CHARACTERIZATION OF REFUSE-DERIVED FUEL (RDF), ANALYSIS OF PROPERTIES AND ASSESSEMENT OF POTENTIAL THERMOCHEMICAL VALORIZATION AS ALTERNATIVE FUEL IN CEMENT INDUSTRY

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ABSTRACT

Alternative fuels, such as Refuse-Derived Fuel (RDF) – a fraction separated from municipal and commercial wastes with a high calorific value – can undoubtedly serve as a viable and beneficial alternative for combustion in the cement industry. This includes aspects such as waste management and reduction, energy and mass recovery, lower GHG etc.[1]. The effectiveness of utilizing RDF in the cement industry depends on various factors, including the quality of the RDF produced (i.e., high/low calorific value), combustion technology efficiency, and adherence to environmental regulations (i.e., low concentration of various impurities such as chlorides, etc.)[2], [3]. While RDF is a value-added product compared to the original waste, its diverse blend of materials requires additional effort for the prediction of its physical properties and chemical composition. This study focuses on assessing the properties of a typical RDF sample fuel, encompassing physical analysis, proximate and ultimate analysis, and thermal analysis. The aim is to further explore the potential use of RDF as an energy-efficient material. A conventional coal sample was also analyzed as a base case reference fuel.

Manual material sorting revealed that the RDF sample primarily consists of plastic and paper (approximately 75%), with the remaining fractions predominantly composed of organics, wood, and textiles. Tandem elemental analysis was conducted using standard ASTM D 5291 combustion and thermoconductivity detection (LECO CHN828), Energy Dispersive X-ray Spectroscopy (EDS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Thermogravimetric Analysis with Differential Scanning Calorimetry (TGA-DSC) was performed to determine the kinetic release of volatiles and combustion of solid residue. The High Heating Value (HHV) of RDF was established using an isoperibol bomb calorimeter, measuring 19.2 MJ/kg. Morphological characterization of the samples was carried out through Scanning Electron Microscopy (SEM), while structural parameters such as crystallinity and average crystal size were assessed via X-Ray Diffraction (XRD).

The outcomes of this study will be further utilized to validate an in-house developed combustion model to predict flame characteristics, species evolution and concentrations, and char burnout coupled with a CFD model of a real cement kiln.

KEYWORDS: refuse-derived fuel (RDF); properties assessment; alternative fuel; thermochemical valorization

INTRODUCTION

Municipal and commercial wastes are produced to an increasing extent, and due to mismanagement of these wastes, there are major socioeconomic, health and environmental costs [1]. Municipal waste accounts for only about 10 % of total waste generated when compared with the data reported according to the Waste Statistics Regulation [4]. The difficulty in management of those wastes is caused by its complex and undifferentiated composition, the direct proximity of the waste produced to citizens, the high public visibility of this issue, and its impact on the environment and human health[5]. However, municipal and commercial wastes are great resources for energy recovery in the form of heat and electricity, syngas, char and pyrolysis oils [2], due to their high calorific value. These wastes constitute the Refuse-Derived Fuel (RDF), an alternative fuel that is often being used in cement kilns, boilers and for power generation [2]. RDF is produced from mixed combustible portions of waste, including household, commercial and industrial/trade waste [5] and comprises of combustibles such as plastics, paper materials and wood.

Cement industry is a field with high energy requirements and a large carbon footprint. Therefore, it is necessary to find new alternative ways of operating the cement kilns, which will have lower environmental costs. RDF could be a solution to this problem, provided that it will be effective to utilization, due to its quality (i.e., high/low calorific value), combustion technology efficiency, and adherence to environmental regulations (i.e., low concentration of various impurities such as chlorides, etc.) [2-3].

This paper is a study dealing with the analysis of an RDF sample, and an attempt to make useful characterization of the fuel to determine its acceptability or unacceptability as a cement kiln fuel.

METHODOLOGY

Two samples were examined; one Petroleum coke (i.e. pet coke) sample and one RDF sample (Fig.1).

