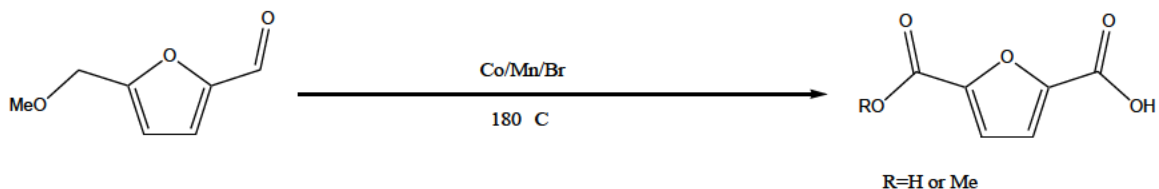


## Experiment: OxE-081



Target: Oxidation of HMF, AMF and mixtures HMF/AMF. For it, some parameters are fixed as P= 20 bar; T=180 °C; Cat conc (Co+Mn)=5.4 mol %; Co/Mn= 1. The variable Br/(Co+Mn) was varied from 0.1 to 1. Besides, the use of 5-methylfuran as substrate for the production of FDCA was also tested.

Main objective: **Oxidation of AMF, HMF and mixtures HMF/AMF**

Table 1: Chemicals

Name	Saccharine	MMF	MeOH	DMSO
Supplier		New batch		
Cas nr				
Lot nr				
Mw (g/mol)				
info				
Name	AcOH	AcOH	AcOH	
Supplier				
Cas nr				
Lot nr				
Mw (g/mol)				
info				

Table 2: Apparatus

Apparatus	HPLC06
Brand / type	Agilent
Guard Column	none
Column	Sunfire C18, 4.6*10 cm, 3.5 um, part no. 186002553
Flow (ml/min)	1.0
Oven temp ( °C)	40.0
Mobile phase	Gradient: 0.2% TFA with MeOH : ACN (50:50)
Method name analyzing	080313-Oxe-gradient-35min.met
Apparatus	HHP QCS
Stirring speed (rpm)	750
QCS Heating T ( °C)	194 (results in 180 °C inside the reactor)
Huber T ( °C)	135

Table 3: Catalysts

Cat	Supplier	Lot number	Cas nr	Avantium nr	MW	Purity
Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O		B225016	6147-53-1	N7019	249.08	98-102
Mn(OAc) <sub>2</sub> ·4H <sub>2</sub> O	Alpha	0884600	6156-78-1	105A	245.09	Mn=22%
NaBr	Aldrich	90517008	7647-15-6	143	102.89	99+
Co(OAc) <sub>3</sub>	Aldrich					

Experimental REMARK:

Date weighing, diluting Cat's :  
 Date weighing, diluting Cat's :  
 Date weighing, dissolving substrate :  
 Date starting reaction of experiment :  
 Date weighing, dissolving and adding Saccharine stock solution :  
 Date of analyzing with the HPLC :  
 HPLC-analyzing according HPLC-6 logboek :

**Experimental**  
 if done make X

- \_\_\_\_\_ Load blocks according table 12 till 16. Weighing tolerance **± 0.3 mg**
- \_\_\_\_\_ Add stirring magnet and cap with Avantium disk 11352955. **These caps leaked so old ones "Big" used.**
- \_\_\_\_\_ Close the blocks according OP-CH-100: Manual HPHQCS.
- \_\_\_\_\_ Bring under pressure with Air till **20 Bar** at RT according OP-CH-99: Pressuriser Work procedure
- \_\_\_\_\_ Plac in preheated HTHP QCS # LR-041 of **160 or 180 °C**, according settings in table 2, during **1 or 0.5 hours**.
- \_\_\_\_\_ Fill in logboeknr.: HTHPQCS-E13
- \_\_\_\_\_ Place immediately after the reaction time in an ice bath during 30 minutes.
- \_\_\_\_\_ Open and thereby decompress reactors in a fumehood.
- \_\_\_\_\_ **Add 5.0 ml of Saccharine stock solution, table 5 and stir for 1 hour until all the products were dissolved.**
- \_\_\_\_\_ Transfere these dilutions to 7 times to 8 ml vials with Pasteur's pipettes.
- \_\_\_\_\_ Dilute 700 times by 10 µl of dilutions 78 times + 990 µl of **Water** in HPLC vials.

