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Solar pyrolysis of cotton stalk in molten salt for bio-fuel production

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A B S T R A C T

Solar pyrolysis of cotton stalk was carried out in a molten salt reactor heated by 4 kW solar simulator. The effects of pyrolysis temperature and mass ratio of molten salt to biomass on pyrolysis products properties were investigated. The use of molten salt as pyrolysis media increased gas yield. At 850 °C, the gas yield (mainly of CO and H₂) continued to rise from 41.35 wt% to 82.57 wt% when mass ratio of molten salt to cotton stalk increased from 0 to 10. Pyrolysis in molten salt significantly decreased bio-oil acids and phenols, while increased aromatics among pyrolysis temperature range of 450–850 °C. There was positive correlation between the increased content of aromatics and mass ratio of molten salt to cotton stalk (from 0.5 to 10). The bio-char carbon content showed a general decreasing trend while oxygen, BET surface area and pore volume increased with using molten salt as pyrolysis media. Bio-char obtained from CS1MS5 pyrolysis at 850 °C had the highest BET surface area of 972.57 m²/g and the biggest total pore volume of 0.6203 cm³/g. High quality pyrolysis products with more uniform chemistry suggest catalytic reactions occur inside the solar reactor due to the intermediates degradation with molten salt.

Keywords:

Solar pyrolysis

Molten salt

Cotton stalk

Bio-gas

Bio-char

1. Introduction

Due to the negative environmental impacts of fossil fuels and the increasing global energy demands, biofuels are receiving increasing attention as the best short-term substitute for petroleum fuels. Pyrolysis is a promising thermochemical process for converting biomass into biofuels (bio-gas, bio-oil and bio-char) [1]. However, the thermal energy driving the pyrolysis process is typically drawn from combustion of the feedstock or other fossil energy sources. To produce a truly carbon-neutral fuel and maximize the yield of biofuel per unit biomass consumed, the energy driving the pyrolysis reactions must come from a renewable energy source. Concentrated solar energy fits the requirements of a heat source for an externally heated pyrolysis process. Solar radiation is concentrated using mirrors to provide temperatures high enough to drive biomass pyrolysis reactions that are able to store this solar thermal energy in a chemical form as biofuels [2–4].

Supplying process heat with concentrated solar energy has

numerous advantages over conventional pyrolysis [5]. There is no need for partial combustion which allowing all of the feedstock to be upgraded into bio-fuel; the product gas contains low CO₂ and N₂, and no other combustion by-products; the energetic value of the product is greater than that of the feedstock. Besides, pyrolysis driven by direct concentrated solar irradiation has the benefits of high temperatures and rapid heating rates [6]. The biomass can be rapidly heated to around 500 °C and thus maximizes exposure to the higher temperatures that favor vapors formation. Hence, high yields of bio-oil will be obtained at normal pyrolysis temperatures of about 500 °C because vapors passing from the high temperature region (the focus of concentrated solar radiation) to the low temperature zone (the surrounding gas) are quickly condensed, thus minimizing the secondary decomposition of primary tar into gas [7]. Fuel calorific value of carbonaceous feedstock can be upgraded by direct solar pyrolysis process, which enables the storage of solar energy in chemical form as bio-oil, bio-char and bio-gas whose proportion mainly depending on the temperature [8,9].

The previous work on pyrolysis driven by direct irradiation of concentrated solar energy has demonstrated many benefits, however issues related to transient sensitivity, poor heat transfer and

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tar production have been persistent motivating the search for an improved approach to solar pyrolysis. Concentrated solar energy can be effectively stored in molten salt, then providing high temperature heat for biomass pyrolysis [10]. The use of molten salts allowed the continuous operation of solar pyrolysis system. Besides, the biomass particles can be dispersed in molten salt, which is beneficial to enhancing the bio-fuels production rate and yield. This can be attributed to two main reasons [11]: fast heat transfer rate and catalytic effect of alkali metal-based catalyst. The fast heat transfer was attributed to a high convective heat transfer with high heat capacity [12]. The alkali metal cations play an important role in the catalytic phenomenon of biomass pyrolysis with three main steps: (1) biomass devolatilization; (2) tar and char formation and (3) tar dissociation by molten salt [13].

Several researchers have performed laboratory bench scale experiments using molten salt for biomass pyrolysis. The temperature, amount and composition of molten salt have been shown to influence the pyrolysis reactions. The heating rates of sapwood pyrolysis at 600–900 °C in molten salt were 4–10 times higher than those without molten salt, the heating rate can be up to 4100–16700 °C/min in a mixture of sodium chloride (NaCl) and potassium chloride (KCl) at 900 °C [14]. Maximum heating rates for cylindrical beech wood pellet (30 mm length and 3.5 mm diameter) pyrolysis in LiNaKF salt were 46–56 °C/s [15]. The total energy input required for wood pyrolysis at 900 °C equal about 20% of its heating value [16].

Besides, molten salt changed the proportion of three-state products. When wood pyrolysis in molten carbonates, the yield of liquid products decreased while the yields of gas and char increased [17]. Higher gas yield and less complex bio-oil composition were obtained in a bath of nitrate molten salts (60 wt% NaNO₃ and 40 wt% KNO₃) at 500 °C [18]. The yields of bio-oil obtained from cellulose/rice stalk pyrolysis in mixtures of metal chlorides and nitrates molten salts at temperatures ranges of 400–600 °C increased and then decreased with increasing temperature, and the optimal temperature was 530 °C [19]. Lignin was pyrolyzed in mixtures of molten salt (ZnCl₂ and KCl) with molar ratios of 3/7 and 7/6 at temperatures from 500 to 800 °C [20]. It was found that a molar ratio of 7/6 at 600 °C had a high selectivity to cresols with a maximum yield of 4.6 wt%. The effect of salt amount was also investigated with different salt-to-lignin ratios (1, 2 and 3) [21]. In addition, the lowest yields of gas products and the highest yield of phenolic compounds except for phenol were obtained at salt-to-lignin ratio of 1. The presence of molten salt in cellulose pyrolysis could increase its conversion to syngas by 30% at 850 °C and the maximum conversion of 98 wt% was achieved at 915 °C [22]. The use of molten salt increased the total hydrocarbon compounds with decreasing oxygenated compounds during coal pyrolysis [23].

