Fast pyrolysis characteristics of two typical coastal zone biomass fuels by thermal gravimetric analyzer and down tube reactor

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**ARTICLE INFO**

**Keywords:**
Biomass
Fast-pyrolysis
Bio-oil
TGA
Down tube reactor

**ABSTRACT**

This study aimed at investigating fast pyrolysis behavior and products distribution of two typical coastal zone biomass fuels (Jerusalem artichoke stalk (JAS) and reeds (Re)) by TGA and a homemade down tube reactor. The kinetic analysis with different ramping rates was conducted by FWO and DAEM models. The liquid, gaseous and solid products are characterized to study the influence of temperature. Results indicate that high heating rates may be overcome some resistances to mass or heat transfer inside the particles of biomass, and lead to a higher conversion rates and Re species is preferable to JAS in terms of thermochemical conversion because of the lower apparent activation energy for total conversion. Moreover, the pyrolysis conditions - temperature under fast pyrolysis in a down tube pyrolysis unit will make the covalent bonds in the biomass degradation more rapidly, gave significant influence on the yields and properties of liquid, gaseous and solid products.

1. Introduction

Biomass as the only renewable carbon sources in nature are considered to be huge amount, environmentally friendly and carbon neutral resources (Kumar et al., 2018). Exploiting biomass as an energy source not only maximizes deal with the agricultural and forestry waste, but also refining high value-added products. Pyrolysis is a thermochemical process that can be categorized as two different processes based on the operational conditions: fast and slow pyrolysis. In general, biomass fast pyrolysis process, with and without catalyst, provides about 58 to 77% condensable gas, 13 to 28% noncondensable gases, and 6 to 13% char (Chen et al., 2015), which can be directly or refined to be used as fuels for vehicles, gas turbine fuels and chemical raw materials, etc.

Some of the several bench and pilot scale reactor technologies for fast pyrolysis include fluidized bed reactors, ablative pyrolysis reactors, and entrained flow pyrolysis reactors. However, due to the fact that the ordinary fluidized bed requires gas to promote the fluidization of the biomass feedstock, the cooling load is large, and some fine powder in the bio-oil produced is difficult to remove, which affects the reaction conditions for improving the yields of the target bio-oil component (Li et al., 2017). Ablative pyrolysis reactor requires mechanical actuation and more complex than other types of reactors (Peacocke and Bridgwater, 1993). For entrained flow pyrolysis reactors, biochars buildup can be a troublesome, liquid yields are usually lower than fluid bed systems (Brown et al., 2001). However, the down tube reactor has proven to be a suitable alternative with free-fall reactor to implement the fast pyrolysis process. It has several features, including of parallel flow of the gravitational force field, short solidification or gas-solid contact time, rapid heating rates, uniform radial distribution, small catalyst back mixing, and flexible adjustment of solid/gas or solid/solid ratio. It is not only maintaining the advantages of fluidized bed reactor in modified high liquid yield and large-scale production, but also the vapors can be cooling rapidly to make the bio-crude products. Moreover, the cooling load and energy consumption of down tube reactor are greatly reduced, and is easy to remove dust in oil relatively (Warnecke, 2000). Therefore, the down tube reactors will be the best reactor to be developed and applied for the biomass fast pyrolysis and oil upgrading modification technology.

Coastal zone, is a narrow interface zone between marine and terrestrial areas. It providing rich agricultural lands, and is typically held as public heritage and connects land and sea (Ramesh et al., 2015). However, coastal wet lands and coastal agricultural zones are seriously affected by the salinity issue. Coastal wetlands comprise various habitat types, including salt marshes, mangroves, seagrasses, salt swamps, and sand dunes, because of their transitional situation between sea and terrestrial ecosystems, affected by salinity (Paul and Lade, 2014). Saline-alkali soils are a major area in the vicinity of seawater as in
coastal regions. The crops living on saline-alkali soils have high salt-tolerant content due to salt inhibits plant photosynthesis, protein synthesis and lipid metabolism (Paul and Lade, 2014). Jerusalem artichoke stalk (Helianthus tuberosus L. JAs) is one of the most promising non-food biofuel crops due to its wide adaptability, high resistance, high biomass production, extensive use and environmental friendliness. In addition, it can tolerate 7–10 g salt/kg soil in coastal mudflat areas. The Key Lab of Marine Biology of Jiang-su province studied the introduction, selection and breeding of energy crops in Laizhou, Shandong province, and Dafeng, Jiangsu province, and screened out Jerusalem artichoke Nanyu1 and Nanyu2 genotypes that have high seawater tolerance, substantial biomass production and high energy density (Long et al., 2007). JAs can be used as a source of biomass for direct pyrolysis to produce electricity on a large scale. The stalks contain mainly inulin, fructooligosaccharides and fructose (structural carbohydrates (cellulose and hemicellulose)). The common reed (bulrush), Phragmites australis (Cav.) Trin. exSteu. (Re), described as it is one of the most widely distributed plant species on the planet, covering approximately ten million hectares, commonly found in coastal wetlands and along the upland edge of tidal marshes due to their higher salt tolerance (Zhao et al., 2011). Re is an especially promising energy plant and chemical feedstock due to it would loses its green and becomes dry under natural conditions throughout the late fall and winter, this greatly reduces the cost of drying process.

