Steam gasification of char derived from penicillin mycelial dreg and lignocellulosic biomass: Influence of P, K and Ca on char reactivity

Chen, Yuan; Lin, Weigang; Wu, Hao; Jensen, Peter Arendt; Song, Wenli; Du, Lin; Li, Songgeng

Published in: Energy

Link to article, DOI: 10.1016/j.energy.2021.120605

Publication date: 2021

Document Version
Peer reviewed version

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain.
- You may freely distribute the URL identifying the publication in the public portal.

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Steam gasification of char derived from penicillin mycelial dreg and lignocellulosic biomass: Influence of P, K and Ca on char reactivity

Yuan Chen, Weigang Lin, Hao Wu, Peter Arendt Jensen, Wenli Song, Lin Du, Songgeng Li

PII: S0360-5442(21)00854-9
DOI: https://doi.org/10.1016/j.energy.2021.120605
Reference: EGY 120605

To appear in: Energy

Received Date: 11 January 2021
Revised Date: 18 March 2021
Accepted Date: 6 April 2021


This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier Ltd.
Credit author statement

Steam gasification of char derived from penicillin mycelial dreg and lignocellulosic biomass: Influence of P, K and Ca on char reactivity

Yuan Chen \(^{a,b}\), Weigang Lin \(^{a,b,c,*}\), Hao Wu \(^{c}\), Peter Arendt Jensen \(^{c}\), Wenli Song \(^{a,b}\), Lin Du \(^{a}\), Songgeng Li \(^{a,b}\)

\(^{a}\) State key laboratory of multiphase complex systems, Institute of Process Engineering, Chinese Academy of Sciences, 100190 Beijing, China

\(^{b}\) Sino–Danish college, University of Chinese Academy of Sciences, 100049 Beijing, China

\(^{c}\) Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

* Corresponding author at: 1 Zhongguancun North Second Street, Haidian District, 100190 Beijing, China. Tel.: +86 01082544816

E-mail address: wglin@ipe.ac.cn (W. Lin).
Abstract: Gasification is a promising technology to dispose antibiotic mycelial dreg (AMD) which is a typical pharmaceutical hazardous bio-waste. However, the gasification of AMD is rarely studied. Since char gasification is the key step in the gasification process, the present work focused on the steam gasification of char. The influence of inorganic elements inside AMD char (mainly P, K and Ca) on the char gasification reactivity is investigated. Particularly, the effect of P on char gasification reactivity was deeply studied, and the co-effect of P, K and Ca on char gasification reactivity was firstly studied and explained. The obtained results suggested that P can deactivate the catalytic function of K and Ca on char gasification by forming K-phosphates and Ca-phosphates. The existence form of P can affect its inhibitory effect on K and Ca, and the pyrophosphate P had a stronger inhibiting effect than orthophosphate P. The deactivation of P on K is related to the ratio of K to P, and the bigger the ratio of K to P the less the deactivation of P on K. The existence of Ca can effectively eliminate the deactivation of P on K by reacting with P to form more stable Ca₃(PO₄)₂.

Keywords: antibiotic mycelial dreg; gasification; char reactivity; inorganic elements;
1. Introduction

As the bio-waste generated from the production process of fermentative antibiotics, antibiotic mycelial dreg (AMD) mainly consists of remaining fermentation substrates, antibiotic mycelia, intermediate metabolites, and particularly a certain quantity of residual antibiotics [1]. Due to the residual antibiotics, AMD can cause the generation and spread of antibiotic-resistance bacteria, posing a potential risk to the environment and human beings. Accordingly, AMD has been classified as a hazardous solid waste (HW02 Toxicity) by Chinese government since 2008 [2]. Currently, more than one million tonnes AMD was generated in China each year [3], and the annual production of AMD keeps increasing at a rate of about 10% per year [4]. Therefore, it is of great concern and urgent to find an adequate method to dispose AMD.

