PAPER • OPEN ACCESS

Optimizing process parameters and materials for the conversion of plastic waste into hydrogen

To cite this article: Sakib Tanvir Hossain and M A Parvez Mahmud 2024 *Eng. Res. Express* **6** 045319

View the article online for updates and enhancements.

Engineering Research Express

PAPER

Optimizing process parameters and materials for the conversion of plastic waste into hydrogen

Sakib Tanvir Hossain[1] ⬥ and M A Parvez Mahmud[2] ⬥

[1] Institute of Innovation, Science and Sustainability, Federation University Australia, Victoria, 3842, Australia
[2] School of Mathematical and Physical Sciences, University of Technology Sydney, NSW, 2007, Australia

E-mail: Parvez.Mahmud@uts.edu.au

Abstract

This study has investigated hydrogen production from waste plastics using pyrolysis, steam methane reforming, and water-gas-shift reactions modelled via Aspen Plus. After evaluating multiple alternatives, polypropylene (PP) was selected as the feedstock. The research has been focused on how reformer temperature, steam-to-fuel ratio (S/F), reformer pressure, and pyrolysis temperature impact syngas composition, heating values, syngas (H_2/CO) ratios, and yields of hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). Key findings have indicated that raising reformer temperatures to around 1000°C maximizes hydrogen production in syngas, reaching peak levels of 2360 Nm^3/Ton and 2525 Nm^3/Ton for reformer temperature and steam-to-fuel ratio (S/F) ratios, respectively, via processes like steam methane reforming and the water-gas-shift reaction. Moreover, other parameters like steam-to-fuel (S/F) ratio and reformer pressure have produced the highest amount of hydrogen at 0.25 and 1 atm, respectively. Optimizing reformer temperature and steam-to-fuel ratio (S/F) have been selected as key in hydrogen production, with peak lower heating values (LHV) of 1.15 MJ/kg for temperature and 1.035 MJ/kg for S/F ratios, highlighting the importance of balancing these parameters for efficiency. Additionally, syngas' hydrogen (H_2) composition increased with pyrolysis temperature, peaking at 8.5% at 700°C. Finally, this research has provided valuable insights into optimizing process parameters for sustainable hydrogen production. Moreover, the simulation process has provided cost-effective adjustments and informed decision-making for sustainable and scalable technologies, benefiting researchers, investors, engineers, and policymakers involved in innovative hydrogen generation.

1. Introduction

Plastics, characterized as malleable polymeric substances synthesized from hydrocarbons, are amenable to diverse shapes by applying heat and pressure. This versatility facilitates their conversion into various products suitable for industrial and residential applications. Contemporary reliance on plastics has escalated to unparalleled magnitudes (Akhshik *et al* 2018). Globally, 370 million tonnes of plastics annually serve vital roles across multiple industries, while only in 2015, the worldwide generation of plastic waste amounted to 322 million tonnes (Lopez *et al* 2018; Europe 2022b). Plastics' lifespan varies from <1 year to >50 years, culminating in significant waste generation. Significantly, the United States and Europe are identified as principal contributors to plastic waste generation, with annual outputs exceeding 40 and 29 million tonnes, respectively. However, the growing use of plastics is leading to significant obstacles due to the rising amounts of plastic waste and the insufficient methods for its proper disposal. Addressing plastic waste management is critical to preventing environmental contamination (Midilli *et al* 2022). There is a general agreement about the harmful effects of waste plastics on the environment, which emphasizes the importance of finding new and better ways to deal with plastic waste (Geyer *et al* 2017; Akhshik *et al* 2018; Statista 2022; Europe 2022a).

Globally, a mere 9% of the 6.3 billion tonnes of plastics manufactured between 1950 and 2018 have undergone recycling processes, with an additional 12% subjected to thermal destruction. Nevertheless, the residual 79% of plastics emit pollutants such as furans, dioxins, and mercury, detrimentally affecting the environment and marine ecosystems. Annually, roughly 4 to 12 million metric tons of polymers are deposited in oceans (Thompson *et al* 2009; Alabi *et al* 2019). As a result, many countries advocate for and implement legislative measures designed to diminish plastic consumption and foster recycling efforts (d'Ambrières 2019). Transforming plastics effectively into valuable products is essential for safeguarding the environment and utilizing energy from vast quantities of waste. Scholarly research has consistently affirmed the viability of plastic recycling. Among various methods, thermochemical recycling is considered particularly efficacious, converting plastics into synthesis gas suitable for creating different important chemicals (Simões *et al* 2014; Francis 2016; Ahmad *et al* 2020; Ahmed *et al* 2021).

Since plastic waste is rich in hydrocarbons and has substantial energy potential, a sustainable approach involves converting this waste into energy using eco-friendly methods like pyrolysis. Dewangan and team investigated the integration of low-density polyethylene with sugarcane residue within a pyrolysis reactor operating at temperatures ranging from 350 °C to 600 °C. They observed that this combination lowered the levels of oxygen-containing compounds in the syngas and boosted its energy content (Dewangan *et al* 2016). In addition, pyrolysis decomposes materials in an oxygen-free environment, producing clean syngas free of toxic emissions. In the early 1990s, Scott *et al* explored plastic waste pyrolysis, examining thermal and catalytic methods and conducting tests on polyethylene (PE). Their findings indicated promising results for catalytic thermal pyrolysis, meriting additional research for its economic viability (Scott *et al* 1990; Wu and Williams 2010).

Again, recent studies focus on producing hydrogen from waste plastics, diverging from the 96% of hydrogen currently derived from fossil fuels, primarily natural gas. This conventional production employs steam reforming of methane at 700 °C–1000 °C and 0.3–2.5 MPa, using nickel-based catalysts to generate hydrogen and carbon monoxide. The following water-gas shift process, converting carbon monoxide with steam, increases hydrogen yields and produces carbon dioxide (Spath and Mann 2000; Dou *et al* 2016; Guo *et al* 2020; Midilli *et al* 2022; Qin *et al* 2022).

The key outcomes of this reaction are hydrogen (H_2) and carbon monoxide (CO).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

Methane steam reforming process

In the commercial method, a downstream water gas shift reaction system is utilized to enhance hydrogen production, where carbon monoxide is through catalytic means transformed into hydrogen and carbon dioxide.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Water-gas shift process

Hydrogen produced from plastic waste is a substitute for natural gas, addressing waste management and utilizing catalytic steam processing of pyrolysis fumes. This involves pyrolysis to release hydrocarbons, then steam reforming these for hydrogen and carbon monoxide production (Zhang *et al* 2017; Barbarias *et al* 2018; Yao *et al* 2018; Arregi *et al* 2020). This technique simulates the traditional catalytic steam reforming process for natural gas by using gases generated from the pyrolysis of plastics, including a broad spectrum of hydrocarbons from C1 to C60, derived from straight-chain and branched polymers like polyethylene and polypropylene, instead of methane. (Williams 2006). The diversity of hydrocarbon types generated via plastic pyrolysis makes the reaction environment more complex than in the catalytic steam reforming of methane. Santamaria *et al* have undertaken a comprehensive review of the pyrolysis-steam conversion technique employed for discarded plastics and biomass, particularly emphasizing the assortment of catalysts employed within this process (Santamaria *et al* 2021).

However, to run the system well, it is essential to carefully manage and improve how it works. Using process simulation, which is a way to save costs, helps us understand how different factors affect the operation and find the best settings. Past research has shown how creating simulation models using computers can help make processes better, especially for using waste plastics as fuel (Al-Qadri *et al* 2022; Zhao *et al* 2023), coal (Paul *et al* 2021; Zhou *et al* 2023), and biomass (Tavares *et al* 2020; Kourdourli *et al* 2023). Nonetheless, extensive research or documentation on employing simulators such as Aspen Plus to simulate the air gasification of plastic waste needs to be included in the existing literature. Ajorloo *et al* modelled pinewood/HDPE co-gasification in Aspen Plus, finding temperature and steam-to-fuel ratio as critical factors (Ajorloo *et al* 2022). Again, Phan *et al* used a two-phase catalytic steam breakdown-gasification method for generating hydrogen from plastics, analyzing catalyst ratio, temperature, and water rate using a Ni–Mg–Al catalyst (Wu and Williams 2010). Furthermore, Singh and the team designed an Aspen Plus model for the co-gasification of biomass and plastics in a fluidized bed, integrating kinetic equations to investigate the mixing of polyethylene (PE) and polypropylene (PP) (from

Table 1. Proximate and ultimate analysis of plastics (weight percent on an as-received basis).

	Polypropylene (PP) (Alshareef *et al* 2023)	Polystyrene (PS) (Encinar and González 2008)	Polyethylene terephthalate (PET) (Encinar and González 2008)
Proximate Analysis **(Mass fraction %)**			
Fixed Carbon	0	99.8	13.15
Volatile Matter	98.8	0.2	86.85
Ash	0.21	0	0
Moisture Content	0	0	0
Ultimate Analysis (Mass fraction %)			
C	84.85	90.02	62.5
H	13.91	8.48	4.21
N	0.03	0	0
S	0.09	0	0
Cl	0	0	0
O	0.91	1.5	33.29

0%–30%) with lignocellulosic biomass. They examined syngas composition, syngas (H_2/CO) ratio and higher heating value (HHV), aiming to understand the synergistic effects (Singh *et al* 2022).

This investigation has offered a new technique for generating hydrogen from discarded plastics using a three-phase process, including pyrolysis, steam methane reforming, and the water-gas-shift reaction, which was evaluated with Aspen Plus software. It also has evaluated various feedstocks, including polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and their combinations (PP-PS, PS-PET, PET-PP) to ascertain the optimal substrates for hydrogen yield and energy efficiency, identifying polypropylene (PP) and polyethylene terephthalate (PET) as superior for hydrogen production and energy yield, respectively. Moreover, the impact of reformer temperature, steam-to-fuel (S/F) ratio, reformer pressure, and pyrolysis temperature on hydrogen concentration, assessing the lower heating value (LHV) and higher heating value (HHV) of polypropylene (PP) under varying conditions have been investigated thoroughly. It has further explored the syngas (H_2/CO) ratio, methane (CH_4) and carbon dioxide (CO_2) yields, comprehensively analyzing the model's efficacy. Overall, this research has paved the way to advance the sustainable conversion of waste plastics into hydrogen, providing insights into process optimization to enhance efficiency and sustainability. Additionally, it has had significant implications for research, investment, academia, and manufacturing stakeholders, addressing a gap in the existing literature on waste plastic conversion processes.

2. Methodology

The Aspen Plus V12.1 software has been utilized to model hydrogen generation from the gasification of waste plastics in a fluidized bed. This has involved the detailed development process, encompassing the selection of plastics, determination of physical property methods, creation of the process diagram, establishment of starting and working conditions and model verification.

2.1. Characteristics of plastics
For hydrogen production, three distinct kinds of waste plastics have been selected as fuels: polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET). The proximate and ultimate analysis data for these samples have been sourced from existing literature (Encinar and González 2008; Alshareef *et al* 2023), as listed in table 1.

2.2. Thermodynamic calculation methods
For a comprehensive thermodynamic analysis and the key thermodynamic calculations and methods that have been generally applied to each stage of the entire process, pyrolysis, steam methane reformation (SMR) and water-gas shift (WGS), have been involved in converting waste plastics into hydrogen are taken into considerations. Here a more detailed overview of the thermodynamic calculation methods for the whole process has been shown in detail:

2.2.1. Pyrolysis process
Using the Gibbs free energy minimization, the prediction of the equilibrium products from the pyrolysis of plastics was conducted. The products have been varied depending on temperature and the type of plastic used

throughout the process. The Gibbs free energy equation is central to thermodynamics, particularly in determining the spontaneity and equilibrium of chemical reactions (Cengel *et al* 2011). The Gibbs free energy (ΔG) for a system is defined as:

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

Where:

- ΔG is the change in Gibbs free energy.

- ΔH is the change in enthalpy (heat content) of the reaction.

- ΔS is the change in entropy (disorder) of the system.

- T is the temperature at which the reaction occurs.

This is typically an endothermic process requiring external heat input. The overall enthalpy change of the pyrolysis process can be calculated as:

$$\Delta H_{pyrolysis} = H_{products} - H_{plastics} \tag{4}$$

If $\Delta H_{pyrolysis} > 0$, the process is endothermic, meaning it involves heat input to proceed. In most cases, pyrolysis is endothermic because breaking down the strong C-C and C-H bonds in plastics requires significant energy. The energy requirement can vary depending on the type of plastic and the specific pyrolysis conditions (e.g., temperature, pressure) (Ciuta *et al* 2018).

The energy balance equation for the pyrolysis process accounts for the heat required to break down the chemical bonds in the feedstock (such as plastics) and the heat generated or absorbed due to the formation of products (Hussein *et al* 2023). The general form of the energy balance for pyrolysis is:

$$Q_{in} + H_{feed} = H_{products} + Q_{losses} + Q_{out} \tag{5}$$

Where:

- Q_{in} is the heat supplied to the reactor.

- H_{feed} is the enthalpy of the incoming feedstock (plastics).

- $H_{products}$ is the enthalpy of the pyrolysis products (gases, liquids, char).

- Q_{losses} represents heat losses due to radiation, convection, etc.

- Q_{out} is the heat content of the products exiting the reactor.

Combining these components, the energy balance equation ensures that the energy supplied to the system equals the energy carried by the products and the losses, helping optimise the reactor design and operational parameters to achieve efficient pyrolysis.

2.2.2. Steam methane reforming (SMR) process

The steam methane reformation (SMR) process is a key industrial method for producing hydrogen. The Gibbs free energy analysis of the steam methane reformation (SMR) process involves assessing the reaction's spontaneity and equilibrium under specific conditions. For the methane reforming reaction, the standard Gibbs free energy change is calculated using:

$$\Delta G° = \sum \Delta G_f°(products) - \sum \Delta G_f°(reactants) \tag{6}$$

Where, $\Delta G_f°$ is the standard Gibbs free energy of formation for each species.

For the steam methane reformation (SMR) process, according to chemical reaction (1):

$$\Delta G°(reaction) = [\Delta G_f°(CO) + 3\Delta G_f°(H_2)] - [\Delta G_f°(CH_4) + \Delta G_f°(H_2O)] \tag{7}$$

This value can then be used to assess the equilibrium constant K and to determine the extent of reaction at different temperatures. Values for the methane reforming and water-gas-shift reactions are considered to find the overall Gibbs free energy for the steam methane reformation (SMR) process. At industrial operating temperatures (700°C–1000°C), the process is designed to be thermodynamically efficient, ensuring the maximum production of hydrogen (Özkara-Aydınoğlu 2010).

