

## ESI: *In situ* recovery of bio-based ethyl esters via hybrid extraction-distillation

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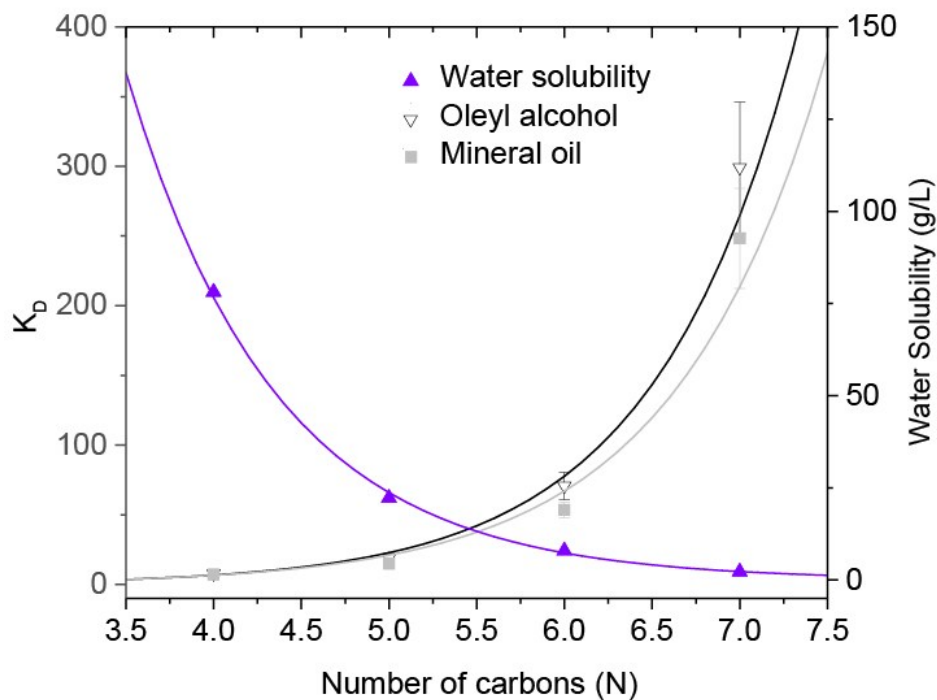
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**Table S1.** Physical properties of ethyl esters used in this study

Compound	Water solubility (g/L)	Normal boiling point (°C)
Ethyl valerate	2.2	145
Ethyl butyrate	7.9	121.1
Ethyl propionate	22.2	98.9
Ethyl acetate	78.1	77.1
Ethyl 3-hydroxypropanoate	409	187

**Table S2.** Spinning band distillation fraction purities with a reflux ratio of 1.0

DISTILLATE SAMPLE	AVERAGE VAPOR TEMP (°C)	WT. % ETHYL ACETATE	WT. % ETHYL PROPIONATE	WT. % ETHYL BUTYRATE	WT. % ETHYL VALERATE
<b>1</b>	25.7	73%	27%	0%	0%
<b>2</b>	32.7	64%	35%	1%	0%
<b>3</b>	37.7	48%	50%	2%	0%
<b>4</b>	43.2	31%	64%	5%	0%
<b>5</b>	46.0	18%	75%	7%	0%
<b>6</b>	49.5	0%	87%	13%	0%
<b>7</b>	53.2	0%	78%	22%	0%
<b>8</b>	52.6	0%	0%	100%	0%
<b>9</b>	51.5	0%	0%	74%	26%
<b>10</b>	71.1	0%	0%	25%	75%
<b>11</b>	68.6	0%	0%	0%	100%
<b>12</b>	54.2	0%	0%	0%	100%