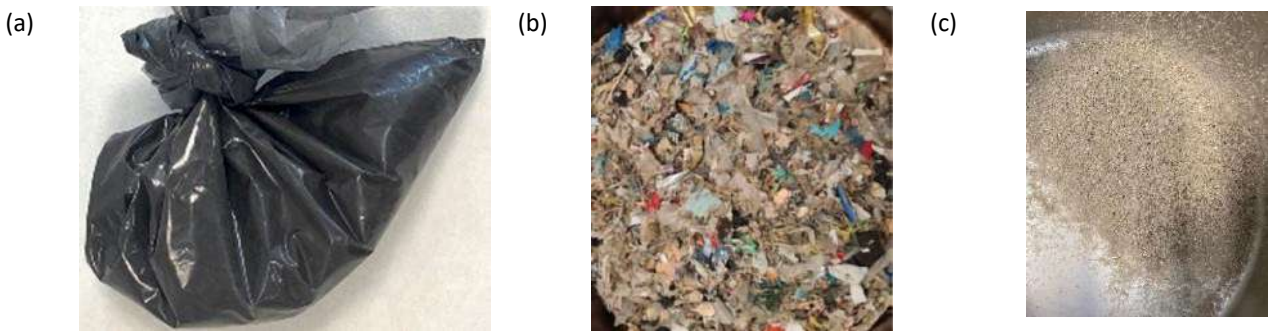


Figure 1. *Image of (a) pet coke sample, (b) RDF sample as-received and (c) RDF sample after milling.*

The morphological and microchemical analysis of the samples was performed by InTouchScope™ JSM-IT 500 Scanning Electron Microscope (SEM) in combination with Energy dispersive X-ray spectroscopy (EDS) by JEOL, Japan. Observation of the materials was performed after coating the surfaces of the samples with conductive gold layers. The determination of the kinetic release of volatiles and combustion of solid residue for the samples was carried out by applying the Thermogravimetric Analysis with Differential Scanning Calorimetry (TGA/DSC) method (NETZSCH, Germany, Jupiter STA 449 F3 model, at maximum temperature 1650^{o}C). Determination of the Particle Size Distribution (PSD) of the samples was carried out by Dynamic Light Scattering (DLS) and Laser Scattering. The DLS method (VASCOγ model from CORDOUAN Technologies, France) focuses on the determination of primary particles, while the determination of the size distribution of aggregated particles was performed by Laser Scattering (Laser Scattering Particle Size Distribution Analyzer-LA-960/HORIBA, Japan). The crystallographic structure of the samples was studied by X-ray Diffraction Crystallography (XRD) (X-Ray Diffractometer, D9 Advance model, Bruker, Germany). Qualitative and quantitative determination of combined elements was performed by Inductively

Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a Plasma 400 Perkin Elmer spectrophotometer equipped with a Ceta6000AT+ ultrasonic nebulizer. The average value of the upper heating value of the solid fuel samples was carried out by calorimetry (Parr 6200 Isoperibol bomb Calorimeter, USA). Elemental analysis was performed based on the Method 2023 – Phenylalanine method on Elemental analysis (LECO CHN828, Michigan). Specifically, for the elemental analysis of the RDF sample the method ASTM D 5291 was used. An analytical scale (Uni Bloc ATX224R, Shimadzu, China) was used for precision weighing of the samples during manual material sorting (max. weight: 220 g, min. weight: 10 mg, accuracy: 0.1 mg). The experimental determination of the weight-based particle size distribution of RDF was carried out by classification per size and per material. Each size fraction and each material by size fraction was weighed. The total manual sorting process lasted 5 days, and weighing took place on the 5th day. During this period, the sample was kept under ambient temperature conditions, allowing thus to reduce the initial moisture content.

RESULTS AND DISCUSSION

Determination of the weight-based particle size distribution of RDF

The weight-based particle size distribution of RDF sample was carried out by classification per size at the ranges >20cm, 15-20cm, 10-15cm, 5-10 cm, 1-5cm, <1cm. The percentages of weight of each size class of materials are listed in Table 1. The largest weight is occupied by the 1-5 cm size fraction with a percentage of 51.21%, followed by the fraction for materials <1 cm, with a percentage of 29.56% and then the 5-10 cm size fraction with a percentage of 16.04%. This is followed by materials of size 10-15 cm (2.88%), materials larger than 20 cm (0.18%) and finally materials of size 15-20 cm (0.14%).

