



Synergistic co-pyrolysis of polyethylene terephthalate and hibiscus rosa-sinensis: Catalytic mechanisms for optimizing pyrolysis yields

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ABSTRACT

This study investigated the co-pyrolysis of Polyethylene Terephthalate (PET) and Hibiscus rosa-sinensis (HRS) biomass as a sustainable approach for waste valorization and biofuels production. This study improves both yield and fuel quality by emphasizing HRS's potential as a valuable co-feedstock for sustainably valorising PET waste and producing biofuels. Various PET and HRS weight ratios (100 %, 95 %: 5 %, 90 %: 10 %, 85 %: 15 %, and 80 %: 20 %) were employed at 350 °C pyrolysis temperature.

Both the experimental and simulation results indicated that product distribution was significantly affected by HRS. The slight addition of HRS (90:10) had a synergistic effect, yielding a maximum oil output of 538 ml and 393 g (78,6 % yield), exceeding the yield from pure PET pyrolysis. The oil yield indicated that the fuel characteristics were superior at this ratio. The octane number increased to 98, the calorific value remained approximately constant at 46.65 MJ/kg, but viscosity and density exhibited variations. Moreover, the addition of HRS significantly increased and accelerated gas yields, particularly CH₄ and H₂, indicating HRS's catalytic role in facilitating cracking and reforming processes.

The catalytic activity of HRS is primarily related to its flavonoid compounds. The flavonoid greatly improves the co-pyrolysis of PET and HRS by encouraging bond cleavage, increasing the formation of oxygenated compounds, making it easier to turn long-chain hydrocarbons into valuable gases, and making the pyrolysis yields better overall in terms of quality and stability. HyperChem simulation results demonstrate alterations in molecular design, polarizability, and energy dynamics, thereby providing a molecular-level understanding of these synergistic effects.

1. Introduction

The global rise in waste plastic pollution has created significant challenges to environmental sustainability, requiring novel waste management approaches. Polyethylene Terephthalate (PET), a commonly utilized polymer in packaging and consumer products, is one of the most significant and enduring contributors to this issue (Zakaria et al., 2023; Bartwal et al., 2025). Recycling methods, such as mechanical and chemical recycling, face technological and economic challenges, leaving much PET untreated.

Recently, pyrolysis has emerged as a viable option, providing both of the advantages of waste reduction and the generation of energy-dense

fuels and chemicals (Peng et al., 2022; Sharma et al., 2022). Pyrolysis is the thermal degradation of hydrocarbon in inert conditions, producing solid, liquid, and gas hydrocarbons yields. The liquid yields have high calorific value and octane number, making it a potential alternative to fossil fuels. Unlike recycling or incineration, pyrolysis reduces landfill use and greenhouse gases, supporting a circular economy (Hasan et al., 2025; Praveenkumar et al., 2024).

However, pure PET pyrolysis faces challenges such as oxidative degradation of fumes, oil instability, and uneven product distribution. To solve these problems, it has looked into co-pyrolysis, which is a method that mixes plastic with other materials to improve the quality and efficiency of the products (Gulab and Malik, 2024; Tee et al., 2025;

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Hassan and Hameed, 2024; Seah et al., 2023; Song et al., 2023). Additionally, combining PET with biomass shows enormous promise, as biomass can facilitate the breakdown of PET molecules, making the resulting products more suitable as alternative fuels to fossil fuels.

Biomass, a renewable organic material mainly composed of cellulose, hemicellulose, lignin, and trace elements like flavonoids, releases volatile compounds like hydrocarbons, H_2 , and CO during pyrolysis (George et al., 2024). When combined with plastics, it improves bond breaking, thermal conductivity, and radical stability, leading to higher liquid and gas yields, less char, and better bio-oil quality (Rahman et al., 2023; Dong et al., 2024). The high hydrogen-to-carbon (H/C) ratio of lignocellulosic biomass makes plastics more carbon-rich (Hu et al., 2024; Speisky et al., 2022). It also provides oxygenated chemicals that make cracking easier. Besides, biomass's abundance and renewability support environmental and economic benefits within circular economy practices (Islam et al., 2024; Tyagi and Anand, 2024).

Among biomass sources, plant materials abundant in antioxidants and phenolics have demonstrated notable potential. Antioxidants such as flavonoid compounds stabilize reactive intermediates, reducing vapor-phase oxidation and enhancing the stability and calorific value of pyrolysis oil. Hibiscus rosa-sinensis (HRS) is a sustainable and underutilized biomass resource with considerable potential for co-pyrolysis applications. In tropical countries, HRS is plentiful, economical, and replete with distinctive chemical components that augment its thermal and catalytic characteristics. The porosity of HRS enhances heat transfer during pyrolysis, while its antioxidant-rich flavonoids stabilize radicals and aid hydrogen transfer (Subramanian and Ragula, 2025; Anand and Sarkar, 2017). These features improve the yield and quality of pyrolysis liquids and gases. Flavonoids also promote PET's hydrocarbon breakdown, increasing valuable hydrocarbons like gasoline fractions, and its stability prevents oxidative degradation, preserving hydrocarbon chains. This makes HRS a highly valuable, sustainable, and cost-effective co-feedstock for waste valorization. HRS may serve as a catalyst in co-pyrolysis at 350 °C, a pyrolysis temperature effective for PET breakdown but insufficient for full degradation of HRS biomass. Its phytochemicals and heat resistance suggest HRS could facilitate PET degradation and improve yields, even with limited thermal decomposition (Gulab and Malik, 2024; Subramanian and Reddy Ragula, 2020).

Nonetheless, these encouraging attributes, the utilization of HRS in PET pyrolysis, are still inadequately investigated. Most research focuses on biomass sources like agricultural waste and wood, which lack HRS's antioxidant properties. The co-pyrolysis of PET and biomass utilizes the complementary characteristics of these feedstocks to attain synergistic results. PET, a synthetic polymer made of carbon, hydrogen, and oxygen, undergoes decomposition through pyrolysis, yielding aromatic and aliphatic hydrocarbons, as well as smaller flavonoid molecules. In contrast, biomass emits volatile substances abundant in oxygenated and short-chain hydrocarbons. The combination of radicals and reactive intermediates from one feedstock promotes the degradation of the other, resulting in the formation of more stable molecules and alternative cracking routes (Wang et al., 2021; Zeng et al., 2024; Zeng et al., 2025; Li et al., 2025).

The antioxidant properties of phenolic substances are crucial for HRS. These chemicals stabilize free radicals produced during PET disintegration, mitigating undesired secondary reactions and facilitating the synthesis of stable hydrocarbons. Concurrently, the high porosity of HRS facilitates heat transport, guaranteeing consistent decomposition and equitable product distribution. These mechanisms raise oil yields and improve the quality of gaseous products, such as hydrogen and methane, further validating the potential of HRS as a co-feedstock.

Determining the ideal PET-to-HRS ratio is crucial to weigh synergistic advantages against possible disadvantages. Initial research shows that small increases in biomass (like 10 %) are enough to reach this balance, which improves oil yield and stability without making big sacrifices (Subramanian and Ragula, 2025). This study aims to assess the impact of different concentrations of HRS on the pyrolysis of PET in

which HRS can improve fuel production. The inquiry precisely measures the alterations in the characteristics of pyrolysis oil fuel—calorific value, viscosity, and stability—as well as the yield and composition of gaseous products, including methane and hydrogen. The synergistic pyrolysis of PET and HRS will be examined. This method offers significant insights into the fundamental mechanisms of degradation and transformation, uncovering paths that can be directed to enhance the recovery of precious resources. HRS as a co-feedstock in PET pyrolysis improves efficiency and product quality by enabling in-situ upgrading (Gulab et al., 2024). Its phenolics and flavonoids may modify PET breakdown, increase oil yield, and enhance fuel properties (Zhang et al., 2014), while also boosting gases like methane and hydrogen (Farobie et al., 2024). This sustainable method optimizes PET pyrolysis through biomass co-processing.

Finally, investigating the potential of HRS as a co-feedstock for PET pyrolysis is crucial, particularly regarding its catalytic and synergistic effects on enhancing fuel yield and quality. This research presents a sustainable approach to waste valorization by integrating renewable biomass with plastic waste, thereby supporting energy production and environmental conservation goals. The study aims to establish a foundational understanding for future advancements in biomass-assisted pyrolysis through comprehensive testing and analysis, with significant implications for both academic research and industrial applications.

2. Methodology

2.1. Pyrolysis feedstocks

2.1.1. Polyethylene terephthalate (PET)

PET utilized in this research was obtained from post-consumer PET beverage containers. Before use, the PET bottles were thoroughly cleaned to eliminate any remaining pollutants, including labels and caps. Thereafter, the PET was manually sliced into flakes of roughly 1 × 1 cm to guarantee uniformity and enable consistent feeding into the pyrolysis reactor. Table 1 shows the composition of the PET used in this study, highlighting the primary polymeric constituent as well as the additives and trace contaminants present in the material (Konkol et al., 2003). Meanwhile, Table 2 and Table 3 present the proximate and ultimate analysis for PET, detailing its elemental composition and other related properties essential for understanding its pyrolysis behaviour.

2.1.2. Hibiscus rosa-sinensis (HRS)

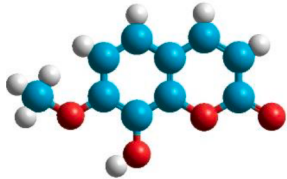
HRS flowers were chosen as the biomass co-feedstock for this research. Following harvest, the HRS flowers were subjected to a drying procedure in a convection oven at 60 °C for 24 h to reduce moisture content and guarantee uniform biomass quality for pyrolysis. The desiccated HRS flowers were further pulverized to a particle size of under 2 mm with a knife to improve thermal contact and facilitate uniform pyrolysis. The compositions of HRS influence its pyrolytic behaviour and yields of pyrolysis, shown in Table 4. Meanwhile, Tables 5, 6 explain the proximate and ultimate analysis of HRS, describing its components and relevant characteristics that are essential to understanding its pyrolysis behaviour.

2.2. Experimental setup and procedures

The pyrolysis experiments were conducted in a stainless-steel reactor that was designed to evenly distribute heat and keep the reaction parameters under control. The reactor, measuring 20 cm in diameter and 15 cm in height, afforded adequate volume for the feedstock mixes to undergo heat breakdown. A type-K thermocouple positioned in the reactor's core continuously monitored the pyrolysis temperature, linked to a Proportional-Integral-Derivative (PID) controller that managed the heat source. The PID controller was set up to keep the pyrolysis temperature at 350 °C all the time. A solenoid valve controlling an LPG burner made it possible for automatic adjustments. Maintaining

Table 1
Composition of Polyethylene Terephthalate (PET) and Its Additives.

Main Component	Percentage (% by weight)	Descriptions
Polyethylene Terephthalate	95 %	Primary polymeric constituent; repeating ethylene terephthalate units.
Additives and Trace Contaminants	5 %	Comprises processing aids, stabilizers, colorants, and possible trace contaminants from post-consumer PET sources (e.g., other polymers, beverage residues).



Molecules structures
of Polyethylene Terephthalate (PET)

Table 2
Proximate Analysis of PET.

	Moisture content	Volatile Matters	Fixed Carbon	Ash content
Proximate Analysis (wt % dry basis)	0.0	90.35	8.52	1.09

Table 3
Ultimate Analysis of PET.

	C	H	N	S	O
Ultimate Analysis (wt % dry basis)	61.80	4.38	0.0	0.0	33.82

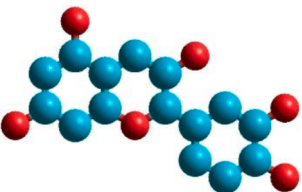
consistent temperature control is essential for optimizing pyrolysis reactions and guaranteeing experimental reproducibility (Djurdjevic et al., 2024)

Nitrogen environment was created within the reactor to inhibit combustion by suppressing Oxygen. Nitrogen gas, delivered at a flow rate of 10 ml/min via a flow regulator, purged the reactor prior to and during each operation. This inert atmosphere prevented undesired combustion processes, enhancing the quality and stability of the pyrolysis products.

Volatile matters generated during pyrolysis exited the reactor and traversed a system of copper pipes for condensing and trapping. The copper coil, with a length of 500 cm and a diameter of 9.5 mm, was occupied in an ice bath to promote effective heat exchange and the condensation of volatile fractions into liquid oil. Non-condensable gases were sent to a sensor array for immediate analysis. The sensors, comprising MQ-4 (methane), MQ-8 (hydrogen), MQ-7 (carbon monoxide), and MQ-135 (carbon dioxide), were integrated with an Arduino Uno microcontroller for ongoing data logging. These sensors delivered

Table 4
Standard Composition of HRS Biomass (Dry Weight Basis).

Main component	Percentage (% by weight)	Descriptions
Bioactive Compounds	3–8 %	Flavonoid compounds (significantly influences electron donation)
flavonoid		
Structural Carbohydrates	40–60 %	Cellulose, Hemicellulose, and Lignin - main constituents of biomass and constitute a substantial fraction of the dry weight
Other extractives and minor components	20 – 35 %	Lipids (fats and oils), Proteins, Ash, and other minor extractives. These denote the residual fractions required to approach 100 %
Moisture	2 %	



Molecular structures of
flavonoid

accurate measurements of gas composition, enhancing the quantitative evaluation of pyrolysis products.

Fig. 1 illustrates a schematic of the experimental apparatus, including the pyrolysis reactor, condenser, PID control system, and gas sensors while Fig. 2 presents the experimental flow diagram that explains the procedures. This integrated system facilitated thorough regulation of reaction conditions and detailed characterization of product yields and attributes. In the meantime, Table 7 shows the experimental conditions, including the parameters measured and their respective values, as outlined in the table. This analysis of conditions is essential for ensuring the reproducibility of the experiment, understanding the influence of various parameters on the pyrolysis process, and providing a comprehensive context for interpreting the results accurately.

For these co-pyrolysis tests, PET and HRS were mixed physically in five different weight ratios: 100 % PET, 95 % PET: 5 % HRS, 90 % PET: 10 % HRS, 85 % PET: 15 % HRS, and 80 % PET: 20 % HRS. The PET-HRS combinations were created shortly before each pyrolysis experiment to

Table 5
Proximate Analysis of HRS.

	Moisture content	Volatile Matters	Fixed Carbon	Ash content
Proximate Analysis (wt % dry basis)	5.04	66.04	17.80	11.08

Table 6
Ultimate Analysis of HRS.

