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Production of ethyl acetate from pyrolysis of lignin model compound guaiacylglycerol-β-guaiacyl using TGA-MS

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Production of Ethyl Acetate from pyrolysis of lignin model compound guaiacylglycerol-β-guaiacyl ether using TGA-MS

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Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes
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The University of Dublin

Fondúireacht Eolaíochta Éireann
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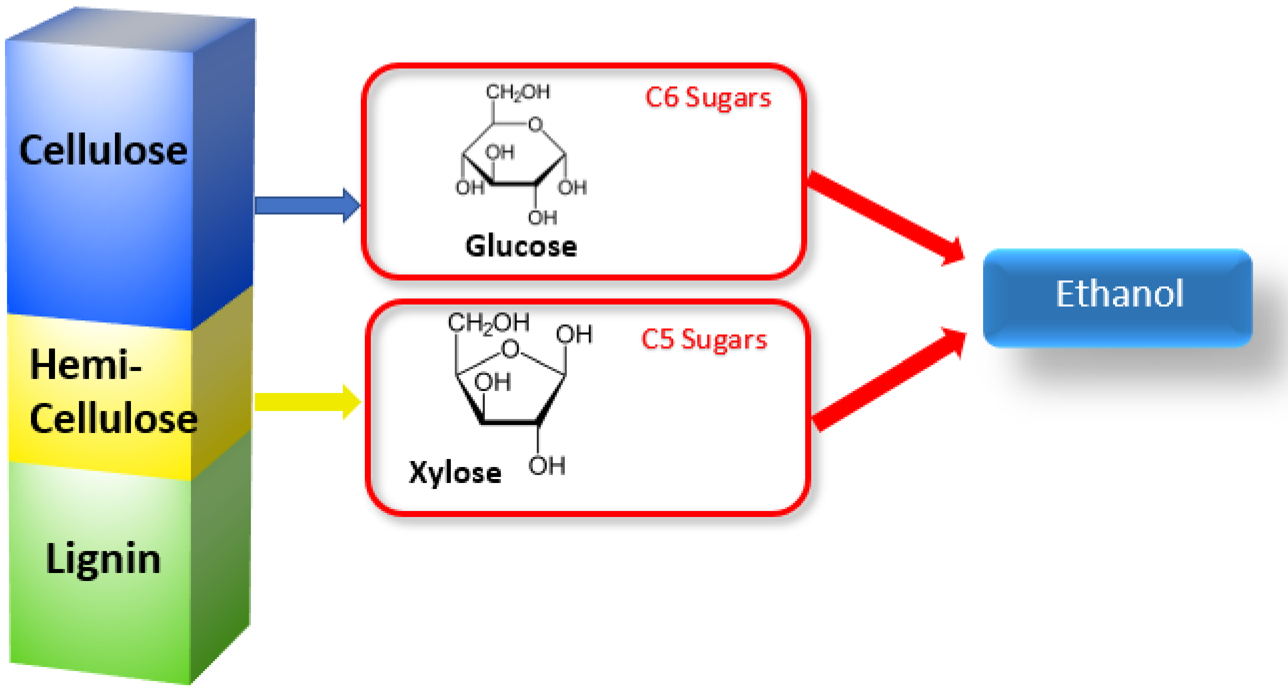
1. Biomass Constituents