Table 1. *Weight and percentages of weight of each size class of materials.*

Length (cm)	Weight (gr)	%
>20	0.5172	0.175701
15-20	0.3976	0.135071
10-15	8.4891	3
5-10	47.2071	16.03695
5-1	153.1572	51.21321
Total	87	29.55519

Material types that have been identified by oral observation are: Thin plastic, Thin plastic with aluminum coating, Hard plastic, Metal, Wood, Rubber, Rubber, Paper, Foam, Glass, Soil. Soil occupies the highest weight percentage (29.50%) followed by fine plastic (25.45%). The third position is significantly far in percentage from the previous two and is occupied by hard plastic (11.13%), followed by paper (10.39%) and fabric (9.64%). In smaller percentages are thin plastic with aluminum (3.83%), stones (3.15%), foam (1.13%), glass (1.09%) and finally with very small percentages are rubber (0.82%) and metal pieces (0.58%).

Table 2. *Weight and percentages of weight of each size class of materials.*

Material	Weight (gr)	%	Material	Weight (gr)	%
Metallic	1.6978	0.58	Thin plastic with aluminum	11.2981	3.83
Rubber	2.4252	0.82	Fabric	28.4349	9.64
Glass	3.2138	1.09	Paper	30.6357	10.39
Foam flex	3.3286	1.13	Hard plastic	32.8315	11.13
Stones/marble/ceramic	9.2766	3.15	Thin plastic	75.0656	25.45
Wood	9.6967	3.29	Soil	87.000	29.50
		Total	294.9045	100	

Morphological and microchemical analysis by Scanning Electron Microscopy (SEM/EDS)

The SEM images for both RDF and pet coke samples, at different size scales are listed below. The magnification range was x30 - x2000.

From the low magnification SEM images it is observed that the pet coke sample shows homogeneity

and from the high magnification images it appears that there are aggregates of about 10 μm in size. It is also observed that the RDF sample consists of fibres and aggregates.

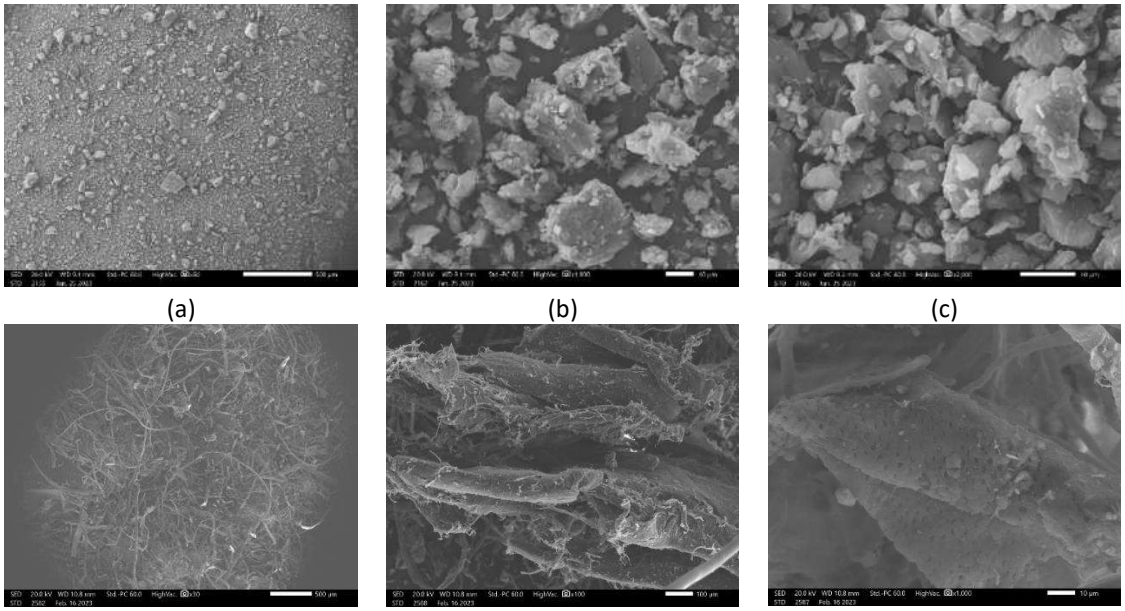


Figure 2. *SEM Images of pet coke sample at magnification (a) x50, (b) x1000, (c) x2000 and RDF sample at magnification (d) x30, (e) x100, (f) x1000*

