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The effect of potassium salts and ash from biomass combustion on the degradation of MEA.

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c-capture

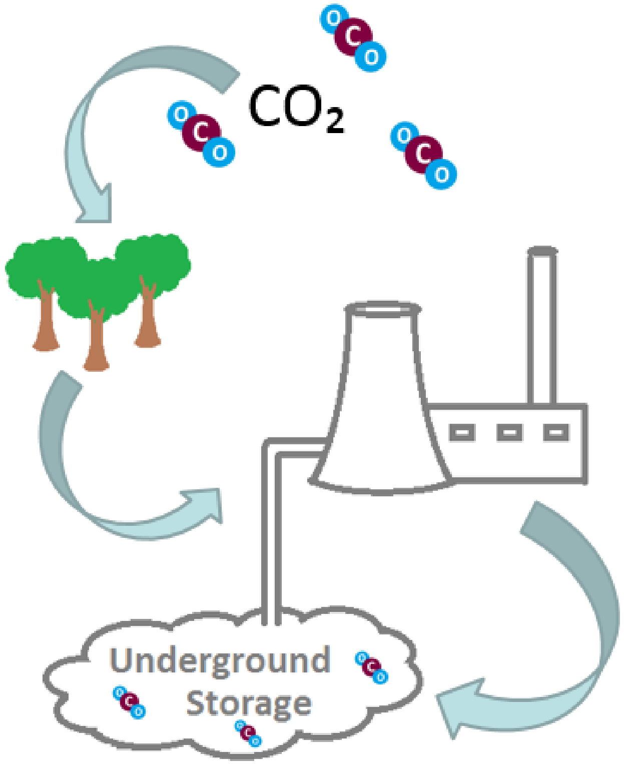
SUPERGEN Bioenergy Hub

UKCCS RESEARCH CENTRE

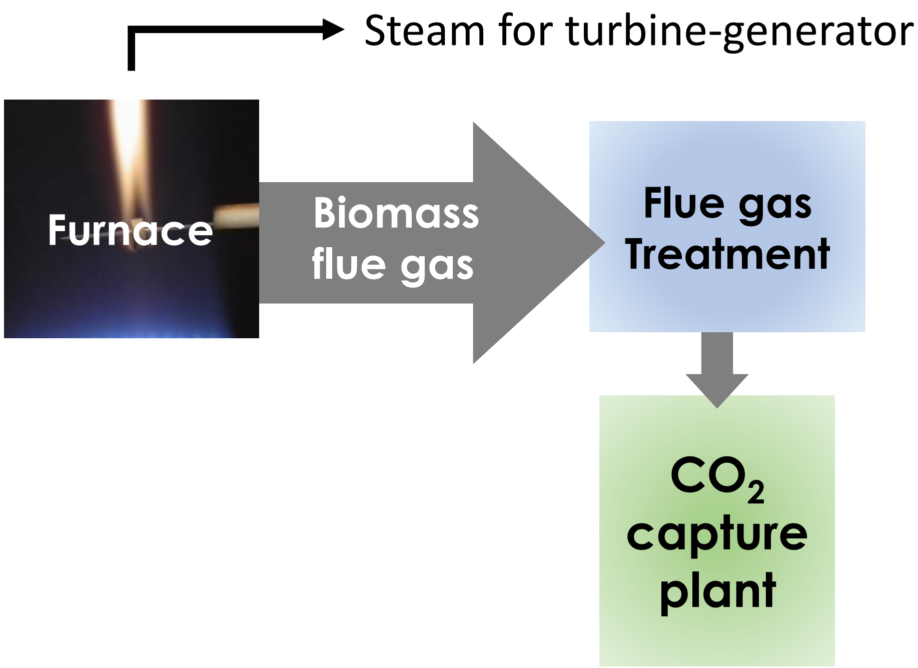
PCCC4 Post Combustion Capture Conference

Introduction to Biomass with Carbon Capture and Storage (BECCS):

- CCS operated with fossil fuels alone is a **low carbon technology**.
- Biomass combustion by itself is also a **low carbon technology**.
- Biomass combustion combined with CCS, known as BECCS, is the most promising carbon **net negative emission** technology currently available.



Introduction to Biomass Combustion:



- Biomass ashes typically has lower metal content compared to coal, except for potassium (K).
- K is volatilised during all stages of biomass combustion.
- KCl can condense on fly ash particles.

Biomass and Coal ash composition:

Parameter	Wood ash (wt%)	Olive ash (wt%)	Coal ash (wt%)
SiO_2	16.6	11.2	58.2
Al_2O_3	2.5	1.2	20.8
Fe_2O_3	2.1	0.9	9.3
K_2O	10	32.3	1.7
Cl	0.01	0.26	0.01
CaO	29.3	10.3	2.9
MgO	5.9	3	1.4
Na_2O	2.2	0.6	2.3

Fe is a known catalyst to MEA degradation[1].

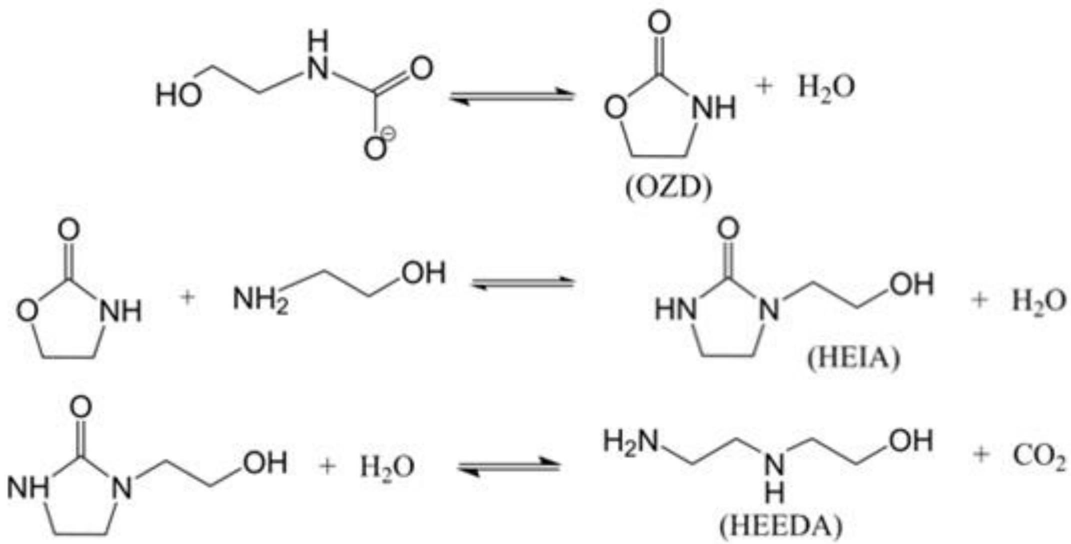
K is known to be volatile at combustion temperatures (>850°C).

