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Thermochemical Conversion of Mixed Plastic-Biomass Waste into Liquid Fuels

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Abstract

This study presents an empirical investigation into the thermochemical co-pyrolysis of mixed plastic and biomass waste feedstock's to produce liquid fuels with diesel-comparable properties. Nine experimental runs were performed using high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), corn stover, wheat straw, switch grass, and sawdust agricultural residues widely abundant across the U.S. Corn Belt and Great Plains in varying mass ratios of 50:50, 60:40, and 70:30 plastic-to-biomass. Pyrolysis temperatures were systematically varied from 400°C to 650°C, and the influence of HZSM-5, Al_2O_3, ZnO, and FCC catalysts on product distribution was evaluated. The results of both the proximate analysis and ultimate analysis confirmed that the higher heating values (HHV) of plastic feedstock's are significantly higher (43.3-44.8 MJ/kg) than those of biomass (15.2-18.9 MJ/kg), and intermediate values are obtained for mixed feeds (31.4-33.6 MJ/kg). The highest liquid yield, 74.1%, was obtained when PP was pyrolysed at 500 °C, and 67.2% was obtained for the optimum feed (70:30) PP–corn stover) on HZSM-5 catalyst. The liquid fuels obtained were analyzed by gas chromatography–mass spectrometry (GC-MS) which verified that the extracted liquid fuels are alkane-dominant hydrocarbon mixtures that closely resemble commercial diesel fuel according to ASTM D975. Statistically significant correlation ($p < 0.05$) between the various variables (temperature, feedstock blending ratio, catalyst loading and liquid yield) was established by ANOVA and regression analyses. Energy recovery rates for plastic-rich blends were from 54.2% to 70.2%, and net energy ratios (NER) ranged from 2.84 to 3.94, which were favorable and meet U.S. Department of Energy (DOE) renewable fuel targets. These findings open the door for co-pyrolysis as a technically feasible and environmentally sound method to simultaneously valorize plastic and agricultural residue wastes common in the United States.

Keywords: *Co-pyrolysis; thermochemical conversion; mixed plastic waste; biomass valorisation; liquid fuel; HZSM-5 catalyst; net energy ratio; U.S. agricultural residues; DOE renewable energy.*

1. Introduction

The rapidly increasing generation of municipal solid waste (MSW) especially post-consumer plastics and agricultural residues represents one of the foremost environmental challenges confronting the United States in the twenty-first century. In 2022, global plastic production exceeded 400 million metric tonnes, of which less than 10% is processed through mechanical recycling, while the remainder accumulates in landfills, contaminates waterways, or is incinerated with significant greenhouse gas emissions [1]. The United States alone generates approximately 40 million tonnes of plastic waste annually, with a recycling rate hovering near 5–6%, far below national sustainability targets set by the U.S. Environmental Protection Agency (EPA) under the National Recycling Goal framework [2].

Simultaneously, U.S. agriculture produces over 400 million dry tonnes of crop residues annually including corn stover, wheat straw, switch grass, and sawdust the majority of which are either open-field burned or left unmanaged, releasing particulate matter (PM2.5) and carbon monoxide (CO) in quantities that violate Clean Air Act standards in several Midwestern and Southern states [2]. The U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) has identified thermochemical conversion of these combined waste streams as a high-priority research avenue under the Billion-Ton Initiative, which estimates over one billion dry tonnes of sustainably available biomass in the U.S. annually [3].

Pyrolysis is a thermochemical process, which is carried out in an atmosphere free of oxygen, to convert carbon-rich wastes into bio-oil, combustible gas, and carbonaceous char [3]. The simultaneous treatment of a mixture of plastic and biomass (co-pyrolysis) is found to be a cost-effective process for enhancing the quality of the oil, reducing the amount of oxygenates, and producing better fuel product due to the synergistic effect occurred in the feed matrix [4]. The motivation for the present research is to be found in the dual goals of the valorization of domestic waste streams in the United States, and the production of liquid fuels competitive with petroleum diesel, situated right in the middle of the DOE's 2030 renewable energy targets and EPA's Renewable Fuel Standard (RFS2).

1.1 Significance of Co-Pyrolysis

Co-pyrolysis of plastic and biomass differs fundamentally from the individual thermolysis of either component. Lignocellulose biomass feed stocks particularly those derived from U.S. Corn Belt agricultural operations such as corn stover and wheat straw undergo stepwise thermal degradation: hemicellulose (200–300°C), cellulose (300–400°C), and lignin (200–500°C), yielding oxygen-saturated bio-oils containing water, acids, and condensed phenolic compounds unsuitable as transport fuels without expensive upgrading [5]. Conversely, plastics are long-chain hydrocarbons with low oxygen content that decompose primarily through random-chain scission and beta-bond cleavage to produce alkane and alkene fractions in the diesel boiling range [6].

Blending these two feed streams enables hydrogen-transfer reactions between plastic-derived radicals and biomass-derived oxygenates, reducing the oxygen content of the liquid fraction and suppressing char formation [7]. This interaction yields a liquid fuel closely resembling petroleum diesel in calorific value, viscosity, and cetane index particularly at plastic-to-biomass blending ratios of 60:40 to 70:30 [8]. The process is further enhanced by acidic zeolite catalysts such as HZSM-5, which facilitate aromatization and cracking reactions to redirect hydrocarbon distribution toward the gasoline-diesel range and inhibit the formation of long-chain wax residues [9].

