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Improvements on combustion properties of asphaltite and correlation of activation energies with combustion results

Cahit Hiçyılmaz [1], N. Emre Altun *

Department of Mining Engineering, Middle East Technical University, 06531, Ankara, Turkey

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Abstract

Processing of Şırnak Asphaltite sample by gravity and flotation concentration methods was investigated to decrease its ash content. Finely disseminated inorganic constituents of asphaltite revealed the difficulty of operation. Ash content of asphaltite was reduced from 44.86% to 31.44% by gravity concentration method with a 75% combustible recovery. On the other hand, it was possible to reduce ash content to 24% by flotation with almost same combustible recovery. Combustion characterization of raw and improved asphaltites was performed by non-isothermal thermogravimetric experiments. The data obtained were analyzed for the determination of activation energy of asphaltite samples. Processing proved to improve the combustion characteristics of asphaltite where activation energies showed the same trend with ash contents of asphaltite samples and decreased from 47.75 kJ/mol of raw asphaltite to 30.24 kJ/mol. As a result, activation energies were correlated with ash contents, calorific values, burn-out temperatures and sulfur contents of processed samples.

Keywords: Asphaltite; Gravity concentration; Flotation; Combustion characteristics; Thermogravimetry; Activation energy

1. Introduction

Asphaltite is a petroleum originated substance and formed by metamorphism. The low oxygen content of asphaltites (<2%) is the best evidence about its origin. It is a hard and a blackish material, with a relatively high softening point of about 200–315 °C. It is soluble by carbon disulfide. Asphaltite deposits of Mesozoic–Cenozoic age contain high amount of quartz, pyrite, carbonates and clay minerals [1].

Asphaltite is not only utilized as fuel, but also for the production of ammonia in the world. In addition, it can be converted into a variety of secondary products such as light hydrocarbon gases, tar and high quality fuel char via pyrolyis.

Türkiye has large sources of asphaltite in the southeastern part of Anatolia in an area of 1700 km^2. The asphaltite reserves in Türkiye are approximately 82 million tonnes [2]. It is marketed around the southeastern part of Anatolia for domestic heating. However, the quality of these asphaltite reserves is poor in terms of their ash and sulfur contents.

Some investigations have been performed about the asphaltites of Şırnak–Türkiye to remove ash and sulfur constituents by chemical and physico-chemical (i.e. flotation) methods [3–5]. However, the studies related to processing of it by gravity and flotation method and discussing the improvements from the view of combustion characteristics has not been studied. Therefore, this research aims to investigate the combustion characteristic and reaction kinetics of raw or improved asphaltites

Table 1
Proximate and elemental analysis of asphaltite

Proximate analysis	Wt. (%) (air-dried)	Elemental analysis	Wt. (%) (air-dried)
Moisture	0.66	C	46.96
Ash	44.86	H	3.46
Volatile matter	33.25	N	0.83
Fixed carbon	21.23	O	1.56
Calorific value (kcal/kg)	4701	S (total)	5.53

* Corresponding author. Tel.: +90 312 210 58 11; fax: +90 312 210 12 65.
E-mail addresses: cahith@metu.edu.tr (C. Hiçyılmaz), naltun@metu.edu.tr (N.E. Altun).
[1] Tel.: +90 312 210 58 13; fax: +90 312 210 12 65.

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Table 2
Ash, total sulfur, calorific value, combustible recovery and thermogravimetric properties of raw and improved asphaltites by gravity concentration

Sample	Ash (%)	Total sulfur (%)	Calorific value (kcal/kg)	Combustible recovery (%)	Burn-out temp. (°C)	Activation energy, E (kJ/mol)	Operation condition
Raw	44.86	5.53	4380	–	846	46.76	–
Jig conc.	39.76	4.72	4764	77.53	828	44.38	−9.53 mm sample
Reichert sp. conc.	37.56	4.23	4919	70.02	865	42.24	−0.6 mm sample
Reichert sp. conc.	35.16	3.78	5128	78.41	823	41.54	−0.3 mm sample
Humphreys sp. conc.	31.44	3.01	5440	75.84	819	40.05	−0.3 mm sample
Shaking table conc.	36.10	4.08	5010	94.47	826	41.76	−0.3 mm sample

and to install a relationship between activation energies and ash contents, calorific values, burn-out temperatures and sulfur contents of processed asphaltites.

