Supplementary Material

Investigating physicochemical properties of MgO catalysts for the gas phase conversion of glycerol

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Calculations

Equation (1) was used to calculate the glycerol conversion (C_{gly}) based on the molar difference between the carbon moles of glycerol fed into the reactor $g_{m\ in}$ compared to those detected in the reaction mixture $g_{m\ out}$:

$$C_{GLY}\ (\%) = \left(\frac{g_{m\ in} - g_{m\ out}}{g_{m\ in}}\right) \text{ x } 100 \qquad (1)$$

The product selectivity (S_x) for any product, x, was calculated from the moles of carbon recovered in product x, (x_{cm}) divided by the sum of moles of carbon in all detected products, y_{Cm} (2):

$$S_x\ (\%) = \left(\frac{X_{cm}}{\sum_y y_{cm}}\right) \times 100 \qquad (2)$$

The carbon balance X_{cb} (3) was calculated by dividing the sum of the carbon moles of the reaction products X_{cp}, coke X_{coke} and unreacted glycerol g_{mol} by the amount of carbon moles injected into the reactor g_{mi}. Sum of reaction product carbon moles was calculated *via* combining the products identified in the liquid fractions, (GC1) with that of the gas fraction of the reaction stream (GC2). Liquid HMWPs were not included in this calculation as unanalysed.

$$X_{cb}(\%) = \left(\frac{X_{cp} + X_{coke} + g_{mo}}{g_{mi}}\right) \text{ x } 100 \qquad (3)$$

Carbon deposition in the form of catalyst coke (4) was estimated from the mass loss *via* TGA of the post reaction catalyst. The mass of carbon lost was converted to the number of moles of carbon retained on the catalyst (X_{coke})m_{lost}, by the moles of carbon fed into the reactor g_{mi}.

$$Coke\ (\%) = \left[\frac{m_{lost}}{g_{mi}}\right] \times 100 \qquad (4)$$

Space time yield of product *x* was calculated (5) from the mass of product m_x produced per hour (reaction time Rt), per mass of catalyst (m_{cat}, Kg).

$$STY_X\ \ (g_X\ h^{-1}\ kg_{cat}^{-1}) = \left(\frac{m_X\ (g)}{Rt(h)\ x\ m_{cat}(kg)}\right) \qquad (5)$$

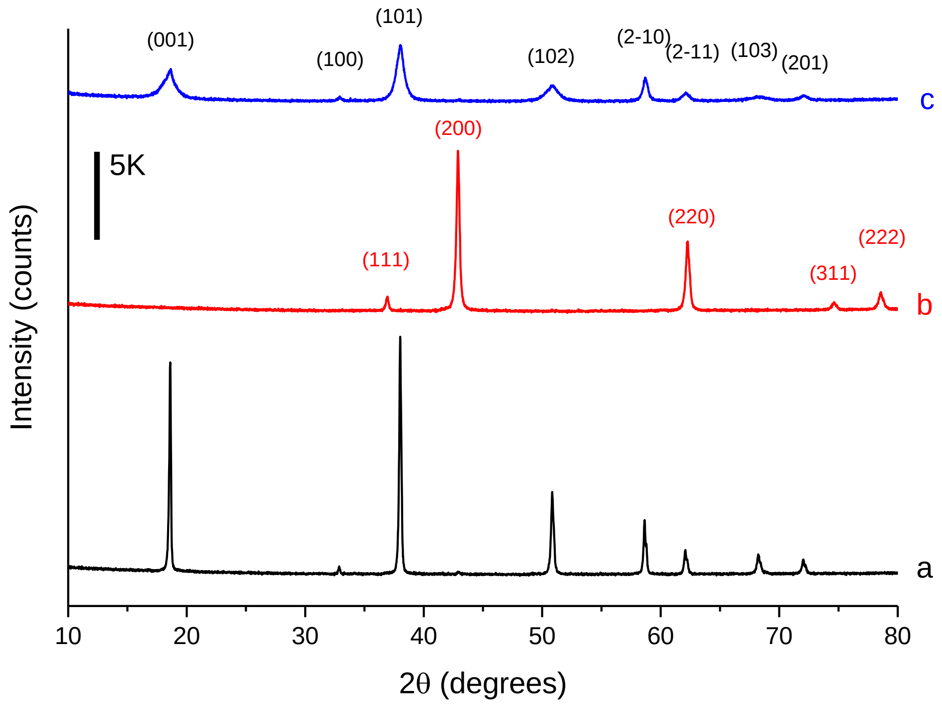

Figure S1: XRD patterns for (a) commercial $Mg(OH)_2$, (b) MgO after calcination at 450 ˚C for 2 h, (c) $Mg(OH)_2$ after refluxing in water and drying at 110 ˚C for 16 h.

