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

Electronic Supporting Information

Describing Oxymethylene Ether Synthesis based on the application of Non-Stoichiometric Gibbs Minimisation

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UNCONSTRAINTED GIBBS MINIMIZATION TECHNIQUE

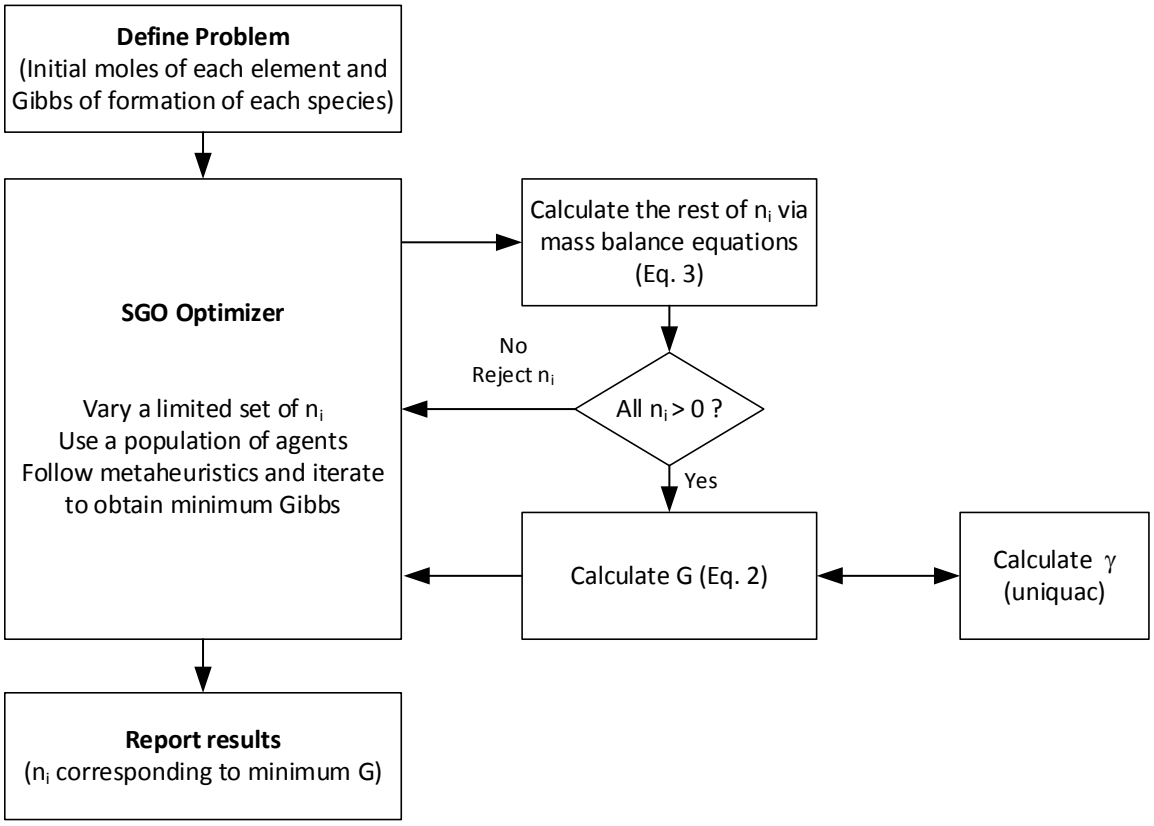

Figure S1 Scheme of the unconstrained Gibbs minimisation approach

IMPLEMENTATION ON OME LIQUID-PHASE REACTION

Table S1 Standard Gibbs of formation values at T = 333.15 K for different species in the system calculated using data extraction method

Species	**Std. Gibbs Energy of formation (Liquid) at 333.15 K (kJ/mol)**
OME_1	-207.12
OME_2	-316.79
OME_3	-426.46
OME_4	-536.13
OME_5	-645.80
OME_6	-755.48
OME_7	-865.15
OME_8	-974.82
MG_1	-336.55
MG_2	-448.66
MG_3	-558.37
MG_4	-668.07
MG_5	-777.78
MG_6	-887.49
MG_7	-997.20
MG_8	-1106.90
HF_1	-273.69
HF_2	-383.12
HF_3	-491.55
HF_4	-599.98
HF_5	-708.42

HF_6	-816.85
HF_7	-925.28
HF_8	-1033.71
FA	-94.81
MeOH	-158.01
H_2O	-231.38

Table S2. UNIFAC structural groups with size- and surface parameters (Adapted from Schmitz *et al.* (Ref. 1) and (Kuhnert et al. (Ref. 2))

Structural group	**Number**	***R***	***Q***
CH_2O	1	0.9183	0.78
H_2O	2	0.92	1.4
H_3C-O-CH_2O-CH_3	3	2.9644	2.716
HO-CH_2O-H	4	2.6744	2.94
OH	5	1	1.2
CH_2	6	0.6744	0.54
CH_3O	7	1.1459	1.088
CH_2OH	8	1.2044	1.124
CH_3OH	9	1.4311	1.432
(CH_2O)OME	10	0.9183	0.78

Table S3. UNIFAC interaction parameters a_{km}/K (Adapted from Schmitz *et al.* (Ref. 1) and (Kuhnert et al. (Ref. 2))

k	***m***									
	1	2	3	4	5	6	7	8	9	10

1	-	867.8	0	189.2	237.7	83.36	0	238.4	238.4	0
2	-254.5	-	$a_{2,3}$(T)	189.5	-229.1	300	-219.3	$a_{2,8}$(T)	289.6	$a_{2,10}$(T)
3	0	$a_{3,2}$(T)	-	$a_{3,2}$(T)	237.7	83.36	0	0	410	26
4	59.2	-191.8	$a_{2,3}$(T)	-	-229.1	300	-142.4	289.6	289.6	59.2
5	28.06	353.5	28.06	353.5	-	156.4	112.8	-137.1	-137.1	28.06
6	251.5	1318	251.5	1318	986.5	-	447.8	697.2	697.2	251.5
7	0	423.8	0	774.8	1164.8	273	-	238.4	238.4	0
8	-128.6	$a_{8,2}$(T)	0	-181	249.1	16.5	-128.6	-	0	-128.6
9	-128.6	-181	-71.21	-181	249.1	16.5	-128.6	0	-	-128.6
10	0	670.7	141.5	189.2	237.7	83.36	0	238.4	238.4	-

$a_{2,3}$(T)=-225.5+0.7205(T/K) ; $a_{3,2}$(T)=1031.0-1.749(T/K) ;$a_{8,2}$(T)=-1018.57+329900/(T/K) ;$a_{2,8}$(T)=451.64-114100/(T/K) ; $a_{2,10}$(T)=168.9-0.8776(T/K)

Table S4 UNIFAC group assignment for all components adapted from K (Adapted from Schmitz *et al.* (Ref. 1) and (Kuhnert et al. (Ref. 2))

Substance/Group	**CH_2O (FA)**	**H_2O**	**$C_3H_8O_2$ (OME_1)**	**$OH(CH_2O)H$ (MG_1)**	**OH**	**CH_2**	**CH_3O**	**CH_2OH**	**CH_3OH**	**CH_2O (OME)**
FA	1									
Water		1								
Methanol									1	
Methylal (OME_1)			1							
MG_1				1						
HF_1							1	1		
$MG_{n>2}$	n-1				2	1				
$HF_{n>2}$	n-1						1	1		
$OME_{n>2}$			1							n-1

EXPERIMENTAL VALIDATION

Table S5 Different educts used for chemical equilibrium of the OME system Adapted from the supporting information of Schmitz et al. (Ref. 2)

Educt	Total Mass of Educt (g)	FA (mass fraction)	Water (mass fraction)	MeOH (mass fraction)
1	820	0.4841	0.0226	0.4933
2	790	0.3669	0.2225	0.4106
3	798	0.4743	0.1866	0.3391
4	776	0.3682	0.3454	0.2865
5	779	0.3447	0.0227	0.6315
6	763	0.2824	0.2181	0.4992
7	763	0.4713	0.0288	0.4996
8	801	0.3970	0.0152	0.5879
9	813	0.5697	0.0235	0.4014
10	791	0.4289	0.113	0.4580
11	799	0.5140	0.1209	0.3651

Table S6 Equilibrium composition of the OME synthesis for different reaction conditions and different feed compositions in comparison to the literature values (Ref. 1 and 2).

				[wt.%]										
EQ (OME 1:TRI)	**T [°C]**	**Exp.**	**p [bar]**	**TRI**	**OME_1**	**OME_2**	**OME_3**	**OME_4**	**OME_5**	**OME_6**	**OME_7**	**OME_8**	**MEFO**	**MeOH**
3:1	50	B	1.5	1.28	39.12	24.76	15.57	9.17	5.02	2.70	1.39	0.65	0.00	0.13
	50	Own	3	1.22	44.08	24.59	13.99	8.03	3.89	1.79	0.81	0.34	0.01	1.25
	65	B	1.9	1.45	39	24.72	15.53	9.16	5.00	2.71	1.39	0.65	0.00	0.16

	65	Own	4	1.44	44.20	24.33	13.77	8.02	3.91	1.87	0.81	0.34	0.05	1.26
	80	B	2.6	1.62	38.96	24.69	15.43	9.10	4.96	2.67	1.37	0.65	0.09	0.17
	80	Own	6.3	1.61	44.07	24.67	13.84	7.85	3.81	1.82	0.82	0.36	0.40	0.75
2:1	50	B	1.5	1.69	33.83	23.59	16.32	10.64	6.45	3.84	2.21	1.24	0.00	0.03
	50	Own	4	2.07	35.50	22.71	15.32	10.66	6.23	3.63	1.95	1.05	0.02	0.86
	65	B	1.9	1.91	33.85	23.52	16.21	10.57	6.41	3.83	2.19	1.27	0.00	0.03
	65	Own	5	2.26	35.91	22.64	15.19	10.47	6.07	3.44	1.93	1.07	0.15	0.87
	80	B	2.6	2.14	33.67	23.52	16.18	10.55	6.40	3.82	2.17	1.24	0.00	0.05
	80	Own	8	2.62	37.80	22.46	14.50	9.67	5.44	3.08	1.67	0.87	1.21	0.67
2.5:1	50	Own	4	1.56	40.34	23.59	14.67	9.29	4.93	2.59	1.27	0.61	0.00	1.16
	65	Own	5.5	1.84	40.76	23.04	14.40	9.12	4.89	2.60	1.34	0.66	0.13	1.22
	80	Own	9.5	2.15	40.99	23.48	14.22	8.68	4.48	2.29	1.09	0.50	1.31	0.80

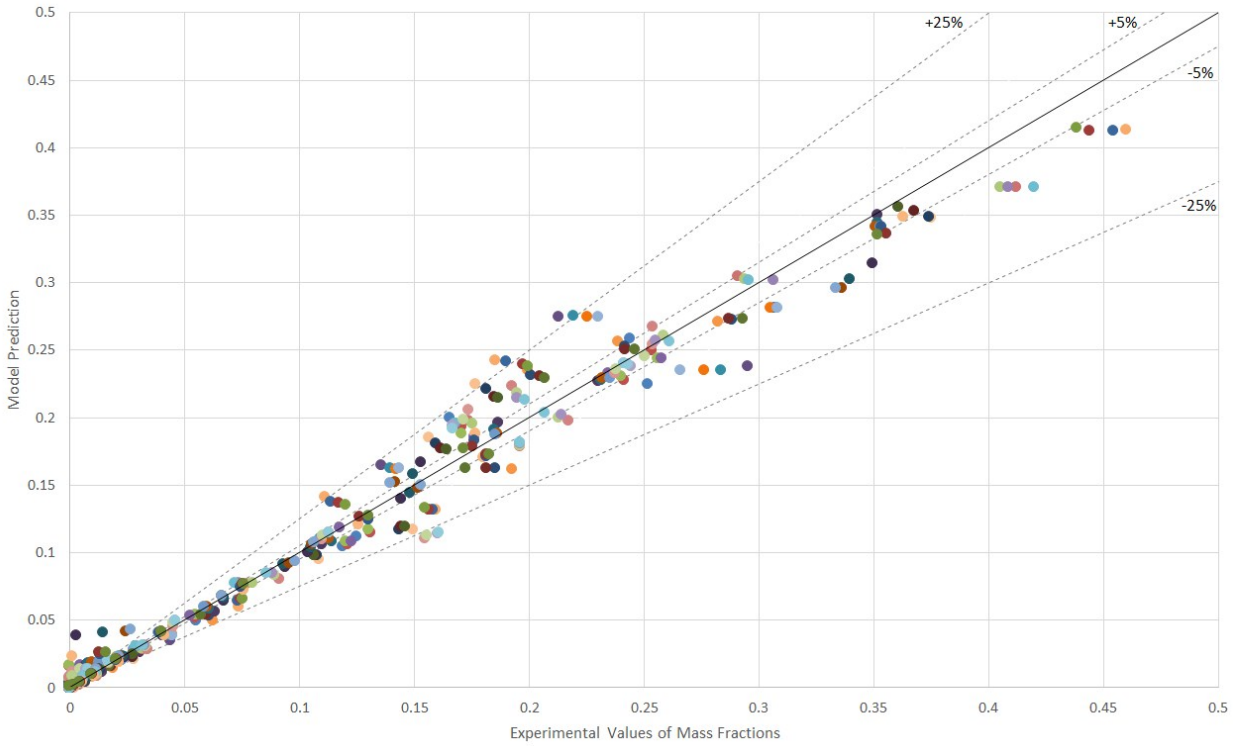

Figure S2 A parity plot of overall mass fractions of FA, MeOH, water and OME of the different educts at equilibrium calculated by the model to the literature experimental values from Schmitz et al. (Ref. 1)

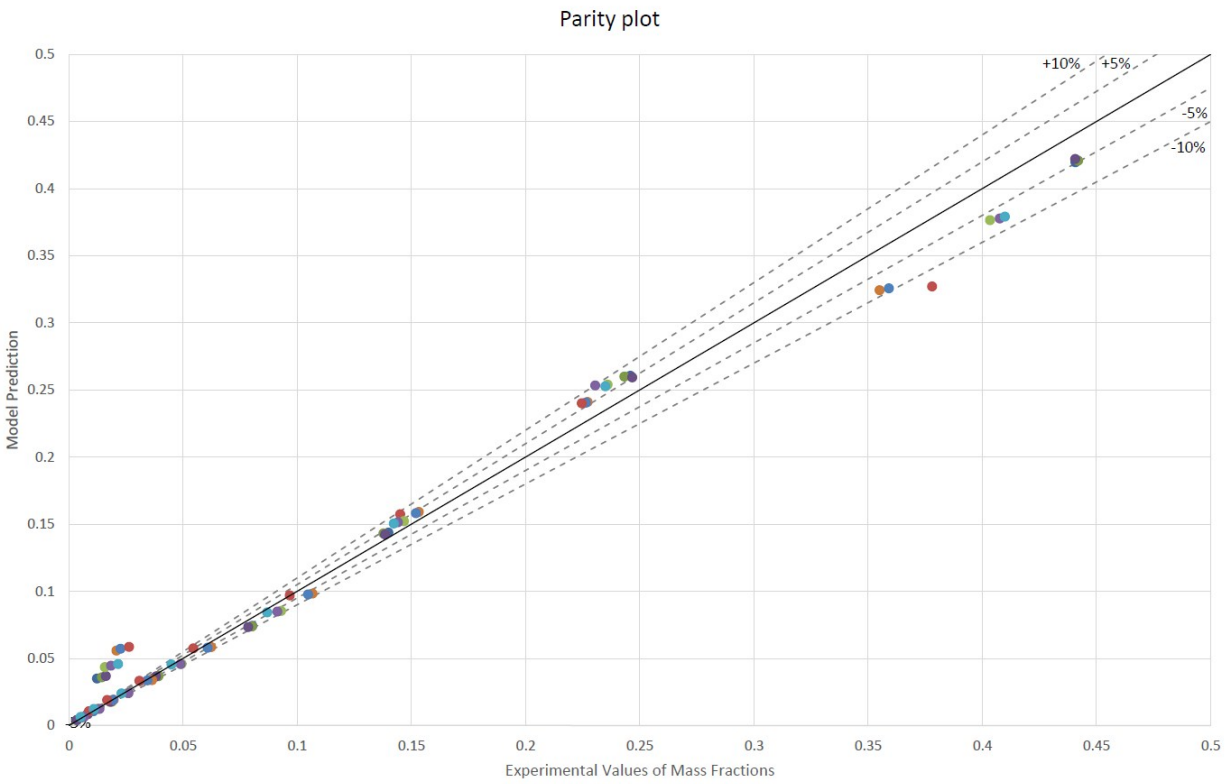

Figure S3 Parity plot between the equilibrium overall mass fractions of FA, MeOH, water and OME of different educts and reaction conditions calculated by the unconstrained Gibbs energy minimisation equilibrium model to the experimental values reported in Table S6

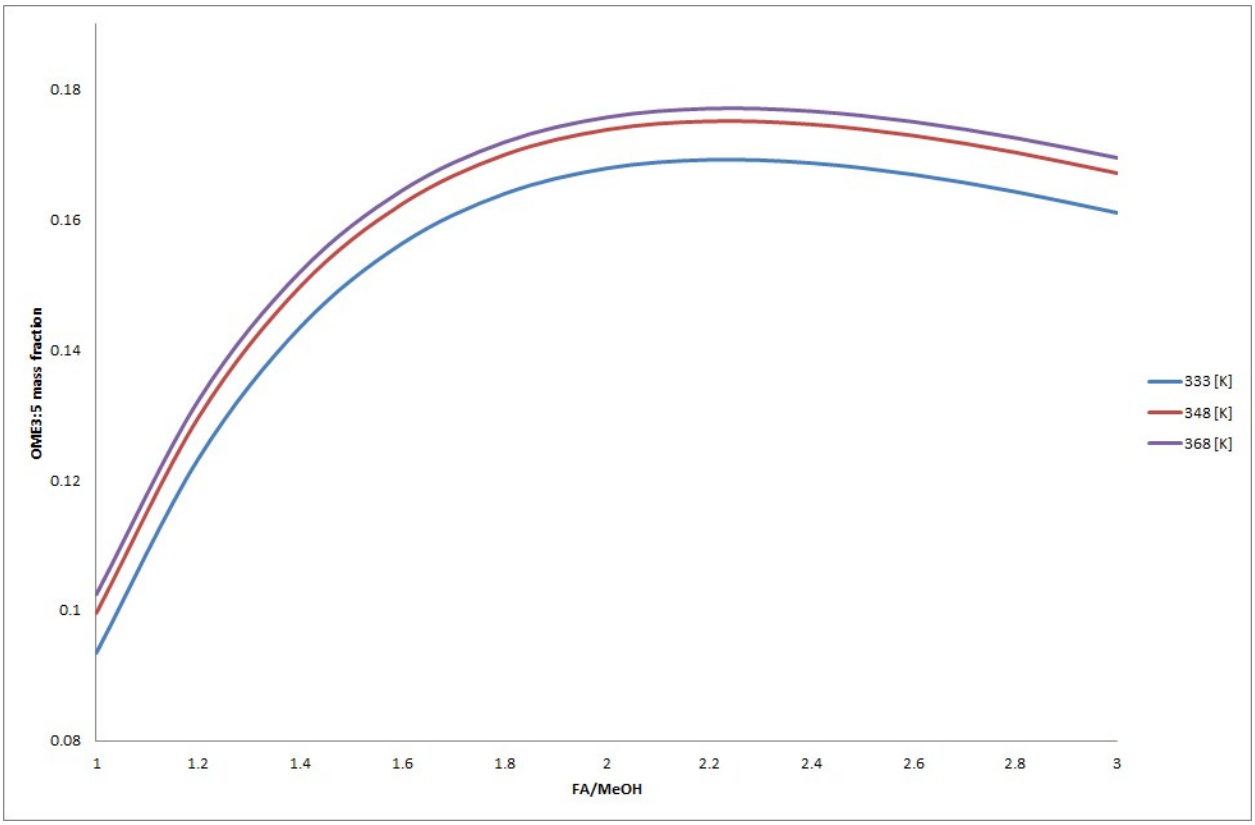

Figure S4 Effect of FA and MeOH ratio for anhydrous feeds on the $OME_{3\text{-}5}$ equilibrium composition

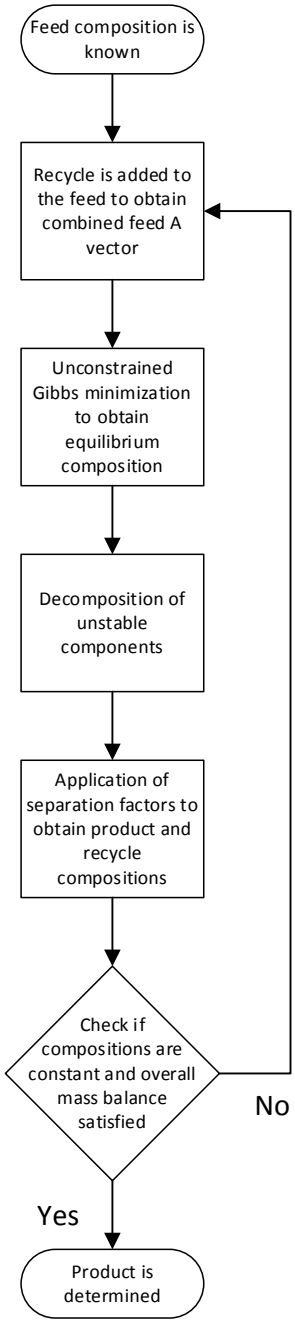

Figure S5 The recycle calculation algorithm

Table S7 Fuel properties of DME, OME and diesel (EN 590) as sourced from Refs. 3, 4, and 5.

Component	M [g/mol]	Oxygen-content [wt. %]	Cetane number	Density at 15°C [kg/m³]	Melting point [°C]	Boiling point [°C]	v at 40°C [mm²/s]	LHV [kWh/kg]	Equivalent to diesel [m³/m³]
DME	46.1	34.7	55	668	-141	-25	<0,1	7.5	1.96
OME_1	76.1	42.1	29	866.8	-105	42.3	$0.58_{(20°C)}$	6.5	1.75
OME_2	106.1	45.2	63	970	-69.7	105	$0.66_{(20°C)}$	5.4	1.75
OME_3	136.1	47	67	1,031	-42.5	155.9	1.08	5.4	1.75
OME_4	166.2	48.1	76	1,075	-9.8	201.8	1.72	5.3	1.73
OME_5	196.2	48.9	90	1,106	18.3	242.3	2.63	5.1	1.72
OME_6	226.2	49.5	-	1,135	45.8	273	-	-	-
OME_7	256.3	49.9	-	1,157	72.4	297	-	-	-
OME_8	286.3	50.3	-	-	-	-	-	-	-
OME_{3-5}	166.2	48.8	70-100	1,070	-19	155-242	1.89	5.4	1.8
Diesel	-	-	>51	820-840	-20_{winter} / 0_{summer}	170-390	2-4.5	11.833	1

References

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