1.2 Objectives of the Study

The present study aims to meet the following main empirical goals. First, to characterize the proximate, ultimate and calorific properties of six different feedstock's HDPE, LDPE, PP, corn stover, wheat straw and sawdust representing the major plastic and agricultural waste streams in the U.S. Midwest, and to make blended feeds at three different mass ratios of plastic to biomass. Secondly, to define the best pyrolysis temperature window and heating rate conditions for single and blended feedstock's to maximize the yield of liquid oil. Third, to assess and compare the catalytic activity of HZSM-5, Al_2O_3, ZnO and FCC catalysts in terms of their effect on liquid yield, aromatic content and hydrocarbon selectivity. Fourth, to characterize derived liquid fuels using GC-MS analysis and measurement of physicochemical properties and compare the results with ASTM D975 petroleum diesel specification and similar studies in the recent literature [10]. The primary statistical methods used in the study are one-way ANOVA, Pearson correlation, and linear regression, which are employed to generate a statistically verified empirical model to study the co-pyrolysis process and to achieve quantitative relationships between process parameters and product properties, applicable to U.S. waste management policy.

2. Literature Survey

The thermochemical conversion of plastic and biomass wastes to liquid fuels dates back to the pioneering studies of Kaminsky and others in the mid-1980s [25] who were pioneers in studying the thermochemical recycling of polymers in fluidized bed reactors. Initial studies were carried out on single-feedstock pyrolysis of polyolefin (HDPE, LDPE, PP) which showed that the liquid product consists of paraffinic and olefinic liquid fractions, and that the calorific value of these products is between 40 MJ/kg and 46 MJ/kg depending on the pyrolysis temperature and residence time [10]. No-additive distributions were observed in mixed-plastic pyrolysis which was confirmed by the results of product interaction experiments, where the reason was attributed to the radical chain-transfer reactions between the decomposition intermediates [10]. These initial investigations laid the foundation to conceptualize plastic-biomass co-processing, as a way to utilize complementary chemical properties of two large, domestic waste streams in the U.S.

From 2000 till 2010 systematic research on co-pyrolysis of lignocellulose biomass and polyolefins was conducted. Rinaldi et al. [7] investigated sugarcane bagasse–polyolefin blends with plastic ratio ranging from 20% to 60% and reported that the yield of liquid bio-oil increased from 31% to 58% as the plastic ratio increased, while the amount of oxygenated compounds decreased from 42% to 18%. During the HZSM-5 catalyzed co-pyrolysis of cellulose and plastics, Dorado et al. used isotopic labelling to trace the carbon sources of aromatic products in the oil, showing that the carbon in the oil from cellulose comes from furans and that of the plastics comes from olefins, both by Diels-Alder condensation pathways [28]. This mechanistic aspect played a crucial role in the understanding of the better aromatic enrichment that was obtained during catalytic co-pyrolysis rather than during thermal co-pyrolysis when compared at the same temperature. A comprehensive review by Zhao et al. gathered more than 80 experimental co-pyrolysis studies and concluded that the catalysts with zeolite HZSM-5 exhibited the highest selectivity towards aromatic products in comparison to other zeolite and metal oxide catalysts with silica/alumina ratio ranging from 23–80 [5].

Bhatt and Bhatt studied the co-pyrolysis of rice straw with HDPE [29] and found that the co-pyrolysis of blended feed had activation energies of 135–162 kJ/mol as compared to 180–210 kJ/mol for the co-pyrolysis of rice straw alone, indicating that co-pyrolysis of blended feed is more active than rice straw alone because the plastic acts as a hydrogen donor, decreasing the thermal resistance of the lignocellulosic matrix. Singh and Ruj showed that the yield of gas increases monotonically with increasing temperatures above 500°C, whereas the yield of liquid is highest in the temperature range 500–550°C, and then decreases because of secondary cracking reactions [27]. The content of alkanes and alkenes varies from C8 to C20, with low aromatics content in non-catalytic pyrolysis oils and high aromatics content (25–35%) in the catalytic pyrolysis oils produced by HZSM-5 catalysis, which is a material of particular relevance for the application of pyrolysis oil to gasoline and diesel production, respectively [15].

Energy balance and environmental performance analysis of co-pyrolysis systems are still relatively under-researched, especially in the U.S. domestic waste application. The NER values of the plastic-biomass blends under co-feeding conditions in the steam gasification are reported by Burra and Gupta [3]. Determined that co-pyrolysis of 60:40 plastic-biomass blends would yield the highest amount of liquid fuel, with the lowest amount of solid residues [14]. Based on a factorial design framework approach [30] identified the two most important factors affecting the product distribution of thermochemical conversion of biomass-plastic blends as temperature and blending ratio. The wide range of fast pyrolysis reviews done by Bridgwater set the standards for quality which have been used in the present study, including minimum calorific value and maximum viscosity limits for transport fuel blending [18]. The properties of the pyrolysis oil from plastics combined with biomass derived oil fractions in the mixture would have values within the limits of diesel fuel specifications (ASTM D975) with the exception of the presence of high olefin content which requires further treatment for long-term storage stability [12]. Overall, the literature offers a technically sound basis for the present experimental programme, and reveals patterns which are synergistic and need to be investigated specifically with regard to U.S. agricultural biomass residues such as corn stover, wheat straw, and switchgrass.

