

## Parametric study of pyrolysis and steam gasification of rice straw in presence of $K_2CO_3$

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**Abstract**—A parametric study of pyrolysis and steam gasification of rice straw (RS) was performed to investigate the effect of the presence of  $K_2CO_3$  on the behavior of gas evolution, gas component distribution, pyrolysis/gasification reactivity, the quality and volume of synthetic gas. During pyrolysis, with the increase in  $K_2CO_3$  content in RS (i) the instantaneous  $CO_2$  concentration was increased while CO concentration was relatively stable; (ii) the yield of  $CO_2$  and  $H_2$  increased on the cost of  $CH_4$ . During steam gasification of RS, with the increase in  $K_2CO_3$  content in RS (i) the instantaneous concentration of  $CO_2$  and  $H_2$  increased while instantaneous concentration of CO and  $CH_4$  decreased; (ii) the yield of  $CO_2$  and  $H_2$  production and total yield increased; and (iii) yield of CO and  $CH_4$  production followed the order: 9%  $K_2CO_3$  RS < 6%  $K_2CO_3$  RS < raw RS < 3%  $K_2CO_3$  RS < water-leached RS. Water-leached RS showed the highest pyrolysis reactivity, while steam gasification reactivity was proportional to  $K_2CO_3$  content in RS. The results of this study reveal that the presence of  $K_2CO_3$  during pyrolysis and steam gasification of RS effectively improves production of  $H_2$  rich gas.

Keywords: Pyrolysis, Steam Gasification, Biomass, Rice Straw,  $K_2CO_3$

### INTRODUCTION

Rice is grown in over a hundred countries. Approximately 480 million metric tons (Mt) of milled rice was produced in 2014 [1]. Asian countries—China, India Indonesia, Bangladesh, Vietnam, Myanmar, Thailand, the Philippines, Japan, Pakistan, Cambodia, the Republic of Korea, Nepal, and Sri Lanka—account for 90% of the world's total rice production [1]. For every ton of grain harvested, about 1.35 tons of rice straw remain in the field [2]. Research is going on to explore efficient processes for energy recovery from agricultural waste [3,4]. According to Chakma et al. [5] the production of different biofuels from rice crop residues is economically viable. Bioenergy from rice crop residues provides simultaneous solution to issues of energy security and climate change risk in developing nations [6]. Gasification is considered as a key technology for energy recovery from biomass. It offers high flexibility in processing different kinds of feedstock materials as well as in the generation of different products [7]. Catalytic gasification is an efficient way to convert carbonaceous materials to optional gaseous products [8].

The initial step of gasification is pyrolysis, in which volatiles are released, leaving behind the solid char. Pyrolysis is followed by char gasification in which volatiles and char are further reacted and converted into the final products in the presence of reactive agents [9]. There is not a clear boundary line about these two stages

and the two processes interact with each other. The presence of inherent alkali and alkaline earth metallic species enhances the heterogeneous char gasification, as well as the homogeneous water-gas shift, steam-tars reforming, and hydrocarbon reforming reactions on biomass gasification [10]. The purpose of our study was to evaluate the effect of presence of  $K_2CO_3$  during the pyrolysis and steam gasification of RS on gas evolution behavior, gas component distribution and quality and volume of gas in a laboratory fixed-bed reactor under atmospheric pressure. We also analyzed the effect of the presence of  $K_2CO_3$  on reactivity during both pyrolysis and gasification. A fixed-bed gasifier was selected for this study due to its simplicity and production of relatively high  $H_2$  content in the gaseous product [11].

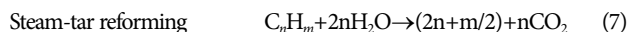
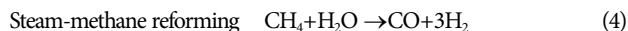
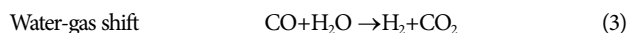
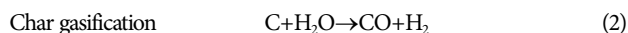
### PYROLYSIS AND GASIFICATION REACTIONS

To clarify the reaction mechanisms of biomass gasification, researchers usually study gasification by two stages: pyrolysis and char gasification. During pyrolysis, volatiles ( $CO$ ,  $CO_2$ ,  $CH_4$  and  $H_2$ ), tar and char are produced by thermal-chemical decomposition of biomass (cellulose, hemicellulose and lignin) [12]. During steam gasification, homogeneous and heterogeneous reactions between pyrolysis gas, tar, char and steam occur simultaneously. Steam as a gasifying agent is considered as one of the most effective techniques to produce synthetic gas with higher  $H_2$  content [13]. The main reactions during pyrolysis and steam gasification are as under [14-16].



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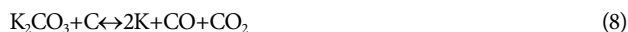
Potassium catalyst undergoes similar redox cycles under steam gasification conditions [23]. McKee [24] tried to explain the mechanism of redox cycle in localized sites where the catalyst and carbon interact as the following.



