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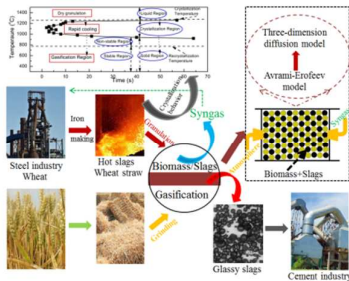
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Graphical Abstract

Syngas production was achieved using low temperature biomass gasification combined with heat recovery from hot slags.



Characteristics of low temperature biomass gasification and syngas release behavior using hot slags

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Abstract

This study proposed an emerging method to prepare the syngas using integrated low temperature biomass gasification combined with heat recovery from hot slags. A series of non-isothermal and isothermal gasification experiments were performed in the temperature range of 250-500°C to determine the effect of the presence of slags on the gasification. The results showed that the addition of slags remarkably increased the production of syngas in the temperature range of 425~500°C and during the gasification at 450°C with the mass ratio of wheat straw to slags of 1:1, the syngas with the amount of 0.149 L CO, 0.036 L H₂ and 0.069 L CH₄ can be produced per gram of wheat straw. The kinetic mechanism of biomass gasification changed from an Avrami–Erofeev model to a three-dimension diffusion model with the addition of slags. Although the presence of slag altered the mechanism of gasification, it did not lower the degree of gasification, and therefore the waste heat from hot slags can be used to produce syngas. Accordingly an industrial prototype plant composed of multiple systems was proposed, through which an energy saving relevant to 19.1 million tons of standard coal and an emission reduction of 69.9 million tons of CO₂ emissions would be achieved in China.

Keywords: Biomass gasification; Waste heat recovery; Hot slag; Syngas production

1. Introduction

To lower the reliance of energy supply on fossil fuel and to reduce the greenhouse gas (GHG) emission and environmental pollution, it is crucial to recover the waste heat and reduce the CO₂ emission from traditional industrial sectors ^[1-2]. In the steel industry, hot slags untapped at temperatures up to 1550°C carry a large amount of high quality energy, the recovery of which represent the last potential of energy reduction ^[3-4]. In China, the output of crude steel was more than 710 million tons in 2012 ^[5] and accordingly the produced slags during blast furnace process were more than 200 million tons, the total waste heat of which was equivalent to 16 million tons of standard coal. Conventionally, the slags can be rapidly quenched by water to avoid crystallization and the slags obtained this way are in a glassy state with strong hydraulicity ^[6] and can therefore be used as cementitious materials ^[7]. However, the thermal energy of the hot industrial slags from the steel industry is largely wasted in this water-quenched method and consequently the recovery rate of waste heat of slags is less than 2% in China ^[8] and there is a great potential for energy extraction.

In addition, hot slags are produced periodically resulting in the time in-continuity of heat supply ^[9] and many chemical methods are therefore exploited, which are believed as a promising way to transfer the in-continuous waste heat into continuous chemical energy in syngas ^[10-13]. Methane reforming ^[10-11] and coal gasification have been investigated ^[12-13] and the production of CO and H₂ was achieved. Furthermore, it was found that hot slags can act not only as heat carrier, but also as good catalysts in some chemical reactions ^[11-13]. This catalytic effect could originate from the

crystallization behaviors in the slags, which actually should be avoided from the point of view of material recycling of the solid slags. Although syngas production was achieved, the recycling of the material resources of slags has been limitedly discussed in these studies [11-13].

As a primary energy resource, biomass is believed to be promising in the near future because of its wide availability, renewability in nature and CO₂-neutrality [14-15]. In China, the crop residues were more than 803 million tons in 2009 [16] and the government attaches great importance to the usage of biomass energy. Recently biomass gasification technology has been extensively investigated and conventionally four reactive agents are widely used, *i.e.*, air [17], oxygen [18], steam [19-20] and carbon dioxide [21], or mixture of these [17-18, 22]. Fixed bed system is widely used to perform the biomass gasification [14, 20, 22] and generally the content of syngas is detected by gas analyzer [14, 20]. Recently, the co-gasification between biomass and other energy resource, such as bituminous coal and petroleum coke have been extensively studied and the synergistic effect of different gasification materials has been identified [18, 23]. The objective of an ongoing investigation by the current authors is to explore an emerging heat recovery method, low temperature biomass gasification using hot slags, considering both the waste heat recovery and the material recycling of slags.

To recover the waste heat of slags, a multi-stage control method was proposed in our previous work [24] and the property change of slags during cooling process was studied [25]. The whole temperature range of slags could be divided into liquid region, crystallization region and solid region. Generally, the temperature of the biomass

gasification is lower than 1000°C^[14], which is located in the solid region and it is therefore possible that the hot slags are taken as heat carrier for biomass gasification. While the advantageous role of the thermal energy in the slag is obvious, it is not known whether the presence of slag could hinder biomass gasification or even exhibit a possible catalytic effect, and therefore the present study was motivated. Moreover, there is a great challenge in the steel industry for meeting CO₂ targets^[26], which increases the possibility of using biomass gasification to recover waste heat from hot slags. The produced CO and H₂ can be potentially used directly as reactive gas to reduce the iron in the steel industry^[27]. In this study, a mixture of oxygen and steam was used to perform the gasification, which has been proved as good medium to perform biomass gasification elsewhere^[18, 28] and a series of non-isothermal and isothermal experiments were conducted using samples with various biomass/slag (B/S) ratios, which may provide a pathway for waste heat recovery from slags and biomass utilization.

2. Materials and Methods

2.1. Materials analysis

The wheat straw, a typical agricultural residue in Central China, was collected from Henan province. The results of ultimate and proximate analyses are listed in **Table 1**. Based on the ultimate analysis, the chemical formula of the raw material is derived as CH_{1.39}O_{0.90}. This study was mainly focused on the characteristics of the syngas release including the syngas yield and release kinetics; however, it should be pointed out that the pressure of gases during gasification could remarkably increase

due to the release of the high content of volatile in biomass, which may show some specific utilization for energy generation and could be our future work. Before gasification, the wheat straw was crushed into particles of sizes less than 200 meshes using a rotary cutting mill and then dried for 24 h at 105°C. Water quenched blast furnace (BF) slags from Shougang Corporation, China, were used and the chemical compositions were analyzed by X-ray fluorescence (XRF, S4-Explorer, Bruker), as shown in **Table 1**. BF slags alone account for more than 70% energy of slags^[6] and therefore this study concentrated on BF slags. Before mixture, these slags were crushed and ground to 200 meshes and characterized by X-ray diffraction (XRD, D/Max 2500, Rigaku) technique to confirm the glassy state. A series of gasification experiments were performed using 0.1g, 0.25g and 0.5 g biomass and found that under the present experimental conditions, the syngas production including CO, H₂ and CH₄ showed well linear relationship versus biomass amount. In the present experiment, 0.25g wheat straw was used with the B/S mass ratios of 1:0 (**S1**), 1:1 (**S2**) and 1:3 (**S3**) during each gasification process.

