Energy 44 (2012) 509–514

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Catalytic gasification of tobacco rob in steam–nitrogen mixture: Kinetic study and fuel gas analysis

Yi Yang [a,*], Shiping Jin [a], Yixin Lin [a], Suyi Huang [a], Haiping Yang [a,b]

[a] School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China
[b] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form
29 March 2012
Accepted 28 May 2012
Available online 2 July 2012

Keywords:
Steam–nitrogen gasification
Tobacco rob
Catalysts
Kinetic

ABSTRACT

Tobacco rob (TR) gasification experiments were carried out using thermogravimetric analyzer and gas chromatographic analyzer (TG–GC). Under the catalytic and non-catalytic condition, the pyrolysis characteristics, gasification characteristics and kinetics of TR were investigated in nitrogen-steam atmosphere. In the gasification process, the volumetric model was used in modeling pyrolysis of TR and the shrinking model was applied for investigating the gasification of pyrolysis chars. The experimental results showed that the TR gasification started above 750 °C without catalysts. Both NiO and dolomite could decrease the gasification temperature and enhance water gas shift reactions. The composition of gasification production was detected by gas chromatograph. The H_2 yield (34 mol/kg) of TR gasification with NiO was the most. The dolomite had more remarkable effect on improving CO yield (23 mol/kg).

1. Introduction

Agricultural and forestry wastes and, in general, all biomass residues, can be used as raw materials for the generation of power, liquid fuels, fuel gas, chemicals and active carbon. Thermochemical methods, such as direct combustion, pyrolysis and gasification, are the most appropriate and the most commonly commercially employed for these purposes [1]. Most of the biomass is composed of numerous components and thus has a heterogeneous property. In most cases, biomass is a mixture of hemicellulose, cellulose, lignin, ash, and minor amounts of other organics, which each pyrolyze or degrade at different rates and by different mechanisms and pathways [2].

Tobacco plants were widely cultivated in China as an important cigarette material. The tobacco production was 500–550 million tons in China each year. However, tobacco rob (TR) accounted for more than 60% of the total tobacco plants production which could not be used for cigarette production, and the cost was great to deal with them. Thus, TR was often treated by burning as agricultural wastes. It led to serious environmental problems and enormous waste of resources. So, the reutilization of this waste and the exploitation for potential bioenergy would be indispensable. Thus, this study primarily focused on this feedstock and its experimental results.

Some catalysts have been used in steam gasification processes to enhance the yield of gaseous products, and minimize the tar content of the product. The most appropriate catalysts for steam gasification are oxides and alkaline earth metals [3]. Dolomite catalyst is concluded to produce more gaseous products [4]. On the other hand, metal oxide traces in char catalyze water–gas shift reaction [5]. The use of dolomite or oxidation nickel as catalysts in biomass pyrolysis or gasification had been attracted much attention, because it was inexpensive and abundant and it could significantly reduce the tar content of the product gas [6]. Likewise, during TR gasification process, dolomite and NiO/γ-Al_2O_3 catalyst were used to eliminate tar.

In recent years, gasification of original samples of pyrolysis chars with steam or CO_2 was also commonly studied for both coal and biomass samples, including investigation on gas product [7], and related outcomes. According to the literature, it was hard to determine reaction kinetics and detailed mechanism of gasification process. This may be due to difficulties in real-time measuring of gas product analysis, and disturbance caused by catalysts. The technology of thermogravimetric analysis (TGA) couple with gas chromatograph (GC) is able to provide the reaction kinetics and gas product distribution of traditional gasification. There has been some literature concerning the thermogravimetric analysis–gas chromatograph (TG–GC) of volatile products from biomass [8–10]. According to the literature, one of the most attractive

---

[*] Corresponding author. Tel./fax: +86 (0)27 87559603.
E-mail address: yangyi7231@yahoo.com.cn (Y. Yang).

0360-5442/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2012.05.051

advantages of TG–GC is that it is able to afford the real-time and sensitive detection of evolved gases, which is an important and often a difficult task in many thermal applications.