## PYROLYSIS AND GASIFICATION REACTIONS CATALYZED BY $\text{K}_2\text{CO}_3$

A catalyst has the main influence on the yield distribution percentage because it has the ability to decompose feed material significantly [17]. Mudge et al. [18] found  $\text{K}_2\text{CO}_3$  was an effective catalyst for conversion of wood to synthesis gases and methane-rich gas. Lang [19] testified that alkali and alkaline earth metals, especially in the form of carbonate, are the superior catalysts for the gasification reactions. Li et al. [20] reported improvements in gas yield during the atmospheric steam gasification of peat catalyzed by  $\text{K}_2\text{CO}_3$  when studied at the temperature range from 973 °K to 1,123 °K. High temperature and long reaction time favor the increase in gas yield, but they reduce caloric value of the gas product.

Karimi and Gray found  $\text{K}_2\text{CO}_3$  as better catalyst than  $\text{Na}_2\text{CO}_3$  for the steam gasification of bitumen coke [21]. According to McKee [22] potassium undergoes redox cycle for  $\text{CO}_2$  gasification, in which the potassium catalyst is reduced and oxidized as illustrated in reactions (8), (9) and (10).



The sum of reactions (8), (9) and (10) gives the reverse Boudouard reaction:

Wang et al. [25] proposed oxygen transfer and intermediate hybrid mechanism as shown in Fig. 4(a) to explain the reasons for the increase in instantaneous release concentration of  $\text{CO}_2$  and  $\text{H}_2$  increase with the increase in potassium content. However, according to Wu et al. [26] the above mechanism failed to explain the selectivity of catalytic gasification. Wu et al. [26] also suggested a modified mechanism of  $\text{K}_2\text{CO}_3$ -catalyzed steam gasification of ash-free char which is shown in Fig. 4(b).

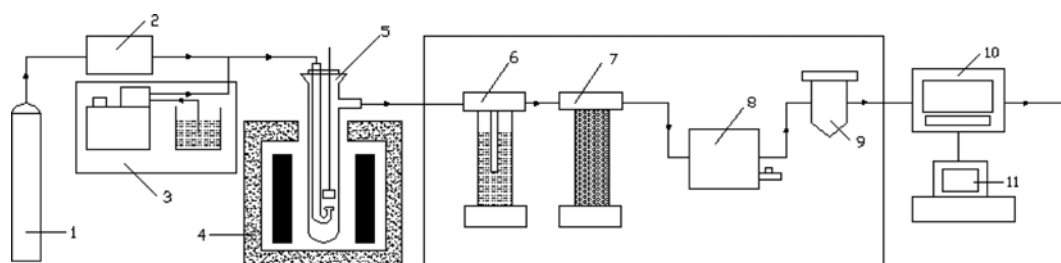
## EXPERIMENTAL SECTION

### 1. Materials Pretreatment

RS sample was obtained from Shenyang city, Liaoning province, China. Air-dried biomass was ground and sieved to a size of 0.15-0.25 mm. The elemental and proximate analyses of RS selected as raw material are given in Table 1. Inherent potassium in RS sample was removed by leaching the sample with deionized water. During leaching the sample at a ratio of 80 ml/g (deionized water to biomass) was placed into a constant temperature water bath oscillator maintained at 30 °C temperature for 3 h; after that the solution was filtered and residue was dried at 105 °C in the oven for 12 h. The potassium content of raw RS and water leached RS was determined by ICP-E8300. The removal efficiency of potassium content during leaching was up to 90.5%. In biomass gasification the catalysts can be added directly to the biomass by dry

**Table 1. The elemental and proximate analyses of RS**

Elemental analysis (wt%)														Proximate analysis (wt%)			
H	C	N	S	O	Cl	K	Na	Ca	Mg	Al	Si	Fe	Ti	Ash	VO	FC	M
5.53	39.77	0.82	0.24	53.6	0.44	0.81	0.32	0.45	0.018	0.35	4.99	0.349	0.005	15.84	71.55	6.62	5.99



**Fig. 1. The experimental setup for pyrolysis and steam gasification of RS.**

(1) Nitrogen cylinder

(2) Mass flow meter

(3) Steam generating device

(4) Gasifier

(5) Quartz tube reactor

(6) Dust removing device

(7) Decoking unit

(8) Gas pump

(9) Condensing unit

(10) On-line infrared gas analyzer

(11) Computer

mixing or wet impregnation [27]. We used  $K_2CO_3$  as potassium additive and adopted impregnation method to add  $K_2CO_3$  to water leached RS to prepare the samples containing mass concentration of 3%, 6%, 9%  $K_2CO_3$ .

## 2. Experimental Setup and Procedure

### 2-1. Pyrolysis Experiment

The experimental apparatus is shown in Fig. 1. One-gram sample in quartz crucible with micropores was placed in the most upper part of the quartz tube reactor.  $N_2$  was purged (in a 200 ml/min flow rate) into the quartz tube reactor and reactor temperature was raised to 750 °C. After 15 min of achieving 750 °C the

sample was moved to reaction zone to start pyrolysis experiment. On-line infrared gas analyzer (GASBOARD-3100 type produced by Wuhan Sifang) was used to record instantaneous gas volume concentration data. The pyrolysis reaction lasted for 20 min.