	C	H	N	S	O
Ultimate Analysis (wt % dry basis)	33.88	4.56	2.45	0.71	58.4

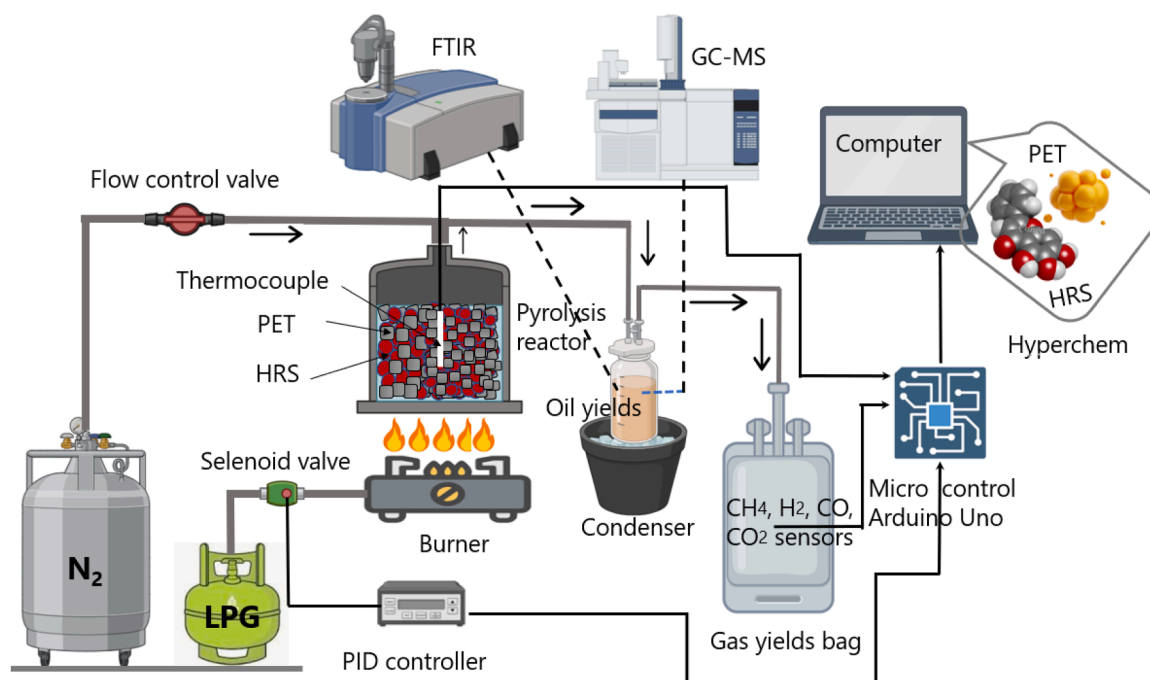


Fig. 1. An experimental setup for PET-HRS co-pyrolysis.

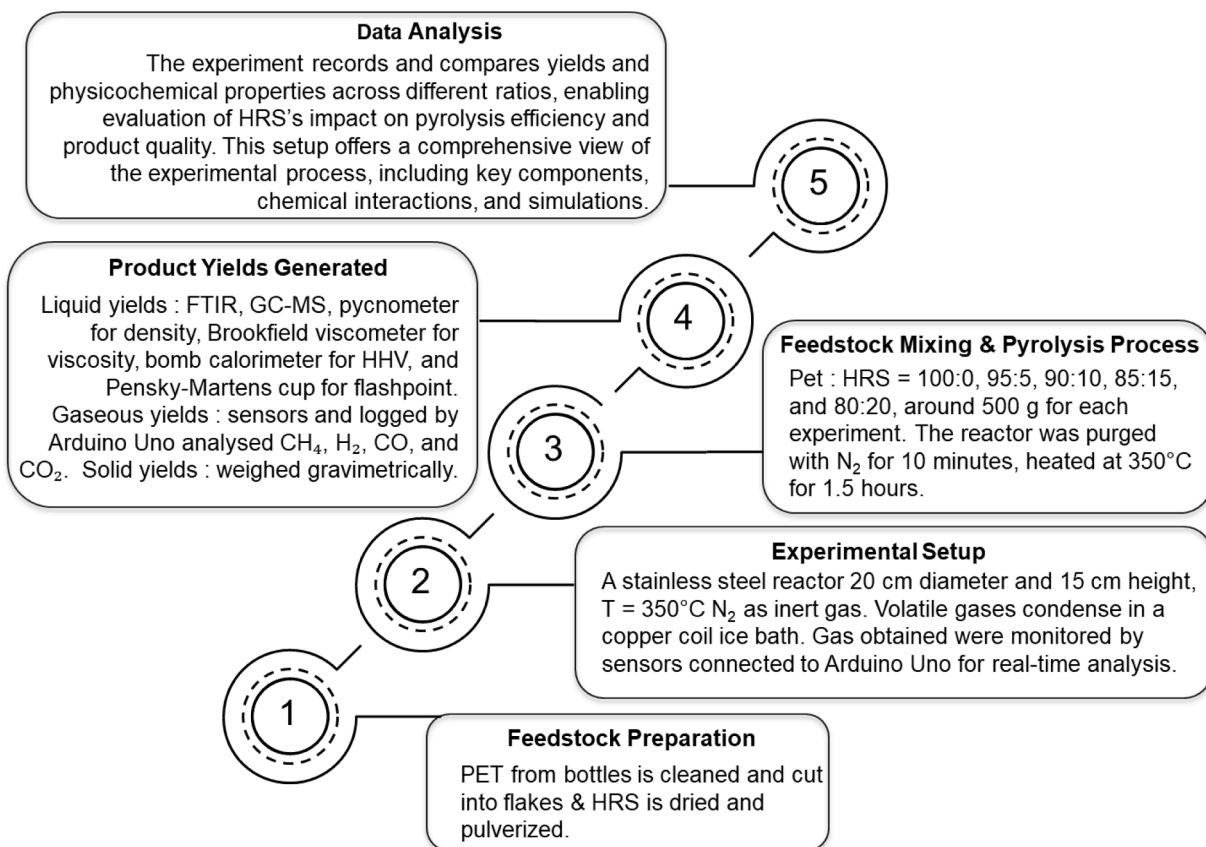


Fig. 2. Experimental flow diagram.

guarantee feedstock homogeneity. The mass was approximately 500 g to maintain uniformity throughout all experimental samples. The designated ratios were selected to methodically examine the impact of HRS concentration on the pyrolysis behaviour of PET, encompassing the

yields of liquid oil, gas, and solid, in addition to the physicochemical characteristics of the resultant products.

Prior to heating, the reactor was purged with Nitrogen for 10 min at a flow rate of 10 ml/min to remove Oxygen and establish an inert

Table 7

Experimental conditions.

Temperature profile	Reactor temperature maintained during pyrolysis	350 °C (constant)
Feedstock ratios	PET to HRS mixtures	100:0, 95:5, 90:10, 85:15, 80:20
Feedstock quantity	Total mass of each sample	~ 500 g
Pyrolysis duration	Total heating time	5400 s (1.5 h)
Flow Rate of Nitrogen	During inert purge and pyrolysis	10 mL/min
Heating method	Heating source	LPG burner controlled via PID
Cooling method	Post-reaction cooling	Ambient temperature in inert atmosphere
Gas sampling	Gas analysis via sensors	Continuous in real-time
Condensation system	Copper coil in ice bath	500 cm in length, 9.5 mm diameter
Sensor monitoring	Gases analysed with MQ sensors	CH ₄ , H ₂ , CO, CO ₂
Chemical analysis	Analytical methods for products	FTIR, GC–MS, density, viscosity, HHV, flashpoint
Molecular modelling	HyperChem simulations of PET and HRS components	Geometry optimization, molecular dynamics, quantum calculations

environment, an essential measure to avoid combustion. The burner was fired, and the PID controller sustained a constant temperature of 350 °C during the pyrolysis process, which lasted 5400 s (1.5 h). Throughout this interval, the feedstock experienced decomposition into volatile matters and solid residues. The volatile matter products passed via the Copper condenser, where the condensable components were converted into pyrolysis oil, while the non-condensable gases were sent to the sensor array for examination. The Arduino Uno captured sensor data at one-second intervals, providing extensive time-series information on gas compositions.

Subsequent to the heating phase, the reactor was permitted to cool to ambient temperature while sustaining the Nitrogen flow. The liquid oil was volumetrically collected and quantified, while the solid yields was weighed to ascertain its production. In each experiment, all five PET-to-HRS ratios were used, which made it possible to directly compare how the product was distributed and how good it was across different feedstock compositions.

2.3. The yields of product analysis measurements

This study's product analysis concentrated on two main fractions: liquid yields and gaseous yields. Both product phases demonstrate considerable promise for fuel use. The pyrolysis products—liquid oil, gas, and solid—underwent comprehensive physicochemical studies to assess their quality and prospective applications. A Gay-Lussac pycnometer was used to find out how dense the pyrolysis oil was, which made sure that the mass-to-volume measurements were correct in normal conditions. A rotational viscometer (BROOKFIELD DV-II+) was used to measure viscosity. This showed how the oil flowed and how adding biomass changed its rheological properties. A bomb calorimeter was utilized to determine the higher heating value (HHV), an essential parameter for assessing the oil's efficacy as a fuel. Flashpoint tests were performed in accordance with Pensky-Martens Closed Cup Tester (ASTM D93) standards to ascertain the ignition temperature of the oil vapours, hence assuring safety while handling and storage.

Real-time gas analysis addressing methane (CH₄), hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂), measured using the sensor array. The Arduino Uno microcontroller continuously recorded sensor data, aggregating it over time to determine the total volume and relative proportions of each gas. The gas composition elucidated the synergistic impacts of PET and HRS during pyrolysis, emphasizing hydrogen and methane production as markers of fuel potential.

It was used gravimetric analysis to accurately measure the residual

solid product of pyrolysis and determine its yield as a proportion of the established feedstock mass. This measurement was utilized to verify the mass balance of the pyrolysis process and to confirm compliance with the principle of mass conservation.

2.4. Molecular modelling

Following experimental investigations, chemical analysis and the examination of PET - HRS behaviour were conducted by developing molecular environment models and analysing their molecular properties using HyperChem software. It is to elucidate the molecular mechanisms governing the co-pyrolysis of PET and HRS. This model, as shown in Fig. 3, aims to enhance comprehension of the impact of HRS as a co-pyrolizer on the thermal degradation of PET and the resultant product attributes. The simulations were mostly about looking at reaction pathways and guessing how the yields and properties of solid, liquid, and gaseous products would change. These properties include density, calorific value, flash point, viscosity, and potential octane number. The goal was to improve the interpretation of experimental data from GC–MS and FTIR analyses.

As part of the simulation method, representative molecular models of PET fragments and key HRS components (notable bioactive chemicals) are made. The models were subjected to geometry optimization, and in certain cases, molecular dynamics simulations were utilized to investigate interactions between PET and HRS (flavonoid compounds). After that, quantum mechanical or semi-empirical calculations were used to find out important molecular properties, such as the structure of the molecules, their polarizability, dipole moment, kinetic energy, and energy total. The goal of the study was to find out why product yields and physicochemical properties change at the molecular level. This is accomplished by comparing computational results across various PET-to-HRS ratios to verify and analyse the processes found in the experimental outcomes, hence confirming their consistency.

2.5. Statistical analysis

In this study, a statistical approach was adopted to ensure the reliability and robustness of the experimental results. Each pyrolysis experiment was conducted in triplicate to confirm the consistency of findings, as shown in Figs. 4–16. This repetition is crucial for validating hypotheses, enhancing the accuracy of experimental data, and ensuring reproducibility. To quantify the variability, averaged results were

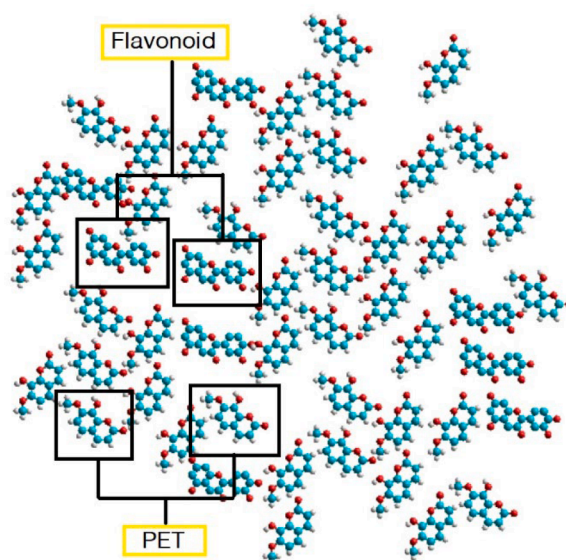


Fig. 3. Molecular model of PET - HRS co-pyrolysis.

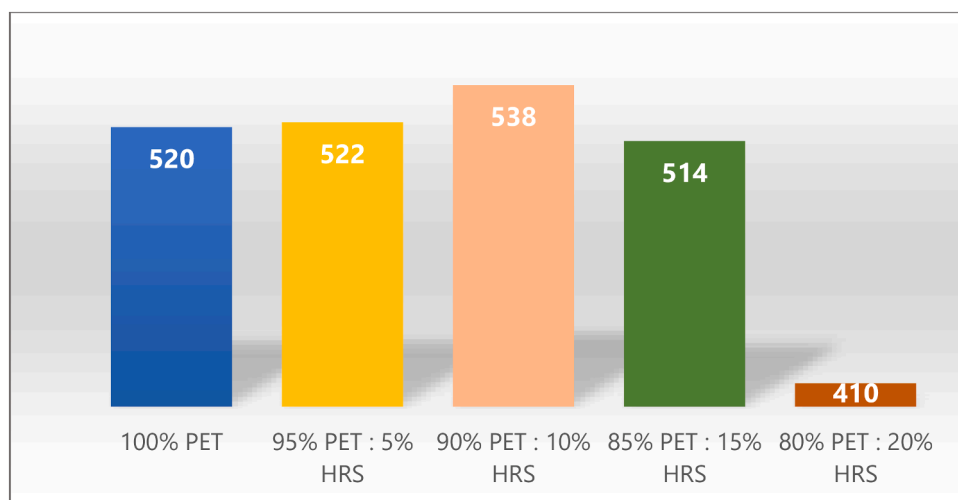


Fig. 4. The volume of liquid yields (in ml) generated in PET – HRS pyrolysis.

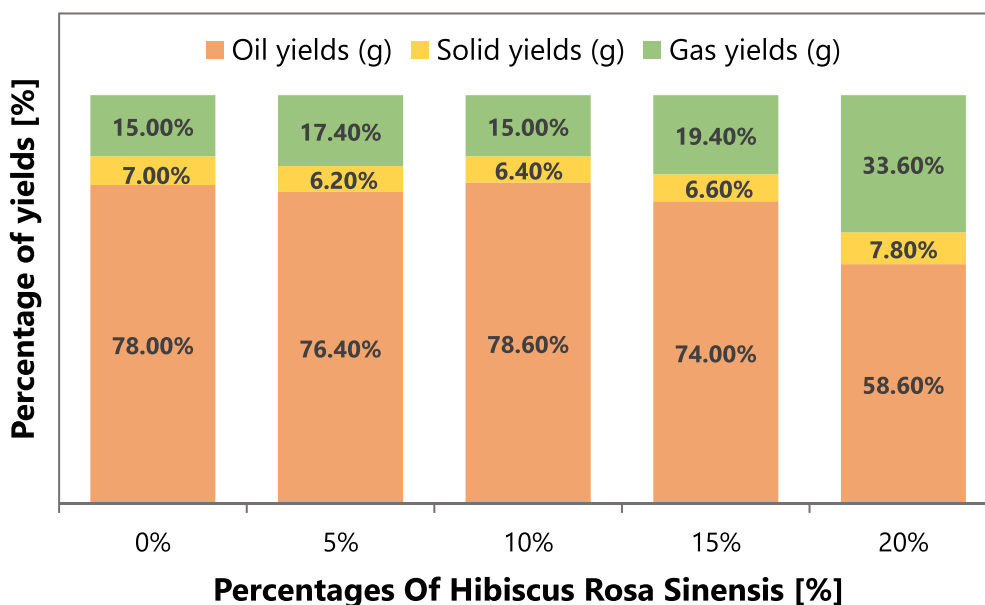


Fig. 5. Product yields in PET – HRS pyrolysis.

accompanied by standard deviation calculations, providing insights into measurement precision. These statistical measures not only strengthen the conclusions drawn from the data but also allow for a comprehensive understanding of the pyrolysis process under varying conditions. Furthermore, this rigorous approach lays the groundwork for future research endeavours to effectively build upon these findings.

