PYROLYSIS OF TOBACCO RESIDUE: PART 1. THERMAL

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The pyrolysis of two types of tobacco residue was carried out at different pyrolysis temperatures between 300 and 600 °C and a residence time of 1 h in a nitrogen atmosphere. The effect of pyrolysis temperature on the product distributions was investigated and the composition of the bio-oils identified. The variation in product distribution depended on both the temperature and the type of tobacco residues. The maximum liquid yields were obtained at 400°C for one sample and at 500°C for the other. The compositions of bio-oils from the pyrolysis of the two samples were found to be very similar. N-containing compounds were found to be the major compounds identified in ether extracts for both samples.

Keywords: Biomass; Tobacco residue; Pyrolysis; Bio-char

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INTRODUCTION

The term "biomass" refers to any plant-derived organic substance. There are two main processes to convert biomass into fuels and/or chemical feedstocks: biological and thermochemical. Thermochemical conversion of biomass is achieved by pyrolysis, gasification, and combustion processes (Bridgwater 2006). Pyrolysis is one of the promising technologies for liquefaction of biomass (Beis et al. 2010; Bridgeman et al. 2007; Karagoz 2009; Stojanowska and Jones 2005). Biomass is converted into gaseous, condensable liquid products, and residual solids in the pyrolysis process.

Currently the most important biomass resources are in the form of agricultural crops, wastes, and residues, forestry products and wastes, animal wastes, and municipal solid wastes. Agricultural products have been considered as a potential feedstock to produce liquid fuels and /or valuable chemicals. Tobacco is one of the most valuable agricultural products as long as it is treated with respect (Rodgman and Perfetti 2008). Tobacco is produced from the dried leaves of plants in the genus *Nicotiana*. Products from tobacco can be used for a variety of purposes including biofuel. Thus, research efforts with tobacco plants will play an increasingly important role in the development of agricultural science (Rodgman and Perfetti 2008).

Most of the early studies on pyrolysis of tobacco and tobacco residues were focused on determining the chemical compounds of tobacco smoke (Yi et al. 2004; Bi et al. 2005; Liu et al. 2010). Limited information is available in the literature concerning the production of condensable liquid products from the pyrolysis of tobacco (Putun et al. 2007; McGrath et al. 2009). Fast and slow pyrolysis of tobacco residue was investigated under various conditions. The maximum oil yield (27wt. %) was obtained at the pyrolysis temperature of 550°C (Putun et al. 2007).

The focus of this study is to investigate processability of pyrolysis of two types of tobacco residue sample and to obtain bio-fuel and/or valuable chemicals. In this work, the pyrolysis of two types of tobacco residue was carried out in relation to different pyrolysis temperatures between 300 and 600 °C and a residence time of 1 h in a nitrogen atmosphere. The effect of pyrolysis temperature on the product distributions was investigated and the composition of bio-oils identified. Functional group chemical analysis of tobacco sample, and bio-char was also carried out using Fourier transform infra-red spectrometry with an accessory for attenuated total reflectance (FTIR-ATR).

EXPERIMENTAL

Materials

Tobacco residues were kindly provided by European Tobacco Company, Mersin Turkey. Tobacco samples were used as received and kept in closed plastic bags before being tested. Two types of tobacco residues originated from the mixture of Virginia, Burley and Oriental was used in the pyrolysis experiments. Tobacco residues are denoted as TR1 (rejected from packaging, tobacco stem) and TR2 (rejected from silo, tobacco dust). Table 1 shows the proximate and ultimate analyses of the tobacco residues pyrolysed. All chemicals and solvents used in this study were of analytical grade.