While there is a substantial amount of literature on pyrolysis of different lignocellulosic-based biomass, literature data on pyrolysis of JAs or Re are scarce. Encinar et al. (2009) explored the influence of the operating variables and determined the optimal conditions of the pyrolysis process for JAs waste. Experimental results showed that the temperature has a greater impact on the solid and liquid yields and gas phase yield. The variation of the initial sample mass and the particle size do not exert a defined influence in the yield of the three phases. Also, Li et al. (2013) studied the pyrolytic characteristics of Jerusalem artichoke tubers at heating rates of 5, 10, 20 and 30 °C min⁻¹, and used distributed activation energy model (DAEM) to study the pyrolysis kinetics. Results showed that there were three distinct stages of mass loss and the major loss occurs between about 190–380 °C. Heating rate brought a lateral shift toward right in the temperature. Barbootti et al. (2012) evaluated the possibility of common reed as a candidate biomass feedstock by the thermogravimetry. TG analysis indicated that the material loses 4% of its weight below 150 °C through dehydration. The main decomposition reaction occurs between 200 and 390 °C. Kinetic analysis helped in the resolution of the temperature ranges of the overlapping steps. Anastasakis et al. (2016) chose heating rate (600 °C/s) and holding time (10 s) at peak pyrolysis temperature simulated the industrial processes by a heated foil reactor coupled to an FTIR spectrophotometer for herbaceous (reed) biomasses. The results indicated that the maximum tar yield of 23.3 wt% of dry reed at 600 °C, char yield of 16.7 wt% at 800 °C and of 32.4 wt% at 700 °C for reed, maximum CO yield of 18 wt% at higher pyrolysis temperatures (> 700 °C). While most available studies emphasized the effects of pyrolysis condition by TGA or TG-FTIR on different biomasses, a detailed study of the pyrolysis mechanisms and products of coastal biomass for high salt-tolerant JAs and RE in a down tube reactor under high heating rate is non-existent but critically needed.

More so, there is a research gap in pyrolysis behaviors of coastal zone biomass with high salt-tolerant in a down tube reactor. In this study, we aim to fill this gap by investigating pyrolysis apparent kinetics and product distribution of JAs and Re biomasses with high salt-tolerant in a down tube reactor to evaluate the yield and quality of the products (bio-oils, biochars and pyrolysis gas) systematically. This paper is separated into two parts. The first part investigates the devolatilization behaviour of JAs and Re biomass fuels by Thermal Gravimetric Analyzer (TGA) under high heating rate conditions simulating free-fall processes in a down tube reactor. The second part of the research work emphasizes on the products distribution with an aim to investigate the product yields under fast pyrolysis of JAs and Re fuels in the free-fall reactor. The influence of temperature on fast pyrolysis in a down tube pyrolysis unit was clarified simultaneously.

2. Materials and methods

2.1. Biomass samples

High seawater tolerance Jerusalem artichoke stalks (JAs) were provided by the Key Lab of Marine Biology of Jiangsu province, China. Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences provided Reed (Re) samples, it was taken at wetland of the Yellow River Delta, Shandong province, China. All biomass samples powder (particle size ≤ 1 mm) were dried at 100 °C. The proximate analysis was calculated according to the Chinese National Standards (GB/T 28731–2012) (Liting Han and Chen, 2008) and the ultimate analysis was measured by an Elementar Analysensysteme GmbH (Vario MACRO cube, Germany). In order to investigate the difference on pyrolysis activity and conversion between two types of fuels, AAEM species (Na⁺, K⁺, Mg²⁺, Ca²⁺) contents was detected by inductively coupled plasma mass spectrometry (ICP-MS, 2030, Shimadzu Company, Japan).

2.2. Experiment apparatus

2.2.1. TG analysis

In order to determine the kinetics of devolatilization procedure, the Thermal Gravimetric Analyzer (NETZSCH Instruments, STA 449 F3 Jupiter®, Germany) was adopted. The main advantage of this analyzer type is that it is possible to reproduce similar conditions to industrial processes by employing very high heating rates (500–550 °C/min) and temperatures. The analyzer was placed in a continuous atmosphere of inert nitrogen (99.999 purity) at a flow rate of 100 mL/min to investigate the mass loss of JAs, RE and the formation of volatiles. The operation process of TGA based as per reported method (Zhao et al., 2014). Heating rate (100, 300 and 500 °C/min) and holding time (10 s) at pyrolysis temperature (1000 °C) were chosen to correspond to conditions encountered in free-fall reactor processes. At the same time, the high heating rates can be minimizing heat and mass transfer effects in the calculations of kinetic parameters.

2.2.2. The design of down tube reactor

The down tube reactor was designed and home-installed following the aforementioned literatures (Wang et al., 2018), and on this basis getting improved. The pyrolysis device was mainly used to accomplish research objectives that exploring the correlation between fast pyrolysis reaction conditions of biomass and target product yields. The device was shown in Fig. 1, which mainly consisted of the nitrogen supply unit, biomass feeding unit, down tube reactor unit, liquid collector, and gas measuring device unit. Among them, in the down-tube reactor, we designed a reaction platform to promote complete pyrolysis of biomass, and the platform was covered with a wire mesh cup so that we could collect biochar. The entire reactor was heated by an insulated electric furnace with a temperature control system. The lower part of the reaction tube is connected to the collector, the inner diameter is 10 mm, and external heat insulating cotton is applied to prevent the pyrolysis steam from condensing on the tube wall. The liquid condensation separation collector is a rigid plastic tube with a built-in absorbent packing absorbent cotton for fully absorbing liquid bio-oil and allowing small molecules to pass. The absorbent cotton is generally two layers and is replaced once after each experiment.

About 1 g of the pretreated biomass sample loaded into a rubber tube. The rubber tube is clamped on both sides with a spring clip and then connected to the biomass injection hole. High-purity nitrogen (99.999%) was first purged the reactor at a flow rate of 100 mL/min for 10 min. The reactor tube was subsequently heated to 650 °C at 10 °C/min. When the setting temperature was reached, constant temperature
for 10 min, the spring clip was turned to ensure that the sample slips into the reactor instantaneously. Biomass samples undergoes high heating rate during slipping. Pyrolysis time was set to about 10 min to ensure the complete release of volatiles. The condensable gas can condense quickly after passing through the condensing unit. Non-condensed gas is collected by air bag after passing through the gas-purifying unit. Biochars was collected after cooling to room temperature.

