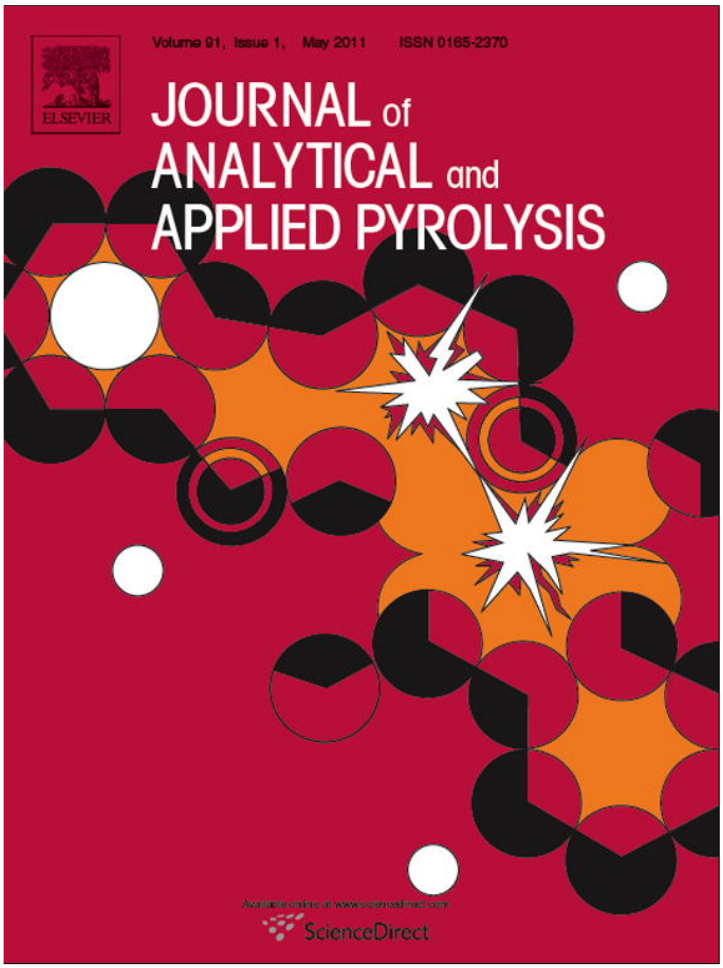

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Production of fungicidal oil and activated carbon from pistachio shell

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ABSTRACT

The main objective of this study was to evaluate the feasibility of pistachio shell as a biomass feedstock for the production of fungicidal oil and a precursor for the production of activated carbon by physical activation. For this purpose, pistachio shell was pyrolyzed in a fixed bed reactor at the different temperatures (300–600 °C). The pyrolysis products were identified as gas, bio-oil, aqueous solution and char. The product distribution from pyrolysis process did not significantly change when the pyrolysis temperature was above 300 °C. The pyrolysis gas product had low calorific value since it contained the high proportion of carbon oxides. Because of their high oxygen content, the bio-oils were found not to be used as a fuel. Thus, the bio-oil was tested again four different types of fungi (pathogenetic, wood decaying and saprophyting). It was shown fungicidal activity again all tested fungi at the concentration of 10–50 mg ml^{-1}. The pyrolysis char was evaluated as a precursor for the production of activated carbon. The surface area and micropore volume of the activated carbon produced from the char by CO_2 activation at 900 °C were found to be 708 $m^2 g^{-1}$ and 0.280 $cm^3 g^{-1}$, respectively.

1. Introduction

Biomass feedstock including energy crops, wood or agricultural residues and by-products usually applied as biomass fuels are of significant interest, because they form one of the largest alternative energy sources in the world. In addition, they can also be precursors for the materials of various applications, such as chemicals and adsorbents. There are many conversion technologies, such as thermochemical and biochemical process, for utilizing biomass as energy and chemical feedstock. One of them is pyrolysis which is a thermochemical process to obtain solid (char), liquid (bio-oil or pyrolytic tar) and gas products in the absence of oxygen. The yields of pyrolysis products depend on the process conditions including pyrolysis temperature, heating rate, and residence time. Many kinds of biomass species such as cotton stalk [1], cashew nut shell [2], rice husk [3], linseed [4], orange peel [5], wood [6], have been subjected to different pyrolysis conditions to produce fuels, chemicals and other products in literature.