Table S1. Crystallite sizes for $Mg(OH)_2$ before and after reflux and drying

Sample	Crystallite size / nm
Commercial $Mg(OH)_2$	51
MgO after 2 h calcination at 450 °C	32
$Mg(OH)_2$ after reflux and drying	11

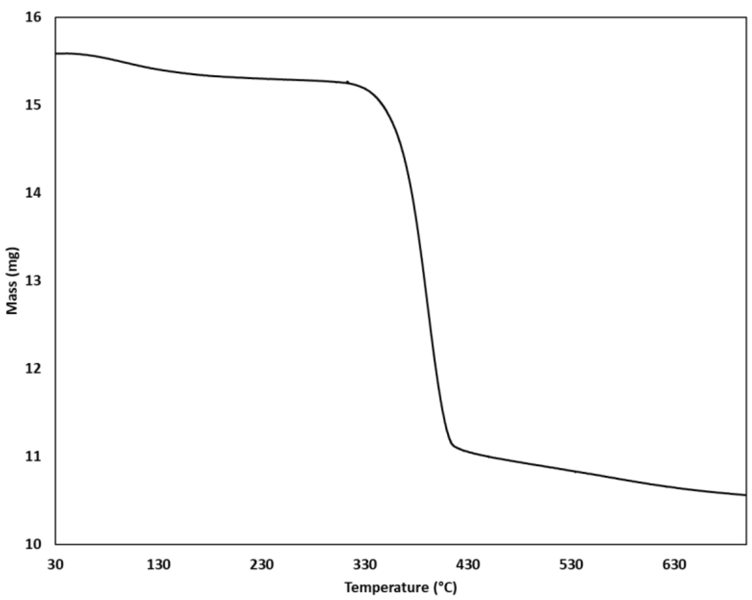

Figure S2. Thermogravimetric analysis (TGA) of $Mg(OH)_2$ showing mass loss as temperature is increased.

Table S2. Literature values for DRIFTS adsorption bands basic sites and CO_2 species.

	OH	O^{2-}	Mg^{2+} -O^{2}
Reference	Bicarbonate / hydrogen carbonates **(cm^{-1})**	Monodentate carbonates **(cm^{-1})**	Bidentate & tridentate carbonates **(cm^{-1})**
1	1220 asymmetric 1480 asymmetric 1650 asymmetric	1360–1400 symmetric 1510 – 1560 asymmetric	1610 – 1630 symmetric 1320–1340 symmetric
2		1370−1590 general area attributed 1440 v_{3high} DFT (110) 1378 v_{3low} DFT (110)	1270 – 1390 general area attributed 1620 – 1710 general area attributed 1680 v_{3high} Drifts 1650-1730 v_{3high} DFT 1125-1200 v_{3low} DFT 1651 v_{3high} Drifts (tridentate 100) 1304 v_{3low} Drifts (tridentate 100) 1600-1650 v_{3high} DFT (tridentate 100) 1280-1300 v_{3low} DFT (tridentate 100)

			1516 ν_{3high} Drifts (tridentate 100) 1347 ν_{3low} Drifts (tridentate 100) 1560 ν_{3high} DFT (tridentate 100) 1330 ν_{3low} DFT (tridentate 100)
3	1655–1658 ν_2 1405–1419 ν3 1220–1223 ν4	1510–1550 ν_{3high} 1390–1410 ν_{3low} 1035–1050 ν_1	
4	1480 ν_3 1250 ν_4	1590,1510 ν_{3high} 1415 ν_{3low}	1385,1335 ν_{3low}
5	1650 ν_2 1510,1408 ν3 1220 ν4		
6		1550 ν_{3high} 1410 ν_{3low} 1050 ν_1	
7		1520 ν_{3high} 1370 ν_{3low} 1060 ν_1	1670, 1630 ν_{3high} 1270 ν_1
8		1550 ν_{3high} 1410 ν_{3low} 1050 ν_1	1670,1630 ν_{3high} 1315,1280 ν_{3low} 1000,850 ν_1 950,830 ν_1

Table S3. Product list from GC analysis.

