Effect of palygorskite clay on pyrolysis of rape straw: an in-situ catalysis study

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Abstract:

Biomass tar restricts the wide application and development of biomass gasification technology. In the present paper, palygorskite, a natural magnesium-containing clay mineral, was investigated for catalytic pyrolysis of rape straw in-situ and compared with the dolomite researched widely. The two types of natural minerals were characterized with XRD and BET. The results showed that combustible gas derived from the pyrolysis increased with an increase of gasification temperature. The $H_{conversion}$ and $C_{conversion}$ increased to 44.7% and 31% for the addition of palygorskite and increased to 41.3% and 31.3% for the addition of dolomite at the gasification temperature of 800 ^{o}C, compared with 15.1% and 5.6% without addition of the two types of material. It indicated more biomass was converted into combustible gases implying the decrease of biomass tar under the function of palygorskite or dolomite and palygorskite had a slightly better efficiency than that of dolomite in the experimental conditions.

Keywords: In-situ catalytic cracking, palygorskite clay, dolomite, pyrolysis

1. Introduction

Under the pressure to make cleaner less expensive fuels and environmental protection, biomass gasification offers the potential for producing fuel gas that can be used for power generation or synthesis gas applications. Pyrolysis of biomass has several environmental advantages over fossil fuels, such as lower emission of CO_2 and other greenhouse gases [1]. However, one of the major issues in biomass gasification is dealing efficiently with tar reduction during the pyrolysis process. This presents a significant impediment to the application of biomass gasification. The condensed compounds present in tar may cause problems in downstream handling, making catalytic hot gas cleaning a necessary step in most gasification applications. Catalytic decomposition appears to be a very attractive way to convert tar components into H_2, CO, etc [2-7].

Most research has focused on steam reforming of various hydrocarbon feedstock over supported-Ni and expensive metal catalysts [2-5, 8-16]. Furusawa *et al.* [11] reported that Co/MgO catalyst had higher activity than any types of Ni/MgO catalysts. This was attributed to the difference in catalytic performance between Co/MgO and Ni/MgO. In general, Ni catalysts showed high catalytic activity for the removal of tar and are very efficient in tar removal. However, coking on the catalyst surface and sintering of Ni particles caused the loss of the catalytic activity [13]. In addition, to avoid a fast deactivation of Ni catalyst by coke,

researchers used CeO_2 as a catalyst additive. It is well known that CeO_2 supported catalysts can promote the reaction of active carbon with O_2 enhancing the catalytic activity and resistance to coking [14-16]. However, these catalysts were difficult to apply in industry due to the carbon deposition and high cost. Therefore, natural minerals, containing dolomite [17-19], olivine [1, 20-23], ilmenite [24], monolith [25], limestone [26] and others, are getting increased attention by many researchers. It has also been reported that the product gas was cleaned and the total product gas yield was increased by using calcined dolomite both in-bed and downstream of a biomass gasifier [17]. Corella *et al.* [23] reported that the use of calcined dolomite inside the gasifier could decrease the tar amount from 6.5 wt% (without dolomite) to 1.3 wt%. Rapagna *et al.* [21] investigated the catalytic activity of olivine and observed that it had a good performance in terms of tar reduction. Lopamudra *et al.* [22] investigated effect of the pretreatment of olivine on catalytic cracking of biomass tar. The report of Min *et al.* [24] indicated that ilmenite has good activity for the steam reforming of tar into gases due to its highly dispersed iron-containing species. In short, natural minerals have a catalytic reactivity which may improve the decomposition of biomass tar.

Besides, palygorskite as a catalyst or catalyst support was investigated in our research [27-30]. The results showed palygorskite was a good catalyst and a better catalyst support for catalytic cracking of biomass tar. However, all the published works concerned the catalytic

performance of palygorskite clay by an ex-situ reaction. Palygorskite as an in situ catalyst has never been studied, although it was proved to be a good catalyst and a better catalyst support for decomposition of biomass tar. To improve the gasification efficiency of biomass, palygorskite as an in situ catalyst for catalytic pyrolysis of biomass was investigated and compared with dolomite in the present study. The aim is to investigate the feasibility of palygorskite as an in-situ catalyst for catalytic pyrolysis of biomass and decomposition of biomass tar, and to find a new way for the application of biomass energy—catalytic pyrolysis of biomass using natural mineral, a material with low cost and a large number of storage, and broad the application field of palygorskite clay.

2. Experimental

2.1 Materials preparation

Palygorskite clay (The formula of the ideal unit cell is (Mg, Al, $Fe)_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$. However, the actual composition of palygorskite varies because of partial replacement of magnesium by aluminum or/and iron) was collected from Guanshan palygorskite clay mine, Mingguang city, Anhui province, China.

