Research article

Synergetic biofuel production from co-pyrolysis of food and plastic waste: reaction kinetics and product behavior

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A B S T R A C T

This study aimed to develop a process for producing bio-oil, char, and value-added chemicals from food waste and plastic waste blend using co-pyrolysis under controlled conditions. The food waste (rice, vegetables, and fish) was blended in definite ratios (70:30, 60:40, and 50:50 w/w) with polyethylene terephthalate (PET). Experiments were conducted at various temperatures (250, 300, and 350 °C) and reaction times (30, 60, 90, and 120 min). A kinetic analysis was performed to fit experimental data, and reaction kinetics were observed to follow Arrhenius behavior. Maximum yields of bio-oil and bio-char, 66 and 40 wt% respectively, were attained at 350 °C, with yields being strongly influenced by variations in temperature and weakly affected by variations in reaction time. Co-pyrolysis promoted the formation of carboxylic acid, hydrocarbons, and furan derivatives. Formation of carboxylic acid could be increased by increasing the ratio of plastic waste. A maximum carboxylic acid content of 42.01% was achieved at 50% of plastic waste. Meanwhile, a maximum aliphatic hydrocarbon content of 44.6% was obtained with a ratio of 70:30 of food waste to plastic waste at 350 °C. Overall, pyrolysis of food and plastic waste produced value-added compounds that can be used as biofuels and for a variety of other applications.

1. Introduction

Currently, the principal energy sources used in daily living are petroleum-based fossil fuels. The massive consumption of petroleum fuels is depleting these energy sources and creating environmental issues due to the increased pollution emissions from burning these fuels (SO_2, NOx, and CO_2). The depletion of these energy sources causes many new issues, including waste treatment, which must be addressed immediately. The issue of waste treatment has arisen because the consumption of plastic materials has increased dramatically due to their practicality, low-cost, and high resistance. Plastic accounts for about 8% of municipal solid waste, and this is made up of a variety of plastics, including 40.5 wt% HDPE (High-Density Polyethylene) and LDPE (Low-Density Polyethylene), 19.6 wt% PP (Polypropylene), 11.9 wt% PS (Polystyrene), 10.7 wt% PVC (Polyvinyl Chloride), 8.1 wt% PET (Polyethylene Terephthalate), about 5 wt% ABS (Acrylonitrile Butadiene Styrene), and 4.2 wt% other polymers [1].

In the context of producing clean energy, lignocellulosic biomass has maintained its position and relevance in the industrial development of thermochemical conversion plants during the last decade [2]. In general, biomass is clean, abundant, low-cost, easy to grow, and a renewable resource [3]. Food waste is a type of biodegradable waste that comes from a variety of places, including households, food processing facilities, and the catering industry [4, 5, 6]. The main organic components of food waste are carbohydrates (starch, cellulose, and hemicellulose), lignin, protein, lipids, and organic acids [7, 8], making food waste a prospective source for chemical, material, and fuel production. A number of food waste disposal techniques have been banned in many countries, including landfill and animal feeding, while decomposition is limited by the rate of reaction and post-decomposition expenses.

Several approaches have been developed to utilize food waste to produce heat, power, biogas, biochar, bio-oil, and other important products using incineration [9], gasification [10, 11], hydrothermal liquefaction [12, 13], and pyrolysis [14, 15]. However, incineration creates unpleasant gases and ash; gasification requires a lot of energy and has a high operating cost; and hydrothermal liquefaction has a high capital cost (expensive autoclaves), insufficient protection, and an unobservable reaction process [16].

As a result, the advantages of pyrolysis, such as its wide range of products, high efficiency, and environmental friendliness, have become more visible. Pyrolysis is the thermal degradation of organic molecules in an inert atmosphere, anaerobically changing its structure at a comfortable temperature (300–800 °C), leading the substance to decompose into gas, bio-oil, and solid hydrocarbons [17, 18, 19]. Pyrolysis has recently been recognized as a viable technique for managing a variety of biomass sources through the production of high calorific value liquid and gas products, as well as a carbon-rich solid that can be used as activated carbon, soil ameliorant, and in other applications [20]. This process is generally defined as a series of steps in which biomass is depolymerized, monomers are changed or evaporated, and vapors reach the catalyst to be turned into end products [21].

With the growth of food waste and plastic waste production, there is a strong interest in the practical and long-term management of these wastes. However, there are just a few prominent findings on the co-pyrolysis of food waste and plastic waste mixtures generated in commercial establishments. To date, the pyrolysis of food waste and plastic waste for energy recovery has only been attempted by Klaimy et al., [22]; and Liu et al., [23]. Even though the pyrolysis of pure polymers has been extensively studied, the pyrolysis of plastic mixtures has received less attention. Recently, Hu et al. [24] evaluated the pyrolysis behavior of real-world plastic, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), Polypropylene (PP), Polystyrene (PS), and tire, in experiments carried out in a TG-FTIR analyzer. The viscosity and density of the pyrolytic oil were found to be a consequence of the remaining oxygen concentration [24]. In an attempt to fills gaps in existing knowledge, this study reports the effect of univariate optimization and interaction process parameters during co-pyrolysis on product yield and quality. The main objective of this study was to evaluate the impact of temperature (250, 300, and 350 °C), reaction time (30, 60, 90, and 120 min) and ratio of food waste to plastic waste on yield and compositional characterization of bio-oil. Despite the fact that numerous researchers have investigated the hydrothermal decomposition of food waste [25, 26, 27], to the best of the authors' knowledge, there is no information about decomposition kinetics provided in the literature. Hence, this study aims to investigate the kinetics of the hydrothermal co-pyrolysis degradation of food waste and to evaluate the degradation pathways and their kinetic data.

