

Power-to-chemicals: sustainable liquefaction of food waste with plasma-electrolysis

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Abstract The increasing amount of food waste from various industrial, agricultural, and household sources is an environmental burden if managed inappropriately. Numerous waste management approaches have been developed for the disposal of food waste, but still suffer from either high cost, production of toxic by-products, or secondary environmental pollutions. Herein, we report a new and sustainable plasma electrolysis biorefinery route for the rapid and efficient liquefaction of food waste. During the plasma electrolysis process, only the solvent is added to liquefy the waste, and anions in the waste can contribute to catalyzing the biowaste conversion. While liquefying the waste, the highly reactive species produced in the plasma electrolysis process can efficiently reduce the content of O, N, and Cl in the liquefied products and oxidize most of the metals into solid residues. Especially, the removal rate of Na and K elements was greater than 81%, which is significantly higher than using the traditional oil bath liquefaction, resulting in a relatively high-quality biocrude oil with a high heating value of 25.86 MJ·kg⁻¹. Overall, this proposed strategy may provide a new sustainable and eco-friendly avenue for the power-to-chemicals valorization of food waste under benign conditions.

Keywords plasma electrolysis, food waste, liquefaction, resource recovery

1 Introduction

Due to the increasing demands for food and natural resources worldwide and the perishable nature of numerous foods (both fresh produce and products), food waste has become a substantial and global concern with substantial economic, social, and environmental costs [1]. Globally, roughly one-third of food resources are lost along the food supply chain from the production stages to the consumer, i.e., an annual loss of about 1.6 billion tons of food, according to the Food and Agriculture Organization [2]. Moreover, the carbon footprint of food waste is estimated to contribute to the emissions of greenhouse gases by accumulating around 3.3 billion tons of CO₂ into the atmosphere every year globally [1,3,4]. These challenges demand not only the improvement of waste management systems for effective reutilizing and upcycling of food wastes, but also the development of sustainable and cost-efficient approaches that do not produce new wastes and produce little or no carbon emissions.

Conventional food waste management approaches which are still widely applied worldwide include incineration, landfills, composting and application as animal feeds [1]. Among those, the incineration of food waste with high water content is energy-intensive due to the water evaporation along the process and causes high CO₂ emissions. The landfill strategy results in serious environmental concerns since the nutritional compositions of wastes provide an excellent breeding environment for various microorganisms, thus contributing to severe bacterial contaminations and infectious diseases. Composting generally requires large

Received June 20, 2022; accepted September 12, 2022

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disposal space and is relatively expensive owing to the long-distance transportation and waste collection, as well as a long reaction time. Feed for livestock is regarded as a cost-effective approach for the treatment of biowastes in the long run, but this application is strictly regulated because of the diversified and unknown substances in the biowastes [5]. Therefore, there is an immediate need to develop green approaches for transforming food waste streams into diversified value-added products, which can contribute to zero-carbon emissions and support the establishment of sustainable circular economy [6].

Recently, thermochemical processes have been extensively investigated to dispose food waste into value-added chemicals and minimize environmental impacts. They provide a simple and convenient avenue to minimize the waste volume (> 80%), shorten reaction periods [7], enhance energy recovery efficiency, and extend the types of waste that can be disposed of. For example, Wang et al. [8] treated food waste by hydrothermal liquefaction and found that an alkaline catalyst inhibited the yield of bio-oil but positively increased the yield of coke. They also developed a high-temperature pyrolysis process to treat food residues to produce biochar. However, these methods are time-consuming with the high energy consumption, and retain a relatively high metal ion content in the obtained product.

Electricity-driven biorefinery may offer another viable way for sustainable production of green chemicals and fuels from the agricultural and food-processing wastes, e.g., through the plasma electrolysis (PE) strategy. An illustration of food waste management process by the PE was shown in Scheme 1. Previously, we have developed a PE liquefaction process for the efficient catalytic liquefaction of wood chips within 150 s and with a low-energy consumption [9,10]. They found that the reactive species ($\cdot\text{CH}_x$, $\cdot\text{OH}$, $\cdot\text{H}$, etc.) generated from the in-liquid

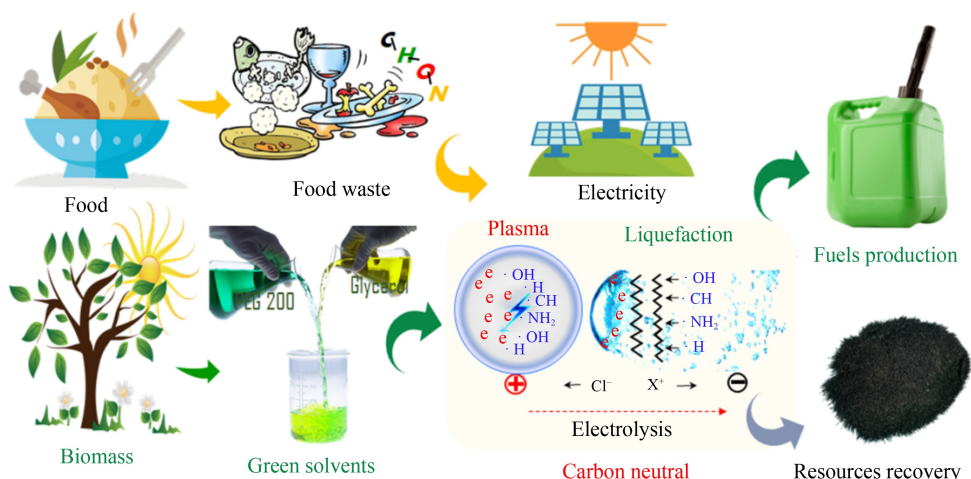
plasma discharges could not only heat the solution but also facilitate the catalytic liquefaction of biomass [11]. Subsequent studies also demonstrated the universality of this proposed technology for the catalytic liquefaction of lignocellulosic biomass [12] and microalgae conversion into value-added chemicals [13]. However, the presence of strong acids, alkalis or inorganic salts as catalysts results in extra challenges for the equipment maintenance [14], and subsequent characterizations of the produced compounds further hinder the mechanism studies.

Here we report a catalyst-free approach based on the electricity-driven in-liquid PE to tackle the overwhelming problems of valorization of food waste, with the only addition of solvent to liquefy the food waste stream, and the schematic diagram of the developed PE system was shown in Fig. S1 (cf. Electronic Supplementary Material, ESM). The effects of water content in food wastes and treatment time on the liquid yield and the reduction of metal and non-metal elements are investigated. The concentration of anions in the samples as well as the catalytic effects of each of these ions under acid, neutral, and alkali conditions are determined. Further analysis of the obtained products from the developed PE process and favorable comparison with conventional liquefaction methods are carried out to evaluate this potential approach for reutilizing food waste residues as an energy source.