Ca and Mg are less volatile at combustion temperatures, but will still be present in biomass fly ashes.

1. da Silva, E.; Lepaumier, H.; Grimstvedt, A.; Vevelstad, S.J.; Einbu, A.; Vernstad, K.; Svendsen, H.F. and Zahlsen, K.Ind. Eng. Chem. Res., 2012, **51**, 13329-13338

Introduction to MEA degradation:

Main thermal degradation products include:



2-Oxazolidone (OZD) [1,2,3]

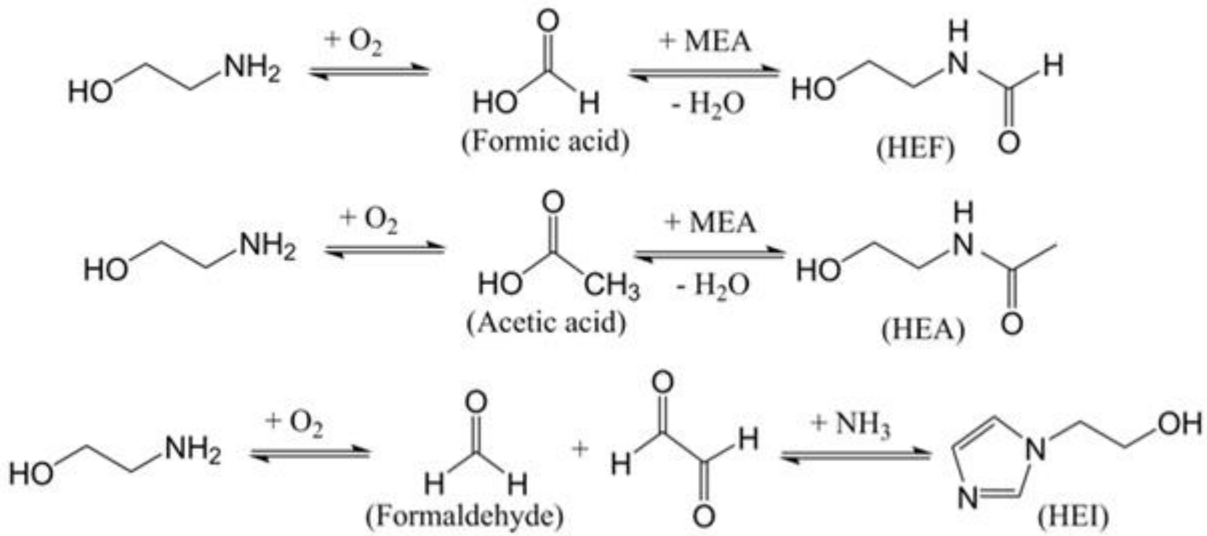
1-(2-Hydroxyethyl)-2-imidazolidinone (HEIA) [1,2,4,5]

N-(2-Hydroxyethyl) ethylenediamine (HEEDA) [1,2,5]

1. Davis, J., Rochelle, G., Energy Procedia, 2009, **1**, 327–333.
2. Lepaumier et al., Ind. Eng. Chem. Res., 2009, **48**, 9061-67.
3. Strazisar et al., Journal of Energy and Environmental Research 1, 2001, 32–39.
4. Strazisar, B.R., Anderson, R.R. & White, C.M., Energy and Fuels, 2003, **17**, 1034–1039.
5. Supap et al., Ind. Eng. Chem. Res., 2006, **45**, 2437–2451.

Introduction to MEA degradation:

- Main oxidative degradation products include:



N-(2-Hydroxyethyl) formamide (HEF) [6,7,8]

N-(2-Hydroxyethyl) acetamide (HEA) [6,7,8]

N-(2-Hydroxyethyl)-imidazole (HEI) [9,10]

- Pilot plant degradation mostly matches oxidative degradation products.

6. Lepaumier et al., Ind. Eng. Chem. Res., 2009, **48**, 9061-67.
7. Strazisar, B.R., Anderson, R.R. & White, C.M., Energy and Fuels, 2003, **17**, 1034–1039.
8. Supap, T., Idem, R., Tontiwachwuthikul, P., Energy Procedia, 2011, **4**, 591–598.
9. Lepaumier et al., Energy Procedia, 2011, **4**, 1652–1659.
10. Sexton, A.J., Rochelle, G.T., Ind. Eng. Chem. Res., 2011, **50**, 667–673.

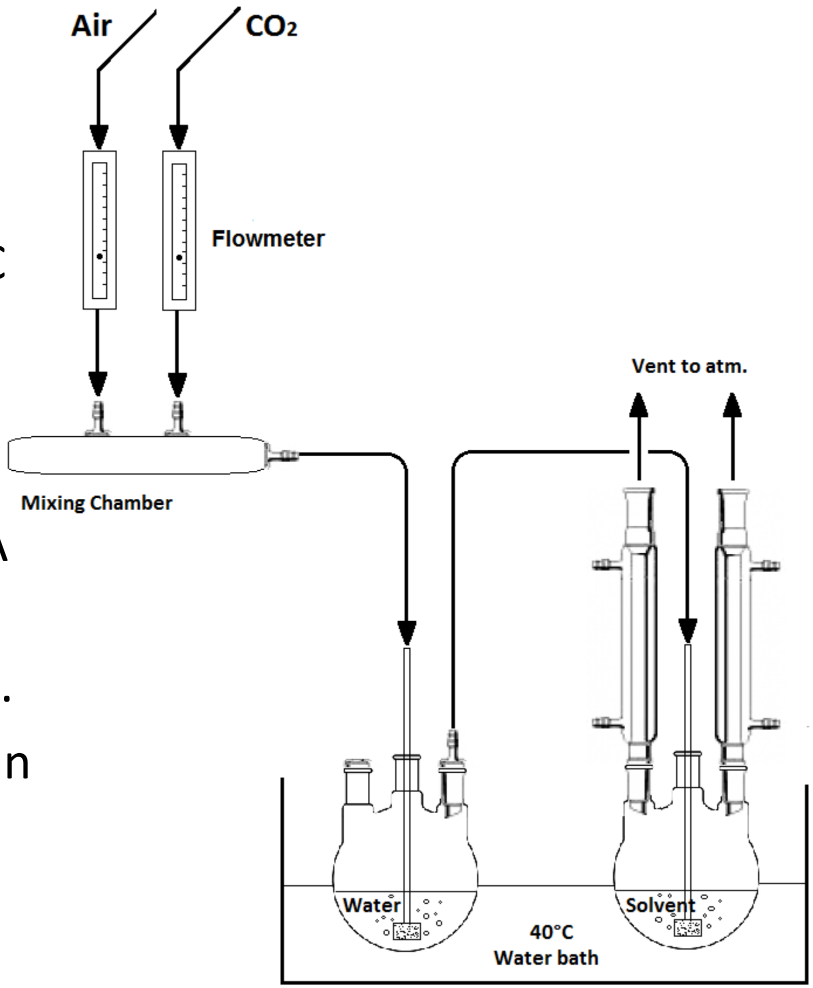
Aims:

- Identify degradation products in thermally and oxidatively degraded solvents from the laboratory.
- Compare the quantities of products formed with the addition of biomass and coal fly ashes.
- Establish the effects of high quantities of potassium salts from biomass combustion on the degradation process.

