Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 3, 991–997

STUDY ON THE COMBUSTION KINETIC CHARACTERISTICS OF BIOMASS TAR UNDER CATALYSTS

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TG and DTA experiments were performed to investigate the biomass tar combustion behavior in coexistence of dolomite and mayenite at two different heating rates as 5 and 15°C min^{-1}. Different reaction kinetic mechanisms with the classical Arrhenius model were used to treat TG data, and showed that the first-order combustion model fitted the data well. Three stages combustion model was proposed and applied for the calculation of kinetics parameters successfully. The starting temperature of high temperature combustion stage moved up near 100°C because of the coexistence catalysts, and the combustion amount of biomass of the stage also improved nearly 10 mass%. By calculation a uniform trend of decreasing activation energies was observed with the addition of dolomite and mayenite, and also greatly improved the amount and speed of tar combustion process.

Keywords: *biomass tar, combustion, dolomite, kinetic model, mayenite, TG*

Introduction

Tar is an unavoidable waste or by-product during biomass thermal conversion such as biomass pyrolysis, gasification, or fossil thermal conversion such as coal carbonization or liquefaction [1], for example, coal tar account for 2.5~4.0% of the amount of the feed coal during the process of coal carbonization; tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater in the product gases for biomass gasification; Tar from biomass pyrolysis is often called as 'pyrolysis oil', which is the main aim product of this process. So the research on combustion behavior of biomass tar will favor the understanding the development of energy thermal conversion process. Thermo-analytical tools such as thermo-gravimetry (TG) and differential thermal analysis (DTA) can play an important role in this regard. The use of thermal method for characterization of fuel such as coal, lignin or tar is certainly not new, and much work has been carried out to study the combustion process. Nevertheless, only a very few investigations are currently available on the thermo-chemical behavior of biomass tar especially in coexistence with catalysts.

Biomass oil derived via slow pyrolysis process blended with ethanol and burned in a circular jet spray at atmospheric pressure were studied by Stamatov [2]. It showed that biomass pyrolysis oil flames were shorter, wider and brighter than diesel fuel flames at the same conditions, and could be regarded as one potential energy resource. Karaosmanoglu [3] studied the characteristic of tar oil as combustion energy from biomass pyrolysis. It found that pyrolytic oil was a carbon rich, hydrocarbon mixture bearing oxygen at a considerable ratio and containing ash, sulphur and nitrogen in very small quantities. And Dasa [4] studied the stability and combustion characteristic of Cashew nut shell (CNS) pyrolysis oil. Zhang [5] deduced the kinetic parameters of bio-oil from flash pyrolysis of biomass (wood chip). Aprameya [6] studied the pyrolysis and combustion behavior of heavy oil and its asphaltenes by TG. Kök [7] investigated the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix by TG and DTA technical, and also proposed four stages combustion kinetic model. Kök [8] also studied the reaction rates related to an in-situ combustion process and heating rate. In summary, tar is potential combustion oil, and also its low sulphur content is quite promising for its evaluation as fuel from the point of view environmental pollution. However, biomass tar combustion is extremely complicated and its combustion behavior and mechanism still requires further study, especially in coexistence of catalysts.

In this study, thermogravimetric analyzer was adopted to obtain information on the combustion behavior of biomass tar in coexistence of dolomite and mayenite. Three stages reaction kinetics model was proposed and analyzed. The effect of catalysts (dolomite/mayenite) on biomass combustion in air environment was studied. The apparent activation energy (*E*) and pre-exponential factor (*A*) for combustion kinetic were available. It shows that dolomite and mayenite can improve the tar combustion properties efficiently.

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1388–6150/$20.00

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Experimental

Sample preparation

The tar studied in this research was supplied from fowl droppings gasification process. The chemical analysis of the tar obtained by a CHN coder was shown in Table 1. 10 mass% of catalysts were added to the tar in order to see the effect of catalyst on combustion.

