

## Combined Pyrolysis and Steam Gasification of Hohhot Coal, China

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(Received: 27 February 2012;

Accepted: 4 January 2013)

AJC-12653

The product gas release rate and gas product composition of combined pyrolysis and steam gasification of demineralized Hohhot coal catalyzed by KOH under different temperature and pressure were investigated on a laboratory fixed-bed reactor. The reactions of raw coal, demineralized coal, Ca(OH)<sub>2</sub> loaded and Ni(NO<sub>3</sub>)<sub>2</sub> loaded samples were also performed to figure the catalysts effect. It was observed that the catalysts and the mineral in raw coal have less effect on pyrolysis than steam gasification. Potassium hydroxide has the best catalytic performance among the investigated samples. The peak values of H<sub>2</sub>, CO and CH<sub>4</sub> release rates of KOH-added sample during the pyrolysis and steam gasification increase with temperature while the release rate of CO<sub>2</sub> reach its maximum value at 750 °C. Operation pressure has a negative effect on product gas release rates of KOH catalyzed pyrolysis and gasification except for CH<sub>4</sub>. High temperature was in favour of CO concentration while high pressure was beneficial to CO<sub>2</sub> and CH<sub>4</sub> contents. Both temperature and pressure had adverse effects on H<sub>2</sub> content.

**Key Words:** Pyrolysis, Steam gasification, Gas release rate, Gas composition.

### INTRODUCTION

Hohhot has one of the largest deposits of coal in China and this is an important resource for the country. Hohhot coal will be an important energy source for the future. It will also play an important role in providing affordable energy. The continued use of Hohhot coal will depend on the development of technologies that minimize environmental impacts and reduce the emission of greenhouse gases. Coal gasification is one of the most extensive use of large-scale coal technology in the whole world. Moreover, gasification of coal with steam is widely considered because it is a clean method of utilizing coal and it can increase the H<sub>2</sub> content in product gas<sup>1</sup> and the introduction of catalysts will significantly reduce gasification temperature, which means coal can convert under mild conditions. As one of the major fields of carbonaceous material utilization, catalytic gasification has already obtained fruitful achievements on different gasification materials<sup>2-4</sup> and different catalysts<sup>5-7</sup>. In the 1970's, Exxon company's development of coal steam gasification process for the purpose of producing substitute natural gas, is a meaningful progress to the catalytic gasification industry<sup>8</sup>.

So far the catalytic steam gasification of coal char has been extensively investigated, but most of the researches were based on TG method and focused on the gasification reactivity and carbon conversion<sup>9,10</sup> rather than the characteristic of gas

release rate and gas composition. Moreover, few researches have considered the catalysis effect on mother coal pyrolysis and its influence on the later char gasification. This paper chose Hohhot coal, for its importance of social and economic development of China, as the research object to study the characteristic of product gas of combined pyrolysis and steam gasification in a fixed-bed reactor system. A gas analyzer, which can detect the instantaneous contents of CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> at the same time, combined with a flowmeter, were used to determine the instantaneous product composition and flowrate *in situ*.

### EXPERIMENTAL

**Sample preparation:** The proximate analysis showed that the coal contained 12.9 % ash, 34.3 % volatile matter and 52.8 % fixed carbon, on the dry basis. The ultimate analysis showed that the coal consisted of 72.8 % C, 4.0 % H, 1.1 % N and 0.6 % S, on the dry ash-free basis. The ash was composed of 46.18 % SiO<sub>2</sub>, 19.83 % Al<sub>2</sub>O<sub>3</sub>, 4.37 % Fe<sub>2</sub>O<sub>3</sub>, 12.28 % CaO, 2.51 % MgO, 0.77 % Na<sub>2</sub>O, 1.18 % K<sub>2</sub>O, 11.10 % SO<sub>3</sub> and others. In order to eliminate the effect of minerals on the reactivity of samples, coal demineralization was conducted with two acids (HCl and HF), employing the method of Sun *et al.*<sup>11</sup>. The proximate analysis showed that the demineralized coal contained 0.9 % ash, 33.3 % volatile matter and 65.8 % fixed carbon, on the dry basis. The ultimate analysis showed that