Moreover, there are numerous studies focusing on the influences of reactive atmospheres during gasification of biomass. Steam, steam–oxygen, steam–air, hydrogen, etc. were widely applied in these studies. But, there is few detailed information about the combined effects of steam and nitrogen in a same gasification process. Therefore, this study aimed to investigate the thermogravimetric property, reaction kinetics, and gas product distribution of gasification of TR samples under the atmosphere of steam–nitrogen mixture with NiO and dolomite as catalysts by utilizing the TG–GC technology, and then to further discuss characteristics and novel discoveries in gasification of biomass.

2. Experimental section

2.1. Materials

The TR samples were collected from tobacco waste which was from farm in Enshi City, Hubei Province, China. The samples were dried under the sun for a period of 7 days to reduce the moisture content and then were shredded into particles of sizes of approximately 75 μm. Ultimate analysis of the TR sample was obtained with a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis gave the weight percent of carbon, hydrogen, nitrogen, and sulfur in the sample simultaneously, and the weight percent of oxygen was determined by difference. The proximate and ultimate analyses and the heating value of the sample were listed in Table 1.

Two types of pure chemicals, including NiO and dolomite, were introduced in the thermal system as catalyst to improve the yields of gas product form biomass gasification. These chemicals had an average diameter of 0.1 mm or less. Their BET surface areas were measured using ASPA2010 with liquid N_2 at 77 K. It was found that dolomite contain very low surface area (0.31 m^2/g) while those of NiO are higher (108.5 m^2/g). The pore volume of NiO and dolomite are 0.341 ml/g and 0.07 ml/g, respectively.

2.2. Apparatus and procedures

A process flow diagram of TR gasification process in steam–nitrogen atmosphere is shown schematically in Fig. 1. In this process, TG–GC measurements were performed by a simultaneous thermal analyzer coupled with a dual Channels Micro-Gas Chromatograph (Micro-GC, Varian, CP-4900). Non-isothermal thermogravimetric analysis (TGA) experiments, where the sample was heated under the dynamic atmosphere of the mixture of nitrogen (50 ml/min) and steam (50 ml/min) were conducted using a Ther-Max 500 analyzer. In order to avoid heat and mass transfer limitations, the masses of the original biomass samples were selected as only 5 mg. The samples were spread uniformly on the bottom of the crucible made of alumina. The catalysts were directly dry-mixed with biomass samples [11] and the total sample mass was 10 mg. Thus, the weight ratio of TR to catalyst was kept at 1:1. The TR samples were performed at a constant heating rate of 20 °C/min under a nitrogen atmosphere. During the experiments, the flow rate of nitrogen was fixed at 50 ml/min. The temperature was raised from ambient to 150 °C to be sure of complete removal of the moisture content of the samples and then steam was fed to the system. The temperature raised from 150 to 950 °C under atmosphere of 100 ml/min of mixture of steam and nitrogen in equal volumetric ratio and held 30 min at this temperature. The product syngas flow is introduced to a three way valve that allowed for either flowing into gas flow meter to check the gas yield or introducing the syngas directly to the micro GC for detailed analysis of the gas. The two columns used are: (1) column A: Molecular sieve 5A (MS-5A), Ar carrier gas for analysis of H_2, CH_4, and CO at 95 °C; (2) column B (Porapak Q-PPQ, He carrier gas) for the analysis of CO_2 and some hydrocarbons (C_2H_4 and C_2H_6) at 60 °C.

The reproducibility of the experimental results was checked and errors were lower than 5%. Each data given was the mean value of at least two trials, or even more, whenever deviations were higher than 5%.

Table 1
Ultimate analysis and proximate analysis of the sample.

Ultimate analysis (wt.%)		Proximate analysis (wt.%)	
C	42.33	Moisture content	12.82
H	5.596	Volatile matter	67.34
O[a]	35.86	Fixed carbon	17.30
N	0.758	Ash	2.54
S	0.096	Low heating value (M J/kg)	16.67
		Molecular formula	$CH_{1.58}O_{0.61}$

[a] By difference.

3. Results and discussion

3.1. Mechanism of catalytic steam gasification of TR

The purpose of using catalyst includes: (1) cracking of tar; (2) to decrease the gasification temperature; (3) to enhance steam reforming and water gas shift reactions in order to produce hydrogen-rich gas and more product gas.

