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A promising new on-line method of tar quantification by mass spectrometry during steam gasification of biomass

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ABSTRACT

This paper presents an on-line method of measuring at $\text{mm}^3 \text{m}^{-3}$ level some organic compounds such as BTX (Benzene, Toluene, Xylene) and PAH (Polycyclic Aromatic Hydrocarbon) which are called “tar” for biomass gasification applications. This method is based on the ion molecule reaction (IMR) mass spectrometer (MS) principle. Due to the low energy of ionization of Hg, Xe or Kr almost no overlapping spectra can damage the interpretation of the detected results. IMR-MS results of concentrated (above $\text{cm}^3 \text{m}^{-3}$) and trace (below $\text{cm}^3 \text{m}^{-3}$) tars are presented after a bubbling fluidized bed and a tar cracker respectively. Results are compared with other measurement methods such as microgas chromatography for benzene and toluene or Tar Protocol or Solid Phase Adsorption technique both methods for BTX and PAH giving good confidence to the results.

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1. Introduction

Contaminants present in the gas obtained from the biomass gasification may induce saturation of the gas cleaning systems or degradation of the catalysts used for fuel synthesis. They are important to be measured on-line in order to detect rapidly their variations for process control. Furthermore, after gas cleaning systems, they are at a trace level, i.e. at $\text{mm}^3 \text{m}^{-3}$ level. These contaminants are gaseous organic compounds such as BTX (Benzene, Toluene, Xylene) and PAH (Polycyclic Aromatic Hydrocarbon) which are called “tar” for biomass gasification applications. Some gaseous inorganic components as sulfured species (H_2S , COS, thiophene...) are also contaminants.

On-line measurements of BTX are currently made by micro-gas chromatography with a thermal conductivity detector ($\mu\text{GC-TCD}$). The detection limit is above several $\text{cm}^3 \text{m}^{-3}$ [1]. Naphthalene can also be measured on-line directly in the gas phase by FTIR (Fourier Transform Infra-Red) [2]. Naphthalene, fluoranthene and pyrene by LIF (Laser Induced Fluorescence) [3–5]. The detection limit is above several $\text{cm}^3 \text{m}^{-3}$ level for FTIR. LIF presents strong interferences with other species present in the gas. Molecular beam mass spectrometry (MBMS) is another on-line method capable of measuring all tars from BTX to PAHs and others [6] using a specific gas sampling to collect condensable species thanks to a molecular beam inlet system. This method suffers from the conventional high ionization energy (70 eV) when the

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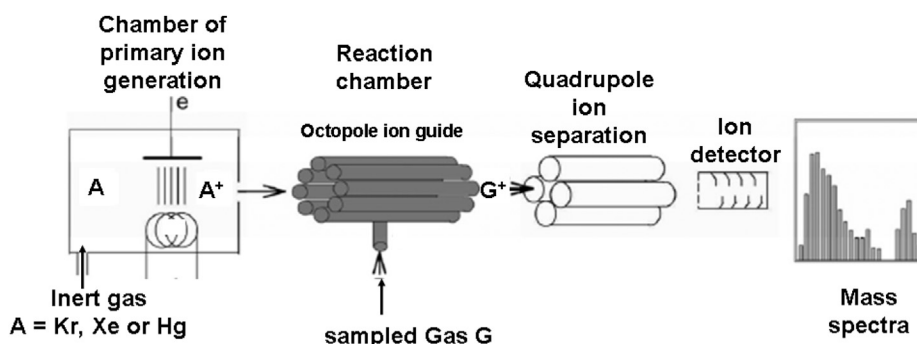


Fig. 1 – IMR-MS principle (partly reported from Ref. [17]).

electronic impact (EI) method is employed. Indeed the major drawback with this ionization energy is the fragmentation of molecules leading to complex mass spectra and multiple overlapping intensities in complex gas mixtures. To overcome this limitation several soft ionizations have been used with photoionization techniques such as Resonance-Enhanced Multiphoton Ionization (REMPI) or Single-Photon Ionization (SPI) with Time-Of-Flight Mass Spectrometry (TOFMS) [7–9]. However, mainly identification and few quantifications are performed. Other methods measuring on-line total tar contents exist, such as the ECN Tar Dew Point [10], the FID (Flame Ionization Detector) tar analyzer (TA 120-3) currently used by IFK University of Stuttgart [11] or the PID (Photo-Ionization Detection) tar analyzer recently developed by Ahmadi [12] but the nature of the species is not known for these methods.