2 Experimental

2.1 Raw materials

Food waste was collected from the kitchen waste bins in the Haiyun Canteen of Xiamen University, China. The leftovers (100.00 g) were dried at 110 °C for 24 h in a drying box, yielding a mass of about 33.33 g.



Scheme 1 Illustration of food waste management process by the PE. Green and sustainable solvents can be potentially produced from renewable biomass sources at large scales. This study reports a catalyst-free approach based on the electricity-driven in-liquid plasma discharges to convert the biomass and recycle resources from food wastes, nearing the ultimate carbon-neutral processes.

2.2 Liquefaction equipment and product separation

The experimental system included a tungsten electrode (purity 99.99%, diameter 1.5 mm), reaction vessel (explosion-proof quartz reactor), direct current (DC) pulse power supply (MAO-7HD), oscilloscope (TBS1102B), platinum electrode thermometer (Pt-100, MaserAC), and a condensation system. The raw materials and liquefier were added into a three-necked flask and stirred. The two electrodes entered the solution 20 mm from each side of the reactor, forming a 10 mm gap between the two electrodes. The other ends of the two electrodes were connected to the positive and negative poles of the pulsed DC power supply. The applied voltage, duty cycle, and frequency of the power supply were 0–750 V, 10%–80%, and 100–1000 Hz, respectively. A condenser tube was connected to the top of the reactor to recover the evaporated aqueous solution and light oil, and a gas collection bag was connected to the end of the condensing system. More details about the plasma device and operation procedure can be found in our published studies [9,12].

After PEL, a suction filter was used to separate the liquid product from the solid product of the solution. The solid product was washed with acetone and filtered 3–4 times, and the filtrate was passed through a rotary evaporator to remove the acetone to obtain the final liquid product. The filtered solid product was placed in an oven and dried at 105 degrees for 12 h. The liquid yield calculation formula is:

Liquid yield

$$= \frac{\text{Mass of solution after PE} - \text{Mass of solvent after PE}}{\text{Mass of biomass loaded}} \times 100\%,$$

where “Mass of solution after PE” is the mass of food waste and solvent mixture treated by PE, and “Mass of solvent after PE” is the mass of solvent treated by PE.

2.3 Measurement of metal content in waste streams

After weighing 25.00 g of dried waste material into a mould, X-ray fluorescence (XRF, S8 TIGER) was used to analyze the relative content of the metal elements and oxides. The metal content in the aqueous solution, bio-oil, waste material, and residues, was measured using the metal ion probe [15]. The detailed measurement was commercially conducted in Kaishipu (Shanghai) Testing Technology Co., Ltd.

2.4 Measurement of anion concentrations in liquefied products, aqueous solutions and residues

The solid residue pretreatment followed the procedure of Osman et al. [16], with a 1.00 g sample of the mixed waste material (not dried) or solid residues (not dried after filtration) being added to 10 mL ultrapure water in a

test tube, and stirred for 24 h. After sonication for 10 min, the sample was centrifuged at 3800 r·min^{−1} for 10 min. The supernatant was passed through a C18 column, transferred to 10 mL volumetric flask, and used ultrapure water to make a fixed volume. The concentrations of ammonium ions, nitrite, and nitrate anions were measured with a spectrophotometer and a microplate reader, respectively [17].

The titration method was employed to measure the carbonate concentration in an aqueous solution, bio-oil, leftovers, and solid residues [18], which was commercially performed in Kaishipu (Shanghai) Testing Technology Co., Ltd. Nitrite and ammonium standard solutions were used (Griess Reagent, Nessler reagent) to calibrate samples [19]. Because the solution contained both nitrite and nitrate ions, solutions were divided, each of which was 2.5 mL. In one sample, the concentration of nitrite ions was obtained by the above method. Nitrate reductase (NADPH) was added to the second sample to reduce nitrate to nitrite, with Griess reagent added to determine the total nitrite concentration. The nitrite content measured in the first sample was subtracted from the total nitrite content to determine the nitrate content [20].

3 Results and discussion

From the bulk 5000 g food waste material, the main constituents were found to be 32.34% rice, 16.12% green vegetables, 8.35% lean meat, 5.53% eggs, and 2.61% tofu. These five foods accounted for 64.95% of the total. Of these, rice, vegetables, and lean meat accounted for 56.81% of the leftovers. The rice, greens, and lean meat obtained from the canteen leftovers were in a 4:2:1 ratio, to simulate real leftover conditions but in a controlled means. The sample was mixed and processed to a paste. To further assess the impact of other food additions, eggs and tofu were added at various proportions and their impacts on the liquid yield were assessed. The main ingredients of rice, vegetables, lean pork, eggs, and tofu are shown in Table 1, which shows that the main components of eggs and tofu were basically the same as those of the paste (rice, green vegetables, and pork) but that the eggs and tofu had more protein and fat. Results indicate that the addition of eggs or tofu had little effect on the liquid yield, as shown in Fig. S2 (cf. ESM). Therefore, a paste of rice, vegetables, and lean meat was used as the raw material in the subsequent experiments.

3.1 Influence of water content on PE

3.1.1 PE characteristics

A 10 g sample (rice, vegetables, lean meat: 5.70, 2.85, 1.45 g, respectively, water = 66.7%) was studied in the PEL process. The current versus voltage curve

Table 1 Composition of leftovers

Material	Crude fiber	Protein	Fat	Carbohydrate	Water content	Ref.
Rice	1.44%	2.91%	3.55%	26.32%	65.12%	[21]
<i>Brassica chinensis</i> L.	4.70%	2.01%	—	15.74%	72.89%	[22]
Lean pork	—	29.57%	6.76%	—	55.87%	[23]
Egg	—	15.8%	26.43%	3.58%	52.65%	[24]
Tofu	0.10%	15.70%	8.60%	4.30%	69.80%	[25]

(characteristic curve, CV) obtained using an oscilloscope during PE is shown in Fig. 1. Figure 1(a) shows that the electrolysis occurred in two phases. The voltage and current curve of Phase 1 is shown in Fig. 1(b), and the voltage and current curve of Phase 2 is shown in Fig. 1(c). The CV in the PEL only appeared in Phase 2. The waste sample contained a high water content, so an experiment was designed to analyze the influence of water on the CV. The sample was heated to 115 °C in an oil bath to remove the water, and the measured CV is shown as Phase 2 in Fig. 1(a) (Phase 1 did not appear). The corresponding voltage and current with time are shown in Fig. 1(c). After the solution cooled, 6.67 mL (the same content as in the sample) of deionized water was added to the solution. The CV is shown in Fig. 1(a), which reveals that Phase 1 appeared. This indicated that Phase 1 was caused by the water in the waste sample and corresponded to the electrolyzation of water. Phase 2 (Fig. 1(b)) is related to the liquefaction of the waste material. The energy of a single pulse, 4.10 J (Fig. 1(b)), can be calculated from the area of a single pulse, 6.02 J (Fig. 1(c)). Both are spark discharges. This is different from a previously reported mode of discharge (filamentary discharge) [9], which was obtained by the PE of cellulosic biomass. The pulse energy (E_p) of a spark discharge is higher than that of a filamentary discharge, and the number of active particles produced is also higher than that of a filamentary discharge. The reason for the different discharge modes appears to be that the waste material contains more electrolytes than that of cellulosic biomass.