Additionally, molecular modelling simulation studies were integrated to validate regression models, ensuring they accurately reflected real-world conditions. This method facilitated the identification of significant trends and the prediction of outcomes, enhancing the interpretation of experimental data. The regression models are depicted in Figs. 17–22. This detailed statistical approach not only confirmed the reliability of the experimental results but also provided a clear picture of the complex relationships in the pyrolysis system. This comprehensive analysis paves the way for more targeted research initiatives aimed at optimizing pyrolysis processes. By leveraging these insights, future studies can explore innovative techniques to improve efficiency and yield in similar systems.

3. Results and discussion

3.1. Product yields distribution

PET and HRS pyrolysis resulted in three primary yields: liquid yields (pyrolysis oil), solid yields, and gas yields. The distribution of these yields varied significantly with the PET-to-HRS ratio, highlighting the critical role of feedstock composition in shaping pyrolysis yields. As observed in the experiments, moderate additions of HRS enhanced liquid oil production, while higher biomass content increased solid and gas yields. These results indicate that the chemical and thermal properties of PET and HRS work together to create complex synergistic effects during co-pyrolysis.

3.1.1. Liquid yield formation

Fig. 4 illustrates the experimental results regarding liquid product yields from the pyrolysis of a PET and HRS mixture. Notably, the integration of HRS into PET significantly influenced the quality and volume of pyrolysis oil, with a peak liquid yield of 538 ml observed at a 90:10 PET-to-HRS ratio. This yield exceeded the 520 ml achieved from pure

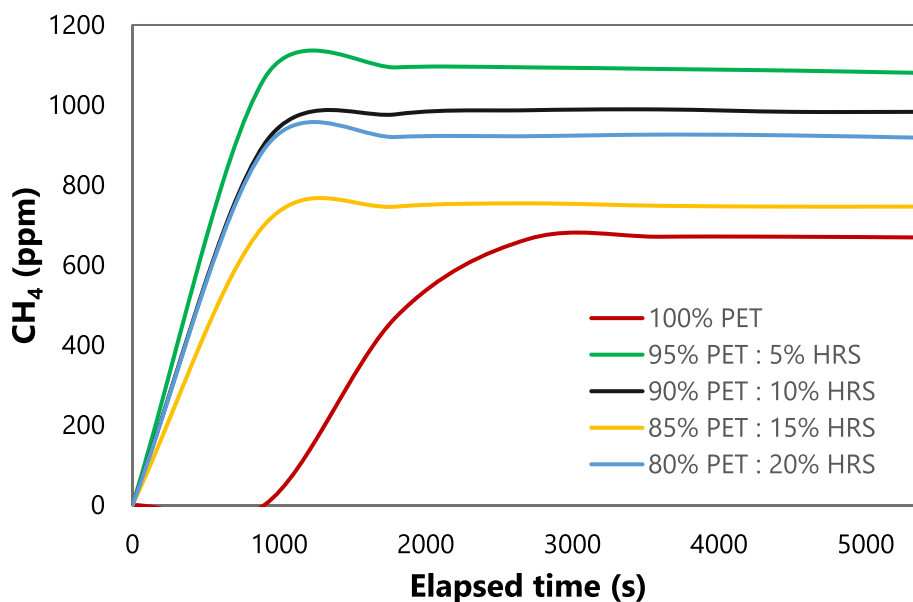


Fig. 6. CH_4 of gas yields produced in elapsed time.

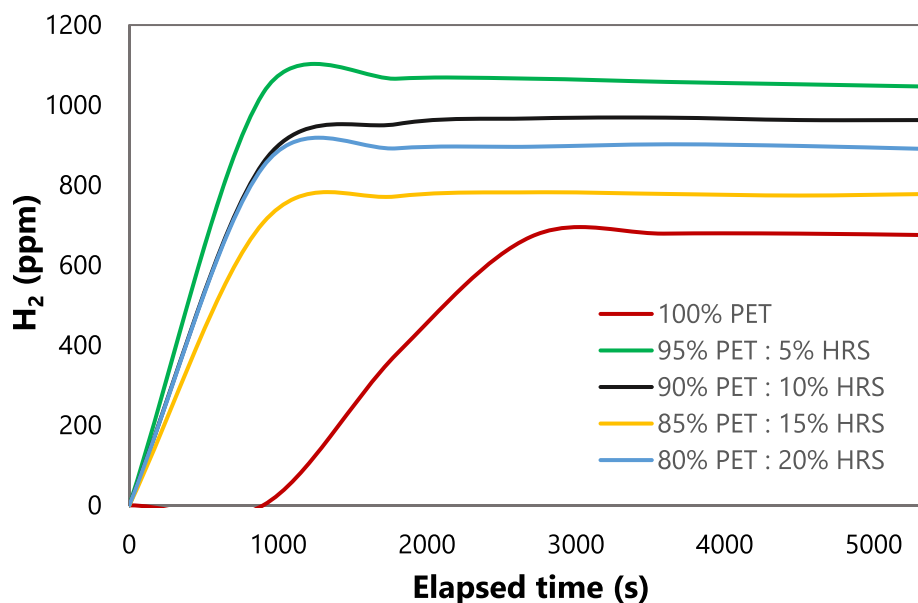


Fig. 7. H_2 of gas yields produced in elapsed time.

PET (100 % PET), demonstrating the synergistic benefits of incorporating biomass in the pyrolysis process. Moderate additions of HRS provided oxygenated functional groups, which facilitated bond cleavage in PET, therefore enhancing the production of volatile hydrocarbons. These oxygenated intermediates play a crucial role in promoting the thermal breakdown of PET, resulting in improved yields of the liquid phase, which is corroborated by the subsequent characterization of the oil's physicochemical properties.

Fig. 5 further delineates the product yields derived from pyrolysis, categorized into oil, solid, and gaseous fractions. For all PET: HRS variations, the total product mass is 500 g, consistent with the law of mass conservation, indicating that the feedstock before pyrolysis and the resultant products remain constant. Here, it becomes evident that HRS co-feeding leads to diverse product distributions, expressed as percentages. The analysis clarifies that the maximum oil yield of 393 g (78.6 % of yields) occurred at the 90 % PET: 10 % HRS mixture, slightly surpassing the 390 g (78 % of yields) from pure PET. The result reinforces

the hypothesis that moderate HRS additions can lead to enhanced oil production, benefiting from a potentially ideal balance of bioactive compounds. Conversely, further increases in HRS concentration—specifically at 15 % and 20 %—resulted in declines in liquid yields to 514 ml and 410 ml, respectively. This decrease can be attributed to a higher representation of oxygen-rich biomass constituents that divert carbon away from liquid hydrocarbon production towards solid yield formation, thus aligning with findings indicated in prior studies regarding high biomass content undermining pyrolysis oil stability and calorific value (GONG et al., 2024; Gupta et al., 2018; McCormick et al., 2016).

The role of oxygenated compounds may also be linked to the oil's physicochemical properties, as elaborated from Figs. 13, 14, 15, 16, 17. The calorific value, viscosity, density, and flashpoint of pyrolysis oil are essential markers for its applicability as a sustainable alternative fuel. As seen in varied compositions of PET and HRS, the interaction between these substrates significantly alters the quality and usability of the

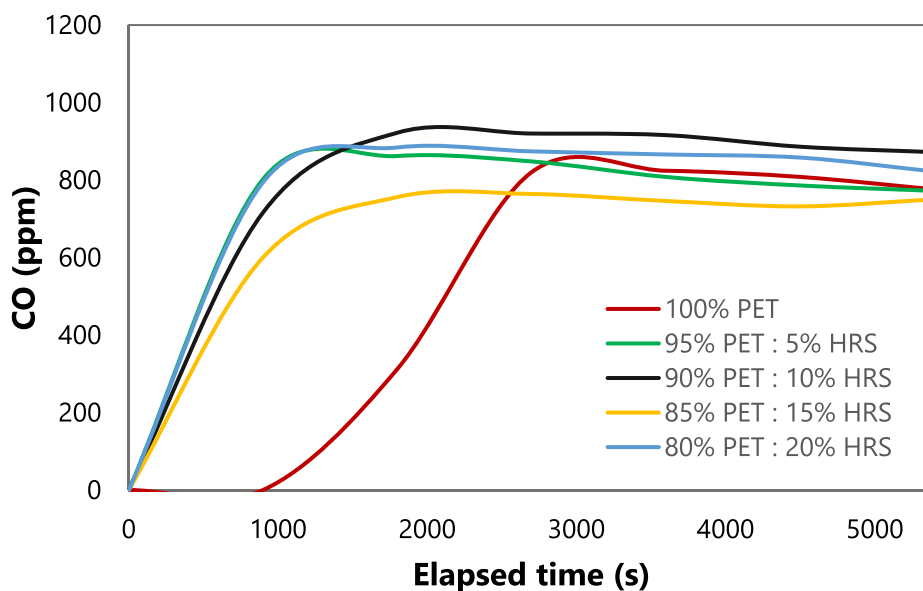


Fig. 8. CO of gas yields produced in elapsed time.

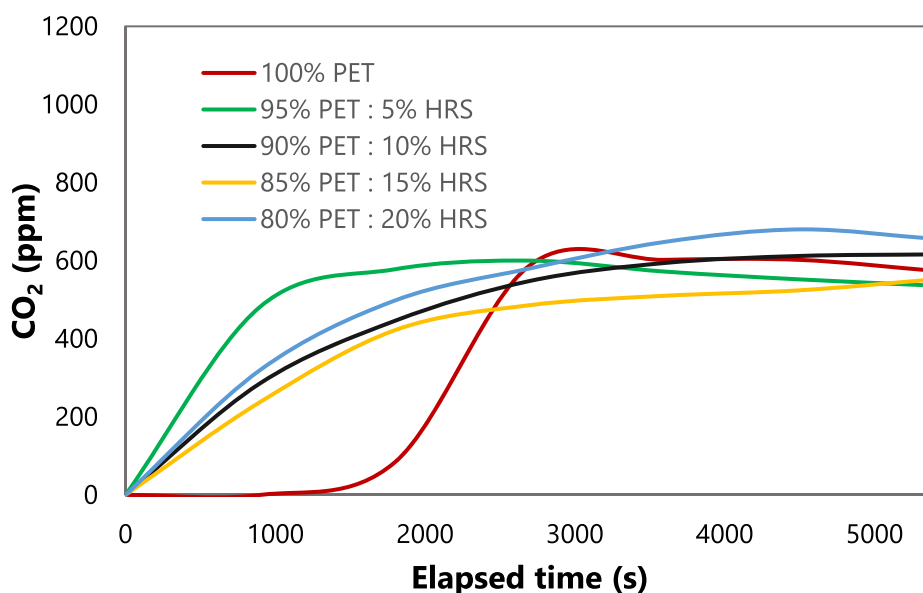
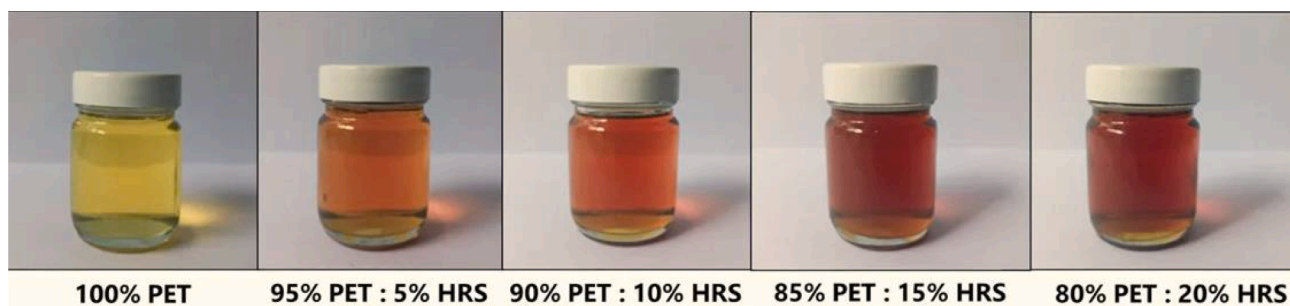
Fig. 9. CO₂ produced in elapsed time.

Fig. 10. Snapshot of oil yields.

derived oil, enhancing its compatibility with commercial fuels.

Then, the formation of liquid yield in PET-HRS pyrolysis, the influence of biomass on chemical processes, and the resulting

physicochemical enhancements contribute to the oil's suitability for various fuel applications.

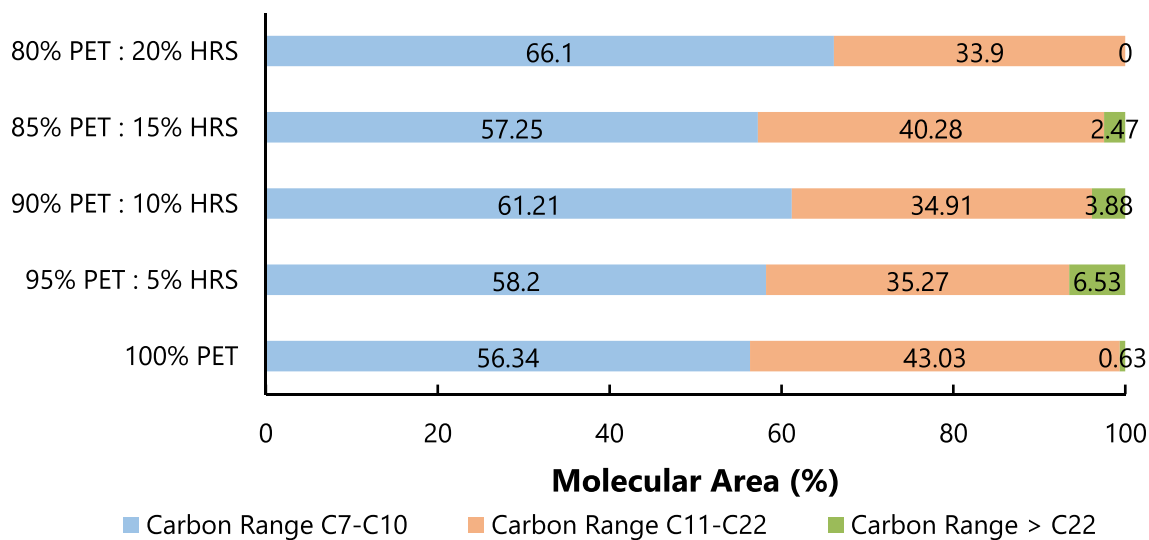


Fig. 11. Oil yield Carbon Range Profile Distribution.

