

Article



# Upgrading Mixed Agricultural Plastic and Lignocellulosic Waste to Liquid Fuels by Catalytic Pyrolysis

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Abstract: Agriculture generates non-recyclable mixed waste streams, such as plastic (netting, twine, and film) and lignocellulosic residues (bluegrass straw/chaff), which are currently disposed of by burning or landfilling. Thermochemical conversion technologies of agricultural mixed waste (AMW) are an option to upcycle this waste into transportation fuel. In this work, AMW was homogenized by compounding in a twin-screw extruder and the material was characterized by chemical and thermal analyses. The homogenized AMW was thermally and catalytically pyrolyzed (500–600 °C) in a tube batch reactor, and the products, including gas, liquid, and char, were characterized using a combination of FTIR, GC-MS, and ESI-MS. Thermal pyrolysis wax products were mainly a mixture of straight-chain hydrocarbons  $C_7$  to  $C_{44}$  and oxygenated compounds. Catalytic pyrolysis using zeolite Y afforded liquid products comprised of short-chain hydrocarbons and aromatics  $C_6$  to  $C_{23}$ . The results showed a high degree of similarity between the chemical profiles of catalytic pyrolysis products and gasoline.

**Keywords:** thermochemical conversion; catalytic pyrolysis; waste upcycling; agricultural mixed waste; zeolite Y catalyst; transportation fuel

# 1. Introduction

Plastics have long been used in agriculture to increase the yield and quality of the crop [1]. At the end of the harvest season, agricultural lignocellulosic and plastic wastes are often disposed by open burning or landfilling. Improper disposal of agricultural mixed waste (AMW) can have significant adverse environmental consequences; for example, open burning causes significant air pollution [2], and landfilling leads to the generation of greenhouse gases [3] and microplastics [4]. Alternative waste management technologies, such as thermochemical conversion, can help mitigate the negative environmental impact of AMW. Particularly, because agricultural plastic waste is petroleum-based, it is a good candidate to be exploited for product and energy recovery [5]. The use of thermochemical conversion technologies, such as pyrolysis, for lignocellulosic agricultural residue results in low quality energy products. The liquid pyrolysis products (bio-oil) of agricultural residue contain numerous oxygenated compounds, such as sugars, aldehydes, ketones, acids, and phenols. The presence of these compounds leads to low heating values, thermal instability, and corrosiveness of the energy product [6]. In contrast to the lignocellulosic residue, synthetic polymers deliver liquid products (oils and waxes) of higher quality due to their high carbon content. Co-pyrolysis of lignocellulosic biomass with synthetic polymers has shown promise in enhancing the properties of the obtained oil.

Studies have shown that co-pyrolysis of lignocellulosic biomass and synthetic polymers generates liquid products of high quality. Paradela et al. have reported that an increase in the plastics content in the blend of pine, plastics, and tires not only increases liquid yield (from 33% to 92% w/w) and favors the formation of lighter compounds (less distillation residue) but also promotes the conversion of aromatic compounds into alkanes



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and alkenes [7]. Rutkowski studied the bio-oil characteristics of beverage carton packaging waste and reported that non-catalytic pyrolysis of their feedstock leads to the formation of levoglucosan as a major liquid product of cardboard decomposition [8] and long-chain hydrocarbons as the product of thermal decomposition of polyethylene (PE) layers [9]. Chen et al. also reported that the co-pyrolysis of wastepaper and PE significantly enhances the oil yield and the fuel properties of the obtained oil [10]. Waste plastics exhibit synergistic effects during co-pyrolysis and provide the proper hydrogen/carbon ratio. Waste plastic is a good hydrogen source, and its use as a co-reactant in the catalytic pyrolysis of biomass increases aromatic carbon efficiency and decreases coke production. Up to 40% of gross waste plastics are made up of PE, making it a great candidate for catalytic co-pyrolysis [11].

Other studies have shown that pyrolysis of plastic waste can result in the generation of a mixture of hydrocarbons under various pyrolysis conditions [12–17]. However, there are concerns about the economic and energy consumption feasibility of the process. Moreover, quite often, the pyrolysis process produces liquid oil that contains long carbon chain compounds [18]. The oil has lower quality because of its low octane number, presence of solid residues [19], and impurities such as sulfur, nitrogen, chlorine, and phosphorous [20]. To overcome these issues, catalytic pyrolysis of plastics has become a topic of interest in the past decade [21]. Various catalysts have been utilized, such as Red Mud and ZSM-5 [22], fluid catalytic cracking (FCC) [23], HZSM-5 [24], zeolite Y [25], ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) [26], and natural zeolite [27], to enhance the quality of the catalytic pyrolysis oil.

The first step in catalytic pyrolysis is the thermal cracking on the external surface of the catalyst. The porous structure inside the catalyst works as a channel for selective movement and breakdown of large hydrocarbon chains into smaller fragments [23]. Generally, the degradation of heavier alkenes occurs on the outer surface of the catalyst, and further degradation and product selectivity take place in the internal pores of the catalyst [28]. It was possible to combine the catalyst with the feedstock in the reactor or with the organic vapors produced in a separate catalyst chamber. Lopez et al. [22] and Chen et al. [15] reported that a liquid phase or direct contact with feedstock improves the cracking process by reducing the reaction temperature and retention time. However, in the case of direct contact, it is difficult to recover the catalyst due to the sticky nature of plastic feedstock [27]. Several catalysts, such as zeolite Y and ZSM-5, have shown to be effective under vapor phase contact with feedstock [22].

Catalyst characteristics such as surface area, pore size, pore volume, and acidity are the main factors influencing its activity in the pyrolysis process [28]. Syamsiro et al. have reported that using a catalyst with a high surface area allows for more contact between reactants and the catalyst surface, which results in an increased rate of cracking reaction to produce more gases than liquid oil [27].

The three main types of catalysts used in catalytic pyrolysis include FCC, silicaalumina catalysts, and zeolites [27]. FCC catalysts are mainly used in petroleum refineries for cracking heavy oil into gasoline and liquid oil petroleum. These catalysts have been used in the pyrolysis process successfully [27]. Silica-alumina catalysts are amorphous catalysts that have Lewis acid sites as electron acceptors and Brønsted acid sites with ionizable hydrogen atoms [27]. It has been shown that the acidity of these catalysts affects the production of liquid oil from plastic waste, and lower acidity results in higher yield [29]. Zeolite catalysts are crystalline alumino-silicates molecular sieves that have a 3D framework consisting of cavities and channels. The main characteristic of these catalysts is their ionexchange capabilities and open pores. Different ratios of  $SiO_2/Al_2O_3$  in zeolites determine their reactivity and affect the final products of the pyrolysis process. Zeolite catalysts generally increase volatile hydrocarbon production and have a low rate of deactivation.

Among these catalysts, FCC catalysts increase liquid oil yields and the use of spent catalysts (i.e., previously used in refineries) instead of virgin catalysts makes them more economical [30]. It is noteworthy that the introduction of zeolite Y in FCC catalyst formulations in the 70s and 80s resulted in a drastic increase in the gasoline yield [31].

Yuan et al. co-pyrolyzed rice husks and PVC with MgO/MgCO<sub>3</sub>, which resulted in a significant decrease in acid content and increased hydrocarbon content [32]. Miandad et al. have reported that natural and synthetic zeolite catalysts can be used for the catalytic pyrolysis of four major types of plastic wastes such as PE, PS, PP, and PET. Their resultant liquid oils have high higher heating values (HHV, 40.2–45 MJ·kg<sup>-1</sup>), which is similar to conventional diesel [33]. Syamsiro et al. also used zeolite Y and natural zeolite catalysts for sequential pyrolysis and catalytic reforming of municipal plastic wastes and produced high-quality liquid and solid products with higher HHV than those of biomass and lowrank coal [27]. Generally, the primary function of the catalysts is to increase the proportion of lighter hydrocarbons in the oil through cracking reactions [34] and improve the overall process energy efficiency [22] (i.e., achieving higher quality products at lower temperatures). Zeolite Y has been used as the main cracking catalyst in FCC. It contains an internal porous structure that can convert longer-chain hydrocarbons to smaller molecules through the formation of carbenium ions via proton transfers in the hydrocarbon's Brønsted and Lewis acid sites [35]. Since the pores of zeolite Y are small (7.3 Å), the larger molecules in the wax oil will need to be thermally cracked first before passing through the pores. Lee successfully used multiple zeolite catalysts, including zeolite Y, for the upgrading of pyrolysis wax oil, obtained from municipal plastic waste, in a continuous plug flow reactor at 450 °C [25]. The catalyst pore dimensions were shown to play a vital role in the conversion of wax into light hydrocarbon and catalysts with more than one dimension, such as zeolite Y, show a high conversion rate.

Thus, this work aims to investigate the thermal and catalytic (using Zeolite Y) decomposition of agricultural plastic waste mixed with lignocellulosic biomass via pyrolysis on a batch reactor and characterize the gaseous, liquid, and solid products by a combination of electrospray ionization-mass spectrometry (ESI-MS), gas chromatography-mass spectrometry (GC-MS), GC, proximate/ultimate analysis, surface area measurements, and Fourier transform infrared (FTIR) spectroscopy. The biomass and plastic waste feed stocks were also characterized by compositional analysis, thermogravimetric analysis (TGA), and FTIR spectroscopy.

## 2. Results and Discussion

# 2.1. Agricultural Mixed Waste (AMW) Characterization

Two batches of AMW were collected from rural Idaho farms and used as feedstock. The first batch contained wheat chaff and mixed plastic (CMP), and the second batch contained bluegrass straw and mixed plastics (BMP). The lignocellulosic portion of each batch was separately analyzed. The plastic portion of the waste consisted of 69% net wrap (NW), 22% twine 1 (T1), and 9% twine 2 (T2), all of which were separately analyzed and then extruded. Homogenized mixed plastic (MP) was also analyzed after the extrusion of NW, T1, and T2.

Density was used to identify the ratio of lignocellulosic content (L) to plastic (P) in each feedstock. L:P was 16.8:83.2 for CMP and 36.2:63.8 for BMP. FTIR spectroscopy was used to identify the plastic-type and lignocellulosic material as well as the blended AMW. NW was identified as PE, while T1 and T2 were polypropylene (PP) (detailed results are presented in Figure S1 in Supplementary Materials).

The results of chemical composition, proximate, ultimate, and calorific value analyses of bluegrass straw (BG), chaff, MP (extruded mixture of NW, T1, T2), BMP, and CMP are presented in Table 1. The low N contents of BG and chaff were expected as both feedstocks have very little protein. This finding was in line with the literature [36]. Fixed carbon (FC) values of 21.5% and 15.5% for BG and chaff, respectively, were in the range reported for straw [37–39]. The calorific values for BG and chaff were 19.7 and 17.5 MJ·kg<sup>-1</sup>, respectively. The calorific value for MP was 46.21 MJ·kg<sup>-1</sup> and was in the range of reported values [40]. BMP and CMP calorific values were 35.4 and 39 MJ·kg<sup>-1</sup>, respectively. Considering the L:P ratio found via density analysis, these values were reasonable.