Dolomite ($CaMg(CO_3)_2$) was collected from Huaguo mountain, Xuyi county, Jiangsu province, China. The two types of materials underwent drying, crushing and sieving to obtain powder with particles less than 0.075 mm in size. Then, palygorskite clay and dolomite were

calcinated at different temperatures (300, 500, 800 ^{o}C) for 1 h in flowing nitrogen and cooled to room temperature for further characterization.

Rape straw was collected around Hefei city, China. The rape straw were smashed and sieved to obtain the particle size lower than 2 mm. The weight percentage of C, H and N was 46.83 %, 6.596 % and 0.442 %, respectively, detected before pyrolysis.

2.2 Materials characterization

C, H, N was measured with an element analyzer VARIO ELIII with a high purity of oxygen and a decomposition temperature of 1100^{o}C.

X-ray diffraction (XRD) was performed using a Rigaku powder diffractometer with Cu Kα radiation. The tube voltage was 40 kV, and the current was 100 mA. The XRD diffraction patterns were taken in the range of 5-70° at a scan speed of 4° min^{-1}. Phase identification (Search-Match) was carried out by comparison with those included in the Joint Committee of Powder Diffraction Standards (JCPDS) database.

13-point BET-nitrogen isotherms were used to quantify changes in the specific surface area. Raw palygorskite and raw dolomite were degassed at 90 ^{o}C for 12 h before analysis were conducted. Annealed palygorskite and annealed dolomite were degassed at 150 ^{o}C for

12h before analysis were conducted. The multi-point BET surface area of each sample was measured at atmospheric pressure using Quantachrome NOVA 3000e Surface Area and Pore Size Analyzer. The adsorption isotherms achieved a p/p_o range of 0.05-0.35.

2.2 Testing methods

Fig. 1 shows the diagram for in-situ catalytic cracking of rape straw pyrolysis gases with palygorskite or dolomite. The experimental setup involves a sample introduction system, hot cracking system, and detection system. Firstly, the furnace was heated to the desired temperature. Secondly, 10±0.1g of rape straw was mixed with palygorskite or dolomite and then put into a hopper. Thirdly, carrier gas (160 mL/min), hopper, reaction tube (550×30mm), ice bath (to condensate biomass tar), wetting flow-meter (to detect production gases) and gas chromatograph (GC, to detect combustible gas concentration) were connected and the air tightness was examined. Then the valve of hopper was loosened and then the pyrolysis reaction of rape straw was started. The reaction time was 10 minutes for every experiment.

To calculate the pyrolysis efficiency, the composition of pyrolysis gases mainly contained H_2, CO, CH_4, C_nH_m and little light hydrocarbon after condensation. According to the report [31], hydrogen (H) from dry wood was mainly converted into CH_4 (more than 30% mol of H at 900^{o}C), H_2 (from 9 to 36% mol. from700 to 1000^{o}C), H_2O, and C_2H_4. Thus, combustible gases (H_2, CO and CH_4 except C_2H_4) were detected by a gas chromatograph

(GC-7890T) equipped with a C2000 column (2m×4mm) and a thermal conductivity detector (TCD) with argon as carrier gas to measure H_2, N_2, CO and CH_4. The column temperature, evaporation chamber temperature, the temperature and bridge current of detector were 70°C, 120°C, 100°C, 100 mA, respectively.

$$Total \cdot combustible \cdot gas(TCG, mL/g \cdot straw) = \frac{V_{H_2} + V_{CO} + V_{CH_4}}{10}$$

where, V_{H_2}, V_{CO}, V_{CH_4} represented the total volume of H_2, CO, CH_4, which were calculated from the result of GC and wetting flow-meter after the pyrolysis of 10g rape straw. In addition, $C_{conversion}$ and $H_{conversion}$ were calculated as follows:

$$C_{conversion}(\%) = (\frac{V_{(CO+CH_4)}}{22.4} \times 10^{-3} \times 12)/(W_{straw} \times 46.83\%) \times 100\% = \frac{12 \times V_{(CO+CH_4)}}{46.83 \times 22.4}$$

$$H_{conversion}(\%) = (\frac{2V_{H_2} + 4V_{CH_4}}{22.4} \times 10^{-3} \times 1)/(W_{straw} \times 65.96\%) \times 100\% = \frac{10 \times (2V_{H_2} + 4V_{CH_4})}{65.96 \times 22.4}$$

, where V_{CO} represents the CO yield (mL) after pyrolysis and W_{straw} denotes the weight of rape straw.

