Journal of Analytical and Applied Pyrolysis 121 (2016) 205–212

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Fructose and inulin: Behaviour under analytical pyrolysis

Arianna Massaro, Maria Perla Colombini, Erika Ribechini*

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124 Pisa, Italy

ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form 25 July 2016
Accepted 25 July 2016
Available online 28 July 2016

Keywords:
Fructose
Inulin
Topinambour (Jerusalem artichoke)
EGA-MS
Py(HMDS)-GC/MS
Di-fructose dianhydrides

ABSTRACT

EGA-MS (evolved gas analysis–mass spectrometry) and Py(HMDS)-GC/MS (pyrolysis-gas chromatography coupled with mass spectrometry with *in situ* derivatisation using hexamethyldisilazane as a silylating agent) were used to study the behaviour under pyrolytic conditions of fructose, inulin and topinambour (Jerusalem artichoke), a tuber, in which inulin coexists with other organic and inorganic species. The aim was to acquire a complete picture of the chemical characteristics and reactivity of fructose and its polymers (fructans). In fact, fructans constitute the reserve carbohydrates of several botanical species and are important substrates for obtaining high value-added products.

EGA-MS of inulin and topinambour provided information on their different thermal and chemical complexities. Despite tuber being constituted mostly by inulin, its thermogram was much more complex than obtained for inulin alone. The EGA curve of topinambour extended for a wider temperature range and provided mass spectra containing several peaks related to the fragmentation of compounds different from those obtained in the analysis of inulin. The evolution of levoglucosan clearly indicates the presence of glucose units in the tuber. The pyrolysis of fructose and inulin carried out by Py-GC/MS generated a high number of pyrolysis products, the main ones being dihydroxyacetone, 5-hydroxymethyl-2-furaldehyde, and 2,6-anhydrofructofuranose. The similarity between the two pyrograms suggests that under pyrolysis conditions, one of the first reactions of inulin is the cleavage of the glycosidic bond. An important difference was obtained in the pyrolysis of inulin alone, which led to the formation of di-fructose dianhydrides. A different quali-quantitative distribution of the pyrolysis products was obtained for topinambour likely due to the different monosaccharides in the topinambour composition from fructose, as well as to the presence of significant amounts of inorganics.

1. Introduction

Pyrolysis is a promising tool capable of efficiently converting biomass into bio-oils, which can be further transformed into biofuels and/or value-added chemicals [1–3]. To date, however, we are far from having ideal pyrolysis processes and technologies [3]. Therefore, the knowledge and the optimization of the chemical steps that lead to obtaining bio-oils are essential in order to achieve better results.

Analytical pyrolysis is thus becoming very useful as it reveals the chemistry of the decomposition pathway of biomass by carrying out a comprehensive control of the experimental parameters. The vast number of papers [4–20] on the mechanisms affecting lignocellulosic materials, raw biomasses, extracted lignin and cellulose as well as standard molecules carried out by analytical pyrolysis based techniques, demonstrates the high interest in this topic.

Analytical pyrolysis studies on fructose and its polymers (fructans), such as inulin and fructooligosaccharides, are less well documented [21,22,10]. However, fructans constitute the reserve carbohydrates of several botanical species and thus of agricultural and forest residues, as well as the residues of many processing industry, and they are considered as important substrates for obtaining high value-added products [23–26]. Studying the behaviour under pyrolytic conditions of fructose and inulin remains an open issue and an important step in acquiring a complete picture of their chemical characteristics and reactivity.

Our main aim was thus to provide a comprehensive study of such substances using techniques based on analytical pyrolysis, EGA-MS (evolved gas analysis–mass spectrometry) and Py(HMDS)-GC/MS (pyrolysis- gas chromatography coupled with mass spectrometry with *in situ* derivatisation using hexamethyldisilazane as silylating agent). Regarding the *in-situ* derivatisation, HMDS was used because it is able to convert non-volatile and polar pyrolysis products into suitable compounds for separation and analysis by gas chromatography [4,8,27,28,19].

* Corresponding author.
E-mail address: erika.ribechini@unipi.it (E. Ribechini).

http://dx.doi.org/10.1016/j.jaap.2016.07.021
0165-2370/

In our investigations, we used a "simple to complex" approach which begins with fructose and then moves on to inulin before studying a more complex system, such as topinambour (Jerusalem artichoke, *Helianthus tuberosus)*, a tuber, where such carbohydrates coexist with other organic and inorganic species.

2. Materials and methods

2.1. Chemicals and samples

1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma-Aldrich, Milan, Italy) was used as a silylating agent for the *in situ* derivatisation of pyrolysis products.

D(−)-Fructose (chemical purity ≥99.9%, Sigma-Aldrich, Milan, Italy), inulin from *Dahlia tubers* (Sigma-Aldrich, Milan, Italy), and Jerusalem artichoke (known also as topinambour) were used in this study. Jerusalem artichoke was milled using a ball mill Mini-Mill Pulverisette 23 with a zirconium oxide (ZrO_2) grinding bowl and balls (Fritsch GmbH, Germany). It was then oven dried at 60 °C for 15 h before being analysed.

