Study on the pyrolysis of different coal in atmospheres of argon, carbon dioxide, and steam

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Abstract. The pyrolysis process is fundamental in many deep coal utilization technologies. The comparison of conversion of three different types of coal was carried out utilizing thermal analysis in the atmosphere of argon, carbon dioxide, and steam within the temperature range from ambient temperature to 1000 °C. The anthracite, bituminous coal, and lignite of Siberian deposits were studied. It was found that within the temperature range of 20-700 °C for bituminous coal and lignite, and within 20-800 °C for anthracite, the differences between mass loss rate in inert medium and other studied samples were insignificant. While flue gases (from fossil fuels burnt with low excess air ratio) in general consist of carbon dioxide and steam. Thus, they could be used for the pyrolysis of studied fuels within the mentioned temperature ranges.

1. Introduction

The technologies of fossil fuel chemistry for the production of different products like liquid fuel [1, 2], and sorbents for water treatment [2] are becoming more and more relevant nowadays. The majority of them include [3] the pyrolysis process, and for many of them, it’s the core process. While classic definition of the term “pyrolysis” means conversion during heating in the inert medium [4] or vacuum [5]. Such a solution is very expensive due to poor heat exchange properties of inert gases and the high-cost of vacuuming. That’s why pyrolysis using hot flue gases [6] which are easy to produce, is a very promising solution for many applications. However, carbon dioxide and steam in flue gas could interact with the carbon of fuel at high temperatures thus decreasing the amount of final product. The rate of these reactions could be assumed to be negligibly low at low temperatures. However, the exact reaction rate depends on many factors like level of carbon metamorphism, maceral composition, etc.

The purpose of current work was to determine the characteristics of conversion of three different coals in the atmosphere of argon, carbon dioxide, and steam to justify the maximal temperature at which the difference between conversion in inert and flue gases was insignificant.

2. Materials and methods

2.1. Sample characterization

The coals of three types were studied: anthracite, T-grade bituminous coal of Kuznetsk deposit, and 2B-grade lignite of Kansk-Achinsk deposit. Later in the article, these samples will be referred to as A, B, and L. Initial samples were crushed and sieved to obtain fraction lower than 80 µm to eliminate diffusional resistance during thermal analysis. The proximate analysis was performed using standard
ISO methodic, while the elemental composition was carried out using EURO EA 3000 elemental analyzer (Eurovector, Italy). Obtained proximate and ultimate analysis results are presented in Table 1. The proximate analysis results are presented on the as-received basis, while ultimate analysis results are given on the dry ash-free basis.

| Sample | Proximate analysis* | Ultimate analysis |
|--------|---------------------|-------------------|
|        | M       | A    | VM | FC  | H  | C  | N  | O  |       |
| A      | <1      | 10   | <1 | 90  | 2  | 95 | <1 | <1  |       |
| B      | 3       | 21   | 20 | 66  | 4  | 68 | 3  | 4   |       |
| L      | 7       | 16   | 32 | 45  | 4  | 50 | 2  | 28  |       |

* M – moisture content; A – ash content; VM – volatile matter content; FC – fixed carbon content

2.2. Thermal analysis
Thermal analysis experiments were performed using STA 449 F3 Jupiter (Netzsch, Germany). The measurements were carried out using samples with weight ~20 mg in corundum crucible. The heating rate was 20 °C/min within the temperature range from 20 to 1000 °C. The flow rate of Ar, H₂O, or CO₂ was 150 ml/min (maximal flow rate for this analyzer) with a simultaneous 10 ml/min flow rate of argon through the thermal weight scheme to prevent damage. Before experiments with Ar and CO₂, the chamber of the analyzer was blown with corresponding gas for 30 minutes to remove atmospheric air. For the measurements in the steam atmosphere, the initial measurements (up to 120 °C) were carried out in an atmosphere of argon. After reaching 150 °C, the chamber of the thermal analyzer was blown for 30 minutes with steam at a constant temperature to completely substitute argon with steam. Then the heating was continued at the same regime as in other media. The mass loss during this 30 minute blowdown period was less than 1% for all samples, so this period was excluded from consideration.

2.3. Conversion parameter definition
While for both anthracite and bituminous coal samples the complete conversion wasn’t reached in studied temperature range, the majority of standard methods for kinetic analysis couldn’t be applied. However, the few of them were applied in the present article to perform the numerical characterization of the conversion process. The temperatures of the intense conversion onset and maximal reaction rate were determined according to the technique presented in [7]. While pyrolysis in inert argon medium was considered to be some kind of "reference" process, the difference between the mass of sample at the same temperature in argon and reactive steam or carbon dioxide medium was determined. The temperature of the beginning of intense conversion onset was chosen to be the temperature at which the comparison was carried out.