Insert Figure 1 here

3. Results and discussion

3.1 XRD characterization

Figure 2 represents the XRD patterns of palygorskite and annealed palygorskite (300, 500, 800 °C), where Cps represents counts per second. Three phases can be identified from these XRD patterns. The peaks at 2θ=8.44°, 13.68°, 16.2°, 27.52°, 34.09° were found and

identified as palygorskite. The peaks intensity decreased with an increase of annealing temperature and almost disappeared after annealing at 800^{o}C, which should be attributed to the collapse of palygorskite structure under the function of high temperature. The result was in good agreement with these reports [19, 27]. The peaks at 2θ=20.76^{o}, 26.67^{o}, 67.34^{o} were observed and attributed to quartz and can be observed after annealing at all temperatures. The peaks at 2θ=30.88^{o}, 41.19^{o}, 44.89^{o}, 50.97^{o}, 59.91^{o} were observed and identified as dolomite. The dolomite takes up about 7.5 wt% in the palygorskite clay, which was calculated roughly according to the result of X-ray fluorescence (XRF) which indicated this palygorskite used in the experiments was mainly composed of Al_2O_3 9.4wt%, MgO 9.9 wt%, Fe_2O_3 5 wt% and CaO 2.3wt%. All XRD peaks of dolomite disappeared when the annealing temperature reached 800^{o}C. As is well-known, dolomite possessed catalytic reactivity assigned to the formation of CaO-MgO when the annealing temperature was over 750^{o}C. Therefore, the peak at 2θ=42.43^{o} can be observed and ascribed to MgO and FeO when palygorskite clay was annealed at 800 ^{o}C. However, the characteristic reflection of MgO mainly appeared at 2θ=37^{o} and 2θ=42.47^{o}, where the reflection at 2θ=37^{o} has the strongest intensity, as shown in Fig. 3. Furthermore, the intensity of reflection at 2θ=42.47^{o} was the strongest in the newly formed reflection. Therefore, the reflection at 2θ=42.47^{o} should be ascribed to the overlap of the reflection of FeO and MgO. Anyway, wustite ($Fe_{0.942}O$)formed after heating at 800 ^{o}C, which was assigned to the collapse of the palygorskite structure. It is normal for wustite to be

observed as Fe can substitute for Mg and/or Al in the structure of palygorskite and the result of XRF also demonstrated the existence of Fe in this palygorskite clay. That is to say, the palygorskite clay used in this study was mainly composed of palygorskite and dolomite (lower than 7.5 wt%).

Insert Figure 2 here

Fig. 3 illustrates the XRD patterns of dolomite and annealed dolomite. Two phases were observed from dolomite and annealed dolomite at 300 and 500^{o}C. Two peaks at 2θ=23.92^{o}, 26.57^{o} were observed and identified as quartz. These peaks at 2θ=30.78^{o}, 41.06^{o} were found and identified as dolomite. However, these peaks for dolomite almost disappeared after annealing at 800^{o}C and displaced by two new phases based on the results of XRD patterns. The peak at 2θ=29.22^{o} was attributed to $CaCO_3$ and the peaks at 2θ=37^{o}, 42.47^{o}, 53.37^{o} were attributed to MgO. That is to say, dolomite was unstable and decomposed into $CaCO_3$ and MgO when anneal temperature reached 800^{o}C, which was consistent with previously reported [32, 33]. Ratko *et al.* [32] reported that dolomite was decomposed at a temperature below 800 ^{o}C producing a high concentration of carbon dioxide.

3.2 Nitrogen adsorption-desorption characterization

The specific surface area (SSA) of palygorskite, dolomite, annealed palygorskite and

dolomite is presented in Table 1. Palygorskite and dolomite were annealed at different temperatures for 1 h before characterization. The SSA of palygorskite experienced a dramatic decrease with the increase of annealing temperatures. Especially, the SSA of palygorskite was only 20.5 $m^2 \cdot g^{-1}$ after annealing at 800 ^oC. The change of SSA of palygorskite with increasing temperature was ascribed to folded channels and the collapse of palygorskite structure, which was in good agreement with the results of XRD and in line with other reports [34-36]. In contrast, no obvious change of SSA of dolomite was found after annealing at 300^oC and 500 ^oC. However, the SSA of dolomite increased to 13.4 $m^2 \cdot g^{-1}$ after annealing at 800 ^oC, which was assigned to the decomposition of dolomite. Under the function of high temperature, dolomite was decomposed into $CaCO_3$ and MgO based on the result of XRD and pore structure was formed due to the release of CO_2 at the same time [32]. Therefore, dolomite had a larger SSA after annealing at 800^oC.

Table 1 SSA of palygorskite and dolomite annealed at different temperatures ($m^2 \cdot g^{-1}$).

