

Co-Production of Carbon Nanotubes and Hydrogen from Waste Polypropylene Using an Fe/Al₂O₃ Catalyst: Waste Valorization Beyond Fuel

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Abstract

The conversion of waste polypropylene into hydrogen and carbon nanotubes (CNTs) offers a potential pathway for transforming persistent plastic waste into products with complementary energy and materials value. This study is designed to investigate the catalytic decomposition of waste polypropylene using an iron-loaded alumina ($\text{Fe}/\text{Al}_2\text{O}_3$) catalyst, with particular emphasis on the simultaneous production of hydrogen-rich gas and carbon nanomaterials. A two-stage pyrolysis–catalytic decomposition configuration is proposed to separate polymer cracking from the subsequent catalytic transformation of volatile hydrocarbons. The effects of catalyst temperature, iron loading, catalyst-to-plastic ratio, residence time and catalyst reuse are to be evaluated against polypropylene conversion, hydrogen yield, carbon deposition, CNT selectivity and structural quality. Gas chromatography is proposed for quantitative gas analysis, while scanning and transmission electron microscopy, Raman spectroscopy, X-ray diffraction and thermogravimetric analysis will be used to establish the identity, morphology, crystallinity and purity of the carbon products. Carbon and hydrogen balances will provide a quantitative basis for comparing energy recovery with materials recovery. Previous studies demonstrate the feasibility of producing hydrogen and CNTs from polypropylene using iron-containing alumina catalysts; therefore, the principal contribution of this investigation must be established through reproducible measurements, systematic parameter optimization and an integrated assessment of product quality and catalyst stability. The resulting framework is intended to support the development of waste-to-resource technologies that extend plastic valorization beyond conventional fuel production.

1. Introduction

The accumulation of post-consumer plastic waste presents a persistent environmental challenge because the durability that makes plastics technologically useful also complicates their end-of-life management. Polypropylene (PP), a widely used polyolefin, is particularly suitable for thermochemical conversion because its hydrocarbon backbone can generate volatile compounds that serve as precursors for hydrogen and carbon nanomaterial production. Although mechanical recycling remains important wherever material quality and contamination permit, thermochemical routes may provide additional options for selected waste streams that are difficult to recycle conventionally.

Catalytic pyrolysis offers an alternative to treating waste plastics solely as sources of combustible oils and gases. During thermal decomposition, polypropylene generates a complex mixture of hydrocarbons. Subsequent catalytic cracking and dehydrogenation can convert these intermediates into smaller gaseous molecules, hydrogen and carbonaceous deposits. Under appropriate conditions, iron-containing catalysts can promote the nucleation and growth of tubular graphitic structures, creating a pathway in which the same waste feedstock supplies both an energy-related product and a potentially valuable functional material.

Alumina-supported iron is of interest because the support can disperse the active metal, influence metal-particle stability and provide a surface for hydrocarbon conversion. Nevertheless, the formation of carbon nanotubes is not guaranteed by carbon deposition alone. Amorphous carbon, graphitic particles, nanofibres and other morphologies may coexist with CNTs. Consequently, gravimetric carbon yield must be distinguished from verified CNT yield, and hydrogen production must be quantified independently rather than inferred from the apparent degree of cracking.

Previous research has already established the feasibility of hydrogen and CNT co-production from waste plastics. Yao and co-workers reported that Fe/ γ -Al₂O₃ generated 22.9 mmol H₂ per gram of plastic and approximately 195 mg of carbon nanotubes per gram of plastic among the monometallic catalysts examined in their study of real-world waste plastics. Their results also demonstrated that catalyst composition and operating conditions influence both products [1]. Further research has investigated Fe/Al₂O₃-catalysed conversion of different waste plastics and the relationship between feedstock composition and carbon-product characteristics [2]. More recently, plasma-assisted processing of polypropylene over Fe/ γ -Al₂O₃ has demonstrated the importance of activating pyrolysis vapours and controlling CNT growth [3].

These studies establish a substantial foundation, but they also impose a clear requirement on subsequent research: a new investigation should not claim novelty merely because it combines polypropylene, iron and alumina. Its contribution must arise from a clearly defined experimental question, such as the effect of iron loading on the trade-off between hydrogen formation and CNT quality, the response of real post-consumer polypropylene to operating conditions, or the stability of the catalyst over repeated cycles.