Methods

Pyrolysis Procedure

Pyrolysis experiments were carried out in relation to different pyrolysis temperatures between 300 °C and 600 °C and a residence time of 1 h in nitrogen atmosphere. The reactor was purged before experiments by nitrogen gas flow of 30 mL min^{-1} for 30 min to remove air inside, and the purging with nitrogen was continued after the end of the reaction was completed, which includes cooling down of the reactor to room temperature. The pyrolysis reactor was a fixed bed design of stainless steel with 6 cm diameter and 21 cm height. The pyrolysis vapors on exiting the reactor were passed through three condensers. The first two stages of condensation were carried out with glass condensers cooled with a water and ice mixture. The third condenser was cooled using water. Tobacco residue samples of 25g (dry basis) were placed into the reactor. The system was heated at a rate of 5 °C min^{-1} to the desired temperature, and held at that desired temperature for 60 min. The volatile products were swept by nitrogen gas (30 mL min^{-1}) from reactor to collection flasks. The pyrolysis products were classified into three groups: gases (products that were not condensable at water–ice mixture cooling temperature), liquid products, and solid residues (bio-char). The pyrolysis experiments were repeated three times with an average standard deviation of 2 wt% for liquid, solid, and gaseous yields.

Analysis procedure

Liquid products were extracted with an equal quantity of diethyl ether. The ethereal solutions thus obtained were dried over anhydrous sodium sulfate, filtered, and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether,

this fraction was called diethyl ether extract (bio-oil). The diethyl ether extracts were analyzed by GC-MS. The separation was made on a 30m×0.25mm i.d. phenyl methyl siloxane capillary column HP-5MS using a 6890 Gas Chromatograph Agilent. The GC oven temperature was programmed to start at 40 °C, held for 10 min, then raised at a rate of 2 °C to 170 °C, held for 5min, then raised to 250 °C at a rate of 8 °C, held for 15 min, then raised to 300 °C at a rate 15 °C, and held at this final temperature for 10 min. The injector temperature was 250 °C with split mode. A 1 mL min^{-1} of helium was used as the carrier gas. The end of the column was directly introduced into the ion source of Agilent 5973 series mass selective detector operated with electron impact ionization mode. The data acquisition system used was G1035A software with a NIST library.

Solid residue (bio-char) products were analyzed in terms of their elemental analysis using a LECO CHNS 932. Higher Heating value of biomass, and chars were calculated according to the Dulong formula, which has been widely used by other researchers (Brown et al. 2010; Xu and Lad 2008).

Functional group chemical analysis of tobacco residue samples and selected chars was carried out using Fourier transform infra-red spectrometry with accessory for attenuated total reflectance (FTIR-ATR). A Perkin Elmer FTIR 100 spectrometer was used for functional group chemical analysis of tobacco residue samples and selected chars.

Table 1. Properties of Tobacco Residues

	Type of Biomass	
Proximate Analysis	TR1	TR2
Moisture (wt.%, as received)	12.30	5.20
Volatile matter (wt.%, dry basis)	72.75	68.80
Fixed carbon[a]	1.69	6.10
Ash (wt.%, dry basis)	13.26	19.90
Ultimate Analysis (daf[b], wt %)		
C	42.39	44.78
H	6.49	6.04
N	2.23	2.77
S	0.41	0.43
O[c]	48.48	45.98
HHV[d], MJ kg^{-1}	14.98	15.59

[a, c] by difference

[b] daf: dry basis ash free

[d] Higher Heating Value (HHV) calculated by the Dulong Formula, that is, HHV=0.338C+1.428(H-O/8) +0.095S

RESULTS AND DISCUSSION

The results from the pyrolysis of samples TR1 and TR2 are summarized in Table 2. The variation in product distribution depended on both the temperature and the type of tobacco residues. The liquid yields were lower and solid residue yields were higher for TR2 than for TR1 at all tested temperatures.

