Thermochimica Acta 486 (2009) 1–4

Contents lists available at ScienceDirect

Thermochimica Acta

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

Thermogravimetric study on stem biomass of *Nicotiana tabacum*

Yong Joo Sung[a], Yung Bum Seo[b,*]

[a] KT&G Central Research Institute, 302 Shinseong-Dong, Yuseong-Gu, Daejeon, Republic of Korea
[b] Dept. of Forest Products, College of Life Science and Agriculture, Chungnam National University, Daejeon, Republic of Korea

ARTICLE INFO

Article history:
Received 10 March 2008
Received in revised form 3 December 2008
Accepted 7 December 2008
Available online 13 December 2008

Keywords:
Thermogravimetric analysis
Tobacco
Stem
Biomass
Hot water extraction

ABSTRACT

The non-isothermal behavior of the stem biomass of *Nicotiana tabacum* was investigated in depth using thermogravimetric analyzer (TGA). The thermal behavior of tobacco stems showed different patterns depending on decomposition conditions as well as tobacco varieties.

The higher contents of the volatile components and simple sugar in the bright stem resulted in the greater thermal decomposing in the temperature range ca. 120–250 °C. The structural difference in hemicellulose and cellulose depending on tobacco varieties could be detected by the temperature difference in the derivative TG result. The thermal analysis of the freeze-dried soluble obtained from hot water extraction of tobacco stem demonstrated that the distinct weight loss of the bright stem at around 570 °C was due to oxidation of the residual char originated from the soluble fraction, such as simple sugar.

1. Introduction

The stem biomass of *Nicotiana tabacum* L. (commonly called tobacco) is one of the major agricultural by-products originated from tobacco leaf processing factories and cigarette manufacturing mills. Since the tobacco stem biomass forms more than 20 wt.% of the whole tobacco leaf [1], the proper utilization of the stem has been a major issue for the economics of tobacco business. Actually, the physical and morphological properties of the tobacco stem are not suitable for direct application to the cigarette, therefore various processes have been developed, for example, the expanding process for the expanded tobacco stem and the papermaking process for the reconstituted tobacco sheet [2]. These processed stems provide not only the economic benefits but also the improved physical properties such as the higher filling power which provide fewer materials per a cigarette. And the great potential for reducing the potential risk components in smoke and the increasing demand for safer cigarette make the processed stems become one of the major components of the modern blended cigarette [3,4]. Although the significance of the tobacco stem biomass has been increasing in tobacco industry, there has been relatively little information on the tobacco stem, especially on the thermal behavior of tobacco stem.

For the practical reason, intensive studies have been conducted to reveal the thermal behavior of tobacco materials [5–10], to find the pyrolysis products from tobacco leaves and ingredients [11–14], and to understand the actual burning mechanism in cigarette [15,16]. And many studies on the chemical composition of tobacco leave show that there are significant differences in chemical composition between tobacco lamina and tobacco stem [17–19]. The stem usually has more rigid structure and higher proportion of cell wall biopolymer such as cellulose, pectin, lignin and less soluble materials such as non-polymeric constituents, which may lead to a different thermal behavior of tobacco stem. In order to utilize the tobacco stem more usefully, the deeper knowledge about the properties of tobacco stem especially the thermal behavior would be greatly required as regards with the chemical components of the stem.

In this study, the thermal behavior of tobacco stems were deeply investigated depending on decomposition conditions as well as tobacco varieties. Especially, the differences in thermal decomposing pattern were rationalized by relating with the difference in chemical composition between tobacco stems and extracted samples. And it was examined whether the changes in the chemical composition and in the structural cell wall biopolymer of tobacco stem could be distinguished by using TGA method. Therefore, the usability of TGA method for the researches on the developing the stem treatment processes was demonstrated.

2. Experimental

2.1. Materials

Two typical types of tobacco stem biomass, bright stems and burley stems were applied to this study. The samples were collected from a commercial tobacco leaf factory in KOREA, 2007. The stem samples were ground and sieved, and particles ranging in size from

* Corresponding author. Tel.: +82 42 821 5759; fax: +82 42 823 8050.
E-mail address: ybseo@cnu.ac.kr (Y.B. Seo).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.12.010

35 mesh and 60 mesh were selected for experiments to minimize the effects of sample size on the extraction analysis and the thermal decomposing behavior.

2.2. Chemical composition analyses

The chemical compositions of the stems were analyzed according to other researches [17,20]. Total ash content was obtained gravimetrically by combustion of stem samples at 550 °C for 2 h in a muffle furnace.