Table 1 Characteristics of the wheat straw and BF slags

	Proximate analysis/%				Ultimate analysis/%					Higher heating value (MJ/kg)	
	Moisture	Volatile	Ash	Fixed carbon	C	H	O	N	S		
Biomass	5.73	74.20	9.88	15.93	41.37	4.80	49.52	0.81	0.11	16.48	
	SiO ₂	K ₂ O	CaO	Cl	MgO	S	P ₂ O ₅	Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃	
Ash (XRF)	53.76	20.09	6.14	3.30	2.38	2.12	1.35	1.11	1.07	0.92	
	CaO	SiO ₂	MgO	Al ₂ O ₃	S	Fe ₂ O ₃	Na ₂ O	TiO ₂	MnO	K ₂ O	Cl
Slag (XRF)	37.88	34.61	15.62	8.56	0.92	0.60	0.54	0.45	0.36	0.26	0.02

2.2. Crystallization property analysis of BF slags

According to our previous work ^[24-25], an understanding of the crystallization behaviors of the slags is fundamental to exploit reasonable waste heat recovery methods. Isothermal experiments were carried out using Single Hot Thermocouple Technique (SHTT) for visualizing phase transformation and measuring crystallization behaviors of slags. The working mechanism was briefly introduced here ^[29]. The slag was first melted by heating it to 1550°C, held for 120 s to eliminate the bubbles and homogenize the chemical compositions; then the liquid slag was rapidly quenched to a holding temperature and it took some time to crystallize, defined as incubation time, and all the processes were performed in the atmosphere of air. Generally, the relation between incubation time and holding temperature is presented in Time Temperature Transformation (TTT) curve. Based on the TTT curve, the temperature range describing the slag characteristic could be divided into three regions, which are liquid region, crystallization region and solid region, respectively. This provided the

scientific basis for waste heat recovery from slags and also favors the selection of a reasonable gasification condition. It should be pointed out that the recrystallization also occurs as the solid slag is heated to the certain temperature, recrystallization temperature. This represents the stability of solid slags, which can be measured by thermogravimetric-differential thermal analysis (TG-DTA, S60/58341, Setaram).

2.3. Gasification apparatus and setup

Gasification processes were carried out in a fixed bed system, which was mainly composed of reactive gas control part, steam generator, tube furnace reactor, gas condenser and purifier and gas analyzer, as shown in **Figure 1**. A quartz tube reactor, with the length of 110 mm and the inner diameter of 30mm, was used in this study, which was externally heated by an electric furnace and quartz boats were used to hold the reactants.

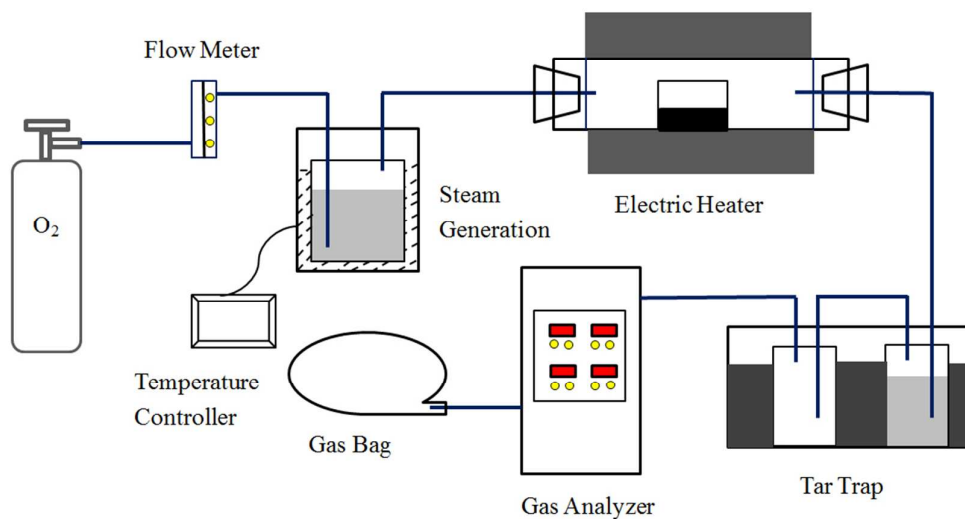


Fig.1. Schematic of biomass gasification system

The flow rate of gasification agent was 300 ml/min with the oxygen/steam ratio of 30%:70%. In order to ensure that the inlet gas composition has an accurate

oxygen/steam ratio of 30%:70%, the temperature of the humidifier (steam generator) was accurately controlled at 90°C and then the oxygen flowed through the humidifier with a flow rate of 90 ml/min to obtain a gasifying agent of 90 ml oxygen and 210 ml steam; meanwhile, to avoid the condensation of steam, the pipe that the gasification agent flows through was heated at 120°C by a heating tape. In order to clarify the effect of slags on biomass gasification, both non-isothermal and isothermal experiments were performed. For the non-isothermal process, the quartz boat was first placed in the middle of the tube and the gasification agent was then pumped into the system to fully expel the air. The furnace was then heated from room temperature (25°C) to 1000°C at 10°C/s, during which the gasification reaction occurred. For the isothermal experiments, the quartz boat was first loaded on the right side of the tube and the reactive agent was then pumped into the system to fully expel the air. When the temperature reached the holding temperature, the quartz boat was rapidly pushed into the middle of the tube to start the gasification process. After purification by a gas condenser and purifier, the volume and composition of the syngas was later detected by the gas analyzer (Testo pro350, Testo). Besides, the morphology and the facial distribution of the elements of the slag/ash after gasification were measured by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) (Hitachi S4800, Bruker); simultaneously, the Brunauer-Emmett-Teller (BET) surface area of the slag/ash was measured by an surface area and pore size analyzer (ASAP 2010, Micrometrics).

3. Results and discussion

3.1. Crystallization behavior of slags

The TTT curve for slags presents the crystallization ability of slags, which mainly determines the further utilization of the solid slags. If the cooled slag is to be utilized for applications such as cementitious materials, then a glassy structure is required. As shown in **Figure 2**, the TTT curve showed the double “C” shape, which suggested that two different crystallization events occurred. Additionally, several characteristics related to the crystallization behaviors of slag can be derived based on TTT curve. First, the highest temperature that crystal could form in the slag melts was 1270°C, which was defined as crystallization temperature and second, the lowest temperature that crystallization phenomena could be observed was 920°C. It should be pointed that there is a slight kink at 1160 °C, namely “nose position”, which significantly characters the crystallization behavior of slags. At the temperature of this position, the incubation time is the shortest and it is easy for crystal to form in the slags. Based on these temperature points, the temperature regions of slag cooling path can be reasonably divided^[24-25]. The region at 1550~1270°C was defined as liquid region, in which the slag would be expected to be in a completely liquid phase. The region between 1270°C and 920°C was defined as crystallization region, in which crystal could form in the slag. The region below 920°C was defined as glassy region, in which the slag would be expected to be in a glassy phase and there was no crystal precipitated because of the high resistance of mass transfer of ions in the slag.