Material	Raw	300^oC	500^oC	800^oC
Palygorskite	213.5	112.9	82.4	20.5
Dolomite	5.3	4.5	3.6	13.4

3.3 Effect of pyrolysis temperature

Fig. 4 displays the pyrolysis efficiency as a function of pyrolysis temperature without addition of palygorskite and dolomite. Obviously, TCG volume increased with an increase of

pyrolysis temperature due to the endothermic reaction. Almost no H_2 was detected after the pyrolysis of rape straw at 400 or 500^{o}C. However, H_2 volume increased from 9.35 to 60.48mL·g^{-1} when pyrolysis temperature increased from 600 to 800^{o}C. CH_4 volume had the similar change with H_2. Little CH_4 was detected after the pyrolysis of straw at 400 and 500^{o}C, however it increased from 10.63 to 25.42 mL·g^{-1} when pyrolysis increased from 600 to 800 ^{o}C. It has been wildly accepted for the enhancement of high temperature for pyrolysis of biomass. In addition, the $H_{conversion}$ and $C_{\text{conversion}}$ had an obvious increase with an increase of pyrolysis temperature, as is shown in Fig. 5. The $H_{conversion}$ increased to 15.3% as well as the $C_{conversion}$ increased to 9.6% when pyrolysis temperature came to 800 ^{o}C. At low pyrolysis temperature, $C_{conversion}$ was higher than $H_{conversion}$ in contrast with the opposite results when pyrolysis temperature was over 600^{o}C. It is obvious that high temperatures provided more energy and made the break of C-H and C-C bond easy. Therefore, high temperature considerably benefited the further pyrolysis of straw, which agrees well with the previously reported [31].

Insert Figs 4 and 5 here

3.4 Effect of the ratio between palygorskite and straw

Fig. 6 illustrates the pyrolysis efficiency as a function of palygorskite percentage in the mixtures. The experiments were carried out at an identical pyrolysis temperature of 500 ^{o}C. The TCG increased under all ratios when the mixture of palygorskite and straw was put into pyrolysis reactor. Especially, there was a maximum TCG of 79.81mL·g^{-1} when the

224 palygorskite percentage reached 3% (3 g palygorskite in 100 g straw). However, TCG
225 increased first and then decreased with an increase of the percentage. To eliminate the testing
226 error, several times of repeat testing was taken and the results displayed the similar data. The
227 reason for the best catalytic efficiency at the percentage of 3% was speculated to the effect of
228 heat conductivity due to more palygorskite. Although no direct evidence supported the
229 explanation, it is easy to understand that heat conductivity needed time. Therefore, it would
230 take more time to reach the furnace temperature because of the addition of more palygorskite.
231 Therefore, the percentage of 3% between natural mineral and straw was selected in the
232 following works. Fig. 7 showed the $H_{conversion}$ and $C_{conversion}$ of straw pyrolysis as a function of
233 ratio between palygorskite and straw at the pyrolysis temperature of 500^{o}C. It was observed
234 that $H_{conversion}$ increased with the increase of the palygorskite percentage between palygorskite
235 and straw. However, the fluctuation of $C_{conversion}$ was observed in Fig. 7. The $C_{conversion}$ had a
236 maximum of 8.1% when the percentage reached 3% between palygorskite and straw. The
237 result is consistent with the change of TCG as mentioned above. It indicates that more carbon-
238 containing matter in biomass is converted to gases implying less biomass tar is formed during
239 the gasification process. The more carbon is converted into combustible gases, the better
240 utilization for the biomass in gasification technology. Anyway, the addition of palygorskite
241 clay enhanced the pyrolysis of straw increasing the TCG and $H_{conversion}$ and $C_{conversion}$. Therefore,
242 palygorskite possesses the potential as an in-situ catalyst for the biomass gasification technology.

Insert Figs 6 and 7 here

As is well-known, thermal treatment temperature affected the SSA and surface physicochemical properties of palygorskite [27]. Thus, the high annealing temperature (800^{o}C) was considered at the same experimental conditions. Compared with the result of pyrolysis reaction without palygorskite, H_2, CH_4 and TCG volume increased in contrast with the decrease of CO volume when the addition of palygorskite annealed at 800 ^{o}C, as is shown in Table 2. However, when it is compared with the results where palygorskite annealed at 500 ^{o}C was used, H_2, CO, TCG and $C_{conversion}$ have an obvious decrease in contrast to the increase CH_4 volume and $H_{conversion}$, which not sure whether means more biomass tar will be produced in the process of gasification due to the less production of gases but at least improved the gasification efficiency. That is to say, the utilization of palygorskite anneal at 800^{o}C was better than without palygorskite, but was worse than palygorskite annealed at 500 ^{o}C. The reason was ascribed to the catalytic reactive and the decrease of specific surface area as the annealing temperature increases to 800 ^{o}C. On the other hand, iron oxide would be formed after self-annealing of palygorskite at 800 ^{o}C, as shown in Fig. 2 and magnesium oxide and a little of calcium oxide were formed after the self-annealing of dolomite at 800^{o}C. Uddin *et al.* [37] reported that the activity of the iron oxide catalysts for tar decomposition seemed stable with cyclic use but the activity of the catalysts for the water gas shift reaction decreased with