Most of these studies were focused on the distribution and composition of products obtained from pyrolysis in molten salt. However, little information is available on the formation mechanism and mutual transformation process of products during solar pyrolysis of biomass in molten salt, despite this information is very important for realizing the high-valued conversion of biomass. Therefore, it is necessary to deeply investigate all products (bio-oil, bio-char and bio-gas) for revealing pathways of intermediates degradation with molten salt. In this study, solar pyrolysis of cotton stalk in molten salt (Li₂CO₃-Na₂CO₃-K₂CO₃) was conducted in a 4 kW solar simulator reactor. The effects of temperature (450, 550, 650, 750 and 850 °C) and molten salt amount (the mass ratio of molten salt to biomass was 0.5, 1, 5 and 10) on the molten salt pyrolysis of biomass were investigated by characterizing the total products.

2. Experimental

2.1. Experimental sample

2.1.1. Cotton stalk

Cotton stalk (CS) was crushed into small particles with size of 0.1–0.4 mm, and then dried at 105 °C for 24 h. The proximate analysis of the air-dried cotton stalk feedstock was 77.49 wt% volatile, 4.60 wt% ash, 16.04 wt% fixed carbon, and 1.86 wt% moisture. The elemental composition of the dried feedstock was 46.56 wt% carbon, 6.04 wt% hydrogen, 41.82 wt% oxygen, and 0.79 wt% nitrogen.

2.1.2. Molten salt

Lithium, sodium and potassium carbonates (analytical purity > 99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were well-mixed with mass ratio of 1:1:1. Then, the ternary eutectic blend salts were put in a corundum crucible and heated to 600 °C for 2 h in muffle furnace. The salts were crushed into fine particles by a grinder once they were cooled down to atmospheric temperature. The fine particle salts were defined as molten salts (MS), and the melting point of MS was approximately 400 °C [24].

2.1.3. Pyrolysis feedstock

For each pyrolysis experiment, about 1 g of cotton stalk was weighted then well mixed with MS. The mass ratio of MS to cotton stalk for mixture were 0, 0.5, 1, 5, 10 denoted as CS, CS1MS0.5, CS1MS1, CS1MS5 and CS1MS10, respectively.

2.2. Experimental procedure

2.2.1. Experimental setup

Solar pyrolysis experiments were performed in molten salt reactor heated by a 4 kW solar simulator instead of the real sun as shown in Fig. 1. Solar simulators can overcome the shortcomings of real sunlight such as the periodicity and randomness of solar irradiance [25]. What's more, they can present significant advantages in terms of size, cost and operational flexibility [26]. They are very important and valuable for fast and cost-effective indoor laboratory in certain research fields, such as the pyrolysis [27] and gasification [28] of carbonaceous feedstock.

The solar simulator consists of three 5 kW xenon arc lamps and three accompanying parabolic concentrators. The lamps and concentrator are adjusted to the right position making sure the focus in the same point. The position of solar simulator focus can be changed by adjustable screw devices. The solar simulator can produce concentrated radiation similar to the solar spectral pattern (mostly in the visible and IR spectra) [29], with irradiative flux densities ranging from 0.2 to 1.5 MW/m² within 800 mm diameter circle. A shutter with moving parallel carbon composite blades modulates the concentrated flux impinging molten salt reactor and finally the pyrolysis sample temperature. The molten salt reactor is a 30 mm diameter by 40 mm long cylindrical graphite crucible within a 150 mm transparent Pyrex balloon enclosure, which is positioned vertically at the solar simulator focus. Temperature sensor (K-type thermocouple) is sited at the rear of the reactor in contact with the reactor inner wall to measure the sample temperature. The required heating rate and temperature are set on a PID controller, which controls the shutter opening based on the measured sample temperature. The balloon is swept with nitrogen flow controlled by a mass flowmeter for keeping wall clean.

2.2.2. Experimental procedure

The pyrolysis sample was weighed and placed into the graphite crucible (molten salt reactor). The graphite crucible was put inside

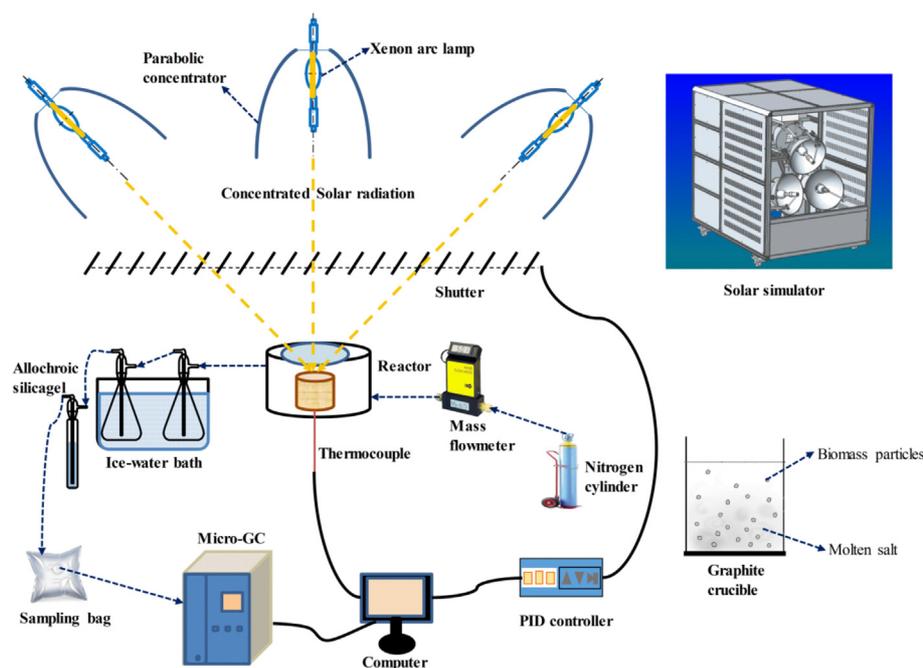


Fig. 1. Schematic of the solar pyrolysis in molten salt experimental setup.