Table 1 Element composition of tar by CHN

C	45.21%
H	6.43%
N	6.20%
Ignition loss	42.16%

Catalysts: Calcination of natural dolomite was carried out in muffle oven at 1000°C for 2 h in air environment and used in this study. The component analysis of calcined dolomite was shown in Table 2. The catalyst before and after calcinations were characterized by XRD to study the effect of tar combustion, the results were shown in Fig. 1, which show that the natural dolomite are mainly $CaCO_3$ and dolomite ($CaMg(CO_3)_2$), and the calcined dolomite are CaO and MgO.

Table 2 Composition of calcined dolomite

Composition	CaO	MgO	SiO_2	Fe_2O_3
Mass%	55.896	39.983	4.051	0.070

Mayenite ($Ca_{12}Al_{14}O_{33}$) was prepared by the mixture $Ca(OH)_2$ and $Al_2(OH)_3$ in stoichiometric ratio and calcined at 1000°C for 4 h in air environment. The XRD pattern was shown in Fig. 2, which shows that the mayenite are mainly $Ca_{12}Al_{14}O_{33}$ (mayenite).

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed with Rigaku Thermo Plus TG8120 thermogravimeter analysis system. The TG and DTA curves were obtained using the following experimental conditions: atmosphere. Air; flow rate 50 mL min^{-1}; mass of tar sample is 20–25 mg; heating rates: 5 and 15°C min^{-1}; temperature range: 25~1000°C. Prior to experiments, TG/DTA equipment was calibrated and experiments were performed more twice for repeatability.

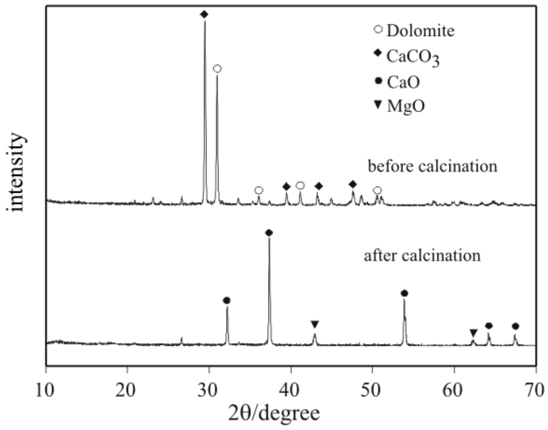

Fig. 1 X-ray diffraction pattern of dolomite before and after calcination

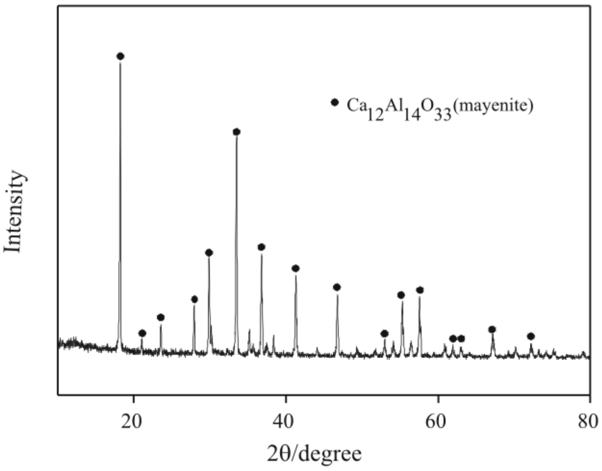

Fig. 2 X-ray diffraction pattern of mayenite

Kinetic theory

About the reaction kinetics of solid such as coal, lignin, fuel, different reaction model was used by different researches [9–17], such as Arrhenius-type kinetic model [9–11], Coats–Redfern model [12–16], Horowitz–Metzger [17].

Tar from biomass gasification, is one kind black and high viscosity liquid containing more than one hundred compounds, can be regarded as one material whose properties are between liquid such as crude and solid such as coal, asphaltene. Theoretically, the combustion of tar can be initiated whenever oxygen comes into contact with tar when the temperature reaches some degree. However, the reaction process is exceeding complex and many competing processes contribute to the thermal analysis curves, and also biomass tar from different sources also express different combustion characterizations. In this research, for all DTA curves of our samples, during the temperature range of 30~200°C, it appears one endothermic peak, it is the volatilization of water and some smaller molecular compounds contained in tar. Then a widen and gently exothermic period will appear in the DTA curves because of the low temperature oxidation, and when the temperature reaches some degrees, the exothermic peak appears, which results from tar high-temperature combustion reaction. So according to the analysis of DTA curves, in this study, three stages reaction kinetic model was proposed and used.