2. Materials and methods

### 2.1. Pyrolysis of food and plastic waste

Food waste and plastic waste pyrolysis were conducted using a semi-continuous batch reactor, schematically illustrated in Figure 1. The reactor consists of a heater, feed holder, semi-continuous reactor, condensers, sampling port, thermocouple, and pressure gauge. Stainless

Table 1. Proximate and Ultimate analysis of raw materials.

	Food waste	Plastic waste
	Proximate (wt%)	Proximate (wt%)
Moisture content	87.0	0.201
Fixed carbon	5.10	n/a
Volatile matter	71.01	99.65
Ash	70.34	0.151
	Ultimate (%wt)	Ultimate (%wt)
C	47.45	84.32
H	3.89	15.48
N	3.89	n/a
O	41.6	0.22
S	0.29	n/a
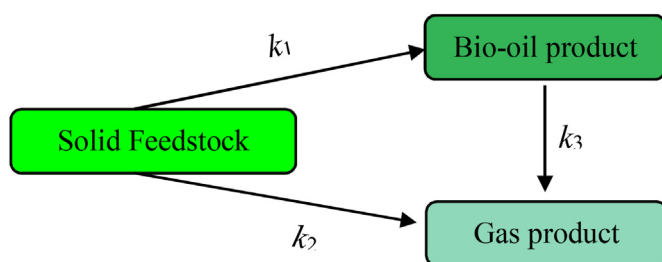
Figure 2. Reaction pathways of food and plastic waste decomposition during pyrolysis.
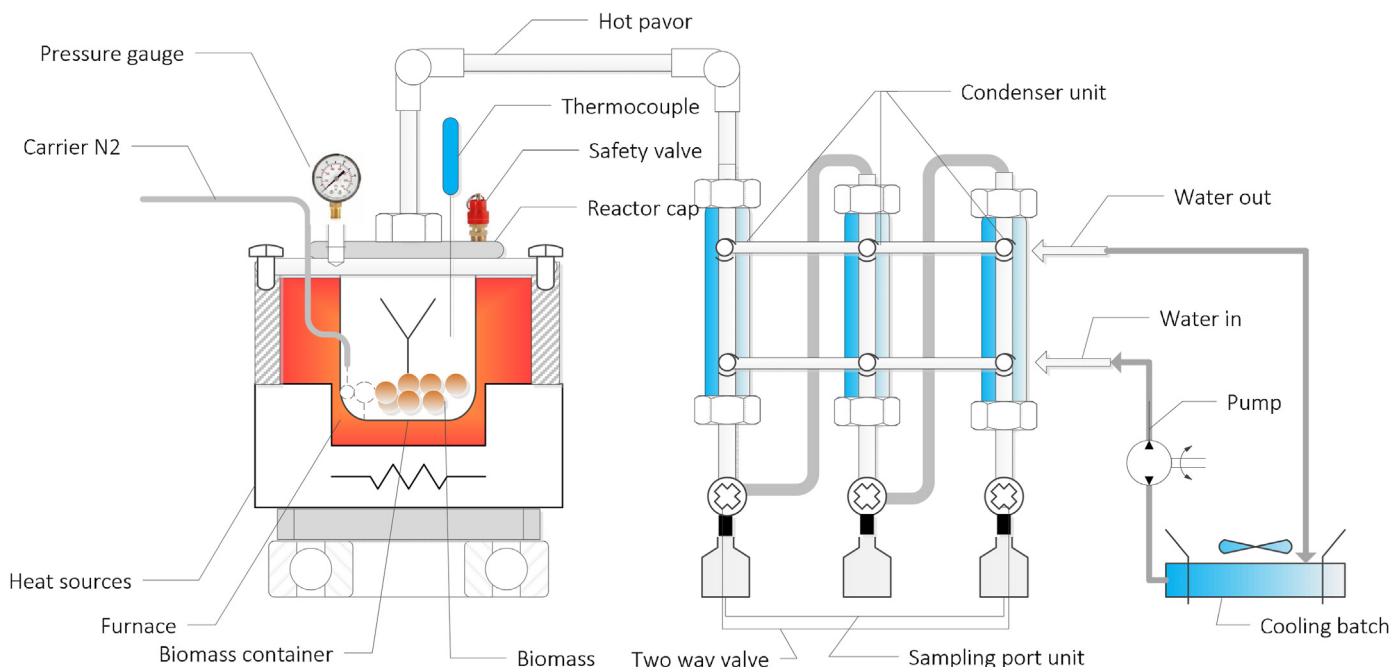
Figure 1. Experimental apparatus.