The EDS results for both RDF and pet coke samples are depicted below. From the elemental EDS analysis at a random point in the sample, it is observed that pet coke is mainly composed of carbon (C), oxygen (O), sulphur (S) and calcium (Ca). Small amounts (below 0,4 %) of copper (Cu), silicon (Si), aluminium (Al), iron (Fe), etc. were also detected.RDF is mainly composed of carbon (C), oxygen (O), calcium (Ca),. Small amounts (less than 0.4%) of silicon (Si), sulphur (S), aluminium (Al), chlorine (Cl), sodium (Na), iron (Fe), magnesium (Mg), potassium (K) and titanium (Ti) were also detected.

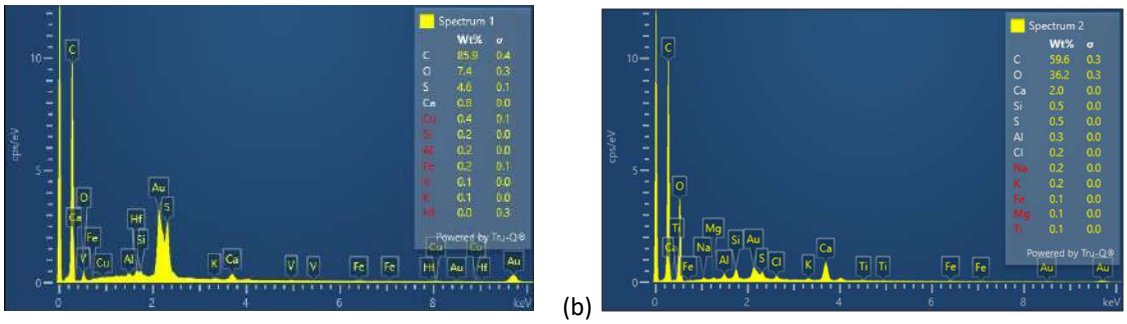


Figure 3. *Presentation of EDS results at random point of the (a) pet coke and (b) RDF samples*

Thermogravimetric Analysis with Differential Scanning Calorimetry (TGA-DSC) for the determination of kinetic release of volatiles and combustion of solid residue

The pet coke sample was heated from ambient temperature to 1,000ºC at a rate of 5ºC/min with air flow during thermogravimetric analysis. From the results presented in Figure 4, it is observed that the greatest weight loss starts from 310.8°C and stops at 548°C, during which the weight of the sample is reduced by 97.24%. This loss occurs due to the combustion of the sample, and release of the volatile components. The residue corresponding to 2.05 % is the ash, which is an inert material. There is also a strong heat release due to combustion, as expected.

The RDF sample was heated from ambient temperature to 1300ºC at a rate of 5ºC/min with air flow during thermogravimetric analysis. In Figure 5, where the thermogravimetric analysis of RDF is depicted, it is observed that the total weight loss up to 1,300ºC is about 88%, therefore the residual mass and therefore the ash content of RDF is about 12%. Also the weight loss at 200-360º C and

360-400°C occurs due to oxidation of the sample. It also appears that there is a strong heat release due to combustion, as expected. The two strong phenomena overlap and therefore quantification of the thermal effect of combustion is not possible, at least based on the heating protocol followed.