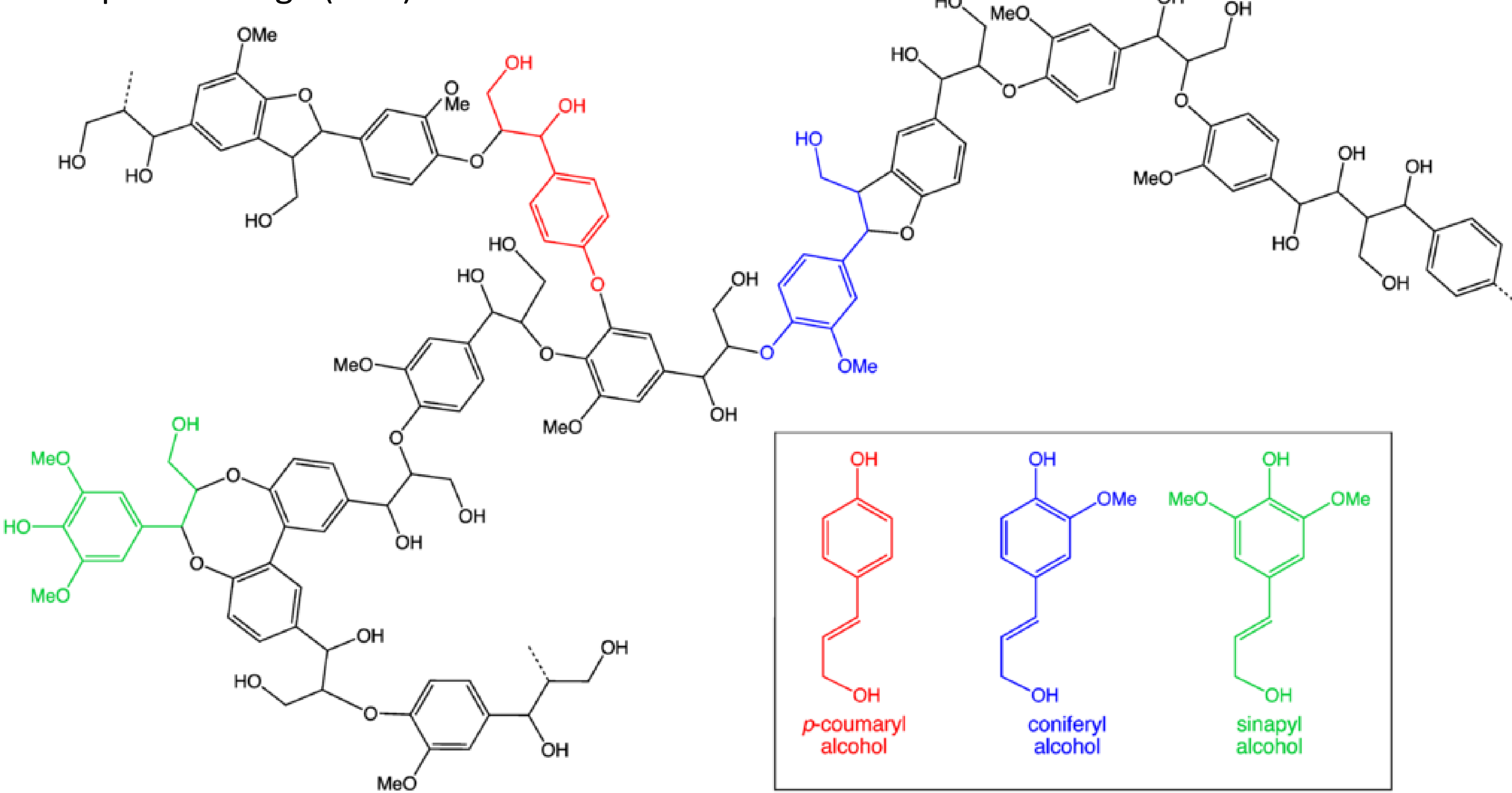
- Sugar Stream: Cellulose & hemicellulose ⟶ Ethanol.
- Lignin Stream: 2% Commercially utilized[1].
- Increasing efficiency = Increasing economic attractiveness.



1. A Shrotri, H Kobayashi, and A Fukuoka. Advances in catalysis Proceedings of the Combustion Institute, 60:59–123, 2017.

2. Lignin

- 20-40% dry weight of plant matter
- 3 monolignol units – p-hydroxyphenol (H), guaiacyl (G) and syringyl (S).
- β-O-4 linkage (50%)[2].