Table 4: Substrate MMF solutions, in table 11 to 26

Sol A HMF (100 mg/ml)	Amount	Sol B HMF/AMF (113.34 mg/ml)	Amount
HMF [g]	0.500	AMF [g] [53.34 mg/ml]	0.263
V AcOH [ml]	5	HMF [g] [60 mg/ml]	0.302
Total V [ml]		V AcOH [ml]	5
Concentration (mg/ml)	99.96	Total V [ml]	
Date		Concentration (mg/ml)	113.04
Samples prepared with this solution.		Date	
		Samples prepared with this solution.	
Sol C HMF/AMF (120 mg/ml)	Amount	Sol D AMF (133.33 mg/ml)	Amount
AMF [g] [80 mg/ml]	0.396	AMF [g]	0.669
HMF [g] [40 mg/ml]	0.194	V AcOH [ml]	
V AcOH [ml]	5	Total V [ml]	5
Total V [ml]	5	Concentration (mg/ml)	
Concentration (mg/ml)	118.04	Date	133.88
Date		Samples prepared with this solution.	
Samples prepared with this solution.			

Sol E 5MF (87.30 mg/ml)	Amount	Sol E 5MF (87.30 mg/ml)	Amount for E-1	Amount for E-2
5-MF [g]	0.430	5-MF [g]	0.4379	0.4351
V AcOH [ml]		V AcOH [ml]		
Total V [ml]	5	Total V [ml]	5	5
Concentration (mg/ml)	85.96	Concentration (mg/ml)	87.58	87.02
Date		Date		09sep09
Samples prepared with this solution.		Samples prepared with this solution.	090909-OxE081-V37 till V44	090909-OxE081-V49 till V56

Sol F DMF (76.22 mg/ml)	Amount for F-1	Amount for F-2
DMF [g]	0.3814	0.3807
V AcOH [ml]		
Total V [ml]	5.0	5.0
Concentration (mg/ml)	76.28	76.14
Date		10sep09
Samples prepared with this solution.	090910-OxE081-V45 till V48	090909-OxE081-V57 till V60

Table 5: Saccharine stock solution (11.04 mg/ml)

	amount	amount
m Saccharine [g]	2.7725	
V DMSO [ml]		
Total V [ml]	250	
Concentration (mg/ml)	11.09	
Date		
Samples prepared with this solution.		

Table 10: List of catalysts.

Name	Solvent	Solvent [m]	Co(OAc) <sub>2</sub> 4H <sub>2</sub> O		Mn(OAc) <sub>2</sub> 4H <sub>2</sub> O		NaBr		Co/Mn	Br/(Co+Mn)
			[mg]		[mg]		[mg]			
			Need	Done	Need	Done	Need	Done		
Cat-081-01	AcOH	25	66.66	66.4	65.59	64.4	55.07	54	1/1	1.0
Cat-081-02	AcOH	25	66.66	65.3	65.59	64.6	38.55	38.4	1/1	0.7
Cat-081-03	AcOH	25	66.66	65.2	65.59	69.2	22.03	21.5	1/1	0.4
Cat-081-04	AcOH	25	66.66	65.8	65.59	66.5	5.51	4.9	1/1	0.1

