

## PYROLYSIS OF TOBACCO RESIDUE. PART 2: CATALYTIC

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The pyrolysis of tobacco residue in the presence of metal oxides and metal chlorides was investigated at 300, 400, and 500 °C. Catalysts used were Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, AlCl<sub>3</sub>, and SnCl<sub>4</sub> in concentrations from 1 up to 5 wt% of the tobacco residue feedstock. The amount of catalysts and the pyrolysis temperature had significant effect on both product distributions and bio-oil composition. The catalytic effect was dominant at the lowest temperature (300 °C). The pyrolysis temperature was decreased by 200 °C compared to the thermal run. Bio-oil contained a large variety of compounds. Nicotine, which is very stable until temperatures in excess of 600 °C, could be degraded at the lowest temperature by using 1 wt% of AlCl<sub>3</sub> and 1 wt% of Fe<sub>2</sub>O<sub>3</sub>.

*Keywords:* Tobacco residue; Metal oxide; Metal chlorides; Pyrolysis; Bio-char

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### INTRODUCTION

In recent years, biomass has attracted considerable attention all over the world, as it represents a renewable energy source. Biomass is composed mainly of hemicellulose, cellulose, and lignin and may contain minor amounts of other organic and inorganic species depending on the type of biomass. The production of fuels and/or valuable chemicals from biomass is achieved by thermochemical conversion. Thermochemical conversion of biomass includes pyrolysis, gasification, and combustion processes (Bridgwater 2006). Biomass can be converted liquid (bio-oil), solid (bio-char), and gaseous products from pyrolysis. The most commonly used technologies for thermochemical conversion of biomass is pyrolysis, due to its high efficiency. Biomass resources are mainly in the form of wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste, pulp process wastes, and so on. Incineration of agricultural byproducts and residues results in the loss of their energy content. Therefore, production of value-added chemicals or fuels from agricultural residue via thermochemical conversion is very important for sustainable energy and society. Agricultural byproducts and residues can be considered as an important biofuel feedstock.

Tobacco is one of the most valuable agricultural products (Rodgman and Perfetti 2008). A great number of investigations have been carried out for the pyrolysis of tobacco, tobacco components, and tobacco additives. Most of the early studies on pyrolysis of tobacco (Senneca et al. 2007), tobacco components (Baliga et al. 2003), and tobacco additives (Baker and Bishop 2004) were focused on determining the chemical compounds of tobacco smoke in order to determine the effect of tobacco smoke on human health.

There is limited information available in the literature about liquid products from the pyrolysis of tobacco (McGrath et al. 2009) and tobacco residues (Putun et al. 2007), and these studies concerned non-catalytic pyrolysis processing. There has been a plethora of research on the efforts to use solid acid and base catalysts for the pyrolysis of biomass (Aho et al. 2007; Chen et al. 2008; Iliopoulou et al. 2007; Müller-Hagedorn et al. 2003; Zhong and Wei 2004). Aho et al. (2007) investigated the effect of  $\beta$ -zeolites with varying silica to alumina ratio on the pyrolysis of pine wood. It was reported that the chemical composition of biomass was changed depending on the type of catalysts. Two mesoporous aluminosilicate Al-MCM-41 materials (Si/Al = 30 or 50) were used as catalysts for the pyrolysis of wood. It was found that the use of Al-MCM-41 catalytic materials increased the concentration of phenolic compounds and decreased the concentration of corrosive acids. The catalytic effect of pH-neutral inorganic salts on the pyrolysis temperature of three different wood species was researched (Müller-Hagedorn et al. 2003). It was reported that sodium and potassium chloride have a remarkable effect on the pyrolysis temperature and on the product distribution.

The purposes of the present study are:

1. to obtain valuable chemicals and/or biofuels via catalytic pyrolysis.
2. to explore metal oxides and metal chlorides for liquefaction of tobacco residue.
3. to compare cracking abilities of metal oxide and metal chlorides for degradation of tobacco residue under identical conditions.
4. to identify liquid products from the pyrolysis of tobacco residue in the presence of metal oxide and metal chlorides.

For this purpose, the pyrolysis of tobacco residue in the presence of metal oxides and metal chlorides was investigated at 300, 400, and 500 °C. Additives used were  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AlCl}_3$ , and  $\text{SnCl}_4$  in concentrations from 1 up to 5 wt% of the tobacco residue feedstock. The effects of catalyst type and concentration on product distributions and the compositions of bio-oil obtained from the pyrolysis of tobacco residue were investigated.

## EXPERIMENTAL

### Materials

A tobacco residue sample (particle size is between 1 mm and 10 mm) that had been rejected from packaging tobacco stem was kindly provided by European Tobacco Company, Mersin, Turkey. The properties of the tobacco residue sample can be found elsewhere (Akalin and Karagöz 2011). All chemicals and solvents used in this study were of analytical grade. Anhydrous  $\text{AlCl}_3$  (purity grade  $\geq 98$ , in powder form),  $\text{Al}_2\text{O}_3$  (particle size 70% between 0.063 and 0.2 mm),  $\text{Fe}_2\text{O}_3$  (in powder form) were purchased from Merck. Anhydrous  $\text{SnCl}_4$  (purity grade 99%) was purchased from Aldrich.  $\text{SnCl}_4$  is a colorless liquid with density 2.226g/cm<sup>3</sup>.

## Methods

### *Pyrolysis procedure*

Pyrolysis experiments were carried out in relation to different pyrolysis temperatures between 300 and 500 °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<sup>-1</sup> for 30 min to remove air inside, and the purging the nitrogen was fixed to 30 mL min<sup>-1</sup> and continued at the end of reaction completed, which includes cooling down of the reactor to the room temperature. The pyrolysis reactor was a fixed bed design of stainless steel with 6 cm diameter and 2 cm height. The pyrolysis vapors on exiting the reactor were passed through three condensers. The first two condensations were provided with glass condensers cooled with a water and ice mixture. The third condenser was cooled using water. Tobacco residue sample of 25 g (dry basis) and the required amount of catalysts in concentrations 1, 2.5, and 5wt% of the tobacco residue feedstock was placed into the reactor. The system was heated at a rate of 5 °C min<sup>-1</sup> to the desired temperature, and it was held at that desired temperature for 60 min. The volatile products were swept by nitrogen gas (30 mL min<sup>-1</sup>) 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 3wt% for liquid, solid, and gas yields.

### *Analysis procedure*

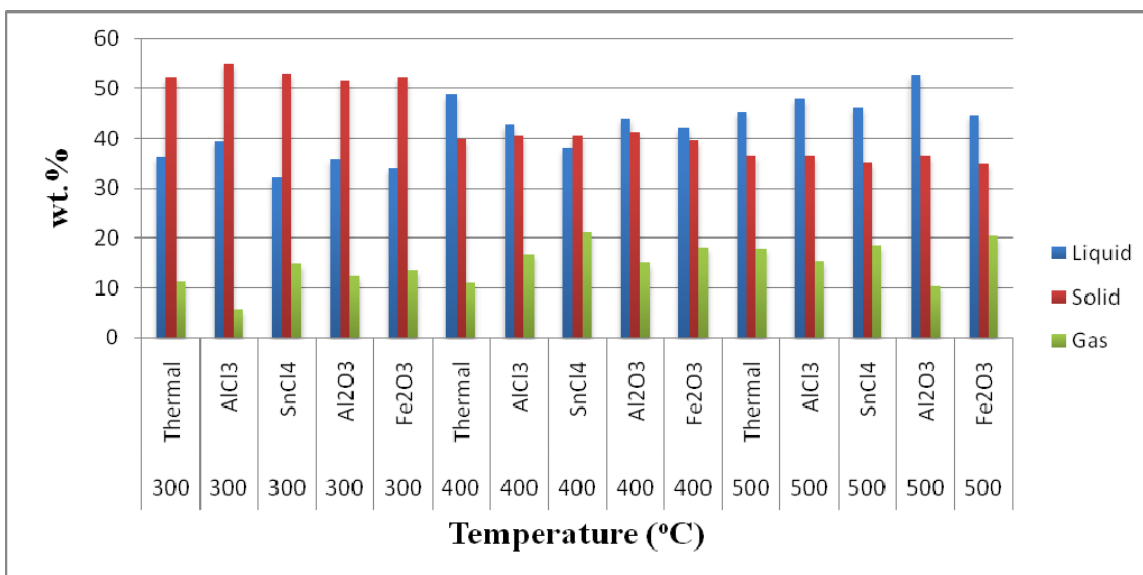
Liquid products were extracted with an equal quantity of diethyl ether. The ethereal solutions thus obtained were dried over anhydrous sodium sulfate, filtered, and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was called diethyl ether extract (bio-oil). 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 5 min, then raised to 250 °C at a rate of 8 °C/min and held for 15 min, then raised to 300 °C at a rate of 15 °C/min, and held at this final temperature for 10 min. The injector temperature was 250 °C with split mode. A 1 ml min<sup>-1</sup> of helium was used as the carrier gas. The end of the column was directly introduced into the ion source of an Agilent 5973 series mass selective detector operated in the electron impact ionization mode. The data acquisition system used was G1035A software with a NIST library.

