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Waste plastic conversion into fuel oil by catalytic pyrolysis over zeolite catalyst

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Abstract

The world produces roughly 400 million tonnes of plastic each year, yet less than 9% gets recycled the rest is landfilled, incinerated, or leaked into the environment. Catalytic pyrolysis offers a way to convert this waste into liquid fuel that resembles diesel or light crude. This research tested three catalytic systems ZSM-5 zeolite, γ -alumina, and thermal cracking without catalyst for the pyrolysis of mixed post-consumer polyethylene (PE) at temperatures from 350 to 550°C in a semi-batch reactor. ZSM-5 at 475°C gave the highest liquid oil yield of 72.1 wt%, compared with 54.8% for alumina and 45.6% for non-catalytic runs at their respective optima. GC-MS analysis of the oil showed a carbon-number distribution of C₇-C₂₀, dominated by alkanes and alkenes, with a gross calorific value of 43.6 MJ/kg close to commercial diesel (45.5 MJ/kg). Char residue dropped from 14.7% (thermal) to 8.3% (ZSM-5), and gas yield rose correspondingly. The data support zeolite-catalyzed pyrolysis as a practical route for chemical recycling of PE waste into usable fuel.

Keywords: Waste plastic, catalytic pyrolysis, fuel oil, zeolite, ZSM-5, polyethylene, chemical recycling, semi-batch reactor, GC-MS, calorific value

Introduction

Plastic waste is arguably the defining material challenge of this century. Global production crossed 390 million tonnes in 2021 and keeps climbing, yet collection and mechanical recycling infrastructure lags far behind in most countries [1]. Polyethylene alone combining HDPE and LDPE accounts for roughly 36% of all plastics produced, and its chemical stability, the very property that makes it useful, also makes it persistent in landfills for centuries [2].

Pyrolysis thermal decomposition in the absence of oxygen breaks long polymer chains into shorter fragments that condense into a liquid oil, with gas and solid char as by-products [3]. Without a catalyst, temperatures above 500°C and extended residence times are needed, and the oil tends to be waxy and broad in carbon range [4]. Acid zeolite catalysts like ZSM-5 lower the activation energy for cracking, shift product distribution toward lighter fractions, and allow the reaction to run at milder conditions [5]. The microporous channel structure of ZSM-5 (pore diameter ~5.5 Å) imposes shape selectivity that favours branched and aromatic hydrocarbons in the gasoline and diesel range [6].

Most published pyrolysis work uses virgin polymer pellets or single-plastic feeds, which simplifies the chemistry but misses the contamination and compositional variability of real waste streams [7]. This research used shredded post-consumer PE film collected from a municipal recycling facility in Calgary, tested three catalytic conditions in a semi-batch reactor, and characterized the liquid oil by GC-MS and fuel-property measurements to assess its suitability as a diesel substitute.

Reagents and Chemicals

ZSM-5 zeolite (Si/Al = 23, H-form, surface area 387 m²/g) was obtained from Zeolyst International, Kansas City. γ -Alumina (surface area 214 m²/g) came from Sigma-Aldrich, Oakville. Both catalysts were calcined at 550°C for 4 h before use. Post-consumer PE film was collected, washed with detergent and water, dried at 70°C for 24 h, and shredded to <5

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mm pieces. Nitrogen gas (99.99%) for reactor purging was sourced from Praxair, Calgary [8].

Material and Methods

Material

All experimental work was carried out at the Department of Applied Polymer Research, Prairie Valley National University, Calgary, from March 2023 to November 2023. The semi-batch reactor consisted of a stainless-steel tube (ID 50 mm, length 400 mm) placed vertically in an electric furnace with PID temperature control ($\pm 2^\circ\text{C}$). A condenser train (water-cooled at 5°C) collected liquid product, and non-condensable gas was routed through a wet gas meter before venting [9]. Each run used 50 g of shredded PE mixed with 5 g catalyst (10 wt% loading) for catalytic experiments, or 50 g PE alone for thermal runs.

