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CO-COMBUSTION COAL AND WASTE ALTERNATIVE FUEL:
THERMOGRAVIMETRIC ANALYSIS

SPOLUSPALOVÁNÍ UHLÍ A ALTERNATIVNÍHO PALIVA:
TERMOGRAVIMETRICKÁ ANALÝZA

Abstract

Combustion of coal together with a relative small percentage of waste alternative fuel (WAF) may be a choice for the management of these wastes. Co-combustion coal and their blends of 5%, 10% and 50% (wt.%) with waste alternative fuel were tested in a thermogravimetric analyser (TGA) in the temperature range from ambient to 1000°C under the heating rate of 10 °C min⁻¹. Combustion characteristics such as volatile release, ignition and burnout were also studied for the fuel blends. The method of direct non-linear regression was used for calculation of apparent kinetic parameters of oxidation processes from thermogravimetric (TG) curves. The coal oxidation is the first-order reaction. The study has been conducted aiming at widening the spectrum of fuels utilised by co-combustion.

Abstrakt

Spalování uhlí s relativně malým procentem alternativního paliva představuje možnost pro nahlázení s těmito odpady. Spoluspalování uhlí a jejich směsí 5%, 10% a 50% (hm%) s alternativním palivem bylo hodnoceno termogravimetrickým analyzátozem v teplotním rozsahu do 1,000°C a rychlosti ohřevu 10°C min⁻¹. Spalovací charakteristiky jako tškání, vznícení a zapálení byly také studovány u směsí paliva. Pomocí metody přímé nelineární regrese (PNR) byly stanoveny formální kinetické parametry (aktivační energie, frekvenční faktor) oxidace z TG křivek pro řád reakce roven jedné. Studie byla provedena za účelem rozšíření spektra paliv pro spoluspalování.

1 INTRODUCTION

One realistic option contributing to fulfil the provisions of the Kyoto Protocol, committing the European Union to achieve over the period from 2008 to 2012 an overall greenhouse gas emission reduction by 8% compared with the 1990 levels, is represented by the substitution of fossil fuels with low-carbon fuels for energy production purposes. Co-combustion coal and waste alternative fuel may be one of the options for the management of these wastes. Combustion characteristics of fuel before it is used in energy production can be determined by using thermo-analytical techniques such as TG, DTG, DTA, DSC and TMA which cover a wide range of applications in research, development and economic assessment of fuels. They have been used in a wide variety of areas related to proximate analysis, coal reactivity, and heat effects associated with coal pyrolysis, combustion, co-combustion and heat of hydrogenation. Thermogravimetric analysis (TGA) is the simplest and the most effective techniques to observed the burning profile of a fuel.

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2 EXPERIMENTAL STUDY

2.1 Materials and techniques

Brown coal (C) and waste alternative fuel (WAF) have been used in this work. The C comes from the north coalfield of Bohemia and it is usually exploited in circulating fluidised-bed power station in Tisová at about 850 °C. WAF containing plastics (1-20%), fabric and carpets (45-75%), rubber (5-15%), paper (1-10%) and wood (1-10%) comes from the supply company. C was crushed, ground in the segmental mill, sieved and fractions below 0,1 mm were used for the measurements. WAF ground to cutting mill SM 100 for 3 min at 1390 rpm = particle size 6 mm and ultra centrifugal mill ZM 200 for 6 min at 18 000 rpm = particle size 0,05 mm.

Samples were prepared as a mixture of 5 %, 10 % and 50 % WAF with C.

The thermal analysis was carried out using simultaneous TG-DTA apparatus NETZSCH STA 409 EP. All the experiments were conducted under the identical conditions: the samples (10¹ mg in weight) were heated up to 1,000 °C in the crucibles (aluminium oxide) in a dynamic atmosphere of dry air at the heating rate of 10 cm³ min⁻¹.

2.2 Determination of apparent kinetic parameters

The method of direct non-linear regression [5] was used for calculation of apparent kinetic parameters of oxidation processes from thermogravimetric (TG) curves.