The PE process is mainly generated by the breakdown of the gasified solution with several different stages, as shown in Fig. S3 (cf. ESM). The discharge type is commonly determined by the E_p [26]. Generally, the E_p of the filamentary discharge is < 1 J, while the spark discharge is $1 \text{ J} < E_p < 10 \text{ J}$. Based on the energy calculation from the voltage and current vs. time in Fig. 1(c), the E_p of the PE process is ~ 6 J, as referred to as the spark discharge. In contrast, the voltage and current vs. time curves of the filamentary discharge are shown in Ref. [17], with the E_p of ~ 0.1 J. Clearly, the E_p of the filamentary discharge is significantly lower than that of the spark discharge. The greater E_p in PE, the higher the electron energy in the discharge area [27], and thus the higher concentrated free radicals.

In addition, a spectrometer was used to measure the

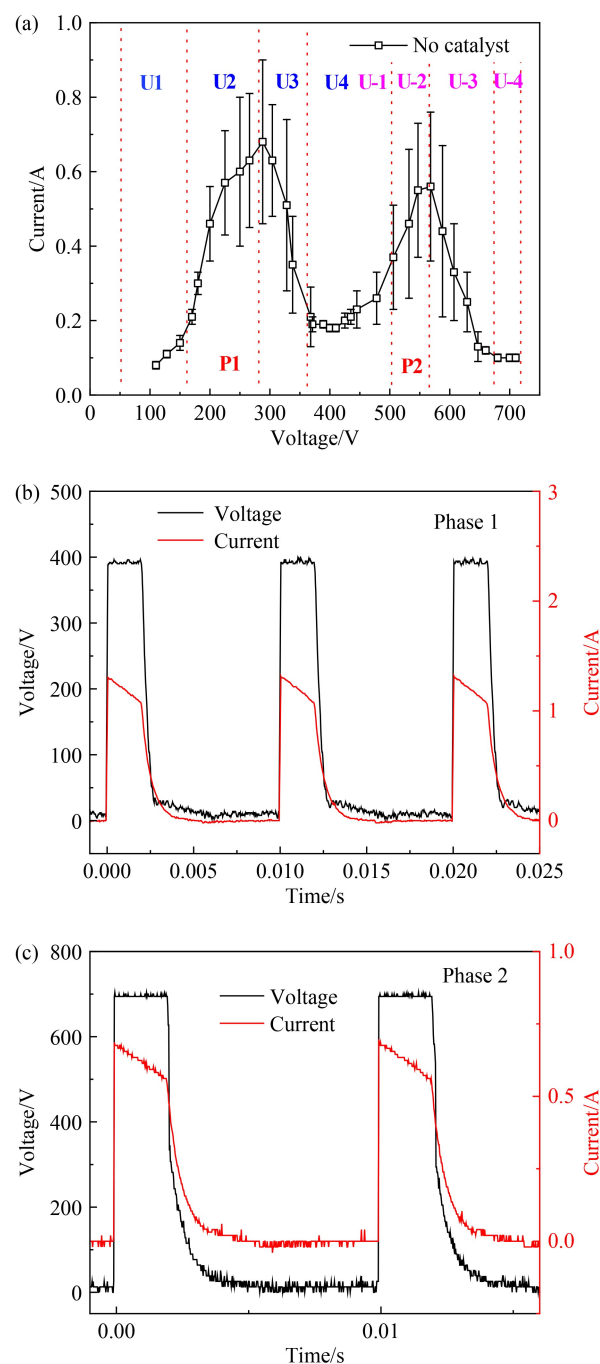


Fig. 1 The CV and the voltage and current with time curves of PE. (a) The CV (voltage vs. current curve); (b) voltage and current vs. time in Phase 1; (c) voltage and current vs. time in Phase 2.

optical emission spectrum of the PE discharge, as shown in Fig. S4 (cf. ESM). Compared with the filamentary discharge emission spectrum in Ref. [17], more types of emission lines (i.e., NH_2 and H_α) with higher intensity are observed in the spectrum of spark discharge. It can be seen from Fig. S4 that many radicals are generated, such as $\cdot\text{OH}$, $\cdot\text{CH}$, $\cdot\text{NH}_2$, $\cdot\text{H}_\alpha$, $\cdot\text{H}_\beta$ and $\cdot\text{C}_2$. Among these lines, $\cdot\text{OH}$ at 309 nm is mainly derived from $\text{e}^- + \text{H}_2\text{O} \rightarrow \cdot\text{OH}$ (A) + $\cdot\text{H} + \text{e}^-$ [28], which indicates that $\cdot\text{H}$ and $\cdot\text{OH}$ radicals can be produced during the discharge. The $\cdot\text{CH}$ at 431 nm mainly comes from $\cdot\text{H} + \cdot\text{CH}_2 \rightarrow \cdot\text{CH} + \text{H}_2$ ($1 \times 10^{-11} \exp(900/T_g)$). The presence of $\cdot\text{C}_2$ Swan band system ($\text{d}^3\Pi_g \rightarrow \text{a}^3\Pi_u$ transition with $\Delta v = 0$) at 516 nm should correspond to the presence of C in the solid residue [28,29]. These free radicals diffusing into the solution can engage in a series of chemical reactions to decompose solid macromolecules into small molecules [11]. Kleinert [30] also reported that cellulose could be degraded by using UV-induced free radicals. Nakamura et al. [31] employed UV radiation to produce $\cdot\text{OH}$ and $\cdot\text{C}_2$ free radicals to convert the glucose units in cellulose into 5-hydroxymethylfurfural.

3.1.2 The influence of water content on liquefaction

Different amounts of water were added to the dried waste material providing water contents of 16.67%, 33.33%, 50.00%, and 66.67% (raw material). The sample was liquefied by PE with no added catalyst. The liquid yield and solution temperature curves are shown in Fig. 2. The liquid yield did not decrease with the water content; only the liquefaction time increased, as shown in Fig. 2(a). Figure 2(b) shows that the temperature rose slowly between 100–130 °C (Phase I, water electrolysis stage). When the temperature exceeded 130 °C, it increased linearly. This stage lasted approximately 4 min and corresponded to the liquefaction stage of the waste material. This is approximately the same time as the electrolytic liquefaction of the dry raw material. These experiments show that the liquid yield of the paste (74.5%) was almost the same as that of the dry raw material (75.2%). Therefore, in the subsequent experiments, the waste samples were only mixed to a paste.

