Fuel Processing Technology 139 (2015) 226–235

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Detailed identification and quantification of the condensable species released during torrefaction of lignocellulosic biomasses

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ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form 30 June 2015
Accepted 2 July 2015
Available online 5 August 2015

Keywords:
Lignocellulosic biomass
Torrefaction
Mild pyrolysis
Volatiles
Condensable species
Gas analysis
GC–MS
Adsorption

ABSTRACT

Torrefaction is a mild thermal pretreatment which improves biomass properties and releases condensable species. Condensable species released during torrefaction of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C were investigated. A fixed-bed reactor was used for the laboratory scale experiments. A micro-GC, Karl Fischer titrator and GC-MS were used to analyse incondensable gases, water and other condensable species, respectively. The overall mass balance ranged from 96 to 103 wt.%. The quantification rate of condensable species was on average 77 wt.%. In addition to the major species usually reported in the literature – water, acetic acid, 2-propanone,1-hydroxy- – we show that large amounts of some anhydrosugars were produced. Additionally, 85 condensable species were identified. Among these species, many terpenes and terpenoids in pine were identified by adsorption on SPME fibre. Finally, the influence of temperature and of the nature of biomass on the yields of condensable species was highlighted.

1. Introduction

Lignocellulosic biomass is a particularly interesting energy source, as it is renewable, quite abundant and available all over the world. It is the source of a large range of products (materials, chemicals, and energy). It could also be an alternative to fossil fuels in countries without their own sources. Lignocellulosic biomass is already used for combustion and gasification processes, for the production of heat, power, and fuel. However, this type of biomass is heterogeneous, hygroscopic, has a low density, high moisture content, and low calorific value and can easily aggregate when used in powdery form [23]. These drawbacks can be addressed by torrefaction.

Biomass torrefaction – also called mild pyrolysis – is a thermochemical treatment at low temperatures (200–300 °C), at atmospheric pressure and in an inert atmosphere, which produces a solid. This torrefied solid has lower H:C and O:C ratios, higher energy content, is more hydrophobic, easier to grind and fluidize than the raw biomass [24]. These modifications make the biomass more suitable for the gasification process, particularly in an entrained flow reactor for instance. It is also more resistant to fungi and bacteria, thereby simplifying storage of the feedstock [15].

The torrefied solid usually represents between 60% and 90% db of the initial mass, depending on the operating conditions. The remaining fraction is released as volatile matter. Approximately one-third of this volatile matter is composed of incondensable gases – mainly CO_2 and CO; two-thirds of which are condensable species, with approximately one-half water and the other half acids, alcohols, aldehydes, ketones, furans, sugars [17]. These condensable species are generally considered as waste or effluent, or are burnt to produce heat [20]. Since the torrefied solid is the main torrefaction product, most studies have focused on its characterisation. Hence, very few studies have focused on the identification and quantification of the condensable species. However, these species could damage the production unit at industrial scale, and would require a gas treatment unit, before being emitted into the atmosphere. On the other hand, they could be reused to produce chemical species as an alternative to petroleum-based products. The management of these torrefaction condensable species is thus a crucial issue in industrialisation of the process.

The articles that deal with the analysis of torrefaction condensable species are listed in Table 1. In addition, Tumuluru et al. [22] summed up the analytical techniques for volatiles and other products of biomass torrefaction and pyrolysis. The major condensable species of torrefaction generally identified are water, acetic acid, 2-propanone,1-hydroxy-, methanol, formic acid, furfural, formaldehyde [6,11,17–19,26].

Several compounds which are used in the chemical industry are also released during torrefaction of lignocellulosic biomass. For instance,

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http://dx.doi.org/10.1016/j.fuproc.2015.07.001
0378-3820/

Table 1
Recovery and analytical techniques for the analysis of torrefaction condensable species.

