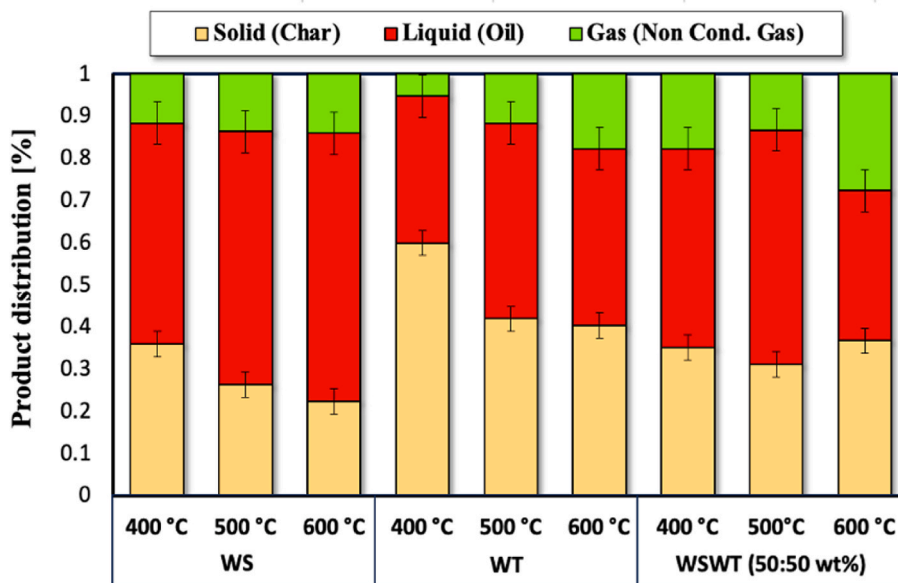


Fig. 3. Product distribution at different temperatures.

more efficient thermal degradation and stabilize the liquid products. Additionally, the co-pyrolysis process resulted in a more balanced gas composition, with increased methane production and reduced formation of undesirable byproducts, such as tars and chars, compared to the individual pyrolysis of each material. This outcome is supported by previous studies by Rejeb et al. [19], which have also reported improved product yields and higher-value chemical production through the co-pyrolysis of biomass with polymeric materials. Generally, the liquid product yields peak at a medium temperature (500 °C) for WT and WSWT, whereas WS deviates from this trend, showing increased liquid yields at 600 °C, likely due to excessive water formation at higher temperatures. This behavior indicates a unique characteristic of WS in handling higher temperatures by shifting more towards liquid and aqueous production rather than transitioning towards gaseous products, as is typically expected [30]. At 600 °C, while the liquid yield generally decreases for most materials, it is compensated by an increase in the

production of non-condensable gases. This shift from liquid to gas phase products at higher temperatures aligns with common pyrolytic reactions where thermal cracking intensifies, leading to a higher fraction of gaseous emissions. These findings highlight the benefits of co-pyrolysis, including enhanced efficiency, higher-quality products, and reduced waste byproducts.

3.3. Characteristic of bio-oil

Fig. 4 displays the relative peak percentage of various chemical groups identified in the pyrolysis products of different feedstock ratios, ranging from WS100 to WT100, including blended ratios such as WS25-WT75; WS50-WT50 and WS75-WT25. Aliphatics represent a significant component across all samples, indicating a consistent presence of non-aromatic hydrocarbons in the pyrolysis outputs, which could be attributed to the decomposition of polymeric materials present in both waste

