Kinetics Dynamics Characteristics of Carbon Deposition on the Gas and Soot Formation in Ethanol Pyrolysis

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ABSTRACT

Ethanol is a promising energy to replace traditional fuels such as oil, coal and natural gas. The utilization of Ethanol is gradually common in agricultural, industrial and commercial fields. Pyrolysis is a typical approach to gain power from Ethanol and the gas production under various experimental conditions has been intensive studied. Excessive carbon deposition influences the effective use of Ethanol thus analyzing its formation process and kinetics dynamics characteristics during pyrolysis is much significant. This paper sets up an experimental system which can adjust pyrolysis temperature ranging from 1050℃ to 1250℃. Mass flowmeter and continuous injection pump were employed to control concentration and flow velocity of the mixture. Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatograph (GC) confirmed the stable pyrolysis of Ethanol. Thermogravimetric experiments were carried out when carbon deposition was obtained after 6 hours of Ethanol pyrolysis. Key characteristics of carbon deposition include reaction energy, pre-exponential factor and combustibility index. Based on the quality loss curve of carbon deposition in oxygen atmosphere, these factors were calculated. It is found that pyrolytic carbon produced under a lower temperature is easier to be transformed, collected and eliminated. The combustibility index of graphite, fault coal and other traditional materials verified the importance of reducing carbon deposition during Ethanol pyrolysis.

Keywords: Ethanol pyrolysis, carbon deposition, reaction energy, combustibility index

1. INTRODUCTION

Development of renewable energy results from perceived risk of using traditional fuels. The perceived risk includes a big contrast between short-term consumption of fossil fuels and millions of years energy storing. The shortage of traditional energies leads to a 'post-petroleum era'. What's worse, fossils fuels cause serious problems, such as acid rain, greenhouse effect and severe haze. According to the above reasons, lots of renewable energies have been researched and applied. Hydropower is used for power generation (Wu 2010). Direct solar is beneficial to photovoltaic and water heaters (Al-Hasan 1998). Tidal comes from barrage and tidal stream (Rourke 2010). Beyond these new energy sources, Ethanol with its excellent performance of sufficient burning, environmental protection and price moderate has been widely used in various fields (Pimentel 2003, Antolini 2007, Balat 2009).

The attempt to Ethanol application was dated back to 1908 with initial focus on pyrolysis time, pressure and temperature. With the deepen of research, various products were manufactured through pyrolysis of Ethanol and its mixture. Hydrogen was a typical one with advantages like high thermal value, non-toxic and harmlessness. Guo et al., utilized the heavy magnesium water with an addictive of Ethanol to prepare magnesium oxide with its purity of 99.7%. Their conclusions pointed to the fact that the optimum purity of magnesium oxide crystal was obtained with Ethanol volume fraction of 40% when pyrolysis at 70 ℃ (Guo 2009). Zhang et al., prepared Co/McM-41 mesoporous molecular sieve through chemical vaporing deposition and found the best Ethanol pyrolysis condition was 750 ℃ (Zhang 2013). Nowadays, Ethanol application is gradually mature and the mixture of Ethanol and other fuels has aroused great interests among researchers. Ceviz et al., studied the property changes of gasoline when mixed with E0, E5, E10, E15 and E20. Experimental results illustrated that the engine performance of power, emission and economics were improved as increasing percentages of Ethanol (Ceviz 2005). Yiiksel demonstrated that CO and HC emission for gasoline mixed Ethanol was much lower compared with gasoline alone (Yücesu 2006). Although there is various analysis on gas productions during Ethanol pyrolysis, the formation of carbon deposition and its reactivity under different pyrolysis conditions still need further study.

Ethanol is a common addictive to various fuels aiming to affect the amount of carbon deposition during mixture reactions. Zhao et al., conducted thermogravimetric experiments with different volume ratios of diesel and Ethanol. The investigation involved activation energy, combustion property and burn-out characteristic of the produced carbon deposition (Xia 2014). Ruiz et al., studied mixture pyrolysis of Ethanol with acetylene and ethylene, respectively. The conclusion pointed out to the fact that low ratio of Ethanol and acetylene could effectively increase reactivity of the pyrolytic carbon, which had an inner connection with the ratio of carbon and hydrogen elements (Ruiz 2007). According to complex influence of ethanol on carbon productions, the importance to investigate carbon deposition during ethanol pyrolysis is much more obvious.

