



The objective of this experiment is to study the stability of the final compounds (FDCAR) in the oxidation of MMF.

Main objective: **Stability of products**

Table 1: Chemicals

Name	HMF	MMF	Saccharine Block 2 + 3	MeOH
Supplier			Acros Organic	Fisher Scientific
Cas nr			81-07-2	67-56-1
Lot nr			A0259796	0896339
Mw (g/mol)			183.19	
info			98+%	HPLC-grade
Name	AcOH Block 2 + 3	AcOH Block 1	Saccharine Block 1	DMSO
Supplier	Mix from 4 bottles	Fluka	Aldrich	Sigma Aldrich
Cas nr	64-19-7	64-19-7	81-07-2	67-68-5
Lot nr	80160	80160	S37371-017	8202S
Mw (g/mol)	60,05	60,05	183.19	78.13
info			98+%	For HPLC

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)old Block 1	247 (results in 220 C inside the reactor)
Huber T C)	175
Huber T C)	115
QCS Heating T (C)Block 2, 60 Bar	179 (results in 160 C inside the reactor)
QCS Heating T (C)Block 3, 20 Bar	174 (results in 160 C inside the reactor)

Table 3: Catalysts

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

Experimental REMARK:

	Block 1	Block 2 and 3
Date weighing, dissolving and adding Cat and substrate	: 12MAY09	15JUN09
Date starting reaction of experiment	: 12MAY09	15JUN09
Date weighing, dissolving and adding Saccharine stock solution	: 12MAY09	15JUN09
Date of analyzing with the HPLC	: 13MAY09 by Paul	15JUN09
HPLC-analyzing according HPLC-6 logboek	:	

Experimental

Done by ABE:

Load blocks according table1 till 16. Weighing tolerance **± 0.3 mg**.

Add stirring magnet.

Close with teflon/rubber cap.

Bring under pressure with Air till **60 Bar** at RT

Placed in preheated HTHP QCS of **180 °C**, according settings in table 2, during **1 hours**.

Placed immediately after the reaction time in an ice bath during 35 minutes.

Open and thereby decompress reactors.

Add 1.0 ml of DMSO. Stirring for 20 minutes

Add 5.0 ml of Saccharine stock solution, table 5.

These dilutions where stirred for 10 minutes.

These dilutions to 7 times were transferred to 8 ml vials. Stirring during a whole night.

Done by CMD:

Dilutions to 700 times were made by 10 µl of dilutions 8 times + 990 µl of **Water** in HPLC vials.

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

Block 1	amount
m Saccharine [g]	2.2080
V MeOH [ml]	
Total V [ml]	200.0
Concentration (mg/ml)	11.04
Date	15may09
Samples prepared with this solution.	090512-OxE-073-V01 till V09

Block 2 and 3	amount
m Saccharine [g]	1.1043+0.2206
V DMSO [ml]	
Total V [ml]	100+20
Concentration (mg/ml)	11.041
Date	15jun09
Samples prepared with this solution.	090615-OxE-073-V09 till V28 + BI-FDCA-10 and -5mg BI-FDCAhalfEt-10 and -5mg

Table 6: Blancs solutions

Blanks	Amount (mg)	HPLC name
FDCA1/2Me 10	10.0	090615-OxE-073-BI-FDCAhalfEt-10
FDCA1/2Me 5	5.0	090615-OxE-073-BI-FDCAhalfEt-5
FDCA 10	9.9	090615-OxE-073-BI-FDCA-10
FDCA 5	5.2	090615-OxE-073-BI-FDCA-5

Table 10: List of catalyts.

Name	Solvent	Solvent [ml]	Co(OAc) ₂ 4H ₂ O		Mn(OAc) ₂ 4H ₂ O		NaBr		Co/Mn/Br	Color
			[mg]		[mg]		[mg]			
			Need	Done	Need	Done	Need	Done		
Co/Mn/Br-01	AcOH	50	39		191.9		80.6		1 / 5 / 5	

Co/Mn/Br-02	AcOH	50	39		191.9		161.1		1 / 5 / 10	
Co/Mn/Br-04	AcOH	50	39		191.9		322.2		1 / 5 / 20	
Co/Mn/Br-05	AcOH	50	39		191.9		483.3		1 / 5 / 30	
Co/Mn/Br-07	AcOH	50	39		115.2		161.1		1 / 3 / 10	
Co/Mn/Br-09	AcOH	50	39		115.2		322.2		1 / 3 / 20	
Co/Mn/Br-13	AcOH	25	39		191.9		80.6		1 / 5 / 5	
Co/Mn/Br-14	AcOH	25	39		191.9		161.1		1 / 5 / 10	
Co/Mn/Br-15	AcOH	25	39		191.9		322.2		1 / 5 / 20	
Co/Mn/Br-16	AcOH	25	39		191.9		483.3		1 / 5 / 30	
Co/Mn/Br-17	AcOH	25	39		115.2		161.1		1 / 3 / 10	
Co/Mn/Br-18	AcOH	25	39		115.2		322.2		1 / 3 / 20	

Table 11: Block 1 /Temp = 220 C / P= 60 bar (Air) / T₀=14.27

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V _{AcOH}	V _{Cat}	Cat concentration	Solvent	HPLC name
				[ml]	[ml]	[mol %]		
1	FDCA	49.9	---	1.0	---	---	AcOH	OxE073-V1
2	FDCA	49.9	---	1.0	---	---	AcOH	OxE073-V2
3	FDCA1/2Me	---	---	---	---	---	---	---
4	FDCA1/2Me	49.8	---	1.0	---	---	AcOH	OxE073-V4
5	FDCA	50.7	Co/Mn/Br-15	---	1.0	---	AcOH	OxE073-V5
6	FDCA	50.7	Co/Mn/Br-15	---	1.0	---	AcOH	OxE073-V6
7	FDCA1/2Me	46.9	Co/Mn/Br-15	---	1.0	---	AcOH	OxE073-V7
8	FDCA1/2Me	50.3	Co/Mn/Br-15	---	1.0	---	AcOH	OxE073-V8

Table 11: Block 2 /Temp = 180 C / P= 60 bar (Air) / T₀=12.00

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V _{AcOH}	V _{Cat}	Water added	Solvent	HPLC name
				[ml]	[ml]	[μL]		
1	FDCA1/2Me	64.7	None	1.5	0	---	AcOH	OxE073-V9
2	FDCA1/2Me	64.5	None	1.5	0	---	AcOH	OxE073-V10
3	FDCA1/2Me	64.8	Co/Mn/Br 01	0.5	1.0	---	AcOH	OxE073-V11
4	FDCA1/2Me	64.6	Co/Mn/Br 01	0.5	1.0	---	AcOH	OxE073-V12
5	FDCA1/2Me	64.5	Co/Mn/Br 09	0.5	1.0	---	AcOH	OxE073-V13
6	FDCA1/2Me	65.9	Co/Mn/Br 09	0.5	1.0	---	AcOH	OxE073-V14
7	FDCA1/2Me	64.3	Co/Mn/Br 01	0.5	1.0	20	AcOH	OxE073-V15
8	FDCA1/2Me	64.5	Co/Mn/Br 01	0.5	1.0	20	AcOH	OxE073-V16
9	FDCA1/2Me	63.6	Co/Mn/Br 09	0.5	1.0	20	AcOH	OxE073-V17
10	FDCA1/2Me	64.1	Co/Mn/Br 09	0.5	1.0	20	AcOH	OxE073-V18

Table 11: Block 2 /Temp = 180 C / P= 20 bar (Air) / T₀=12.00

Time 1 hours

R Nr.	Substrate name	Substrate	Cat Code	V _{AcOH}	V _{Cat}	Water added	Solvent	HPLC name
				[ml]	[ml]	[μL]		
1	FDCA1/2Me	64.8	None	0.5	1.0	---	AcOH	OxE073-V19
2	FDCA1/2Me	63.9	None	0.5	1.0	---	AcOH	OxE073-V20
3	FDCA1/2Me	64.2	Co/Mn/Br 01	0.5	1.0	---	AcOH	OxE073-V21
4	FDCA1/2Me	63.9	Co/Mn/Br 01	0.5	1.0	---	AcOH	OxE073-V22
5	FDCA1/2Me	64.1	Co/Mn/Br 09	0.5	1.0	---	AcOH	OxE073-V23
6	FDCA1/2Me	64.0	Co/Mn/Br 09	0.5	1.0	---	AcOH	OxE073-V24
7	FDCA1/2Me	64.4	Co/Mn/Br 01	0.5	1.0	20	AcOH	OxE073-V25
8	FDCA1/2Me	63.8	Co/Mn/Br 01	0.5	1.0	20	AcOH	OxE073-V26
	FDCA1/2Me	65.0	Co/Mn/Br 09	0.5	1.0	20	AcOH	OxE073-V27
	FDCA1/2Me	64.1	Co/Mn/Br 09	0.5	1.0	20	AcOH	OxE073-V28