2. S.Kim. et al. Computational study of bond dissociation enthalpies for a large range of native and modified lignins.

3. Guaiacylglycerol-β-guaiacyl Ether (GGE)

- $C_{17}H_{20}O_6$
- Lignin Model Compound
- Two guaiacyl subunits connected by β-O-4 aryl ether linkage
- Boiling Point – 553°C
- Molecular Weight – 320 g/mol

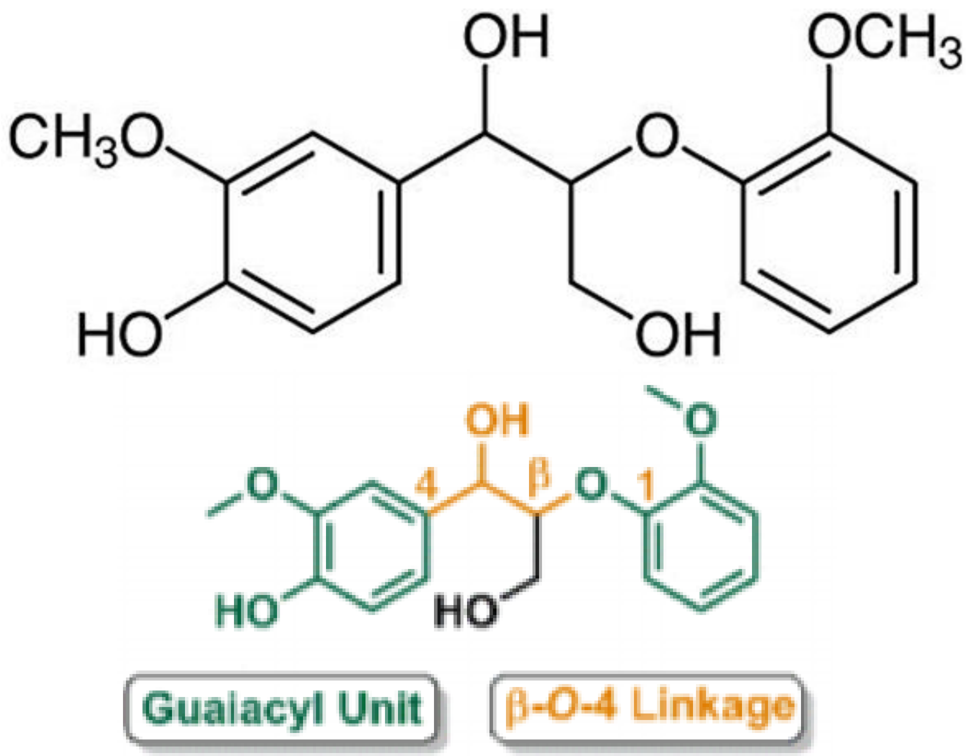


Figure 3. Structure of guaiacylglycerol-β-guaiacyl

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4. Thermogravimetric Analysis (TGA)

- TGA – Measuring mass change over temperature range
- 5mg GGE
- 30-700^{o}C at 20^{o}C/min
- Using Accupik = more reproducible results – reducing evaporation
- Similar TGA curves to lignin