Analysis	BG	Chaff	MP	BMP	СМР
C (%)	$37.0 \pm 1.8$	$32.2\pm1.6$	$74.2\pm2.9$	$69 \pm 3.1$	$72.7\pm3.5$
N (%)	$1.2\pm0.04$	$1.2\pm0.06$	$0.9\pm0.03$	$0.3\pm0.02$	$0.4\pm0.01$
Ash (%)	$17.1\pm0.8$	$5.46\pm0.26$	$1.02\pm0.04$	$3.73\pm0.17$	$5.9\pm0.27$
Fixed Carbon (%)	$21\pm0.9$	$15.5\pm0.7$	0.0	$8.1\pm0.4$	$5.3\pm0.25$
Volatile Matter (%)	$61.9\pm1.3$	$71\pm0.9$	$98.98 \pm 0.3$	$88.17\pm0.5$	$89\pm0.8$
Density (g cm <sup>-3</sup> )	$1.45\pm0.07$	$1.34\pm0.03$	$0.95\pm0.02$	$1.09\pm0.01$	$1.04\pm0.04$
Calorific Value (MJ·kg <sup>-1</sup> )	$19.7\pm0.4$	$17.5\pm0.2$	$46.2\pm0.9$	$35.4\pm0.3$	$39\pm0.2$
Extractives (%)	$2.1\pm0.3$	$3.2\pm0.5$	-	-	-
Carbohydrate (%)	$55.0 \pm 1.8$	$58.0\pm0.6$	-	-	-
Lignin Content (%)	$22.98\pm0.5$	$23.6\pm0.23$	-	-	-

**Table 1.** Proximate and ultimate analyses, density, calorific values, and chemical content of bluegrass (BG), chaff, mixed plastic (MP), BMP, and CMP.

Lignin contents of BG and chaff were 23.0% and 23.6%, respectively. Acid-soluble lignin and Klason lignin contents were 4.34% and 18.64% for BG and 3.86% and 19.69% for chaff, respectively. Lignin values were consistent with previous findings [41]. The carbohydrate contents of BG and chaff were, respectively, 55% and 58%, and comparable to wheat straw [41].

The CH<sub>2</sub>Cl<sub>2</sub> extractives yields were 3.2% and 2.1% for BG and chaff, respectively. Fatty acid methyl esters (FAME) analysis of the extract identified palmitic acid (C16:0), linoleic acid (C18:2), and oleic acid (C18:1) as the most abundant fatty acids (Table 2). Trace amounts of lauric (C12:0), myristic (C14:0), stearic (C18:0), and arachidic (C20:0) acids were also detected. FAME results were consistent with prior findings for lignocellulosic agricultural residues [42,43].

Fatty Acid	Retention Time (min)	${ m M}^+$ (m/z)	(mg/g Dry BG)	(mg/g Dry Chaff)
Lauric Acid	24.70	200	$0.04\pm0.004$	$0.06\pm0.004$
Myristic Acid	28.70	228	$0.08\pm0.01$	$0.51\pm0.04$
Palmitic Acid	32.80	270	$5.25\pm0.4$	$12.47\pm0.04$
Linoleic Acid	34.72	294	$0.57\pm0.05$	$1.87\pm0.09$
Oleic Acid	36.08	296	$0.67\pm0.05$	$0.82\pm0.03$
Stearic Acid	36.56	298	$0.12\pm0.01$	$0.26\pm0.02$
Arachidic Acid	40.01	304	$0.10\pm0.01$	$0.16\pm0.01$

Table 2. Fatty acid methyl ester analysis of bluegrass (BG) and chaff CH<sub>2</sub>Cl<sub>2</sub> extracts.

# 2.2. TGA

TGA was used to study the thermal kinetic decomposition characteristics of the AMW samples with and without a 50% catalyst (Figure 1). Differential thermogravimetric (DTG) curves are also shown in Figure 1. The thermal decomposition onsets, major peak, and final decomposition temperatures are given in Table 3.

According to Raveendran et al., the process of biomass pyrolysis typically involves three steps: (i) dehydration; (ii) devolatilization, which produces biochar; and (iii) the gradual transformation of the biochar that has already been produced [44]. The evaporation of water and light volatiles was responsible for the initial decomposition stage for chaff and BG, which occurred at <300 °C and was associated with very little mass loss [45]. The majority of the weight loss occurred between 300 and 410 °C, where two distinct DTG peaks were present and corresponded to the steep weight loss [46]. The weight loss between 325 and 400 °C was attributed to cellulose degradation [45,47,48]. Over 90% of the material eventually deteriorated. Levoglucosan and other oligomers were created from the breakdown of cellulose through trans-glucosidation [49]. The peak around 470 °C was likely related to the breakdown of lignin [50,51]. A modest weight loss was observed above 500 °C, which was attributed to the biochar's sluggish transformation [52].



**Figure 1.** TGA (**left**) and DTG (**right**) thermograms of bluegrass (BG), chaff, net wrap (NW), twine 1 (T1), twine 2 (T2), mixed plastic (MP), bluegrass mixed plastic (BMP), chaff mixed plastic (CMP), BMP-catalyst (1:1), and CMP-catalyst (1:1) at  $\beta$  20 °C/min heating rates.

**Table 3.** Thermal degradation behavior determined by TGA of bluegrass (BG) straw, chaff, net wrap (NW), twine 1 (T1), twine 2 (T2), mixed plastic (MP), bluegrass mixed plastic (BMP), chaff mixed plastic (CMP), BMP-catalyst (1:1), and CMP-catalyst (1:1) at  $\beta$  20 °C/min heating rate.

Samples	1st Onset (°C)	2nd Onset (°C)	1st Peak (°C)	Major Peak (°C)	Final Decomposition (°C)
BG	243	-	-	352	385
Chaff	291	-	-	349	401
NW	472	-	-	519	530
T1	479	-	-	511	521
T2	478	-	-	514	524
MP	482	-	-	512	526
BMP	316	488	365	520	534
CMP	310	492	332	527	539
BMP + Cat	316	423	373	447	485
CMP + Cat	330	426	346	453	484

All plastic samples exhibited one-step breakdown [53,54]. The highest degradation rate for T1, T2, NW, and MP (extruded mixture of NW, T1, and T2) occurred between 520 and 530 °C [55]. The major DTG peaks reduced in size in the presence of catalysts because low molecular weight alkanes degraded more quickly at lower temperatures. According to other studies, the presence of zeolite catalysts with a high acidity level speeds up the breakdown of polymers into shorter fragments and gaseous products [56,57]. In thermal conversion procedures, the catalyst's crystalline structure encourages hydrogen transfer reactions that result in high conversions [58,59].TGA was a helpful tool to establish a suitable operating temperature frame for pyrolysis. The results suggested that 500 to 600 °C was an appropriate temperature range for pyrolysis.

Based on a linear regression model, the apparent  $E_a$  was estimated using the isoconversional technique, as described below, and data given in Table 4. Figure 2 shows a linear regression of the FWO method in the conversion ( $\alpha$ ) range of 10% to 90%. For BG and chaff, Figure 2a,b display two sets of parallel iso-conversional lines, one set representing  $10\% \le \alpha \le 70\%$  and the other representing  $\alpha \ge 80\%$ . For the T1, T2, NW, and MP plastic samples (Figure 2c–f), the slope was similar for all conversion rates, suggesting a similar kinetic behavior. In the BMP and CMP thermographs (Figure 2g–h), there were two sets of parallel iso-conversional lines due to the mixed nature of the feedstock. The behavior was likely due to different response mechanisms between the plastic and lignocellulosic portions [46,60,61].

	bluegrass mixed plastic (BMP) determined by TGA.									GA.						
Conversion	Cha	ıff	BS		NV	v	T1		1	Γ2	MI	,	CM	ИР	BM	Р
α	Ea (J/mol)	R <sup>2</sup>	Ea (J/mol)	R <sup>2</sup>	E <sub>a</sub> (J/mol)	R <sup>2</sup>	Ea (J/mol)	R <sup>2</sup>	E <sub>a</sub> (J/mol)	R <sup>2</sup>	Ea (J/mol)	R <sup>2</sup>	E <sub>a</sub> (J/mol)	R <sup>2</sup>	Ea (J/mol)	R <sup>2</sup>
10% 20% 30% 40% 50% 60% 70% 80% 90% Average	117 146 155 158 160 156 170 303 336 189	0.99 0.99 0.99 0.99 0.99 0.99 0.98 0.76 0.68	152 173 198 206 212 221 246 494 312 246	0.986 0.985 0.991 0.992 0.993 0.993 0.998 0.607 0.480	203 200 201 201 201 200 200 200 200 200 201	0.957 0.92 0.949 0.963 0.973 0.977 0.981 0.984 0.988	246 236 228 219 214 211 209 207 222	0.996 0.995 0.996 0.996 0.996 0.996 0.996 0.995 0.995	169 176 179 178 178 176 175 175 175 175 175	0.995 0.994 0.993 0.992 0.993 0.993 0.993 0.993 0.994 0.995	236 231 227 224 222 218 217 215 214 223	0.987 0.985 0.984 0.985 0.984 0.983 0.983 0.982 0.981 0.98	195 229 214 212 212 210 209 210 213 211	0.988 0.998 0.994 0.996 0.997 0.998 0.998 0.999 0.999	176 186 194 232 228 229 229 233 235 216	0.999 0.999 0.883 0.989 0.994 0.996 0.996 0.996 0.995
			log β (K/min)	1.70 - 1.50 - 1.30 - 1.10 - 0.90 - 0.70 -	÷	· · · · · · · · · · · · · · · · · · ·		(a)	1.70 - 1.50 - 1.30 - 1.10 - 0.90 - 0.70 -	• Δ		°	(b)			
				0.50	20 1.40	1.60	1.80	2.00	0.50	1.40	1.60	1.80	2.00			
			log ß (K/min)	1.80 · · · · · · · · · · · · · · · · · · ·	<b>\$€</b> <b>*</b> <b>*</b> <b>*</b> <b>*</b> <b>*</b> <b>*</b> <b>*</b>	0 	• • • • • • • • • • • • • • • • • • •	(C) 1.40	1.80 - 1.60 - 1.40 - 1.20 - 1.00 - 0.80 - 0.60 _ 1.20	1.25	+	0.	(d)			
			/min)	1.80 • 1.60 • 1.40 •	<b>€₽</b> - <b>?</b> ×4 †			(e)	1.80 • 1.60 • 1.40 •	<b>*</b>	4		(f)			
			log ß (K	1.20 - 1.00 - 0.80 - 0.60 -		*******	• + • • •	<sup>1</sup> 0	1.20 • 1.00 • 0.80 • 0.60		**** ° ********	р + о	-			
			(K/min)	1.20 1.80 1.60 1.40	0 1.25	1.30	1.35	1.40 (g)	1.20 1.80 1.60 1.40	1.25 X	1.30	1.35 0	(h)			
			β β	1.00 0.80 0.60	0 1.4	0		1.80	1.00 - 0.80 - 0.60 -	1.40	▲ 1.	+ 0 + 0	1.80			
						10 <sup>3</sup> /T (K	-1)				10 <sup>3</sup> /T (K <sup>-1</sup>	)				
					01	.0% +20%	▲ 30% ×4	0% \$ 50	% - 60% •	70% <b>∆</b> 80%	♦ 90%					

**Table 4.** Activation energy values ( $E_a$ ) at various conversion factors ( $\alpha$ ) for chaff, bluegrass straw (BS), net wrap (NW), twine 1 (T1), twine 2 (T2), mixed plastic (MP), chaff mixed plastic (CMP), and bluegrass mixed plastic (BMP) determined by TGA.

**Figure 2.** Determination of apparent activation energy ( $E_a$ ) according to the FWO method at heating rates ( $\beta$ ) of 5, 10, 20, and 50 °C/min for (**a**) Chaff, (**b**) BG straw, (**c**) NW, (**d**) T1, (**e**) T2, (**f**) MP, (**g**) CMP, and (**h**) BMP.