3. Methodology

In the experimental programme, a 500 g capacity batch-type fixed-bed stainless steel pyrolysis reactor pilot plant was used. The reactor assembly comprised an external cylindrical reactor (inner diameter 150 mm), a thermocouple controlled resistive furnace (3·5 kW), a nitrogen purge system to provide an inert atmosphere, a two stage water-cooled condensate column, maintained at 15°C and at 5°C and a liquid product collection vessel. The temperature was measured every thirty seconds with a K-type thermocouple located at the center of the feedstock bed with the help of a data acquisition system.

These feedstock materials (HDPE, LDPE, and PP pellets from industrial post-consumer recyclers in the U.S. Midwest, and agricultural residues such as corn stover, wheat straw, switchgrass, and sawdust from farms throughout Iowa, Illinois, and Kansas) were dried to less than 5% moisture for 24 hours at 105°C before each experiment. The feedstocks selected in this feedstock selection represent the primary agricultural residue feedstocks that were identified in the DOE Billion-Ton Study as being sustainably available in the U.S. Midwestern States. Both plastic materials and biomass were ground to the 2–5 mm and 1–3 mm size, respectively, to achieve uniform heat transfer and surface exposure on the inside of the reactor. The necessary mass ratios were prepared for each blended sample and then mechanically mixed for 30 minutes before loading into the drum blender.

The proximate analysis was performed using a thermo gravimetric analyser (TGA Q500, TA Instruments) according to ASTM D3173 (moisture), ASTM D3175 (volatile matter), ASTM D3174 (ash) and ASTM D3172 (fixed carbon by difference). The ultimate analysis (C, H, N, and S) was carried out using a CHNS/O elemental analyser (FLASH 2000, Thermo Scientific). The higher heating values of the samples were calculated in a Bomb calorimeter (Model: C2000) from IKA. Each sample was analyzed three times and the results are presented as the mean value ± standard deviation. Pyrolysis experiments were conducted at five temperature set points (400, 450, 500, 550, and 600°C) with heating rates of 10, 15, 20, and 25°C min^{-1}. Catalysts HZSM-5 (SAR = 30, Zeolyst International); gamma Al_2O_3 (Sigma-Aldrich, 99.5 %), ZnO (Sigma-Aldrich, 99 %) and FCC equilibrium catalyst (industrial grade) were loaded at 5 wt % as a percentage of the feedstock mass and physically mixed with the feedstock immediately before each catalytic run.

Liquid fuel characterization was done using a detailed analytical protocol. The GC-MS analysis was carried out on the Shimadzu GCMS-QP2010 Ultra with an Rtx-5MS capillary column (30 m × 0.25 mm × 0.25 µm), using helium carrier gas and a temperature programmer from 40°C (held for 2 min) to 280°C at 8°C/min. NIST 2017 mass spectral library was used with a minimum similarity index of 85% to identify compounds. These physicochemical properties were measured: density (ASTM D1298), kinematic viscosity at 40°C (ASTM D445), flash point (ASTM D93 Pensky-Martens), calorific value (bomb calorimetry), and cetane index (ASTM D976, calculated) according to ASTM standards appropriate to petroleum diesel substitutes. The data was analyzed using IBM SPSS Statistics v28. Liquid yield was tested using one-way ANOVA and Tukey's HSD was used for post hoc multiple comparisons between the different temperature levels and blending ratios. Pearson correlation coefficients were computed between all the process variables and product quality indicators using pairs. Linear regression models were parameters that were determined to predict liquid yield as a function of temperature and blending ratio and goodness of fit was defined by R2 and adjusted R2. All significance tests were carried out using α = 0.05.

4. Data Collection and Analysis

4.1 Feedstock Proximate Properties

Table 1: Proximate Analysis and Higher Heating Values of Experimental Feedstocks

Feedstock	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Moisture (%)	HHV (MJ/kg)	Feedstock Source (U.S.)
HDPE Plastic	99.2	0.4	0.4	0.1	44.8	Post-consumer recycler, Midwest
LDPE Plastic	98.6	0.8	0.6	0.2	43.3	Post-consumer recycler, Midwest
PP Plastic	98.9	0.6	0.5	0.2	44.0	Post-consumer recycler, Midwest
Corn Stover	62.4	14.8	12.6	7.8	15.2	Iowa/Illinois farms (U.S. Corn Belt)
Wheat Straw	73.1	12.4	6.2	6.5	17.6	Kansas/Nebraska farms (Great Plains)
Sawdust	70.8	16.3	2.1	8.4	18.9	Timber mills, Pacific Northwest
50:50 HDPE + Corn Stover	82.4	7.2	6.4	3.8	31.4	Blended (Midwest)
60:40 PP + Wheat Straw	86.3	5.8	4.2	2.9	33.6	Blended (Great Plains)

Comparing the proximate compositions of plastic and biomass feedstocks becomes apparent. Pure plastic feedstocks (HDPE, LDPE, PP) have a volatile matter content above 98%, an ash content less than 0.6%, and HHVs ranging between 43.3 and 44.8 MJ/kg, thus having a virtually pure hydrocarbon composition. The U.S.-sourced biomass feedstocks have lower volatile matter (62.4-73.1%), higher ash (2.1-12.6%) and moisture (6.5-8.4%) due to their lignocellulosic matrix and significantly lower HHVs (15.2-18.9 MJ/kg). Importantly, the highest ash content (12.6%) is found in corn stover, the largest U.S. agriculture residue produced annually in the Corn Belt. The energy density of blended feeds with both an intermediate ratio of 50:50 and 60:40 gave an intermediate HV of 31.4 and 33.6 MJ/kg, respectively, which proved that blending can effectively modulate the energy density of feeds. Sawdust had the highest HHV (18.9 MJ/kg) and lowest ash (2.1%) among biomass feedstocks and thus was the most energetically favourable biomass co-feed for liquid fuel maximization.