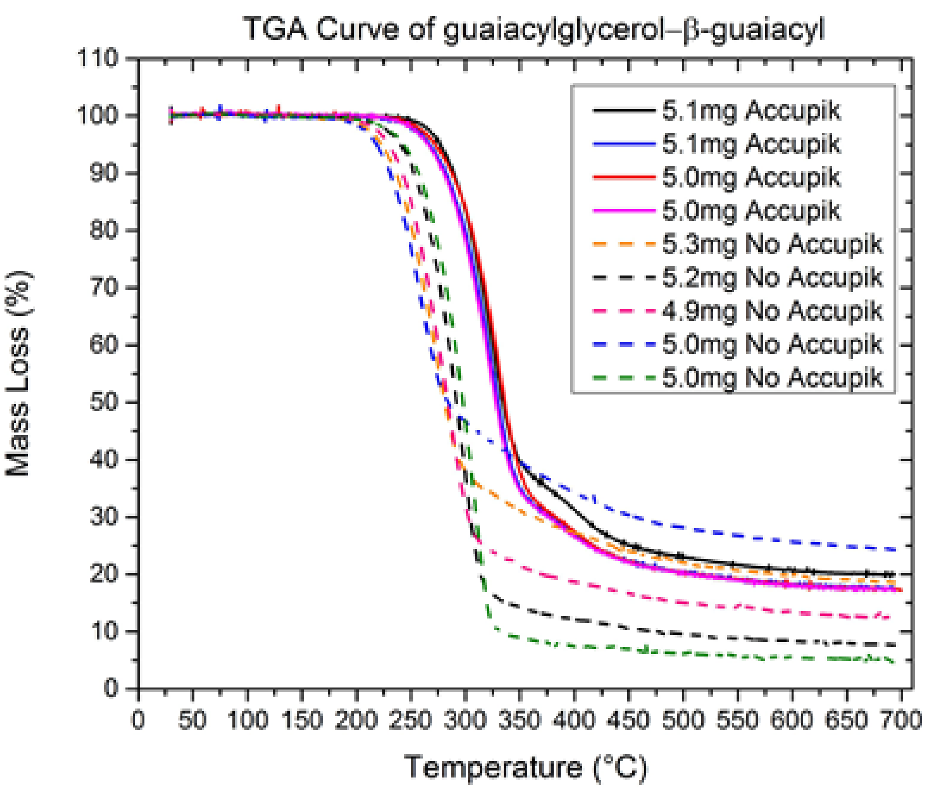

Figure 4. TG Graph of GGE with and without Accupik

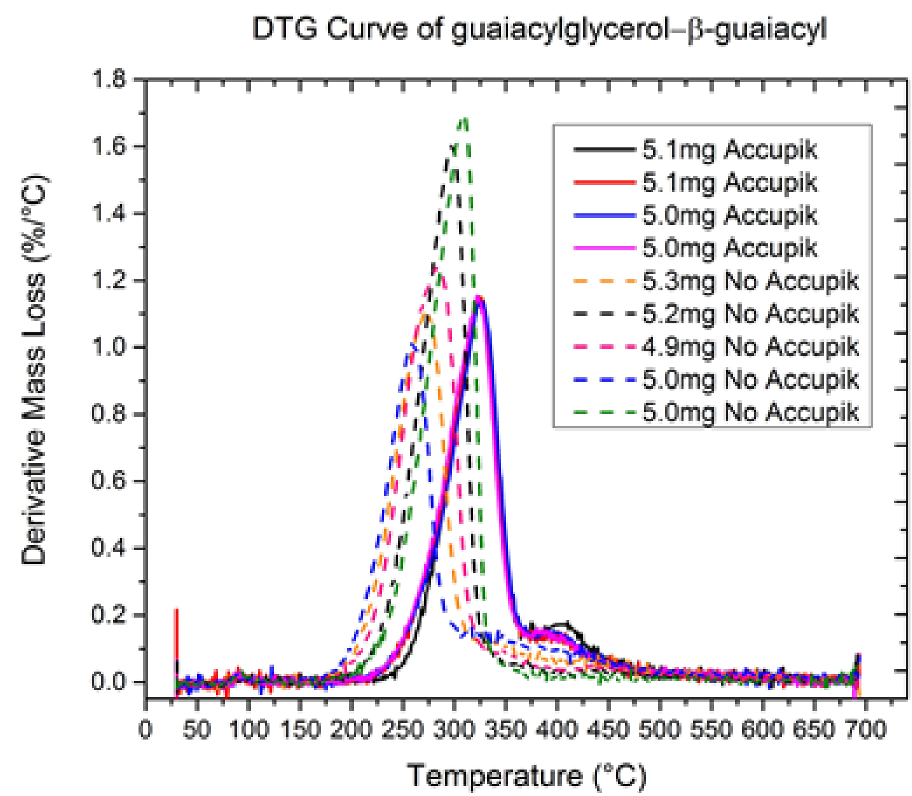

Figure 5. Derivative TG Graph of GGE with and without Accupik

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5. Electron Ionisation Mass Spectrometry (EI-MS)

- Uptake of gaseous molecules from TGA combustion chamber via flowline
- Analyte molecules ionised
- Detector response over a range of mass-to-charge (m/z) values measured
- Enables identification of compounds present in chamber during pyrolysis