For example, the pyrolysis liquids obtained from biomass has been used as sterilizing agent, smoke flavours, antimicrobial and growth promoting agent etc. [7,8]. Besides, it has also been used as a source of wood preservatives. As known, there are two types of wood preservatives commercially; oil-based and water-based namely. They are effective against a wide variety of wood-destroying organisms such as fungus whereas there are some environmental concerns with these preservatives because of high aquatic toxicity and their residuals [9]. Thus, researchers have developed environmental-friendly preservatives which do not damage the natural environment. Due to its chemical composition, pyrolytic tar obtained from fast and slow pyrolysis of wood has been used for wood protection as potential chemical preservative. In contrast to coal tar, pyrolytic tars derived from wood do not contain polynuclear aromatic hydrocarbons (PAH), it contains many phenolic compounds which have antifungal properties as wood preservatives [10–12]. Mohan et al. [9] tested antifungal properties of several pyrolytic oils and lignin-rich fractions obtained from pine wood, pine bark, oak wood and oak bark. They stated that phenolic compounds are most likely to be responsible for fungal inhibition and bio-oil fungicidal activities are comparable to some other oils/preservatives reported in the literature.

Moreover, pyrolysis of lignocellulosic materials produce non-graphitizable, high-purity chars of appropriate hardness and bulk density, which are very adequate as precursors for production of high quality activated carbons. Activated carbons with a variety of pore size distributions can be produced from lignocellulosic materials by modifying the preparation conditions of either physical or chemical activation procedures.

In both methods there is a reaction of the precursor with the activating agent to develop the porosity, but they differ both in the practical procedure and the mechanism [13]. The physical activa-

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tion involves carbonization of a carbonaceous precursor followed by the activation of the resulting char in the presence of some activating agents such as carbon dioxide, steam or both. The physical activation method has advantage over chemical activation, if the bio-oil derived from carbonization step is used as chemical feedstock or fuel.

Because of its low ash content and reasonable good hardness, production of activated carbon from pistachio shell was studied by Yang et al. They investigated the effects of the preparation variables (pyrolysis temperature, CO_2 flow rate, carbonization temperature and time) on the surface area and pore structure of activated carbon in physical activation process [14,15]. They also investigated the effects of different parameters such as the impregnation ratio, the activation temperature, the hold time and the activation condition (nitrogen gas or vacuum) on pore development in chemical activation process [16–20].

They obtained the activated carbon having a BET surface area and micropore volume of 2527 $m^2\,g^{-1}$ and 0.43 $cm^3\,g^{-1}$ by activation with $ZnCl_2$ [16] whereas they obtained the activated carbon having the highest BET surface area and micropore volume of 1064 $m^2\,g^{-1}$ and 0.210 $cm^3\,g^{-1}$, respectively by physical activation with CO_2 [14]. On the other hand, activated carbon having a BET surface 1300 $m^2\,g^{-1}$ with a loss of char mass of 70 wt% was obtained from pistachio shell by steam activation [21].

The main biomass sources in Turkey are food processing wastes, industrial wastes, and forestry wastes. One of the main food processing wastes is pistachio shell since Turkey is the third biggest pistachio producer in the world with an annual production of 120 thousands tones [22]. Pistachio are used fresh, or processed into candies, baked goods, and ice cream. Due to the processing activities, huge amount of residues (pistachio shells) are generated and they are disposed by burning.

Although there are number of studies on the preparation of pistachio shell-based activated carbon, there is no research on the production of fungicidal oil from pistachio shell by pyrolysis. Hence, the aim of this study was to evaluate the feasibility of pistachio shells as a biomass feedstock for production of fungicidal oil and a precursor for production of activated carbon.

2. Materials and methods

2.1. Materials

Pistachio (*Pistacia vera* L.) shell samples were supplied by a food company in Gaziantep, Turkey and used as received. The proximate, ultimate and component analyses of pistachio shell are shown in Table 1. All chemicals used in this study were analytical grade.

Table 1
Proximate, ultimate and component analyses of pistachio shell.

Proximate analysis (as received, wt%)	
Moisture	6.99
Volatile matter	80.01
Fixed carbon	12.08
Ash	0.09
Ultimate analysis (dry, wt%)	
C	42.41
H	5.64
N	0.07
S	0.01
O[a]	51.87
HHV[b] (MJ kg^{-1})	17.88
Component analysis (dry, wt%)	
Cellulose	53.98
Hemicellulose	20.10
Lignin	25.25
Extractives[c]	0.67

[a] Calculated from difference.
[b] High heating value.
[c] Toluene/alcohol (2/1) (v/v).

2.2. Experimental setup

2.2.1. Pyrolysis

Pistachio shell samples were pyrolyzed in a fixed bed design using a stainless steel reactor (L, 210 mm; Ø, 60 mm) which was placed in an electrical heating furnace. In a typical pyrolysis experiment, a quantity of 100 g of biomass was filled in and then the reactor temperature was increased by a slow heating rate of 10 °C min^{-1} up to pyrolysis temperature and hold for 1 h at the desired temperature. The reactor was continuously purged with nitrogen at a flow rate 25 ml min^{-1}. The nitrogen gas swept the volatile products from the reactor into the ice-cooled traps. The total liquid products were condensed in a series of traps. First trap was air-cooled and the other two traps were ice-cooled. The gases were collected in a Tedler bag. After pyrolysis, furnace was cooled to room temperature in a nitrogen gas stream. All traps were weighted before and after each run. Total liquid amount was determined by difference. The yields of liquid products and char were determined by weighting. The amount of gas was determined by difference. The liquid product consisted of two phases; aqueous phase and bio-oil phase. The bio-oil product was collected in first trap, whereas ice cooled traps contained aqueous product.