The first stage is volatilization process, which is mainly water and low molecular mass compounds, then will enter into one low temperature oxidation stage (LTO), in general this oxidation reaction will mainly produce small quantities of carbon dioxide and presumable acids, aldehydes, ketones and peroxides [18]. With the temperature raise, a sharp and big exothermic peak will appear because of the high temperature combustion (HTC), where carbon dioxide is the major product.

Based on three stages reaction kinetic model, if it assumes that volatiles are released according to a set of parallel reactions for lumped components, then, the overall mass loss rates is a linear combination of the single component rates. Hence, the kinetic mechanism proposed here for tar reaction in TG consists of *N* independent parallel reaction as Fig. 3.

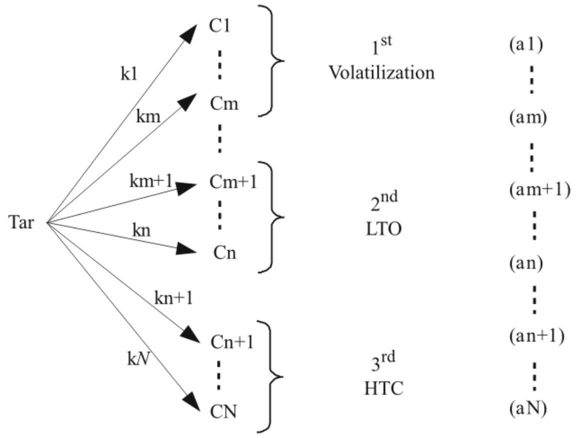

Fig. 3 Tar combustion reaction model

Where tar is the parent fuel which produces the lumped volatile products C_i (i =1, ..., N). From the chemical point of view, reactions a_1, ..., a_m are associated with tar compounds volatilization, reactions a_{m+1}, ..., a_n are associated with tar compounds LTO, and reactions a_{n+1}, ..., a_N are associated with tar compounds LHC. The number of reactions m, n and N strictly required for an accurate description of the experiments is included among the model parameters to be determined.

Because of the complexity of tar, tar combustion or decomposition are often considered as a single reaction in which all tar components are regarded just only one group (tar mixture) and assumed to disappear by several simultaneous reactions of (steam-, dryhydro-, thermal-, ...), reforming, cracking, etc. The overall rate of tar disappearance was thus given by the sum of the rates of all of the elementary individual reactions involved in the network. And this handling method was accepted by most of researchers and Labs [1, 19]. In this study, we also adopt this method, i.e. all the reactions m in volatilization stage were regarded as one group reaction, and all the reactions n and N were used this method.

The mathematical procedure used in the present study, in the analysis of TG/DTA data for determining the combustion kinetics, is based on the Coats-Redfern method used by many other investigators [12–16, 20, 21], which is an integral method developed by Coats and Redfern [22]. Based on this theory, tar volatilization/combustion rate equation can be expressed as Eq. (1).

$$\mathrm{d}\alpha/\mathrm{d}t=k(1-\alpha)^{\mathrm{n}} \tag{1}$$

where α is volatilization/combustion conversion rate, n is assuming order of the reaction, the correct order presumed should lead to the best linear plot. In most conditions, the first-order linear rate is adopted by researchers. In this study, n=1/2, 1, 3/2, 2 three conditions were considered. k is reaction rate constant.

The extent of conversion, or fraction of material combusted, can be defined by the following expression.

$$\alpha=(W_0-W_{\mathrm{t}})/(W_0-W_\infty) \tag{2}$$

W_0 is the sample mass at start time (mg), W_t is sample mass at time t (mg). W_∞ is sample mass at the end time (mg).

The temperature dependence of reaction rate constant k can be expressed by the following Arrhenius Eq. (3).

$$k=A\mathrm{e}^{-\mathrm{E}/\mathrm{RT}} \tag{3}$$

A is pre-exponential factor, min^{-1}, E is apparent reaction activity energy, J mol^{-1}.