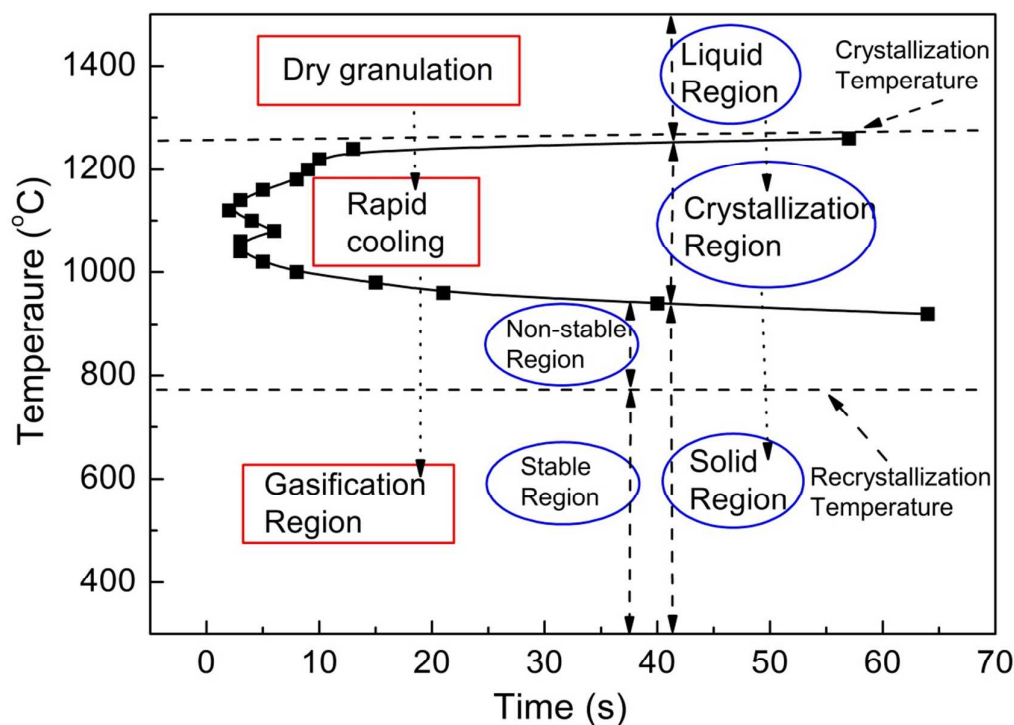


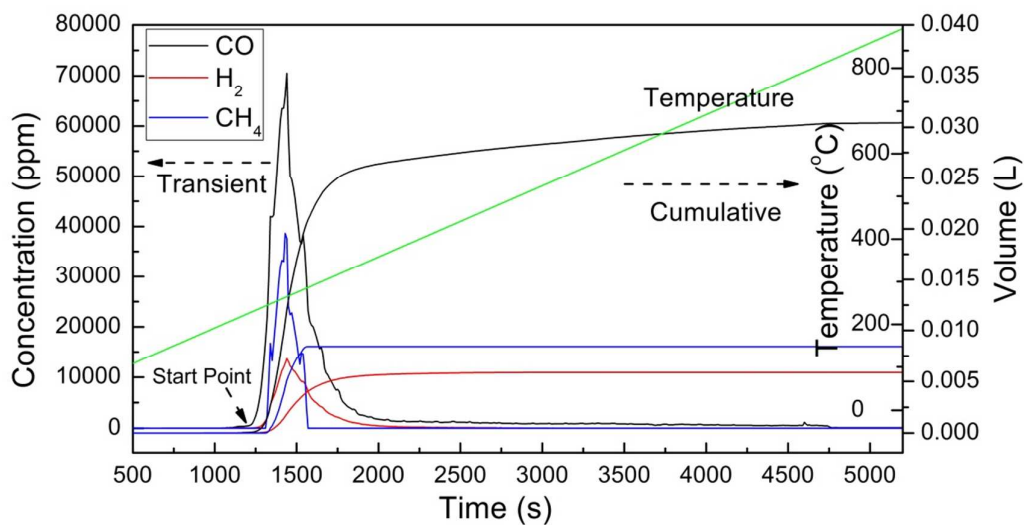
Fig.2. Crystallization behavior and cooling path of BF slags

These results derived from TTT curve are indicative of a two-step heat recovery process from hot slags. First, the liquid slag would be granulated into small particles and rapidly cooled to the temperature below 920°C to avoid crystallization and the waste heat in this region can be extracted through heat exchange between hot slags and air (or steam). Second, the solid slag would be made to contact ground biomass and the waste heat could enable the gasification to occur. The temperature region below 920°C covered the temperature region generally used for biomass gasification [14]. Moreover, the recrystallization temperature of the glassy slags was measured as 790°C by a TG/DTA method, which divided the solid region into stable region and non-stable region. To avoid crystallization and confirm the further recycling the slags, the gasification should be performed at temperatures below 790°C and therefore the present gasification temperatures were selected.

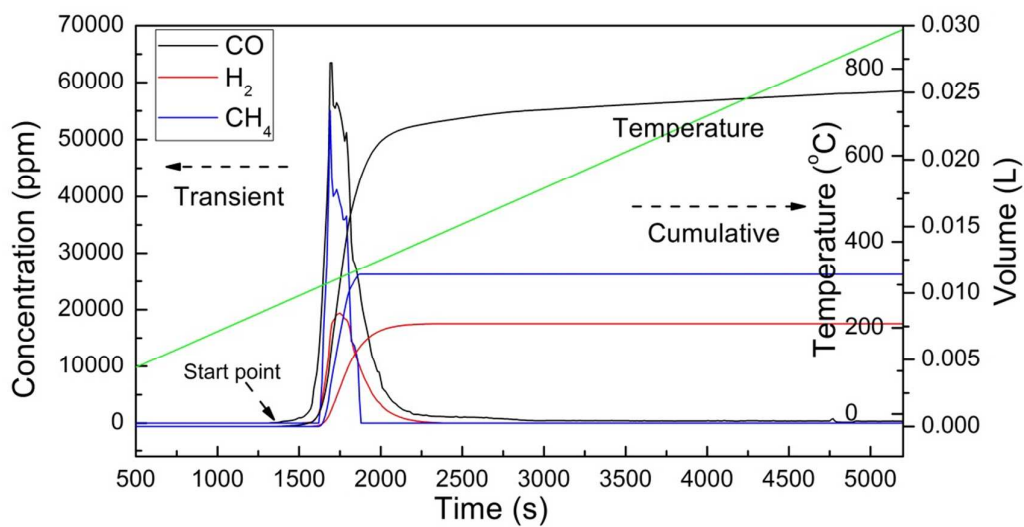
3.2. Non-isothermal gasification

During the non-isothermal process, the gas release was detected by a gas analyzer and the transient behavior of biomass gasification was recorded. **Figure 3** shows the transient and cumulative syngas production and it can be seen that the syngas was released in a specific temperature region. At $\sim 250^{\circ}\text{C}$, the gas release started and at $\sim 500^{\circ}\text{C}$, the gas release was completed; a peak in gas release curve can be identified at $\sim 320^{\circ}\text{C}$. The results show that, when comparing the S1, S2 and S3, the onset of gasification temperature was delayed with the addition of slags.

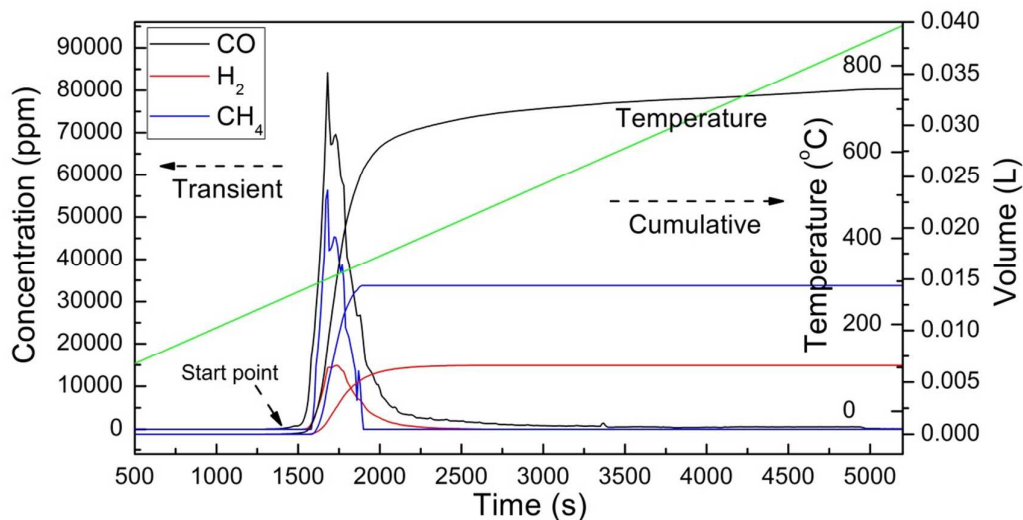
Biomass gasification can be generally divided into two stages, de-volatilization and char reaction^[20-22], and the former is especially important because of the high content of volatile in biomass. This phenomenon was also observed in the present experiments (**Figure 3**). It can be seen that the syngas release curve can be separated into two regions, and the former region of the gas release curves for three samples was sharp, whereas the latter region of the gas release curve was flat. This may suggest that there were two reaction steps in biomass gasification even though it was hard to completely separate de-volatilization and char reaction^[20]. From the curves of cumulative syngas production, it can be seen that the order of the syngas amount was that $\text{CO} > \text{CH}_4 > \text{H}_2$. It is also noted that the amount of syngas production slightly increased with addition of slags, which was also clearly observed in the isothermal experiments.



