Fuel 235 (2019) 944–953

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Resolution-enhanced Kendrick mass defect plots for the data processing of mass spectra from wood and coal hydrothermal extracts

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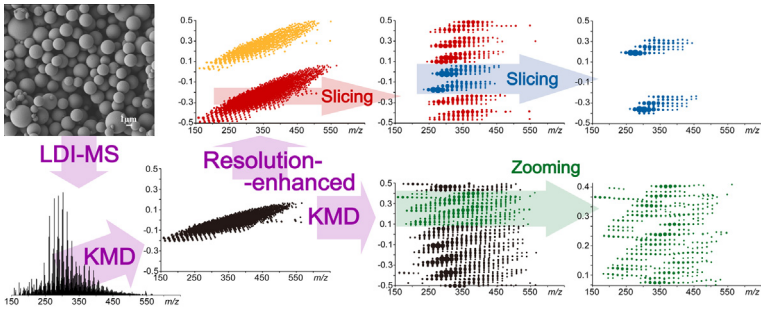
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Kendrick mass defect analysis
Hydrothermal extraction
Coal
Organic microsphere
High-resolution mass spectrometry
Data processing

ABSTRACT

The Kendrick mass defect (KMD) analysis conveniently turns a complex high-resolution mass spectrum into a compositional map with informative clustering of points depending on the elemental composition of the associated ions. It has nevertheless been left unchanged for thirty years with the use of chemical moieties such as methylene as base units for the computation of "regular" mass defects displayed in condensed plots regardless of the samples. The concept of "resolution-enhanced" KMD analysis using the mass of the repeating unit divided by an integer as the new fractional base unit has been recently introduced for the computation of expanded plots from polymeric mass spectral data with a dramatically improved separation of ion series. This user-friendly data processing is extended to the case of carbonaceous samples for the first time with the analysis of water-insoluble organic microspheres recovered from the hydrothermal extraction of wood and coals. In a didactic discussion with illustrative examples, the direct resolution-enhanced KMD analysis, the consecutive resolution-enhanced analysis of a part of a regular KMD plot or the systematic slicing of plots in a multistep procedure are shown to produce simple resolution-enhanced KMD plots or resolution-enhanced zooming from complex mass spectra. The

Abbreviations: LDI-HRMS, laser desorption/ionization high-resolution mass spectrometry; FE-SEM, field-emission scanning electron microscopy; MD, Mass defect; KM, Kendrick mass; KMD, Kendrick mass defect; IUPAC, International Union of Pure and Applied Chemistry; JRP, Japanese red pine; DM, Dong-Ming Chinese brown coal; LY, Loy-Yang Australian brown coal; daf, dry ash free; db, dry basis; JRPOM, hydrothermally extracted water-insoluble organic microspheres from JRP; DMOM, hydrothermally extracted water-insoluble organic microspheres from DM; LYOM, hydrothermally extracted water-insoluble organic microspheres from LY

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https://doi.org/10.1016/j.fuel.2018.08.085
Received 5 April 2018; Received in revised form 19 July 2018; Accepted 20 August 2018
Available online 28 August 2018

combination of these techniques in a unique “advanced KMD analysis” toolkit is expected to revolutionize the data processing of high-resolution mass spectra with unprecedented separating and unraveling capabilities.

1. Introduction

Coal and biomass are regarded as important resources for chemicals and materials [1]. Hydrothermal treatment (hot water as the reaction/extraction medium) has proven to be an effective, green and suitable method for their conversion [2–10]. The products after hydrothermal extraction typically consist of the extraction residue (coal: upgraded coal; biomass: hydrochar), gaseous products (mainly carbon dioxide), and the extract. The latter is divided into water-soluble and water-insoluble extracts at room temperature and ambient pressure [6,7].

It has been recently found that the water-insoluble extracts from woody biomass and brown coals have uniform nano- or micro-spherical morphology (woody biomass: 0.1–6.9 μm [11]; brown coal: 0.2–3.8 μm [12]). These extracts differ completely from carbonaceous microspheres or hydrochars obtained from hydrothermal carbonization of carbohydrates in chemical composition, formation mechanism and starting materials. Extracts from brown coals have been successfully used as templates to synthesize hollow metal oxide materials, paving the way to potential applications in materials science.

The characterization of water-insoluble extracts is limited so far to an elemental analysis or the evaluation of functional groups and molecular weight distributions. Laser desorption/ionization high-resolution mass spectrometry (LDI-HRMS) may nevertheless offer a first insight into their molecular composition via a simple analytical procedure [10]. If the analytical technique is straightforward, the resulting mass spectra are notoriously complex with several thousands of peaks to be assigned manually. The present article reports on a new user-friendly data processing methodology based on the latest innovations in mass defect (MD) analysis of mass spectra to overcome this issue.