3. Results and discussion

3.1. Initial experimental TG and DTG-curves
Obtained experimental TG and DTG-curves for samples of anthracite, bituminous coal, and lignite are presented in Figs. 1, 2, and 3, respectively. The several characteristic mass loss stages could be distinguished on all TG- and DTG-curves. The first one took place at temperatures below 200 °C and was likely caused by moisture desorption from the sample because it appeared in all media. The lower humidity desorption rate in the steam medium was connected to lower drying rates at temperatures below the boiling point. The second stage took place within the temperature range of 400-900 °C for bituminous coal and lignite sample. However, while for lignite, the DTG-curves within the temperature range of 400-600 °C were nearly similar in all media, for bituminous coal the mass loss rate in CO₂ medium was lower than that in argon and steam. It could be caused by the strong
endothermal effect of reactions between carbon dioxide and the fixed carbon of the sample. For anthracite, due to the low content of volatiles, this stage was nearly absent.

Figure 1. Experimental TG- (a) and DTG-curves (b) for anthracite sample.

Figure 2. Experimental TG- (a) and DTG-curves (b) for bituminous coal sample.

Figure 3. Experimental TG- (a) and DTG-curves (b) for lignite sample.
The insignificant difference between the volatiles release stage in different media for the lignite sample could be caused by the predominant sublimation of organic compounds. While sublimation didn’t include chemical reactions with gas and didn’t depend on its type. For bituminous coal samples, the released gas composition significantly depended on a chemical reaction in carbon lattice and included reactions with ambient gases.

The last stage for all samples was observed only in reactive media at temperatures higher than 600 °C for bituminous coal and lignite samples, and higher than 800 °C for anthracite sample. The reaction rate in steam is much higher than that in carbon dioxide resulting in more complete conversion in corresponding experiments at the final temperature of 1000 °C.

### 3.2. Calculated conversion parameters

Calculated parameters of conversion in different media are presented in Table 2. Presented results were in good agreement with the data of Fig. 1-3, and described earlier results. The volatile matter release stage for bituminous coal and lignite samples in different media was studied earlier and could be found in [8]. The only mass loss stage in argon was connected to volatile matter release while in other media several mass loss stages could be observed (Fig. 1-3). The volatile matter release stage in all media was nearly similar, that’s why in Table 2 the data on characteristic temperatures in argon are given for the first stage, while the results in carbon dioxide and steam are given for the second stage.

#### Table 2. Conversion parameters in different media.

| Sample | Tico*, °C | Tmrr**, °C | Δm***, wt.% |
|--------|----------|------------|--------------|
|        | 1st stage | 2nd stage  |              |              |
|        | Ar | CO₂ | H₂O | Ar | CO₂ | H₂O | CO₂ | H₂O |
| A     | 640 | 777 | 883 | 992 | 999 | 1000 | 1,42 | 9,05 |
| B     | 336 | 582 | 589 | 560 | 868 | 730  | -2,01 | -1,29 |
| L     | 377 | 688 | 666 | 456 | 899 | 805  | 0,44  | 3,14 |

* Tico is the temperature of intense conversion onset; ** Tmrr is the temperature of maximal reaction rate; ***Δm is the difference between the mass of samples in argon and given medium at Tioo in this medium.

Based on the results presented in Table 2, it could be seen that maximal reaction rate temperatures of the second stage were higher for CO₂ compared to H₂O. However, the temperatures of the intense conversion onset were nearly similar. This is in good correlation with presented literature data on conversion kinetics of carbon in carbon dioxide and steam media [9, 10]; in terms of Arrhenius equation, the activation energy of both these reactions is nearly similar, while frequency factor of reaction with H₂O is much higher than in CO₂. It means that temperature intervals of fuel mass loss in both these media would be similar (without taking into account burnout) while the reaction rate in steam would be higher.

The difference between mass at a temperature of the intense oxidation onset in inert medium and other media was quite small with the only exception of anthracite in the steam medium. Additionally, the difference between the mass of the sample in inert gas and steam at 777 °C (temperature of intense oxidation onset in carbon dioxide) was determined and equal to 1,54 wt.% For bituminous coal, the mass of the sample in CO₂ and H₂O media at determined temperature was even higher, likely, due to the endothermal character of reactions of carbon with such media [9].

### Conclusions

The conversion of three coal samples in the atmosphere of argon, carbon dioxide, and steam was studied using thermal analysis. The characteristic temperatures of intense conversion onset were close for bituminous coal and lignite with a difference of less than 25 °C. For anthracite, this difference was larger – close to 100 °C. The opposite situation was observed for temperatures of maximal reaction rate – they were nearly similar for anthracite and quite different for bituminous coal and lignite: the
difference was 138 °C and 94 °C, respectively. The maximal reaction rate in carbon dioxide medium was higher meaning it is more preferable as pyrolysis agent compared to steam. The difference between the mass of samples at the temperatures of intense conversion onset in reactive and inert media was quite low (lesser than 4 wt. % with the only exception for anthracite in steam medium). To sum up, the mixture of carbon dioxide and steam (which could be obtained by burning solid or gaseous fuel with low oxidizer-fuel ratio) could be effectively used for pyrolysis purposes at temperatures below the determined values of intense conversion temperatures, i.e. lower than 777 °C for anthracite, lower than 582 °C for bituminous coal, and lower than 666 °C for lignite. For bituminous coal using such gases, pyrolysis could result even in a higher mass of solid residue due to the endothermal character of reactions between carbon and carbon dioxide or steam. For pyrolysis in a higher temperature range, carbon dioxide could be recommended because its activity was lower compared to steam.

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