3.2 Optimization of PEL

3.2.1 Liquefaction time

The liquid yield and temperature curves under different pH conditions are shown in Fig. 3. H_2SO_4 and NaOH were added separately to investigate the effect of solution pH on the liquefaction process. Figure 3(a) shows that the liquid yield with sulfuric acid addition was 95%, at a processing time of 6 min. When alkali was used in the liquefaction process, the liquid yield was only 62.4%,

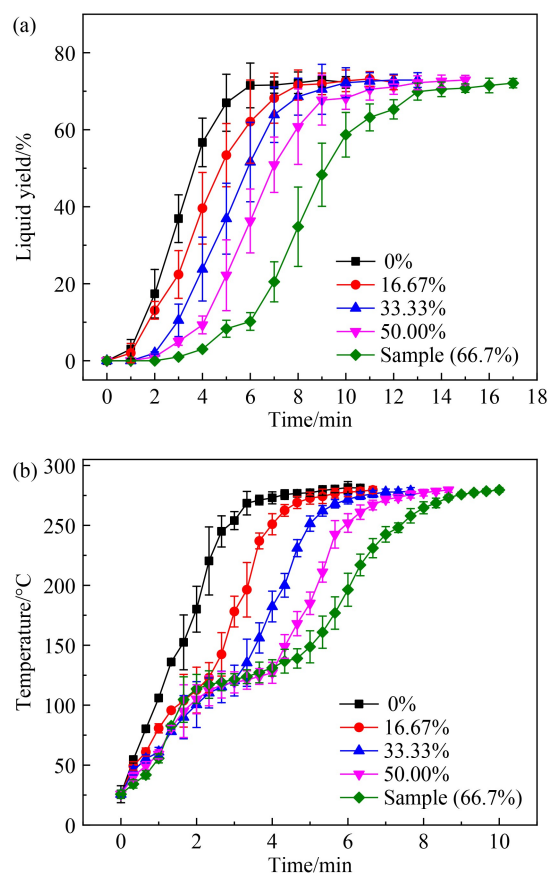


Fig. 2 Influence of different amounts of water on (a) liquid yield and (b) temperature (polyethylene glycol (PEG 200)/glycerol: 3/1, liquid–solid ratio: 7/1, no catalyst added).

which is lower than that with no catalyst added (74.5%). Overall, these experimental results indicate that the liquid yield of food waste under alkaline conditions is significantly lower than that under acidic conditions. Figure 3(b) shows that the temperature of the solution was similar for all pH conditions, but the liquid yield varied significantly. This is due to the almost same composition of the mixed solution (solvent and food waste) with the same boiling point. However, during the PE, cellulosic biomass in food waste can be hydrolyzed to form glucose units (Eq. (1)) [32]. These glucose molecules can be further oxidized by plasma-generated hydroxyl radicals to form D-glucuronic acid (Eq. (2)) [33], and proteins and lipids in food waste can also be hydrolyzed and oxidized to form organic acids [34,35]. With the H^+ ions produced from the ionization of these organic acids, relevant anions can be generated simultaneously. These H^+ ions produced during PE can break the glycosidic bond in cellulose, which is beneficial to the liquefaction of biomass [36]. Thus, during the alkaline PE process, the H^+ ions generated by PE will neutralize OH^- ions in the alkaline solution, which reduces the pH of the solution. The decrease in OH^- concentration also affects the liquid yield of food waste. In contrast, more H^+ ions will be produced in the acidic PE process, and contribute to the liquefaction of

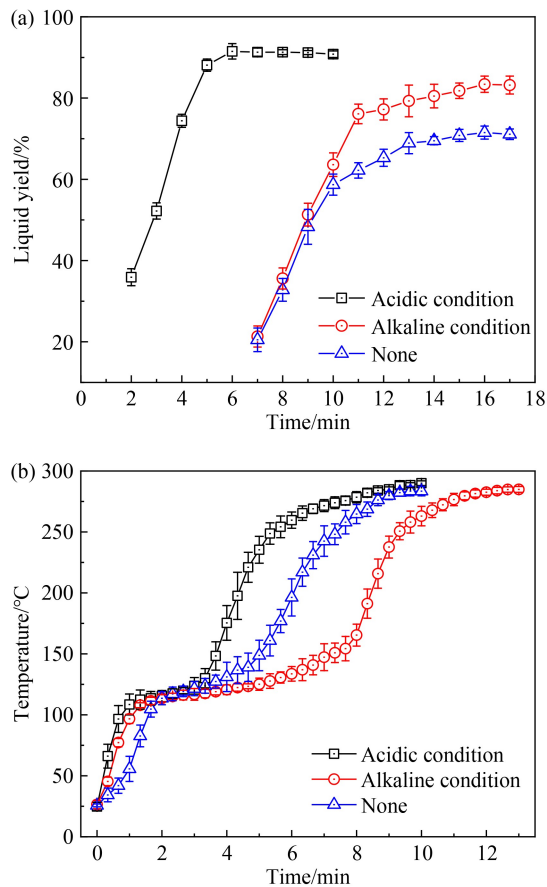
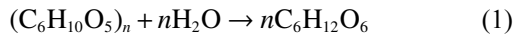


Fig. 3 The effect of time on (a) the liquid yield and (b) temperature with different pH conditions (PEG 200/glycerol: 3/1 (volume ratio); liquid–solid ratio: 7/1 (mass ratio without water); pH control: 1.25% H_2SO_4 , 1.25% NaOH (mass ratio)).

food waste. More details about the effects of the solution pH on the food waste liquefaction can be found in the next section.



The pH of the solutions was measured, as shown in Table S1 (cf. ESM). Clearly, the pH of the solution under the alkaline condition decreased from 12.78 to 8.03 in 12 min. This indicates that H^+ was generated in the PEL process, which can react with OH^- ions and reduce the catalytic effect. The decrease in pH under alkaline conditions resulted from the organic acids produced by the alcoholysis of carbohydrates, proteins, and lipids. In contrast, the pH of the solution changed slowly under acidic conditions [37]. The experimental results show that the optimal treatment times for acidic, no catalyst added, and alkaline conditions were 6, 12, and 14 min, respectively.