Experimental Method:

- Thermal degradation experiments used sealed stainless steel vessels stored at 135°C for 5 weeks.

- Oxidative degradation experiments sparged 0.15L/min compressed air through 30% MEA for 21 days[1].
    - Samples fully loaded prior to air sparging.
    - Sparged with CO_2 every 3 days to maintain high loading
    - Aliquot also taken every 3 days.



1. da Silva, E.; Lepaumier, H.; Grimstvedt, A.; Vevelstad, S.J.; Einbu, A.; Vernstad, K.; Svendsen, H.F. and Zahlsen, K.Ind. Eng. Chem. Res., 2012, **51**, 13329-13338

Analysis of degraded solvents:

- ^{1}H NMR used as initial measurement of loading and degradation product formation.
- GC-MS used for volatile degradation products.
- Known thermal and oxidative degradation products were purchased from Sigma Aldrich and used to confirm peaks and calibrate equipment.

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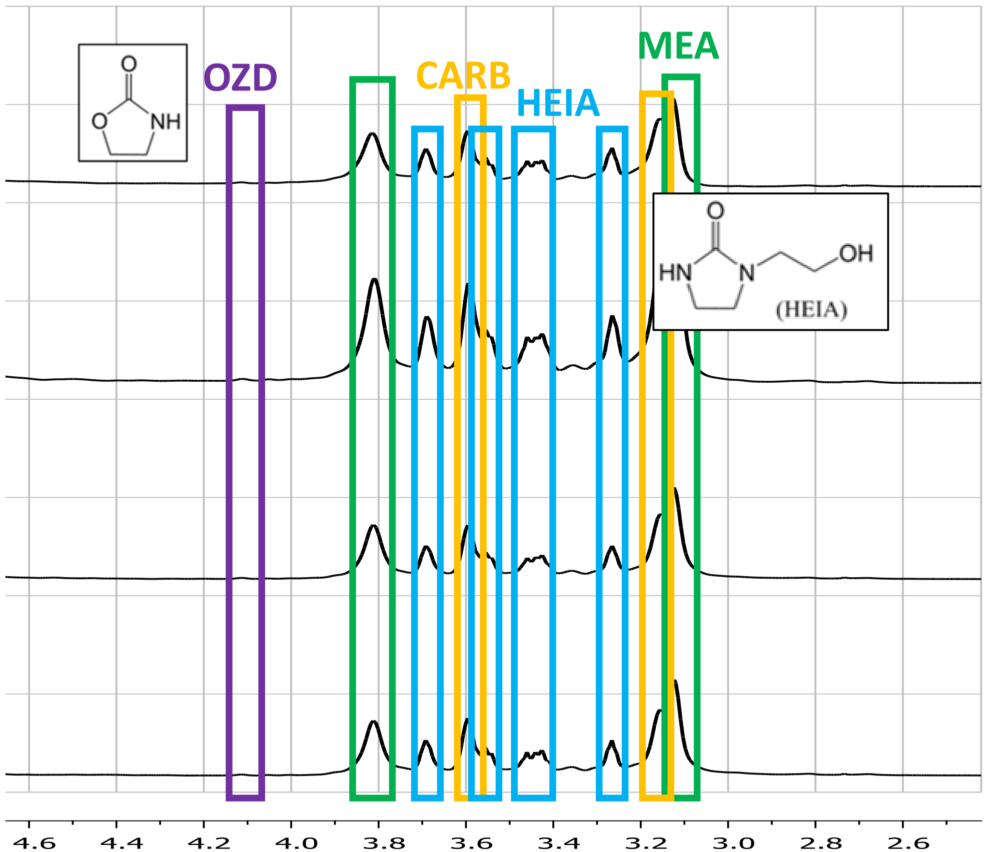
Identification of thermal degradation products using ^{1}H NMR:



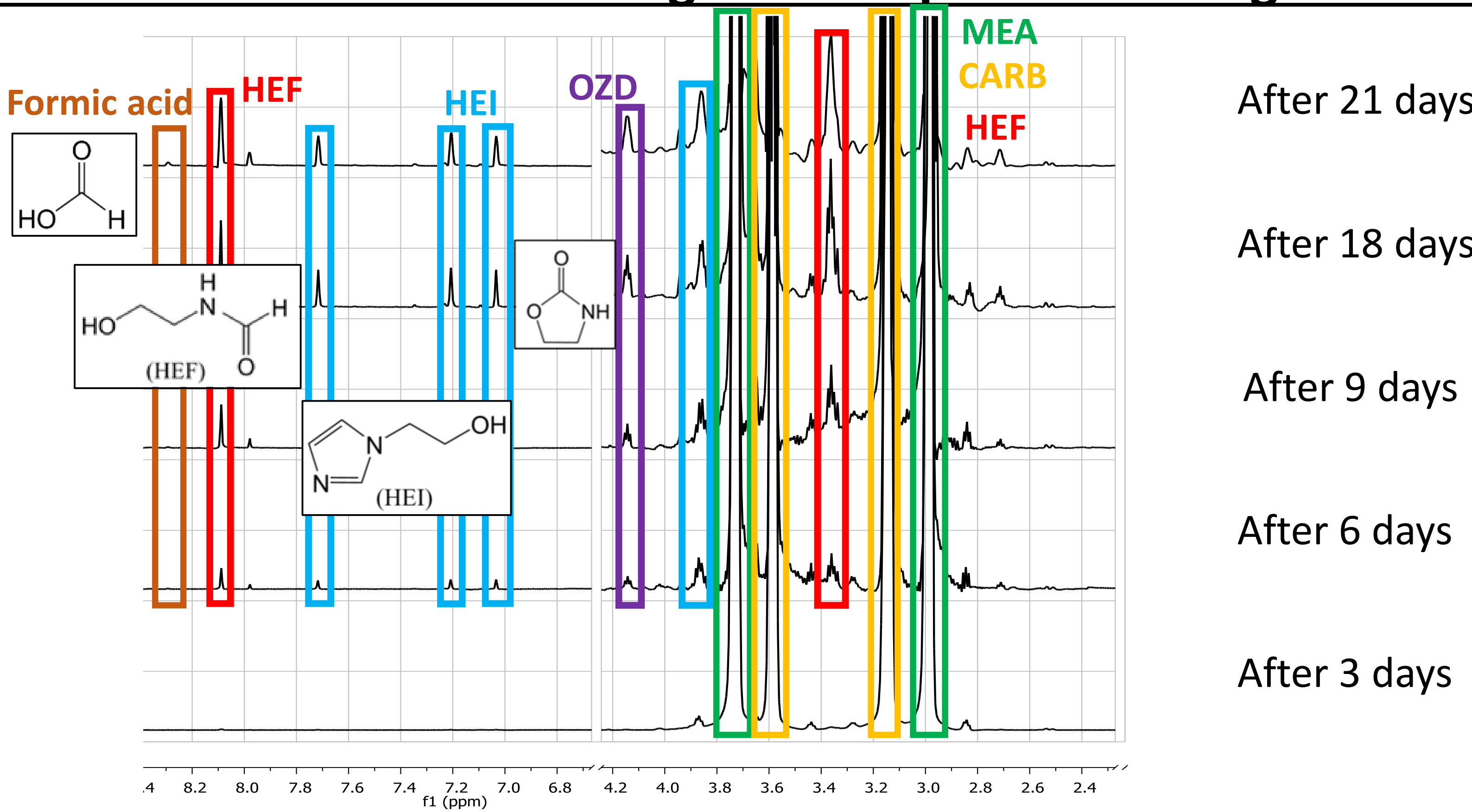
30% MEA with KCl (10mM)