# 2.3. DSC and DTA

DSC was used to determine the melting behavior of T1, T2, and NW and the extruded samples, MP, BMP, and CMP. DSC and DTA thermograms of the analyzed samples are shown in Figure 3. Average DSC melting peaks and percent crystallization of NW, T1, T2, MP, BMP, and CMP samples are given in Table 5. All thermograms show a major and a minor endothermic melting peak, with the distinct peaks for MP, BMP, and CMP. The NW thermogram show a single peak at 130 °C t that corresponds to PE. T1 and T2 display two endothermic peaks around 150 and 160 °C associated with PP. MP, BMP, and CMP show two peaks at 132 and 160 °C consistent with the mix of PE and PP. The peak at 132 °C was sharper and more distinct than the peak at 160 °C because of the larger proportion of net wrap compared to twine in the mixture.



**Figure 3.** (left) DSC thermograms of NW, T1, T2, MP, BMP, and CMP and (right) DTA thermograms of MP, BMP, CMP, MP-catalyst, BMP-catalyst, and CMP-catalyst.

**Table 5.** Average DSC melting peaks and percent crystallinity of NW, T1, T2, MP, BMP, and CMP samples.

Samples	First Peak Tm (°C)	$\Delta H_m$ (J/g)	Xc (%)	Second Peak Tm (°C)	$\Delta H_m$ (J/g)	Xc (%)
Net wrap (NW)	$130.9\pm0.4$	$123\pm1$	$41.9\pm0.4$	-	-	
Twine 1 (T1)	$155.2\pm0.3$	$29.8\pm3$	$14.4\pm0.6$	$165.6 \pm 1$	$104\pm2$	$50.1 \pm 1$
Twine 2 (T2)	$154.0\pm0.2$	$30.7\pm3$	$14.8\pm0.6$	$163.8 \pm 1$	$97.1\pm3$	$46.9\pm1$
Mixed Plastic (MP)	$133.3\pm0.5$	$106\pm2$	$40.1\pm0.5$	$160.2\pm0.8$	$12.1\pm2$	$57.7\pm1$
BMP	$131.6\pm0.4$	$60.8\pm1$	$23.3\pm0.7$	$158.9\pm0.8$	$7.53\pm2$	$32.8\pm0.3$
CMP	$132.7\pm0.3$	$75.0\pm1$	$28.9\pm0.8$	$159.7\pm0.7$	$9.51\pm2$	$40.3\pm0.3$

DTA was used to observe the exothermic or endothermic behavior of the MP, BMP, and CMP samples at higher temperatures with and without a catalyst. The DTA thermogram of the MP showed major endothermic and exothermic peaks at 148 and 462 °C, respectively. The peak at 148 °C was associated with the plastic melting, and the peak at 462 °C was associated with the decomposition of the plastic. Consistent with these results, Çanlı et al. reported 110 °C as the starting melting point and 475 °C as the degradation point for LDPE in DTA analysis [62]. The first endothermic peak appeared at approximately 147 °C in MP (-109.4 J/g), BMP (-85.8 J/g), and CMP (-93.1 J/g), and major exothermic peaks appeared at approximately 467 °C in MP (1133 J/g), BMP (560 J/g), and CMP (664 J/g). The exothermic peaks were associated with the degradation of plastic and biomass [63]. MP, BMP, and CMP mixed with a Zeolite Y catalyst (1:1) showed two distinct endothermic peaks at approximately 146 and 430 °C. The first peak was associated with the melting of

the plastic in MP (-78.7 J/g), BMP (-41.56 J/g), and CMP (-80.2 J/g) samples, and the second peak was associated with catalytic degradation of the plastic and biomass in MP (-380.1 J/g), BMP (-307.3 J/g), and CMP (-309 J/g) samples.

# 2.4. Analytical Py-GCMS of AMW

A wide range of volatile organic compounds were released during the thermochemical breakdown of lignocellulosic biomass and plastic. These biomass-derived substances are typically produced by the thermal cracking of lignin, hemicellulose, and cellulose fractions. Py-GCMS provided a reliable way to identify potential chemical components that may have resulted from thermal degradation processes [64]. To identify the potential pyrolysis products of each individual component of BMP and CMP, analytical pyrolysis GC-MS was carried out at 500 °C (Supplementary Material Figures S1 and S2). The detected chemicals along with their concentrations (%) are presented in the Supplementary Materials, Table S1. Acetic acid and cyclopropyl-carbinol and 1-hydroxyl-2-propanone were found to be the most abundant chemicals in chaff and BG samples. The majority of these came from the breakdown of hemicellulose [64]. There were also aliphatic oxygenated organic molecules, phenol, furan derivatives, and aromatic compounds. Py-GC-MS results for NW, T1, and T2 samples indicated the presence of PE and PP degradation products such as alkanes and alkenes from C<sub>3</sub> to C<sub>35</sub>, suggesting a high potential for conversion to fuel [65,66].

## 2.5. Pyrolysis Process and Product Yield

To produce lower molar mass products, BMP and CMP samples were subjected to thermal and catalytic pyrolysis at 500, 550, and 600 °C. Most of the condensable products were collected in the U-tube condenser and impinger. The non-condensable (gaseous) products were collected in a gas sampling bag. Pyrolysis product yields are shown in Figure 4. The thermal pyrolysis at 500 °C had the highest wax yield at 70% for BMP and 73% for CMP. The highest total liquid product yield was 50% in BMP and 46% in CMP for catalytic pyrolysis at 600 °C. Compared to the thermal pyrolysis process, catalytic pyrolysis produced substantially more gaseous products, with the maximum at 500 °C at 50% for CMP. The higher percentage of gaseous products implied that significantly larger number of lighter hydrocarbons were produced during catalytic pyrolysis. These findings corroborated with previous findings for the products of catalytic pyrolysis of plastic waste [33]. Syamsiro et al. reported a 52% liquid product yield for catalytic pyrolysis of municipal solid plastic waste using zeolite Y and reported a maximum liquid product yield of 54% for catalytic pyrolysis of polystyrene using natural zeolites [27]. The slightly higher yield figures in this work may have been the result of adding the impinger collection stage. All samples were catalytically pyrolyzed initially with the new catalyst and three further times with the recovered catalyst. The catalyst remained effective, and the product yields from experiments using recovered catalyst remained comparable to those from the initial experiment using new catalyst. The product yields were within the reported range given in the literature [66].

## 2.6. Products Characterization

# 2.6.1. Analysis of Wax and Liquid Products by ESI-MS

Positive ion ESI-MS of wax and liquid products of thermal and catalytic pyrolysis of BMP and CMP was carried out to measure the molar mass distribution of volatile and non-volatile compounds in the wax and liquid products (Figure 5 and Supplementary Material Figure S3). The results of the computed  $M_w$  and  $M_n$  are provided in Table 6.



**Figure 4.** Product yields of thermal pyrolysis (TPy) and catalytic pyrolysis (CatPy) of BMP and CMP at 500 °C, 550 °C, and 600 °C.



**Figure 5.** Positive-ion ESI-MS spectra of the products of liquid products of catalytic pyrolysis of BMP at (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C, and CMP at (**d**) 500 °C, (**e**) 550 °C, and (**f**) 600 °C.

Sample Name	Pyrolysis	Temperature (°C)	M <sub>n</sub>	$\mathbf{M}_{\mathbf{w}}$	Monomer/Oligomer
		500	695	952	0.29
	Thermal	550	662	873	0.33
BMP		600	645	907	0.35
		500	594	827	0.31
	Catalytic	550	562	787	0.37
		600	506	753	0.41
		500	702	969	0.27
	Thermal	550	690	979	0.30
CMP		600	648	879	0.34
		500	647	895	0.29
	Catalytic	550	622	859	0.36
	5	600	592	837	0.39

**Table 6.** Weight  $(M_w)$  and number  $(M_n)$  average molar mass of thermal pyrolysis and catalytic pyrolysis of BMP and CMP at 500, 550, and 600 °C were determined from positive ion ESI-MS data.

Significant [M+H]<sup>+</sup> peaks were found in the thermal pyrolysis products of BMP and CMP at m/z 125, 139, 151, 163, 165, 179, 193, and 323, which were tentatively attributed to guaiacol, hydroxymethylfurfuryl, ethyl guaiacol, eugenol/isoeugenol, coniferyl aldehyde, and cellobiosan. These compounds were derived from the lignocellulosic bluegrass or chaff portion of the BMP and CMP [8,67,68]. A series of ions (m/z 14 apart) corresponding to hydrocarbon dienes from C<sub>14</sub> (m/z = 196) to C<sub>27</sub> (m/z = 252), alkenes from C<sub>7</sub> (m/z = 113) to C<sub>33</sub> (m/z = 282), and alkanes from C<sub>7</sub> (m/z = 102) to C<sub>38</sub> (m/z = 298) were also identified in the ESI-MS. There were several intense peaks in the m/z 300–350 range, possibly associated with lignin [69–71]. The ESI-MS results were further confirmed by the GC-MS results presented in the next section.

Products of catalytic pyrolysis did not contain any peaks for oxygenated compounds or dienes, in contrast to those of thermal pyrolysis. Instead, the results showed substantial  $[M+H]^+$  peaks for aromatics from C<sub>8</sub> (m/z = 109) to C<sub>13</sub> (m/z = 179), alkanes from C<sub>7</sub> (m/z = 105) to C<sub>15</sub> (m/z = 215), and alkenes from C<sub>8</sub> (m/z = 115) to C<sub>10</sub> (m/z = 143). Benzene and toluene were not observed because they had a  $[M+H]^+$  below m/z 100. The ESI-MS findings demonstrated that, in comparison to thermal pyrolysis, catalytic pyrolysis led to greater breakdown of aliphatic molecules into short-chain hydrocarbons and aromatics.

The  $M_w$  and  $M_n$  for the products of thermal and catalytic pyrolysis and their monomer to oligomer ratio are listed in Table 6. During thermal and catalytic pyrolysis, as temperature increases, the  $M_n$  decreases by an average of 7% (thermal) and 15% (catalytic) in BMP and 8% (thermal) and 9% (catalytic) in CMP. Thermal degradation and sample reactions with the catalyst led to the drop in average molar mass [66]. Ion intensities were used to estimate the composition of monomer (m/z 100–300) to oligomer (m/z 301–2000) compounds (Table 6). The ranges were selected to represent low and high molar masses [8]. In thermal pyrolysis, the monomer to oligomer ratio increased by 21% in BMP and 26% in CMP. In catalytic pyrolysis, the ratio increased by 32% in BMP and 41% in CMP. The larger increase in the ratio during catalytic pyrolysis was the result of the formation of substantially more short-chain alkanes and aromatic compounds.

## 2.6.2. Analysis of Wax and Liquid Products by GC-MS

The wax and liquid products of thermal and catalytic pyrolysis were analyzed by GC-MS. The wax product of thermal pyrolysis of BMP and CMP was brown in color. The wax samples contained a variety of long-chain alkanes, alkenes, and dienes as well as oxygenated chemicals. Alkanes and olefins with different chain lengths ( $C_7$ – $C_{44}$ ) and a negligible number of aromatic hydrocarbons (0.26 to 0.36% in BPM and 0.41 to 1% in CMP) were produced during thermal pyrolysis (Supplementary Material Figure S4 and Table S2). These results corroborated previous waste plastic thermal pyrolysis findings [72]. A significant number of oxygenated compounds were observed in the wax product (9 to 16% in BPM and 16 to 22% in CMP). In addition, long-chain alkanes and alkenes ( $C_{17}$ – $C_{38}$ )

were the most abundant substances in the condenser, and short-chain alkenes were the most abundant substances in the impinger ( $C_7$ – $C_{10}$ ) (Supplementary Material Figure S5 and Table S3). The results suggested that the conversion was incomplete during thermal pyrolysis. The compounds from BMP and CMP pyrolysis were only partially cracked and their average chain lengths decreased with temperature [67]. The presence of oxygenated compounds and the lack of aromatics were discouraging factors as they significantly lowered the quality of the liquid product.

