Supplementary information for

On the chemical interactions of the biomass processing agents γ-valerolactone (GVL) and N-methylmorpholine-N-oxide (NMMO)

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1. Values of Figures 1, 3, and 4

Table 1: Values of Figure 1, A.

GVL loss (%), 100 °C [Figure 1, A]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
1.5	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0.1	0.1	0.3	0.3
7.5	0	0	0.2	0.5	0.5	0.6
10	0	0	0.3	0.5	0.8	0.8

NMMO loss (%), 100 °C [Figure 1, A]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
1.5	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
7.5	0	0	0	0	0	0
10	0	0	0	0	0	0

Table 2: Values of Figure 1, B.

GVL loss (%), 125 °C [Figure 1, B]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	0	0	0	0	0.1	0.2
1	0	0	0.1	0.2	0.3	0.3
1.5	0	0.1	0.2	0.2	0.4	0.6
2	0	0.2	0.2	0.3	0.6	0.7
3	0	0.3	0.4	0.5	0.8	0.8
4	0.2	0.3	0.5	0.7	1	1.3
5	0.2	0.4	0.7	0.9	1.3	1.6
7.5	0.4	0.6	0.9	1.3	1.7	2.6
10	0.4	0.8	1.2	1.6	2.6	3.3

NMMO loss (%), 125 °C [Figure 1, B]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	2.5	8.6	1.8	0	0	0
1	1.3	3.6	0.7	0	0	0
1.5	1.1	2	0.4	0	0	0
2	0.6	1.7	0.4	0	0	0
3	0.4	1.2	0.2	0	0	0
4	0.2	0.9	0.2	0	0	0
5	0.2	0.6	0.1	0	0	0
7.5	0.1	0.4	0.1	0	0	0
10	0.1	0.3	0.1	0	0	0

Table 3: Values of Figure 1, C.

GVL loss (%), 150 °C [Figure 1, C]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	0.2	0.5	0	0	0.2	0.6
1	0.2	0.5	0	0	0.5	1.1
1.5	0.1	0.5	0.4	0.5	1	1.7
2	0.3	0.8	0.5	0.5	1.3	2.1
3	0.1	1	0.7	0.8	1.9	2.5
4	0.2	1.1	0.8	1.1	2.5	3.9
5	0.2	1.1	0.8	1.2	3.1	4.4
7.5	0.2	1.4	1.2	1.9	4.4	6.9
10	0.2	1.7	1.5	2.4	6	9.1

NMMO loss (%), 150 °C [Figure 1, C]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	23.5	86.4	18.4	0	0	0
1	12.8	36.4	7.2	0	0	0
1.5	11.1	35.1	4.5	0	0	0
2	10.5	33.4	4.4	0	0	0
3	10.5	28	3.9	0	0	0
4	9	23	2.5	0	0	0
5	7.2	16	1.8	0	0	0
7.5	3.7	9.8	0.9	0	0	0
10	1.4	3.2	0.7	0	0	0

Table 4: Values of Figure 1, D.

GVL loss (%), 180 °C [Figure 1, D]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	1	3.9	0	0	0.9	1.2
1	1.2	8.6	0.5	0.8	1.9	2.4
1.5	1.4	9	0.9	1.6	2.6	3.4
2	1.7	9.5	1.2	2.2	3.5	4
3	2.3	10.3	2	3.1	4.6	5.3
4	2.6	11.2	2.8	4	6.4	7.6
5	3.4	12.4	3.6	5.2	7.4	9.5
7.5	4.8	14.9	4.9	8.2	13.3	15.1
10	6.9	17.3	6.2	11.6	17.4	19.2

NMMO loss (%), 180 °C [Figure 1, D]

NMMO in GVL (wt%)	NMMO/H_2O (molar ratio) 1:2	1:3	1:4	1:5	1:7.5	1:10
0.5	34	100	100	23	0	0
1	16	100	92	4	0	0
1.5	13.4	100	76	0	0	0
2	8.3	96	51	0	0	0
3	5.2	67	36	0	0	0
4	4.1	53	23	0	0	0
5	3	41	16	0	0	0
7.5	2.1	26	16	0	0	0
10	2.1	23	9	0	0	0

Table 5: Values of Figure 3, A.

GVL loss (%), 100 °C [Figure 3, A]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	3.8	3.4	2	1.8
60:40	5.6	4.1	2.9	2.6
70:30	7.2	5.9	4.1	3
80:20	8.2	8.1	7.9	4.2
90:10	8.1	7.9	9.8	6.4
100:0	12.2	10.2	11.3	5.8

NMMO loss (%), 100 °C [Figure 3, A]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	18	26	38	74
60:40	24	35	49	80
70:30	31	44	62	93
80:20	40	54	73	98
90:10	46	63	85	100
100:0	48	74	98	100

Table 6: Values of Figure 3, B.

GVL loss (%), 125 °C [Figure 3, B]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	8.9	9.4	6.5	3.3
60:40	10.1	8.8	7.9	5.4
70:30	12.1	9.9	8.5	6.8
80:20	13.9	11	10.2	7.2
90:10	15	13.6	12.2	7.4
100:0				

NMMO loss (%), 125 °C [Figure 3, B]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	24	31	48	84
60:40	36	44	58	98
70:30	48	59	72	100
80:20	50	74	86	100
90:10	54	90	94	100
100:0				

Table 7: Values of Figure 3, C.

GVL loss (%), 150 °C [Figure 3, C]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	29.9	21.3	15.8	11.1
60:40	31.4	22	16.6	12.3
70:30	31	22.3	16.9	11.4
80:20	31.8	24.8	17.4	11.6
90:10				
100:0				

NMMO loss (%), 150 °C [Figure 3, C]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	64	72	100	100
60:40	72	84	100	100
70:30	85	94	100	100
80:20	92	100	100	100
90:10				
100:0				

Table 8: Values of Figure 3, D.

GVL loss (%), 180 °C [Figure 3, D]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	34.4	29	18.4	8.6
60:40	35.6	29.4	19.2	9.4
70:30				
80:20				
90:10				
100:0				

NMMO loss (%), 180 °C [Figure 3, D]

GVL/H_2O (molar ratio)	NMMO charge (wt%) 20	15	10	5
50:50	100	100	100	100
60:40	100	100	100	100
70:30				
80:20				
90:10				
100:0				

Table 9: Values of Figure 4.

GVL:H_2O 60:40, 150 °C [Figure 4, A]	GVL loss (%)	NMMO loss (%)
Biomass	16.6	100
Cellulose	1.4	10.4
Lignin	55.7	100
Xylan	4.3	4.5
Model mix	12.9	100

GVL:H_2O 80:20, 150 °C [Figure 4, B]	GVL loss (%)	NMMO loss (%)
Biomass	17.4	100
Cellulose	0.9	16.8
Lignin	62.9	100
Xylan	7.1	32.4
Model mix	19.3	98.4

GVL:H_2O 60:40, 180 °C [Figure 4, C]	GVL loss (%)	NMMO loss (%)
Biomass	19.2	100
Cellulose	3	18.3
Lignin	77.2	100
Xylan	6.1	38.6
Model mix	22.4	100

GVL:H_2O 80:20, 180 °C [Figure 4, D]	GVL loss (%)	NMMO loss (%)
Biomass		
Cellulose	2.8	25.4
Lignin		
Xylan	10.5	50.4
Model mix		

2. Hazard classification NMMO[1]

Classification and labelling according to (EC) No 1272/2008

Hazard statements

H315	Causes skin irritation (category 2).
H319	Causes serious eye irritation (category 2).
H335	Specific target organ toxicity - (single exposure) (category 3). May cause respiratory irritation.

Precautionary statements

P261	Avoid breathing dust.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Pictogram

Warning

3. Hazard classification NMMO-Monohydrate[2]

Classification and labelling according to (EC) No 1272/2008

Hazard statements

H315	Causes skin irritation (category 2).
H319	Causes serious eye irritation (category 2).
H335	Specific target organ toxicity - (single exposure) (category 3). May cause respiratory irritation.

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1 https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=AT&language=EN-generic&productNumber=224286&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F224286%3Flang%3Dde, 12.5.2021

2 https://www.alfa.com/de/msds/?language=EE&subformat=CLP1&sku=A15996, 12.5.2021

Precautionary statements

P302 + P352	IF ON SKIN: Wash with plenty of soap and water.
P337 + P313	If eye irritation persists: Get medical advice/attention.
P304 + P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P312	Call a POISON CENTER or doctor/physician if you feel unwell.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P332 + P313	I f skin irritation occurs: Get medical advice/attention.

Pictogram

Warning

4. Known incidents in the past five years, involving NMMO and/or GVL systems

Year, region, institution (anonymized)	**Biomass processing system used**	**Description of the incident**
2020, South Asia, company A	NMMO pretreatment of bamboo biomass, followed by GVL pulping	Uncontrolled exothermicity during pulping at 180°C, charring. Situation improved by washing after the NMMO step.
2020, Middle America, company B	NMMO preactivation of maize stalks, followed by GVL pulping	Black discoloration and temperature rise during pulping at 160 – 180°C. Washing after NMMO step lowered NMMO content to <1% (rel. to GVL) and overcame the color problem.
2019, South America, research institution I	Simultaneous acidic hydrolysis and NMMO preactivation	Strong exothermicity at already 85 °C due to Polonowski-type degradation of NMMO.
2019, South Asia, company A	NMMO pretreatment of palm oil empty fruit bunches, followed by GVL pulping	Uncontrolled exothermicity upon distillation/purification of GVL due to accumulated NMMO from carryovers.
2019, South Asia,	Three-step sequence of GVL	Strong discoloration in step 3 at

research institution II	– aqueous NMMO – GVL treatment for delignification and saccharification of palm oil biomass	185 °C, disappeared with a better washing after step 2 and lowering the temperature to 170°C.
2019, Africa, research institution III	NMMO preactivation of rice straw, followed by ionic liquid pretreatment and GVL pulping	Instabilities (exothermicities, complete charring) in GVL step above 150 °C. Thorough washing and elimination if the ionic liquid step removed the problem.
2018, Europe, research institution IV	Attempted esterification of NMMO-pretreated woody biomass	Vigorous exothermicity and breaking of reaction vessel (90 °C), due to instability of NMMO towards acylating agents.
2018, South Asia, research institution II	Dissolution of GVL-pulped bamboo in NMMO-monohydrate for fiber spinning (Lyocell)	Charring and black discoloration of spinning dope (105 °C, 10% pulp), disappeared when pulp was thoroughly washed free of GVL before.
2016 South Asia, company C	NMMO preactivation of biomass, followed by GVL pulping	Uncontrolled exothermicity during pulping at 175 -180 °C with charring. Situation improved by washing after the NMMO step.
2016 Europe, research institution V	Dissolution of hardwood dissolving pulp in NMMO for fiber spinning (Lyocell)	Charring and black discoloration of spinning dope (120 °C), disappeared when pH was kept above neutral and complexation agents were added.
2016 South America, research institution VI	GVL delignification of eucalyptus followed by dissolution in NMMO	Charring and black discoloration of spinning dope (temp. not known), system was stable when pulp was thoroughly washed free of GVL before.