The rate of temperature increase is higher in the acidic condition than that under other conditions. Since H^+ ions have a much higher specific charge (charge-to-mass ratio) than OH^- ions, they are much easier to accelerate to

promote collisions with other species and to increase the thermal impact in the plasma environment. The thermal impact in the PE process mainly comes from resistance heating and the heating from the plasma-generated reactive species. When a high voltage is applied between the two electrodes, the electrons and H^+ move directionally under the action of the electric field to generate a current. The heating power can be calculated based on the equation $W = I^2R$, where I is the current and R is the solution resistance (solvent and food waste). On the other hand, the reactive species generated by the discharge have high energy, and the mass transfer, diffusion and collisions with other species would also heat the solution [11]. Higher temperature provides an environment that is more conducive to molecular dehydration and promotes interactions between energetic radicals and carbon-enriched materials. Moreover, the H^+ ions in the acidic solution can break the glycosidic bonds in cellulose, which is beneficial to the liquefaction of biomass. All these factors contribute to the difference of ~20% in the acidic and alkaline PE processes.

3.2.2 Effect of pH on liquid yield

The influence of solution pH on the liquid yield is directly demonstrated in Fig. 4, which shows that the liquid yield increased significantly with H_2SO_4 . However, the liquid yield decreased linearly with NaOH . Figure 4 also shows that 1.25% (mass ratio to the mixed solvent and food waste) H_2SO_4 or NaOH had the highest liquid yields. Results indicate that the solution pH has a great influence on liquid yield, and a high yield of leftover oil can be achieved at $\text{pH} < 7$, mainly due to the cleavage of β -O-4 bonds (glycosidic bonds) in cellulose and lignin by H^+ through charge transfer [38]. The degradation of cellulose can generate glucoside, and the glucoside can be

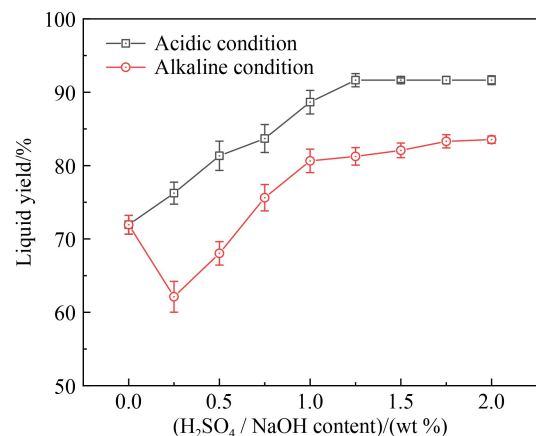


Fig. 4 The effect of solution pH on liquid yield (PEG 200/glycerol: 3/1 (volume ratio), liquid–solid ratio: 7/1 (mass ratio without water); solution pH adjusted by the addition of H_2SO_4 and NaOH ; treatment time: 6 min (acidic condition), 16 min (alkaline condition)).

decomposed in the alcohol solution to further produce a levulinic acid-like product. In contrast, the H^+ ions generated by PE will neutralize OH^- in the alkaline solution. The decrease in OH^- concentration affects the liquid yield of food waste. However, it should be noted that the relatively higher liquid yield under the alkaline condition than the none catalyst condition is that the electrolyte content is 0.3418 g (8 mmol) higher than that without any catalyst, and the treatment time is 4 min longer, resulting in a relatively complete liquefaction.

3.2.3 Liquid–solid ratio

The main component of the waste material was cellulosic biomass (Table 1). Polyol was chosen as the solvent with the liquid–solid ratio changed to measure the liquid yield. The results are shown in Table 2. Clearly, in all pH conditions, the liquid yield of food waste increased with the increasing liquid–solid rates. Moreover, when the liquid–solid ratio was greater than 7/1, the liquid yield rose slowly. Therefore, the liquid–solid ratio was set at 7/1 in subsequent experiments.

3.2.4 Solvent ratio

In this experiment, the total volume of the solvent was unchanged (20 mL). The ratio of PEG 200 and glycerin was changed, and the liquid yield is shown in Table S2 (cf. ESM). Table S2 shows that the optimal volume ratio of PEG 200 to glycerol was 3:1 providing the highest liquefaction yield. Therefore, the optimal parameters for the PEL processing of the waste material obtained by the single factor method were: PEG200/glycerol, v/v 3/1; pH condition: 1.25 wt % H_2SO_4 or NaOH; time: sulfuric acid = 6 min, none = 10 min, NaOH = 16 min. The corresponding liquid yields were 91.45%, 71.27%, and 81.65%, respectively. The method was also used to obtain the parameters of the dried waste material by oil bath heating. The optimal parameters were: PEG200/glycerol: v/v 3/1; pH condition: 1 wt % H_2SO_4 or NaOH; time: sulfuric acid = 12 min, none = 21 min, NaOH = 25 min. The corresponding liquid yields were 84.68%, 58.48%, and 62.66%, respectively.

Table 2 The influence of liquid–solid ratios on the liquefaction^{a)}

Liquid–solid ratios/(wt %)	Liquid yield/%		
	Acidic condition	Alkaline condition	None
3	42.21 ± 1.21	39.35 ± 1.08	37.07 ± 1.75
4	67.11 ± 1.13	45.64 ± 1.11	42.75 ± 1.56
5	90.32 ± 0.77	58.73 ± 0.78	52.67 ± 0.68
6	91.59 ± 0.58	72.46 ± 1.59	64.18 ± 0.87
7	91.88 ± 0.82	81.78 ± 1.84	69.74 ± 0.37
8	91.73 ± 0.47	82.83 ± 0.58	70.86 ± 0.67
9	91.88 ± 0.65	82.92 ± 0.47	72.37 ± 0.47

a) PEG 200/glycerol: 3/1 (volume ratio); pH control: 1.25% H_2SO_4 , 1.25% NaOH (mass ratio); H_2SO_4 , 6 min, none, 10 min, NaOH, 16 min.

The best parameters of the two liquefaction methods (PE and oil bath) are different in heating times, resulting in different liquid yields. The reason for the high liquid yield of PE is the free radicals generated by plasma. The diffusion of these free radicals into the solution can significantly increase the liquefaction effect and shorten the liquefaction time. The elemental analysis of the products obtained by these two methods is shown in Table S3 (cf. ESM) [11]. Table S3 shows that $O_{\text{bio-oil}} < O_{\text{leftovers}} < O_{\text{residue}}$, $C_{\text{bio-oil}} > C_{\text{leftovers}} > C_{\text{residue}}$, and $H_{\text{bio-oil}} > H_{\text{leftovers}} > H_{\text{residue}}$. Comparing the bio-oil obtained by PE with that obtained by oil bath heating, $C_{\text{PE}} > C_{\text{oil bath}}$, $H_{\text{PE}} > H_{\text{oil bath}}$, and $O_{\text{PE}} < O_{\text{oil bath}}$. The reason is that the plasma-generated active species, including electrons and $\cdot OH$, $\cdot CH_3$, $\cdot C_2$, etc., have strong oxidizing capacity. These species react with the macromolecules in the solution, tying up the oxygen needed to produce oxides. After liquefaction, a bio-oil with low oxygen content was obtained.