steel was used to construct this lab-scale reactor. The reactor was then heated at an initial temperature of 25 °C and then increased to the desired temperatures of 250, 300, and 350 °C. The three-stage condensers were installed to condense the purified gas into a liquid. The food waste used in this study consisted of rice, vegetables, and fish; however, the compounds of food waste were not considered in this study, but rather will become part of future research. The plastic waste used was PET waste. In individual co-pyrolysis experiments, 20 g of feedstock was placed in a 500 mL capacity of the batch, which was kept in wool insulation. For the co-pyrolysis experiments, four different types of feedstock were prepared by mixing the food waste with plastic waste in the following ratios: (1) food waste only (denoted as 100FW);
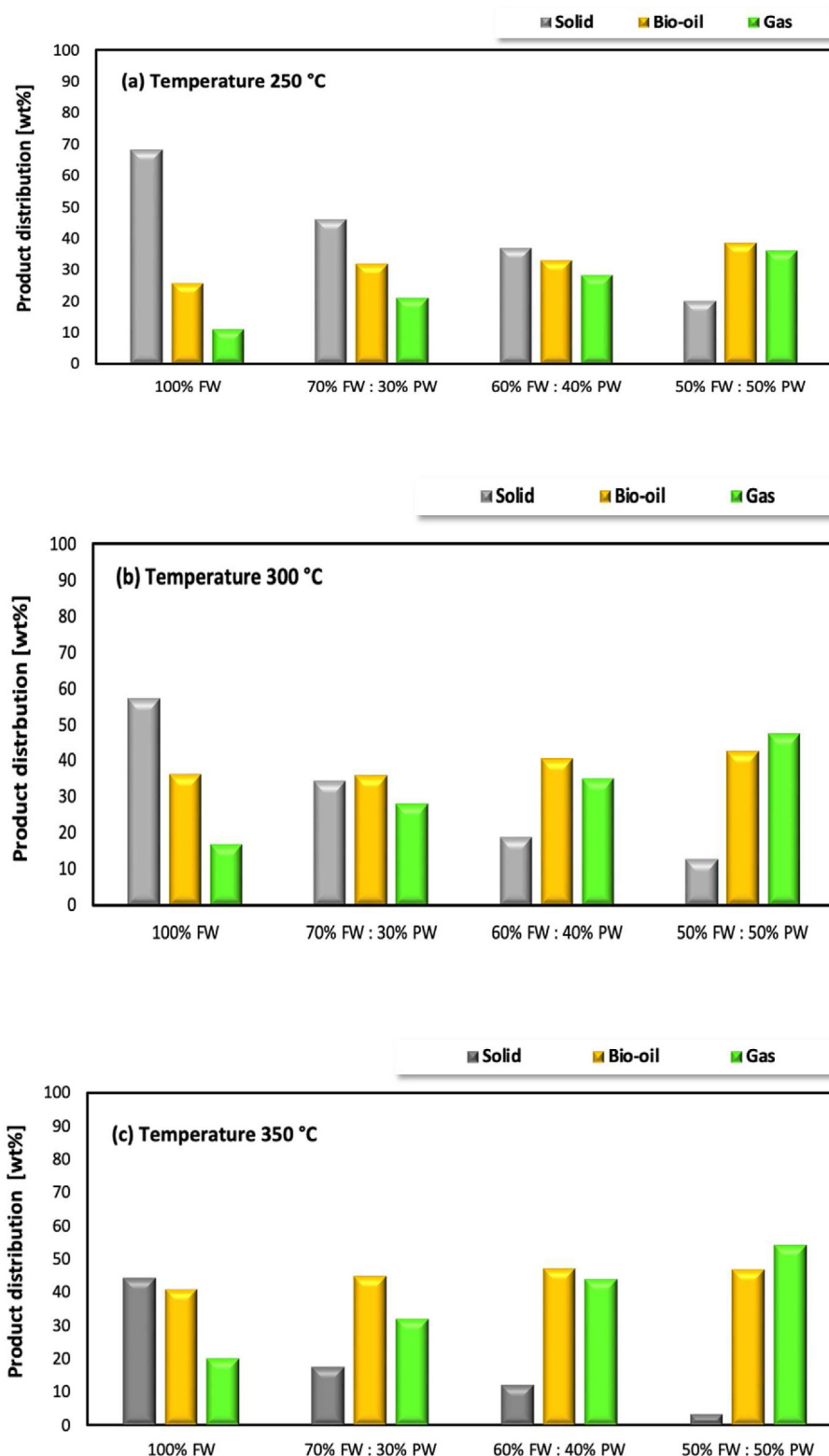

Figure 3. Product distribution of the co-pyrolysis of blended food waste and plastic waste at different temperatures: (a) 250 °C, (b) 300 °C, and (c) 350 °C.

(2) a mixture of food waste and plastic waste in a ratio of 70:30 (denoted as 70FW:30PW); (3) a mixture of food waste and plastic waste in a ratio of 60:40 (denoted as 60FW:40PW); and (4) a mixture of food waste and plastic waste in a ratio of 50:50 (denoted as 50FW:50PW). Pyrolysis was carried out at a rate of 30 °C/min. The pyrolysis system was monitored and controlled using thermocouples and a pressure gauge. All of the experiments were conducted in duplicate. The yield of products (bio-oil, solid, and gaseous) were calculated using the following Eqs. (1), (2), and (3).