the transparent Pyrex balloon and set at the solar simulator focus. The balloon was purged in 3 min by nitrogen gas with a flow rate of 2000 ml/min for inert atmosphere. Then the pyrolysis unit swept by 500 ml/min nitrogen was heated to target temperatures (450, 550, 650, 750 and 850 °C) at heating rate of 10 °C/s with PID controller on. The pyrolysis temperature was remained stable for 30 min until the reaction was completed. The gas mixture produced from pyrolysis was cooled by the ice-water mixture condensing unit for the condensable volatiles collection, whereas the non-condensing gas was collected with gas bag. After each run, the solid residues were retained in graphite crucible after turning off the solar simulator. The carrier gas flow was still on for 5 min until solid residues cooled to the ambient temperature. Each experiment was run at least three times to ensure the repeatability. The RSD for the experiment was less than 5%. The error bars indicate 95% confidence intervals.

2.2.3. Product recovery and characterization

According to molten salt mass ratio in pyrolysis feedstock, the solid residues was washed with sufficient amount of hydrochloric acid solution (1 mol/L) for removing molten salt. The mixture was stirred in the magnetic agitator for 3 h at room temperature. After stirring, suction filtration device was utilized to filter and wash suspension mixture until the filtrate was neutral. The solid left after filtration was dried at 105 °C in oven to constant weight, and then was weighed and recorded as the “bio-char” yield. The “gas” yield was calculated by combining the volumes of all the gases collected in the gas bag. The “bio-oil” yield was calculated by the mass difference of the conical condenser after the reaction.

The bio-char was weighed and characterized as our previous study [30]. Ultimate analysis was carried out in a CHNS/O elementary analyzer (Vario Micro Cube, Germany). The specific surface area and pore size distribution were analyzed with Surface Area and Porosity analyzer (TriStar II, Micromeritics Instrument Corp., Norcross, USA). Prior to each analysis, the sample was degassed at the temperature of 150 °C under a vacuum for 20 h. Nitrogen adsorption isotherm was obtained at the temperature

of –196 °C in the relative pressures (P/P_0) range between 0.05 and 0.99. The BET surface area, micropore volume and total pore volume were calculated with the Brunauer–Emmett–Teller (BET) equation, t-plot method and single point adsorption total pore volume analysis, respectively [31].

The gas compositions were analyzed using a dual-channel gas chromatography (Panna A91, Panna Instruments Co., Ltd, Changzhou, China). H_2 , N_2 , O_2 , CO_2 , CH_4 and CO were separated by Porapak Q column and 5 A zeolite molecular sieve column with He as carrier gas and analyzed by a thermal conductivity detector (TCD). Olefins and alkanes (C_{2+}) were separated using a Al_2O_3/KCl capillary column with N_2 as carrier gas and analyzed by a flame ionization detector (FID). Content of N_2 in produced gas was calculated as the reference to obtain the yield of each gas. Heating program of columns was set as below, columns was maintained at 80 °C for 4 min and heated to 150 °C at a heating rate of 10 °C/min, then maintained at 150 °C for 6 min.

The main compositions of bio-oil were determined using gas chromatography-mass spectrometry (GC-MS; Agilent 7890 A series GC coupled with an HP5975 MS detector) with He. The detail of GC-MS and test method has already been described in our previous study [32]. All the compounds were identified based on NIST mass spectral data library with response factors for GC quantification determined by internal standard method [4].

3. Results and discussion

3.1. Final product distribution

Fig. 2 compares the products distribution from solar pyrolysis of cotton stalk without and with molten salt. For CS pyrolysis (without molten salt), the gas yield noticeably increased from 24.09 wt% to 41.35 wt% when pyrolysis temperature increased from 450 to 850 °C shown in Fig. 2a, while the liquid yield significantly decreased from 42.08 wt% to 33.65 wt% indicated in Fig. 2b, char yield decreased from 34.64 wt% to 25.11 wt% depicted in Fig. 2c. This result suggests that the increase in the gas yield is primarily

