J Therm Anal Calorim (2009) 97:637–642
DOI 10.1007/s10973-009-0367-y

TG-FTIR coupling to monitor the pyrolysis products from agricultural residues

Bruno S. Souza · Ana Paula D. Moreira ·
Ana Maria R. F. Teixeira

ICTAC2008 Conference

Abstract Thermogravimetry has been widely used for the characterization of several biomasses but the most useful information given by this technique has been normally concerned to the relative amounts of humidity, hemi-cellulose, cellulose and lignin present in the biomass. TG-FTIR has been used to yield qualitative data about the pyrolysis products, in an exploratory way, by some authors. In the present paper, this technique was employed to reach comparative data about the products of pyrolysis of biomasses that are potentially available at economic bases for the production of biofuels. Agricultural residues such as coconut shell, sugarcane bagasse, corn stalks and peanut shell were chosen to be investigated. For all samples, the thermogravimetric curves showed a mass loss between 35 and 400 °C changed up to 73%, while that the loss between 400 and 800 °C changed up to 26%. TG-FTIR indicated tendencies in the rate of the formation of important species during the pyrolysis process of the four biomasses studied. The interpretation of the spectra allowed the proposition of characteristic absorbance ratios and the comparison of these values allowed inferences about the relative abundances of components formed in the pyrolysis of the biomasses. As an example of the possible inferences reached, among the species formed in the pyrolysis condensate, called bio-oil, the formation of carboxylic acids has to be specially considered due to their corrosivity. Thus, the data produced indicated that a bio-oil derived from peanut shell should be a little less acidic while the one derived from sugarcane bagasse should be showed more acidic among the biomasses studied.

Keywords Bio-oil · TG-FTIR · Biomass

Introduction

The generation of liquid fuels from biomass is a subject that deserves massive efforts by the scientific and technological communities in the world, especially their use in engines replacing fossil fuels [1–3]. This fact can take part in a decisive role in the abatement of the emissions of the greenhouse gas CO_2 [1]. Bio-oils, which are liquids derived from the condensation of the fluid effluent from the pyrolysis of biomass [4]. They are among the most well accepted candidates for bio-oil. However, there are technological barriers to be overcome, mainly regarding their stability, miscibility with hydrocarbons and especially their corrosivity. They are very corrosive because of high yields of carboxylic acids forming during the pyrolysis process. Their reactivity is related to several other oxygenated compounds, including aldehydes. The requirement of a treatment of such abundance of acids and other oxygenated substances contribute to the difficulties found in the economics of this route for bio-fuels.

Residual biomasses were studied because their availability is the best-accepted solution for the possible problems related to the competition of bio-fuels and food.

B. S. Souza (✉) · A. M. R. F. Teixeira
Instituto de Química, Programa de Pós-Graduação em Química,
Universidade Federal Fluminense – UFF, Centro Niterói,
RJ 24020-150, Brazil
e-mail: bruffno@yahoo.com.br

A. P. D. Moreira
Instituto de Química, Departamento de Química Analítica,
Universidade Federal Fluminense – UFF, Centro Niterói,
RJ 24020-150, Brazil

Dealing with residual feedstocks, however, it brings the understanding of analytical tools able to provide data for the tuning of the processes. Thermogravimetric tests in inert atmosphere were carried out to evaluate the thermal behavior of the biomasses. The gases were directed into FTIR through a heated interface. FTIR spectra provided information about the products yielded, such as CO_2, CO and C–H bonds.

Agricultural residues such as coconut shell, sugarcane bagasse, corn stalks and peanut shell were chosen to be investigated with the TG-FTIR technique. Thermogravimetric analysis has shown to be a very useful technique for studying the pyrolysis of a wide range of solid samples but the composition of evolved gas in each mass loss steps cannot be observed only by using TG. On other hand, Fourier transform infrared spectroscopy (FTIR) results can be used to evaluate the functional groups and indicate the existence of some emissions [5, 6].

TG combining with FTIR is a useful tool in dynamic analysis because it monitors continuously both the time dependent evolution of the gases and the mass of the non-volatile materials (residue) [5, 7]. In this study, volatile products from TG during TG-FTIR experiment were swept into gas cell immediately by carrier-gas so that secondary reactions were minimized. The results of mass loss and composition of evolved gases obtained through the study provide plentiful information to understand the pyrolysis products of biomass samples.