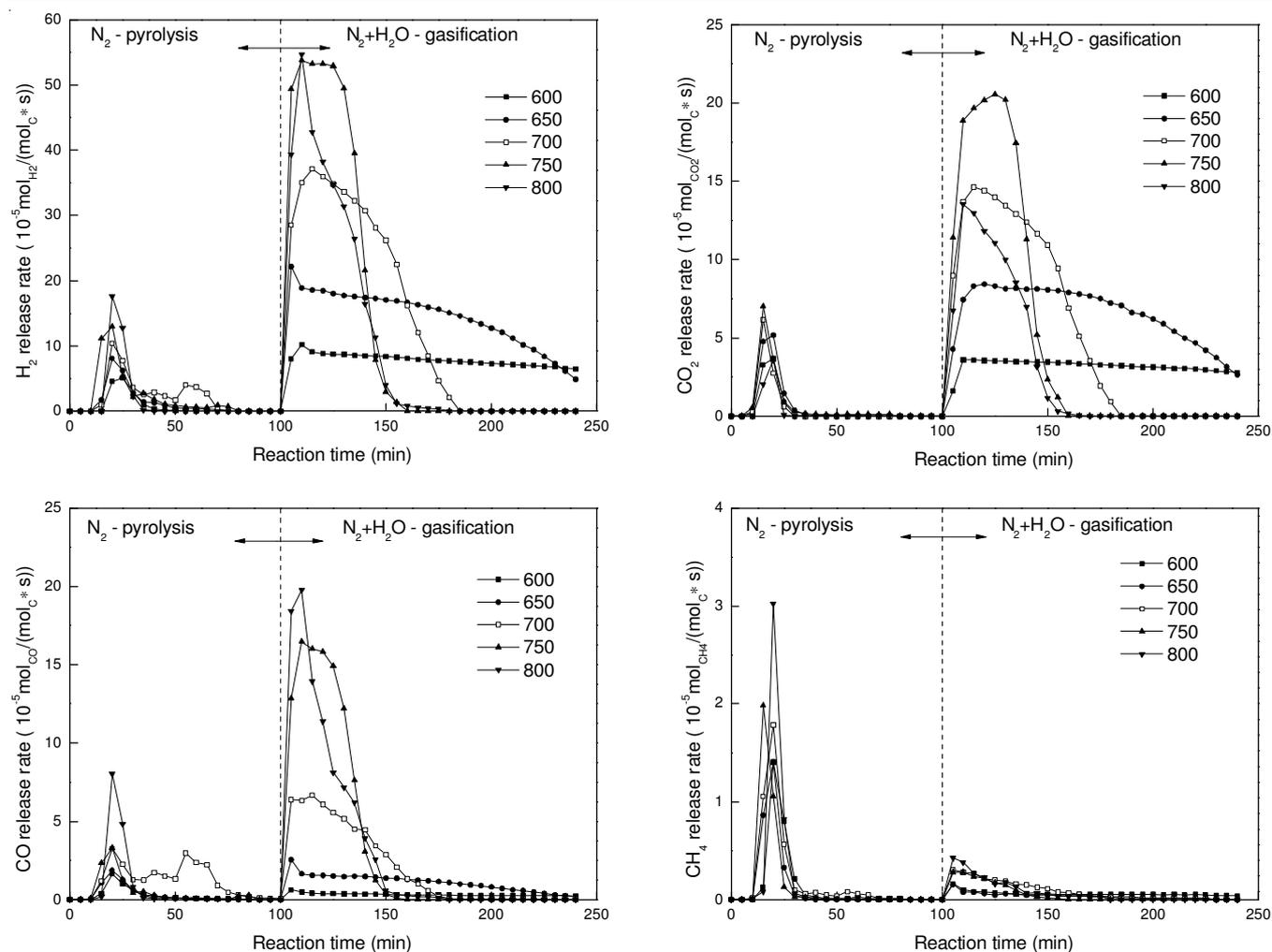


Fig. 1. Product gas release rate of KOH loaded coal at different temperature

the coal consisted of 82.2 % C, 4.8 % H, 1.0 % N and 0.6 % S, on the dry ash-free basis.