(a)



(b)



(c)

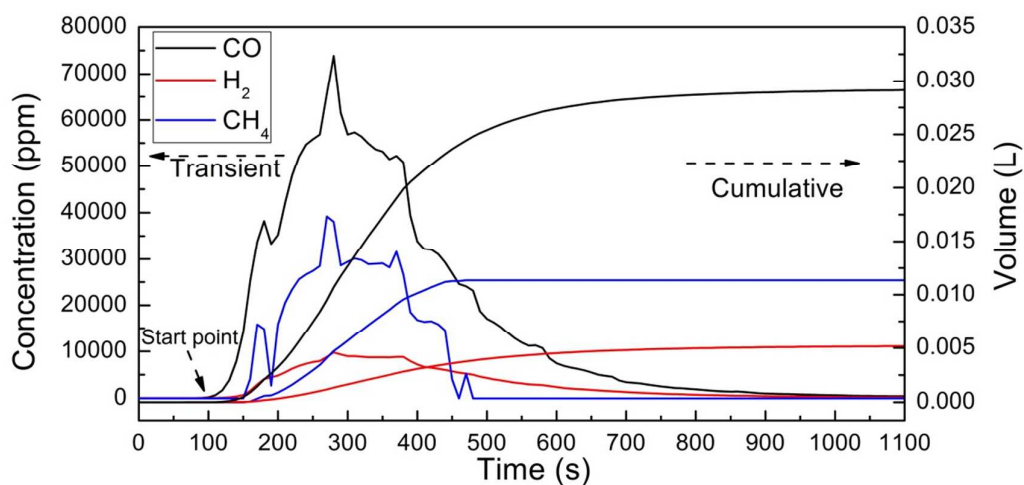
Fig.3. Non-isothermal syngas release for samples (a) S1, (b) S2 and (c) S3.

3.3. Isothermal gasification

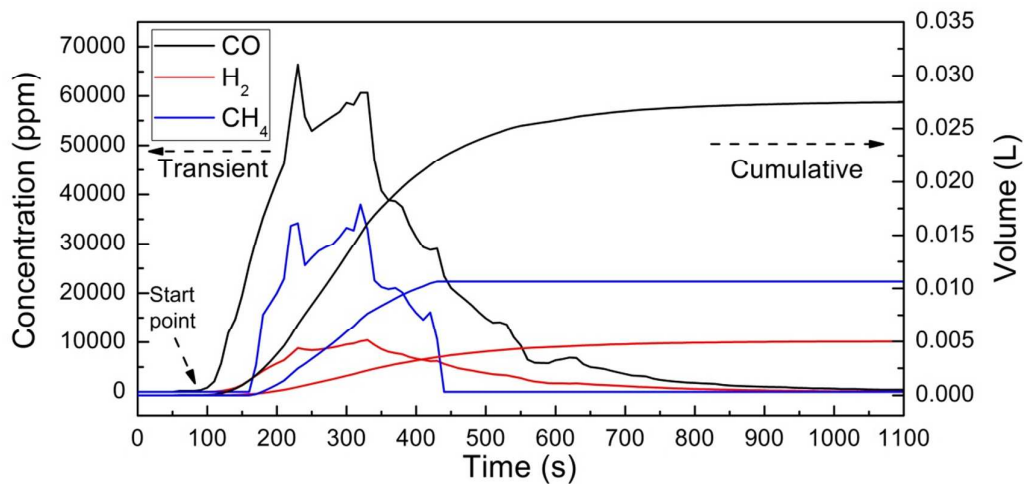
3.3.1. Kinetics of syngas release

The isothermal experiments were performed at 250~500°C. **Figure 4** shows the transient syngas release and calculated cumulative syngas production at 400°C. The transient curves at different temperatures showed a similar shape and therefore only the gas release curve at 400°C is presented here as a typical example. It can be seen that the produced gases showed the order that $\text{CO} > \text{CH}_4 > \text{H}_2$ and the gas release curves showed the characteristic shape composed of a sharp side in the former stage and a flat side in the later stage. This indicated that the gas release process was composed of at least two stages, namely de-volatilization and char reaction^[20-22]. The de-volatilization process accounted for the main process of gas release because of the high content of volatile, so the transient curve of gasification process was mainly composed of one sharp peak. The char reaction occurred at a slow rate and lasted for a

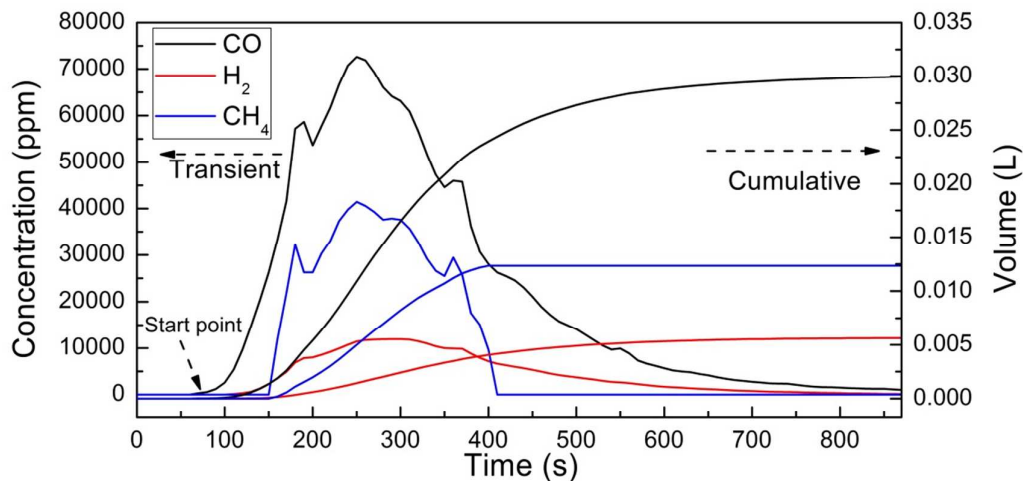
long time due to the low gasification temperature, and therefore the later stage of the curve showed a flat shape. These curve shapes of transient gas production was similar to a previous study on gasification of pine wood chips^[20]. Additionally, the gas release process was rapidly completed in several minutes as a whole.



(a)



(b)



(c)

Fig.4. Transient and cumulative syngas production at 400°C for samples (a) S1, (b) S2 and (c) S3.

In this study, the apparent kinetics of biomass gasification was interpreted. The kinetic equation of common type can be generally written as follows^[30-32]:

$$\frac{dx}{dt} = k(T)f(x) \quad (1)$$

where x is the conversion degree of syngas which is deduced by the division of the total syngas production by the syngas production at a time point, t is time, k is apparent gasification rate constant, T is the absolute temperature, and $f(x)$ is the differential function of reaction mechanism.

