Influence of limestone fillers on combustion characteristics of asphalt mortar for pavements*

Wu Ke(吴 珂)[a], Zhu Kai(朱 凯)[a], Wu Hao(吴 昊)[b], Han Jun(韩 君)[a,c], Wang Jin-Chang(王金昌)[a], Huang Zhi-Yi(黄志义)[a,†], and Liang Pei(梁 培)[d,‡]

[a] *College of Civil and Architecture Engineering, Zhejiang University, Hangzhou* 310027, *China*
[b] *Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, Building* 229, *DK*-2800 *Kgs. Lyngby, Denmark*
[c] *Jiangsu Bao Li Asphalt Co. LTD, Wuxi* 214422, *China*
[d] *College of Optical and Electronic Technology, China Jiliang University, Hangzhou* 310018, *China*

(Received 23 October 2013; revised manuscript received 28 November 2013; published online 29 May 2014)

Asphalt materials will be ignited and release significant toxic fumes within tunnel fires. Thus, combustion characteristics of asphalt materials used in road tunnel should be studied in order to limit such an adverse effect. In the present work we study the influence of limestone fillers on combustion characteristics of asphalt mortar by thermogravimetric and kinetic analysis. It is shown that the combustion of asphalt mortar is not just a linear superposition of asphalt and limestone. The limestone will increase the ignition point and the activation energy of the primary volatile release, and will catalyze the char formation from the primary volatile release. Kinetic analysis shows that the primary volatile release stage of asphalt mortar combustion can be explained by a three-dimensional diffusion model, the secondary volatile release and char combustion stage can be explained by a model under the assumption of random nucleation and nuclei growth, whereas the limestone decomposition stage appears to follow the one-dimensional phase boundary model.

Keywords: asphalt mortar, limestone, combustion, kinetic analysis

PACS: 47.70.–n, 05.20.Dd, 42.70.Jk **DOI:** 10.1088/1674-1056/23/7/074703

1. Introduction

Due to several characteristics of asphalt, such as smoothness, seamlessness, low noise level, short construction period, and easy maintenance, utilization of asphalt concrete in road tunnels is a new trend. However, asphalt materials are flammable.[1] Asphalt mixtures ignite between 428 °C and 530 °C, and the gas temperatures in heavy goods vehicle fires can reach up to 1000 °C in a few minutes.[2] In the case of tunnel fires, the presence of asphalt concrete may cause severe consequences such as casualties, equipment damage, traffic congestion,[3] and releasing a large amount of toxic fume.[4] In order to minimize the adverse effect of asphalt during tunnel fire, a thorough understanding of the combustion characteristics of asphalt is indispensable.

However, there have been only a few studies on the flame retardant[5–9] and combustion kinetics[10–13] of asphalt. Reaction order models are commonly used to explain the multi-stages of asphalt combustion.[10–12] The asphalt compositions are usually classified into four categories: saturates, aromatics, resins, and asphaltenes.[14] Each composition has its own combustion activity. In particular, the asphaltene has a quite different combustion mechanism from the other ingredients.[15] The reaction order models that are applicable to homogeneous[16,17] reactions are of insufficient accuracy to describe the asphalt combustion processes. Therefore, the multi-stage models with different combustion mechanisms in each stage are needed to fit the combustion process of asphalt and asphalt mortar. The kinetic parameters are meaningful, only when the appropriate models are chosen. The simple reaction order models in the literature for the pyrolysis and combustion of asphalt[10–12] are not able to fully describe the complicated combustion processes.

In road pavements, asphalt is mixed with mineral fillers which are able to absorb the asphalt to their surface to form more structured asphalt. The mixture, often called asphalt mortar, has a strong influence on the pavement performance. Asphalt mortar may have quite different combustion characteristics from the asphalt. Xu and Huang[18] used magnesium hydroxide (MH) as a flame retardant which can partly replace the mineral fillers. They found that the thermal stability of asphalt mortar is improved by MH. However, in asphalt mortar the value of filler-asphalt ratio is more than 1, the content value of mineral fillers in asphalt mortar is much more than that of flame retardants. Hu *et al.*[19] found that when an alkaline filler replaces the mineral filler in flame-retarded asphalt mixtures, the alkaline filler can also restrain smoke without

*Project supported by the Natural Science Foundation of Zhejiang Province, China (Grant No. LY14E080014) and the National Natural Science Foundation of China (Grant Nos. 61154002 and 51078331).