This paper introduces a novel method to carry out an experimental analysis on Ethanol pyrolysis. The chemical compositions of obtained productions were studied by thermal-gravimetry in an oxygen atmosphere. Reaction energy, pre-exponential factor

and combustibility index of the carbon deposition were also calculated through Coats-Redfern integral method. Moreover, the comparison of activation energy between pyrolytic carbon and other typical fuels demonstrates the fact that carbon deposition during Ethanol pyrolysis was much more difficult to be transformed or eliminated.
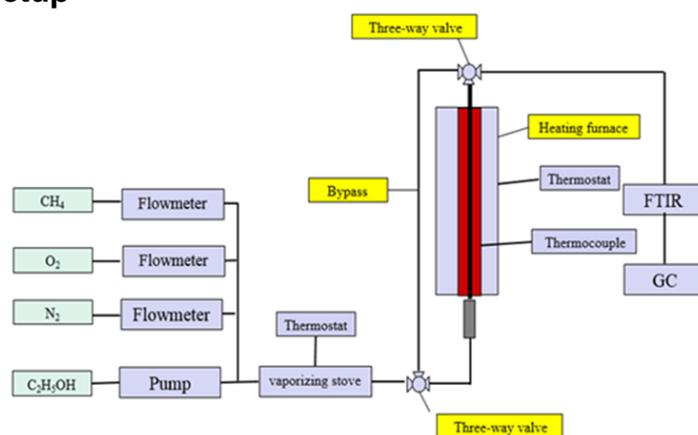
2. Experimental setup

Fig. 1. Experimental schematic of Ethanol pyrolysis

Figure 1 shows the experimental system including gas distribution section, reactant pyrolysis section and production monitoring section. In the gas distribution part, Ethanol was loaded into a 20 ml type syringe which was installed at a continuous injection pump to control the inflow volume. Nitrogen was defined as the carrier gas controlled by a flowmeter. A vaporizing stove was fixed at a constant temperature of 100 ℃. Reaction gas flew through a quartz glass tube inside a heating furnace. Thermocouple together with temperature controller adjusted pyrolysis temperature of the vertical heating furnace from 1050 ℃ to 1250 ℃. The FTIR and GC were employed to monitor pyrolysis productions in real time. Table 1 shows detailed parameters during Ethanol pyrolysis. Each set of the three experiments was conducted 6 hours to obtained an obvious amount of carbon deposition.

Table 1. Experimental conditions

Item	$[C_2H_5OH]$ (ml/h)	$[N_2]$ (ml/min)	Concentration （percentage）	Temperature （℃）	Residence time （s）
1	1.90	250	5.02	1050	7.26
2	1.90	250	5.02	1150	7.26
3	1.90	250	5.02	1250	7.26

N_2 is measured by a mass flowmeter at room temperature. Ethanol is injected as liquid in a 20 ml syringe at room temperature.

The experimental procedure of Ethanol pyrolysis was divided into two parts. The first part was aimed to ensure a completed mixing and reduce experimental errors. Nitrogen and liquid Ethanol was injected into the experimental system successively. The mixture reached 100 ℃ at the vaporizing stove leading to a completed gasification

and well mixing. The gaseous reactants of both nitrogen and Ethanol flew through a bypass near the vertical tube furnace. FTIR matched primary concentrations of reactant with expected set values before normal pyrolysis. And then the second part was carried out by switching the three-way valve to let reactant flow through the quartz glass which had been fixed at a constant temperature previously. After 6 h ethanol pyrolysis, carbon deposition inside the glass tube was fetched out and then stored in a glass desiccator for 20 h. Thermal-gravimetry experiments were proceeded by taking 10 mg carbon deposition under different experimental temperature.

3. Experimental results and discussions

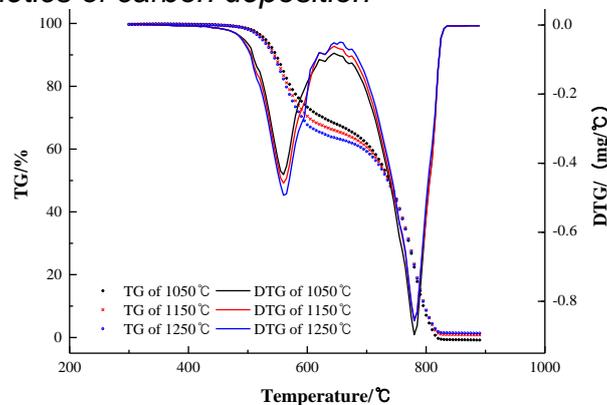## 3.1 Pyrolysis kinetics of carbon deposition

Fig. 2. TG and DTG curves of carbon deposition

Figure 2 illustrates weight loss process of pyrolytic carbon in oxygen atmosphere. Based on different temperature intervals, the experiment was divided into two parts. The first interval displayed oxidation reactions of volatile component at a temperature range from 500 ℃ to 600 ℃. As the increasing of temperature, volatile component kept precipitating out and reacted with oxygen. The calculation results from TGA experiments illustrate that the amounts of volatile component were 24.99%, 27.74% and 30.41% respectively. In addition to that, the peak of decomposition increases. When the temperature reach 650 ℃，soot began to react. The calculation results from DTG experiments illustrate that the amounts of soot particle were 67.93%, 65.79% and 63.47% respectively. The peak of decomposition rate decreases.