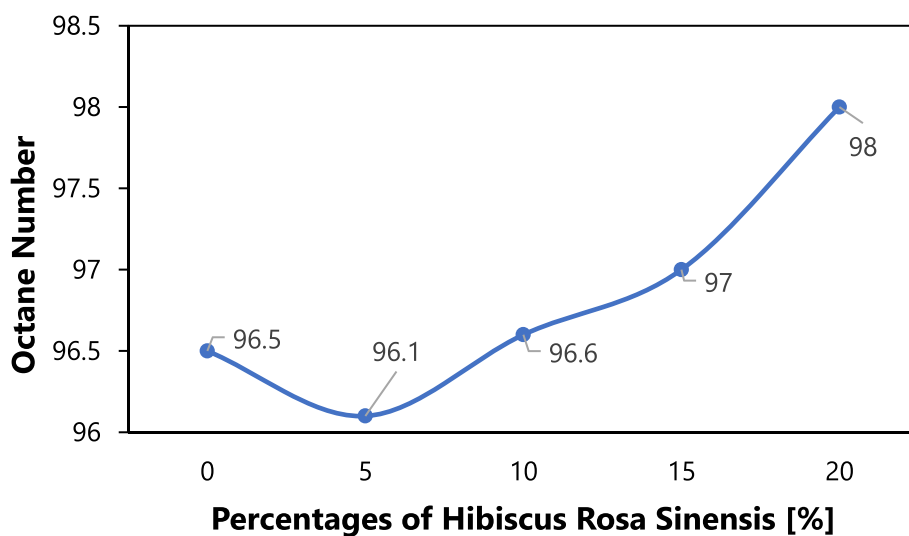


Fig. 12. The improvement of Octane Number of oil yields.

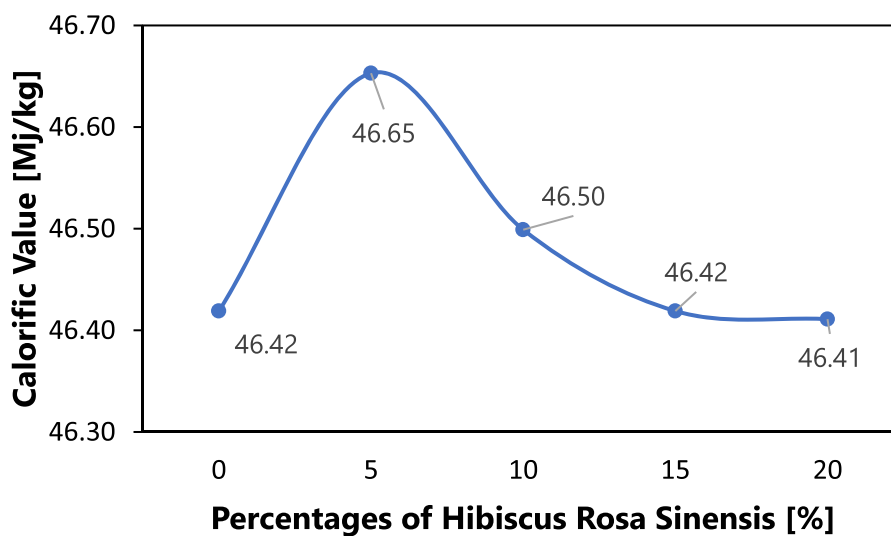


Fig. 13. Calorific Value of PET – HRS in different ratio.

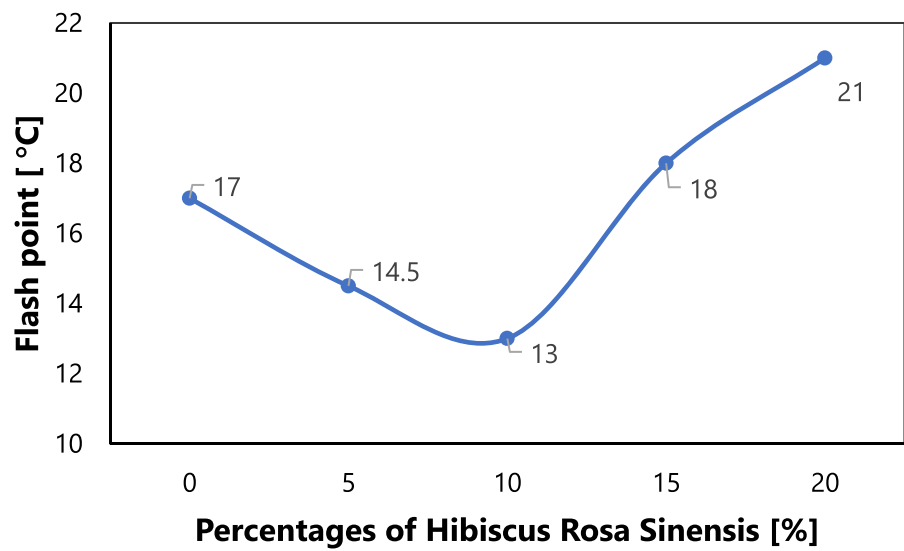


Fig. 14. Flashpoint of PET – HRS in different ratio.

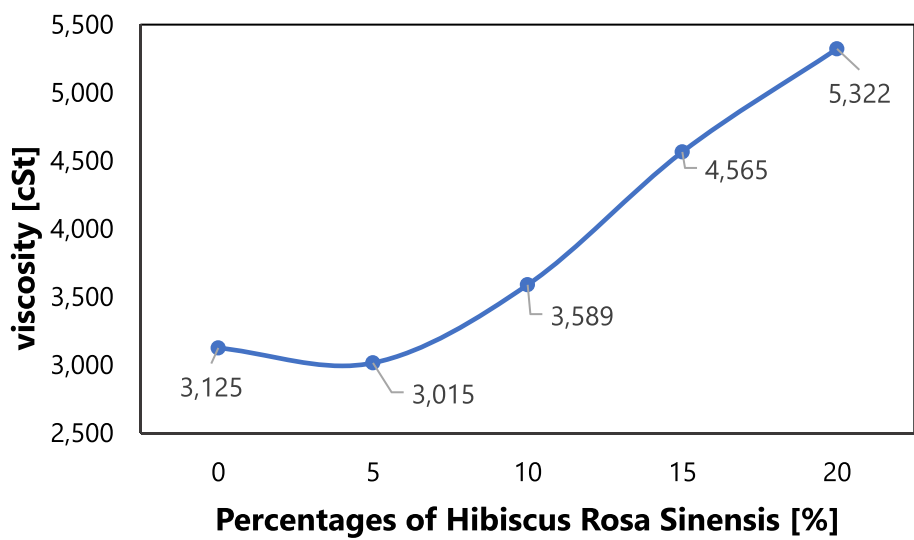


Fig. 15. Viscosity of PET – HRS in different ratio.

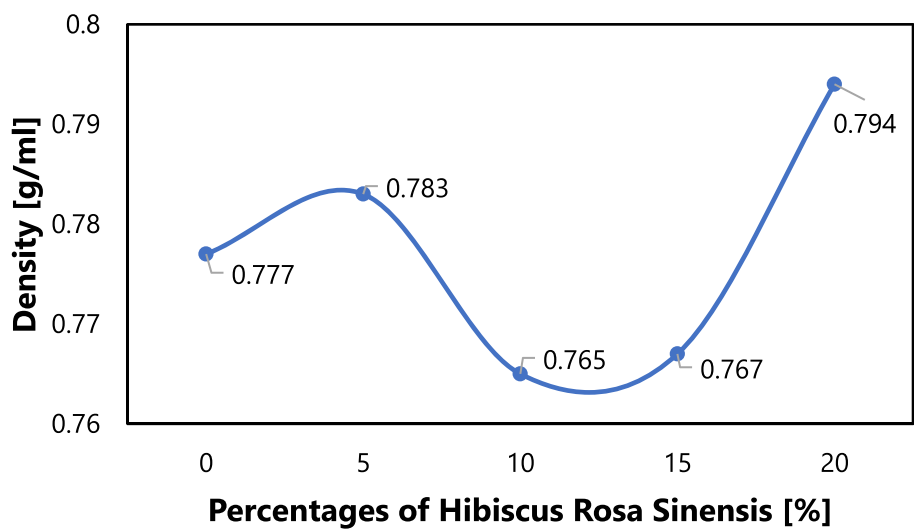


Fig. 16. Density of PET – HRS in different ratio.

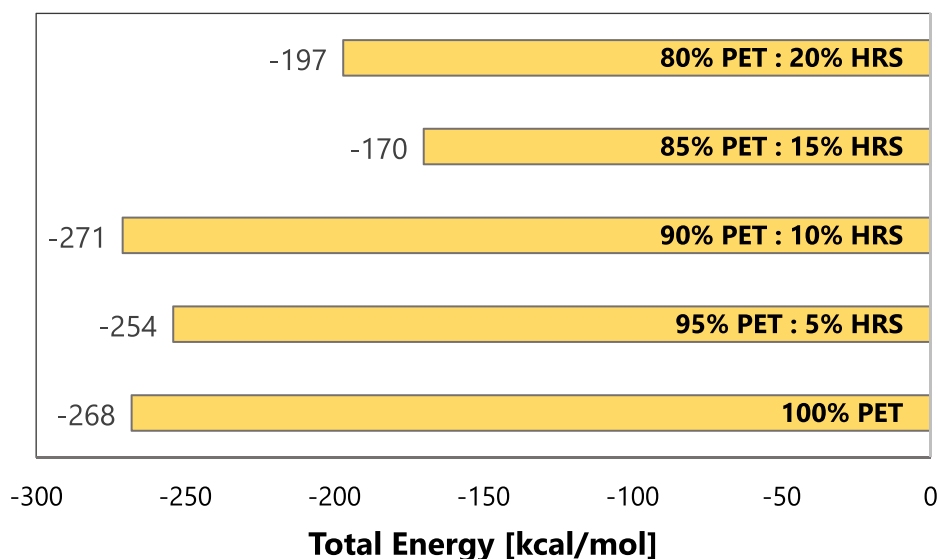


Fig. 17. Total energy profiles of PET-HRS co-pyrolysis at different ratios.

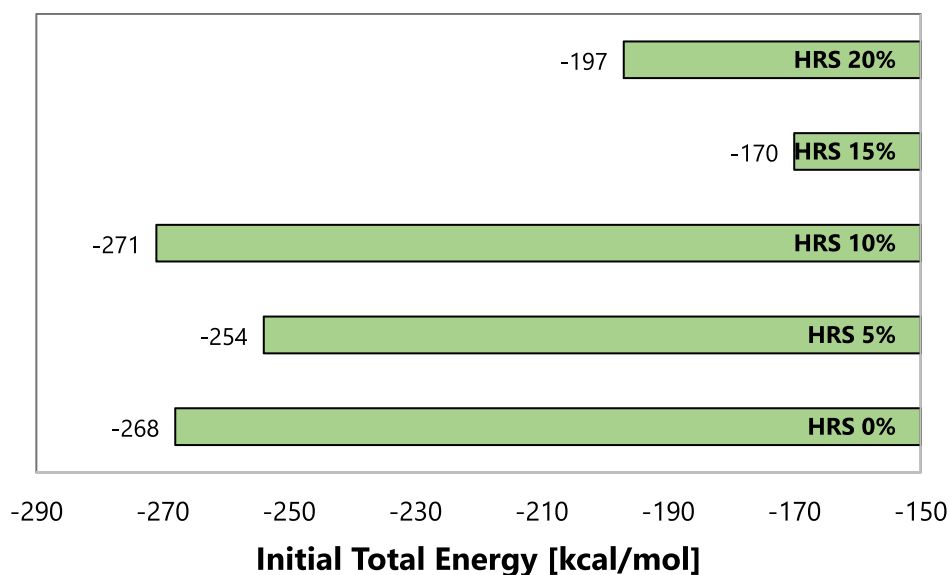


Fig. 18. Initial total energy trends in PET-HRS co-pyrolysis simulations.

3.1.2. Solid yields formation

Fig. 5 illustrates the trade-offs in product distribution that result from HRS co-feeding in PET pyrolysis. The solid yield profile shows a predominant increasing trend across the analysed HRS compositions. Pure PET yielded a substantial solid yield of 35 g (7 % of yields); however, the addition of HRS, even at a 5 % concentration, significantly reduced the solid output to 31 g (6,2 % of yields). As the HRS fractions increased, solid yields consistently rose, reaching 32 g (6,4 % of yields) at 10 % HRS, 33 g (6,6 % of yields) at 15 % HRS, and peaking at 39 g (7,8 % of yields) for the 80 % PET: 20 % HRS blend. This continual rise highlights the significant role of HRS biomass in producing solid residues during the co-pyrolysis process.

The increase in solid yield with higher HRS content underscores the impact of biomass on solid product generation. Pure PET only makes 35 g of solid, however, an 80:20 mixture of PET and HRS makes 39 g, which is a huge improvement due to the lignocellulosic nature of HRS. This composition includes fixed carbon and ash components that are more likely to contribute to solid residues during thermal decomposition at 350 °C. Increased solid yields were observed when PET and HRS were

heated. This was due to the significant role of HRS's lignocellulosic content. HRS comprises fixed carbon and ash constituents that exhibit greater resistance to thermal degradation than pure PET. During pyrolysis, HRS generates oxygenated molecules, including hydroxyl and carbonyl groups, which facilitate the production of solid residues.

This occurs because oxygenated chemicals typically show varying thermal stabilities and frequently produce solid residues upon pyrolysis. Moreover, HyperChem simulations indicate an elevation in total energy and molecule polarization inside the mixture including HRS. The presence of these polar functional groups enhances the polarization of the pyrolysis products and alters their dipole moment, hence influencing the course of the chemical reaction upon heating. The integration of HRS in the PET pyrolysis process increases solid yields by generating supplementary solid components from the degradation of HRS lignocellulosic compound, hence complicating the process and improving the characteristics and overall pyrolysis yields.

Besides, the elevated solid yield corresponds with anticipated biomass behaviour, as thermal degradation processes often produce carbon-dense residues (Romero et al., 2023). The integration of HRS into

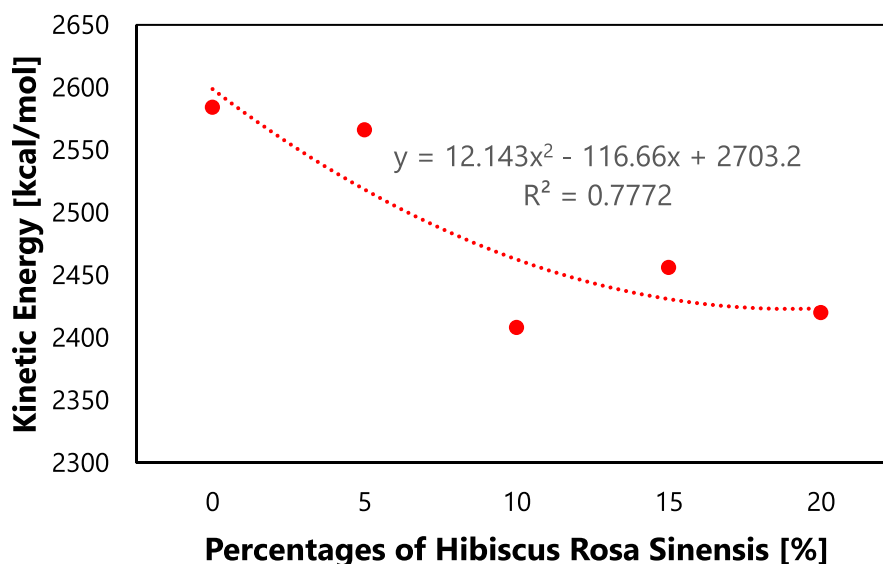


Fig. 19. Kinetic energy dynamics during PET-HRS co-pyrolysis at 350 °C.