Selected bio-chars were analyzed in terms of their elemental analysis using a LECO CHNS 932. Higher heating value of the selected bio-chars was calculated according to the Dulong formula.

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

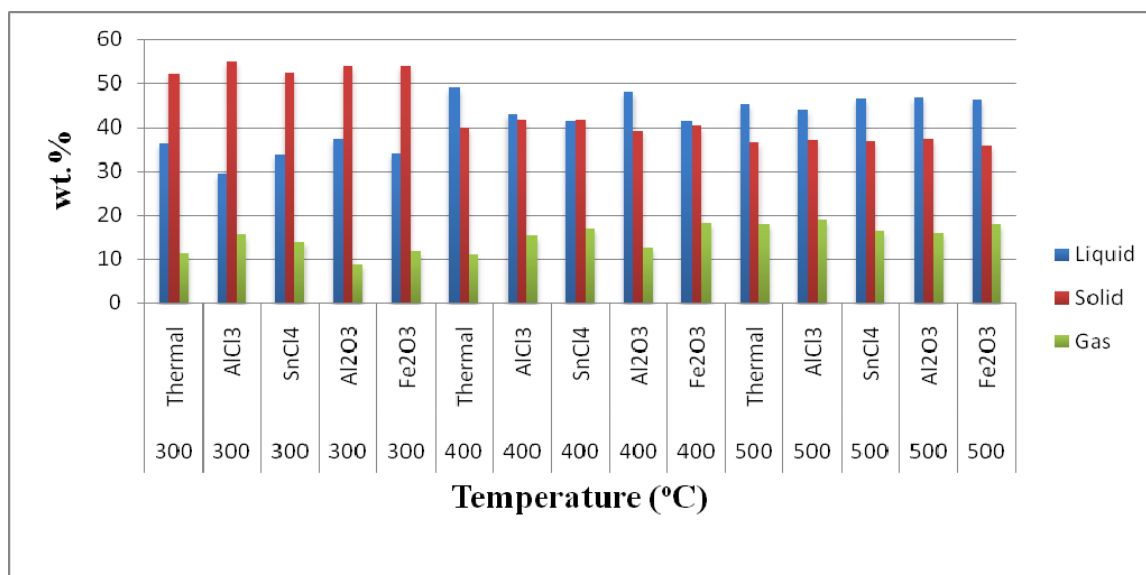
## RESULTS AND DISCUSSION

The results from the pyrolysis of tobacco residue in the absence and presence of metal chloride ( $\text{AlCl}_3$ , and  $\text{SnCl}_4$ ) and metal oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) in concentration 1wt% of the tobacco residue sample at the temperatures of 300, 400, and 500 °C are presented in Fig. 1. As can be seen from Fig. 1, both temperature and catalyst type affected the product distributions. At the temperature of 300 °C, the liquid yield was the highest in the case of  $\text{AlCl}_3$ , whereas other tested catalysts produced less liquid products than that of thermal run. The solid residue yield was higher than 50wt% for all runs at 300 °C. With increasing temperature from 300 to 400 °C, an increase in liquid yields and a decrease solid residue yields were observed for all tested runs. When the temperature was increased to 400 °C, the formation of more gaseous products took place, as expected for all catalytic runs. The slow pyrolysis pine wood was investigated in a static batch reactor in relation to different pyrolysis temperatures between 300 to 720 °C (Williams and Besler 1996). It was reported that when the pyrolysis temperature was increased, the yield of solid char decreased, while gas and oil product yields increased. Our results are in good agreement with this previous study. Further increase in the temperature (to 500 °C) led to the formation of more liquid products for all catalytic runs. The thermal run gave a slightly less liquid product at 500 °C than that of 400 °C. The  $\text{Al}_2\text{O}_3$  gave the highest liquid yield among the catalysts used. The yields of bio-char decreased when the temperature was increased for all runs. Similar results have been reported in the literature (Apaydin-Varol et al. 2007). Slow pyrolysis of pistachio shell was carried out in a fixed-bed reactor in relation to different pyrolysis temperatures between 300 to 700 °C (Apaydin-Varol et al. 2007). It was shown that the increase in temperature led to decrease bio-char yield and the lowest char yield was obtained at 700 °C.



**Figure 1.** Product distributions from the pyrolysis of tobacco residue in the absence and presence of metal chloride ( $\text{AlCl}_3$ , and  $\text{SnCl}_4$ ) and metal oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) in concentration 1wt% of the tobacco residue sample at the temperatures of 300, 400, and 500 °C. The results for the thermal run were taken from (Akalin and Karagöz 2011) for purpose of comparison.

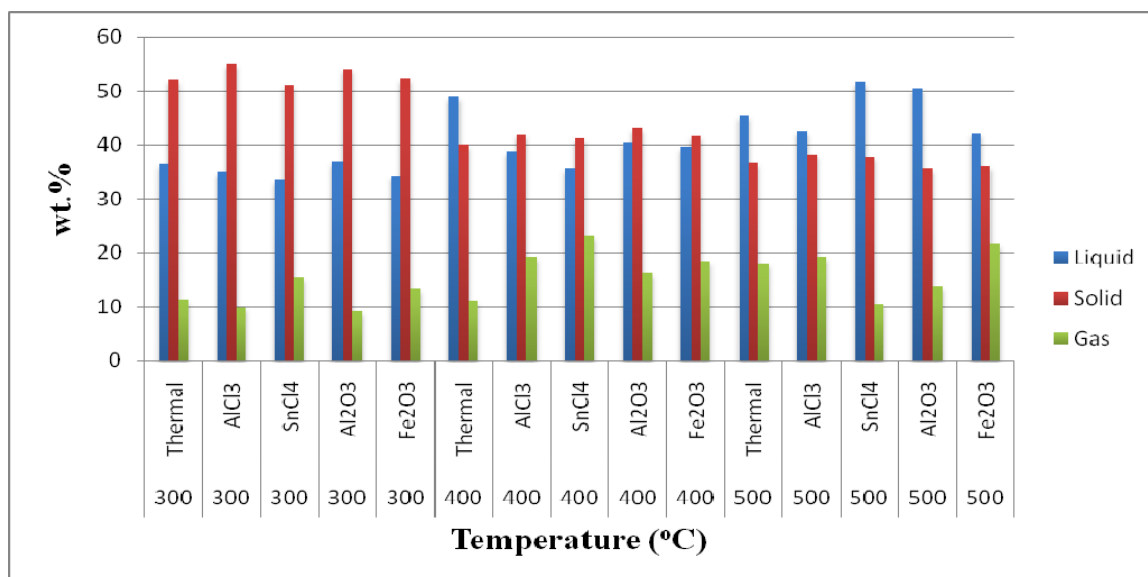
Figure 2 presents the product distributions of tobacco residue samples in the presence of 2.5wt% catalysts. The product distributions from thermal pyrolysis of tobacco residue sample were also incorporated into Fig. 2 for comparison purpose. When the temperature was increased from 300 to 400 °C, the yields of liquid products increased and the yields of solid residue decreased for all runs including the thermal run. Further increase in the temperature (from 400 °C to 500 °C) led to degradation of liquids and formation of more gas products in the cases of thermal run and Al<sub>2</sub>O<sub>3</sub>. The other tested catalysts produced more liquid products. This might be due to differences in interaction between tobacco residue and other tested catalysts. When the temperature was increased from 400 to 500 °C, the yields of solid char products decreased for all runs. The maximum gas yield (19.01wt %) at 500°C was obtained over AlCl<sub>3</sub>.



