Journal of the Korean Society of
Tobacco Science Vol. 30, No. 2, 94～102 (2008)
Printed in Republic of Korea

Comparison of Pyrolysis Patterns of Different Tobacco Leaves by Double-Shot Pyrolysis-GC/MSD Method

Chang-Gook Lee*, Jae-Gon Lee, Hee-Jin Jang, Young-Ju Kwon, Jang-Mi Lee, Jae-Jin Kwag, Soo-Ho Kim, Yong Joo Sung, Chang-Ho Shin, Kun-Soo Kim and Moon-Soo Rhee

KT&G Central Research Institute
(Received November 18, 2008)

ABSTRACT : In this paper, we describe our study on the characterization of tobacco leaves by their pyrolysis patterns. Two kinds of tobacco leaves were pyrolyzed and analyzed by Double-Shot Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) methods. Three grades of Korean flue-cured tobacco leafsuch as B1O, AB3O, CD3L and burley tobacco leaves such as B1T, AB3T, CD3W were pyrolyzed with six discrete but stepwise heating temperature ranges, those are from 100℃ to 150℃, 150℃ to 200℃, 200℃ to 250℃, 250℃ to 300℃, 300℃ to 350℃ and finally from 350℃ to 400℃. Using the resultant 52 pyrolytic components identified in the programs as components, principal component analysis (PCA) showed statistical classification between flue-cured and burley tobacco lamina. Among six pyrolysis temperature ranges, the best discrimination was achieved at the temperature range from 250℃ to 300℃ and from 300℃ to 350℃.

***Key words** : pyrolysis, Principal Component Analysis (PCA), discrimination*

Pyrolysis of tobacco *Nicotiana tabacum* leaves has received significant interest over the years due to the susceptibility of tobacco leaves to thermal degradation during smoking. A variety of pyrolysis studies on this subject have been reported (Scheijen, *et al.,*1987; Müller, 1985; Scheijen, *et al.,* 1991). Some of these were about tobacco leaf characterization (Halket, *et al.,* 1985; Crispino, *et. al.,* 2007). Tobacco is a complex plant biomass containing small organic and inorganic molecules and biopolymers. The biopolymer consistsof cellulose, hemicellulose, pectin, lignin, protein and peptides, nucleic acid, etc (Bokelman, *et al.,* 1983; Milne, *et. al.,* 1983). Pyrolysis studies using Py-GC/MS methods have been conducted to reveal the pyrolytic behavior of some tobacco components (Schlotzhauer, *et. al.,* 1992). Tobacco lamina in the column of smoking cigarette is exposed to high temperature of the burning corn and is subject to a severe pyrolytic degradation and thermal decomposition when the cigarette is puffed. The extent of these thermolysis is governed by the kinds of tobacco fillers, packing density, burning rate, availability of air at the site of pyrolysis, so the composition of generated smoke changes case by case. The taste of cigarette smoke is governed largely by the composition of tobacco leaves. The cigarette smoke is composed of a variety of compounds, which depend not only on the type of tobacco

*연락저자 : 305-805 대전광역시 유성구 신성동 302 번지, KT&G 중앙연구원
*Corresponding author : *KT&G Central Research Institute, 302 Shinseong-dong, Yuseong-gu, Daejeon 305-805, Korea (phone: 82-42-866-5597 fax: 82-42-866-5426 e-mail: cg4tang@ktng.com*

being smoked, but also on the conditions of smoking. Real cigarette smoke has complete information about the thermal behavior of tobacco leaf which is contained in cigarette column, but the conventional analysis procedure for cigarette smoke is composed of multiple steps including cigarette preparation, sorting according to physical properties such as weight and pressure drop, smoking with machine by standard method, trapping the real smoke with appropriate methods, separation and purification and then analysis with instrument. These procedures require lots of labors and time and furthermore the smoke composition can be altered from the intrinsic information the cigarette has originally, so the information about the nature of tobacco leaf may be lost during these laborious steps. So many tobacco scientists have used the pyrolysis technique over the last few decades to investigate the smoking phenomenon as model studies for smoking (Faix, *et al.* 1992). The objective of this study is to investigate whether the Pyrolysis-GC/MSD method is possible in discriminating the different tobacco leaves with convenience and rapidity. We present the statistical differentiation between different tobacco leaves according to their thermal degradation behaviors.

MATERIALS AND METHODS

Tobacco leaf samples

Three grades of flue-cured tobacco leaves including B1O, AB3O and CD3L and three grades of burley tobacco leaves including B1T, AB3T and CD3W, which were grown in Korea, discriminated and graded by leaf expert after harvesting and aging, prepared for pyrolysis experiment. Additionally one oriental tobacco leaf, IZMIR, and one puffed burley stem and tobacco fillers of three commercial cigarette brands(α,β,γ) were prepared too. These tobacco leaves were homogenized and dried at 40℃ for 6 h in oven.