The catalyst was added to the demineralized coal using wet mixing method. The sample was then dried, ground and sieved to make sure the particle size is smaller than 150  $\mu\text{m}$  and then placed in a desiccator in reserve. The catalyst loading is 10 wt % of coal which is calculated by the mass of metal.

The experiments were carried out in a laboratory fixed-bed reactor. The 10 g sample was placed in the constant temperature zone of the reactor. The inlet flowrate of inert gas nitrogen was set to 1 L/min. The reactor was then heated at a nominal heating rate of 40  $^{\circ}\text{C}/\text{min}$  from room temperature to gasification temperature. The sample was subjected to pyrolysis in nitrogenous atmosphere during the heating period. Once the internal temperature of the reactor's constant temperature zone kept stable at the stated temperature and the pyrolysis gas production was negligible, the gas flow was shifted to the mixture of nitrogen and steam to start the steam gasification. The flowrate of the gas mixture was 2 L/min and the ratio was 1:1. The product gas composition and flow rate were recorded by computer once per second.

Preliminary experimental results indicated when the particle size was smaller than 150  $\mu\text{m}$  and the steam flow rate was not less than 1 L/min, the influence of internal and external diffusion under atmospheric pressure has been basically eliminated.

## RESULTS AND DISCUSSION

**Product gas release rate:** Potassium hydroxide was used as the catalyst to study the influence of temperature and pressure on product gas release rate during the combined pyrolysis and steam gasification. Fig. 1 shows the gas release rates of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  at atmospheric pressure and different temperature. The peak values of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  release rates during the pyrolysis and the steam gasification increase with temperature within the experimental temperature range, while the release rate of  $\text{CO}_2$  reach its maximum value at 750  $^{\circ}\text{C}$ . It indicates that temperature is a disadvantage for the formation of  $\text{CO}_2$  above 750  $^{\circ}\text{C}$  for the reduction of  $\text{CO}_2$  by C is easy to happen at high temperature while the water-gas-shift reaction gets more difficult. During the steam gasification, the release rates of all product gas are quite low at 600  $^{\circ}\text{C}$ , which means most of the reactants haven't obtain enough energy from heating to overcome the activation energy barrier. As the gasification temperature increases, both the activated carbon ratio and the collision frequency of surface carbon atoms with  $\text{H}_2\text{O}$  molecules increase, thus the product gas release rates have a substantial growth from 600  $^{\circ}\text{C}$  to 750  $^{\circ}\text{C}$ . However, the release rate growth with temperature is no longer significant once the gasification temperature is higher than 750  $^{\circ}\text{C}$ .