### 2-2. Gasification Experiment

Compared with the pyrolysis experiment, the steam gasification experiment has an extra device (steam generating). Experimental procedure is basically the same as for the pyrolysis experiment. At 750 °C, steam was introduced into the reactor (at flow rate of 2 ml/min) under 200 ml/min  $N_2$  entrainment. In addition, the quartz crucible was replaced by 200 mesh copper network during gasifi-

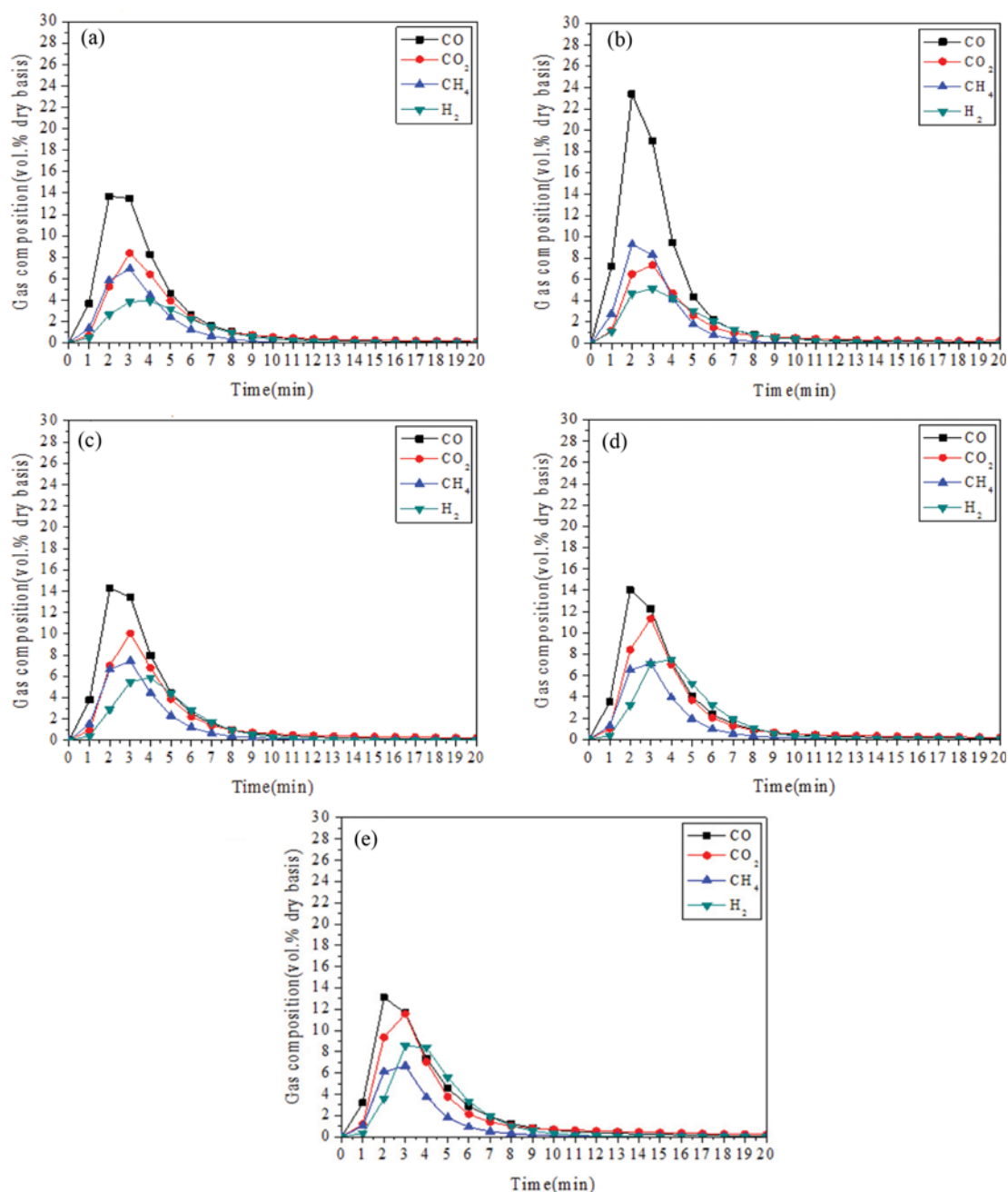


Fig. 2. The effect of presence of  $K_2CO_3$  on gas transient release behavior during pyrolysis of (a) Raw RS, (b) water leached RS, (c) 3%  $K_2CO_3$ -RS, (d) 6%  $K_2CO_3$ -RS (e) 9%  $K_2CO_3$ -RS.

cation in order to make RS contact with steam more intimate.

**3. Analysis Methods**

During RS pyrolysis and steam gasification process the instantaneous release concentration (volume percent of each component in gas) was recorded by GASBOARD-3100 on-line infrared gas analyzer. The carbon conversion rate (X) of RS during pyrolysis and steam gasification was calculated by the following equation [28].

$$X = \frac{\int_{t_0=0}^{t=t} \left( \frac{200 \times 10^{-3} \times (\varphi_{CO} + \varphi_{CO_2} + \varphi_{CH_4})}{22.4 \varphi_{N_2}} \times 12 \right) dt}{m_o} \times 100 \quad (15)$$

where  $m_o$  is the carbon mass of RS,  $t_o$  is the initial time of RS pyrolysis/steam gasification, and  $\varphi_{CO}$ ,  $\varphi_{CO_2}$ ,  $\varphi_{CH_4}$  and  $\varphi_{H_2}$  are CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> instantaneous volume fraction at time t.