Experimental

Four biomass samples with different origin are studied in this work, namely, coconut shell, sugarcane bagasse, corn stalks and peanut shell. Each material was crushed and sieved, and the 0.125–0.250 mm fraction was selected. The samples were dried at room temperature for 48 h before each experiment. After drying, the samples were characterized.

Thermogravimetric data are obtained using a Netzsch STA 409 thermal analyzer. All the experiments were conducted in an alumina crucible with 10 mg of the sample and at a heating rate of 20 °C min^{-1}. Each sample was heated from 25 to 800 °C under dynamic atmosphere (nitrogen, 50 cm^3 min^{-1}).

FTIR measurements were carried out using a Nicolet Nexus Spectrometer. TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during TG runs are carried out coupling the FTIR spectrometer to the TG balance. The transfer line and the head of the TG balance were heated at a constant temperature of 320 °C and the spectral region was 4,000–400 cm^{-1}.

Results and discussion

The TG and DTG curves of biomass samples are shown in Fig. 1. The onset temperature of pyrolysis for all materials is in the range of 150–250 °C. The main mass loss ends at 400 °C for all biomass samples and it is followed by a slow and continuous mass change with a long tail of devolatilization. At the first stage in the curves (until 100 °C) water release takes place, being that the highest water content was observed for corn stalk. After that, at the second stage, the mass rapidly decreases due to cellulose volatilization; then, in the third stage, the slow mass loss can be observed due to lignin decomposition. In general, the lignin is harder to decompose than cellulose since part of lignin consists of benzene rings [8]. The most important characterization parameters are cited in Table 1. All of them were obtained from the TG curves, except for the ash content, obtained by the thermal treatment of a five-gram sample of the biomass at 575 ± 25 °C, for 5 h (TAPPI T15m-58).

Considering each biomass sample, the profile of TG curves (Fig. 1) for coconut shell and sugarcane bagasse is very similar indicating that both exhibit a similar devolatilization behavior. The temperature at the maximum mass loss rate is the characteristic temperature in the initial and terminal of each pyrolysis stage was determined in DTG curves. The DTG curves showed that coconut shell and sugarcane bagasse exhibit three well distinct mass losses with maximum mass loss rate. These DTG peak temperatures are 200, 270 and 320 °C for coconut; 210, 295 and 338 °C for sugarcane bagasse. For corn stalk and peanut shell the main decomposition or pyrolysis stage started slowly after dehydration and increased sharply after 240 °C.

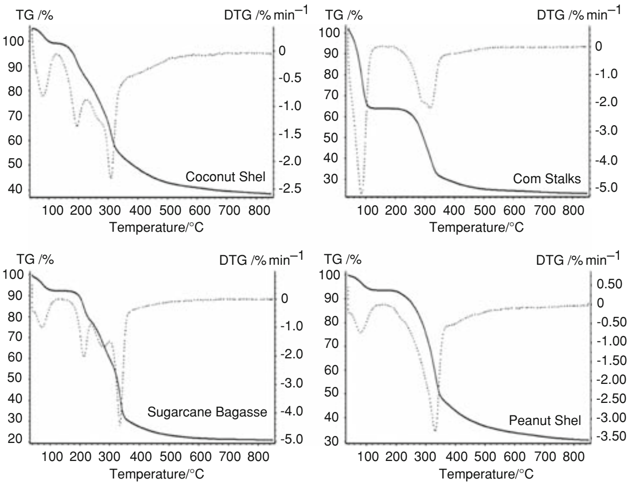

Fig. 1 TG and DTG curves of biomass samples

Table 1 Characterization parameters for the biomasses studied

Parameters/mass%	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
Volatile matter	35.41	54.25	50.34	65.09
Fixed carbon	26.65	33.26	40.43	25.66
Humidity	1.67	3.71	2.47	1.31
Ash	36.27	8.78	6.76	7.94

In the case of corn, considering the temperature range in which the pyrolysis occurs the DTG exhibits a single peak indicating a maximum mass loss rate at 330 °C, whereas, the peanut shell had presented two mass losses at 315 and 345 °C. In accordance to literature [9] the different reactivity and volatile matter release determine the devolatilization of biomass materials. Biomass is comprised of hemicellulose, cellulose, lignin, a little of extract and ash. These components result in different pyrolysis products because of different mechanisms of thermal decomposition [10]. Hemicellulose is the most reactive among all components and the temperature range of devolatilization is very narrow, while the lignin decomposes in a wider temperature range than the other components.