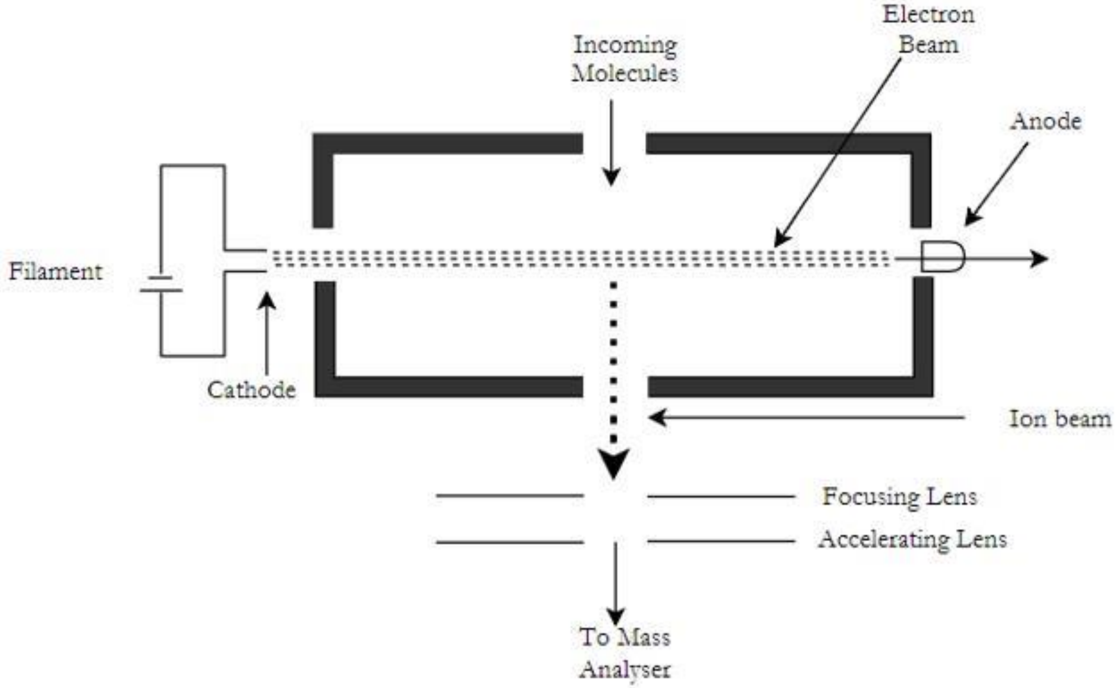

Figure 6. Ionisation chamber of EI-MS

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6. TGA-MS

- Peaks at m/z values: 43, 61, 70, 73, 88
- Peaks coincide with onset of mass loss from TGA data - intermediaries

- Range of 5 m/z
- Scan time = 7.6 seconds
- 266 data points per m/z value
- Electron Energy = 70eV
- Emission Current = 500µA