The calculation is based on the kinetic equation (1)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (1)$$

If the time step is set small enough, the derivatives in Eq. (1) may be replaced by differences. We assume that the TG curve is composed of very small linear segments of the length Δt , in which the reaction rate is constant:

$$\Delta\alpha = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \Delta t \quad (2)$$

where α is the degree of conversion, t - time (s), T - absolute temperature (K), R - molar gas constant (8.314 J. K⁻¹ mol⁻¹), A - frequency factor (s⁻¹), E - activation energy (J. mol⁻¹) and n is the reaction order.

Assuming the α_0 and t_0 at the beginning of the α vs. t curve, further points of the curve can be calculated from the recurrence relation

$$\alpha_i = \alpha_{i-1} + A \exp\left(-\frac{E}{RT_{i-1}}\right)(1-\alpha_{i-1})^n (t_i - t_{i-1}) \quad (3)$$

If the TG curve consists of p various processes with kinetic parameters A_j , E_j and n_j ($j=1$ to p), Eq. (3) can be used for calculation of extent of conversion for individual reactions. In this case, the equation describing the whole curve can express as a sum of particular equations:

$$\alpha_i = \sum_j \alpha_{j,i-1} + \sum_j A \exp\left(-\frac{E_j}{RT_{i-1}}\right)(1-\alpha_{j,i-1})^{n_j} (t_i - t_{i-1}) \quad (3)$$

This equation enables to determine apparent kinetic parameters of multistep reactions by means of non-linear optimization.

In our calculations we assumed, similarly to other authors, that the coal oxidation is the first-order reaction and that the effect of diffusion can be neglected under used this experimental conditions.

3 RESULTS AND DISCUSSION

3.1 The oxidation of brown coal

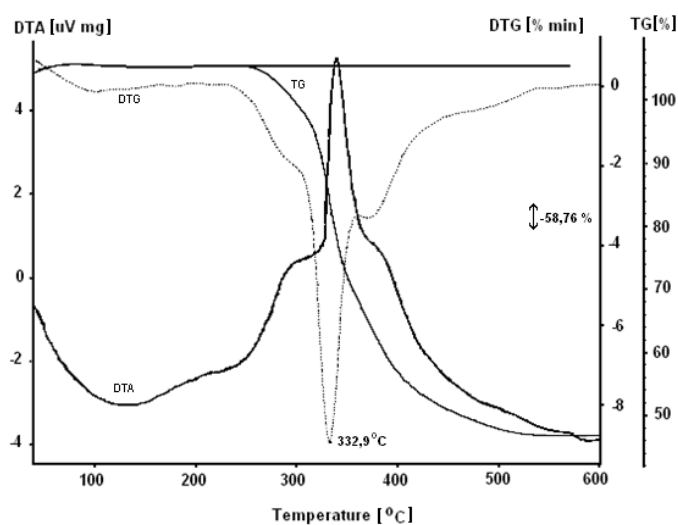


Fig. 1 Thermoanalytical curves of brown coal oxidation.

The coal oxidation proceeds in the temperature range 250 – 600 °C and it is not a single process containing two partially overlapped stages. At lower temperatures (250-350 °C) the process corresponds to the oxidation of coal pyrolysis components accompanied by the release of volatile substances and their oxidation in the gas phase. The resulting semi-coke is subsequently oxidised at higher temperatures (350 – 600 °C). Total weight loss from TG curve is 58.8 % with distinct maximum temperature about 333 °C (DTG curve).

The results of kinetic calculations are summarized in table 1.

Table 1 Kinetic calculation of brown coal oxidation.