2.2.2. Production of activated carbon

In the activation process, the char obtained from pyrolysis at 500 °C was heated to 900 °C under nitrogen atmosphere. As soon as the reactor temperature reached 900 °C, the inert atmosphere was rapidly substituted by flowing carbon dioxide (350 ml min^{-1}). At the end of the desired activation time, the reactor was cooled to room temperature under nitrogen atmosphere. The activated carbon from activation process was weighted (m_2) to calculate the burn-off value. The burn-off value was calculated by

$$\%\,\text{burn-off} = \frac{M - m_2}{M} \times 100$$

where M is the initial mass of char.

2.2.3. Fractionation of bio-oil

Bio-oil phase obtained from pyrolysis of pistachio shell was fractionated into four groups, namely water-solubles, extractives; low molecular weight lignin compounds (LMWL) and high molecular weight lignin (HMWL) compounds. Fractionation process was carried out by a modified method as based on the literature [23]. Thus, the bio-oil was extracted with cold water at 0 °C (1:10, w/w) and powder-like precipitate was filtered, dried and weighed as water-insolubles. The amount of water-solubles was determined by difference. Water-insoluble fraction was extracted with dichloromethane. Dichloromethane soluble fractions consist of extractives and LMWL; Dichloromethane insoluble fractions consist of HMWL. The amount of extractives in bio-oil was determined by hexane soluble. Thus, the bio-oil and hexane (1:10, w/w) mixture was stirred for 2 h and seperated by decantation. Hexane solubles were defined as extractives.

2.2.4. Analysis

Thermogravimetric analysis of pistachio shell was performed by means of a Perkin–Elmer Diamond TG/DTA thermogravimetric analyzer under nitrogen atmosphere. The flow rate of purge gas was kept at 200 ml min^{-1}. The sample was heated from the ambient temperature up to 740 °C with heating rate of 10 °C min^{-1}.

The collected gas product in Tedlar bag was analyzed by HP model 5890 series II gas chromatography, with a thermal conductivity detector. A stainless steel packed column (6.0 m × 1/8 in

Porapack Q, 2.0 m × 1/8 in. 5A molecular sieve, serially connected to each other) was used. The separation of CO_2, C_1, C_2, C_3, C_4 and C_5 hydrocarbons was made with Poropack Q column and the separation of O_2, N_2 and CO was carried out with MS 5A column.

The bio-oils samples were extracted with ethyl acetate (1:1, v/v) that allows qualitative analysis of the phenolic compounds. Then, the ethyl acetate extracts were analyzed by a gas chromatography-mass selective detector system (Agilent 6890N Network GC System 5973 Network series). The used column was a HP-5MS fused silica capillary column with a 30 m × 0.25 mm i.d. The GC initial oven temperature was 40 °C for 10 min, then ramped up to 175 °C at 2 °C min^{-1} for 20 min, and then to 200 °C at 1 °C min^{-1} and then to 250 °C at 4 °C min^{-1} for 20 min. The data acquisition system was done with G1035A software with a NIST library database.

The amount of total phenols in aqueous phases and bio-oil was determined by colorimetry (reaction of phenols with 4-nitroaniline to a yellow complex) with the photometer by Hach Lange-DR2800.

Component analysis (extractives, lignin, hemicellulose and cellulose) of pistachio shell was carried out according to literature [24].

The elemental analysis of pistachio shell, bio-oils and chars was carried out by a LECO CHNS 932 elemental analyzer according to ASTM D5291-96. Water contents of bio-oils were determined by Karl–Fischer Volumetric Titrator (Mettler Toledo DL 31). The gross calorific values of bio-oils and pistachio shell were determined using an IKA C-2000 basic model calorimeter according to ASTM D240-02. The proximate analyses of chars and pistachio shell were done according to ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatile matter.

Measurements of specific surface areas of the activated carbons produced from pistachio shell have been made by N_2 adsorption (at 77.3 K), using Quantachrome Inst., Nova 2200e model surface and pore size analyzer. The micropore volume (V_{micro}) was determined by using *t*-plot method. The surface area and pore volume results were obtained by using Quantachrome Novawin2 software. The mesopore volume (V_{meso}) was calculated by subtracting V_{micro} from V_{total}. ($V_{meso} = V_{total} - V_{micro}$). The amount of surface oxygen groups on the activated carbons has been determined by Boehm titration method [25]. The scanning electron microscope (SEM) images of char and activated carbons were recorded by using JEOL JSM-6060.