**RESULTS AND DISCUSSION**

**1. The Effect of Potassium on Transient Gas Components During Pyrolysis and Steam Gasification of RS**

Since pyrolysis and steam gasification are not completely independent and interact with each other, it is hard to divide the two stages clearly. However, they have different reaction characteris-

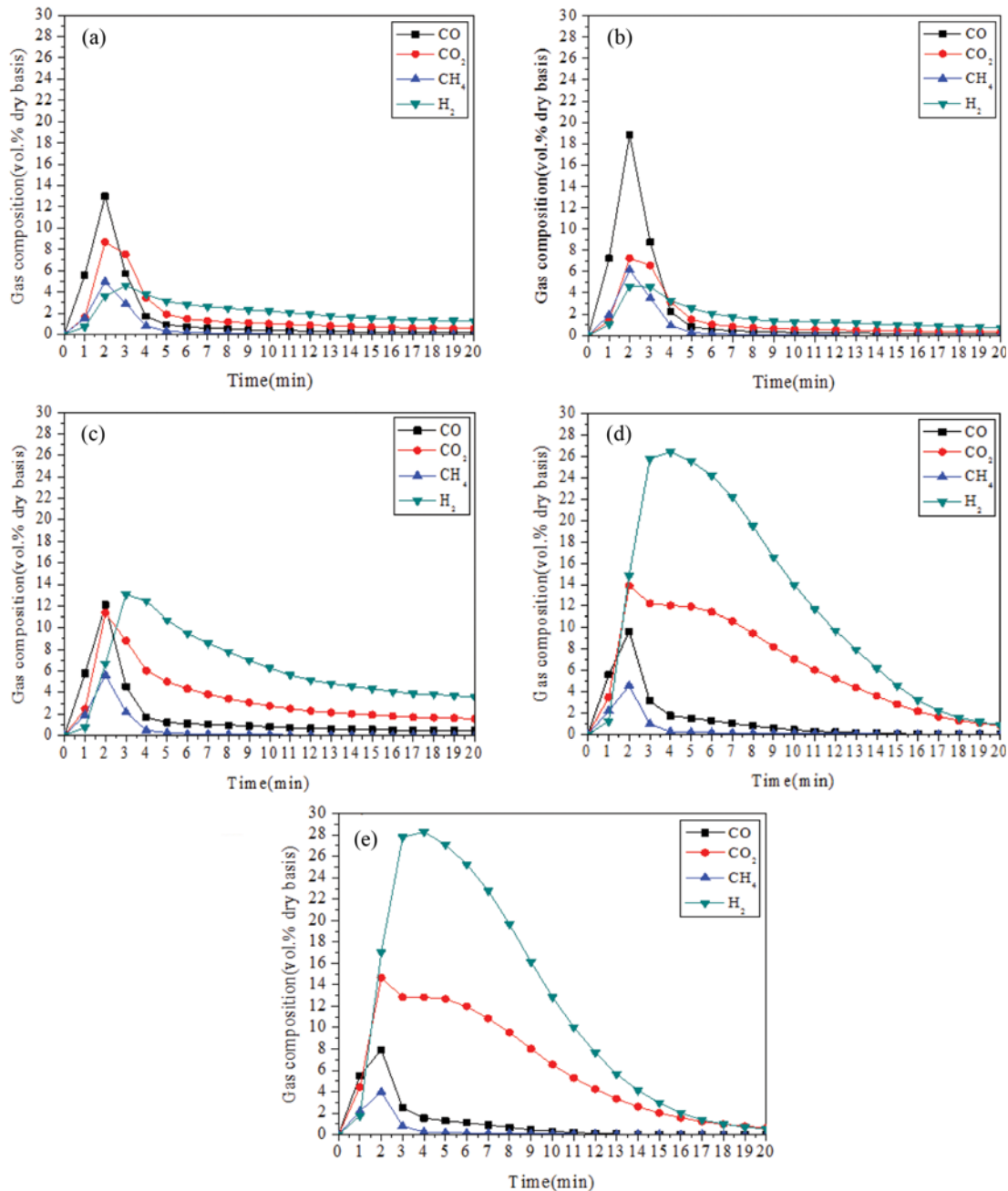


Fig. 3. The effect of presence of K<sub>2</sub>CO<sub>3</sub> on gas transient release behavior during steam gasification of (a) Raw RS, (b) water leached RS, (c) 3% K<sub>2</sub>CO<sub>3</sub>-RS, (d) 6% K<sub>2</sub>CO<sub>3</sub>-RS, (e) 9% K<sub>2</sub>CO<sub>3</sub>-RS.

tics, and a qualitative manner was used to analyze them.

