Support Information for

Microwave-assisted HMF production from water-soluble sugars using betaine-based natural deep eutectic solvents (NADES)

Gustavo R. Gomes and Julio C. Pastre

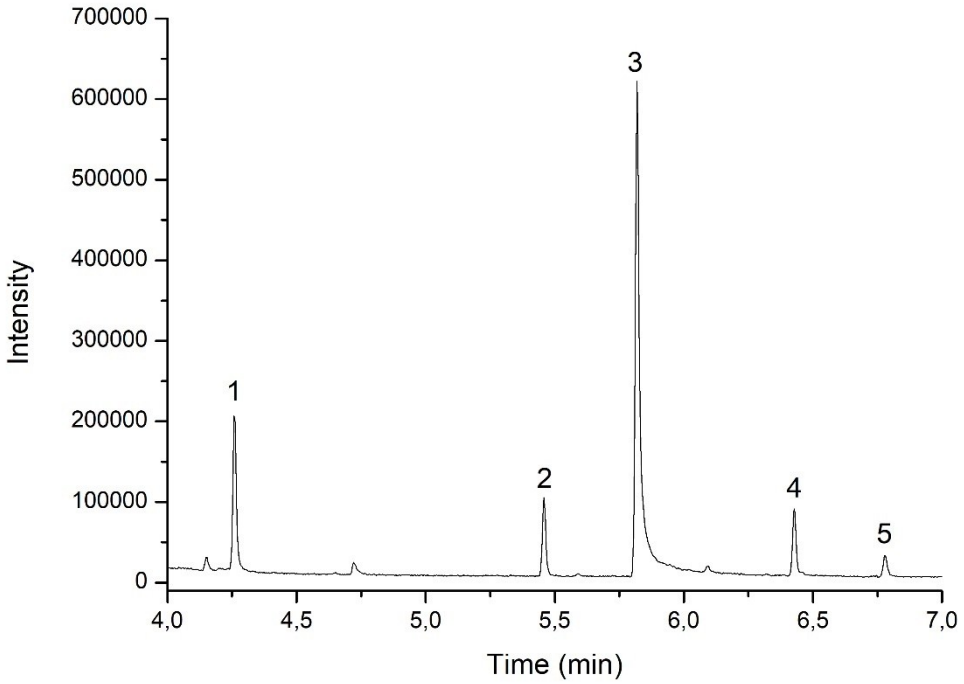
Institute of Chemistry, University of Campinas - UNICAMP, PO Box 6154, 13083-970 Campinas, SP, Brazil

Keywords: HMF, natural deep eutectic solvent, betaine, fructose, sucrose

Summary

List of Figures

List of Tables



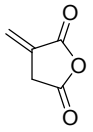
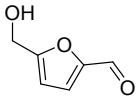
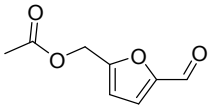
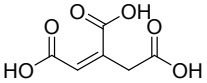
Peak	t_R (min)	Compound	NIST similarity index (%)
1	4,26	 Itaconic anhydride	77
2	5,46	unknown	
3	5,82	 HMF	96
4	6,43	 5-(acetoxymethyl)-furfural	95
5	6,78	 Aconitic acid	78

Figure S1. GC-MS analysis of fructose dehydration using BHC/CA/H_2O under conventional heating.

Table S1. ANOVA analysis of the 2^2 full factorial design for fructose dehydration under microwave irradiation.

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	2325.76	1	2325.76			
Model	747.00	3	249.00	106.71	0.0093	significant
A-Tempertature	*225.00*	*1*	*225.00*	*96.43*	*0.0102*	
B-Time	*81.00*	*1*	*81.00*	*34.71*	*0.0276*	
AB	*441.00*	*1*	*441.00*	*189.00*	*0.0052*	
Pure Error	4.67	2	2.33			
Cor Total	3077.43	6				

Table S2. ANOVA analysis of the 2^2 full factorial design for sucrose dehydration under microwave irradiation.

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	613.44	1	613.44			
Model	266.75	3	88.92	38.11	0.0257	significant
A-Temperature	*0.25*	*1*	*0.25*	*0.11*	*0.7745*	
B-Tme	*210.25*	*1*	*210.25*	*90.11*	*0.0109*	
AB	*56.25*	*1*	*56.25*	*24.11*	*0.0391*	
Pure Error	4.67	2	2.33			
Cor Total	884.86	6				

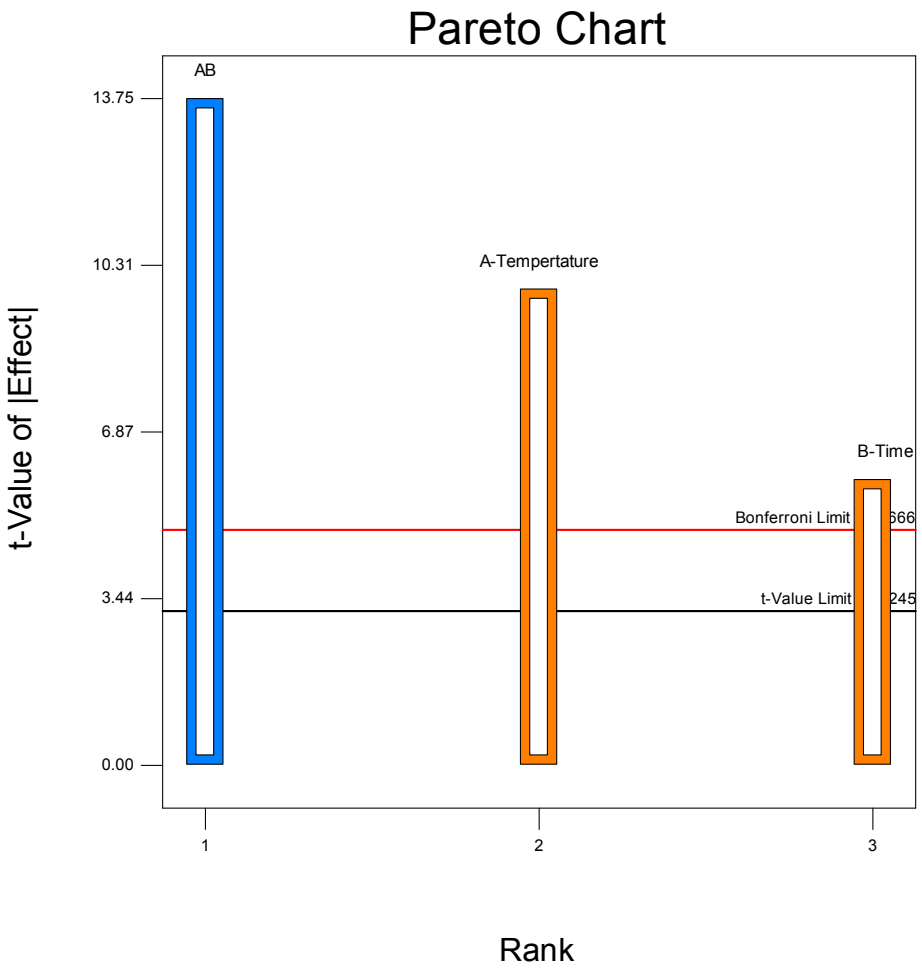


Figure S2. Pareto chart of the 2^2 full factorial design for fructose dehydration under microwave irradiation.