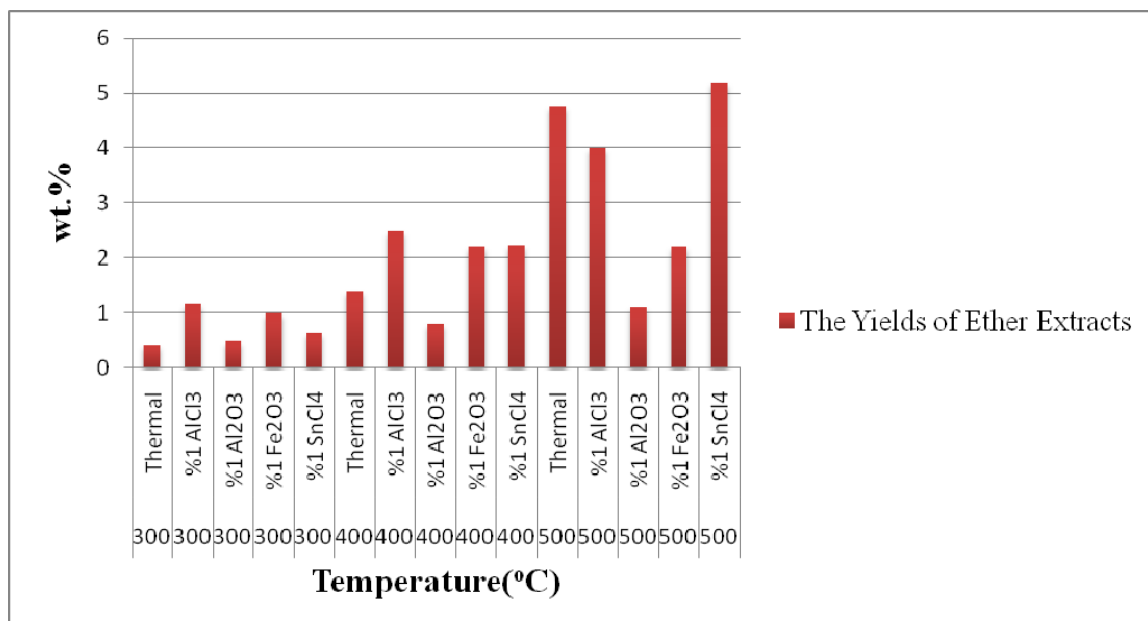
**Figure 2.** Product distributions from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 2.5wt% of the tobacco residue sample at 300, 400, and 500 °C. The results belong to thermal run was taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.

Figure 3 presents the product distributions of tobacco residue sample in the presence of 5wt% catalysts. When the temperature was increased from 300 to 400 °C and further increase to 500 °C, an increase in liquid yields and a decrease solid residue yields were observed for all catalytic runs. The maximum liquid yield (51.70wt%) was obtained over SnCl<sub>4</sub>, whereas Fe<sub>2</sub>O<sub>3</sub> gave the lowest liquid yield at 500 °C. The maximum gas yield was also obtained over Fe<sub>2</sub>O<sub>3</sub> at 500 °C.

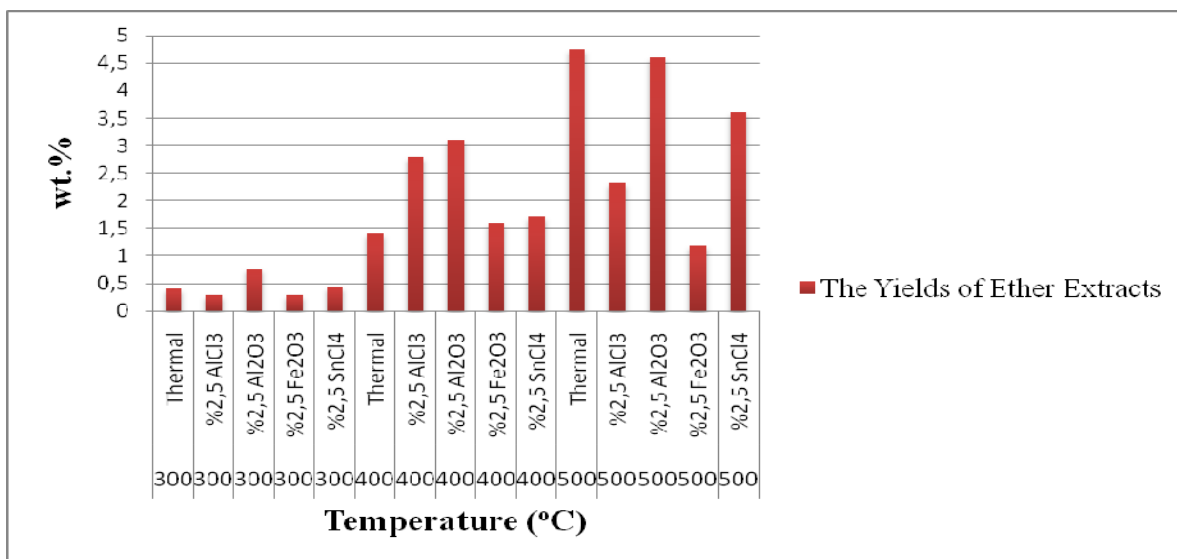
The yields of ether extracts from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 1, 2.5 and 5wt% of the tobacco residue sample at the temperatures of 300, 400, and 500 °C are presented in Figs. 4, 5, and 6, respectively. The increase in the temperature led to the formation of more ether extracts in the cases of 1 and 5wt% catalysts loading. In the cases of 2.5wt% loading of Fe<sub>2</sub>O<sub>3</sub> and AlCl<sub>3</sub>, the ether extract yields decreased when the temperature was increased from 400 to 500 °C. The maximum ether extract yield was obtained from SnCl<sub>4</sub> at 500°C in the case of 1wt% loading.



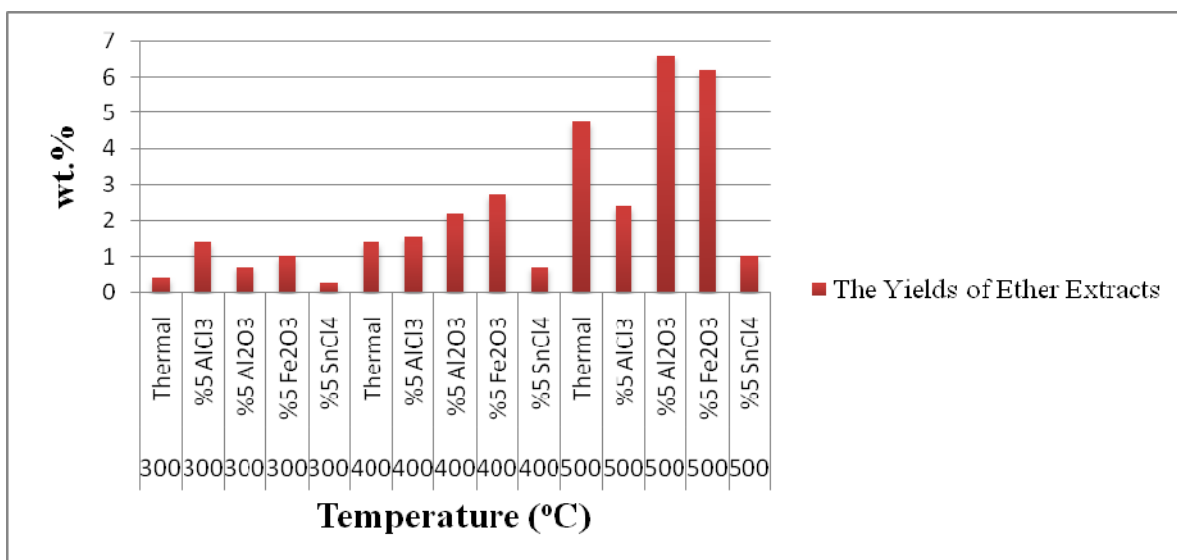
**Figure 3.** Product distributions from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 5wt% of the tobacco residue sample at the temperatures of 300, 400, and 500°C. The results belong to thermal run was taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.