$$bio-oil~(\%) = \frac{W_{bio-oil}}{W_{initial~feedstock}} \times~100 \tag{1}$$

$$solid~(\%) = \frac{W_{solid~product}}{W_{intial~feedstock}} \times~100 \tag{2}$$

$$gaseous~(\%) =~100 - (solid + bio-oil) \tag{3}$$

2.2. Analytical method

Solid products were dried and weighed using an electric balance. The chemical composition of bio-oil samples was examined using a GC–MS (QP-2010) with a capillary column coated with white Rtx-5MS (inner diameter of 60 mm × 0.25 mm and film thickness of 0.25 μm). 1 mL of the sample was dissolved in methanol and placed into the column. The GC heating process started at 150 °C and continued for 5 min. The temperature was then raised to 300 °C. An automatic proximate analyzer was used to determine the proximate analysis of the feedstock (FW and PW) (SDTGA5000, Sundy, China). A CHNOS analyzer (VarioEL III, Germany) was used to do the final analysis. The proximate and ultimate analyses are presented in Table 1.

2.3. Reaction modeling

To evaluate the effect of temperature on product distribution, food waste and plastic waste pyrolysis kinetics were studied. The solid, liquid, and gas yields were used to create a kinetic model. With the assumption of first-order reaction, the mechanism of feedstock degradation during co-pyrolysis is shown in Figure 2.

A reaction model was developed based on the product yields at 100% of food waste achieved in this work. The solid feedstocks were converted to the gaseous phase (x), while others were directly changed into the bio-oil phase (y) (k_{ct-y}) (k_{ct-x}). The bio-oil phase could then be converted to gas (k_{y-x}). The reaction network established the kinetic parameters used to match the experimental and modeling data. The change in each product yield can be expressed as follows:

$$\frac{dX(ct)}{dt} = -\left(k_{ct-y} + k_{ct-x}\right)X(ct) \tag{4}$$

$$\frac{dX(y)}{dt} = k_{ct-y}X(ct) - k_{y-x}X(y) \tag{5}$$

$$\frac{dX(x)}{dt} = k_{ct-x}X(ct) + k_{y-x}X(x) \tag{6}$$

where *k*, *t*, and X(x) are the reaction rate constant [min^{-1}], reaction time [min], and the yield of product, respectively. Solid (char + tar) phase to bio-oil phase, solid (char + tar) phase to gas phase, and bio-oil phase to gas phase are represented by the subscripts *ct-y*, *ct-x*, and *y-x*, respectively. Non-linear regression with the least-squares-error (LSE) approach was used to get a rate of reaction constants. This is a typical methodology in regression analysis that compares experimental and calculation data to find the best fit between them.

3. Results and discussion

3.1. Effect of co-pyrolysis conditions on product distribution

Figure 3 shows the product distribution from the co-pyrolysis process at different temperatures (250, 300, and 350 °C). The percentage of bio-oil for each temperature was in the range of 40–60%. Temperature had a considerable impact on the distribution of bio-oil products, transforming them from solid to bio-oil and then to gaseous products. It was observed that increasing co-pyrolysis temperature from 250-350 °C resulted in the percentage of bio-oil rising from 20-48% at 250 °C, 30–50% at 300 °C, and 35–66% at 350 °C. A maximum 66% of bio-oil yield was obtained at 350 °C. This could be due to the lignin molecules being strengthened during the thermal process of creating liquid hydrocarbons at higher temperatures [27]. It also confirms that the secondary reaction of the heavy molecular
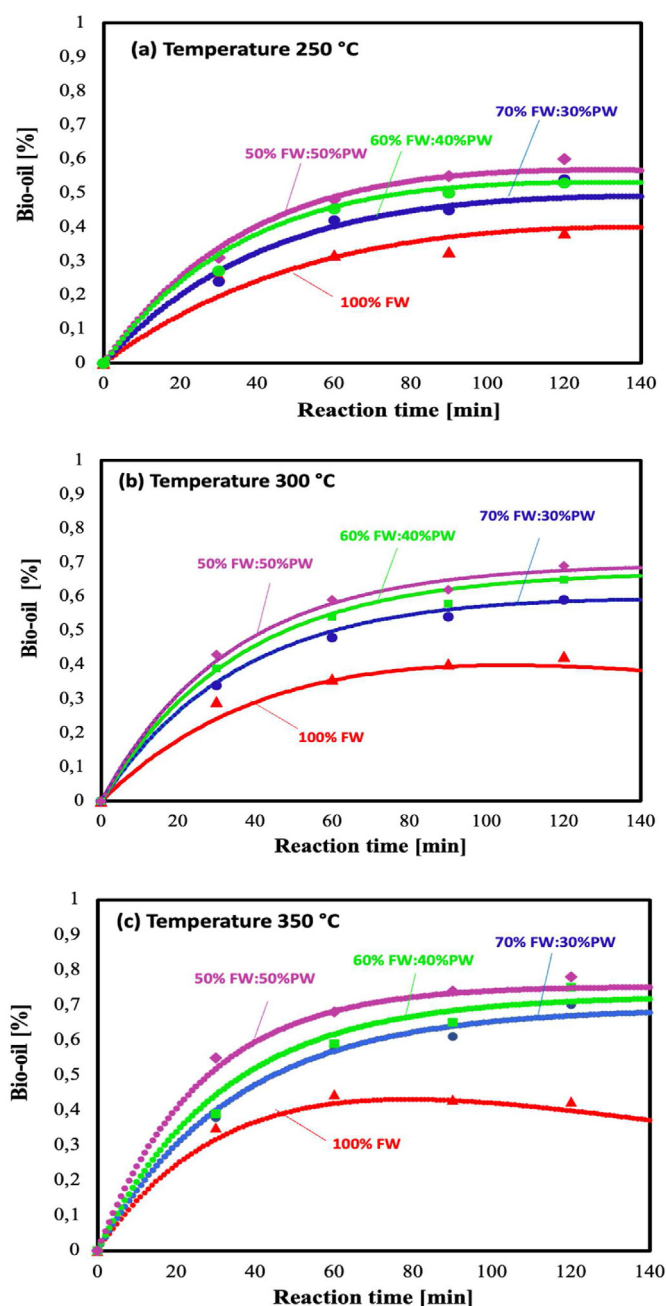