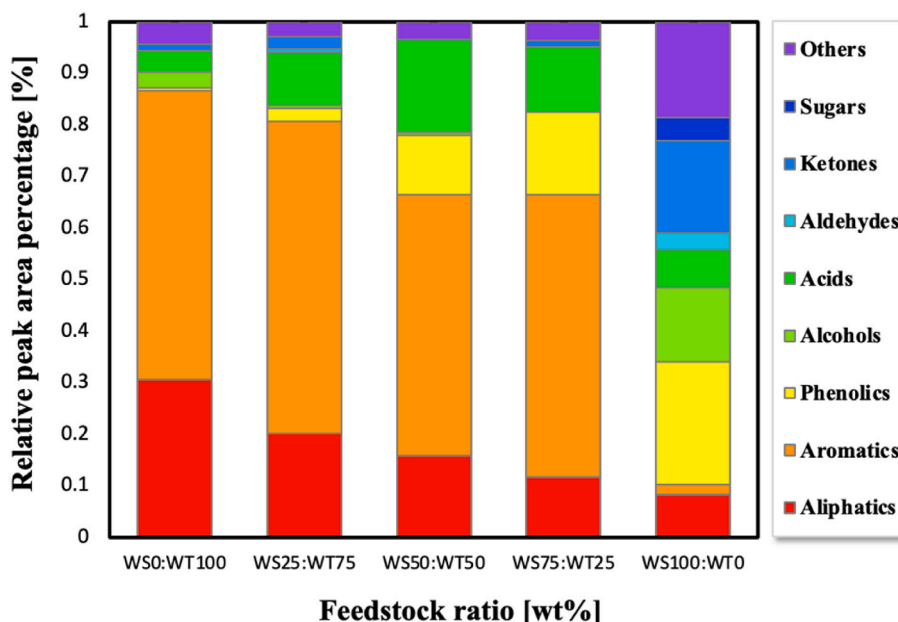


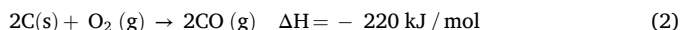
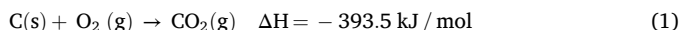
Fig. 4. The selective bio-oil compound obtained in WS; WT and WSWT co-pyrolysis at 600 °C.

tires and synthetic waste [31]. Aliphatics content shows a consistent decrease in their concentration as the proportion of WT in the mixture increases. For instance, they dominate at WS100:WT0, accounting for nearly 30 % of the total composition, but decrease to just above 10 % at WS0:WT100. This suggests that WS-rich feedstocks are particularly high in aliphatic compounds.

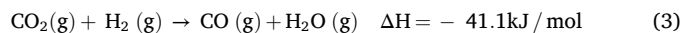
Aromatics and phenolics exhibit noticeable increases with the augmentation of WT content. Specifically, aromatics nearly double, escalating from approximately 10 % in the WS100:WT0 blend to around 20 % in the WS0:WT100 blend. This trend indicates that lignin-rich feedstocks are superior sources of these compounds [32,33]. Phenolics demonstrate an even more significant rise, increasing from less than 10 % to nearly 30 % over the same range. This trend suggests that WT-rich feedstocks are superior sources of these compounds, which hold value for their chemical properties in various industrial applications. Other components, including acids, alcohols, aldehydes, ketones, sugars, and others, also show variations across different ratios but generally represent smaller proportions of the total composition. Notably, alcohols and acids exhibit moderate consistency across the samples, indicating their pervasive presence irrespective of the feedstock type.

3.4. Reaction during pyrolysis of WS, WT and WSWT

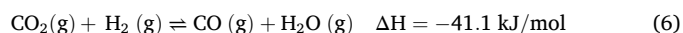
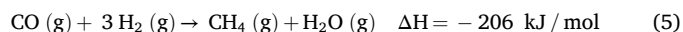
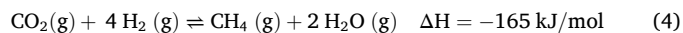
The pyrolysis behavior was investigated in terms of the gas flow rates of CO, H₂, CH₄, and total C_xH_y (primarily consisting of CH₄, C₂H₂, C₂H₄, C₂H₆, and C₃H₈), as well as the total syngas yield and its evolutionary flow rate at various temperatures. The heating value of the evolved syngas (energy output) and the energy input to the reactor were determined to gain insights into the performance regarding the quality of syngas production, energy recovery, and overall efficiency in the lab-scale fixed bed reactor. Equations (1)–(6) represent the main global reactions occurring during the pyrolysis of WS, WT, and their blends in an N₂ atmosphere.



The percentage of CO₂ was diminishing with the increase of the pyrolysis temperature, at 500 °C and 600 °C, because of the presence of the reverse water gas shift reaction.



The Water-Gas Shift Reaction (WGSR) is a reversible exothermic process; thus, the reaction equilibrium shifts to the left with increasing temperatures [34]. WGSR maximizes CO conversion in the low-temperature range (200–250 °C), while in the high-temperature range (300–450 °C), the reaction favors CO formation, known as the reverse WGSR. The percentage of CO₂ decreases, primarily due to this reverse WGSR which transforms CO₂ back to CO. Although WGSR is not one of the principal pyrolysis reactions, it cannot be omitted in the analysis of chemical reactions involving syngas [35,36]. At 600 °C, the percentage of CO decreased while CH₄ continued to increase from 400 °C, indicating that methanation reactions occurred.



3.5. Effect of pyrolysis temperature on gas production

The gas compositions resulting from the various pyrolysis experiments are shown in Fig. 5. Since the experiments were conducted in an inert nitrogen atmosphere, the data were normalized to a nitrogen-free basis.