The inorganic compounds were analyzed quantitatively by using inductively coupled plasma-atomic emission spectrophotometry (ICP-AES, PerkinElmer). The sample pre-treatment procedure and the ICP operating conditions were done according to the literature [21].

2.3. Thermal analysis

The non-isothermal analysis of the tobacco stems was conducted with a TGA standard equipment (TA Instruments, model SDT 2960). The sample weighing approximately 10 mg ± 0.5 mg of each kind of tobacco stems was pyrolyzed with a heating rate of 10 °C/min from room temperature up to 900 °C. The volatiles were carried out by either air or nitrogen gas with a flow rate of 100 ml/min.

2.4. Hot water extraction

A 1.00 g sample of grounded tobacco stem was weighted into a 250 mL glass flask and 100.00 g of distilled water was added. The sample was boiled under reflux condenser for 1 h cooled, and filtered on Whatman No. 5 Paper with normal laboratory vacuum. The residual fraction on the Whatman paper was washed thoroughly with distilled water and dried in an oven at 100 °C for 3–4 h to permit a more specific examination of the thermal decomposing of cell wall biopolymers [12]. The filtrate was separately collected and dried with a freeze dryer (Ilshin Lab Co., Ltd.) with −50 °C condition, in order to reduce the loss of the volatile compound in the filtrate by hot drying process.

3. Results and discussion

3.1. Characterization of tobacco stems

Although the chemical composition of tobacco leafs varies not only in stalk position but also in the cultivation factors such as weather, fertilizing, soil, place, and harvesting, etc. [19], there was a distinct difference in chemical composition originated from the tobacco types. In case of tobacco stem, the chemical composition also varies greatly depending on the tobacco types as summarized in Table 1.

The remarkable differences between burley stem and bright stem were found in the contents of nitrate, total ash, various reducing sugar and crude fiber, etc. [17]. While burley stem has much higher contents of nitrate and total ash than those of bright stem, very little sugar was found in burley stem. Bright stem was composed of more than 20% of simple sugar compounds based on the total weight, which resulted in the higher water soluble contents.

3.2. Thermal behavior of tobacco stems in nitrogen and air atmosphere

The typical thermal decomposing patterns of the tobacco stem samples are shown in Fig. 1. The weight loss below 120 °C was originated from the moisture retained in the stems, which resulted in about 10% weight loss [7]. In the temperature range ca. 120–250 °C, the higher weight loss of bright stem might be come from the higher contents of the volatile components and non-polymeric constituents in it than those in burley stems [13].

Table 1
Composition of burley tobacco stem and bright tobacco stem (all values expressed on a percentage dry weight basis).

Components (wt.%)	Burley stem biomass	Bright stem biomass
Hot water solubles	45.8	55.5
Total alkaloids	0.66	0.52
Nitrate	7.29	0.32
Total reducing sugars	Trace	20.73
Glucose	0	5.17
Fructose	0	6.15
Sucrose	0.38	2.08
Citric acid	0.77	0.34
Malic acid	2.21	4.81
Oxalic acid	1.23	1.06
Protein type nitrogen	0.88	0.91
Ethyl ether extractive	0.56	1.42
Crude fiber	19.9	15.0
Total ash	26.2	16.1
Ca	2.12	1.92
K	8.92	3.80
Mg	0.60	0.57
Na	0.01	0.01
P	0.46	0.37

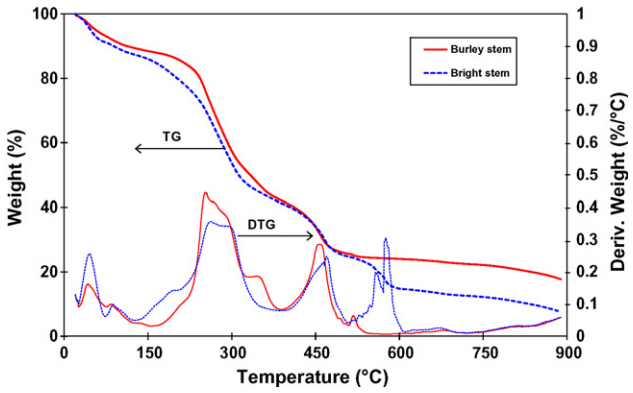

Fig. 1. TG and derivative TG curves for two tobacco stems obtained in air gas flow of 100 ml/min and at heating rate of 10 °C/min.

The main thermal degradation took place between 250 and 500 °C. In this temperature range, two strong peaks in the DTG curve were observed. The peak around 260 °C was originated from the thermal decomposition of cell wall biopolymer such as cellulose, hemicellulose, sugars, lignin, pectin etc. And the peak around 465 °C was due to the combustion of the residual char of the carbohydrates [13,22,23]. Table 2 shows the temperature of DTG peaks under air atmosphere.