Accordingly, the present study is framed around the following research question: Can the operating conditions of Fe/Al₂O₃-catalysed polypropylene conversion be optimized to obtain reproducible hydrogen production and high-quality CNTs while maintaining a closed carbon balance and acceptable catalyst stability?

The specific objectives are:

1. To quantify polypropylene conversion and the distribution of gaseous, condensable and solid products.
2. To determine hydrogen yield and composition using calibrated gas analysis.
3. To distinguish verified CNT production from total carbon deposition.
4. To correlate operating conditions with CNT morphology, graphitic order and catalyst properties.
5. To evaluate repeatability, catalyst deactivation and the implications of the combined energy–materials recovery route.

The central hypothesis is that an intermediate operating window may provide a more favourable balance between hydrogen generation, carbon nanotube formation and structural quality than conditions selected to maximize any single output.

2. Materials and methods

2.1. Feedstock preparation and characterization

Post-consumer polypropylene should be collected from a traceable source, manually sorted, washed where necessary, dried to constant mass and cut into appropriately sized pieces. Polymer identity should be confirmed using Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) or another validated method. Thermogravimetric analysis (TGA) can establish the principal decomposition interval and residual inorganic fraction.

The initial characterization should document moisture, ash content, polymer identity and any detectable contaminants. Where the study uses only clean laboratory-grade polypropylene, the manuscript should state this explicitly and avoid generalizing the results to mixed municipal plastic waste.

2.2. Catalyst preparation

Fe/Al₂O₃ should be prepared using a specified method, such as incipient-wetness impregnation or controlled wet impregnation of alumina with an iron precursor. The iron precursor, solvent, nominal loading, drying conditions, calcination temperature, heating rate and duration must be recorded. A consistent preparation protocol is necessary to separate the effect of iron loading from variations in catalyst synthesis.

The nominal iron content should be reported separately from the experimentally measured loading. Inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray fluorescence or an appropriate alternative may be used to verify metal content. BET surface-area analysis, X-ray diffraction and electron microscopy should be used, where available, to assess support properties, crystalline phases and metal dispersion.

2.3. Pyrolysis–catalytic reactor configuration

A two-stage reactor is proposed. In the first stage, polypropylene is thermally decomposed under an inert carrier gas. The resulting vapours are transported to a second, temperature-controlled zone containing Fe/Al₂O₃, where hydrocarbon cracking, dehydrogenation and carbon deposition occur.

The system should include calibrated temperature measurement, controlled gas flow, a sealed gas-transfer line, condensate collection, appropriate gas sampling and safe exhaust treatment. Reactor geometry, catalyst-bed dimensions, particle size, carrier-gas identity, feed rate, pressure and vapour residence time must be documented.

A practical initial screening range is 700–900°C for the catalytic zone, informed by previous studies of plastic-derived hydrogen and CNT formation [1,2]. This range is a proposed experimental window, not a report of conditions already tested in the present study. The selected operating range must be compatible with the reactor, catalyst and institutional safety procedures.

2.4. Experimental design

The study should use a staged design rather than changing all parameters simultaneously.

First, perform baseline experiments without catalyst and with alumina alone. Next, evaluate Fe/Al₂O₃ at several catalyst temperatures. Subsequently, investigate iron loading and catalyst-to-plastic ratio around the most promising temperature range. Finally, repeat the selected condition and conduct catalyst-reuse tests.

Each condition should be independently replicated, preferably at least three times. Randomized run order, consistent feedstock preparation and predefined procedures for handling missing or anomalous measurements should be adopted. Report means, standard deviations, replicate counts and uncertainty intervals.

2.5. Gas analysis and hydrogen quantification

Permanent gases should be quantified using calibrated gas chromatography, with a suitable detector configuration for hydrogen and the relevant light hydrocarbons. Gas composition alone is insufficient: the total dry-gas volume or molar flow must also be measured.

Gas measurements should be corrected for sampling losses, water vapour where relevant, calibration factors and the reference temperature and pressure. Any hydrogen concentration reported in volume percent must be distinguished from the total hydrogen yield.

