

### Supplementary material.

**Table S1** Composition of the previously described medium [20] used for preculture and batch studies

Component	Formula	Concentration in Stock solution, g L <sup>-1</sup>
<b>Mineral solution</b>		<b>33.3x</b>
Ammonium chloride	NH <sub>4</sub> Cl	100
Sodium chloride	NaCl	80
potassium chloride	KCl	10
potassium dihydrogen phosphate	KH <sub>2</sub> PO <sub>4</sub>	10
Magnesium sulfate	MgSO <sub>4</sub>	20
Calcium chloride	CaCl <sub>2</sub>	4
<b>Vitamin solution</b>		<b>100x</b>
Pyridoxine	C <sub>8</sub> H <sub>11</sub> NO <sub>3</sub>	0.01
Thiamine	C <sub>12</sub> H <sub>17</sub> ClN <sub>4</sub> OS	0.005
Riboflavin	C <sub>17</sub> H <sub>20</sub> N <sub>4</sub> O <sub>6</sub>	0.005
Calcium pantothenate	Ca(C <sub>9</sub> H <sub>16</sub> NO <sub>5</sub> ) <sub>2</sub>	0.005
Liponic acid	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	0.005
Para amino benzoic acid	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	0.005
Nicotinic acid	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.005
Vitamin B12	C <sub>72</sub> H <sub>100</sub> CoN <sub>18</sub> O <sub>17</sub> P	0.005
D-biotin	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> S	0.002
Folic acid	C <sub>19</sub> H <sub>19</sub> N <sub>7</sub> O <sub>6</sub>	0.002
2-mercapto ethane sulfonic acid	C <sub>2</sub> H <sub>6</sub> O <sub>3</sub> S <sub>2</sub>	0.02
<b>Trace element solution</b>		<b>100x</b>

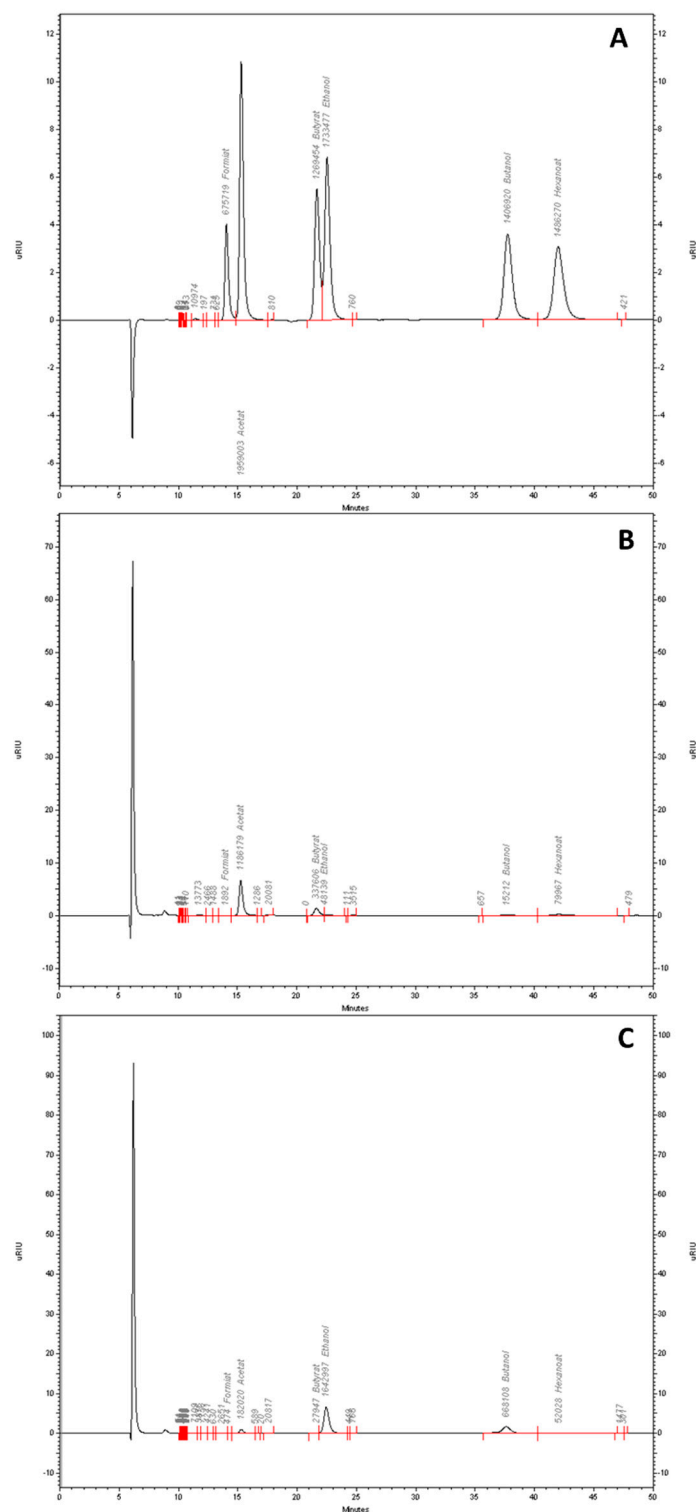
Nitrilotriacetic acid	$\text{C}_6\text{H}_9\text{NO}_6$	2.00
Manganese sulfate	$\text{MnSO}_4$	1.00
Ammonium iron sulfate	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	0.80
Cobalt chloride	$\text{CoCl}_2$	0.20
Zinc sulfate	$\text{ZnSO}_4$	0.20
Copper chloride	$\text{CuCl}_2$	0.02
Nickel chloride	$\text{NiCl}_2$	0.02
Sodium molybdate	$\text{Na}_2\text{MoO}_4$	0.02
Sodium selenate	$\text{Na}_2\text{SeO}_4$	0.02
Sodium wolframate	$\text{Na}_2\text{WO}_4$	0.02

**Medium concentration**

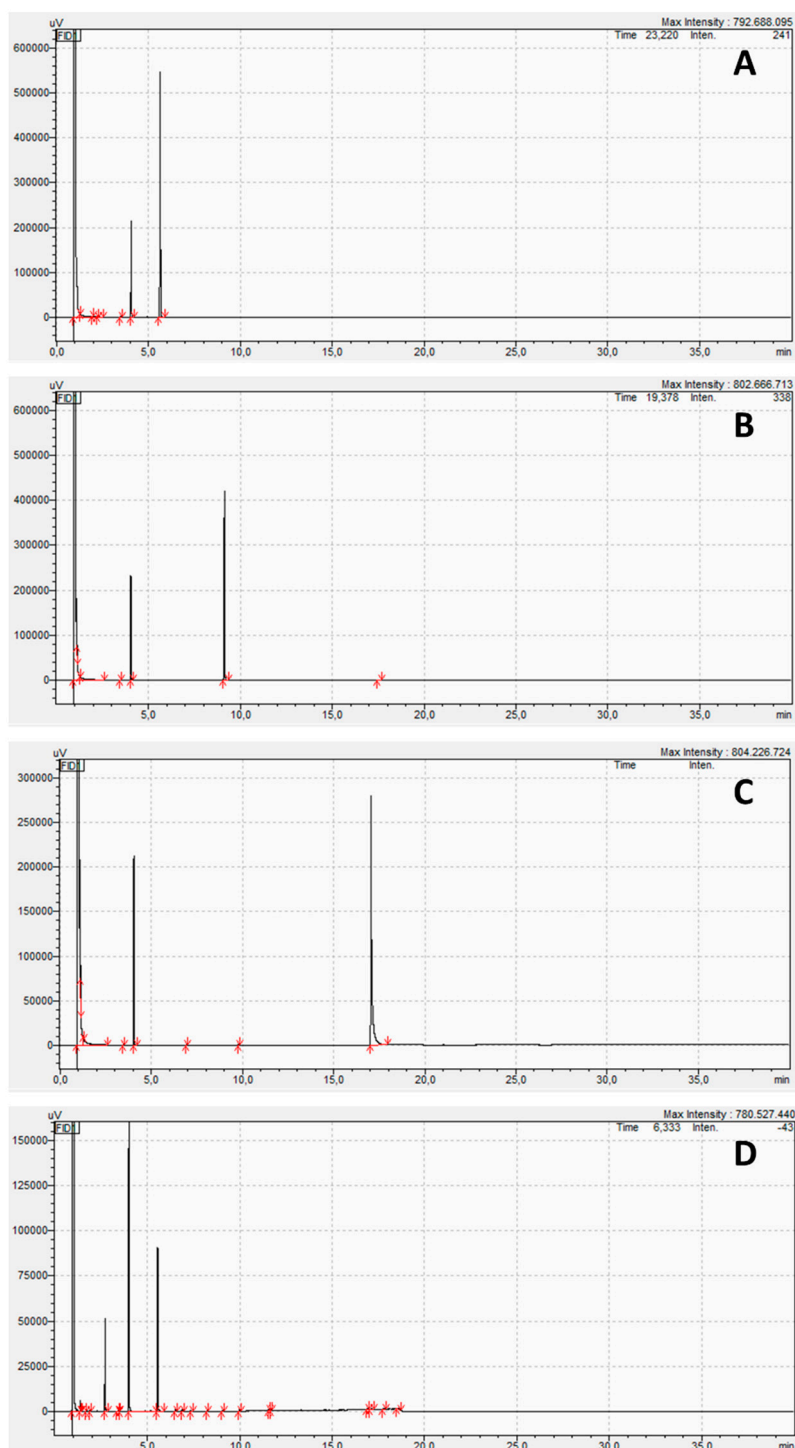
<b>Yeast extract</b>		1.0 g L <sup>-1</sup>
<b>Cysteine hydrochloride</b>	$\text{C}_3\text{H}_7\text{NO}_2\text{S HCl}$	0.5 g L <sup>-1</sup>
<b>Morpholino ethanesulfonic acid<sup>a)</sup></b>	$\text{C}_6\text{H}_{13}\text{NO}_4\text{S}$	15.0 g L <sup>-1</sup>
<b>Polypropylene glycol (1:10)<sup>b)</sup></b>		0.1 mL L <sup>-1</sup>

a) used only for heterotrophic preculture in anaerobic flasks

b) only for reactor studies



**Figure S1** Chromatograms of the organic acids and alcohols measured by HPLC (Finnigan Surveyor, Thermo Fisher Scientific, Waltham, USA) equipped with a refractive in-dex (RI) detector (Finnigan Surveyor RI Plus Detector, Thermo Fisher Scientific, Waltham, USA) and an Aminex-HPX-87H ion exchange column (Biorad, Munich, Germany). Separation of organic acids and alcohols was carried out at a constant flow rate of  $0.6 \text{ mL min}^{-1}$  of  $5 \text{ mM H}_2\text{SO}_4$  as eluent at a column temperature of  $60^\circ\text{C}$ . (A) all products; (B) sample of the first reactor after 167 h; (C) sample of the second reactor after 167 h of process time.



**Figure S2** Chromatograms of the gas chromatographic (GC) analysis, automated by using an autosampler (AOC-20s, Shimadzu Corp., Kyoto, Japan) and a GC auto-injector (AOC-20i, Shimadzu Corp., Kyoto, Japan), which took a sample volume of 5  $\mu\text{L}$  with a split of the injector of 50. The stationary phase: GC capillary column (FameWax, Restek), mobile phase (4.35  $\text{mL min}^{-1}$ ; 4.96 bar): helium. The column temperature was increased from 50  $^{\circ}\text{C}$  to 180  $^{\circ}\text{C}$  at 7  $^{\circ}\text{C min}^{-1}$  after each sample injection. After the products were separated on the GC capillary column, they were detected by a flame ionization detector (FID-2010 Plus, Shimadzu Corp., Kyoto, Japan) operated at a temperature of 250  $^{\circ}\text{C}$  with flow rates of 40  $\text{mL min}^{-1}$  ( $\text{H}_2$ ) and 400  $\text{mL min}^{-1}$  (He), respectively. (A) 1-Pentanol and 1-Hexanol; (B) 1-Pentanol and 1-Octanol; (C) 1-Pentanol and octanoate; (D) sample of the second reactor after 167 h with 1-Pentanol and 1-Hexanol. First peak is hexane.