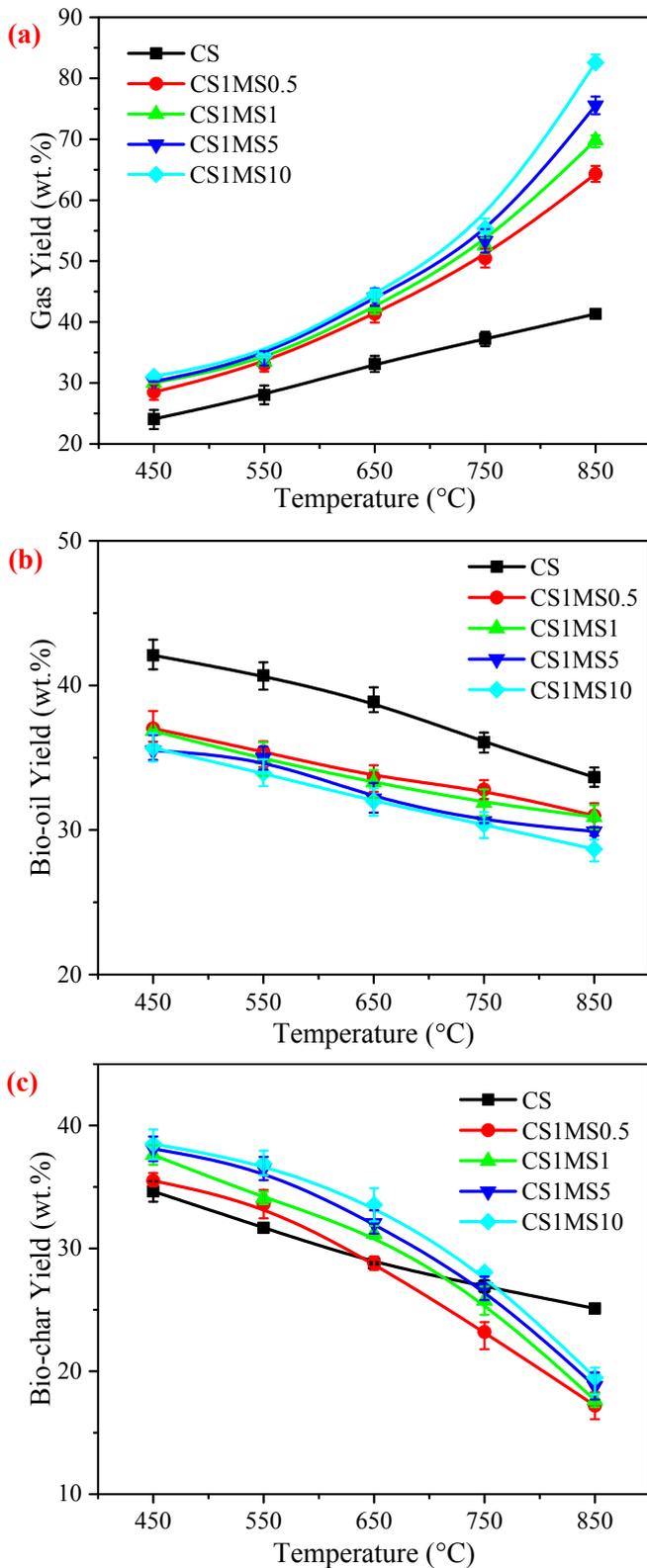


Fig. 2. Effects of temperature and molten salt amount on the product distribution of solar pyrolysis: (a) Bio-gas yield, (b) Bio-oil yield, and (c) Bio-char yield.

ascribed to the secondary tar cracking and char decomposition, which can be confirmed by the reduce in liquid and char yields [2]. The secondary reactions of tar into gas prevail at temperatures

above 600 °C [1]. The changing trend of product distribution with pyrolysis temperature was almost the same for cotton stalk pyrolysis with and without molten salt. For CS1MS10 pyrolysis, the gas yield distinctly increased from 31.07 wt% to 82.57 wt% with pyrolysis temperature rising from 450 to 850 °C (Fig. 2a), while the liquid yield decreased from 35.67 wt% to 28.68 wt% (Fig. 2b), char yield remarkably decreased from 38.50 wt% to 19.50 wt% (Fig. 2c).

For the same pyrolysis temperature, the use of molten salt as pyrolysis media increased gas yield at the expense of liquid product or char. The increase of gas yield was strongly due to the catalytic activity of the alkali species in the molten salt for cotton stalk pyrolysis. Molten salt made sure a fast heat transfer rate because of its high thermal conductivity and heat capacity [11]. Then the cotton stalk thorough dispersion in liquid salt enabled rapid heating for higher pyrolysis rate [22]. It was expected to obtain more primary vapor products due to more rapid devolatilization at pyrolysis [33]. With the help of alkali carbonate salts catalysis effect, the primary vapor secondary cracking reaction into gas product would be promoted at higher pyrolysis temperature [34]. Meanwhile, the char and molten salt might react to produce more gas at higher temperature (>700 °C) [35], and this also made the mass balance of pyrolysis over 100% at high temperature (750 and 850 °C). Then the increase of gas yield became more significant with increasing pyrolysis temperature indicated in Fig. 2a.

At pyrolysis temperature of 850 °C, the gas yield continued to rise from 64.31 wt% to 82.57 wt% when mass ratio of molten salt to cotton stalk increased from 0.5 to 10 shown in Fig. 2a. A higher molten salt mass ratio meant more effective contact of alkali carbonates with the cotton stalk so that the secondary reaction of tar into gas product increased [23]. Meanwhile, more molten salt could participate in the reaction with char, thus producing more gas. However, there was no statistically significant change in gas yield with different molten salt mass ratios when the pyrolysis temperatures were lower than 850 °C. It was mainly attributed to the not so obvious catalytic effect of molten salt (Na_2CO_3 and K_2CO_3) for tar secondary reactions and the reaction with char when the temperature was lower than 800 °C [22].

The existence of molten salt could not only catalyze the decomposition of volatile matter, but also might inhibit the release of volatile matter, thus reducing the yield of the bio-oil and increased the yield of bio-char. Yasunishi, A. et al. [14] has also found that when wood was pyrolyzed in molten carbonates, the yield of liquid products decreased while the yields of gas and char increased. The inhibitory effect of molten salt on volatile release enhanced with the increase of molten salt mass ratio. So the liquid yields obtained from CS1MS5 and CS1MS10 were lower than those from CS1MS0.5 and CS1MS1 indicated in Fig. 2b.

It was observed that molten salt use slightly increased the char yield at low pyrolysis temperatures (450–650 °C) but it further decreased when temperature increased to 850 °C (Fig. 2c). The displacement of pyrolysis reaction at lower temperatures induced by alkali metals favors the charring reactors versus fragmentation and depolymerization reactions in the primary decomposition of biomass, thereby increasing char yield [36]. The decrease of char yield at higher temperatures (750 and 850 °C) were mainly because K_2CO_3 and Na_2CO_3 could further promote the cleavage of C-H and C-O bonds and aromatization of char during pyrolysis [37] while carbon in the char would simultaneously reacted with carbonates as the reaction (1) [38]. However, considering the error bars, there was no big difference of the char yields obtained with different molten salt mass ratios under the same pyrolysis temperature.