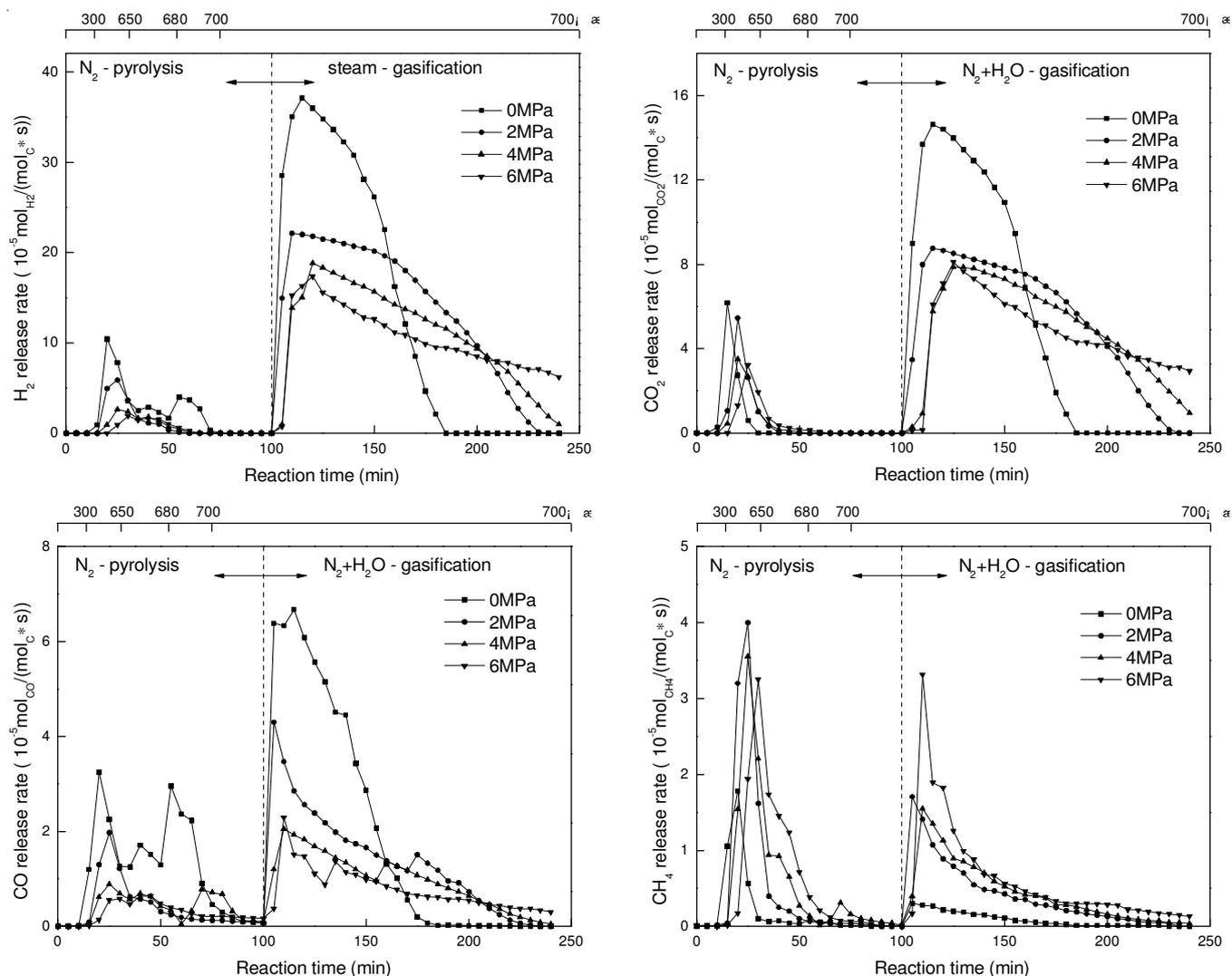


Fig. 2. Product gas release rate of KOH loaded coal at different pressure

The study of pressure effect on KOH catalyzed pyrolysis and steam gasification was performed at 700 °C. Fig. 2 shows the release rates of H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub> under different pressure. According to the experimental data, the highest release rates of H<sub>2</sub>, CO<sub>2</sub> and CO appear at atmospheric pressure, which means increasing operation pressure is detrimental for the catalytic pyrolysis and steam gasification. As the diffusion elimination experiment was carried out at atmospheric pressure, gas diffusion has a certain influence on gasification rate at high pressure. Moreover, the system was pressurized by pure N<sub>2</sub>. The higher the operation pressure is, the smaller the partial pressure ratio of steam to N<sub>2</sub> ( $P_{H_2O}/P_{N_2}$ ) is at the initial period of gasification when the active site concentration is the highest and the gasification rate is the fastest. At that time N<sub>2</sub> concentration on the sample surface is much higher than the concentration of steam, thus reducing the contact of H<sub>2</sub>O molecules with the active sites and resulting in the carbon conversion decrease. For pyrolysis, high pressure will restrain the eduction of volatiles<sup>12</sup> which leads to the decrease of product gas release rates of H<sub>2</sub>, CO<sub>2</sub> and CO. However, the release rate of CH<sub>4</sub> gets higher at high pressure because high pressure will highly promote the cracking of long chain hydrocarbons and the hydrogenation of char to form CH<sub>4</sub>.