30% MEA with wood ash (3.4g/kg)

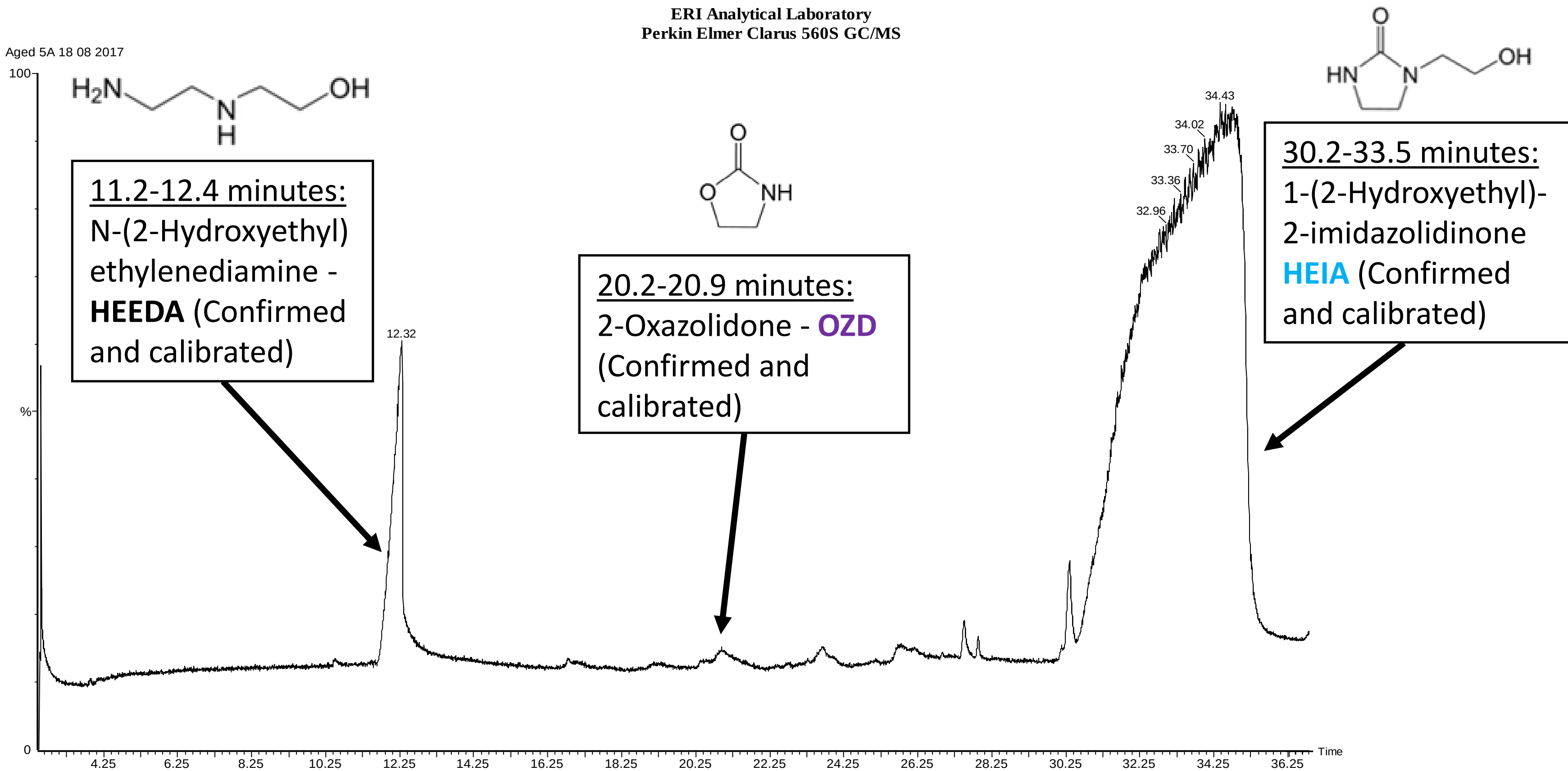
30% MEA with coal ash (3.4g/kg)