2.6. Carbon product recovery and CNT characterization

After cooling, the catalyst bed should be recovered quantitatively. Carbonaceous deposits should be assessed using gravimetry and TGA, with suitable controls to distinguish deposited carbon from changes in catalyst mass. Where necessary, the catalyst may be subjected to a validated separation or purification procedure, with recovery losses reported.

Scanning electron microscopy (SEM) should assess surface morphology, while transmission electron microscopy (TEM) should be used to verify tubular structures, wall morphology and approximate diameter distributions. Raman spectroscopy should provide the D and G band positions and intensity ratio. X-ray diffraction may be used to investigate graphitic ordering and residual crystalline phases.

The total carbon-deposit yield and the verified CNT yield must be reported separately. If CNT mass cannot be quantified independently with defensible uncertainty, it should be described as an estimated CNT fraction rather than an exact yield.

2.7. Statistical analysis

Results should be presented as mean $\pm$ standard deviation for independent replicates. One-way or factorial analysis of variance (ANOVA), as appropriate to the design, may be used to evaluate operating-parameter effects, with effect sizes, confidence intervals and adjusted post-hoc comparisons reported

where applicable. Regression or response-surface analysis may be used to identify interactions between catalytic temperature, iron loading and catalyst-to-plastic ratio.

Statistical significance should not substitute for engineering relevance. The analysis should also consider measurement uncertainty, carbon-balance closure, run-to-run variability and the trade-off between hydrogen output and CNT quality.

3. Data analysis tables

Table 1
Feedstock and catalyst characterization

Parameter	Measurement method
Material identity	FTIR/XRD
Moisture content (wt%)	Gravimetry/TGA
Ash or inorganic residue (wt%)	TGA/elemental analysis
Iron loading (wt%)	ICP-OES/XRF
BET surface area (m ² g ⁻¹)	N ₂ adsorption
Average iron-particle size (nm)	TEM
Major crystalline phases	XRD
Thermal decomposition range (°C)	TGA/DSC

Purpose: Establish the reproducibility of the feedstock and catalyst and identify structural properties that may influence catalytic performance.

Table 2
Experimental matrix for process optimization

Run group	Catalytic temperature (°C)	Fe loading (wt%)	Catalyst/PP mass ratio	Replicates
Thermal baseline	No catalyst	—	0	≥ 3
Support control	Selected temperature	0	Matched to catalyst mass	≥ 3
Temperature screening	700, 750, 800, 850, 900	Fixed	Fixed	≥ 3 per condition
Fe-loading screening	Optimized range	5, 10, 15, 20*	Fixed	≥ 3 per condition
Catalyst-ratio screening	Selected temperature	Selected loading	0.25, 0.50, 1.00*	≥ 3 per condition
Reuse study	Selected temperature	Selected loading	Selected ratio	≥ 3 cycles

Table 3
Literature benchmarks and positioning of the present study

Study	Catalyst/system	Reported result	Implication
Yao et al. (2018) [1]	Fe/ γ -Al ₂ O ₃ ; two-stage pyrolysis–catalysis	22.9 mmol H ₂ g ^{−1} plastic; approximately 195 mg CNT g ^{−1} plastic for the reported Fe/ γ -Al ₂ O ₃ case	Baseline for hydrogen and CNT co-production
Yao and Wang (2020) [3]	Fe- and Ni-based catalysts	FeNi sol–gel catalyst: 25.14 mmol H ₂ g ^{−1} plastic and 360 mg carbon nanomaterials g ^{−1} plastic	Demonstrates the importance of catalyst formulation
Cai et al. (2021) [2]	Fe/Al ₂ O ₃ ; multiple plastic feedstocks	PP and PE produced carbon deposits with reported CNT purity of approximately 80%	Feedstock identity influences product quality
Plasma-assisted PP study (2023) [4]	Fe/ γ -Al ₂ O ₃ with dielectric-barrier-discharge plasma	Approximately 30 mmol H ₂ g ^{−1} plastic and 322 mg CNT g ^{−1} plastic	Highlights the effect of plasma activation
Present investigation	Fe/Al ₂ O ₃ ; waste PP	To be measured	Establishes whether the selected feedstock, operating window and analytical protocol provide a defensible improvement

4. Results and discussion: analytical framework

This section specifies the scientific interpretation to apply after the experimental results have been obtained. It does not claim that the proposed experiments have already been conducted.