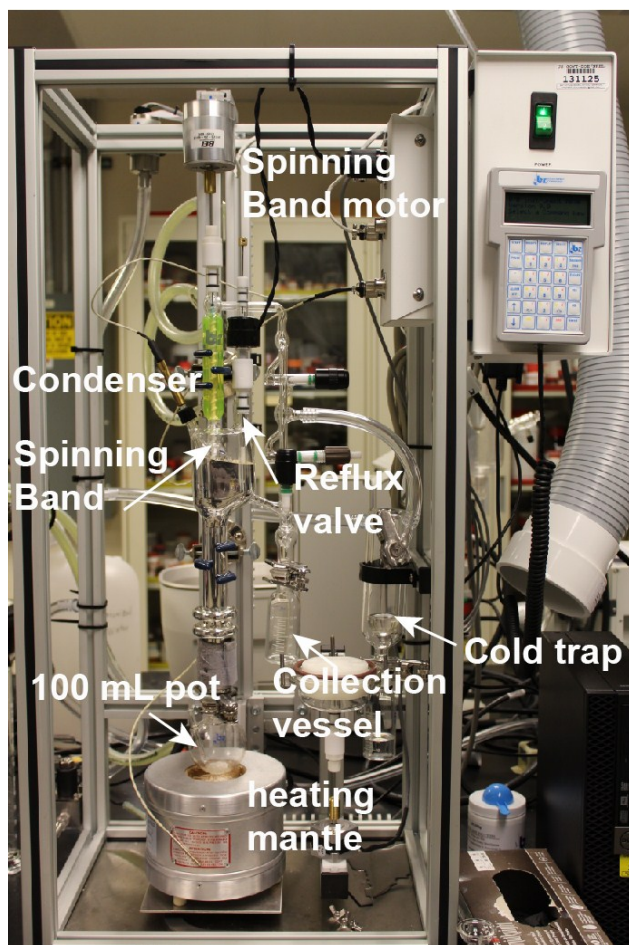


**Fig. S1** The  $K_D$  and water solubility of ethyl acetate, ethyl propionate, ethyl butyrate, and ethyl valerate are plotted against the number of carbon atoms (N) in the ester. The lines correspond to two parameter exponential fits using the following equations respectively.

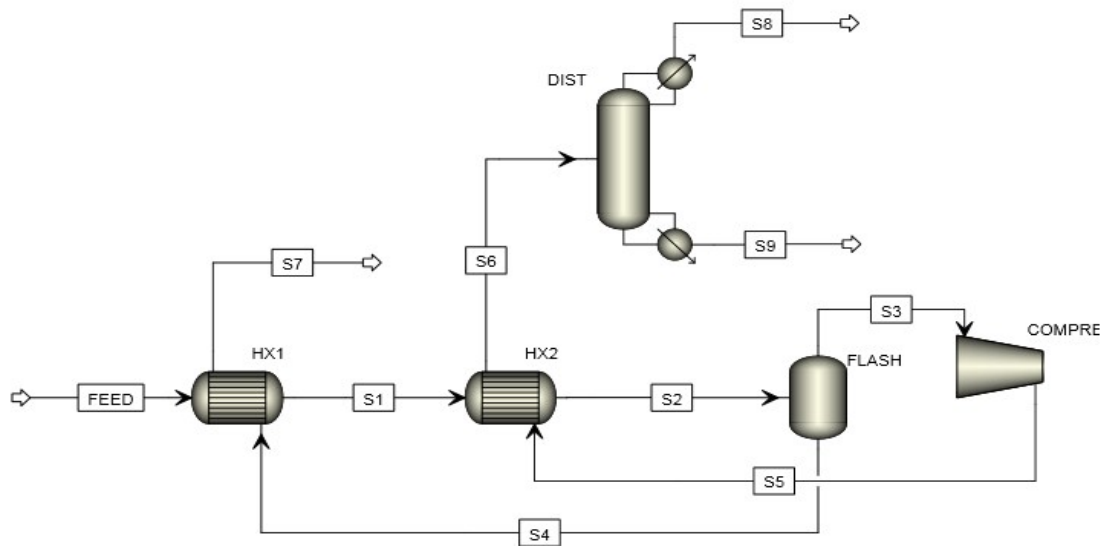
$$8350 \exp(-1.173 N) = \text{Water solubility (S1)}$$

$$A \exp(N \cdot B) = K_D \quad (\text{S2})$$

Where N is the number of carbon atoms in the ester, A is 0.050 for oleyl alcohol or 0.042 for mineral oil, and B is 1.2 for oleyl alcohol and for mineral oil.