For a linear heating rate, say, deg φ min^{-1}.

$$\varphi=\mathrm{d}T/\mathrm{d}t \tag{4}$$

For Eqs (1)–(4), the kinetic parameters could be obtained from thermogravimetry (TG) and derivative thermogravimetry analyzer (DTA) curves obtained from experiment. Combines the Eqs (1)–(4) into Eq. (5).

$$\frac{1}{(1-a)^{\mathrm{n}}}\mathrm{d}a=\frac{A}{\varphi}\mathrm{e}^{-\mathrm{E}/\mathrm{RT}}\mathrm{d}T \tag{5}$$

Then by integral:

$$\int_0^{\mathrm{a}}\frac{1}{(1-a)^{\mathrm{n}}}\mathrm{d}a=\int_0^{\mathrm{T}}\frac{A}{\varphi}\mathrm{e}^{-\mathrm{E}/\mathrm{RT}}\mathrm{d}T \tag{6}$$

The right-hand side of Eq. (6) has no exact integral, but Eq. (7) can be obtained when this term is expanded into an asymptotic series hand higher order terms are ignored by numerical approach.

$$f(a)=\int_0^{\mathrm{a}}\frac{1}{(1-a)^{\mathrm{a}}}\mathrm{d}a= ART^2\left(1-2\frac{RT}{E}\right)\exp\left(-\frac{E}{RT}\right)/(\varphi E) \tag{7}$$

Taking natural logarithms on both sides of Eq. (7) and assuming that $2RT/E<<1$; then:

$$\ln\left(\frac{f(a)}{T^2}\right)=\ln\left(\frac{AR}{\varphi E}\right)-\frac{E}{RT} \tag{8}$$

Then, a plot of $\ln=(f(a)/T^2)$ *vs.* $1/T$ should give a straight line of slope E/R and an intercept of $\ln(AR/\varphi E)$ for an appropriate form of $f(a)$. The criterion used for accepted values of E and A is that the $f(a)$ should yield the best linear correlation coefficient.

For Eq.(8), there are many kinds of expression for the alpha functions ($f(a)$), such as nucleation and growth rate process, reaction order process and diffusion controlling process [23]. In this study, only the reaction orders style is considered, and the reaction orders (n=0.5, 1, 1.5, 2) are considered, the final form of the Eq. (8) for the different reaction orders is shown in Table 3.

The suitable reaction order can be selected according the correlation coefficient. Then from line slope ($-E/R$) and y intercept of the regression line obtained by TG data, the apparent activation energy (E) and the pre-exponential factor (A) can be calculated.

Results and discussion

Selection of reaction order

According to the expression style shown in Table 3 and the kinetic model, the least square method was used to determine the best straight line, linear least square correlation coefficients for the identified rectilinear portions for different reaction order are shown in Table 4. The reaction condition: heating rate (5°C min^{-1}), flow rate of air is 50 mL min^{-1}. From Table 4, it can see that for n=1, the regression coefficient for the combustion of tar and in coexistence with dolomite was in the range of 0.97–0.99, which is better than that of n=0.5, 1.5 and 2 as a whole. The results reveal the best order of reaction for the three assuming selections, so in the following discussion the first-order reaction for tar kinetic model is adopted.

Table 3 The approximate solution *vs.* different reaction order by numerical approach

Reaction order/n	Approximate solution
1	$\ln\left[-\frac{\ln(1-a)}{T^2}\right]=\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}$ (9)
1/2, 3/2, 2	$\ln\left[\frac{1-(1-a)^{1-n}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}$ (10)

Table 4 The correlation coefficient for different reaction orders

	Stages	Correlation coefficient/n			
		0.5	1	1.5	2
Tar, air, without catalyst	Volatilization	0.9760	0.9755	0.9778	0.9187
	LTO	0.9766	0.9880	0.9751	0.6510
	HTC	0.9225	0.9963	0.9803	0.8033
Tar, air, with dolomite	Volatilization	0.9580	0.9874	0.9650	0.9462
	LTO	0.9645	0.9935	0.9943	0.9777
	HTC	0.9601	0.9761	0.9653	0.9776

Combustion process

The rules of dolomite and mayenite and its possible influence on kinetics of biomass burning is not entirely clear, which is very important for the understanding of tar low temperature combustion technology development. The main objective of the oxidation experiment was to obtain sufficient data to establish the reaction kinetics and determine the Arrhenius parameters. In the course of this research, TG-DTA curves were produced for biomass tar and in the coexistence with 10 mass% of dolomite and mayenite respectively. Isothermal experiments were conducted from 25 to 1000°C. An integrative plot of TG-DTA curves in air environment of different heating rates is shown in Figs 4 and 5 respectively, from these curves, three main stages of transition are observed. They are (I) volatilization, (II) low-temperature oxidation (LTO) and (III) high-temperature combustion (HTC).