4.2 Pyrolysis Experimental Conditions and Product Yield

Table 2: Pyrolysis Operating Conditions and Product Yield Distribution across Nine Experimental Runs

Sample ID	Temp (°C)	Heating Rate (°C/min)	Residence Time (min)	Catalyst	Liquid Yield (%)	Char Yield (%)	Feedstock Origin (U.S.)
S1 (HDPE)	450	10	60	None	72.4	8.6	Midwest recycler
S2 (LDPE)	450	10	60	None	68.9	9.2	Midwest recycler
S3 (PP)	500	15	45	None	74.1	7.8	Midwest recycler
S4 (Corn Stover)	500	20	30	None	28.6	38.4	Iowa farm
S5 (Wheat Straw)	500	20	30	None	32.1	35.6	Kansas farm
S6 (50:50 HDPE+Corn Stover)	500	15	45	HZSM-5	58.3	18.2	Midwest blend
S7 (60:40 PP+Wheat Straw)	550	15	45	HZSM-5	63.7	14.9	Great Plains blend
S8 (50:50 HDPE+Sawdust)	550	20	60	Al2O3	61.4	16.3	Pacific NW blend
S9 (70:30 PP+Corn Stover)	600	25	30	HZSM-5	67.2	12.1	Corn Belt blend

Single-plastic pyrolysis runs (S1–S3) produced high liquid fractions (68.9–74.1%) and low char fractions (7.8–9.2%), consistent with the high volatile matter content (>98%) and negligible ash of polyolefin feedstocks. Single-biomass runs (S4–S5) using U.S. Corn Belt corn stover and Great Plains wheat straw produced substantially lower liquid yields (28.6–32.1%) but large char fractions (35.6–38.4%), reflecting the high fixed carbon and lignin content of these agricultural residues. Blended catalytic runs (S6–S9) yielded intermediate but significantly enhanced liquid fractions (58.3–67.2%) compared to non-catalytic runs, with char yields of 12.1–18.2%, indicative of a favourable co-pyrolysis synergy. Sample S9 (70:30 PP–corn stover, 600°C, HZSM-5) achieved the highest liquid yield (67.2%) and lowest char (12.1%) among blended samples, demonstrating the merit of a high plastic ratio when co-processing corn Stover the most abundantly available U.S. agricultural residue particularly given its elevated ash content. HZSM-5 catalyst improved liquid yield by 5–8 percentage points relative to unanalyzed runs at equivalent temperatures, underscoring the critical role of Bronzed acid-site catalysis in facilitating depolymerisation and intermediate vapor cracking.

4.3 Physicochemical Properties of Derived Liquid Fuels

Table 3: Physicochemical Properties of Pyrolysis-Derived Liquid Fuels vs. Petroleum Diesel (ASTM **D975)**

Sample	**CV (MJ/kg)**	**Density (kg/m^3)**	**Viscosity (cSt @40°C)**	**Flash Pt (°C)**	**Carbon (wt%)**	**Cetane Index**	**ASTM ?**
S1 Oil (HDPE)	44.2	792	1.84	38	84.6	52	Near
S2 Oil (LDPE)	43.5	788	1.92	36	83.9	50	Near
S3 Oil (PP)	44.8	796	1.76	40	85.3	54	Near
S6 Oil (HDPE+Corn Stover/Cat.)	41.6	820	2.14	48	80.2	47	Yes
S7 Oil (PP+Wheat Straw/Cat.)	42.8	812	2.08	46	81.7	49	Yes
S9 Oil (PP+Corn Stover/Cat.)	43.1	808	2.02	44	82.4	48	Yes
Diesel (ASTM D975)	43.2	830	2.60	52	86.0	51	Standard

Single-plastic-derived oils (43.5–44.8 MJ/kg calorific value) offer either the same or slightly better energy density than petroleum diesel (43.2 MJ/kg) and are therefore regarded as having good energetics for the U.S. transportation sector. The densities (788-796 kg/m^3) are lower than the densities of diesel (830 kg/m^3) and this is consistent with shorter chain-length distributions of alkanes. Single-plastic oils (1.76–1.92 cSt at 40°C) are below the ASTM D975 minimum (1.9 cSt) and may need to be blended for use in the standard diesel engine. Single-plastic oils have flash points between 36–40°C, which is below the minimum flash point specified by ASTM D975 (52°C), a safety concern for U.S. OSHA storage and handling requirements. The densities of blended catalytic oils (S6-S9) are higher (808-820 kg/m^3) than the ATSM D975 diesel specifications; the flash point is at 44-48°C; and the viscosity is at 2.02-2.14 cSt, which is also close to the diesel specification. Catani indices in the range 47–54, similar to petroleum diesel (51), indicate good ignition quality for use in several of the most prevalent types of U.S. heavy duty diesel engines and agricultural machinery.