2.2. Methods and instrumentation

Evolved gas analysis-mass spectrometry (EGA-MS) measurements were carried out in a micro-furnace pyrolyzer (Multi-Shot EGA/PY-3030D Pyrolyzer, Frontier Lab) directly coupled with a 5973 Mass Selective Detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer via a deactivated and uncoated stainless steel transfer tube (UADTM-2.5N, 0.15 mm i.d. × 2.5 m length, Frontier Lab). The temperature of the micro-furnace pyrolyzer was programmed from 50 °C to 800 °C at a heating rate of 12 °C/min under a helium flow (1 mL/min) with a split ratio 1:50. The micro-furnace interface temperature was kept at 320 °C and the column oven temperature was maintained isothermal at 300 °C. The mass spectrometer was operated in EI positive mode (70 eV, scanning *m*/*z* 50–650). The MS transfer line temperature was 300 °C. The MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at 150 °C. Samples of about 0.2 mg were placed into a steel sample cup.

Py-GC/MS measurements were carried out in a micro-furnace pyrolyser (Multi-Shot EGA/PY-3030D Pyrolyzer, Frontier Lab). The pyrolysis temperature was 500 °C for a period of 20 s with an interface temperature of 280 °C. Roughly 50–100 μg of each sample with HMDS (5 μL) added were put into a stainless steel cup and placed into the micro-furnace of the pyrolyser. The pyrolyser was connected to a gas chromatograph 6890 Agilent (USA) equipped with a split/splitless injector (used with a split ratio of 1:10 at a constant temperature of 280 °C), an HP-5MS fused silica capillary column (stationary phase 5% diphenyl and 95% dimethylpolysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA).

Chromatographic conditions were as follows: initial temperature 50 °C, 1 min isothermal, 5 °C/min to 300 °C, 2 min isothermal. He (purity 99.995%) was used as a carrier gas in constant flow mode at 1.0 mL/min.

The GC was coupled with an Agilent 5973 Mass Selective Detector operating in EI positive mode (70 eV, scanning *m*/*z* 50–650). The MS transfer line temperature was 300 °C. The MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at 150 °C.

Chromatographic peak assignments as well as the identification of the peaks in mass spectra obtained by EGA-MS were performed using mass spectra interpretation, along with a comparison with mass spectral libraries (NIST 2.0 and Wiley) and published mass spectra [4,5,8–10,19,29,30].

3. Results and discussion

3.1. EGA-MS

Fig. 1 shows the thermogram of the evolved gas during the thermal degradation of inulin. The EGA profile shows a single curve between roughly 190 °C and 380 °C, with two maxima, the first at approximately 240 °C and the second at 280 °C. The presence of the

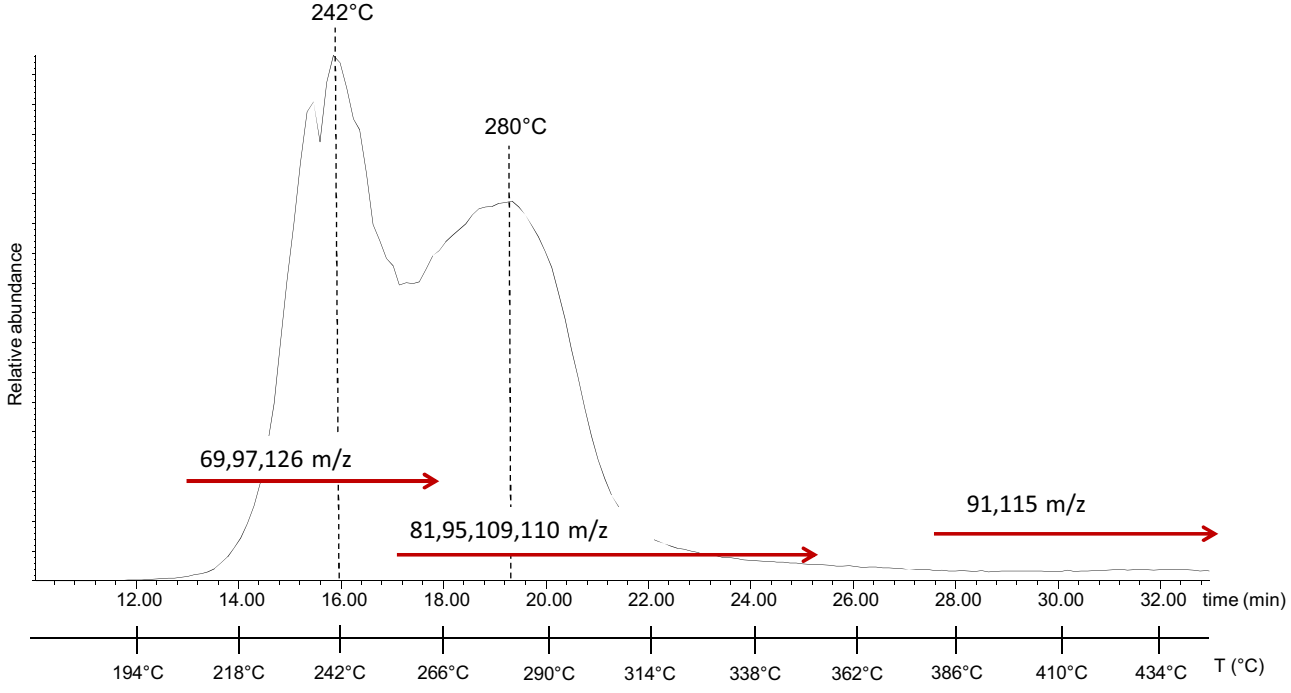

Fig. 1. Thermogram of the evolved gas obtained during the thermal degradation of inulin.