†Corresponding author. E-mail: hzy@zju.edu.cn
‡Corresponding author. E-mail: plianghust@gmail.com

© 2014 Chinese Physical Society and IOP Publishing Ltd

influencing the pavement performances. It is noteworthy that limestone fillers are commonly added into asphalt mortar as mineral fillers for engineering applications.[20] Although the limestone filler is of high practical importance, its influence on combustion properties of asphalt has not been systematically studied.

In the present paper, we study the influence of limestone filler on combustion characteristics of asphalt mortar through the thermogravimetric experiments, and analyze the kinetic parameters by using the experimental data. The results enrich the fundamental knowledge of asphalt mortar combustion. The derived kinetic data are applicable to the modeling of asphalt combustion and helpful for choosing asphalt materials.

2. Experimental part

2.1. Materials

In this research, asphalt and corresponding mortar were used. The asphalt was produced by Sinopec Group in China. The asphalt mortar was produced by mixing 30% asphalt with 70% limestone fillers by weight. The main ingredient of limestone filler is $CaCO_3$ and a small amount of SiO_2, the median particle size was 42 μm, and the specific surface area was 160 m^2/kg.

A LECO-CHNS932 elemental analyzer and a 5E-MACIII infrared fast analyzer were used to carry out proximate and ultimate analysis, respectively. The results of proximate and ultimate analysis of asphalt are given in Table 1.

Table 1. Proximate and ultimate analysis of samples.

	Proximate analysis/wt%,ad				$Q_{net,ad}$/MJ·kg^{-1}	Ultimate analysis / wt%,ad				
	M	A	VM	FC		C	H	N	S	O
Asphalt	1.69	0.02	82.58	15.71	42.514	88.2	5.14	0.65	2.5	3.49

Note: ad denotes air dried basis; M moisture; A ash; VM volatile matter; FC fixed carbon; $Q_{net,ad}$ air dried basis, low heating value.

2.2. Methods

Thermogravimetric analysis (TGA) uses heat to force reactions and physical changes in materials, and provides quantitative measurement of weight change in material associated with dehydration, decomposition, and oxidation of a sample with time and temperature.[21,22] Weight loss (TG) curves may help distinguish different chemical compounds due to unique sequence from physicochemical reactions occurring over specific temperature ranges and heating rates. This technique can give a deep insight into the evolution of combustion reactions and volatiles information.

Here, the TGA experiments were performed by using a thermal analyzer TGA/SDTA 851e (Mettler Toledo, USA and Switzerland). The samples were heated from 50 to 1000 °C at four different heating rates of 5, 10, 20, and 30 °C·min^{-1}. Then the asphalts were heated at a constant temperature of 1000 °C for 15 min. The input gas was composed of 20% oxygen and 80% nitrogen by volume, and the flow rate was 50 mL/min. The samples (10–20 mg) were placed in an alumina crucible with a cross-section area of 4.9×10^{-4} m^2. Before the formal experiments, the temperature and balance calibration were performed, and the experiments were done three times under each condition, the average data was used. The results show that the weight curves are superposed perfectly and the error is allowable.

3. Results and discussion

3.1. Thermogravimetric analysis

Figure 1 shows the TGA results of asphalt and corresponding mortar combustion at a heating rate of 10 °C·min^{-1}.

As shown in Fig. 1, the derivative of weight loss (DTG) curve of asphalt mortar indicates that the combustion process of mortar can be mainly divided into three stages, which are separated by the valley of the peaks in DTG curves.

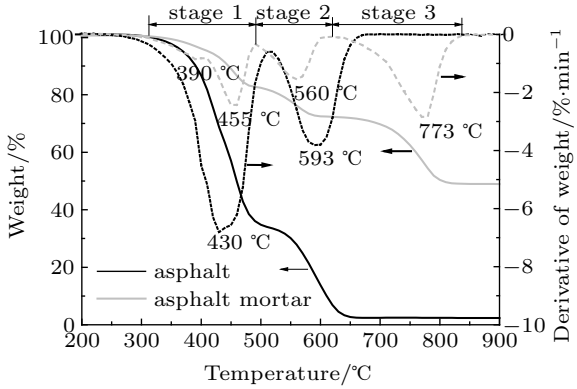


Fig. 1. TG-DTG curves of asphalt and corresponding mortar.