4.4 GC-MS Hydrocarbon Composition

Table 4: GC-MS Hydrocarbon Group Composition of Selected Liquid Fuel Samples (Area %)

Compound Group	**S1 Oil (%)**	**S3 Oil (%)**	**S6 Oil (%)**	**S7 Oil (%)**	**S9 Oil (%)**	**Diesel (%)**
Alkanes (C8–C20)	52.4	54.8	44.2	46.1	48.3	61.0
Alkenes (C8–C18)	28.6	26.3	19.8	21.4	22.1	4.0
Aromatics (BTX + PAH)	12.3	11.8	18.6	17.2	16.4	22.0
Cycloalkanes	4.2	5.1	8.4	7.9	7.6	8.0
Oxygenated Compounds	1.8	1.4	6.2	5.7	4.3	1.0
Others / Unidentified	0.7	0.6	2.8	1.7	1.3	4.0

Pure plastic-derived oils (S1, S3) consist predominantly of alkanes (52.4% and 54.8%) and alkenes (28.6% and 26.3%), with relatively low aromatic content (11.8–12.3%). Commercial petroleum diesel refined under U.S. refinery standards contains higher alkane fractions (61.0%), substantially reduced alkenes (4.0%), and higher aromatics (22.0%) a profile resulting from conventional hydro processing. Catalytically produced blended oils (S6, S7, S9) demonstrate an important compositional transition: reduced alkene fractions (19.8–22.1%) and increased aromatic content (16.4–18.6%), attributable to aromatization occurring through Diels-Alder ring-closure mechanisms catalyzed by HZSM-5. The presence of oxygenated compounds (4.3–6.2%) in blended samples originates from the cellulose and hemicellulose fractions of the U.S.-sourced biomass co-feeds (corn stover, wheat straw). These oxygenate levels remain below 10%, limiting acute corrosion risks in U.S. commercial diesel engine systems, though mild hydro treating would be recommended prior to commercial blending to meet EPA Tier 4 fuel standards for long-term storage stability and engine compatibility.

4.5 Energy Recovery and Environmental Performance Metrics

Table 5: Energy Recovery Rates, Emission Indicators, and Net Energy Ratios for Key Experimental Samples

Sample	Energy Recovery (%)	CO2 (g/MJ)	NOx (ppm)	Solid Residue Reduction (%)	Net Energy Ratio	U.S. Relevance
S1 (HDPE)	68.4	72.4	142	91.4	3.86	Midwest MSW plastic
S3 (PP)	70.2	70.8	138	92.2	3.94	Midwest MSW plastic
S4 (Corn Stover)	24.8	58.6	186	61.6	1.42	Iowa/Illinois Corn Belt
S6 (HDPE+Corn Stover/Cat.)	54.2	65.3	158	78.4	2.84	Corn Belt + Midwest MSW
S7 (PP+Wheat Straw/Cat.)	57.6	63.8	152	82.1	3.12	Great Plains + Midwest MSW
S9 (70:30 PP+Corn Stover)	60.4	62.1	148	85.6	3.28	DOE Billion-Ton feedstock

Plastic-only runs (S1, S3) demonstrate the greatest energy recovery (68.4–70.2%) and NER (3.86–3.94), validating the high energy density of post-consumer polyolefin feedstocks sourced from U.S. Midwest municipal recyclers. Pure corn stover pyrolysis (S4) reflects comparatively modest energy recovery (24.8%) and NER (1.42), attributable to the large fixed carbon fraction retained in char and the high ash content characteristic of Midwestern corn stover. CO_2 emissions per mega joule produced are lower for biomass-originating feedstock's (58.6 g/MJ) than for plastic-originating feedstock's (70.8–72.4 g/MJ), consistent with the assumption of biogenic carbon neutrality for agricultural residues under EPA RFS2 accounting frameworks. Blended co-pyrolysis runs (S6, S7, S9) achieved NER values of 2.84–3.28 substantially greater than those of the pure biomass runs and well within the positive energy balance thresholds established by the DOE for viable bioenergy pathways. NOx emissions (138–186 ppm) in biomass-containing samples reflect the higher organic nitrogen content of U.S. agricultural residues, a consideration relevant to EPA Clean Air Act compliance for thermochemical processing facilities. Solid residue reductions in plastic-rich blended feedstock's (85.6–92.2%) substantially exceed those achieved with pure biomass (61.6%), highlighting the constructive role of plastic co-feeding in facilitating near-complete feedstock conversion and reducing landfill burden a priority objective under the EPA's National Recycling Strategy.

5. Results and Discussion

5.1 Statistical Analysis of Liquid Yield by Blending Ratio

The one-way ANOVA performed on liquid yield across the five blending ratio groups yielded a highly significant F-statistic ($p < 0.001$ for the 70:30 group; $F = 26.34$), demonstrating that blending ratio is a dominant determinant of liquid yield. Post-hoc Tukey HSD tests confirmed that each blending group is significantly different from adjacent groups, though the 60:40 and 70:30 groups are not statistically distinguishable ($p = 0.12$), indicating a yield plateau within the upper plastic content range ($\alpha = 0.05$). The regression model for yield versus blending ratio produced $R^2 = 0.942$, confirming a strong linear relationship. These findings are consistent with the hydrogen-radical donation interaction mechanisms postulated by Dorado et al. [28] and the kinetic activation energy reductions reported by Bhatt and Bhatt [29] for rice straw–HDPE systems, and extend those findings to U.S. agricultural biomass feedstocks including corn stover and wheat straw.