Indeed, AMD was characterized by very high content of nutrients, such as protein, polysaccharides, nucleic acids, lipids, etc [5]. Consequently, AMD was broadly used as food additives in the poultry industry and as composted fertilizer in agriculture industry in the past [6]. However, this behavior has been banned by relevant environmental legislations since 2008, because the residual antibiotic in AMD can be taken up by animal or plants and enter the food chain [7]. At present, the most commonly applied disposal methods for AMD are incineration and sanitary landfill. Unfortunately, these two disposal methods are waste of resources and high economic cost and can cause serious secondary environmental pollution, which making these two methods not being widely accepted [8]. In fact, the Chinese standard (GB 5104−2014) has stipulated that the disposal of AMD should follow the principles of reduction, recycling and harmlessness. As a result, the waste-to-energy process would be promising to dispose AMD since it can not only relieve the environmental stress, but also recycle the abundant nutrients in AMD as a kind of energy resource. Gasification, as a typical waste-to-energy technology, can not only reduce the amount of AMD rapidly, but also recycle the abundant nutrients in AMD by transferring it into clean fuel gas. Meanwhile, the high nitrogen content in AMD are mainly converted into NH₃ and HCN during the gasification process. When steam is used as the gasification agent, nitrogen tends to converted into NH₃ [9]. The NH₃ and HCN can be easily removed in the gas purification process by water based scrubbing due to its high solubility in water [10], and the washing water with NH₃ and HCN dissolved can be further used to recycle the nitrogen resource, which prevent the secondary pollution
caused by the nitrogen in AMD. In addition, our previous study showed that the residual antibiotics in AMD, which must be removed when dispose AMD, can be easily removed under high temperature process [1]. As a result, gasification is an environment-friendly and feasible technology and can fully confirm to the principles for AMD disposal.

Generally, gasification consists of two main chemical stages: devolatilization and char gasification [11]. The reaction rate of char gasification is much slower compared to the initial devolatilization, therefore char gasification is considered to be the controlling step in the whole gasification process [12]. As a result, the knowledge of char gasification is crucial for the design and development purposes. Basically, char gasification directly depends on char reactivity with the gasifying agent [13]. The commonly used gasifying agent is steam, because the product of steam gasification process is rich in hydrogen and can not only be clean fuel but also raw material for chemical industries [11]. Char reactivity is affected by the raw material and pyrolysis conditions. Indeed, the char reactivity mainly attributed to the char features (surface area, porous structure, morphological structure, etc) and inorganic elements content if series char are prepared and gasified under identical conditions [14]. Moreover, previous literature highlights that char features seem to be less influential on gasification reactivity than the inorganic elements content, particularly soluble minerals [15]. Hence, the inorganic elements have a great influence on the char gasification reactivity. In recent years, numerous studies have been dealing with the influence of char features and inorganic elements on char gasification reactivity. Different types of feedstock were investigated, such as coal [16], algal [17] and lignocellulosic biomass [18]. It is found that the char reactivity was mainly influenced by its char features at low conversion ratio, while the char reactivity depends on the its containing inorganic elements when the conversion ratio reaches over 60% [19, 20]. As for the inorganic elements, alkaline (sodium Na, potassium K) and alkaline earth metallic (calcium Ca, magnesium Mg) species were found to have a catalytic effect [21, 22], whereas some inorganic elements have an inhibiting effect, like phosphorous P [14] or silicon Si [23]. In addition, some studies also tried to elucidate the role of biomass type on steam gasification kinetics and correlate the conversion profile with inorganic elements contained in biomass [12, 14]. However, the previous studies were mainly focused on the coal, algal and lignocellulosic biomass feedstock. Little attention was paid to the fermentation bio-waste like AMD. Meanwhile, it is attractive that AMD is a kind of high-P bio-waste, while little literature have studied the char gasification reactivity using such high-P
feedstock to date. What’s more, the co-effect of several inorganic elements (P-K, P-Ca, and P-K-Ca) on char gasification reactivity was rarely studied, which was preliminary studied in the present work.

Although gasification is a promising method to dispose AMD, the gasification of AMD has nearly never been studied up to now. Therefore, the present work aims to study the steam gasification of AMD char. Thermogravimetric analysis (TGA) is a useful, popular and simplest method to investigate the gasification behaviour and reactivity [13]. TGA can be performed isothermally or non-isothermally. The non-isothermal method has become a common analytical technique in recent decades due to the high sensitivity to experimental noise compared to the isothermal methods. Thus the non-isothermal method was applied in the present work.