2.2.5. Fungal cultures and inhibition test

In this study, the anti fungal activity of bio-oil obtained from pyrolysis at 500 °C was tested for four types of fungal cultures. The fungal cultures of *Aspergillus niger* TEM (a saprophytic fungus), *Trichoderma viridae* TEM (a phytopathogenic fungus), *Coriolus versicolor* ATCC 200801 (a white rot fungus), and *Trichophyton rubrum* (a dermatophytic fungus) were obtained from Basic and Industrial Microbiology Section of Biology Department and Medicine Faculty, Aegean University-Turkey, respectively. Prior to testing each test fungus was subcultured on Sabouraud's Dextrose Agar (SDA) and incubated at 27 °C for 10 days to ensure purity of them. SDA Plates 90 mm in diameter were prepared and then three holes were punched in periphery and a forth at the centre. The inhibition test was carried out according to literature [26]. Emulsions containing 2, 10, 20, 30, 40 and 50 mg bio-oil ml^{-1} were prepared by serial dilutions in 1% dimethylsulfoxide. An aliquot of 50 μl of the bio-oils were added to peripheral holes and a 6 mm in diameter cylindrical plug of mycelium cut from the edge of actively growing colony were also added to central hole. 1% dimethylsulfoxide was used as the control. Petri dishes were incubated at 27 °C for 10 days. Distance between peripheral holes and the rim of the fungal colony were measured after 10 days. All experiments were done triplicate.

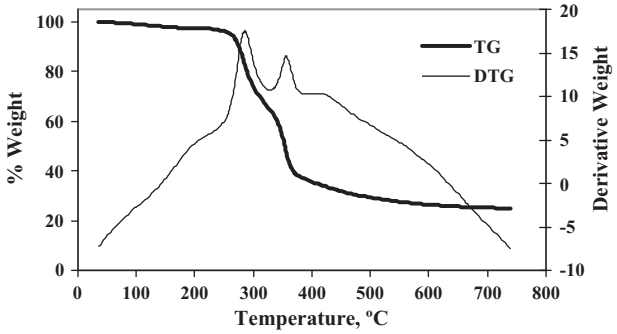

Fig. 1. TG–DTG curves of the pistachio shell.

Then, the inhibition was calculated following formula:

$$\text{Inhibition}\,\% = \frac{1 - [d_t - d_i]}{d_t} \times 100$$

where d_t is total distance between the central hole and the peripheral hole and d_i is the distance between mycelial edge of fungal growth and the peripheral hole.

3. Results and discussion

3.1. Thermogravimetric analysis results

Fig. 1 shows the TG and DTG curves of the pistachio shell decomposition recorded at a heating rate 10 °C min^{-1} under nitrogen atmosphere. The thermal decomposition starts at approximately 235 °C and the main devolatilization takes place between 270 and 400 °C with two stage weight loss. The TG curve shows that the first stage, located between 255 and 320 °C, represents approximately 33 wt% weight loss. The second stage, located 325–500 °C, represent approximately 37 wt% weight loss. Above 500 °C, no appreciable weight loss was observed. This may suggest that no major reaction exists above 500 °C. According to this result, it can be said that choosing pyrolysis temperature as 500 °C is appropriate when obtaining of char for physical activation process is aimed.

Corresponding to the two-stage weight loss on the TG curves, two peaks are observed on the DTG curves. The first peak is observed at 285.5 °C and the second peak is observed at 360.5 °C. Based on the literature [27–29], it seems that the lower temperature DTG peak represents mainly the decomposition of hemicellulose and the higher temperature DTG peak is associated with the decomposition of cellulose and lignin.

In contrast to our result, Hayashi et al. [30] observed one peak between 127 and 627 °C in the thermal degradation of pistachio shell and they suggested that the peak of the cellulose overlaps with that of the hemi-cellulose and therefore only a single peak appeared in the weight loss rate. This contrast may be due to the difference in the kind of pistachio shell.

3.2. Pyrolysis of pistachio shell

3.2.1. Pyrolysis yields

The product yields for the pyrolysis of pistachio shells at different temperatures are given in Table 2. It is clearly seen that the product distribution did not significantly change when the pyrolysis temperature was above 300 °C. There was a little increase in bio-oil product and decrease in char product yield as temperature raised from 400 to 600 °C.

In our previous work, we studied the pyrolysis of cherry seed using same reactor at different temperatures and similarly, product yields did not vary between 400 and 600 °C. Similarly, in the case of pyrolysis of corncob [31] a faster changing in products yields

Table 2
Product distributions from pyrolysis of pistachio shell (wt%).