30% MEA alone

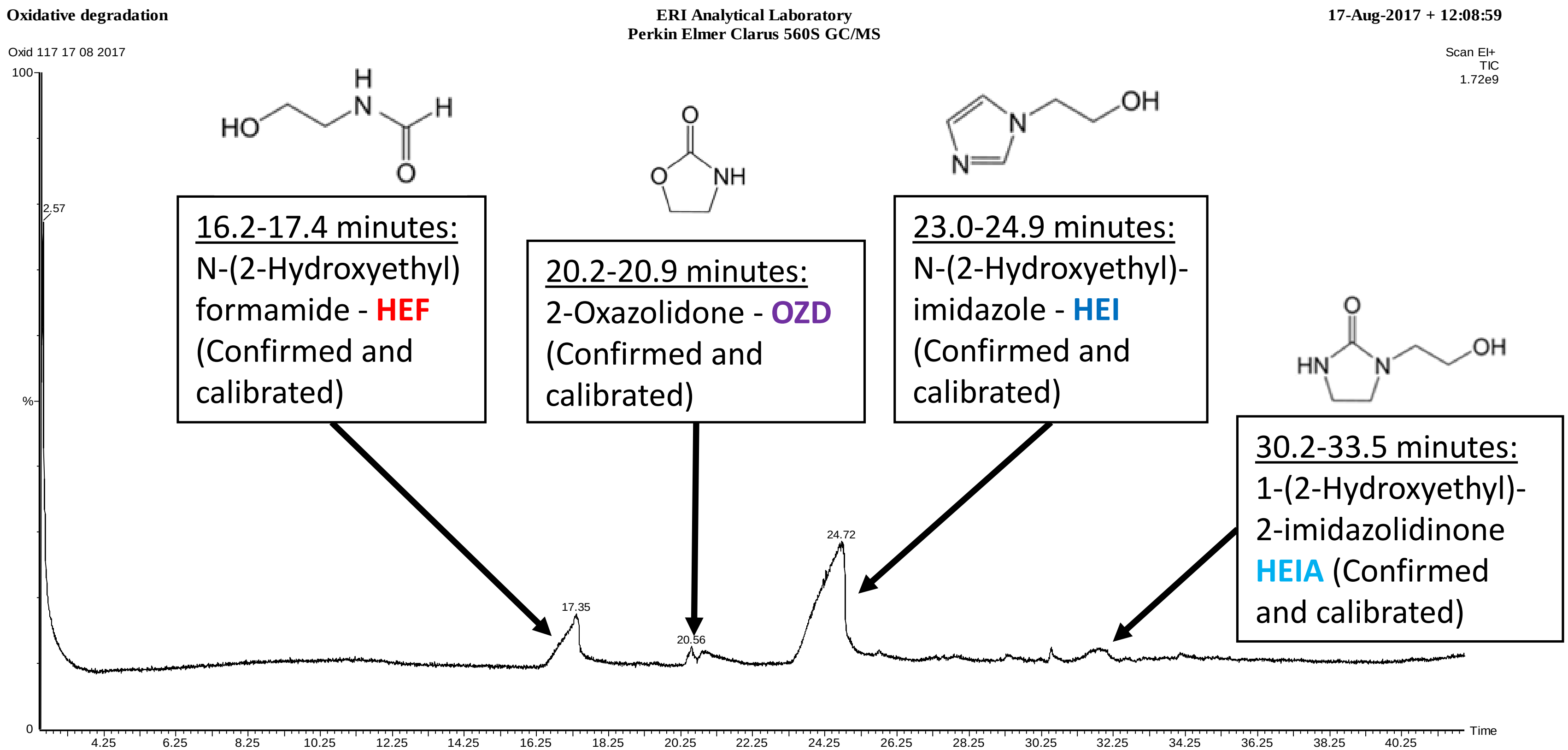
Identification of oxidative degradation products using ^{1}H NMR:



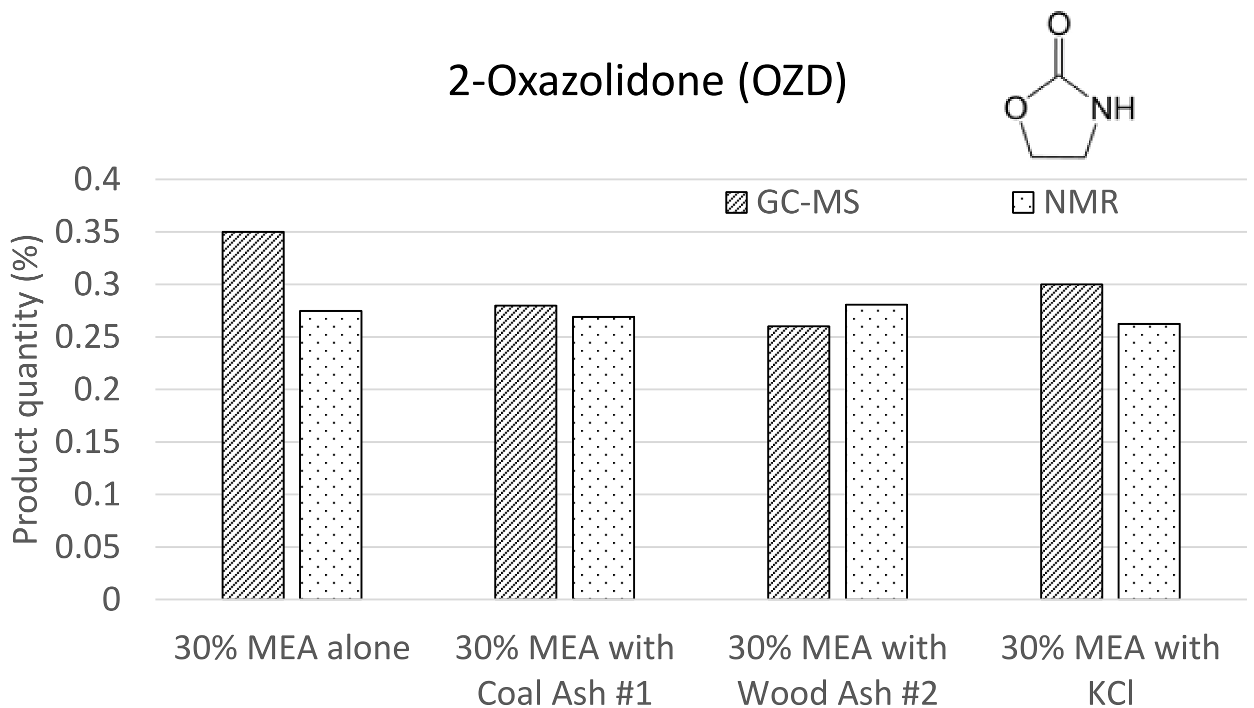
Identification of thermal degradation products using GC-MS:



Identification of oxidative degradation products using GC-MS:

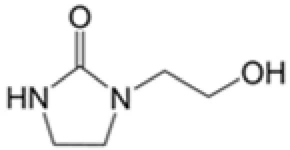


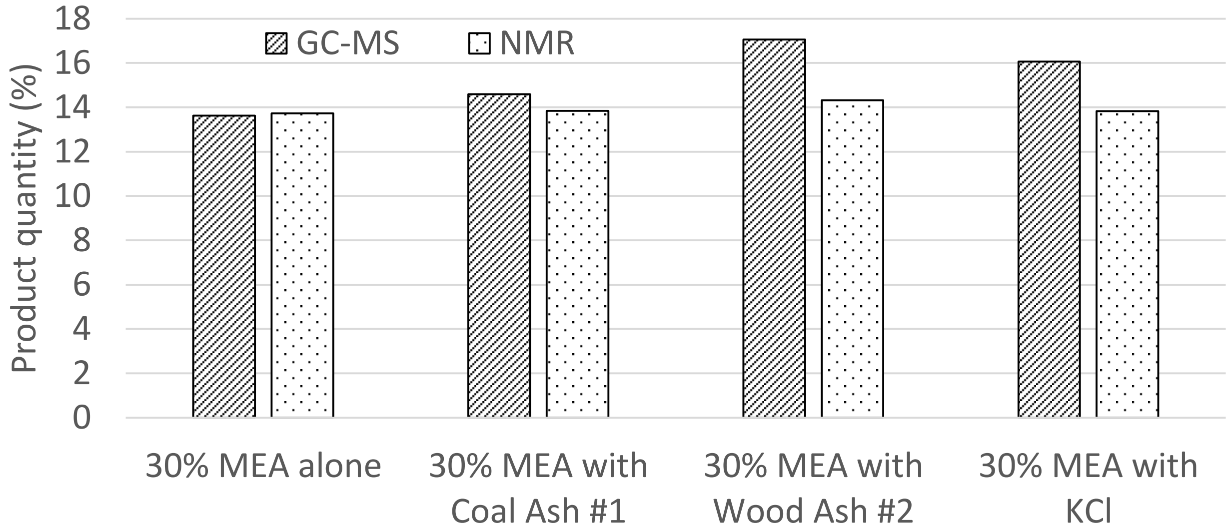
Results from thermal degradation analysis (OZD):