4.1. Influence of catalytic temperature on hydrogen generation

Catalytic temperature is expected to influence the cracking of polypropylene-derived hydrocarbons, the formation of lighter gas molecules, hydrogen release and carbon deposition. At relatively low temperatures, incomplete cracking may leave a larger fraction of condensable hydrocarbons. Increasing temperature may promote secondary decomposition and dehydrogenation, but the resulting hydrogen yield will depend on gas residence time, catalyst properties and the competition between gas formation and carbon deposition.

The temperature profile should therefore be evaluated using both hydrogen yield and CNT yield. A temperature that maximizes hydrogen production may not maximize CNT quality or carbon recovery. The preferred operating condition should be defined using a transparent, multi-objective criterion rather than selecting the largest single value.

4.2. Relationship between hydrogen production and carbon nanotube growth

Hydrogen and CNTs can emerge from related catalytic transformations of hydrocarbon intermediates. Iron-containing particles may facilitate carbon dissolution or diffusion and subsequent precipitation as graphitic structures. However, excessive carbon accumulation can block active sites, alter particle morphology or promote catalyst deactivation.

A convincing interpretation requires the combined evaluation of hydrogen yield, total carbon deposition, CNT selectivity and microscopy. An increase in total solid carbon should not automatically be interpreted as an improvement in CNT production. Likewise, a rise in hydrogen concentration should not be interpreted as an increase in hydrogen yield without a corresponding measurement of total gas production.

4.3. Influence of iron loading and alumina support

Iron loading may affect active-site density, metal-particle size, dispersion and the degree of interaction between the metal and alumina support. Insufficient loading may provide too few effective sites for carbon growth, whereas excessive loading may promote particle aggregation and heterogeneous carbon formation.

The support-only control is particularly important because alumina can influence the cracking environment independently of iron. Comparing the supported catalyst with the support control will help identify the contribution of the active metal. Characterization of fresh and spent catalysts should be

used to assess whether changes in activity are associated with particle growth, carbon encapsulation or other structural transformations.

4.4. Verification of CNT structure and quality

A strong materials-science contribution depends on demonstrating that the recovered carbonaceous material contains CNTs with reproducible structural characteristics. SEM may reveal elongated or filamentous morphologies, but TEM is needed to establish tubular structure and examine wall arrangement. Raman spectra can assess graphitic order and defect-related features, while TGA can estimate oxidation behaviour and residual inorganic matter.

The manuscript should provide representative microscopy images with scale bars, diameter distributions based on a stated number of measured nanotubes, Raman spectra and clearly documented thermal-analysis conditions. If the carbon deposit contains multiple morphologies, the results should report that heterogeneity rather than describe the entire deposit as pure CNTs.

4.5. Mass balance and process reliability

Mass-balance closure is central to the credibility of a waste-valorization study. The carbon entering with polypropylene should be compared with carbon recovered in the gas, condensate, solid deposit, unconverted feed and other identified streams. A large unexplained deficit may indicate unmeasured products, condensate losses, incomplete sampling or analytical bias.

Hydrogen balance can provide an additional consistency check if the elemental composition of the feedstock and all relevant hydrogen-containing products are known. Any unclosed fraction should be reported and investigated, not assigned automatically to a desired product.

4.6. Statistical robustness and uncertainty

The optimum condition should be supported by independent replicates and uncertainty estimates. Temperature, catalyst loading and catalyst-to-feed ratio may interact, so a factorial or response-surface design can be more informative than changing each parameter independently. Regression models should be checked against residual patterns and independent confirmation experiments.

The paper should distinguish statistical significance from practical importance. A small increase in hydrogen yield may not justify a substantial increase in energy demand, catalyst consumption or CNT purification requirements. Conversely, a modest yield accompanied by improved CNT quality and better catalyst stability may be attractive for a materials-oriented application.

4.7. Beyond fuel: environmental and process implications

The defining proposition of this work is the simultaneous recovery of hydrogen and carbon nanomaterials from plastic waste. Its environmental merit, however, cannot be established solely from the value of the products. Reactor heating, carrier-gas consumption, catalyst preparation, hydrogen

purification, CNT separation, waste treatment and catalyst regeneration may contribute materially to the overall footprint.