The burley stem showed no noticeable degradation over 500 °C, while a clear peak at around 570 °C was found in the DTG curve of the bright stem. Under nitrogen atmosphere, no peak at this temperature was detected for both stem samples as shown in Fig. 2. This result indicated that the greater oxidation reaction of the residual char took place during thermal decomposing of bright stem samples under air atmosphere [8].

Table 2
Temperature of DTG peaks under air atmosphere.

	T_p (°C)		
	1st peak	2nd peak	3rd peak
Bright stem	266	472	576
Burley stem	255	460	NA

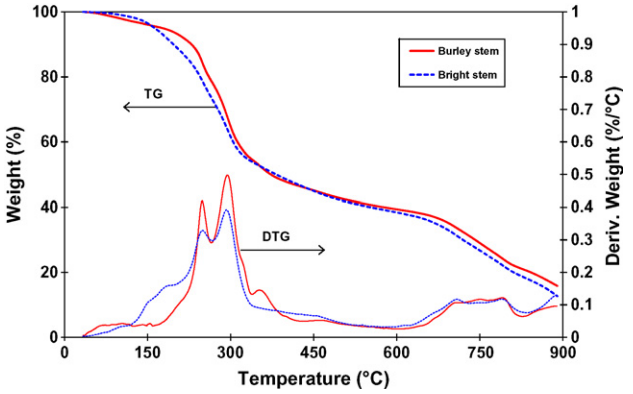

Fig. 2. TG and DTG curves for two tobacco stems obtained in nitrogen gas flow of 100 ml/min and at heating rate of 10 °C/min.

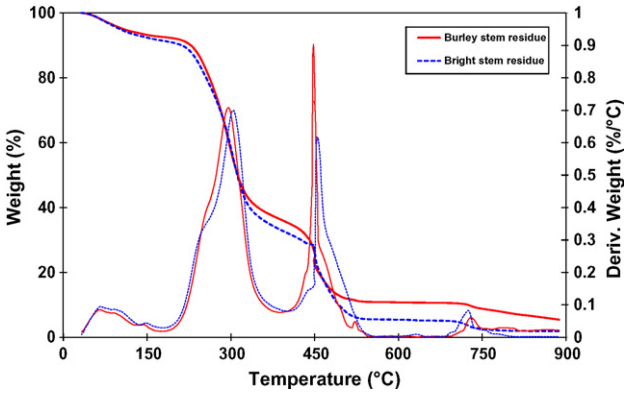

Fig. 3. TG and DTG curve of the residue after hot water extraction of two tobacco stems in air atmosphere.

The more distinct pattern in thermal decomposition of cell wall biopolymer was observed under nitrogen atmosphere as shown in Fig. 2. The broad peak at around 270 °C developed under air atmosphere was recorded as two distinct peaks in DTG curve at nitrogen atmosphere. The first peak appeared at 250 °C for the burley stem and at 253 °C for the bright stem, which were originated from the thermal decomposition of hemicellulose and pectin [23]. The thermal decomposition of cellulose resulted in the second peak shown at around 296 °C for the both samples [24].

As pointed by other researchers [16,25], the condition of atmosphere has great influence on the thermal decomposition of biomass, not only the decomposing rate but also the amounts of thermally decomposed materials, expressed as the thermal weight loss. The amounts of remaining char residue at 880 °C temperature varied between burley stem and bright stem, for example, about 10 wt.% more weight loss for bright stem. However, under nitrogen atmosphere, the gradual weight loss was observed in both tobacco stems after 400 °C and the difference in the remaining char weight at 880 °C between tobacco samples was greatly reduced as shown in Fig. 2. The difference between the residual char weight of samples was only about 2.7 wt.%.

3.3. *Effects of hot water extraction on the thermal behavior of tobacco stem biomass*

Tobacco stem contains significant amounts of non-structural constituents that could affect the thermal decomposition of cell wall polymer and might lead to indistinct decomposition pattern. In order to investigate the thermal behavior of cell wall biopolymer in tobacco stem more precisely, the hot water extraction treatment was applied for removal of the non-structural constituents. Fig. 3 shows the thermal decomposing pattern of the both stem residues under air atmosphere.

The significant changes in DTG curves by extraction took place in the 100–250 °C temperature region. The shoulder of the peak at this temperature, which was observed in DTG of non-extracted samples, was not found. This result indicated that the thermal decomposition between 100 and 250 °C temperature regions was originated from the soluble components of bright stems [5,23].