Fig. 5 illustrates the gas composition at different temperatures (400 °C, 500 °C, and 600 °C) for three types of feedstock: waste tires (WT), waste synthetic (WS), and a blend of waste synthetic and waste tires (WSWT) at 50:50 wt% ratio. As the temperature increased, notable trends were observed: the percentage of hydrogen (H₂) increased across all feedstocks, likely because the WGSR was dominant in the reverse direction, favoring hydrogen consumption at higher temperatures [37, 38]. For WS, there is a marked increase in methane (CH₄) from 400 °C to 600 °C, which could be attributed to the methanation reaction, as suggested by changes in the methanation dynamics at higher temperatures [39]. Conversely, in WT, CO₂ levels decrease significantly by 600 °C, likely due to the reverse Water-Gas Shift Reaction (WGSR), where CO₂ is converted back to CO with rising temperatures, supporting the findings of [40,41]. Interestingly, the WSWT blend shows a balanced gas

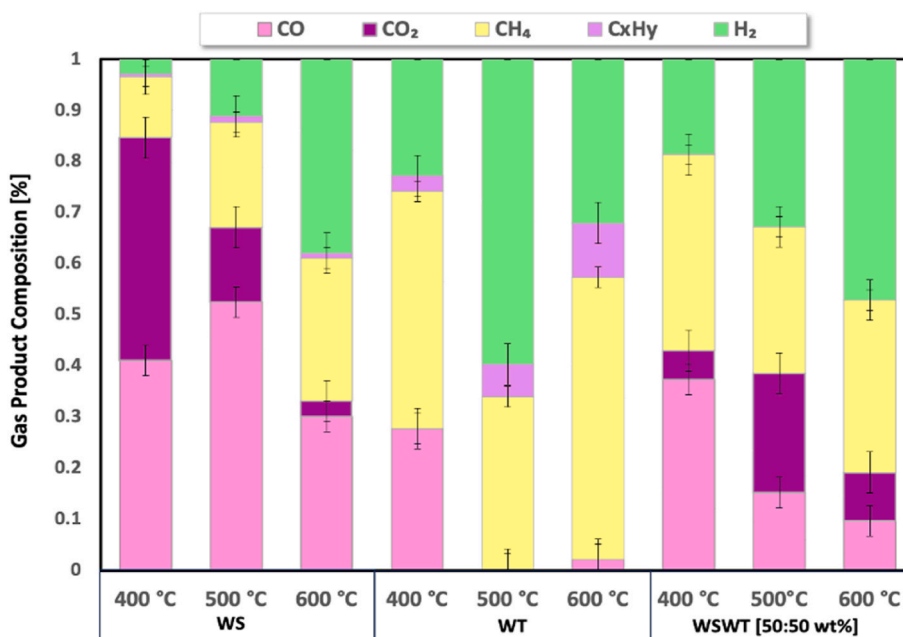


Fig. 5. Effect of temperature on gas production.

composition, suggesting that blending different waste types may stabilize the production of syngas over a broader temperature range, aligning with the concept that mixed feedstocks can optimize syngas quality and yield.

4. Conclusion

This study addresses critical gaps in the current understanding of co-pyrolysis processes, particularly for mixed wastes such as wood sawdust (WS) and waste tires (WT). Prior research has largely overlooked the potential synergistic benefits of co-pyrolyzing these materials and the impact of temperature on the resulting product yields and chemical compositions. Our findings reveal that co-pyrolysis at optimized temperatures significantly enhances the yield and quality of pyrolytic products. Specifically, at 500 °C, WT and its co-pyrolysis mixtures (WSWT) demonstrated peak oil yields of 46.4 wt% and 55.6 wt% respectively, indicating that WT undergoes optimal thermal degradation at this temperature. In contrast, WS reached a higher oil yield of 63.6 wt % at 600 °C, suggesting that WS components require higher temperatures to maximize liquid production, primarily due to the formation of more aqueous and volatile components. GCMS results reveal a dominant presence of aliphatic compounds in WS-rich samples, which gradually decrease as WT content increases, highlighting the differing chemical nature of the feedstocks. Aromatic and phenolic compounds, essential for various industrial applications, notably increase in WT-rich samples, underscoring their potential for producing value-added chemicals from waste. Furthermore, gas production analysis revealed a notable increase in methane production from WS as temperatures rose from 400 °C to 600 °C, while CO₂ levels in WT decreased, likely due to the reverse Water-Gas Shift Reaction converting CO₂ back to CO at higher temperatures. These results suggest new opportunities for more efficient and sustainable waste management practices and mark a pioneering step in the comprehensive study of temperature-dependent effects in the co-pyrolysis of mixed waste materials.

CRediT authorship contribution statement

Imron Masfuri: Writing – original draft, Resources, Project administration, Methodology, Funding acquisition, Formal analysis. **Apip Amrullah:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Obie Farobie:** Writing – review & editing, Data curation, Conceptualization. **Trisno Anggoro:** Resources, Formal analysis, Data curation. **Frendy Rian S:** Resources, Conceptualization. **Wargianto Prabowo:** Methodology, Investigation, Formal analysis. **Erlan Rosyadi:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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