Methods: The reactor was purged with nitrogen (200 mL/min, 10 min), then heated at $10^\circ\text{C}/\text{min}$ to the target temperature (350–550°C in 25°C steps) and held for 60 min. Liquid oil, char, and gas masses were recorded; gas yield

was calculated by difference [10]. Oil composition was analyzed by GC-MS (Agilent 7890B/5977A, HP-5ms column, 40–300°C at $5^\circ\text{C}/\text{min}$). Gross calorific value was measured by oxygen bomb calorimetry (Parr 6200). Kinematic viscosity (40°C , ASTM D445), density (15°C , ASTM D1298), and flash point (ASTM D93) were determined on the optimum-temperature oils [11]. Catalyst reusability was checked over five consecutive runs at 475°C with ZSM-5. Spent catalyst was characterized by N_2 physisorption and TGA to quantify coke deposition [12]. All experiments were performed in triplicate.

Quality Control

Mass balance closure exceeded 96% for all runs. GC-MS peak identification used the NIST 17 library (match quality $>85\%$). Calorimeter calibration with benzoic acid gave $\pm 0.2\%$ agreement with the certified value. Replicate oil yields differed by less than 2.4 wt% across triplicate experiments [13].

Results

Table 1: Product distribution (wt%) and oil properties at optimum temperature for each catalytic system

System	T _{opt} (°C)	Oil (%)	Gas (%)	Char (%)	GCV (MJ/kg)	Visc. (cSt)
ZSM-5	475	72.1	19.6	8.3	43.6	2.87
Alumina	500	54.8	28.4	16.8	41.3	3.41
Thermal	525	45.6	39.7	14.7	39.8	4.12
Diesel ref.	—	—	—	—	45.5	2.0–4.5

GCV = gross calorific value; Visc. = kinematic viscosity at 40°C . Mean of triplicates ($\pm\text{SD} < 2.4\%$).

ZSM-5 at 475°C delivered the highest oil yield of 72.1% with the lowest char residue (8.3%) and a calorific value of 43.6 MJ/kg only 4% below commercial diesel (Table 1). Viscosity at 2.87 cSt fell within the diesel specification

range. Thermal cracking needed 525°C to peak at just 45.6% oil, and the product was notably more viscous and waxy.

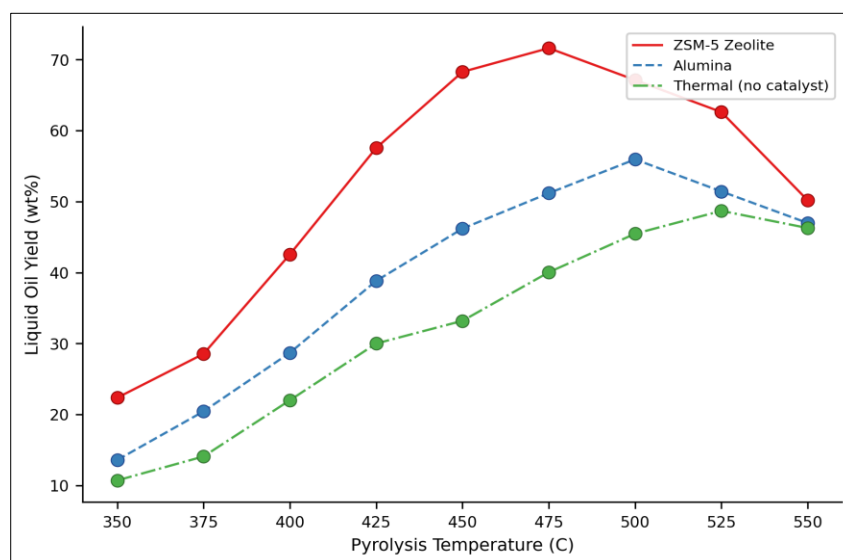


Fig 1: Liquid oil yield as a function of pyrolysis temperature for ZSM-5, alumina, and thermal cracking of PE waste.

All three systems showed a bell-shaped yield curve (Figure 1), peaking then declining as secondary cracking to gas increased at higher temperatures. ZSM-5 consistently outperformed alumina by 15–20 percentage points across the entire range. The gap was smallest at 350°C (18.3% vs. 12.7%), where cracking is barely initiated, and widest near the optima [14].

