

## Supplementary Information

### Demonstration and experimental model validation of the DME synthesis by reactive distillation in a pilot-scale pressure column

Malte Semmel\*<sup>a,c</sup>, Innokentij Bogatykh<sup>b,d</sup>, Benedikt Steinbach<sup>a</sup>, Jörg Sauer<sup>c</sup>, Jens-Uwe Repke<sup>d</sup> and Ouda Salem<sup>a</sup>

<sup>a</sup> Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany.

<sup>b</sup> ASG Analytik-Service AG, Trentiner Ring 30, Neusäss, 86356, Germany.

<sup>c</sup> Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

<sup>d</sup> Technische Universität Berlin, Process Dynamics and Operations Group, Sekr. KWT 9, Straße des 17. Juni 135, Berlin 10623, Germany

#### SI 1. Consistency of measured temperature and dew temperature of analyzed gas phase composition

Figure 1 shows the ratio of the dew temperature of the analyzed gas phase composition and the measured temperature at the two sampling positions available in the reactive section (2 and 3). While a slight scattering of the temperature ratio can be observed the average temperature ratio is 0.9992 and 1.0000 for position 2 and 3, respectively. These results show that temperature measurement and gas phase analysis are in accordance with the VLE of the system, thus providing confidence in the measurements.

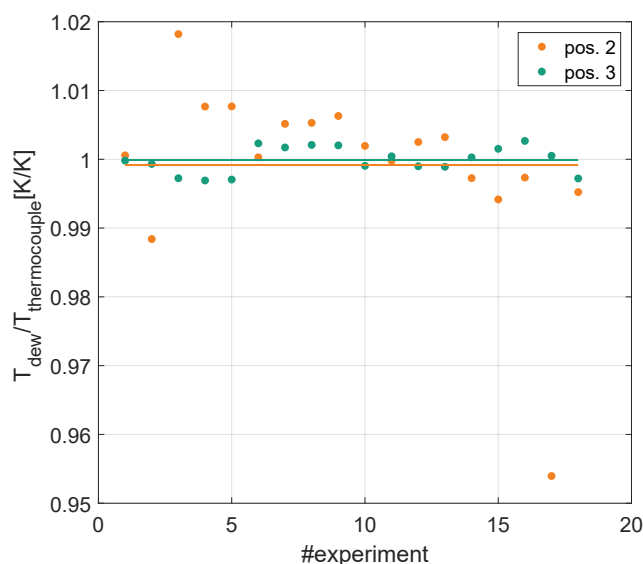


Figure 1: Relative deviation between measured temperature and dew temperature of the measured gas phase composition.

## SI 2. Complete experimental dataset

Table 1: Measured temperature data of all experiments performed in the pilot-scale column.

#Experiment	TI14	TI13	TI12	TI11	TI10	TI9	TI8	TI7	TI6	TI5	TI4	TI3	TI2	TI1
	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]
1	184.1	170.5	152.8	144.1	142.0	135.8	133.2	130.2	126.8	104.6	91.4	55.2	54.4	55.4
2	182.0	165.2	148.0	145.7	145.0	141.9	140.5	137.0	138.3	120.2	99.9	55.9	54.8	54.7
3	185.0	162.7	151.5	143.4	141.3	128.2	126.0	123.2	121.2	100.9	90.1	63.0	57.3	63.9
4	186.2	163.8	151.5	143.5	140.7	127.3	125.1	122.2	117.5	96.5	88.0	56.0	53.5	56.1
5	186.5	172.0	151.5	143.6	140.7	127.6	125.5	122.6	117.8	96.8	88.3	56.0	53.8	56.4
6	185.8	174.7	151.4	144.2	143.1	140.3	139.8	129.8	131.0	103.6	94.7	55.9	54.7	56.5
7	185.7	175.2	151.5	144.2	142.0	139.6	138.9	128.9	131.0	109.9	104.3	72.7	66.3	78.3
8	185.8	168.3	151.5	144.1	141.7	138.8	138.0	129.5	131.3	113.0	108.2	84.1	78.9	87.8
9	185.9	166.8	151.5	144.1	141.5	138.7	137.8	129.5	131.4	114.1	109.7	88.5	85.4	91.0
10	186.0	171.7	155.3	146.1	143.8	135.7	132.7	129.8	126.6	105.8	96.0	60.5	57.9	60.0
11	186.5	173.1	152.3	146.8	146.4	143.3	139.0	136.1	135.3	112.2	101.0	61.2	58.2	60.5
12	186.4	167.9	154.4	147.1	145.9	143.5	139.3	136.0	134.2	116.9	109.6	71.1	65.7	76.0
13	186.5	168.1	154.2	147.1	145.8	143.6	140.0	135.1	134.1	116.2	109.1	70.7	65.8	75.3
14	186.0	171.6	152.4	147.2	146.8	144.5	144.6	139.9	139.5	126.3	116.6	80.8	73.7	88.6
15	185.7	176.7	151.4	147.7	147.2	144.8	145.2	140.4	140.4	124.1	110.1	66.9	61.0	67.3
16	187.1	172.2	154.0	146.9	146.6	144.0	139.1	136.4	136.2	111.3	97.9	57.7	56.1	57.1
17	182.2	175.7	149.8	147.5	146.8	144.0	139.5	130.5	134.2	113.6	78.0	53.9	53.9	54.9
18	186.7	177.5	154.9	151.0	150.5	148.8	149.2	145.1	145.2	127.1	104.2	60.5	57.4	58.7

Table 2: Measured gas phase compositions on the three sampling positions of all experiments performed in the pilot-scale column.

# Experiment	sampling position 1			sampling position 2			sampling position 3		
	$Y_{\text{MeOH, gas}}$	$Y_{\text{H}_2\text{O, gas}}$	$Y_{\text{DME, gas}}$	$Y_{\text{MeOH, gas}}$	$Y_{\text{H}_2\text{O, gas}}$	$Y_{\text{DME, gas}}$	$Y_{\text{MeOH, gas}}$	$Y_{\text{H}_2\text{O, gas}}$	$Y_{\text{DME, gas}}$
	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]
1	1.9%	0.1%	98.0%	39.0%	0.6%	60.3%	91.3%	8.7%	0.0%
2	1.2%	0.1%	98.7%	54.7%	1.0%	44.4%	90.9%	9.1%	0.0%
3	7.0%	0.0%	92.9%	41.9%	0.8%	57.3%	85.8%	9.0%	5.2%
4	3.0%	0.1%	96.9%	31.5%	0.5%	68.1%	86.6%	8.8%	4.6%
5	3.2%	0.1%	96.7%	31.8%	0.5%	67.7%	86.6%	9.0%	4.4%
6	3.0%	0.1%	96.9%	39.5%	0.3%	60.2%	89.8%	10.1%	0.0%
7	13.5%	0.0%	86.5%	47.9%	0.6%	51.6%	89.3%	10.7%	0.0%
8	19.8%	0.0%	80.2%	51.4%	0.7%	47.9%	88.8%	11.1%	0.1%
9	22.6%	0.0%	77.4%	53.3%	0.8%	45.9%	88.6%	11.3%	0.1%
10	3.5%	0.1%	96.4%	38.5%	0.6%	60.8%	90.4%	9.4%	0.2%
11	3.1%	0.2%	96.7%	46.7%	1.1%	52.2%	90.7%	9.3%	0.0%
12	11.1%	0.1%	88.8%	52.5%	1.2%	46.2%	89.9%	10.0%	0.1%
13	10.4%	0.1%	89.5%	52.2%	1.3%	46.6%	89.7%	10.2%	0.2%
14	18.9%	0.3%	80.9%	63.5%	1.8%	34.6%	90.0%	10.0%	0.0%
15	7.4%	0.1%	92.6%	61.0%	1.1%	38.0%	87.2%	12.8%	0.0%
16	1.7%	0.0%	98.3%	46.4%	0.5%	53.1%	88.1%	11.8%	0.0%
17	0.1%	0.0%	99.9%	29.3%	0.3%	70.4%	89.0%	11.0%	0.0%
18	2.8%	0.0%	97.2%	52.8%	9.1%	38.1%	83.7%	16.3%	0.0%

### SI 3. Mass balance and energy balance of column

Since the MeOH dehydration is an equimolar reaction, the overall mass balance of the column is:

$$N_{Feed} = N_{distillate} + N_{bottoms} \quad (1)$$

In the component mole balance, the MeOH conversion  $X_M$  needs to be accounted for. Considering that no significant amounts of the light boiler DME will be in the bottoms product or the heavy boiler water in the distillate, the component mole balances are as follows:

$$\begin{array}{l} \text{MeOH} \\ \text{balance} \end{array} \quad N_{Feed} \cdot y_{MeOH, Feed} = N_{Feed} \cdot y_{MeOH, Feed} \cdot X_M + N_{distillate} \cdot y_{MeOH, distillate} + N_{bottoms} \cdot y_{MeOH, bottoms} \quad (2)$$

$$\begin{array}{l} \text{H}_2\text{O balance} \end{array} \quad N_{Feed} \cdot y_{H_2O, Feed} + N_{Feed} \cdot y_{MeOH, Feed} \cdot \frac{X_M}{2} = N_{bottoms} \cdot y_{H_2O, bottoms} \quad (3)$$

$$\begin{array}{l} \text{DME balance} \end{array} \quad N_{Feed} \cdot y_{MeOH, Feed} \cdot \frac{X_M}{2} = N_{distillate} \cdot y_{DME, distillate} \quad (4)$$

Rearranging the equations (1)-(4) an explicit formula for the calculation of the MeOH conversion can be found based on the measured composition of the bottoms product and the distillate.

$$X_M = \frac{y_{MeOH, Feed} - y_{MeOH, bottoms}}{\frac{y_{MeOH, Feed}}{2 \cdot y_{DME, distillate}} \cdot (y_{MeOH, distillate} - y_{MeOH, bottoms}) + y_{MeOH, Feed}} \quad (5)$$

The energy balance of the column is given by the following equation:

$$N_{Feed} \cdot h_{Feed} + \dot{Q}_{reboiler} = N_{distillate} \cdot h_{distillate} + N_{bottoms} \cdot h_{bottoms} + \dot{Q}_{condenser} \quad (6)$$

Rearranging the energy balance provides the condenser duty. Based on the condenser duty, the mole flow of the condensate can be obtained by an energy balance over the condenser:

$$N_{condensate} = \frac{\dot{Q}_{condenser}}{\Delta h_{condensate}} \quad (7)$$

The enthalpy change of the condensate is calculated considering both the condensation enthalpy and enthalpy change due to subcooling based on the actual composition of the condensate according to the FT-IR analysis and the measured temperature  $T_{in}$  before the condenser and the subcooling temperature:

$$\Delta h_{condensate} = \Delta h_{v, condensate} + c_{p, condensate} \cdot (T_{in} - T_{subcool}) \quad (8)$$

Knowing the mole flow of the condensate from eq. (8) and the measured distillate mole flow, the reflux ratio can be calculated:

$$RR = \frac{N_{reflux}}{N_{distillate}} = \frac{N_{condensate} - N_{distillate}}{N_{distillate}} \quad (9)$$

### SI 4. Models for the Calculation of Thermodynamic and Physical Properties

Table 2 summarizes the models used to calculate the thermodynamic and physical properties in Aspen Plus®. The interested reader is referred to the Aspen Plus® Help for further information on the models.

Table 3: Models used for the calculation of thermodynamic and physical properties in Aspen Plus®.

Property	Route ID	Property	Route ID
PHIVMX	PHIVMX41	SL	SL22
PHILMX	PHILMX94	VV	VV01

HVMX	HVMX41	VL	VL01
HLMX	HLMX94	DL	DL01
GVMX	GVMX23	DV	DV02
GLMX	GLMX94	MUL	MUL01
SVMX	SVMX41	MUV	MUV01
SLMX	SLMX41	KV	KV04
VVMX	VVMX01	KL	KL04
VLMX	VLMX01	SIGL	SIGL01
MUVMX	MUVMX04	PHISMX	PHISMX00
MULMX	MULMX05	HSMX	HSMX02
KVMX	KVMX04	GSMX	GSMX02
KLMX	KLMX03	SSMX	SSMX01
DVMX	DVMX02	VSMX	VSMX02
DLMX	DLMX02	KSMX	KSMX01
SIGLMX	SIGLMX01	PHIS	PHIS00
PHIV	PHIV41	HS	HS02
PHIL	PHIL41	GS	GS02
HV	HV42	SS	SS02
HL	HL41	VS	VS01
GV	GV21	KS	KS01
GL	GL22	WSL	WATSOL00
SV	SV21	HCSL	HCSOL01

### SI 5. Influence of feed stage and feed composition for C400

Figure 2 shows the specific reboiler duty per ton of produce DME in dependence of the feed stage and the water mole fraction of the feed. The absolute methanol flow of the feed was kept constant at 17.5 t/h, while an additional water mass flow was added to achieve the respective molar fraction. The catalyst mass in the RD column was 24 t, resulting in a WHSV of 0.73 h<sup>-1</sup>. The used catalyst for the simulation was C400, the maximum operating temperature in the reactive section was set to 160 °C by varying the column pressure as described in chapter 4.4. The resulting operating pressure of all operating points shown was between 12.9-14.3 bar depending on the feed stage and the feed composition.

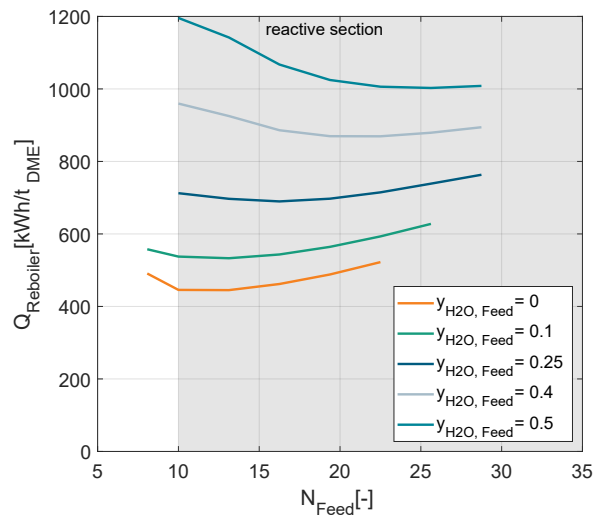


Figure 2: Specific reboiler duty per ton of produced DME in dependence of the feed stage for various molar water fractions in the feed. WHSV=0.73.  $N_{\text{rect, upper}} = 10$ ,  $N_{\text{rect, lower}} = 14$ ,  $N_{\text{reactive}} = 25$ . Use of C400 in the reactive section with  $T_{\text{max}} = 160$  °C.