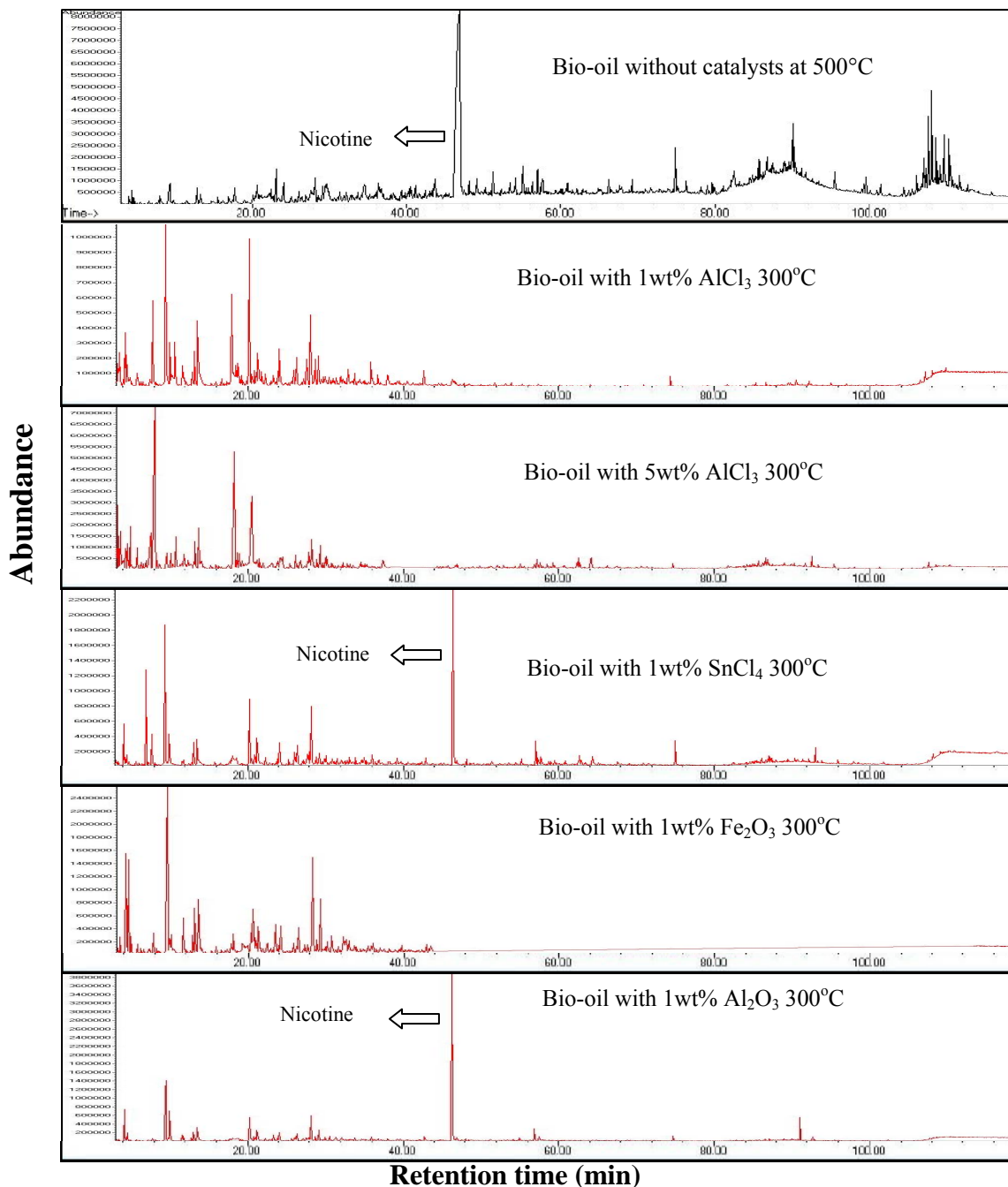
**Figure 4.** The yields of ether extracts from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 1wt% of the tobacco residue sample at the temperatures of 300, 400, and 500 °C. The results belong to thermal run was taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.



**Figure 5.** The yields of ether extracts from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 2.5wt% of the tobacco residue sample at the temperatures of 300, 400 and 500°C. The results belong to thermal run was taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.



**Figure 6.** The yields of ether extracts from the pyrolysis of tobacco residue in the absence and presence of metal chloride (AlCl<sub>3</sub>, and SnCl<sub>4</sub>) and metal oxide (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) in concentration 5wt% of the tobacco residue sample at the temperatures of 300, 400, and 500 °C. The results belong to thermal run was taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.



**Figure 7.** Total ion chromatograms of bio-oil obtained from thermal and catalytic runs

Figure 7 shows total ion chromatograms of ether extracts obtained at 300 °C with catalysts 1wt% loading and at 500 °C without catalysts. It can be seen clearly that the spectrum of the ether extract of thermal run revealed hydrocarbons of longer chain (longer residence time) than those of catalytic runs. The selectivity of the catalysts is poor. Kaminsky and Zorriquetta (2007) carried out catalytic pyrolysis of polyolefins in the



presence of Lewis acids and mixtures of Ziegler–Natta catalyst such as  $\text{AlCl}_3$  and  $\text{TiCl}_4$ . It was reported that the use of catalysts increased the amount of light oil fraction. Both from the previous report (Kaminsky and Zorriquetta 2007) and the present study, it can be concluded that these types of catalysts are effective on the degradation of both synthetic polymers and biomass. By using catalysts, the pyrolysis temperature could be decreased by 200 °C. 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. The degradation of nicotine at 300 °C in the presence of 1wt% of  $\text{AlCl}_3$  and 1wt% of  $\text{Fe}_2\text{O}_3$  shows that they have more cracking ability than  $\text{Al}_2\text{O}_3$  and  $\text{SnCl}_4$  under identical conditions, as the ether extracts contained nicotine in the cases of 1wt% loading of  $\text{Al}_2\text{O}_3$  and 1wt% loading of  $\text{SnCl}_4$ .

GC–MS analysis was carried out to identify compounds of bio-oils (ether extracts) from the pyrolysis tobacco residue in the absence and presence of catalysts. The identified compounds were classified and set out in Table 1. The results of chromatographic areas (percentage of total area) belong to identified compounds. The variation in bio-oil compositions depended on the concentration of catalyst and the type of catalysts. As can be seen from Table 1, various compounds, namely N-containing compounds, phenols, acids and esters, aldehydes and ketones, benzene derivatives, and alcohols, were observed in all runs. The relative concentrations of phenolic compounds were the highest in the case of  $\text{AlCl}_3$  at 300 °C with the amount of catalyst 1wt%. It is considered that most of the phenolic compounds were produced from the decomposition of lignin. The total relative concentration of aldehydes and ketones were higher in the case of catalytic runs than that of the thermal run at 300 °C. The relative concentrations of alcohols were the highest in the case of  $\text{Fe}_2\text{O}_3$  at 300 °C with the amount of catalyst 1wt%. Propylene glycol and 3-furan methanol were observed in all catalytic runs, whereas these compounds were not observed in the thermal run (see Appendix). The pyrolysis of two brown macro algae and one red macro algae was investigated at the temperatures of 300, 400, 500, and 600 °C (Bae et al. 2011). The organic phase contained a large variety of compounds i.e. phenols, nitrogen containing compounds, alkanes, benzene derivatives, alcohols, and so on. Catalytic pyrolysis of pine wood was carried out at 300, 350, 400, and 700 °C in the presence of  $\text{K}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$  (Wang et al. 2010). Identified compounds in organic phase consisted of cyclopentenones, furans, saccharides, ketones, aldehydes, alkenes, acids, alcohols, and phenols. Fast pyrolysis of rice husk was carried out and phase separations of the bio oil were performed by adding inorganic salts into bio oils (Song et al. 2009). Some of the identified compounds in whole bio-oil, upper layer, and the bottom layer were acids, aldehydes, ketones, and phenols. The relative concentrations of the identified compounds in upper layer and the bottom layer were different from each other. Although the type of biomass and the pyrolysis conditions in the previous studies mentioned above were different from our experimental conditions (the type of biomass and pyrolysis conditions), most of the identified compounds in the ether extracts from catalytic and thermal pyrolysis of tobacco residue was found similar. Some compounds such as (S)-3-(1-methyl-2-pyrrolidinyl)-pyridine, and pyrazine derivatives) are special to tobacco residue sample.

**Table 1.** Classification of Identified Compounds in Bio-oils (ether extracts) from the Pyrolysis of Tobacco Residue in the presence of Metal Oxides and Metal Chlorides (See Appendix for detail information).

Type of Compounds	Area, %											
	None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
	500°C	300°C (1wt%)	300°C (2,5wt%)	300°C (5wt%)	400°C (1wt%)	500°C (1wt%)	300°C (1wt%)	500°C (5wt%)	300°C (1wt%)	500°C (5wt%)	300°C (1wt%)	500°C (5wt%)
<i>Alkanes</i>	6.94	0.27		1.81	15.27	5.92	1.28	0.47	1.02	7.85	1.79	3.92
<i>Alkenes</i>	2.91	0.23		0.15	1.65	2.34			0.95	2.90	0.37	3.60
<i>Steroids</i>	4.17				2.65	2.33				2.01		1.22
<i>Phenols</i>	8.23	14.63	12.54	12.27	19.03	15.30	15.75	6.60	9.13	13.99	12.69	17.59
<i>N-containing compounds</i>	41.23	15.35	22.59	8.02	28.46	34.30	25.36	58.96	15.94	39.99	41.95	31.81
<i>Acids and Esters</i>	1.9	0.85	0.52	3.42	0.44	0.97	0.81	0.52	2.44	0.57	1.96	0.26
<i>Aldehydes and Ketones</i>	2.61	22.74	13.46	35.81	0.44	1.73	11.03	8.75	14.35	4.77	9.48	3.11
<i>Benzene Derivatives</i>	0.46	3.49	0.41	1.45	2.01	3.23	2.92	1.55	1.57	1.34	4.88	2.35
<i>Alcohols</i>	2.07	12.26	14.49	4.59	0.83	1.78	15.79	9.26	22.61	3.13	16.85	1.71
<i>PAHs</i>	1.25				1,12	1,91				0.84		0.98
<i>Vitamin E</i>	3.12				2.21	1.82				1.52	0.13	1.62
<i>Others</i>	1.06		0.43	1.4								
<b>TOTAL</b>	<b>77.16</b>	<b>69.82</b>	<b>64.44</b>	<b>68.92</b>	<b>74.11</b>	<b>71.63</b>	<b>72.94</b>	<b>86.11</b>	<b>68.01</b>	<b>78.91</b>	<b>90.1</b>	<b>68.17</b>

<sup>a</sup> taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.