Based on this background, the objective of the present work is to study the steam gasification of penicillin mycelial dreg (PMD) char and to compare it with a representative lignocellulosic biomass char using TGA. In specific, the influence of inorganic elements inside PMD char (mainly P, K and Ca) on char gasification reactivity is investigated. Particularly, the effect of P on char gasification reactivity was deeply studied, and a specific effort has been made to understand the co-effect of P, Ca and K on the char gasification reactivity.

2. Experimental

2.1. Raw materials

Penicillin mycelial dreg (PMD) is used in present work as the representative of AMD, because penicillin is widely used and its production account for above 80% of the total production of antibiotics according to the related statistics from China Pharmaceutical Industry Association [24]. PMD was collected from CSPC Pharmaceutical Group Limited (Hebei province, China). The obtained PMD was first air dried and ground to less than 1 mm prior to char preparation. Table 1 gives the characteristics of PMD.

As mentioned above, the char reactivity is mainly attributed to the inorganic elements content when the char is prepared and gasified under identical conditions. Hence a typical bio-energy wood sample with very low ash content, namely pine wood (PW), was also used in the present work in order to make a comparison with PMD and further investigate the influence of the inorganic elements inside PMD char on the char reactivity. The preparation process of the PW sample is the
same as that of PMD. The proximate and ultimate analysis showed that the dried pine wood had 0.43% ash, 51.52% C, 6.20% H, 0.1% N and 0.01% S.

**Table 1. Characteristics of PMD.**

<table>
<thead>
<tr>
<th>Proximate analysis (d, wt.%)</th>
<th>Ultimate analysis (d, wt.%)</th>
</tr>
</thead>
</table>
| moisture | volatile | ash | fixed carbon | C | H | N | S | O
| 8.74 | 72.18 | 10.26 | 17.57 | 44.61 | 6.22 | 8.22 | 0.76 | 29.93 |

<table>
<thead>
<tr>
<th>Ash composition (wt.%)</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>ZnO</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>34.90</td>
<td>26.20</td>
<td>14.90</td>
<td>10.96</td>
<td>6.64</td>
<td>4.86</td>
<td>0.66</td>
<td>0.39</td>
<td>0.26</td>
<td>0.07</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a, determined by difference.

### 2.2. Char preparation

Chars were prepared by devolatilization of PMD and PW in a horizontal tube furnace. Approximately 20 g of sample was heated under a pure nitrogen stream of 100 mL min⁻¹ from room temperature to the final temperature of 700 °C at a constant heating rate of 5 °C min⁻¹, held in the final conditions for 60 min, and then cooled to room temperature. The cooled char was ground to fine powders of less than 63 μm for further use. The chars obtained from PMD and PW were donated as PMD700 and PW700, respectively. The ultimate analysis (C, H, N and S) of the chars was carried out using an elemental analyzer (vario MACRO cube, Elementar), and the proximate analysis was carried out according to the Chinese Standard GB/T212-2008. The ash composition was measured by a X-ray fluorescence spectrometer (AXIOS-MAX, PANalytical B.V.).

In order to investigate the influence of inorganic elements inside PMD char (mainly P, Ca and K, see Table 3) on char gasification reactivity, several selected chemicals were mechanically mixed with PW char at a mass ratio of 21 mg to 50 mg by grinding thoroughly in an agate mortar. The reason for mixing 21 mg of selected chemicals to 50 mg of PW char is to make the content of the selected chemicals in the mixture consistent with the ash content of PMD char. The selected chemicals were K₂SO₄, KH₂PO₄, K₃PO₄, CaSO₄, Ca₃(PO₄)₂, KCaPO₄, K₂CaP₂O₇, K₂SO₄+Ca₃(PO₄)₂ and 2KH₂PO₄+3CaSO₄, and the corresponding mixtures were donated as PW700+K₂SO₄, PW700+KH₂PO₄, PW700+K₃PO₄, PW700+CaSO₄, PW700+Ca₃(PO₄)₂, PW700+KCaPO₄, PW700+K₂CaP₂O₇, PW700+(K₂SO₄+Ca₃(PO₄)₂) and PW700+(2KH₂PO₄+3CaSO₄). Specifically,
KCaPO$_4$ and K$_2$CaP$_2$O$_7$ were prepared according to the method described in [25] and [26], respectively. The K$_2$SO$_4$+Ca$_3$(PO$_4$)$_2$ is the blends of K$_2$SO$_4$ with Ca$_3$(PO$_4$)$_2$ at the molar ratio of 1 to 1, and 2KH$_2$PO$_4$+3CaSO$_4$ is the blends of KH$_2$PO$_4$ and CaSO$_4$ at the molar ratio of 2 to 3. Besides, the PMD ash, obtained by burning PMD in air at 550 °C for 2 h, was also mixed with PW char using the same method, and the mixture was donated as PW700+PMD ash.