Comparing the oil obtained by PE with that obtained by oil bath heating, $C_{H_2SO_4} > C_{\text{None}} > C_{NaOH}$, $H_H^+ > H_{\text{None}} > H_{OH^-}$, and $O_H^+ < O_{\text{None}} < O_{OH^-}$. These results were caused by the strong oxidation and carbonization of concentrated sulfuric acid. The strong oxidizing effect of PE is the key factor because it can convert the organic macromolecules in the waste material into small molecules through the deoxygenation reaction. The main reactions are: dehydroxylation of alcohols ($C_2H_5OH + H \rightarrow \cdot C_2H_5 + H_2O$) [38] and oxidation of aldehydes ($C_2H_5OH + \cdot CH_3 \rightarrow CH_3OH + \cdot C_2H_5$, $CH_3OH + \cdot OH \rightarrow CH_2O + H_2O + H \cdot$) [39]. The loss of oxygen reduces the oxygen content in the bio-oil and increases its caloric value. The lost oxygen reacts with metals to form metal oxides ($M + H_2O \rightarrow MO + H_2$) [40], which enter the residue after filtering, explaining the significant increase in oxygen content in the residue. In addition, part of the oxygen is converted to gas and escapes the solution. The gases collected in the experiment were mainly CO , CO_2 , and NO_x .

3.3 Main elements and oxides in the residue

The leftover waste samples were liquefied by both the PE and oil bath processes under the optimized conditions. The contents of the elements and oxides in the residue were analyzed by XRF when the liquid yield was 55.7% (shortening the liquefaction time of the PE process). The relative elemental content in the waste stream and residues are shown in Table 3, which were found to differ significantly before and after treatment where the relative content of the metal elements in the residue obtained by PE was higher than that from the oil bath, and the relative content of the non-metal elements in the residue of the oil bath was higher than that from the PE. The two liquefaction methods had little influence on the content of the non-metal elements, such as S, P, Si, but a significant influence on the content of metal elements. The relative

Table 3 Relative content of the elements in the leftovers and residues

Element	Leftovers	Residues (PE at the acidic condition)	Residues (oil bath at the acidic condition)	Residues (PE at the alkaline condition)	Residues (oil bath at the alkaline condition)	Residues (PE and none)	Residues (oil bath only)
Na	21.44%	7.90%	6.52%	22.27%	19.52%	19.63%	16.30%
K	6.21%	1.73%	1.81%	8.18%	6.37%	4.62%	5.29%
Ca	9.71%	14.07%	9.06%	26.82%	22.71%	26.04%	21.58%
Mg	0.34%	0.25%	0.00%	1.36%	0.80%	1.46%	0.44%
Cl	48.53%	23.95%	18.84%	20.67%	29.48%	27.08%	33.48%
Fe	0.45%	0.77%	0.00%	1.36%	0.40%	1.22%	0.00%
Zn	0.22%	0.00%	0.00%	0.23%	0.40%	0.00%	0.00%
Al	0.01%	0.00%	0.00%	0.23%	0.40%	0.00%	0.00%
Si	0.68%	0.25%	0.00%	0.23%	0.00%	0.24%	0.00%
P	4.74%	3.21%	5.07%	3.86%	8.37%	3.89%	8.37%
S	7.67%	45.25%	58.70%	11.14%	11.55%	12.65%	14.54%
W	0.00%	2.63%	0.00%	3.64%	0.00%	3.17%	0.00%

content of metal elements in the residue with PE was greater than that of the oil bath heating. The metal relative content in the residue in PEL was $\text{OH}^- > \text{no catalyst added} > \text{H}^+$. The reason is the low solubility of metal ions in alkaline solutions. There was no tungsten element before liquefaction, but tungsten appeared in the solid product after liquefaction. This is caused by the tungsten anode losing electrons so that tungsten ions entered the solution during the PE process.

Table S4 (cf. ESM) shows that the relative content of oxides in the residues analyzed by XRF was: (1) There were no metal oxides in the leftovers before liquefaction, but metal oxides appeared after liquefaction. Indicates that PE heating and oil bath heating are both oxidation processes. This process reduced the content of metals and oxygen in the bio-oil. The oxidation in the PE process is stronger than that of the oil bath, so the content of the metal oxides in the residue was higher. (2) Na, K, etc., can be converted into oxides during liquefaction. The removal rate of the metal elements was best under alkaline conditions. Comparing Tables 3 and S4 show that the non-metal elements S and P were converted into oxides during the liquefaction. (3) The tungsten entering the solution in the PE process was converted into tungsten oxide and existed in the residue in the alkaline condition or when no catalyst was added. As a result, some tungsten was removed from the solution.

Tables 3 and S4 show that the relative content of the 7 elements Na, Mg, K, Ca, Fe, W, and Cl was high. The prepared samples were measured by inductively coupled plasma (ICP)-ion chromatography for the concentration of these 7 elements by Kaishipu (Shanghai) Testing Technology Co., Ltd. and the results are shown in Table S5 (cf. ESM). The data in Table S5 and the relative content of metal elements in Table 3 can be used to calculate the removal rate of the metal elements before and after liquefaction. The calculation formula (3) is [41]:

$$f(x) = \left(1 - \frac{x}{m} \times v\right) \times 100\%, \quad (3)$$

where x is the content of metal elements in the liquid (multiplied by the dilution factor) in ppm (10^{-6}); m is the mass of metal elements in leftovers in mg; v is the volume in L. The removal rate of metal elements in PE was as follows: Na (81.85%), Mg (82.00%), K (81.82%), Ca (98.32%), and Fe (99.25%); that in oil bath was: Na (60.50%), Mg (45.00%), K (44.98%), Ca (62.53%), and Fe (42.86%). The results show that the PEL removed more metal ions than the oil bath.

Thus, a strong oxidation reaction occurs in PEL, allowing the removal of most metals. This strong oxidation is mainly generated by free radicals in the plasma. During the spark discharge, a large number of electrons, ions, radicals and neutral particles can be produced. When electrons diffuse into the solution, they can react with H_2O or solvent to produce $\cdot\text{OH}$ radicals, which would further react with metal ions to form metal oxide residues. The results of X-ray diffraction (XRD) also showed that ionic crystals appeared in the residue after liquefaction, as shown in Fig. S5 (cf. ESM). Clearly, the residues after PE have a polycrystalline structure, while the original structure of dried food waste is amorphous. The XRF results also show that there is no Na oxide in the food waste, and Na_2O products appear in the residue after PE, which was consistent with the structure of XRD.