Based on the linear non-isothermal experiments, Coats-Redfern integral method was introduced to analysis activation energy (E), pre-exponential factor (A) and linear regression coefficient (R^2) of carbon deposition produced under various temperature.

$$ln[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}] = ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad n \neq 1 \tag{1}$$

$$ln\left[\frac{-ln(1-\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad n=1 \tag{2}$$

Equation (1) and (2) stand for common dynamic equations of nonhomogeneous system in non-isothermal conditions. In these equations, α stands for weight loss percentage of carbon particles. T is thermodynamic temperature and R is molar gas constant with its value fixed at 8 .314 J/(mol·K). The pyrolysis kinetics result of carbon deposition is shown in table 2. The three items stand for carbon deposition obtained during Ethanol pyrolysis at 1050 ℃，1150 ℃ and 1250 ℃ respectively. It is confirmed that the reaction energy of carbon deposition increases when Ethanol pyrolysis was conducted at a higher temperature. The results demonstrate that carbon deposition produced at higher temperature is more difficult to be converted or eliminated which brings into correspondence with other researchers' results (Esarte 2011).

Table 2. Ethanol pyrolysis kinetic parameters at different temperatures

Item	Pyrolysis interval（T /°C）	E (kJ·mol^{-1})	A (min^{-1})	R^2
1	500~800	119.89	2.04×10^7	0.93124
2	500~800	123.38	3.91×10^7	0.92373
3	500~800	127.29	7.85×10^7	0.91864

Table 3 shows the pyrolysis kinetics parameters of graphite, fault coal and other materials. The comparison result exhibited a significant value difference of reaction energy between carbon deposition during Ethanol pyrolysis and other materials. To be specific, the smallest reaction energy of carbon deposition was more than 100 kJ·mol^{-1} while the biggest data for other materials was less than 80 kJ·mol^{-1}. According to the comparison, reducing carbon deposition during Ethanol pyrolysis is much more difficult.

Table 3. Pyrolysis kinetics parameters of materials

Samples	Pyrolysis interval（T /°C）	E (kJ·mol^{-1})	A (min^{-1})	R^2
Graphite	619~888	17.70	0.0033	0.88085
Fault coal	411~611	47.53	78.57	0.99046
Pine	226~429	74.11	332526	0.99291
Wheat	203~402	56.07	12192	0.99526
Corn	191~401	44.48	1032	0.99086

3.2 Combustion dynamics characteristics of carbon deposition
In order to have a deep understanding on carbon deposition during Ethanol pyrolysis at various temperature, combustibility index was taken into consideration. The index was related to ignition temperature of carbon deposition which can be regarded as critical temperature between slow combustion and rapid combustion. Equation (3) was employed to calculate the combustibility index. $\left(\frac{dw}{dt}\right)_{max}$, $\left(\frac{dw}{dt}\right)_{mean}$, T_i and T_h stand for maximum combustion velocity, average burning rate, ignition temperature and burnout temperature respectively.

$$S = \frac{(\frac{dw}{dt})_{max} * (\frac{dw}{dt})_{mean}}{T_i^2 * T_h}$$

(3)

Table 4 shows the combustibility index of carbon deposition when Ethanol pyrolysis was conducted. The three items stand for carbon deposition obtained during different pyrolysis temperature of 1050 ℃，1150 ℃ and 1250 ℃. The combustibility index reduced from 8.435×10^{-12} mg^2/(min^2·K^3) to 7.520×10-12 mg^2/(min^2·K^3) as increasing pyrolysis temperature. The results demonstrate that carbon deposition produced at higher temperature was harder to be burnt out. What's more, the reproducible capability was also stronger than before.

Table 4. Combustion characteristic index of sediments

Items	Ignition temperature (K)	Burnout temperature (K)	average burning rate (mg/min)	combustibility index
1	932.33	1084.31	0.351	8.435×10^{-12}
2	935.02	1089.93	0.322	7.654×10^{-12}
3	939.18	1092.72	0.320	7.520×10^{-12}

4. CONCLUSIONS

This paper studied kinetics dynamics characteristics of carbon deposition during Ethanol pyrolysis at various temperature. The volatile components increase while soot particles decrease as increasing pyrolysis temperature. Higher activation energy contributed to the chemical stability and lower combustibility index verified the strong renewable capacity. The kinetics performance of carbon deposition produced at higher temperature reveals a harder conversion, collection and elimination procedure.

Acknowledgements

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