repeated use. Other iron-containing catalysts were also investigated [38-40]. This research indicated iron oxide or iron-containing catalysts had a good catalytic reactivity for removal of biomass tar. Therefore, the pyrolysis efficiency was still improved after the addition of palygorskite, despite the decrease of SSA for palygorskite.

Table 2 Effect of palygorskite heat treatment temperature on gases volume

Material	Anneal temperature/^{o}C	Gas volume/(mL·g^{-1} H_2	CO		CH_4	$H_{conversion}$	$C_{conversion}$
		TCG					
3%(palygorskite:straw)	500	9.0	70.8	<0.01	79.8	1.2	8.1
	800	6.0	26.1	4.1	36.1	1.9	3.5
Straw	——	0.5	32.1	<0.01	32.5	0.1	3.7

3.5 A comparison between dolomite and palygorskite

Table 3 showed the effect of dolomite and palygorskite on gases volume of straw pyrolysis. The percentage between palygorskite or dolomite and straw was 3:100. The two types of materials were annealed at 500 ^{o}C for 1 h before use. On the one hand, the addition of both dolomite and palygorskite clay considerably improved the gasification efficiency, especially for the pyrolysis temperature of 800 ^{o}C, increasing the H_2, CO, CH_4 and TCG volume. On the other hand, it was observed that TCG, H_2, CO, CH_4 volume after the pyrolysis of straw with palygorskite were more than that after pyrolysis with dolomite at 500 ^{o}C, as is shown in Table 3. When the pyrolysis temperature reached 800 ^{o}C, the

279 improvement of palygorskite clay was just slightly better than that of dolomite. In addition,
280 $H_{conversion}$ and $C_{conversion}$ had an increase after the addition of palygorskite or dolomite when the
281 reaction temperature was 500^{o}C. What's more important, $H_{conversion}$ and $C_{conversion}$ increased to
282 44.7 and 30.9% for the addition of palygorskite and increased to 41.3 and 31.3% for the
283 addition of dolomite at the pyrolysis temperature of 800 ^{o}C. The higher pyrolysis temperature
284 was, the more apparent the improvement of the pyrolysis efficiency of straw. Additionally,
285 high temperature can better the pyrolysis efficiency and provide enough energy for catalytic
286 cracking of biomass tar than that at 500 ^{o}C. Corella *et al.* [41] and Orio *et al.* [42] extensively
287 studied the performance of calcined dolomite (CaO·MgO) for hot gasification-gas cleaning.
288 The results showed anneal dolomite had a good performance for removal of biomass tar.
289 Meanwhile, the SSA of dolomite increased from 3.6 to 13.4 $m^2 \cdot g^{-1}$ when the annealing
290 temperature increased from 500 to 800^{o}C, as is reported in Table 1. Therefore, the pyrolysis
291 efficiency was improved apparently after the addition of dolomite. However, the catalytic
292 reactivity of palygorskite clay is slightly better than that of dolomite in the present studies.
293

294 **Table 3 Effect of palygorskite and dolomite on gases volume**

Material	Pyrolysis temperature/^{o}C	Gases volume/mL/g·straw				$H_{conversion}$	$C_{conversion}$
		H_2	CO	CH_4	TCG		
3% (palygorskite:straw)	500	9.0	70.8	<0.01	90.0	1.2	8.1
	800	187.1	198.9	71.5	457.5	44.7	30.9
3%(dolomite:straw)	500	3.3	28.1	8.4	39.8	2.7	4.2

Straw only	800	178.5	210.4	63.3	452.2	41.3	31.3
	500	0.5	32.1	<0.01	32.5	0.1	3.7
	800	60.5	58.4	25.4	144.3	15.1	9.6

4. Conclusions

A new way of biomass gasification with palygorskite, a natural mineral with low cost and abundant storage, was provided. Pyrolysis temperature favored the gasification efficiency of straw regardless of with or without palygorskite. The addition of palygorskite improved the catalytic pyrolysis of straw regardless of the ratio between palygorskite and straw and improved the gasification efficiency of straw. The addition of palygorskite annealed at 800 ^{o}C increased CH_4 and $H_{conversion}$ compared with that annealed at 500 ^{o}C, however dramatically decreased the H_2, CO, TCG and $C_{conversion}$ due to the evident decrease of specific surface area. In addition, palygorskite and dolomite can dramatically improve the pyrolysis efficiency regardless of pyrolysis temperature. However, palygorskite had a slightly better efficiency than that of dolomite in the experimental conditions. This result can provide information on the potential application of palygorskite in biomass gasification technology to be determined.