Temperature (°C)	300	400	500	600
Gas[a]	21.0	20.1	19.3	19.0
Aqueous phase	21.3	24.2	24.8	25.2
Bio-oil	27.9	30.6	31.3	32.6
Char	29.8	25.1	24.6	23.2

[a] Calculated from mass balance.

between the temperatures 350 and 400 °C and a slower changing between the temperatures of 400 and 600 °C were observed. However, bio-oil yield reached a maximum value at 500–550 °C in many studies to slow pyrolysis of lignocellulosic materials [32,33] and above these temperatures bio-oil yields decreased while gas yield increased. Meanwhile, the char yield continuously decreased with increasing temperature. The differences in the results obtained from present study and previous studies may be due to the mainly difference in the biomass species. It is worthwhile noting that our results were also different that of previous study on pistachio shell pyrolysis by a heating rate of 7 °C min^{-1}. Apaydin-Varol et al. [34] observed that gas yield continuously increased while char yield decreased by increasing temperature from 300 to 700 °C. They obtained the maximum bio-oil yield (~20.5 wt%) at the temperature between 500 and 550 °C.

By considering the slow pyrolysis studies in literature, the bio-oil yield obtained from pyrolysis of pistachio shell in this study seems to be reasonable. Maximum bio-oil yields were found to be 66.0 wt% for bagasse [35], 25.8 wt% for soybean [36], 23 wt% for hazelnut shell, 44 wt% for sunflower, 32 wt% for *Euphorbia rigida* [37], 24.5 wt% for cottonseed cake [38].

3.2.2. Composition of bio-oil

Because of the large number oxygen containing compounds, characterization of bio-oil differs from that of hydrocarbon based fuels. Due to this reason, the characterization procedure in this study was carried out by fractionation according to literature [23]. As seen from Fig. 2, the fractions consist of water soluble compounds, extractives, low molecular and high molecular weight lignin compounds. Water content was also included in bio-oil composition. Bio-oil composition was independent on the pyrolysis temperature and consisted of mainly water soluble compounds (38–39 wt%) and water (41–43 wt%). Water soluble compounds generally are acids, sugars, alcohols, catechols and phenols [39]. Extractives (~7 wt%) contained hexane-soluble compounds, consisting mainly of hydrocarbons. Similarly, Mullen et al. obtained the bio-oils from fast pyrolysis of barley straw and barley hulls containing 60.4 wt% and 64.0 wt% of water-solubles, respectively [40]. Acetic acid, acetol and levoglucosan (carbohydrate degradation products) were found in high concentrations in the water-solubles

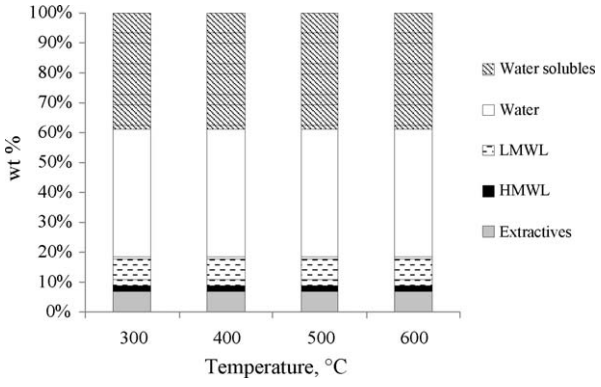

Fig. 2. Composition of bio-oils obtained from pyrolysis of pistachio shell.

Table 3
Properties of bio-oils obtained from pyrolysis of pistachio shell.

Temperature (°C)	300	400	500	600
Ultimate analysis (wt%)				
C	26.37	32.36	36.63	36.86
H	5.87	7.10	7.18	6.51
N	2.78	2.10	2.81	2.59
S	0.03	0.01	0.06	0.04
O[a]	64.95	58.43	53.32	54.00
Water content (wt%)	43.78	42.44	38.42	38.19
HHV[b] (MJ kg^{-1})	12.53	12.75	13.59	14.01

[a] Calculated from difference.
[b] High heating value.

of bio-oils. In another study, the proportion of water-solubles was 80 wt% of bio-oil obtained from straw [39].

In previous study [34] relating to slow pyrolysis of pistachio shell, the amount of extractives in bio-oil were found to be about 42 wt% and the rest was called as asphaltenes like in hydrocarbon fuel. Unfortunately, we cannot explain the reason for differences in results.

Although pyrolysis of pistachio shell produce reasonable yield of bio-oil, they contained low amount of carbon (Table 3). Due to the high content of water, bio-oil had low calorific value. Although the liquid products obtained from pyrolysis were not homogenous, consisted of aqueous and oil phases, oil phase (bio-oil) contained still huge amount of water. This shows that bio-oil contained the some chemicals which act as emulsifier. Overall, it is clear that bio-oils are not appropriate for utilization as a fuel.