2.3. Experimental procedure

2.3.1. Apparent reaction kinetics analysis

In order to provide a theoretical basis for optimizing the reflection operation and better design of reactors, it is necessity to carry out the researches on the pyrolysis mechanisms and kinetics of JAs and Re under high heating rate. The kinetic analysis of pyrolysis of biomass resources by thermochemical analysis technology can reveal the physical and chemical changes occurring in the pyrolysis process, and grasp the characteristics, process characteristics and pyrolysis laws of biomass pyrolysis products comprehensively (El-Sayed and Mostafa, 2014). The core of thermal analysis kinetics is to determine the mechanism of its reaction and related kinetic parameters. Among them, pyrolysis activation energy is an important parameter of kinetics. According to different calculation methods, it can be divided into model-free and model-fitting methods. However, model-fitting methods may reach analogous conclusions: almost any conversion function can satisfactorily fit experimental data at the cost of estimating drastically different kinetic parameter values. The uncertainty in estimating kinetic parameters caused by the use of model-fitting methods can be avoided in the use of isoconversional methods (Sánchez-Jiménez et al., 2013). The model-free methods mainly include Friedman method, Flynn-Wall-Ozawa method (FWO), Kissinger-Akahira-Sunose method (KAS), etc (Chen et al., 2017). In this study, the FWO and DAEM methods were used to simulate the kinetic reaction. The FWO method avoids the choice of the reaction mechanism function, and can directly determine the activation energy value (E_a) to avoid the errors that may be caused by the assumption of the reaction mechanism function (Kandelbauer et al., 2009). The DAEM method can not only obtained the continuous distribution activation energy value, but also grasped the variety trends of activation energy in the whole pyrolysis temperature range. The DAEM model assumes that the pyrolysis process of organic matter is a series of irreversible first-order independent reactions that exhibit a Gaussian distribution function (Shen et al., 2011). For biomass, this assumption is appropriate because biomass consists of a series of chemical structures and extremely complex organic matter that have their own pyrolysis behavior during pyrolysis. In addition, due to the influence of other different types of components around, even if the same organic component exhibits different pyrolysis behavior, the biomass thermal decomposition reaction exhibits a wide distribution of E_a values. Extrapolating these kinetic parameters from experimental data obtained in high heating rate conditions simulating free-fall processes in down tube reactor is therefore of primary importance.

The non-isothermal pyrolysis reaction of a solid sample can be considered as an isothermal process during an infinitesimal reaction time period. The rate of pyrolysis reaction can be expressed by the following typical equation:

$$\frac{dx}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha)$$

(1)

where $t$ is the reaction time, $\alpha$ is the conversion rate, $A$ is pre-exponential factor, $E_a$ is the activation energy, $f(\alpha)$ is the reaction
equation, respectively. \( \alpha \) can be defined by the mass of the sample that has been decomposed, and can also be calculated based on the amount of volatiles that have been released. The calculation equation is as follows:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}
\]

where \( m_0 \) is the sample mass in pyrolysis process when \( t = 0 \), \( m_t \) is the sample mass in when \( t = t \) and \( m_f \) is the mass at the end of the process, respectively.

The pyrolysis conversion rate can be expressed by the following typical equation:

\[
\frac{da}{dT} = \frac{dx}{dt} \frac{df}{dx} = \frac{dx}{dt} \frac{1}{\beta} \tag{3}
\]

The Eq. (1) can also be written as:

\[
\frac{da}{dt} = \frac{k(T)}{\beta} f(\alpha) = \frac{A}{\beta} \exp \left( -\frac{E_a}{RT} \right) \theta(\alpha) \tag{4}
\]

It is assumed that \( g(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)} = \frac{A}{\beta} \int_0^\alpha \exp \left( -\frac{E_a}{RT} \right) dT \)

Approximate processing of temperature integral equation \( g(\alpha) \approx -5.33 - 1.03x \) according to Doyle’s, and taking the natural logarithm of both sides of equation (5), the FWO dynamic equation can be obtained.

\[
\ln \beta \alpha = \ln \left( \frac{AE_a}{Rg(\alpha)} \right) - 5.335 - 1.0516E_a \tag{6}
\]

In the FWO model, \( \ln \beta \alpha \) is also plotted against \( 1/T \) at three different heating rates at the same conversion rate, and the slope of the parallel fitting straight line is \( -1.0516E_a/R \), and \( E_a \) is calculated therefrom.

As mentioned earlier, the DAEM method assumes that the biomass is a series of irreversible first-order independent reactions in the pyrolysis process, and \( E_a \) exhibits a Gaussian distribution trend during the reaction and is represented by the \( f(E) \) function. The DAEM equation can be expressed by the following formula.

\[
1 - \frac{V}{V^*} = \int_0^{\alpha_m} \exp \left( -A \int_0^\alpha \exp \left( -\frac{E_a}{RT} \right) dT \right) f(E) dE \tag{7}
\]

Wherein \( T \) is the reaction temperature, \( V^* \) is the total volatiles in the sample, and \( V \) is the volatiles that have been released at the reaction time \( t \). The reaction activation energy function conforms to the following normalized equation:

\[
\int_0^{\alpha_m} f(E) dE = 1 \tag{8}
\]

Miura et al. proposed a simplified DAEM model and successfully applied it to the calculation of dynamic three-factors in the pyrolysis process of biomass. The Arrhenius equation for simplifying the DAEM model can be expressed by the following formula:

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{A}{E_a} \right) + 0.6075 - \frac{E_a}{RT} \tag{9}
\]

Based on Eq (9), \( E_a \) and \( A \) can be calculated simultaneously by the slope and intercept of the fitted line.