Initially, the thermal behavior of samples was investigated up to 800 °C. However, for all samples, the results generated by TG curves showed that the mass loss between 35 and 400 °C changed from 57 to 73%, while the loss between 400 and 800 °C (which is the final temperature) changed from 17 to 26%. This last yield was considered low and it suggests that the process of pyrolysis for biomass samples investigated in this work can be finished at 400 °C. The amount of residue at 800 °C does not justify the energy consumption to maintain the pyrolysis process at temperatures above 400 °C [9]. The main goal of thermal treatment was to generate and investigate the evolution of volatiles for all samples. Then, the gas generated in the range of 25–400 °C was analyzed by TG-FTIR technique (Fig. 2).

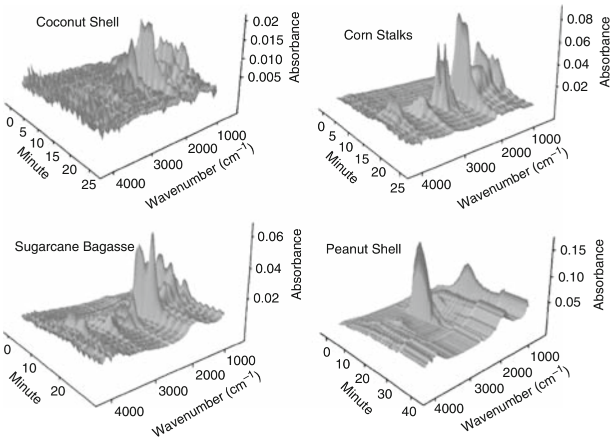

Fig. 2 FTIR spectra of the gases released of biomass during pyrolysis treatment

Comparing themselves the biomass samples, the spectra for each one was taken from the temperature of most intense mass loss. The assignment of peaks in the FTIR spectra was attributed by comparison with literature data [5, 6, 9] by the examination of reference books [11] and by the application of the experience of the authors in the interpretation of FTIR spectra. The use of the absorbance values could in some cases support the conclusions and also allowed some comparisons among the pyrolysis products of the biomasses studied and some inferences on the thermal behavior of the samples. Table 2 shows the regions of the spectra chosen for the present work after these considerations with the corresponding absorbances. These regions were defined according to the information obtained from the evaluation of the spectra to be partially described in this paper. The registered absorbances were the highest ones found in each region chosen.

Firstly, by reviewing some papers that employed the same technique to monitor the pyrolysis of biomass samples [5, 6, 9, 10] it can be seen that some unambiguous assignments can be adopted. The detection of carbon dioxide by duplet at 2,400–2,250 cm^{-1} is undoubted and it is confirmed by a singlet at 680–660 cm^{-1}; the attribution of the duplet 2,200–2,000 cm^{-1} to carbon monoxide is also

Table 2 Spectral regions and absorbances considered in the present work

Wavenumber/cm^{-1}	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
4,000–3,400	0.022	0.0071	0.039	0.017
3,000–2,800	0.019	0.0052	0.017	0.011
2,400–2,250	0.06	0.015	0.158	0.013
2,200–2,000	0.021	0.0073	0.018	0.0041
1,790–1,760	0.071	0.018	0.043	0.05
1,740–1,700	0.05	0.0109	0.038	0.033
1,610–1,590	0.01	0.0034	0.048	0.012
1,480–1,450	0.021	0.0049	0.05	0.015
1,400–1,360	0.034	0.0081	0.036	0.022
1,280–1,260	0.034	0.0071	0.027	0.02
1,190–1,170	0.045	0.013	0.025	0.043
1,100–1,030	0.039	0.0091	0.027	0.018
1,000–970	0.021	0.006	0.024	0.017
680–660	0.034	0.01	0.086	0.024

Table 3 Comparison of the absorbance ratios considering the regions (2,200–2,000 cm^{-1})/(2,400–2,250 cm^{-1})

Sample	Coconut shell	Corn stalk	Sugarcane bagasse	Peanut shell
Absorbance	0.49	0.35	0.32	0.11

Table 5 Comparison of the absorbance ratios considering the regions of the spectra: (4,000–3,400 cm^{-1})/(1,790–1,760 cm^{-1})

Sample	Coconut shell	Corn stalk	Sugarcane bagasse	Peanut shell
Absorbance	0.39	0.31	0.34	0.91

undoubted. The ratio of the highest absorbance values in these regions indicates the relative tendencies of these biomasses between the reactions known as decarboxylation (formation of CO_2) and decarbonylation (formation of CO, which can be the preferred one in some applications of the gaseous products of pyrolysis). These values are somewhat varied in the comparison among the volatiles of the biomasses studied here, as it is shown in Table 3. Only corn stalk and sugarcane bagasse had similar ratios.