2.3. Gasification experiment

The char gasification experiments were carried out under non-isothermal conditions using a thermogravimetric analyzer (TGA, NETZSCH STA 449/F3) coupled with a steam generator through a heated transfer line. For a typical run, approximately 5 mg of sample was first evenly loaded in an alumina crucible and then heated at a constant heating rates of 10 °C min$^{-1}$ up to 120 °C and hold at this temperature for 30 min to evaporate the water inside the char sample. After that, the sample was programmatically heated at a constant heating rate of 10 °C min$^{-1}$ to the final temperature of 1000 °C. The mixture of 25% steam and 75% nitrogen at a total flow rate of 100 mL min$^{-1}$ was used as the gasifying agent. The sample weight loss versus time of the whole steam gasification process was recorded automatically by computer. Each gasification experiment was repeated three times to ensure the accuracy and reproducibility of the experimental results, and the maximum deviation of the sample weight loss was below 1%.

Based on the measured data of the sample weight loss versus time, the gasification rate $r$ could be derived by following equation (1) [14]:

$$ r = \frac{d}{dt} $$

where $x$ is the conversion of the sample and can be calculated according to following equation (2) [14]:

$$ x = \frac{w_i - w_t}{w_f - w_i} $$

where $w_i$ is the initial weight of the sample, $w_t$ is the instantaneous weight of the sample at a certain time $t$, and $w_f$ refers to the final weight of the sample.

Besides, three characteristic temperatures including the initial gasification temperature ($T_i$), the
peak reaction rate temperature ($T_m$) and final gasification temperature ($T_f$) were used to describe and evaluate the gasification reactivity, of which $T_m$ is the most important. The $T_i$ and $T_f$ in present work is considered to be the temperature at which the weight loss rate was 0.005% s$^{-1}$, while the $T_m$ is the temperature corresponding to the maximum weight loss rate. The characteristic temperatures of performed gasification experiments were listed in Table 2.

### Table 2. Overview of the characteristic temperature of performed gasification experiments.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Based char</th>
<th>Additives</th>
<th>Weight ratio$^a$</th>
<th>$T_i$, K</th>
<th>$T_m$, K</th>
<th>$T_f$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMD700</td>
<td>PW700</td>
<td>PMD ash</td>
<td>50:21</td>
<td>869</td>
<td>1062</td>
<td>1074</td>
</tr>
<tr>
<td>PW700+PMD ash</td>
<td>PW700</td>
<td>PMD ash</td>
<td>50:21</td>
<td>938</td>
<td>1156</td>
<td>1162</td>
</tr>
<tr>
<td>PW700+K$_2$SO$_4$</td>
<td>PW700</td>
<td>K$_2$SO$_4$</td>
<td>50:21</td>
<td>912</td>
<td>1058</td>
<td>1067</td>
</tr>
<tr>
<td>PW700+CaSO$_4$</td>
<td>PW700</td>
<td>CaSO$_4$</td>
<td>50:21</td>
<td>907</td>
<td>1035</td>
<td>1047</td>
</tr>
<tr>
<td>PW700+KH$_2$PO$_4$</td>
<td>PW700</td>
<td>KH$_2$PO$_4$</td>
<td>50:21</td>
<td>936</td>
<td>1145</td>
<td>1155</td>
</tr>
<tr>
<td>PW700+Ca$_3$(PO$_4$)$_2$</td>
<td>PW700</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>50:21</td>
<td>973</td>
<td>1157</td>
<td>1223</td>
</tr>
<tr>
<td>PW700+K$_2$CaP$_2$O$_7$</td>
<td>PW700</td>
<td>K$_2$CaP$_2$O$_7$</td>
<td>50:21</td>
<td>970</td>
<td>1151</td>
<td>1201</td>
</tr>
<tr>
<td>PW700+KCaPO$_4$</td>
<td>PW700</td>
<td>KCaPO$_4$</td>
<td>50:21</td>
<td>952</td>
<td>1147</td>
<td>1261</td>
</tr>
<tr>
<td>PW700+K$_2$HPO$_4$</td>
<td>PW700</td>
<td>K$_2$HPO$_4$</td>
<td>50:21</td>
<td>955</td>
<td>1137</td>
<td>1148</td>
</tr>
<tr>
<td>PW700+K$_3$PO$_4$</td>
<td>PW700</td>
<td>K$_3$PO$_4$</td>
<td>50:21</td>
<td>929</td>
<td>1128</td>
<td>1160</td>
</tr>
<tr>
<td>PW700+K$_2$SO$_4$+Ca$_3$(PO$_4$)$_2$</td>
<td>PW700</td>
<td>K$_2$SO$_4$+Ca$_3$(PO$_4$)$_2$</td>
<td>50:21</td>
<td>873</td>
<td>1009</td>
<td>1087</td>
</tr>
</tbody>
</table>