Figure 4. Bio-oil yield at different plastic waste loading and reaction temperatures of (a) 250 °C, (b) 300 °C, and (c) 350 °C.

weight compounds in the pyrolysis vapor were enhanced at the higher temperature, increasing the production of gas products. On the other hand, the solid percentage decreased with increasing temperature: 70-20% at 250 °C, 50-17% at 300 °C, and 40-3% at 350 °C. These results are in line with the findings of Aboulkas et al. [30], and Amrullah et al. [31], who reported that increasing temperature affected bio-oil and gas production, while dehydration and thermal degradation of biomass caused the decreasing solid yield product. Meanwhile, non-condensable gases were observed to increase monotonically in proportion from 6-22% (250 °C), 18–28% (300 °C), and 25–30% (350 °C). This could be the result of the secondary reaction of cracking generating hydrocarbon vapor, which results in a lower percentage of solid and a higher concentration of non-condensable gases [32].

Besides the operating temperature, reaction time also plays a role in bio-oil production. However, the effect of reaction time is less significant than that of temperature. The effect of time on bio-oil yield is depicted in Figure 4. At 250 °C, the bio-oil yield slightly increased from $31.7 \pm 4\%$ to $32.7 \pm 2\%$ when the reaction time was prolonged from 60 min to 90 min. Meanwhile, the bio-oil yield significantly increased from 32.7% to 40.2% at 300 °C with the same reaction time of 90 min. Thus, temperature more significantly affected bio-oil production than reaction time did. These results are supported by the previous work of Palmay et al. [33], who observed that the reaction time has no influence on bio-oil production in terms of thermal pyrolysis of compact polystyrene waste.

3.2. Effect of plastic waste loading and temperature on bio-oil production

Co-pyrolysis of food waste and plastic waste was also compared in bio-oil production. The different percentages of plastic waste loading

were found to affect product distribution (solid, bio-oil, and gas products) as shown in Figure 4. It can clearly be seen that the percentage of bio-oil increased in line with increases in the percentage of plastic loaded and temperature. Bio-oil production with different food and plastic waste ratios (70:30, 60:40, and 50:50) reached 50–70% at 350 °C, respectively - far higher than the 100% of food waste at 30%. Wu et al. [34], observed the same trend in the case of co-pyrolysis of corn stover (CS) and polypropylene (PP). However, the bio-oil yields of Wu et. al.'s study showed lower results than those of this study (PP alone: 57.1% and CS alone: 19.1%). A lower result was observed by Mishra and Mohanty [35] with a maximum bio-oil yield of 44%. Mishra and Mohanty also reported that bio-oil yield from the co-pyrolysis of waste biomass and waste plastics was higher than that of individual biomass (39.2%). Increasing the plastic waste ratio in the raw material enhanced the bio-oil percentage with a significant reduction in the percentage of solids compared to the 100% food waste oil. This could be due to the lack of ash in plastic waste and the effect of ash on biomass, which has been shown to improve the output of pyrolysis volatiles at high reaction temperatures of 350 °C while inhibiting the conversion process at lower temperatures [35].