**Gas composition:** Fig. 3(a) shows the product gas composition of steam gasification at different temperature. It was observed that gasification temperature affects the product composition significantly. At lower temperature (below 700 °C), CO content is insignificant compared with CO<sub>2</sub> and H<sub>2</sub>. As gasification temperature increases, CO<sub>2</sub> content decreases with an increasing rate, while CO concentration has a notable rise on the contrary and is even higher than CO<sub>2</sub> at 800 °C, which makes CO as the most abundant carbon-containing gas component. The content of CH<sub>4</sub> is less than 1 % and the contents variation is not obvious. Hydrogen has the highest concentration in gas composition and its content decreases gradually as the temperature increases.

The main reactions during steam gasification are universally accepted as follows:



The former is an endothermic reaction, while the latter is an exothermic reaction. The effect of temperature on product composition can be interpreted from the thermodynamic equilibrium of the above reactions. High temperature is negative for the exothermic water-gas-shift reaction. It will make the balance move towards the reverse reaction thus decrease the

CO<sub>2</sub> level and increase CO production. Meanwhile, high temperature will boost CO production further by promoting the endothermic carbon steam reaction. Thus the CO<sub>2</sub> content decreases by 10.4 % from 600 to 800 °C, while the CO content increases by a bigger proportion of 16 %. The diminution of H<sub>2</sub> production at higher temperature indicates that temperature has a greater influence on water-gas-shift reaction because the decrement of H<sub>2</sub> production from water-gas-shift reaction is larger than the increment from carbon steam reaction.

As shown in Fig. 3(b), operation pressure has less influence on gas composition than temperature. High pressure has a positive effect on CH<sub>4</sub> contents for the promotion of carbon hydrogenation. CO<sub>2</sub> concentration shows a slight increase with pressure too. However, high operation pressure is not in favour of CO and H<sub>2</sub> production for the thermodynamic equilibrium of steam carbon reaction. Pressurized steam gasification will increase the production of high heat-value gas CH<sub>4</sub>, nevertheless the CH<sub>4</sub> content is still quite low at high operation pressure. Therefore, high pressure has little significance for the production of high heat value gas from steam gasification.

**Catalytic effect of various catalysts:** Fig. 4 shows the effects of KOH, Ca(OH)<sub>2</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> at 700 °C and atmospheric pressure, compared with demineralized coal and raw coal pyrolysis and steam gasification. It is shown that demineralized coal has the average pyrolysis reactivity as most of the investigated samples but the worst gasification reactivity. It indicates that the studied catalysts and the mineral in raw coal have less effect on pyrolysis than steam gasification. However, demineralized sample has the remarkably high release rate of CH<sub>4</sub> during steam gasification process. Raw coal gasification reactivity is higher than the demineralized coal indicating that the minerals contained in raw coal have definite catalytic effect on steam gasification.

Among all the investigated catalysts, KOH shows the best catalytic effect for pyrolysis and steam gasification. The H<sub>2</sub> production of KOH loaded sample can reach 1.30 mol<sub>H<sub>2</sub></sub>/mol<sub>C</sub> while it of demineralized coal is only 0.21 mol<sub>H<sub>2</sub></sub>/mol<sub>C</sub>. As indicated by the research of Dhupe *et al.*<sup>13</sup>, the dispersion of the catalyst is one of the main factors that affect the catalytic performance. Hohhot coal contains a large number of functional groups such as carboxyl, hydroxyl and phenolic hydroxyl. Ion

exchange will occur between these acidic functional groups and the soluble alkaline catalysts, making the alkali metal based catalysts highly dispersed in the coal. Besides, potassium has good mobility at high temperature in the presence of carbon<sup>3,14</sup>. Therefore the potassium metal based catalysts show a better catalytic effect than other catalysts.