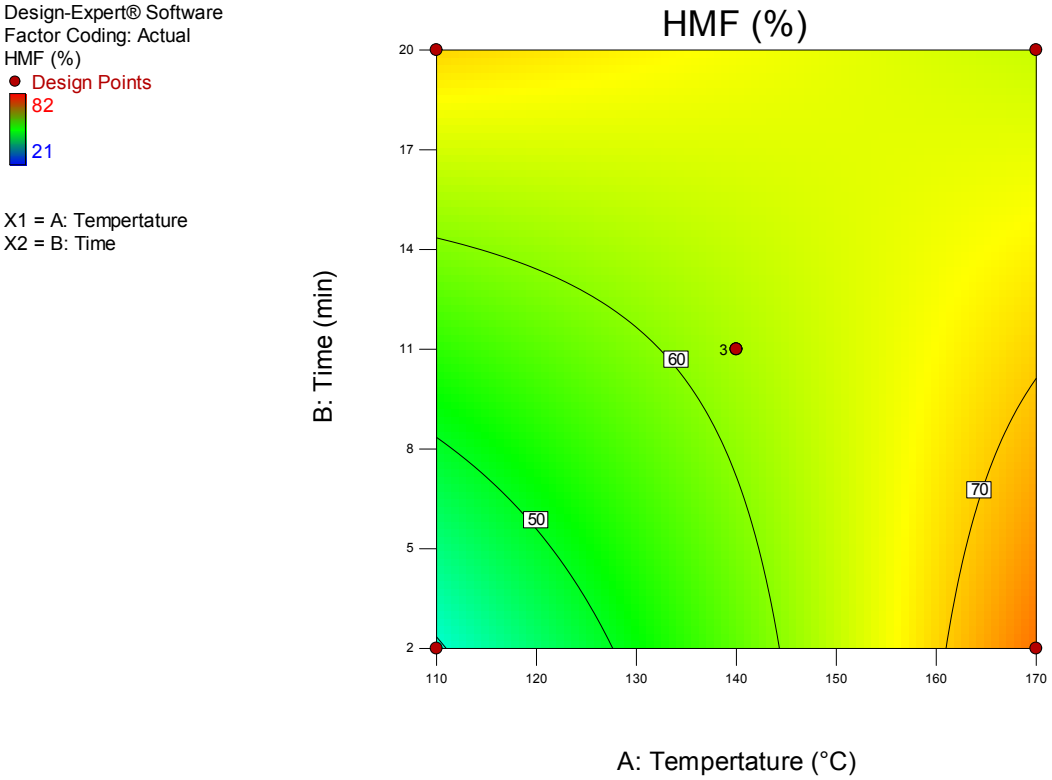


Figure S3. Contour graphic of the 2^2 full factorial design for fructose dehydration under microwave irradiation.

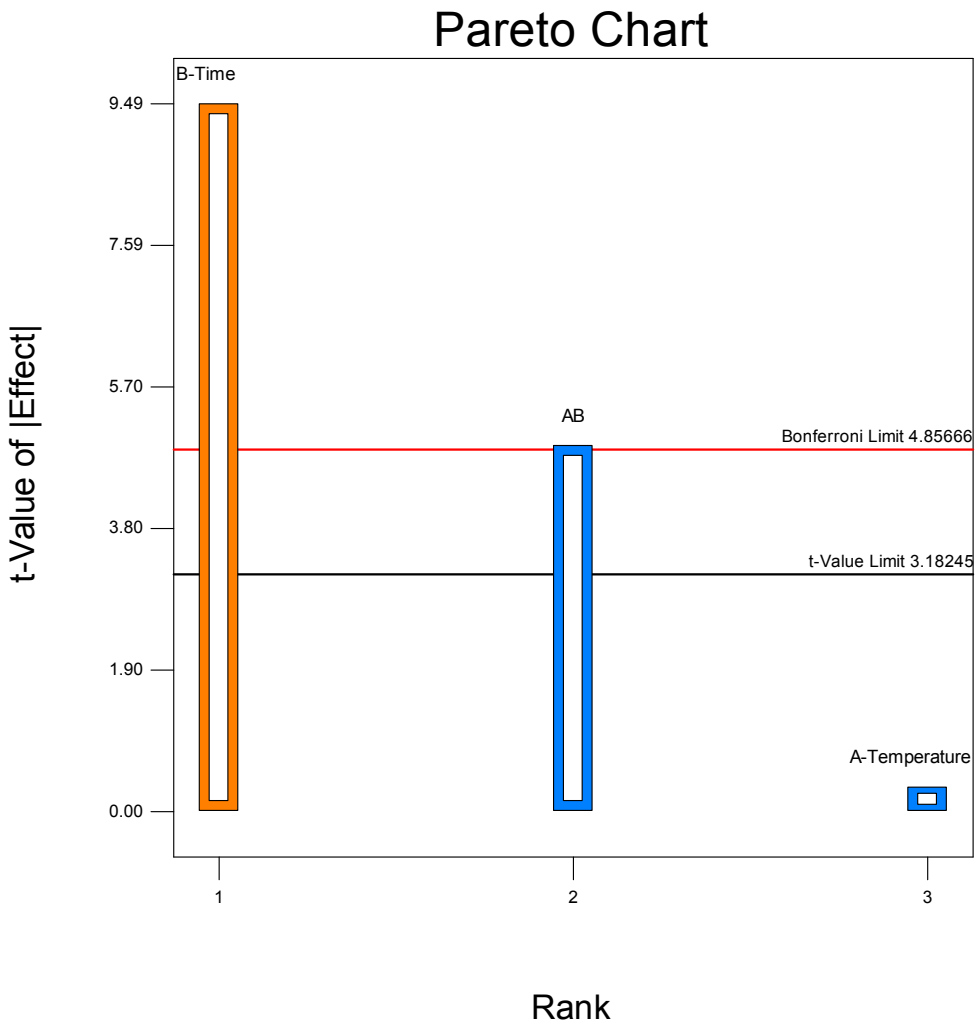


Figure S4. Pareto chart of the 2^2 full factorial design for sucrose dehydration under microwave irradiation.