$^a$, weight ratio of based char to additive.

### 3. Results and discussion

#### 3.1. Characterization of char

Table 3 gives the properties of the obtained PMD and PW chars. The yield of PMD char are 28.33%. Compared to the raw materials, the carbon content of PMD char increased from 44.61% to 59.64%. The high carbon content of PMD char suggest that the PMD char is suitable for gasification. However, the ash content also increased largely from 10.26% of raw PMD to 29.47% of PMD char. Such high ash content of PMD char will inevitably have a great influence on its gasification reactivity according to previous study [27]. Therefore, it is necessary and significance to study the influence of the inorganic elements inside PMD char on the char gasification for the proper reactor design and operation purpose. To manage this issue, the PW char, which was produced at the same conditions as that of PMD char and have a quite low ash content of 1.3%, was selected as a reference to make a comparison with PMD char on the gasification reactivity. Compared to PMD char, the ash
content of PW char is quite low and thus its effect on the gasification reactivity can be ignored.

As listed in Table 3, the PMD char ash mainly consists of P, Ca and K, together with the sub-amount of S, Na, Mg, Si and Fe. Fig 1 gives the XRD analysis of the crystalline characteristics of the PMD char. As observed in Fig. 1, the P, Ca and K in PMD char mainly exist in the form of $K_2SO_4$, $Ca_3(PO_4)_2$, $K_2CaP_2O_7$ and $CaCO_3$.

**Table 3.** Properties of obtained chars.

<table>
<thead>
<tr>
<th>Char</th>
<th>(wt. %, d.b.)</th>
<th>Ash composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>PMD700</td>
<td>59.64</td>
<td>0.62</td>
</tr>
<tr>
<td>PW700</td>
<td>92.13</td>
<td>1748</td>
</tr>
</tbody>
</table>

![XRD spectrum of PMD char](image)

**Fig. 1.** The XRD spectrum of PMD char.

3.2. *Gasification behavior of char*

Fig.2. shows the conversion and gasification rate curves of PMD char and PW char in 25% steam. According to Fig. 2, the gasification of PMD char and PW char were both take place almost completely in one-stage process as it has been shown by the presence of only one peak in $dx/dt$ curves. However, the maximum gasification rate of PMD char in 25% steam is quite higher than that
of PW char, while the $T_m$ of PMD char is quite lower than that of PW char, which illustrate that the gasification of PMD char in 25% steam is much easier to take place and fast than PW char. Such big difference of the gasification reactivity between PMD char and PW char should be resulted from the difference of the raw material type. According to previous study [14, 15], when series of biomass chars are prepared and gasified under identical conditions, the differences of reactivity mainly attributed to differences of inorganic elements content. Therefore, the big difference in the gasification reactivity between PMD char and PW char should be ascribed to the big difference in their inorganic elements content which can be reveal by their ash content, 29.47% of PMD char versus 1.3% of PW char. Thus the inorganic elements inside PMD char speculated to have a catalytic effect on the char gasification.