The catalytic pyrolysis product was a yellow, transparent liquid. The catalytic pyrolysis products displayed a chemical composition profile (Figures 6 and 7) that resembled that of gasoline (Supplementary Material Table S4) [73,74]. The samples contained a mixture of aromatics  $(C_6-C_{23})$  and short-chain alkanes (straight-chain and isomerized) commonly found in gasoline, such as toluene p-xylene, o-xylene, mesitylene, benzene, ethylbenzene, naphthalene, 1-methyl-, 1,2,4-trimethyl benzene, and 1-ethyl-2-methyl-benzene. The alkane, olefin, and aromatic compositions were higher than those observed in gasoline. The chemical profiles of the catalytic pyrolysis liquid products produced at 550 °C for BMP and CMP were closest to that of gasoline (Table 7). As anticipated, the products collected at the impinger were shorter chain compounds (Figure 7 and Supplementary Material Table S5) than those collected from the condenser (Figure 6 and Supplementary Material Table S6). Toluene, 2-methyl- pentane, and p-xylene were the most abundant compounds [60]. The existence of aromatic compounds and the absence of oxygenated compounds represented a major improvement over thermal pyrolysis products [66]. The aromatic chemical profile of the catalytic pyrolysis products in this study closely matched the one reported by Bagri et al. for catalytic pyrolysis of polyethylene [75]. In comparison with thermal pyrolysis, catalytic pyrolysis resulted in significant changes to the carbon number range in products. However, the range of aromatic carbon numbers in the products of catalytic pyrolysis was considerably wider (Supplementary Material Table S7). This result suggested that aromatic carbon mass increased and alkane and olefin carbon mass decreased (Supplementary Material Tables S5 and S6). There were several common steps in aromatization reaction pathways. In mixed feedstock such as BMP and CMP, cellulose must first be cracked and deoxygenated to create small olefins such as C2-C5. The small olefins were oligomerized to create  $C_6-C_{10}$  olefins, which proceeded through hydrogen transfer processes to create dienes, and then cyclization and aromatization reactions to create aromatics [11].

**Table 7.** Yields (g/100g) of branched alkanes, straight alkanes, alkanes, diene, aromatics, and oxygenated compounds in the pyrolysis (thermal and catalytic) products at 500, 550 and 600 °C from BMP and CMP. The proportions are also shown for gasoline as a basis of comparison.

Pyrolysis	Sample	Alkanes	(g/100 g)	Olefins	(g/100 g)	Aromatics	Oxygenated
ryrorysis	Name	Branched	Straight	Alkene	Diene	(g/100 g)	(g/100 g)
nal	BMP500	3.02	27.56	50.32	8.89	0.26	9.96
lern	BMP 550	3.32	19.89	55.49	9.66	0.46	11.19
Th	BMP 600	2.81	18.15	51.37	10.76	0.36	16.54
tic	BMP 500	3.79	4.21	1.6	1.58	88.82	0
taly	BMP 550	12.84	6.16	1.28	1.17	78.54	0
Cat	BMP 600 12.63 37.99		14.86	14.86 1.01		0	
Gase	oline	46.9	0.5	4.0	00	48.6	
nal	CMP500	4.06	20.73	49.11	9.07	1.02	16.01
ern	CMP 550	5.26	21.26	49.66	10.11	0.41	13.29
Th	CMP 600	4.17	15.83	43.65	13.54	0.41	22.40
tic	CMP 500	11.98	3.19	8.02	3.08	73.73	0
taly	CMP 550	7.68	17.01	19.28	2.34	53.70	0
Cai	CMP 600	5.89	40.59	8.04	0.58	44.89	0



**Figure 6.** GC-MS chromatograms of U-tube condenser liquid products of catalytic pyrolysis of BMP (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C and CMP (**d**) 500 °C, (**e**) 550 °C, (**f**) 600 °C.



**Figure 7.** GC-MS chromatograms of impinger trapped products from the catalytic pyrolysis of BMP at (**a**) 500 °C, (**b**) 550 °C, and (**c**) 600 °C and CMP at (**d**) 500 °C, (**e**) 550 °C, and (**f**) 600 °C.

Previous studies showed that the amount of aromatic chemicals increased when zeolite Y was added to the process. Furthermore, the 3D structure of zeolite Y was essential for

the transformation of wax into light hydrocarbons [25]. Zheng et al. reported that the highest yield of aromatic hydrocarbons in catalytic pyrolysis was for LDPE and PP, both of which were present in BMP and CMP [11]. Long-chain hydrocarbons produced by thermal pyrolysis can be transformed into lighter-branched (isomerized) hydrocarbons and aromatics, like those found in gasoline and this study, when using zeolite Y in the catalytic pyrolysis process [76,77]. A list of all identified substances and their abundance concentration is given in the Supplementary Material Tables S2–S6.

## 2.6.3. Gas Analysis by GC-MS

Catalytic pyrolysis led to more efficient breakdowns than thermal pyrolysis of AMW, which subsequently resulted in more gaseous compounds. Zeolite Y facilitated the secondary breakdown of the condensable vapors [54]. The gaseous products from thermal and catalytic pyrolysis were collected and directly analyzed. Thermal pyrolysis products consisted of alkanes, and alkenes ( $C_1$  to  $C_6$ ) such as methane, ethyl-cyclopropane, 1-hexene, 1-pentene, and 2-butene in both BMP and CMP. Oxygenated compounds including dimethyl-cyclopropane, acetaldehyde,  $CO_2$ , and CO were also identified in both samples. In general, CMP showed a greater number of identified gaseous products likely because of the lower L:P ratio (Supplementary Material Table S8). Products of catalytic pyrolysis included alkanes, alkenes, and aromatics ( $C_1$  to  $C_7$ ) [78]. CO<sub>2</sub> and CO were the only oxygenated compounds identified in catalytic pyrolysis gaseous products (Table 8). The most abundant compound was CO in all pyrolysis experiments which has been previously observed and reported by Paradela et al. [7].

**Table 8.** Identified gas products of catalytic pyrolysis of BMP and CMP at 500,550 and 600 °C. The units are percent compound of total collected gas.

			RT	BMP 500	BMP 550	BMP 600	CMP 500	CMP 550	CMP 600
Compound Name	Formula	M+ -	Min	%	%	%	%	%	%
Carbon monoxide	CO	28	1.13	72.9	76.1	32.9	89.5	56.3	3.98
Methane	$CH_4$	16	1.2	-	12.7	8.36	-	13.2	0.75
Carbon dioxide	CO <sub>2</sub>	44	1.48	-	-	15.72	-	1.65	3.99
Ethylene	$C_2H_4$	28	2.02	6.48	1.33	15.29	4.41	3.92	5.99
Ethane	$C_2H_6$	30	2.55	2.20	1.06	6.42	0.64	3.05	5.80
Propene	$C_3H_6$	42	8.77	1.00	2.20	8.52	0.53	2.69	15.7
Propane	$C_3H_8$	44	9.57	2.40	1.72	2.03	0.65	3.18	15.1
Isobutane	$C_{4}H_{10}$	58	16.24	3.11	1.99	1.39	0.84	5.67	17.8
2-methyl-1-propene	$C_4H_8$	56	17.15	0.12	0.44	1.03	-	-	4.90
2-Butene	$C_4H_8$	17.59	56	0.14	0.27	1.14	-	2.23	0.29
Butane	$C_{4}H_{10}$	58	18	0.97	0.36	1.24	-	1.42	4.89
1-Butene	$C_4H_8$	56	18.27	0.11	0.36	0.59	0.37	0.99	2.05
(Z)-2-Butene	$C_4H_8$	56	18.55	0.26	0.35	0.29	-	-	1.13
3-methyl-1-Butene	$C_{5}H_{10}$	70	22.89	-	-	0.32	-	-	0.11
2-methyl-Butane	C <sub>5</sub> H <sub>12</sub>	72	23.61	-	-	-	0.38	3.77	7.28
ethyl-Cyclopropane	$C_{5}H_{10}$	70	24.16	-	-	0.63	-	-	1.16
Isoprene	$C_5H_8$	68	24.57	-	-	0.45	-	-	0.07
1-Pentene	$C_{5}H_{10}$	70	24.76	-		0.23	0.37	1.99	3.97
1,4-Pentadiene	$C_5H_8$	68	25.77	0.96	-	0.26	-	1.02	-
2-methyl-Pentane	$C_{6}H_{14}$	86	29.61	2.56	-	-	0.41	-	0.88
2-methyl-2-Butene,	$C_{5}H_{10}$	70	29.74	5.25	0.74	0.63	-	-	0.06
2,3-dimethyl-pentane	C7H16	100	30.02	-	-	-	-	-	0.56
1-Hexane	$C_6H_{14}$	86	31.07	0.36	-	-	-	-	0.25
2-ethyl-1,3-Butadiene	$C_{6}H_{10}$	82	31.22	0.11	-	-	0.22	-	-
Benzene	$C_6H_6$	78	31.25	0.25	0.46	1.32	0.55	-	2.28
Toluene	C7H8	92	32.23	0.73	-	1.15	1.11	-	-

#### 2.6.4. FTIR

The AMW components and extruded materials before pyrolysis and the thermal and catalytic pyrolysis products of BMP and CMP samples were analyzed using FTIR spectroscopy to obtain their chemical functional groups (Figures 8 and 9). Using the literature as a guide, Table 9 (wax, liquid), and Supplementary Material Table S9 (char) provide band assignments for all samples.



**Figure 8.** FTIR spectra of wax products of thermal pyrolysis of BMP at (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C and CMP at (**d**) 500 °C, (**e**) 550 °C, and (**f**) 600 °C.



**Figure 9.** FTIR spectra of liquid products of catalytic pyrolysis of BMP at (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C; CMP at (**d**) 500 °C, (**e**) 550 °C, (**f**) 600 °C; and (**g**) gasoline.