This paper presents a soft ionization mass spectrometry method based on the ion molecule reaction (IMR) mass spectrometry (MS) principle. Such an IMR-MS method has already been used to measure on-line major components (CO, CO₂ etc.) as well as some inorganic (SO₂, NO) or organic (benzene, acetaldehyde) pollutants at the exhaust of incineration processes [13,14]. However, to our knowledge, this method has never measured the composition of a syngas from a biomass gasification process.

2. Principle of IMR-MS

The IMR method is well known in ion physics. It is an important path of primary ion loss in plasma. The monograph by Harrison is especially recommended for further reading [15]. A simplified description is given in our paper. IMR-MS method is similar to CI-MS (Chemical Ionization Mass Spectrometry) but one of the differences is that the primary ion source is run with an inert gas such as Hg, Xe, Kr instead of a reactant gas such as NH₃, CH₄ or N₂-H₂O mixture. The main pathway in IMR-MS to ionize a sampling gas G with a primary inert gas ion A⁺ (A = Hg, Xe or Kr) is a charge transfer as given in [eq. (1)].



ion molecule reaction.

For CI-MS more complex ionization pathways are occurring as proton transfer [Eq. (2)]



The principle of the IMR-MS method is explained in Ref. [16] and schematized in Fig. 1.

An inert gas (Hg, Xe or Kr) is ionized by electron impact (EI) in the chamber of primary ion ionization as:



primary ionization.

Primary ions A⁺ are conducted to the reaction chamber through a high frequency octopole ion guide. Here the primary ions react with the sampled gas G with the ion molecule reaction [eq. (1)]. Contrary to CI-MS, the chamber of primary ion generation and the reaction chamber are separated in IMR-MS. In addition, the ion molecule reaction happens with a vacuum of ~10 mPa (CI-MS about 100 Pa). The G⁺ ions generated are conducted to a classical quadrupole and a downstream counter to be separated (mass separation), detected and quantified.

The ion molecule reaction [eq. (1)] can only occur if the ionization potential of the primary ion A is higher than the one of the gas sample G. Fig. 2 shows the ionization potential of several molecules of interest and to the inert gas Hg, Xe and Kr.

For example the ionization potential of mercury (IP(Hg) = 10.43 eV) is higher than the one of BTX, PAHs and thiophene (C₄H₄S). If the excess energy IP(Hg) – IP(G) is small (~<1 eV) no fragmentation will occur otherwise it might be used to break the weakest bond of the ionized molecule leaving a lower molecular weight fragment ion. Mercury is able to ionize these species almost without fragmentation as

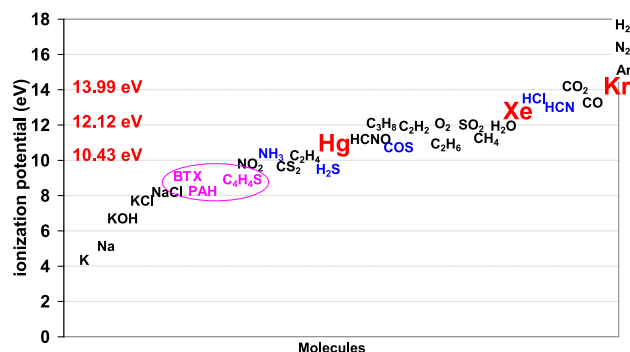


Fig. 2 – Ionization potential of several molecules.

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