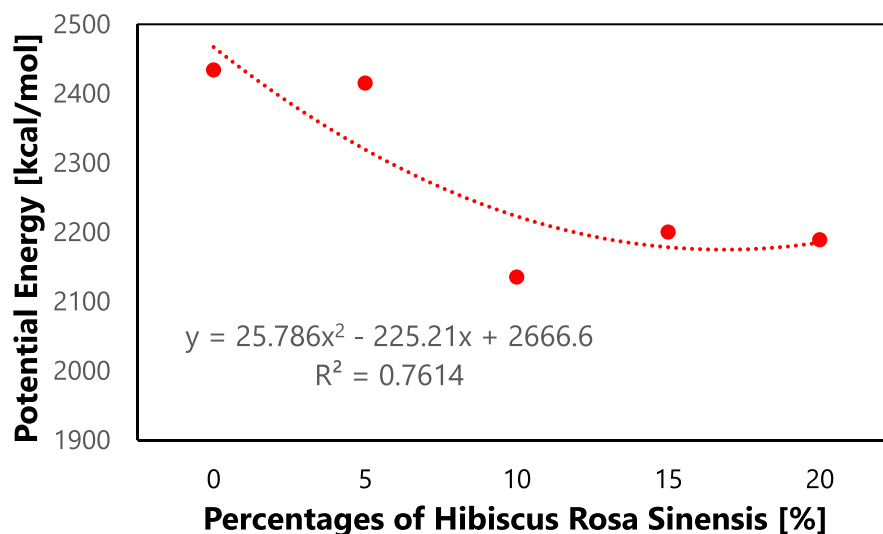


Fig. 20. Potential energy landscape of PET-HRS co-pyrolysis at 350 °C.

the PET feedstock significantly increases solid yield formation during co-pyrolysis due to the inherent char-forming properties of lignin, hemicellulose, and cellulose found in HRS. During thermal degradation, these complex carbohydrates and aromatic polymers quickly contribute to the solid fraction, with their contribution increasing as HRS concentration rises.

It is also expected that interactions between PET and HRS pyrolysis products may play a secondary role. Upon release from HRS, volatile matters can interact with PET-derived fragments in condensation and polymerization processes, resulting in more complex, carbon-rich structures that contribute to enhanced solid yield production.

The pyrolysis temperature of 350 °C employed in this investigation is insufficient for the complete decomposition of HRS. The pyrolysis temperature is sufficient to initiate the degradation of PET, however inadequate to entirely dismantle the molecular structures of HRS biomass, including cellulose and lignin. Another research suggests that significant decomposition of these components typically requires pyrolysis temperatures above 350 °C, with maximum degradation rates observed over 400 °C for lignin

The minimal heat to HRS at 350 °C validates the hypothesis that it

has a catalytic function in the co-pyrolysis of PET and HRS. Rather than serving as the primary substance undergoing significant alterations, HRS appears to control the PET degradation process by functioning as a catalyst. Bioactive substances in HRS, although present in limited quantities, substantially affect PET degradation pathways at this temperature, including oxygenated molecules within phenolic structures (Abate and Belay, 2022). These compounds can interact with PET molecules to facilitate the cleavage of carbon chains and modify product selectivity while little degrading the HRS compounds. The mechanistic specifics of these interactions are further examined in the HyperChem simulation results.

In line with the solid yield trend, which shows a rise with HRS addition, it is important to note that this increase is not solely due to HRS decomposition into solid yield. Various factors contribute to the increased solid yield: (1) a minor contribution from HRS components undergoing initial degradation to generate solid residues at 350 °C, (2) potential synergistic interactions between the decomposition yields of PET and HRS that facilitate solid formation pathways, and (3) the catalytic effect of HRS compounds, which may inadvertently convert a greater fraction of PET fragments into denser, carbon-rich structures

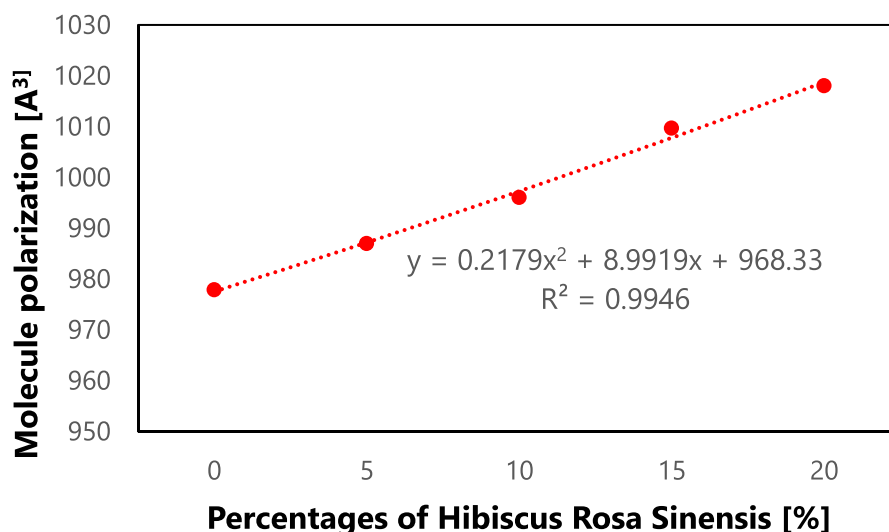


Fig. 21. Molecular polarization of yields from PET-HRS co-pyrolysis.

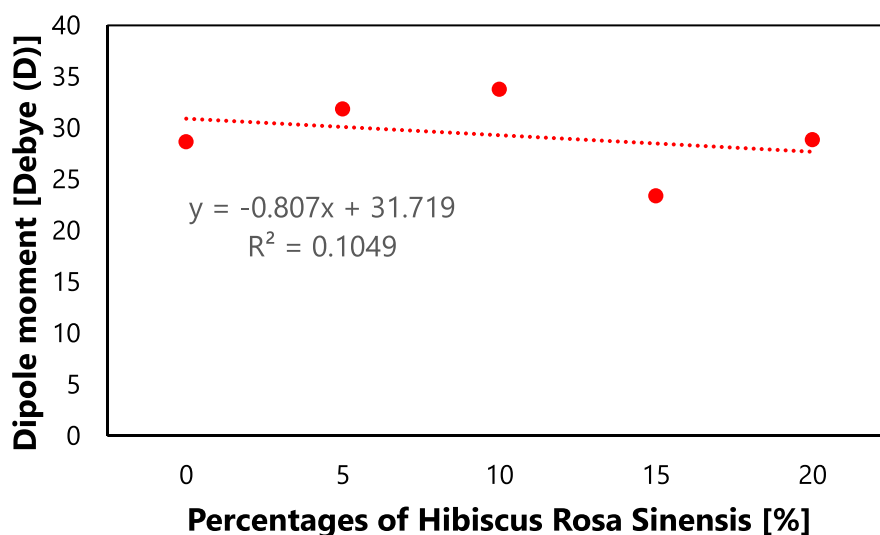


Fig. 22. Dipole moment variations in PET-HRS co-pyrolysis yields.

that accumulate as char, while still aiming to maximize oil yield (Chaturvedi et al., 2024).

3.1.3. Gas yields formation

The gaseous product yields depicted in Fig. 5 indicate that the addition of HRS during PET co-pyrolysis results in a non-linear trend. The pyrolysis of pure PET (100 % PET) yielded the lowest gaseous output at 75 g (15 % of yields). The initial integration of HRS into the feedstock structure resulted in a significant improvement in gas yield. The gaseous yield for the 95 % PET and 5 % HRS mixture increased to 87 g (17,4 % of yields), demonstrating the advantageous impact of a slight number of HRS on gas production.

The increase in gaseous product yield continued with higher HRS, reaching the peak at the 80 % PET: 20 % HRS blend, which produced the maximum gas output of 168 g (33,6 % of yields). The peak value indicates an ideal synergistic effect at this particular PET-to-HRS ratio, hence optimizing the production of gaseous products. The non-monotonic behaviour of gaseous product yields suggests a complex interaction of reaction pathways and possible catalytic influences. The preliminary increase in gas output with minimal HRS integration (up to 20 %) can be explained to various variables. Initially, volatile matter

emitted during the early phases of HRS biomass pyrolysis, even at 350 °C, might improve the total gaseous product yield. Secondly, bioactive chemicals in HRS may catalytically promote secondary cracking events of primary pyrolysis vapours, resulting in the production of lighter gaseous products from both PET and HRS-derived intermediates.

The pyrolysis of the 80 % PET: 20 % HRS can primarily be attributed to enhanced gas yields resulting from the direct pyrolysis of cellulose, hemicellulose, and lignin present in the HRS. These components are inclined to generate higher proportions of solid and gas yields compared to liquid oil yields. Consequently, the increased solid yield in the 80:20 mixture reflects the carbonization of HRS, along with gas yields derived from the decomposition of these compounds, which release important gases such as CO, CO₂, H₂, CH₄ and light hydrocarbons. Additionally, the substantial integration of HRS at this ratio may shift the overall pyrolysis pathways, diverting product selectivity away from liquid oil formation.

The findings align with understanding concerning the molecular characteristics and energy dynamics related to the co-pyrolysis of PET and HRS. The changes in product distribution are affected by both the content of HRS and the changes made in the molecular structure of the pyrolysis products, as demonstrated by HyperChem simulation results. The presence of flavonoids and antioxidant chemicals in HRS is thought

to have catalytic effects in PET co-pyrolysis. Nonetheless, their effectiveness seems to be dependent upon concentration. At 80 % HRS loading, a potential "catalyst overload" effect may arise, whereby these bioactive compounds, together with complicated biomass degradation products, may not predominantly facilitate oil synthesis pathways. The reaction routes are directed towards increased solid and gas yields, influenced by the fundamental pyrolysis properties of the predominant HRS component.

This investigation highlights the importance of adjusting PET-HRS blend ratios. This optimization facilitates the strategic management of pyrolysis product yields, resulting in the achievement of desired distributions. The notable rise in syngas production at elevated HRS ratios corresponds with previous studies, wherein the presence of HRS facilitates the creation of crucial gaseous compounds vital for energy applications. Additionally, the relationships illustrate how the interactions between PET and HRS affect molecular characteristics, hence strengthening the possibility of this biomass integration in developing sustainable energy solutions (Tao et al., 2022).

3.2. Pyrolysis yields for potential fuels

3.2.1. Gas yields

This study investigates the types and yields of gases produced during the pyrolysis of PET and HRS. Particularly, the addition of HRS significantly increases the production of methane (CH_4), hydrogen (H_2), and carbon monoxide (CO). Specifically, hydrogen production saw an increase of 84.54 ppm, methane increased by 86.46 ppm, and carbon monoxide rose by 40.42 ppm compared to pure PET pyrolysis.

Flavonoids and oxygenate compounds in HRS likely act as reactive intermediates, promoting hydrogen transfer and enhancing the cracking of long-chain hydrocarbons from PET. The pyrolysis of the 80 % PET: 20 % HRS yields a notable product distribution, with the highest solid fraction of 39 g (7.8 % of yields) observed across all tested compositions. This solid yield marks a significant increase from the 35 g (7.00 % of yields) from pure PET. Concurrently, this mixture also exhibits the highest gaseous yield of 168 g (33.60 % of yields), while unexpectedly resulting in the lowest liquid oil yield of 293 g (58.60 % of yields) compared to other blends, particularly the peak yield from the 90 % PET: 10 % HRS ratio, which was 393 g (78.60 % of yields).

This deviation in product trends can be attributed to several molecular mechanisms, particularly the increased contribution of HRS. At higher HRS, the direct pyrolysis of cellulose, hemicellulose, and lignin becomes more prominent, leading to higher proportions of solid and gaseous products relative to liquid oil. Consequently, the enhanced solid yield in the 80:20 mixture reflects the effective carbonization of HRS, while the increased gas yield results from the decomposition of these components, releasing gases such as CO, CO_2 , H_2 , CH_4 , and light hydrocarbons.

The addition of 20 % HRS is believed to alter the overall pyrolysis pathways, resulting in a deviation of product selectivity from liquid oil production. The reactive components generated upon heating HRS may interact with the degradation products of PET, hence accelerating the condensation and polymerization activities. This synergy may result in the generation of larger, more complex molecules that accumulate in the solid phase, hence reducing the fraction of liquid oil products. Higher HRS concentrations may induce increased secondary cracking reactions, potentially elucidating the sustained high gas yields despite not having attained their maximum level.

The catalytic effects of flavonoids and antioxidants in HRS appear to influence these pyrolysis yields, although their effectiveness is likely concentration-dependent. At an 20 % HRS, a potential "catalyst overload" effect may occur, shifting the focus away from promoting oil formation pathways toward enhanced solid and gas production. This emphasizes the importance of optimizing PET-HRS blend ratios for strategically manipulating pyrolysis product yields and achieving desirable distributions for hydrogen and methane production.

3.2.1.1. Methane (CH_4) and hydrogen (H_2). The yields of methane and hydrogen demonstrated significant increases with the addition of HRS, as shown in Figs. 6, 7. For instance, the production of methane increases by 118.6 ppm with a 95 % PET: 5 % HRS and reaches an increase of 88.60 ppm with the 80 % PET: 20 % HRS mixture. Similarly, hydrogen production shows an increase of 113.7 ppm with the 95 % PET: 5 % HRS blend and 83.41 ppm with the 80 % PET: 20 % HRS mix. Overall, the average increases in methane and hydrogen production are 86.46 ppm and 84.54 ppm, respectively, when PET is combined with HRS compared to pure PET pyrolysis.

These enhancements are linked to the catalytic effects of antioxidant and flavonoid compounds present in HRS, which promote bond cleavage in PET's long-chain hydrocarbons and facilitate hydrogen transfer reactions. Additionally, the oxygenated compounds in HRS likely enhance reforming reactions that convert CO and hydrocarbons into methane and hydrogen. Such interactions improve the crucial hydrogen-to-carbon monoxide (H_2/CO) ratio, which is essential for applications in fuel cells and chemical synthesis.

The fast generation of CH_4 and H_2 with HRS addition also reduces the time required to reach steady-state gas production, a vital aspect for industrial pyrolysis reactors. The higher throughput and improved yields of hydrogen and methane make co-pyrolysis a promising option for renewable energy systems, ultimately boosting process efficiency and economic viability.

3.2.1.2. Carbon monoxide (CO) and carbon dioxide (CO_2). Carbon monoxide and carbon dioxide production exhibited nuanced trends with varying HRS as illustrated in Figs. 8, 9. The increase in carbon monoxide production observed from the pyrolysis of pure PET compared to HRS shows significant rises, with increments of 40.51 ppm for the 95 % PET: 5 % HRS, 47.53 ppm for the 90 % PET: 10 % HRS, and 49.08 ppm for the 80 % PET: 20 % HRS. Meanwhile, carbon dioxide production also increases, albeit more modestly, with minimal fluctuations at specific HRS ratios. For instance, the 95 % PET: 5 % HRS shows a slight increase of 34.97 ppm, and the 80 % PET: 20 % HRS reports a 37.54 ppm increase.