Analysis of the derivative thermo-gravimetric curve of the tars showed that, the reaction trends of the three conditions (tar, tar coexistence with dolomite and mayenite) are similar at low temperature (<400°C), there are one endothermic peak appear around 120°C in the first reaction stage, which caused by the volatilization of water and some smaller molecular compounds contained in tar. Then the volatilization and combustion of tar became relatively gently before 400°C. A plausible explanation for this is that the tar enters into one properties relatively stable period after the water (around 10 mass% of biomass tar in some case) and low mass molecular evaporate.

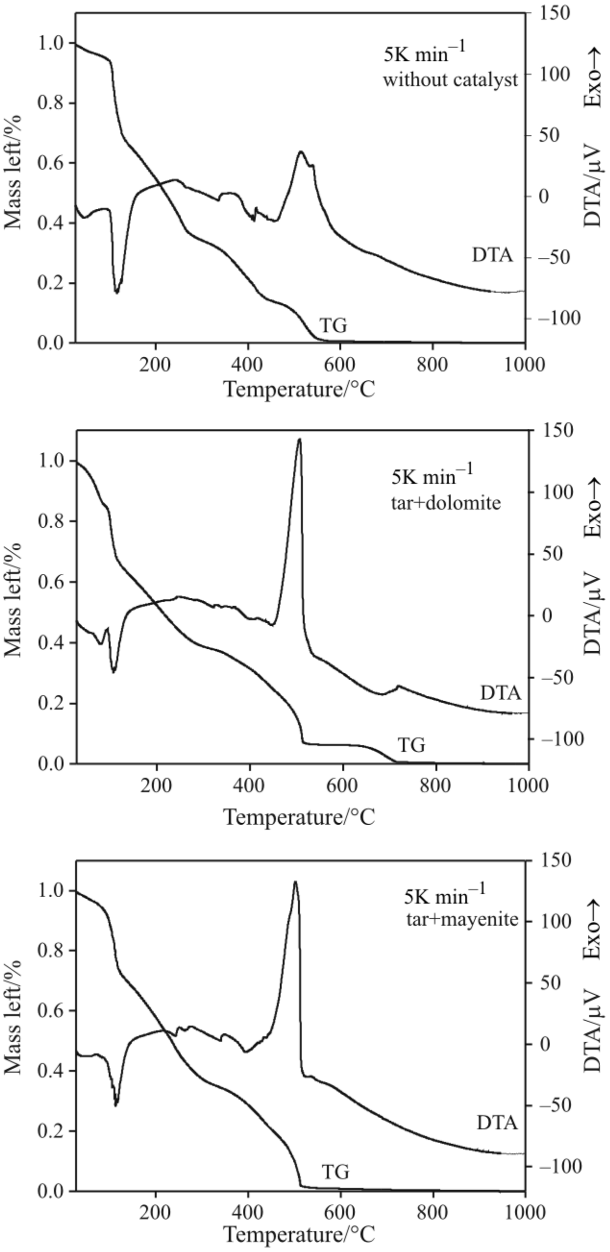

Fig. 4 TG-DTA curves of tar with different catalysts (heating rate 5 K min^{-1})