Table 2. Product Distributions from the Pyrolysis of Tobacco Residues

		Pyrolysis products, wt.%		
Temperature (°C)	Type of biomass	Liquid(L)	Residue (R)	Gas (G)[a]
300	TR1	36.40	52.46	11.14
	TR2	30.60	59.90	9.90
400	TR1	48.86	39.74	11.40
	TR2	33.90	45.00	21.10
500	TR1	45.38	36.65	17.97
	TR2	35.10	43.90	21.00
600	TR1	44.50	33.70	21.80
	TR2	32.30	39.60	28.10

[a] G = 100-(L+R)

$$\text{The yield of liquid products (wt\%)} = \frac{\text{weight of liquid products}}{\text{weight of biomass (dry basis)}} \times 100$$

$$\text{The yield of solid products (wt\%)} = \frac{\text{weight of solid products}}{\text{weight of biomass (dry basis)}} \times 100$$

The solid residue yield was reduced as the pyrolysis temperature was increased, from 52.46 wt% at 300 °C to 33.70 wt% at 600 °C for TR1. The solid residue yield was reduced as the pyrolysis temperature was increased, from 59.90 wt% at 300 °C to 39.60 wt% at 600 °C for TR2. The highest liquid yields were obtained at 400 °C for TR1 and at 500 °C for TR2. In contrast to TR2, the gas yield was almost same with increasing the temperature from 300 to 400 °C in the case of TR1. The increase in the temperature from 500 to 600 °C led to more gas and less liquid formation for both TR1 and TR2. The reason for more gas and less liquid formation is the secondary degradation of the volatile products at higher temperatures. From work by other researchers using biomass it has been observed that high yields of gases were obtained at higher temperatures (Williams and Nugranad 2000; Beaumont and Schwob 1984; Samolada et al. 1990).

Figure 1 shows the yields of ether extracts from the pyrolysis of TR1 and TR2. The yields of ether extracts were higher for TR2 than for TR1 at the temperatures of 300 and 400°C, whereas TR1 produced higher yields of ether extracts than TR2 at higher temperatures (500 and 600 °C). The maximum ether extract yield was obtained from the pyrolysis of TR1 at 600 °C.

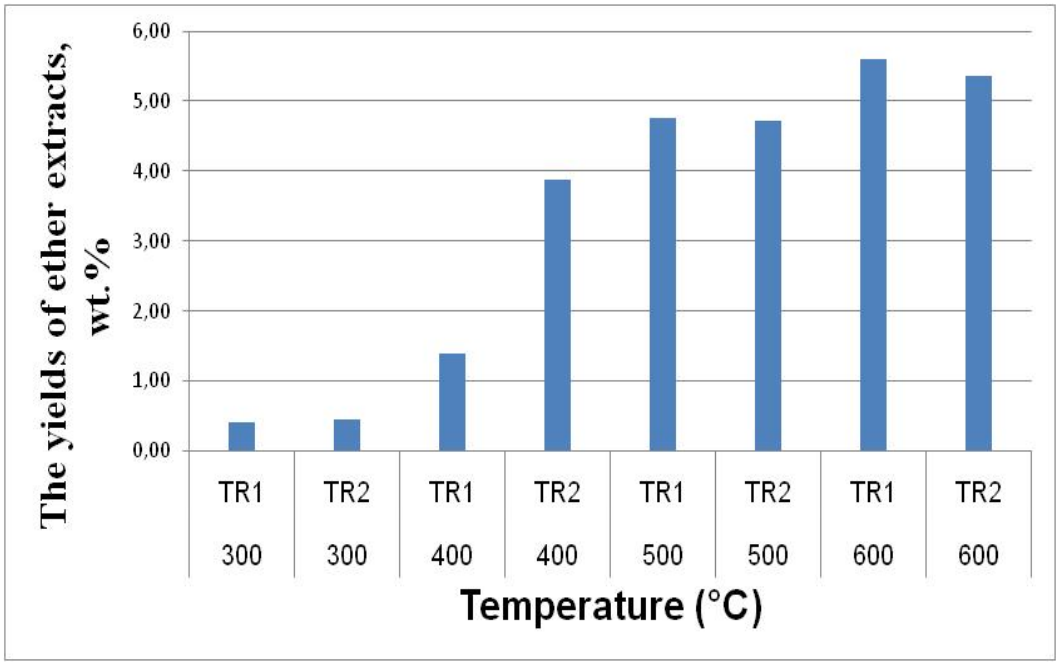

Figure 1. Yields of ether extracts from the pyrolysis of TR1 and TR2 at 300, 400, 500, and 600°C