2.3.2 Products characterization and analysis

Bio-oil is a complex mixture, the upper layer is a light brown oil that dissolves in water, and the lower layer is a black heavy oil that is insoluble in water (Sanna et al., 2011). The chemical properties of the lower heavy oil are more complicated. After acetone and filtration, GC–MS analysis shows that each peak represents a mixture of several substances, which is difficult to search efficiently. Therefore, further exploration and detection methods are needed. Take a certain amount of bio-oil samples separately, mix thoroughly in a constant-temperature magnetic stirrer, and analyze the bio-oil components by GC–MS (Agilent Technologies, 5973–6890 N). The operating parameters are as follows: (1) GC: DB-1701 capillary column (60 m×0.25 mm×0.25 μm), the column temperature is programmed, the initial temperature is 60 °C, and the temperature is raised to 240 °C at 10 °C/min for 10 min. The inlet temperature is 280 °C, split injection, the split ratio is 80:1, the carrier gas is helium. (2) MS: Electron bombardment (EI) ion source, the electron energy is 70 eV, the scanning range is 12–550 amu, the ion source temperature is 150 °C, and the interface temperature is 240 °C. Mass spectrometry analysis of the identified chemicals contrast with the NIST08 library database. This enabled the detection of the yields of the major compounds of primary and secondary pyrolysis reactions as functions of temperature conditions. The compounds were quantified using the absolute area corresponding to each peak per milligram of sample pyrolyzed (Chagas et al., 2016).

Biochar is mostly distributed on the platform wire mesh, which is easy to collect and quantify. In addition, a small amount of biochar adheres to the tar at the bottom of the reactor and in front of the glass condensing tube. This part of biochar needs to dissolve the washing pipe with solvent, and filter then dry. The two parts of biochars were combined and weighed. The biochars were fixed to an adhesive carbon stub and covered with gold using a sputter coater at 30 mA for 5 min (Wang et al., 2018). SEM images were obtained at different magnifications (HITACHI S-4800 Scanning Electron Microscopy, Tokyo, Japan).

Pyrolysis gas was detected by GC, with argon as the carrier gas, the column consists of a capillary column and a packed column. The detector includes a thermal conductivity detector (TCD) and a hydrogen flame ionization detector (FID). The qualitative analysis is performed by a standard gas comparison method, and the quantitative analysis is performed by a single-point external standard method of peak area.

3. Results and discussion

3.1 Sample characteristics

The properties analysis of JAs and Re are listed in Table 1. These values are comparable to the results of similar biomass in the aforementioned literatures (Patuzzi et al., 2013; Sun et al., 2012). The content of volatile matter determines whether the biomass species is suitable for the thermal conversion process. The volatile matter contents of the samples were 67.40 and 72.12 wt% for JAs and Re, respectively. The differences of JAs and Re in the content of volatile matter could be attributed to the chemical component, molecular structure, component proportion and various extractives (Yang et al., 2006). Another point need to focus on is the amount of ash, Re (8.47%) has a higher ash content than in JAs (3.34%). There are controversial in the role of ash now. Many researchers believed that ash content can limit heat and mass transfer while producing all kinds of problems such as agglomeration, slagging, and fouling in boilers (Hu et al., 2017). However, some experts hold the view that ash is also a good heat carrier and contributed to the pyrolysis process (Zhang et al., 2010). The alkali and alkaline earth metallic (AAEMs) species have the significant enhancement for the biomass pyrolysis. From Table 1 (a), we can found that the Re has a higher AAEMs (mainly K+, Na+, Ca2+ and Mg2+) content than JAs. Wang et al. (2018) found that these inorganic elements can be present in biomass in numerous forms, such as a free ion and salts. Furthermore, covalent bonds between inorganic elements and the organic biomass structure are seen as well (e.g. proteins). The HHV value of JAs and Re is 15.69 MJ/kg and 16.16 MJ/kg, respectively.

According to the ultimate analysis, the N and S content range at 0.1–1.5%, evidencing that biomass is a green, clean energy source and it is an important driving force for improving environmental quality. Re and JAs biomass fuels were found that the main components are cellulose, hemicelluloses and lignin. Additionally, extractives of biomass
also proved by Zhou et al. (2016). The phenomenon can be attributed to heating rates of 100 °C/min, which means that more Re samples are (15.65 wt%) contain large quantities than JAs (30.68 wt%) was found to contain large quantities than JAs. As observed, JAs and Re species shows a trend that the mass lose effects at 250–350 °C, the phenomenon is more obvious in the DTG curves of Re, and JAs are only re-fi-marks. This phenomenon indicates that the high heating rate is benefi-cial to the devolatilization and inhibition for biochar formation. The main reason of this phenomenon maybe attributed to that the pro-longed preheating in the low temperature range of 250–300 °C dehy-drates and carbonizes of the cellulose component inside the biomass, causing generate large amounts of biochars after reformed the cellulose structure (Várhegyi et al., 1994). This reaction can also be explained by the fact that the cellulose polymer tends to be carbonized by dehy-drination and crosslinking reaction at a low temperature (Shen and Gu, 2009).

Total mass losses for the JAs were determined as 79.05, 80.69 and 83.16% on original basis at the heating rates of 100, 300 and 500 °C/ min, respectively. The mass losses for the Re were determined as 70.29, 71.66 and 75.21%, respectively. From these we can see that the conversion rate increases slowly from the 100–300 °C/min, and the conversion rate increases faster when the heating rate reaches 500 °C/min. This phenomenon may be attributed to some resistances to mass or heat transfer inside of the biomass at lower heating rate, these resistances maybe overcomed by means of strengthened driving forces of mass and heat transfer inside the particles of biomass as an increase in heating rate, and lead to a higher conversion rate (Haykiri-Acma et al., 2006). Analysis from the product perspective, high heating rate is more conduc-tive to the biomass pyrolysis reaction. The higher the heating rate, the shorter residence times experienced by the samples, which is not conduc-tive to the occurrence of secondary reaction. Thus, fast pyrolysis maybe favorable to the formation of bio-oil (tar).