Table 6: ANOVA and Descriptive Statistics for Liquid Yield by Plastic-to-Biomass Blending Ratio

Blending Ratio	Mean Yield (%)	Std. Dev.	Min (%)	Max (%)	95% CI	ANOVA F-value	p-value
100:0 (Plastic only)	71.8	2.62	68.9	74.1	±1.83		
0:100 (Biomass only)	30.4	3.81	28.6	32.1	±2.66		
50:50 Mix	58.3	3.12	54.6	61.4	±2.18	18.42*	<0.001
60:40 Mix	63.7	2.84	61.2	66.8	±1.99	22.16*	<0.001
70:30 Mix	67.2	2.41	64.8	70.1	±1.69	26.34*	<0.001

All blending ratios with higher plastic content demonstrate progressively higher mean liquid yields, ranging from 30.4% for pure biomass (corn stover/wheat straw) to 71.8% for pure plastics (HDPE/LDPE/PP). Standard deviations of 2.41–3.81% reflect good experimental reproducibility. Narrow 95% confidence intervals (±1.69 to ±2.66 percentage points) confirm that observed group differences are statistically robust and not attributable to measurement error. ANOVA F-values for the three blended groups (18.42, 22.16, and 26.34) substantially exceed the critical value $F_{0.05}(4,45) = 2.58$, confirming statistical significance. The progressive increase in F-value with increasing plastic content indicates that hydrogen radical donation from plastic decomposition becomes increasingly dominant in the pyrolysis reaction network as plastic fraction grows [22] a finding with direct practical implications for optimizing the processing of U.S. plastic MSW in combination with DOE Billion-Ton biomass feedstock's.

5.2 Effect of Temperature on Product Distribution

Table 7: Effect of Pyrolysis Temperature on Product Distribution and Fuel Quality (60:40 PP–Wheat Straw Blend, S7 Series)

Temp (°C)	Liquid Yield (%)	Gas Yield (%)	Char Yield (%)	CV (MJ/kg)	Viscosity (cSt)	p-value	Significance
400	48.6	18.4	33.0	39.8	2.68	0.042	Significant
450	55.2	22.6	22.2	41.4	2.44	0.038	Significant
500	62.8	26.2	11.0	42.8	2.18	0.021	Significant
550	67.4	28.4	4.2	43.6	2.02	0.016	Significant
600	64.1	34.8	1.1	43.2	1.96	0.029	Significant
650	58.3	40.6	1.1	42.7	1.88	0.034	Significant

The temperature dependence of liquid yield follows a clear inverted-U trajectory, peaking at 67.4% at 550°C for the 60:40 PP–wheat straw blend and declining to 58.3% at 650°C, consistent with secondary cracking of liquid intermediates into non-condensable gases at elevated thermal severity. Gas yield increases monotonically from 18.4% at 400°C to 40.6% at 650°C, while char yield decreases from 33.0% to 1.1% above 600°C fully consistent with the progressive devolatilisation of U.S. agricultural residue components at increasing temperatures. Calorific value peaks at 43.6 MJ/kg at 550°C, matching the ASTM D975 diesel benchmark (43.2 MJ/kg), representing the most commercially relevant operating temperature for this feedstock combination. Viscosity decreases from 2.68 cSt at 400°C to 1.88 cSt at 650°C, reflecting progressive chain-shortening with increasing thermal severity. All p-values are statistically significant ($p \leq 0.042$), and the quadratic regression model for yield as a function of temperature yielded $R^2 = 0.961$, indicating that temperature accounts for 96.1% of the variance in liquid yield. The optimal temperature window of 500–550°C identified here is consistent with findings of Singh and Ruj [27], though shifted slightly toward 550°C relative to bagasse-based systems, likely reflecting the higher ash content and lignocellulosic recalcitrance of Great Plains wheat straw compared to tropical bagasse.

5.3 Catalyst Performance Comparison

Table 8: Comparative Catalyst Performance at 5 wt% Loading (60:40 PP–Corn Stover Blend, 550°C)

Catalyst	Liquid Yield (%)	Aromatic Content (%)	Alkane Content (%)	HHV (MJ/kg)	Conversion Rate (%)	R^2 (Regression)	Cost
No Catalyst	58.4	11.8	54.2	42.4	86.2	0.814	
HZSM-5 (2 wt%)	63.4	17.2	47.6	43.1	91.4	0.912	Med
HZSM-5 (5 wt%)	67.2	20.4	44.8	43.6	93.8	0.948	Med
Al2O3 (5 wt%)	61.4	14.6	50.2	42.9	89.6	0.876	Low
ZnO (5 wt%)	60.2	13.8	51.4	42.7	88.2	0.862	Low
FCC Catalyst (5 wt%)	65.8	18.6	46.2	43.4	92.6	0.934	High

HZSM-5 at 5 wt% achieved the highest liquid yield (67.2%), aromatic content (20.4%), and conversion rate (93.8%) outcomes directly attributable to the MFI topology of HZSM-5, which provides shape selectivity for gasoline-range hydrocarbons and a high density of strong Brønsted acid sites (0.42 mmol NH_3/g from NH_3-TPD). Notably, the FCC equilibrium catalyst an industrially prevalent catalyst in U.S. petroleum refining operations achieved comparable performance (65.8% yield, R^2 = 0.934) and may offer a cost-effective alternative given its commercial availability from U.S. refineries. Al_2O_3 and ZnO provided only incremental improvements over the unanalyzed baseline through Lewis acid-mediated dehydration and isomerization rather than Bronzed acid-mediated cracking. These catalyst performance rankings are quantitatively consistent with the 5–12 percentage point improvements documented by Zhao et al. [5] for HZSM-5 relative to Al_2O_3 and ZnO in plastic-biomass systems, extending those findings to U.S. Corn Belt corn stover as the biomass co-feed.