A preliminary process assessment should therefore distinguish laboratory-scale technical feasibility from environmental and economic performance at scale. Claims of reduced emissions, net-zero conversion or commercial viability should be made only when supported by an appropriate life-cycle assessment, energy balance and techno-economic analysis.

Schematic of the polypropylene pyrolysis zone, Fe/Al₂O₃ catalytic bed, temperature-control system, condensate trap and gas-analysis line.

SEM and TEM micrographs of the recovered carbon, including scale bars and a statistically supported CNT diameter distribution.

Raman spectra and D/G band analysis, supported by XRD and TGA to distinguish graphitic structure from non-CNT carbon deposits.

Measured hydrogen yield, verified CNT yield and carbon closure plotted against catalytic temperature, with uncertainty bars.

6. Conclusions

This study establishes an experimental framework for evaluating the co-production of hydrogen and carbon nanotubes through Fe/Al₂O₃-catalysed conversion of waste polypropylene. By combining controlled pyrolysis, quantitative gas analysis, carbon-product characterization and elemental mass-balance calculations, the proposed investigation aims to determine whether waste polypropylene can serve as a precursor for both hydrogen and high-value carbon nanomaterials.

The principal contribution will depend on demonstrating a reproducible relationship between operating conditions, hydrogen yield, verified CNT formation, structural quality and catalyst stability. Particular attention must be given to distinguishing total carbon deposition from CNT yield and to accounting for the carbon distributed across gaseous, condensable and solid products.

The broader significance of this approach lies in evaluating plastic waste as a potential source of functional materials rather than exclusively as a feedstock for combustible products. Its environmental and economic advantages, however, must ultimately be assessed in relation to process energy requirements, catalyst durability, product purification and recovery efficiency. The experimental findings will determine whether the selected Fe/Al₂O₃ system offers a meaningful contribution to integrated plastic-waste valorization.

Declarations

Competing interests:

The authors declare no competing interests, if this statement accurately reflects their circumstances.

Ethics approval:

Not applicable to experiments involving only polymer materials and catalysts, provided no human participants, animals or other ethically regulated materials are involved.

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7. Figures 1,2,3 and 4 are AI assisted.

Figures

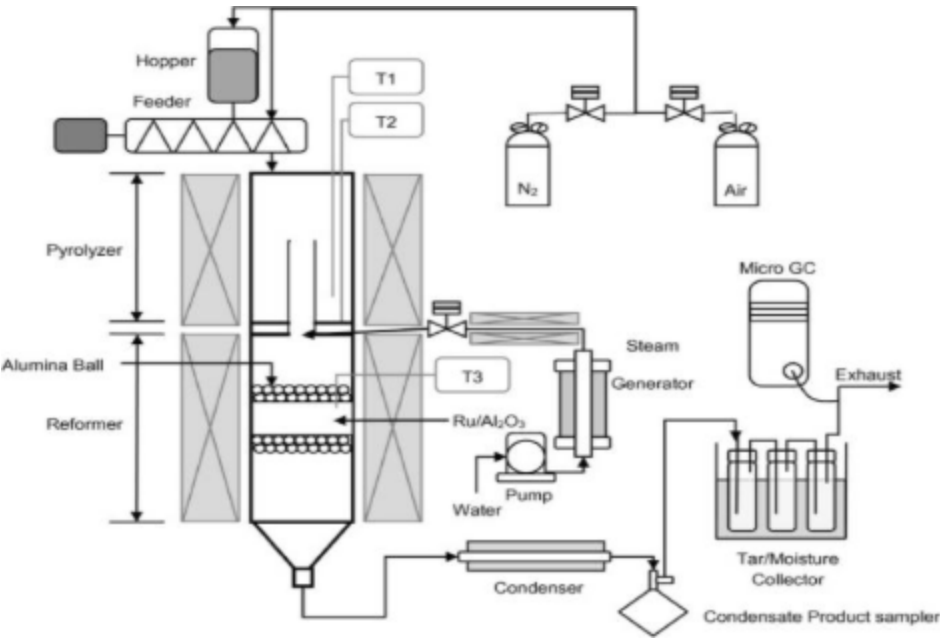


Figure 1

Experimental reactor configuration

Schematic of the polypropylene pyrolysis zone, Fe/Al₂O₃ catalytic bed, temperature-control system, condensate trap and gas-analysis line.

