



Energetic and ecological effect of small amount of metalline powders used for doping waste-derived fuels



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ABSTRACT

The synthesis of an effective composite fuel from industrial wastes almost always requires mixing several components with different properties. Features of certain components can effectively compensate for the limitations of others, eventually improving the fuel as whole. We propose the optimization of the waste-derived coal-water slurry (CWS) by doping it with a small amount (2–5 wt%) of non-hydrocarbon dopants (metal-bearing powders with aluminium, iron, copper and chalk). It allows the stabilization of the combustion temperature (or even its increase), while keeping the ignition delays at the reasonable level (~ 2 s at 1000 K). Doping the CWS by 2–5 wt% of chalk powder allows a radical decrease in the production of harmful exhausts (up to an order of magnitude regarding the SO_2 and 2–5 times regarding NO_x). A strong ecological effect was observed when the fuel is doped by iron powder, too. Therefore, the usage of non-organic dopants is a very promising way to prepare environmentally friendly fuel compositions with high power efficiency.

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1. Introduction

The optimal combustion of any fuels requires satisfying a set of conditions regarding the furnace temperature, fuel content and atomization level, etc. [1–3]. Multi-component fuel compositions have evident difficulties with the optimization of the burning regime due to different favorable conditions needed for different components. However, such fuels are very popular due to the possibility to compensate for the downsides of some components by the upsides of others. Coal-water slurries (CWS) became popular in this way due to the low air pollution and good energy performance as compared to usual coals [4–6].

The preparation of CWS is a popular way to utilize coal-processing waste like sludges, filter cakes, low grade coals, etc. [4,7,8]. These waste-derived fuel compositions are suitable for industrial and domestic heaters because of their fire-safe storage and low price consisting mostly of transportation costs. However, better functional properties of CWS can be achieved after doping them by waste petrochemicals [9,10]. It improves the ignition parameters as well as the calorific value of CWS together with the additional utilization of oil-processing waste. A typical amount of the petrochemical dopant is up to 10–15 wt% because higher concentrations

lead to strong negative changes in the rheological properties of the fuel [9].

However, sometimes we need further modification of the properties of fuel compositions, which cannot be done by petrochemicals. For example, the external limitations related to fuel viscosity or the content of exhausts can restrict fuel doping by oil-based waste. Some of our previous works [7,8] describe the ignition properties of the fuel compositions doped by a small amount (less than 5 wt%) of metal and metal oxide powders. Non-combustible and highly inert particles of TiO_2 allow the stabilization of the combustion temperature together with a relatively good ignition delay time [7]. CWS doping by petrochemicals with a small amount of aluminium powder gives different effects (like an increase in the combustion temperature by more than 100 K, stabilization of the combustion heat for a wide range of furnace temperatures, etc.) depending on the powder concentration and furnace temperature [8]. The usage of aluminium powder as a dopant for CWS is an economically attractive way because the coal ash always contains a lot of alumina (15–35 wt%). Thus, doping just leads to an increase in this number making the ash an attractive raw material for the reduction of the aluminium from oxide. Aluminium is quite expensive, but our fuel composition keeps practical attraction even taking in account the price of 50 kg of aluminium per 1 ton of the CWS.

In this paper, we investigate experimentally the *thermal* and *ecological* effect of doping of the waste-derived CWS by different metalline powders with waste engine oil. In contrast to

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aluminium, the new dopants introduce new chemical reactions going on during the CWS combustion. They lead to significant changes in the chemical content of the exhausts, which was analyzed in this paper. The dopants aimed at the improvement of environmental friendliness mostly decrease combustion efficiency but this looks like a reasonable price for cleaner heat production.

An essential part of the metal remains in ash as solid insoluble substances and does not spread any harmful effects to the environment. Most of the chemical elements composing the dopants or produced after their combustion are already present in the coal ash and, therefore, our approach does not add any new chemicals to the ash. The dopants were chosen to be cheap and widespread, thus, the results will be interesting for numerous people who deal with the ignition and combustion of waste-derived fuels.

2. Materials and methods

2.1. Preparation of the fuel compositions

All fuel compositions were based on the filter cake of fiery coal, which contains ~62 wt% of coal powder (particle size less than 100 μ) and water. This coal processing waste is described in detail in numerous papers [1,4,7,8] and, therefore, it is very convenient as a test sample. The CWS was doped by a mixture of waste motor oil (MO) and a certain amount of metal or metal salt powders. This slurry fuel differs from the earlier observed [7,8] because it contains a different petrochemical component with lower viscosity (MO instead of fuel oil). The final fuel compositions can be divided into four classes:

1. Aluminized CWS (10 wt% of MO with 2–3–5 wt% of aluminium powder PAP-2 [11] and 88–87–85 wt% of filter cake correspondingly);
2. Ironized CWS (10 wt% of MO with 2–5 wt% of iron powder [12] (particle size 40 – 160 μ) and 88–85 wt% of filter cake);
3. The CWS doped by copper powder [12] (10 wt% of MO with 5 wt% of copper powder (particle size 40 – 100 μ) and 85 wt% of filter cake);
4. The CWS doped by calcium carbonate (10 wt% of MO with 2–5 wt% of chalk powder (particle size 50 – 100 μ) and 88–85 wt% of filter cake).