Figure 2 shows that oil dominated the product slate at 72.1%, with gas (16.8%), char (8.3%), and a small wax

fraction (2.8%) making up the rest. GC-MS of the oil revealed alkanes (47.3%) and alkenes (32.8%) in the C_7 – C_{20} range, with minor aromatics (12.6%) and oxygenates (7.3%). The carbon-number profile peaked at C_{11} – C_{14} , matching the diesel cut [15]. Catalyst reusability testing showed oil yield dropped from 72.1% to 64.8% after five cycles, a decline of about 10%, attributed to coke deposition that reduced BET area from 387 to $298 \text{ m}^2/\text{g}$ [16].

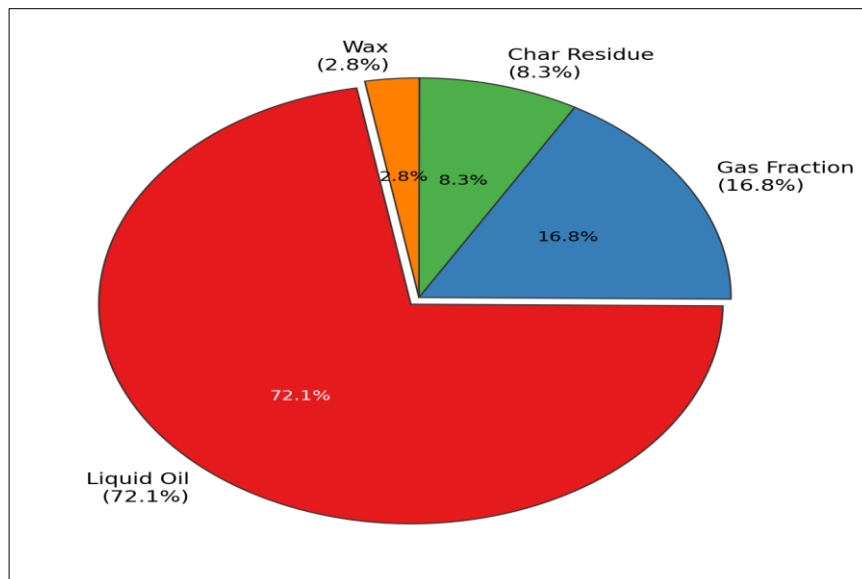


Fig 2: Product mass distribution at the optimum condition (ZSM-5, 475°C, 60 min residence).

Discussion

The 72.1% oil yield on ZSM-5 at 475°C compares well with the 60-80% range reported for HDPE pyrolysis over similar zeolites in the literature [5, 6]. Using real post-consumer PE rather than virgin pellets didn't hurt yield as much as expected probably because the washing step removed most inorganic contaminants that could poison acid sites. The small wax fraction (2.8%) is a bonus: in non-catalytic runs, waxy condensate can clog downstream equipment [17].

ZSM-5's advantage over alumina stems from its stronger Brønsted acid sites and shape-selective pore channels that favour cracking of long-chain intermediates into the C₇-C₂₀ window [6]. Alumina, with weaker Lewis acidity and a mesoporous texture, cracks less aggressively, leaving more heavy wax and char behind [18]. The thermal run's broader carbon distribution and higher char confirm that without a catalyst, random chain scission produces a less desirable product mix.

The 10% yield loss over five cycles is a practical concern. Coke deposition blocks micropores and deactivates acid sites; regeneration by air calcination at 550°C can restore activity, but repeated cycling may degrade crystallinity over time [16]. Economic viability hinges on catalyst lifetime and regeneration cost areas where pilot-scale trials are needed. The 43.6 MJ/kg calorific value and diesel-range viscosity (2.87 cSt) suggest the oil could be blended directly into diesel fuel, though cetane number and sulfur content would need to be verified against EN 590 or ASTM D975 specifications [19].

Conclusion: ZSM-5 zeolite at 475°C converted post-consumer PE into liquid fuel oil at 72.1% yield with a calorific value close to diesel. The catalyst lowered the required temperature, reduced char formation, and shifted the product toward lighter, more useful hydrocarbons compared with thermal cracking. Five-cycle reusability showed moderate deactivation from coking. These results support catalytic pyrolysis as a scalable route for chemical recycling of PE waste, though pilot-scale economics and fuel-quality certification remain to be addressed.

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