**Fig. S2** The laboratory scale ‘spinning band’ distillation column used to separate esters from oleyl alcohol.



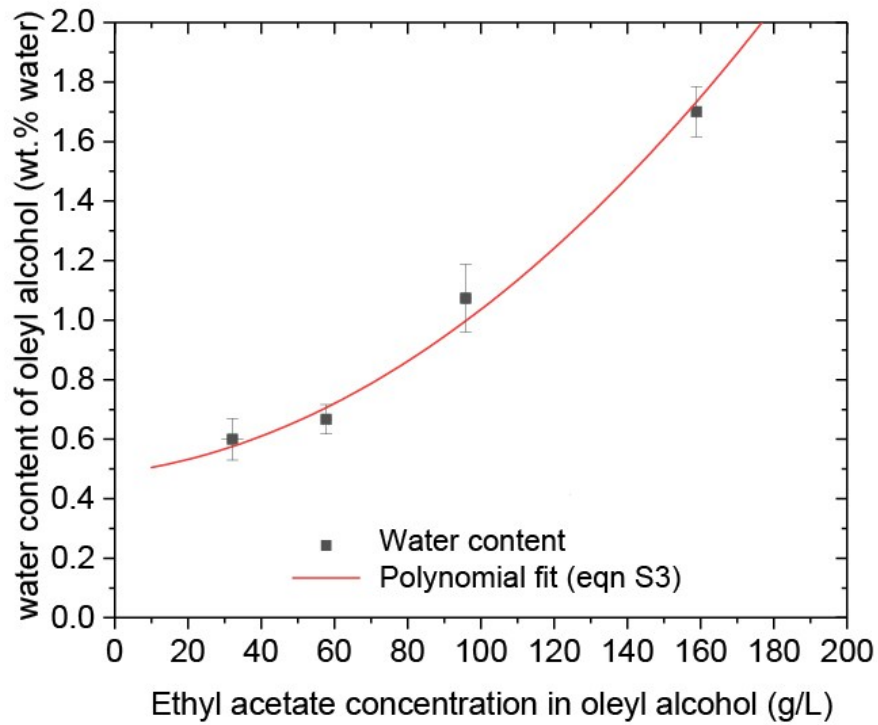
**Fig. S3** Process flow diagram for the recovery of esters from oleyl alcohol (HED-ISPR process). An additional preheater was added between the second heat exchange (HX2) and the flash vessel (FLASH) to preheat the feed stream to the flash temperature for cases where insufficient heat was recovered from the compressed flash distillate and bottoms stream. The flash was set at 0.01 atm and the temperature was varied to achieve a 95% recovery of ethyl acetate in the distillate stream (S3). The compressor was set at 5 atm and used to preheat the feed stream. Stream 6 was sent to stage 3 of a 3-stage distillation column set at 0.11 atm and a reflux ratio of 0.1. The bottoms rate was set to achieve a 99% recovery and 95% purity of esters in the distillate stream (S8). In order to not overheat Stream 1 to above the required flash vessel temperature, in some cases, a heat exchanger was used after the compressor which provided excess heat to power the reboiler of the distillation column (80% heat recovery was assumed).

**Table S3.** Mass flow rate, temperature, and pressure of streams in Fig. S3 at a feed ethyl acetate concentration of 20.7 g/L.

Streams	FEED	S1	S2	S3	S4	S5	S6	S7	S8	S9	ET-ACET
<b>Toal mass flow (kg/hr)</b>	100.0	100.0	100.0	100.0	2.5	97.4	2.5	97.4	2.5	0.5	2.0
<b>Ethyl acetate (kg/hr)</b>	2.1	2.1	2.1	2.1	2.0	0.1	2.0	0.1	2.0	0.1	1.9
<b>Oleyl alcohol (kg/hr)</b>	97.4	97.4	97.4	97.4	0.1	97.3	0.1	97.3	0.1	0.1	0.0
<b>Water (kg/hr)</b>	0.5	0.5	0.5	0.5	0.5	0.0	0.5	0.0	0.5	0.4	0.1
<b>Temperature (°C)</b>	37.0	60.5	75.8	94.2	94.2	94.2	433.8	70.5	85.8	21.6	20.5
<b>Pressure (atm)</b>	1.0	1.0	1.0	1.0	0.0	0.0	5.0	0.0	5.0	0.1	0.1

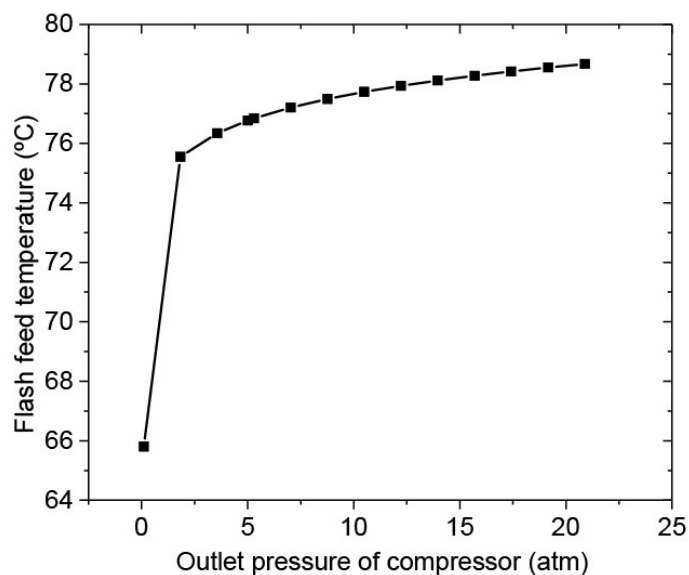
**Table S4.** Energy input of process units of Fig. S3 at a feed ethyl acetate concentration of 20.7 g/L