Compared with JAs, the pyrolysis of the Re is somewhat different: the value of $T_i$ and $T_m$ were lower. The mass loss of Re at 300 °C/min started at 239.9 °C, JAs was 261.5 °C. $T_m$ presents the same trend. (E-supplementary data of this work can be found in online version of the paper). Why does this happen? On one hand, JAs was found richer in cellulose, while Re was richer in hemicellulose and lignin. Zhou et al. (2013) found that the decomposition of hemicellulose and cellulose mainly occurred range about 210–300 °C and 300–450 °C. On the other hand, JAs and Re crops living on coastal zone have high salt-tolerant content due to salt inhibits plant photosynthesis, protein synthesis and lipid metabolism. This phenomenon may due to the fact that the actions of AAEMs (especially K+ and Na+) as catalysts during biomass pyr-olysis (Eom et al., 2012). This, along with the lower cellulose and higher hemicellulose content of Re, can also explain the slight shift to lower temperatures for Re devolatilization when compared to JAS (Table 1).

3.2. TG/DTG analysis

The devolatilization behavior of JAs and Re biomass fuels by TGA under high heating rate conditions (100, 300, 500 °C/min) are shown in Fig. 2. The pyrolysis characteristic parameters ($T_f$: initial temperature, $T_m$: maximum degradation rate temperature, $T_p$: final temperature, $R_{max}$: maximum mass loss rate, $m$: residue quality, $Di$: devolatilization index) at different heating rates are mainly used to characterize the pyrolysis characteristics of biomass intuitively. (E-supplementary data of this work can be found in online version of the paper).

As observed, JAs and Re species shows a trend that the mass loss curves shift to the high temperature and the mass of residue decrease as the heating rate increases, which is consistent with the results by Ding et al. (2017). The higher the heating rate, the higher initial temperature ($T_i$) and maximum rates of mass losses ($R_{max}$), the lower residue quality ($m$). (E-supplementary data of this work can be found in online version of the paper). The main thermal degradation temperature of JAs and Re are occurs in the temperature range of 200–600 °C. Among them, a small peak were observed at the stage of 250–350 °C, the phenomenon is more obvious in the DTG curves of Re, and JAs are only reflected at heating rates of 100 °C/min, which means that more Re samples are decomposed or converted than JAs before 350 °C. This occurrence was also proved by Zhou et al. (2016). The phenomenon can be attributed to abundant hemicellulose contents units in the Re, hemicellulose present in Re (30.68 wt%) was found to contain large quantities than JAs (15.65 wt%) confirmed in the Table 1 (b). Moreover, this small peak gradually disappeared as the heating rate rises, which was reflected in the DTG images of the two species. When biomass under low heating rate conditions, cellulose and hemicellulose constituents may be sequentially thermal cracking separately, exhibiting characteristic individual decomposition peaks. However, as the heating rate increases, both constituents are simultaneously cracking and several adjacent peaks are combined together to form overlapping wider and higher peaks, and no separate peaks appear. This conclusion was also confirmed in the pyrolysis of coal under high heating rate (Tian et al., 2016). On the other hand, another effect of the heating rate is that the high heating rate leads to a decrease in the mass of the residue. Taking JAs as an example, $m$ (100 °C/min) is 16.45%, and $m$ reduced by 1.63% as the heating rate increases to 500 °C/min. Whereas, $m$ reduced highly by 5.02% as the heating rate increases to 500 °C/min for Re. (E-supplementary data of this work can be found in online version of the paper).

Table 1

Properties analysis of biomass fuels. JAs: Jerusalem artichoke stalks; Re: Reed.

(a) Proximate analysis (% wt, ad. Basis)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coastal biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>JAs 15.76</td>
</tr>
<tr>
<td></td>
<td>Re 5.89</td>
</tr>
<tr>
<td>Ash</td>
<td>JAs 3.34</td>
</tr>
<tr>
<td></td>
<td>Re 8.47</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>JAs 67.40</td>
</tr>
<tr>
<td></td>
<td>Re 72.12</td>
</tr>
<tr>
<td>Fix carbon</td>
<td>JAs 13.50</td>
</tr>
<tr>
<td></td>
<td>Re 13.52</td>
</tr>
</tbody>
</table>

(b) Ultimate analysis (% wt, def. Basis)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coastal biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>JAs 45.36</td>
</tr>
<tr>
<td></td>
<td>Re 42.78</td>
</tr>
<tr>
<td>H</td>
<td>JAs 6.11</td>
</tr>
<tr>
<td></td>
<td>Re 5.17</td>
</tr>
<tr>
<td>O</td>
<td>JAs 47.26</td>
</tr>
<tr>
<td></td>
<td>Re 50.51</td>
</tr>
<tr>
<td>N</td>
<td>JAs 0.75</td>
</tr>
<tr>
<td></td>
<td>Re 1.33</td>
</tr>
<tr>
<td>S</td>
<td>JAs 0.52</td>
</tr>
<tr>
<td></td>
<td>Re 0.21</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>JAs 15.69</td>
</tr>
<tr>
<td></td>
<td>Re 16.16</td>
</tr>
</tbody>
</table>

3.3. Kinetic analysis

The main reaction zone of biomass thermal cracking was analyzed by thermogravimetric method, and the reaction kinetic parameters were obtained to establish the apparent reaction kinetics model of the interval. Based on the FWO and DAEM methods, the conversion rate ($\alpha$) is chosen from 0.1 to 0.9, and good liner relationships are shown in the JAs and Re linear plots (E-supplementary data of this work can be found in online version of the paper). Then the apparent activation energy

\[
\text{Activation energy} = \text{E Activation} = RT \ln \left( \frac{\text{A}_{\text{obs}}}{\text{A}_{\text{calc}}} \right)
\]

where $R$ is the gas constant, $T$ is the temperature, $A_{obs}$ is the observed rate constant, and $A_{calc}$ is the calculated rate constant. (E-supplementary data of this work can be found in online version of the paper).
values calculated by the slopes ($-1.052E_a/R$) and ($-E_a/R$) corresponding to various conversion rates, as listed in Table 2. From Table 2, the regression coefficients ($R^2$) of $E_a$ calculated by different kinetic methods were very high, indicating that the selected kinetic methods can achieve a high fitting effect on different samples.

Owing to the errors take place under high conversion ($\alpha = 0.85$, 0.90) by using differential iso-conversion model, so we chose conversion rate range of 0.10–0.80. The mean values of $E_a$ calculated using FWO and DAEM models were 255.0 and 225.4 kJ/mol for JAs, 238.2 and 226.6 kJ/mol for Re, respectively. These values were closed to the aforementioned literature (Hu et al., 2017; Li et al., 2013). Apparent activation energy for total conversion of Re was found to be lower than that of JAs as was expected due to its lower temperature decomposition as shown before. Therefore, the Re reaction rate is faster than JAs, hence Re species is preferable to JAs in terms of thermochemical conversion.

JAs and Re were typical lignocellulosic biomass, and cellulose, hemicellulose, lignin are the main components. The apparent activation energies vary with conversion significantly maybe attributed to the $E_a$ of individual thermal decomposition of the above biopolymer components (Ojha et al., 2017). (E-supplementary data of this work can be found in online version of the paper). The pyrolysis of biomass exists multistep complex processes of those components. At the initial stage of the reaction, the $E_a$ increases vary with the $\alpha$, which may be due to the release of inherent moisture and other low temperature decomposing components. When the conversion rate is further increased,

**Table 2**
Calculation results of the apparent activation energy ($E_a$) and pre-exponential factors ($A$) by the FWO and DAEM method. JAS: Jerusalem artichoke stalks, Re: Reed.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>FWO method</th>
<th>DAEM method</th>
<th>FWO method</th>
<th>DAEM method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>$R^2$</td>
<td>$A$ (s$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.10</td>
<td>214.7</td>
<td>1.000</td>
<td>145.9</td>
<td>2.4E+15</td>
</tr>
<tr>
<td>0.15</td>
<td>211.5</td>
<td>0.992</td>
<td>159.3</td>
<td>2.6E-16</td>
</tr>
<tr>
<td>0.20</td>
<td>220.2</td>
<td>0.982</td>
<td>171.9</td>
<td>2.55E+17</td>
</tr>
<tr>
<td>0.25</td>
<td>216.2</td>
<td>0.981</td>
<td>196.4</td>
<td>3.06E-19</td>
</tr>
<tr>
<td>0.30</td>
<td>222.3</td>
<td>0.969</td>
<td>202.0</td>
<td>5.61E-19</td>
</tr>
<tr>
<td>0.35</td>
<td>252.0</td>
<td>0.954</td>
<td>230.2</td>
<td>1.24E-22</td>
</tr>
<tr>
<td>0.40</td>
<td>288.4</td>
<td>0.933</td>
<td>264.6</td>
<td>8.41E+24</td>
</tr>
<tr>
<td>0.45</td>
<td>314.5</td>
<td>0.932</td>
<td>289.3</td>
<td>6.53E+26</td>
</tr>
<tr>
<td>0.50</td>
<td>311.8</td>
<td>0.920</td>
<td>286.6</td>
<td>1.78E+26</td>
</tr>
<tr>
<td>0.55</td>
<td>301.2</td>
<td>0.921</td>
<td>276.4</td>
<td>1.14E+25</td>
</tr>
<tr>
<td>0.60</td>
<td>291.3</td>
<td>0.923</td>
<td>266.9</td>
<td>9.37E+23</td>
</tr>
<tr>
<td>0.65</td>
<td>270.0</td>
<td>0.945</td>
<td>246.5</td>
<td>9.51E+21</td>
</tr>
<tr>
<td>0.70</td>
<td>251.4</td>
<td>0.945</td>
<td>228.8</td>
<td>1.71E+20</td>
</tr>
<tr>
<td>0.75</td>
<td>236.2</td>
<td>0.946</td>
<td>214.2</td>
<td>6.00E+18</td>
</tr>
<tr>
<td>0.80</td>
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<td>0.932</td>
<td>202.0</td>
<td>3.26E+17</td>
</tr>
<tr>
<td>0.85</td>
<td>257.1</td>
<td>1.000</td>
<td>234.1</td>
<td>6.17E+19</td>
</tr>
<tr>
<td>0.90</td>
<td>449.0</td>
<td>0.912</td>
<td>422.6</td>
<td>7.25E+33</td>
</tr>
<tr>
<td>Average</td>
<td>255.0</td>
<td>0.952</td>
<td>225.4</td>
<td>5.68E+25</td>
</tr>
</tbody>
</table>

I: main thermal cracking stage ($\alpha$ is from 0.3 to 0.7), II: total process ($\alpha$ is from 0.1 to 0.9).
hemicellulose starts to pyrolysis. After \( \alpha = 0.50 \), the \( E_a \) decrease with the conversion increasing until about \( \alpha = 0.80 \), which is possibly attributed to the pyrolysis of cellulose crystal, whose decomposed activation energy is decreased with the conversion increasing. Other similar downturn results were obtained from the pyrolysis of pine wood, rice husk and bamboo (Bambusa Chungii) (Hu et al., 2016). Such declining \( E_a \) demonstrates that there were mechanisms change happening in corresponding conversion range (Vyazovkin et al., 2011). Due to the complexity of the biomass components, the pyrolysis reactions have both chemical bond cleavage reactions and accompanying processes of free radical formation, reaction and disappearance. When the chemical bond breaks to form a radical, the radical reaction is relatively easy and does not required a high reaction activation energy. Finally, a sharply increases of \( E_a \) mainly caused by the pyrolysis of higher thermal stability of lignin and higher ordered cellulose.