GC–MS analysis was carried out to identify compounds of bio-oils (ether extracts) from the pyrolysis tobacco residues at 500 °C. The results of the chromatographic areas (% of total area) are set out in Table 3 for compounds of bio-oils from the pyrolysis of tobacco residues at 500ºC. The compounds were grouped and ordered according to increasing retention time. The difference from 100% represented the proportion of unidentified compounds. Bio-oil contained a large variety of compounds including N-containing compounds, phenols, alkanes, alkenes, steroids, acids and esters, ketones, benzene derivatives, alcohols, PAHs, and Vitamin E. By comparing the peak areas and the relative abundance in terms of area percentage, it is clearly seen that N-containing compounds were the major compounds identified in ether extract for both TR1 and TR2.

Among the N-containing compounds, (S)-3-(1-methyl-2-pyrrolidinyl)-pyridine (Nicotine) was the major component. Thermal transfer of nicotine to the gas phase from various tobacco types was investigated by TG/DTA/MS analysis (Seeman et al. 1999). It was reported that nicotine in the absence of oxygen will not begin to decompose thermally until temperatures in excess of 600 °C. It can be concluded that nicotine itself is also stable under our pyrolytic conditions and could be transferred to the diethyl ether extract.

Table 3. Identified Compounds in Bio-oils (ether extracts) from the Pyrolysis of Tobacco Residues at 500 °C

R.T. (min)	Quality	Name of Compounds	Area, %	
			TR1	TR2
Alkanes				
43.75	93	Tridecane		0.30
49.75	94	Cyclododecane		0.57
50.33	94	Tetradecane	0.39	0.33
56.45	95	Pentadecane	0.59	0.72
67.26	83	Ethyl- cyclododecane		0.20
67.67	95	Heptadecane	0.15	0.26
67.72	93	Tetradecane	0.29	
72.89	86	Octadecane		2.22
85.66	95	Cyclopentadecane		0.40
95.59	97	Tetracosane		0.83
95.64	99	Docosane	0.49	0.14
101.59	99	Octacosane	1.02	1.37
104.64	97	Pentacosane	0.46	
107.16	96	Heneicosane		1.73
107.18	97	Tricosane	0.79	
107.61	97	Nonadecane	1.88	0.35
107.78	98	Hentriacontane		3.68
108.76	93	Triacontane	0.88	
109.08	99	Dotriacontane	1.21	
Sum			8.15	13.1
Alkenes				
4.35	94	2-Methyl-1,3,5-hexatriene	0.04	0.07
8.31	76	Trimethyl-1,3-cyclopentadiene	0.03	
9.70	93	1,2-Dimethyl-4-methylene-cyclopentene	0.08	
23.19	94	D-Limonene	0.96	1.5
55.96	97	1-Pentadecene	0.25	
61.73	94	1-Hexadecene		0.14
75.26	90	[R-[R*,R*-(E)]]- 3,7,11,15-Tetramethyl-2-hexadecene	0.30	
89.05	91	1-Heptadecene		0.29
90.28	91	2,6,10,14,18-Pentamethyl-2,6,10,14,18-eicosapentaene	1.25	1.58
Sum			2.91	3.58
Steroids				
105.28	84	Cholesta-3,5-diene	0.37	0.27
107.46	99	Stigmastan-3,5-dien	0.53	0.44
108.41	97	Stigmasta-4,6,22-trien-3.beta.-ol		0.23
108.48	94	Acetate(ester) 3,4-dedihydro- Stigmasterol	0.22	
109.33	99	Campesterol	0.58	0.43
109.82	93	Stigmasterol	1.08	0.95
110.67	99	Sitosterol-. gamma	0.66	0.37
110.93	99	Fucosterol	0.16	
111.85	95	Spinasterone	0.38	0.41
112.86	93	Stigmast-4-en-3-one	0.19	
Sum			4.17	3.1