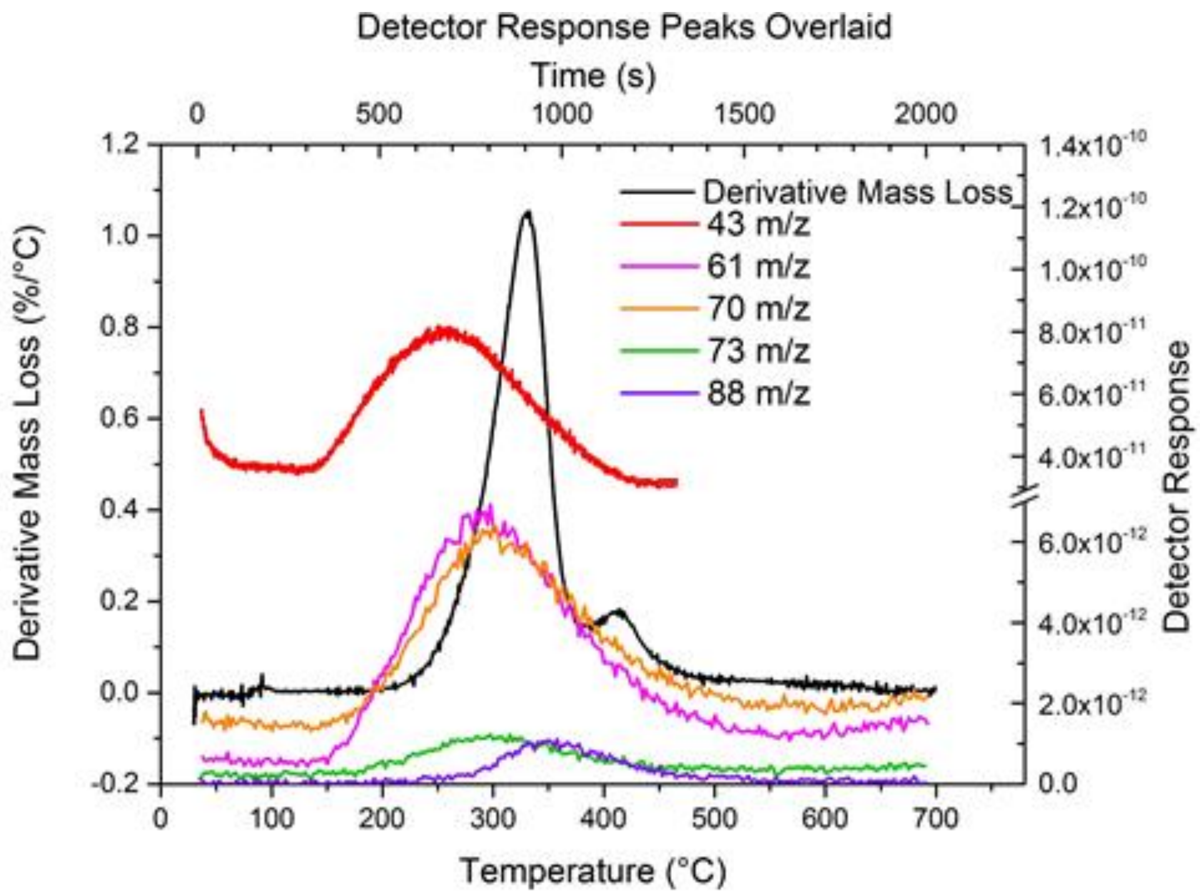
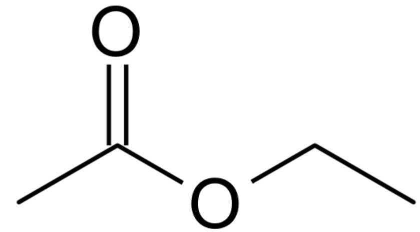


Figure 7. Detector responses from MS overlaid onto DTG curve of GGE in experiment 70-75m/z was scanned

7. Ethyl Acetate



- Mass-to-charge ratio (m/z) – 88
- Ethyl Acetate Origin: 1. Pyrolysis reactions of GGE
  2. Product of gas phase reactions in combustion chamber
  3. Produced due to severe fragmentation in ionisation chamber