3.2. Pyrolysis gas composition

Fig. 3 shows the yields of H₂, CO₂, CO, CH₄ and C₂₊ during pyrolysis of cotton stalk without and with molten salt at different temperatures. For CS pyrolysis (without molten salt), the H₂ releasing clearly increased from 2.15 to 81.64 ml/g with pyrolysis temperature increasing from 450 to 850 °C shown in Fig. 3a. And CO distinctly increased from 42.07 to 138.55 ml/g depicted in Fig. 3b, CH₄ noticeably increased from 8.93 to 47.86 ml/g indicated in Fig. 3c, C₂₊ increased from 5.00 to 18.68 ml/g as shown in Fig. 3d. While, temperature had a limited influence on the yield of CO₂ in this temperature range (Fig. 3e). Below 450–550 °C, most of

permanent gases directly came from degradation of biomass chemical structures (hemicellulose, cellulose and lignin) as volatile secondary reactions was negligible [1]. However, the increase of H₂ and CO were mainly due to tar secondary reactions as temperature increases above 450–550 °C [39]. Simultaneously, most of the remaining tars convert into CH₄ and C₂₊ [4].

The changing trend of gas compositions with pyrolysis temperature was almost the same for cotton stalk pyrolysis with and without molten salt. For CS1MS10 pyrolysis, H₂ yield clearly increased from 11.33 to 162.43 ml/g with pyrolysis temperature increasing from 450 to 850 °C shown in Fig. 3a. And CO distinctly increased from 36.60 to 388.68 ml/g depicted in Fig. 3b, CH₄

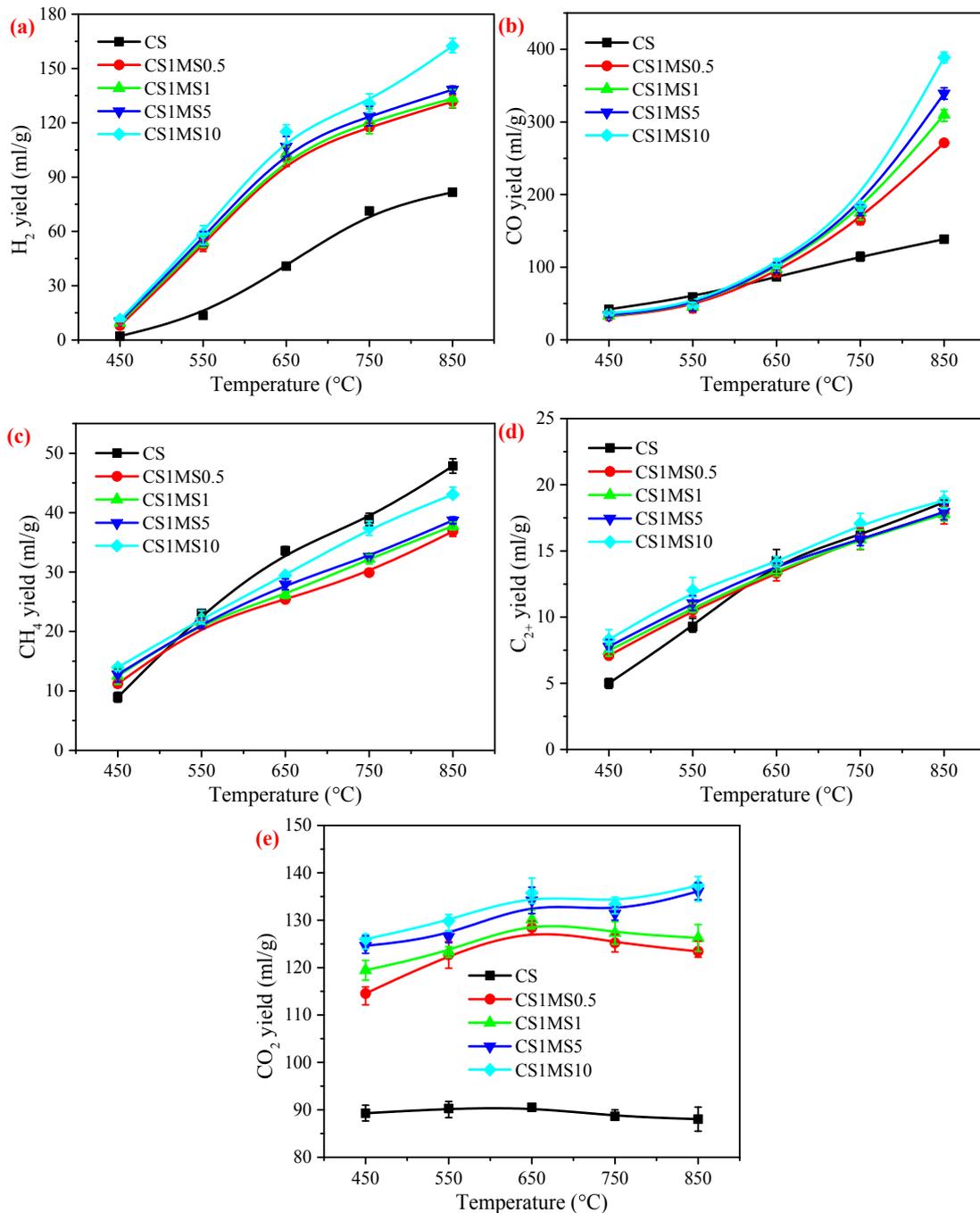
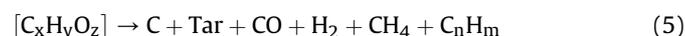
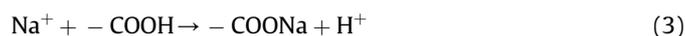


Fig. 3. Effects of temperature and molten salt amount on the gas product compositions of solar pyrolysis: (a) H₂ yield, (b) CO yield, (c) CH₄ yield, (d) C₂₊ yield, and (e) CO₂ yield.

noticeably increased from 13.96 to 43.07 ml/g indicated in Fig. 3c, C_{2+} increased from 8.30 to 18.81 ml/g as observed in Fig. 3d. At the same pyrolysis temperature, H_2 yield showed a general increasing trend with molten salt media (Fig. 3a). With Na containing molten salt, the added Na^+ and $-COOH$ or $-OH$ groups in cotton stalk reacted as reactions (2) and (3) for releasing H^+ , which promoted H_2 formation [40]. Furthermore, the increase trend of H_2 yield became more pronounced with pyrolysis temperature rising. It was mainly due to the enhancing catalytic activity of the alkali species in the molten salt for tar cracking reaction (4) at higher temperatures [11].