For each reaction, the standard enthalpy of formation ($\Delta H_f°$) of the reactants and products is needed to ensure the total heat input equals the sum of heat required for the endothermic reactions plus any losses. The overall enthalpy change of the steam methane reformation (SMR) process can be calculated according to chemical reaction (1):

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}; \Delta H° = +206.1 \, KJ/mol \tag{8}$$

To optimize the process, the heat which is released from the exothermic water-gas-shift reaction can be used to partially supply the energy needed for the steam methane reformation (SMR) reaction (Lutz *et al* 2003).

The overall energy balance of the steam methane reformation (SMR) process involves calculating the total heat input required for the endothermic reforming reaction and any heat losses within the system. The balance ensures that the heat supplied matches the energy needed to sustain the reactions and maintain the reactor at the desired temperature (Kaiwen *et al* 2018). The overall energy balance of the steam methane reformation (SMR) process:

$$Q_{in} + Q_{reactants} = Q_{products} + Q_{losses} + Q_{net} \tag{9}$$

Where:

- Q_{in} is the heat supplied externally.

- $Q_{reactants}$ is the enthalpy of the reactants, including methane and steam.

- $Q_{products}$ is the enthalpy of the products, primarily hydrogen, carbon monoxide, and carbon dioxide.

- Q_{losses} is the heat losses due to imperfect insulation, radiation, and other inefficiencies.

- Q_{net} is the net heat needed or released.

2.2.3. Water-gas shift (WGS) reaction

The Gibbs free energy balance for the water-gas-shift (WGS) reaction is crucial in determining the reaction's spontaneity and equilibrium at various temperatures. The Gibbs free energy change for the WGS reaction at standard conditions ($\Delta G°$) is negative, indicating that the reaction is spontaneous under these conditions (Smith RJ *et al* 2010). The standard Gibbs free energy change is calculated as, according to chemical reaction (2):

$$\Delta G° = [\Delta G_f°(CO_2) + \Delta G_f°(H_2)] - [\Delta G_f°(CO) + \Delta G_f°(H_2O)] \tag{10}$$

As temperature increases, $\Delta G°$ becomes less damaging, meaning the reaction becomes less favorable at higher temperatures, but it is still generally spontaneous under typical reaction conditions (200°C–450°C).

Understanding the enthalpy balance in reactor design helps integrate the water-gas-shift (WGS) reaction with other processes, ensuring efficient energy use. The overall enthalpy change of the water-gas-shift (WGS) reaction can be calculated (Smith *et al* 2010), according to chemical reaction (2):

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}; \Delta H° = -41.2 \, KJ/mol \tag{11}$$

The overall energy balance of the water-gas-shift (WGS) reaction involves accounting for the heat generated by the exothermic reaction and ensuring this heat is managed effectively within the process. In practical systems, this often involves designing the reactor with heat exchangers to recover and reuse the heat efficiently, maintaining optimal reaction temperatures (typically 200°C–450°C, depending on whether a high-temperature or low-temperature shift is used) (Smith *et al* 2010). The overall energy balance of the water-gas-shift (WGS) process:

$$Q_{in} + \Delta H_{reactants} = Q_{out} + \Delta H_{products} + Q_{losses} \tag{12}$$
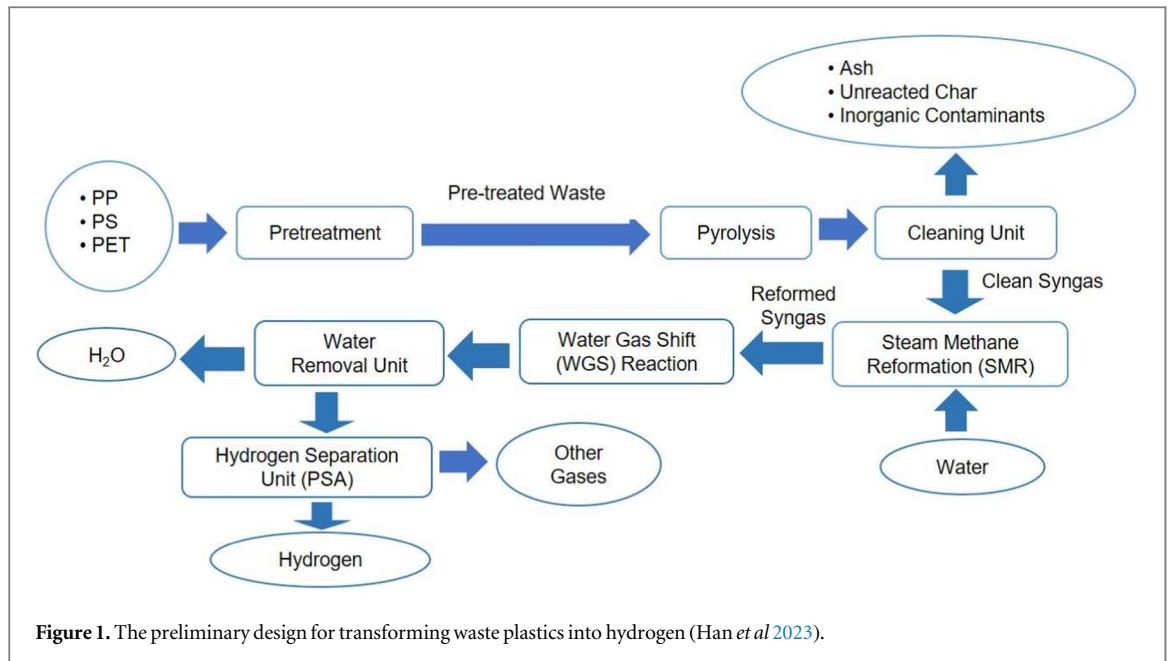
Where:

- Q_{in} is the external heat added (if any).

- $\Delta H_{reactants}$ is the enthalpy of the reactants (CO and H_2O).

- Q_{out} is the heat released by the reaction.

- $\Delta H_{products}$ is the enthalpy of the products (CO_2 and H_2).

- Q_{losses} accounts for heat losses due to inefficiencies, radiation, or convection.

By balancing these components, the overall energy management of the water-gas shift (WGS) reaction ensures optimal operation and integration with other processes, such as steam methane reforming, to maximize hydrogen production efficiency.

2.3. Overall thermal balance

The thermal balance of the entire process, including the steam methane reformation (SMR) process and water-gas-shift (WGS) reactions, involves accounting for all the heat inputs, outputs and losses within the system. The main components include:

Figure 1. The preliminary design for transforming waste plastics into hydrogen (Han *et al* 2023).

- Energy is required to maintain reaction temperatures, typically supplied externally. This energy is considered as heat input.

- Heat is generated and released by the exothermic water-gas-shift (WGS) reaction.

- Heat is consumed by the endothermic steam methane reforming (SMR) process.

- Integrating heat, which is released by the water-gas-shift (WGS) reaction to drive the steam methane reforming (SMR) process or preheat feedstocks.

- Energy is lost through radiation, convection, and inefficiencies. This energy is known as heat consumption.

The balance ensures that the total heat input matches the sum of heat consumed by reactions, heat, which is recovered, and losses, optimizing the process efficiency (Duncan 2014). The following equation can express the thermal balance of the entire process involving the steam methane reforming (SMR) process and the water-gas shift (WGS) reaction.

$$Q_{in} + \Delta H_{reactants} = \Delta H_{SMR} + \Delta H_{WGS} + Q_{out} + Q_{losses} \tag{13}$$

Where:

- Q_{in} is the external heat supplied.

- $\Delta H_{reactants}$ is the enthalpy of the feed (CH_4, H_2O).

- ΔH_{SMR} is the heat absorbed by the endothermic steam methane reforming (SMR) process.

- ΔH_{WGS} is the heat released by the exothermic water-gas shift (WGS) reaction.

- Q_{out} is the heat carried by the products (H_2, CO_2).

- Q_{losses} accounts for heat losses through radiation, convection, etc.

This equation ensures that the energy input into the system equals the energy consumed, produced, and lost, maintaining the energy balance for the process.

2.4. Transforming discarded plastics into hydrogen

Figure 1 shows the preliminary layout for hydrogen production from discarded plastics via pyrolysis, steam methane reformation, and a water-gas-shift unit. Initially, waste plastics undergo mechanical pre-treatments like collection, crushing, and sorting before being fed into the decomposer for pyrolysis. The selection process for waste plastics in the pretreatment phase has been started by identifying and collecting suitable plastics such as polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) from various sources, followed by meticulous sorting using manual or automated technologies to segregate these plastics by type and colour. The

Figure 2. Diagram of the process for transforming waste plastics into hydrogen.
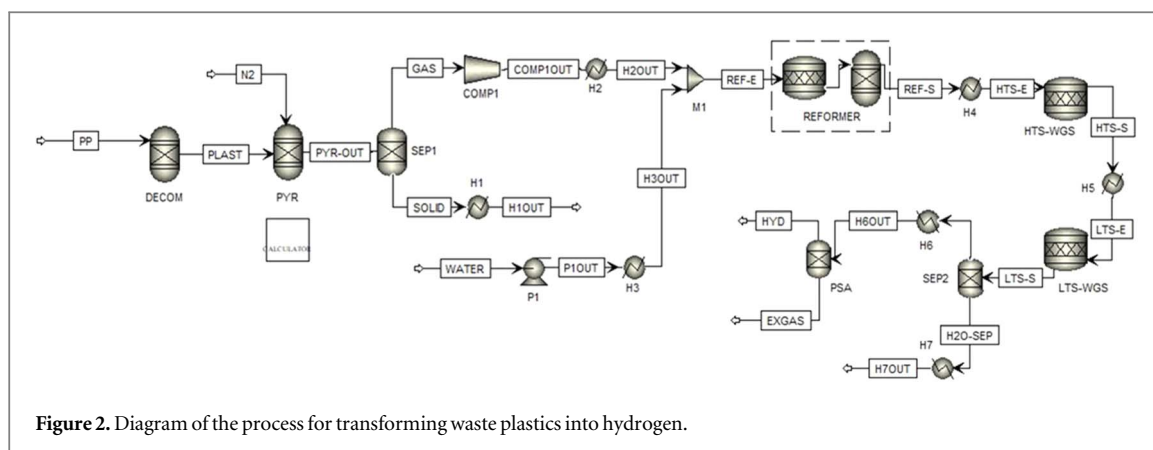
removal of contaminants and assessment of the material quality to ensure only the best, high-quality plastics proceed have been included in this process.

In the depicted process (figure 1), pyrolysis thermally decomposes pre-treated plastics at 300 °C to 700 °C in an oxygen-free environment, efficiently producing syngas and solid residues like char and ash. The resulting syngas from plastic waste gasification with nitrogen is cleaned to remove particulates and tar, creating a mix of nitrogen (N_2), hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), vapour (H_2O) and impurities like ammonia (NH_3) and hydrogen sulfide (H_2S), along with unreacted char and ash. The cleaning phase targets impurity removal, complemented by shredding to increase surface area, drying, and decontamination, with homogenization and pre-conditioning with catalysts optimizing chemical reactions for efficient processing.

In the following purification unit, these inorganic impurities and solid particles, including unconverted char and ash, are removed from the product. Following this, the process has been moved into the steam methane reformation (SMR) unit; in the reformer, methane (CH_4) has been transformed into carbon monoxide (CO) and hydrogen (H_2) using steam, according to the chemical reaction (1). The syngas is mixed with steam and heated over a nickel-based catalyst at temperatures between 700°C to 1100°C (Park *et al* 2019).

The reformed syngas has been then directed to the water gas shift (WGS) reactor, where carbon monoxide (CO) has been converted into hydrogen (H_2) and carbon dioxide (CO_2), reducing CO content and increasing CO_2 levels, according to the chemical reaction (2). Positioned strategically, the water-gas-shift (WGS) enhances the efficiency of the hydrogen production process by transforming a potential waste product into a valuable resource while also producing carbon dioxide that can be captured for environmental management, thereby optimizing hydrogen yield and contributing to the system's sustainability (Amadeo and Laborde 1995). Afterwards, water was separated in the water extraction unit, where the purified and dried syngas were transferred to the hydrogen extraction unit (PSA) to achieve high-purity hydrogen.

The hydrogen production process through pyrolysis, steam methane reformation (SMR) and the water gas shift (WGS) reactor has been analyzed using Aspen Plus. This analysis considers the entire process's mass-energy balance and chemical equilibrium, as depicted in figure 2.

2.5. Process model development

Before starting simulations, it's crucial to specify the correct stream classes. Aspen Plus has categorized material streams into mixed, conventional, and nonconventional solids in this process model. The software's libraries have been used to determine the thermodynamic properties of chemical components. Gases have been designated as mixed sub-streams, char as a conventional solid sub-stream, and plastics and ash as a nonconventional solid. Given their varied solid structure, the plastics have been categorized as nonconventional components, defined by their ultimate and proximate analyses, as detailed in table 1.

The HCOALGEN and DCOALIGT algorithms, built into the software, were selected to calculate the enthalpy and density of nonconventional solids. HCOALGEN determines the enthalpy based on composition and processing conditions, aiding in the energy balance calculations necessary for processes like combustion or gasification. DCOALIGT, on the other hand, estimates the density of these materials using principles adapted from the ideal gas law, which is essential for material handling and reactor design (Upreti 2017; Foo 2022).

The physical characteristics of the standard components have been computed using the Peng-Robinson equation with the Boston Mathias modification (PR-MB). This describes a thermodynamic model, precisely the Peng-Robinson equation of state (EOS), enhanced in 1976 better to predict vapour-liquid equilibria in the petroleum and chemical sectors. The Boston-Mathias modification further adjusts this model to improve the handling of both polar and non-polar compounds' thermodynamic properties (Mathias and Copeman 1983).

Table 2. Catalogue of chemical species employed in the simulation.

Component ID	Type	Component Name	Formula
C	Solid	CARBON-GRAPHITE	C
S	Solid	SULFUR	S
H_2	Conventional	HYDROGEN	H_2
O_2	Conventional	OXYGEN	O_2
N_2	Conventional	NITROGEN	N_2
PLASTIC	Nonconventional		
ASH	Nonconventional		
CO_2	Conventional	CARBON-DIOXIDE	CO_2
CO	Conventional	CARBON-MONOXIDE	CO
CH_4	Conventional	METHANE	CH_4
NH_3	Conventional	AMMONIA	H_3N
H_2O	Conventional	WATER	H_2O
H_2S	Conventional	HYDROGEN-SULFIDE	H_2S

The Boston-Mathias modification of the Peng-Robinson equation enhances the alpha function for improved fit to experimental data at high temperatures and pressures (Peng and Robinson 1976):

$$P = \frac{RT}{V - b} - \frac{a.\alpha(T)}{V^2 + 2bV - b^2} \tag{14}$$

Where:

- P is the pressure,

- T is the temperature,

- R is the gas constant,

- V is the molar volume,

- a and b are substance-specific parameters,

- $\alpha(T)$ is a function of temperature that incorporates the effects of molecular attraction, modified by Boston-Mathias as:

$$\alpha(T) = \left[1 + c\left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \tag{15}$$

In the Boston-Mathias modification, c is adjusted better to match the behaviour of the fluid under various conditions. This modification often provides better accuracy in predicting phase equilibria and critical properties for a wide range of substances, making it particularly useful in process simulation software and engineering calculations (Poling *et al* 2001; Kontogeorgis and Folas 2009).