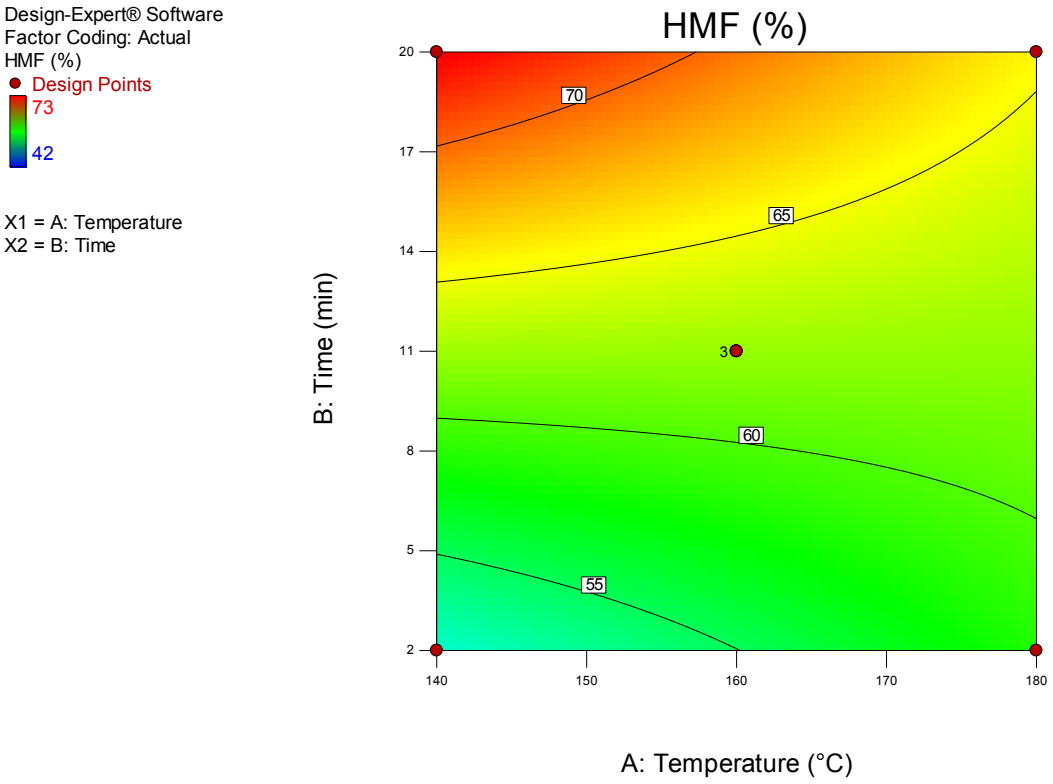
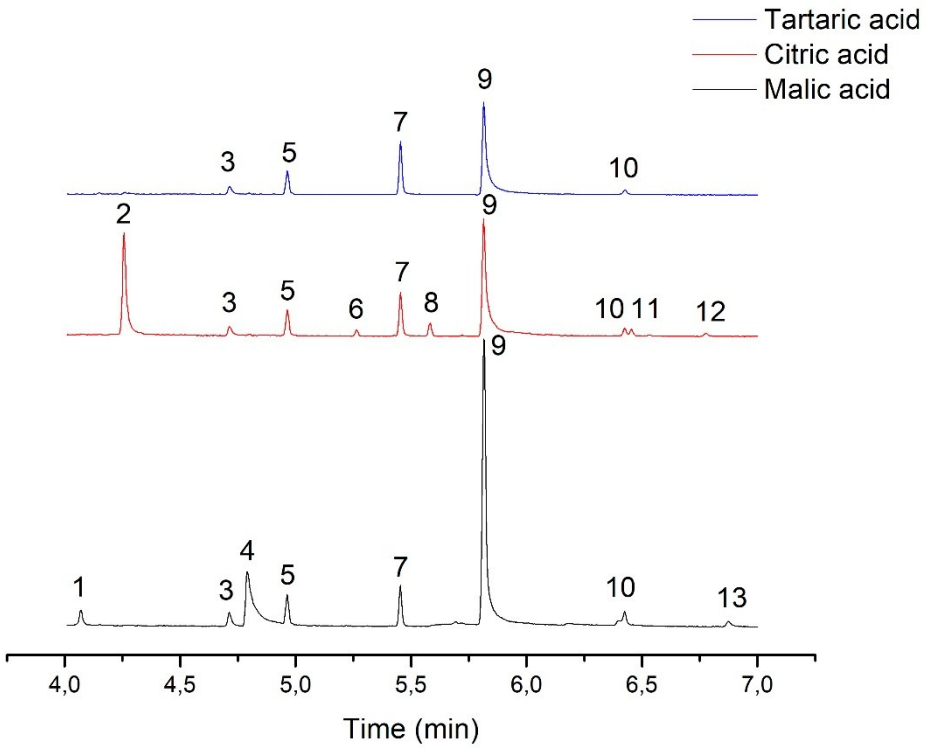
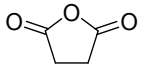
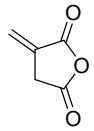
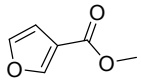
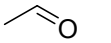
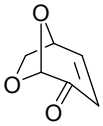
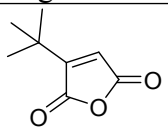
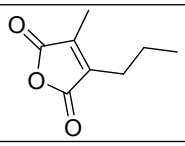


Figure S5. Contour graphic of the 2^2 full factorial design for sucrose dehydration under microwave irradiation



Peak	t_R (min)	Compound	NIST similarity index (%)
1	4,07	 Succinic anhydride	77
2	4,26	 Itaconic anhydride	66
3	4,71	 Methyl 3-furoate	55
4	4,79	 Acetaldehyde	77
5	4,96	 Levoglucosenone	96
6	5,26	 3-(tert-butyl)furan-2,5-dione	53
7	5,46	unknown	
8	5,58		90

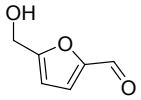
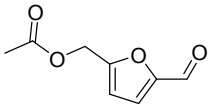
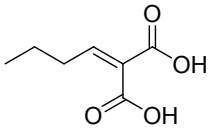
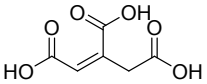
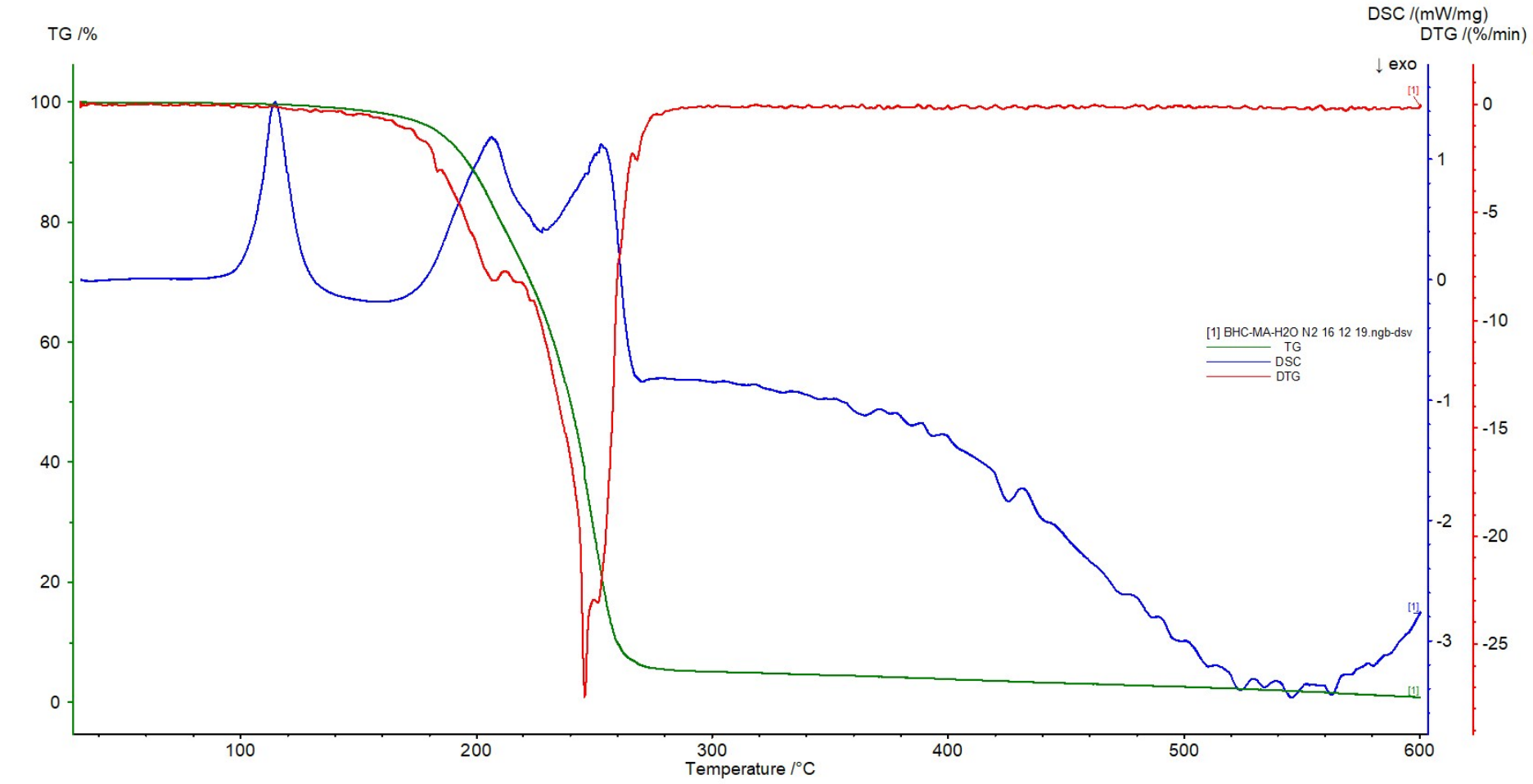
		3-methyl-4-propylfuran-2,5-dione	
9	5,82	 HMF	96
10	6,43	 5-(acetoxymethyl)-furfural	90
11	6,46	 2-butylidenemalonic acid	33
12	6,78	 Aconitic acid	63
13	6,88	Unknown	