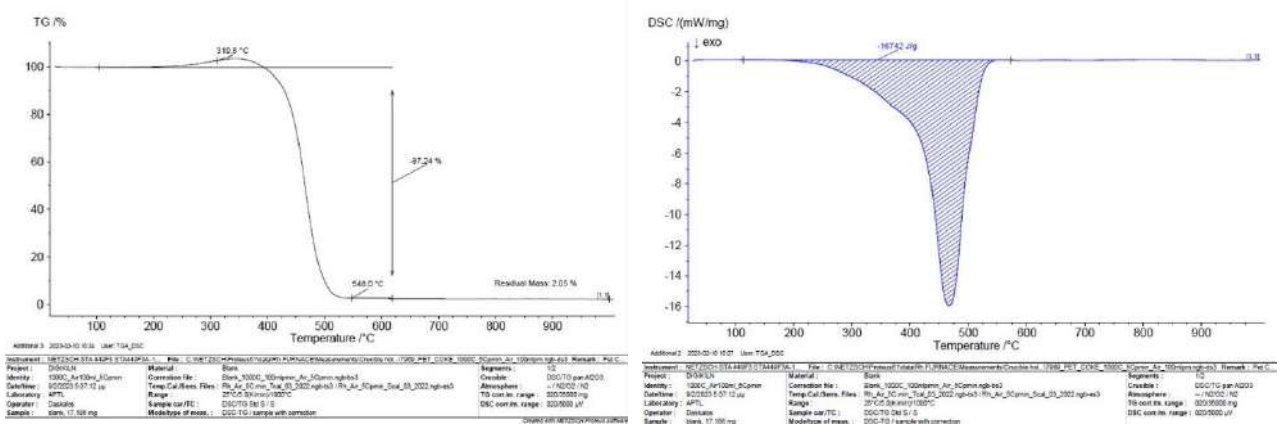


Figure 4. *Results of thermogravimetric analysis of pet coke.*

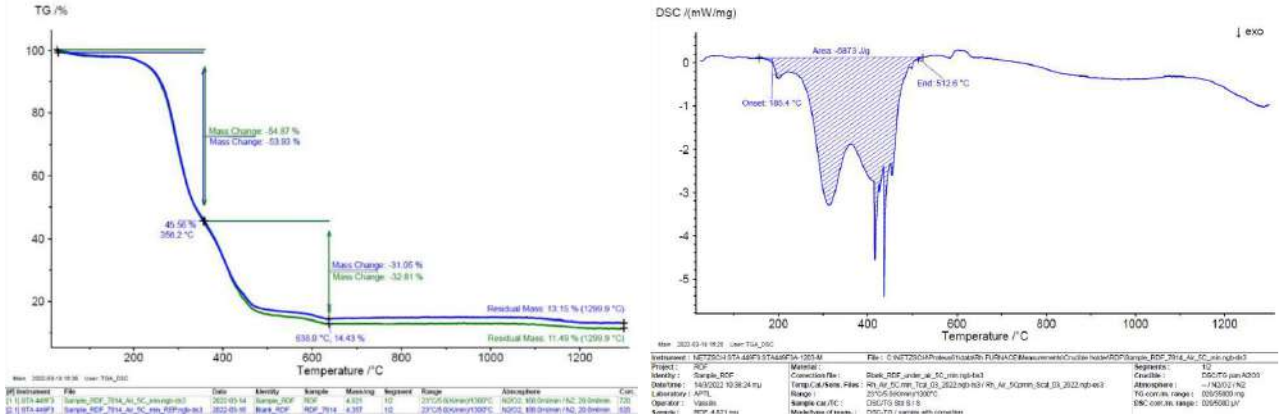


Figure 5. *Results of thermogravimetric analysis of RDF*

Particle Size Distribution (PSD) with Dynamic Light Scattering (DLS)

The DLS particle size distribution curves for both RDF and pet coke samples are shown below. For pet coke (Fig. 6) two peaks are observed (180nm and 650nm), which coincide for the distribution as a function of number with the distribution as a function of volume. The main peak as a function of number of particles is located at ~ 180nm, while the main peak as a function of volume is located at ~650nm, with the former being smaller.