Alternatively, by rearranging **Eq. (1)** and integrating, the following equation can be deduced:

$$F(x) = \int_0^x \frac{dx}{f(x)} = k(T)t \quad (2)$$

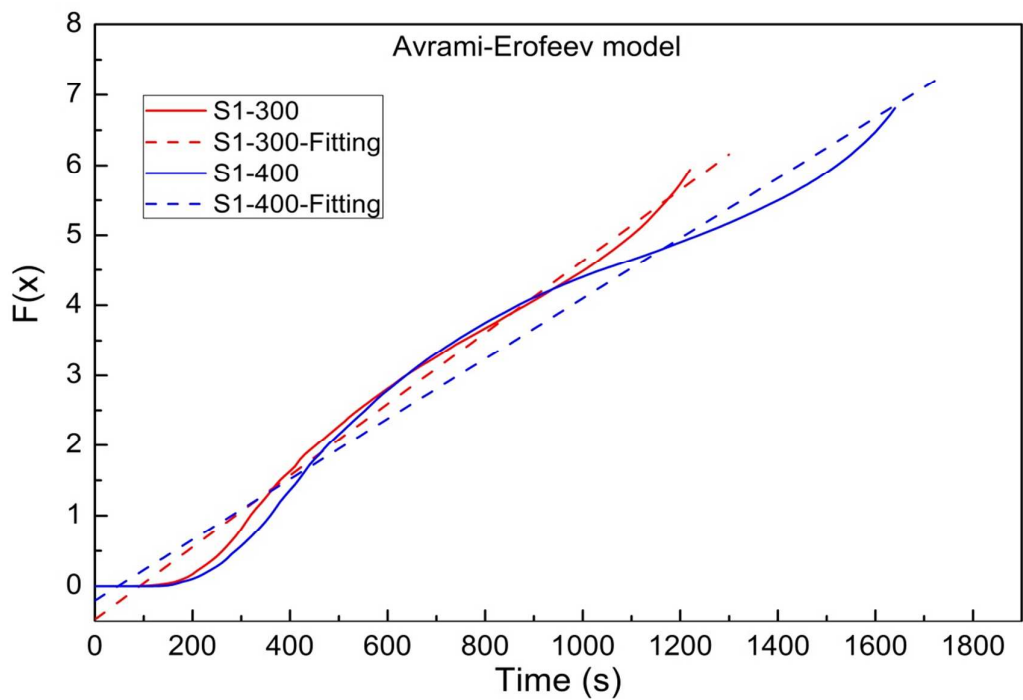
where $F(x)$ is the integral mechanism function. To analyze the linear relationship between $F(x)$ and t using different mechanism functions, the most probable

reaction mechanism could be obtained. By plotting $F(x)$ versus t using various mechanism functions including nucleation growth, chemical reaction and mass diffusion and comparing the correlation coefficients (R^2) of all plots, it was found that the experimental data could be reasonably reproduced by an Avrami–Erofeev model (**Eq. (3)**) for sample S1 and three-dimension diffusion model (**Eq. (4)**) for sample S2 and S3, as shown in **Figure 5**.

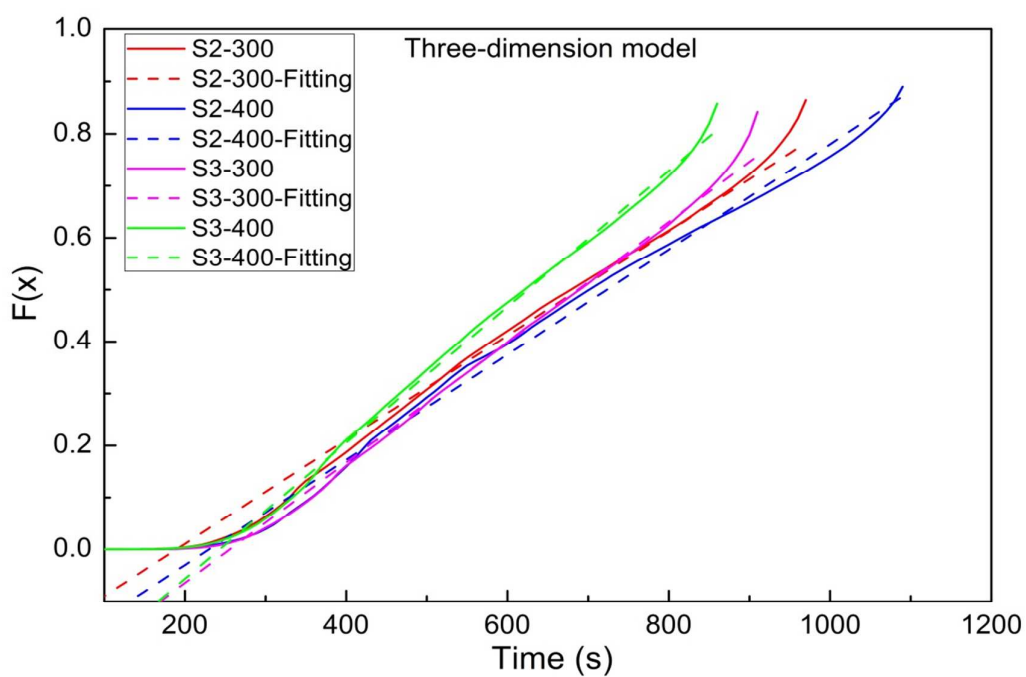
$$F(x) = -\ln(1-x) \quad (3)$$

$$F(x) = [1 - (1-x)^{1/3}]^2 \quad (4)$$

Avrami–Erofeev model is generally applicable to materials whose porosity changes during the reaction ^[31-32] and the rate-controlling step is the nucleation process, which is probable to interpret the biomass gasification because of the high content of volatile. As for samples S2 and S3, the presence of the slag suppressed the contact between biomass and reactive atmosphere, which increased the resistance of mass transfer; therefore the rate-controlling step would shift towards gas diffusion and it was reasonable to use a three-dimension diffusion model to reproduce the biomass/slag gasification process.



(a)



(b)

Fig.5. Mechanism model for samples (a) Avrami–Erofeev model for sample S1 (b)

Three-dimension diffusion model for sample S2 and S3

3.3.2. Calculation of syngas production

To investigate the effect of gasification temperature and B/S ratio on the biomass gasification, the total syngas production was calculated according to the transient curves, as depicted in **Figure 4**. **Figure 6** showed the relation between syngas production per gram of biomass and gasification temperature. First, it can be seen that the syngas yield was closely related to the gasification temperature. For sample S1 without slags, the production of syngas slightly increased at 250-400°C, while it greatly decreased at 400-500°C. Actually, the combustion of biomass was apparently observed at 500°C, indicating that the char reaction increased and therefore more CO₂ was formed. Second, the optimum temperature for biomass gasification at 250-500°C can be obtained in views of the maximum production of syngas, which was 450°C for these samples.