Some considerations can be made about other assignments found in the literature. For example, the absorptions found in the range of 4,000–3,400 cm^{-1} are well known to be due to –OH groups or, in some cases, to –NH groups, which are not considered here. Some authors attribute these absorptions readily to water. However, another unambiguous assignment is the one of the peak between 1,790 and 1,760 cm^{-1} to the C=O group of carboxylic acids. This peak, for the biomasses studied was in most of the cases, except for the peanut shells, is the most intense one in the spectrum, showing that the decision to attribute the –OH absorptions only to water has to be very careful. These absorptions may certainly be due to –OH groups in other substances, as, for example, carboxylic acids. However, specifically for the production of fuels, an important indication would be the selectivity of the pyrolysis pathway of a given biomass to decarboxylation in comparison to dehydration, because the later eliminates hydrogen, which would have to be added again into the fuel by hydrotreatment, for example. An indication was obtained from the ratios of the absorbances in the adequate regions of the spectra, as shown in Table 4.

If direct indications from these data can be taken, the sugarcane bagasse is more suitable to dehydration than the other biomasses studied, while the peanut shell is the least one among them. However, this ratio could bring information both about the abundance of carboxylic acids and water. An evaluation of the validity of this ratio as a relative indicator was done by the comparison of another ratio of absorbances, as it can be seen in Table 5. It is visible that the ratio of hydroxyl groups to carboxyl groups is almost 3 times the average of the ratios for peanut shells, which is cited to be the one with less tendency to dehydrate. So, no proportionality is believed to be present, in the case of these samples, involving the –OH and –COOH contents. The obvious conclusion is that another hydroxy-containing substance dominates the absorptions between 4,000 and 3,400 cm^{-1}, and that is, of course, water. So, the data in Table 4 can be considered, indeed, an indication to the tendency of dehydration compared to decarboxylation. A final remark is the fact that, as in the comparison of decarboxylation and decarbonylation, it can be seen from Table 4 that this selectivity depends a lot on the nature of the biomass.

Table 4 Comparison of the absorbance ratios considering the regions (4,000–3,400 cm^{-1})/(2,400–2,250 cm^{-1})

Sample	Coconut shell	Corn stalk	Sugarcane bagasse	Peanut shell
Absorbance	0.47	0.37	1.31	0.25

If there is no selectivity in the pyrolysis of peanut shells to yield neither water nor oxygenates, the conclusion is that decarboxylation must play a major role in this case, which had already been addressed by the data in Table 3, in comparison with carbon monoxide. As another indication, a comparison with methane was also desired, because that would lead to possible inferences about the energetic applications of the gas yielded. The absorptions of C–H bonds found between 3,000 and 2,800 cm^{-1} are normally attributed to hydrocarbons, often specifically to methane. This region of the spectrum is quite unspecific, because most of the organic compounds have C–H bonds. However, another region of the spectrum where it is well-known that C–H bonds show important absorptions is between 1,480 and 1,450 cm^{-1}, considering the limits used in the present paper. That would indicate a considerable presence of hydrocarbons with two carbon atoms or more, or other components of other chemical functionalities. This would also be an important indication of the quality of the volatile products of the pyrolysis of the biomasses for energy purposes, because it indicates the possibility of other components of considerable heat value in the gas and/or condensed liquid yielded.

The attribution, by several authors of the total hydrocarbon content in the pyrolysis gases to methane is in agreement with the examination of these regions of the present spectra, because no important absorption between 1,480 and 1,450 cm^{-1} is seen in the pyrolysis products of most of the biomasses here, except for peanut shells. Then, both the absorptions between 3,000 and 2,800 cm^{-1} and between 1,400 and 1,360 cm^{-1} would be used, for this kind of analysis, mainly to monitor the formation of methane, and the ones between 1,480 and 1,450 cm^{-1} would indicate the formation of other components, being two or more carbon atom hydrocarbons one of the possibilities. That was seen in the present study only for peanut shells. The inference from the fact that an important absorption is seen in this region for the products of the pyrolysis of this specific biomass is that it would be possible to have more of those components yielded from its pyrolysis, in comparison to the other biomasses studied. Table 6 shows that the ratios of the absorbances in these regions can also be an indication. In the case of the ratio of absorbances (1,400–1,360 cm^{-1})/(3,000–2,800 cm^{-1}), the values were rather constant for all the samples studied, indicating they monitor the same substance. In the case of (1,400–1,360 cm^{-1})/(1,480–1,450 cm^{-1}), the gases from corn stalks, sugarcane bagasse and coconut shells had constant ratios, but that value was quite different for the peanut shells, indicating the presence of other important C–H bonds besides the ones of methane. Though many substances could also change the ratio (1,400–1,360 cm^{-1})/(3,000–2,800 cm^{-1}), those are probably not produced in these pyrolysis experiments, or they do not reach the FTIR detector.