3.2.3. Composition of pyrolysis gases

The compositions of the gaseous products produced from pyrolysis of pistachio shell at representative temperature (500 °C) determined by GC–TCD are shown in Table 4. As seen from the table, CO and CO_2 are the major gaseous products. This result is in well agreement with the previous studies on biomass pyrolysis [41–44].

For example, in the pyrolysis of rapeseed oil cake at 500 °C, the CO_2 content was 68.79 wt% and CO content was 7.65 wt% [41]. CO_2 is a product of the primary pyrolysis of cellulose and hemicellulose [45] where CO are mainly formed from secondary cracking of volatiles, followed by a reduction of CO_2 ($C + CO_2 = 2CO$) at high temperature (>500 °C) [46].

Due to the high proportion of carbon oxides containing, pyrolysis gas had a low calorific value in this study. It may be provided dome part of the energy requirements of the pyrolysis plant. The heating value of gas was calculated as 14.73 MJ $N\,m^{-3}$. This heating value is the mean heating value of the gas mixture and it has been calculated from the concentration of each individual gas and its corresponding heating value.

Table 4
Composition of gaseous products obtained from pyrolysis of pistachio shell at 500 °C (mol%).

Gas products	
H_2	2.68
CH_4	13.40
CO	38.59
CO_2	40.88
C2	2.15
C3	1.43
C4	0.46
C5	0.40
HHV (MJ $N\,m^{-3}$)[a]	14.73

[a] High heating value.

Table 5
Some properties of chars obtained from pyrolysis of pistachio shell.

Temperature (°C)	300	400	500	600
Ultimate analysis (wt%)				
C	68.74	71.54	82.43	87.33
H	3.38	4.64	3.09	2.57
N	0.27	0.21	0.16	0.16
S	0.07	0.05	0.11	0.14
O[a]	27.54	23.56	14.21	9.80
Ash content (wt%)	0.608	0.609	0.698	0.695
HHV[b] (MJ kg^{-1})	29.70	29.79	31.17	33.40

[a] Calculated from difference.
[b] High heating value.

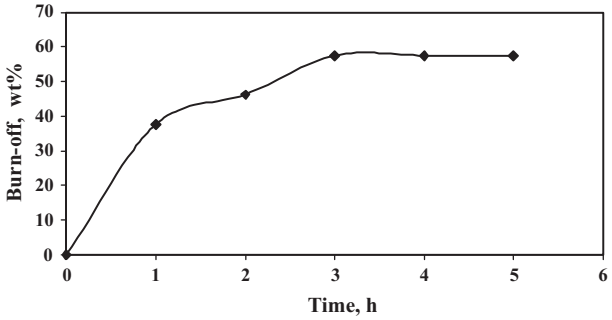

Fig. 3. Carbon burn-off in CO_2 for the char derived from pistachio shell in relation to activation time.

3.2.4. Pyrolysis chars

The characteristic of chars obtained from pyrolysis of biomass is depended on the pyrolysis conditions such as temperature and heating rate as well as the composition of the biomass. Table 5 shows the effect of pyrolysis temperature on elemental composition of char produced from pistachio shell. The ash contents and heating value of chars were also included in Table 5. Oxygen content of char decreased as the temperature was increased with temperature accompanying with the loss of the carbonyl groups [1]. The ash content of chars was not changed as the temperature increased whereas carbon content of chars increased. The calorific value of chars was found to be higher than that of chars obtained from barley straw, barley hulls, barley distiller's dried grains [40], grapeseed, chest nutshell [47] etc. Due to the high heating value and low ash and sulphur content, chars can be used as solid fuel. They are also one of the raw materials for production of activated carbon.

3.3. Fungicidal value of bio-oil

As we mentioned before, bio-oil contains huge amount of oxygenated compounds including carbohydrate degradation products and lignin degradation products. Because of these, bio-oil can be used as feedstock for many purposes. For example, because of its phenol and derivatives (from thermal degradation of lignin), it can be used as antioxidant [8] and fungicide [9]. The one of the aims of this article was to investigate the fungicidal properties of bio-oil obtained from pistachio shell. As seen in Table 6, bio-oils contained phenolic compounds about 1.5 wt% which were mainly monomeric phenols (Table 7).

Table 6
The amount of total phenols (wt%).

Temperature (°C)	300	400	500	600
Aqueous phase	0.21	0.25	0.27	0.29
Bio-oil	1.39	1.42	1.49	1.51

Table 7
Main phenolic compounds in ethylactate extracts from bio-oil obtained from pyrolysis of pistachio shell at 500 °C.