Process Units	Energy Input (MJ/hr)
Preheater (PREHEAT1)	4.38
Flash	1.85
Compressor	1.88
Distillation column	1.082
Total energy input	9.19

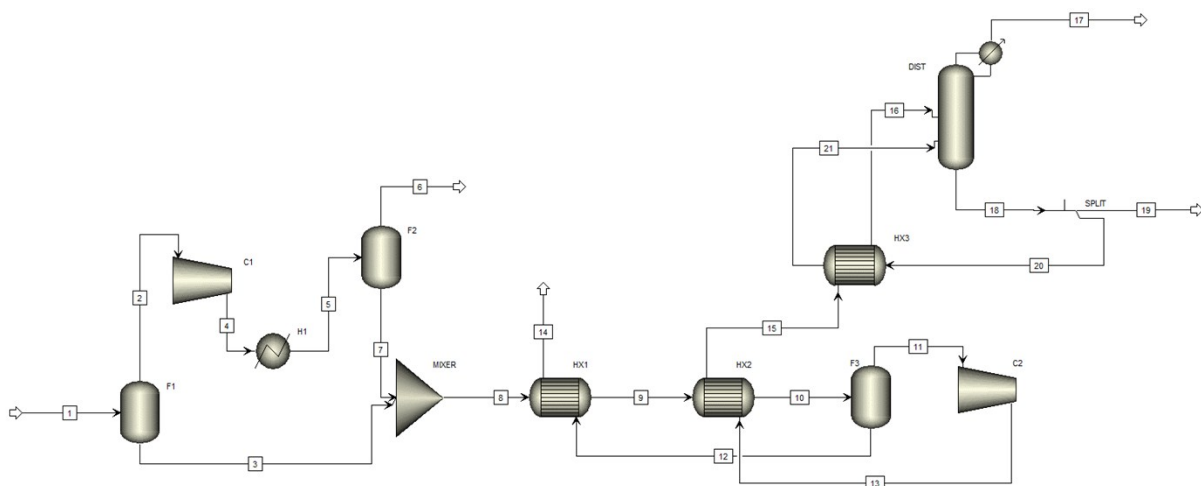


**Fig. S4** The co-extraction of water and ethyl acetate is a function of the concentration of ethyl acetate in oleyl alcohol. Karl Fisher data was fit to a polynomial (eqn. S3) to estimate the water content in feed streams with a concentration ranging from 13.9 g/L to 126 g/L ethyl acetate in oleyl alcohol.

$$4 \times 10^{-5} [ORG]_{EQ} + 0.0015 [ORG]_{EQ} + 0.49 = \text{water content (wt. \%)} \quad (\text{S3})$$



**Fig. S5** A pressure-temperature sensitivity analysis is shown for the compressor in the ISPR-HED case. In the above plot, the outlet pressure of the compressor is varied and the resultant temperature of the feed stream (S2 in Fig. S3 – the process flow diagram) after HEX2 (see Fig. S3) to the flash is shown. A maximum 5 atm pressure was set for the ISPR-HED case because further increasing the pressure adds compressor duty with insignificant temperature gains.



**Fig. S6** Aspen Plus process flow diagram with heat integration for the recovery of ethyl acetate from water. The feed stream contained varying amounts of ethyl acetate and water. The feed stream entered the flash (F1) set at 37°C and 0.1 atm. The CO<sub>2</sub> from the bioreactor was flashed off with some ethyl acetate and water in Stream 2. A compressor at 15 bar was used alongside a heat exchanger set to 20°C and 15 bar to condense the stream. Stream 5 entered a second flash (F2) set at 20°C and 1 bar in order to separate the CO<sub>2</sub> (S6) from the remaining ethyl acetate and water (S7). Stream 3 and Stream 7 were combined with a mixer before being preheated, forming a completely gas phase-free stream which is suitable for pumping through the two heat exchangers (HX 1 and HX2) before flash vessel 3. Stream 10 entering the flash was preheated via heat exchanger 1 and 2 (HX 1 and HX2). A countercurrent heat exchanger with a 10 °C minimum approach temperature was used with the shortcut calculation method. The preheated stream then entered the flash tank (F3) at 0.25 atm and the flash temperature was set to achieve a 99% recovery of ethyl acetate (optimized for minimum energy input – see Fig. S7 below). The distillate stream (S11) was then fed to a compressor at 0.31 atm. The compressed distillate stream was then used to preheat the feed stream to the flash tank and the bottoms from the distillation column (DIST) prior to entering DIST (reflux ratio varied between 0.54-2.8). A design specification of 99% recovery of ethyl acetate in the overhead was set.

**Table S5A.** Mass flow rate, temperature, and pressure of streams in Fig. S6 at a feed ethyl acetate concentration of 20 g/L.

Streams	1	2	4	5	6	8	9	10
<b>Total mass flow (kg/hr)</b>	50.5	1.8	1.8	1.8	0.5	50.0	50.0	50.0
<b>Ethyl acetate (kg/hr)</b>	1.0	0.8	0.8	0.8	0.1	0.9	0.9	0.9
<b>Water (kg/hr)</b>	49.0	0.6	0.6	0.6	0.0	49.0	49.0	49.0
<b>CO2 (kg/hr)</b>	0.5	0.5	0.5	0.5	0.4	0.1	0.1	0.1
<b>Temperature (°C)</b>	37.0	37.0	446	20.0	20.0	34.5	39.8	45.8
<b>Pressure (atm)</b>	1.0	0.1	14.8	14.8	1.2	0.1	0.1	0.1

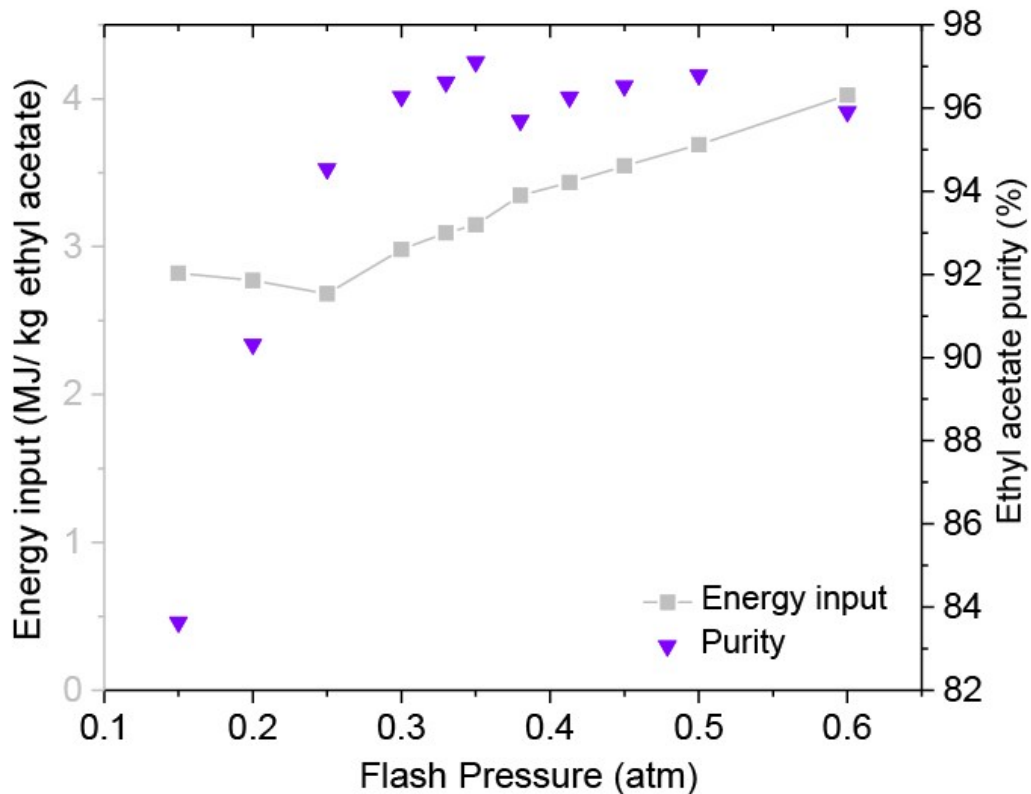
**Table S5B.** Mass flow rate, temperature, and pressure of streams in Fig. S6 at a feed ethyl acetate concentration of 20 g/L.

<b>Streams</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>	<b>18</b>	<b>19</b>
<b>Total mass flow (kg/hr)</b>	19.4	30.6	19.4	30.6	19.4	19.4	0.9	20.1	18.5
<b>Ethyl acetate (kg/hr)</b>	0.9	0.0	0.9	0.0	0.9	0.9	0.8	0.1	0.1
<b>Water (kg/hr)</b>	18.4	30.6	18.4	30.6	18.4	18.4	0.0	20.0	18.4
<b>CO2 (kg/hr)</b>	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.0	0.0
<b>Temperature (°C)</b>	65.0	65.0	76.6	49.8	55.8	55.8	12.3	46.4	46.4
<b>Pressure (atm)</b>	0.3	0.3	0.3	0.3	0.3	0.3	0.1	0.1	0.1

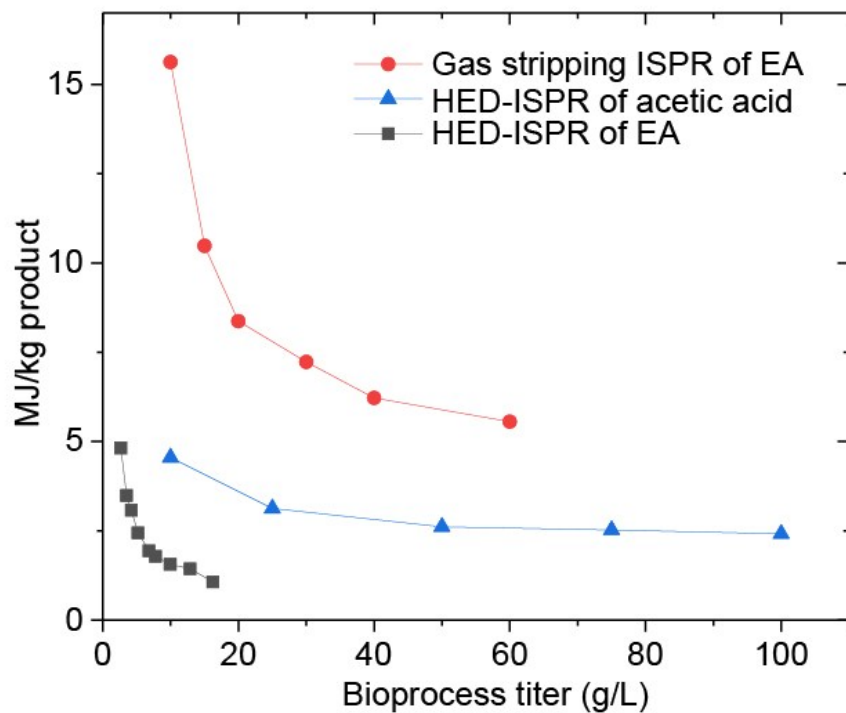
**Table S6.** Energy input of process units of Fig. S6 at a feed ethyl acetate concentration of 20 g/L

<b>Process Units</b>	<b>Energy Input (MJ/hr)</b>
Flash 1 (F1)	1.79
Flash 2 (F2)	0.09
Flash 3 (F3)	3.10
Compressor 1 (C1)	0.74
Compressor 2 (C2)	0.84
Distillation Column	0.14
<b>Total Energy Input</b>	<b>6.70</b>

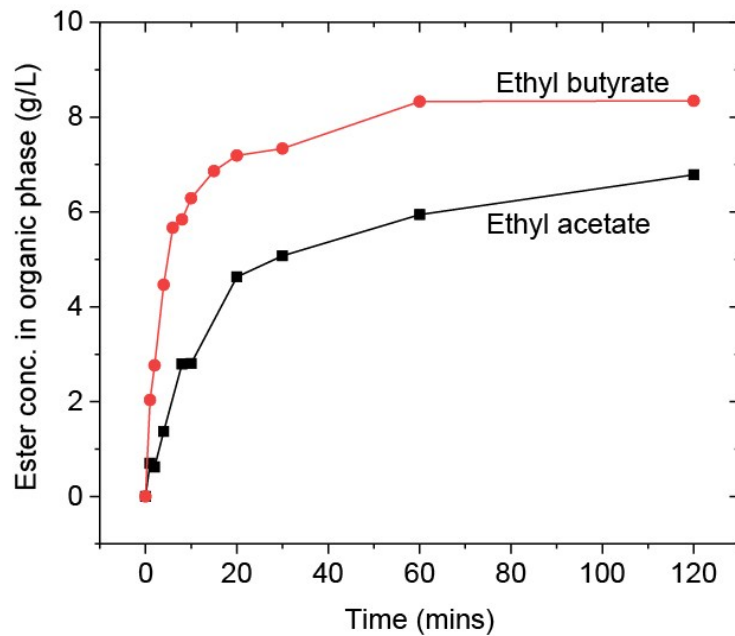




**Fig. S7** Optimization of energy input for ethyl acetate recover from an aqueous stream (gas stripping process). The flash temperature and pressure were chosen to minimize the total flash heating duty by first selecting a range of flash pressures from 0.15 atm to 0.6 atm. At each pressure, the temperature was varied to achieve 95% ethyl acetate recovery from the feed. As the flash pressure decreases, the purity of the distillate decreases and more water per ethyl acetate is flashed, which leads to an increase in energy input below 0.25 atm.



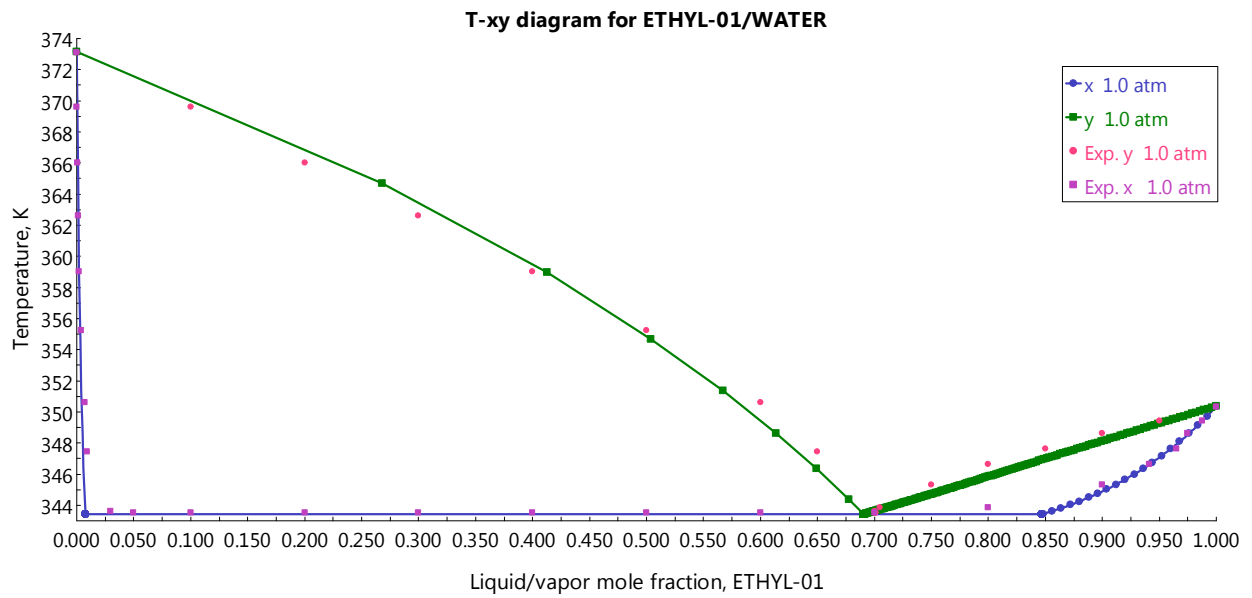
**Fig. S8** The computed heating and vacuum pump duty for three processes is shown. The HED-ISPR process for EA (ethyl acetate) recover was developed in this manuscript and the process flow diagram is shown in Fig. S3. This process was designed to produce ethyl acetate at a 95 wt.% purity and 99% recovery. The data for the HED-ISPR system for acetic acid recovery is adopted from Saboe *et al.* (2018)<sup>1</sup> and was designed to produce acetic acid at a 98 wt.% purity and 99% recovery. The gas stripping process was developed in this study (process flow diagram shown in Fig. S7) and was designed to produce ethyl acetate with the highest purity and recovery (a purity of 90 wt. % and recovery of 90 wt. % was achieved for bioprocess titers greater than 30 g/L).



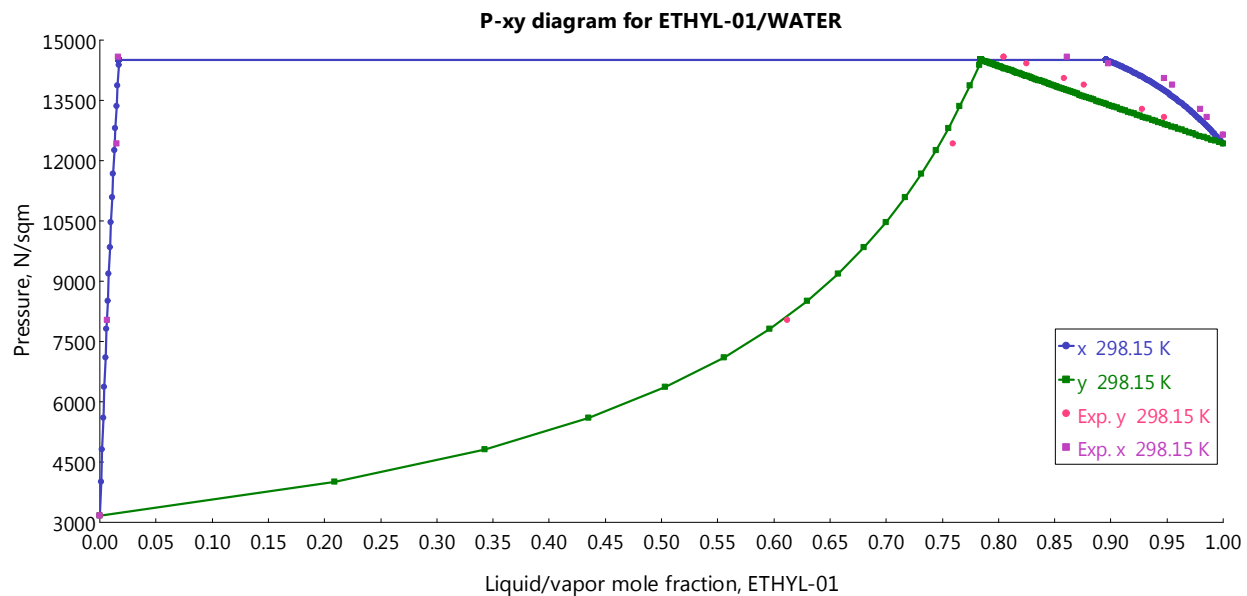
**Fig. S9** The concentration of ethyl acetate and ethyl butyrate in the organic phase are shown as a function of time. An overlayer of 50 mL of oleyl alcohol ( $5 \text{ cm}^2$  of surface area) was added to 100 mL of a solution of ethyl acetate or ethyl butyrate.

## ASPEN plus methods

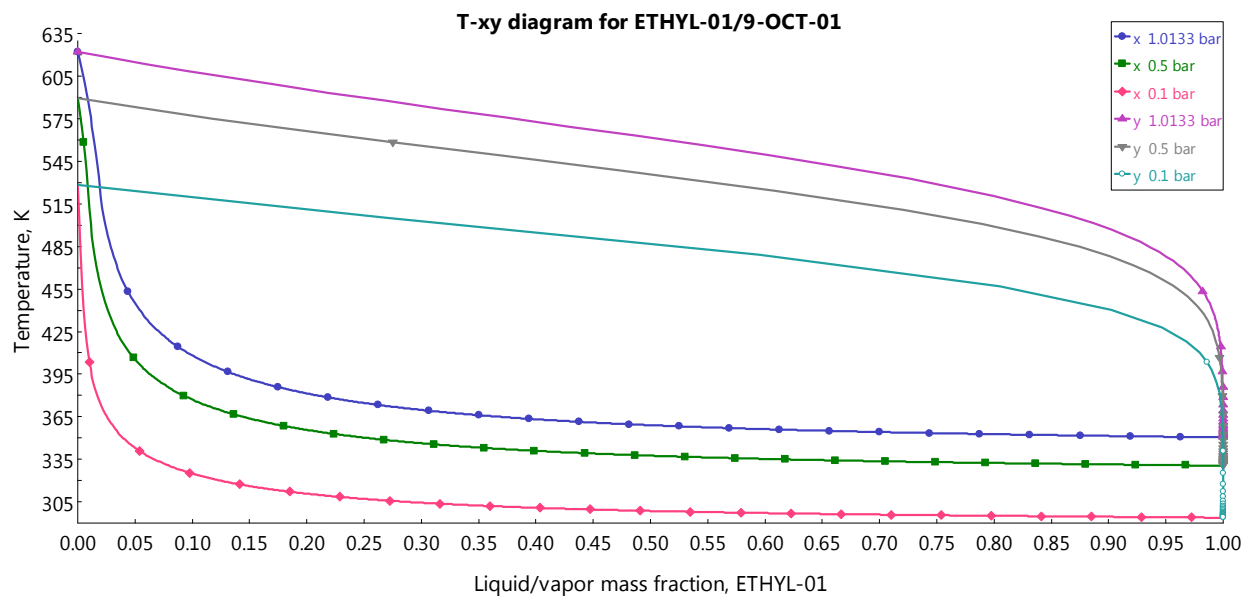
### Thermodynamic Property Methods



**Fig. S10** In the gas-stripping simulations, the NRTL property method was used for all unit operations and streams. Experimental data available in ASPENplus was regressed to fit the NRTL property method model. The T-xy diagram for the regressed NRTL model is plotted alongside experimental data above.<sup>2</sup>



**Fig. S11** A P-xy diagram for ethyl acetate/water equilibrium was also generated and fit from experimental data.<sup>3</sup>



**Fig. S12** In the ethyl acetate and oleyl alcohol (9-OCT-01) separation simulation, the UNIFAC property method was used for all unit operations and streams. A T-xy diagram for the mass fraction of ethyl acetate at various pressures was generated.

## References

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2. M. Kato, H. Konishi and M. Hirata, *J. Chem. Eng. Data*, 1970, **15**, 435-439.
3. J. Staroske and H. Schuberth, *Z. Phys. Chem.*, 1988, **269**, 572-575.