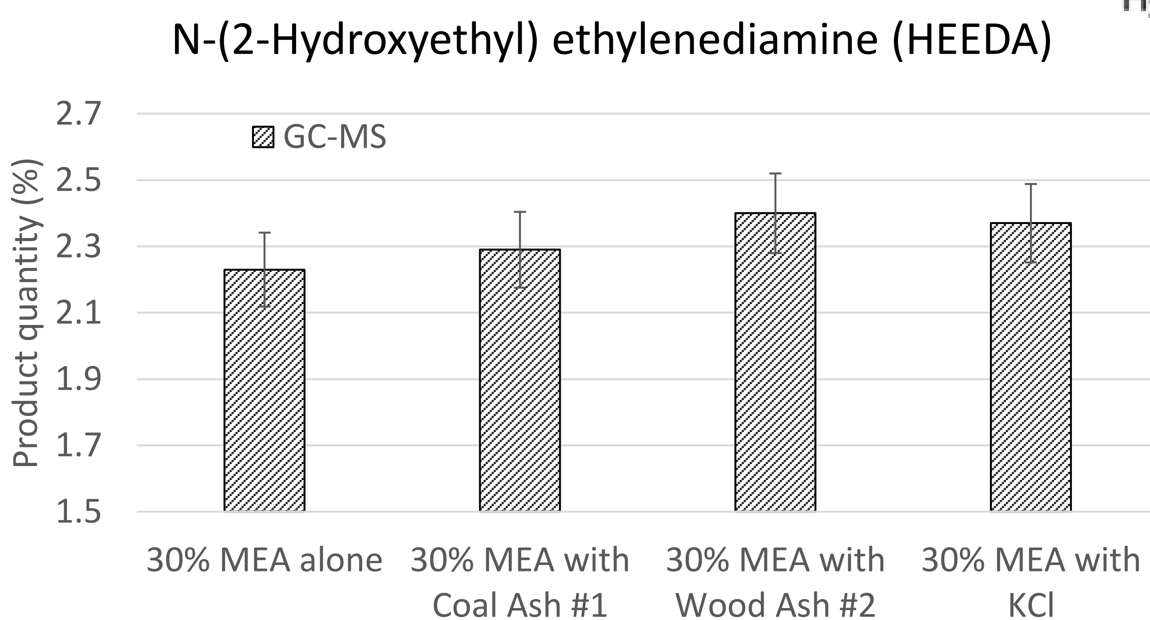
Results from thermal degradation analysis (HEIA):

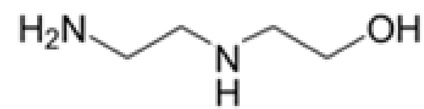
1-(2-Hydroxyethyl)-2-imidazolidinone (HEIA)



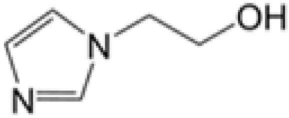


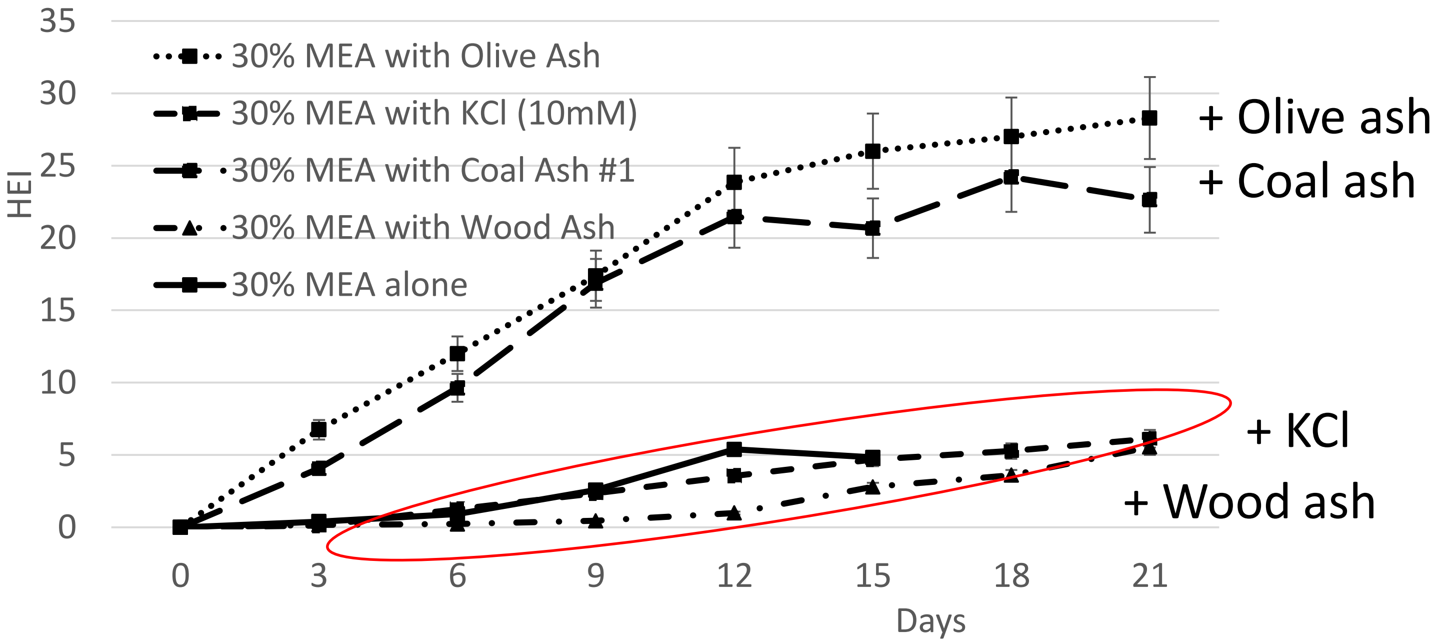
Results from thermal degradation analysis (HEEDA):