In general, steam gasification reactions include two steps [12]. The first step is a thermo-chemical decomposition of TR with production of tar, char and volatiles, this step termed primary pyrolysis could perform at a lower temperature ~300 °C, and last until a temperature of 600 °C or even higher. The second step includes reactions of CO, CO_2, H_2 and H_2O with the hydrocarbon gases and carbon in TR, thereby producing gaseous products. The catalytic steam gasification mechanism of TR might be described by the following reactions as shown in Eqs. (1)–(6):

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 + Q \quad (1)$$

$$C + CO_2 \rightarrow 2CO + 162.4\ \text{MJ/kmol} \quad (2)$$

$$C + H_2O \rightarrow CO + H_2 + 131.3\ \text{MJ/kmol} \quad (3)$$

$$CO + H_2O \rightarrow H_2 + CO_2 - 41.2\ \text{MJ/kmol} \quad (4)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 + 206.3\ \text{MJ/kmol} \quad (5)$$

$$\text{Tar} + n_1H_2O \rightarrow n_2CO_2 + n_3H_2\ (\Delta H\ 298\ \text{K} > 0) \quad (6)$$

3.2. Catalytic gasification kinetics

3.2.1. Gasification with different catalysts

The TG and DTG profiles of TR gasification and catalytic gasification using different catalysts were showed in Fig. 2 and Fig. 3. Moisture release peaks were not considered and mass losses during moisture removal were not included on these profiles. At the temperature lower than 150 °C, the small change of conversion in the samples was attributed to vaporisation of moisture that was attached on the surface of the samples. The TR samples started to decompose and release volatile matter around 200 °C. The TG curves of the biomass samples showed only two major weight loss

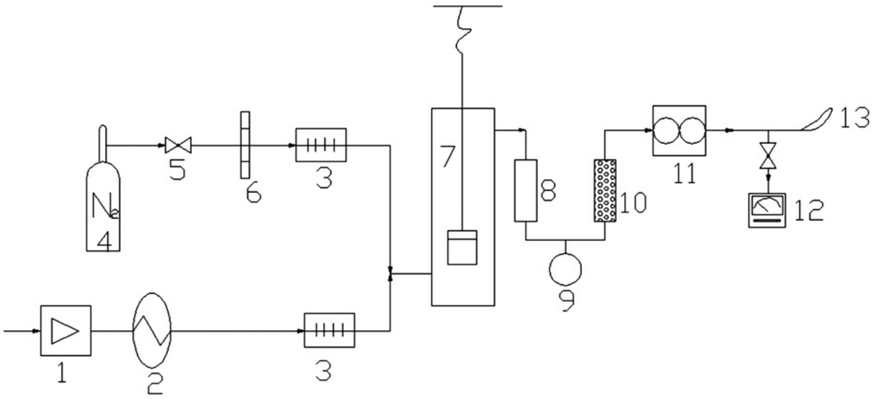

Fig. 1. Flowchart of experimental apparatus. 1. micro constant flow pump; 2. electric heater; 3. pipe electric heater; 4. nitrogen gas tank; 5. valve; 6. flow meter; 7. thermal analyzer; 8. condenser; 9. tar collector; 10. filter 11. gas meter; 12. Micro-Gas Chromatograph; 13. exhaust gas burner.

stages between 220 and 380 °C, and 580 and 800 °C. It was clear that the slop of the curve changed between the two temperature intervals. Slope between 220 and 380 °C was higher than that 580 and 800 °C. The mass loss at different catalysts exhibited similar patterns. It was observed at temperature between 600 and 800 °C that the TG curve shifted to the left with the addition of catalysts. This result suggested that the catalysts could decrease the gasification temperature. Several distinct mass loss zones observed were associated with degradation dynamics of main constituents. The first major mass loss stage between 220 and 380 °C was attributed to thermal decomposition of the hemicellulose and cellulose [13,14]. The second weight loss stages between 580 and 800 °C represented the endothermic reactions of gasification of the char and the steam cracking and reforming of the tars [15].