Using molten salt as pyrolysis media also increased CO yield by 1–3 times compared to those without molten salt when temperature was above 550 °C. The catalytic cracking of tar at higher temperatures for producing CO as (4) was enhanced by molten salt [40]. With the use of molten salt (Na_2CO_3 and K_2CO_3), CO_2 produced during primary pyrolysis stage would react with carbon bonded with Na or K as reactions (5), (6) and (7) before its evolution from biomass or coke surface [23]. What's more, the char would react with carbonates over 700 °C for generating CO by an intermolecular redox reaction (1) [38]. The extend of these reactions increased with temperature rising, and therefore CO yield increase became more and more significant with increasing temperature.



In contrast, a lower CH_4 production was in the molten salt pyrolysis when temperature was above 550 °C (Fig. 3c). It was consistent with a report that 30% of CH_4 conversion at 900 °C in molten salt as (8) [41]. A comparison between pyrolysis without and with molten salt showed that variation on the yields of C_{2+} were very small (Fig. 3d). It was also reported by Blasi et al. [36]. Significant increase was observed for CO_2 with the use of molten salt (Fig. 3e). The increase of CO_2 was mainly due to CO conversion via water gas shift reaction (9) and partly because of carbonate salt decomposition reactions (10), (11) [12,23].



It indicated that the increase of mass ratio of molten salt to cotton stalk from 0.5 to 10 could promote H_2 and CO production at pyrolysis temperature of 850 °C. Increasing molten salt content increased the secondary reaction of tar since more tar could contact with the salt. However, there was almost no change in H_2 and CO yields with different molten salt mass ratios when the pyrolysis temperatures were lower than 850 °C. As shown in Fig. 3c and e, the yields of CH_4 and CO_2 obtained with 10 and 5 mass ratio of molten salt to cotton stalk was higher than those with 0.5 and 1 mass ratio

of molten salt to cotton stalk. This may be because more alkali metal salts (Na, K) could promote the cracking and catalytic reforming reactions between organic compounds and methane [42].

3.3. Bio-oil characterization

Fig. 4 describes the composition of bio-oil from cotton stalk pyrolysis without and with molten salt at temperatures of 450–850 °C. Bio-oil contained a wide range of organic compounds that can be divided into several main groups: Acids, Linear alcohols/aldehydes/ketones, Furans, Cyclopentanones, Phenols, Aromatics and N-species. For cotton stalk pyrolysis (Fig. 4a), the relative content of aromatics tended to increase from 10.07% to 45.30% with the pyrolysis temperature from 450 to 850 °C. Significantly higher aromatic hydrocarbons could be attributed to the enhanced formation of polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene, anthracene, naphthalene with temperature rising [43]. While acids, linear alcohols/aldehydes/ketones and phenols gradually reduced from temperature 450–850 °C. This was because these functional groups were mainly formed from the

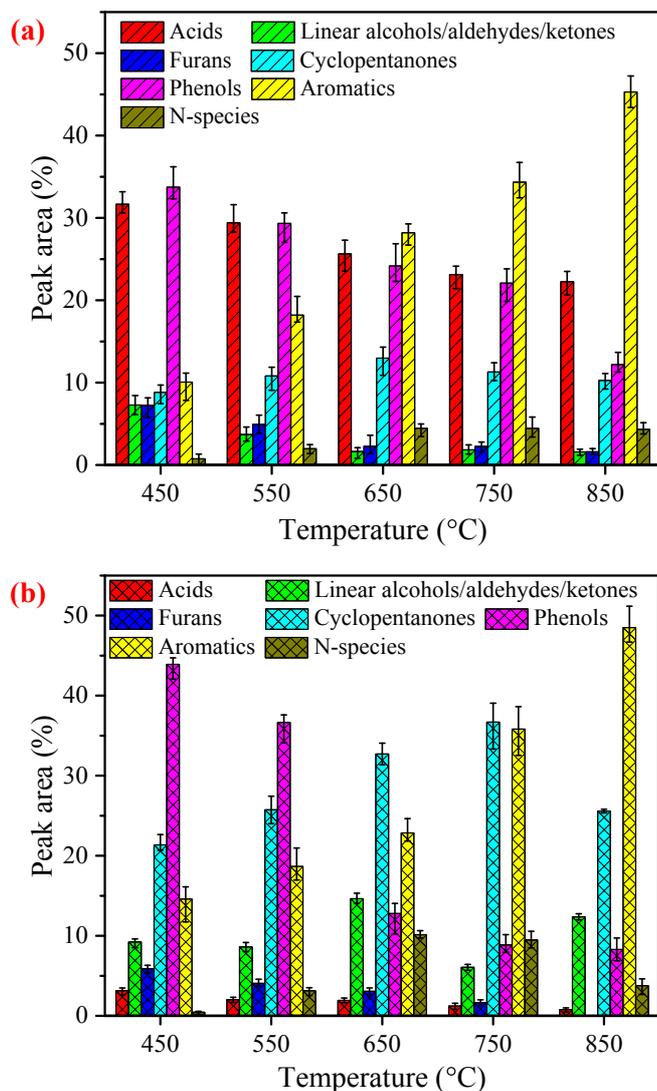


Fig. 4. Effects of temperature on the bio-oil chemical composition from solar pyrolysis of: (a) CS and (b) CS1MS1.

depolymerization of hemicellulose and cellulose at temperature lower than 350 °C [44]. As the final pyrolysis temperature increased, the functional groups experienced secondary cracking for producing more stable species.