The elemental compositions of the selected bio-chars from catalytic and thermal pyrolysis of tobacco residue are shown in Table 2. The results for elemental compositions of the selected bio-chars are given on a dry basis, ash free. The amount of carbon was the highest in the case of  $\text{AlCl}_3$  at  $500^\circ\text{C}$  with the amount of catalyst 1wt%, whereas it was found to be the lowest in the case of  $\text{SnCl}_4$  at  $300^\circ\text{C}$  with the amount of catalyst 1wt%. In catalytic runs, HHV values for bio-chars were found between 21.48 and  $26.24 \text{ MJ kg}^{-1}$ . The HHV value for the bio-char obtained from thermal run was higher than those of catalytic runs.

**Table 2.** Elemental Analysis of Selected Bio-chars

Type of bio-char	Elemental Compositions, (daf <sup>a</sup> , wt.%)					
	C	H	N	S	O <sup>b</sup>	HHV <sup>c</sup> , ( $\text{MJ.kg}^{-1}$ )
Thermal*	75.77	3.41	4.98	1.07	14.77	27.94
$300^\circ\text{C}$ 1wt% $\text{AlCl}_3$	67.93	4.14	3.53	0.66	23.74	24.70
$300^\circ\text{C}$ 5wt% $\text{AlCl}_3$	63.60	3.78	3.08	0.47	29.07	21.75
$400^\circ\text{C}$ 1wt% $\text{AlCl}_3$	67.75	2.76	2.71	0.71	26.07	22.25
$500^\circ\text{C}$ 1wt% $\text{AlCl}_3$	76.98	1.95	2.93	0.74	17.4	25.77
$300^\circ\text{C}$ 1wt% $\text{SnCl}_4$	62.68	3.88	3.24	0.54	29.66	21.48
$500^\circ\text{C}$ 5wt% $\text{SnCl}_4$	74.39	2.00	2.89	0.39	20.33	24.41
$300^\circ\text{C}$ 1wt% $\text{Fe}_2\text{O}_3$	71.83	3.9	3.08	0.64	20.55	26.24
$500^\circ\text{C}$ 5wt% $\text{Fe}_2\text{O}_3$	73.92	1.68	2.40	0.89	21.11	23.70
$300^\circ\text{C}$ 1wt% $\text{Al}_2\text{O}_3$	69.60	4.02	3.22	0.61	22.55	25.30
$500^\circ\text{C}$ 5wt% $\text{Al}_2\text{O}_3$	71.22	1.84	2.68	0.56	23.7	22.52

<sup>a</sup> daf: Dry basis ash free

<sup>b</sup> By difference

<sup>c</sup> Higher Heating Value (HHV) calculated by the Dulong Formula, that is,  
 $\text{HHV} = 0.338\text{C} + 1.428(\text{H}-\text{O}/8) + 0.095\text{S}$

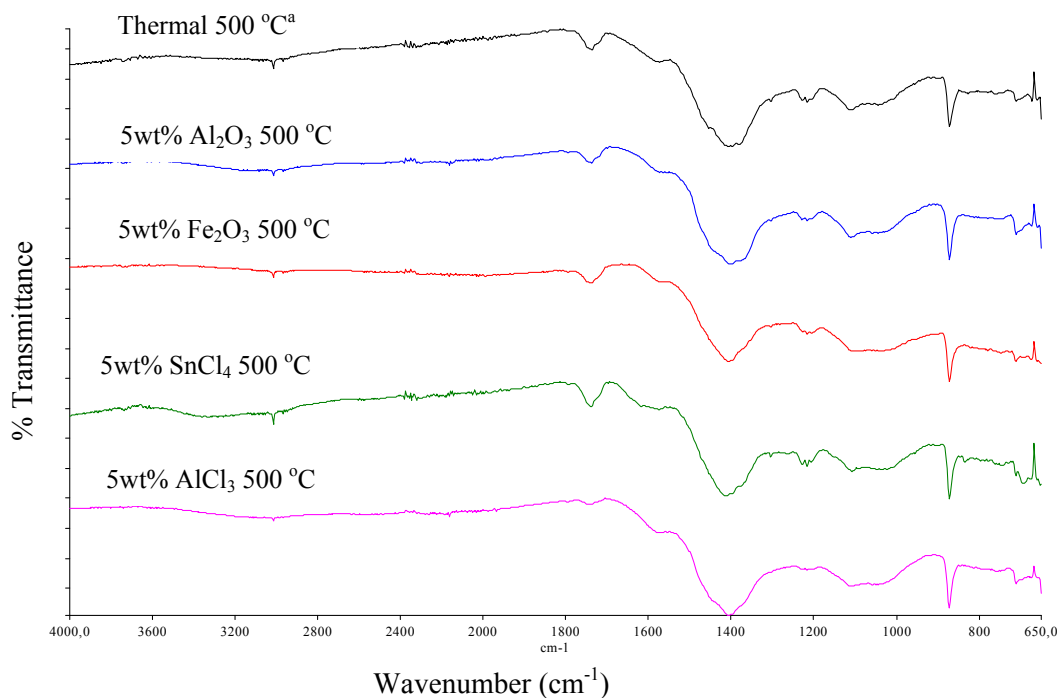
\* taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.

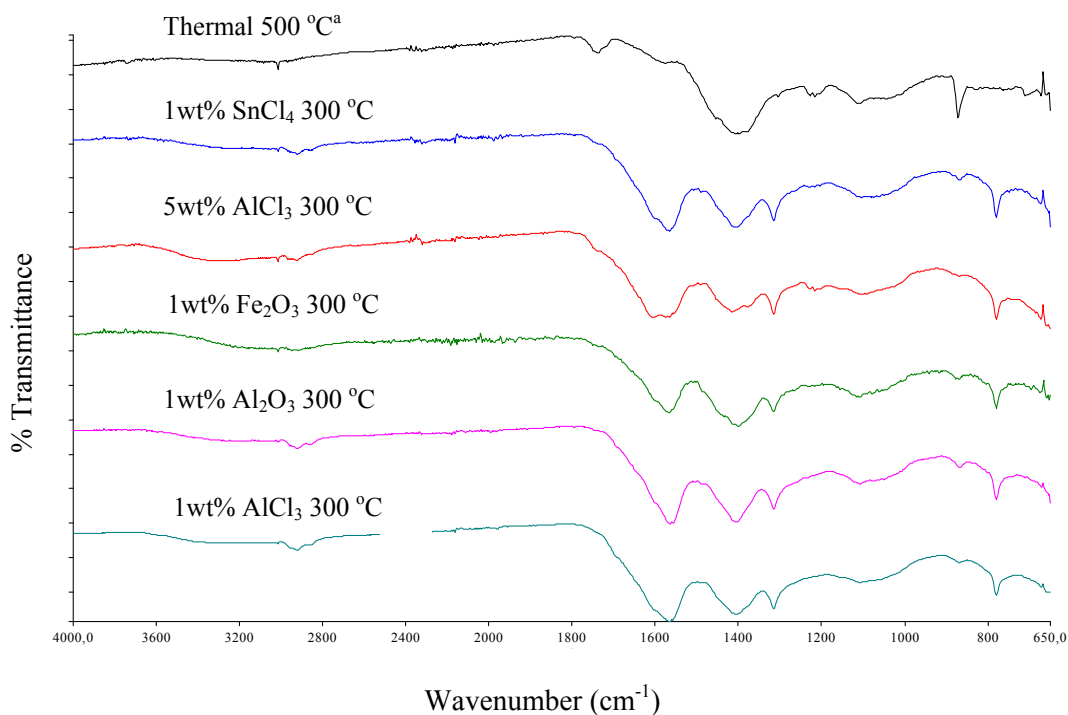
Table 3 shows the ash contents of the selected bio-chars produced from catalytic runs. As can be seen from Table 3, the ash contents of the bio-chars were changed depending on both temperature and the type of additives. The ash contents of the bio-char were increased by increasing both the temperature and catalyst amount.

. **Table 3.** Ash Contents of the Selected Bio-chars

Type of bio-char	Ash, (dry basis, wt. %)
300 °C 1wt% AlCl <sub>3</sub>	27.32
300 °C 5wt% AlCl <sub>3</sub>	29.70
400 °C 1wt% AlCl <sub>3</sub>	35.90
500 °C 1wt% AlCl <sub>3</sub>	39.00
300 °C 1wt% SnCl <sub>4</sub>	24.60
500 °C 5wt% SnCl <sub>4</sub>	39.60
300 °C 1wt% Fe <sub>2</sub> O <sub>3</sub>	28.93
500 °C 5wt% Fe <sub>2</sub> O <sub>3</sub>	43.90
300 °C 1wt% Al <sub>2</sub> O <sub>3</sub>	29.44
500 °C 5wt% Al <sub>2</sub> O <sub>3</sub>	42.50

Functional group analysis the selected bio-chars was carried out with FTIR spectrometry. Figure 8 shows the FTIR spectra of the selected bio-chars obtained from the thermal run and obtained from catalytic run ( at 500°C with the amounts of catalyst of 5wt%).

**Figure 8.** FTIR spectra of the selected bio- chars



**Figure 9.** FTIR spectra of the selected bio-chars ( <sup>a</sup> taken from the reference (Akalin and Karagöz 2011) for purpose of comparison.

As can be seen from Fig. 8, the FTIR spectra of catalytic runs and thermal run were the same. The peak at  $1731\text{ cm}^{-1}$  wavenumber is assigned to the formation of carbonyl groups. The peak at  $873\text{ cm}^{-1}$  represents wagging of aromatic CH groups. Absorption seen at  $1400\text{ cm}^{-1}$  wavelength represents mostly aromatic bands. Figure 9 shows the FTIR spectra of the selected bio-chars obtained from thermal run and obtained from catalytic run (at  $300\text{ °C}$  with the amounts of catalyst of 1wt%). The main difference between the FTIR spectra of thermal run and the FTIR spectra of catalytic runs is that the peak representing the carbonyl groups at  $1731\text{ cm}^{-1}$  wavenumber was lost in catalytic runs at  $300\text{ °C}$  with the amounts of catalyst of 1wt%. The other characteristic bands in the FTIR spectra of catalytic runs (at  $300\text{ °C}$  with the amounts of catalyst of 1wt%) were almost the same with the FITR spectra of thermal run and catalytic runs at  $500\text{ °C}$  with the amounts of catalyst of 5 wt%.

## CONCLUSIONS

1. The use of metal oxide ( $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ ), and metal chlorides ( $\text{AlCl}_3$ , and  $\text{SnCl}_4$ ) in the pyrolysis of tobacco residue reduced the pyrolysis temperature significantly.
2. The use of a small amount of catalysts (1wt%) had significant effect on the composition of bio-oils. The spectrum of the ether extract of thermal run contained hydrocarbons of longer chain (longer residence time) than those of catalytic runs.
3. The use of higher amount of catalysts (5wt%) at the highest temperature ( $500\text{ °C}$ ) decreased the catalytic activity.

4. The degradation of nicotine at 300 °C in the presence of 1wt% of AlCl<sub>3</sub> and 1wt% of Fe<sub>2</sub>O<sub>3</sub> showed that they have more cracking ability than Al<sub>2</sub>O<sub>3</sub> and SnCl<sub>4</sub> under identical conditions.
5. The HHV value of bio-char obtained from the pyrolysis of tobacco residue in the presence of Fe<sub>2</sub>O<sub>3</sub> with the amount of catalyst of 1wt% at 300 °C was the highest.
6. The FTIR spectra of catalytic runs at 300 °C with the amounts of catalyst of 1wt% showed that there are no any carbonyl groups. The overall spectrum of selected biochars indicated the presence aromatic character, predominantly.
7. The ash contents of the bio-char were increased by increasing both the temperature and catalyst amount.

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**Appendix (Expanded Version of Table 1).** Identified Compounds in Bio-oils (ether extracts) from the Pyrolysis of Tobacco Residue in the presence of metal oxides and metal chlorides.

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Alkanes</i>														
21.17	91	Decane						0.11						0.14
29.29	76	Bicyclo[3.3.1]nonane				1.09				0.34	1.02		1.42	0.66
36.77	83	Dodecane						0.42				0.25		0.30
37.76	89	2,6-Dimethyl- undecane						0.22				0.13		0.20
43.75	93	Tridecane						0.32				0.25		0.30
49.75	94	Cyclododecane						0.06						
50.33	94	Tetradecane	0.68			0.03	1.69	0.88				0.36		
56.45	95	Pentadecane	0.59				0.86	0.50	0.12			0.45		0.52
62.14	96	Hexadecane						0.18				0.34		0.18
67.67	95	Heptadecane	0.15				1.36		0.08					0.52
72.89	86	Octadecane				0.16	0.90	1,29	0.48			1.44		0.18
95.59	97	Tetracosane					0.88		0.07					0.46
95.64	99	Docosane	0.49			0.09	0.26		0.19	0,03			0.05	



## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Alkanes (continued)</i>														
101.59	99	Octacosane	1.02				2.55	0.76				0.53		
104.64	97	Pentacosane	0.46					0.46						
107.16	96	Heneicosane				0.09	1.87	0.72				1.28		
107.18	97	Tricosane	0.79											
107.61	97	Nonadecane	1.88				1.40							
107.73	92	Eicosane		0.27		0.18	0.52		0.34	0.10			0.32	0.46
107.78	98	Hentriacontane				0.17	2.72					2.82		
108.76	93	triacontane	0.88				0.26							
109.08	99	Dotriacontane	1.21											
Sum			6.94	0.27		1.81	15.27	5.92	1.28	0.47	1.02	7.85	1.79	3.92
<i>Alkenes</i>														
4.35	94	2-Methyl-1,3,5-hexatriene	0.04				0.15							
8.31	76	Trimethyl-1,3-cyclopentadiene	0.03				0.02							

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Alkenes (continued)</i>														
9.70	93	1,2-Dimethyl-4-methylene-cyclopentene	0.08											
9.84	95	2,5,5-Trimethyl-cyclopentadiene					0.12							
15.94	72	Methyl cycloheptene		0.23							0.23	0.16		
21.33	94	Cis-2,6-Dimethyl-2,6-octadiene							0.14					0.55
22.51	90	1-Methyl-4-(1-methylethyl)-cyclohexene							0.44			0.59		0.72
22.79	70	2,5-Dimethyl-2,4-hexadiene									0.51		0.24	
23.19	94	D- Limonene	0.96				0.34	1.28			0.21	2.15	0.13	2.08
27.32	76	1-Ethyl cyclohexene				0.15								
31.60	93	1-Phenyl-1-butene										0.15		
55.96	97	1-Pentadecene	0.25				1.02	0.48						0.25
61.73	94	1-Hexadecene												
75.26	90	[R-[R*,R*-(E)]]- 3,7,11,15-Tetramethyl-2-hexadecene	0.30											

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Alkenes (continued)</i>														
90.28	91	2,6,10,14,18-Pentamethyl- 2,6,10,14,18-eicosapentaene	1.25											
Sum			2.91	0.23		0.15	1.65	2.34			0.95	2.90	0.37	3.60
<i>Steroids</i>														
105.28	84	Cholesta-3,5-diene	0.37											
107.46	99	Stigmastan-3,5-diene	0.53				0.54	0.58				0.38		
108.48	94	Acetate(ester)-3,4-dedihydro- stigmasterol	0.22											
109.33	99	Campesterol	0.58				0.37	0.33				0.35		0.25
109.82	93	Stigmasterol	1.08				0.95	0.84				0.72		0.54
110.67	99	Sitosterol-.gama	0.66				0.79	0.58				0.56		0.43
110.93	99	Fucosterol	0.16											
111.85	95	Spinasterone	0.38											.
112.86	93	Stigmast-4-en-3-one	0.19											
Sum			4.17				2.65	2.33				2.01		1.22