3.3. Bio-oil characteristics

GC/MS analysis was used to identify the composition of bio-oil produced by the co-pyrolysis of FW and mixed FW:PW. The bio-oil from the co-pyrolysis of this feedstock contained a variety of compounds, and the details of the identified compounds in FW and mixed FW:PW at different temperatures are presented in Table S1. The effect of temperature (250, 300, and 350 °C) and plastic waste loading, during the co-pyrolysis
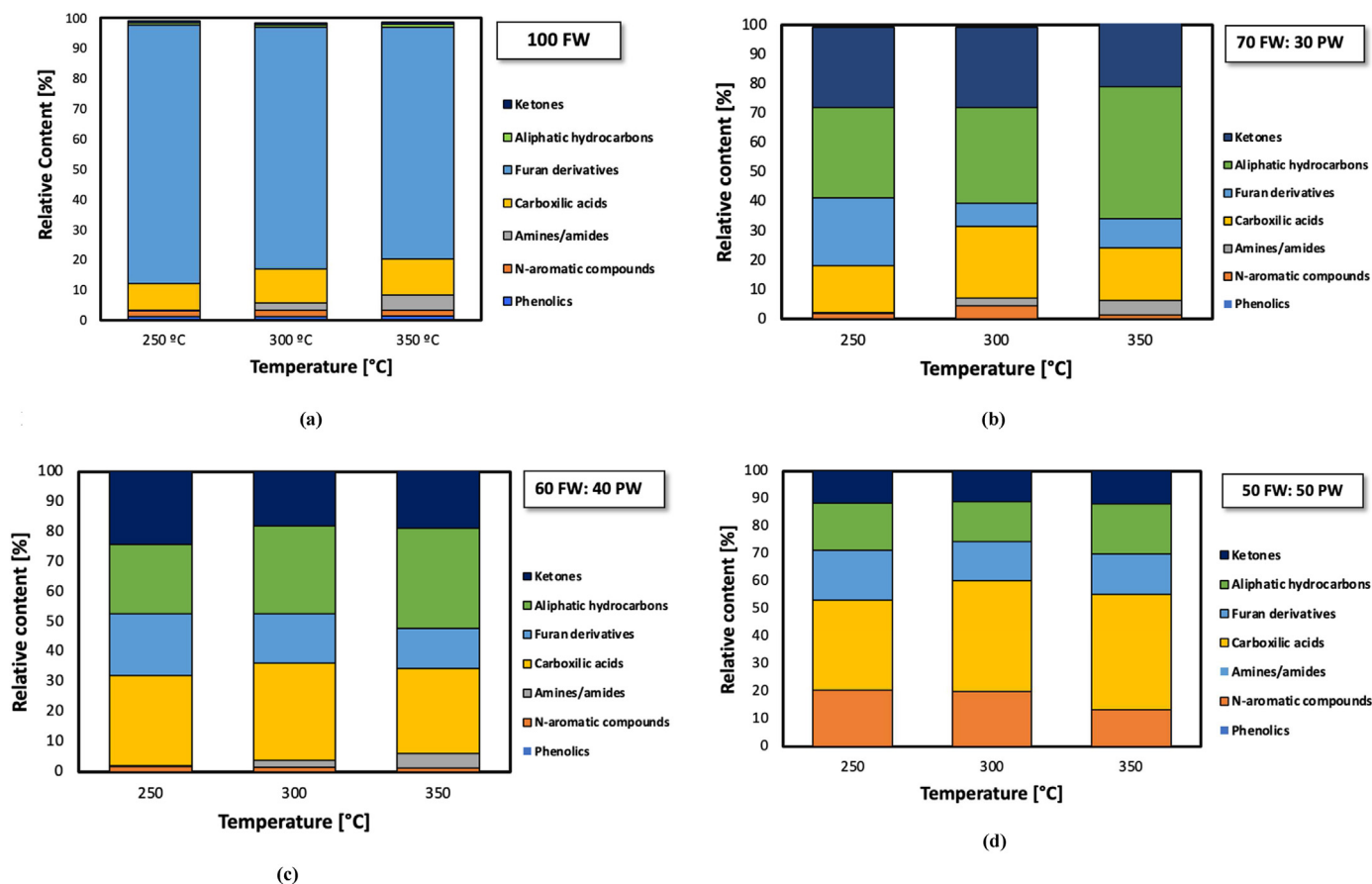
Figure 5. (a) Categories of chemical compounds produced at various compositions of 100FW at a temperature of 250–350 °C. (b) The main categories of bio-oil from co-pyrolysis of FW and PW at varied blend ratios (70FW: 30PW) at a temperature of 250–350 °C. (c) The main categories of bio-oil from co-pyrolysis of FW and PW at varied blend ratios (60FW: 40PW) at a temperature of 250–350 °C. (d) The main categories of bio-oil from co-pyrolysis of FW and PW at varied blend ratios (50FW: 50PW) at a temperature of 250–350 °C.

process, on the properties of bio-oil is shown in Figure 5. Temperature and plastic waste loading were found to affect the chemical compositions of bio-oil. Figure 5(a) shows the categorized chemical compounds produced from various 100% food waste compositions at 250–350 °C. The bio-oil high heating values (HHV) 14.2, 21.9, 34.67, and 42.5 MJ/kg were determined for 100FW, 70FW:30PW, 60FW:40PW, and 50FW:50PW, respectively. This is evidence that a high ratio of plastic waste can increase the HHV of bio-oil. The high HHV bio-oils may have potential applications as a liquid fuel. These findings are in line with the earlier work of Ly et al. [37], which obtained the HHV of bio-oil in the range of 27.60–31.34 MJ/kg for raw catalytic food waste.