Figure S6. GC-MS analysis of sucrose dehydration mediated by NADES under microwave irradiation.

A)


TG /%
DSC /(mW/mg)
DTG /(%/min)
↓ exo
100
80
60
40
20
0
1
0
-1
-2
-3
-5
-10
-15
-20
-25
100
200
300
400
500
600
Temperature /°C
[1] BHC-MA-H2O N2 16 12 19.ngb-dsv
TG
DSC
DTG

B)

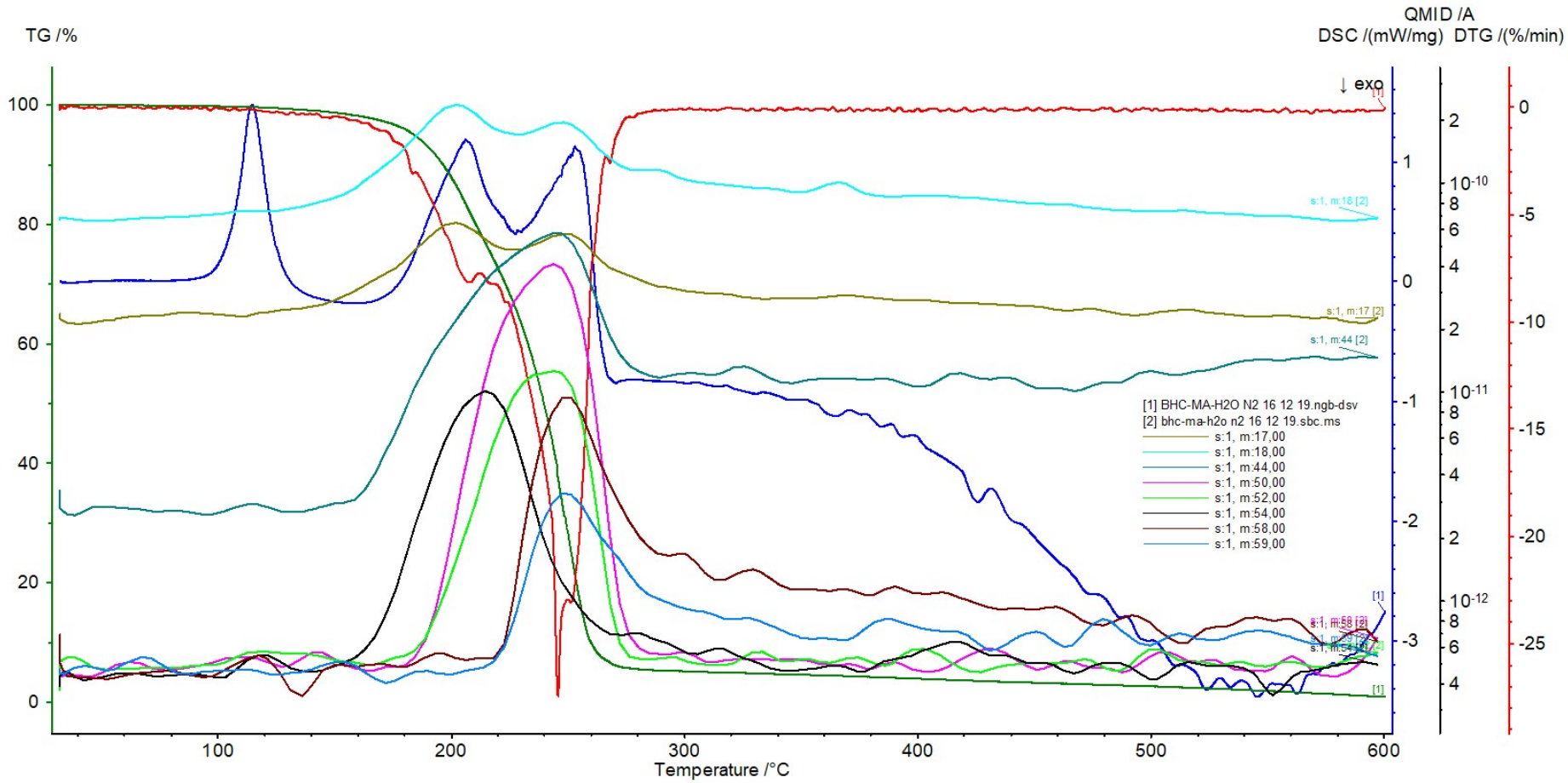
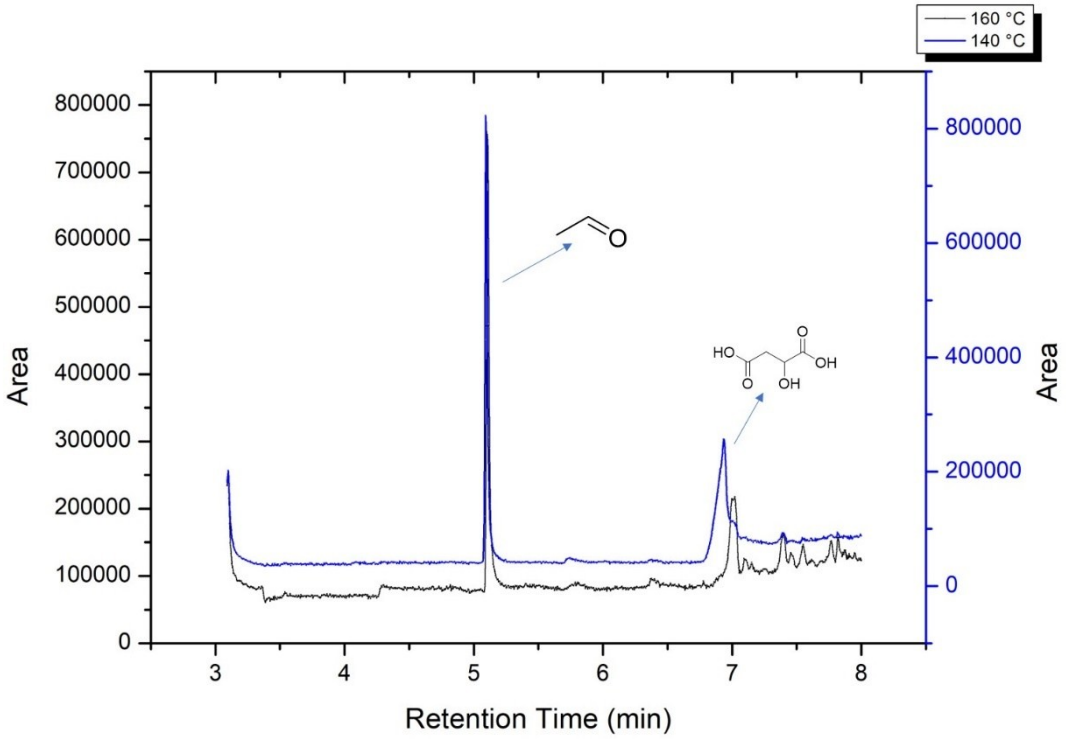