Pyrolysis and qualitative analysis of the pyrolysate by GC-MS

The GC/MS instrument consisted of an Agilent 6890 gas chromatograph equipped with an DB-5 MS capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness). The double-shot pyrolyzer (2020iD) was directly connected to the GC injector maintained at 240℃ with a 100 : 1 split ratio at the initial time. The detector consisted of an Agilent 5973 mass selective detector operating in the scan mode. Mass spectra were recorded in the electron ionization (EI) mode at 70 eV, scanning the m/z 30-500 range. Interface and source temperatures were 250℃ respectively. The carrier gas used was helium with a controlled flow rate of 1.0 mL/min. The GC oven temperature was programmed from 50℃(3 min) to 180℃(20 min) by ramping rate of 3℃/min then heated to 240℃(for 30min) with ramping rate of 5℃/min. The tobacco leaves were grinded and 3.0 mg of grinded sample was loaded into the sample cup of pyrolyzer, which was then introduced in the furnace and heated from 100℃ to 150℃ (A) with heating rate of 50℃/min. Then the thermally evolved components from sample were introduced into the column of GC-MS. Operation of scan mode of MS started as soon as the furnace temperature reach target temperature (150℃) and sample cup is retracted from the furnace, After the first run of Pyrolysis-GC/MS analysis, the sample cup were introduced again into the furnace and pyrolyzed by heating at the temperature range of next step 150℃ to 200℃ (B), from 200℃ to 250℃ (C), from 250℃ to 300℃ (D), from 300℃ to 350℃ (E) and finally from 350℃ to 400℃ (F) with the same heating rate. This stepwise pyrolysis gave six pyrograms (total ion chromatograms) for one tobacco sample. Identification of each pyrolysate compounds was conducted by comparing its mass spectra with those of library (Wiley7n.l)

Principal component analysis (PCA)

In this work, principal component analysis (PCA) was performed using the software SPSS 12.0 (Apache Software Foundation). A data matrix shown in table 1 was constructed with 6 columns representing tobacco samples and 52 rows corresponding pyrolysis products. Factors with two eigenvalues were selected. The varimax rotation method was applied.