3.4. Fast pyrolysis product distribution

Simulated the conditions under high heating rates can be achieved using a down tube reactor. The down tube reactor was used in order to investigate the product distributions resulting from fast pyrolysis of JAs and Re. The influence of temperature on fast pyrolysis in a down tube pyrolysis unit was clarified simultaneously. The products of biomass pyrolysis were divided into three phases: solid, liquid and gas (Fig. 3). Different biomasses have a certain influence on the yield of pyrolysis products. The trend of each species product yields were similar as experimental temperatures (550–850 °C) increases for Re and JAs, both biomasses show a gradual decrease in char yield, increasing dramatically in the yield of gaseous products, and the maximum yield of bio-oil was obtained at 550–650 °C. Additionally, Re displayed the higher gas product yields, and JAs illustrated more bio-oil yields. The bio-oil yields initially showed a decreasing trend from 44.4 to 36.68 wt% for Re as the temperature increases from 550 °C through to 850 °C. However, JAs bio-oil yield was increasing from 54.08 to 55.68 wt% from 550 °C through to 650 °C, decreasing to 53.22 wt% from 650 °C through to 850 °C subsequently, which was the highest in a certain temperature in 650 °C. It is therefore can thus be inferred that more yields of bio-oil can be originated from JAs compared with Re. Similar results have been obtained from other researchers for the pyrolysis of different biomass species. Pidtasang et al. (2013) showed that, compared to the low temperature, a higher temperature of 550 °C resulted in increased gas yield and reduced liquid and char yield during pyrolysis of eucalyptus bark. Guizani et al. (2017) also reported that increasing temperature for woody biomass pyrolysis from 500 to 600 °C resulted in decreased production of oil from 62.4 wt% to 39.7 wt% in a lab-scale drop tube reactor.

It is worth noting that owing to the high heating rate, volatile matter was released at larger quantities as pyrolysis temperatures rises to a certain point. High heating rates should result in a more rapid heat transfer to the loaded sample in the down tube reactor. Li et al. (2016) also observed this fact. The combination of fast pyrolysis and a certain point temperature will make the covalent bonds in the biomass degradation more rapidly. In general, the alternation of the pyrolysis product distribution is due to competition between the formation of condensable gas and the cracking reaction. By JAs as an example, the pyrolysis temperature increases from 550 °C to 650 °C, both tar production and cracking rate increase. However, in the temperature range, the production rate is greater than the cracking rate, so the liquid yield increases. The yield of liquid product reaches a maximum value with the increase of pyrolysis temperature. Beyond this temperature, volatile matter undergoes secondary tar reactions (Hassan et al., 2016). Due to the increase of secondary reaction, the cracking rate is higher than the production rate, so the liquid yield decreases (Pilon and Lavoie, 2013). Bio-oil yields decreased as temperature from 650 to 850 °C, reaching a lowest value of 53.22% for JAs, and 36.68% for Re, respectively. In this experiment, due to the narrow experimental temperature range, the highest point of tar production was not observed in the Re. Furthermore, the thermogravimetric analysis showed high cel lulose content in JAS; and cellulose normally yields high liquid yields. Additionally, it is likely that the high inorganic content of these biomass resulted in a catalytic effect on the fast pyrolysis products.

Both biomasses show a similar decreasing trend in yield of bio-char as temperature increased from 550 °C to 850 °C. The formation of reducing biochar can therefore be linked mostly to the content of lignin and partly from hemicellulose. The decreasing biochar yield impacted by the fast pyrolysis may be explained by lignin hinders the polymerisation of levoglucosan from cellulose compared to low heating rate. Bio-char yields were however different at lower temperature (550 °C), Re char yields were found lower than JAs (32.84% and 35.08%, respectively), indicating the devolatilization of Re at lower temperatures are more rapidly converted to bio-oil and pyrolysis gas than JAS. Additionally, Re was evidenced higher inorganic content. Inorganic substances play a catalytic role in the pyrolysis process (Giudicianni et al., 2014).

JAS and Re have a higher inorganic content and are advantageous for the formation of lighter compounds. Both biomasses showed an increase in pyrolysis gas yields as pyrolysis temperature increased from 550 to 850 °C, this phenomenon is more obvious in the data of Re. At the final studied temperature (850 °C) pyrolysis gas yields of 35.25 wt% and 20.51 wt% were obtained for Re and JAs, respectively. Gas yield increase maybe originates from tar decomposition/cracking and biochar gasification reactions. The reason is that a continuous increase in gas yields while at the same time tar and biochar yields decline as temperature increases. Analyze from the perspective of physiochemistry, the increased gas yield during investigations at the combination of fast pyrolysis and 850 °C temperature would have resulted from the relatively more uniform degradation of the covalent bonds in the biomass with the activation energy provided by the rapidly increasing temperature. These yields were close to the Anastasakis (Anastasakis et al., 2016) during pyrolysis of wood (40.3 wt%, 1000 °C) and reed (35.9 wt%, 1000 °C).