Figure S7. Thermal analysis of BHC/MA/H_2O (A) TG-DSC-DTG and (B) TG-MS

A)



B)

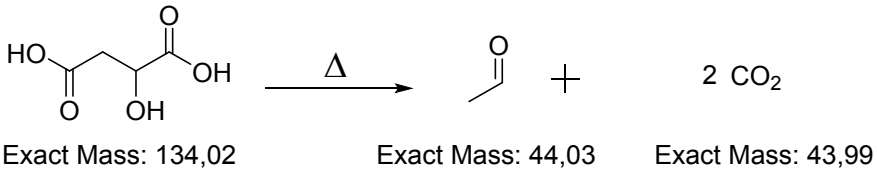
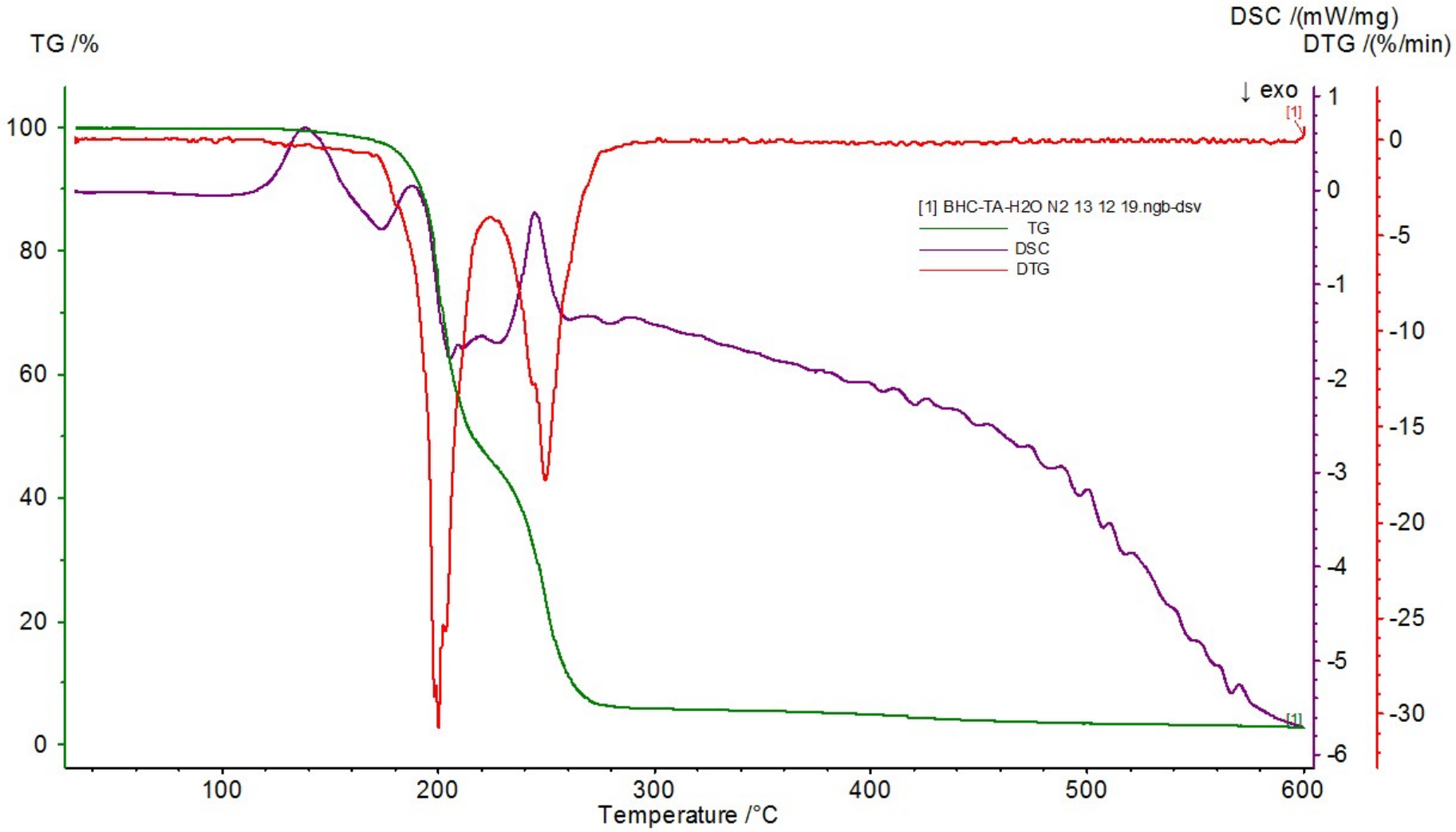


Figure S8. (A) GC-MS analysis of ethyl acetate fraction of BHC/MA/H_2O thermal degradation experiments (B) Reaction scheme for the decarboxylation of malic acid.

A)


TG /%
DSC /(mW/mg)
DTG /(%/min)
↓ exo
[1]
[1] BHC-TA-H2O N2 13 12 19.ngb-dsv
TG
DSC
DTG
100
80
60
40
20
0
1
0
-1
-2
-3
-4
-5
-6
0
-5
-10
-15
-20
-25
-30
100
200
300
400
500
600
Temperature /°C

B)