Process	Type of reactor	Recovery technique for volatile species	Method of analysis	Species analysed	References
Torrefaction	3 L laboratory reactor	Quench on a pool of condensers. Temperature not specified.	Gas chromatography. Analysis conditions not specified.	Water, acetic acid, methanol, formic acid, furfural. No quantification.	Bourgois and Guyonnet [5]
Torrefaction	Batch reactor	2 impinger bottles in series, filled with water and cooled to 5 °C	GC–MS, FC-FID and IEC. Analysis conditions not specified.	34 species identified. No quantification.	Bergman et al. [4]
Torrefaction	Batch reactor	Cold trap cooled to -5 °C. The condensable species were then collected with butan-2-ol	HPLC with Chrompack organic acid column, with detection based on refraction index	Water, acetic acid, formic acid, methanol, lactic acid, furfural, 2-propanone,1-hydroxy- and phenol quantified.	Prins et al. [18]
Torrefaction and pyrolysis	TGA	FTIR (Brücker)	FTIR	Water, acetic acid, formic acid, methanol, furfural identified. No quantification.	Repellin [19]
Torrefaction	TGA	FTIR (Nicolet Magna-IR AEM)	FTIR	Absorbance of acetaldehyde, formaldehyde, acetic acid, formic acid, methanol and methane measured. FTIR not calibrated.	Bridgeman et al. [6]
Torrefaction	Batch reactor	Two-neck flask immersed in liquid nitrogen	Infrared gas analysis (Gasboard-5110)	Water, acetic acid and other oxygenates.	Deng et al. [12]
Torrefaction	TGA	Condenser cooled to -5 °C in an ice bath. The condensable species were then collected with isopropanol.	GC–MS (Perkin Elmer Clarus 500)	Acetic acid, acetic anhydride, furfural, 3-methylbutanol identified.	Wannapeera et al. [26]
Torrefaction	Thermal desorption tube	Adsorption on Tenax tube and thermal desorption into GC–MS	GC–MS and TD (Perkin Elmer Turbomatrix)	Acetic acid, furfural, methylfurfural, hydroxymethylfurfural, phenol,2-methoxy-, phenol,2,6-dimethoxy-, vanillin, syringaldehyde, acetovanillin, acetosyringon identified. GC-MS not calibrated.	Candelier et al. [7]
Torrefaction	Batch reactor	2 condensers in series. Temperature not specified	GC-MS (Agilent 6890 and 5973)	Mainly monoaromatics identified, including: phenol, phenol,2-methoxy-, phenol,4-methyl-, eugenol, vanillin.	Chen et al. [9]
Torrefaction	Batch reactor	Condenser cooled to -10 °C. The condensable species were then collected with acetone.	GC-MS	Acetaldehyde, acetic acid, formaldehyde, formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, propanoic acid quantified. 30 to 44 wt.% of condensable species quantified (except water).	Dupont [13]
Torrefaction	TGA	TGA coupled with MS (Netzsch, QMS 403C)	TGA coupled with MS	Water, acetic acid, formic acid, formaldehyde, chloromethane, hydrogen sulphide, carbonyl sulphide identified.	Shang et al. [21]
Torrefaction and pyrolysis	Auger reactor	2 condensers in series cooled to -5 °C.	Karl Fischer titration (Metrohm, 787KF Titrino) for water; GC-FID (Agilent HP 4890).	Water, acetic acid, 2-cyclopenten-1-one, 2-propanone,1-hydroxy-, propanoic acid, 2-furanmethanol, phenol, phenol,4-ethyl-2-methoxy-, phenol,2-methoxy-, eugenol, isoeugenol and vanillin quantified.	Zheng et al. [27]
Torrefaction	Batch reactor	FTIR for the permanent gases; not detailed for the condensable species	GC-MS and GC-FID	Formaldehyde, acetaldehyde, acetone, methanol, ethanol, glycolaldehyde, acetic acid, water, glyoxal, lactic acid and formic acid quantified.	Anca-Couce et al. [2]
Torrefaction	Batch reactor	Condenser cooled to -10 °C. The condensable species were then collected with acetone.	Karl Fischer titration (Mettler Toledo V20), GC-MS (Agilent 6890 and 5975)	Acetic acid, formaldehyde, formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, propanoic acid quantified.	Commandré and Leboeuf [11]
Torrefaction	Batch reactor	Analysis in gaseous phase. Quench on two condensers, one cooled to 0 °C, the other one to -70 °C	FTIR (Nicolet Magna-IR 550)	Water, acetic acid, formic acid, formaldehyde, furfural, methanol quantified.	Nocquet et al. [17]

methanol is used in the synthesis of formol, MTBE and acetic acid. Furfural and propanoic acid are used as intermediates in organic synthesis. Formic acid is used as a preservative, as well as in dyeing factories. Glycolaldehyde is widely used in the food industry as a cross-linking and food browning agent, and also as an intermediate to produce ethylene glycol [25].

The aim of the present study was to undertake the most complete qualitative and quantitative analysis possible of the condensable species released during torrefaction of lignocellulosic biomass.

To this end, torrefaction experiments were carried out at three temperatures – 250, 280 and 300 °C – and on four biomass samples – pine, ash wood, miscanthus and wheat straw – as representatives of four biomass families, softwood, hardwood, energy crop and agricultural residues, respectively.

2. Materials and methods

2.1. Feedstock

Four biomass samples – pine, ash wood, miscanthus and wheat straw – were studied to assess the influence of the nature of the biomass on the formation of condensable species. Pine and ash trees were harvested in Aveyron (France), miscanthus and wheat straw in Montans (France).

The biomass was chosen as representative of four different families of biomass: hardwood, softwood, energy crop and agricultural residues. Indeed, Dupont [13] showed that one biomass is sufficient to describe the torrefaction behaviour of the whole family of biomasses. The main properties of the samples are listed in Tables 2 and 3.