In the DTG curve of the stem residue after extraction, the bright stem residue showed very similar thermal decomposing pattern as that of burley stem residue. It also became clear that the thermal decomposition of burley stem took place at the slightly lower temperature, as much as about 10 °C less than that of bright stem, for example, 295 °C vs. 305 °C for the first peak and 446 °C vs. 460 °C for the second peak in the DTG curve. This result indicated the biopolymer of burley stem was thermally decomposed at a lower temperature than that of bright stem, which might come from the difference in fine structure of hemicellulose and cellulose, for example, the lower crystallinity and/or the lower degree of polymerization of the biopolymer in the burley stem [26].

At around 570 °C, there was a strong peak in the DTG curve of bright stem before extraction as shown in Fig. 1. After extraction treatment, the peak was not shown in the DTG curve of bright stem residue. This result implied that the distinct thermal decomposition of the bright stem at this temperature might specifically be due to the soluble fraction. In order to examine this hypothesis, the soluble fractions obtained from hot water extraction process were freeze-dried and thermally degraded with the same experimental conditions. The TG and DTG of the soluble fractions of bright stem and burley stem were shown in Fig. 4.

For both stem soluble fractions, the gradual degradation took place from 120 to 450 °C. In case of the bright stem soluble, the sharp thermal decomposition was found at around 580 °C, which could match the peak of the bright stem in Fig. 1. This distinct oxidation of bright stem soluble resulted in more than 20% weight loss of the remaining ash compared with the residual char weight of burley stem soluble over 580 °C.

Under nitrogen atmosphere, the residue of both tobacco stems showed very similar thermal decomposition profiles (Fig. 5). This result implied that the difference in thermal behavior between both tobacco stems might come not only from the difference in the soluble fraction but also from the different carbohydrate oxidation reaction in the presence of oxygen, for example, more complete oxidation for the bright stem [8].

In addition, the most distinct change in thermal decomposition pattern after hot water extraction treatment could be the shrink of the peak at around 255 °C. According to other researches [24],

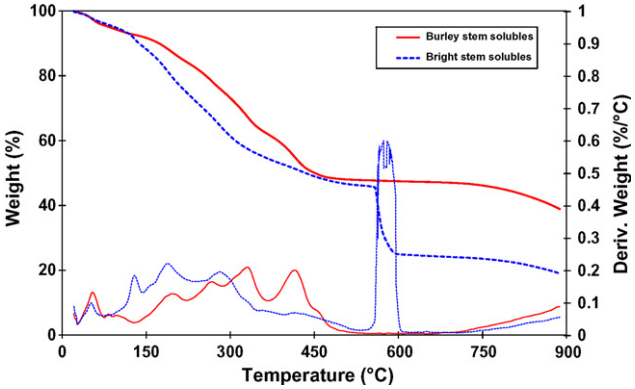

Fig. 4. TG and DTG curve of the freeze-dried soluble obtained from the hot water extraction of two tobacco stems in air atmosphere.

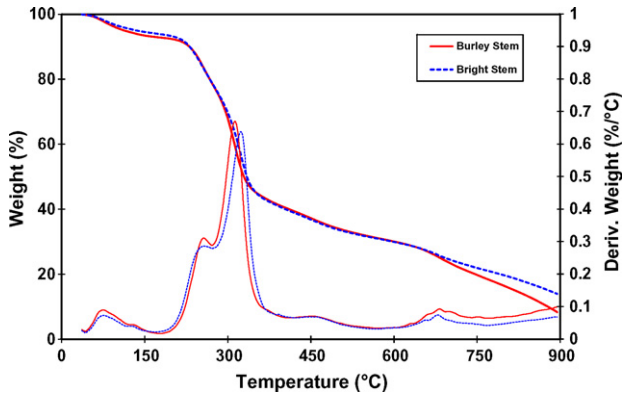

Fig. 5. TG and DTG curve of the residue after hot water extraction of two tobacco stems in nitrogen atmosphere.

the thermal decomposition in this temperature was dominated by the decomposition of the simple polysaccharides such as sugar and hemicellulose. Since some of those could be dissolved and removed by the hot water extraction, the relative amounts of non-soluble components such as cellulose were increased, which might result in the more distinct peak at 313 °C for burley stem residue and at 325 °C for bright stem residue.

4. Conclusion

The role and usability of tobacco stem for cigarette design have been increasing these days, especially for the lower tar products. In this study, a relationship between the chemical compositions and the non-isothermal behavior of the tobacco stems were investigated by comparing those of burley tobacco stem and bright tobacco stem.