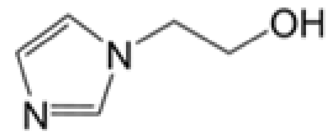


Results from oxidative degradation ^{1}H NMR analysis:

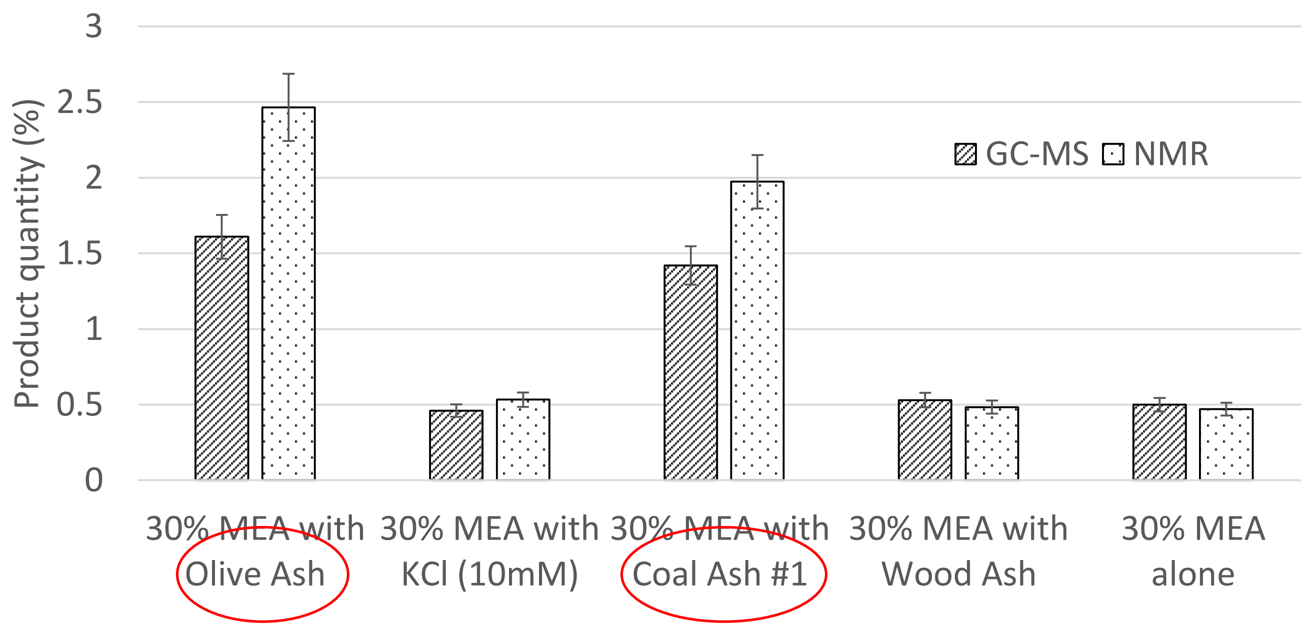




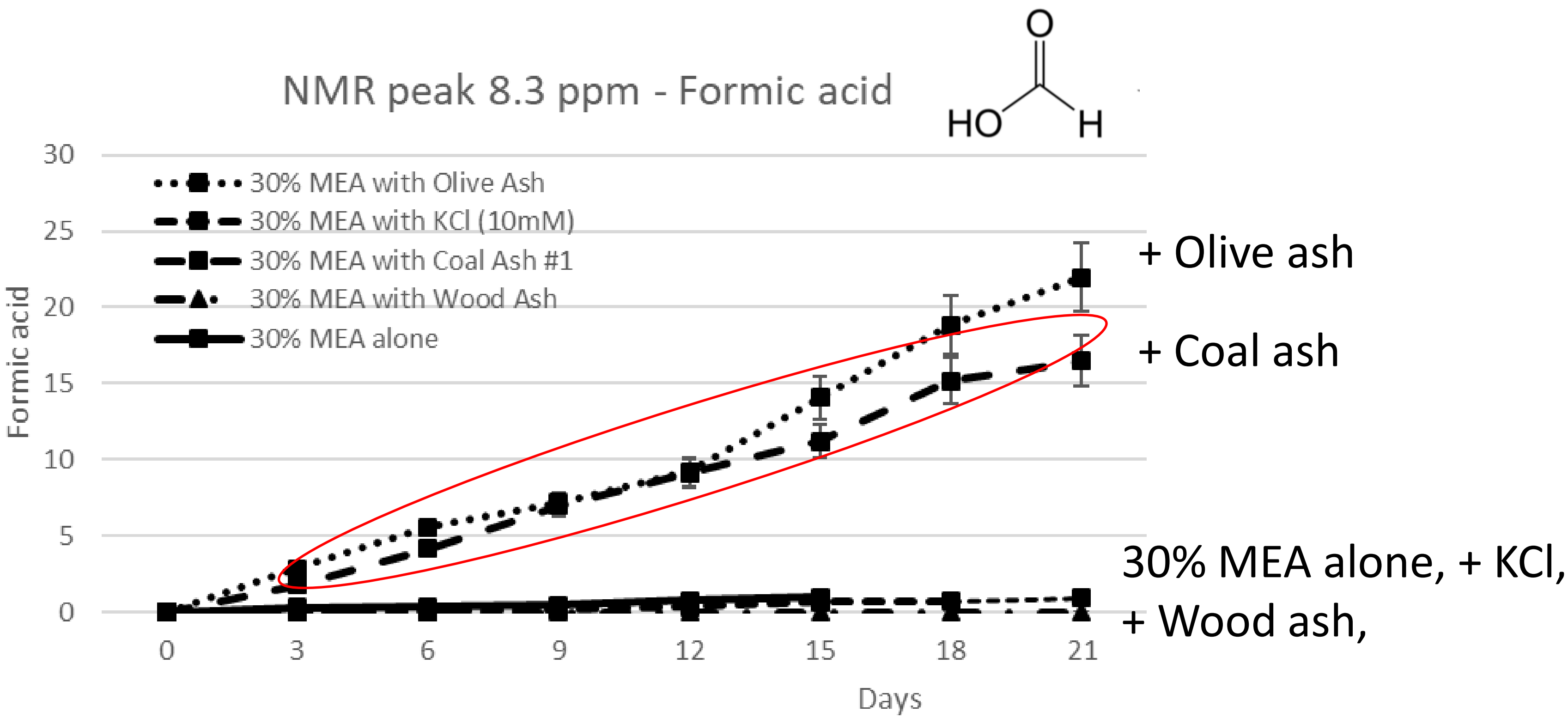
Results from oxidative degradation analysis:



N-(2-Hydroxyethyl)-imidazole (HEI)



Results from oxidative degradation ^{1}H NMR analysis:



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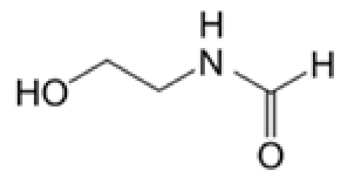
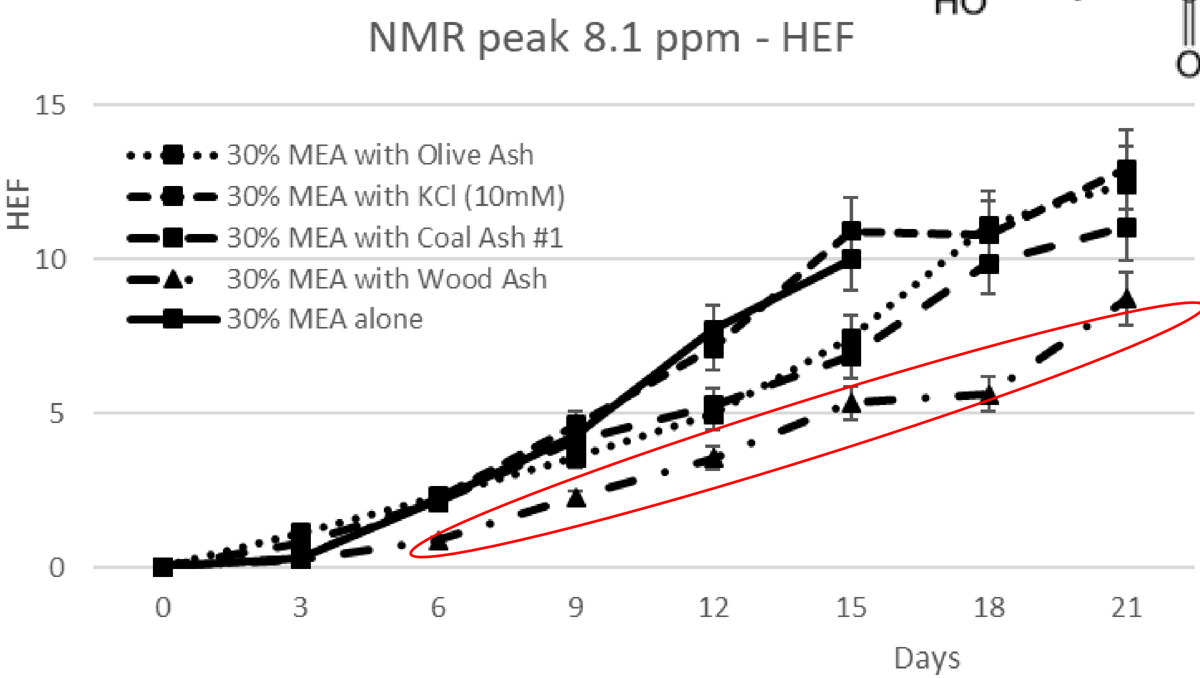
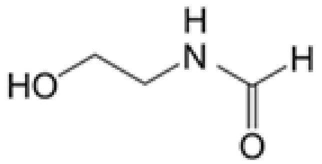


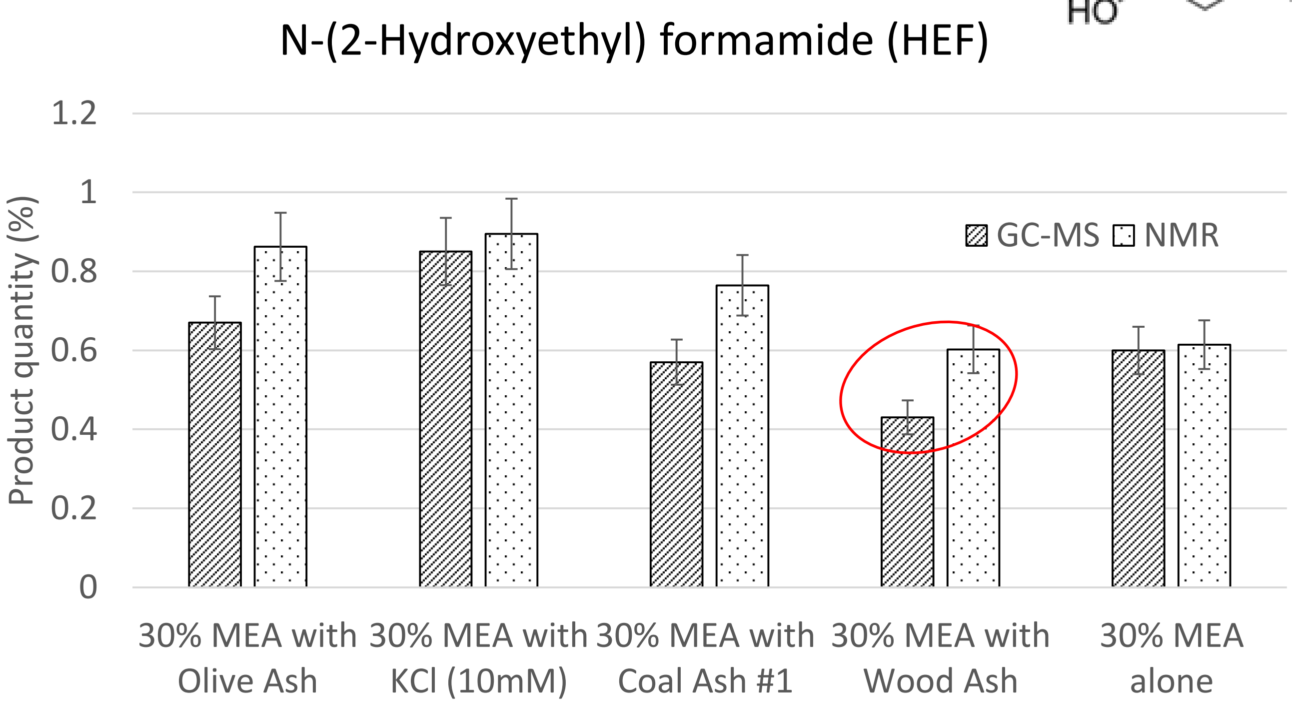


30% MEA alone, + KCl, + Coal ash, + Olive ash

+ Wood ash

Results from oxidative degradation analysis:





Summary:

- THERMAL degradation experiments were complete at 135 °C for 5 weeks.
  - Wood ash and KCl were seen to catalyse HEEDA and HEIA formation.

- OXIDATIVE degradation experiments were complete at 40 °C for 3 weeks.
  - Coal and Olive ash appear to increase the formation HEI.
  - Biomass wood ash appears to reduce HEF & HEI formation.
  - KCl reduced HEI formation.

- More generally, high grade biomass ashes may reduce MEA degradation.

- Further testing required for confirmation but may support the case for using CCS with biomass combustion.

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Thanks for listening!

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