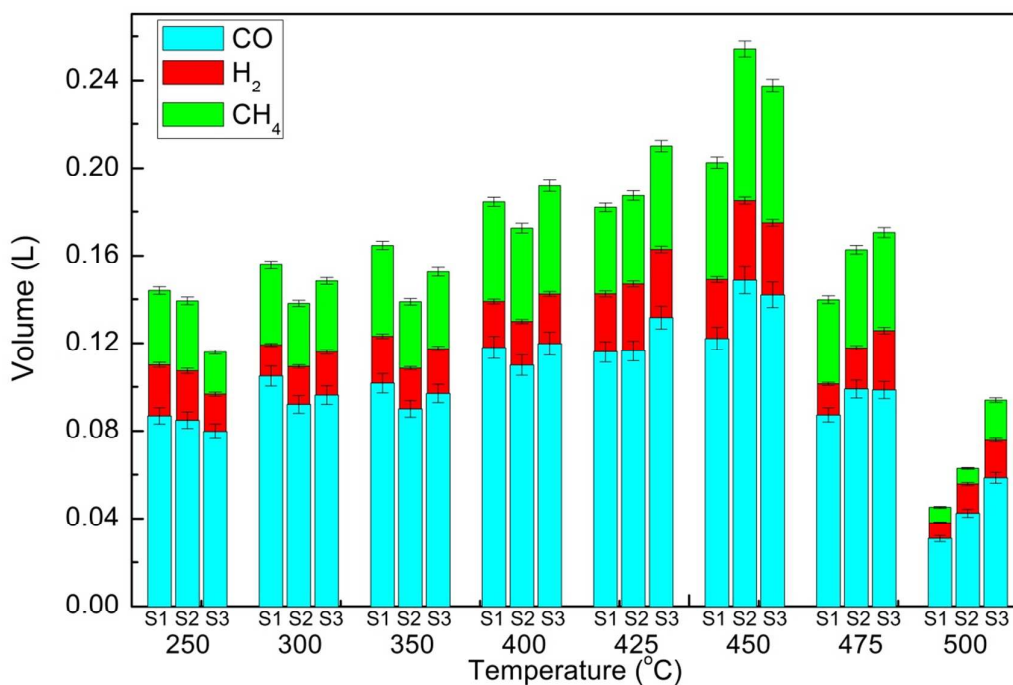


Fig.6. Major Gas yield in terms of gasification temperature per gram of biomass

Additionally, it can be observed that the B/S ratio did not influence the gas production at low temperatures (250~400°C). However, there was an apparent increase of syngas production at 425~500°C, which could originate from the effect of the addition of slags on the reaction of biomass. The added slags reduced the contact between atmosphere and biomass, suppressed the biomass combustion and CO₂ release, and therefore could indirectly improve the production of syngas.

3.3.3. Characterization of hazardous gas and solid residues

In this study, the release of the polluted gases, namely NO_x and SO₂, was also detected by the gas analyzer and the results showed that the concentration of NO₂ and NO during the whole process for all samples was less than 2ppm and 5 ppm, which might result from the low gasification temperature; furthermore, no SO₂ emission was detected in the present experiments. This low emission of NO_x and SO₂ would cause relatively minor environmental pollution and suggested another advantage of low temperature biomass gasification using hot slags.

To further explore the track of S and N elements, the facial distributions were measured by SEM with EDX. As shown in **Figure 7**, the S, N and Cl elements were uniformly distributed in the residual slag/ash, which were generated from the biomass ash (**Table 1**) and were the characteristic elements of biomass resources ^[14, 16]; in contrast, the Si and Ca elements were only distributed in the slag particles, which were the characteristic elements of hot slags ^[6, 25]. Additionally, **Figure 8** showed the morphology of the slag/ash and it can be noted that the surface of the slag particles became coarser because biomass ash was produced and adhered to the slag particle

surfaces. Furthermore, the BET surface area of the slag particles were measured and it was found that the specific surface area increased from $1.25\text{m}^2/\text{g}$ of the original slags to $2.18\text{m}^2/\text{g}$ and $2.70\text{m}^2/\text{g}$ of the produced mixtures of slag and ash after gasification for sample S3 at 425°C and 450°C , respectively, which suggested that the produced biomass ash adhered to the slag surface and therefore increase the specific surface area of the solid residues. Because the gasification occurred at relatively low temperatures, the produced biomass ash was in solid state ^[33], which could not effectively conglomerate and therefore uniformly distributed on the surface of slag particles. The change in surface morphology caused by adherence of biomass ash and slag might be the reason for the observed change in mechanism towards gas phase diffusion control when slag is added to biomass.