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Phenols</i>														
20.53	94	Phenol	0.32	8.13	6.75	7.78	2.78	3.83	5.13	4.27	6.07	3.80	4.65	3.84
27.70	96	2-Methyl-phenol	1.01	0.83	0.23	0.67	1.61	2.18	0.90		2.19	0.67	0.92	2.29
27.87	97	4-Methyl phenol				1.17	1.93	0.10	0.73	0.46		1.84	0.70	1.55
28.29	95	2-Methoxy-phenol	0.89	3.44	2.14	1.38	0.91		4.61	1.69		1.50	4.03	2.37
29.62	95	3-Methyl-phenol	1.36	1.86				3.31	0.70			1.33		
29.63	91	2,6-Dimethyl-phenol						0.62				0.48		0.75
34.62	94	4-Ethyl-phenol				0.29	0.99	0.25	0.26	0.18		1.23	0.25	
34.74	96	2,4-Dimetyl-phenol	1.2			0.19	2.12	1.29	0.48		0.87	1.94	0.16	1.24
36.03	96	2-Methoxy-4-methyl- phenol			0.11	0.10	0.43							
36.19	91	2-Ethyl-5-methyl- phenol	0.22				0.47	0.74						
36.50	90	2-Ethyl- phenol	0.97	0.37		0.13	0.94		0.46			0.59		1.88
36.51	93	3,4-Dimethyl-phenol					0.32	1.48	0.19					0.23
39.77	87	4-Ethyl-2-methyl-phenol					1.91							

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Phenols (continued)</i>														
36.89	93	2,3-Dimethyl- phenol	0.24			0.10	1.82	0.20	0.74				0.38	
41.31	87	3-Ethyl-5-methyl-phenol	0.88				0.84						1.36	
43.10	81	2,3,5,6-Tetramethyl-phenol					0.53							
43.20	96	2,4,6-Trimethyl-phenol	0.20				1.17	1.18				0.61	0.48	
44.87	87	Diethyl-phenol					0.26							
47.00	93	2,6-Dimethoxy- phenol			0.30	0.22		0.12					0.44	
57.11	94	2,6-Bis(1,1-dimethylethyl)-4-methyl- phenol	0.94		3.01	0.24			1.55				1.54	
Sum			8.23	14.63	12.54	12.27	19.03	15.30	15.75	6.60	9.13	13.99	12.69	17.59
<i>N-containing compounds</i>														
4.03	87	Pyrazine		0.11	0.18									
4.37	91	Pyridine		2.1	3.35	4.51		0.25	0.52	0.97		0.37	0.40	0.35
4.52	90	Pyrrole	0.21			0.27		0.43	0.43	0.37	2.19	0.88	0.48	0.92
6.68	96	2-Methyl-pyridine	0.10		0.82	0.03		0.23	0.07	0.75	0.33	0.18		0.18

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>N-containing compounds (continued)</i>														
7.37	80	Methyl pyrazine		0.72	0.69									
4.29	81	4-Pyridine amine						0.49			0.42	0.07		
9.42	87	3-Methyl-pyridine	1.38	1.83				1.10			0.93	0.60	0.35	0.71
12.79	97	2-Ethyl pyridine	0.04							0.06	0.19			
13.32	93	2,6-Dimethyl pyrazine	0.04	3.16	3.77			0.06	0.57	0.81		0.12	0.80	
13.96	91	Ethyl pyrazine									0.54			
15.14	90	2,5-Dimethyl-1H -pyrrole						0.05				0.20		0.33
17.03	95	3-Ethyl pyridine	0.29		0.58			0.25	0.19	0.31	0.89		0.41	
17.40	93	2,5-Dimethyl pyridine			0.14			0.17			0.17			0.22
17.63	93	2,4-Dimethyl pyridine			0.47						0.21			
18.70	96	2,3-Dimethyl pyridine			0.96			0.01			0.07			
19.56	93	Benzonitrile						0.13			0.61			
21.14	90	2-Ethyl-6-methyl- pyrazine		0.67				0.12	0.58	0.25	0.91	0.08	0.58	

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>N-containing compounds (continued)</i>														
21.46	81	Trimethyl-pyrazine		1.20		0.12			0.35	2.60	0.95	1.96		2.17
21.48	93	1-Methyl-1H-Pyrrole-2-carboxaldehyde				0.57								
21.67	93	3-Pyridinecarbonitrile									0.16			
22.38	91	1H-Pyrrole-2-carboxaldehyde		0.85		1.20				0.69		1.11	0.26	0.59
23.69	83	1-(2-Pyridinyl)-ethanone								0.25		0.52		
26.40	94	1-(1H-Pyrrole-2-yl)-ethanone		1.37	0.54	0.73	0.19			2.10	0.97			1.30
27.15	87	4-Methoxy- benzene amine				0.06								0.16
29.63	91	1-(3-Pyridinyl)-ethanone									0.37		0.15	
30.61	74	4,5-Dihydro-5,5-dimethyl-4-isopropylidene-1H-pyrazole				0.14								
31.81	95	3-Ethyl-2,5-dimethyl-pyrazine			0.31					0.40	0.25			0.83
32.06	92	Benzyl nitrile	0.41			0,08		0.19						0.18
32.08	95	5H-5-Methyl-6,7-dihydrocyclopentapyrazine		0.38						0.39		0.31		
32.27	92	3-Methyl-1H-indene						0.76					1.31	
32.40	90	3-Pyridinol								1.79	1.87			

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>N-containing compounds (continued)</i>														
32.75	90	2-Methyl- indene					0.43	0.43				1.26		0.83
33.79	95	2,3,5-Trimethyl-6-ethyl pyrazine	0.32	0.64	0.29			0.43	0.52					0.36
34.12	91	1-(3-Pyridinyl)- ethanone			0.45						0.52			
34.98	70	4-Methoxy- benzene amine							0.55					
35.97	72	(E)- 2-Methyl-5-(1-propenyl)- pyrazine									0.63			
36.40	70	N,N-Dimethyl-2-pyrimidineamine									0.18			
36.88	97	Cyclohexapyrazine		0.53	0.45				0.63	0.34	0.37		0.38	
38.12	87	(Z)-,2,5-Dimethyl-3-(1-propenyl)- pyrazine		0.35									0,22	
38.81	95	Quinoline						0.26			0.29			
39.94	94	1,3-Dimethyl-1H-indene						0.21						0.53
42.86	94	2-Methyl- cyclohexapyrazine		0,71					0.51	0.21	0.52		0.56	
43.17	91	Indole					0.76	0.88			0.20	0.75		
43.86	90	5H-1-Pyridine	0.96											
46.81	94	(S)-3-(1-Methyl-2-pyrrolidinyl)- pyridine (nicotine)	33.48	0.73	9.09		18.97	24.08	13.03	48.34		29.93	31.34	25.44



## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>N-containing compounds (continued)</i>														
49.26	94	4-Methyl-1H-indole	0.87				1.52	0.26				0.89		0.30
51.38	94	3-(3,4-Dihydro-2H-pyrrole-5-yl)-pyridine	0.80				4.87	0.59	0.43	1.16		0.53	0.34	0.48
54.92	74	1-Ethyl-1H-indole						0.27						
55.11	91	3-Methyl-1-phenyl- 1H-pyrazole						1.36						
55.25	95	3-(1-Methyl-1H-pyrrole-2- yl)-pyridine	1.40							0.19		1.70	0.38	1.05
55.63	93	1,2-Dimethyl-1H-indole	0.22				0.58	0.33						
57.72	97	2,3'-Dipyridyl	0.54		0.50	0.31	0.44	0.33	0.90	0.71		0.41	0.66	0.28
60.90	87	5-Phenyl-1,4-dimethyl-imidazole						0.28				0.30		
78.26	90	Hexadecane nitrile	0.17				0,70							
Sum			41.23	15.35	22.59	8.02	28.46	34.30	25.36	58.96	15.94	39.99	41.95	31.81
<i>Acids and Esters</i>														
3.36	91	Hydroxy-acetic acid methyl ester			0.12									
3.81	87	Propanoic acid				1.22			0.20	0.09	0.16		0.12	

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Acids and Esters (continued)</i>														
4.19	78	2-Hydroxy propanoic acid methyl ester		0.14	0.40									
12.82	78	2-Acetate-1,2-propanediol		0.71		0.40			0.21	0.13	0.84		0.48	
12.88	78	2-Methyl- butanoic acid				0.11								
19.28	87	Methyl ester furan carboxylic acid				0.43					0.57		0.18	
19.89	72	3-Methyl- pentanoic acid				1.01			0.40	0.30	0.87		1.18	
35.50	86	Benzoic acid				0.14								
76.38	80	Bis(2-methylpropyl) ester- 1,2-benzenedicarboxylic acid	0.39											
80.02	95	Methyl ester hexadecanoic acid	0.33											0.26
82.60	97	n-Hexadecanoic acid	1.10			0.11	0.44	0.97				0.57		
86.39	92	Methyl ester-14-methyl heptadecanoic acid	0.08											
Sum			1.9	0.85	0.52	3.42	0.44	0.97	0.81	0.52	2.44	0.57	1.96	0.26
<i>Aldehydes and Ketones</i>														
3.13	86	2-Pentanone				0.29						0.03		0.05