Table 2 lists all species used in the simulation model. Additionally, specific assumptions were made to facilitate the modelling process.

2.6. Model assumptions

The non-kinetic numerical model utilizes stoichiometric and non-stoichiometric thermodynamic equilibrium methods, which involve Gibbs's free energy minimization approach. In this respect, the gasifier has been designed under the following presumptions.

- The operation has been presumed to occur in a stable state with constant flow and under uniform temperature conditions. Moreover, all chemical reactions have been assumed to achieve equilibrium, with sufficient residence time to reach both chemical and thermodynamic equilibrium. Furthermore, the ash has been regarded as inert and has not been engaged in any chemical reactions (Tauqir *et al* 2019).

- All pressure, which have been considered as lost within the system, have been disregarded, and char has been assumed to consist solely of carbon (Rosha *et al* 2022).

- Any nitrogen and sulfur, which have been presented in the feedstock, have been assumed to react, producing ammonia (NH_3) and hydrogen sulfide (H_2S) (Vera Marcantonio 2020).

Table 3. Initial condition of polypropylene (PP) flow.

Stream	T (°C)	P (atm)	Mass flowrate (kgh⁻¹)	Molar flowrate (kmolh⁻¹)	Molar composition					
					CH_4	CO_2	H_2O	N_2	CO	H_2
PLAST	25	1	15.15	0.3607	0	0	0	0.14	0	0.49

- Various gases such as hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nitrogen (N_2), vapour (H_2O), ammonia (NH_3), hydrogen sulfide (H_2S) and sulfuric acid (HCl) have been formed in the gasification process (Vera Marcantonio 2020).

- Ideal conditions have been considered for all gases (Marcantonio *et al* 2019).

- The model has omitted the generation of tar and other complex hydrocarbons (Singh *et al* 2022).

- All components, except for ash, have been involved in chemical reactions and interact evenly (Dhrioua *et al* 2022).

Assuming stable operation, constant flow, and uniform temperature in hydrogen production from waste plastics, the initial modelling process has been simplified, focusing on equilibrium conditions to streamline design and feasibility studies. These assumptions have reduced complexity in simulations, enabling more explicit initial assessments and designing optimizations before more detailed analyses. Moreover, disregarding pressure losses and assuming char is pure carbon has simplified initial process modelling by focusing on ideal thermodynamics and main chemical reactions, streamlining early design evaluations (Marcantonio *et al* 2023). This approach clarifies system performance and reaction efficiency by assuming nitrogen and sulfur in feedstock form ammonia (NH_3) and hydrogen sulfide (H_2S), simplifying modelling under high-temperature gasification conditions.

These assumptions streamline process design and environmental compliance by predicting and managing emissions like hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nitrogen (N_2), ammonia (NH_3) and hydrogen sulfide (H_2S) from organic material breakdown during gasification, assuming ideal gas conditions which have simplified state equation use, focusing on primary process dynamics by ignoring complexities like gas compressibility. Excluding tar and complex hydrocarbon streamlines models to primary reactions, enhancing operational focus while assuming all components except ash, which are reactive, have simplified mass and energy balances, emphasizing conversion efficiency (K T *et al* 2023). These assumptions are helpful in preliminary modelling to reduce computational complexity and provide more precise insights into core process behaviours.

2.7. Model description
The model development includes the following steps:

- Arranging the process layout by linking unit blocks with material flows.

- Choosing system elements from the ASPEN database.

- Categorizing conventional and non-conventional components and designating corresponding stream classes.

- Establishing operating conditions for unit blocks and streams, such as thermodynamic characteristics, flow rates, composition, and chemical reactions.

The process layout for the suggested hydrogen production system has been shown in figure 2. This figure has been created based on the conceptual design shown in figure 1, and the processes illustrated in figure 2 have been elaborated upon below. The gasification process consists of four sub-processes: decomposition, pyrolysis, steam methane reformation (SMR) and water gas shift (WGS) reactor. Distinct units in the Aspen Plus simulator have represented these sub-processes. The polypropylene (PP) stream has been initially introduced into the DECOM reactor to simulate the decomposition phase. The initial condition of the plastic flow through the PLAST stream is given in table 3.

The initial conditions in the stream PLAST at 25°C and 1 atm likely represent ambient conditions to simplify the setup and reduce operational complexities in a process simulation or experiment. The selected mass flowrate of 15.15 kg h⁻¹ and molar flowrate of 0.3607 kmol/h are probably determined based on the equipment's capacity and the scale of the experiment, aimed at achieving a balance between material throughput and practical analysis time. Table 4 has provided explanations for the unit blocks within the model. The PLAST

Table 4. Overview of units employed in the ASPEN PLUS simulation.

Block	Block Type	Description
DECOM	RYield	Converts nonconventional plastic waste into conventional components at 500°C and 1 atm.
PYR	RGibbs	Converts conventional plastic components into syngas at 500°C and 1 atm.
SEP1	Sep	Separate the solid particles like ash, unreacted Char, and inorganic contaminants from the PYR-OUT stream.
COMP1	Compr	Increase the pressure of the syngas feedstock from 1 atm to 10 atm.
H1	Heater	Reduce the temperature of the extracted solids from 500°C to 38°C.
H2	Heater	Increase the temperature of the syngas products from 500°C to 850°C.
P1	Pump	Enforce water at 10 atm and 25°C to mix with the syngas products to conduct steam methane reformation (SMR) in the reformer.
H3	Heater	Increase the water temperature from 25°C to 850°C to form steam.
M1	Mixer	Mix the syngas from the H2OUT stream and steam from H3OUT to enter the reformer.
REFORMER	RStoic & RGibbs	Reform methane (CH_4) with steam by SMR process and produce CO in the gas components.
H4	Heater	Reduce the temperature of the stream, REF-S, from 850°C to 650°C.
HTS-WGS	RStoic	Converts carbon monoxide (CO) with the hot stream at 650°C from the stream HTS-E and reduces the CO component.
H5	Heater	Reduce the temperature of the stream, LTS-E, from 650°C to 250°C.
LTS-WGS	RStoic	Converts more carbon monoxide (CO) with a hot stream at 250°C from the stream LTS-E and reduces the CO component.
SEP2	Sep	Separate hot steam from the stream LTS-S to H_2O-SEP.
H6	Heater	Reduce the temperature of the gaseous stream to 38°C to the stream H6OUT.
PSA	Sep	Separate hydrogen (H_2) from other gases, which are moved through EXGAS.
H7	Heater	Reduce the temperature of the stream H_2O-SEP to 38°C to convert the hot steam to water.

stream has transferred the decomposed plastic to the PYR (pyrolysis) chamber, where N2 has been added to facilitate the pyrolysis process at 500°C. Subsequently, pyrolysis products have been directed to the separator (SEP1) via the PYR-OUT stream. SEP1 has removed solid particles such as ash, unreacted char, and inorganic contaminants, which have been carried away by the SOLID stream.

The gas feedstock (GAS) first entered the COMP1 compressor, where the syngas pressure increased. WATER has been combined with GAS in the MIXER (M1), which has flown through the pump (P1). Post-M1, the stream REF-E has been directed into the REFORMER, where it has encountered two types of reactors, namely RStoic and RGibbs. In the water gas shift (WGS) reactor section, the stream has passed through two RStoic reactors: HTS-WGS and LTS-WGS. Subsequently, the stream LTS-S has moved to the SEP2 separator, which has isolated steam via the H_2O-SEP.

The high-temperature shift (HTS-WGS) and low-temperature shift (LTS-WGS) reactors are key for converting syngas carbon monoxide (CO) and vapour (H_2O) to carbon dioxide (CO_2) and hydrogen (H_2), with HTS-WGS using iron oxide catalysts at 350°C to 450°C for rapid CO conversion. LTS-WGS using copper-based catalysts at 200°C to 250°C for near-complete conversion. This ensures maximum hydrogen yield and purity, enhancing efficiency in processes requiring high hydrogen purity like pressure swing adsorption (PSA) (Levenspiel 1998; Sherif *et al* 2014). So, the remaining gas products have been sent to the pressure swing adsorption (PSA) unit, where hydrogen has been extracted through the HYD stream, and the residual gases have been exited through EXGAS. Detailed mainstream parameters of the hydrogen production process have been thoroughly presented in Table 5.

2.8. Performance parameters

The critical parameters for assessing the performance of the reformer in response to variations in process operating conditions include the syngas lower heating value (LHV), energy yield, hydrogen (H_2) yield, carbon dioxide (CO_2) yield, methane (CH_4) yield, and higher heating value (HHV), reformer temperature, steam-to-fuel (S/F) ratio, reformer pressure, pyrolysis temperature, syngas (H_2/CO) ratio.

Pyrolysis temperature is the heat level where organic materials like biomass, coal, and plastics thermally decompose in oxygen-free conditions, producing gases, liquids, and solids such as bio-oil, syngas, and char (Moldoveanu 2009). The temperature range for pyrolysis typically varies from about 300°C to 800°C, depending on the material being processed and the desired end products. The lower heating value (LHV) of syngas measures energy output, excluding water vaporization heat during oxidation, and varies with the content of hydrogen, carbon monoxide, and methane. For example, lower heating value (LHV) from biomass downdraft gasification typically reaches about 4.86 MJ/Nm^3 (Khlifi *et al* 2024).

Table 5. Mainstream parameters of the hydrogen (H_2) production.

Stream	T (°C)	P (atm)	Mass flowrate (kgh^{-1})	Molar flowrate (kmolh^{-1})	Molar composition					
					CH$_4$	CO$_2$	H$_2$O	N$_2$	CO	H$_2$
PYR-OUT	500	1	48.28	4.84	0.02	2.7E-06	0.0005	0.002	2.2E-05	0.02
GAS	500	1	48.28	4.84	0.05	5.9E-06	0.0011	0.004	4.8E-05	0.04
COMP1OUT	998	10	48.28	4.84	0.05	5.9E-05	0.0011	0.004	4.8E-05	0.04
WATER	55	1	60	3.33	0	0	1	0	0	0
P1OUT	55	10	60	3.33	0	0	1	0	0	0
REF-E	850	10	108.28	8.17	0.02	2.6E-06	0.0312	0.002	2.2E-05	0.02
REF-S	850	10	108.28	11.49	2.3E-05	0.002	0.014	0.01	0.003	0.07
HTS-E	650	10	108.28	11.49	0.005	0.002	0.014	0.002	0.013	0.07
HTS-S	650	10	108.28	11.49	0.006	0.012	0.004	0.002	0.003	0.08
LTS-E	250	10	108.28	11.49	0.006	0.012	0.004	0.002	0.003	0.08
LTS-S	250	10	108.28	11.49	0.006	0.015	0.0013	0.002	0.0008	0.08
SYNGAS	250	10	105.68	11.35	0.006	0.015	0	0.002	0.0008	0.08
H$_2$O-SEP	250	10	2.61	0.14	0	0	1	0	0	0
H6OUT	38	10	105.68	11.35	0.006	0.015	0	0.002	0.0008	0.08
HYD	38	10	17.86	8.86	0	0	0	0	0	1
EXGAS	38	10	87.82	2.50	0.007	0.018	0	0.0024	0.001	0

Reformer temperature, critical for efficiency and syngas composition, is the operating temperature in processes like steam methane reforming, where methane converts into hydrogen, carbon monoxide, and dioxide. (Lutz *et al* 2003). The syngas (H_2/CO) ratio, reflecting the hydrogen to carbon monoxide proportion in syngas, is influenced by factors like reformer temperature, pressure, and feedstock, with steam methane reformation (SMR) temperatures of 800°C to 950°C optimizing hydrogen production and achieving a high H_2/CO ratio (Carapellucci and Giordano 2020; Gao *et al* 2023).

The reformer pressure in the steam methane reformation process is usually 15 to 30 bar (atmospheric pressure) (Van Hook 1980). This range is optimized to balance the production of hydrogen (H_2) and carbon monoxide (CO), ensuring efficient conversion of methane (CH_4) while managing the equilibrium of the reactions involved. The S/F ratio (steam-to-fuel ratio) in the steam methane reformation process is crucial for optimizing hydrogen production and preventing catalyst coking, typically ranging from 2.5 to 3.5 moles of steam per mole of methane (Numaguchi and Kikuchi 1988). This ratio controls the reaction efficiency and syngas composition.

The higher heating value (HHV) is the gross calorific value. It represents the total heat released when a fuel is completely combusted and all the products have returned to their original temperature, including the condensation of water vapour in the combustion products (Cohce *et al* 2011). The higher heating value (HHV) for syngas typically ranges from 10 to 20 MJ/m^3, depending on process conditions, feedstock, and composition, with higher methane content leading to an HHV.

Hydrogen yield is calculated as in (16) (Song *et al* 2012).

$$\text{Hydrogen } (H_2) \text{ yield (Nm}^3\text{/Ton feed)} = \frac{H_2 \text{ flow rate(Nm}^3\text{/hr)}}{\text{feedstock flow rate (Ton/hr)}} \tag{16}$$

$$\text{Carbon dioxide } (CO_2) \text{ yield (Nm}^3\text{/Ton feed)} = \frac{CO_2 \text{ flow rate (Nm}^3\text{/hr)}}{\text{Feedstock flow rate (Ton/hr)}} \tag{17}$$

$$\text{Methane } (CH_4) \text{ yield (Nm}^3\text{/Ton feed)} = \frac{CH_4 \text{ flow rate (Nm}^3\text{/hr)}}{\text{Feedstock flow rate (Ton/hr)}} \tag{18}$$

The higher heating value (HHV) of the syngas is calculated using the following formula (Li *et al* 2004).

$$\text{Higher heating value (HHV)} = 12.63 \, yCO + 12.75 \, yH_2 + 39.82 \, yCH_4 \, [\text{MJ/Nm}^3] \tag{19}$$

where yCH_4, yH_2 and yCO represent the mole fractions of methane (CH_4), hydrogen (H_2), and carbon monoxide (CO), respectively, in the generated syngas. The lower heating value (LHV) is the response; the performance indicators are defined below (Kaewluan and Pipatmanomai 2011).

$$\text{Lower heating value (LHV)} = 10.79 \, yH_2 + 12.62 \, yCO + 35.81 \, yCH_4 \, [\text{MJ/Nm}^3] \tag{20}$$

where yCH_4, yH_2, and yCO are the mole fractions of methane (CH_4), hydrogen (H_2), and carbon monoxide (CO) respectively, in the syngas produced. Energy yield is the total energy consumption per kgh^{-1} of hydrogen (E_{H_2}) and the production of hydrogen of each process Q_{H_2}, kgh^{-1} (Phan *et al* 2022).