2. Experimental

The experiments were carried out with asphaltite samples taken from Avgamasya vein of Şırnak. Characterization of sample was retained by proximate, elemental and mineralogical analysis. Table 1 shows proximate and elemental analysis of the sample. Mineralogical analysis, on the other hand, showed that, the sample had high amount of carbonate minerals such as calcite, dolomite, ankerite and siderite within 5–10 μm size. In addition, mica, quartz and clay minerals were also observed during microscopic studies. Pyrite around 20–25 μm, sphalarite, titanium minerals such as rutile and anatase were the other constituents of inorganic materials. Mineralogical analysis, as a result, showed that inorganic minerals disseminated within the asphaltite down to 5–25 μm.

Improvement studies were carried out in two topics, namely gravitational and flotation concentrations. Gravitational concentration experiments were performed using jig, shaking table, Reichert spiral and Humphreys spiral. Flotation experiments were carried out with a Denver Sub-A type laboratory flotation cell. Effect of pH, collector type, pulp density and regulators were investigated. Cleaning and recleaning of products by flotation were also performed. Size reduction for gravity and flotation methods was done via crushing and grinding with laboratory type Denver jaw crusher and rod mill, respectively. In flotation, pulp was conditioned for 5 min after the reagents were added. Flotation time was kept constant as 3 min. Unless otherwise discussed, pulp density was 20% solid by weight. Products were dried and analyzed for ash content and combustible recovery. Ash content was determined at 700 °C according to ASTM D3174-04 standard [6] and combustible recovery (R_{com}) was calculated by Eq. (1).

$$R_{com} = \frac{\text{Product Wt.\%}(100-\text{Product Ash\%})}{100-\text{Feed Ash\%}} \quad (1)$$

The products were also evaluated from the view of combustion properties and activation energies. Combustion properties of

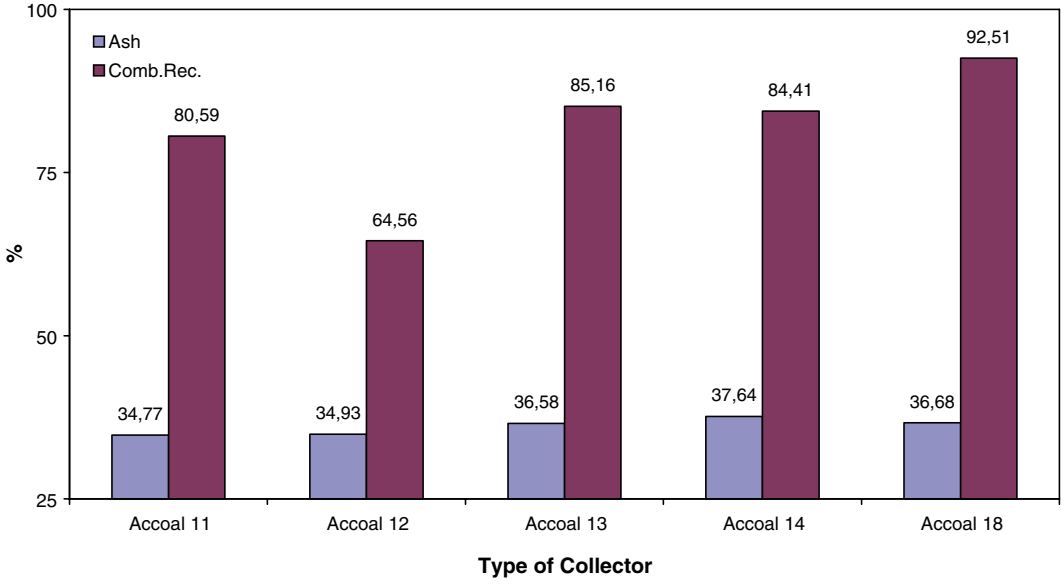

Fig. 1. Effect of type of collector (collector amount = 240 g/ton; pH = natural).