Free radicals can be determined by the emission spectrum of the plasma, including $\cdot\text{OH}$, $\cdot\text{CH}_x$, $\cdot\text{H}_\alpha$, $\cdot\text{C}_2$, etc. When these species diffuse into the solution, they quickly remove the oxygen of organic macromolecules from the sample and convert the organic macromolecules into small liquid molecules. In addition to O, the removal rate of N and Cl was also high. The N content in the bio-oil treated with PE was only 0.11%, with the Cl content also reduced from the original 21891.22 to 35.77 ppm. The nitrogen in the samples was mainly in the form of amino groups in proteins, and Cl existed mainly in the form of Cl^- . The amino groups were converted into ammonia gas, which was released during PE by the following process: $\text{CH}_3\text{C}(\text{OH})\text{NH} + \text{CH}_3\text{CONH}_2 \xrightarrow{\text{e}}$

$\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3\text{CN} + \text{NH}_3$. The Cl^- reacted with water to generate Cl_2 and H_2 during the PE by the following process: $2\text{XCl} + 2\text{H}_2\text{O} \xrightarrow{\text{e}^-} 2\text{XOH} + \text{H}_2 + \text{Cl}_2$ [42]. The removal of N and Cl was mainly caused by the gain and loss of electrons during PE [43]. In summary, the removal of O, N, and Cl is not only conducive to the increase in the calorific value of bio-oil but also improves the quality of the bio-oil.

Compared with the conventional oil bath, the developed PE process is also more oxidative due to the production of reactive oxygen species, as shown in Fig. S4. To analyze the origin of oxygen atoms, we carried out three sets of experiments. In each group, 15 mL of PEG 200 and 5 mL of glycerol were mixed with 6 mmol of ammonium chloride as solutions. In two groups, 2 mmol H^+ (52.3 μL H_2SO_4) or 2 mmol OH^- (0.08 g NaOH) were added, and no additions were included in the third group. Each group was treated with PE for 12 min. The ammonia, nitrate and nitrite ions in the treated solution were measured, as shown in Table S6 (cf. ESM). Results show that both NO_3^- and NO_2^- appeared in the solution after the PE process. Since the solvent is a polyhydric alcohol solution, it can be seen that the oxygen in the nitrate and nitrite originates from the hydroxyl groups of the solvent. The produced reactive oxygen species can oxidize the negative trivalent nitrogen in the ammonia root to positive trivalent and positive pentavalent. The metal elements in the food waste can also be oxidized to metal oxides.

Compared with the PE, the content of free radicals produced by the oil bath heating process is lower, leading to a relatively low metal removal rate. To analyze the mass balance of the metal elements in the PE and oil bath processes, the distribution of five metal elements (Na, Mg, K, Ca, Fe) before and after liquefaction is shown in Table S7 (cf. ESM). It also can be seen from Table S7 that the content of metal oxide residues after the PE is higher than that of the oil bath treatment.

We also found that the liquid yield of the PEL waste sample reached 74.5% without an added catalyst. This showed that the waste material contained anions that could catalyze the leftovers. The anions in the waste stream included Cl^- , nitrite, nitrate, carbonate, and ammonium ions as well as sulfate and phosphate. Neither sulfate nor phosphate have a catalytic effect on cellulose biomass [9,12]. Consequently, the following section focuses on the catalytic effect of nitrate, nitrite, carbonate, and ammonium ions.

Based on the absorbance curve for nitrite ion standard solutions, the linear relationship between the concentration of nitrite and the optical density is calculated, as shown in Fig. S6 (cf. ESM). For the nitrate ions measurement, nitrate ions in the solution are firstly reduced to nitrite ions, the original nitrite can be subtracted from the total nitrite to obtain the original nitrate concentration. The method for measuring the concentration of ammonium in the solution is similar to that for nitrite ion.

The carbonate content was measured by Kaishipu (Shanghai) Testing Technology Co., Ltd. The concentration of nitrite, nitrate, carbonate, and ammonium ions is shown in Table S8 (cf. ESM). Results show that the waste stream contained more nitrate, nitrite, and carbonate ions than the product. These anions with catalytic effects needed to be verified one by one with different catalysts.

The effects of NO_2^- , NO_3^- , NH_4^+ , CO_3^{2-} on the liquefaction rate under different pH are shown in Fig. 5. Figure 5(a) shows that the increase in nitrate and nitrite under acidic conditions (pH = 5.80) increased the liquid

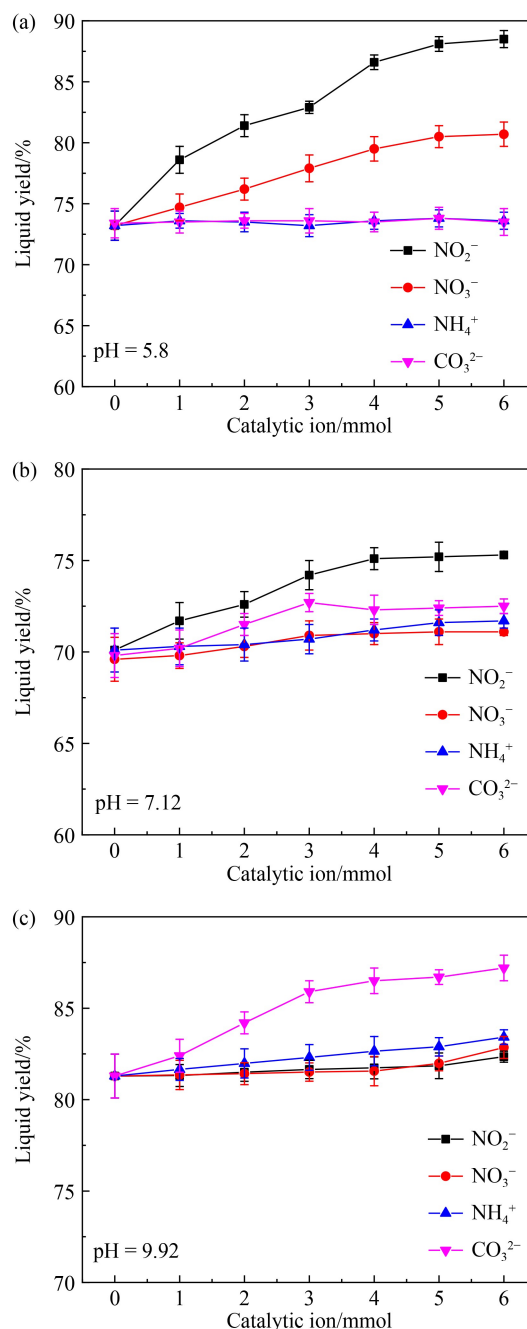


Fig. 5 Catalytic effect of anions under different pH conditions. (a) acidic; (b) neutral; (c) alkaline conditions.

yield by 8% and 15%, respectively. However, the increase in carbonate and ammonia had little effect on the liquid yield. The reason is the oxidation of nitrite and nitrate under acidic conditions. The oxidation of nitrite is stronger than that of nitrate [44], and the corresponding liquid yield is also higher than that of nitrate. Carbonate and ammonia are decomposed by heat in acidic conditions and thus cannot increase the liquid yield. Under alkaline conditions (pH = 9.92), the increase in carbonate had a greater impact on the liquid yield (the liquid yield increased by 12%), followed by nitrite (3%), ammonia, and nitrate. When no catalyst was added (pH = 7.11), the order of influence on the liquid yield was: nitrite (11%), carbonate (7%), ammonia (3%), and nitrate. Thus, the waste material was liquefied under the catalysis of nitrite and carbonate ions.