Stage 1 corresponds to the temperature range of 320–490 °C which is inconsistent with the pyrolysis temperature range of asphalt in inert atmosphere (290–500 °C).[23] In this stage, the first weight loss peak is observed on the DTG curve at about 455 °C, which is probably related to the release of primary volatile matters. The main components of the volatiles are from the breakage of some weak bonds caused by molecular chain ruptures and cycloreversion reactions.[12]

In stage 2 (490–620 °C) about 10% weight is lost due to the release of secondary volatiles and char combustion. In this stage, hydrogen and methyl are removed,[12] and char is formed due to the condensation of free radical molecules. Finally asphaltenes decompose,[24] and the char is combusted.

Finally, stage 3 corresponds to the third major peak that appears on the DTG curve. The weight loss in this stage is about 24% in a temperature range of 620–820 °C, which is in coincidence with the temperature range of limestone decomposition shown in Fig. 2, so the weight loss in this stage is mainly caused by the limestone decomposition. X-ray analysis of mineral composition is performed on residues formed at 500 °C and 900 °C as Fig. 3 shows. The results reveal that the unexpected characteristics of $CaCO_3$ appear in the second stage at 500 °C, and a little $CaSO_4$ is formed by the reaction between $CaCO_3$ and SO_2 is produced by asphalt combustion. At 900 °C, decarbonation is triggered and CaO is formed after the third stage of asphalt mortar combustion.

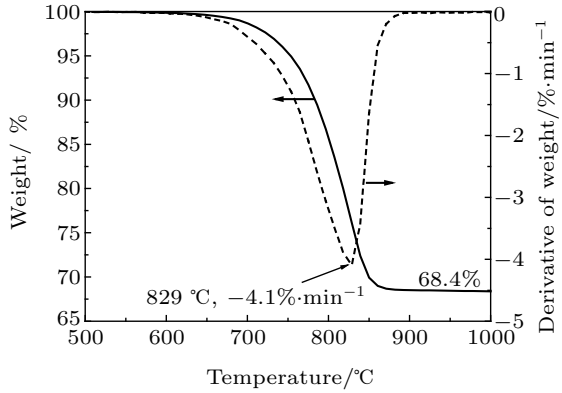


Fig. 2. TG-DTG curve of limestone decomposition.

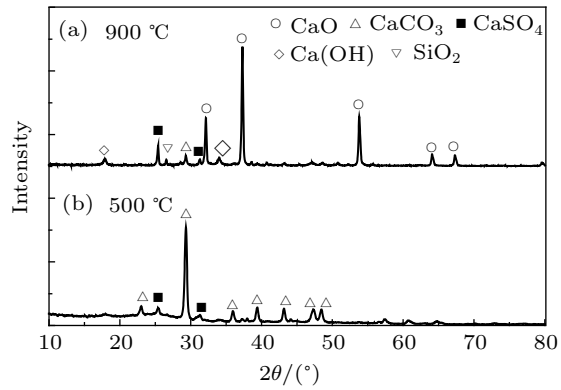


Fig. 3. XRD patterns of asphalt mortar residues formed at (a) 900 °C and (b) 500 °C, respectively.

Compared with the combustion process of asphalt mortar, we can find only two weight loss peaks in the DTG curve of asphalt, because there are no limestone fillers in asphalt. In addition, the weight loss rate of asphalt is much higher than that of asphalt mortar in the first and second stage, owing to the high volatile percentage.

The weight loss of each stage is shown in Table 2. When the limestone and residue are not taken into account, asphalt loses more weight in stage 1, but asphalt mortar loses more weight in stage 2 when char is formed. This indicates that less primary volatile is released, when the asphalt is mixed with limestone fillers. Thus, it is suggested that limestone may inhibit the release of the primary volatile.[25]

Table 2. Weight losses of asphalt and asphalt mortar combustion.

Samples	Weight loss /%		
	stage 1	stage 2	stage 3
Asphalt	65.9	31	–
Asphalt[a)]	67.6	31.8	–
Asphalt mortar	16.9	10.3	23.5
Asphalt mortar[a)]	61.2	37.4	–

[a)]Limestone and residue are not taken into account.