The different rates of instantaneous conversion, dX/dt, were obtained from TG analysis at different catalysts, shown in Fig. 3. The differential DTG curve of each sample has one extensive peak, occurred between 300 and 350 °C. The maximum peaks were attributed to the decomposition of cellulose and hemicellulose. Moreover, the DTG curves presented that adding catalysts tended to slightly delay thermal degradation processes. With the addition of catalysts, the maximum rate of mass loss also decreased from 24.3%/min to 21.08%/min. The possible reason could be that the primary pyrolysis process of TR samples was mainly controlled by reaction kinetics; as adding the catalysts which covered on the surface of TR particles partly, the process was mainly controlled by gas diffusion, since the resultant product gas inside the mixture particle had more difficultly to diffusing out [16]. It can be seen from the Fig. 3 that catalysts caused the second peak of the curves to move leftward. This result suggested that adding catalysts tended to promote gasification processes toward lower temperature. These results were in similar trends with previous reports [7,12]. From Fig. 3, the DTG curve of TR + dolomite showed an additional peak between 700 and 800 °C. According to the literature data [17], this additional peak could be attributed to the decomposition of dolomite.

3.2.2. *Kinetic model for TR gasification reaction*

Direct gasification of TR can be classified into two steps: biomass pyrolysis and char gasification. In this study, the pyrolysis step could perform at lower temperature ∼200 °C, and last until a temperature of about 600 °C. The thermal treatment removed the moisture and the volatile matter contents of the biomass. The gasification step was the reaction between steam and the remaining solid char at higher temperature.

All existing models can be classified into two groups: theoretical and semi-empirical. Well-known examples of theoretical kinetic models include the volumetric model and shrinking model [18]. The volumetric model does not consider the structural changes of the biomass during gasification, assuming that the gasifying agents

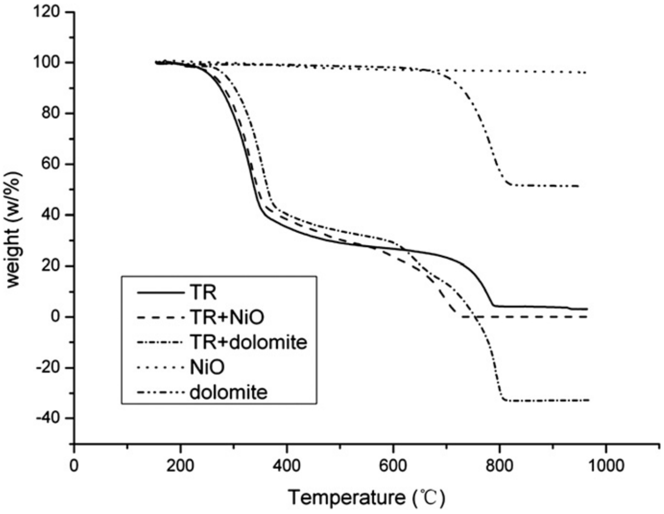

Fig. 2. TG curves of TR catalytic gasification at a heating rate of 20 °C/min.

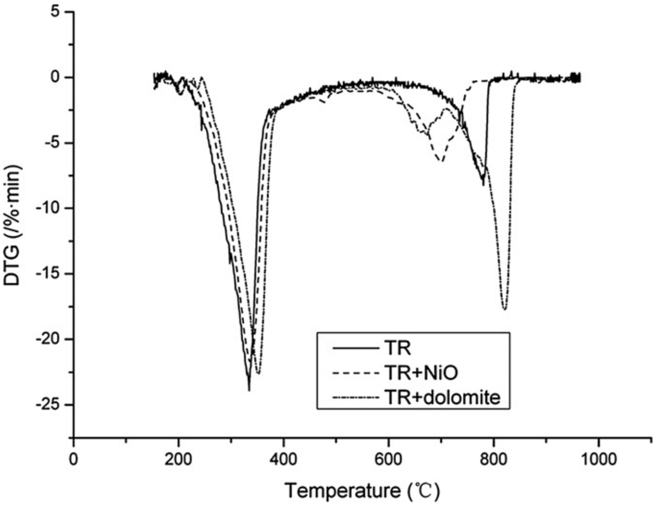

Fig. 3. DTG curves of TR catalytic gasification at a heating rate of 20 °C/min.

react with biomass at all active sites, which are uniformly distributed on both the outside and inside the particle surface. A shrinking core model, proposed for the reactions of a porous solid and gas with a moving boundary, assumes that a porous particle consists of spherical non-porous grains and the reaction takes place on their surface [18]. In this work the volumetric model could be suitable for the TR pyrolysis step. The shrinking core model could be applied to the char gasification step.