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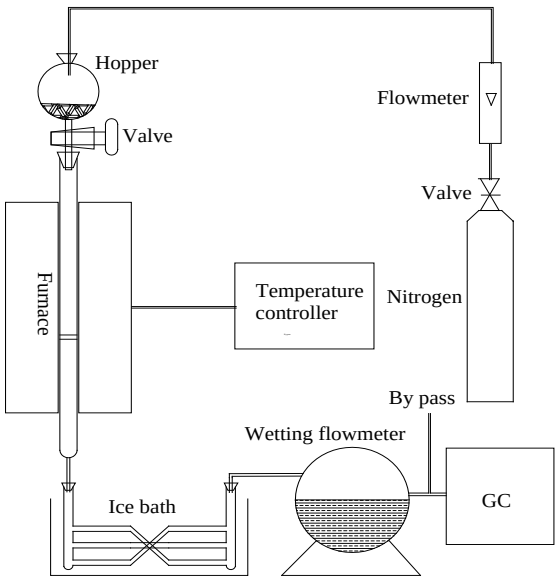

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427 **Fig. 1. Schematic diagram of in-situ catalytic cracking of rape straw with natural**

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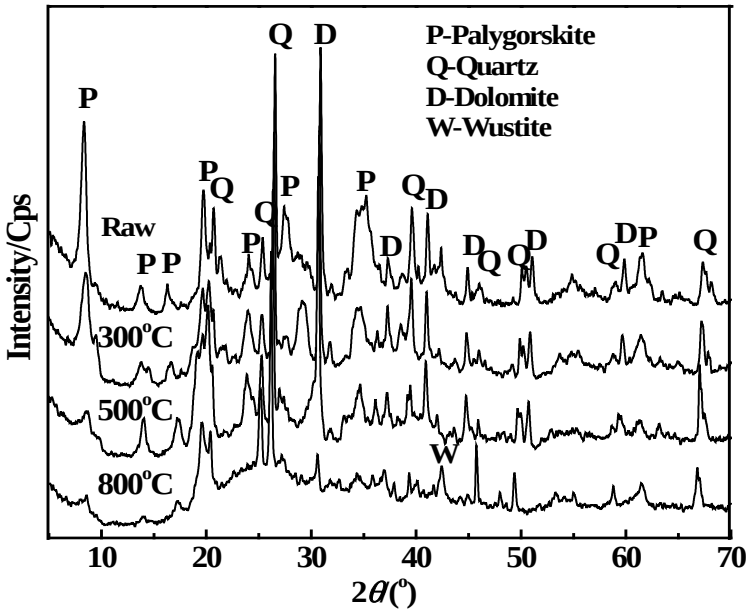

Fig. 2 XRD patterns of palygorskite annealed at different temperature.

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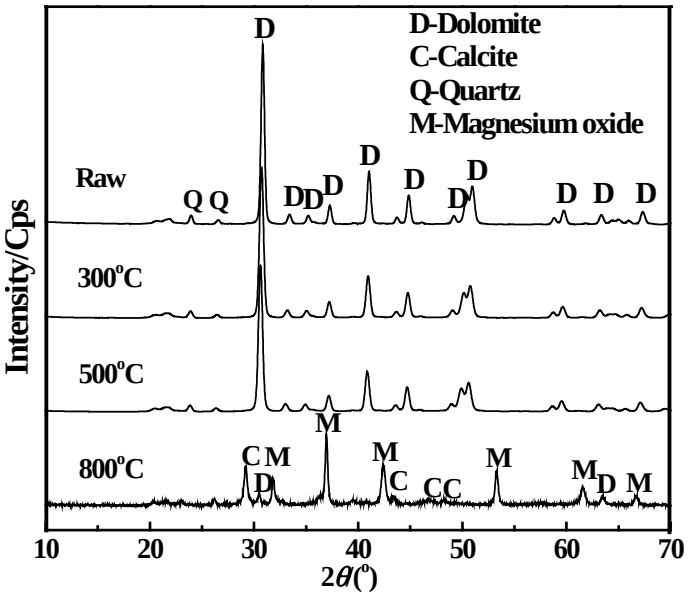

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435 **Fig. 3. XRD patterns of dolomite annealed at different temperatures**