In addition, the content of anions in the bio-oil was significantly reduced. The reason is that the liquefaction product is weakly acidic and the anions volatilize at high temperatures. The experimental results show that the catalytic effect of the ammonia ion is weak under neutral and alkaline conditions. A possible reason is that ammonia is oxidized into nitrous and nitric acids by the plasma [45,46], weakening its catalytic effect. To confirm the above results 15 mL PEG 200, 5 mL glycerin, 2 mmol of ammonium chloride, and 6.67 mL water (no waste material) were used as solvents at different pHs. The content of ammonia, nitrate, and nitrite was measured with the results shown in Table S6. These results show that when the temperature of the solution was 285 degrees, most of the ammonia outgassed from the solution, and only a small amount of ammonia, nitrite, and nitrate remained.

The functional groups of the raw materials and products before and after liquefaction were analyzed by infrared spectroscopy, as shown in Fig. S7 (cf. ESM). Unlike the

infrared spectrum of the cellulose degradation products, a new spectral line appeared at 573 cm^{-1} . The peaks are the $-\text{NH}_2$ and $-\text{NH}$ characteristic absorption peaks [47]. Results show that the 573 nm peak for the raw materials was higher than that for the liquefied product. The reason is that the protein, fibers, and lipids in the waste material are decomposed under PE, which reduces the nitrogen content in the product.

Gas chromatography–mass spectroscopy (GC–MS) revealed nine main types of compounds: alcohols, acids, ammonia, aldehydes, phenols, ketones, quinolines, indoles, and hydrocarbons in the product. These are comparable to those reported in the literature [48]. The main gases produced by PE were H_2 (30.84%), CO (0.73%), CO_2 (8.66%), CH_4 (0.47%), NH_3 (48.32%), Cl_2 (10.33%), NO_x (0.52%), etc., as determined by GC–MS.

As shown in Fig. 6, the possible mechanisms of food waste conversion in the PE process are proposed. Food wastes mainly contained protein, cellulose, hemicellulose, lignin, lipids, carbohydrates, etc., which are also consistent with the main composition and products in Ref. [49]. Among those, lignin can be hydrolyzed into benzene ring oligomers, then produce phenol by dehydration cyclization; cellulose hydrolysis can form monosaccharides, and further dehydration contributes to the formation of acid, ketone, alcohol and epoxide; protein hydrolysis can produce amino acids, which can be converted to organic acids by deamination. Further decarboxylation of organic acids can produce alkane alkenes; lipid hydrolysis can produce glycerol and fatty acids. Glycerol dehydration can form aldehydes, while fatty acids can be decarboxylated into alkane olefins. It should be noted that most of NH_4^+ in the electrolysis process can be converted into ammonia by electrons, rather than the maillard reactions. In addition, due to the complex composition of food waste, further studies of the

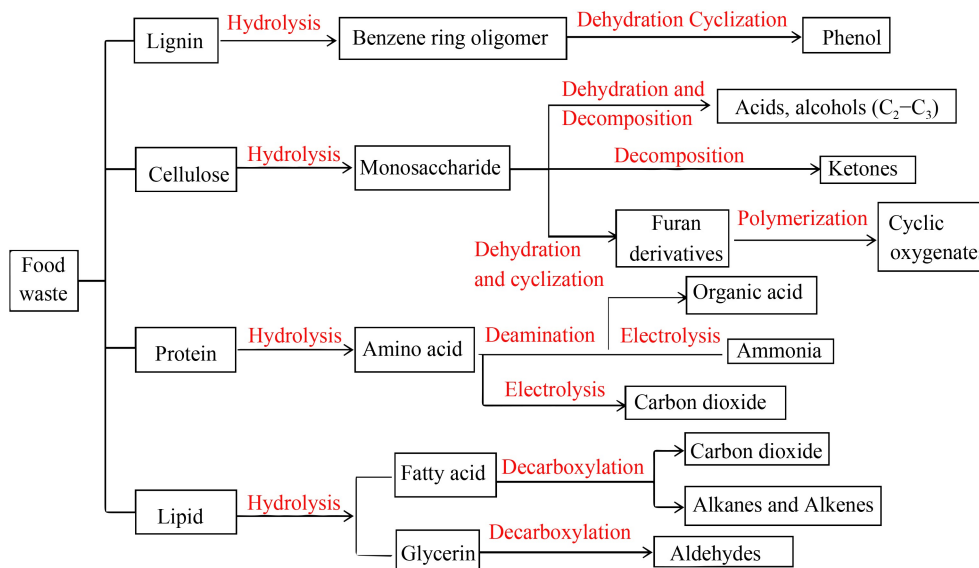


Fig. 6 Possible mechanisms of food waste (lignin, cellulose, protein and lipid) conversion in the PE process.

radicals-induced chemical reactions during PE should be investigated.

4 Conclusions

This study demonstrated that pulsed energy delivered by PE efficiently liquefied waste food under different pH conditions, producing bio-oil, and recycling ammonium, chlorine, and metal oxides. The liquid yield was 74.52% with no catalyst added. The content of C and H in the bio-oil increased, and the O content decreased, resulting in an HHV of 25.86 MJ·kg⁻¹. The bio-oil contained a high proportion of aldehydes and cyclic oxygenates. The XRF and ICP-MS results indicated that chloride ions and amino groups generated ammonia and chlorine gas by gaining and losing electrons during the electrolysis and that metal elements were oxidized by free radicals to generate metal oxides. These experiments show that nitrite and carbonate have a catalytic effect under neutral conditions with no added catalyst. This strategy may offer a green avenue for clean chemical production and sustainable resource recovery from food waste and provide new insights and guiding principles for modern biorefineries.

Acknowledgements Project supported by the National Natural Science Foundation of China (Grant No. 51877184).

Electronic Supplementary Material Supplementary material is available in the online version of this article at <https://dx.doi.org/10.1007/s11705-022-2255-y> and is accessible for authorized users.

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