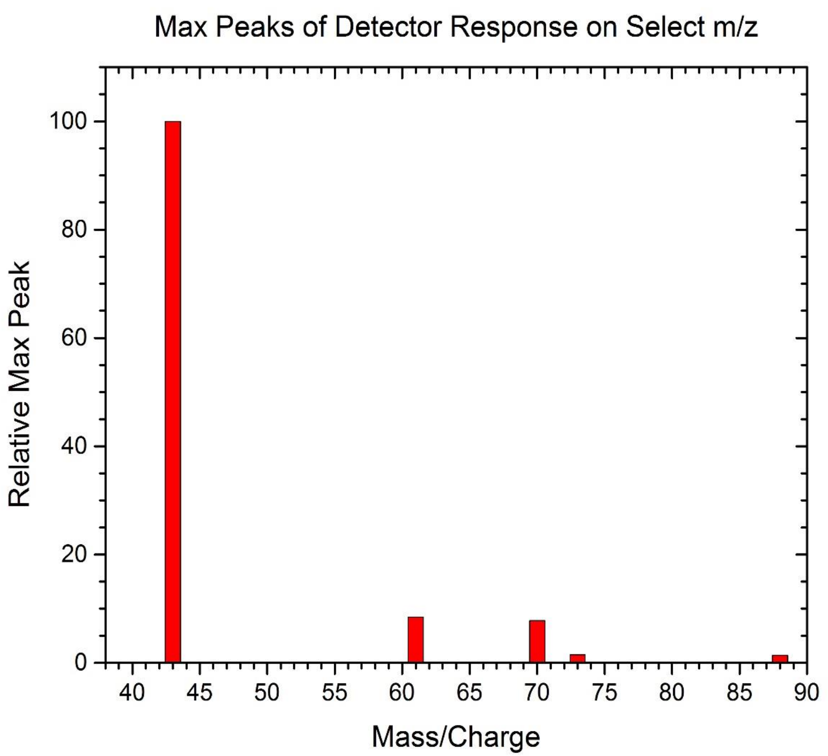


Figure 8. Relative maximum detector responses from MS

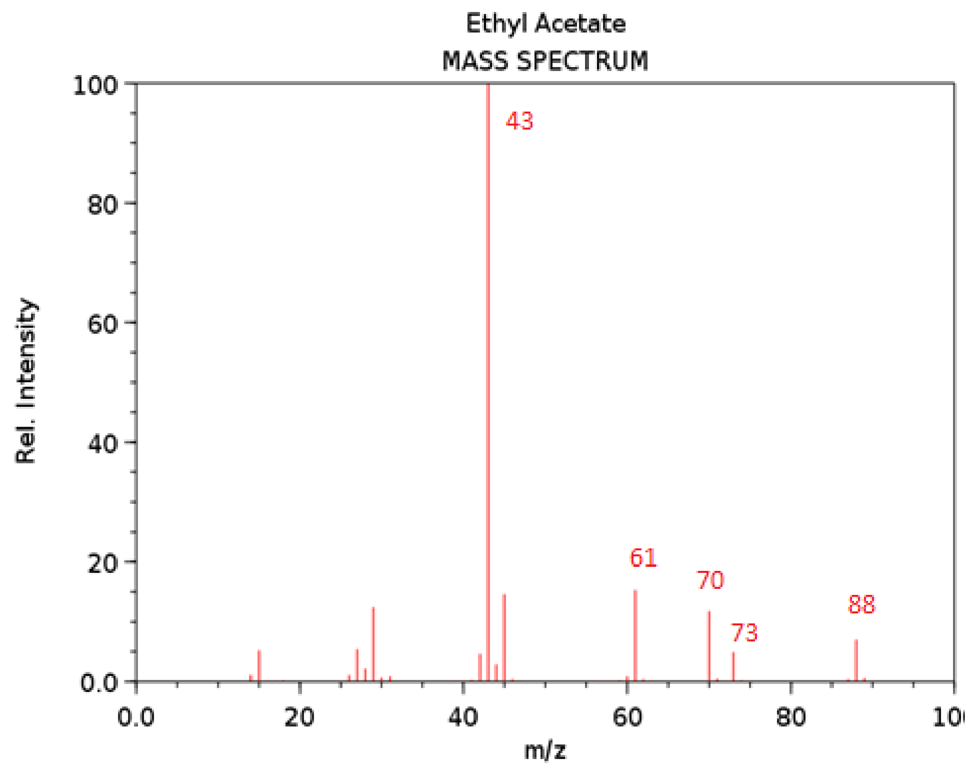


Figure 9. EI Mass spectrum of ethyl acetate. Source: NIST

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Conclusion

1. **Use of Accupik produces more reproducible results**
   - Limiting Evaporation of GGE

2. **Peaks in detector responses represent important intermediaries**
   - Peaks coincide with onset of mass loss

3. **Production of ethyl acetate during experiment**
   - Ethyl Acetate responsible for increased detector response at these m/z values

4. **Origin of ethyl acetate unknown**
   - Further research needed
   - Present prior to entering mass spec?

Thank You For Listening

Questions?