RESULTS AND DISSUSSION

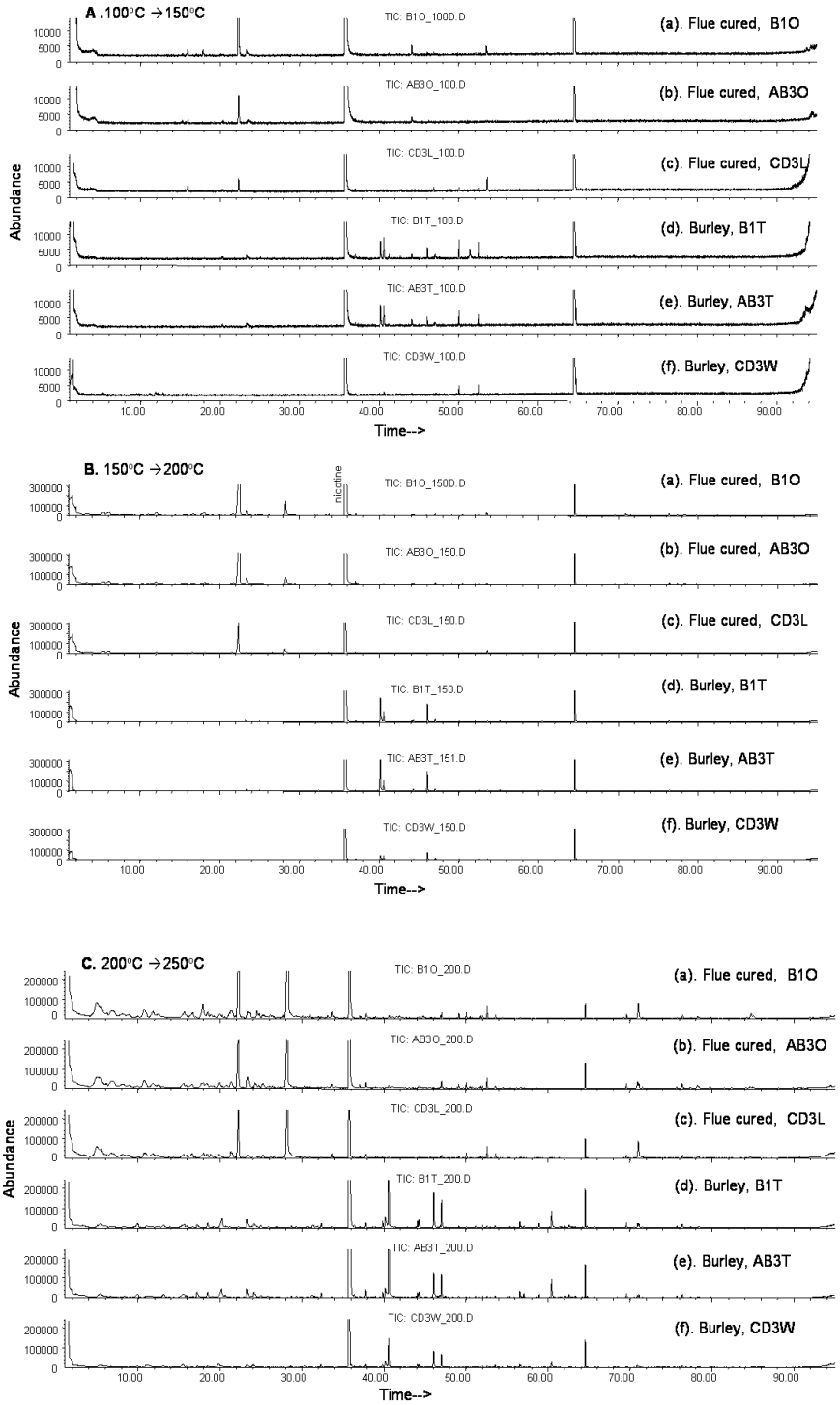
Pyrolytic pattern of tobacco leaves

Fig 1 shows pyrograms of two kinds of tobacco leaves, those are three flue-cured tobaccos [B1O(a), AB3O(b), CD3L(c)]and burley tobaccos [B1T(d), AB3T(e), CD3W(f)], which were pyrolyzed at six stepwise temperature ranges$^{(A\text{-}F)}$. At each temperature ranges, upper three pyrograms of flue-cured tobacco show apparently different pyrolysis pattern from lower three pyrograms of burley ones. Peaks in each pyrogram are the pyrolytic products generated by thermal degradation of tobacco leaves. Table 1 is the results of semi-quantification of components appeared in each pyrograms (total ion chromatogram) in peak area value.

Principal component analysis (PCA)

To investigate which temperature range shows the best discrimination between two kinds of tobacco leaves, principal component analysis (PCA) was conducted on the results obtained at each pyrolysis temperature range using the **table 1** as data matrices. Pyrolysis during first temperature range, that is from 100℃ to 150℃, gives just nicotine and neophytadiene (**fig 1 A**) and did not differentiate flue-cured leaves from burley tobacco leaves because required second principal component could not be extracted from the data. Probably the evolved compounds are not pyrolytic products of tobacco leaves but volatile compounds just evaporated from tobacco leaves. These volatile compounds arose from very small tobacco sample (3 mg) and severe sample treatments such as grinding, drying in oven might alter the original contents of flavor compound in tobacco samples. For these reasons, the pyrolytic compounds, exactly evaporated flavor compounds, did not represent the intrinsic pyrolytic character of tobacco leaf itself and from this result we can not extract second principal component in PCA. Pyrolysis over subsequent temperature range, from 150℃ to 200℃, gave 18 pyrolytic products such as furfural, furfuryl alcohol, 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one, 5, 6-dihydro-2H-Pyran-2-one, nicotine, solanon, nornicotine, myosmine, nicotyrine, anabasine, 2, 3′-bipyridyl, megastigmatrienone isomers, cotinine, N-(b)-formylnornicotin, neophytadiene and cholic acid (fig 1.B). In pyrolysis over this temperature range, volatile components still arose from tobacco sample but, in some extent, pyrolysis also occurred and two kinds of tobacco leaves can be distinguished roughly by PCA with eigen values of *PC 1*: 3.752, *PC 2*: 2.098 (fig. 2. B). Pyrolysis during 3rd(C), 4th(D), 5th(E) and last temperature range(F) gave hyroxymethylfurfural, indole, 3-Oxo-α-ionol, corylone, palmitic acid, phenol, 1, 2-benzenediol, 1, 4-benzenediol, levoglucosan, 5-phenyl-1, 4-dimethyl imidazole, *dl*-limonene, methyl-2-furoate, 5-hydroxymethyldihydrofuran-2-one, 1, 4:3, 6-dianhydro-*d*-glucopyranose, 2, 3-dihydrobenzofuran, 2-methoxy-4-vinylphenol, 2, 6-dimethyl-1, 4-benzenediol, 2, 6, 10-trimethyl-2, 6, 10-dodecatriene and so forth (fig 1. C, D, E, F). Rasing pyrolysis temperature ranges, the proportion of volatile component of tobacco decreased but proportion of pyrolytic components increased. Principal component analysis of 4th(D, from 250℃to 300℃, and 5th(E, from 300℃to 350℃ temperature range gave distinct classification between flue-cured and burley tobacco leaves with eigen value of *PC 1: 3.083, PC 2: 2.622* and *PC 1: 4.744, PC 2: 1.035*, respectively. But at the highest temperature range (F, from 350℃ to 400℃ gave poor discrimination with eigen value of

Comparison of Pyrolysis Patterns of Different Tobacco Leaves
by Double-Shot Pyrolysis-GC/MSD Method