Invariably, a MD analysis is based on the compilation of the fractional parts of the exact mass-to-charge ratios (m/z) from high-resolution mass spectra as they contain information about the elemental composition of ions (Eq. (1)) [13]. In the IUPAC mass scale (reference: $m(^{12}C) = 12$), ions whose elemental composition differs by a number of ^{12}C atoms only have the same MD while adding/removing any other element or isotope modifies it. Plotting MDs as a function of m/z (MD plot) clusters homologous ions into horizontal lines which facilitates their visual identification.

$$\text{mass defect (MD)} = \text{round}(m/z) - m/z \quad (1)$$

For petroleum or coals, methylene CH_2 is a typical repeating moiety which may be worth being highlighted rather than C. The change of basis from the IUPAC scale ($m(CH_2) = 14.0157$) to a new mass scale based on $m(CH_2)$ arbitrarily set at 14 [14] (Eq. (2)) and the associated plots form the Kendrick mass defect (KMD) analysis [15,16]. It has been extensively used to turn complex mass spectra from petroleum [17,18], natural organic matter [19] and hydrothermal extracts from brown coals [10] into two-dimensional maps with intuitive point alignments.

$$\text{Kendrick mass(KM)} = m/z \cdot \frac{14}{14.0157}$$
$$\text{KMD} = \text{round(KM)} - \text{KM} \quad (2)$$

Lately, the KMD analysis has been extended to polymer ions [20] by choosing the exact mass of the repeating unit R of a polymer backbone as the reference mass to compute defects (Eq. (3)). The resulting KMD plots separate the polymer ions based on their end-groups, charge state or co-monomeric content [21,22].

$$\text{KM(R)} = m/z \cdot \frac{\text{round(R)}}{\text{R}}$$
$$\text{KMD(R)} = \text{round(KM(R))} - \text{KM(R)} \quad (3)$$

A breakthrough has eventually been made last year with the introduction of the fractional base unit R/X with X being a positive integer [23] (Eq. (4)). Such mathematical moiety improves the visualization of complex mass spectral data in “resolution-enhanced” KMD plots [23] in opposition to the “regular” KMD plots computed with the molecular moiety R. Points are separated in a better extent along the whole KMD range with less overlapping and apparent realignments in the case of low-accuracy data [24,25].

$$\text{KM(R,X)} = m/z \cdot \frac{\text{round}(\frac{\text{R}}{\text{X}})}{\frac{\text{R}}{\text{X}}}$$
$$\text{KMD(R,X)} = \text{round(KM(R, X))} - \text{KM(R, X)} \quad (4)$$

Limited to mass spectral data of polymers at the time of writing, this concept is obviously extendable to any KMD plot with any base unit beyond the repeating unit R. It would be favourably used for the data processing of mass spectra from carbonaceous samples using CH_2/X as the base units with the ambition of revolutionizing the KMD analysis of coals and petroleum. An “advanced KMD analysis” combining regular and resolution-enhanced KMD plots from LDI mass spectra is reported for the first time. Hydrothermal water-insoluble extracts from two brown coals and one wood biomass are used as archetypal carbonaceous samples as a proof of principle of the procedure with no ambition to fully characterize them. It is shown that a direct resolution-enhanced KMD plot computed with CH_2/X as base unit, a sequential KMD analysis with the resolution-enhanced zooming of a part of the regular KMD plot or the systematic slicing of the KMD plot as well as their combination in multi-step processing help at producing very simple compositional maps with instant separation/assignment of ions series from very complex starting mass spectra.

2. Materials and methods

2.1. Biomass and brown coal samples

A wood sawdust (Japanese red pine noted JRP), a Chinese brown coal (Dong-Ming coal noted DM) and an Australian brown coal (Loy-Yang coal noted LY) were used as the feedstock samples. Table 1 lists the analyses of JRP, DM, and LY including elemental composition, ash content and water content (moisture).

2.2. Hydrothermal extraction and production of extracts

The apparatus is a semi-continuous system [10] shown in Fig. S1 in the Supporting Information. In a typical experiment, ~1.5 g of the feedstock sample (JRP, DM or LY) were placed on filter 1 (Swagelok, SUS316, 11.2 mm outer diameter and 0.5 μm pore size) in the reactor. Distilled water was supplied continuously into the system at a flow rate of 1 mL min^{-1} using a high-performance liquid chromatography pump.

Table 1
Elemental composition, ash content, and moisture of feedstock.

Feedstock	Ultimate analysis (wt%, daf)					Ash (wt%, db)	Moisture (wt%)
	C	H	N	S	O (diff.)		
JRP	48.6	6.1	0.0	0.0	45.3	0.1	9.7
DM	62.6	4.0	0.9	0.2	32.3	13.3	34.4
LY	66.6	5.3	0.5	0.2	27.4	1.5	58.0