Contents

1 Experimental

1.1 General remarks

1-octanol (≥ 99%), 1,4-dioxnae (99.8%),2 4-pentadienoic acid (≥ 97%), α-angelica lactone (98%), butanol (99.8%), diethylene glycol dimethyl ether (≥ 99.5%), *iso*-propanol (≥ 99.9%), magnesium sulfate (≥ 99.5%), and levulinic acid (≥ 98%) were purchased from Sigmα-ALdrich. Ethanol (≥ 99.9%) were purchased from Chemsolute and γ-Methylene-γ-butyrolactone (>98%) was purchased from TCI. Zeolites of HBEA-25, HBEA-150, H-MFI 25, and HMFI-400 were purchased from Süd-Chemie. $15\%WO_3/ZrO_2$ and SO_4^{-2}/ZrO_2 were purchased from Saint-Gobain. γ-Al_2O_3 (product code: 568129) was purchased from Sasol. Amberlyst® 15Dry was purchased from Sigmα-ALdrich and Amberlyst® 36Dry was purchased from The Dow Chemical Company. All chemicals were dried over anhydrous magnesium sulfate or molecular sieves and stored under argon. The catalyst were dried in the oven at 110°C for 24 hours and stored under vacuum. GC analysis was performed on an Agilent HP6890.

1.2 P-Toluenesulfonic acid catalyzed addition of BuOH to α-AL

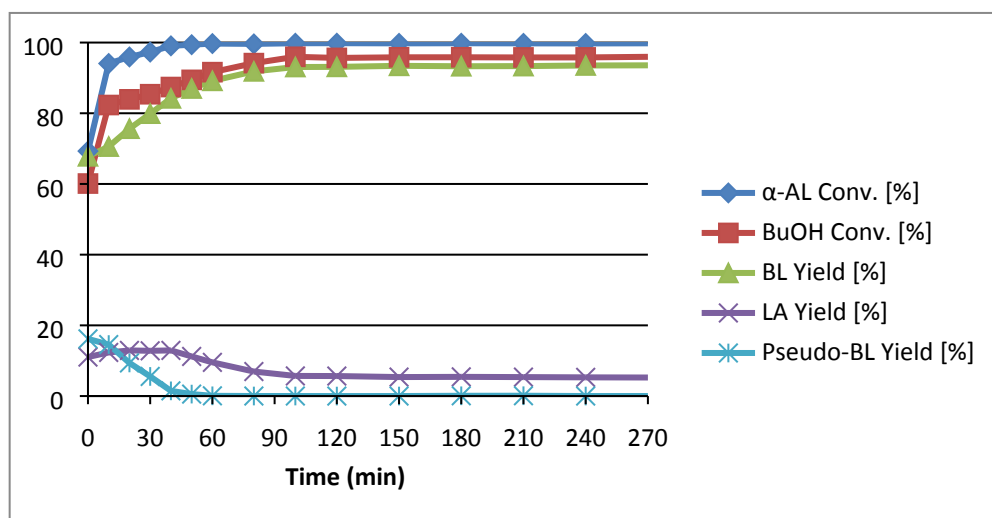Figure S 1. *p*-Toluenesulfonic as a catalyst in the conversion of α-AL to BL. Conditions: 50°C; α-AL (5.00 g, 51.00 mmol); BuOH (3.78 g, 51.00 mmol); *P*TSA (257 mg).

1.3 GC-MS analysis for butyl levulinate and pseudo-butyl levulinate

Unknown; InLib=-709

100—

99

43

50—

57

72

41

39

61

101

117

81 84

97

129

157

173

30   40   50   60   70   80   90   100   110   120   130   140   150   160   170   180

Pseudo-BL

(Text File) WC-LAB-P-152-8_140723_001#2702 RT: 18.22 AV: 1

Name: WC-LAB-P-152-8_140723_001#2702 RT: 18.22 AV: 1
MW: N/A ID#: 12 DB: Text File
Comment: T: {0,0} + c EI Full ms [33.00-500.00]
49 m/z Values and Intensities:

37	1	38	3	39	77	40	11	41	234	42	42	43	744	44	22	45	15	50	3
51	5	52	2	53	23	54	13	55	111	56	169	57	338	58	16	59	2	61	194
62	3	69	4	70	6	71	258	72	276	73	186	74	17	75	7	81	30	82	2
83	2	84	1	86	2	97	3	99	999	100	115	101	177	102	7	103	1	113	4
116	1	117	89	118	5	128	15	129	29	130	11	157	21	158	1	173	5		

Unknown; InLib=244

100—

99

43

74

50—

56

41

71

101

39

53

61

81   86

117

130

143

157

172

30   40   50   60   70   80   90   100   110   120   130   140   150   160   170   180

BL

(Text File) WC-LAB-P-152-8_140723_001#2584 RT: 17.43 AV: 1

Name: WC-LAB-P-152-8_140723_001#2584 RT: 17.43 AV: 1
MW: N/A ID#: 11 DB: Text File
Comment: T: {0,0} + c EI Full ms [33.00-500.00]
53 m/z Values and Intensities:

37	1	38	3	39	73	41	275	42	62	43	916	44	30	45	19	50	3	51	4
52	2	53	19	54	8	55	151	56	330	57	257	58	34	59	4	60	2	61	23
69	4	70	11	71	247	72	41	73	129	74	550	75	181	76	8	77	1	81	27
82	2	83	3	86	1	87	1	97	1	98	99	99	999	100	93	101	316	102	15
103	2	115	1	116	11	117	119	118	6	129	7	130	67	131	6	143	1	157	41
158	3	172	1	173	2														

Hit 1 : Pentanoic acid, 4-oxo-, butyl ester
C9H16O3; MF: 942; RMF: 942; Prob 89.7%; CAS: 2052-15-5; Lib: mainlib; ID: 65337.

GC-MS library

100—

99

43

74

50—

56

41

71

29

117

15

31

39

53

81   87

130

143

157

172

10   20   30   40   50   60   70   80   90   100   110   120   130   140   150   160   170   180

(mainlib) Pentanoic acid, 4-oxo-, butyl ester

Name: Pentanoic acid, 4-oxo-, butyl ester
Formula: C9H16O3
MW: 172 Exact Mass: 172.109944 CAS#: 2052-15-5 NIST#: 292186 ID#: 65337 DB: mainlib
Other DBs: Fine, TSCA, RTECS, HODOC, NIH, EINECS, IRDB
Contributor: NIST Mass Spectrometry Data Center, 1998.
61 m/z Values and Intensities:

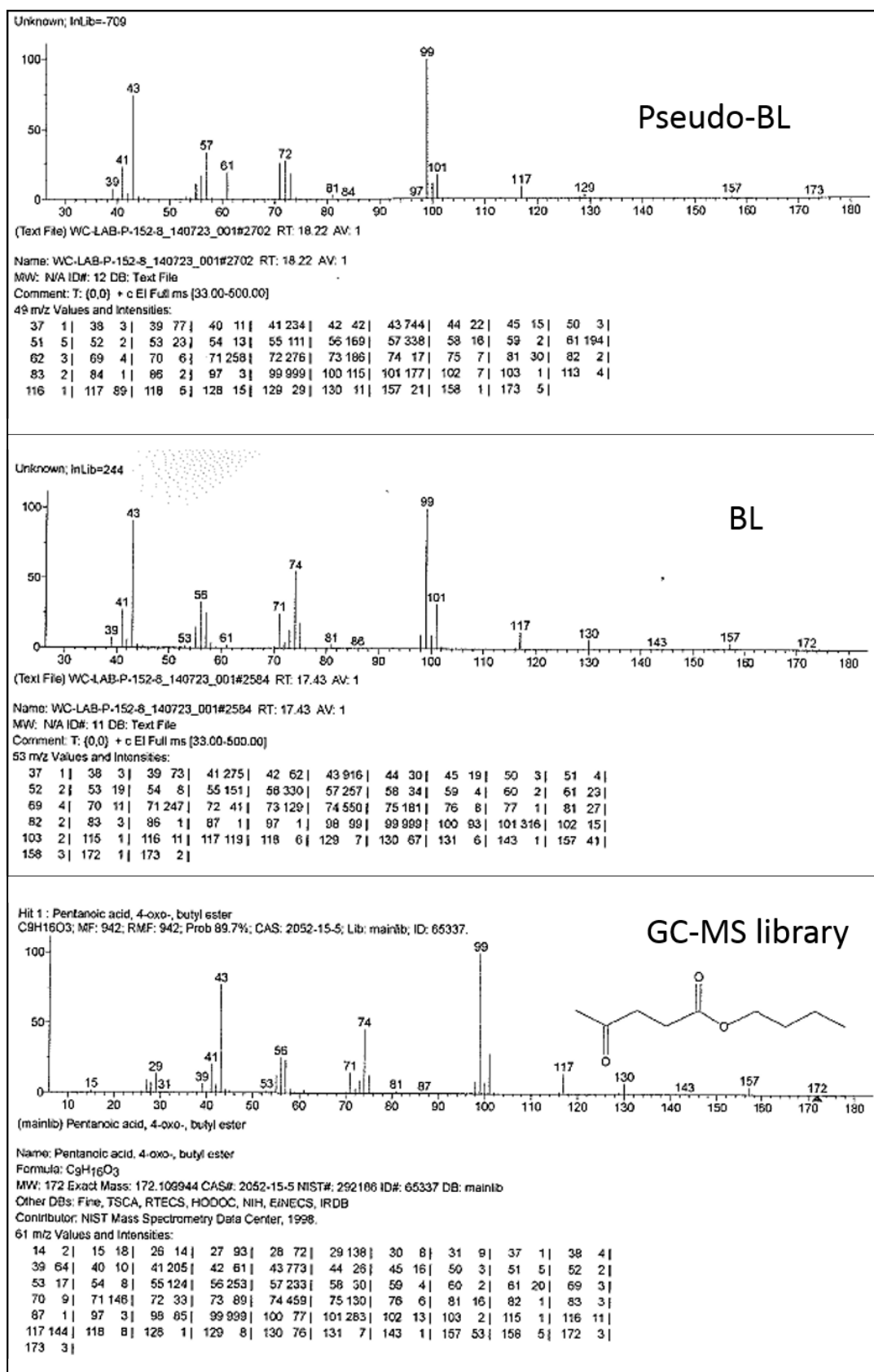| 14 | 2 | 15 | 18 | 26 | 14 | 27 | 93 | 28 | 72 | 29 | 138 | 30 | 8 | 31 | 9 | 37 | 1 | 38 | 4 |
39	64	40	10	41	205	42	61	43	773	44	26	45	16	50	3	51	5	52	2
53	17	54	8	55	124	56	253	57	233	58	30	59	4	60	2	61	20	69	3
70	9	71	146	72	33	73	89	74	459	75	130	76	8	82	1	83	3		
87	1	97	3	98	85	99	999	100	77	101	283	102	13	103	2	115	1	116	11
117	144	118	8	128	1	129	8	130	76	131	7	143	1	157	53	158	5	172	3
173	3																		

Figure S 2. The GC-MS spectra for *pseudo*-BL (Up) and BL (Middle) obtained in the reaction mixture in comparison to the spectra found in the MS library (Down). The obtained spectra of BL matches the one found in the MS library with ca. 90% probability while it is only 15% in the case of *pseudo*-BL.

2 Catalysts characterization

Table S 1. Textural properties of the catalysts

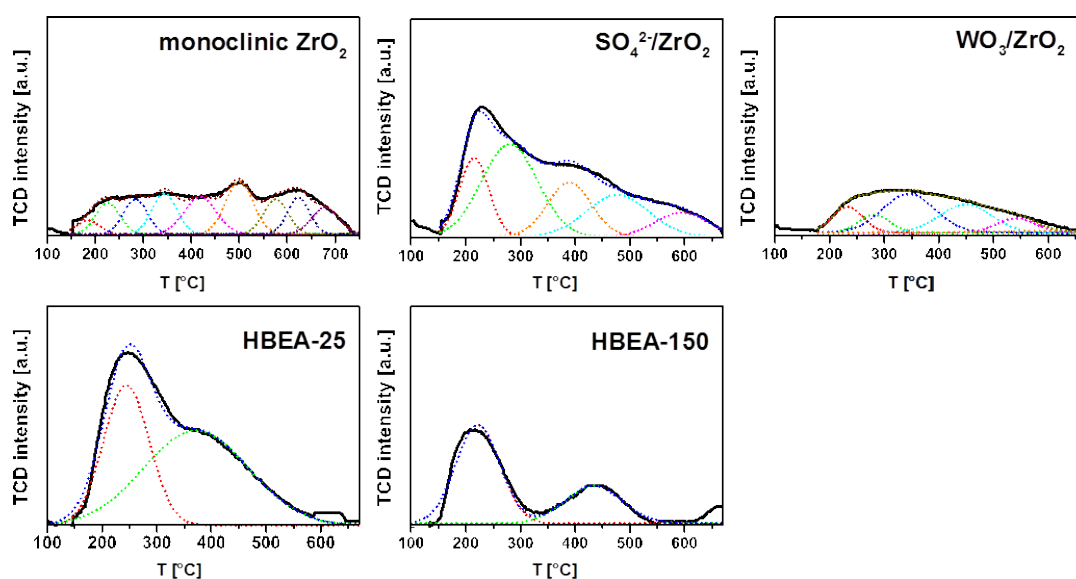| Catalyst	S_{BET} [m²/g]	V_{pore} [cm³/g]
HBEA-25	502	0.39
HBEA-150	577	0.34
ZrO2	103	0.3
SO_4^{2-}/ZrO_2	121	0.11
15%WO_3/ZrO_2	104	0.15

Figure S 3. TPD-spectra of catalysts tested in the conversion of α-AL to LAE

Table S 2. Acid sites quantification by NH₃-TPD

Catalysts	Weak acid [mmol/g]	Strong acid [mmol/g]	total acidity [mmol/g]	Weak acid [10^{-3} mmol/m²]	Strong acid [10^{-3} mmol/m²]	Total acidity [10^{-3} mmol/m²)
HBEA-25	0.17	0.26	0.43	0.035	0.052	0.087
HBEA-150	0.11	0.05	0.16	0.019	0.082	0.101
WZ	0.07	0.09	0.15	0.063	0.085	0.148
SZ	0.20	0.14	0.34	1.620	1.180	2.800
Amberlyst 36	NA	NA	5.4*	NA	NA	160**

* the data for Amberlyst-36 acidity was obtained from the supplier (SIGMA ALDRICH) not measured by NH₃-TPD

** Specific surface area of Amberlyst (data provided by the supplier) is 33 m²/g

3 Kinetics study

In order to perform kinetic studies, LA concentration is considered constant and does not influence the formation of *pseudo*-BL and BL. Then the reaction takes place consecutively through the following mechanism (as previously described by Pathway 1 in **Scheme 2**): (α-AL = AAL)

$$AAL + BuOH \overset{k_1}{\Rightarrow} pseudo{-}BL \overset{k_2}{\Rightarrow} BL \tag{1}$$

According to equation (1), the reaction rate expression for each corresponding compounds can be derived as follows:

$$\frac{d[AAL]}{dt} = -k_1[AAL][BuOH] \tag{2}$$

$$\frac{d[pseudo-BL]}{dt} = -k_2[pseudo{-}BL] + k_1[AAL][BuOH] \tag{3}$$

$$\frac{d[BL]}{dt} = k_2[pseudo{-}BL] \tag{4}$$

The reaction rate constant was solved by minimizing the sum square of the corresponding concentration obtained from the model and experimental data (through equation (5)) using solver *add-in* and the resulting values of k are summarized in Table S2:

$$S = \sum_{i=1}^{n} (C_{exp-i} - C_i)^2 \tag{5}$$

Where:

C_{exp-i} = actual concentration of compound-*i* (mol fraction of *i*)

C_i = concentration of compound-*i* obtained from the model (mol fraction of *i*)
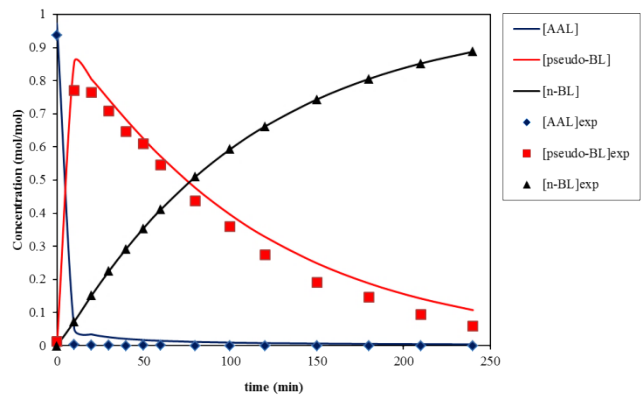
Figure S 4. Concentration profile of the addition reaction of α-AL and BuOH over A36 at 50°C
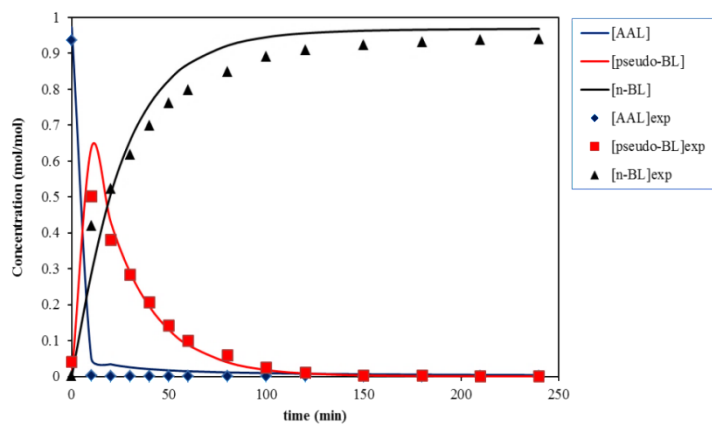
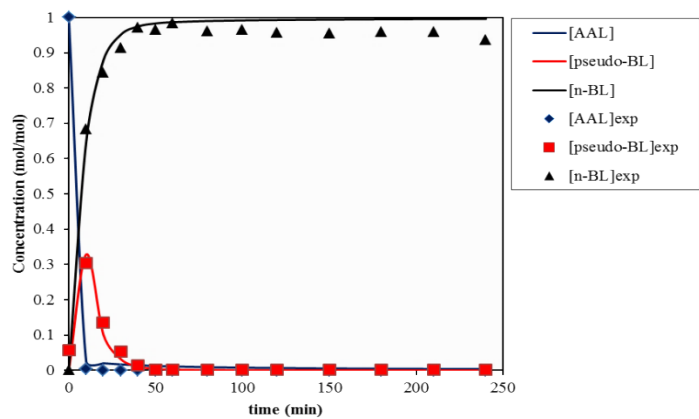**Figure S 5.** Concentration profile of the addition reaction of α-AL and BuOH over A36 at 75°C

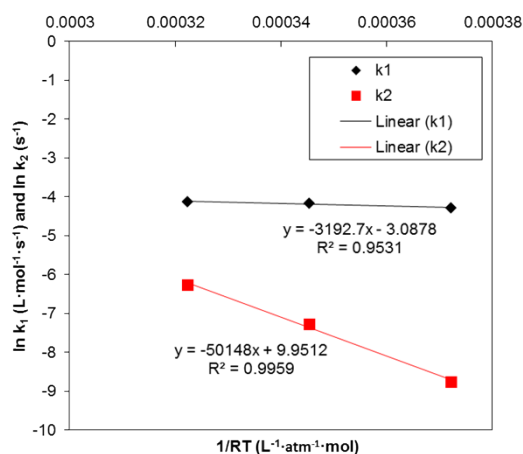**Figure S 6.** Concentration profile of the addition reaction of α-AL and BuOH over A36 at 100°C

Figure S 7. Arrhenius plot for the formation of pseudo-BL and BL

Table S 3. Reaction rate constants as a function of temperature

Temperature (°C)	k_1 (L·mol^{-1}·s^{-1})	k_2 (s^{-1})
50	0.014	0.00016
75	0.015	0.00069
100	0.016	0.00190

4 Influence of water on the addition of alcohols to α-AL

As expected, water influences the reaction system significantly. Figure S 8 shows the significant changes in the reaction outcomes in the presence of 5 and 10 mol% water with respect to α-AL.
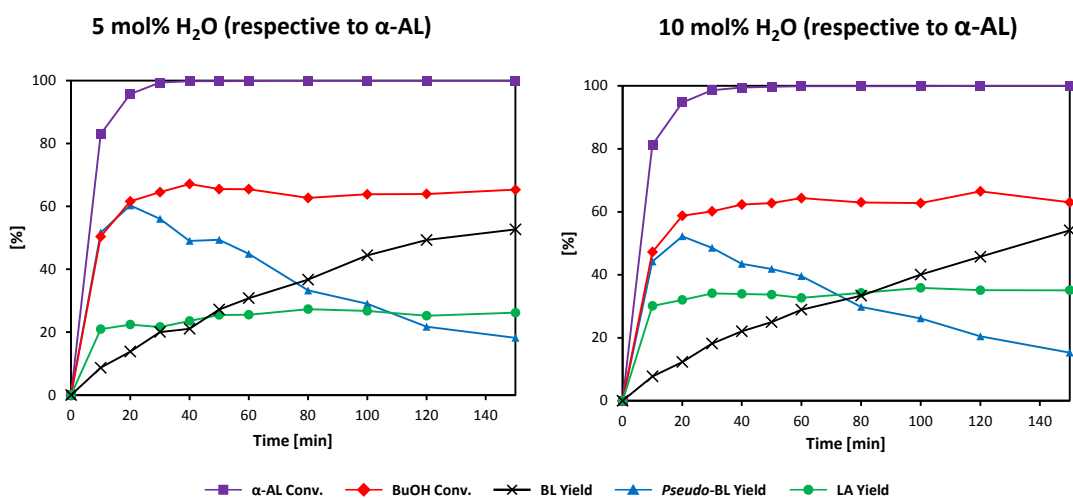
Figure S 8. Influence of 5 and 10 mol% water loading on the addition reaction of α-AL and BuOH.

- **Influence of water on the conversion of BuOH:** Interestingly, for both 5 and 10 mol% water, the conversion of BuOH reached steady-state after 40min with a maximum conversion of 60.2-64.5%. Extending the reaction time to 150 min did not significantly influence the conversion of BuOH which basically remained constant.

- **Influence of water on the conversion of α-AL:** Under water free conditions full conversion of α-AL is reached after 10 min. In the presence of water, the conversion is slowed down. Nevertheless, after 30 min complete conversion of α-AL could be achieved independent of the amount of water in the system (5 or 10 mol%).

- **Effect of water on the formation of LA:** In the absence of water only small amount of LA are present in the reaction systems (max. 10% yield, after 6 h reaction). However, the addition of water facilitates LA formation. 20.3 and 34.1 % yield of LA were observed after 30 min reaction time for an addition of 5 and 10 mol% water, respectively. Important to note, LA production basically happens in the first 10 min of reaction with minor changes for longer reaction times (LA can reach 26.1 and 35.2 % yield after 150 min reaction).

- **Effect of water on the formation of pseudo butyl levulinate (*pseudo*-BL):** In the absence of H_2O, *pseudo*-BL was rapidly generated with 42.0 % yield at very short reaction time (10 min) and then decline progressively to nearly zero at 120 min. However, water is able to delay the conversion of *pseudo*-BL to BL. The trends for the two water concentrations are nearly comparable. The highest yields of *pseudo*-BL are obtained after 20 min for both initial water concentrations. Adding 5 and 10 mol% water leads to 61.2 and 52.2% yield of *pseudo*-BL, respectively. Compared to water-free conditions, the maximum *pseudo*-BL yields are certainly higher mainly caused by the delayed transformation into BL. However, also in the presence of water the concentration of *pseudo*-BL slowly decreases and after 150 min the yield of *pseudo*-BL are only 18.2 and 15.3% *pseudo*-BL for 5 and 10 mol% water.

- **Effect of water on the formation of BL:** According to the reaction network, BL is generated consecutively after the formation *pseudo*-BL. The observed slow transformation of *pseudo*-BL causes overall low yields of BL. In line, for water free conditions 90 %yield of BL could be reached after 150 min. In contrast, only 52.7-54.1% yield of BL could be achieved for the same reaction conditions and in the presence of water.

Overall, water significantly affects the reaction. A slower conversion of α-AL, and an incomplete conversion of BuOH were observed. Concerning product formation, it is obvious that the formed LA has a negative effect on the production of esters (*pseudo*-BL and BL). The origin of hindered ester formation could be a higher activation energy of esterification compared to addition as well as the fact that esterification is limited by chemical equilibrium.