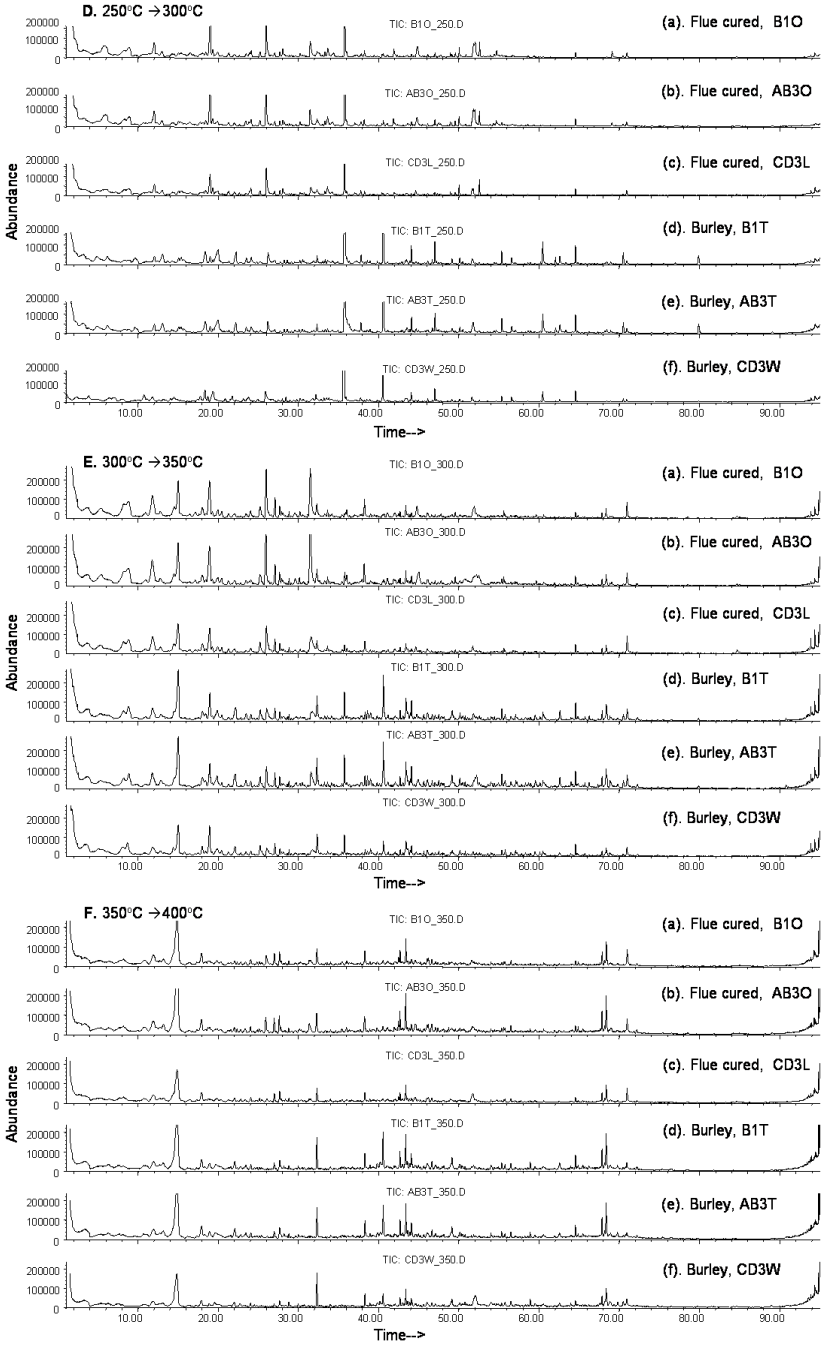


Fig. 1. Pyrograms of six tobacco leaves, three grades of flue-cured including B1O(**a**), AB3O(**b**), CD3L(**c**) and three grades of burley including B1T(**d**), AB3T(**e**), CD3W(**f**) under six stepwise temperature range, 100°C →150°C (**A**), 150°C → 200°C (**B**), 200°C → 250°C (**C**), 250°C → 300°C (**D**), 300°C → 350°C (**E**) and 350°C → 400°C (**F**) with heating rate of 50°C/min.

Table 1. The results of pyrolysis of six tobacco leaves, three grades of flue-cured including B1O**(a)**, AB3O**(b)**, CD3L**(c)** and three grades of burley including B1T**(d)**, AB3T**(e)**, CD3W**(f)**under six discrete temperature range, 100℃ → 150℃**(A)**, 150℃ → 200℃**(B)**, 200℃ → 250℃**(C)**, 250℃ → 300℃**(D)**, 300℃ → 350℃**(E)** and 350℃ → 400℃**(F)** with heating rate of 50℃/min.