The higher contents of the volatile components and non-polymeric constituents such as simple sugar in bright stem biomass resulted in the greater weight loss than that of burley stem biomass in the temperature range ca. 120–250 °C. The bright stem showed greater oxidation, which resulted in the obvious peak in the DTG curve at around 570 °C and about 10 wt.% additional weight loss of the bright stem. The thermal analysis of the freeze-dried soluble showed that the rapid thermal decomposition of the bright stem at around 570 °C was due to the residual char originated from the soluble fraction. The thermal decomposing temperature of polysaccharides of burley stem was lower than those of bright stem, which was shown more obviously in nitrogen atmosphere. This diversity must be originated from the difference in fine structure of the polysaccharides such as hemicellulose and cellulose of stem biomass. This study showed the thermogravimetric analysis could be very useful analysis method not only for distinguishing different types of tobacco stem, but also for the evaluation of the changes in chemical composition and biopolymer structure induced from the stem treatment processes, for example, the expanded stem process.

References

[1] B. Ward, in: D.L. Davis, M.T. Nielsen (Eds.), Tobacco: Production, Chemistry and Technology, Blackwell Science Limited, Oxford, UK, 1999, pp. 330–337.
[2] A. Norman, in: D.L. Davis, M.T. Nielsen (Eds.), Tobacco: Production, Chemistry and Technology, Blackwell Science Limited, Oxford, UK, 1999, pp. 353–387.
[3] N. Baskevitch, Tob. Int. 189 (1987) 20–30.
[4] F. Abdallah, Tob. Rep. 5 (2003) 58–61.
[5] H.R. Burton, Beitr. Tabakforsch. 8 (1975) 78–83.
[6] R.R. Baker, Thermochim. Acta 28 (1979) 45–57.
[7] J.L. Valverde, C. Curbelo, O. Mayo, C.B. Molina, Trans. IchemE 78 (2000) 921–924.
[8] T. Longanezi, M.P.A. Campos, C.G. Mothé, Thermochim. Acta 392 (2002) 51–54.
[9] R.R. Baker, S. Coburn, C. Liu, J. Tetteh, J. Anal. Appl. Pyrolysis 74 (2005) 171–180.
[10] L. Nappi, C. Liu, Proceedings of the third European Combustion Meeting ECM, 2007, pp. 1–6.
[11] W.S. Schlotzhauer, R.F. Arrendale, O.T. Chortyk, Beitr. Tabakforsch. 13 (1985) 74–80.
[12] Y. Ishizu, K. Kaneki, K. Izawa, Beitr. Tabakforsch. 15 (1991) 1–10.
[13] V. Oja, M. Hajaligol, B.E. Waymack, J. Anal. Appl. Pyrolysis 76 (2006) 117–123.
[14] O. Senneca, S. Ciaravolo, A. Nunziata, J. Anal. Appl. Pyrolysis 79 (2007) 234–243.
[15] S. Yi, M.R. Hajaligol, S.H. Jeong, J. Anal. Appl. Pyrolysis 74 (2005) 181–192.
[16] O. Senneca, R. Chirone, R. Salatino, L. Nappi, J. Anal. Appl. Pyrolysis 79 (2007) 227–233.
[17] G.H. Bokelman, W.S. Ryan, E.T. Oakley, J. Agric. Food Chem. 31 (1983) 897–901.
[18] E.T. Oakley, J. Agric. Food Chem. 32 (1984) 1192–1194.
[19] J.C. Leffingwell, in: D.L. Davis, M.T. Nielsen (Eds.), Tobacco: Production, Chemistry and Technology, Blackwell Science Limited, Oxford, UK, 1999, pp. 265–284.
[20] G.H. Bokelman, W.S. Ryan, Beitr. Tabakforsch. 13 (1985) 29–36.
[21] S.E. Cho, M.J. Kim, S.U. Ji, Y.H. Kim, Y.K. Min, J. Kor. Soc. Tob. Sci. 28 (2006) 51–57.
[22] R.A. Fenner, Recent Adv. Tob. Sci. 14 (1988) 82–113.
[23] W. Wang, Y. Wang, L. Yang, B. Liu, M. Lan, W. Sun, Thermochim. Acta 437 (2005) 7–11.
[24] J. Reina, E. Velo, L. Puigjamer, Thermochim. Acta 320 (1998) 161–167.
[25] J.J.M. Órfão, F.J.A. Antunes, J.L. Figueiredo, Fuel 78 (1999) 349–358.
[26] M.E. Calahorra, M. Cortazar, J.L. Egulazabal, G.M. Cuzman, J. Appl. Polym. Sci. 37 (1989) 3305–3314.