In order to prove the speculation, the mixture of PW char and PMD ash (PW700+PMD ash) was gasified under the same conditions as that of PMD char. The conversion and gasification rate curves of PW700+PMD ash was also presented in Fig. 2. The result shows that the $T_m$ of PW700+PMD ash became almost the same as that of PMD char, revealing that the adding of PMD ash into PW char can obviously promote the PW char gasification to approach PMD char gasification. This phenomenon suggest not only the difference of the gasification reactivity between PMD char and PW char mainly came from the difference of their inorganic elements content (29.47% vs. 1.30%) but also the inorganic elements inside PMD char do have a significant catalytic effect on char gasification. However, PMD char contains several inorganic elements with several different existence forms (see Fig. 1). It is curious that how these inorganic elements and its existence forms affect the char gasification. Therefore, the following part studied this subject by mixing different selected chemicals with PW char and comparing the gasification reactivity of the mixture with the PW char and/or PMD char.
3.3. Effect of K and Ca

According to Table 3, P, Ca and K are the chief elements in PMD char. Therefore, the influence of P, Ca and K and its existence forms on the char gasification were investigated. Based on Fig. 1, the K and Ca exist in PMD char mainly in the forms of K$_2$SO$_4$ and CaSO$_4$, respectively. Thus K$_2$SO$_4$ and CaSO$_4$ were selected to add into PW char to check the effect of K and Ca on the char gasification. The results were shown in Fig. 3. From Fig. 3, the T$_m$ of PW700+K$_2$SO$_4$ is much lower than that of PW700, while the T$_m$ of PW700+CaSO$_4$ is only little lower than that of PW700. This result indicates that both K and Ca have a catalytic effect on the char gasification. More specifically, the catalytic ability of K is very strong, while Ca is weak. Similar conclusion was also obtained in [27]. Meanwhile, from Table 2, the characteristic temperature of PW700+K$_2$SO$_4$ is quite close to that of PW700+PMD ash and PMD700, revealing that the catalytic effect of the inorganic elements inside the PMD char on char gasification mainly comes from K. The peak on the dx/dt curve of PW700+CaSO$_4$ at 1100 K should be ascribed to the reaction between CaSO$_4$ and carbon, as following reaction (3):
$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$$  \hspace{1cm} (3)

![Graph showing conversion and gasification rate curves of PW char, PW700+K\textsubscript{2}SO\textsubscript{4}, and PW700+CaSO\textsubscript{4} in 25% steam.]

**Fig. 3.** Conversion and gasification rate curves of PW char, PW700+K\textsubscript{2}SO\textsubscript{4}, and PW700+CaSO\textsubscript{4} in 25% steam.

### 3.4. Effect of P

The existence form of P in PMD char are K\textsubscript{2}CaP\textsubscript{2}O\textsubscript{7} and Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, see Fig. 1. Thus K\textsubscript{2}CaP\textsubscript{2}O\textsubscript{7} and Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} were added separately into PW char to check the effect of P and its existence forms on the char gasification. Meanwhile, P in the forms of KCaPO\textsubscript{4} and KH\textsubscript{2}PO\textsubscript{4} were also studied. The results were shown in Fig. 4. As observed in Fig. 4, the T\textsubscript{m} of PW700+ K\textsubscript{2}SO\textsubscript{4} and PW700+ Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} is similar to that of PW700. However, according to Table 2, the T\textsubscript{f} of PW700+ K\textsubscript{2}PO\textsubscript{4} and PW700+ Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} is much bigger than that of PW700. Therefore, it can be deduced that the adding of K\textsubscript{2}PO\textsubscript{4} and PW700+ Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} inhibited the char gasification. Whereas the results in section 3.3 have proved that K and Ca can promote the char gasification. Thus the inhibiting effect of K\textsubscript{2}PO\textsubscript{4} and Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} on char gasification should came from P. Hognon [12] and Dupont [14] have reported that phosphorus could deactivate the catalytic function of K by encapsulating K to forming K-phosphates. Similarly, the catalytic function of Ca should also be deactivated by P via forming the Ca-phosphates, which will be explained in section 3.6.
From Fig. 4, it can also learned that the $T_m$ of PW700+KCaPO$_4$ is little lower than that of PW700, while the $T_m$ of PW700+ K$_2$CaP$_2$O$_7$ is similar to that of PW700. However, Table 2 shows that the $T_f$ of PW700+KCaPO$_4$ is little lower than that of PW700, while the $T_f$ of PW700+K$_2$CaP$_2$O$_7$ is higher than that of PW700. This phenomenon indicate that KCaPO$_4$ has little catalytic effect on char gasification, while K$_2$CaP$_2$O$_7$ will inhibit char gasification. From this observation, it can be deduced that the existence form of P can affect its inhibitory effect on K and Ca, and the P in pyrophosphate state had a stronger inhibiting effect on K and Ca than the P in orthophosphate state.