Peak area (X100000)

No.	R_t	Compounds	A. 100℃—>150℃						B. 150℃—>200℃						C. 200℃—>250℃						D. 250℃—>300℃						E. 300℃—>350℃						F. 350℃—>400℃					
			B1O	AB3O	CD3L	B1T	AB3T	CD3W	B1O	AB3O	CD3L	B1T	AB3T	CD3W	B1O	AB3O	CD3L	B1T	AB3T	CD3W	B1O	AB3O	CD3L	B1T	AB3T	CD3W	B1O	AB3O	CD3L	B1T	AB3T	CD3W	B1O	AB3O	CD3L	B1T	AB3T	CD3W
1	5.30	Furfural	0.0	0.0	0.0	0.0	0.0	0.0	73.5	73.5	73.5	24.4	165.6	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	6.10	Furfuryl alcohol	0.0	0.0	0.0	0.0	0.0	0.0	73.6	73.6	73.6	95.9	18.3	5.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	10.95	5-Methyl furfural	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	39.3	51.2	29.8	6.6	18.6	6.5	0.0	0.0	0.0	0.0	0.0	0.0
4	11.25	Glycerol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	12.08	Phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	116.1	99.9	70.4	45.1	63.7	0.0	280.1	324.1	199.2	123.0	158.1	106.6	122.8	145.5	5.3	63.0	71.1	47.5
6	14.42	Corylone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97.9	97.4	58.6	58.1	68.6	54.4	0.0	0.0	0.0	0.0	0.0	0.0
7	14.88	dl-Limonene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	292.3	333.9	223.8	398.9	423.3	262.5	757.9	916.8	370.6	759.4	791.8	426.5
9	17.75	4-Methyl phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	71.7	110.9	61.0	83.2	72.5	44.9
10	18.03	Methyl-2-furoate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	73.6	83.6	59.5	79.0	90.5	65.3	0.0	0.0	0.0	0.0	0.0	0.0
11	18.96	Cyclobutanol(?) (unknown)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	245.9	222.1	131.2	38.6	31.1	0.0	296.7	328.9	183.5	167.5	154.8	185.2	0.0	0.0	0.0	0.0	0.0	0.0
12	22.28	2,3-Dihydro-3,5-dihydroxy-	19.9	3.0	2.5	0.0	0.0	0.0	1308.2	1024.8	330.9	26.0	0.2	53.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
13	23.23	5,6-Dihydro-2H-Pyran-2-one	0.0	0.0	0.0	0.0	0.0	0.0	41.0	51.7	7.0	25.0	19.1	0.0	578.5	371.7	279.8	1.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
14	24.08	3-Ethyl phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	31.2	31.9	22.0	23.4	30.6	19.8
15	25.25	5-Hydroxymethyldihydrofuran-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	81.8	89.5	84.1	59.0	49.6	60.6	0.0	0.0	0.0	0.0	0.0	0.0
16	25.99	1,2-Benzenediol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	286.6	202.5	161.1	64.2	69.1	82.5	281.5	333.5	211.0	75.2	122.4	45.1	0.0	0.0	0.0	0.0	0.0	0.0
17	27.10	1,4:3,6-Dianhydro-d-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	76.5	91.4	70.5	51.4	54.9	52.5	50.1	63.6	31.3	30.2	35.1	11.5
18	27.66	2,3-Dihydro benzofuran	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.3	55.0	42.6	32.1	40.4	28.8	51.5	67.9	44.8	46.1	70.8	40.8
19	28.38	HMF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1033.8	489.3	625.8	1.3	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	28.85	Decahydronaphthalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	19.3	21.6	17.3	18.1	20.1	20.1	0.0	0.0	0.0	0.0	0.0	0.0
21	31.49	1,4-Benzenediol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98.8	92.6	60.0	14.6	0.0	0.0	417.3	479.9	230.8	92.4	162.2	82.5	0.0	0.0	0.0	0.0	0.0	0.0
22	32.33	Indole	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	0.9	1.7	17.3	16.5	10.2	0.0	0.0	0.0	0.0	0.0	0.0	76.7	83.9	61.0	110.6	111.3	100.9	74.7	99.5	48.5	117.7	123.3	112.6
23	33.64	2-Methoxy-4-vinylphenol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	33.6	32.1	26.9	18.6	22.4	21.2	0.0	0.0	0.0	0.0	0.0	0.0
24	35.76	Nicotine	1890.5	1916.8	710.1	1382.3	1299.7	376.3	651.6	7582.1	2669.2	6000.0	5252.0	1779.5	1758.3	2903.6	969.5	5854.2	6160.0	2015.2	318.7	714.5	292.1	1875.6	1926.9	902.5	10.5	48.4	29.1	93.4	109.6	67.7	0.0	0.0	0.0	0.0	0.0	0.0
25	37.05	Solanon	0.0	0.0	0.0	0.0	0.0	0.0	7.7	11.4	4.9	7.3	3.9	3.9	5.8	8.6	4.9	3.1	4.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
27	38.29	3-Methyl-1H-Indole	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77.1	82.2	35.0	59.4	90.8	46.7