Figure 3. Comparison of hydrogen (H_2) production and energy yield among the plastic fuels.
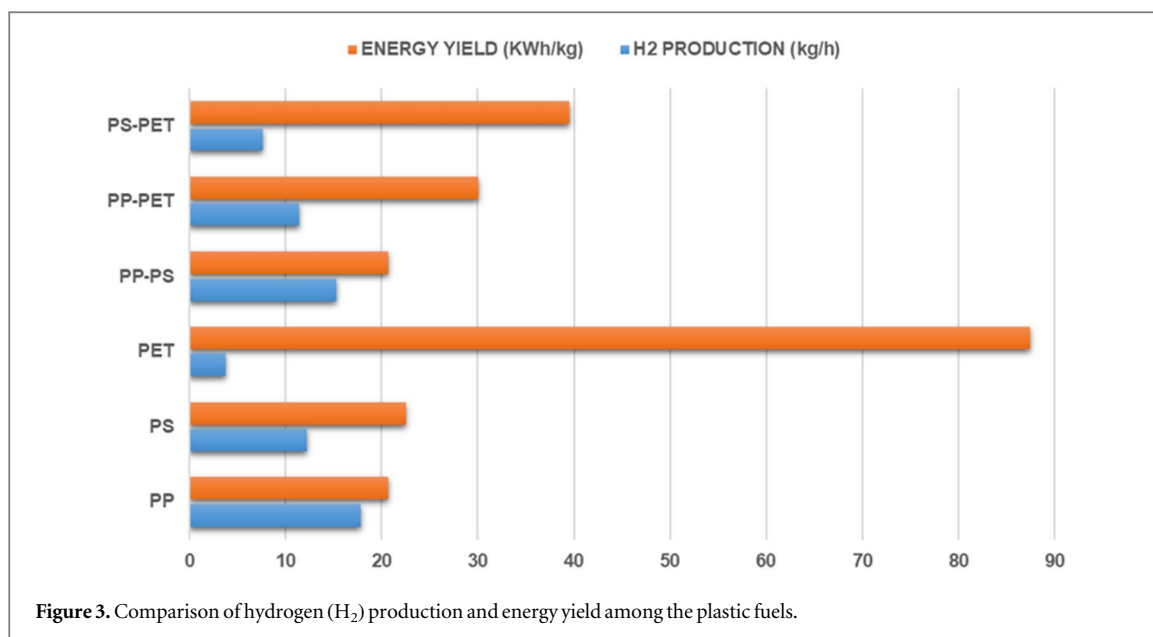
$$\text{Energy yield, } E_{H_2} = E_{total}/Q_{H_2}(\text{kW} \times \text{hkg}^{-1}) \tag{21}$$

3. Results and discussion

Multiple comparisons with experimental data have been carried out to validate the newly developed model's practicality using various oxidizing agent mixes. These comparisons have indicated that the model's predictions are reasonable and closely aligned with actual results.

3.1. Comparison of hydrogen (H_2) production and energy yield

In this research, three types of waste plastics have been utilized for hydrogen (H_2) production: polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). The study also has considered mixtures of these fuels, such as PP-PS, PP-PET, and PS-PET (50–50 wt%), to compare energy yields and hydrogen (H_2) production rates. Pyrolysis of polypropylene typically yields oil/wax rich in alkenes, alkanes, alkadienes, gas, minimal char, and hydrogen-rich alkene gases like ethene, propene, and butene from thermal degradation of similar polyalkene structures (Shalaby 1981; Wampler 1989). But, polystyrene (PS) yields mainly styrene and aromatic hydrocarbons with low gas output and no char, while polyethylene terephthalate (PET) generates carbon dioxide, carbon monoxide, and significant char (Scott *et al* 1990; Williams and Williams 1998).

In case of mixtures of the plastics Williams *et al* analysed hydrogen (H_2), ethene, propene, and butene levels were significantly higher than expected in the pyrolysis process, particularly in the PP/PS combination, which produced more alkene gases than anticipated (Williams and Williams, 1999). Figure 3 presents a detailed comparison of hydrogen (H_2) production and energy yield among these fuels. The graph highlights that polypropylene (PP) has demonstrated the highest hydrogen (H_2) production rate at around 18 kg h^{-1}, whereas polyethylene terephthalate (PET) has the lowest, nearly 5 kg/h. Among the mixed fuels, PP-PS has produced the second-highest amount of hydrogen (H_2), significantly around 16 kgh^{-1}.

On the other hand, the energy yield of various plastics, measured in kilowatt-hours per kilogram (kWh/kg), indicates the energy that can be extracted from a kilogram of plastic through processes such as pyrolysis, gasification, or combustion (Rogoff and Screve 2019). PET (polyethylene terephthalate) has the highest energy yield, nearly 85 KWh/kg, making it the most energy-efficient material for hydrogen production. PS-PET and PP-PET combinations also have shown considerable energy yields of around 30–35 KWh/kg, offering a good balance between energy efficiency and hydrogen production. In contrast, PS (polystyrene) and PP (polypropylene) have much lower energy yields, under 25 KWh/kg, indicating that while these materials may be less energy-efficient, they might be chosen when higher hydrogen production is prioritized over energy yield.

The energy yields of plastics like polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) are shaped by their chemical structures. Simpler hydrocarbons in PP and PS yield more energy, while stable aromatics in PET yield less and are influenced by processing methods like pyrolysis or gasification, which, along with blends or additives, impact decomposition temperatures and energy efficiency. This variability is critical for

Figure 4. Impact of reformer temperature on syngas composition.
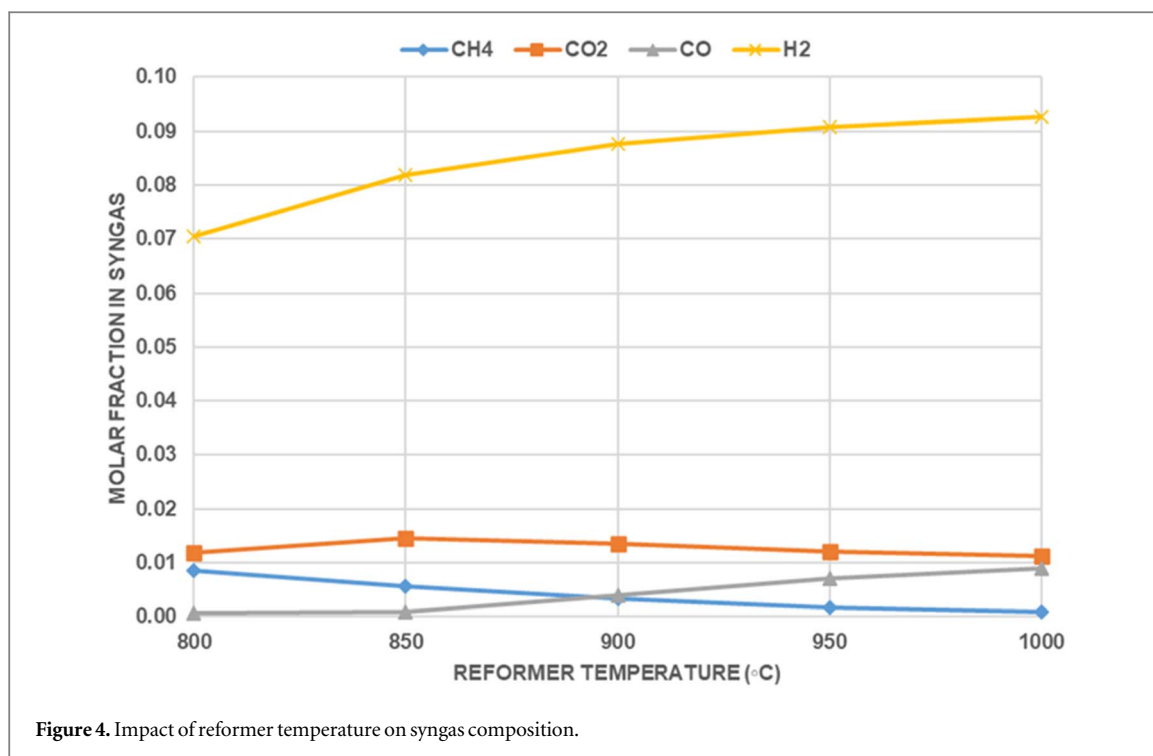
optimizing recycling and waste-to-energy processes to balance environmental and economic outcomes (Flory 1953; Callister and Rethwisch 2020).

Ultimately, the assumptions simplify the model by ensuring that all energy has been used for syngas production without friction or tar formation losses. Assuming complete char conversion to gas maximizes hydrogen yields from various plastics, and omitting tar enhances energy efficiency by eliminating the need to manage it. Additionally, considering all components except ash as reactive optimizes the conversion process, leading to higher syngas production, system efficiency, and increased energy output and hydrogen production.

3.2. Impact of reformer temperature

The reformer temperature has played a pivotal role in the steam methane reformation (SMR) process, with an elevation in gasification temperature anticipated to augment char conversion and facilitate tar decomposition. This section has explained the impact of reformer temperature on the composition of syngas, including the syngas (H_2/CO) ratio, lower heating value (LHV), and yields of hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). For the reformation of polypropylene (PP) plastic, the temperature has been modulated within a spectrum of approximately 750 to $1100°C$, maintaining constancy across other parameters such as pyrolysis temperature at $500°C$, steam-to-fuel (S/F) ratio at 1 and reformer pressure at 10 atm.

Figure 4 delineates the effects of temperature on polypropylene (PP) plastic reformation, showing that higher reforming temperatures have raised the concentrations of carbon monoxide (CO) and hydrogen (H_2) in the syngas while simultaneously decreasing the amounts of carbon dioxide (CO_2) and methane (CH_4).

The molar fraction of hydrogen has reached its apex at 0.09 at $1000°C$, whereas carbon monoxide formation has been absent at $800°C$, subsequently ascending to a 0.01 molar fraction by $1000°C$. At high temperatures, steam methane reformation (SMR) and water-gas-shift (WGS) reactions have been intensified, leading to increased production of hydrogen (H_2) and carbon monoxide (CO) (Twigg 1989; Hou and Hughes 2001). Higher temperatures have increased hydrogen (H_2) and carbon monoxide (CO) output while reducing methane (CH_4) and carbon dioxide (CO_2) levels but have diminished the efficiency of the water-gas-shift (WGS) process. These observations have aligned with established scholarly literature (Ramzan *et al* 2011; S Jarungthammachote 2007).

Assuming chemical equilibrium explains the steady increase in hydrogen production with temperature, maintaining stable concentrations of carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). At the same time, the ideal gas assumption ensures predictable gas behaviour and smooth concentration trends. Finally, disregarding pressure ensures that temperature alone drives changes in gas composition, creating a consistent and predictable output pattern in the system despite pressure variations.

The lower heating value (LHV) is the energy released from the complete combustion of a given fuel quantity, excluding the heat required for water vaporization in the combustion byproducts (Sommas Kaewluan 2011).
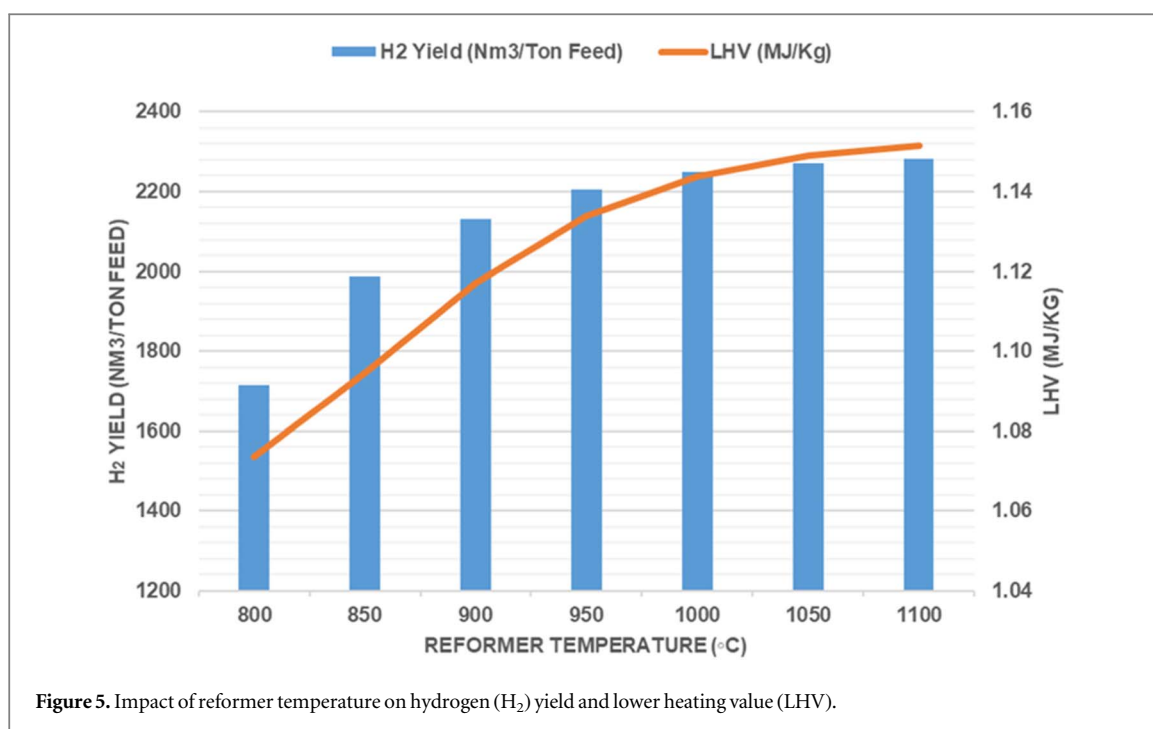
Figure 5. Impact of reformer temperature on hydrogen (H$_2$) yield and lower heating value (LHV).

This research has examined the influence of reformer temperature within the water gas shift reactor's third stage, employing various metal-based catalysts at temperatures ranging from 800 to 1100°C while maintaining other experimental variables constant, including a final pyrolysis temperature of 500°C and a steam reforming temperature of 850 °C. Steam has been introduced at a 60 kg h^{-1} rate during the second and third stages.