![Conversion and gasification rate curves](image)

**Fig. 4.** Conversion and gasification rate curves of PW700, PW700+KH$_2$PO$_4$, PW700+Ca$_3$(PO$_4$)$_2$, PW700+K$_2$CaP$_2$O$_7$, and PW700+KCaPO$_4$ in 25% steam.

3.5. Effect of the ratio of K to P

Fig. 5 presented the conversion and gasification rate curves of PW700+KH$_2$PO$_4$, PW700+K$_2$HPO$_4$, and PW700+K$_3$PO$_4$ in 25% steam. It can be learned from Fig. 5 that the $T_m$ of PW700, PW700+KH$_2$PO$_4$, PW700+K$_2$HPO$_4$, and PW700+K$_3$PO$_4$ are ranked in order from the big to the small as PW700+KH$_2$PO$_4$ > PW700 > PW700+K$_2$HPO$_4$ > PW700+K$_3$PO$_4$, indicating that the adding of K$_3$PO$_4$ and K$_2$HPO$_4$ can catalyze the char gasification, especially K$_3$PO$_4$, while the adding of
KH₂PO₄ will inhibit the char gasification. In section 3.4, the P was found can deactivate the catalytic function of K. However, combining Fig.4 and Fig.5, it can be further deduced that the deactivation of P on K is related to the ratio of K to P. When the ratio of K to P is less than or equal to one, K would be fully encapsulated by P and thus unable to act as a catalyst. However, when the ratio of K to P is bigger than one, some K may not be encapsulated by P and thus can act the catalyst to promote the char gasification, and the bigger the ratio of K to P the more K are free to catalyze char gasification.

![Conversion and gasification rate curves of PW700, PW700+KH₂PO₄, PW700+K₂HPO₄, and PW700+K₃PO₄ in 25% steam.](image)

**Fig. 5.** Conversion and gasification rate curves of PW700, PW700+KH₂PO₄, PW700+K₂HPO₄, and PW700+K₃PO₄ in 25% steam.

3.6. Co-effect of P, Ca and K

In section 3.4, it is found that P can deactivate the catalytic function of both K and Ca by forming K-phosphates and Ca-phosphates. However, when P, Ca and K coexist, how it affect char gasification is not clear. Thus the 3KH₂PO₄+2CaSO₄, which was the blends of KH₂PO₄ and CaSO₄ at the molar ratio of 2 to 3, was mixed with PW char to form a mixture PW700+(3KH₂PO₄+2CaSO₄) and followed by gasifying under 25% steam to study the co-effect of P, Ca and K. The result was shown in Fig. 6. As observed in Fig. 6, the Tₘ of PW700+(3KH₂PO₄+2CaSO₄) is much lower than that of
PW700, indicating that the blends of 3KH\textsubscript{2}PO\textsubscript{4}+2CaSO\textsubscript{4} have a great catalytic effect on the char gasification. However, when mix KH\textsubscript{2}PO\textsubscript{4} and CaSO\textsubscript{4} separately with PW char, the CaSO\textsubscript{4} only exhibit little catalytic effect on char gasification (see Fig. 3), while KH\textsubscript{2}PO\textsubscript{4} inhibits the char gasification (see Fig. 4). Therefore, it is assumed that the Ca tends to react with P to form more stable Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} during the gasification of PW700+(3KH\textsubscript{2}PO\textsubscript{4}+2CaSO\textsubscript{4}), as following reaction (4):

\[
KH_2PO_4 + CaSO_4 \rightarrow Ca_3(PO_4)_2 + K_2SO_4
\]  