The components displayed in the GC-MS analysis findings at a temperature of 250 °C only consist of three components: alcohols, acids, and nitrogen compounds. These results agree well with Mohan et al. [19], who showed that bio-oil has at least a set of components in the form of phenol, alcohol, acid, and aldehyde. Furthermore, the number of acid compounds was reduced at the operating temperatures of 300 °C and 350 °C. The GC-MS test results indicate that this is due to the carbon chain breaking down into its derivative chemicals. The compounds, including alcohols, phenols, and even aldehyde groups, were identified in the second test of this temperature range. The effect of biomass ratio (100FW, 70FW:30PW, 60FW:40PW, and 50FW:50PW) on bio-oil characteristics at different reaction temperatures was investigated in this study. It was confirmed that an increasing ratio of plastic waste (PET) enhances hydrocarbon formation. It was also confirmed that PET improves hydrogenation processes as a hydrogen donor, resulting in higher H/C ratios and lower O/C ratios [37]. This result proves that PET increases the hydrogenation process, which reduces oxygen [38]. Furthermore, the increase in C in bio-oil mixed
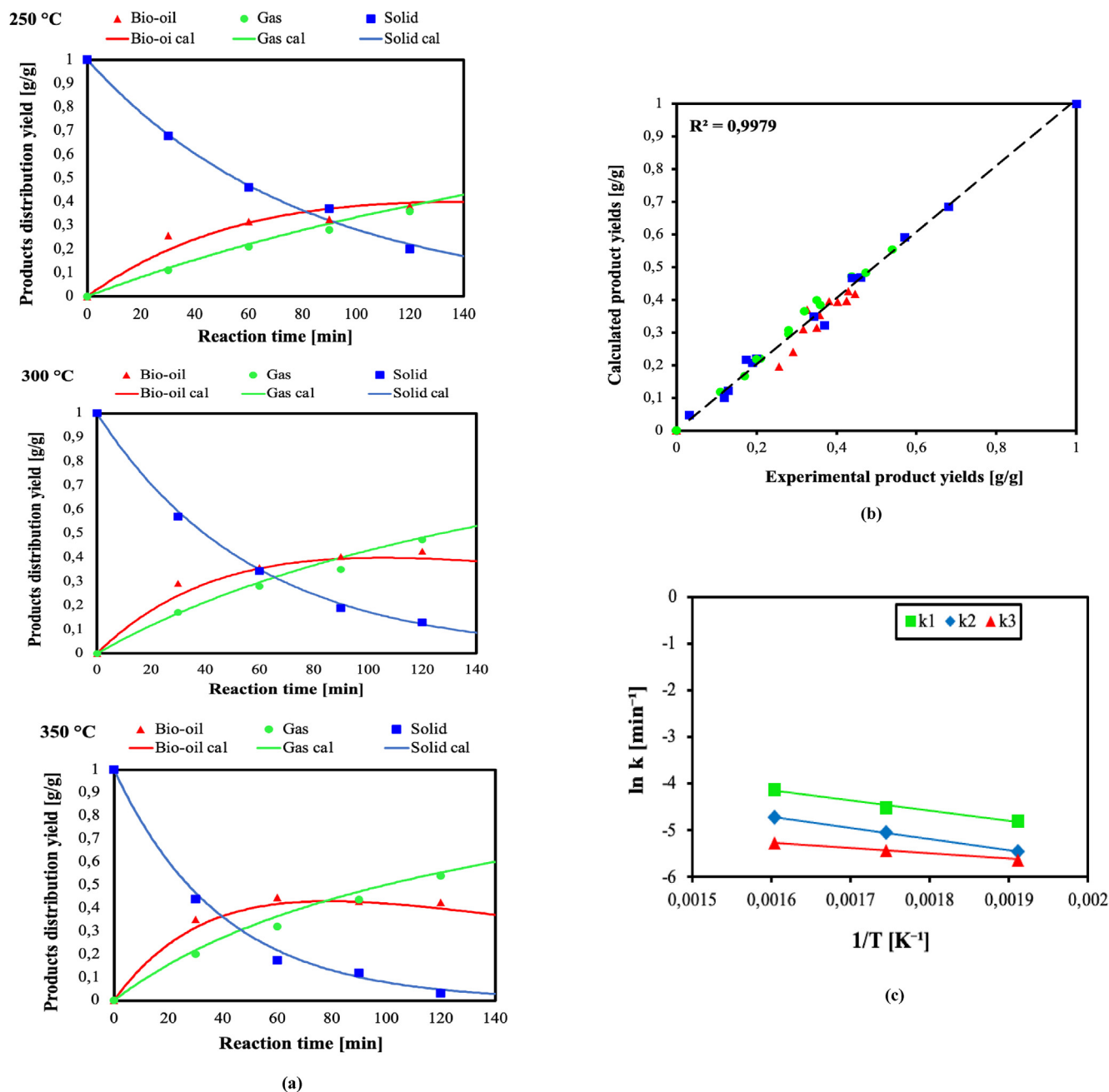

Figure 6. (a) Concentrations of solid, bio-oil, and gaseous products (Experimental condition Temp. 250 °C, 300 °C, and 350 °C at 100FW). (b) Parity plot (Comparison of experimental and calculated data) (exp. conditions: Temp. 250 °C, 300 °C, and 350 °C at 100FW). (c) Arrhenius plot (exp. conditions. 250 °C, 300 °C, and 350 °C at 100FW).

Table 2. Kinetic parameters, Activation Energy, and Pre-Exponential Factor of Each Reaction of Food Waste.

Reaction direction	Kinetic parameter	Reaction rate constant [min⁻¹]			Activation energy, Ea [kJ mol⁻¹]	Pre-exponential factor, A [min⁻¹]
		250 °C	300 °C	350 °C		
solid → bio-oil	k_1	0.008	0.011	0.016	18.08	1.943
solid → gas	k_2	0.004	0.006	0.006	19.98	2.361
bio-oil → gas	k_3	0.003	0.004	0.005	35.19	3.808

compared to food waste could be attributed to plastic waste activating deamination and decarboxylation processes [39]. This is evident through the lower amounts of nitrogen-based molecules and carboxylic acids. In general, crude bio-oil derived from various feedstocks is a complex mixture containing many organic compounds with carbon numbers ranging from C_2 to C_{27} [40]. Hydrocarbons, furans, nitrogen-containing compounds, phenols, alkanes, aldehydes/ketones, carboxylic acids/esters, and traces of other compounds can be divided into eight categories based on their functional groups: hydrocarbons, furans, nitrogen-containing compounds, phenols, alkane, aldehydes/ketones, carboxylic acids/esters, and traces of other compounds [41, 42].