	The	rma Pyrolysis l	вмр	Cata	lytic Pyrolysis	ВМР	The	mal Pyrolysis	СМР	Cata	ytic Pyrolysis	СМР
		Wax			Liquid			Wax		Liquid		
Bond/ Functional Group	500 ° C	550 °C	600 ° C	500 ° C	550 ° C	600 ° C	500 ° C	550 ° C	600 ° C	500 ° C	550 ° C	600 ° C
	Wavenumber (cm <sup>-1</sup> )											
Out-of-plane Bend O-H	-	-	-	-	618	620	-	-	-	-	-	-
Out-of-plane Ring C=C bending	-	-	-	692	692	691	-	-	-	691	691	692
=C-H Bend (Alkene)	719	719	719	-	-	-	719	719	719	-	-	-
Aliphatic CH <sub>2</sub> Rocking	730	730	730	728	729	730	730	730	730	728	728	728
=C-H Bend (Alkene)	-	-	-	742	742	742	-	-	-	742	742	742
C-H "oop" aromatics	-	-	-	770	770	770	-	-	-	768	768	768
Aromatic C–H out of plane bending	-	-	-	784	784	784	-	-	-	784	784	784
=C-H Bending Alkene	-	-	-	795	-	-	-	-	-	795	795	795
Aromatic C–H out of plane bending	-	-	-	809	811	811	-	-	-	807	807	807
Aromatic C–H out of plane bending	-	-	-	835	835	835	-	-	-	835	835	835
Aromatic C–H out of plane bending	-	-	-	-	848	847	-	-	-	847	847	847
C-H "oop" aromatics	886	887	887	875	875	874	887	887	887	874	877	877
O-H bend carboxylic acids	908	908	908	-	-	-	908	908	908	-	-	-
CH <sub>2</sub> wagging or twisting	970	974	974	-	960	-	974	974	974	-	-	966
=C-H bend alkenes	993	993	993	-	-	-	993	993	993	-	-	-
aromatic C-H in-plane deformation	1047	1047	1047	1034	1037	-	1047	1047	1047	1037	1038	1038
C-C-H bending		-	-	1120	1124	-		-	-	1120	1120	1120
C-H wag (-CH2X) alkyl halides	-	1166	1166		1157		1166	1166	1166	1157	1157	1157
C-H in-plane bending	-	-	-	-	1267		-	-	-	1271	1271	1271
CH- Symmetric bending	1376	1376	1376	1378	1378	1378	1376	1376	1376	1377	1377	1377
C-H in-plane wagging	1461	1462	1462	1455	1455	1455	1462	1462	1462	1456	1456	1456
Aromatic skeletal vibration (C=C)	1401	1402	1402	1455	1405	1405	1402	1402	1472	1405	1400	1405
C C stratch (in ring) aromatics (Phonyl compounds)	1516	14/2	1472	1508	1495	1495	1472	1472	1472	1495	1495	1495
C-C sueler (in-ring) atomatics/ Thenyi compounds	1510	-	-	1508	1508	1500	-	-	-	1500	1500	1500
C-C (aromatic) ring stretch, sp <sup>2</sup> CH <sub>2</sub> (olefinic)	-	-	-	1607	1605	1606	-	-	-	1607	1607	1607
Conjugation												
-C=C- stretch alkene	1641	1641	1641	-		-	1641	1641	1641	-	-	-
H–C=O: C–H stretch aldehydes	-	-	-	2730	2730	2730	-	-	-	2730	2730	2730
C–H symmetrical stretching from CH <sub>2</sub> from	2848	2847	2847	-	-	-	2847	2847	2847	-	-	-
aliphatic chain												
C–H Stretch Methyl (–CH <sub>3</sub> )	-	-	-	2860	2860	2859	-	-	-	2859	2859	2859
C–H asymmetrical stretching from CH <sub>2</sub> from	2915	2915	2915	2921	2921	2921	2915	2915	2915	2923	2923	2923
aliphatic chain	2/15	2015	2015	2721	2721	2/21	2015	2015	2010	2725	2725	2725
C–H asymmetrical stretching from CH <sub>3</sub> from	2957	2960	2960	2961	2964	2962	2960	2960	2960	2957	2957	2957
aliphatic chain	2757	2,000	2,00	2,01	2704	2702	2700	2700	2,00	2)31	2)31	2757
$sp^2$ CH <sub>2</sub> olefinic (nonterminal = CHC)	-	-	-	3017	3018	3016	-	-	-	3016	3016	3019
O-H stretching Cellulose, Hemicellulose, Lignin	3077	3076	3076	-	3050	3049	3080	3076	3076	-	-	-
O-H stretching vibration, H-bonded, (alcohols,	2407				2411	2407						
phenols)	3407	-	-	-	5411	3407	-	-	-	-	-	-
• ·												

**Table 9.** FTIR spectra band assignments for products of thermal and catalytic pyrolysis in BMP 500 °C, 550 °C, 600 °C, and CMP 500 °C, 550 °C, 600 °C.

## 2.6.5. FTIR of AMW and Extruded Materials

NW and twine (T1 and T2) spectra resembled those of PE and PP (Supplementary Material Table S10 and Figure S6). At 2949–2850 cm<sup>-1</sup>, a high, sharp absorption band was observed that corresponds to C–H stretching vibrations and distinguishes saturated hydrocarbon bonds. The presence of alkenes was indicated by the significant absorption peaks at 1650 cm<sup>-1</sup>, and 1000–717 cm<sup>-1</sup> as those regions represent =C–H stretching vibration, –C=C– stretching vibration, and –C=C– bending vibration, respectively. Due to the scissoring vibration of CH<sub>2</sub>, the absorption bands at 1460 cm<sup>-1</sup> indicated the presence of the methylene group [79]. Band assignments at 1370, 1730, and 2914 cm<sup>-1</sup> represented all three lignocellulosic components including cellulose, hemicellulose, and lignin [80].

## 2.6.6. FTIR of Wax and Liquid Products

FTIR spectra of thermal pyrolysis products (Figure 8) resembled that of paraffin [66]. The O-H stretching vibrations (3600–3200 cm<sup>-1</sup>) appeared to have been eliminated by thermal pyrolysis in all samples [81]. FTIR spectra bands around 2915 cm<sup>-1</sup> and 2847 cm<sup>-1</sup> showed that aliphatic functional groups exhibited both symmetric and asymmetric C–H stretching.

FTIR spectra of the liquid products from catalytic pyrolysis of BMP and CMP showed a high degree of similarity with that of gasoline (Figure 9). The liquid products had bands at 2960 cm<sup>-1</sup> and 2925 cm<sup>-1</sup> associated with the asymmetric stretching of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>), respectively. The bands between 720 and 840 cm<sup>-1</sup> that could be attributed to the aromatic C–H out-of-plane bending [82]. For all bands between 1375 and 1610 cm<sup>-1</sup>, the liquid products showed lower intensities. C–H deformation bands were observed at 1465 cm<sup>-1</sup>. The bands at about 1608 cm<sup>-1</sup> were associated with aromatic C–C stretching vibrations, and the band around 1375 cm<sup>-1</sup> was attributed to CH<sub>3</sub> symmetrical deformations. The coupled vibrations of the methyl and methylene groups' symmetric stretching were responsible for the vibrational band between 2875 and 2850 cm<sup>-1</sup>. In comparison to the one found in gasoline, these bands were present in all liquid products, but they were stronger and had a smaller shoulder (for methylene stretches) [82–84].

#### 2.6.7. Gas Analysis by FTIR

The gaseous products from thermal and catalytic pyrolysis of BMP and CMP were analyzed by FTIR spectroscopy (Supplementary Material Figures S7 and S8). Natural gas (consisting of methane, ethane, propane, butane, pentane, and hexane), CO, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> were analyzed separately as reference standards. Gaseous products from thermal and catalytic pyrolysis for BMP and CMP showed the presence of natural gas (methane), CO, and CO<sub>2</sub> fingerprints which aligned with the GC-MS results.

## 2.6.8. FTIR of Solid Products

The solid product (char) from the pyrolysis of AMW was analyzed by FTIR spectroscopy (Supplementary Material Figure S9). FTIR band and functional groups are given in Supplementary Material Table S9. The FTIR spectra of thermal and catalytic pyrolysis char samples only showed bands associated with lignocellulosic materials, suggesting that the plastic position in both BMP and CMP had fully degraded. In lignocellulosic biomass, cellulose, hemicellulose, and lignin were the three primary components [80]. Absorptions due to C–H stretching occurred at 2914 cm<sup>-1</sup> and were likely associated with cellulose, hemicellulose, and lignin. Additionally, the band at 1417cm<sup>-1</sup> was found to be attributed to symmetric CH<sub>2</sub> bending vibration in cellulose, carboxyl vibration in glucuronic acid with xylan, and C-H in-plane deformation with aromatic ring stretching in lignin. The aromatic ring stretching and vibration (C=C-C) in lignin was associated with the absorption band at 1584 cm<sup>-1</sup> [85]. The C–O–C stretching at the  $\beta$ -(1 $\rightarrow$ 4)-glycosidic links in cellulose and hemicellulose causes the bands at 873 cm<sup>-1</sup> [80]. The bands between 645 and 798 cm<sup>-1</sup> were aromatic C-H stretching vibrations and =C-H bending (alkene) indicating that the biochar included hydrocarbons. Biochar can be added to agricultural soil to enhance soil quality through adding aggregates and solids, expanding microbiome populations, minimizing fungal populations, and reducing the requirement for fertilizer. Crop yields and soil quality can be improved by biochar; however, certain drawbacks need to be considered [86].

## 3. Materials and Methods

# 3.1. Materials

Agricultural mixed waste (AMW) was collected from farms in northern Idaho. The AMW contains NW, twine (composed of low-density polyethylene, and PP), mixed with lignocellulosic residues such as wheat chaff and bluegrass straw (Figure 10). Zeolite Y (Alfa Aesar (45870), hydrogen, powder form, surface area: 780 m<sup>2</sup>/g, SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>: 30:1) was used as received. Regular gasoline (Conoco gas station in Moscow, ID, USA) was used as standard.

#### 3.2. Density

A Quantachrome Ultra-Pycnometer 1000 was used to measure the density of all AMW components. Using each component density in Equations (1) and (2), the L:P ratio was determined.

$$Y = \frac{dF - d1}{d2 - d1} \tag{1}$$

$$X = 1 - Y \tag{2}$$

where, *dF* was the density of mixture (CMP or BMP), *d*1 was the density of mixed plastic, *d*2 was the density of lignocellulosic portion (chaff or bluegrass straw), *Y* was the percent of the lignocellulosic material in AMW batch, and *X* was the percentage of the plastic mixture in AMW batch.



**Figure 10.** Photographs showing (**a**) Chaff Mixed Plastic (CMP), (**b**) Bluegrass Mixed Plastic (BMP) as received.

## 3.3. Compounding

The AMW was manually fed and compounded into an extruded rod (9 mm OD) using a co-rotating twin-screw extruder (Leistritz 18 mm dia, L/D ratio of 40, 200 rpm, barrel temperature 160 °C, 4.7 kW motor, and base torque of 18%). The extruded rod was milled using a plastic granulator with a screen size of 6 mm (Sterling BP608, New Berlin, WI, USA), and the granules were re-extruded again using a K-Tron weight loss feeder operating at  $0.5 \text{ kg} \cdot \text{h}^{-1}$  to create a homogeneous material for subsequent pyrolysis experiments.

## 3.4. Calorific Value, Fixed Carbon, Volatile Matter (VM) on Raw and Extruded AMW

Calorific value was determined following the ASTM D5865-04 using a Parr oxygen bomb calorimeter (model number 1261) on 1 g of extruded sample (in duplicate). Ash content, fixed carbon (FC), and volatile matter (VM) were all measured in duplicate using proximate analysis following ASTM E870-82. Samples for FC and VM were burned at 950 °C for 7 min in a muffle furnace. Ash content was determined at 600 °C for at least 16 h. The elements C, N, and H were measured using an elemental analyzer (Costech, the ESC 4010).

# 3.5. Moisture Content Measurement and Wax Extraction

A Mettler Toledo moisture analyzer was used to obtain the moisture content of the separated chaff and BG samples. The lignocellulosic samples (4.0 g) were Soxhlet extracted in duplicate using  $CH_2Cl_2$  (150 mL) for 16 h, and extractives were determined gravimetrically, according to ASTM D1108-96.

# 3.6. Carbohydrate, Lignin, and FAME Analysis on Lignocellulosic Residue

Fatty acid methyl ester (FAME) derivatives were used to determine lipids content on chaff and BG CH<sub>2</sub>Cl<sub>2</sub> extracts. The samples (2 mg) were heated for 90 min at 90 °C in a sealed 5 mL reacti-vialTM containing CH<sub>3</sub>OH, H<sub>2</sub>SO<sub>4</sub>, and CHCl<sub>3</sub> (1.7:0.3:2.0 v/v/v, 2 mL) to create their FAME derivatives. 1-Naphthaleneacetic acid was added as an internal standard (200 g·mL<sup>-1</sup> in CHCl<sub>3</sub>). Gas chromatography-mass spectrometry (GC-MS) was used to analyze the FAME derivatives using an ISQ-Trace1300 (ThermoScientific) system with a ZB-5 (30 m × 0.25 mm, Phenomenex) capillary column under a temperature gradient of 40 °C (1 min) to 320 °C at 5 °C·min<sup>-1</sup>. Genuine C<sub>12</sub> to C<sub>20</sub> fatty acid standards and spectrum matching with the NIST mass spectral library from 2017 were used to identify the eluted chemicals.