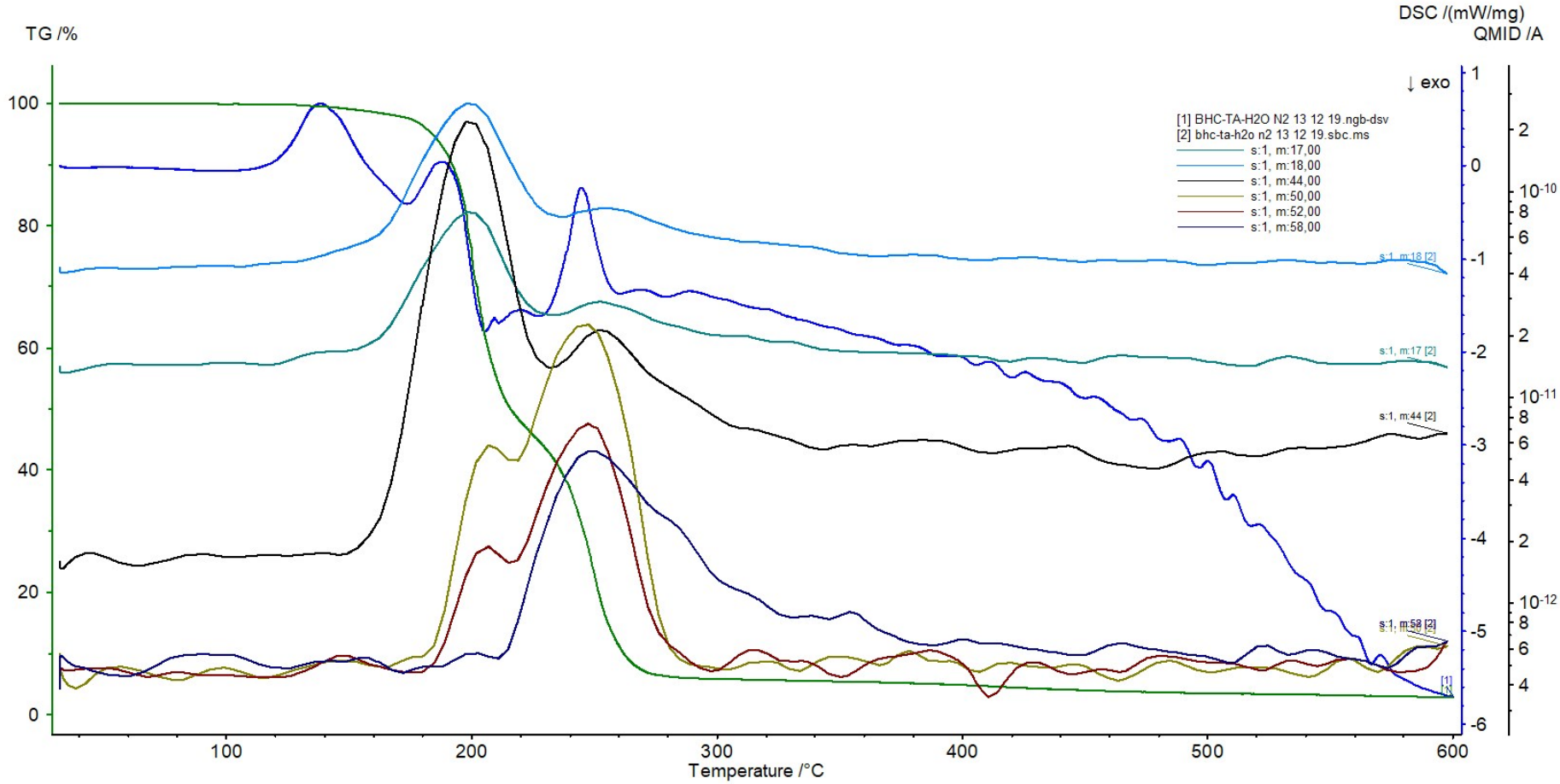
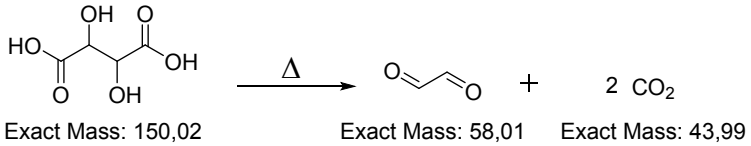


Figure S9. Thermal analysis of BHC/TA/H_2O (A) TG-DSC-DTG and (B) TG-MS

A)



B)

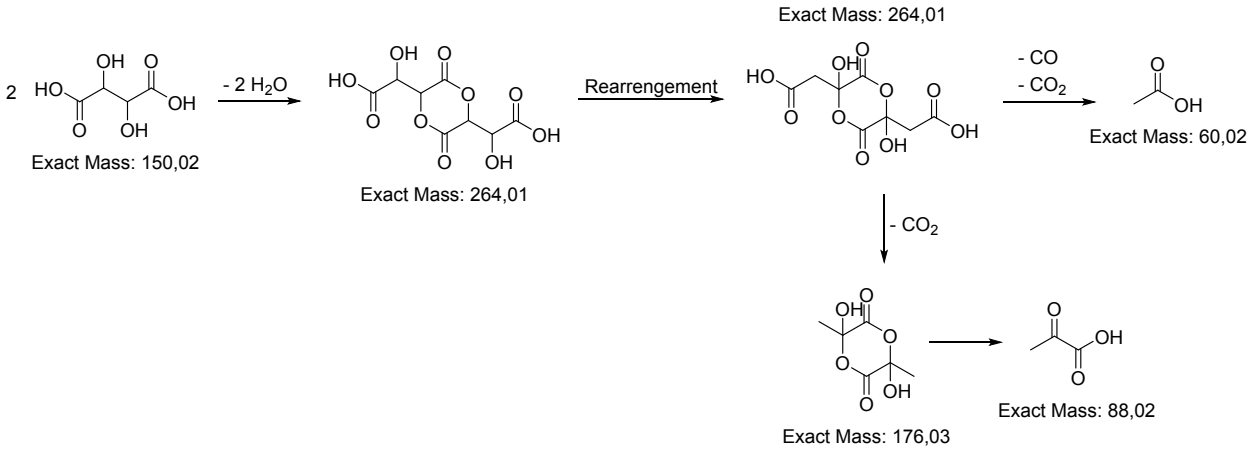
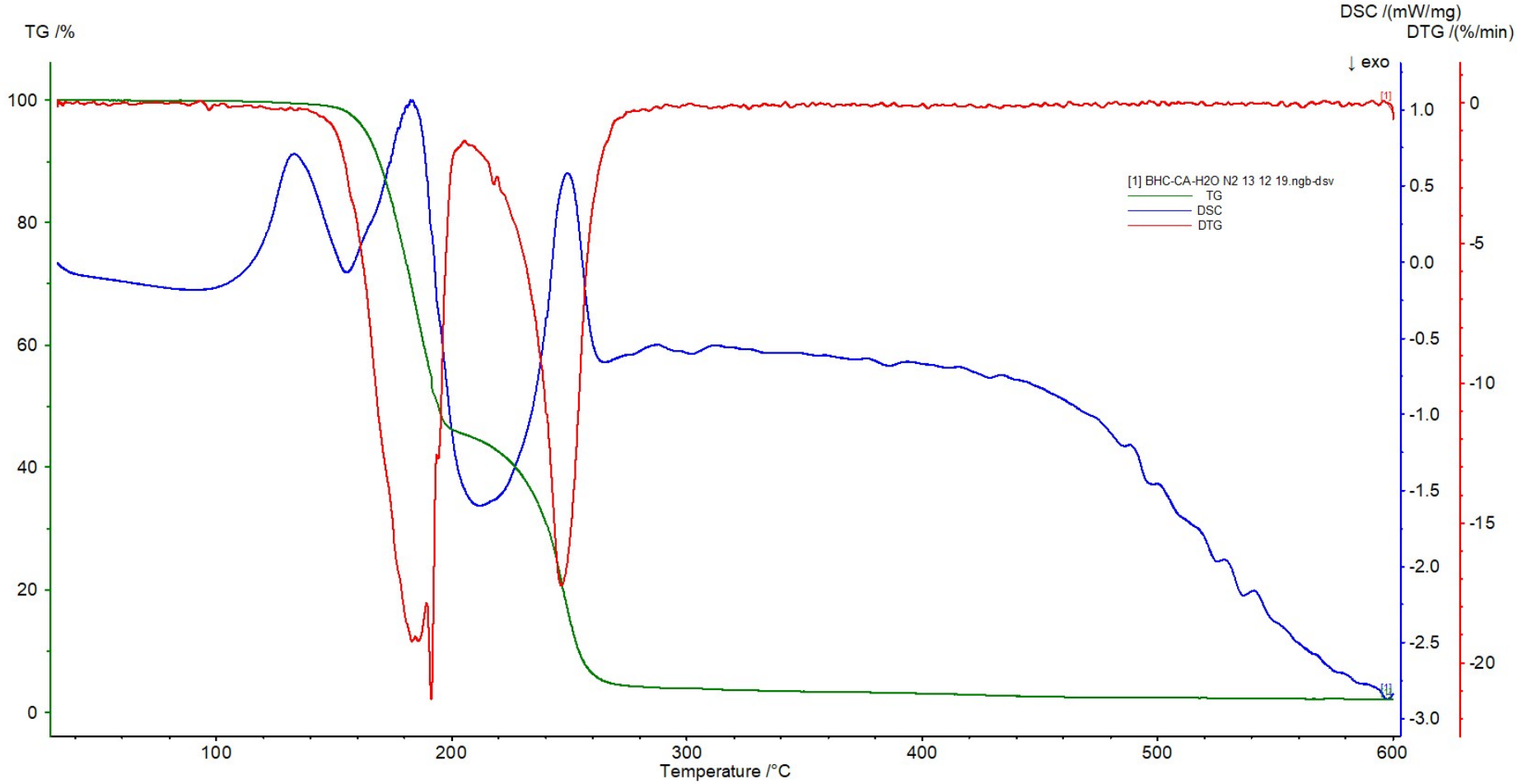