For cotton stalk pyrolysis with molten salt (Fig. 4b), the changing trend of bio-oil composition with pyrolysis temperature was very different from that without molten salt. Molten salt pyrolysis caused a noticeable decrease in bio-oil acids content (3.14%–0.77% versus 31.67%–22.26% of original cotton stalk) among pyrolysis temperature range of 450–850 °C. The decrease of acids was mainly due to enhanced catalytic cracking of the cracking of carboxylic acids by molten salt components ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) [45]. Moreover, alkali and alkaline earth metals in molten salt were able to promote the catalytic conversion of acidic substances and oxygenates in the bio-oil through ketonization and the aldol reaction for more ketones production [46]. However, the cyclopentanones content in molten salt pyrolysis was more than twice that of pyrolysis without molten salt. The addition of Li, Na or K in molten salt would be attributed to the improvement of cyclopentanones formation, as they would enhance the cleavage of C-O bond and the formation of new C-C bond in bio-oil [47]. When cotton stalk was pyrolyzed in molten salt, phenols significantly decreased. In the presence of alkali and alkaline earth metal catalyst, lignin-derived phenolics undergo oxygen-aromatic carbon bond cleavage to form aromatic hydrocarbons [48,49]. It was also confirmed by the fact that molten salt presence increased the relative content of aromatics in the bio-oil.

The main functional groups (Acids, O-species (furans/aldehydes/ketones/alcohols), Phenols and Aromatics) are selected for further comparison indicated in Fig. 5. As depicted in Fig. 5a, the reduction of acids in pyrolysis bio-oil was most evident when the mass ratio of molten salt to cotton stalk was 10. The most obvious decrease of acid was mainly due to optimum catalytic effect achieved with this

mass ratio [19]. However, with the mass ratio of molten salt to cotton stalk increased from 0.5 to 10, the relative content of acids in pyrolysis bio-oil gradually decreased. As shown in Fig. 5b, the o-species (furans/aldehydes/ketones/alcohols) increased when mass ratio of molten salt to cotton stalk increased from 0.5 to 10 at lower pyrolysis temperature (450, 550 and 650 °C). Ketonization and the aldol reactions for more ketones and alcohols production were promoted due to the effective contact of bio-oil compounds with more molten salt catalyst at high mass ratio of molten salt to cotton stalk. However, the o-species might be transformed into gaseous products, which would reduce its relative content at high temperature. Increasing molten salt mass ratio promoted the catalytic cracking of phenols when pyrolysis temperature above 550 °C indicated in Fig. 5c. It should be noted from Fig. 5d that there was positive correlation between the increased content of aromatics and mass ratio of molten salt to cotton stalk (from 0.5 to 10). In fact, the higher the molten salt ratio was used, the better dispersion of cotton stalk in molten salt obtained. Then increasing molten salt content increased the secondary tar reaction of into aromatics since it enhanced the catalytic effect of molten salt (Na_2CO_3 and K_2CO_3) [23].

3.4. Bio-char characterization

The elemental analysis of bio-char obtained from pyrolysis of cotton stalk without and with molten salt are listed in Table 1. For cotton stalk pyrolysis, the carbon content in bio-char increased with increasing pyrolysis temperature while the hydrogen and oxygen contents declined sharply. The carbonaceous structure graphitization at high temperatures lead to increased the carbon content [33]. The decrease of hydrogen and oxygen contents was due to the char weak bonds cracking and cleavage [50]. The changing trend of bio-char composition with pyrolysis temperature

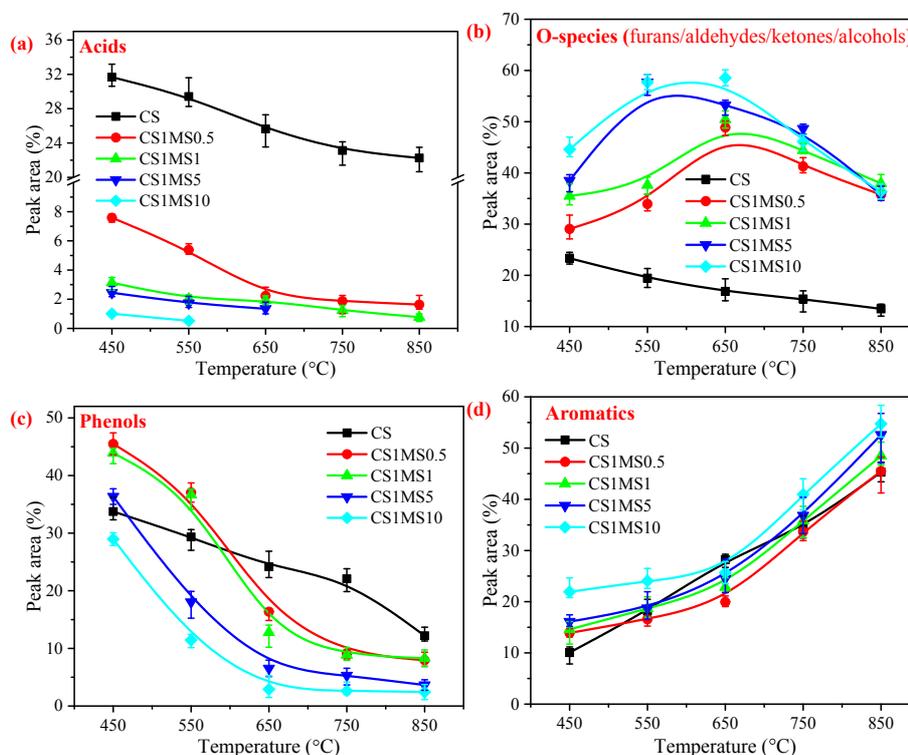


Fig. 5. Effects of temperature and molten salt amount on the main functional group distribution of bio-oil from solar pyrolysis: (a) Acetic acid, (b) O-species (furans/aldehydes/ketones/alcohols), (c) Phenols, and (d) Aromatics.