Figure 5 shows the impact of temperature on hydrogen generation through the pyrolysis-catalytic steam reforming water-gas-shift (WGS) process using polypropylene, indicating that higher temperatures boost hydrogen (H$_2$) yields, with a maximum yield of 2360 Nm^3/Ton achieved at 1100 °C. Simultaneously, the lower heating value (LHV) has gradually risen from just over 1.04 MJ/kg to about 1.16 MJ/kg, indicating that higher temperatures have enhanced the reforming reactions, leading to more efficient hydrogen production with more excellent energy content.
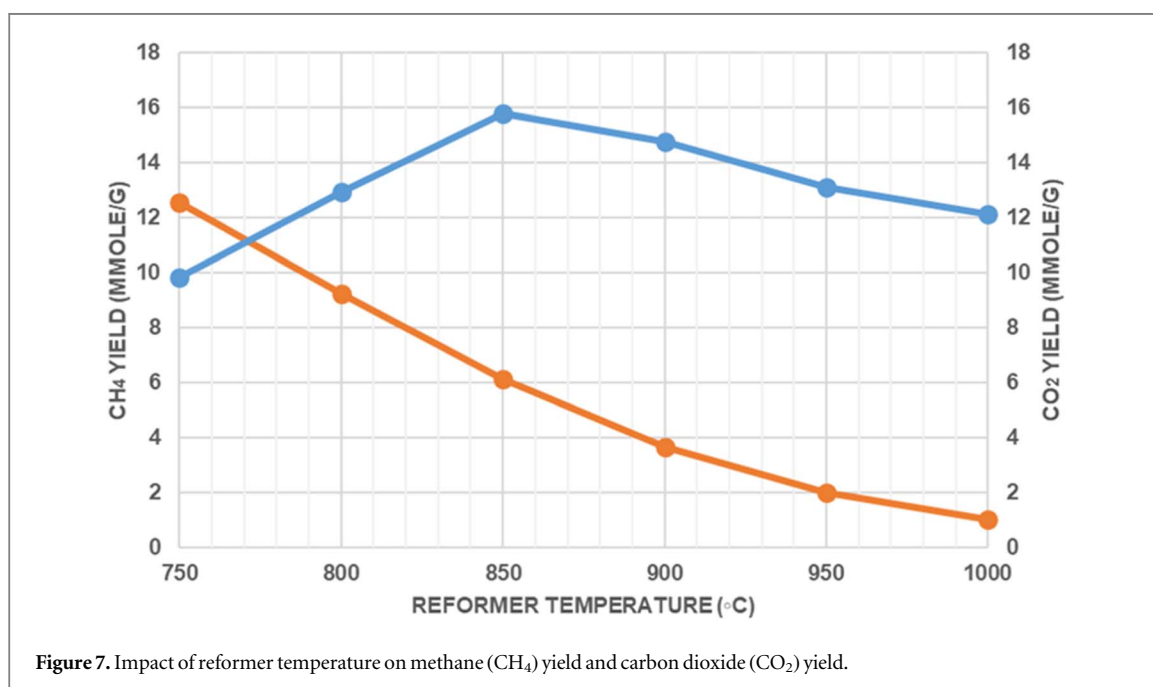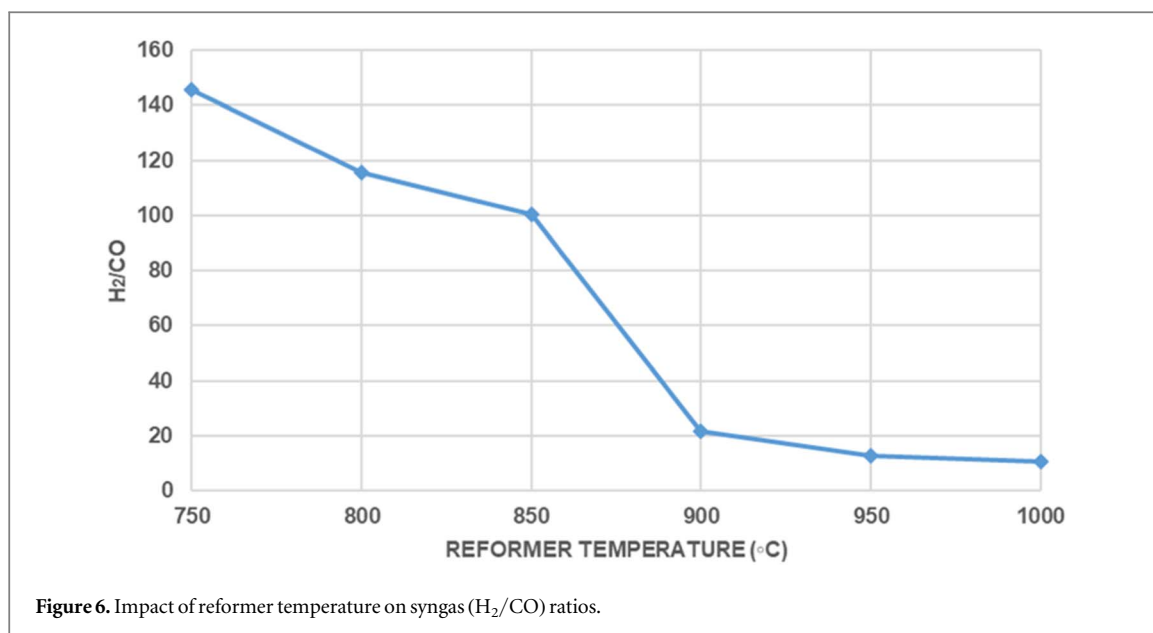
The increase in hydrogen yield and lower heating value (LHV) with rising reformer temperatures can be attributed to enhanced chemical kinetics and shifts in chemical equilibrium. Higher temperatures have accelerated reaction rates in steam methane reformation and push equilibrium toward more excellent hydrogen production, while the increased proportion of hydrogen in the gas mix has raised the overall energy content, optimizing hydrogen production efficiency in industrial processes.

Finally, assuming complete reactivity of carbon in the feedstock increases hydrogen yields and energy density (LHV) as the reformer temperature rises while excluding tar formation maintains high hydrogen yields by avoiding energy loss from inefficient breakdowns. Ideal gas conditions ensure consistent improvements in hydrogen production with increasing temperatures, eliminating deviations due to natural gas behavior.

Again, high temperatures in steam methane reforming (SMR) reduce the syngas (H$_2$/CO) ratio by favoring carbon monoxide (CO) production over hydrogen (H$_2$), as the water-gas shift (WGS) reaction becomes less efficient at higher temperatures (Salaudeen *et al* 2018; Ebrahimi *et al* 2020). This reaction dynamics has led to a higher relative concentration of carbon monoxide (CO) compared to hydrogen (H$_2$), resulting in a lower syngas (H$_2$/CO) ratio. Therefore, while higher temperatures have increased overall gas production, they have tended to decrease the proportion of hydrogen in the output, making temperature optimization crucial for achieving the desired syngas (H$_2$/CO) ratio in industrial applications.

Figure 6 displays the three-stage process's hydrogen/carbon monoxide molar ratio at different reformer temperatures. The figure has highlighted the syngas (H$_2$/CO) ratios, with the highest and, thus, most efficient ratios being attained at a reformer temperature of 750°C.

This temperature has aligned with the apex of hydrogen yield. At 750°C, the syngas (H$_2$/CO) ratio has reached approximately 140, exhibiting a progressive decline with an increase in reformer temperature. Elevating the catalyst temperature to 850°C has resulted in a syngas (H$_2$/CO) ratio of around 100, precipitously dropping to 20 at 900°C. Ultimately, at a temperature of 1000°C, the syngas (H$_2$/CO) ratio stabilizes at approximately 10. The assumption of chemical equilibrium explains the decrease in the syngas (H$_2$/CO) ratio with increased temperature favouring carbon monoxide production. In contrast, complete carbon reactivity ensures all carbon

Figure 6. Impact of reformer temperature on syngas (H_2/CO) ratios.

Figure 7. Impact of reformer temperature on methane (CH_4) yield and carbon dioxide (CO_2) yield.

converts to syngas, maintaining a smooth syngas ratio focused solely on gas-phase reactions without interference from char or tar.

Figure 7 displays how reformer temperature affected methane (CH_4) and carbon dioxide (CO_2) yields in a process. As the temperature has increased from 750°C to 1000°C, methane (CH_4) yield has initially peaked at 850°C before declining, while CO_2 yield has decreased steadily throughout the temperature range. However, as the temperature rises beyond this point, other reactions, such as methane cracking or further reforming, become more dominant, reducing the methane (CH_4) yield (Amin *et al* 2011). This has suggested that mid-range temperatures have optimized methane production, but higher temperatures have likely promoted its breakdown or conversion, reducing carbon dioxide (CO_2) formation.

The steady decrease in carbon dioxide (CO_2) yield with rising temperatures suggests suppression of CO_2 formation or its conversion into carbon monoxide (CO), reflecting temperature-dependent equilibrium shifts and reaction kinetics crucial for optimizing syngas composition and efficiency in reforming processes (Smith RJ *et al* 2010). This has highlighted the importance of temperature control in optimizing syngas composition. The absence of tar ensures methane's availability for reforming, causing a sharp decline in methane yield with rising temperatures as it converts to hydrogen and carbon monoxide (CO). At the same time, the ideal gas assumption

Figure 8. Impact of steam-to-fuel (S/F) ratio on the makeup of syngas.
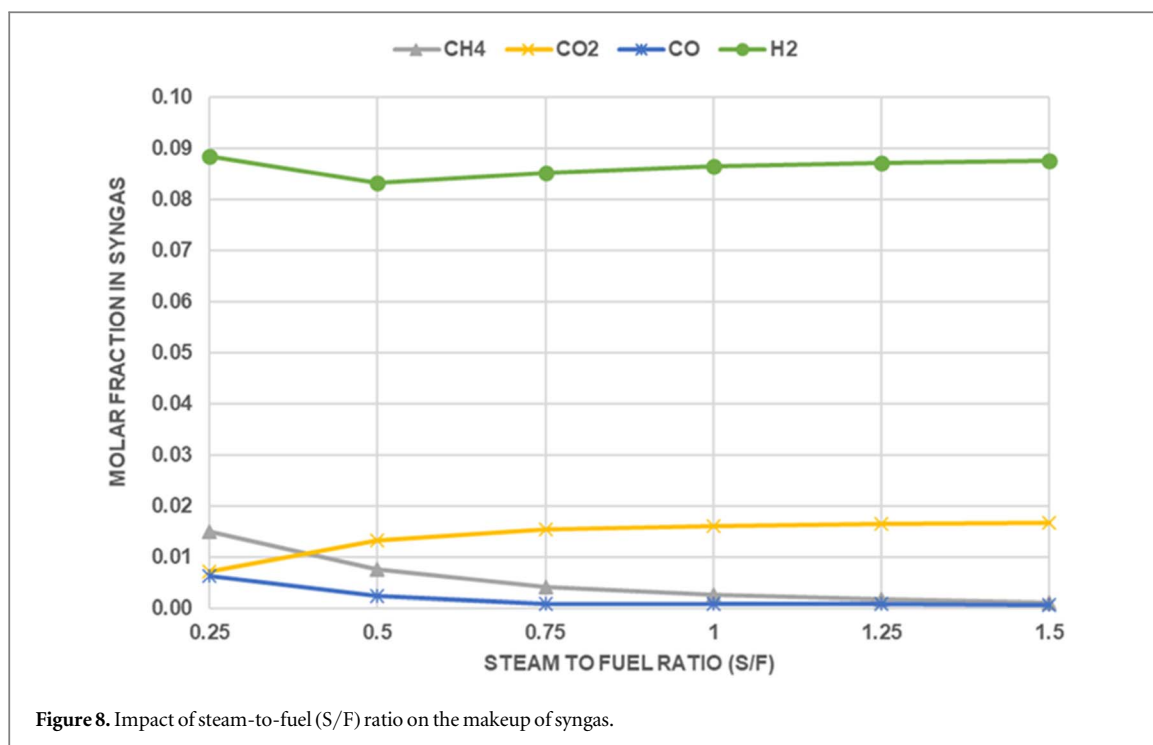
maintains a consistent relationship between carbon dioxide (CO_2) and temperature, peaking and then declining as the water-gas-shift reaction reaches equilibrium at higher temperatures.

3.3. Impact of steam to fuel (S/F) ratio

The steam-to-fuel (S/F) ratio in steam methane reforming (SMR) significantly affects hydrogen production and syngas composition. In contrast, a higher steam-to-fuel (S/F) ratio enhances hydrogen yield by facilitating more steam for reforming and the water-gas shift reaction, increasing carbon dioxide (CO_2) and reducing carbon monoxide (CO) (Ganguli and Bhatt 2023). This segment has elucidated the influence of steam-to-fuel (S/F) on syngas composition, lower heating value (LHV) and yields of hydrogen (H_2). For the reformation of polypropylene (PP) plastic, the steam-to-fuel (S/F) has been modulated within a spectrum of approximately 0.25 to 3.5, maintaining constancy across other parameters such as pyrolysis temperature at 500°C, reformer temperature at 850°C and reformer pressure at 10 atm.

Figure 8 has elucidated the influence of the steam-to-fuel (S/F) ratio on the syngas composition from polypropylene (PP) reformation, with ratios ranging from 0.25 to 1.5. It has also depicted how varying the steam-to-fuel (S/F) ratio affects syngas composition; increasing the ratio slightly boosts hydrogen (H_2) content, as more steam promotes hydrogen production. Meanwhile, the carbon monoxide (CO) and methane (CH_4) fractions have been decreased, reflecting their conversion into hydrogen (H_2) and carbon dioxide (CO_2). A notable decrease in carbon monoxide (CO) concentration from 0.8% to 0.0% has been occurred, attributed to carbon monoxide's (CO) conversion to carbon dioxide (CO_2) via the water-gas-shift (WGS) reaction, which has enhanced by increased steam availability at higher steam-to-fuel (S/F) ratios, aligning with Pinto *et al*'s findings on biomass and plastic waste co-gasification (Pinto *et al* 2002). The absence of tar formation ensures complete hydrocarbon conversion into syngas, maximizing methane reforming and enhancing hydrogen (H_2) production while increasing steam-to-fuel ratios and maintaining chemical equilibrium shift reforming reactions towards higher hydrogen output, keeping carbon dioxide (CO_2) and carbon monoxide (CO) levels stable through the water-gas-shift reaction.