Figure S10. Reaction schemes of thermal degradation of tartaric acid forming (A) glyoxal and (B) acetic and pyruvic acids.

A)


TG /%
DSC /(mW/mg)
DTG /(%/min)
↓ exo
[1] BHC-CA-H2O N2 13 12 19.ngb-dsv
TG
DSC
DTG
Temperature /°C
100
80
60
40
20
0
100
200
300
400
500
600
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
-5
-10
-15
-20

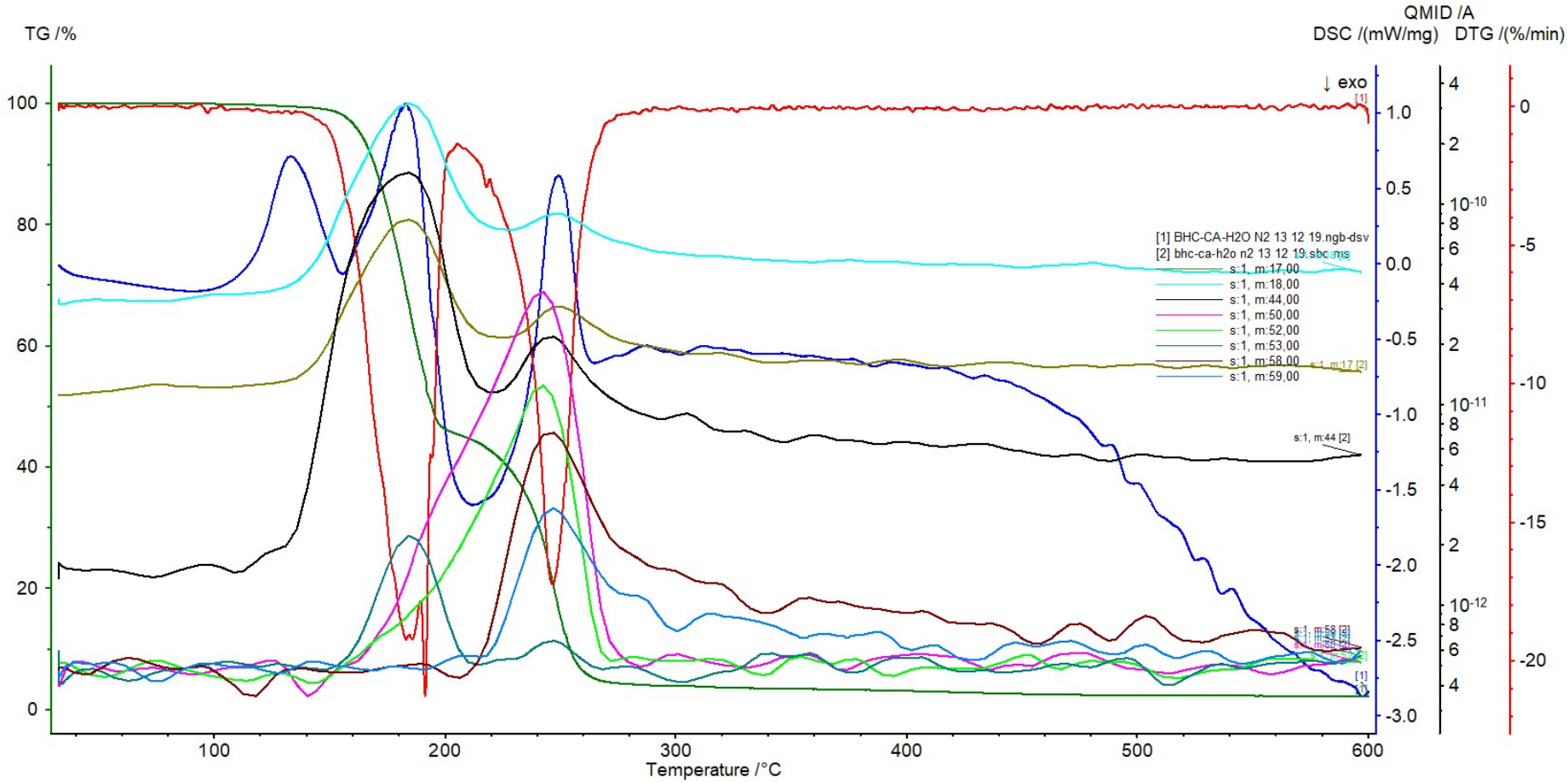


Figure S11. Thermal analysis of BHC/CA/H_2O (A) TG-DSC-DTG and (B) TG-MS

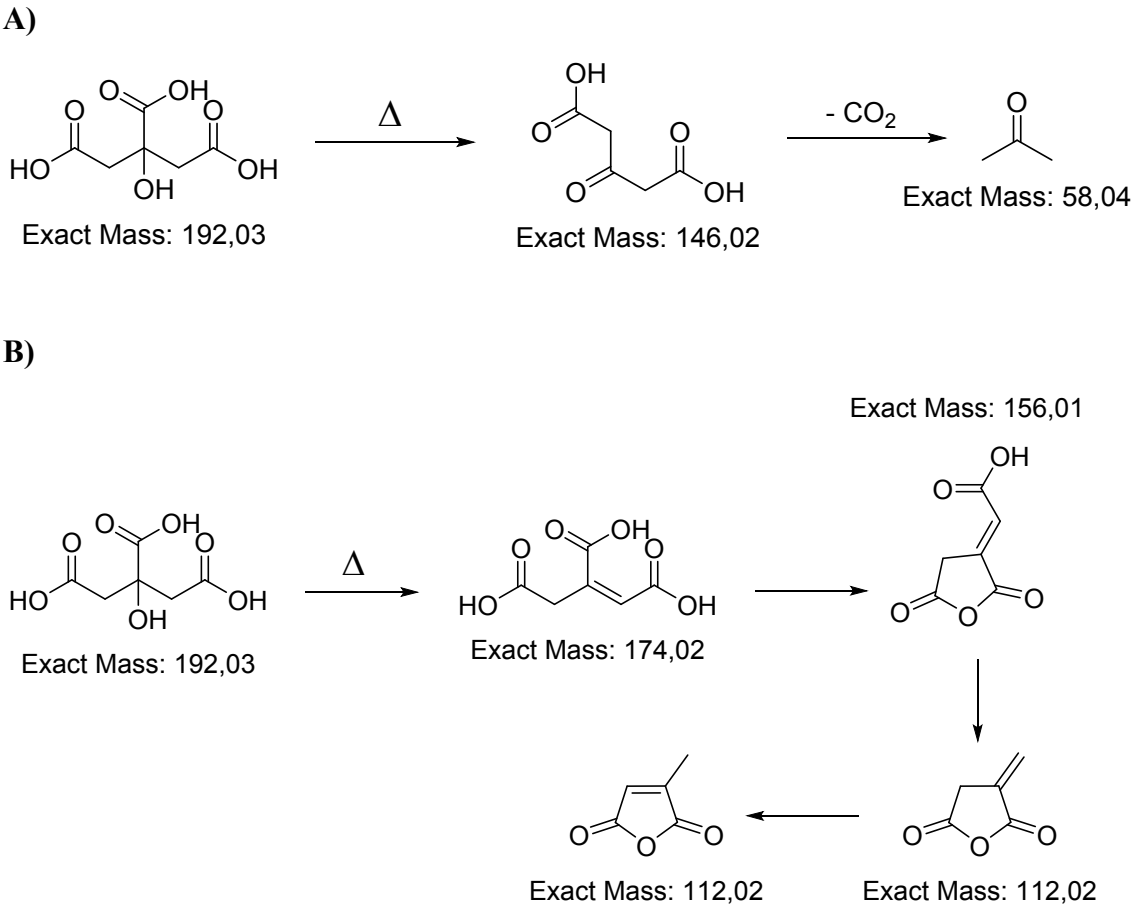
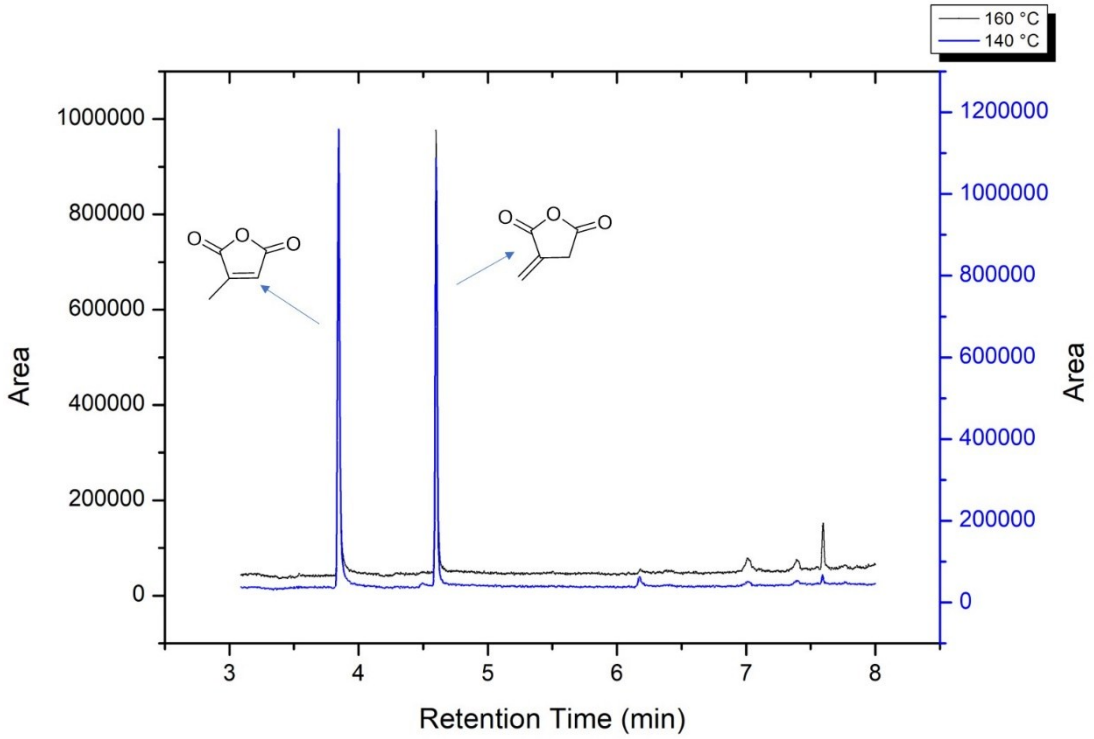