The rate equations used for determining the kinetic parameters are as follows. Volume reaction model:

$$dX/dt = k_v(1-X) \tag{7}$$

Shrinking core model:

$$dX/dt = k_r(1-X)^{2/3} \tag{8}$$

Where k_v and k_r is the rate constant for the surface reaction, X is the conversion ratio.

The conversion ratio (X) was calculated by the following equations:

$$X = \frac{W_0 - W_t}{W_0 - W_a} \tag{9}$$

where W_0 is the initial sample mass, W_t the sample mass at a time t and W_a the ash mass determined from the invariable weight after reaction.

The reaction rate constant k was expressed by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{10}$$

T was the temperature, A was the pre-exponential factor, t was the time, E was the activation energy, R was the universal gas constant (8.314 J/k mol).

In the volumetric model, temperature changes at a constant positive rate $\beta = dT/dt$. Hence, combining Eqs. (7) and (10) leads to Eq. (11):

$$\frac{dX}{dT} = \frac{A(1-X)}{\beta}\exp(-E/RT) \tag{11}$$

The function $p(x)$ may be introduction such that:

$$p(x) = \int_x^{\infty} \frac{e^{-x}}{x^2}dx \tag{12}$$

where $x = E/RT$. Hence Eq. (11) reduces to:

$$\ln(1-X) = -\frac{AE}{\beta R}p\left(x\right) \tag{13}$$

Doyle's approximation [19] of $p(x)$ is derived by observing a linear relationship between $\ln p(x)$ and x:

$$p(x) \approx \exp(-5.3308 - x) \tag{14}$$

Hence Eq. (13) may be manipulated to a linear form to yield:

$$\ln[-\ln(1-X)] = \ln\frac{AR}{\beta E} - 5.3308 - 1.0516\frac{E}{RT} \tag{15}$$

Hence for a given heating rate, E may be estimated from value of the slope of a plot of $\ln[\ln(1-X)]$ versus $1/T$.

In the shrinking model, β was the heating rate. Eq. (8) could be rearranged to:

$$\frac{dX}{dT} = \frac{A}{\beta}\cdot\exp\left(-\frac{E}{RT}\right)\cdot(1-X)^{2/3} \tag{16}$$

The kinetic parameters of Eq. (16) were obtained by non-linear regression analysis of the DTG curves according to the Coats–Redfern methods [20]. Data from experiments were used to estimate the kinetic parameters. The equation derived to calculate the activation energy values was as follows:

$$\ln\left\{\frac{3\left[1-(1-X)^{1/3}\right]}{T^2}\right\} = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{17}$$

Hence for a given heating rate, E may be estimated from the slope of a plot of $\ln\{3[1-(1-X)^{1/3}]/T^2\}$ versus $1/T$.

3.2.3. *Results of kinetics analysis*

3.2.3.1. Pyrolysis kinetics. In the TGA result, several data (mass change by temperature or time) were selected to satisfy a best linear regression of Eq. (15). Their corresponding temperature range and results of kinetics analysis were listed in Table 2. All the regression results had nearly extreme coefficients of determination, R^2 (from 0.971 to 0.997). Therefore, the assumption that pyrolysis of biomass undergoes a first-order reaction should be proper. From Table 2, it can be seen that both biomass pyrolysis and catalytic pyrolysis exhibited typical, muti-step reaction characteristics. In the first-step reaction, the activation energy ranged from 73.81 to 83.45 kJ/mol for TR pyrolysis and catalytic pyrolysis. The apparent activation energy for the catalytic pyrolysis is lower than for non-catalytic pyrolysis. This observed behavior may be due to the presence of catalysts which increased the rate of reaction. According to the literature data, similar results were studied by Lu [21]. During the second-step reaction, the activation energy for TR pyrolysis was 6.13 kJ/mol, but the value changed to 10.42 and 6.56 kJ/mol with NiO and dolomite, respectively. The activation energy showed a decreasing tendency with the increase in temperature. This was attributed to the fact that most of cellulose and hemicelluloses were decomposed at the pyrolytic conversion from 1% to 60% with increasing temperature. The decrease of activation energy at higher conversion may be attributable to further decomposition of lignin. These results were similar trends with previous reports [22,23].