Interestingly, carbon dioxide production dipped slightly with the 10 % and 15 % HRS ratios, suggesting potential competing reaction pathways where intermediate oxygenated compounds engage with radicals and hydrocarbons, temporarily suppressing CO_2 formation. At higher HRS levels, the excess Oxygen from biomass likely promotes oxidative decomposition, leading to increased CO_2 output.

These trends demonstrate the significant role of biomass in modulating the gas composition during pyrolysis. Although higher CO_2 yields raise environmental considerations, they are somewhat offset by the carbon-neutral nature of biomass, as plants sequester carbon during their growth.

3.2.1.3. Enhanced gas yields in PET-HRS co-pyrolysis. The co-pyrolysis of PET with HRS highlights remarkable shifts in product yields compared to pure PET pyrolysis. With escalating HRS ratios, gas yields increase substantially, reaching 168 g at the 80 % PET: 20 % HRS, a stark contrast to the 75 g obtained from pure PET. This shift indicates a preference for gaseous product formation due to the synergistic interactions of PET and HRS components that drive the pyrolytic process toward elevated gas production.

The presence of flavonoids in HRS is a crucial factor in this yield transformation. Phytochemical analyses reveal high concentrations of these antioxidant compounds, known for their catalytic activity. It is hypothesized that flavonoids facilitate the cracking and reforming reactions during co-pyrolysis, leading to increased gas yields of CH_4 , H_2 , CO, and CO_2 . The observed correlation between flavonoid content and catalytic activity is promising for biomass utilization in plastic waste valorization, leveraging the inherent catalytic properties of natural compounds.

3.2.2. Oil yields

The physicochemical properties of pyrolysis oil serve as key indicators for its potential as a sustainable alternative fuel. The co-pyrolysis of PET and HRS resulted in significant variations in calorific value, viscosity, density, and flashpoint, reflecting the synergistic effects of the combined feedstock. These changes underscore the influence of HRS content on oil quality, usability, and its compatibility with commercial fuels.

Fig. 10 illustrated visual analysis of the pyrolysis oil across different PET-to-HRS ratios reveals notable differences in colour and viscosity. Oils derived from pure PET exhibited a lighter coloration, resembling conventional gasoline, while those with higher proportions of HRS displayed darker hues similar to diesel fuel. This change suggests alterations in chemical composition, likely influenced by HRS on pyrolysis pathways. The enhanced yield at 90 % PET: 10 % HRS highlights the potential of moderate HRS additions to improve both the effectiveness and sustainability of PET pyrolysis.

Snapshots evidence illustrates a consistent trend: the progressive darkening of pyrolysis oil as HRS content increases. This correlation indicates that the increasing HRS weight ratio directly affects the oil's color, potentially signifying changes in its chemical makeup. Specifically, the shift from a light-yellow hue in the 100 % PET sample to a deep reddish-brown in the 80:20 PET-HRS mixture suggests the formation of chromophoric compounds that absorb light in the visible spectrum, attributed to the thermal decomposition of HRS components.

The consistency of the oil's clarity across samples, despite differing color intensities, implies that the pyrolysis process efficiently converted both PET and HRS into liquid products without significant solid residues. This characteristic is crucial for practical applications, as the absence of particulates simplifies handling and processing. The color variation likely reflects differences in the molecular composition of the oil rather than the presence of impurities. Gas Chromatography-Mass Spectrometry (GC-MS) will be employed to identify specific compounds responsible for these observed color changes and to understand their implications on the oil's properties and potential applications.

The progressive darkening of pyrolysis oil is corroborated by data, demonstrating significant shifts in chemical composition (Calderon-Arrieta et al., 2024). The 100 % PET, characterized by a high olefin content (74.33 %), contributes to its lighter coloration (Tang et al., 2019), as shown in Fig. 10. As the proportion of HRS increases in the feedstock, there is a notable reduction in olefins, along with fluctuations in alkane and aromatic content. The 80:20 PET-HRS blend, which appears darkest, exhibits a substantial reduction in olefins (25.74 %) and a significant increase in aromatics (17.04 %) compared to pure PET. This indicates that HRS thermal decomposition introduces aromatic compounds that contribute to the intensified coloration.

The carbon range data shown in Fig. 11 reveals further insights into the length of the carbon chain within the pyrolysis oil. For the 100 % PET pyrolysis oil, compounds predominantly fell within the C7-C10 (56.34 %) and C11-C22 (43.03 %) ranges, consistent with the thermal breakdown of PET polymer chains. As HRS ratios increase, the length of carbon chain changes notably. In the 80:20 PET-HRS, the proportion of C7-C10 compounds rises to 66.1 %, while C11-C22 compounds decrease to 33.9 %, and compounds over C22 disappear. This trend indicates that HRS contributes to the formation of smaller molecules during pyrolysis, likely due to the decomposing lignocellulosic components of HRS, which yield short-chain compounds such as furans, aldehydes, and carboxylic acids.

The findings underline the significant role that HRS plays in influencing the thermal decomposition pathways of PET, leading to distinct length of carbon chain distributions and chemical compositions in the resulting pyrolysis oils (Baranitharan et al., 2023; Oyedun et al., 2014; Park et al., 2019)

3.2.2.1. Octane number. The experiment results indicated a clear trend

of increasing octane numbers in pyrolysis oil derived from PET with the progressive addition of HRS biomass, as depicted in Fig. 12. Specifically, the octane number rises from 96.5 RON for pure PET to 98.0 RON at 80 %: 20 % of PET - HRS ratio, outstanding many commercial fuels in quality. This improvement highlights the significant synergistic effect of HRS during the pyrolysis process, promoting the development of fuel components with superior anti-knocking properties.

At lower concentrations (95 % PET: 5 % HRS), a slight reduction in octane number may suggest that this initial HRS concentration is not sufficiently effective in catalyzing the desired transformations, potentially leading to the formation of intermediate products that negatively affect the octane rating. However, once this threshold is surpassed, HRS progressively drives the reaction toward higher-octane components.

HyperChem simulations further elucidate the structural and energetic changes accompanying HRS incorporation. These simulation results indicate an increase in the abundance of branched and shorter-chain hydrocarbons, which are inherently more resistant to auto-ignition, thereby contributing to the higher-octane numbers observed. The increase in polarizability with elevated HRS ratios suggests enhanced intermolecular interactions that may improve fuel vaporization and combustion efficiency. Additionally, fluctuations in dipole moments indicate changes in molecular polarity, which could influence the fuel's ability to form homogeneous mixtures with air—an essential factor for efficient combustion.

Kinetic energy calculations further substantiate the role of HRS as a reactive agent. The heightened kinetic energy of pyrolysis products at increased HRS concentrations indicates the presence of reactive species, including oxygenated compounds and free radicals derived from HRS. These species aid in promoting more complete combustion, reducing knocking, and enhancing the overall octane number.

Bonding energy analyses reveal that HRS significantly alters the pathways of bond cleavage and formation during pyrolysis. This alteration favors the preferential formation of higher-octane components, affirming HRS's catalytic role in optimizing the composition of pyrolysis products.

The integration of both experimental data and computational findings illustrates how HRS co-feeding considerably enhances the octane number of PET pyrolysis oil. Through a combination of structural and energetic modifications, HRS encourages the formation of branched and short-chain hydrocarbons, enhances intermolecular interactions, and drives a shift towards more reactive species, ultimately producing a fuel with improved anti-knocking characteristics. This study also emphasizes the viability of using biomass co-feeding as a strategy to enhance the quality of pyrolysis oil generated from waste plastics, thus contributing to the development of sustainable, high-performance fuels.

3.2.2.2. Calorific value. Fig. 13 shows the experimental results demonstrate that co-pyrolysis of PET with HRS maintains a high heating value (HHV) in the resulting pyrolysis oil, with peak values observed at lower HRS concentrations. Specifically, the HHV reaches 46.653 MJ/kg at the 95 % PET: 5 % HRS, slightly outpacing the HHV of 46.419 MJ/kg from pure PET. This consistency in HHV—despite increasing HRS content—highlights the potential of HRS as a viable co-feedstock without markedly compromising the energy density of the pyrolysis oil.

The slight enhancement noted at lower HRS concentrations may be attributed to the synergistic interaction between carbon-rich PET and the hydrogen-rich components of HRS, resulting in a favorable balance of hydrocarbons and oxygenated compounds. The high HHV values—consistently exceeding 40 MJ/kg—position the produced pyrolysis oil as a feasible substitute for conventional fossil fuels such as diesel and gasoline, particularly for the 95:5 and 90:10 PET - HRS blends, which demonstrate an optimal balance between substantial energy content and application potential.

HyperChem simulation results support the notion that the introduction of HRS alters the molecular composition and energy distribution

of the pyrolysis products, thereby maintaining and slightly enhancing the calorific value. The simulations reveal that lower HRS concentrations favour the formation of hydrocarbons with higher hydrogen-to-carbon ratios, which directly contribute to the increased HHV. Additionally, while HRS-derived oxygenated compounds may reduce HHV, their impact is balanced by the generation of highly energetic short-chain hydrocarbons.

Specifically, bonding energy analyses show that HRS facilitates specific bond cleavage and formation pathways, leading to a higher yield of energy-dense molecules. Kinetic energy calculations reinforce the increased reactivity of the pyrolysis products, suggesting that HRS enhances the reactions responsible for releasing energy during combustion. Polarizability analyses demonstrate that HRS improves intermolecular interactions, which may also facilitate energy transfer during combustion.

The integration of experimental findings with computational insights provides a holistic understanding of the mechanisms by which HRS enhances the HHV of PET pyrolysis oil. The simulations confirm that HRS acts as a co-catalyst, fostering the production of energetically favourable hydrocarbon species and ensuring that the resulting oil remains competitive with traditional fuels. These insights emphasize the feasibility of employing HRS co-pyrolysis to produce high-quality fuels from plastic waste, thus advancing sustainable energy solutions.

3.2.2.3. Flashpoint. The experimental analysis of flashpoint—a crucial safety parameter—reveals a complex relationship with HRS content in PET co-pyrolysis, shown in Fig. 14. Initial results demonstrate a decline in flashpoint with moderate HRS additions (14.5 °C at 95 % PET: 5 % HRS and 13 °C at 905 PET: 10 % HRS), indicating an increase in lighter volatile compounds. However, at higher HRS concentrations (20 %), the flashpoint rebounds to 21 °C, suggesting a significant influence of HRS loading on the oil's volatility and ignition characteristics. The initial decrease in flashpoint is likely due to the introduction of lighter, more volatile compounds released from the decomposition of HRS components. In contrast, the increase observed at higher HRS concentrations may be attributed to the formation of heavier, less volatile compounds, potentially including higher molecular weight aromatics.

These variations in flashpoint underscore the need to consider the intended applications of the pyrolysis oil. Lower flashpoints can be advantageous for applications requiring easy ignition, such as in industrial burners. Conversely, higher flashpoints are essential for enhancing safety during storage and transportation, thereby reducing the risk of accidental ignition. Consequently, optimizing the HRS content becomes critical to modify the flashpoint for specific application requirements, including blending with conventional fuels.

HyperChem simulation results reveal that the observed changes in flashpoint are directly related to the molecular composition and volatility of the pyrolysis products, which are modulated by the HRS content. Molecular design analyses indicate that lower HRS ratios result in a higher proportion of short-chain, volatile hydrocarbons, contributing to the decreased flashpoint. In contrast, at higher HRS concentrations, the presence of larger, more complex aromatic compounds leads to an increase in flashpoint due to their reduced volatility.

Additionally, dipole moment analyses suggest variations in the polarity of the pyrolysis products, which may further influence their volatility. Increased polarity enhances intermolecular interactions, potentially reducing volatility and increasing flashpoint. Polarizability analyses also affirm this finding, showing modifications in intermolecular forces that affect evaporation rates. Kinetic energy calculations provide insights into the reactivity of the pyrolysis products, indicating that higher HRS concentrations may lead to the formation of more stable compounds, thereby contributing to the elevated flashpoint.

The comprehensive integration of experimental data and computational findings sheds light on the mechanisms governing flashpoint modulation in PET pyrolysis oil through HRS co-feeding. The simulation

results verified that HRS significantly alters the molecular composition and volatility of the pyrolysis products, allowing for made-to-order control over flashpoint characteristics. This information highlights the potential of biomass co-pyrolysis to produce pyrolysis oil with desired safety attributes, supporting the development of safer and more versatile biofuel alternatives.

3.2.2.4. Viscosity and density. The experimental results indicate a strong correlation between HRS content and the viscosity (Fig. 15) and density (Fig. 16) in PET of pyrolysis oil yields. Specifically, both viscosity and density increased significantly with rising HRS ratios. For instance, viscosity increased from 3.125 cSt for pure PET to 5.322 cSt at the 80 % PET: 20 % HRS blend, while density rose from 0.765 g/ml to 0.794 g/ml over the same range. These enhancements suggest compositional changes within the pyrolysis oil, largely attributed to the introduction of polymeric fragments and phenolic compounds derived from HRS. Heavier molecules are known to enhance intermolecular interactions, hence leading to the observed increases in viscosity. The higher density at increasing HRS ratios reflects a more compact molecular structure due to a greater presence of aromatic and oxygenated fractions.

These modifications in viscosity and density carry important implications for the storage, transport, and combustion characteristics of the pyrolysis oil. While the inclusion of HRS improves certain fuel properties, the observed increases in viscosity and density suggest that excessive biomass content could necessitate additional refining processes to ensure compatibility with combustion engines. Thus, it is crucial to optimize the PET-HRS ratio to achieve a balance between enhanced fuel properties and operational feasibility.

HyperChem simulation results further illustrate that the increases in viscosity and density are closely tied to the molecular composition and intermolecular interactions of the pyrolysis products influenced by HRS content. Such analyses demonstrate that higher HRS ratios tend to foster the formation of larger, more complex molecules, including phenolic compounds and polymeric fragments, which contribute to the increased viscosity and density of the resulting oil.

Intermolecular interaction analyses, derived from polarizability and dipole moment calculations, indicate that the presence of oxygenated compounds and aromatic structures from HRS enhances these intermolecular forces, leading to increased viscosity. Density calculations based on simulated molecular configurations confirm experimental trends, showing a higher packing density of molecules at elevated HRS ratios, which contributes to the observed increase in bulk density.

Integrating experimental and computational insights provides a thorough understanding of the mechanisms governing viscosity and density changes in PET pyrolysis oil due to HRS co-feeding. This research underscores the potential of biomass co-pyrolysis to produce pyrolysis oil with optimized flow characteristics, fostering the development of versatile biofuel alternatives.

3.3. Effect of PET and HRS co-pyrolysis in molecular properties

The simulations provide valuable insights into the energy dynamics, molecular properties, and reaction mechanisms involved in the pyrolysis process. The analysis encompasses several key parameters; molecular structure, polarizability, and energy dynamics including total energy, initial total energy, pyrolysis kinetic energy, pyrolysis potential energy, molecular polarization, and dipole moment, across varying PET and HRS ratios. It shows from Figs. 17, 18, 19, 20, 21, 22. The results highlight the significant influence of HRS addition on the energy requirements and product characteristics of PET pyrolysis. Specifically, the simulations reveal that pure PET pyrolysis exhibits the lowest total energy, indicating the formation of the most stable products (Fig. 17). However, the introduction of HRS leads to a progressive increase in total energy, suggesting a decrease in product stability. This trend is

attributed to the complex molecular structure of HRS, which comprises cellulose, hemicellulose, and lignin, resulting in the generation of oxygenated compounds that are generally less stable than the hydrocarbon products derived from PET pyrolysis. The analysis of initial total energy further supports these findings, demonstrating a similar trend of increasing energy with increasing HRS content (Fig. 18).