Table 3 (Continued)

R.T. (min)	Quality	Name of Compounds	Area, %	
			TR1	TR2
Phenols				
20.53	87	Phenol	0.32	0.83
27.70	96	2-Methyl-phenol	1.01	0.57
28.29	90	4-methoxy-phenol	0.89	2.06
29.62	95	3-methyl-phenol	1.36	
29.63	91	2,6-Dimethyl-phenol		0.28
34.74	96	2,4-dimethyl-phenol	1.2	0.55
36.19	91	2-Ethyl-5-methyl-phenol	0.22	
36.50	90	2-Ethyl-phenol	0.97	
36.89	93	2,3-Dimethyl-phenol	0.24	0.19
41.31	87	3-Ethyl-5-methyl-phenol	0.88	
43.20	96	2,4,6-Trimethyl-phenol	0.20	0.05
45.28	86	2,5-Diethylphenol		0.22
57.11	94	Butylated Hydroxytoluene	0.94	0.11
Sum			8.23	4.75
N-containing Compounds				
4.37	91	Pyridine		0.06
4.52	90	Pyrrole	0.21	0.21
6.68	96	2-Methyl-pyridine	0.10	
9.42	87	3-Methyl-pyridine	1.38	0.47
12.79	97	2-Ethyl-pyridine	0.04	
13.32	87	2,5-Dimethyl-pyrazine	0.04	
15.14	90	2,5-Dimethyl-1H-pyrrole		0.09
17.03	95	3-Ethyl-pyridine	0.29	0.08
19.56	93	Benzonitrile		0.09
32.06	92	Benzyl nitrile	0.41	0.1
33.79	95	2,3,5-Trimethyl-6-ethylpyrazine	0.32	
43.17	91	Indole		1.11
43.86	90	5H-1-Pyrindine	0.96	
46.81	94	(S)-3-(1-methyl-2-pyrrolidinyl)-pyridine	33.48	23.79
49.26	94	4-Methyl-1H-indole	0.87	0.76
51.38	94	3-(3,4-dihydro-2H-pyrrol-5-yl)- pyridine	0.80	0.88
55.25	95	3-(1-Methyl-1H-pyrrol-2- yl)- pyridine	1.40	1.54
55.63	93	1,2-Dimethyl-1H-indole	0.22	0.25
57.72	97	2,3'-Dipyridyl	0.54	0.71
59.73	83	8-Quinolinamine		0.26
67.54	95	Cotinine		0.62
78.26	90	Hexadecanenitrile	0.17	
87.30	95	Hexadecanamide		0.18
Sum			41.23	31.2

Table 3. (Continued)