3.2.3.2. Char gasification kinetics. The main constituent of char is carbon. Therefore, the main reaction is the water gas reaction (3). Carbon-monoxide may undergo a water gift shift reaction (4). Table 3 reports the kinetic parameters obtained for gasification of chars with steam–nitrogen mixture. If the values of activation energies obtained from the pyrolysis and the steam gasification processes were compared, it was observed that the activation energy for steam gasification was higher than for pyrolysis from Table 2 and Table 3. This was attributed to the fact that the presence of steam as a gasifying agent slowed down the rate of gasification.

Table 2
The kinetic analysis of TR pyrolysis.

	Temperature (°C)	Conversion (%)	E (kJ/mol)	A (1/min)	R^2
TR	217–357	0.9–61.4	83.45	$9.39E + 14$	0.997
	357–737	61.4–82.0	6.13	$1.07E + 07$	0.974
TR + NiO	219–381	1.4–60.2	73.81	$8.26E + 13$	0.990
	381–659	60.2–84	10.42	$3.47E + 07$	0.983
TR + dolomite	231–363	1.4–57.4	81.33	$4.50E + 14$	0.995
	363–605	57.4–73.2	6.56	$1.06E + 07$	0.989

R^2: coefficient determination.

Table 3
The kinetic analysis of char gasification.

	Temperature (°C)	Conversion (%)	*E* (kJ/mol)	R^2
TR	754–800	86.0–98.9	95.33	0.983
TR + NiO	666–717	87.9–99.1	81.11	0.971
TR + dolomite	618–725	73.2–94.9	83.60	0.975

R^2: coefficient determination.

Thus, higher temperature was required for complete gasification [24]. It was clear that the activation energies showed a decreasing tendency with the presence of catalysts. In addition, the remaining solid char that can be gasified at lower temperature are supposed to have lower activation energy. Thus, there was a positive effect for char gasification with the presence of catalysts. From Table 3, it can be seen that the activation energy for non-catalytic gasification was 95.33 kJ/mol, but the value changed to 81.11 and 83.60 kJ/mol with NiO and dolomite, respectively. NiO appeared a stronger effected on the char gasification process than dolomite. According to the kinetics analyses discussed above, too many data may result in poor result of linear regression that comes from a composite effect of multi-components. Therefore, thermogravimetric data over a small interval of temperature or time can provide a good linear regression in the kinetics analysis as illustrated in this study, in spite of which method of integration or other calculation applied.

3.3. Gas product analysis

By means of TG–GC analysis, thermogravimetric data can be obtained as well as information about the product distribution. The yields of individual gas species from TR gasification at different catalysts are plotted in Fig. 4. It indicated that the main gas products were H_2, CO, CO_2, CH_4, and some C_2 hydrocarbons (C_2H_4 and C_2H_6). In contrast, there were a great difference between gasification (run 1) and catalytic gasification (run 2 and run 3), it was concluded that the introduction of steam increased H_2, CO and CO_2 yield, while CH_4, C_2H_4 and C_2H_6 yield decreased, which was caused by the participation of the catalysts improving in gas-phase reaction and gasification of tar and char. The similar finding on other biomass materials for gasification was also reported by Yu [25] and Garcia [26]. The highest H_2 and CO_2 yield were obtained with NiO (run 2). This result showed that the presence of NiO could induce the equilibrium for the two reactions (Eqs. (3)–(4)) to be shifted toward H_2 and CO_2 production. In contrast, with regards to CO production, the highest yield was found with dolomite (run 3). This was attributed to the decomposition of dolomite at temperature higher than 800 °C, meanwhile the CO_2 content increased gradually, which could improved Boudouard reaction (2) to increase the yield of CO. Thus, the catalysts could enhance the yield and quality of product gas in steam gasification of TR.