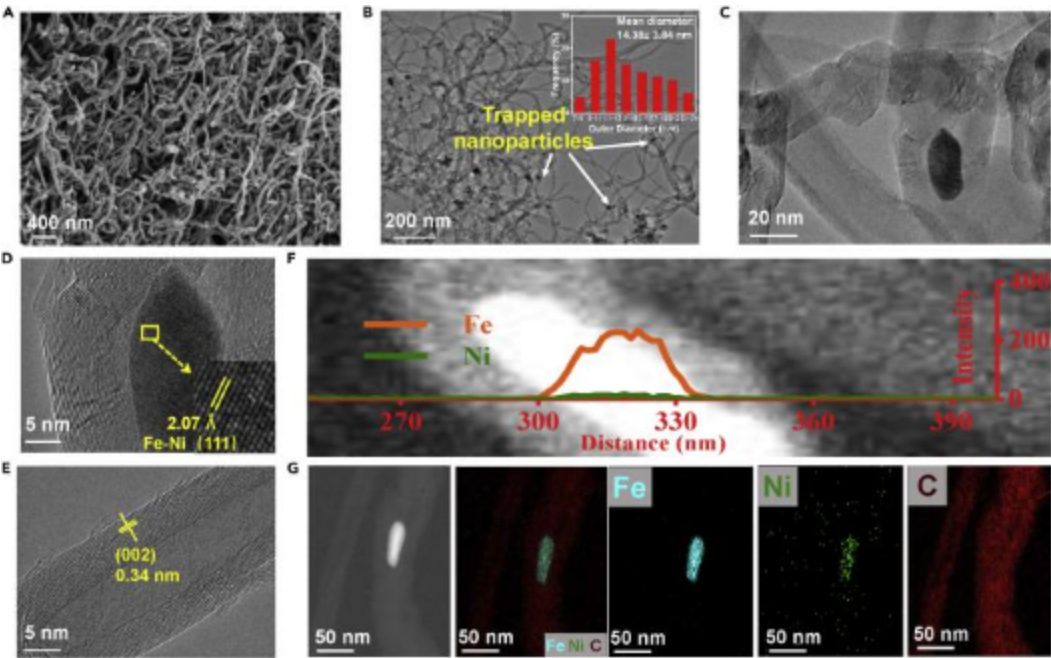


Figure 2

Morphological characterization

SEM and TEM micrographs of the recovered carbon, including scale bars and a statistically supported CNT diameter distribution.

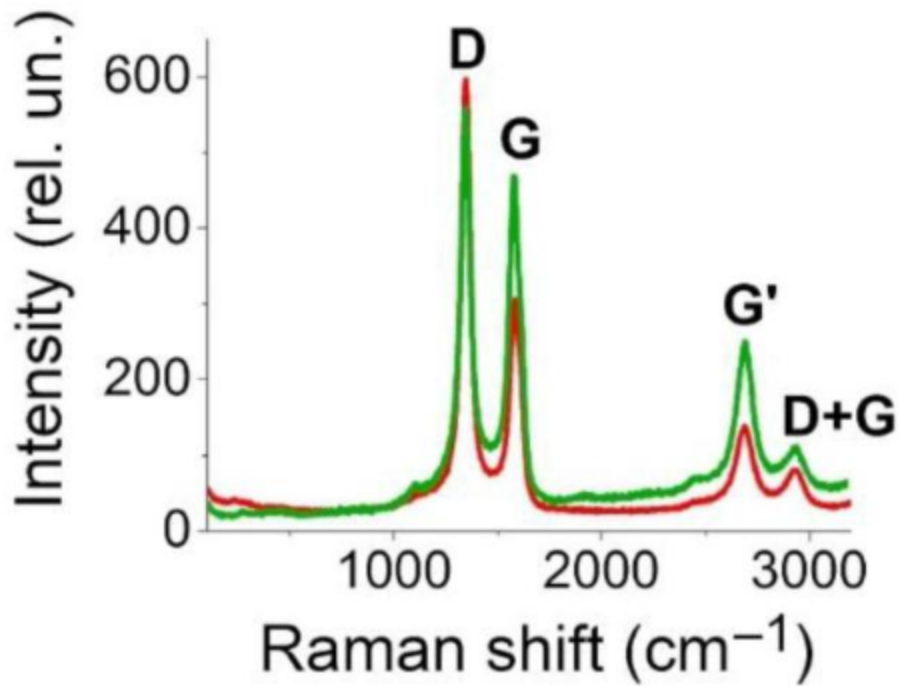


Figure 3

Structural characterization

Raman spectra and D/G band analysis, supported by XRD and TGA to distinguish graphitic structure from non-CNT carbon deposits.