28	40.14	Nornicotine	0.0	0.0	0.0	3.6	8.9	0.0	0.0	0.0	0.0	189.0	339.3	39.7	0.0	0.0	0.0	64.1	39.9	33.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
29	40.56	Myosmine	0.0	0.0	0.0	2.9	3.0	0.0	0.0	0.0	0.0	0.0	61.6	21.6	0.0	11.1	3.4	268.4	253.9	87.3	13.6	19.1	6.2	239.6	230.1	89.3	9.7	25.7	16.2	161.2	139.8	48.7	0.0	0.0	0.0	0.0	0.0	0.0
30	42.50	2,6-Dimethyl-1,4-benzenediol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.5	15.9	16.7	25.1	27.6	17.7	36.0	38.5	19.2	11.1	15.3	7.2
31	43.30	2,6,10-Trimethyl-2,6,10-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	40.1	51.5	39.5	97.6	125.8	69.0	96.5	122.7	62.0	113.2	127.9	52.4
32	44.10	Nicotyrine	0.0	0.0	0.0	0.0	0.0	0.0	5.5	3.8	0.0	5.7	3.1	0.0	3.8	2.9	0.0	18.6	14.3	7.1	10.5	14.5	4.3	55.3	47.6	29.1	15.4	30.8	13.8	63.7	70.6	39.6	0.0	0.0	0.0	0.0	0.0	0.0
33	44.30	Anabasine	0.0	0.0	0.0	0.0	0.0	0.0	2.9	2.0	0.0	12.2	13.9	0.0	0.0	0.0	0.0	28.8	22.0	10.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
34	44.86	Levoglucosan (or d-Allose)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	92.4	58.8	23.8	14.9	17.7	4.1	83.8	140.2	38.0	31.0	75.1	27.9	0.0	0.0	0.0	0.0	0.0	0.0
35	46.05	Unknown	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	109.0	106.9	48.1	0.0	0.0	0.0	121.2	82.8	57.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
36	47.03	2,3'-Bipyridyl	0.0	0.0	0.0	0.0	0.0	0.0	7.2	5.7	1.9	16.5	11.9	7.8	17.0	24.7	6.8	84.5	67.8	37.1	14.7	16.1	7.1	68.7	60.7	40.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
37	50.04	Megastigmatrienone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.9	2.4	1.4	14.1	9.7	6.7	6.3	6.0	0.0	27.1	30.0	26.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
38	50.13	5-Phenyl-1,4-dimethyl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	20.2	18.4	7.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
39	50.05	Megastigmatrienone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.2	12.8	12.6	1.6	0.9	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
40	51.84	Quinic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	156.8	186.6	57.0	40.2	76.8	26.5	106.1	247.1	56.6	41.8	150.8	20.3	0.0	0.0	0.0	0.0	0.0	0.0
41	52.58	Megastigmatrienone	0.0	0.0	0.0	0.0	0.0	0.0	2.0	1.8	1.9	1.4	2.0	1.5	32.2	26.2	28.1	4.3	5.4	3.3	36.6	40.4	41.8	10.9	9.1	4.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
42	53.60	3-Oxo-a-ionol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.7	8.5	12.4	7.5	5.6	7.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
43	56.59	Cotinine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.9	3.4	0.0	0.0	0.0	0.0	19.3	19.4	8.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
44	60.46	N-(b)-Formylnornicotine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.7	3.5	0.0	0.0	0.0	0.0	57.4	58.8	20.1	2.9	2.6	0.0	83.9	87.0	34.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
45	65.56	Neophytadiene	162.9	116.9	271.7	176.1	151.0	221.1	331.1	306.9	387.8	516.7	354.4	434.2	37.0	60.7	46.8	89.7	76.5	62.6	12.2	18.0	16.5	47.5	47.3	27.3	15.0	25.2	22.9	51.1	47.4	33.4	9.1	23.9	14.1	41.8	40.8	19.1
46	67.86	Farnesol isomer B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.1	16.9	12.9	26.4	34.8	13.2	49.8	72.9	34.7	65.8	70.5	40.4
47	68.49	Farnesol isomer B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	31.0	46.7	33.3	74.9	81.5	35.1	87.0	125.4	63.4	130.2	128.7	81.8
48	69.57	Cholic acid	0.0	0.0	0.0	0.0	0.0	0.0	2.7	2.7	0.0	2.4	0.0	0.0	10.7	13.2	7.2	11.7	9.6	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
51	70.46	Unknown	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.8	8.8	4.5	42.9	38.0	11.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
52	70.94	Palmitic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	75.7	28.6	87.3	14.9	7.3	8.0	14.6	13.1	18.1	13.8	16.4	8.6	67.7	62.8	74.3	52.6	72.2	42.9	81.4	74.0	59.2	36.2	26.8	41.0