Product	**Retention time / minutes**		
	GC1 (liq FID)	GC1 (gas FID)	GC1 (Gas TCD)
Acetaldehyde	2.1	2.05	
Propionaldehyde	2.6		
Acetone	2.8	2.35	
Acrolein	3.0	2.64	
Butyraldehyde	3.3		
Methanol	3.5	2.95	
2-propanol	3.9		
Ethanol	4.0		
2,3-butanedione	4.6		
2-butanol	5.4		
1-propanol	5.7		
3-hexanone	6.0		
2-hexanone	6.3		
2-methyl-1-propanol	6.9		
allyl alcohol	7.0		
Cyclopentanone	8.6		
Hydroxyacetone	8.8		
3-ethoxy-1-propanol	8.9		
acetic acid	9.4		
Glycidol	9.9		
propionic acid	10.1		
1,2-propanediol	10.8		
ethylene glycol	11.0		
1,3-propanediol	12.3		
Phenol	15.2		
unreacted glycerol	17.2		
CO			4.5
CO_2			5.4

Table S4. Influence of heat treatment temperature – catalyst product selectivity results. Reaction conditions; 360 °C, 50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours

Carbon mole selectivity / %	MgO_450	MgO_550	MgO_650	MgO_750
Acetaldehyde	19.7	17.4	20.2	21.6
Propionaldehyde	0.6	0.1	0.6	0.6
Acetone	0.1	0.3	0.1	0.1
Acrolein	13.4	11.2	12.7	12.8
Butyraldehyde	0.0	0.0	0.0	0.0
Methanol	11.9	10.1	9.8	11.4
2-propanol	0.6	0.0	0.4	0.6
Ethanol	0.0	0.6	0.1	0.0
2,3-butanedione	1.2	1.4	1.1	1.3
2-butanol	0.1	0.1	0.0	0.1
1-propanol	0.1	0.1	0.1	0.0
3-hexanone	0.0	0.1	0.0	0.0
2-hexanone	0.0	0.0	0.0	0.0
2-methyl-1-propanol	0.0	0.0	0.0	0.0
allyl alcohol	0.8	0.7	0.6	0.8
Cyclopentanone	0.6	0.7	0.3	0.6
Hydroxyacetone	23.2	28.3	23.7	23.9
3-ethoxy-1-propanol	0.9	0.7	0.9	0.9
acetic acid	0.5	1.3	0.5	0.4
Glycidol	1.0	0.9	2.9	1.6
propionic acid	0.3	0.9	0.2	0.2
1,2-propanediol	2.1	2.7	2.6	2.2
unknown(s)	8.3	8.1	8.4	7.6
ethylene glycol	8.2	9.3	9.2	8.1
1,3-propanediol	0.8	0.5	0.8	0.6
Phenol	0.1	0.2	0.3	0.0
CO	2.8	2.2	2.7	2.8
CO2	2.7	1.8	1.9	2.0
Glycerol conversion %	87	84	75	80
Carbon balance %	74	78	98	79
MeOH S.T.Y g h^{-1} kg h^{-1}	80	77	90	83
coke % carbon	3	2.9	3.2	2
carbon deposition mg g^{-1}	89	79	106	44

Table S5. Total organic carbon CHN analysis – MgO_650. Reaction conditions; 360 °C ,50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours.