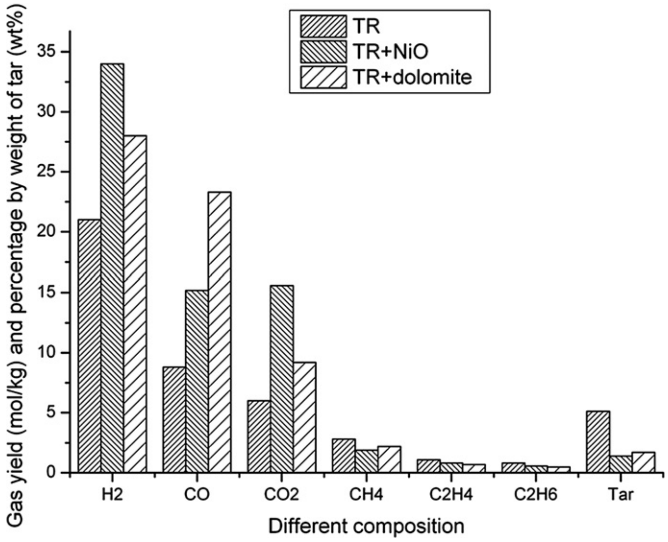

Fig. 4. Gas yield and percentage by weight of tar in steam gasification for non-catalytic and catalytic processes.

3.4. Five stages in steam gasification of biomass

According to the TG–GC results and relevant discussion mentioned above, the gasification of biomass can be divided into five stages. In the zeroth stage, the initial weight loss until 150 °C can be contributed to the loss of moisture in the sample under inert conditions. Once the temperature is high enough (150–250 °C), A rapid thermal degradation is noticed for part of the biomass (like hemicellulose). This is the first stage in pyrolysis of biomass to produce light hydrocarbons. In the second stage (250–500 °C), it is known that the most part of the biomass (hemicellulose and cellulose) start to decompose at this temperature range, then most of the gas products will be produced. At higher temperature (500–600 °C), decomposition at this temperature range progress slowly due to the unreacted lignin or char. Moreover, the productions of H_2 and CO_2 in the third stage may prove the possibility of self-gasification of residual char generated in earlier stages. In the fourth stage (>600 °C). More gaseous products are obtained from the reactions between remaining solid char and steam. However, the presence of steam as a gasifying agent slows down the rate of gasification. Therefore, char gasification reactions are slower than that of pyrolysis and is the rate limiting step in the overall gasification process.

4. Conclusions

The kinetic parameters and characteristics of catalytic gasification of TR were investigated by TG–GC. The catalyst could decrease the gasification temperature, enhance the reaction rate and improve the fuel gas yield. The gasification of biomass can be divided into five stages. Only moisture and light hydrocarbons were detected in the zeroth and the first stage, respectively. Most of gas products were generated in the second stage. The gases produced in earlier stage may provide the evidence of self-gasification of residual char at 500–600 °C. The water gas reactions between remaining char and steam occurred at higher temperature in fourth stage.

The results indicated that there was a strong potential for producing fuel gas from TR which are essentially waste materials by gasification process with inexpensive and abundant dolomite or NiO as catalyst.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 51076057). The authors are grateful to the Analytical and Testing Center of State Key Laboratory of Coal Combustion for carrying out the ultimate analysis.

References

[1] Luo SY, Xiao B, Hu ZQ, Liu SM, Guan YW. Experimental study on oxygen-enriched combustion of biomass micro fuel. Energy 2009;34:1880–4.
[2] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Organic Geochemistry 1999;30:1479–93.

[3] Encinar JM, Gonzalez JF, Rodriguez JJ, Ramiro MJ. Catalysed and uncatalysed steam gasification of eucalyptus char: influence of variables and kinetic study. Fuel 2001;80:2025–36.

[4] Rapagna S, Jand N, Foscolo PU. Catalytic gasification of biomass to produce hydrogen rich gas. International Journal of Hydrogen Energy 1998;23:551–7.