R.T. (min)	Quality	Name of Compounds	Area, %	
			TR1	TR2
Acids and Esters				
76.38	80	Bis(2-methylpropyl) ester- 1,2-benzenedicarboxylic acid	0.39	
80.02	95	Methyl ester-hexadecanoic acid	0.33	0.16
82.60	97	n-Hexadecanoic acid	1.10	1.02
86.39	92	Methyl ester-14-methyl-heptadecanoic acid	0.08	
Sum			1.9	1.18
Ketones				
5.59	90	Cyclopentanone	0.04	0.06
7.98	95	2-Methyl-cyclopentanone	0.08	
8.39	76	3-Methyl-cyclopentanone	0.06	0.06
12.92	94	2-Methyl- 2-cyclopenten-1-one	0.49	0.42
15.65	89	2-Ethyl- cyclopentanone	0.20	0.14
17.81	96	3-Methyl-2-cyclopenten-1-one	0.60	0.29
19.15	83	3-Methyl- 2(5H)-furanone	0.06	
24.19	91	2,3-Dimethyl-2-cyclopenten-1-one	0.81	0.53
99.43	86	(E,E)- 6,10, 14-trimethyl-5,9,13-Pentadecatrien-2-one	0.27	
Sum			2.61	1.5
Benzene Derivatives				
4.79	95	Toluene	0.08	0.03
9.90	95	1,3-Dimethyl-benzene	0.15	0.25
11.58	96	Styrene	0.09	
20.15	95	1,3,5-Trimethyl-benzene	0.14	
Sum			0.46	0.28
Alcohols				
9.41	96	2-Furanmethanol		0.69
23.92	91	Benzyl Alcohol		0.17
79.76	93	3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol	0.45	
86.88	96	(Z)6,(Z)9-Pentadecadien-1-ol	1.62	
Sum			2.07	0.86
PAHs				
43.61	93	2-Methyl-naphthalene		0.34
40.72	87	1,2-Dihydro-3-methyl-naphthalene	0.53	
50.69	96	2,7-Dimethyl-naphthalene		0.20
50.87	97	2,6-Dimethyl- naphthalene		0.30
57.53	95	1,4,6-Trimethyl-naphthalene	0.26	0.12
66.28	87	3-(1,1-Dimethylethyl) -1,2-dihydro- naphthalene	0.46	
Sum			1.25	0.96
Vitamin E				
106.91	94	Tocopherol-.gamma	0.34	0.29
108.25	99	Vitamin e	2.78	1.83
Sum			3.12	2.12
Others				
32.80	95	2-Methylindene	0.19	0.54
34.72	76	1-Methylene-1H-indene		0.23
40.37	90	1,3-Dimethyl-1H-indene	0.87	0.40
Sum			1.06	1.17
TOTAL			77.16	62.63

The other N-containing compounds were mostly pyridine derivatives for both TR1 and TR2. Chitin and tobacco were pyrolyzed separately and in admixture under identical conditions (Schlotzhauer et al. 1976). It was reported that the major basic components of tobacco pyrolysis were pyridine and nicotine. Our results are in good agreement with this previous report. Alkanes having high boiling points, i.e. docosane, octacosane, heneicosane, etc., were also identified in ether extracts. Bio-oils both from TR1 and TR2 contained phenol derivatives. Recently, McGrath and coworkers (2009) have investigated formation of phenolic compounds from the pyrolysis of three main tobacco types at temperatures between 350 and 600 °C. It was reported that the tar fraction from the pyrolysis tobacco at 600 °C was dominated by phenol, mono-, di-, and tri-methyl phenols. Steroids and Vitamin E were also found in both TR1 and TR2. Pyrolysis of two types of tobacco, bright and burley were studied using thermo-gravimetry mass spectrometry (TG–MS) and field ionization mass spectrometry (FIMS) analyses (Oja et al. 2006). Steroids such as stigmasterol, campesterol, and Vitamin E were observed in the pyrolysis of tobacco samples.

Functional group analysis of tobacco residue samples and selected chars was analyzed by FTIR spectrometry. Figure 2 shows the FTIR spectra of tobacco residue samples and selected chars. The FTIR spectra of TR1 and TR2 sample and their corresponding chars at 500 °C were almost the same. TR1 and TR2 samples showed broad bands at 3280 cm^{-1}, as OH and NH groups overlapped. This band represents both hydrogen bonded OH and NH groups. The peak at 2918 cm^{-1} wavenumber represents aliphatic CH_2. The peak at 2845cm^{-1} is assigned to CH stretching vibrations of alkane functional groups. The peaks at 1603 and 1537cm^{-1} are assigned to NH bending vibration. The peak at 1380 cm^{-1} wavenumber represents C-H bending vibration of methyl group. The peak at 1231 cm^{-1} represents C-O bending vibration. The peak at 1026 cm^{-1} is assigned to C-H out-of-plane bending vibrations of alkene groups. The overall spectrum of tobacco residue samples are indicated the presence of multiple molecular components as tobacco consist of cellulose, hemicellulose, lignin, starch, sucrose, glucose, fructose, alkaloids, and other plant components.