The product gas release rates of Ca(OH)<sub>2</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> loaded samples are higher than the demineralized and the raw coal, indicating that Ca and Ni have a certain catalytic effect but their catalytic activity are lower than KOH. The CO<sub>2</sub> release rate of Ca(OH)<sub>2</sub> loaded sample is near zero during the whole pyrolysis process indicated that Ca(OH)<sub>2</sub> is apt to react with CO<sub>2</sub> to form CaCO<sub>3</sub> at high temperature which will lead to the loss of catalytic activity. Transition metals Ni is apt to form stable bonds with sulphur from coal, causing catalysts deactivation by irreversibly poisoning<sup>15</sup>, which results in the poorest activity of Ni(NO<sub>3</sub>)<sub>2</sub> loaded samples.

### Conclusion

As gasification temperature increases, the peak values of H<sub>2</sub>, CO and CH<sub>4</sub> release rates increase during the pyrolysis and the steam gasification while the release rate of CO<sub>2</sub> reach its maximum value at 750 °C. For gas composition, the CO<sub>2</sub> and H<sub>2</sub> contents decrease with temperature while CO content has a notable increase on the contrary.

Operation pressure has a negative effect on product gas release rates of KOH catalyzed pyrolysis and gasification except for CH<sub>4</sub>. As operation pressure increases, CH<sub>4</sub> and CO<sub>2</sub> concentration increase while CO and H<sub>2</sub> level decrease.

The studied catalysts and the mineral in raw coal have less effect on pyrolysis than steam gasification. Among all the investigated catalysts, KOH shows the best catalytic effect for both pyrolysis and steam gasification. The H<sub>2</sub> production of KOH loaded sample is 1.30 mol<sub>H<sub>2</sub></sub>/mol<sub>C</sub> while it of demineralized coal is only 0.21 mol<sub>H<sub>2</sub></sub>/mol<sub>C</sub>. The low activity of Ca(OH)<sub>2</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> is due to the poisoning during gasification.

### ACKNOWLEDGEMENTS

This study is sponsored by National Key State Basic Research Development Program of China (973Program, 2010CB227000) and Fundamental Research Funds for the Central Universities.

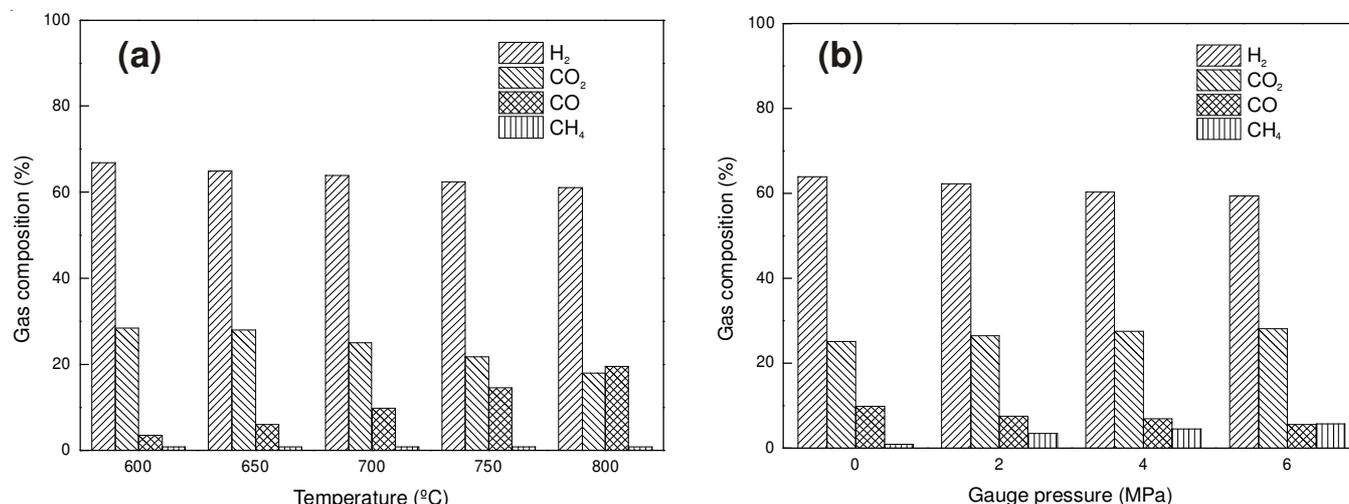


Fig. 3. Gas composition of KOH loaded coal (a: different temperature, b: different pressure)