No.	R.T. (min)	Quality	Name of compounds	Relative area (%)
1	19.66	94	Phenol	0.39
2	25.46	97	2-Methyl phenol	0.35
3	27.12	95	3-Methyl phenol	0.38
4	27.69	97	2-Methoxy phenol	2.78
5	35.51	95	2-Methoxy-4-methyl-phenol	2.26
6	36.46	91	2-Hydroxy phenol	3.88
7	40.18	95	3-Methoxy-2-hydroxy phenol	1.84
8	41.59	85	4-Ethyl-2-methoxy phenol	1.67
9	42.69	94	4-Methyl-2-hydroxy phenol	0.81
10	46.52	93	2,6-Dimethoxy phenol	8.61
11	47.45	93	2-Methoxy-4-propyl phenol	0.41
12	52.54	81	2-Methoxy-4-(1-propenyl) phenol	6.68
13	67.07	88	2,6-Dimethoxy-4-(2-propenyl)-phenol	2.63

Although fungi having wood decaying properties were mostly evaluated in the literature about the antifungal activity of bio-oil, fungi used in this study were selected according to their pathogenetic, wood decaying and saprophyting. As seen from Table 8, bio-oil produced from pistachio shell was shown fungicidal activity again all tested fungi at the concentration of 10–50 mg ml^{-1}. The fact that the bio-oil showed fungicidal activity again four different types of fungi are due to its phenolic contents. Suzuki et al. suggested that 4-ethyl-2-methoxyphenol and 4-propyl-2-methoxyphenol might have some preservation effects [11]. Similarly, Mohan et al. reported that 4-propyl-2-methoxyphenol could contribute to decay resistance [9]. These results are agree-

Table 8
Anti-fungal activity of bio-oil obtained from pyrolysis of pistachio shell.

Concentration (mg ml^{-1})	*T. viridae*			*A. niger*			*T. rubrum*			*C. versicolor*		
	d_t	d_i	Inhibition (%)	d_t	d_i	Inhibition (%)	d_t	d_i	Inhibition (%)	d_t	d_i	Inhibition (%)
50	23	16	69.5	23	15	65.2	23	22	95.6	23	19	82.6
40	23	15	65.2	23	13	56.5	23	22	95.6	23	16	69.6
30	23	12	52.2	23	11	47.8	23	20	86.9	23	14	60.9
20	23	13	56.5	23	8	34.8	23	15	65.2	23	10	43.5
10	23	5	21.7	23	4	17.4	23	11	47.8	23	7	30.4
2	23	0	0	23	0	0	23	0	0	23	0	0

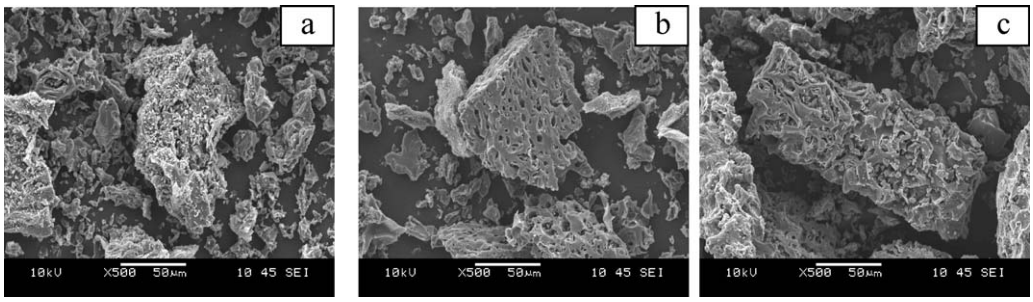

Fig. 4. SEM micrographs of char (a) and activated carbons produced by physical activation for 2 h (b) and 5 h (c).

ment with our findings (Table 7). It should be noted that it was also observed that the color around the fungal colony changed from white to brown during the test with *C. versicolor*. This may be due to metabolizing of the lignin and phenolic compounds in bio-oil by *C. versicolor* having lignolytic activity.

One of the most important distinctive feature of bio-oil is the fact that it showed very good fungicidal activity at the concentration of 30 mg ml^{-1} and above against *T. rubrum* which is a dermatophytic fungus. Taking into consideration the continuous increase of fungal resistance against a wide range of antifungal drugs, bio-oil may be unconventional sources of antifungal treatment due to phenolic content [48].

3.4. Production of activated carbon

In this study, the char obtained from pyrolysis of pistachio shell at 500 °C was activated with CO_2 at 900 °C for changing between 1 and 5 h. Fig. 3 shows the influence of activation time on the degree of burn-off in CO_2 achieved for char. The carbon burns off exhibited a considerable increase till the activation time of 1 h and then gradually increase between 1 and 3 h. A burn-off value of 57.5 wt% was obtained for the activation time of 3 h and the burn-off value was not changed by further increased in activation time.