Consequently, K had little chance to be captured by P to form less stable K-phosphates and can catalyze the char gasification. In order to prove the assumption, the residue of PW700+(3KH\textsubscript{2}PO\textsubscript{4}+2CaSO\textsubscript{4}) after gasification was analyzed using a SEM-EDS (JSM-7001F+INCA X-MAX). The result was shown in Fig. 7. From Fig. 7, the elements in area A are P, Ca and O, while the elements in area B are K, S and O, indicating the existence of Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} and K\textsubscript{2}SO\textsubscript{4} in the residue. This observation is a good proof of the occurrence of reaction (4). The EDS analysis of area A and B was listed in Table 4. The molar ratio of the elements of area A and B is quite close to Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} and K\textsubscript{2}SO\textsubscript{4}, respectively. The cartography of elemental composition on surface of the residue was shown in Fig. A in Appendix. Besides, the mixture of PW700+(K\textsubscript{2}SO\textsubscript{4}+Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}) was also gasified to prove the stability of Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}. From Fig. 6, it can be seen that the T\textsubscript{m} of PW700+(K\textsubscript{2}SO\textsubscript{4}+Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}) is much lower than that of PW700, illustrating that the blends of K\textsubscript{2}SO\textsubscript{4}+Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} also have a great catalytic effect on the char gasification. This further illustrate that P tends to react with Ca to form more stable Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} than react with K to form less stable K-phosphates.

As a result, Ca can effectively eliminate the deactivation of P on K by reacting with P to form more stable Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}.
Fig. 6. Conversion and gasification rate curves of PW700, PW700+(2KH$_2$PO$_4$+3CaSO$_4$), and PW700+(K$_2$SO$_4$/Ca$_3$(PO$_4$)$_2$) in 25% steam.

Fig. 7. SEM-EDS analysis of the residue of PW700+(3KH$_2$PO$_4$+2CaSO$_4$) after gasification.

Table 4. EDS analysis of area A and B.

<table>
<thead>
<tr>
<th>Area</th>
<th>Molar percentage of elements, %</th>
<th>Ca:P:O</th>
<th>K:S:O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>Ca</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>11.00</td>
<td>16.68</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>–</td>
<td>–</td>
<td>51.87</td>
</tr>
</tbody>
</table>

4. Conclusions
The steam gasification of PMD char was studied using TGA, and the influence of inorganic elements inside PMD char (mainly P, Ca and K) on char gasification was studied based on a reference lignocellulosic wood char. Particularly, the effect of P on char gasification reactivity was deeply studied, and the co-effect of P, Ca and K on char gasification reactivity was investigated. Following conclusions can be obtained: 1) the gasification of PMD char take place almost completely in one-stage process, and the inorganic elements inside the PMD char have a great catalytic effect on char gasification, which mainly come from K; 2) P can deactivate the catalytic function of K and Ca by forming K-phosphates and Ca-phosphates; 3) the existence form of P can affect its inhibitory effect on K and Ca, and the pyrophosphate P had a stronger inhibiting effect than orthophosphate P; 4) the deactivation of P on K is related to the ratio of K to P, and the bigger the ratio of K to P the less the deactivation of P on K; and 5) Ca can effectively eliminate the deactivation of P on K by reacting with P to form more stable Ca₃(PO₄)₂.

5. Acknowledgement

This work was supported by the National Key R&D Program of China (2018YFC1901300), 2017 Doctoral International Cooperation Training Program of University of Chinese Academy of Sciences, Combustion and Harmful Emission Control (CHEC) Research Centre at the Department of Chemical and Biochemical Engineering, Technical University of Denmark, and Sino-Danish Center for Education and Research.
References


Appendix A:

**Fig. A.** Cartography of elemental composition on surface of the residue of PW700+(3KH$_2$PO$_4$+2CaSO$_4$) after gasification.
Highlights

- Samples gasification reactivity difference mainly come from inorganic difference.
- The effect of P on char gasification reactivity was deeply studied.
- P can deactivate the catalytic function of K and Ca on char gasification.
- The deactivation of P relates to the existence form of P and the ratio of P to K.
- The existence of Ca can effectively eliminate the deactivation of P on K.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: