Turkish Journal of Earth Sciences

http://journals.tubitak.gov.tr/earth/

Research Article

Turkish J Earth Sci
(2014) 23: 668-672
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doi:10.3906/yer-1312-20

Utilization of petrographic analysis for determination of petroleum coke mixtures

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Received: 20.12.2013 • **Accepted:** 13.06.2014 • **Published Online:** 03.11.2014 • **Printed:** 28.11.2014

Abstract: This study was carried out on mostly imported, processed petrocokes, which are also commercially known as "petcoke" or "petroleum coke". Petrocoke is imported in great amounts and is occasionally consumed domestically without conscientious thought. It is not a well-known material, though there is an idea of its genesis. The samples, their analysis, and their images are essential to be kept in mind for further investigations, since it is not an environmentally friendly material. Petrographic and chemical analyses were conducted on all samples. Trace element and FT-IR analyses were made on a few representative samples. It is possible to distinguish petrocokes from coal samples by means of coal petrography. Even mixtures of the petrocokes with coals can be detected very well. Some trace elements such as V, U, and Ni have much higher contents in petrocokes. They may cause environmental impacts.

Key words: Petrocoke, petrocoke–coal blend, petrocoke determination, petrocoke petrographic analysis, FT-IR analysis, trace elements in petrocokes, petroleum coke

1. Introduction

This study was realized on mostly imported, processed petroleum product samples that are commercially known as "petrocoke", "petcoke", or "petroleum coke. Petrocoke belongs to a group of materials with high carbon content. It is produced by the coking of feedstock obtained from residues of primary and secondary oil refining processes (Radenovic and Terzic, 2010). Petrocoke is produced at refineries in 3 different types: green (raw) coke, calcined coke, and needle coke. Due to its low ash and volatile matter and its high calorific value, petrocoke is used in power plants, cement and brick factories, magnesite plants, and lime manufacturing. In iron and steel industry, low-sulfur-containing mixtures of them with coals are utilized since coking coal prices are considerably high.

As stated, petrocoke is generally utilized in some industrial areas, but it recently began to be used for domestic heating in developing countries such as Turkey because of its low price and high calorific value. However, it is thought to cause environmental problems. Sulfur, nickel, and vanadium, elements that are released with petrocoke combustion in vast amounts, give rise to air pollution and cause fouling and corrosion in furnaces (http://www.enerji.gov.tr/index.php?dil=en&sf=webpages&b=komurN&bn=511&hn=&nm=40717 &id=40729).

Determination of petrocoke is important because it is used in consumption without concern for the environment or the effects that it may cause. The users may not have any idea of its hazardous effects. The main purpose of this article is to analyze petrocokes using the petrographic and chemical properties of coal–petrocoke blends. For this purpose, chemical, petrographic, trace element, and FT-IR analyses were applied to establish a base for the determination of petroleum-derived materials, cokes, and their various mixtures with the fuels, since their appearance and determinations are quite difficult to define.

2. Materials and methods

In this study, a total of 12 samples, including 3 of petrocoke, 4 of calcined petrocoke, 3 of calcined petrocoke/petrocoke blend, 1 of bituminous coal, and 1 of petrocoke/bituminous coal blend, were selected from the samples thought to be of suspicious mixtures and brought to the General Directorate of Mineral Research and Exploration (MTA) laboratories for analysis. Petrographic and chemical analyses were conducted on all samples. Trace element and FT-IR analyses were made for 4 representative samples for each group. All analyses were conducted in the MTA Mineral Analyses and Technology Department Laboratories in Turkey.

For the petrographic analyses, the samples were crushed to less than 1 mm (–18 mesh) in size, mounted in epoxy resin, and polished. The petrographic analyses were performed using a Leica DM4000 M LED microscope.

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For the chemical analysis, the samples were crushed to 250 µm (–60 mesh) in size. Moisture, volatile matter, and ash contents were determined with ASTM D 7582-12 standard procedures (ASTM International, 2012). Total sulfur content and calorific value analyses of the samples were made according to the ASTM D 4239-14 (ASTM International, 2014) and the ASTM D 5865-13 (ASTM International, 2013) standards, respectively.

Trace element analyses (As, Cl, Cd, Cu, Pb, U, V, Ni) were conducted using ISO standard 11466:1995 (International Organization for Standardization, 2010) with Agilent ICP-OES 725 and Thermo ICP-MS instruments.

For FT-IR analyses, KBr-sample mixture pellets were analyzed to be used in a PerkinElmer spectrometer.

3. Results

3.1. Chemical analysis

The moisture content of calcined petrocoke samples is considerably lower than those of the others. Moisture contents of the calcined petrocoke–petrocoke blend, petrocoke, and bituminous coal samples are similar to each other (Table 1). However, the petrocoke–bituminous coal blend moisture content is much higher than those of the others. The ash and volatile matter contents are higher in the bituminous coal sample. In contrast, its low calorific value is lower than those of the petrocoke and the mixed samples. Sulfur content is low in the bituminous coal. Low moisture, ash, and volatile matter contents of the petrocoke samples are thought to result from the heat treatment.

3.2. Elemental analysis

Petrocoke contains numerous toxins including heavy metals and polycyclic aromatic hydrocarbons that are carcinogenic (http://www.epa.gov/osp/tribes/NatForum06/3_2.pdf). In this study, in particular, analyses of air-pollutant elements were made. According to the results (Table 2), uranium, vanadium, and nickel contents of petrocoke, calcined petrocoke, and petrocoke–bituminous coal blend samples are considerably higher

Table 1. Proximate analysis (%) results of the samples.

No.	M*	Ash*	Ash**	VM*	VM**	TS*	TS**	LCV*	LCV**	Type
1	9.29	0.36	0.40	11.6	12.8	5.10	5.62	7496	8324	P
2	8.23	0.46	0.50	11.7	12.7	5.07	5.53	7591	8325	P
3	9.62	0.48	0.53	11.6	11.7	3.96	4.38	7468	8325	P
4	8.91	0.25	0.27	11.9	13.1	5.08	5.57	7510	8302	P
5	8.41	0.42	0.46	11.8	12.9	5.12	5.59	7572	8321	P
6	5.44	0.41	0.44	10.7	11.3	4.56	4.82	7774	8255	CP
7	4.34	0.51	0.53	10.9	11.4	4.71	4.93	7885	8269	CP
8	9.10	11.7	12.8	19.0	20.9	0.28	0.31	6315	7005	Bt
9	8.83	0.16	0.17	11.5	12.6	4.98	5.46	7531	8317	P+CP
10	8.46	0.38	0.41	11.9	13.0	4.98	5.44	7618	8376	P+CP
11	8.33	0.23	0.26	12.1	13.2	5.11	5.57	7572	8313	P+CP
12	14.57	0.40	0.47	10.8	12.6	4.78	5.59	7016	8312	Bt+P

*: As received; **: dried basis; M: moisture; VM: volatile matter; TS: total sulfur; LCV: low calorific value (as kcal/kg); P: petrocoke; CP: calcined petrocoke; Bt: bituminous coal.

Table 2. Trace element analysis results (ppm) of the samples.

Sample No	As	Cd	Cu	Pb	U	V	Ni	Cl
1 (P)	22	<1	26	28	45	30,000	8000	72
6 (CP)	<1	<1	<1	4	40	11,000	3000	ND
8 (Bt)	3	3	<1	10	15	1000	300	ND
12 (Bt+P)	69	<1	149	55	132	7000	22,000	38

P: Petrocoke; CP: calcined petrocoke; Bt: bituminous coal; ND: not detected.

than those of the others. Similarly, As, Cu, and Pb contents are higher in the petrocoke and petrocoke–bituminous coal samples. Cadmium content of the bituminous coal sample seems to be much higher than that of the others.

3.3. Petrographic analysis

Organic petrography is quite practical for detecting the types of organic materials such as lignite, bituminous coal, and petrocokes. Plant tissues and their fragments can clearly be observed in coals, which are definite and well known by organic petrographers. Petrographic appearances of coal macerals exhibit distinct natural patterns; therefore, they can easily be separated from petrocokes in blends. Under a microscope, organic materials are seen in different shades of gray. Vitrinite macerals have medium gray and inertinite macerals have whitish gray colors in bituminous coals (Taylor et al., 1998). Liptinites, which have the highest volatile and hydrogen content, possess the darkest gray colors among the macerals (Figure 1a).

The organic structures and tissues cannot be recognized in the petroleum materials at all (Figure 1b). When the organic materials lose their volatiles and hydrogen elements, their colors become light gray and whitish gray. In the studied samples, this color change can be traced under the microscope easily. As implied, macerals are not identified in petrocokes as in coals; the materials are generally observed with their gray and whitish gray colors. Since petrocokes are processed products, they mostly exhibit unnatural patterns and morphologies, which are

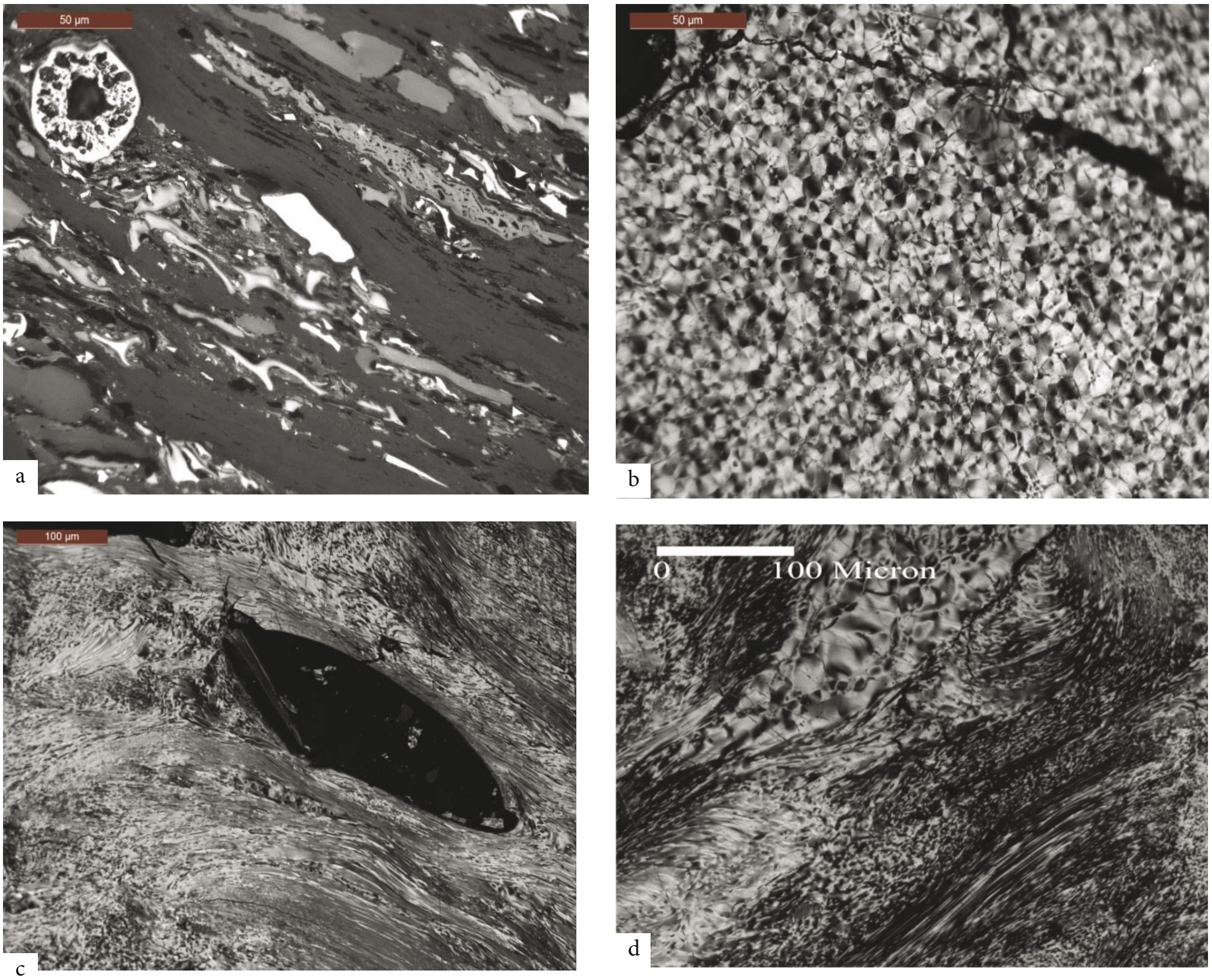

Figure 1**a.** A typical bituminous coal contains different macerals with their textures and colors. Vitrinite (gray) is dominant; inertinite (white) and liptinite (dark gray) are less common. **b.** Petrocoke shows unnatural forms and textures. The equal granular mosaic texture is formed after calcination. **c.** Petrocoke shows undulated color of the ingredients. The grayish colors indicate much moisture and volatile matter content. **d.** Petrocoke exhibits different colors. The grayish colors imply much moisture and volatile matter content. **e.** Calcined petrocoke shows circular forms in the mass, probably formed at the first phase of calcinations. **f.** Calcined petrocoke exhibits various colored mosaic textures with rounded forms. **g.** Calcined petrocoke (whitish on the left) and bituminous coal particles (on the right) together in a sample. **h.** Calcined petrocoke (whitish on the left) and bituminous coal (on the right) together in a sample.

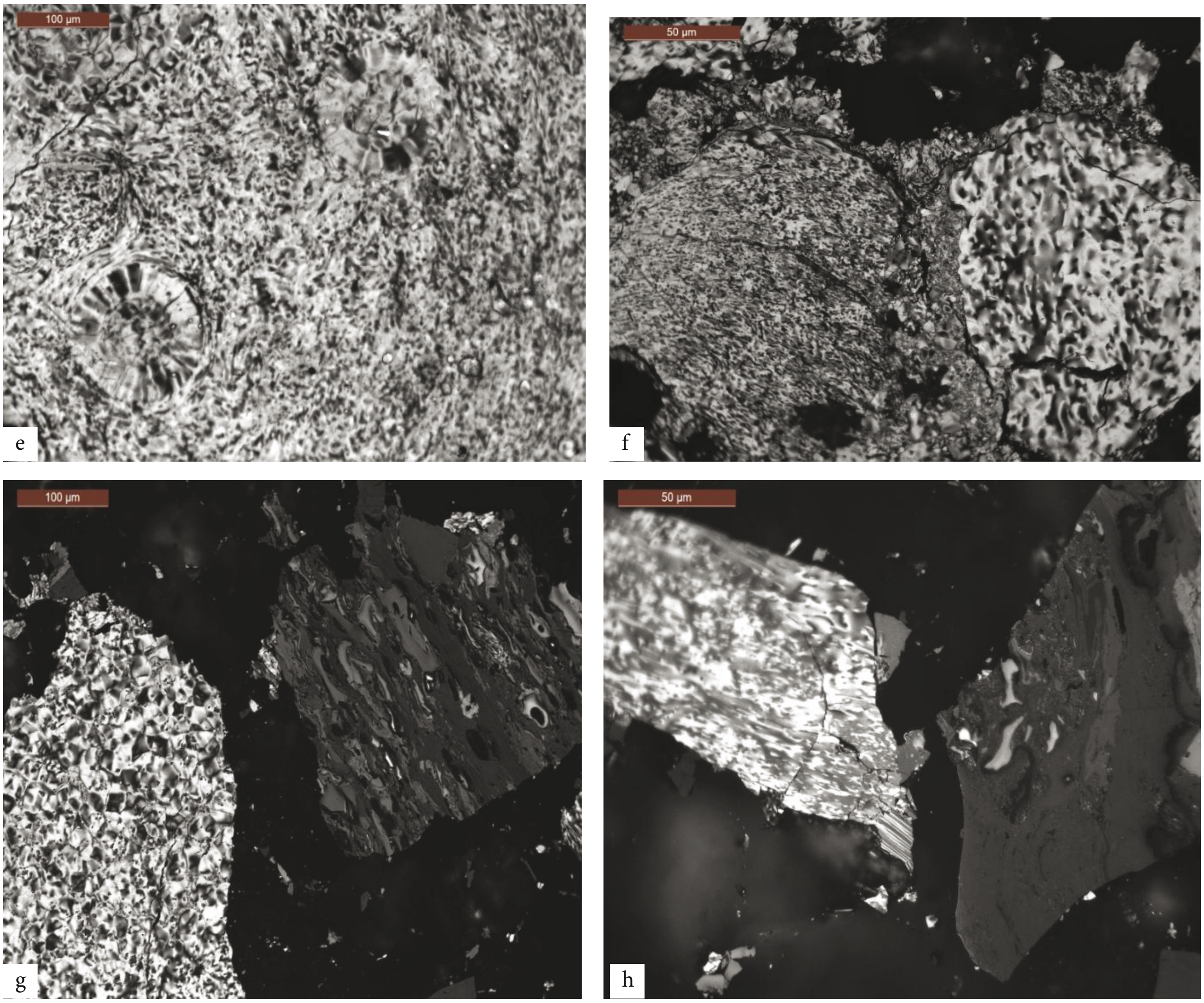

Figure 1. (Continued).

generally referred to as flow and mosaic textures (Figures 1c–1f). The flow texture is like the remnants of paintbrush traces. Petrocokes display grayish elongate undulated lineations, which are not common in natural organics (Figure 1d).

Determination of petrocokes and coals in the blends was carried out with their colors and morphologic features as seen in Figures 1g and 1h.

Petrocoke macerals exhibit nested whitish and gray colors. The grayish appearances are likely to indicate comparatively high content of volatile matters and moisture content. Due to heat and pressure effects, the whitish macerals probably lose their volatiles and moistures. This can also be seen in Table 1 and Figures 1d and 1e. The sum of volatile matter and moisture contents of the petrocokes is higher than that of calcined petrocokes.

3.4. FT-IR analysis

Similar FT-IR spectra were observed for the samples of petrocoke, calcined petrocoke, and petrocoke–bituminous coal mixture (Figure 2). Peaks representing the aromatic carbon region (peak at 1610 cm^{-1}), aliphatic stretching region (3000–2800 cm^{-1}), and hydroxyl group region (3100–3700 cm^{-1}) were similar. Aliphatic stretching peaks were more apparent for calcined petrocoke and petrocoke–bituminous coal than for petrocoke. The region between 3700 cm^{-1} and 3100 cm^{-1} was assigned to O-H stretching vibrations and was due to free OH groups and associated OH groups (hydrogen bonding due to OH). In terms of associated OH groups that may be present, free OH groups (3750 cm^{-1}) were seen for petrocoke, calcined petrocoke, and petrocoke–bituminous coal samples. The sheer increase in OH stretching is characteristic of petrocoke–bituminous coal blends.

The peak in the 1100–1200 cm^{-1} region for bituminous coal was assigned to either group, as well as C-O stretching and OH bonding vibrations in phenoxy structures (Niekerk et al., 2008). Low intensity aromatic -CH out-of-plane (bending) bands were observed between 900 and 700 cm^{-1} in all the samples (Sonibare et al., 2010).

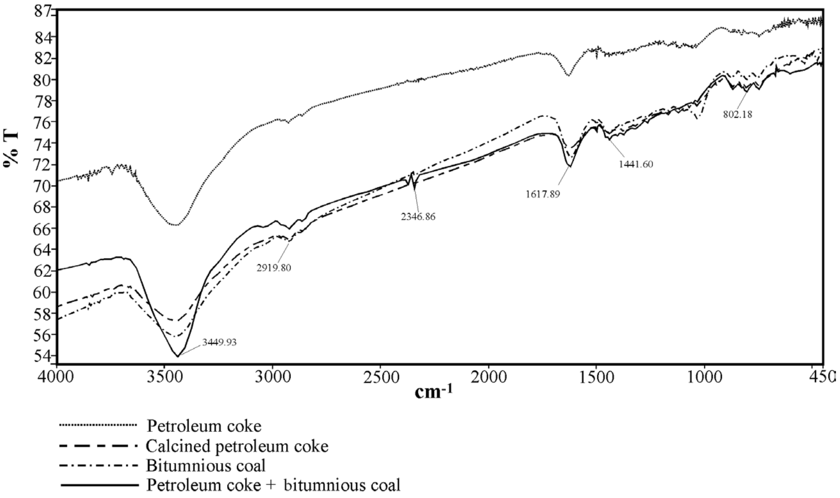

Figure 2. FT-IR spectra of the samples.

4. Discussion

As a result, it is possible to distinguish petrocokes in the mixtures. As seen, it is quite difficult to distinguish petrocokes from the coal blends with only chemical analyses. FT-IR analyses of organics partially help to distinguish their presence. Some trace elements such as V, Ni, and U have much higher contents in petrocokes. Concentrations of vanadium, nickel, and uranium in petrocoke–coal blends ought to be considered with great care.

Petrocokes are rather difficult materials to study by microscope, since they are synthetic, but their petrographic analysis is more practical when compared to the other analysis methods to be used for their determination.

In calcined petrocokes the texture is more like a mosaic texture and the pattern is much smaller than in ordinary petrocokes. The calcined ones often possess spherical shapes or grains with rounded corners (Figures 1e and 1f). Probably the circular form starts with heat effect. The initial forms of calcined petrocokes are likely to be circular grains in the mass (Figure 1e). Later the grains detach and are liberated as variously sized spherical grains.

Mineral matter has rarely been detected in petrocokes by microscopes. Since the petrocokes are processed under high temperatures, even pyrites partially disappear. With heat, the minerals probably lose their properties and combinations. Therefore, either their volume decreases or they burn out.

Acknowledgments

The authors are thankful to General Directorate of Mineral Research and Exploration Mineral Analysis and Technology Department executives Gökçe Gürtekin, Tolga Görmüş, Abdullah Ulaş, Güldane Demirtaş, and Berna Yüksel for their contributions.

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