After this assignment, the comparison of the production of carbon dioxide to methane can be done by the ratios of absorbances of the adequate regions of the spectra, as it is shown in Table 7.

The pyrolysis of sugarcane bagasse will certainly yield a gas more suitable for heat generation applications, among the gases from the pyrolysis of these biomasses, because of the relative abundance of methane. Again, the tendency of considerable decarboxylation of peanut shells by pyrolysis is confirmed. Though the discussion about the gas species is of fundamental importance to understand the reaction pathways, the most interesting products for the production of fuels are the condensable ones, because of the densification of the energetic species. A major problem about these condensable products, mainly represented by the oxygenates, it is their corrosivity. This aspect is understood by the importance of carboxylic acids, mentioned before, in the pyrolysis products. That is why the spectra were mainly used to understand the selectivity to carboxylic acids. The main parameters used for inferences about the reaction pathways are the ones cited in Table 8.

Table 6 Comparison of the absorbance ratios considering regions of the spectra

Wavenumber/cm^{-1}	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
(1,400–1,360)/(1,480–1,450)	1.6	1.7	0.7	1.5
(1,400–1,360)/(3,000–2,800)	1.8	1.6	2.1	2.0

Table 7 Comparison of the absorbance ratios considering regions of the spectra (2,400–2,250 cm^{-1})/(1,400–1,360 cm^{-1})

Sample	Coconut shell	Corn stalk	Sugarcane bagasse	Peanut shell
Absorbance	1.9	1.8	0.6	4.4

Table 8 Comparison of the absorbance ratios considering regions of the spectra

Wavenumber/cm^{-1}	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
(1,790–1,760)/(2,400–2,250)	1.2	1.2	0.3	3.8
(1,790–1,760)/(4,000–3,400)	3.2	2.5	1.1	2.9
(1,790–1,760)/(1,740–1,700)	1.4	1.7	1.1	1.5

The first and second ratios indicate the selectivity in the formation of oxygenates in comparison to carbon dioxide and water. Obviously, the peanut shells shall yield less condensates. However, the bio-oil derived from these condensates shall be a little less acid than the ones derived from the other biomasses. That means that there is less oxygen retained in the condensates. The species that shall be more important for this bio-oil, when compared to the other ones, are the carbonylated components, like aldehydes, which are responsible for the instability of the fuels. The other important absorptions of the spectra are also related to oxygenates. They are also briefly discussed here.

Besides the strong peak in the range of 1,790–1,760 cm^{-1}, due to the presence of the C=O bonds, the one due to the C–O bond of the carboxyl group is also an important characteristic of carboxylic acids. This is normally believed to be in the range of 1,280–1,260 cm^{-1}. However, the absorption in the range of 1,190–1,170 cm^{-1}, which was always more intense in all of the spectra obtained here, was also considered as a possibility studied by the ratios of absorbances. The absorbance in the range of 1,100–1,030 cm^{-1} was also included for comparison, because this one can be certainly attributed to a C–O bond involving a saturated carbon, so it is not related to the carboxyl groups. In the present paper it is attributed to alcohols. The data in Table 9 show that the absorbance ratios involving the region between 1,280 and 1,260 cm^{-1} vary as much as the ratios involving the 1,100–1,030 cm^{-1} region. Therefore, it is possible that the C–O absorption of the carboxyl group is observed in the range of 1,190–1,170 cm^{-1}, because the variations found for the absorbance ratios to the ones of the C=O bond were much smaller.