Furthermore, the kinetic and potential energy profiles of the pyrolysis process are significantly affected by the PET:HRS ratio, shown in Figs. 19, 20. The simulation results indicated that pure PET pyrolysis requires the highest kinetic and potential energy inputs, implying a higher energy barrier for the initiation of the reaction. Conversely, the addition of HRS reduces both the kinetic and potential energy requirements, suggesting that HRS facilitates the pyrolysis process by lowering the activation energy. However, this facilitation comes at the cost of product stability, as evidenced by the higher total energy values. The molecular properties of the pyrolysis products are also influenced by the PET-HRS ratio. The simulation results reveal a clear trend of increasing molecular polarization with increasing HRS content, as depicted in Fig. 21. This observation is attributed to the presence of polar functional groups in HRS-derived compounds, such as hydroxyl groups, which enhance the overall polarity of the pyrolysis products. The increased polarity may have implications for the reactivity and potential applications of the products. In contrast, the dipole moment analysis does not exhibit a clear correlation with the PET-HRS ratio, shown in Fig. 22. The dipole moment values fluctuate irregularly, suggesting that the polar nature of the pyrolysis products is influenced by a complex interplay of various factors, including the specific molecular structures of the products and their interactions.

The simulation results provide a comprehensive understanding of the pyrolysis behaviour of PET and HRS blends. The results demonstrate that HRS addition significantly alters the energy dynamics, molecular properties, and product characteristics of PET pyrolysis. While HRS facilitates the pyrolysis process by reducing the kinetic and potential energy requirements, it also leads to the formation of less stable, more polar products.

3.3.1. Electrostatic force distribution and molecular polarity in PET-HRS pyrolysis products

The molecular visualization of post-pyrolysis electrostatic forces across varying PET-HRS ratios reveals a significant modulation of charge distribution and molecular polarity as a function of HRS content. It is depicted in Fig. 23. In pure PET pyrolysis (100 % PET), the electrostatic contours exhibit a dispersed and low-intensity pattern, indicative of predominantly non-polar species such as hydrocarbons. Conversely, the introduction of 95 % PET: 5 % HRS results in a notable concentration and intensification of electrostatic contours, suggesting the formation of more polar molecular species.

This trend is further substantiated in blends with higher HRS ratios (90 % PET: 10 % HRS, 85 % PET: 15 % HRS, and 80 % PET: 20 % HRS), where a progressive increase in contour concentration and intensity is observed with increasing HRS content. This observation aligns with

previous findings from FTIR analysis and HyperChem simulations, which demonstrated an enrichment of oxygenated compounds upon HRS addition. These oxygenates, including aldehydes, ketones, carboxylic acids, and phenols (Fig. 24), are characterized by polar functional groups, thereby contributing to the enhanced molecular polarity.

The observed modulation of electrostatic forces carries significant implications for the physicochemical properties and potential applications of the pyrolysis products. Products exhibiting higher electrostatic forces (high polarity) are likely to be more amenable to applications requiring strong intermolecular interactions, such as solvents or chemical feedstocks. Conversely, products with lower electrostatic forces (low polarity) may be better suited for fuel applications (Oyedun et al., 2014).

The electrostatic force visualization provides compelling evidence that HRS addition significantly alters the molecular composition and polarity of PET pyrolysis products. The observed increase in molecular polarity with increasing HRS content underscores the formation of oxygenated compounds, which ultimately dictates the potential applications of the pyrolysis products.

3.4. Effect of PET – HRS pyrolysis on molecular structure

The FTIR analysis reveals significant alterations in the molecular structure of pyrolysis products as the HRS ratio increases within the PET and HRS mixture, as shown in Fig. 25. The FTIR spectrum of pure PET (100 % PET) exhibits characteristic peaks corresponding to ester functional groups ($\text{C}=\text{O}$ stretching around 1720 cm^{-1}), aromatic rings ($\text{C}-\text{H}$ bending around $700\text{--}900\text{ cm}^{-1}$), and aliphatic chains ($\text{C}-\text{H}$ stretching around $2850\text{--}2950\text{ cm}^{-1}$). Upon the introduction of HRS, the spectra demonstrate the emergence of novel peaks or changes in the intensity of existing peaks, indicative of the formation of additional functional groups. These peaks are predominantly attributed to oxygenated compounds derived from HRS pyrolysis, such as hydroxyl groups ($-\text{OH}$ stretching around $3300\text{--}3400\text{ cm}^{-1}$), carbonyl groups ($\text{C}=\text{O}$ stretching around $1650\text{--}1750\text{ cm}^{-1}$), and ether groups ($\text{C}-\text{O}$ stretching around $1000\text{--}1200\text{ cm}^{-1}$). This transformation signifies that HRS contributes to the complexity of the pyrolysis products by generating more polar and Oxygen-containing compounds.

These observed changes in the FTIR spectra agree with the HyperChem simulation results, which demonstrated an increase in total energy and molecular polarization with the addition of HRS. The appearance of oxygenated functional groups from HRS can elucidate the elevated total energy, as these compounds are generally less stable compared to the hydrocarbon products from PET. Furthermore, the presence of polar functional groups like hydroxyl and carbonyl enhances the molecular polarity of the pyrolysis products. These alterations may also influence the molecular dipole moment, although the specific relationship might be intricate and subject to other factors. Overall, the FTIR analysis provides experimental evidence that validates the HyperChem simulation findings, affirming that HRS addition substantially modifies the composition and properties of PET pyrolysis products.

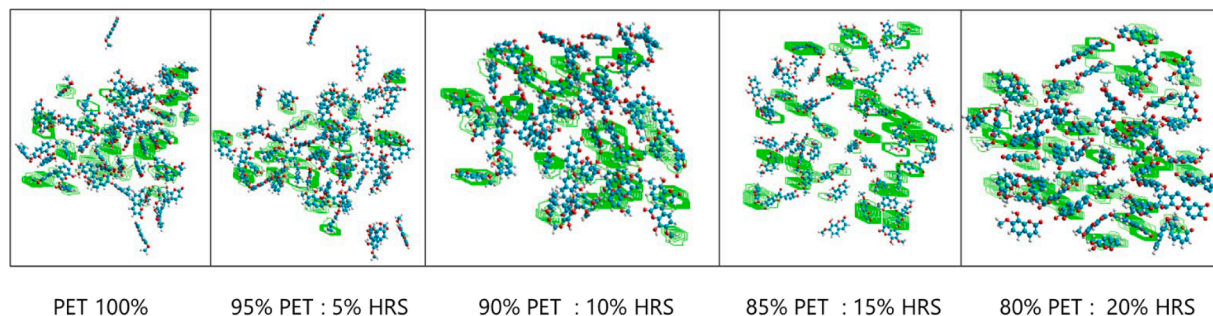


Fig. 23. Electrostatic forces in various PET-HRS ratios.

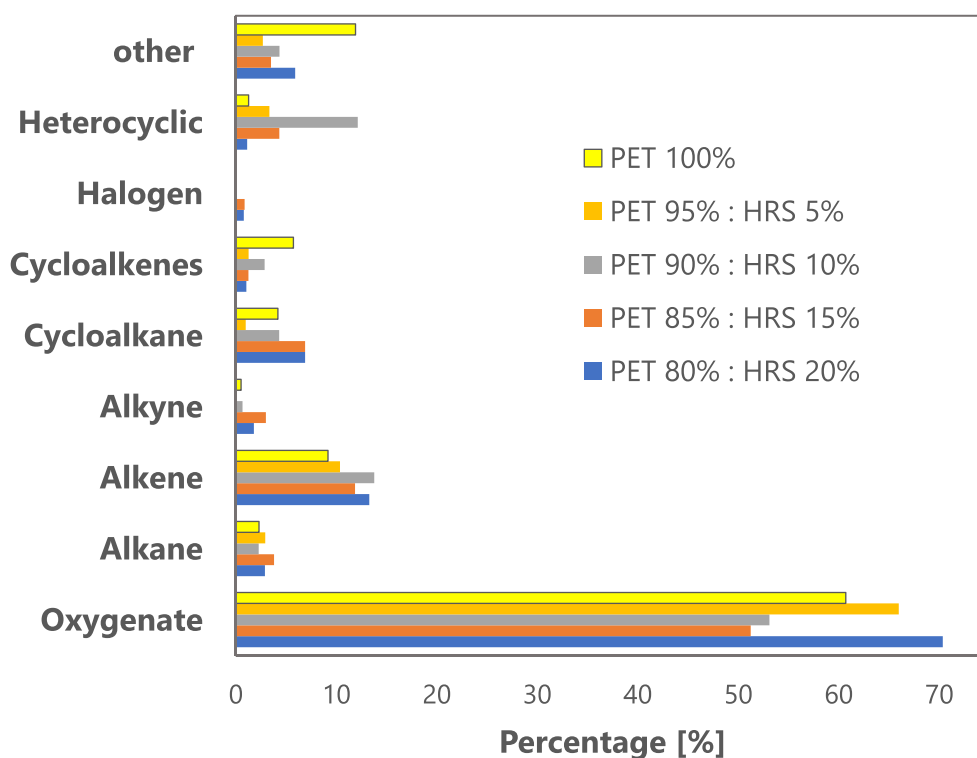


Fig. 24. Oil yields hydrocarbon compositions of GC-MS measurement.

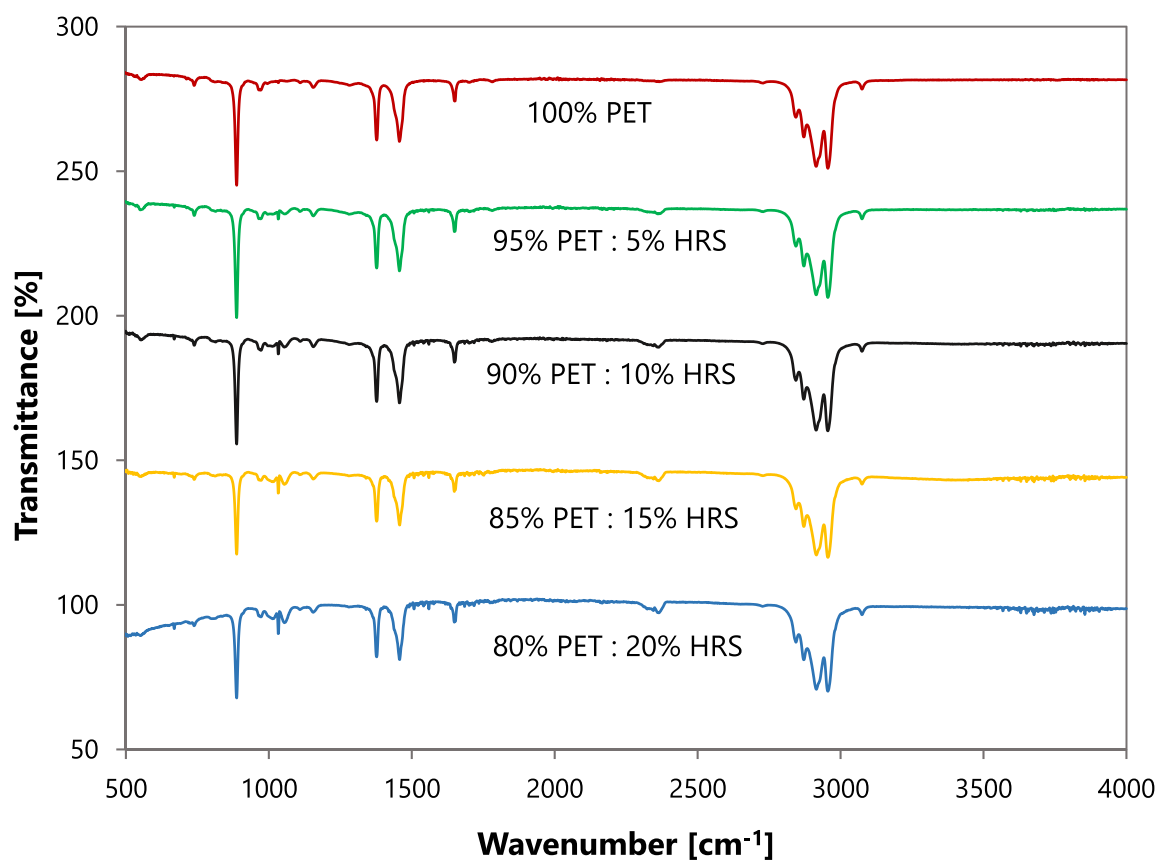


Fig. 25. The formation of functional groups in oil yields as measured by FTIR.

3.5. Effect of PET – HRS pyrolysis in oil yields compounds

The characterization of pyrolysis oil from the co-pyrolysis of PET and HRS provides valuable insights into the compositional differences of the yields products, as demonstrated by analysis techniques; Gas Chromatography-Mass Spectrometry (GC–MS) and Fourier Transform Infrared Spectroscopy (FTIR). The pyrolysis oil derived from pure PET is predominantly composed of hydrocarbon compounds, particularly aromatic hydrocarbons and their derivatives, which align with the expected breakdown of the PET polymer chain.

Incorporating HRS into the feedstock introduces a notable presence of oxygenated compounds—such as phenols, furans, and carboxylic acids—originating from the thermal decomposition of lignocellulosic biomass components, including cellulose and hemicellulose. The FTIR spectra (Fig. 25) reveal characteristic functional group absorptions like C=O, O–H, and C–O stretching vibrations that increase in intensity with higher HRS ratios, confirming the enhanced oxygen content and presence of biomass-derived functional groups in the pyrolysis oil.

The compositional analysis, illustrated in Fig. 24, reflects a distinct correlation between the PET-HRS blend ratios and oil yields hydrocarbon compositions. Notably, the oxygenate content shows a steady increase with higher HRS content, peaking at an 80 % PET: 20 % HRS ratio, whereas pure PET yields the lowest oxygenate concentration. In contrast, the proportion of hydrocarbons—including alkanes, alkenes, alkadienes, cycloalkanes, and cycloalkenes—demonstrates an inverse trend, with pure PET exhibiting the highest hydrocarbon, as shown in Fig. 24.

This phenomenon underscores the significant impact of HRS on the formation of oxygenated compounds during pyrolysis, largely attributed to the decomposition of its cellulose, hemicellulose, and lignin components. Additionally, an increase in halogenated and heterocyclic compounds at higher HRS ratios suggests interactions between PET and HRS that lead to the formation of novel compounds. The diversity noted in the "other" category across different blends indicates a complex mixture of unidentified products.

Moreover, the progressive darkening of the pyrolysis oil corroborates shifts in chemical composition as evidenced by GC–MS and highlighted in the findings, shown in Fig. 26. For instance, the 100 % PET sample is characterized by a high olefin content (74.33 %), contributing to its lighter coloration. However, as the proportion of HRS rises in the feedstock, olefin content decreases significantly to 25.74 % in the 80:20 PET-HRS blend, while aromatic content increases substantially (17.04 %). This shift suggests that thermal decomposition of HRS introduces more aromatic compounds, affecting the oil's colour.