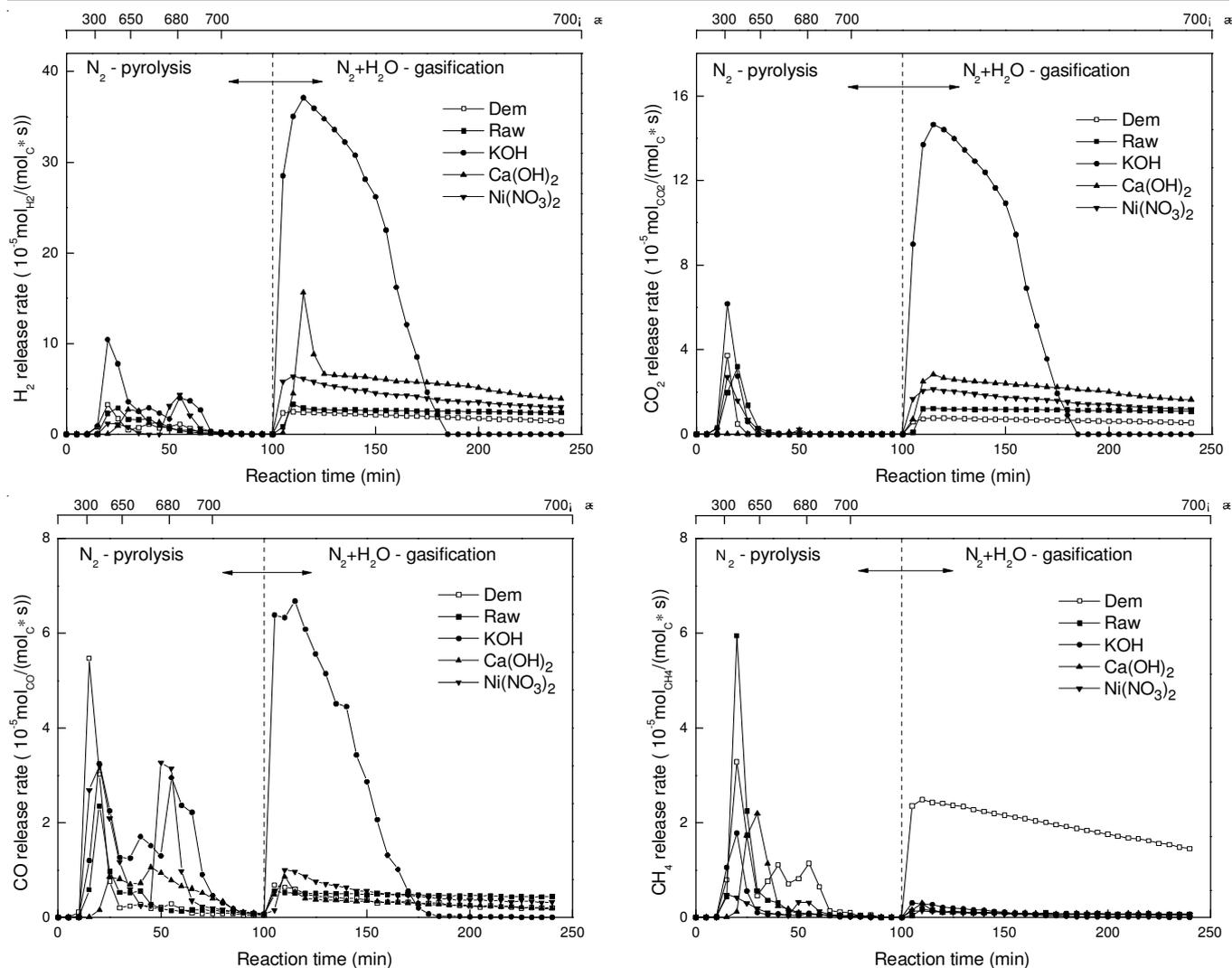


Fig. 4. Product gas release rate of various catalysts loaded coals

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