The lower heating value (LHV) represents the net heat generated through the total combustion of a defined fuel volume, deducting the energy expended in vaporizing water within the combustion effluents (Sommas Kaewluan 2011). Figure 9 has delineated the impact of the steam-to-fuel (S/F) ratio on hydrogen (H_2) yield and lower heating value (LHV), revealing a marked decrease in LHV as the steam-to-fuel (S/F) ratio has escalated from 1 to 3.5, with lower heating value (LHV) diminishing from 1.01 MJ/Kg to approximately 0.96 MJ/Kg. Hydrogen (H_2) yield has shown a slight fluctuation but generally remains high, indicating effective hydrogen production across the range. This phenomenon has been attributable to the diminishing molar fractions of carbon monoxide (CO) concomitant with increased steam-to-fuel (S/F) ratios. Equation (20) has underscored
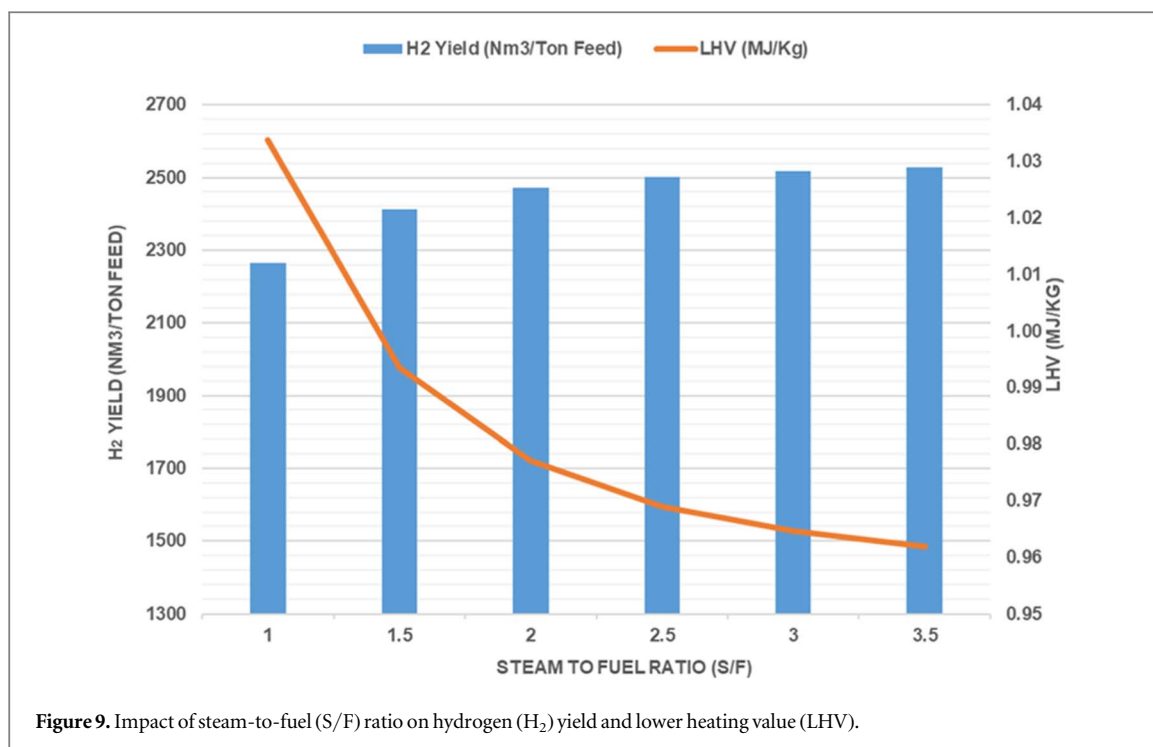
Figure 9. Impact of steam-to-fuel (S/F) ratio on hydrogen (H_2) yield and lower heating value (LHV).

carbon monoxide's (CO) predominant impact on lower heating value (LHV) relative to hydrogen (H_2); despite methane (CH_4) possessing a lower heating value (LHV) triple that of hydrogen (H_2) and carbon monoxide (CO), its quantitative presence within the gas has remained minimal.

However, the lower heating value (LHV) has decreased steadily with increasing steam-to-fuel (S/F) ratio. This suggests that while more steam enhances hydrogen output, it lowers the energy content per syngas unit, affecting its overall efficiency. In contrast, hydrogen (H_2) yield has shown a noticeable increase, from 2275 to 2525 Nm^3/Ton feed, with the rise in plastic content used as fuel.

These experimental findings align with reported trends and quantities in hydrogen (H_2) yield increase (Lopez *et al* 2015). This observation can be clarified by noting that the higher flow rate of syngas is a consequence of the decreased steam-to-fuel ratio, which in turn has caused a decrease in the fuel's ash content. To conclude, the assumption of complete reactivity ensures full carbon conversion in the feedstock to gas, increasing hydrogen yield with higher steam-to-fuel ratios for efficient hydrogen production, while ideal gas behaviour accounts for the smooth decrease in lower heating value (LHV) as added steam dilutes energy content without non-ideal gas effects.
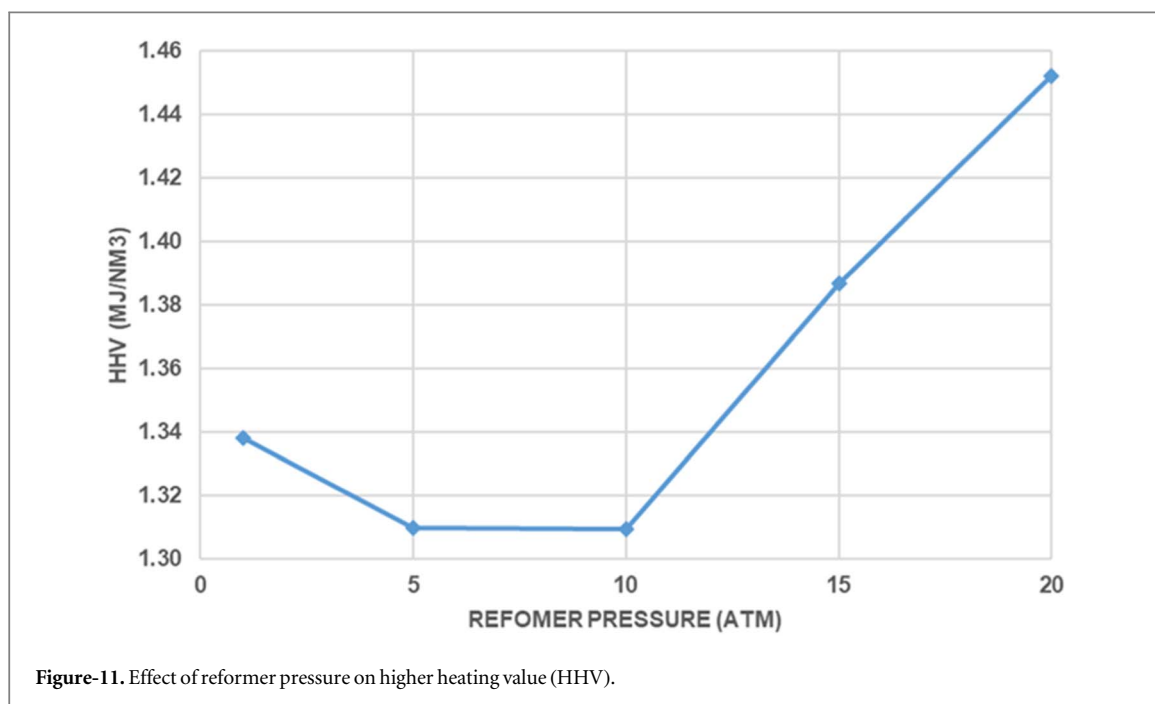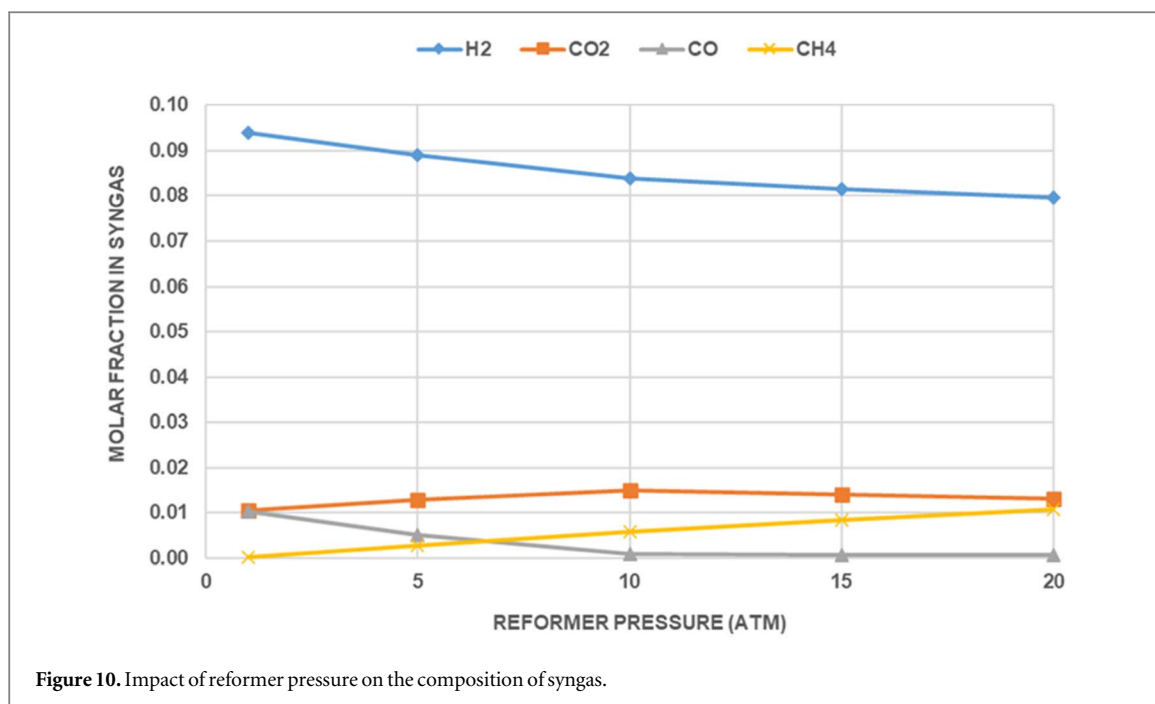
3.4. Impact of reformer pressure

Reformer pressure critically impacts the steam methane reformation (SMR) process by affecting efficiency, reaction equilibrium, and syngas composition, with higher pressures shifting the equilibrium towards less hydrogen and more methane and carbon monoxide, favouring the endothermic steam reforming reaction at lower pressures. However, higher pressures enhance downstream separation and hydrogen recovery via pressure swing adsorption (PSA) by increasing hydrogen's partial pressure (Ganguli and Bhatt 2023).

This segment has elucidated the influence of reformer pressure on syngas composition and higher heating value (HHV). For the reformation of polypropylene (PP) plastic, the pressure has been modulated within a spectrum of approximately 1 to 20 atm, maintaining constancy across other parameters such as pyrolysis temperature at 500°C, reformer temperature at 850°C and steam-to-fuel (S/F) of 1. Figures 10 and 11 have illustrated the effect of altering the reformer pressure on the composition of the product gas and its higher heating value (HHV) in the context of polypropylene (PP) waste plastic conversion. This investigation has involved adjusting the pressure within the 1 to 20 atm range, with all other process conditions have been held constant.

With increasing pressure, the concentrations of hydrogen (H_2) and carbon monoxide (CO) in the product gas have declined, while the amounts of carbon dioxide (CO_2) and methane (CH_4) have increased. Notably, the carbon dioxide (CO_2) content initially increased but then declined after reaching its peak.

Elevating the pressure has led to reduced amounts of hydrogen (H_2) and carbon monoxide (CO) while simultaneously causing an increase in the proportions of carbon dioxide (CO_2) and methane (CH_4). This has

Figure 10. Impact of reformer pressure on the composition of syngas.

Figure-11. Effect of reformer pressure on higher heating value (HHV).

occurred because higher pressure conditions favour the reaction side with fewer gas molecules . Methane content has risen from 0% to 1% as higher pressures have favoured methanation over steam methane reformation, reducing hydrogen (H_2) and carbon monoxide (CO) production but enhancing methane generation (Salaudeen *et al* 2021). Assuming no pressure losses stabilizes hydrogen fractions and causes minor changes in methane (CH_4) and carbon monoxide (CO) levels. At the same time, ideal gas behaviour predicts smooth hydrogen (H_2) decrease with increasing pressure, favouring methane formation over hydrogen production.

Figure 11 illustrates the relationship between reformer pressure and syngas' higher heating value (HHV) in the steam methane reformation (SMR) process. It shows pressure has increased higher heating value (HHV) of syngas despite reduced hydrogen (H_2) and carbon monoxide (CO) levels, with HHV initially dropping to 1.31 MJ/Nm^3 at 5 atm and then rising to 1.45 MJ/Nm^3 between 10 and 20 atm, indicating a reduction in energy content which has suggested that higher pressures have led to a more energy-dense syngas. This enhancement is

Figure-12. Influence of pyrolysis temperature on syngas makeup.
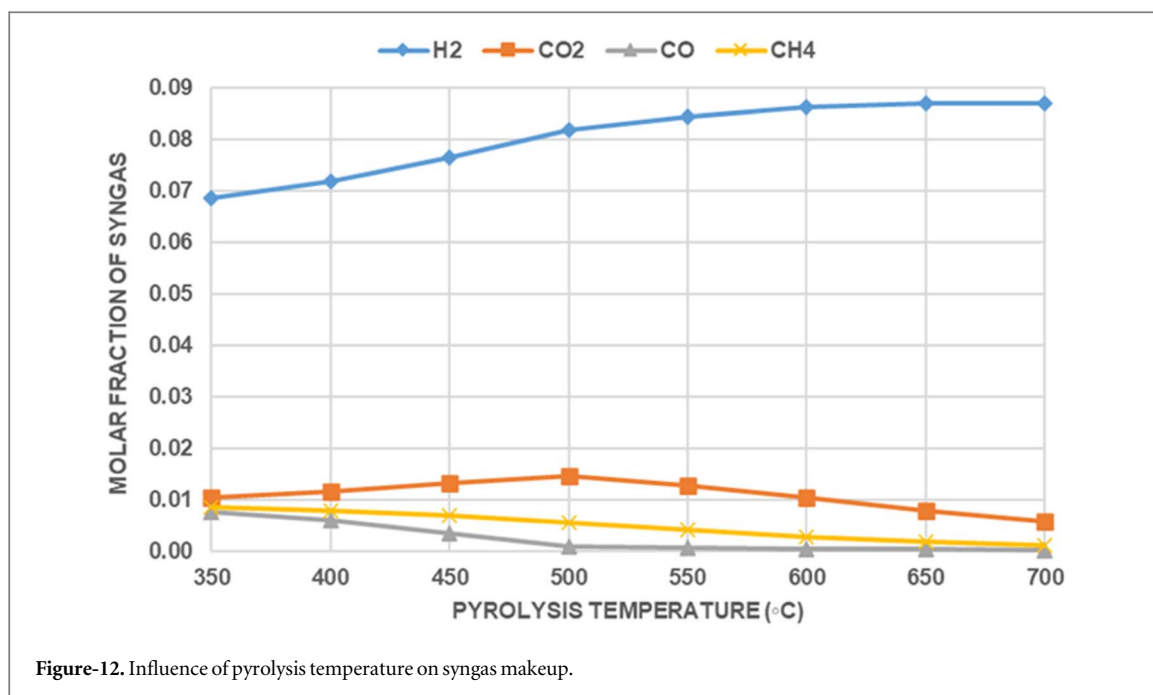
primarily due to the increased formation of methane (CH_4), a highly energy-rich component in the syngas mix (Ganguli and Bhatt 2023).