Figs. 2 and 3 show the effect of  $K_2CO_3$  on gas transient release behavior of RS pyrolysis and steam gasification, respectively. As shown in Figs. 2 and 3 during RS pyrolysis process, compared to raw RS in water leached RS the instantaneous release concentration of  $CO$ ,  $CH_4$ ,  $H_2$  increased and instantaneous release concentration of  $CO_2$  decreased. This was mainly because potassium was removed from RS sample. Compared with raw RS pyrolysis, impregnated 3%, 6%, 9% potassium RS released progressively high concentration of instantaneous  $H_2$ ,  $CO_2$ . These results are in agreement with the earlier studies by Tada and Yasunishi [29]. The presence of potassium promotes formation of C=O double bond compound and generates some small molecules (such as hydroxyacetaldehyde, acids,  $CO_2$ , etc.) [30,31]. According to Nishimura et al. [32]  $K_2CO_3$  promotes straw cellulose structure decomposition by the following two ways: (1) promotes cleavage of hydrogen bond, C-C and C-H bond; and (2) promotes complete decomposition of cellulose glucosidic by heterolytic mechanism and generates some small molecules, such as acetic acid, formic acid, glyoxal, hydroxyacetaldehyde and acetol [32]. Hence RS impregnated with  $K_2CO_3$  during pyrolysis releases high instantaneous concentration of  $H_2$ ,  $CO_2$ .

When gas transient release behavior of five cases was compared (Fig. 3), the maximum appearance time of  $CO$  from gasification

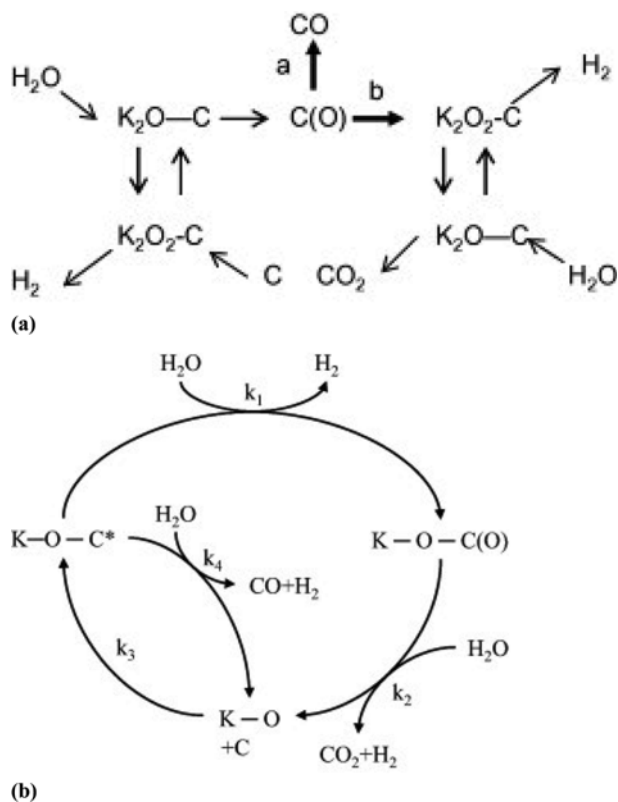


Fig. 4. (a) An oxygen transfer and  $C(O)$  intermediate hybrid reaction scheme during steam gasification of RS catalyzed by potassium proposed by Wang et al. [25], and (b) the mechanism of  $K_2CO_3$ -catalyzed steam gasification of char for kinetic modeling suggested Wu et al. [26].

had no obvious change. For water leached RS,  $H_2$  appeared 1 min early. For 3%  $K_2CO_3$  RS and 6%  $K_2CO_3$  RS no change in  $H_2$  appearance time was noticeable, and for 9%  $K_2CO_3$  RS,  $H_2$  appearance was delayed by 1 min. This was because the volatilization of pyrolysis and char gasification interacts with each other during steam gasification. Pyrolysis gases  $CO$ ,  $CH_4$ , tar and other hydrocarbons react with steam by water-gas shift reaction (3), steam-methane reforming reaction (4), and steam-tar reforming reaction (7) to affect both gas composition as well as distribution. The presence of  $K_2CO_3$  promotes all above reactions besides secondary cracking reaction of tar and other macromolecular hydrocarbons. As shown in Fig. 3, compared with gas transient release behavior of water leached RS gasification, it was found that  $CO$ ,  $CH_4$  instantaneous release concentration of raw RS, impregnated 3%  $K_2CO_3$ , 6%  $K_2CO_3$ , 9%  $K_2CO_3$  RS increased significantly, while the  $CO_2$ ,  $H_2$  instantaneous release concentration decreased (except for 3%  $K_2CO_3$  which increased). Summarizing the results, with increase of impregnated  $K_2CO_3$  content in RS,  $CO$ ,  $CH_4$  instantaneous release concentration decreased gradually and  $CO_2$ ,  $H_2$  instantaneous release concentration increased progressively. In addition,  $H_2$  instantaneous release concentration presented a sharp trend in the case of 6%  $K_2CO_3$  RS gasification and this trend decreased for 9%.  $K_2CO_3$ . The mechanism proposed by Wigmans et al. [25] in Fig. 4 well explains the reason for increase in release instantaneous