The main categories of bio-oil from co-pyrolysis of food waste only and food and plastic waste blend are summarized in Figures 5(b), (c), and (d). Individual co-pyrolysis of food waste biomass indicated the preponderance of carboxylic acids, furan derivates, and nitrogen-containing chemicals (12%, 75%, and 2% respectively), with comparatively low hydrocarbons. This finding agrees with a previous study by Tang et al. [44], which observed that bio-oil derived from algal pyrolysis is primarily composed of N_2 and oxygen-containing molecules, with a lower proportion of hydrocarbons. A high content of oxygenated compounds (furan, acid) (80%; 12%) was found in this study. This is most likely the result of pyran ring-openings and aromatization, producing short-chain hydrocarbons that can be oxidized to produce furans or acids [44]. Increasing plastic waste loading enhanced the proportion of hydrocarbons up to 40% at a 70FW:30PW mixture ratio and reduced the proportion of carboxylic acid to 3%. It is important to note that at 70FW:30PW; 60FW:40PW; 50FW:50PW, the carboxylic acid fraction at considerable revealed changes. This may be due to the oligomerization reaction that occurs during the condensation process, and the secondary reaction that takes place in the reactor, in line with the increase in plastic waste loaded [45, 46]. Thus, this study indicates that the synergistic impact created by the coupling of food and plastic waste biomass during co-pyrolysis improves bio-oil quantity and quality.

3.4. Detailed reaction rate of food waste and plastic waste mixed during the co-pyrolysis process

Comprehensive kinetics research is required to investigate the properties of pyrolytic bio-oils of food waste and plastic waste at various operating temperatures. A reaction model has been presented in this paper that is dependent on the product yields achieved in this study. The pyrolytic bio-oil content of much of char and tar was directly converted into a bio-oil. Meanwhile, some solid feedstocks were converted to gaseous products. Either way, the bio-oil was also converted to gaseous products. The reaction network determined the kinetic parameters to fit the experimental data to the model measurement (Eqs. (4), (5), and (6)). To establish reaction rate constants, non-linear regression with the least-squares-error (LSE) approach was employed (i.e., a typical method in regression analysis that compares experimental data and calculation data to find the best fit between them). The calculated concentrations of solid, bio-oil, and gaseous products are depicted in Figure 6(a), along with the experimental results. The parity plot in Figure 6(b) shows experimental data for product concentration to values generated with the model using the LSE approach. According to the high coefficient of determination (R^2) obtained, the model predictions fit the experimental data quite well. The activation energy and pre-exponential factor were estimated utilizing the Arrhenius equation to

simulate the temperature dependence of the reaction rate constants. The Arrhenius plots of the individual rate constants for thermal degradation during the co-pyrolysis process of food and plastic waste are shown in Figure 6(c). The value for the activation energies and pre-exponential factors obtained for co-pyrolysis of food waste and plastic waste are presented in Table 2. The activation energy (E_a) and pre-exponential factor (A) were calculated using the straight-line fit of ln k vs 1/T. Activation energies between 18 to 35 kJ/mol were obtained for food waste and plastic waste co-pyrolysis, which are values lower than those reported by Tang et al [48], who calculated activation energies in the range of 34.17–183.58 kJ/mol at 400, 500, and 600 °C. This difference may be due to the differences in reaction temperature used in each study. Pre-exponential factors of 1.943, 2.361, and 3.808 min⁻¹ were obtained for the conversion of solid to bio-oil, solid to gas, and bio-oil to gas products, respectively. Interestingly, the activation energy for the conversion of solid to gas was higher (19.98 kJ/mol) than that of solid to bio-oil (18.08 kJ/mol). This could be explained by the fact that more energy is required to break down solids into gas products than to convert solids into liquids.

4. Conclusion

This study has demonstrated the effect of temperature, reaction time, and feedstock ratio on the co-pyrolysis of blended food waste and plastic waste. Temperature (250–350 °C) and food waste to plastic waste ratio contribute to the products produced in the co-pyrolysis process. A maximum of 66% bio-oil was obtained at 350 °C, followed by increased plastic waste co-pyrolysis mixtures. On the other hand, reaction time was found to have a weak effect on bio-oil production. A 90 min reaction time produced a maximum bio-oil yield of 62% compared to the not much higher 66% for a reaction time of 120 min. Solid percentage decreased with increasing temperature, decreasing from 70 to 20% at 250 °C, 50 to 17% at 300 °C, and 40 to 3 % at 350 °C. GC/MS showed enhanced hydrocarbons of up to 40% and reduced carboxylic acids by 3% followed by increased plastic waste loading. The major compounds were carboxylic acids, furan derivatives, and nitrogen-containing chemicals, in amounts of 12%, 75%, and 2% respectively, with comparatively amounts of low hydrocarbons. Finally, the degradation kinetic model fits well with the experimental results, and activation energies were found to be in the range of 18.08–35.19 kJ mol⁻¹.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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