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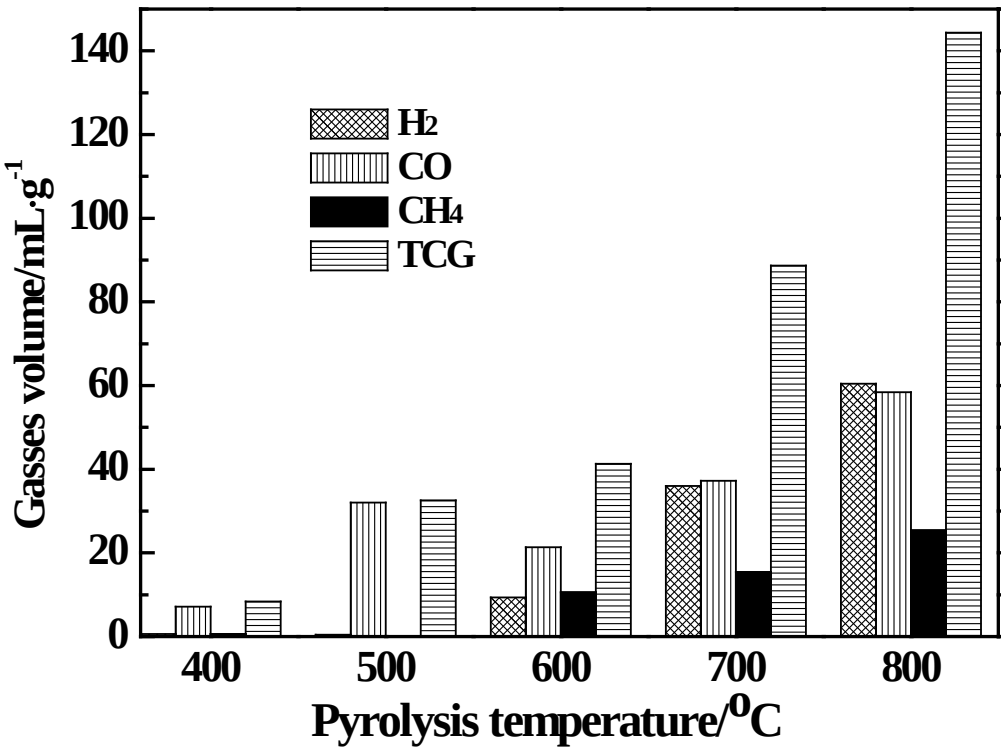


Fig. 4. Effect of pyrolysis temperature on gas volume

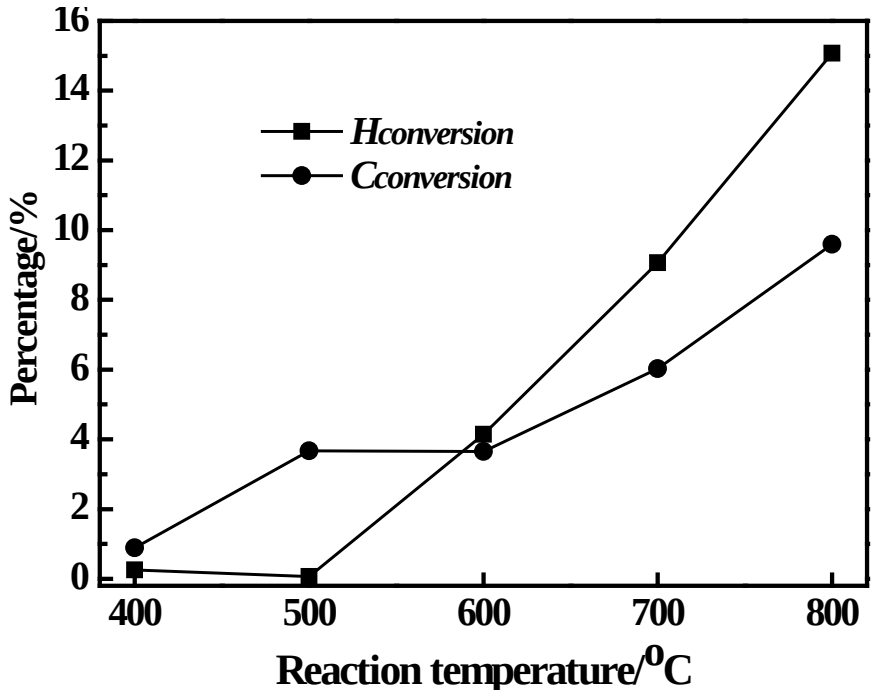
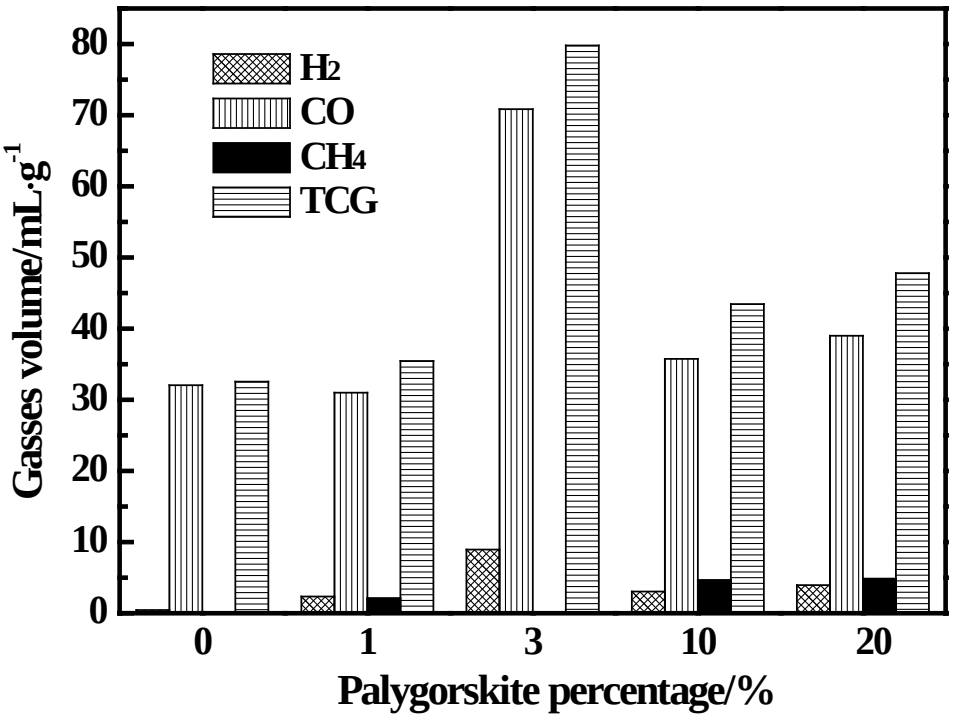