The bands at 3280 cm^{-1} due to hydrogen bonded OH and NH groups were totally absent for both TR1 and TR2 derived chars. The peak at 1731 cm^{-1} wavenumber is an indication of the formation of carbonyl groups. Sharma et al. (2002) characterized char from the pyrolysis of Tobacco, and they reported that the C=O stretch was seen in the region between 1731 and 1525 cm^{-1}. Absorption seen at 1400 cm^{-1} wavelength represents mostly aromatic bands. The peak at 873cm^{-1} represents wag of aromatic CH groups. The overall spectrum of tobacco residue chars are indicated the presence aromatic character dominantly.

The elemental compositions of the bio-chars from the pyrolysis of TR1 and TR2 at 500°C are shown in Table 4. The results for elemental compositions of the bio-chars are given on a dry basis ash free. Tobacco residue samples produced the bio-chars with high ash contents. Ash contents of the bio-chars were 40.8wt% for the TR1 derived bio-char and 47.3wt % for the TR2 derived bio-char.

Figure 2. . FTIR spectra of tobacco residue samples and selected chars obtained from the pyrolysis of TR1 and TR2 at 500°C.

Ash content of the tobacco residue samples is a key parameter that affects the quality of bio-chars. The ash contents in bio-chars were 2 to 3 times higher than that of tobacco residue samples. TR1 derived bio-char contained in slightly higher amount of carbon and lower amount of oxygen content than that of TR2 derived bio-char. HHV values for bio-chars derived from TR1 and TR2 were 27.94 and 26.76MJ kg^{-1}, respectively.

Table 4. Elemental Analysis of Bio-chars Obtained from the Pyrolysis of TR1 and TR2 at 500°C

Elemental compositions, (daf[a], wt %)	Type of biochar	
	TR1	TR2
C	75.77	73.62
H	3.41	3.38
N	4.98	4.95
S	1.07	0.98
O[b]	14.77	17.07
HHV[c], ($MJ.kg^{-1}$)	27.94	26.76

[a] daf: dry basis ash free; [b] by difference; [c] Higher Heating Value (*HHV*) calculated by the Dulong Formula, that is, $HHV = 0.338C + 1.428(H-O/8) + 0.095S$

CONCLUSIONS

1. Pyrolysis of two types of tobacco residues were carried out in relation to temperature at 300, 400, 500, and 600 °C. The liquid yields were lower and solid residue yields were higher for sample TR2 (rejected from silo, tobacco dust) than for TR1 (rejected from packaging, tobacco stem) at all tested temperatures. TR1 produced higher yields of ether extracts than TR2 at the temperatures of 500 and 600 °C.
2. Bio-oils both from TR1 and TR2 contained a large variety of compounds including N-containing compounds, phenols, alkanes, alkenes, steroids, acids and esters, ketones, benzene derivatives, alcohols, PAHs, and Vitamin E.
3. N-containing compounds were found to be the major compounds identified in ether extract for both TR1 and TR2.
4. Tobacco residue samples produced the bio-chars with high ash contents. The overall spectra of tobacco residue chars were consistent with the dominance of aromatic groups in the material.

ACKNOWLEDGMENTS

The authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK) for the pyrolysis setup being provided for other projects (109M745). Otherwise, this research work would not have been possible. We gratefully acknowledge European Tobacco Company, Mersin, Turkey for providing tobacco residue samples.

REFERENCES CITED

Beaumont, O., and Schwob, Y. (1984). "Influence of physical and chemical parameters on wood pyrolysis," *Ind. Eng. Chem. Process. Des. Dev.* 23, 637-641.

Beis, S. H., Mukkamala, S., Hill, N., Joseph, J., Baker, C., Jensen, B., Stemmler, E. A., Wheeler, M. C., Frederick, B. G., van Heiningen, A., Berg, A. G., and DeSisto, W. J. (2010). "Fast pyrolysis of lignins," *BioRes.* 5(3), 1408-1424.