The carbon range analysis illustrates further insights into the length of carbon chain distribution of the pyrolysis oil. In the absence of HRS, the dominant compound size in 100 % PET pyrolysis oil is categorized within the C7-C10 (56.34 %) and C11-C22 (43.03 %) ranges. However,

with increased HRS ratios, this distribution shifts. For the 80:20 PET-HRS sample, the proportion of smaller C7-C10 compounds rises to 66.1 %, while larger C11-C22 compounds decrease to 33.9 %, resulting in the disappearance of compounds over C22. This suggests HRS plays a vital role in forming smaller molecules during pyrolysis, including short-chain compounds like furans, aldehydes, and carboxylic acids.

These findings emphasize the substantial influence of HRS on the thermal decomposition pathways of PET, leading to distinct the length of carbon and chemical compositions of the produced pyrolysis oils. The GC–MS and FTIR results also function as data validation for the Hyperchem simulation performed to examine the catalytic mechanism of HRS in the pyrolysis of PET-HRS.

3.6. Synergistic effect of PET and HRS

The synergistic effect observed in the co-pyrolysis of PET and HRS is both a complex and significant phenomenon. This study reveals that this synergy is primarily inferred from deviations in product yields—including liquid, solid, and gas—across various PET-to-HRS ratios. Changes in physicochemical properties, such as calorific value, octane number, and molecular composition, further underscore the interactions that exceed simple additive behaviours, implying synergistic mechanisms.

This synergy peaks notably at the 90:10 PET-to-HRS blend ratio, attributed to optimal interactions between PET decomposition pathways and the catalytic effects of bioactive compounds in HRS, particularly flavonoids. These compounds facilitate bond cleavage and promote the formation of oxygenated intermediates that enhance fuel quality and favourably shift energy distribution.

Molecular modelling simulations played a crucial role in identifying this synergistic effect, with results validated through experimental data. These simulations demonstrated that increasing HRS ratios led to elevated molecular polarization and shifts in the product distribution toward oxygenates and aromatic compounds, aligning with flavonoids' catalytic role. Reaction pathways favoured at specific feedstock ratios and temperatures align with the formation of hydrocarbons, phenolics, and short-chain oxygenates.

HyperChem simulations reveal that interactions between PET and HRS molecules become increasingly synergistic as intermolecular forces weaken, shown by decreasing kinetic energy (KE) values. At the optimal 90:10 ratio, the system achieves a stabilized reactive configuration, encouraging selective bond cleavage and product formation. Fig. 19 illustrates this relationship, correlating with the highest recorded levels of oxygenated hydrocarbons and heterocyclic compounds.

Further validation comes from GC–MS analysis, in which the 90:10 PET-to-HRS sample exhibited the highest concentration of oxygenated and heterocyclic hydrocarbons (Fig. 23). These stable molecules with polar functional groups contribute to reduced molecular mobility,

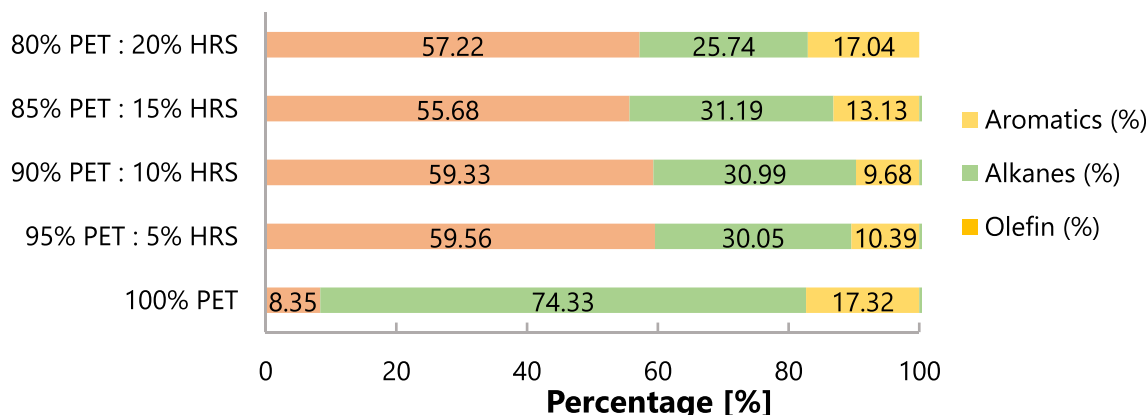


Fig. 26. Distribution of Aromatic, Alkane, and Olefin Compounds in oil yield of PET-HRS pyrolysis.

reflecting lower average KE and enhanced thermal selectivity. This process promotes the formation of valuable intermediates rather than undesirable tars or gases.

Mechanistically, synergy is governed by several factors. Flavonoids act as catalysts, stabilizing radicals and facilitating radical transfer at moderate pyrolysis temperatures ($\sim 350^\circ\text{C}$), impacting yields and product composition. Additionally, the high porosity of HRS enhances heat transfer, promoting uniform decomposition and facilitating interactions between PET fragments and biomass-derived intermediates.

The results indicate that the synergistic effect is most pronounced at ratios where the catalytic influence of HRS's bioactive components, combined with optimal heat transfer and radical stabilization, maximizes product yields without compromising stability.

3.7. The catalytic mechanism of flavonoids in PET-HRS pyrolysis

The analysis of pyrolysis products from different ratios of PET and HRS reveals a distinct shift in product distribution, highlighting the significant influence of HRS addition. The incorporation of HRS results in a considerable increase in oxygenated compounds, especially in the 80 % PET: 20 % HRS blend, while the proportion of hydrocarbons decreases. This trend suggests a complex interplay between the components of PET and HRS during pyrolysis, wherein flavonoids—key constituents of HRS—are hypothesized to play a crucial catalytic role.

Based on the experimental and the simulation results, the mechanism of HRS in co-pyrolysis influenced by flavonoids can be illustrated in Fig. 27. Characterized by their complex polyphenolic structures, flavonoids may enhance the co-pyrolysis process by facilitating the breakdown of PET polymer chains and HRS components, thus increasing the formation of oxygenated compounds (Hujuri et al., 2013; Wang et al., 2023). The degradation of flavonoids also contributes to this oxygenate-rich product profile. Furthermore, these bioactive compounds promote dehydrogenation and reforming reactions, that influence the production of essential gases such as methane, hydrogen, carbon monoxide, and carbon dioxide.

The presence of aromatic rings in flavonoid structures is particularly significant, as these contribute to the formation of aromatic compounds within the pyrolysis products, improving the quality of the resulting liquid fuels. The interaction between flavonoids and other HRS

components, including cellulose, hemicellulose, and lignin, fosters a synergistic effect that drives the conversion of biomass into gaseous and liquid products. Additionally, the antioxidant properties of flavonoids enhance the stability of the pyrolysis products by mitigating oxidative degradation.

Flavonoids play a significant catalytic role in the co-pyrolysis of PET and HRS, primarily due to their complex polyphenolic structures that facilitate various chemical reactions throughout the pyrolysis process. One of the key mechanisms by which flavonoids influence product yields is through their ability to interact with PET polymer chains and HRS compounds, promoting bond cleavage. This interaction effectively breaks down PET into smaller hydrocarbon fragments, increasing the availability of reactive sites for subsequent reactions. As a result, the breakdown of PET into shorter-chain hydrocarbons enhances the efficiency of thermal degradation, leading to higher yields of beneficial products, including liquid fuels and gases.

The integration of HRS into the PET pyrolysis feedstock also significantly boosts the formation of oxygenated compounds, particularly at an 80 % PET: 20 % HRS ratio. During their degradation, flavonoids release volatiles that are rich in Oxygen, such as phenolic compounds, which participate in secondary reactions that contribute to the creation of additional oxygenated species. This not only improves the quality of the resulting oil but also enhances its performance.

Furthermore, flavonoids promote dehydrogenation reactions during pyrolysis, facilitating the conversion of larger hydrocarbons into lighter and more valuable gaseous products, such as methane, carbon monoxide, and hydrogen. By stabilizing reactive intermediates and encouraging reforming reactions, flavonoids streamline the transformation of heavier hydrocarbons into smaller, high-value gaseous products.

The presence of aromatic rings in flavonoid structures significantly impacts the quality of the pyrolysis products. As HRS undergoes thermal decomposition, these aromatic compounds are generated, enhancing the overall quality of the liquid fuels produced. Their formation not only boosts the calorific value of the oil but also improves its stability and compatibility with existing fuel molecular structure.

Flavonoids also possess antioxidant properties that help stabilize reactive species formed during pyrolysis. By minimizing oxidative degradation during and after the pyrolysis process, these compounds maintain the quality and stability of the pyrolysis products, thereby

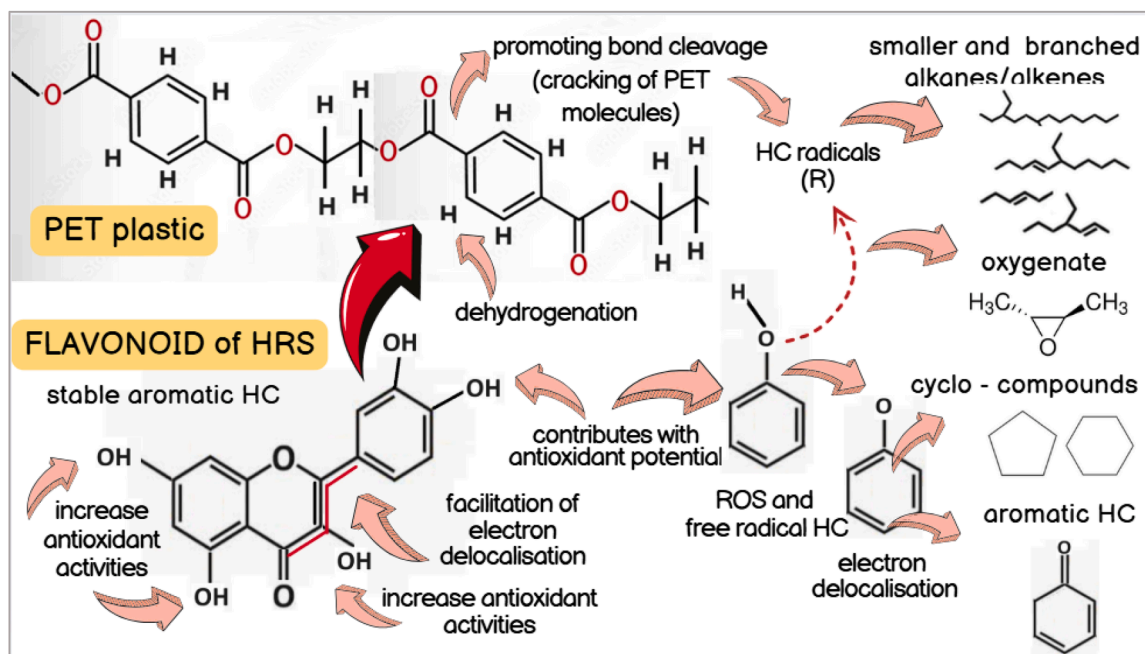


Fig. 27. Catalytic Mechanisms of Flavonoids in PET-HRS Pyrolysis.

enhancing both the overall yield and composition of the oil.

Finally, the integration of HRS results in significant alterations to the molecular composition of the pyrolysis oils. Specifically, the addition of HRS leads to a reduction in olefin content and a corresponding increase in aromatic compounds. This indicates that flavonoids modify the thermal decomposition pathways of PET, resulting in distinct shifts in product distribution and the length of carbon chain.

The observed increase in oxygenated compounds with higher HRS ratios, along with the corresponding decrease in hydrocarbons, underscores the catalytic role of flavonoids in shaping the product composition. This finding emphasizes the potential to influence the inherent catalytic characteristics of biomass components to modify the distribution of pyrolysis products.

Finally, the integration of HRS as a co-feedstock in PET pyrolysis not only enhances the efficiency of the process but also significantly alters the chemical composition and quality of the resulting bio-oil. By harnessing the catalytic properties of HRS, particularly through its flavonoid content, this study underscores the potential of biomass co-pyrolysis in optimizing fuel yields and qualities, ultimately contributing to more sustainable waste management solutions.

4. Conclusion

This research examined the co-pyrolysis of PET and HRS as a sustainable approach for waste valorization and biofuel generation. The results emphasize the promise of HRS as a significant co-feedstock, improving both yield and fuel quality obtained from PET pyrolysis. Different PET-HRS weight ratios were assessed at a pyrolysis temperature of 350 °C, demonstrating that the inclusion of HRS markedly affected product dispersion, as indicated by both experimental and simulation findings as follows:

1. The integration of a small number of HRS at a 90:10 ratio produced a synergistic effect, resulting in an enhanced liquid oil yield of 538 ml, surpassing the 520 ml achieved from the pyrolysis of pure PET. The ideal ratio of 90:10 resulted in a peak oil production of 393 g, slightly exceeding the yield from pure PET (390 g). An extensive evaluation of the liquid yield revealed improved fuel properties at the 90:10 ratio, with a high-octane number (98), a competitive calorific value (46.65 MJ/kg), and alterations in viscosity and density.
2. Furthermore, the integration of HRS markedly enhanced the valuable gas yields, especially of CH₄ and H₂, highlighting the catalytic function of HRS in promoting cracking and reforming processes. The catalytic activity is predominantly linked to the flavonoid content in HRS. The flavonoids augment the co-pyrolysis of PET and HRS by facilitating bond cleavage, enhancing the production of oxygenated compounds, and promoting the transformation of long-chain hydrocarbons into valuable gaseous products, thus improving the overall quality and stability of the pyrolysis products.
3. The HyperChem simulation results clarify changes in molecular structure, polarizability, and energy dynamics, providing a molecular-level comprehension of these synergistic effects. This study together illustrates the significant potential of HRS as a co-feedstock for the sustainable valorization of PET waste, enhancing advancements in biofuel production technology.

Declaration of use of generative – AI

We hereby declare that the following generative AI tools were utilized during the course of this research and manuscript preparation:

Gemini and ChatGPT - for organizing and structuring manuscript effectively.

SciSpace and Elicit - for organizing and managing research materials and references efficiently.

QuillBot - for enhancing the clarity and coherence of the written

content through paraphrasing and grammar checking.

CANVA - for designing and creating visual materials, including figures and presentations that support the findings of this study.

BioRender - for creating professional scientific figures and diagrams that visually represent the data and concepts discussed.

Following the utilization of GEN-AI, the authors carefully evaluated and revised the articles and writing format as necessary, assuming full responsibility for the publication's subject matters.

CRediT authorship contribution statement

Ahmad Yani: Visualization, Methodology, Investigation. **Widya Wijayanti:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Mega Nur Sasongko:** Supervision, Resources, Data curation. **Slamet Wahyudi:** Supervision. **Purbo Suwandono:** Validation, Software. **Musyarah Musyarah:** Software.

Declaration of competing interest

The authors declare that there are no financial or personal relationships that could be construed as a potential conflict of interest regarding the research presented in this manuscript. All authors have disclosed any relevant affiliations or funding sources that may have influenced the study. The research was conducted independently, and the findings and conclusions drawn in this paper are solely those of the authors.

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