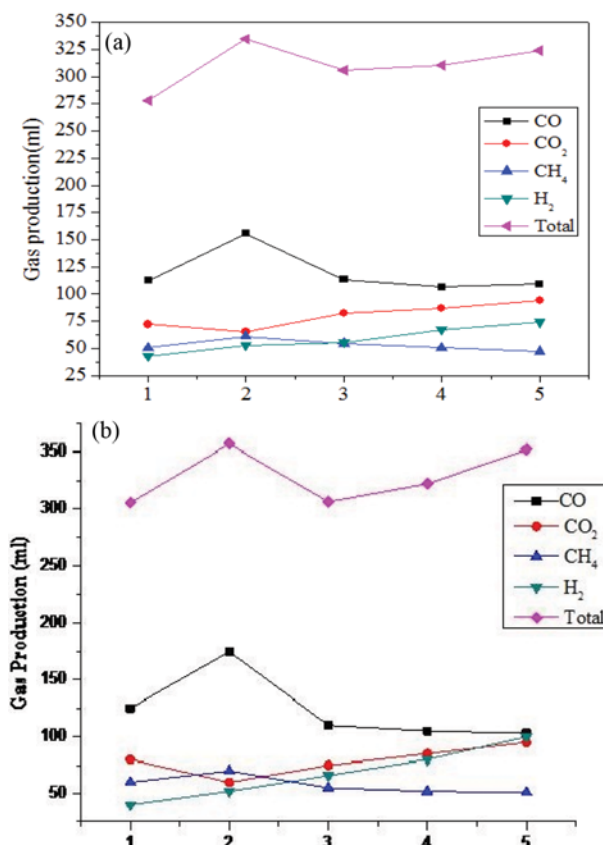


Fig. 5. The effect of  $K_2CO_3$  on gas component distribution and total gas yield during (a) pyrolysis, and (b) steam gasification of (1) Raw RS, (2) water leached RS, (3) 3%  $K_2CO_3$  RS, (4) 6%  $K_2CO_3$  RS, and (5) 9%  $K_2CO_3$  RS.

concentration of  $\text{CO}_2$ ,  $\text{H}_2$  with the increase of  $\text{K}_2\text{CO}_3$  content in RS.  $\text{K}_2\text{CO}_3$  catalysis RS pyrolysis by promoting  $\text{CO}_2$ ,  $\text{H}_2$  generation, and promoting  $\text{CO}$ ,  $\text{CH}_4$ , tar and hydrocarbons reacting with steam to contribute  $\text{CO}_2$  and  $\text{H}_2$ . When pyrolysis happens, char is produced instantaneously, so reaction (2) is accompanied with the entire pyrolysis process.

## 2. The Effect of Potassium on Gas Component Distribution and Total Yield of Gas Production During RS Pyrolysis and Steam Gasification

Fig. 5 shows the effect of  $\text{K}_2\text{CO}_3$  on individual component as well as total gas production from pyrolysis and steam gasification of RS. During pyrolysis,  $\text{CO}$  production in water leached RS was largest, and after  $\text{K}_2\text{CO}_3$  was impregnated,  $\text{CO}$  production decreased.  $\text{CO}_2$  production increased with the increase in  $\text{K}_2\text{CO}_3$  content, while the production of  $\text{CH}_4$  decreased slightly.  $\text{H}_2$  production followed the order: raw RS < water leached RS < 3%  $\text{K}_2\text{CO}_3$  RS < 6%  $\text{K}_2\text{CO}_3$  RS < 9%  $\text{K}_2\text{CO}_3$  RS. Total gas production increased with the increase of potassium content in RS.

During RS steam gasification,  $\text{CO}$  production followed the order: 9%  $\text{K}_2\text{CO}_3$  RS < 6%  $\text{K}_2\text{CO}_3$  RS < raw RS < 3%  $\text{K}_2\text{CO}_3$  RS < water leached RS.  $\text{CO}_2$ ,  $\text{CH}_4$  production exhibited the same regularity as during pyrolysis.  $\text{H}_2$  production and total production were in proportional to  $\text{K}_2\text{CO}_3$  content in RS and followed the order: water leached RS < raw RS < 3%  $\text{K}_2\text{CO}_3$  RS < 6%  $\text{K}_2\text{CO}_3$  RS < 9%  $\text{K}_2\text{CO}_3$  RS. This is

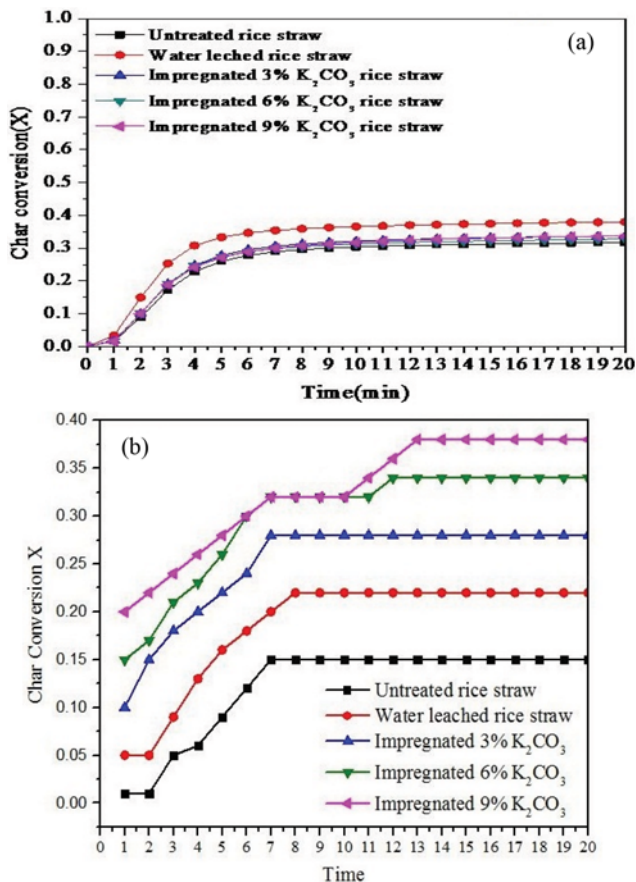


Fig. 6. The effect of  $\text{K}_2\text{CO}_3$  on reactivity during (a) pyrolysis and (b) steam gasification of raw RS, water leached RS, 3%  $\text{K}_2\text{CO}_3$  RS, 6%  $\text{K}_2\text{CO}_3$  RS and 9%  $\text{K}_2\text{CO}_3$  RS.