Bi, X., Sheng, G., Feng, Y., Fu, J., and Xie, J. (2005). "Gas- and particulate-phase specific tracer and toxic organic compounds in environmental tobacco smoke," *Chemosphere* 61, 1512-1522.

Bridgeman, T. G., Darvell, L. I., Jones, J. M., Williams, P. T., Fahmi, R., Bridgwater, A. V., Barraclough, T., Shield, I., Yates, N., Thain, S. C., and Donnison, I. S. (2007). "Influence of particle size on the analytical and chemical properties of two energy crops," *Fuel* 86, 60-72.

Bridgwater, T. (2006). "Biomass for energy," *J. Sci. Food Agric.* 86, 1755-1768.

Brown, T. M., Duan, P., and Savage, P. E. (2010). "Hydrothermal liquefaction and gasification of *Nannochloropsis* sp.," *Energ. Fuel* 24, 3639-3646.

Karagoz, S. (2009). "Energy production from the pyrolysis of waste biomasses," *Int. J. Energy Res.* 33(6), 576-581.

Liu, C., Feng, S., van Heemst, J., and McAdam, K. G. (2010). "New insights into the formation of volatile compounds in mainstream cigarette smoke," *Anal. Bioanal. Chem.* 396-5, 1817-1830.

McGrath, T. E., Brown, A. P., Meruva, N. K., and Chan, W. G. (2009). "Phenolic compound formation from the low temperature pyrolysis of tobacco," *J. Anal. Appl. Pyrol.* 84, 170-178.

Oja, V., Hajaligol, M. R., and Waymack, B. E. (2006). "The vaporization of semi-volatile compounds during tobacco pyrolysis," *J. Anal. Appl. Pyrol.* 76, 117-123.

Putun, A. E., Onal, E., Uzun, B. B., and Ozbay, N. (2007). "Comparison between the "slow" and "fast" pyrolysis of tobacco residue," *Ind. Crop Prod.* 26, 307-314.

Rodgman, A., and Perfetti, T.A. (2008). "Introduction," in: *The Chemical Components of Tobacco and Tobacco Smoke*, Taylor & Francis Group: CRC Press.

Seeman, J. I., Fournier, J. A, Paine III, J. B., and Waymack, B. E. (1999). "The form of nicotine in tobacco. Thermal transfer of nicotine and nicotine acid salts to nicotine in the gas phase," *J. Agric. Food Chem.* 47 (12), 5133-5145 and references therein.

Samolada, M. C., Stoicos, T., and Vasalos, I. A. (1990). "An investigation of the factors controlling the pyrolysis product yield of Greek wood biomass in a fluidised bed," *J. Anal. Appl. Pyrol.* 18, 127-141.

Schlotzhauer, W. S., Chortyk, O. T., and Austin, P. R. (1976). ''Pyrolysis of chitin, potential tobacco extender," *J. Agric. Food Chem.* 24-1, 177-180.

Sharma, R. K., Wooten, J. B., Baliga, V. L., Martoglio-Smith, P. A., and Hajaligol, M. R. (2002). "Characterization of char from the pyrolysis of tobacco," *J. Agric. Food Chem.* 50, 771-783.

Stojanowska, G., and Jones, J. M. (2005). "Influence of minerals and added calcium on the pyrolysis and co-pyrolysis of coal and biomass," *J. Energy Inst.* 78(3), 126-138.

Williams, P. T., and Nugranad, N. (2000). "Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks," *Energy* 25-6, 493-513.

Xu, C., and Lad, N. (2008). ''Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water," *Energ Fuel* 22, 635-642.

Yi, S. C, Hajaligol, M. R., and Jeong, S. H. (2004). "The prediction of the effects of tobacco type on smoke composition from the pyrolysis modeling of tobacco shreds," *J. Anal. Appl. Pyrol*. 74(1-2), 181-192.

Article submitted: November 17, 2010; Peer review completed: March 11, 2011; Revised version received and accepted: March 14, 2011; Published: March 16, 2011.