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Full Length Article

Solid fossil fuels thermal decomposition features in air and argon

Svetlana A. Epshtein, Elena L. Kossovich *, Vladimir A. Kaminskii, Nikolay M. Durov, Nadezhda N. Dobryakova

National University of Science and Technology "MISiS", 4, Leninsky prospect, Moscow 119049, Russian Federation

HIGHLIGHTS

- Coals oxidation is described by TGA data processing.
- TGA experiments were held in inert and oxidizing environments.
- Sample set contains coals of different nature and ranks.
- Two groups of coals are found in context of their interaction with oxygen.
- New kinetic model is proposed to mathematically process TGA data.

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ABSTRACT

Investigation and characterization of coals oxidation is one of the most current problems due to the fact that it may lead to quality loss and spontaneous combustion hazards at mining, storage and utilization. A detailed analysis was performed for thermogravimetric analysis of selection of coals with a wide rank range, different structural characteristics, petrographic and elements composition and origins during experiments in inert and oxidizing environments. It was found that for both the considered environments, the coals thermogravimetric curves retain their space disposition order. Values of the temperatures corresponding to maximal decomposition rates correlate with coal rank as for inert, as for oxidizing environments. For bituminous coals and anthracite, temperatures corresponding to maximal decomposition rate drifted to the zone of higher temperatures in case of experiments in air in comparison with tests in inert. For lignites, they moved to lower temperature intervals. Values of the maximal thermal decomposition rate for bituminous coals well correlate with aromaticity degree. For lignites, the maximal decomposition rates in air and argon have comparable values, whereas for high-rank coals and anthracite they grow in oxidizing environment in comparison with inert one. Kinetic parameters were evaluated for the most common stages of coals mass change during thermogravimetric experiments in air and argon. Kinetic parameters of coals pyrolysis and combustion correlate not only with rank but also with aromaticity degree. For bituminous coals at high temperature intervals at experiments in inert environment, there was found a decrease of activation energy values with rank and aromaticity degree growth. As for corresponding values for bituminous coals tested in oxidizing environment, there was an increase of activation energy with rank and aromaticity degree. Two groups were allocated for coals in context of their interaction with oxygen. The first group included lignites and peat and is characterized by enhanced volatiles release at temperatures over 100 °C. The second one contains coals that are prone to oxygen adsorption at low-temperature intervals (up to 300–400 °C) (bituminous coals and anthracite). New parameter was proposed for preliminary describing coals group affiliation. This parameter denotes mass gain or decrease for coals tested in oxidizing environment. The complex of kinetic parameters may serve as an additional but informative tool to view at coals oxidation mechanisms. This, presumably, could be performed at simultaneous characterization of thermogravimetric data with heat flow and gas analysis.

1. Introduction

Characterization of different solid fossil fuels behavioral features is becoming increasingly popular due to the related issues

* Corresponding author.
E-mail addresses: apshtein@yandex.ru (S.A. Epshtein), e.kossovich@misis.ru (E.L. Kossovich), vkamin123@yandex.ru (V.A. Kaminskii), nickmih@bk.ru (N.M. Durov), n.dobryakova@misis.ru (N.N. Dobryakova).

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of mining, storage and utilization. Recent researches are concentrated on variation of quality, characteristics and combustion properties of fossil fuels with rank [1–4], oxidation degree [5] and structure [6]. One of the most relevant problem nowadays is studying of solid fossil fuels oxidation that may lead to quality loss and spontaneous combustion hazards at mining, storage and utilization [7]. In order to study the effects of structure and properties of coals and other solid fossil fuels at their pyrolysis and combustion behavior, thermogravimetric analysis (TGA) is widely applied [8,9].

Coals pyrolysis stages detailed experimental and analytical investigation was shown in [10]. It was shown that vitrinite reflectance index of coals is in a good correlation with thermal decomposition kinetic parameters obtained from TGA studies [11,12].

Propensity of coals of different rank to oxidation and spontaneous combustion was studied in [13,14], where authors introduced new parameters derived from TGA tests and found correlation between them with rank. As part of analysis of coals thermochemical behavior during oxidation, authors of [4] discussed that thermogravimetric (TG) curves shapes variate with coals rank. They tested low- and high-rank coals in oxygen-containing gas flow. And observed that for the high-rank coal there exists a pronounced stage of oxygen adsorption (mass increase at temperatures 150–300 °C), whereas for low-rank coals such phenomena were not found at similar thermal intervals. TGA of bituminous coals in environments containing different values of oxygen concentration were performed by [14–18] and the phenomenon of oxygen adsorption at low-temperature intervals (up to 400 °C) also was highlighted. In [13] it was shown that for bituminous coals such stage remains for all the considered heating rates, and, along with the heating rate growth, the oxygen adsorption becomes less pronounced, whereas for lignites no mass growth was found for all the heating rates. In [19] authors revealed that for the low-rank coal there exist no such stage for tests in oxidizing environment, and increase of heating rate reduces mass loss rate. In [15], while investigating of a bituminous coal, authors revealed that growth of oxygen concentration in atmosphere of TG experiment enhances its adsorption into coal matter at low-temperature intervals, and increase of heating rate induces growth of the maximal weight loss rate and the corresponding temperatures. As for lignites, increase of oxygen concentration in experiment environment lead to pronounced shifts of maximal weight loss rate temperatures to the lower values [20]. Some low-temperature coal oxidation features were observed and discussed in [17,18,21], such as thermal decomposition kinetic parameters comparison at low and high temperature intervals.