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Aldehydes and Ketones (continued)</i>														
3.54	78	3-Hydroxy-2-butanone			0.9				0.08	0.04	0.32		0.07	
5.59	90	Cyclopentanone	0.04	0.52		0.56		0.11	0.25	0.16	0.34	0.22	0.16	0.24
6.48	87	Dihydro-2-methyl-3(2H)-furanone		0.14		0.17					0.05			
7.76	95	Furfural		3.57		15,03			2,01				0.40	0.03
7.91	76	2-Cyclopenten-1-one			1.99						1.05	0.17		
7.98	95	2-Methyl-cyclopentanone	0.08	0.28		0.28		0.18	0.18	0.26	0.28	0.23	0.18	0.32
8.39	76	3-Methyl-cyclopentanone	0.06			0.15		0.06			0.18			0.14
10.61	72	1-(Acetyloxy)-2-propanone		2.78	3.54	1.51								
12.92	94	2-Methyl- 2-cyclopenten-1-one	0.49	1.90	1.05	1.18		0.64	1.64	2.03	2.20	0.74	1.30	0.87
13.59	91	1-(2-Furanyl)-ethanone		2.84		1.78			1.63	1.13	3.01	0.28	1.34	0.19
15.20	90	2-Cyclohexen-1-one				0.22					0.23			
15.65	89	2-Ethyl- cyclopentanone	0.20	0.07								0.39		0.41
17.50	92	Benzaldehyde				0.33								

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Aldehydes and Ketones (continued)</i>														
17.81	96	3-Methyl-2-cyclopenten-1-one	0.60	1.26		0.09		0.28	0.54	1.65		0.38	0.92	0.27
18.00	94	5-Methyl-2-furan carboxyaldehyde		4.43	3.84	11.46			0.25		1.39			
19.15	83	3-Methyl- 2(5H)-furanone	0.06		0.31	0.16					0.32		0.19	
21.75	91	1-Acetyloxy-2-butanone			0.57									
22.88	91	Dihydro-5,5-dimethyl-2-(3H)-furanone			0.22									
23.42	92	3-Methyl-1,2-cyclopentandione		0.82			0.16	0.43						
23.46	94	2-Hydroxy-3-methyl-2-cyclopenten-1-one									1.82	0.55	0.85	0.12
23.49	80	3-Methyl-2-cyclohexen-1-one				0,10								
23.50	96	3,4-Dimethyl-2-cyclopenten-1-one			0.43				0.12	0.35			0.62	
23.88	97	2-Hydroxy-3-methyl-2-cyclohexen-1-one				0.76								
24.19	91	2,3-Dimethyl-2-cyclopenten-1-one	0.81	3.16		0.39	0.28		2.40	2.09	2.11	1.14	1.78	0.44
25.75	87	3,4-Dimethyl-2-hydroxy cyclopent-2-ene-1-one									0.67		0.57	
26.29	86	2,3,4-Trimethyl-2-cyclopenten-1-one				0.33			0.54	0.52				

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Aldehydes and Ketones (continued)</i>														
27.09	90	3-Ethyl-2-cyclopenten-1-one		0.41		0.15				0.47	0.52	0.38		0.38
30.80	96	3-Ethyl-2-hydroxy-2-cyclopenten-1-one			0.44	0.27						0.55	0.72	
31.54	81	5-Ethyl-2-fural aldehyde		0.41					0.55					
35.27	95	1-(2-Methylphenyl)-ethanone		0.15				0.03	0.37			0.09		0.03
44.42	93	5-Acetoxyethyl-2-furaldehyde				0.09								
49.91	93	Vanillin			0.17	0.14								
58.03	80	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone				0.09								
64.25	72	1-Cyclohexyl-3-ethoxy-butan-2-one				0.28								
99.43	86	(E,E)- 6,10,14-Trimethyl-5,9,13-pentadecatrien-2-one	0.27											
Sum			2.61	22.74	13.46	35.81	0.44	1.73	11.03	8.75	14.35	4.77	9.48	3.11
<i>Benzene Derivatives</i>														
4.79	95	Toluene	0.08			0.85		0.17	0.13			0.33		0.49
9.90	95	1,3-Dimethyl benzene	0.15	0.69		0.60		0.27			1.28	0.14	4.17	0.26

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Benzene Derivatives (continued)</i>														
10.03	97	P-xylene		2.20			0.39	1.48	2.79	1.55	0.29	0.56	0.71	0.85
11.58	96	Styrene	0.09					0.12						0.31
19.08	94	1-Ethyl-2-methyl benzene												0.17
20.15	95	1,3,5-Trimethyl benzene	0.14					0.27						0.27
25.66	91	Methyl-(1-methylethyl) benzene						0.20						
30.30	94	1,2,4,5-Tetramethyl benzene						0.12						
31.18	83	1-Methyl-4-(2-propenyl) benzene						0.17						
34.96	83	(3-Methyl-2-butenyl) benzene						0.11						
36.00	90	1-Methyl-3-(1-methyl-2-propenyl)-benzene										0.31		
38.23	72	Ethyl-1,2,4-trimethyl-benzene		0.60			0.15							
38.66	90	2,4-Dimethylanisole					0.59	0.32						
44.52	87	1,6-Dimethyl cyclohexene			0.41									
Sum			0.46	3.49	0.41	1.45	2.01	3.23	2.92	1.55	1.57	1.34	4.88	2.35

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Alcohols</i>														
4.22	90	Propylene glycol		1.19	4.67	1.08	0.13	0.31	1.36	3.38	5.25	0.65	2.33	0.32
9.41	96	3-Furan methanol		9.53	8.30	0.95	0.70	1.35	12.86	5.24	14.95	1.67	13.23	1.27
23.92	91	Benzyl alcohol		0.69		0.59		0.12	0.79	0.21	0.75	0.10	0.75	0.12
30.16	94	Phenyl ethyl alcohol		0.50	0.76	0.94			0.78	0.43	0.96		0,54	
37.40	94	1,2-Benzenediol			0.76	1.03								
43.34	93	1,4-Benzenediol									0.70	0.71		
74.80	72	Phytol		0.35										
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	12.26	14.49	4.59	0.83	1.78	15.79	9.26	22.61	3.13	16.85	1.71
<i>PAHs</i>														
34.71	93	Naphthalene						0.23						0.19
43.61	93	2-Methyl naphthalene					0.42	0.29				0.42		0.53

## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>PAHs (continued)</i>														
40.72	87	1,2-Dihydro-3-methyl naphthalene	0.53					0.51						
50.87	97	2,6-Dimethyl- naphthalene					0.26	0.21						
57.53	95	1,4,6-Trimethyl naphthalene	0.26				0.44	0.26						0.26
66.28	87	3-(1,1-Dimethylethyl) -1,2-dihydro naphthalene	0.46					0.41				0.42		
Sum			1.25				1,12	1,91				0.84		0.98
<i>Vitamin E</i>														
106.91	94	Tocopherol-gama	0.34					0.19						
108.25	99	Vitamin E	2.78				2.21	1.63				1.52	0.13	1.62
Sum			3.12				2.21	1.82				1.52	0.13	1.62
<i>Others</i>														
3.44	95	2,3-Dimethyl furan				0.12								
19.80	80	Dihydro-5-methyl-2-(3H)-furanone			0.43									
24.22	81	2-Acetyl-2-methylfuran				0.20								



## Appendix (Continued)

R. T. (min)	Quality	Name of Compounds	Area, %											
			None <sup>a</sup>	AlCl <sub>3</sub>					SnCl <sub>4</sub>		Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	
			500°C	300°C (%1)	300°C (%2,5)	300°C (%5)	400°C (%1)	500°C (%1)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)	300°C (%1)	500°C (%5)
<i>Others (continued)</i>														
24.48	94	3,4-Dimethyl-2,5-furandione				0.78								
29.66	81	3-Ethyl-4-methyl-2,5-furandione				0.30								
32.80	95	2-Methyl indene	0.19											
40.37	90	1,3-Dimethyl-1H-indene	0.87											
Sum			1.06		0.43	1.4								
<i>TOTAL</i>			77.16	69.82	64.44	68.92	74.11	71.63	72.94	86.11	68.01	78.91	90.1	68.17

<sup>a</sup> taken from the reference (Akalin and Karagöz 2011) for purpose of comparison