We have chosen these very substances for fuel doping for two reasons: they are natural and do not lead to any more environmental pollution by new chemicals and they are widespread for mass usage. Most of the possible products of fuel combustion induced by the proposed dopants are insoluble solids that will precipitate comprising to the ash. Aluminium, iron, copper, calcium and their oxides are naturally present in the ash of bituminous coals, so our intervention just changes their concentration. Some of these dopants are generally recognized means of stimulation of the combustion or pollution control [13–15].

Most of the solid dopants were powders made up of particles that are smaller than coal particles. The final fuel compositions were homogenized by mechanical mixing for half an hour to ensure a highly uniform substance. The slurry was viscous enough to keep the uniformity for 2 days [16]. Some properties of the organic fuel components are shown in Table 1.

It is clear from the Table that the main part of the fuel composition (except metal dopants) has a calorific value of ~13 MJ/kg. It is approximately 40% of the calorific value of typical anthracite coal but taking into account the price of the waste-derived fuel which approaches the price of used dopants, this fuel is economically attractive. The main problem is just in suitability of the principal combustion parameters for a certain application.

Table 1

Physical and chemical properties of the main fuel components.

<i>Filter cake of the fiery coal</i>	
Fraction of coal part in wet state, wt%	62.1
Combustion heat in wet state, MJ/kg	9.46
Combustion heat in dry state, MJ/kg	15.23
Yield of volatiles in dry state, wt%	14.8
Ash content in dry state, wt%	50.89
Carbon content in dry state, wt%	87.47
Hydrogen content in dry state, wt%	5.039
Nitrogen content in dry state, wt%	2.15
Sulfur content in dry state, wt%	0.444
Oxygen content in dry state, wt%	4.77
Therm. cond. (dry) at 400 K, W/(m K)	0.49
Specific heat (dry) at 400 K, J/(kg K)	2435.5
<i>Waste motor oil</i>	
Density at 293 K, kg/m ³	871
Moisture content, wt%	0.28
Ash content, wt%	0.78
Ignition point, K	491
Combustion heat, MJ/kg	43.98
Evaporation heat, MJ/kg	0.178
Therm. cond. at 400 K, W/(m K)	0.107
Specific heat at 400 K, J/(kg K)	1760

2.2. Measurement methods of the fuel combustion parameters

We have analyzed three important parameters of the fuel: ignition delay time, maximum combustion temperature and content of gaseous exhausts. These values clearly explain the influence of dopants on the ignition, combustion efficiency and ecological impact of the chosen composite fuel. The scheme of the experimental setup for thermal and temporal measurements is shown in Fig. 1a.

A small portion of the fuel was placed onto the tip of a thin wire and then introduced into the tube muffle furnace by a motorized linear translation stage controlled from a computer. It allows fast introduction of the fuel into the middle of the furnace (in 1–1.5 s) with a very good repeatability of the introduction time. The Nabertherm R 50/250/13 muffle furnace allows keeping the stable temperature inside the furnace in the range of (300–1500 K). The fuel ignition and combustion were observed in the steady state atmosphere. The dominating heat transfer mechanism was radiative heating rather than convective heating like in the previous investigations [7,8].

The weight of the fuel sample was controlled through its volume using an electronic batcher. Time measurements were done using quasi-spherical droplets with a radius ~1 mm ($V \sim 4 \text{ mm}^3$). The fluctuations of the droplet volumes were less than 5%. At the same time, the product of the specific heat and density of the fuel varies by less than 2% from the average value (~3.5 MJ/kg) for all the fuel compositions.

The volume of the fuel samples for gas analysis was ~500 mm³ ($R \sim 5 \text{ mm}$), which allowed effective measurements. In this case, the sample was fixed on the bigger holder with basket-like netting tip.

Observations of the temporal parameters of the fuel ignition were done from the other face of the furnace tube by the Phantom V411 high-speed video camera. The camera was equipped with macro optics, which allowed the effective designation of the ignition and quenching. The video was recorded at a resolution of 800 × 600 px and with a frame rate of 2500 fps. This means that the time resolution was not worse than 0.4 ms and the corresponding systematic errors of the time measurements did not exceed this value.

The moment of the fuel ignition was determined from the analysis of the sequence of video frames (Fig. 2). The first stage of the ignition is a gas-phase ignition of volatiles around the fuel droplet.

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