This has suggested that higher reformer pressures have favoured the production of syngas with a higher energy content due to the increased formation of energy-rich components like methane (CH_4), which significantly has enhanced the higher heating value (HHV), even with reduced hydrogen (H_2) and carbon monoxide (CO) levels (Singh *et al* 2022). Assuming no pressure losses keeps syngas energy content stable, with higher pressures increasing the higher heating value (HHV) due to enhanced methane production. At the same time, ideal gas behaviour ensures consistent HHV increases with pressure, avoiding deviations from real gas effects.

3.5. Influence of pyrolysis temperature

Pyrolysis temperature significantly impacts hydrogen production and syngas composition in steam methane reforming (SMR); higher temperatures enhance methane breakdown into hydrogen and carbon monoxide, boosting hydrogen production efficiency. However, excessively high temperatures may increase carbon formation on the catalyst, potentially reducing efficiency (Lee *et al* 2021).

In this model, the pyrolysis temperature has emerged as a pivotal determinant of the syngas composition's molar fractions, as illustrated in figure 12, with the temperature spectrum under investigation ranging from 350 to 700°C, maintaining constancy across other parameters such as steam-to-fuel (S/F) ratio at 1, reformer temperature at 850°C and reformer pressure at 10 atm. Initially, an ascending trajectory has been observed in the fractions of hydrogen (H_2) and carbon dioxide (CO_2). Nonetheless, the hydrogen (H_2) fraction has plateaued at 8.5% with temperature escalation. In contrast, carbon dioxide (CO_2) has attained a maximum at 500°C, which undergoes a steep decline to approximately 0.6%, indicating that temperature changes within this range less influence CO_2 production.

In contrast, carbon monoxide (CO) and methane (CH_4) have commenced at 1% and gradually diminished, culminating in 0% towards the process's conclusion, reflecting its more excellent conversion into hydrogen and other products at elevated temperatures. Moreover, Increasing temperatures convert more carbon monoxide (CO) to carbon dioxide (CO_2) via the water-gas-shift reaction, with CO_2's molar fraction showing a stable yet slightly downward trend, indicating its production is less sensitive to temperature variations within this range (Lee *et al* 2021). Overall, higher pyrolysis temperatures enhance hydrogen production and reduce methane and carbon monoxide in syngas, while the absence of tar leads to efficient hydrocarbon conversion, increasing hydrogen fractions. Assuming complete carbon reactivity in the feedstock ensures full conversion to syngas, further boosting hydrogen levels with rising temperatures.

3.6. The joint impact of pyrolysis and reforming temperatures on hydrogen (H_2) generation

Figure 13 has outlined the combined effects of pyrolysis and reformer temperatures on hydrogen (H_2) generation. An increase in reformer temperature has correlated with a progressive rise in hydrogen (H_2) generation, plateauing at 1000°C. Moreover, within a delineated range (400°C to 700°C), augmenting the pyrolysis temperature modestly boosts hydrogen (H_2) output. Notably, at a reformer temperature of 1000°C, the
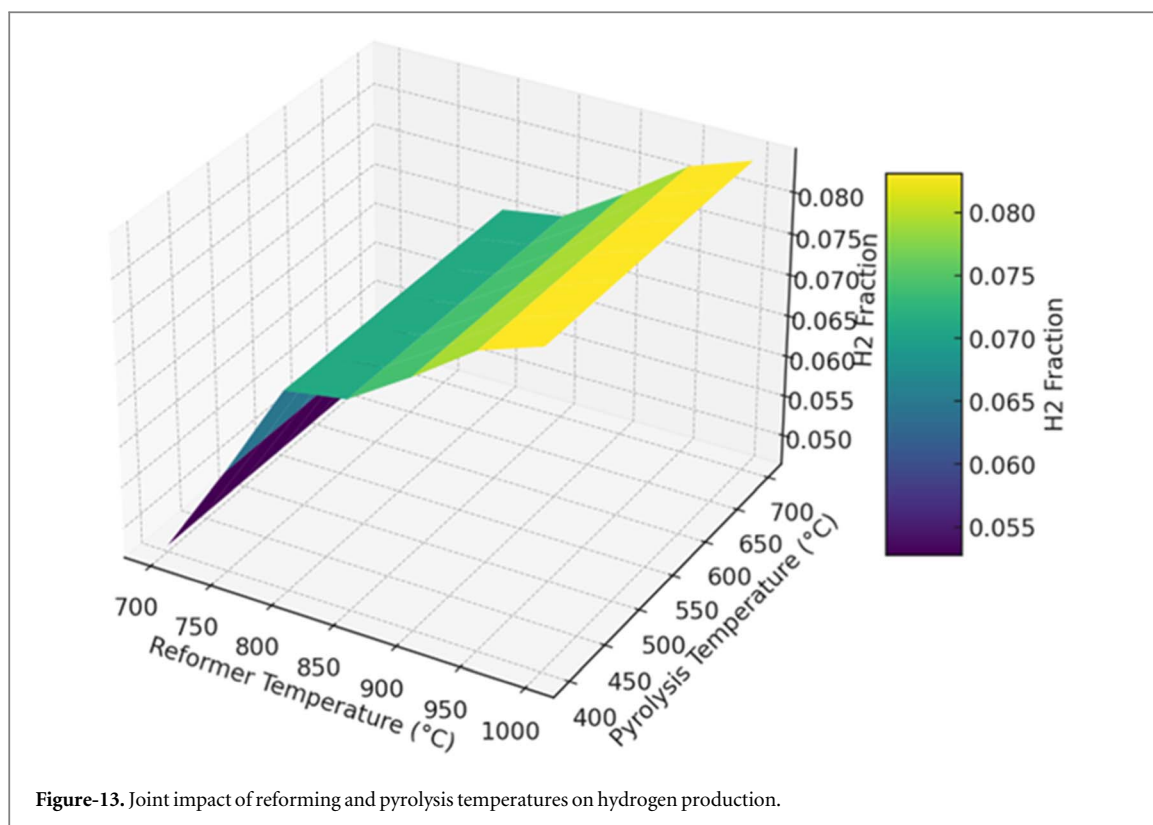
Figure-13. Joint impact of reforming and pyrolysis temperatures on hydrogen production.

hydrogen (H_2) fraction has attained an approximate value of 8.2%. These observations have been congruent with existing literature, which has suggested that the steam reformation of methane (CH_4) is optimally conducted at elevated temperatures between 750°C and 900°C, thereby substantiating the model's validity (Wenjun Duan *et al* 2015). The ideal reformer temperature of 800°C has achieved maximum efficiency, exceeding this wastes energy and has reduced economic viability (Li *et al* 2018).

Hydrogen output in this process system depends on the reformer's temperature, with the optimal reactor temperature set at 1000°C and pyrolysis maintained at 700°C. Assuming chemical equilibrium and ideal gas behaviour, hydrogen production consistently increases with rising reformer and pyrolysis temperatures, as higher temperatures favour hydrogen-producing reactions and ensure a smooth, predictable increase in hydrogen (H_2) levels.

4. Scope and limitations

The model used Aspen Plus software to simulate the process, including pyrolysis, steam methane reformation (SMR), and the water-gas-shift (WGS) reaction. The model has focused on the efficient conversion of polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) into hydrogen, which has offered a pathway for hydrogen production from waste plastics, addressing waste management and sustainable hydrogen generation. It has several limitations that need to be addressed for real-world applications. There are some limitations of the model, which are summarised here:

· The model's assumptions of no pressure losses and ideal gas behaviour oversimplify real-world operations where pressure drops and non-ideal gas behaviour can reduce system efficiency and impact gas yields.

· This model produces a significant amount of carbon dioxide (CO_2), which is released with exhaust gases. This gas is harmful to the environment and hampers the ecosystem very severely.

· The model is primarily designed for only three types of plastics (polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET)), limiting its applicability to other plastics or mixed plastic waste streams. Other plastics may behave differently under pyrolysis, affecting hydrogen yields and byproduct formation.

Using stoichiometric and non-stoichiometric methods with Gibbs free energy minimization, the model has shown a scope of accurate prediction of the system thermodynamics and product yields while incorporating

error analysis to assess reliability and refine idealized assumptions. Model validation through comparison with experimental data can enhance the accuracy and predictive capabilities, while the article has also evaluated various operational scenarios to optimize yields and efficiency.

The exclusion of tar and other heavy hydrocarbons from the model might lead to overestimating hydrogen yield. In pyrolysis processes, tar formation is standard and can reduce gas yields and affect reactor performance, necessitating more accurate handling in future models. The study has shown how to consider catalysts used in reforming or cracking processes to improve efficiency.

5. Conclusion

In this article, Aspen Plus has been employed to simulate the model to scrutinize hydrogen (H_2) production from waste plastics via a tripartite process. The study has also elucidated that numerous process parameters significantly affect syngas composition, its lower heating value (LHV), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2) yields, the syngas (H_2/CO) ratio and the syngas's higher heating value (HHV). Key outcomes of the research are delineated below:

- For hydrogen (H_2) generation, this study has employed three distinct types of waste plastics: polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) in addition to evaluating mixtures of these substrates, including PP-PS, PP-PET, and PS-PET, each at a 50–50 weight percentage. Comparative analysis has revealed polyethylene terephthalate (PET) to be the most productive in energy yield, achieving approximately 90 kWh/kg. At the same time, polypropylene (PP) has been identified as the least productive, yielding marginally over 20 kWh/kg. Conversely, polypropylene (PP) has been demonstrated to have the highest hydrogen (H_2) production rate at around 18 kg h^{-1}, whereas polyethylene terephthalate (PET) has the lowest, nearly 5 kg/h.

- Elevated reformer temperature, pyrolysis temperature, reformer pressure and steam-to-fuel (S/F) ratios have collectively enhanced the syngas composition's hydrogen (H_2) concentration. The optimised reformer temperature, steam-to-fuel (S/F) ratio, pyrolysis temperature and reformer pressure at around 1000°C, 0.25, 700°C and 1 atm, respectively, have maximized hydrogen production in syngas.

- As the reformer temperature and steam-to-fuel (S/F) ratio increased, the syngas lower heating value (LHV) increased and decreased. At the same time, the hydrogen (H_2) yield also increased, reaching a peak of 2360 Nm^3/Ton and 2525 Nm^3/Ton, respectively.

- As the reformer temperature has been increased from 750°C to 1000°C, the yield of methane (CH_4) has decreased significantly, while the yield of carbon dioxide (CO_2) also has decreased but at a slower rate.

- The higher heating value (HHV) of hydrogen has remained relatively stable at low reformer pressures (around 1.32 MJ/Nm^3) but has experienced a sharp increase as the pressure has risen above 10 atm, reaching approximately 1.46 MJ/Nm^3 at 20 atm.

- Higher reformer and pyrolysis temperatures jointly contribute to an increased hydrogen fraction, with the highest yields achieved at the maximum temperatures of both parameters.

Finally, this investigation has significantly contributed to hydrogen technology, particularly within renewable energy, by charting a novel path to produce green hydrogen as an alternative to traditional gasification processes. Consequently, the insights garnered from this study are anticipated to enrich future experimental research by applying the innovative three-stage production process in the field.

Future research should aim to investigate the impact of diverse plastic feedstock compositions, especially by including a broader range of plastic types, to improve hydrogen production efficiency significantly. This approach could also pave the way for capturing significant amounts of CO_2, which is released with exhaust gases and is detrimental to the environment. Additionally, future models should consider using catalysts in reforming or cracking processes to enhance efficiency.

Data availability statement

The data cannot be publicly available upon publication because no suitable repository exists for hosting data in this field of study. The data supporting this study's findings are available upon reasonable request from the authors.

ORCID iDs

Sakib Tanvir Hossain https://orcid.org/0009-0003-1800-7200
M A Parvez Mahmud https://orcid.org/0000-0002-1905-6800

References

Ahmad N, Ahmad N, Maafa I M, Ahmed U, Akhter P, Shehzad N, Hussain M and Javaid M 2020 Conversion of poly-isoprene based rubber to value-added chemicals and liquid fuel via ethanolysis: effect of operating parameters on product quality and quantity *Energy* **191** 116543

Ahmed U, Hussain M A, Bilal M, Zeb H, Ahmad N, Ahmad N and Usman M 2021 Production of hydrogen from low rank coal using process integration framework between syngas production processes: techno-economic analysis *Chemical Engineering and Processing-Process Intensification* **169** 108639

Ajorloo M, Ghodrat M, Scott J and Strezov V 2022 Modelling and statistical analysis of plastic biomass mixture co-gasification *Energy* **256** 124638

Akhshik M, Panthapulakkal S, Tjong J and Sain M 2018 A comparative life cycle assessment based evaluation of greenhouse gas emission and social study: natural fibre versus glass fibre reinforced plastic automotive parts *International Journal of Global Warming* **15** 350–69

Alabi O A, Ologbonjaye K I, Awosolu O and Alalade O E 2019 Public and environmental health effects of plastic wastes disposal: a review *J. Toxicol. Risk Assess* **5** 1–13

Al-Qadri A A, Ahmed U, Abdul Jameel A G, Zahid U, Usman M and Ahmad N 2022 Simulation and modelling of hydrogen production from waste plastics: technoeconomic analysis *Polymers* **14** 2056

Alshareef R, Nahil M A and Williams P T 2023 Hydrogen production by three-stage (i) pyrolysis,(ii) catalytic steam reforming, and (iii) water gas shift processing of waste plastic *Energy & Fuels* **37** 3894–907

Amin A M, Croiset E and Epling W 2011 Review of methane catalytic cracking for hydrogen production *Int. J. Hydrogen Energy* **36** 2904–35

Arregi A, Seifali Abbas-Abadi M, Lopez G, Santamaria L, Artetxe M, Bilbao J and Olazar M 2020 CeO_2 and La_2O_3 promoters in the steam reforming of polyolefinic waste plastic pyrolysis volatiles on Ni-based catalysts *ACS Sustainable Chemistry & Engineering* **8** 17307–21

Barbarias I, Lopez G, Artetxe M, Arregi A, Bilbao J and Olazar M 2018 Valorisation of different waste plastics by pyrolysis and in-line catalytic steam reforming for hydrogen production *Energy Convers. Manage.* **156** 575–84

Callister W D Jr and Rethwisch D G 2020 *Materials Science and Engineering: an Introduction* ed L Ratts *et al* (Wiley)

Carapellucci R *et al* 2020 Steam, dry and autothermal methane reforming for hydrogen production: a thermodynamic equilibrium analysis *J. Power Sources* **469** 228391

Cengel Y A, Boles M A and Kanoğlu M 2011 *Thermodynamics: an Engineering Approach* ed M Kanoglu *et al* (McGraw-Hill) ch. 1 1–41

Ciuta S, Patuzzi F, Baratieri M and Castaldi M J 2018 Enthalpy changes during pyrolysis of biomass: interpretation of intraparticle gas sampling *Appl. Energy* **228** 1985–93