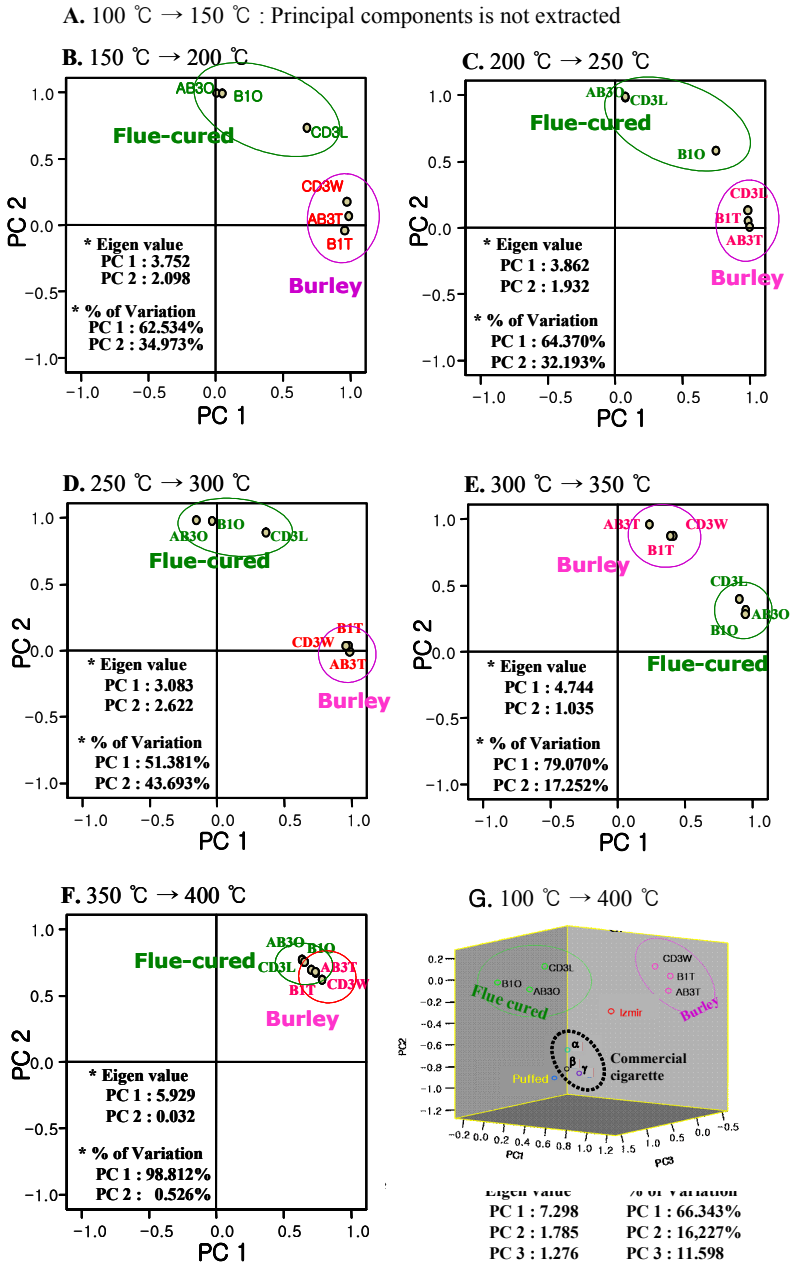


Fig. 2. Principal component analysis on pyrolysis of six tobacco leaves, three grades of flue-cured including B1O(a), AB3O(b), CD3L(c) and three grades of burley including B1T(d), AB3T(e), CD3W(f) under six discrete temperature range, 100℃→150℃A), 150℃→200℃B), 200℃→250℃C), 250℃→300℃D), 300℃→350℃E), 350℃→400℃F) and Entire temperature range from 100℃ →450℃G)with heating rate of 50℃min (orient tobacco such as IZMIR and burley stem expanded tobacco, and three commercial cigarette brands α,β,γ were additionally analyzed and discriminated by PCA.)

PC 1: 5.929, PC 2: 0.032. As the tobacco samples were exposed to higher temperature, they underwent more severe pyrolysis. Their characteristic pyrolysis products have already escaped from sample matrix in the previous pyrolysis step and remaining residue became close to char state. Hence, pyrolysis at higher temperature range, in this case from 350℃ to 400℃ could not generate useful information for the leaf discrimination. Pyrolysis experiments over the whole temperature range from 100℃ to 450℃ for three flue-cured and three burley tobacco leaves, plus three commercial cigarette brands α, β,γ and puffed tobacco made of burley stem and oriental tobacco IZMIR were done. PCA on this broad temperature range gave discrimination between each tobacco leaves with eigen value of *PC 1: 7.298, PC 2: 1.785, PC 3: 1.276*. (fig 2. G). Though the number of sample was very small in this study, and the sample cigarettes had been processed tobaccos by casing and flavoring, the PCA result shows the possibility of differentiating cigarette fillers from raw tobacco materials by pyrolysis.

CONCLUSIONS

Pyrolytic products of tobacco leaves, mixture of compounds generated from tobacco lamina, give characteristic information about tobacco leaf itself. So different kind of tobacco leaves such as flue-cured and burley tobacco can be distinguished by principal component analysis of the pyrolysis results. These two kinds of tobacco were originally classified according to their species, and the pyrolytic behavior was also differentiated from each other. Good discrimination of tobacco leaves is achieved at temperature ranges of 250℃~300℃ and 300℃~350℃. Though pyrolysis method gives indirect clue of real smoke, it is quite simple, convenient and undergo less loss of information compared to traditional direct analysis of real smoke. These model studies of pyrolysis could give birth to indirect but largely reliable information about smoke components of cigarettes made of different kinds of tobacco lamina.