Fig. 5 Effect of pyrolysis temperature on $H_{coversion}$ and $C_{conversion}$



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448 **Fig. 6 Effect of ratio between palygorskite and straw on gases volume**

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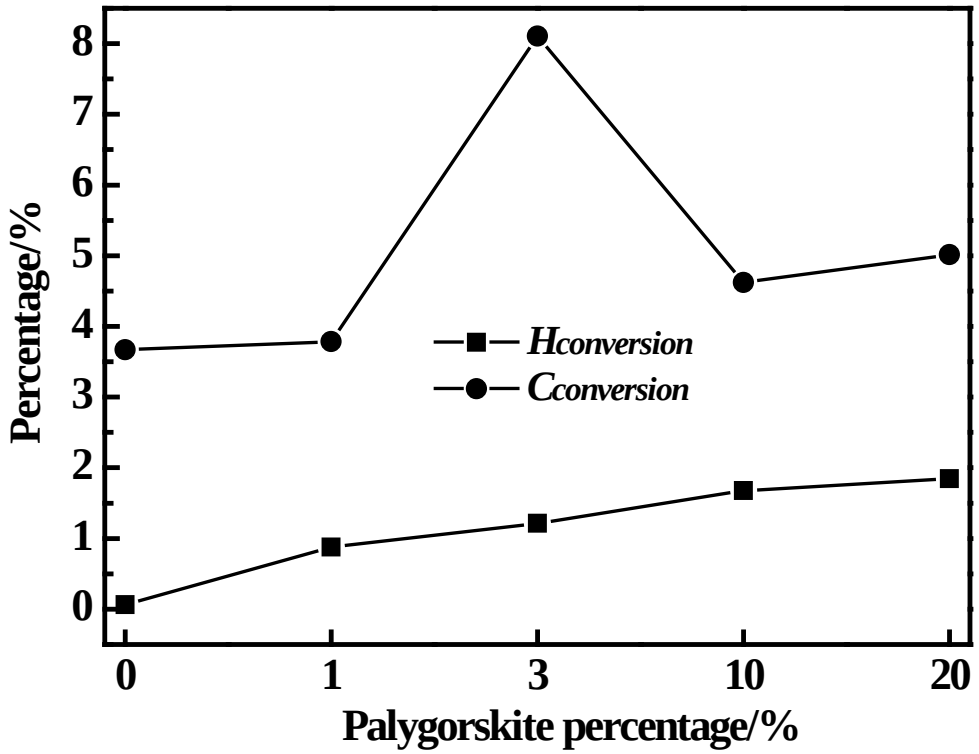

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451 **Fig. 7. Effect of Ratio between palygorskite and straw on $H_{coversion}$ and $C_{conversion}$**

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