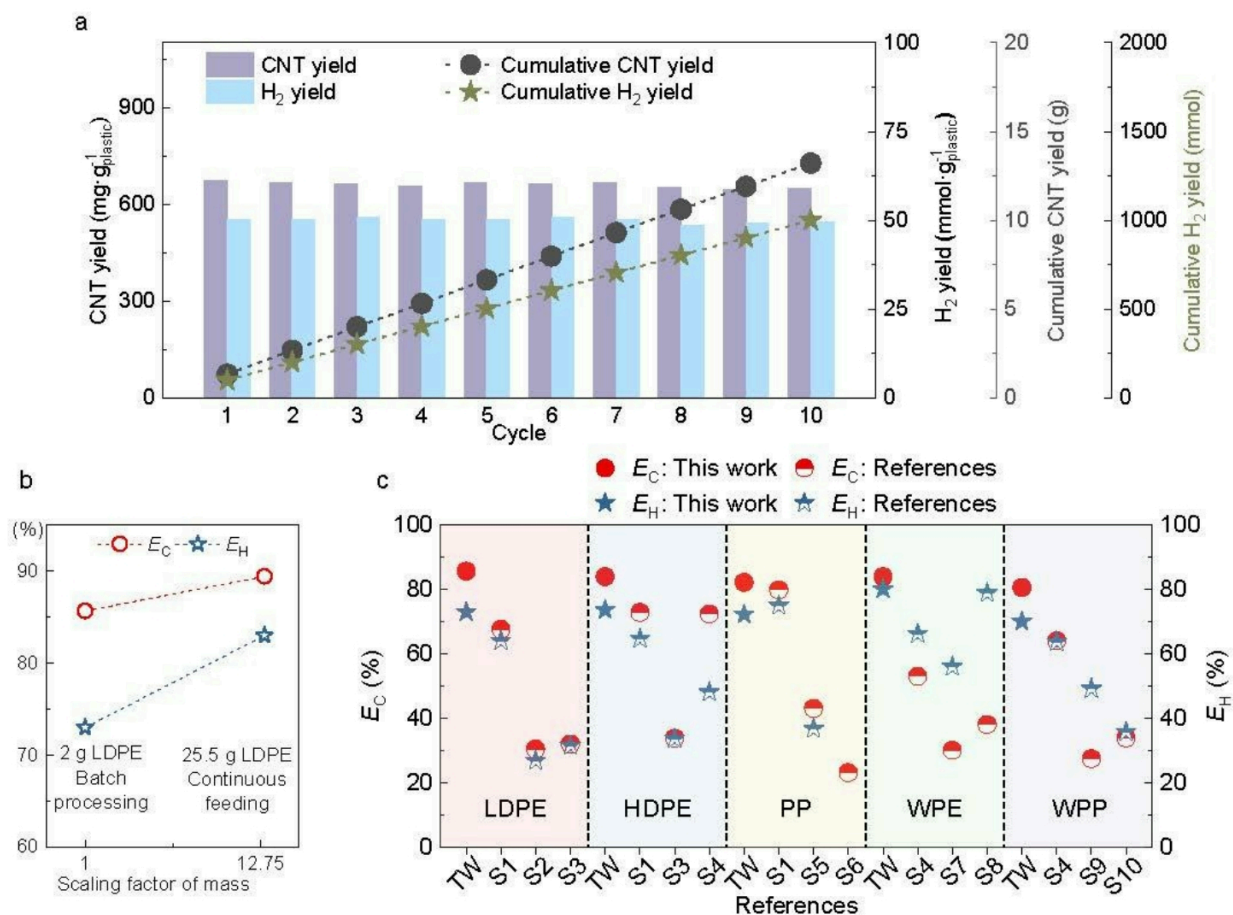


Figure 4

Process optimization

Measured hydrogen yield, verified CNT yield and carbon closure plotted against catalytic temperature, with uncertainty bars.