	Temperature range T [°C]	Activation energy E_A [kJ mol ⁻¹]	Frequency factor A [s ⁻¹]
1. process	250 - 350	155	$1.445 \cdot 10^{11}$
2. process	350 - 600	60	$1.148 \cdot 10^2$

3.2 The oxidation of waste alternative fuel

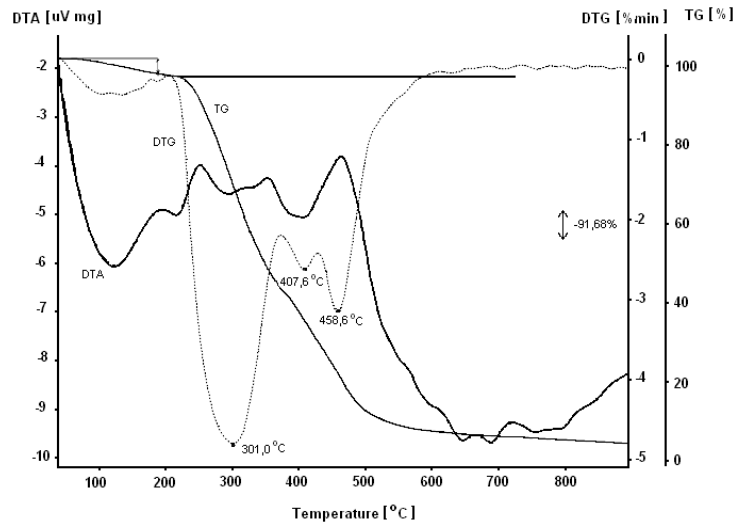


Fig. 2 Thermoanalytical curves oxidation of waste alternative fuel.

The WAF oxidation proceeds in the same temperature range 250 – 600 °C such as coal oxidation. This is not a single process too containing several partially overlapped stages with two significant maximum temperatures about 301 °C and 459 °C (DTG curve). Total weight loss from TG curve is 95.5 %.

The results of kinetic calculations are summarized in table 2.

Table 2 Kinetic calculation of waste alternative fuel oxidation.

	Temperature range T [°C]	Activation energy E_A [kJ mol ⁻¹]	Frequency factor A [s ⁻¹]
1. process	200 - 350	70	$1.047 \cdot 10^4$
2. process	350 - 600	55	$2.466 \cdot 10^1$

3.3 The oxidation of brown coal blends and WAF

Following three thermoanalytical curves show co-combustion of brown coal and waste alternative fuel in the different weight ratio: coal and 5 % WAF (Fig. 3), coal and 10 % WAF (Fig.4) and coal and 50 % WAF (Fig. 5). To compare the effect of WAF addition, the temperatures of reaction maximum and weight losses were read from TG and DTG curves (table 3).

Table 3. The temperatures of reaction maximum and weight losses.

	Temperature T_{max} [°C]	Weight loss Δm [%]
C + 5% WAF	393.5	64.4
C + 10% WAF	401.2	68.4
C + 50% WAF	439.4	70.9

Higher addition of WAF shifts the oxidation maximum towards higher temperatures together with increasing weight loss.

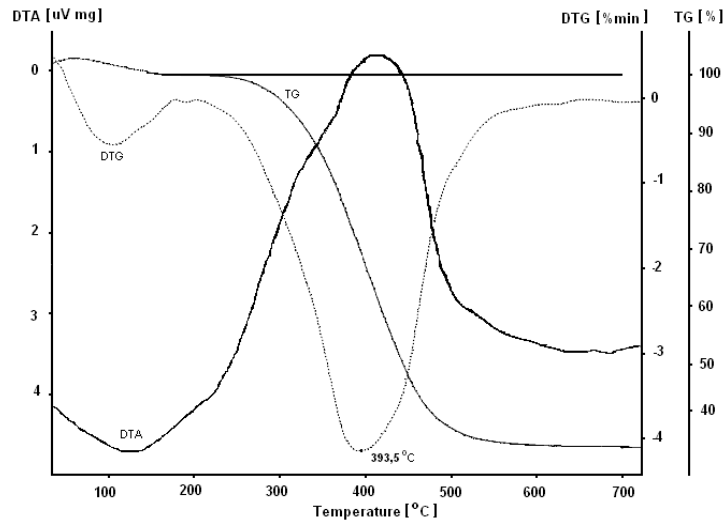


Fig. 3 Thermoanalytical oxidation curves of coal and 5% waste alternative fuel.