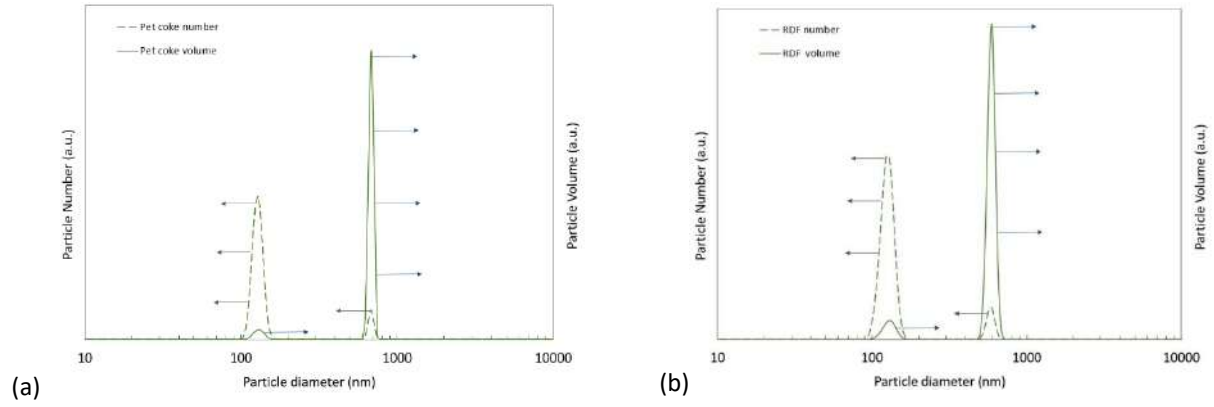


Figure 6. *Particle size distribution curve with DLS of (a) pet coke and (b) RDF sample.*

For RDF sample two peaks are also observed (170nm & 550nm), which coincide for the distribution as a function of number with the distribution as a function of volume. The main peak as a function

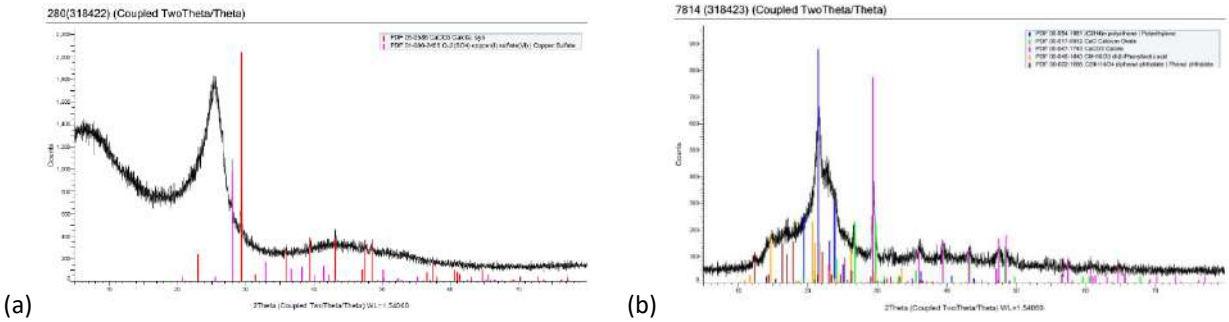
of number of particles is located at about 170nm, while the main peak as a function of volume is located at about 550nm, with the former being smaller.

Calorimetry results

Two measurements of High Heating Value (HHV) were performed on pet coke sample and the average value was calculated at 34.57 MJ/kg. On RDF were performed three measurements and the average value was calculated at 19.2 MJ/kg.

X-ray Diffraction Crystallography, XRD

The XRD results for both RDF and pet coke samples are depicted below, where only the crystalline phases spectra of are shown. In pet coke (Fig. 7a), graphite predominates, with small amounts of $CaCO_3$ and $Cu_2(SO_4)$ present.



(a) (b)

Figure 7. *X-ray diffraction results for the (a) pet coke and (b) RDF sample*

Elemental analysis

For pet-coke, the results of the elemental analysis showed that in the sample the percentage of carbon is 49.6%, hydrogen is 6.91% and nitrogen is 1.64%. From the elemental analysis of the RDF sample carried out by ASTM D 5291, it can be seen that the sample consists of 50.48% carbon (C) and 7.4% hydrogen (H). The remaining percentage is probably occupied by quantities of minor elements such as chlorine (Cl), calcium (Ca), etc.

CONCLUSIONS

From the characterization carried out on the two fuels, it is observed that RDF could be an acceptable and promising alternative fuel while further investigation would be recommended.

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