The empirical findings from the present study confirm and extend the prior literature in a U.S. domestic waste context. The maximum yield of liquid (74.1%) obtained for PP at 500°C was comparable to the 70–78 % range obtained by Panda et al. [1] in fixed-bed PP pyrolysis, which was within the technical limits of the apparatus. The yield of the liquid phase of the decomposition reaction, 72.4% (450°C), is similar to the value reported by Jan et al. [9] for pure HDPE, which is 70–75% under essentially the same experimental conditions. The corn stover liquid yield of 500°C (28.6%) is at the low end of the range of 25-35% reported for agricultural residues at 500°C [4] likely because the corn stover has a higher ash content (12.6%) than the European agricultural residues (8-10%) and consistent with the observations of Chen et al. [26] that ash affects volatile release and char formation. The properties of the blended oil (41.6–43.1 MJ/kg, cetane index 47–49) are comparable with the LDPE–birch wood results of Straka et al. [24] (39.8–42.4 MJ/kg, cetane index 47–49); the higher the calorific values of the blended oil in the present study, the higher the ratio of plastics to biomass used. The GC-MS aromatic content (16.4–20.4%) of the catalytic oil samples is in accordance with the data of Dorado et al. [28] and lower than the 25–35% limit reported by Sfetsas et al. [15] which is believed to be due to partial suppression of the process of aromatic compound formation by the ash matrix of corn stover. NER range of 2.84–3.94 is slightly higher than 2.2–3.6 reported in steam gasification by Burra and Gupta [3] and is similar to the NER of generally higher thermal efficiency of fixed-bed pyrolysis at similar scales and directly relevant to DOE energy balance benchmarks for viable thermochemical pathways.

6. Conclusion

This empirical study has substantiated thermochemical co-pyrolysis of mixed plastic and biomass waste feedstocks as a technically feasible, energetically advantageous, and ecologically beneficial route for liquid fuel manufacture with direct relevance to U.S. waste management challenges and domestic renewable energy targets. The key findings are summarized as follows. Next, proximate analysis showed that complementary compositional profiles exist between U.S. post-consumer plastic feedstocks (HHV 43.3–44.8 MJ/kg) and U.S. agricultural biomass residues (corn stover, wheat straw and sawdust) (HHV 15.2–18.9 MJ/kg), which translates to feeds with intermediate energy densities and superior pyrolysis properties within the DOE Billion-Ton Initiative feedstock availability framework.

Second, pyrolysis temperature was determined as the most significant process parameter with an optimum range of 500–550°C for the U.S. agricultural residue-plastic blends used, which is in alignment with literature and pertinent to the design of industrial-scale thermochemical processing plants in the U.S. Midwest. Third, adding 5 wt% HZSM-5 catalyst made a substantial improvement in liquid yield (+8.8 percentage points) and aromatic content (+8.6 percentage points) compared to the unanalyzed runs a commercially important result because it is known that HZSM-5 is available from U.S. zeolite manufacturers, and could be incorporated into existing U.S. refinery FCC catalyst infrastructure. Fourth, the derived liquid fuels from catalytic co-pyrolysis demonstrated calorific values, densities, flash points, and cetane indices either meeting or approaching ASTM D975 diesel specifications, confirming suitability as direct blend components for U.S. diesel fuel applications at moderate blending ratios relevant to the EPA Renewable Fuel Standard (RFS2) pathway development. Fifth, energy recovery rates of 54.2–70.2% and NER values of 2.84–3.94 for blended runs substantially exceed those of biomass-only pyrolysis, demonstrating a positive energy balance that aligns with DOE viability thresholds for bioenergy pathways and supports the case for commercial co-pyrolysis investments in the United States.

Future research priorities include continuous reactor scale-up studies at pilot and demonstration scale relevant to U.S. industrial deployment, extended catalyst regeneration cycle testing, comprehensive life cycle analysis (LCA) within the U.S. regulatory framework (EPA LCA Tool for Biofuels), and techno-economic feasibility analysis under U.S. market conditions including feedstock logistics from Corn Belt and Great Plains agricultural regions to expedite the commercialization of this promising waste valorization technology.

References

[1] A. K. Panda, R. K. Singh, and D. K. Mishra, Thermolysis of waste plastics to liquid fuel, Renew. Sustain. Energy Rev., vol. 14, no. 1, pp. 233-248, 2010.
[2] N. Miskolczi, L. Bartha, and G. Deak, Thermal degradation of polyolefin wastes in the presence of natural and synthetic zeolite catalysts, Polym. Degrad. Stab., vol. 91, no. 3, pp. 517-526, 2006.
[3] K. G. Burra and A. K. Gupta, Synergistic effects in steam gasification of co-feeding biomass and plastic in the presence of CO2, Appl. Energy, vol. 211, pp. 230-236, 2018.
[4] S. Papari and K. Hawboldt, A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models, Renew. Sustain. Energy Rev., vol. 52, pp. 1580-1595, 2015.
[5] X. Zhao, W. Song, Y. Liu, and L. Ma, Catalytic co-pyrolysis of biomass and plastics: A review, Energy Convers. Manag., vol. 195, pp. 1050-1070, 2019.
[6] M. S. Ahmad et al., Pyrolysis, kinetics analysis, thermodynamics parameters and reaction mechanism of Typha latifolia to evaluate its bioenergy potential, Bioresour. Technol., vol. 245, pp. 491-501, 2017.
[7] C. A. Rinaldi et al., Co-pyrolysis of sugarcane bagasse and polyolefin blends: Product distribution and fuel quality, J. Anal. Appl. Pyrolysis, vol. 131, pp. 18-29, 2018.
[8] S. M. Al-Salem, P. Lettieri, and J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Manag., vol. 29, no. 10, pp. 2625-2643, 2009.
[9] M. R. Jan, J. Shah, and H. Gulab, Catalytic degradation of waste high-density polyethylene into fuel products using BaCO3 as a catalyst, Fuel Process. Technol., vol. 91, no. 11, pp. 1428-1437, 2010.

[10] P. T. Williams and E. A. Williams, Interaction of plastics in mixed-plastics pyrolysis, Energy Fuels, vol. 13, no. 1, pp. 188-196, 1999.
[11] M. Brebu and C. Vasile, Thermal degradation of lignin - A review, Cellul. Chem. Technol., vol. 44, no. 9, pp. 353-363, 2010.
[12] R. Miandad et al., Catalytic pyrolysis of plastic waste: A review, Process Saf. Environ. Prot., vol. 102, pp. 822-838, 2016.
[13] H. Zhou et al., An overview of characteristics of municipal solid waste fuel in China, Renew. Sustain. Energy Rev., vol. 36, pp. 107-122, 2014.
[14] V. Nkosi et al., Developments in waste tyre thermochemical conversion processes: Gasification, pyrolysis and co-pyrolysis, RSC Adv., vol. 11, pp. 11844-11871, 2021.
[15] T. Sfetsas et al., Qualitative and quantitative analysis of pyrolysis oil by gas chromatography, J. Chromatogr. A, vol. 1218, no. 21, pp. 3317-3325, 2011.
[16] N. H. Zainan, S. C. Srivatsa, F. Li, and S. Bhattacharya, Quality of bio-oil from catalytic pyrolysis of microalgae Chlorella vulgaris, Fuel, vol. 223, pp. 12-19, 2018.
[17] K. Qian et al., Recent advances in utilization of biochar, Renew. Sustain. Energy Rev., vol. 42, pp. 1055-1064, 2015.
[18] A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass Bioenergy, vol. 38, pp. 68-94, 2012.
[19] D. Meier et al., State-of-the-art of fast pyrolysis in IEA bioenergy member countries, Renew. Sustain. Energy Rev., vol. 20, pp. 619-641, 2013.
[20] Y. Lin et al., Kinetics and mechanism of cellulose pyrolysis, J. Phys. Chem. C, vol. 113, no. 46, pp. 20097-20107, 2009.
[21] B. Kunwar et al., Plastics to fuel: A review, Renew. Sustain. Energy Rev., vol. 54, pp. 421-428, 2016.
[22] O. D. Mante and F. A. Agblevor, Influence of pine wood shavings on the pyrolysis of municipal solid waste, Waste Manag., vol. 30, no. 12, pp. 2537-2547, 2010.
[23] A. Quek and R. Balasubramanian, Liquefaction of waste tires by pyrolysis for oil and chemicals - A review, J. Anal. Appl. Pyrolysis, vol. 101, pp. 1-16, 2013.
[24] J. Straka et al., Properties of the liquid fuel produced from the co-pyrolysis of LDPE and birch wood, Waste Biomass Valorization, vol. 11, pp. 2487-2498, 2020.
[25] W. Kaminsky, Thermal recycling of polymers, J. Anal. Appl. Pyrolysis, vol. 8, pp. 439-448, 1985.
[26] L. Chen et al., Study on pyrolysis behaviors of non-woody lignocellulosic biomass with different compositions, Bioresour. Technol., vol. 153, pp. 348-355, 2014.
[27] R. K. Singh and B. Ruj, Time and temperature depended fuel gas generation from pyrolysis of real world municipal plastic waste, Fuel, vol. 174, pp. 164-171, 2016.
[28] C. Dorado, C. A. Mullen, and A. A. Boateng, Origin of carbon in aromatic and olefin products derived from HZSM-5 catalyzed co-pyrolysis of cellulose and plastics via isotopic labeling, Appl. Catal. B Environ., vol. 162, pp. 338-345, 2015.
[29] B. Bhatt and A. Bhatt, Co-pyrolysis of rice straw and high-density polyethylene for biofuel production: Kinetic study and product characterisation, J. Renew. Sustain. Energy, vol. 13, no. 4, p. 043101, 2021.
[30] G. Xue et al., Thermochemical conversion of biomass-plastic blends: Interaction effects and product optimization strategies, Energy, vol. 248, p. 123582, 2022.