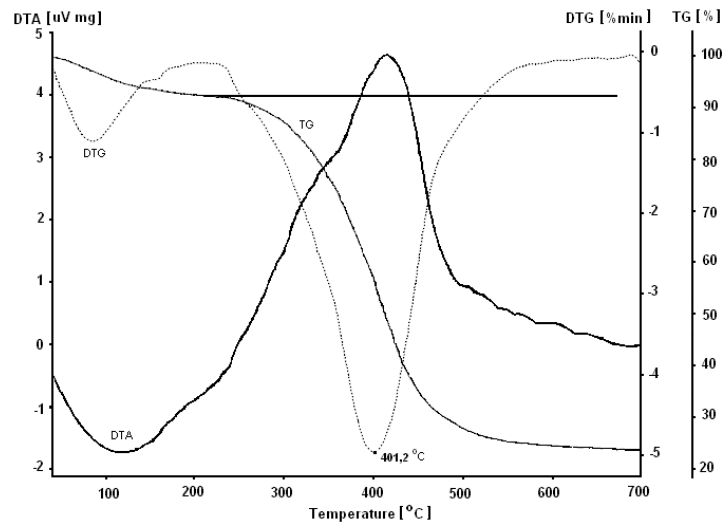


Fig. 4 Thermoanalytical oxidation curves of coal and 10% waste alternative fuel.

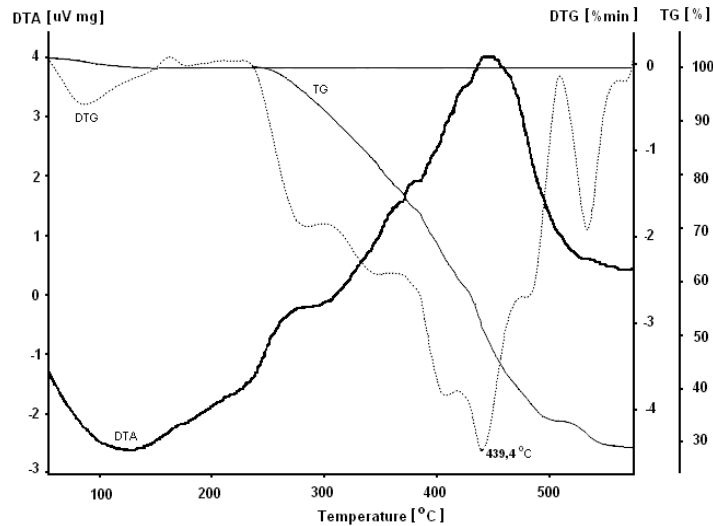


Fig. 5 Thermoanalytical oxidation curves of coal and 50% waste alternative fuel.

CONCLUSIONS

The co-combustion behaviour of brown coal with the waste alternative fuel and their blends has been investigated using the TGA analysis. The conclusions drawn resulting from the present study are summarized as follows.

- finding the optimal ratio of coal and waste alternative fuel
- extend extension of the range of fuels for co-combustion
- determination of apparent kinetic parameters using TGA

Thermogravimetric analysis allowed to ascertain differences between coal and waste alternative fuel combustion. The oxidation of waste alternative fuel is does not one process but it consists of several partially overlapped stages.

The optimal ratio of coal and waste alternative fuel is C + 10 % WAF because the oxidation of this blend is resembling/similar to coal combustion. This ratio is suitable in term of distribution parts of heating effect, incineration and after-flame time.

The combustion of the studied wastes is characteristic for each kind of material. No general conclusions may be established on the groups of measured wastes but the present study proves that thermogravimetric analysis is a very useful tool for a first, simple and fast assessment of wastes combustion behaviour and fuel properties before their incineration.

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