Solely TGA of coals do not provide unambiguous information on oxidation mechanisms because non-stationary heating regime leads to simultaneous proceeding of various processes, e.g. physical and chemical sorption, oxidation, decomposition, etc. Therefore, the majority of the coal thermogravimetric analysis researches nowadays are dedicated to combining of TGA and differential scanning calorimetry (DSC) or differential thermogravimetric methods (DTA), along with the recently developed approach of simultaneous TGA/Fourier transform infrared spectroscopy (FTIR) for studying the thermal decomposition features of coals. Such combinations of research methods are especially important in context of studying of coals propensity to oxidation, in order to obtain more information on the mechanisms of coals interaction with oxygen. For example, TG-FTIR was used for the quantitative characterizing of coals oxidation degree by analyzing the volatiles gas composition [22–24]. On the other hand, TGA of coals could serve as a supplementary but comprehensive tool for characterization of the prevailing mechanisms of oxidation and spontaneous combustion. To this end, one may use comparative analysis of solid fossil fuels behavior at low- and high-temperature intervals in inert and oxidizing environments during the TGA experiments, as shown in [25]. Unfortunately, only a few papers were found with comparative analysis (see, e.g., [15,18,25,26]), and there is lack of unified information of such type for coals of different rank and structure.

In this work we performed thermogravimetric analysis of coals in inert (argon) and oxidizing (air) gas flow under coherent conditions of experiment. A sample set of 15 coals with wide rank range, different structure, of various basins and origins was used. Mass loss patterns obtained in air and argon were compared at low- and high-temperature intervals for each sample. Kinetic parameters were evaluated by model [27] and compared for low- and high-temperature intervals for all the samples at experiments in air and argon. Also, a new parameter was introduced for indication of dominating processes of oxygen sorption or enhanced matter decomposition of coals at low-temperature intervals prior to combustion stage. Complex of kinetic parameters and the introduced one could serve as an additional informative tool (along with heat flow measurements, gas analysis, etc.) for clarification of coals oxidation mechanisms. This data may be useful for prognosis of coals propensity to spontaneous combustion as well as characterization of tendency to oxidation in context of quality loss at mining and storage, coals gasification, and many other related issues.

2. Materials and methods

2.1. Coals samples characterization and preparation

In the work the studies were performed at coals of different rank and origins from different deposits of the Russian Federation. The sample set of coals counts 14 items. Characteristics of samples are shown in Table 1. On using samples chemical composition data, the atomic ratio H/C (at.) was determined. This atomic ratio well correlates with aromaticity degree f_a, as it was shown previously by [28–30]. Therefore, further in the text we will use this parameter, H/C, as substituent of coals aromaticity degree.

Data shown in Table 1 reveals that the selected samples set contains coals with different metamorphism degree, petrographic and chemical compositions.

All lignites are characterized by very close values of vitrinite reflectance index (R_{or}, %) (range 0.30–0.38%) but by relatively wide range of H/C. For example, lignite 5 has the largest value of H/C ratio and low index R_{or}. At the same value of R_{or}., lignites 3 and 5 differ by H/C. There also exist variations in petrographic composition of coals: lignites 5 and 2 are mostly consist of vitrinite (V_t), whereas ##3 and 4 have much lower V_t percentage. A major share of samples is occupied by bituminous coals of different ranks. Their vitrinite reflectance indexes vary from 0.5 to 1.8%, carbon 76–88%, hydrogen 3.90–5.70%, atomic ratio H/C is 0.53–0.91 at. Also, the bituminous coals samples have different petrographic composition with vitrinite share varying from 31 to 94%. An oxidized bituminous coal also was included (#6) characterized by higher moisture, volatile matter, lower carbon and hydrogen contents along with higher H/C ratio in comparison with coals with the same rank. Also, within the chosen set of solid fossil fuels, there exists anthracite with high Sulphur contents, lowest H/C ratio (i.e. highest aromaticity degree) and with $R_{or.}$ = 3.58%. And, a sample of peat was included. This sample is characterized by high hydrogen content and low carbon one. H/C for peat has the largest value among all the samples set.

As it was expected, there is a good correlation between vitrinite reflectance index and atomic ratio H/C of the studied samples (Fig. 1). With R_{or} growth, the atomic ratio values of H/C decrease, but for lignites there exist high level of dispersion. At the moment, this samples set was used partially in work [31] aimed at evaluation of coals propensity to oxidation and spontaneous combustion.