To further investigate the differences between asphalt and corresponding mortar, the weight loss curves of asphalt and limestone are added by their weight percentage in asphalt mortar. From Fig. 4, we can find several differences between the TG curve of asphalt mortar and the linear superposition of asphalt and limestone, although the reaction between $CaCO_3$ and asphalt mortar is only a physical blending process. The temperature corresponding to the maximum weight loss rate in stage 1 of asphalt mortar is higher than that of asphalt. Simultaneously, the ignition point and the temperature of primary volatile release of asphalt mortar are slightly higher than those of the corresponding asphalt (as given in Table 3). This may be explained by the fact that asphalt mortar has a large number of mineral fillers, and more polar components of asphalt are adsorbed on the surface of the filler. Simultaneously, an increase of ash content will lead to a decrease in effective specific surface area,[26] which results in a reduced reaction rate. Hence, the increase in ash content is beneficial to retarding the combustion, as Xu (2012) presented.[18] The results can also be verified by the kinetic analysis in Subsection 3.2. The second peak on the DTG curve of asphalt mortar appears earlier than that of asphalt, which indicates that limestone may catalyze the release of secondary volatiles, because alkaline-earth metal (Ca) is an excellent catalyst for the carbon–oxygen reaction.[25]

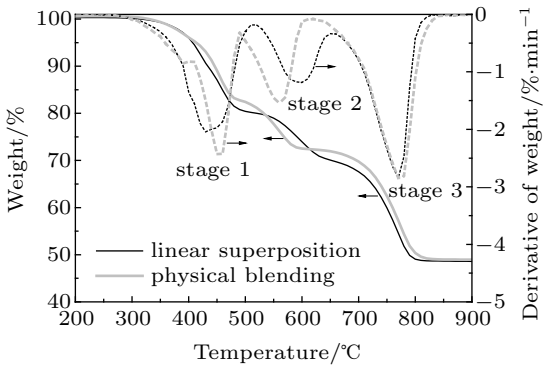


Fig. 4. Comparison between linear superposition of asphalt and limestone with asphalt mortar.

Table 3. Special temperatures in combustion process.

Samples	T_i / °C	Reaction region temperature/°C		
		stage 1	stage 2	stage 3
Asphalt	384	310-520	520-650	–
Asphalt mortar	405	320–490	490–620	620–820

3.2. Kinetic analysis

The kinetic parameters[27,28] were determined under the assumption of single reactions for each stage of thermal converse. The stages are separated by the peak valleys on the DTG curves. The three stages of asphalt mortar combustion correspond to the stage of primary volatile release, the stage of secondary volatile release and the char combustion, and the stage of limestone decomposition, respectively. The temperature range of each stage is shown in Table 3.

In non-isothermal reaction with a constant heating rate of $\beta = \mathrm{d}T/\mathrm{d}t$, the kinetic equation can be written as follows:

$$\mathrm{d}\alpha/\mathrm{d}T = k(T)f(\alpha) = (A/\beta)\exp(-E/RT)f(\alpha), \qquad (1)$$

where α is the degree of conversion, T the combustion temperature at time t (in K), A the pre-exponential factor (in s^{-1}), E the activation energy (in $\mathrm{J{\cdot}mol^{-1}}$), $R = 8.314\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ is the universal gas constant, $k(T)$ the temperature dependence of rate constant, $f(\alpha)$ a function, the type of which depends on reaction mechanism.

The kinetic analysis has been performed using equations which are described in detail in our previous work[30] along with TG and DTG data under four different heating rates. The kinetic models having good linearity can be found in Table 4, and the values of correlation coefficient $f(\alpha)$ of each stage are all above 0.99. This indicates that primary volatile release of asphalt and asphalt mortar are both accordant with three-dimensional diffusion model subjected to kinetic diffusion control. During the secondary volatile release stage, the optimal correlation coefficients of the combustion reaction of asphalt and asphalt mortar are both obtained with function 2, namely under the assumption of random nucleation and its subsequent growth model. The model suggests that the reaction occurs at the points with lattice defects, and the adjacent decomposition products aggregate into a new nuclear. The surrounding molecules then continue to react in the nuclear interface until the solid phase decomposition is completed. Finally, function 3 is suitable for the last stage of the combustion of asphalt mortar, which indicates that limestone decomposition is a phase boundary reaction following a power law.

Table 4. Algebraic expressions of functions $f(\alpha)$ and its corresponding mechanism.