Figure S12. Reaction scheme of thermal degradation of citric acid forming (A) acetone and (B) itaconic and citraconic anhydrides.

A)


160 °C
140 °C
Area
Area
Retention Time (min)
0
200000
400000
600000
800000
1000000
1200000
3
4
5
6
7
8

B)

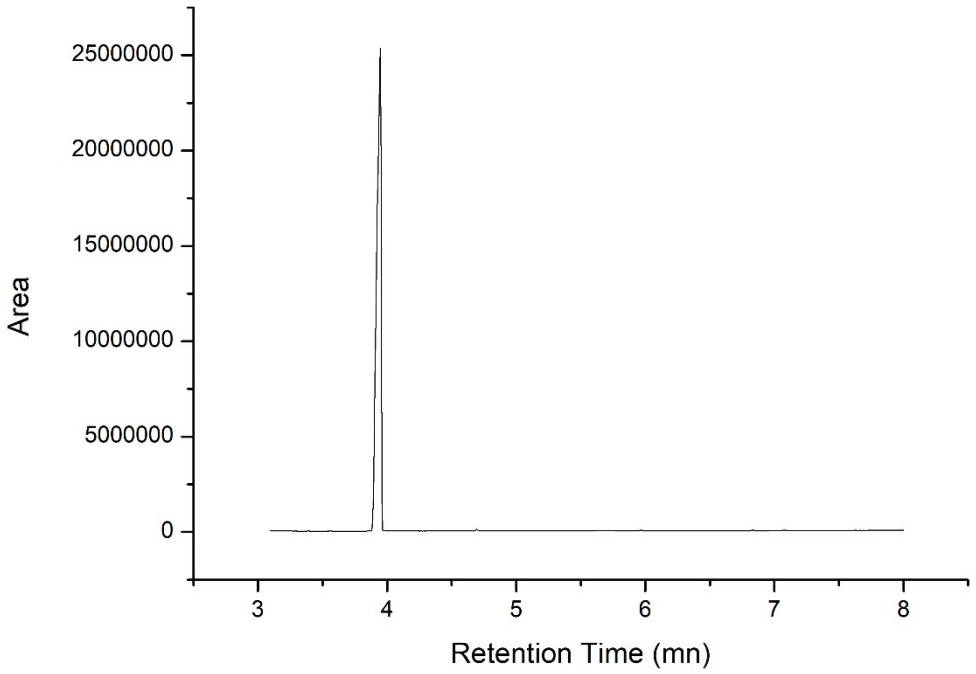

Area
Retention Time (mn)
0
5000000
10000000
15000000
20000000
25000000
3
4
5
6
7
8

Figure S13. GC-MS analysis of (A) ethyl acetate fraction of BHC/CA/H_2O thermal degradation experiments and (B) citraconic anhydride (authentic sample from commercial sources).