Table 11: Block 1 **Blocknr:** /Temp = 180 °C / P= 20 bar (Air) / T<sub>0</sub>=

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V <sub>Cat</sub>	Cat concentration	O <sub>2</sub> /MMF	HPLC name
		[ml]		[ml]	[mol %]	[mol ratio]	
1	HMF	0.5 ml A	Cat-081-01	1.0	4	2.69	OxE081-V1
2	HMF	0.5 ml A	Cat-081-01	1.0	4	2.69	OxE081-V2
3	HMF/AMF (3/2)	0.5 ml B	Cat-081-01	1.0	4	2.69	OxE081-V3
4	HMF/AMF (3/2)	0.5 ml B	Cat-081-01	1.0	4	2.69	OxE081-V4
5	HMF/AMF (2/3)	0.5 ml C	Cat-081-01	1.0	4	2.69	OxE081-V5
6	HMF/AMF (2/3)	0.5 ml C	Cat-081-01	1.0	4	2.69	OxE081-V6
7	AMF	0.5 ml D	Cat-081-01	1.0	4	2.69	OxE081-V7
8	AMF	0.5 ml D	Cat-081-01	1.0	4	2.69	OxE081-V8
9	HMF	0.5 ml A	Cat-081-02	1.0	4	2.69	OxE081-V9
10	HMF	0.5 ml A	Cat-081-02	1.0	4	2.69	OxE081-V10
11	HMF/AMF (3/2)	0.5 ml B	Cat-081-02	1.0	4	2.69	OxE081-V11
12	HMF/AMF (3/2)	0.5 ml B	Cat-081-02	1.0	4	2.69	OxE081-V12

Table 12: Block 1 **Blocknr:** /Temp = 180 °C / P= 20 bar (Air) / T<sub>0</sub>=

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V <sub>Cat</sub>	Cat concentration	O <sub>2</sub> /MMF	HPLC name
		[ml]		[ml]	[mol %]	[mol ratio]	
1	HMF/AMF (2/3)	0.5 ml C	Cat-081-02	1.0	4	2.69	OxE081-V13
2	HMF/AMF (2/3)	0.5 ml C	Cat-081-02	1.0	4	2.69	OxE081-V14
3	AMF	0.5 ml D	Cat-081-02	1.0	4	2.69	OxE081-V15
4	AMF	0.5 ml D	Cat-081-02	1.0	4	2.69	OxE081-V16
5	HMF	0.5 ml A	Cat-081-03	1.0	4	2.69	OxE081-V17
6	HMF	0.5 ml A	Cat-081-03	1.0	4	2.69	OxE081-V18
7	HMF/AMF (3/2)	0.5 ml B	Cat-081-03	1.0	4	2.69	OxE081-V19
8	HMF/AMF (3/2)	0.5 ml B	Cat-081-03	1.0	4	2.69	OxE081-V20
9	HMF/AMF (2/3)	0.5 ml C	Cat-081-03	1.0	4	2.69	OxE081-V21
10	HMF/AMF (2/3)	0.5 ml C	Cat-081-03	1.0	4	2.69	OxE081-V22
11	AMF	0.5 ml D	Cat-081-03	1.0	4	2.69	OxE081-V23
12	AMF	0.5 ml D	Cat-081-03	1.0	4	2.69	OxE081-V24

Table 13: Block 3 **Blocknr:** /Temp = 180 °C / P= 20 bar (Air) / T<sub>0</sub>=

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V <sub>Cat</sub>	Cat concentration	O <sub>2</sub> /MMF	HPLC name
		[ml]		[ml]	[mol %]	[mol ratio]	
1	HMF	0.5 ml A	Cat-081-04	1.0	4	2.69	OxE081-V25
2	HMF	0.5 ml A	Cat-081-04	1.0	4	2.69	OxE081-V26
3	HMF/AMF (3/2)	0.5 ml B	Cat-081-04	1.0	4	2.69	OxE081-V27
4	HMF/AMF (3/2)	0.5 ml B	Cat-081-04	1.0	4	2.69	OxE081-V28
5	HMF/AMF (2/3)	0.5 ml C	Cat-081-04	1.0	4	2.69	OxE081-V29
6	HMF/AMF (2/3)	0.5 ml C	Cat-081-04	1.0	4	2.69	OxE081-V30
7	AMF	0.5 ml D	Cat-081-04	1.0	4	2.69	OxE081-V31
8	AMF	0.5 ml D	Cat-081-04	1.0	4	2.69	OxE081-V32
9	MF	0.5 ml E	Cat-081-01	1.0	4	2.69	OxE081-V33
10	MF	0.5 ml E	Cat-081-01	1.0	4	2.69	OxE081-V34
11	MF	0.5 ml E	Cat-081-03	1.0	4	2.69	OxE081-V35
12	MF	0.5 ml E	Cat-081-03	1.0	4	2.69	OxE081-V36