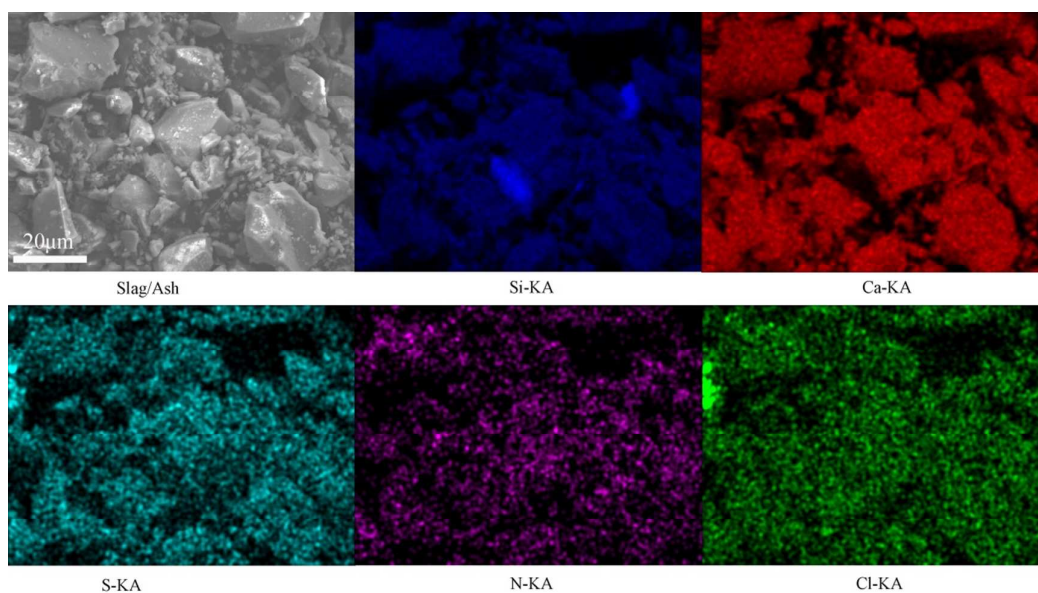


Fig.7. Facial distribution of the characteristic elements in solid residues

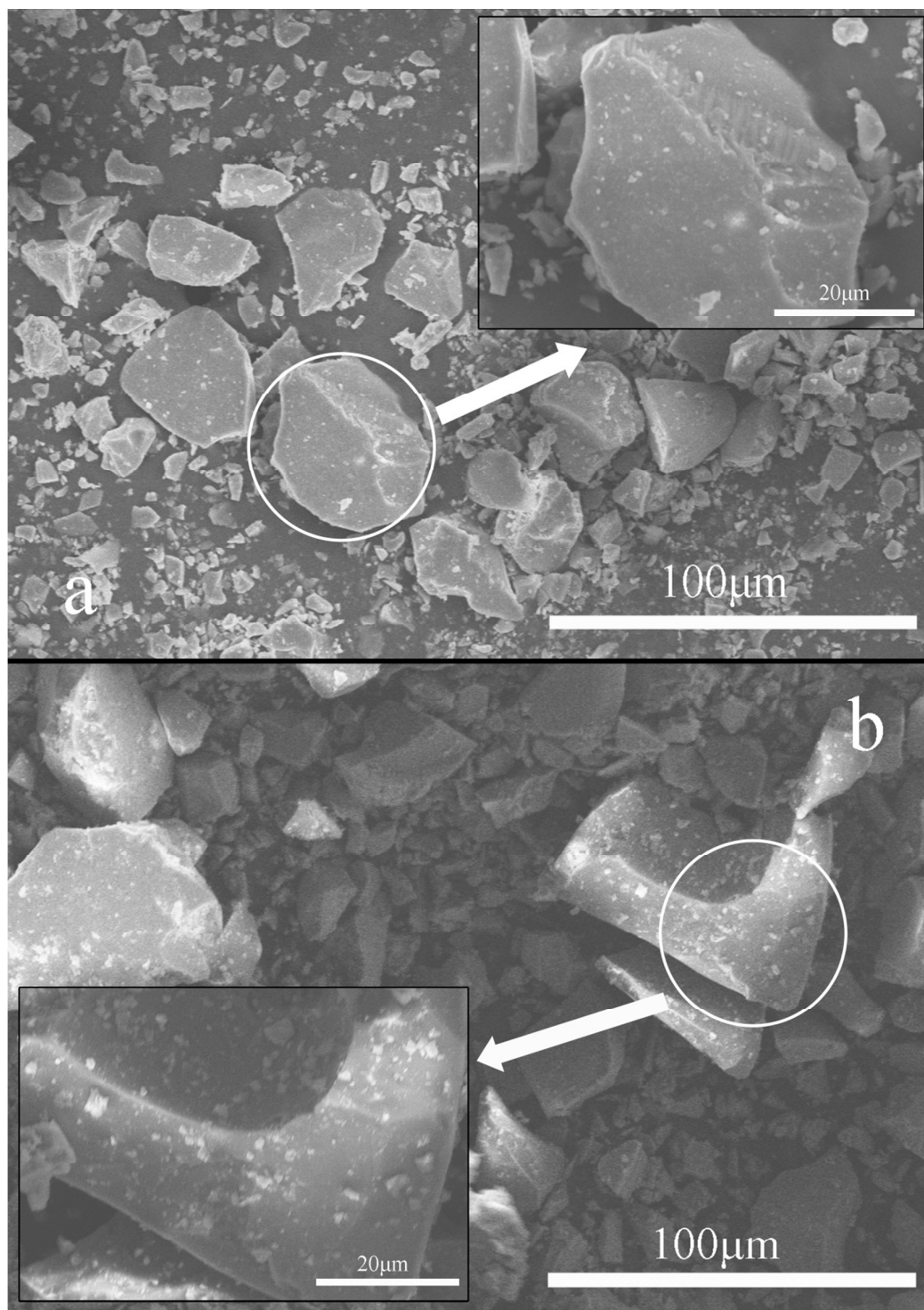


Fig.8. Surface morphology of the slag particles (a) Original slags and (b) Slag/Ash after gasification (S3 at 450°C)

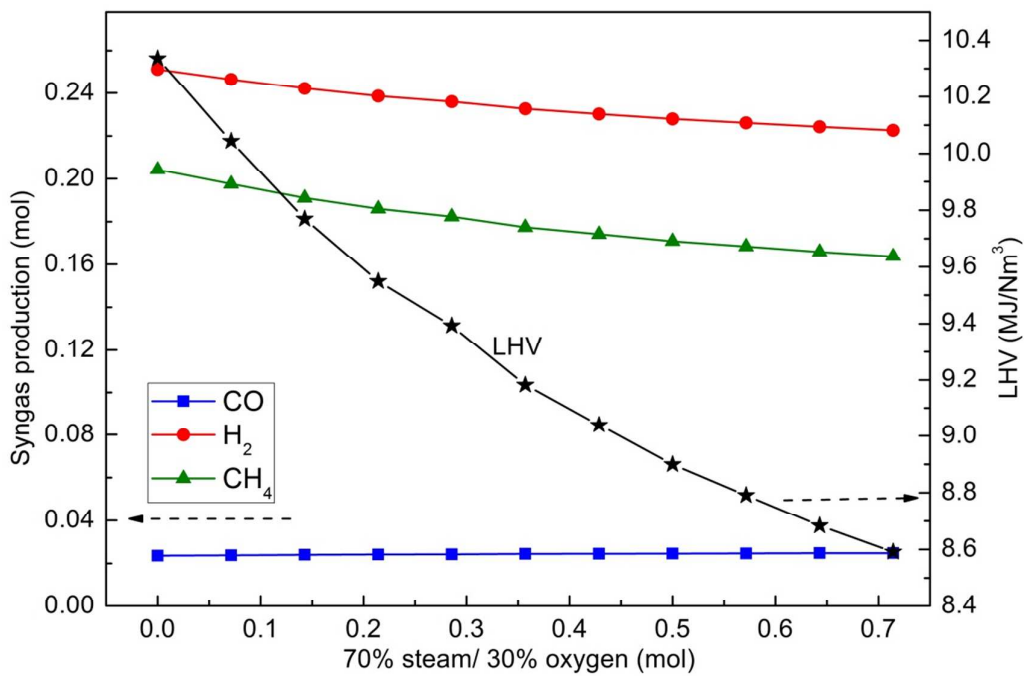
3.3.4. Thermodynamics of biomass gasification by FactSage

The syngas composition and production was greatly influenced by the reaction medium and the atmosphere with the oxygen/steam ratio of 30%:70% was adopted to predict the syngas formation; while exploration of other reaction medium is also of great significance, and constitutes our future work. The experiments suggest that the presence of slags do not lower the degree of gasification under the conditions studied. Thus, syngas production during the biomass gasification using hot slags could be approximated through calculations by FactSage^[34]. Considering that the optimum gasification temperature for these samples was 450°C, the equilibrium syngas production was calculated at 450°C in different atmospheres as an example. To simplify the calculation process, the amount of C, H and O atoms were assumed to be 1mol, 1.39mol and 0.90mol, respectively and the reactive steam and oxygen was varied from 0.05 mol to 0.5 mol. Then the lower heating value (LHV) of the syngas was calculated according to the following equation^[31, 35]:

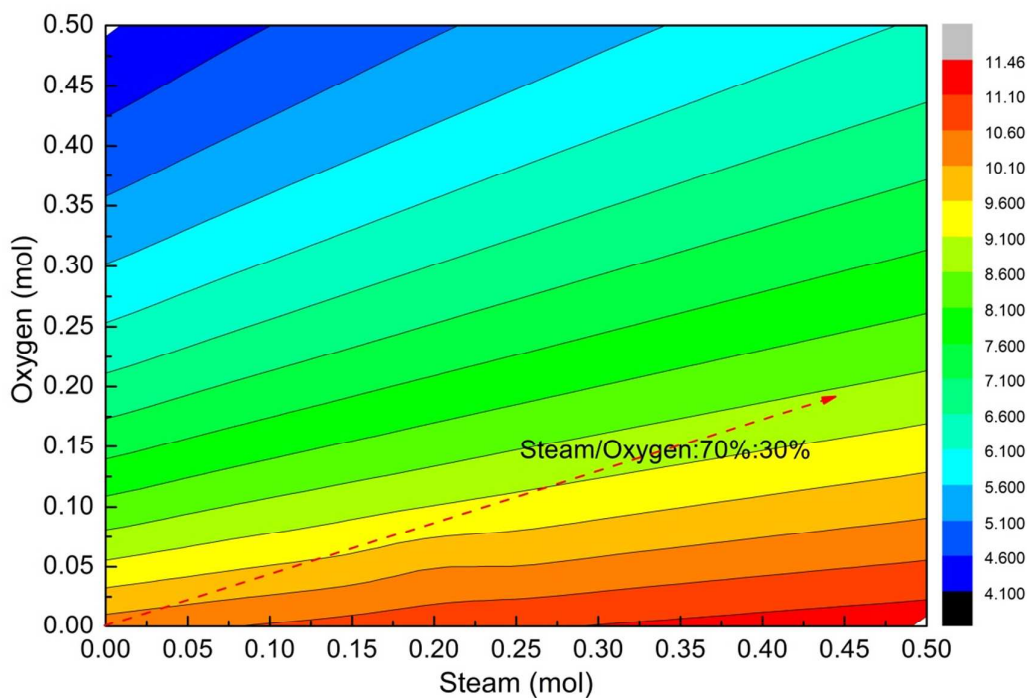
$$LHV = (30[\text{CO}] + 25.7[\text{H}_2] + 85.4[\text{CH}_4] + 151.3[\text{C}_m\text{H}_n]) \times 4.2 / 1000 \text{ MJ/Nm}^3 \quad (5)$$

Figure 9(a) shows the syngas production calculated at 450°C in atmospheres of 70%steam/30%oxygen. It can be observed that the production of H₂ and CH₄ greatly decreased while that of CO slightly increased with increasing reactive agent, and therefore the total syngas production and the LHV decreased. Meanwhile, it should be pointed out that the relative content of CO and H₂ between calculation and experiments were different, which could originate from two factors. The reason was mainly due to the simplification and assumption made during the FactSage calculation.