REFERENCES

Halket, J. M., Schulten, H. R., (1985) Rapid characterization of tobacco by combined direct pyrolysis-field ionization mass spectrometry and pyrolysis-gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrol*, 8: 547-560.

Müller, B. H., (1985) Experiences with grade assessment by "condensate predictions" from tobacco pyrolysis. *J. Anal. Appl. Pyrol*, 8: 577-585.

Schlotzhauer, W. S., Chortyk, O. T., (1987) Recent advances in studies on the pyrosynthesis of cigarette smoke constituents. *J. Anal. Appl. Pyrol,* 12: 193-222..

Scheijen, M. A., Boon, J. J., (1991) Micro-analytical investigations on lignin in enzyme-digested tobacco lamina and midrib using pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography / mass spectrometry. *J. Anal. Appl. Pyrol*, 19: 153-173..

Schlotzhauer, W. S., Snook, M. E., Chortyk, O. T., Wilson, R. L., (1992) Pyrolytic evaluation of low chlorogenic acid tobaccos in the formation of the tobacco smoke co-carcinogen catechol. *J. Anal. Appl. Pyrol,*22: 231-238.

Faix, O., Bremer, J., Meier, D., Fortmann, I., Scheijen, M. A., Boon, J. J., (1992) Characterization of tobacco lignin by analytical pyrolysis and Fourier transform-infrared spectroscopy. *J. Anal. Appl. Pyrol*, 22: 239-259.

Bokelman, G. H., Ryan Jr, W.S., Oakley, E. T., (1983) Fractionation of bright tobacco. *J. Agric. Food. Chem*, 31: 897-901.

Milne, T. A., Soltys, M. N., (1983) Direct mass-spectrometric studies of the pyrolysis of

carbonaceous fuels : I. A flame-pyrolysis molecular-beam sampling technique. *J. Anal. Appl. Pyrol*, 5: 93-110..

Milne, T. A., Soltys, M. N., (1983) Direct mass-spectrometric studies of thepyrolysis of carbonaceous fuels : II. Qualitative observations of primary and secondary processes in biomass. *J. Anal. Appl. Pyrol*, 5: 111-131.

Crispino, C. C., Fernades, K. G., Kamogawa, M. Y., Nobrega, J. A., Nogueira, A. R., Ferreira, M. C., (2007) Multivariate Classification of cigarettes according to their elemental content determination by inductively coupled plasma optical emission spectroscopy. *Analytical Sciences,* 23: 435-438.

Bokelman, G. H., Ryan Jr, W.S., Oakley, E. T., (1983) Fractionation of bright tobacco. *J. Agric. Food. Chem*, 31: 897-901.

Crispino, C. C., Fernades, K. G., Kamogawa, M. Y., Nobrega, J. A., Nogueira, A. R., Ferreira, M. C., (2007) Multivariate Classification of cigarettes according to their elemental content determination by inductively coupled plasma optical emission spectroscopy. *Analytical Sciences,* 23: 435-438.

Faix, O., Bremer, J., Meier, D., Fortmann, I., Scheijen, M. A., Boon, J. J., (1992) Characterization of tobacco lignin by analytical pyrolysis and Fourier transform-infrared spectroscopy. *J. Anal. Appl. Pyrol*, 22: 239-259.

Halket, J. M., Schulten, H. R., (1985) Rapid characterization of tobacco by combined direct pyrolysis-field ionization mass spectrometry and pyrolysis-gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrol*, 8: 547-560.

Milne, T. A., Soltys, M. N., (1983) Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels : I. A flame-pyrolysis molecular-beam sampling technique. *J. Anal. Appl. Pyrol*, 5: 93-110..

Milne, T. A., Soltys, M. N., (1983) Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels : II. Qualitative observations of primary and secondary processes in biomass. *J. Anal. Appl. Pyrol*, 5: 111-131.

Müller, B. H., (1985) Experiences with grade assessment by "condensate predictions" from tobacco pyrolysis. *J. Anal. Appl. Pyrol*, 8: 577-585.

Scheijen, M. A., Boon, J. J., (1991) Micro-analytical investigations on lignin in enzyme-digested tobacco lamina and midrib using pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography / mass spectrometry. *J. Anal. Appl. Pyrol*, 19: 153-173..

Schlotzhauer, W. S., Chortyk, O. T., (1987) Recent advances in studies on the pyrosynthesis of cigarette smoke constituents. *J. Anal. Appl. Pyrol,* 12: 193-222..

Schlotzhauer, W. S., Snook, M. E., Chortyk, O. T., Wilson, R. L., (1992) Pyrolytic evaluation of low chlorogenic acid tobaccos in the formation of the tobacco smoke co-carcinogen catechol. *J. Anal. Appl. Pyrol,* 22: 231-238.