Table 1

Effect of pyrolysis temperature and mass ratio of molten salt to biomass on char composition.

Char samples	Ultimate analysis (wt.%, daf)			
	C	H	N	O ^a
CS-450	81.97	3.51	1.89	12.63
CS-550	86.06	3.10	1.76	9.08
CS-650	90.13	2.45	1.44	5.98
CS-750	93.42	1.96	1.31	3.31
CS-850	94.42	1.56	1.34	2.69
CS1MS0.5-550	83.70	2.66	1.27	12.37
CS1MS0.5-850	84.92	1.02	0.62	13.44
CS1MS1-550	75.79	2.59	1.19	20.43
CS1MS1-850	81.85	1.75	0.28	16.12
CS1MS5-550	77.86	3.60	1.27	17.27
CS1MS5-850	83.71	1.25	0.16	14.88
CS1MS10-450	74.16	3.51	1.29	21.04
CS1MS10-550	78.54	2.61	1.23	17.63
CS1MS10-650	78.44	2.31	1.01	18.24
CS1MS10-750	79.16	2.11	0.45	18.28
CS1MS10-850	78.98	1.53	0.09	19.40

daf: dry ash free basis.

^a By difference.

was different for cotton stalk pyrolysis with and without molten salt. At the same pyrolysis temperature, carbon content showed a general decreasing trend while oxygen increased with molten salt media. The decrease of carbon content was mainly due to the enhanced C-C bonds cleavage by alkaline metals in molten salt [36]. Alkaline cations due to small size could penetrate into the biomass/char structure and cause the bond of oxygen as reactions (2) and (3) [40]. However, there was no obvious influence of molten salt mass ratio on bio-char composition.

Table 2 lists the BET surface area and pore volume of bio-char obtained from pyrolysis of cotton stalk without and with molten salt. For cotton stalk pyrolysis, the BET surface area increased from 2.12 to 222.31 m²/g as temperature increased from 450 to 850 °C. Meanwhile, the micropore volume increased from 0.0011 to 0.0978 cm³/g, the total pore volume increased from 0.0038 to 0.1395 cm³/g. Intensifying volatile release with increasing temperature caused the increase of surface area and pore volume [50]. The changing trend of bio-char BET surface area and pore volume with pyrolysis temperature was almost the same for cotton stalk pyrolysis with and without molten salt. At the same pyrolysis temperature, BET surface and pore volume showed an obvious increasing trend with molten salt media. For CS1MS10 pyrolysis, the BET

surface area increased from 1.90 m²/g to 873.44 m²/g as temperature increased from 450 to 850 °C. And the micropore volume increased from 0.0009 to 0.3210 cm³/g, the total pore volume increased from 0.0051 to 0.5567 cm³/g.

At 850 °C, the BET surface area of CS1MS10 bio-char increased about 4 times compared with that of CS bio-char. Simultaneously, both of micropore and total pore volumes increased about 4 times. The use of molten salt catalyzed the pyrolysis reaction of cotton stalk, which enhanced volatile release for creating bio-char with higher BET surface area and pore volume. In addition, the generated H₂O and CO₂ during pyrolysis process reacted with carbon for porous carbon formation, which called activation process [51]. Molten salt just could promote the activation process for more porous bio-char with high surface area and pore volume. However, bio-char obtained from C1MS5 pyrolysis at 850 °C had the highest surface area of 972.57 m²/g and the biggest total pore volume of 0.6203 cm³/g. BET surface area and pore volume of bio-char decreased with mass ratio of molten salt to cotton stalk increasing from 5 to 10. The results proved that loading excessive amounts of molten salt could enter the inner interspace through the surface crack of char, which resulted in blocking some micropores and decreasing the specific surface of bio-char [40].

4. Conclusion

Solar pyrolysis of cotton stalk in molten salt media has been investigated with a 4 kW solar simulator. At pyrolysis temperature of 850 °C, the syngas mainly composed of CO and H₂, continued to rise from 41.35 wt% to 82.57 wt% when mass ratio of molten salt to cotton stalk increased from 0 to 10. Pyrolysis in molten salt significantly decreased bio-oil acids (3.14%–0.77% versus 31.67%–22.26% of original cotton stalk) and phenols, while increased aromatics among pyrolysis temperature range of 450–850 °C. There was positive correlation between the increased content of aromatics and mass ratio of molten salt to cotton stalk (from 0.5 to 10). The bio-char carbon content showed a general decreasing trend while oxygen, BET surface and pore volume increased with using molten salt as pyrolysis media. BET surface area and pore volume of bio-char decreased with mass ratio of molten salt to cotton stalk increasing from 5 to 10. Solar pyrolysis of biomass in molten salt can be considered as a promising method for producing syngas (rich in H₂ and CO), high quality bio-oil (little acids) and bio-char (large BET surface area), which storing solar energy in chemical form at the same time.

Table 2

Effect of pyrolysis temperature and mass ratio of molten salt to biomass on char surface area and pore volume.

Char samples	BET surface area (m ² /g)	Pore volume of micropore (cm ³ /g)	Total pore volume (cm ³ /g)
CS-450	2.12	0.0011	0.0038
CS-550	11.63	0.0155	0.0155
CS-650	84.24	0.0320	0.0556
CS-750	192.26	0.0854	0.1157
CS-850	222.31	0.0978	0.1395
CS1MS0.5-550	5.68	0.0040	0.0087
CS1MS0.5-850	802.29	0.2935	0.4900
CS1MS1-550	1.41	0.0018	0.0041
CS1MS1-850	904.60	0.3128	0.5387
CS1MS5-550	1.94	0.0027	0.0070
CS1MS5-850	972.57	0.2881	0.6203
CS1MS10-450	1.90	0.0009	0.0051
CS1MS10-550	6.08	0.0035	0.0080
CS1MS10-650	340.41	0.1533	0.2060
CS1MS10-750	641.49	0.2784	0.3895
CS1MS10-850	873.44	0.3210	0.5567

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