Carbon component	%
Catalyst coking (TGA)	3.2
Gas analysis (GC)	8.7
Liquid analysis (GC)	85.7
Liquid analysis (CHN)	85.1
Total Carbon	98

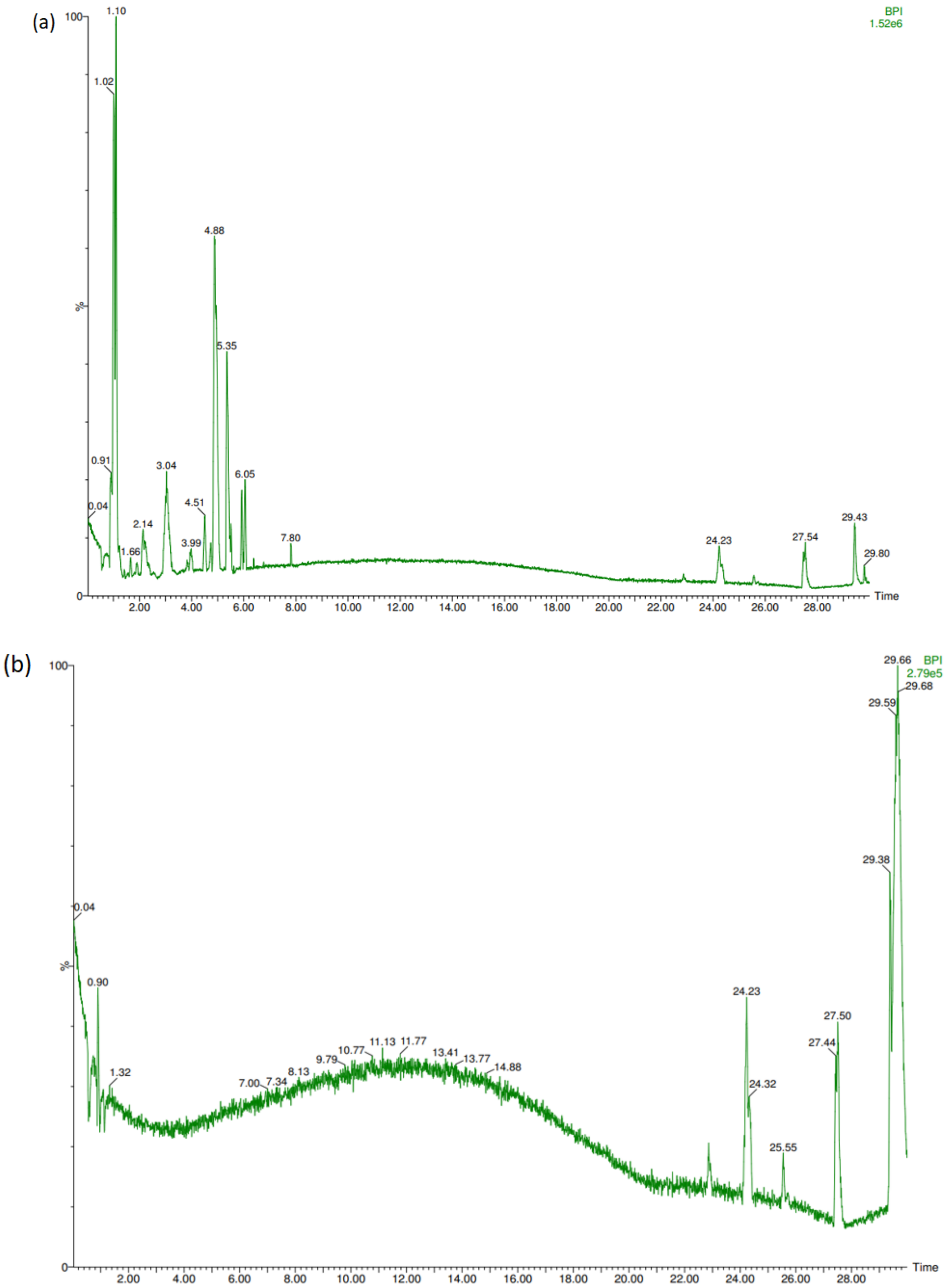

Figure S3. LCMS chromatogram for the reaction mixture of MgO_450 (a) and MgO_650 (b) at 360 °C 50 wt.% glycerol.