The surface area and the pore size distribution of the activated carbon is an important specification in determining the utilization of the final product. Surface properties of activated carbons versus activation time are given in Table 9. The BET surface area and micropore volume of activated carbon exhibited a similar trend. By increasing activation time, they both increased.

Activation of char improves pore formation and further creates new pores, resulting in increasing BET surface area and micropore volume of the activated carbons for increasing activation time. This evidence can be clearly seen from the scanning electron micrographs of the char and activated chars in Fig. 4.

In contrast to our result, Yang and Lua [14] observed different trend in preparation of activated carbon from pistachio shell. The micropore volume and BET surface area peaked at 1.5 and 2 h, respectively, and thereafter, decreased with increasing activation time. The difference may be due to the activation condition such as CO_2 flow rate and activation temperature. It should be noted that although the BET surface area of activated carbon obtained in this study was lower than that of activated carbon obtained by Yang et al., micropore volume of former was higher than that of latter.

Table 9
The effect of activation time on surface properties of activated carbons produced from pistachio shell derived char.

Activation time (h)	1	2	3	5
BET surface area ($m^2 g^{-1}$)	123.6	588.6	555.5	708.6
Micropore surface area ($m^2 g^{-1}$)	nd	554.2	467.8	604.6
Mesopore surface area ($m^2 g^{-1}$)	nd	34.4	87.7	104.0
Total pore volume ($cm^3 g^{-1}$)	nd	0.293	0.275	0.359
Micropore volume ($cm^3 g^{-1}$)	nd	0.223	0.216	0.280
Mesopore volume ($cm^3 g^{-1}$)	nd	0.070	0.059	0.079
Average pore diameter (Å)	nd	9.95	1.97	2.02

nd: not determined.

On the other hand, the chemical nature of activated carbons significantly influences its adsorptive properties as well as surface area and porosity. In this study, the oxygen-containing functional groups on activated carbon surfaces were determined by Boehm titration. The oxygen functional groups are very important characteristics of the activated carbons because they determine the surface properties of the carbons and hence their quality as adsorbents [49]. The amount of basic surface oxygen groups (chromene and pyrone) of activated carbons was found to be 0.893 and 0.962 mmol g^{-1} for 2 h and 5 h, respectively. However, there were no acidic groups (carboxyl, lactonic hydroxyl, carbonyl groups) detected on the activated carbon surfaces. This result shows that all surface acidic oxygen groups were decomposed during activation at 900 °C. It has been reported, that carboxylic acids and lactones were decomposed by CO_2 evolution at the temperatures of 200–500 °C and 600–800 °C, respectively [50]. Groups such as phenols, carbonyls, ethers and quinines were decomposed up to 1000 °C by CO evolution. As conclusion, the obtained activated carbon with basic surface chemical properties is suitable for acidic gas adsorption such as sulphur dioxide, phenols, acidic dye etc.

4. Conclusions

In this study, conversion of pistachio shell to useful products by pyrolysis and activation methods has been investigated. Thermogravimetric analysis showed that the thermal decomposition of pistachio shell starts at approximately 235 °C and no major reaction exists above 500 °C.

The pyrolysis of the pistachio shell was carried out in fixed-bed reactor at different pyrolysis temperatures (300–600 °C). The products obtained from pyrolysis were gas, bio-oil, aqueous solution and char. The product distribution from pyrolysis did not significantly change when the pyrolysis temperature was above 300 °C.

The gas product obtained from pyrolysis contained the high proportion of carbon oxides so it has low calorific value. It was suggested that pyrolytic gas can provide some part of the energy requirements of the pyrolysis process.

The bio-oils obtained from pyrolysis were not suitable for the use as a fuel because of their high oxygen content. Thus, the bio-oils were suggested to be used as chemical feedstock. The fungicidal properties of bio-oil again four different types of fungi were also tested in this study. The bio-oil was shown fungicidal activity again all tested fungi at the concentration of 10–50 mg ml^{-1}.

The pyrolysis chars had high calorific values and low ash content below 1 wt% with very low sulphur concentration making them attractive for use as a solid fuel or as raw material for production of activated carbon. The present study shows that pistachio shell can be effectively used as a raw material for the preparation of activated

carbon by physical activation. The activated carbon having a surface area and micropore volume of 708 $m^2 g^{-1}$ and 0.280 $cm^3 g^{-1}$, respectively, was produced from the char by CO_2 activation.

Consequently, the results of this work showed that pistachio shell can be used for production of both fungicidal oil and activated carbon. Antifungal properties of bio-oil is valuable for wood decay prediction agent alone or combination with commercial biocides, such as cresoate and pentachlorophenol.

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