Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information On: Poly(Oxymethylene) Dimethyl Ethers - A combined chemical equilibrium investigation towards increasingly efficient and a potentially sustainable synthetic route

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Sources for Thermodynamic Standard Properties in Literature

Table S1 Sources for standard Gibbs energy of formation Δg°_{if}

Literature sources	Estimation methods
• DIPPR 801 project, Design institute for physical properties • NIST, the National Institute for Standards and Technology • NBS Technical Note 270 • JANAF (Joint Army-Navy-Air Force) tables	• Method of Joback (1984; 1987) • Method of Constantinou and Gani (1994) • Method of Benson (1968; 1969) • CHETAH-software from ASTM (1998)

Thermodynamic Chemical and Phase Equilibrium Model parameters

Table S2 Parameters A, B for chemical equilibrium constants (Kj) fitted to experimental data [1,2]

$\ln K(T) = A + \frac{B}{T}$	**A**	**B**
$FA + H_2O \leftrightharpoons MG_1$	-2.3250	2579.0
$FA + MG_{n-1} \leftrightharpoons MG_n; \quad n \geq 2$	-2.4334	3039.4
$FA + MeOH \leftrightharpoons HF_1$	-1.9020	3512.0
$FA + HF_{n-1} \leftrightharpoons HF_n; \quad n \geq 2$	-2.2496	3008.8
$HF_1 + MeOH \overset{H^+}{\leftrightarrow} OME_1 + H_2O$	0.8147	340.25
$FA + OME_{n-1} \overset{H^+}{\leftrightarrow} OME_n; \; n \geq 2$	-2.4154	3029.6
$3FA \overset{H^+}{\leftrightarrow} TRI$	-4.3253	7347.3

Table S3 UNIFAC group assignment for all components

Substance \ Group	**CH_2O (FA)**	**H_2O**	**$C_3H_8O_2$ (OME1)**	**$OH(CH_2O)H$ (MG1)**	**OH**	**CH_2**	**CH_3O**	**CH_2OH**	**CH_3OH**	**CH_2O (OME)**
Formaldehyde	1									
Water		1								
Methanol									1	
Methylal (OME1)			1							
MG1				1						
HF1							1	1		
MGn>2	n-1				2	1				
HFn>2	n-1						1	1		
OMEn>2			1							n-1
Trioxane	3									

Table S4 UNIFAC Interaction parameters aij (K) [3,4]

Group i \ Group j	**CH_2O (FA)**	**H_2O**	**OME1**	**MG1**	**OH**	**CH_2**	**CH_3O**	**CH_2OH**	**CH_3OH**	**CH_2O (OME)**
CH_2O FA	-	867.8	0.0	189.2	237.7	83.36	0.0	238.4	238.4	0.0
H_2O	-254.5	-	$a_{2,3}$(T)	189.5	-229.1	300.0	-219.3	$a_{2,8}$(T)	289.6	$a_{2,10}$(T)
OME1	0.0	$a_{3,2}$(T)	-	$a_{3,2}$(T)	237.7	83.36	0.0	0.0	410.0	26,0
MG1	59.2	-191.8	$a_{2,3}$(T)	-	-229.1	300.0	-142.4	289.6	289.6	59.2
OH	28.06	353.5	28.06	353.5	-	156.4	112.8	-137.1	-137.1	28.06
CH_2	251.5	1318	251.5	1318	986.5	-	447.8	697.2	697.2	251.5
CH_3O	0.0	423.8	0.0	774.8	1164.8	273.0	-	238.4	238.4	0.0
CH_2OH	-128.6	$a_{8,2}$(T)	0.0	-181.0	249.1	16.5	-128.6	-	0.0	-128.6
CH_3OH	-128.6	-181.0	-71.21	-181.0	249.1	16.5	-128.6	0.0	-	-128.6
CH_2O (OME)	0.0	670.7	141.5	189.2	237.7	83.36	0.0	238.4	238.4	-

Here, $a_{2,3}$(T)=-225.5+0.705(T/K); $a_{3,2}$(T)=1031.0-1.749(T/K); $a_{8,2}$(T)=-1018.57+329.9(T/K); $a_{2,8}$(T)=451.64-114100(T/K); $a_{2,10}$(T)=168.9-0.8776(T/K)

Experimental data T1 and T2

Table S5 Experimental data of OME-synthesis on T1

Test 13 – Autoclave – D50WX2 – Experimental data						
p-FA = 119.94 g MeOH = 80.20 g			Catalyst Mass = 1.0048 g MeOH for cat. loading = 7.41 g			
sample Time (min)	MeOH (%wt.)	OME1 (%wt.)	OME2 (%wt.)	OME3 (%wt.)	OME4 (%wt.)	OME5 (%wt.)
0	25.83	0.00	0.000	0.000	0.000	0.000
10	12.38	12.37	9.27	4.97	2.63	1.30
30	12.02	15.23	11.41	5.45	4.12	2.42
60	11.58	14.88	10.89	4.84	3.81	2.26
90	11.13	13.64	9.63	5.99	3.89	2.39
120	11.01	14.15	9.97	5.59	4.07	2.55
180	10.63	13.30	9.31	5.73	3.90	2.49
240	12.45	16.91	11.59	6.79	4.84	3.22
AV	**11.48**	**14.69**	**10.47**	**5.74**	**4.11**	**2.56**

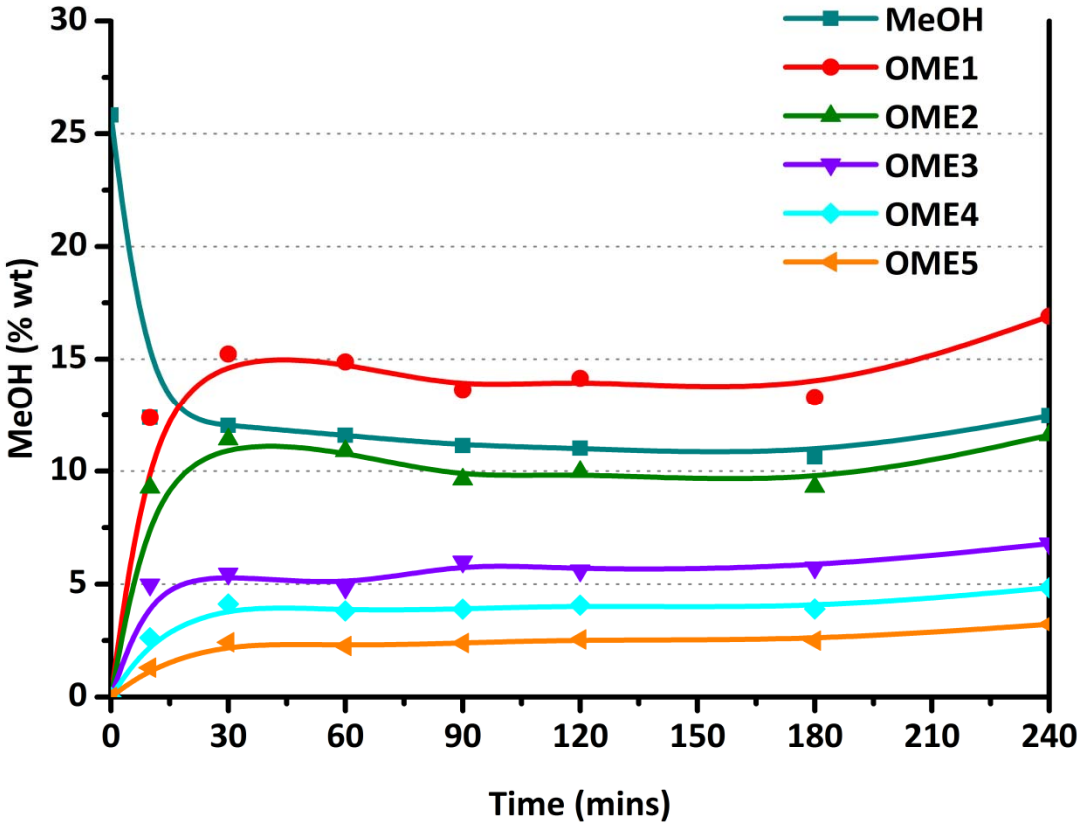

Figure S1 Graphic progress of OME-synthesis on T1

Table S6 Experimental data of OME-synthesis on T2

Test 14 – Autoclave – A36 – Experimental data							
	p-FA = 120.05 g MeOH = 80.25 g				Catalyst Mass = 1.0038 g MeOH for cat. loading = 6.41 g		
sample Time (min)	MeOH (%wt.)	FA (%wt.)	OME1 (%wt.)	OME2 (%wt.)	OME3 (%wt.)	OME4 (%wt.)	OME5 (%wt.)
0	29.37	57.21	0.00	0.00	0.000	0.00	0.00
6	23.98	--	4.55	2.81	1.20	0.60	0.25
12	18.71	43.81	8.15	5.67	2.30	1.29	0.60
21	16.49	--	10.55	7.45	2.68	1.67	0.79
31	14.68	36.35	12.73	9.32	4.56	2.19	1.00
61	12.07	33.47	13.67	10.04	5.23	2.97	1.47
102	11.63	32.33	14.00	10.14	5.40	3.20	1.77
184	11.20	32.04	13.69	9.72	5.65	3.69	2.27
270	11.86	31.96	15.01	10.39	5.71	3.93	2.44
441	11.17	31.74	15.77	11.05	6.24	4.46	2.60
AV	**11.41**	**31.91**	**14.83**	**10.39**	**5.87**	**4.03**	**2.44**

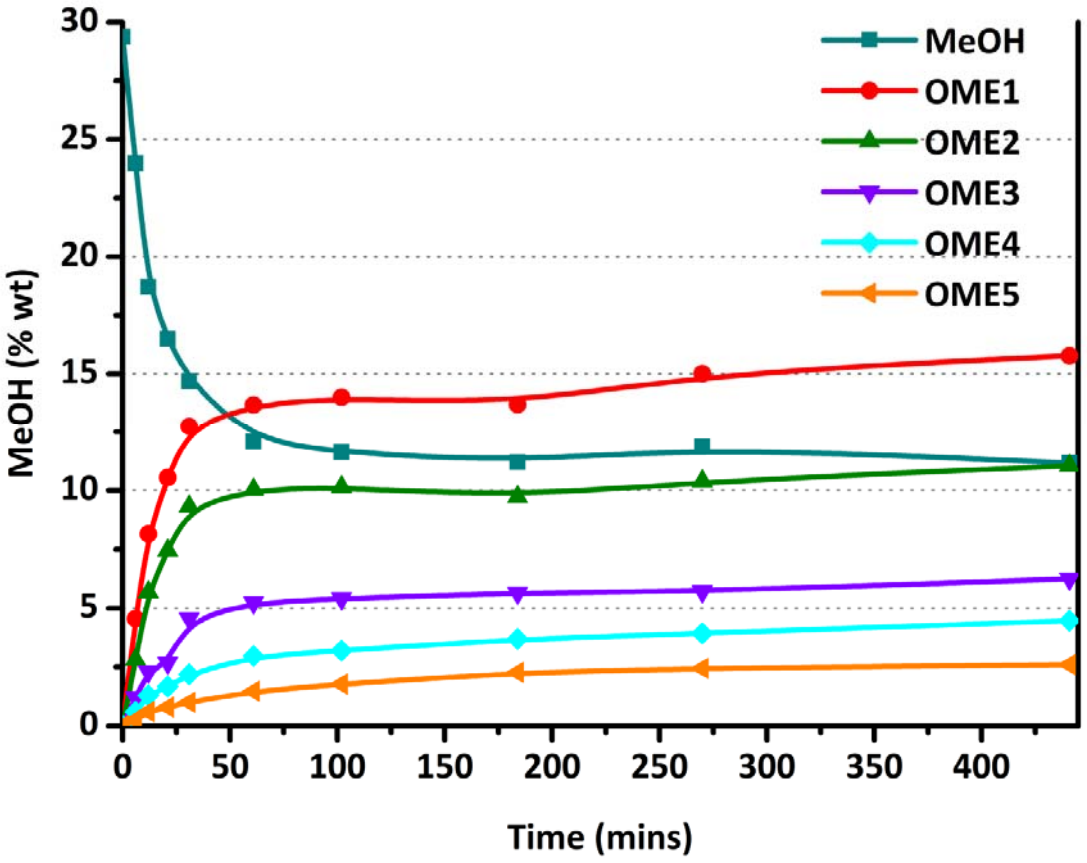

Figure S2 Graphic progress of OME-synthesis on T2

References

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