Cohce M, Dincer I and Rosen M 2011 Energy and exergy analyses of a biomass-based hydrogen production system *Bioresour. Technol.* **102** 8466–74

d'Ambrières W 2019 Plastics recycling worldwide: current overview and desirable changes. Field Actions Science Reports *The journal of field actions*(Special Issue 19) 12–21 (https://journals.openedition.org/factsreports/5102)

Dewangan A, Pradhan D and Singh R 2016 Co-pyrolysis of sugarcane bagasse and low-density polyethylene: influence of plastic on pyrolysis product yield *Fuel* **185** 508–16

Dhrioua M, Ghachem K, Hassen W, Ghazy A, Kolsi L and Borjini M N 2022 Simulation of biomass air gasification in a bubbling fluidized bed using aspen plus: a comprehensive model including tar production *ACS Omega* **7** 33518–29

Dou B, Wang K, Jiang B, Song Y, Zhang C, Chen H and Xu Y 2016 Fluidized-bed gasification combined continuous sorption-enhanced steam reforming system to continuous hydrogen production from waste plastic *Int. J. Hydrogen Energy* **41** 3803–10

Duncan A 2014 *Introduction to Chemical Engineering Processes* ed A Duncan (Global Media)

Ebrahimi P, Kumar A and Khraisheh M 2020 A review of recent advances in water-gas shift catalysis for hydrogen production *Emergent Materials* **3** 881–917

Encinar J and González J 2008 Pyrolysis of synthetic polymers and plastic wastes. Kinetic study *Fuel Process. Technol.* **89** 678–86

Flory P J 1953 *Principles of Polymer Chemistry* ed P J Flory (Cornell University Press)

Foo D *et al* 2022 *Chemical Engineering Process Simulation* ed D Foo (Elsevier)

F Pinto cf, André R N, Miranda M, Gulyurtlu I and Cabrita I 2002 Co-gasification study of biomass mixed with plastic wastes *Fuel* **81** 291–7

Francis R 2016 *Recycling Of Polymers: Methods, Characterization And Applications* ed R Francis (Wiley)

Ganguli A and Bhatt V 2023 Hydrogen production using advanced reactors by steam methane reforming: a review *Frontiers in Thermal Engineering* **3** 1143987

Gao Y, Wang M, Raheem A, Wang F, Wei J, Xu D, Song X, Bao W, Huang A and Zhang S 2023 Syngas production from biomass gasification: influences of feedstock properties, reactor type, and reaction parameters *ACS omega* **8** 31620–31

Geyer R, Jambeck J R and Law K L 2017 Production, use, and fate of all plastics ever made *Sci. Adv.* **3** e1700782

Guo X, Song Z and Zhang W 2020 Production of hydrogen-rich gas from waste rigid polyurethane foam via catalytic steam gasification *Waste Management & Research* **38** 802–11

Han D G, Erdem K and Midilli A 2023 Investigation of hydrogen production via waste plastic gasification in a fluidized bed reactor using Aspen Plus *Int. J. Hydrogen Energy* **48** 39315–29

Hou K and Hughes R 2001 The kinetics of methane steam reforming over a Ni/α-Al_2O catalyst *Chem. Eng. J.* **82** 311–28

Hu Li A R, Saravanamurugan S, Pandey A, Sangwan R S, Yang S and Luque R 2018 Carbon-increasing catalytic strategies for upgrading biomass into energy-intensive fuels and chemicals *American Chemical Society* **8** 148–87

Hussein Z A, Shakor Z M, Alzuhairi M and Al-Sheikh F 2023 Kinetic and thermodynamic study of the pyrolysis of plastic waste *Environmental Processes* **10** 27

Kaewluan S and Pipatmanomai S 2011 Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidised bed gasifier *Energy Convers. Manage.* **52** 75–84

Kaiwen L, Bin Y and Tao Z 2018 Economic analysis of hydrogen production from steam reforming process: a literature review *Energy Sources Part B* **13** 109–15

Khlifi S, Pozzobon V and Lajili M 2024 A comprehensive review of syngas production, fuel properties, and operational parameters for biomass conversion *Energies* **17** 3646

Kontogeorgis G M and Folas G K 2009 *Thermodynamic Models For Industrial Applications: From Classical And Advanced Mixing Rules To Association Theories* ed G M Kontogeorgis and G K Folas (Wiley)

Kourdourli F, Estel L, Taouk B and Abdelouahed L 2023 Modeling of hydrogen production from biomass bio-digestion under Aspen Plus *Comput. Chem. Eng.* **175** 108273

K T A A *et al* 2023 Aspen plus simulation of biomass gasification: a comprehensive model incorporating reaction kinetics, hydrodynamics and tar production. Process Integration and optimization for *Sustainability* **7** 255–68

Lee S, Kim H S, Park J, Kang B M, Cho C-H, Lim H and Won W 2021 Scenario-based techno-economic analysis of steam methane reforming process for hydrogen production *Applied Sciences* **11** 6021

Levenspiel O 1998 *Chemical Reaction Engineering* ed W Anderson and K Santor (Wiley)

Li X, Grace J, Lim C, Watkinson A, Chen H and Kim J 2004 Biomass gasification in a circulating fluidized bed *Biomass Bioenergy* **26** 171–93

Lopez G, Artetxe M, Amutio M, Alvarez J, Bilbao J and Olazar M 2018 Recent advances in the gasification of waste plastics. a critical overview *Renew. Sustain. Energy Rev.* **82** 576–96

Lopez G, Erkiaga A, Amutio M, Bilbao J and Olazar M 2015 Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor *Fuel* **153** 393–401

Lutz A E, Bradshaw R W, Keller J O and Witmer D E 2003 Thermodynamic analysis of hydrogen production by steam reforming *Int. J. Hydrogen Energy* **28** 159–67

Marcantonio V, De Falco M, Capocelli M, Bocci E, Colantoni A and Villarini M 2019 Process analysis of hydrogen production from biomass gasification in fluidized bed reactor with different separation systems *Int. J. Hydrogen Energy* **44** 10350–60

Marcantonio V, Di Paola L, De Falco M and Capocelli M 2023 Modeling of biomass gasification: from thermodynamics to process simulations *Energies* **16** 7042

Mathias P M and Copeman T W 1983 Extension of the peng-robinson equation of state to complex mixtures: evaluation of the various forms of the local composition concept *Fluid Phase Equilib.* **13** 91–108

Midilli A, Kucuk H, Haciosmanoglu M, Akbulut U and Dincer I 2022 A review on converting plastic wastes into clean hydrogen via gasification for better sustainability *Int. J. Energy Res.* **46** 4001–32

Moldoveanu S C 2009 *Pyrolysis Of Organic Molecules: Applications To Health And Environmental Issues* ed S C Moldoveanu (Elsevier)

Naveed Ramzan A A, Naveed S and Malik A 2011 Simulation of hybrid biomass gasification using Aspen plus: a comparative performance analysis for food, municipal solid and poultry waste *Biomass Bioenergy* **35** 3962–9

Numaguchi T and Kikuchi K 1988 Intrinsic kinetics and design simulation in a complex reaction network; steam-methane reforming *Tenth International Symposium On Chemical Reaction Engineering* **3** 2295–301

Özkara-Aydınoğlu Ş *et al* 2010 Thermodynamic equilibrium analysis of combined carbon dioxide reforming with steam reforming of methane to synthesis gas *Int. J. Hydrogen Energy* **35** 12821–8

Park H-G, Han S-Y, Jun K-W, Woo Y, Park M-J and Kim S K 2019 Bench-scale steam reforming of methane for hydrogen production *Catalysts* **9** 615

Paul T R, Nath H, Chauhan V and Sahoo A 2021 Gasification studies of high ash Indian coals using Aspen plus simulation *Mater. Today Proc.* **46** 6149–55

Peng D-Y and Robinson D B 1976 A new two-constant equation of state *Industrial & Engineering Chemistry Fundamentals* **15** 59–64

Phan T S, Minh D P, Espitalier F, Nzihou A and Grouset D 2022 Hydrogen production from biogas: process optimization using ASPEN Plus® *Int. J. Hydrogen Energy* **47** 42027–39

Plastics Europe 2022 *Plastics - the Facts 2021* https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/

Plastics Europe 2022 *The Circular Economy for Plastics – a European Overview* https://plasticseurope.org/knowledge-hub/the-circular-economy-for-plastics-a-european-overview-2/

Poling B E, Prausnitz J M and O'connell J P 2001 *The Properties Of Gases And Liquids* Fifth, ed B E Poling, J M Prausnitz and J P O'Connell (McGraw-Hill) (https://doi.org/10.1036/0070116822)

Qin L, Xu Z, Zhao B, Zou C, Chen W and Han J 2022 Kinetic study on high-temperature gasification of medical plastic waste coupled with hydrogen-rich syngas production catalyzed by steel-converter ash *J. Energy Inst.* **102** 14–21

Rogoff M J and Screve F 2019 *Waste-To-Energy: Technologies And Project Implementation* 3rd edn, ed M L Leticia (Academic) (https://doi.org/10.1016/B978-0-12-816079-4.00001-3)

Rosha P, Kumar S, Vikram S, Ibrahim H and Ala'a H 2022 H2-enriched gaseous fuel production via co-gasification of an algae-plastic waste mixture using Aspen PLUS *Int. J. Hydrogen Energy* **47** 26294–302

Salaudeen S A, Acharya B, Heidari M, Arku P and Dutta A 2018 Numerical investigation of CO_2 valorization via the steam gasification of biomass for producing syngas with flexible H_2 to CO ratio *Journal of CO₂ Utilization* **27** 32–41

Salaudeen S A, Acharya B and Dutta A 2021 Steam gasification of hydrochar derived from hydrothermal carbonization of fruit wastes *Renewable Energy* **171** 582–91

Santamaria L, Lopez G, Fernandez E, Cortazar M, Arregi A, Olazar M and Bilbao J 2021 Progress on catalyst development for the steam reforming of biomass and waste plastics pyrolysis volatiles: a review *Energy & Fuels* **35** 17051–84

Scott D, Czernik S, Piskorz J and Radlein D S A 1990 Fast pyrolysis of plastic wastes *Energy & Fuels* **4** 407–11

Shalaby S W 1981 Thermoplastic polymers *Thermal Characterization of Polymeric Materials* ed E A Turi (Elsevier Science) 3 237–354

Sherif S A, Goswami D Y, Stefanakos E L and Steinfeld A 2014 *Handbook of hydrogen energy* ed F Kreith and D W Pepper (CRC press)

Simões C L, Pinto L M C and Bernardo C 2014 Environmental and economic analysis of end of life management options for an HDPE product using a life cycle thinking approach *Waste Management & Research* **32** 414–22

Singh M, Salaudeen S A, Gilroyed B H and Dutta A 2022 Simulation of biomass-plastic co-gasification in a fluidized bed reactor using Aspen plus *Fuel* **319** 123708

S Jarungthammachote A D 2007 Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier *Energy* **32** 1660–9

Smith R J B, Loganathan M and Shantha M S 2010 A review of the water gas shift reaction kinetics *Int. J. Chem. Reactor Eng.* **8** 1

Sommas Kaewluan S P 2011 Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidised bed gasifier *Energy Convers. Manage.* **52** 75–84

Song T, Wu J, Shen L and Xiao J 2012 Experimental investigation on hydrogen production from biomass gasification in interconnected fluidized beds *Biomass Bioenergy* **36** 258–67

Spath P L and Mann M K 2000 *Life Cycle Assessment Of Hydrogen Production Via Natural Gas Steam Reforming* Golden, CO (United States) National Renewable Energy Lab (NREL) (https://doi.org/10.2172/764485)

Statista 2022 *New York* https://statista.com/study/22965/new-york-statista-dossier

Tauqir W, Zubair M and Nazir H 2019 Parametric analysis of a steady state equilibrium-based biomass gasification model for syngas and biochar production and heat generation *Energy Convers. Manage.* **199** 111954

Tavares R, Monteiro E, Tabet F and Rouboa A 2020 Numerical investigation of optimum operating conditions for syngas and hydrogen production from biomass gasification using Aspen Plus *Renewable Energy* **146** 1309–14

Thompson R C, Moore C J, Vom Saal F S and Swan S H 2009 Plastics, the environment and human health: current consensus and future trends *Philosophical transactions of the royal society B: biological sciences* **364** 2153–66

Twigg M V *et al* 1989 *Catalyst Handbook* 2nd edn, ed M V Twigg (Wolfe Pub. Ltd) (https://doi.org/10.1201/9781315138862)

Upreti S R *et al* 2017 *Process Modeling And Simulation For Chemical Engineers: Theory And Practice* ed S R Upreti (Wiley) (https://doi.org/10.1002/9781118914670)

Van Hook J P *et al* 1980 Methane-steam reforming *Catalysis Reviews—Science and Engineering* **21** 1–51

Vera Marcantonio E B A D M *et al* 2020 Development of a chemical quasi-equilibrium model of biomass waste gasification in a fluidized-bed reactor by *Using Aspen Plus. Enregies* **13** 53

Wampler T P *et al* 1989 Thermometric behavior of polyolefins *J. Anal. Appl. Pyrolysis* **15** 187–95

Wenjun Duan Q Y, Wang K, Qin Q, Hou L, Yao X and Wu T 2015 ASPEN Plus simulation of coal integrated gasification combined blast furnace slag waste heat recovery system *Energy Convers. Manage.* **100** 30–6

Williams P T *et al* 2006 Yield and composition of gases and oils/waxes from the feedstock recycling of waste plastic *Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels* ed D J Scheirs and P W Kaminsky (Wiley) 285–313

Williams P T and Williams E 1998 Recycling plastic waste by pyrolysis *J. Inst. Energy* **71** 81–93

Wu C and Williams P T 2010 Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production *Int. J. Hydrogen Energy* **35** 949–57

Yao D, Yang H, Chen H and Williams P T 2018 Investigation of nickel-impregnated zeolite catalysts for hydrogen/syngas production from the catalytic reforming of waste polyethylene *Appl. Catalysis* B **227** 477–87

Zhang Y, Huang J and Williams P T 2017 Fe–Ni–MCM-41 catalysts for hydrogen-rich syngas production from waste plastics by pyrolysis–catalytic steam reforming. *Energy & Fuels* **31** 8497–504

Zhao Y, Yao J, Chen G, Liu J, Cheng Z, Wang L, Yi W and Xu S 2023 Energy, efficiency, and environmental analysis of hydrogen generation via plasma co-gasification of biomass and plastics based on parameter simulation using Aspen plus *Energy Convers. Manage.* **295** 117623

Zhou B, Chang J, Li J, Hong J, Wang T, Zhu Z, Zhang L and Ma C 2023 Two-stage gasification process simulation and optimization of pulverized coal for hydrogen-rich production using Aspen plus *Int. J. Hydrogen Energy* **49** 849–60