The extractive-free chaff and BG samples were analyzed for carbohydrate and lignin contents. Klason and acid-soluble lignin content were measured by digesting extractive-free

biomass (200 mg) in sulphuric acid (2 mL, 72%) for 60 min at 30 °C, followed by secondary hydrolysis (4% H<sub>2</sub>SO<sub>4</sub>, 30 min, 121 °C) in an autoclave in accordance with ASTM D 1106-96. The Klason lignin concentration was determined gravimetrically, and the acid-soluble lignin was determined by measuring the absorbance at 205 nm of the filtered hydrolysate with an absorption coefficient of 110  $L\cdot g^{-1}\cdot cm^{-1}$  (Genesys 50, Thermoelectron).

According to ASTM E 1758-01, neutral carbohydrate analysis was carried out on the secondary hydrolysis filtrate (5 mL). The monosaccharides were measured using differential refractive index detection (Waters model 2414) with HPLC (two Rezex RPM columns, 7.8 mm  $\times$  300 mm, Phenomenex) at 85 °C on elution with water (0.5 mL·min<sup>-1</sup>) [22].

## 3.7. Thermal Analysis

# 3.7.1. TGA

The thermal stability and impact of catalyst addition on the thermal breakdown of AMW samples TGA was performed using a Perkin–Elmer TGA-7 instrument (Shelton, CT, USA). The AMW and mixture of AMW and zeolite Y catalyst (1:1) were used in the experiments. 8 mg of the material was heated under nitrogen ( $30 \text{ mL} \cdot \text{min}^{-1}$ ) from  $30 \degree \text{C}$  to  $900 \degree \text{C}$  at  $10 \degree \text{C} \cdot \text{min}^{-1}$ .

## 3.7.2. Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)

Using Perkin–Elmer DSC-7 instruments, triplicate analyses of the AMW samples (6–8 mg) were performed from 40 to 200 °C at 10 °C·min<sup>-1</sup> under N<sub>2</sub> (20 mL·min<sup>-1</sup>). The Pyris v.13.3.1 software was used to evaluate the DSC data. The following equation (Equation (3)) is used to determine the percentage of crystallinity in the plastics:

$$X_c = \frac{\Delta H_m}{\Delta H_0} \times 100\% \tag{3}$$

 $X_c$  is the percent crystallinity of the wax,  $\Delta H_m$  is the melting enthalpy or enthalpy of fusion calculated from the area under the peak, and  $\Delta H_0$  is the theoretical enthalpy of fusion for low-density polyethylene (293 J·g<sup>-1</sup>) and polypropylene (207 J·g<sup>-1</sup>).

The exothermic and endothermic reactions of the MP, BMP, and CMP samples with temperature were analyzed using a Perkin Elmer DTA-7 instrument from 40 °C to 1000 °C at 20 °C·min<sup>-1</sup> under N<sub>2</sub> (30 mL·min<sup>-1</sup>) [51].

# 3.8. Analytical Py-GCMS

Using a Projector II unit (SGE Analytical Science) connected to a GC-MS (Trace 1300-ISQ, Thermo Scientific, Waltham, MA, USA), analytical pyrolysis was carried out, in duplicate, at 500 °C, and the compounds were separated on a ZB-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \text{ } \emptyset$ ,  $0.25 \text{ } \mu\text{m}$  coating, Phenomenex) from 50 °C (1 min) to 250 °C (10 min) at 5 °C·min<sup>-1</sup>. By comparing mass spectra, utilizing NIST 2017 library matching, and comparing the compounds to standards, the compounds were identified. Each compound's relative abundance was determined relative to the CO<sub>2</sub> peak.

#### 3.9. Thermal and Catalytic Pyrolysis

Samples were thermally pyrolyzed at three temperatures (500, 550, and 600 °C) in a quartz tube reactor (20 mm ID × 300 mm) under N<sub>2</sub> (100 mL·min<sup>-1</sup>) using a mass flow controller (Dakota instruments). For catalytic pyrolysis experiments, a 60 mL·min<sup>-1</sup> N<sub>2</sub> flowrate was used. The reactor setup is shown in Figure 11. All reactor components were weighed before and after each experiment to be able to determine a mass balance and yield. Samples (1.0 g) were secured between glass wool plugs inside a carrier glass tube (16 mm dia × 125 mm) and placed in the furnace heated zone. For catalytic pyrolysis, the sample (0.5 g) was placed in a carrier tube and held in place with glass wool and sandwiched between a mixture of Zeolite Y and sand (1:1, 1.0 g on each side), and secured with class wool plugs. The pyrolysis products were condensed using a U-tube condenser immersed in liquid nitrogen followed by an impinger (10 mL of CH<sub>2</sub>Cl<sub>2</sub> containing 1,2,4-

trichlorobenzene as internal standard) to capture lighter-weight hydrocarbons. In separate experiments, the gaseous products were collected in a Tedlar gas sampling bag (500 mL, SASSCO) after the condenser.



Figure 11. Schematic of the tubular batch reactor.

## 3.10. GC-MS

The products from thermal pyrolysis and catalytic pyrolysis were analyzed in duplicates by GC-MS (Trace 1300-ISQ, Thermo Scientific, Waltham, MA, USA). The wax oil and liquid samples (1.0 mg) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) containing 1,2,4-trichlorobenzene as an internal standard. Separation was achieved using a temperature program of 40 °C (1 min) to 320 °C at 5°C·min<sup>-1</sup> on a ZB-5 capillary column (30 m × 0.25 mm Ø, 0.25 µm coating, Phenomenex). The gas products were injected directly into the GC-MS using a 100 µL syringe and separation was achieved using a TG-BondQ packed column (30 m × 0.32 mm Ø, 10 µm thickness, Thermo Scientific, Waltham, MA, USA) with a temperature program of 35 °C (5 min) to 150 °C (10 min) at 5°C·min<sup>-1</sup>.

# 3.11. ESI-MS

The molar mass of wax and liquid products from the thermal and catalytic pyrolysis experiments was determined by negative ion ESI-MS (m/z 100–2000) on a Finnigan LCQ-Deca instrument (Thermo-Quest). Samples (2 mg mL<sup>-1</sup>) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/methanol/acetic acid (50:49:1) and injected into the ESI-MS at 10 µL min<sup>-1</sup>. The capillary voltage and ion source are 50 V at 275 °C and 4.5 kV, respectively. The numberaverage molar mass (M<sub>n</sub>) and weight-average molar mass (M<sub>w</sub>) were determined using Equations (4) and (5), respectively, where M<sub>i</sub> was mass after accounting for the charge and N<sub>i</sub> was the ion intensity.

$$M_n = \sum N_i M_i / \sum N_i \tag{4}$$

$$M_w = \sum N_i M_i^2 / \sum N_i M_i \tag{5}$$

## 3.12. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of solid samples were obtained using a Thermo-Nicolet iS5 spectrometer with a ZnSe attenuated total reflection (iD5-iTR) accessory. For the dark char samples, a Ge iD5-iTR accessory was employed. Gas was collected and analyzed on a Thermo-Nicolet iS10 FTIR spectrometer equipped with a gas cell (KBr 32 mm windows and 100 mm path length). Omnic v9 software is used to correct the baseline and average the FTIR spectra (Thermo-Nicolet).

## 4. Conclusions

Agricultural mixed waste (AMW) comprising of plastic (netting and twine) and lignocellulosic fiber (wheat chaff and bluegrass) was successfully characterized to determine its composition. The AMW was compounded by extrusion to produce a homogeneous feedstock and then pyrolyzed into wax (paraffins and olefins), liquid oil (oxygenated compounds), gas and char products. The highest wax/oil yields were achieved at 600 °C. The wax products contained oxygenated compounds but could potentially be used as bunker fuel in marine vessels. The gaseous products could be used as a petrochemical feedstock. Catalytic pyrolysis of the AMW using Zeolite Y (catalyst) was successfully applied to produce aromatic compounds in about a 45% yield at 600 °C. The profile of the aromatic components was similar to gasoline, making the liquid product suitable for use as a "drop-in" fuel. The recovered catalyst proved to be as effective as the new catalyst, which could help with the economics of the industrial implementation of the process.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/catal12111381/s1, Figure S1. Py-GC-MS chromatograms at 500 °C of (a) bluegrass (BG), (b) chaff, (c) net wrap (NW), (d) twine 1 (T1), and (e) twine 2 (T2). Figure S2. Py-GC-MS chromatograms at 500 °C of (a) bluegrass-mixed plastic (BMP) and (b) chaff-mixed plastic (CMP). Table S1. Py-GC-MS products identified from chaff, bluegrass (BG), net wrap (NW), twine 1 (T1), twine 2 (T2), chaff mixed plastic (CMP), bluegrass mixed plastic (BMP) at 500 °C. Figure S3. Positive-ion ESI-MS spectra of the products of liquid products of catalytic pyrolysis of bluegrassmixed plastic (BMP) at (a) 500 °C, (b) 550 °C, and (c) 600 °C and chaff-mixed plastic (CMP) at (d) 500 °C, (e) 550 °C, and (f) 600 °C. Figure S4. GC-MS chromatograms of liquid products collected in U-tube condenser from thermal pyrolysis of BMP at (a) 500 °C, (b) 550 °C, and (c), 600 °C and CMP at (d) 500 °C, (e) 550 °C, and (f) 600 °C. Table S2. Identified compounds in the liquid products of thermal pyrolysis of BMP and CMP at 500, 550, and 600 °C collected from the condenser. The units are mg compound per g resultant liquid product. Figure S5. GC-MS chromatograms of impinger trap products of thermal pyrolysis of BMP at (a) 500  $^{\circ}$ C, (b) 550  $^{\circ}$ C, (c) 600  $^{\circ}$ C and CMP at (d) 500  $^{\circ}$ C, (e) 550 °C, and (f) 600 °C. Table S3. Identified compounds collected in an impinger of thermal pyrolysis of BMP and CMP at 500, 550, and 600 °C. The units are mg compound / g resultant product. Table S4. Identified compounds in gasoline used as a standard. The units are mg compound per g resultant liquid product. Table S5. Identified compounds in products of catalytic pyrolysis of BMP and CMP at 500,550, and 600 °C collected from the impinger. The units are mg compound per g resultant product. Table S6. Identified compounds in liquid products of catalytic pyrolysis of BMP and CMP at 500, 550, and 600  $^{\circ}$ C, collected from the condenser. The units are mg compound / g liquid product. Table S7. Carbon number partitioning of alkanes, olefins, aromatics, and oxygenated compounds in the thermal and catalytic pyrolysis products of BMP and CMP. Units are the number of carbons. Table S8. Identified gas products of thermal pyrolysis of BMP and CMP at 500, 550, and 600 °C. The units are percent compound of total collected gas. Table S9. FTIR band and functional group table of thermal and catalytic pyrolysis of BMP and CMP chars at 500, 550, and 600 °C. Table S10. FTIR band and functional group table of bluegrass (BG), net wrap (NW), twine 1 (T1), twine 2 (T2), mixed plastic (MP), chaff mixed plastic (CMP), bluegrass mixed plastic (BMP). Figure S6. FTIR spectra of (a) bluegrass (BG), (b) chaff, (c) net wrap (NW), (d) twine 1 (T1), (e) twine 2 (T2), (f) mixed plastic (MP), (g) chaff mixed plastic (CMP), and (h) bluegrass mixed plastic (BMP). Figure S7. FTIR spectra of gas produced from the thermal pyrolysis of BMP at (a) 500 °C, (b) 550 °C, (c) 600 °C, and CMP at (d) 500 °C, (e) 550 °C, and (f) 600 °C. Figure S8. Gas FTIR spectra of catalytic pyrolysis of BMP at (a) 500 °C, (b) 550 °C, (c) 600 °C, and CMP at (d) 500 °C, (e) 550 °C, (f) 600 °C. Figure S9. FTIR spectra of char from thermal pyrolysis of: BMP at (a) 500 °C, (b) 550 °C, (c) 600 °C; catalytic pyrolysis of BMP at (d) 500 °C, (e) 550 °C, (f) 600 °C; thermal pyrolysis of CMP at (g) 500 °C, (h) 550 °C, (j) 600 °C; and catalytic pyrolysis of CMP at (k) 500 °C, (l) 550 °C, and (m) 600 °C.