mainly due to the catalysis effects of  $\text{K}_2\text{CO}_3$  on mainly reactions (2), (3).  $\text{CO}$  production decreased, while  $\text{CO}_2$ ,  $\text{H}_2$  and total gas production increased. It is observed that the maximum  $\text{H}_2$  yield percentage was produced at 9% of  $\text{K}_2\text{CO}_3$  in the studied range (3%, 6%, and 9%) of  $\text{K}_2\text{CO}_3$  catalyst in both pyrolysis and steam gasification.

## 3. The Effect of $\text{K}_2\text{CO}_3$ on Reactivity During RS Pyrolysis and Steam Gasification

Carbon conversion rate is usually used to evaluate the reactivity during pyrolysis and steam gasification. The reactivity of RS during pyrolysis and steam gasification was analyzed by carbon conversion rate, and results are shown in Fig. 6(a) and (b). During RS pyrolysis process, carbon conversion rate of all five samples of RS (raw RS, water leached RS, 3%  $\text{K}_2\text{CO}_3$  RS, 6%  $\text{K}_2\text{CO}_3$  RS and 9%  $\text{K}_2\text{CO}_3$  RS) reached maximum at 7 min, and there were consistent gas release characteristics during pyrolysis that ended at 7 min (Fig. 6). For all five samples of RS, water leached RS had the highest carbon conversion rate and showed the highest reactivity. Impregnated  $\text{K}_2\text{CO}_3$  RS had almost the same carbon conversion rate. The reasons are that during pyrolysis,  $\text{K}_2\text{CO}_3$  promotes the release of  $\text{CO}_2$  while at the same time inhibits the release of  $\text{CO}$  and  $\text{CH}_4$ . Both promotion and inhibition effect are proportional to  $\text{K}_2\text{CO}_3$  content.

During RS steam gasification process, with the increase of  $\text{K}_2\text{CO}_3$  content in RS both carbon conversion rate as well as steam gasification reactivity increased. This trend increased significantly from 3%  $\text{K}_2\text{CO}_3$  RS to 6%  $\text{K}_2\text{CO}_3$  RS; however, from 6%  $\text{K}_2\text{CO}_3$  RS to 9%  $\text{K}_2\text{CO}_3$  RS this trend was non-significant.

## 4. The Effect of $\text{K}_2\text{CO}_3$ on Quality of Gas Evaluation During RS Pyrolysis and Steam Gasification

$\text{H}_2$  yield and  $\text{H}_2/\text{CO}$  ratio are regarded as a standard to evaluate gasification gas quality [33-35]. Fig. 7 shows the effect of  $\text{K}_2\text{CO}_3$  on  $\text{H}_2$  yield during RS pyrolysis and steam gasification. During pyrolysis as well as steam gasification  $\text{H}_2$  yields followed the order: water leached RS < raw RS < 3%  $\text{K}_2\text{CO}_3$  RS < 6%  $\text{K}_2\text{CO}_3$  RS < 9%  $\text{K}_2\text{CO}_3$  RS, whereas the numerical values were 15.5%, 15.8%, 18.2%,

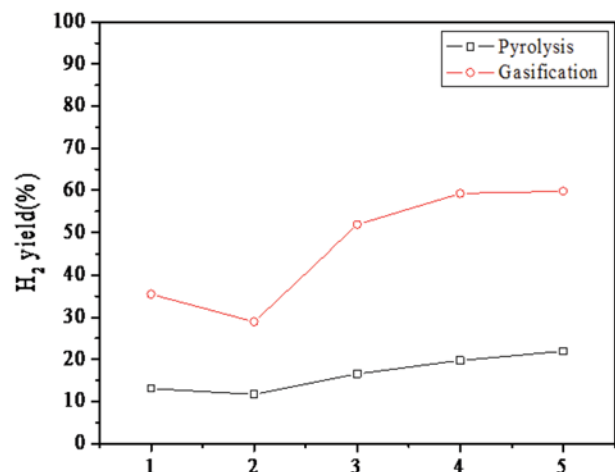


Fig. 7. The effect of  $\text{K}_2\text{CO}_3$  on  $\text{H}_2$  yield during pyrolysis and steam gasification of (1) Raw RS, (2) Water leached RS, (3) 3%  $\text{K}_2\text{CO}_3$  RS, (4) 6%  $\text{K}_2\text{CO}_3$  RS, and (5) 9%  $\text{K}_2\text{CO}_3$  RS.