[5] Franco C, Pinto F, Gulyurtlu I, Cabrita I. The study of reactions influencing the biomass steam gasification process. Fuel 2003;82:835–42.

[6] Hu G, Xu SP, Li SG, Xiao CG, Liu SQ. Steam gasification of apricot stones with olivine and dolomite as downstream catalysts. Fuel Processing Technology 2006;87:375–82.

[7] Li JF, Liu JJ, Liao SY, Yan R. Hydrogen-rich gas production by air-steam gasification of rice husk using supported nano-NiO/γ-Al_2O_3 catalyst. International Journal of Hydrogen Energy 2010;35:7399–404.

[8] Perng LH. Thermal decomposition characteristics of poly (phenylene sulfide) by stepwise Py-GC/MS and TG/MS techniques. Polymer Degradation and Stability 2000;69:323–32.

[9] Shen DK, Gu S, Bridgwater AV. Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR. Journal of Analytical and Applied Pyrolysis 2010;87:199–206.

[10] Sasidharan N, Hariharanath B, Rajendran AG. Thermal decomposition studies on energetic triazole derivatives. Thermochimica Acta 2011;520:139–44.

[11] Sutton D, Kelleherm B, Ross JRH. Review of literature on catalysts for biomass gasification. Fuel Processing Technology 2001;73:155–73.

[12] Luo SY, Xiao B, Hu ZQ, Liu SM, Guo XJ, He MY. Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: influence of temperature and steam on gasification performance. International Journal of Hydrogen Energy 2009;34:2191–4.

[13] Ferdous D, Dalai AK, Bej SK, Thring RW. Pyrolysis of lignins: experimental and kinetic studies. Energy & Fuels 2002;16:1405–12.

[14] Cheng G, Zhang LG, He PW, Yan F, Xiao B, Xu T, et al. Pyrolysis of ramie residue: kinetic study and fuel gas produced in a cyclone furnace. Bioresource Technology 2011;102:3451–6.

[15] Herguido J, Corella J, Gonzalez-Saiz J. Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot plant: effect of the type of feedstock. Industrial & Engineering Chemistry Research 1999;31:1247–82.

[16] Lv PM, Xiong ZH, Chang J, Wu CZ, Chen Y, Zhu JX. An experimental study on biomass air-steam gasification in a fluidized bed. Bioresource Technology 2004;95(1):95–101.

[17] Zhang SY, Hong RY, Cao JP, Takayuki T. Influence of manure types and pyrolysis conditions on the oxidation behavior of manure char. Bioresource Technology 2009;100:4278–83.

[18] Fermoso J, Arias B, Pevida C, Plaza MG, Rubiera F, Pis JJ. Kinetic models comparisons for steam gasification of different nature fuel chars. Journal of Thermal Analysis and Calorimetry 2008;91:779–86.

[19] Starink MJ. The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. Thermochimica Acta 2003;404:163–76.

[20] Coats AW, Redfern JP. Kinetics parameters from thermogravimetric data. Nature 1964;201:68–9.

[21] Lu CB, Song WL, Lin WG. Kinetics of biomass catalytic pyrolysis. Biotechnology Advances 2009;27:583–7.

[22] Varhegyi G, Antal JJM, Jakab E, Szabo P. Kinetic modeling of biomass pyrolysis. Journal of Analytical and Applied Pyrolysis 1997;42(1):73–87.

[23] Jeguirim M, Trouve G. Pyrolysis characteristics and kinetics of Arundo donax using thermogravimetric analysis. Bioresource Technology 2009;100: 4026–31.

[24] Lucas C, Szewczyk D, Blasiak W, Mochida S. High-temperature air and steam gasification of densified biofuels. Biomass and Bioenergy 2004;27:563–75.

[25] Yu QZ, Brage C, Nordgreen T, Sjöström K. Effects of Chinese dolomites on tar cracking in gasification of birth. Fuel 2009;88:1922–6.

[26] Garcia L, Salvador ML, Arauzo J, Bilbao R. Catalytic steam gasification of pine sawdust: effect of catalyst weight/biomass flow rate and steam/biomass ratios on gas production and composition. Energy & Fuels 1999; 13:851–9.