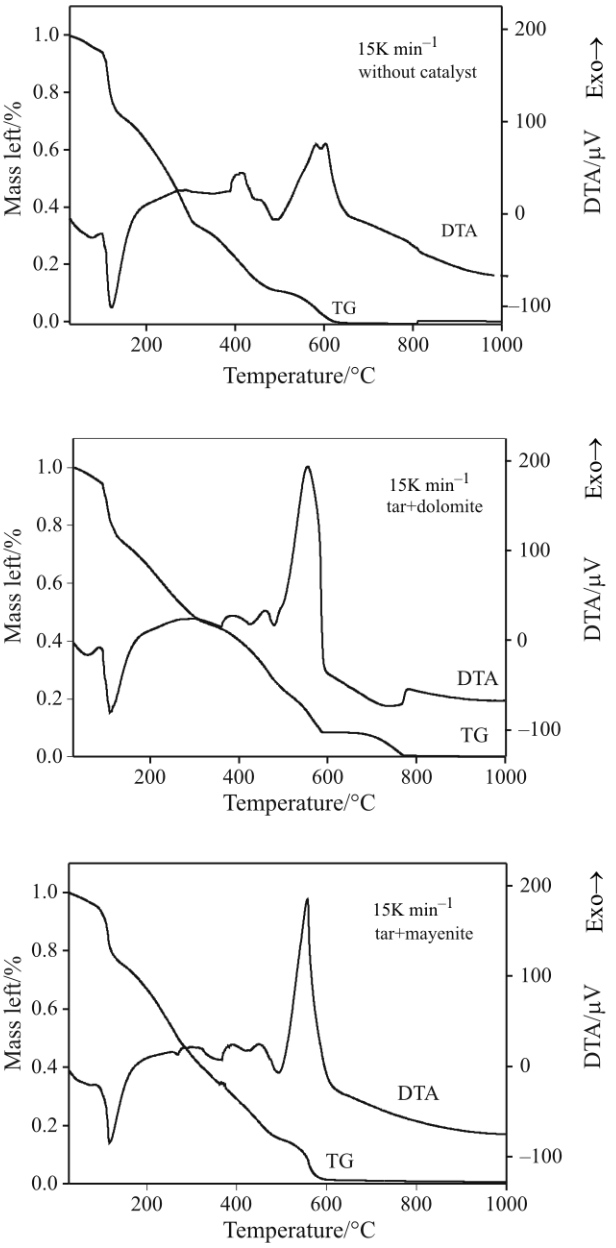

Fig. 5 TG-DTA curves of tar with different catalysts (heating rate 15 K min^{-1})

For tar without catalyst, at the heating rate 5°C min^{-1}, drastic combustion behavior did not occur until the temperature 500°C, but in the coexistence with dolomite, the larger exothermic peak occur on around 450°C, for mayenite, it is near 400°C. It moves up nearly one hundred degree, and also the exothermic peak is sharper and bigger than that without catalyst, which shows that biomass tar combustion releases more energy in coexistence with dolomite and mayenite, and combustion is more sufficient in this stage. Scrutinizing the results obtained, it can also be observed that the total mass loss during the HTC stage is around 31% in the coexistence with dolomite and mayenite, but only around 21% in the case of no catalyst. These results can qualitative show that the coexistence of dolomite and mayenite can benefit the tar combustion process.

By comparison the DTA curves of different heating rate, it is observed that the heating rate has significant effects on the combustion behavior such as combustion peak, burn-out temperatures. Higher heating rate will cause the reactions occurring at higher temperatures, and also probably overlapping the subordinate reaction then causes the TG-DTA curves to change. In this study, it shows that there are near 30°C difference between the heating rate 5 and 15°C min^{-1}.

Table 5 Tar combustion stage and peak temperature (tar-dolomite-mayenite)

	Heating rate / °C min^{-1}	Volatilization/ °C	Peak temp./°C Volatilization	LTO/ °C	HTC/ °C	Peak tem./ °C LTO
Tar without catalysts	5	<140	115	140~470	470~560	526
	15	<140	120	140~490	500~640	580
Tar + 10% dolomite	5	<140	105	140~450	450~520	500
	15	<140	110	140~480	480~580	550
Tar + 10% mayenite	5	<140	112	140~396	396~513	480
	15	<140	115	140~485	485~600	540

Table 6 Kinetic parameters of biomass tar in coexistence of dolomite and mayenite