Furthermore, the syngas production calculated by FactSage was obtained under the equilibrium condition; while during the experimental process, the produced syngas was instantaneously taken away by the gasifying agent. **Figure 9(b)** displays the contour of LHV in different atmospheres and the dash line shows the results in the present experimental conditions. It can be seen that the LHV decreased with increasing oxygen content while increased with increasing steam content. Thus, the key factor to increase the LHV of syngas was to reasonably increase the content of steam in the reactive atmosphere and actually, pure steam was one of the commonest reactive atmospheres for biomass gasification^[19-20]. Additionally, the LHV of the experimentally detected syngas for sample S1, S2 and S3 reacted at 450°C was less than 3.79, 5.24 and 4.17 MJ/Nm³, respectively, which was lower than those calculated by FactSage, which could result from three factors. First, the reactive agent used was much more than the theoretical values to obtain the complete gasification of the biomass, which diluted the syngas and therefore reduced the syngas LHV. Second, the excess oxygen promoted the combustion of the biomass and improved the CO₂ production, which also result in the decrease of the syngas LHV. Third, during the calculation process, the break of the chemical bonds in the biomass was ignored, which could also cause the difference of the syngas production. Although the calculated results differed significantly from the experimentally measured ones, they provided the possible ways to improve the LHV of syngas.



(a)



(b)

Fig.9. Calculation of syngas production (a) Syngas production and LHV at 450°C (b)

Contour of the syngas LHV (MJ/Nm³) in various atmospheres

3.4. Prototype of biomass gasification and heat recovery from slags

According to our study, an integrated prototype with multiple industrial systems was proposed, the concept of which is shown in **Figure 10**. The whole process can be divided into several parts. First, the liquid slags would be granulated into small particles to increase the surface area and the heat transfer efficiency. Second, the slags would be rapidly cooled to 790°C to form glassy phases and avoid inside crystallization. The waste heat in this stage could be transferred into air or steam for further electricity production. Third, the slag particles would be mixed with the ground biomass and the gasification process would be performed. Fourth, syngas would be separated and directly used in the steel industry or exported to other applications as fuel; meanwhile the glassy slags would be applied as raw materials in the cement industry. Thus, a multi-system industrial prototype composed of steel industry, chemical industry and cement industry could be conceptually designed which could simultaneously recover energy and recycle spent materials.

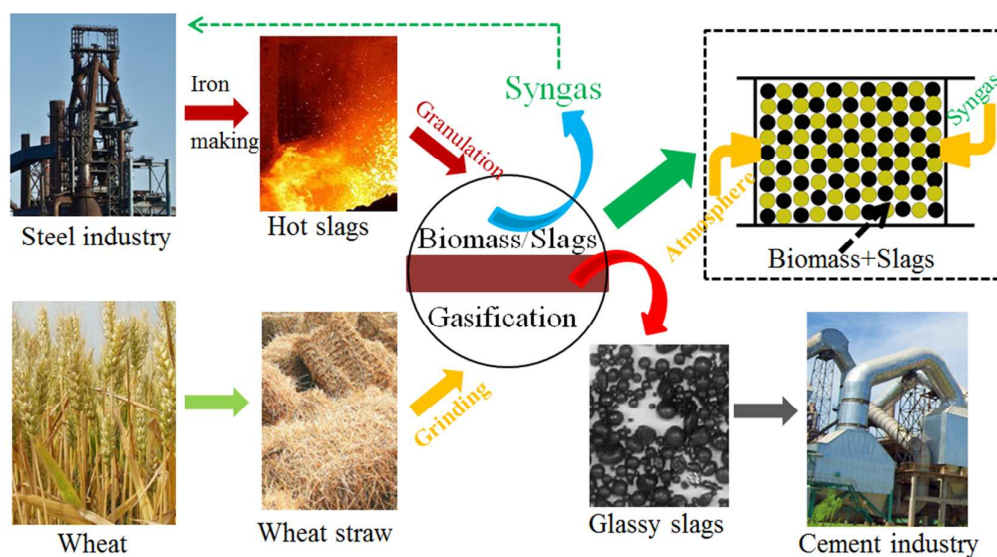


Fig.10. An integrated concept of the proposed prototype

Moreover, the potential of energy savings of this prototype plant based on low temperature biomass gasification using hot slags can be calculated. The produced CO and H₂ are assumed to be used for DRI (direct reduced iron) production^[27]. Based on **Figure 6**, the gasification is assumed to be performed at 450°C with the mass ratio B/S of 1:1, then 0.149 L CO, 0.036 L H₂ and 0.069 L CH₄ can be produced per gram of wheat straw. However, an important issue caused by the biomass ash should be pointed out that according to **Table 1**, the Cl and alkalis in the biomass ash may cause the contamination of slags. In order to effectively avoid the possible contamination, the B/S mass ratios could be further decreased in an actual industrial process and the B/S mass ratios should be adjusted for different kinds of biomasses with varying content of ash. In China, the output of crude steel in 2012 was 710 million tons^[5] and therefore more than 210 million tons of slags were produced with the slag production ratio of 0.3 t slags per ton of steel. Therefore 3.13×10^{10} Nm³ CO, 7.56×10^9 Nm³ H₂ and 1.45×10^{10} Nm³ CH₄ would be produced and this syngas can at least transform 84.7 million t Fe₂O₃ into 59.3 million t Fe. Accordingly, an energy saving relevant to 19.1 million tons of standard coal would be achieved and 69.9 million t CO₂ emissions would be reduced. The potential value of energy saving was even more than the thermal energy untapped in hot slags, which resulted from the oxidation of the biomass. Based on the aforementioned analysis, it can be seen that there is a great potential of energy efficiency improvement and reduction in CO₂ emission in the steel industry from the heat recovery through biomass gasification, considering the possible higher syngas production through further condition optimization.

4. Conclusions

This study proposed an important method of heat recovery from hot slags for syngas production, namely low temperature biomass gasification. The transient release and cumulative production of syngas was clarified and the results showed that the hot slags at 250-500°C used as good heat carrier significantly influenced the gasification process. The presence of the slag did not hinder the degree of gasification, while it altered the mechanism from an Avrami–Erofeev model to a three-dimension diffusion model. The produced biomass ash adhered to the slag particles, which remarkably increased the surface area of the slags and agreed well with the variation of kinetic mechanism. Moreover, the produced syngas can be applied for DRI production, which could remarkably reduce the energy consumption and CO₂ emission in the steel industry and a prototype plant made up of multi-systems was therefore proposed, through which the waste energy and spent material resources were recovered simultaneously.

Acknowledgements

Supports by the National High Technology Research and Development Program of China (863 Program, 2012AA06A114), the Key Projects in the National Science & Technology Pillar Program (2013BAC14B07), and the Common Development Fund of Beijing and the National Natural Science Foundation of China (51172003, 51272005 and 51172001) are acknowledged.

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