No.	Name of the function	Rate-determining mechanism	$f(\alpha)$
1	Jander equation	three-dimensional diffusion, spherical symmetry	$3/2(1-\alpha)^{2/3}\,[1-(1-\alpha)^{1/3}]^{-1}$
2	Avrami–Erofeev equation	assumed random nucleation and its subsequent growth, $n=2$	$2(1-\alpha)\,[-ln(1-\alpha)]^{1/2}$
3	Power law	contracting disk	$(1-\alpha)^0$
4	Avrami–Erofeev equation	assumed random nucleation and its subsequent growth, $n=1$	$1-\alpha$

In order to obtain the active energy E and pre-exponential factor A, equation (1) is transformed into the following integral type of equation with Coats–Redfern method[31] which has been mostly and successfully used for studying the kinetics of dehydration and decomposition of different solid substances:

$$\ln\frac{\int_0^\alpha \mathrm{d}\alpha/f(\alpha)}{T^2} = \ln\frac{AR}{\beta E} - \frac{E}{RT} + \ln\left(1-\frac{2RT}{E}\right) \approx \ln\frac{AR}{\beta E} - \frac{E}{RT}. \qquad (2)$$

From Eq. (2) it follows that $\ln(AR/\beta E)$ is constant and a plot of $\ln[T^{-2}\int_0^\alpha \mathrm{d}\alpha/f(\alpha)]$ against $1/T$ should be a straight line with slope E/R, from which the values of active energy E can be calculated by using the TG data.

Table 5 shows a comparison between combustion kinetic factors of the current study and that of Xu and Huang[12] The activation energy of asphalt mortar in stage 1 is higher that of asphalt, which implies that the volatile material in asphalt is easier to release than that in asphalt mortar, which again proves that the limestone is beneficial to improving flame-retarding effects of asphalt. As Eq. (1) indicates, the reaction rate depends on both reaction mechanism $f(\alpha)$ and $k(T)$, the selection of mechanism function will influence the value of $k(T)$, so the calculated values of activation energy may be different. This is why the activation energy of asphalt is much higher than the result reported by Xu and Huang[12] when a different mechanism function was chosen. In the second stage, the activation energy is much lower, so the asphaltenes and the char will burn strongly in this stage. This result coincides with the previous research result.[16] The activation energy values of asphalt and asphalt mortar are almost the same in the secondary volatile release and char combustion stage. As analyzed in Subsection 3.1, calcium has catalytic action on asphalt combustion, but it is offset by the flame retardant effect at a high mineral filler content value, so the activation energy has no great difference. From Table 5, the activation energy of limestone decomposition is 178 kJ/mol. Due to the differences in crystalline structure and existence of the nature of impurities, the chemical reactivity values of different limestones show a large variation[32] and the activation energy varies between 100 and 4000 kJ/mol.[33] The result of this research project is consistent with the activation energy of high purity limestone, which varies in a range of 155–212 kJ/mol, as reported by Ar and Dogu.[34]

In order to verify the predictability of the models, a couple of experiments at a heating rate of 40 °C/min on asphalt and corresponding mortar are performed. As shown in Fig. 5,

the differences between the results from the models and the experimental values in each combustion stage are acceptable. Therefore, the kinetic models of asphalt and asphalt mortar can be considered to be reliable.

Table 5. A comparison of combustion kinetic factor between current study and research of Xu and Huang.[12]

Samples	Stage 1		Stage 2		Stage 3	
	E	$f(\alpha)$	E	$f(\alpha)$	E	$f(\alpha)$
Asphalt	188	No. 1	106	No. 2	–	–
Asphalt mortar	203	No. 1	105	No. 2	178	No. 3
Asphalt[12]	93	No. 4	101	No. 4	–	–

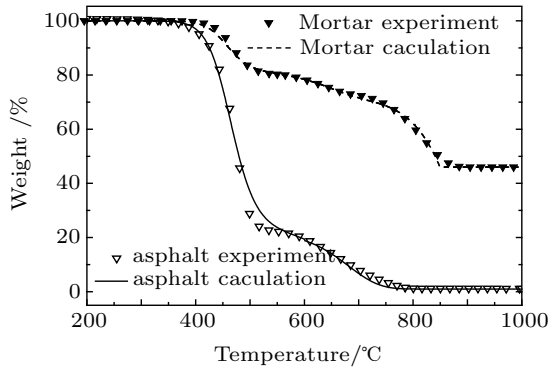


Fig. 5. Comparison between calculation and measurement.

4. Conclusion

(i) Combustion of asphalt mortar is not just a linear superposition of asphalt and limestone. The limestone will increase the ignition point and activation energy of the primary volatile release, which inhibits the ignition of asphalt. Simultaneously, the limestone will promote the release of secondary volatile.

(ii) The combustion process of asphalt mortar can be divided into three stages. Compared with asphalt, asphalt mortar with limestone fillers has an additional stage which is mainly caused by the limestone decomposition at temperatures ranging from 620 to 820 °C.