Table S6. Influence of heat treatment temperature C – catalyst product Space time yield g h^{-1} kg^{-1} cat results. Reaction conditions; 360 °C, 50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours

S.T.Y / g h^{-1} kg^{-1} cat	MgO_450	MgO_550	MgO_650	MgO_750
Acetaldehyde	92	83	118	98
Propionaldehyde	2	1	3	2
Acetone	0	1	1	0
Acrolein	53	45	64	49
Butyraldehyde	0	0	0	0
Methanol	80	77	90	83
2-propanol	3	0	3	3
ethanol	0	3	1	0
2,3-butanedione	6	6	8	6
2-butanol	0	0	0	0
1-propanol	1	1	1	0
3-hexanone	0	0	0	0
2-hexanone	0	0	0	0
2-methyl-1-propanol	0	0	0	0
allyl alcohol	3	3	4	3
cyclopentanone	2	2	1	2
hydroxyacetone	122	152	173	122
3-ethoxy-1-propanol	4	3	6	4
acetic acid	3	8	4	3
Glycidol	8	7	32	12
propionic acid	1	4	0	1
1,2-propanediol	12	15	19	11
unknown(s)	0	0	0	0
ethylene glycol	54	63	71	52
1,3-propanediol	4	3	6	3
phenol	0	1	2	0
CO	17	14	19	16
CO2	25	18	24	18
Glycerol conversion %	87	84	75	80
Carbon balance %	74	78	98	79
MeOH S.T.Y g h^{-1} kg h^{-1}	80	77	90	83
coke % carbon	3	2.9	3.2	2
carbon deposition mg g^{-1}	89	79	106	44

Table S7. Product selectivity - MgO_450 D_2O and H_2O experiments compared. Reaction conditions; 360 °C, 50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours

Carbon mole selectivity / %	D_2O	H_2O
Acetaldehyde	13.8	18.6
propionaldehyde	0.5	0.3
acetone	0.2	0.2
acrolein	10.8	12.5
butyraldehyde	0.0	0.0
methanol	9.9	11.5
2-propanol	0.0	0.4
ethanol	0.5	0.3
2,3-butanedione	0.8	1.2
2-butanol	0.0	0.1
1-propanol	0.1	0.1
3-hexanone	0.1	0.1
2-hexanone	0.0	0.0
2-methyl-1-propanol	0.0	0.0
allyl alcohol	0.7	0.8
cyclopentanone	0.5	0.6
hydroxyacetone	28.6	23.4
3-ethoxy-1-propanol	1.5	0.9
acetic acid	1.0	0.8
Glycidol	0.5	0.8
propionic acid	1.6	0.6
1,2-propanediol	3.0	2.3
unknown(s)	9.6	7.9
ethylene glycol	12.2	9.5
1,3-propanediol	0.8	0.9
phenol	0.2	0.1
CO	1.7	2.7
CO2	1.6	3.4
Glycerol conversion	54	87
Carbon balance	98	74
MeOH S.T.Y. g h-1 kg h-1	65	80
coke % Carbon	3.5	3.2
carbon deposition mg g	95	89

Table S8. Product selectivity - MgO_550 D_2O and H_2O experiments compared. Reaction conditions; 360 °C, 50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours

Carbon mole selectivity / %	D_2O	H_2O
Acetaldehyde	13.0	17.4
Propionaldehyde	0.5	0.1
Acetone	0.1	0.3
Acrolein	10.0	11.2
Butyraldehyde	0.0	0.0
Methanol	10.0	10.1
2-propanol	0.0	0.0
Ethanol	0.5	0.6
2,3-butanedione	0.7	1.4
2-butanol	0.0	0.1
1-propanol	0.1	0.1
3-hexanone	0.1	0.1
2-hexanone	0.0	0.0
2-methyl-1-propanol	0.0	0.0
allyl alcohol	0.8	0.7
cyclopentanone	0.5	0.7
hydroxyacetone	28.6	28.3
3-ethoxy-1-propanol	0.7	0.7
acetic acid	0.9	1.3
Glycidol	0.5	0.9
propionic acid	1.2	0.9
1,2-propanediol	3.6	2.7
unknown(s)	14.3	8.1
ethylene glycol	11.0	9.3
1,3-propanediol	0.9	0.5
Phenol	0.1	0.2
CO	1.4	2.2
CO2	0.5	1.8
Glycerol conversion %	53	80
Carbon balance %	103	78
MeOH S.T.Y g h^{-1} kg h^{-1}	66	77

Table S9. Product selectivity - MgO_650 D_2O and H_2O experiments compared. Reaction conditions; 360 °C, 50 wt.% glycerol/water flow 0.016 mL min^{-1}, 0.5 g MgO, 50 mL min^{-1} Ar, 3 hours

Carbon mole selectivity / %	D_2O	H_2O
Acetaldehyde	17.0	20.2
propionaldehyde	0.6	0.6
acetone	0.5	0.1
acrolein	10.9	12.7
butyraldehyde	0.0	0.0
methanol	10.6	9.8
2-propanol	0.0	0.4
ethanol	0.6	0.1
2,3-butanedione	1.1	1.1
2-butanol	0.0	0.0
1-propanol	0.1	0.1
3-hexanone	0.0	0.0
2-hexanone	0.0	0.0
2-methyl-1-propanol	0.0	0.0
allyl alcohol	0.8	0.6
cyclopentanone	0.6	0.3
hydroxyacetone	26.7	23.7
3-ethoxy-1-propanol	1.0	0.9
acetic acid	1.1	0.5
Glycidol	0.6	2.9
propionic acid	1.2	0.2
1,2-propanediol	2.4	2.6
unknown(s)	9.4	8.4
ethylene glycol	10.2	9.2
1,3-propanediol	0.7	0.8
phenol	0.2	0.3
CO	2.1	2.7
CO2	1.5	1.9
Glycerol conversion %	71	75
Carbon balance %	92	98
MeOH S.T.Y. g h^{-1} kg h^{-1}	80.5	90.0
coke % Carbon	2.0	3.8
carbon deposition mg g^{-1}	56	105

Table S10. Hydroxyacetone reactions over MgO_450 and MgO_650 Product selectivity - Reaction conditions: 320 - 360 °C, 50 wt.% hydroxyacetone/water flow 0.016 mL min^{-1}, 0.5 g catalyst, 50 mL min^{-1} Ar, 3 hours.

Carbon mole selectivity / %	Blank	MgO 450	MgO 450	MgO 650	MgO 650
Reaction Temperature / °C	320	320	360	320	360
acetaldehyde	0.0	12.2	20.3	21.3	26.5
propionaldehyde	0.0	0.0	0.3	0.0	0.0
acetone	0.0	1.2	1.4	1.8	0.4
acrolein	0.0	0.0	0.0	0.0	1.6
butyraldehyde	0.0	0.0	0.0	0.0	0.0
methanol	0.0	1.3	1.3	1.4	1.2
2-propanol	0.0	0.0	0.0	0.0	0.0
ethanol	0.0	0.2	0.2	0.0	0.0
2,3-butanedione	0.0	2.7	2.3	2.4	1.4
2-butanol	0.0	0.0	0.0	0.0	0.0
1-propanol	0.0	0.3	0.2	0.0	0.0
3-hexanone	0.0	1.2	1.8	1.6	1.9
2-hexanone	0.0	0.0	0.0	0.0	0.0
2-methyl-1-propanol	0.0	0.0	0.0	0.0	0.0
allyl alcohol	0.0	0.4	0.0	0.0	0.0
cyclopentanone	5.9	3.9	3.3	3.1	2.6
3-ethoxy-1-propanol	0.0	2.0	1.4	0.9	0.7
acetic acid	10.5	6.2	8.0	9.5	9.2
Glycidol	5.6	4.4	5.2	2.4	8.0
propionic acid	0.0	4.4	4.0	4.2	4.7
1,2-propanediol	0.0	4.5	8.8	11.8	14.5
unknown(s)	78.0	44.9	34.7	24.8	14.4
ethylene glycol	0.0	0.7	0.5	0.0	0.6
1,3-propanediol	0.0	2.4	2.4	3.4	2.9
phenol	0.0	0.0	0.0	0.0	0.0
CO	0.0	1.0	0.5	2.4	3.3
CO2	0.0	6.3	3.3	7.2	8.3
Hydroxyacetone conversion %	1	16	16	0	1
Carbon balance %	101	89	94	105	104

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