Table 14: Block 4 **Blocknr:** /Temp = 180 °C / P= 20 bar (Air) / T<sub>0</sub>=

d.d.:9sep09

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V <sub>Cat</sub>	Cat concentration	O <sub>2</sub> /MMF	HPLC name
		[ml]		[ml]	[mol %]	[mol ratio]	
1	DMF	0.5 ml F-1	Cat-081-01	1.0	4	2.69	OxE081-V37
2	DMF	0.5 ml F-1	Cat-081-01	1.0	4	2.69	OxE081-V38

3	DMF	0.5 ml F-1	Cat-081-02	1.0	4	2.69	OxE081-V39
4	DMF	0.5 ml F-1	Cat-081-02	1.0	4	2.69	OxE081-V40
5	DMF	0.5 ml F-1	Cat-081-03	1.0	4	2.69	OxE081-V41
6	DMF	0.5 ml F-1	Cat-081-03	1.0	4	2.69	OxE081-V42
7	DMF	0.5 ml F-1	Cat-081-04	1.0	4	2.69	OxE081-V43
8	DMF	0.5 ml F-1	Cat-081-04	1.0	4	2.69	OxE081-V44
9	5-MF	0.5 ml E-1	Cat-081-01	1.0	4	2.69	OxE081-V45
10	5-MF	0.5 ml E-1	Cat-081-01	1.0	4	2.69	OxE081-V46
11	5-MF	0.5 ml E-1	Cat-081-02	1.0	4	2.69	OxE081-V47
12	5-MF	0.5 ml E-1	Cat-081-02	1.0	4	2.69	OxE081-V48

Table 14: Block 5 **Blocknr:** /Temp = **180 °C** / P= 50 bar (Air) / T<sub>0</sub>= d.d.: 10sep09 **Time 1 hours**

R Nr.	Substrate name	Substrate [ml]	Cat Code	V <sub>Cat</sub> [ml]	Cat concentration [mol %]	O <sub>2</sub> /MMF [mol ratio]	HPLC name
1	DMF	0.5 ml F-2	Cat-081-01	1.0	4	2.69	OxE081-V49
2	DMF	0.5 ml F-2	Cat-081-01	1.0	4	2.69	OxE081-V50
3	DMF	0.5 ml F-2	Cat-081-02	1.0	4	2.69	OxE081-V51
4	DMF	0.5 ml F-2	Cat-081-02	1.0	4	2.69	OxE081-V52
5	DMF	0.5 ml F-2	Cat-081-03	1.0	4	2.69	OxE081-V53
6	DMF	0.5 ml F-2	Cat-081-03	1.0	4	2.69	OxE081-V54
7	DMF	0.5 ml F-2	Cat-081-04	1.0	4	2.69	OxE081-V55
8	DMF	0.5 ml F-2	Cat-081-04	1.0	4	2.69	OxE081-V56
9	5-MF	0.5 ml E-2	Cat-081-01	1.0	4	2.69	OxE081-V57
10	5-MF	0.5 ml E-2	Cat-081-01	1.0	4	2.69	OxE081-V58
11	5-MF	0.5 ml E-2	Cat-081-02	1.0	4	2.69	OxE081-V59
12	5-MF	0.5 ml E-2	Cat-081-02	1.0	4	2.69	OxE081-V60

Catalysts:

