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Thermochemical treatment of E-waste from small household appliances using highly pre-heated nitrogen-thermogravimetric investigation and pyrolysis kinetics

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ABSTRACT

The EU directive on waste of electrical and electronic equipment (WEEE) 2002/96/EC has set a goal of recovering 70–80% in terms of materials and energy. Nowadays, thermal cracking (pyrolysis) of such waste streams is receiving renewed attention, due to the energy and material recovery that can be achieved and therefore the sustainable waste management. However, it still lacks the kinetic background which is of great importance for a successful design of thermochemical processes. In this study the kinetic parameters of WEEE (originating from small household appliances) pyrolysis using highly pre-heated nitrogen under six different heating rates (1–2.5 K/s) have been estimated using a combination of model-free and model fitted methods. Even though WEEE is heterogeneous material, similar behavior at each of the six different heating rates applied was observed. The activation energy of the pyrolysis process determined with two different model-free methods gave comparable results. Pre-exponential factor and reaction order were determined using the Coats-Redfern method. The estimated kinetic parameters for the WEEE pyrolysis are: $E = 95.54$ kJ/mol, $A = 1.06 \times 10^8$ and $n = 3.38$.

1. Introduction

Around 10 million tonnes of electrical and electronic equipment are placed on the market of EU-27 and about nine million tonnes of waste coming from electrical and electronic equipment are generated yearly. Taking into consideration the technological evolution in electronics industry, their life time is getting shorter with their waste growing with a tremendously fast rate. According to predictions about 12 million tonnes per year will be generated by 2020 [1].

EU, recognizing the problem and in conjunction with the climate change conditions and the depletion of the oil and fossil fuels reserves, has introduced the 2002/96/EC directive [2], demanding 70–80% of the WEEE generated to be recovered in terms of energy and materials. Since thermochemical processes (pyrolysis and gasification) can be providers of both energy and material recovery the scientific community turned its attention to them and especially pyrolysis.

Recycling of WEEE is an important subject not only from a waste treatment and energy recovery perspective but also from the recovery aspect of valuable materials [3]. WEEE is regarded as a resource of metals such as Cu, Al, Fe, Pb, Zn as well as noble metals like Ag, Au, Pt, Pd or even rare elements such like Ta. Effective separation of metals is the key for developing an effective recycling system [3].

WEEE contains about 30% plastics [3,4] and therefore it is imperative to include these plastics in recycling systems. In fact, material characterization revealed housing fractions of e-waste (small WEEE–sWEEE) to be interesting sources for energy recycling [5]. In addition, the pyrolysis residue contains both organic and metallic fractions which can easily be separated enhancing material recovery [6]. It is also reported that sWEEE contributes highly to the pollutant load of residual MSW concerning elements such as Cd, Pb and Br, whereas its introduction into waste incinerators results in high concentrations of heavy metals in the slag, the flue gas or the filter cake [7], which makes pyrolysis a more appropriate method for treatment of sWEEE due to lower operating temperatures that results in very lower emissions of such elements [8]. However, there is significant lack of expertise related to sWEEE treatment [7].

Pyrolysis is the heart of a thermochemical process and the products distribution is strongly affected by the pyrolysis conditions. Thus, reliable pyrolysis conversion rates are needed in a successful design of a thermochemical reactor. Even though that several kinetic data for different kinds of plastics are reported and different

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Abbreviations

WEEE	waste of electrical and electronic equipment
sWEEE	small waste of electrical and electronic equipment
HHV	higher heating value
KAS	Kissinger–Akahira–Sunose
OFW	Ozawa–Flynn–Wall
TG	thermogravimetric
DTG	differential thermogravimetric
LHS	left hand side
RHS	right hand side

Nomenclature

T	temperature (K)
t	time (s)
m	mass of solid (g)
E	activation energy (J mol^{-1})
A	pre-exponential factor (s^{-1})
n	reaction order
R	gas constant 8.314 (J K^{-1} mol^{-1})
Er	error
Ea	characteristic apparent activation energy
f(α)	function depending on the decomposition mechanism
g(α)	integrated function depending on the decomposition mechanism

Greek symbols

α	normalized conversion
β	heating rate (K s^{-1})

Subscripts

0	initial state
t	state at time *t*
f	final state

decomposition mechanisms are proposed, reported data reveals that the decomposition rate of plastics is heavily affected by interactions of different plastics in a mixture [9,10].

Electrical and electronic waste is a heterogeneous material with variations in reported compositions. However waste coming from specified applications (sWEEE) (Blenders, mixers, heaters, toasters, coffee makers, cables, shavers, etc.) is comprised of same kind of materials and if a sophisticated approach of sampling is applied, a sample with representative composition can be obtained.

According to the above mentioned, it is understood that pyrolysis still lacks of kinetic background that will allow the proper and successful design of processes treating sWEEE. Thermogravimetry is a useful, convenient method for the study of a variety of decomposition processes for a range of materials and it has been used for determining kinetic parameters of different fractions of WEEE [11,12]. However, none of the previous studies has treated actual mixed waste coming from a sWEEE processing plant.

Furthermore the use of a highly pre-heated sweeping gas for WEEE pyrolysis has never been investigated. In previous studies, it has been reported that the use of a highly pre-heated agent during thermochemical treatment, result in low char yield [13–15]. Thus the use of pre-heated agent improves the separation between the organic and inorganic matter enhancing both energy as well as material recovery due to the higher volatile matter yield and lower char yield respectively.

In this study the thermal degradation (decomposition behavior as well as kinetic rate) of electrical and electronic waste from small household appliances has been investigated in a try to understand the mechanism of such decomposition and fill in the gap of kinetic data lack for such kind of materials.

The decomposition was investigated under heating rates of 1–2.5 K/s. In order to obtain kinetic parameters, combination of model-free and model fitted methods has been used.

2. Materials and methods

2.1. Materials

The raw material was provided by Stena Metall AB. The waste was originated from small household appliances as this is defined by El-Kretsen report [16] and Annex IB of 2002/96/EC directive [2]. The term "small household appliances" includes all the household appliances excluding white goods, refrigerators, TV and audio appliances.

The waste carefully decontaminated mercury, PCB capacitors, batteries, and other environmentally damaging substances and components according to Swedish Waste Management (Avfall Sverige) demands [17].

According to the sampling procedure 10 l is taken directly from the transportation conveyor four times a day during 4 days and a total amount of 150 l was collected. A representative sample of 2 l was then taken out by mixing and quartering from the whole sample. Then the sampled was run through a hammer mill (20 mm mesh) and grounded into pieces. Sampling of the material was done according to Värmeforsk report 1036 [18].

The proximate and ultimate analyses of the resulting material are shown in Table 1.

Since the material contains a high amount of ash the empirical chemical formula was calculated on dry basis and equals to $CH_{1.41}O_{0.15}N_{0.03}S_{0.0004}$ Higher Heating Value (HHV) of the sample was calculated using the following formula [19]:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash[kJ/g] \quad (1)$$

where C, H, S, O and N are the corresponding weight percentages on dry basis of carbon, hydrogen, sulfur and oxygen respectively. A value of 19.91 MJ/kg was calculated for the sample.

Table 1
Proximate and Ultimate Analyses of Household Electrical and Electronic Waste.

Proximate analysis (%wt)					
Moisture				10.1	
Ash				35.4	
Volatile matter				42.6	
Ultimate analysis (db)					
C	44.3	%wt	Ti	1730	ppm
H	5.2	%wt	Sb	6.01	ppm
N	1.62	%wt	As	<0.1	ppm
O	8.86	%wt	Ba	614	ppm
Cl	4.54	%wt	Pb	49700	ppm
Br	1.183	%wt	B	271	ppm
S	0.053	%wt	Cd	51.1	ppm
Si	14600	ppm	Co	29.7	ppm
Al	9120	ppm	Cu	188000	ppm
Ca	43300	ppm	Cr	179	ppm
Fe	4750	ppm	Hg	1.41	ppm
K	707	ppm	Mo	71.3	ppm
Mg	3090	ppm	Ni	79	ppm
Mn	261	ppm	V	69.2	ppm
Na	469	ppm	Zn	24600	ppm
P	747	ppm			