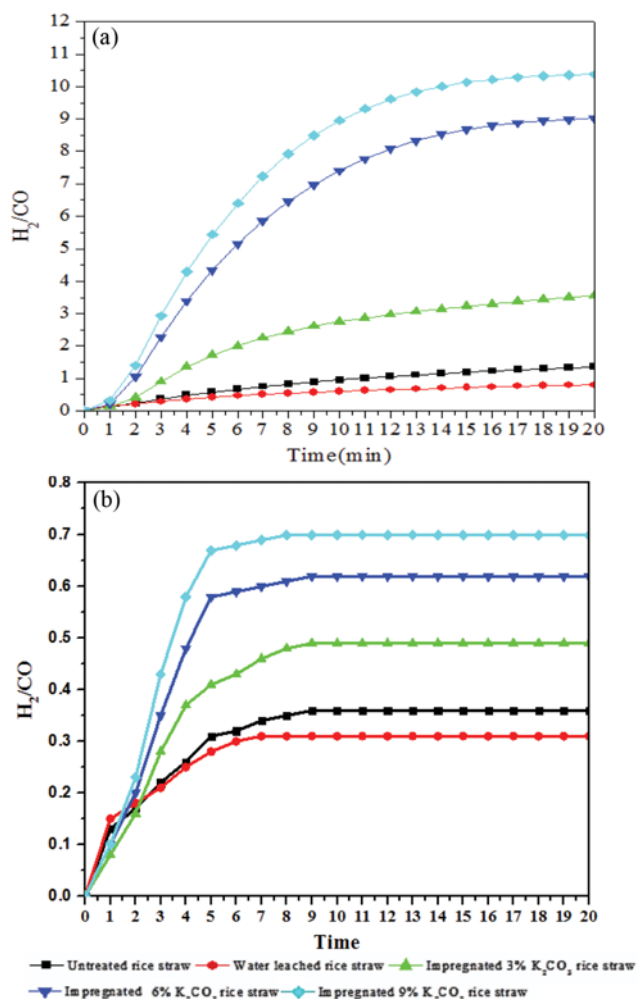


Fig. 8. The effect of  $K_2CO_3$  on  $H_2/CO$  ratio during pyrolysis and steam gasification of raw RS, water leached RS, 3%  $K_2CO_3$  RS, 6%  $K_2CO_3$  RS and 9%  $K_2CO_3$  RS.

21.6% and 22.9%, respectively. While during steam gasification,  $H_2$  yield was 28.9%, 35.5%, 51.9%, 59.2% and 59.8% respectively.

Fig. 8 shows the effect of  $K_2CO_3$  on  $H_2/CO$  ratio during RS pyrolysis and steam gasification. During both RS pyrolysis and steam gasification,  $H_2/CO$  ratio was proportional to  $K_2CO_3$  content. Higher the  $K_2CO_3$  content, the higher  $H_2/CO$  ratio. During RS pyrolysis,  $H_2/CO$  ratio was less than 1, which is unfavorable to gas end-use. However, during steam gasification of RS,  $H_2/CO$  ratio of raw RS gasification was 1; such gas can be applied to engine power. When  $K_2CO_3$  content was higher than 3%,  $H_2/CO$  ratio was much greater than 3, and  $H_2$  yield was more than 50%. A high  $H_2/CO$  ratio is required for producing liquid fuels through Fischer-Tropsch synthesis and also benefits the production of  $H_2$  rich gas [36].

#### CHALLENGES AND FURTHERS STUDIES

Potassium is one of the major nutrients and the potassium content in the RS is comparatively high [37]. The inherent alkali metals account for the high reactivity of biomass char [38]. The impregnation of potassium in RS has advantages of lower operating

temperature, lower investment cost and selectivity to certain gas products (higher  $H_2$  content). However, subsequent recovery of impregnated  $K_2CO_3$  is difficult and not always cost effective. It also increases  $K_2CO_3$  content in the residual ash after char gasification [27]. Besides  $K_2CO_3$  content in RS, other process parameters like steam/biomass ratio, reactor temperature, mean residence time, biomass particle size distribution also play a major role in the  $H_2$  yield during pyrolysis and steam gasification. Their synergistic interactive effect in presence of  $K_2CO_3$  needs further study studies and analyses.

#### CONCLUSIONS

This study evaluated the effect of the presence of  $K_2CO_3$  during the pyrolysis and steam gasification of RS. We found that the increase in  $K_2CO_3$  content in RS during the pyrolysis of RS resulted in increase in instantaneous concentration of both  $H_2$  and  $CO_2$ , while during subsequent gasification the instantaneous concentration of  $CO$  and  $CH_4$  decreased while  $CO_2$  and  $H_2$  increased when the  $K_2CO_3$  content in RS was increased. During gasification, both the production and yield of  $CO_2$  and  $H_2$  increased with the increase in  $K_2CO_3$  content in RS. Water-leached RS showed the highest carbon conversion rate and reactivity during pyrolysis, while  $K_2CO_3$  impregnated RS and raw RS showed almost the same carbon conversion rate. However, the gasification reactivity of RS was proportional to its  $K_2CO_3$  content. When  $K_2CO_3$  content in RS was higher than 3%,  $H_2$  concentration in gas produced was more than 50%. The yield of  $H_2$  was highest at 59.8% when  $K_2CO_3$  in RS was 9% (Fig. 7). These results indicate that the presence of  $K_2CO_3$  during pyrolysis and steam gasification of RS effectively assists in production of  $H_2$ -rich synthetic gas.

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