3.5. Fast pyrolysis product characteristics

3.5.1. Bio-oil analysis

There are more than 100 compounds were appeared in the composition of the bio-oil/tar from Re and JAs in relation to fast pyrolysis (E-supplementary data of this work can be found in online version of the paper). According to the classification of the compound structure, Re tar divided into groups of furans, organic acids, phenols, polycyclic aromatic hydrocarbons, etc. The changes in the four main bio-oil compounds identified at 550, 650, 700 and 850 °C for Re was shown in Fig. 4(a), the components of pyrolysis tar mainly include furans,
phenols and aromatic compounds in JAs. The changes of the three compounds varies with pyrolysis temperature for JAs as shown in Fig. 4(b).

According to the analysis data of GC/MS, guaiac-based compounds are main component of pyrolysis products for Re, which corresponds to the abundant guaiac-based units in reeds, while the main phenolic compounds in the bio-oil of JAs was alkylphenols. The compounds in tar are mainly derived from the destructuring of components (cellulose, hemicellulose, lignin) and the cleavage of reactive bonds (Fagbemi et al., 2001). Among the pyrolysis compounds, 2,3-dihydrobenzofuran is main component of furans which is formed from the covalent bond scission of hemicellulose and cellulose, as well as it is widely used for synthesis of tricyclic compounds, and it is also the intermediate raw material for some important drugs, such as antitumor preparation benzofuran sulfonylurea, HIV protease inhibitor and other special chemicals (Choi et al., 2015). Due to its relatively high content, it is necessary to understand the effect of pyrolysis temperature on it (Fig. 4c). The amount of dihydrobenzofuran increases first and then decreases slowly with temperature increasing, and its amount is the lowest at 550 °C. For JAs, the highest point was reached at 750 °C, then decreased, while Re continued to increase, but decreasing the rate.

It can be seen from the Fig. 4 that the content of various substances in the tar has a tendency of rises and falls, indicating that the products obtained by pyrolysis of the biomass are mutually transformed with temperature changes, which indicates that there may be occurrence the secondary cleavage reactions in the process of biomass pyrolysis. For Re, the concentration of phenols decreases with temperature increases from 550 to 850 °C, while for JAs, the amount of phenols presents increases first and then decreases. This can be explained by the presence of higher lignin amounts in Re than JAs; because guaiacol naturally occur in trees that contain high lignin content. Guaiacol is easily thermal cracking at high temperatures. This phenomenon is consistent with Daniel research (Daniel et al., 2018). The concentration of organic acids increases with temperature from 26.14% at 550 °C to 29.20% at 850 °C.

3.5.2. Pyrolysis gas characteristics

The yield of each gas component can be calculated from the content of detection gas component in combination with the quantification of the sample during the pyrolysis process, that is, the gas volume (mL/g) released per gram of the biomass sample. Fig. 5 depicts the effect of temperature on the yield of the pyrolysis gas (H₂, CH₄, CO, CO₂ and

![Fig. 4. The changes in the main bio-oil compounds identified at 550, 650, 700 and 850 °C. (a: reed, b: Jerusalem artichoke stalk, c: Dihydrobenzofuran compounds).](image)

![Fig. 5. Pyrolysis gas components evolution over temperature during fast pyrolysis. JAs: Jerusalem artichoke stalks; Re: Reed.](image)
small amount of $C_2H_4$, $C_2H_2$) evolved during fast pyrolysis of Re and JAs.

The amount of pyrolysis gas produced by pyrolysis of different biomasses is very different. Compared with Re, the pyrolysis of the JAs in the region of low temperature (550 °C) produced more CO (47.72 mL/g). With the pyrolysis temperature increases to 850 °C, the amount of CO released from the JAs (98.36 mL/g) was similar to Re (96.43 mL/g). In terms of the trend of CO2 yield, Re was much higher than that of JAs, and reaches peak (96.72 mL/g) at around 650 °C. The trends of H2 and CH4 produced by Re and JAs are similar with temperature increases. Moreover, the hydrogen yield rises rapidly as the pyrolysis temperature increases. In the pyrolysis gas of JAs, CO was the dominant gaseous product released than other gases, while CO2 was predominant at pyrolysis gases of Re. In addition to the highest yield of CO2 in the pyrolysis of JAs and Re at 650 °C, followed by a slight predominance at pyrolysis gases of Re. In addition to the highest yield of CO2 in the pyrolysis of JAs and Re at 650 °C, followed by a slight predominance at pyrolysis gases of Re.

3.5.3. Bio-char characteristics

In order to study the effects of temperature on the morphological characteristics of fast pyrolysis bio-chars derived from coastal biomass, the bio-char of Re and JAs at 550, 650, 750 and 850 °C were scanned by SEM images taken from different sections of the Re showed that interior pores. The biomass surfaces were found to rupture drastically with temperature increasing. This is more obvious in the picture of Re in 850 °C, the surface presented the molten state.

4. Conclusions

Overall, fast pyrolysis behavior and products distribution of two typical coastal zone biomass fuels (reed and Jerusalem artichoke stalk) were conducted by TGA and down tube reactor, respectively. Analysis from the product perspective, high heating rate is more conducive to the biomass pyrolysis reaction, which is not conducive to the occurrence of secondary reaction. Kinetics experiments showed Re species is preferable to JAs in terms of thermochemical conversion because of the lower apparent activation energy for total conversion. More interesting, the combination of high heating rate and certain point temperature will make the covalent bonds in the biomass degradation more rapidly, gave profound influence on the products distribution.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [Grant numbers: 2157606571, 21576294 and 21706287]; Shandong Province Major Science and Technology Innovation Project (2018CXGC0301); Qingdao People’s Livelihood Science and Technology Project [Grant number 16-6-2-51-nsh and 18-6-1-101-nsh] and Independent Innovation Research Project of China University of Petroleum (East China) [Grant numbers 18CXS05022A; YJ201601066].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.02.097.

References

142–151.