(iii) The first stage of the combustion of asphalt and asphalt mortar can be explained, respectively, by three-dimensional diffusion model with the Jander equation, the second stage can be explained under the assumption of random nucleation and its subsequent growth model with Avrami–Erofeev equation. The third stage of asphalt mortar combustion appears to follow one-dimensional phase boundary reaction model following a power law. The resulting activation energy of the first stage is higher than those reported previously.

References

[1] Yu J Y, Cong P L and Wu S P 2009 *Construction and Building Materials* **23** 2277

[2] Lönnermark A and Ingason H 2005 *Fire Safety Journal* **40** 506

[3] Schartel B, Bahr H, Braun U and Recknagel C 2010 *Fire and Materials* **34** 333

[4] Wu K, Zhu K, Huang Z Y, Wang J C, Yang Q M and Liang P 2012 *Spectroscopy and Spectral Analysis* **32** 2089 (in Chinese)

[5] Wu S P, Cong P L, Yu J Y, Luo X F and Mo L T 2006 *Fuel* **85** 1298

[6] Wu S P, Mo L T, Cong P, Yu J and Luo X F 2008 *Fuel* **87** 120

[7] Xu T, Huang X M and Zha Y L 2011 *Fire Safety Journal* **46** 330

[8] Qun Y and Guo Z Y 2005 *Road Materials and Pavement Design* **6** 255

[9] Bonatia A, Merusia F, Bochicchiob G, Tessadrib B, Polaccoc G, Filippic S and Giuliania F 2013 *Construction and Building Materials* **47** 990

[10] Benbouzid M and Hafsi S 2008 *Fuel* **87** 1585

[11] Xu T and Huang X M 2010 *Journal of Analytical and Applied Pyrolysis* **87** 217

[12] Xu T and Huang X M 2010 *Fuel* **89** 2185

[13] Bonati A, Merusi F, Polacco G, Filippi S and Giuliani F 2012 *Construction and Building Materials* **37** 660

[14] Aske N, Kallevik H and Sjöblom J 2001 *Energy & Fuels* **15** 1304

[15] Guo A J, Zhang X J and Wang Z X 2008 *Fuel Processing Technology* **89** 643

[16] Wang X W, Cai G B, Jin P 2011 *Chin. Phys. B* **20** 104701

[17] Wang X W, Cai G B, G Y S 2011 *Chin. Phys. B* **20** 064701

[18] Xu T and Huang X M 2011 *Combustion Science and Technology* **183** 1027

[19] Hu S G, Zhang H J and Wang J L 2006 *Journal of Wuhan University of Technology-Materials Science Edition* **21** 146

[20] Kanitpong K and Bahia H 2005 *Transportation Research Record: Journal of the Transportation Research Board* **1901** 33

[21] Zhang Y M, Han R Q, Wu X S and Wang Z H 2011 *Chin. Phys. Lett.* **28** 8202

[22] Zong F J, Ma H L, Liang W, Du W, Zhang X J, Xiao H D, Ma J, Ji F, Xue C S and Zhuang H Z 2005 *Chin. Phys. Lett.* **22** 907

[23] Mothé M G, Leite L F M and Mothé C G 2008 *Journal of Thermal Analysis and Calorimetr* **93** 105

[24] Gonçalves M L A, Teixeira M A G, Pereira R C L, Mercury R L P and Matos J R 2001 *Journal of thermal analysis and calorimetry* **64** 697

[25] Gopalakrishnan R, Fullwood M J and Bartholomew C H 1994 *Energy & fuels* **8** 984

[26] Shirai H, Ikeda M and Tanno K 2011 *Energy & Fuels* **25** 5700

[27] Yang J Z, Xia Z X and Hu J X 2013 *Acta Phys. Sin.* **62** 074701 (in Chinese)

[28] Yang J Z, Xia Z X and Hu J X 2012 *Acta Phys. Sin.* **61** 164702 (in Chinese)

[29] Kök M V and Acar C 2006 *Journal of Thermal Analysis and Calorimetry* **83** 445

[30] Wu K, Zhu K, Han J, Wang J C, Huang Z Y and Liang P 2013 *Chin. Phys. B* **22** 068801

[31] Coats A W and Redfern J P 1964 *Nature* **201** 68

[32] Borgwardt R H and Harvey R D 1972 *Environmental Science and Technology* **6** 350

[33] Khraisha Y H and Dugwell D R 1989 *Chemical Engineering Research & Design* **67** 48

[34] Ar I and Dogu G U 2001 *Chemical Engineering Journal* **83** 131