Table 9 Comparison of the absorbance ratios considering regions of the spectra

Wavenumber/cm^{-1}	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
(1,790–1,760)/(1,280–1,260)	2.1	2.5	1.6	2.5
(1,790–1,760)/(1,190–1,170)	1.6	1.4	1.7	1.2
(1,790–1,760)/(1,100–1,030)	1.8	2.0	1.6	2.8

Table 10 Comparison of the absorbance ratios considering regions of the spectra

Wavenumber/cm^{-1}	Corn stalk	Coconut shell	Peanut shell	Sugarcane bagasse
(1,280–1,260)/(1,610–1,590)	3.4	2.1	0.6	1.7
(1,000–970)/(1,610–1,590)	2.1	1.8	0.5	1.4

If so, the absorbance in the region of 1,280–1,260 cm^{-1} has to be assigned to another kind of C–O bond of an unsaturated carbon. The inference was the presence of phenols. It is well-known that phenols are pyrolytic products of the degradation of the lignin portion of biomasses. A confirmation was tried with the absorptions of C=C and the selected region was 1,610–1,590 cm^{-1}, which would be correlated to the degree of insaturation (including aromaticity) of the products. Since olefins are also important pyrolysis products and are also important in the definition of the insaturation, a specific absorption was attributed to olefins, in the range of 1,000–970 cm^{-1}. The absorbance ratios are in Table 10 but no correlation could be done. It should be said that the more pronounced variations were for the peanut shells. However, their spectrum was the only one where relatively important absorptions of a C-H bond of an unsaturated carbon around 3,100 cm^{-1}, they were seen. Maybe, this aspect will be explored in further works by the authors.

Conclusions

The study allowed a comparison of the pyrolysis process of four biomasses as a possible way to generated fuels. For peanut shells, the reaction is considerably more selective for the production of carbon dioxide and, therefore, for low-heteroatom-content, saturated species. This biomass seems to be the best option for the production by pyrolysis of possible fuels directly from the condensation products. However, the mass yield of condensates is probably limited, because of the great importance of the formation of carbon dioxide. Besides, this tendency to form carbon dioxide also allows the inference that in the evaluation of a possible heat generation application of the gaseous products from the pyrolysis of these biomasses, the characteristics observed for peanut shell were the least suitable ones. While for the sugarcane bagasse the relative abundance of methane brings the inference that the heat value of the gas produced will probably be the most suitable one. The bio-oils derived from the condensation of the pyrolysis products of sugarcane bagasse, however, shall be showed more acidic than the ones produced from peanut shell. This is an indication about the storage and processing problems that may come from the production of these biofuels.

Acknowledgements The authors thank Dr. Marco Antonio Gomes Teixeira for many useful discussions.

References

1. Tonbul Y. Pyrolysis of pistachio shell as a biomass. J Therm Anal Calorim. 2008;91(2):641–7.
2. Candeia RA, Freitas JCO, Souza MAF, Conceição MM, Santos IMG, Soledade LEB, et al. Thermal and rheological behavior of diesel and methanol biodiesel blends. J Therm Anal Calorim. 2007;87(3):653–6.
3. Khelfa A, Les Finqueneisel G, Auber M, Weber JV. Influence of some minerals on the cellulose thermal degradation mechanisms thermogravimetic and pyrolysis-mass spectrometry studies. J Therm Anal Calorim. 2008;92(3):795–9.
4. Yuan HR, Liu RH. Study on pyrolysis kinetics of walnut shell. J Therm Anal Calorim. 2007;89(3):983–6.
5. Zhu HM, Yan JH, Jiang XG, Lai YE, Cen KF. Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis. J Hazard Mater. 2008;153:670–6.
6. Shao J, Yan R, Chen H, Wang B, Lee DH, Liang DT. Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry forier transform infrared analysis. International conference on bioenergy outlook. Singapore. Singapore: American Chemical Society. Energy Fuels. 2008;22:38–45.
7. Buryan P, Staff M. Pyrolysis of the waste biomass. J Therm Anal Calorim. 2008;93(2):637–40.
8. Gani A, Naruse I. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. Renewable Energy. 2007;32:649–61.
9. Biagini E, Barontini F, Tognotti L. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. Ind Eng Chem Res. 2006;45:4486–93.
10. Worasuwannarak N, Sonobe T, Tanthapanichakoon W. Pyrolysis behaviors of rice straw, rice husk and corncob by TG-MS technique. J Anal Appl Pyrolysis. 2007;78:265–71.
11. Silverstein R, Bassier GC, Morrill TC. Identificação Espectrométrica de Compostos Orgânicos. 3rd ed. Rio de Janeiro: Guanabara; 1987. p. 65.