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# References

- 1. Ćilerdžić, J.; Stajić, M.; Vukojević, J. Degradation of wheat straw and oak sawdust by Ganoderma applanatum. *Int. Biodeterior. Biodegrad.* **2016**, *114*, 39–44. [CrossRef]
- 2. Hays, M.D.; Fine, P.M.; Geron, C.D.; Kleeman, M.J.; Gullett, B.K. Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions. *Atmos. Environ.* **2005**, *39*, 6747–6764. [CrossRef]
- 3. Koul, B.; Yakoob, M.; Shah, M.P. Agricultural waste management strategies for environmental sustainability. *Environ. Res.* 2022, 206, 112285. [CrossRef]
- Castillo-Díaz, F.J.; Belmonte-Ureña, L.J.; Camacho-Ferre, F.; Tello-Marquina, J.C. The Management of Agriculture Plastic Waste in the Framework of Circular Economy. Case of the Almeria Greenhouse (Spain). *Int. J. Environ. Res. Public. Health* 2021, 18, 12042. [CrossRef]
- Schettini, E.; Scarascia-Mugnozza, G.; Blanco, I.; Convertino, F.; Vox, G. 12-Agricultural plastic waste. In *Handbook of Sustainable Concrete and Industrial Waste Management*; Colangelo, F., Cioffi, R., Farina, I., Eds.; Woodhead Publishing: Sawston, UK, 2022; pp. 255–268. [CrossRef]
- 6. Saha, K.; Maharana, A.; Sikder, J.; Chakraborty, S.; Curcio, S.; Drioli, E. Continuous production of bioethanol from sugarcane bagasse and downstream purification using membrane integrated bioreactor. *Catal. Today* **2017**, *331*, 6877. [CrossRef]
- 7. Paradela, F.; Pinto, F.; Ramos, A.M.; Gulyurtlu, I.; Cabrita, I. Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 392–398. [CrossRef]
- 8. Sotoudehnia, F.; Rabiu, A.B.; Alayat, A.; McDonald, A.G. Characterization of bio-oil and biochar from pyrolysis of waste corrugated cardboard. *J. Anal. Appl. Pyrolysis* 2020, 145, 104722. [CrossRef]
- 9. Rutkowski, P. Characteristics of bio-oil obtained by catalytic pyrolysis of beverage carton packaging waste. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 609–617. [CrossRef]
- 10. Chen, W.; Shi, S.; Zhang, J.; Chen, M.; Zhou, X. Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization. *Energy Convers. Manag.* **2016**, *112*, 41–48. [CrossRef]
- Zheng, Y.; Tao, L.; Yang, X.; Huang, Y.; Liu, C.; Zheng, Z. Study of the thermal behavior, kinetics, and product characterization of biomass and low-density polyethylene co-pyrolysis by thermogravimetric analysis and pyrolysis-GC/MS. *J. Anal. Appl. Pyrolysis* 2018, 133, 185–197. [CrossRef]
- 12. Achilias, D.S.; Roupakias, C.; Megalokonomos, P.; Lappas, A.A.; Antonakou, E.V. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *J. Hazard. Mater.* **2007**, *149*, 536–542. [CrossRef]
- 13. Borsodi, N.; Miskolczi, N.; Angyal, A.; Bartha, L.; Lengyel, A. Hydrocarbons obtained by pyrolysis of contaminated waste plastics. In Proceedings of the 45th International Petroleum Conference, Bratislava, Slovak Republic, 13 June 2011; p. 10.
- Buah, W.K.; Cunliffe, A.M.; Williams, P.T.Ã. Characterization of Products from the Pyrolysis of Municipal Solid Waste. Process. Saf. Environ. Prot. 2007, 85, 450–457. [CrossRef]
- 15. Chen, D.; Yin, L.; Wang, H.; He, P. Pyrolysis technologies for municipal solid waste: A review. *Waste Manag.* 2014, 34, 2466–2486. [CrossRef]
- 16. Murata, K.; Sato, K.; Sakata, Y. Effect of pressure on thermal degradation of polyethylene. J. Anal. Appl. Pyrolysis 2004, 71, 569–589. [CrossRef]
- 17. Velghe, I.; Carleer, R.; Yperman, J.; Schreurs, S. Study of the pyrolysis of municipal solid waste for the production of valuable products. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 366–375. [CrossRef]
- 18. López, A.; de Marco, I.; Caballero, B.; Laresgoiti, M.; Adrados, A. Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chem. Eng. J.* **2011**, *173*, 62–71. [CrossRef]

- 19. Kim, S.-S.; Kim, S. Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor. *Chem. Eng. J.* **2004**, *98*, 53–60. [CrossRef]
- 20. Miskolczi, N.; Angyal, A.; Bartha, L.; Valkai, I. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor. *Fuel Process. Technol.* **2009**, *90*, 1032–1040. [CrossRef]
- 21. Arabiourrutia, M.; Elordi, G.; Lopez, G.; Borsella, E.; Bilbao, J.; Olazar, M. Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. J. Anal. Appl. Pyrolysis 2012, 94, 230–237. [CrossRef]
- 22. López, A.; de Marco, I.; Caballero, B.; Laresgoiti, M.; Adrados, A.; Aranzabal, A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Appl. Catal. B: Environ.* **2011**, 104, 211–219. [CrossRef]
- 23. Lee, K.-H. Thermal and catalytic degradation of pyrolytic oil from pyrolysis of municipal plastic wastes. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 372–379. [CrossRef]
- 24. Hernández, M.D.R.; Gómez, A.; García, N.; Agulló, J.; Marcilla, A. Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE. *Appl. Catal. A Gen.* **2007**, *317*, 183–194. [CrossRef]
- 25. Lee, K.-H. Effects of the types of zeolites on catalytic upgrading of pyrolysis wax oil. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 209–214. [CrossRef]
- Sarker, M.; Rashid, M.M. Waste Plastics Mixture of Polystyrene and Polypropylene into Light Grade Fuel using Fe2O3 Catalyst. Int. J. Renew. Energy Technol. Res. 2013, 2, 13.
- Syamsiro, M.; Saptoadi, H.; Norsujianto, T.; Noviasri, P.; Cheng, S.; Alimuddin, Z.; Yoshikawa, K. Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors. *Energy Procedia* 2014, 47, 180–188. [CrossRef]
- Miandad, R.; Barakat, M.; Aburiazaiza, A.S.; Rehan, M.; Nizami, A. Catalytic pyrolysis of plastic waste: A review. *Process Saf. Environ. Prot.* 2016, 102, 822–838. [CrossRef]
- 29. Sakata, Y.; Uddin, M.; Koizumi, K.; Murata, K. Thermal degradation of polyethylene mixed with poly(vinyl chloride) and poly(ethyleneterephthalate). *Polym. Degrad. Stab.* **1996**, *53*, 111–117. [CrossRef]
- Anuar Sharuddin, S.D.; Abnisa, F.; Wan Daud, W.M.A.; Aroua, M.K. A review on pyrolysis of plastic wastes. *Energy Convers.* Manag. 2016, 115, 308–326. [CrossRef]
- Vogt, E.T.C.; Weckhuysen, B.M. Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* 2015, 44, 7342–7370. [CrossRef]
- 32. Yuan, R.; Shen, Y. Catalytic pyrolysis of biomass-plastic wastes in the presence of MgO and MgCO3 for hydrocarbon-rich oils production. *Bioresour. Technol.* 2019, 293, 122076. [CrossRef]
- 33. Miandad, R.; Barakat, M.; Rehan, M.; Aburiazaiza, A.; Ismail, I.; Nizami, A. Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts. *Waste Manag.* 2017, *69*, 66–78. [CrossRef] [PubMed]
- 34. Lerici, L.C.; Renzini, M.S.; Pierella, L.B. Chemical Catalyzed Recycling of Polymers: Catalytic Conversion of PE, PP and PS into Fuels and Chemicals over H-Y. *Procedia Mater. Sci.* 2015, *8*, 297–303. [CrossRef]
- 35. Bronsted and Lewis Acid Sites | FSC 432: Petroleum Refining. Available online: https://www.e-education.psu.edu/fsc432 /content/bronsted-and-lewis-acid-sites (accessed on 7 August 2020).
- 36. Islam, K.; Khatun, M.S.; Arefin, A.; Islam, M.R.; Hassan, M. Waste to energy: An experimental study of utilizing the agricultural residue, MSW, and e-waste available in Bangladesh for pyrolysis conversion. *Heliyon* **2021**, *7*, e08530. [CrossRef] [PubMed]
- 37. Boateng, A.; Banowetz, G.; Steiner, J.; Barton, T.; Taylor, D.; Hicks, K.; Elnashaar, H.; Sethi, V. Gasification of Kentucky bluegrass (Poa pratensis I.) straw in a farm-scale reactor. *Biomass-Bioenergy* **2007**, *31*, 153–161. [CrossRef]
- Griffith, S.M.; Banowetz, G.M.; Gady, D. Chemical characterization of chars developed from thermochemical treatment of Kentucky bluegrass seed screenings. *Chemosphere* 2013, 92, 1275–1279. [CrossRef] [PubMed]
- Mohammed, I.Y.; Kabir, G.; Abakr, Y.A.; Apasiku, M.A.A.; Kazi, F.K.; Abubakar, L.G. Bioenergy potential of millet chaff via thermogravimetric analysis and combustion process simulation using Aspen Plus. *Clean. Chem. Eng.* 2022, 3, 100046. [CrossRef]
- 40. A Sharuddin, S.D.; Abnisa, F.; Daud, W.M.A.W.; Aroua, M.K. Pyrolysis of plastic waste for liquid fuel production as prospective energy resource. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, 334, 012001. [CrossRef]
- 41. Ebikade, E.O.; Samulewicz, N.; Xuan, S.; Sheehan, J.D.; Wu, C.; Vlachos, D.G. Reductive catalytic fractionation of agricultural residue and energy crop lignin and application of lignin oil in antimicrobials. *Green Chem.* **2020**, *22*, 7435–7447. [CrossRef]
- Kakkad, H.; Khot, M.; Zinjarde, S.; RaviKumar, A. Biodiesel Production by Direct In Situ Transesterification of an Oleaginous Tropical Mangrove Fungus Grown on Untreated Agro-Residues and Evaluation of Its Fuel Properties. *BioEnergy Res.* 2015, *8*, 1788–1799. [CrossRef]
- 43. Wang, Y.; Cui, T.; Niu, K.; Ma, H. Comparison and Characterization of Oxidation Resistance and Carbohydrate Content in Cd-Tolerant and -Sensitive Kentucky Bluegrass under Cd Stress. *Agronomy* **2021**, *11*, 2358. [CrossRef]
- 44. Raveendran, K. Pyrolysis characteristics of biomass and biomass components. Fuel 1996, 75, 987–998. [CrossRef]
- 45. Jin, W.; Singh, K.; Zondlo, J. Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method. *Agriculture* **2013**, *3*, 12–32. [CrossRef]
- 46. Alvarenga, L.M.; Xavier, T.P.; Barrozo, M.A.S.; Bacelos, M.S.; Lira, T.S. Determination of activation energy of pyrolysis of carton packaging wastes and its pure components using thermogravimetry. *Waste Manag.* **2016**, *53*, 68–75. [CrossRef] [PubMed]
- Sanchez-Silva, L.; López-González, D.; Villaseñor, J.; Sánchez, P.; Valverde, J. Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresour. Technol.* 2012, 109, 163–172. [CrossRef]

- 48. Zhou, C.; Yang, W.; Blasiak, W. Characteristics of waste printing paper and cardboard in a reactor pyrolyzed by preheated agents. *Fuel Process. Technol.* **2013**, *116*, 63–71. [CrossRef]
- 49. Wang, S.; Liu, Q.; Luo, Z.; Wen, L.; Cen, K. Mechanism study on cellulose pyrolysis using thermogravimetric analysis coupled with infrared spectroscopy. *Front. Energy Power Eng. China* 2007, *1*, 413–419. [CrossRef]
- 50. Brebu, M.; Vasile, C. Thermal degradation of lignin—A review. Cellul. Chem. Technol. 2010, 44, 353.
- 51. Pelita, E.; Hidayani, T.R.; Akbar, A. Analysis physical properties of composites polymer from cocofiber and polypropylene plastic waste with maleic anhydrate as crosslinking agent. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, 223, 012060. [CrossRef]
- 52. Ghorbel, L.; Rouissi, T.; Brar, S.; López-González, D.; Ramirez, A.; Godbout, S. Value-added performance of processed cardboard and farm breeding compost by pyrolysis. *Waste Manag.* **2015**, *38*, 164–173. [CrossRef]
- 53. Dubdub, I.; Al-Yaari, M. Pyrolysis of Mixed Plastic Waste: I. Kinetic Study. Materials 2020, 13, 4912. [CrossRef]
- Raveh-Amit, H.; Lemont, F.; Bar-Nes, G.; Klein-BenDavid, O.; Banano, N.; Gelfer, S.; Charvin, P.; Bin Rozaini, T.; Sedan, J.; Rousset, F. Catalytic Pyrolysis of High-Density Polyethylene: Decomposition Efficiency and Kinetics. *Catalysts* 2022, 12, 140. [CrossRef]
- 55. Miandad, R.; Rehan, M.; Barakat, M.A.; Aburiazaiza, A.S.; Khan, H.; Ismail, I.M.I.; Dhavamani, J.; Gardy, J.; Hassanpour, A.; Nizami, A.-S. Catalytic Pyrolysis of Plastic Waste: Moving Toward Pyrolysis Based Biorefineries. *Front. Energy Res.* 2019, 7, 27. Available online: https://www.frontiersin.org/articles/10.3389/fenrg.2019.00027 (accessed on 22 September 2022). [CrossRef]
- López, A.; de Marco, I.; Caballero, B.; Laresgoiti, M.; Adrados, A. Pyrolysis of municipal plastic wastes: Influence of raw material composition. *Waste Manag.* 2010, 30, 620–627. [CrossRef]
- 57. Sangpatch, T.; Supakata, N.; Kanokkantapong, V.; Jongsomjit, B. Fuel oil generated from the cogon grass-derived Al–Si (Imperata cylindrica (L.) Beauv) catalysed pyrolysis of waste plastics. *Heliyon* **2019**, *5*, e02324. [CrossRef] [PubMed]
- 58. Li, X.; Shen, B.; Guo, Q.; Gao, J. Effects of large pore zeolite additions in the catalytic pyrolysis catalyst on the light olefins production. *Catal. Today* **2007**, *125*, 270–277. [CrossRef]
- Mastral, J.; Berrueco, C.; Gea, M.; Ceamanos, J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. *Polym. Degrad. Stab.* 2006, *91*, 3330–3338. [CrossRef]
- Eimontas, J.; Striūgas, N.; Abdelnaby, M.; Yousef, S. Catalytic Pyrolysis Kinetic Behavior and TG-FTIR-GC–MS Analysis of Metallized Food Packaging Plastics with Different Concentrations of ZSM-5 Zeolite Catalyst. *Polymers* 2021, 13, 702. [CrossRef]
- Santos, K.; Lobato, F.S.; Lira, T.; Murata, V.; Barrozo, M. Sensitivity analysis applied to independent parallel reaction model for pyrolysis of bagasse. *Chem. Eng. Res. Des.* 2012, 90, 1989–1996. [CrossRef]
- Çanlı, M.; Keskin, I.; Türemiş, M.; Sirin, K.; Katı, M.I. Characterization and determination of thermal and radioluminescence properties of low-density polyethylene (LDPE)-(nanozeolite + Y2O3) composite. *Polym. Polym. Compos.* 2019, 28, 112–118. [CrossRef]
- Satlewal, A.; Soni, R.; Zaidi, M.; Shouche, Y.; Goel, R. Comparative Biodegradation of HDPE and LDPE Using an Indigenously Developed Microbial Consortium. J. Microbiol. Biotechnol. 2008, 18, 477–482.
- 64. Balogun, A.O.; Sotoudehniakarani, F.; McDonald, A.G. Thermo-kinetic, spectroscopic study of brewer's spent grains and characterisation of their pyrolysis products. *J. Anal. Appl. Pyrolysis* **2017**, *127*, 8–16. [CrossRef]
- La Nasa, J.; Biale, G.; Ferriani, B.; Trevisan, R.; Colombini, M.P.; Modugno, F. Plastics in Heritage Science: Analytical Pyrolysis Techniques Applied to Objects of Design. *Molecules* 2020, 25, 1705. [CrossRef] [PubMed]
- 66. Sotoudehnia, F.; Orji, B.; Mengistie, E.; Alayat, A.M.; McDonald, A.G. Catalytic Upgrading of Pyrolysis Wax Oil Obtained from Waxed Corrugated Cardboard Using Zeolite Y Catalyst. *Energy Fuels* **2021**, *35*, 9450–9461. [CrossRef]
- 67. Sotoudehnia, F.; Mengistie, E.; Alayat, A.; McDonald, A.G. Valorization of waste waxed corrugated cardboard via pyrolysis for recovering wax. *Environ. Prog. Sustain. Energy* **2020**, 40, e13566. [CrossRef]
- 68. SLiang, S.; Han, Y.; Wei, L.; McDonald, A.G. Production and characterization of bio-oil and bio-char from pyrolysis of potato peel wastes. *Biomass-Convers. Biorefinery* **2014**, *5*, 237–246. [CrossRef]
- Jarvis, J.M.; McKenna, A.M.; Hilten, R.N.; Das, K.C.; Rodgers, R.P.; Marshall, A.G. Characterization of Pine Pellet and Peanut Hull Pyrolysis Bio-oils by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* 2012, 26, 3810–3815. [CrossRef]
- Liu, Y.; Shi, Q.; Zhang, Y.; He, Y.; Chung, K.H.; Zhao, S.; Xu, C. Characterization of Red Pine Pyrolysis Bio-oil by Gas Chromatography–Mass Spectrometry and Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* 2012, 26, 4532–4539. [CrossRef]
- Miettinen, I.; Mäkinen, M.; Vilppo, T.; Jänis, J. Compositional Characterization of Phase-Separated Pine Wood Slow Pyrolysis Oil by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* 2015, 29, 1758–1765. [CrossRef]
- 72. Anene, A.F.; Fredriksen, S.B.; Sætre, K.A.; Tokheim, L.-A. Experimental Study of Thermal and Catalytic Pyrolysis of Plastic Waste Components. *Sustainability* **2018**, *10*, 3979. [CrossRef]
- 73. Ali, M.F.; Siddiqui, M.N. The Conversion of Waste Plastics/Petroleum Residue Mixtures to Transportation Fuels. In *Feedstock Recycling and Pyrolysis of Waste Plastics*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2006; pp. 363–380. [CrossRef]
- 74. Luo, G.; McDonald, A.G. Conversion of Methanol and Glycerol into Gasoline via ZSM-5 Catalysis. *Energy Fuels* **2013**, *28*, 600–606. [CrossRef]
- 75. Bagri, R.; Williams, P.T. Catalytic pyrolysis of polyethylene. J. Anal. Appl. Pyrolysis 2002, 63, 29-41. [CrossRef]

- 76. Lee, H.W.; Park, Y.-K. Catalytic Pyrolysis of Polyethylene and Polypropylene over Desilicated Beta and Al-MSU-F. *Catalysts* **2018**, *8*, 501. [CrossRef]
- 77. Co-pyrolysis of Mixed Plastics and Cellulose: An Interaction Study by Py-GC×GC/MS | Energy & Fuels. Available online: https://pubs.acs.org/doi/full/10.1021/acs.energyfuels.7b01887 (accessed on 19 September 2022).
- Paradela, F.; Pinto, F.; Gulyurtlu, I.; Cabrita, I.; Lapa, N. Study of the co-pyrolysis of biomass and plastic wastes. *Clean Technol. Environ. Policy* 2009, 11, 115–122. [CrossRef]
- 79. Xu, F.; Wang, B.; Yang, D.; Hao, J.; Qiao, Y.; Tian, Y. Thermal degradation of typical plastics under high heating rate conditions by TG-FTIR: Pyrolysis behaviors and kinetic analysis. *Energy Convers. Manag.* **2018**, *171*, 1106–1115. [CrossRef]
- Zhuang, J.; Li, M.; Pu, Y.; Ragauskas, A.J.; Yoo, C.G. Observation of Potential Contaminants in Processed Biomass Using Fourier Transform Infrared Spectroscopy. *Appl. Sci.* 2020, 10, 4345. [CrossRef]
- Fonts, I.; Azuara, M.; Gea, G.; Murillo, M.B. Study of the pyrolysis liquids obtained from different sewage sludge. J. Anal. Appl. Pyrolysis 2009, 85, 184–191. [CrossRef]
- Al-Ghouti, M.A.; Al-Degs, Y.S.; Amer, M. Determination of motor gasoline adulteration using FTIR spectroscopy and multivariate calibration. *Talanta* 2008, 76, 1105–1112. [CrossRef]
- Calabrò, E.; Magazù, S. FTIR Spectroscopy Analysis of Molecular Vibrations in Gasoline Fuel Under 200 mT Static Magnetic Field Highlighted Structural Changes of Hydrocarbons Chains. *Pet. Sci. Technol.* 2015, 33, 1676–1684. [CrossRef]
- Dadson, J.; Pandam, S.; Asiedu, N. Modeling the characteristics and quantification of adulterants in gasoline using FTIR spectroscopy and chemometric calibrations. *Cogent Chem.* 2018, 4, 1482637. [CrossRef]
- Wang, X.; Sotoudehniakarani, F.; Yu, Z.; Morrell, J.J.; Cappellazzi, J.; McDonald, A.G. Evaluation of corrugated cardboard biochar as reinforcing fiber on properties, biodegradability and weatherability of wood-plastic composites. *Polym. Degrad. Stab.* 2019, 168, 108955. [CrossRef]
- Allohverdi, T.; Mohanty, A.K.; Roy, P.; Misra, M. A Review on Current Status of Biochar Uses in Agriculture. *Molecules* 2021, 26, 5584. [CrossRef] [PubMed]