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Fragmentation mechanisms of cellulose pyrolysis tars investigated by tunable synchrotron VUV Q-TOF-MS

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High importance to understand the mechanisms of tars ionisation and fragmentation

Need of tars on-line analysis to monitor the thermo-chemical processes and fundamental study on pyrolysis [1]
Soft ionisation conditions should be selected to reduce ions fragmentation
Currently used electronic impact leads to low ionisation accuracy and high fragmentation of tars/ions
Single Photo-Ionisation (SPI) with Vacuum Ultra-Violet (VUV) light has shown high benefits for tars analysis [2]

A unique set-up has been developed in Hefei (China)

Pyrolysis of solid materials in a pre-heated furnace under vacuum
Tars introduced in an ionisation chamber through a heated skimmer
Ionization energy is accurate and tunable thanks to the synchrothron VUV light (S VUV in Fig. 1) [3]
Ions are analysed by a triple quadrupole and time of flight mass spectrometer (Q-TOF-MS)
Molecular structure of ions can be revealed by MS*MS analysis thanks to the Q-TOF-MS

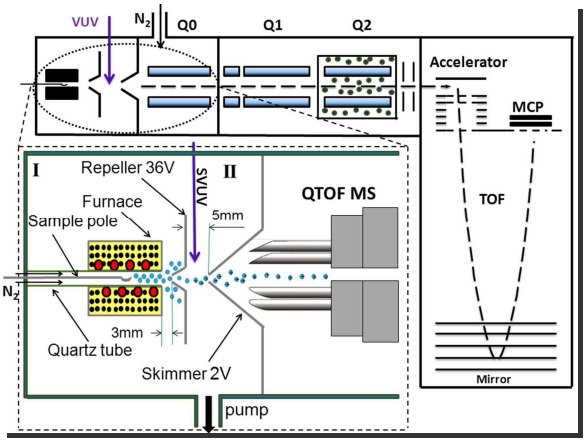
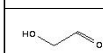
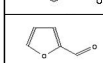
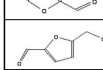
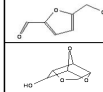


Fig. 1. Pyrolysis furnace coupled to Synchrothron VUV light ionisation and Q-TOF-MS

Effect of ionisation energy on cellulose tars/ions

Minimum ionisation threshold of some major cellulose tars calculated by compound method calculation (CBS-QB3) [4] (Tab. 1)

Structure	g/mol	IE (eV)
	60	9.88
	96	9.19
	126	8.76
	144	9.02
	162	8.82

Tab. 1. Molecular structure and minimum ionisation threshold of some major cellulose primary tars

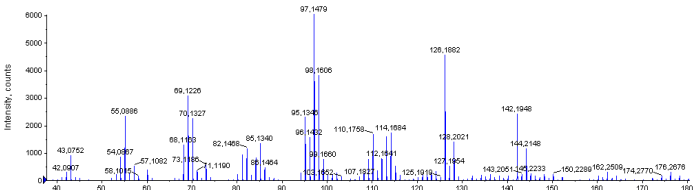


Fig. 2. Exemple of mass spectra obtained for cellulose pyrolysis at a reactor temperature of 350°C, synchrotron VUV IE of 10.5eV

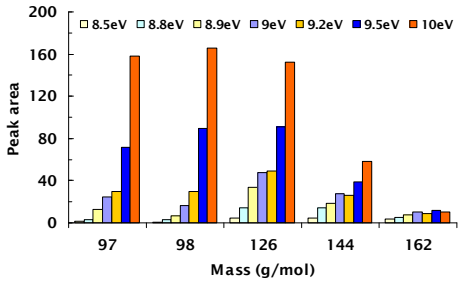
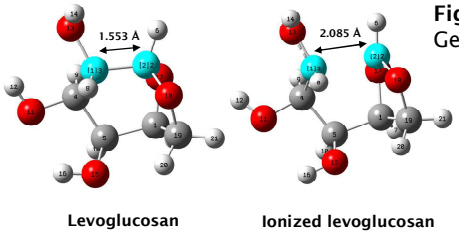


Fig. 3. Effect of ionisation energy (8.5 to 10eV) on the peak areas of main ions

Ionisation AND fragmentation of levoglucosan (mass 162)

Mechanism of levoglucosan ionisation



Levoglucosan Ionized levoglucosan

Fig. 4. Energy calculation at the CBS-QB3 level of theory
Geometry and frequency calculations at the B3LYP/6-311G(d,p)

Large increase of the C(2)-C(3) bond length from levoglucosan molecule to the cation (Fig. 4)

Conclusion

This set-up coupled with ab-initio calculations offers a unique and powerful methodology to get new insights on:

1. ionisation mechanisms of biomass tars
2. molecular structure of some key ions by MS*MS analysis
3. fundamentals of pyrolysis of cellulose, and other solid materials

References

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