	Volatilization		LTO		HTC	
	E_a/ kJ mol^{-1}	A/ min^{-1}	E_a/ kJ mol^{-1}	A/ min^{-1}	E_a/ kJ mol^{-1}	A/ min^{-1}
Tar without catalysts	95.0	$1.5 \cdot 10^{10}$	7.5	$1.2 \cdot 10^{-1}$	72.6	$2.2 \cdot 10^{3}$
Tar + 10% dolomite	64.2	$4.4 \cdot 10^{6}$	2.4	$7.5 \cdot 10^{-3}$	42.9	$2.2 \cdot 10^{2}$
Tar + 10% mayenite	60.3	$7.1 \cdot 10^{6}$	4.7	$9.9 \cdot 10^{-3}$	31.7	$1.6 \cdot 10^{2}$

And in coexistence of mayenite, the difference is larger, it is around 80°C. These results are the same trends identified in [7]. The stages and peak temperatures of biomass tar in the coexistence of dolomite and mayenite of different heating rates are summarized and shown in Table 5.

The summary of the calculation results including apparent activation energy (E) and frequency factor (A) is shown in Table 6, which provides the quantitative explanation for the TG and DTA curves with and without catalysts for tar combustion.

From the results of Table 6, it shows that the apparent activation energy of volatilization stage is very higher. It is because that some biomass internal oxygen is transferred into a liquid composition (biomass tar) in form of water (around 10%), oxygenated aliphatic during biomass gasification, and also with the emulsions effect, these chemically dissolved water in biomass tar do not form separate layer of water and oil, so it is more difficult evaporation that pure water, which also the reason the endothermic peak appears around 120 not 100°C. The adding of catalyst of dolomite and mayenite reduces the higher apparent activation energy of this stage, main reason of this is on account of de-emulsification, but not catalysis, the dolomite and mayenite act as de-emulsifying agents not catalysts.

In LTO and HTC stages, the apparent activation energy of biomass tar is greatly reduced because the coexistence of dolomite and mayenite, and also the catalysis of mayenite is greater than dolomite. According to our former research results [24], it shows that mayenite has occlude superoxide radical (O_2^-) and peroxide radical (O_2^{2-}) by the measured Raman spectrum of mayenite. It is well known that these oxygen radicals are effective for the organic substance oxidative reaction.

In summary, it can conclude that dolomite and mayenite can greatly improve tar combustion efficiency, and effectively reduce the apparent activation energy. It also shows that the mayenite or dolomite is one potential catalyst for tar combustion at low temperature.

Conclusions

The thermogravimetric and derivative thermogravimetric analysis conducted in this study provided valuable information on the tar combustion kinetics and mechanisms, especially in coexistence with different catalysts.

By comparison the calculation result of different reaction order, the first-order reaction model fitted the data well. The kinetic model consisting of three parallel reactions provides a good description of the thermogravimetric curves for the tar. As in the case of air environment, the three stages can be divided to volatilization (concerning about 20% of the sample), low temperature oxidation (LTO) and high temperature combustion (HTC).

By comparison the DTA curves of different heating rate, it is observed that the heating rate has significant effects on the combustion behavior such as combustion peak, burn-out temperatures. Higher heating rate will cause the reactions occurring at higher temperatures, and also probably overlapping the subordinate reaction then causes the TG-DTA curves to change.

The coexistence of dolomite and mayenite greatly improves the amount and speed of combustion process for tar, and the calculation results of E and A also gives the quantity explanation. For the first stage, apparent activation energy is greatly reduced by the adding the dolomite and mayenite because of the de-emulsification. For LTO and HTC stages, the HTC combustion stage move up near 100°C because of the coexistence of dolomite and mayenite, and also the combustion amount of biomass also improved nearly 10 mass%.

Appendix

A	pre-exponential factor/min^{-1}
E	apparent reaction activity energy/kJ mol^{-1}
k	rate constant/min^{-1}
R	gas constant, 8.314 J mol^{-1} K^{-1}
t	reaction time/min^{-1}
T	sample temperature/K
W_0	sample mass at the start time/mg
W	sample mass at time t/mg
W_∞	sample mass at end time/mg
φ	heating rate/°C min^{-1}
a	mass loss ratio

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Received: March 26, 2008
Accepted: May 21, 2008
OnlineFirst: October 12, 2008

DOI: 10.1007/s10973-008-9126-8