Data sets: Model solution preparation, Material balance based on experimental runs, GC-MS analysis of samples, Process model development, Process layout considerations and Energy consumption for CO_2 recycle process

Thesis: *Supercritical Fractionation Process Development: A techno-economic evaluation of retrofitting an apple aroma production facility*

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1. Model solution preparation

Description: Due to the complexity of the volatile profile for apple aroma, a 20 litre model solution was prepared comprised of selected key apple aroma compounds. The analysis of a sample obtained from a similar industrial operation was provided by Elgin Fruit Juices (Pty) Ltd. This analysis assisted with providing a typical analysis of the concentrations of the selected aroma compounds. Based on literature sources, hexanal, trans-2-hexenal and hexanol was selected to represent key apple aroma compounds present in apple aroma. The analysis indicated that the apple aroma concentrate comprised of 0.3% organic compounds. For analysis purposes, a concentration of this sample (the process is termed "folding") from 0.3% to 5% (i.e., a 17-fold, or concentration by a factor of 17) was selected to validate the process model described in this research as shown in the table below:

Compound	Mass fraction in aroma feed solution	Mass fraction in 5% organics concentration
Hexanal	9.01E-04	1.47E-02
trans-2-hexenal	3.56E-03	5.82E-02
hexanol	3.02E-01	4.93

The mass measured for the chemical in the 20 litre solution prepared were as follow:

Compound	Mass (g) in 20 litre solution	Concentration of chemical supplied (%)	Mass required (g)
Hexanal	2.97	98.8	3.00
trans-2-hexenal	11.64	98	11.88
hexanol	985.40	98	1 005.51

The model solution was prepared on the 20th of September 2021 and stored in fridge at 5°C until experiments started.

2. Experiment 1: Validation with model optimum – Material balance

Description: This experiment occurred on the 14th of October 2021 at 06:29 am. The system was purged and all thermal equipment and pressure was set to the conditions listed below. At 07:24 am the column reached a steady temperature and pressure at 07:39 am. The column was drained at 07:49 am and followed by the introduction of feed to the column through MV423. Mass of feed and raffinate (collected at the bottom of the column) was recorded for 1 hour until it established hydrodynamic steady state. Mass of feed was recorded every 5 minutes for the first 50 minutes then every 10 minutes until minute 130. Raffinate was recorded every 10 minutes for the first 50 minutes then every 15 minutes until minute 120. Feed was changed before liquid level reached the feed line at the end of 120 minutes. At 09:41 am chemical steady state evaluation of raffinate started for 105 minutes. The last 4 samples of raffinate were collected for analysis. Combined sample of extract from separators and total average sample from raffinate were collected at the end of the experiment.

2.1. Parameters for experiment 1

Temperature (^oC)	40
Pressure (bar)	70
CO_2 flow rate (kg/hr), FI200	5
Solvent density (kg/m^3)	198
Liquid feed pump rate (rpm), PI210	500

2.2. Results: Mass flow recorded of feed

Time (min)	Feed+ bottle mass (g)	Mass difference (g)	Mass flow rate (kg/hr)
0	3260.95	-	-
5	3172.27	88.68	1.06
10	3123.54	48.73	0.58
15	3036.21	87.33	1.05
20	2928.64	107.57	1.29
25	2833.93	94.71	1.14
30	2748.30	85.63	1.03
40	2540.36	207.94	1.25
45	2490.36	50.00	0.60
50	2353.85	136.51	1.64
70	2223.51	130.34	1.56
80	2027.55	195.96	1.18
90	1837.62	189.93	1.14
100	1658.23	179.39	1.08
110	1423.91	234.32	1.41

120	2802.55	-1378.64	-8.27
130	2697.35	105.20	0.63

2.3. Results: Mass flow rate recorded of raffinate

Time (min)	Raffinate + bottle mass (g)	Mass difference (g)	Mass flow rate (kg/hr)
0	572.76		
10	630.09	57.33	0.34
20	777.50	147.41	0.88
30	966.09	188.59	1.13
40	1153.82	187.73	1.13
50	1340.17	186.35	1.12
75	1590.02	249.85	1.00
90	1834.12	244.10	0.98
105	1968.46	134.34	0.54
120	2114.98	146.52	0.59

3. Experiment 2: Increasing temperature and pressure – Material balance

Description: This experiment occurred on the 14th of October 2021 at 11:15 am. At 11:27 am the system was purged and column drained. At 11:53 am column reach the set parameters as shown below and experiment started for the evaluation of hydrodynamic steady state. Mass of feed and raffinate was recorded every 15 minutes for this experiment for 120 minutes based on the evaluation of the first experiment. At 2:04 pm the evaluation of chemical steady state started and continued for 120 minutes. The last 4 samples were collected for analysis; however, it was later decided to exclude the samples for the analysis. On the other hand, combined samples of extract collected from the separators and average raffinate sample was collected for analysis (refer to Appendices for GC-MS analysis results)

3.1. Set Parameters for experiment 2

Temperature (^oC)	50
Pressure (bar)	100
CO_2 flow rate (kg/hr), FI200	5
Solvent density (kg/m^3)	384
Liquid feed pump rate (rpm), PI210	500

3.2. Results: Mass flow rate recorded of feed

Time (min)	Feed + bottle mass (g)	Mass difference (g)	Mass flow rate (kg/hr)
0	3200.77	-	-
15	3057.25	143.52	1.72
30	2912.63	144.62	1.74
45	2767.01	145.62	1.75
60	2631.38	135.63	0.54
75	2485.21	146.17	1.75
90	2341.61	143.60	1.72
105	2203.02	138.59	0.83
120	2065.37	137.65	1.65

3.3. Results: Mass flow rate recorded of raffinate

Time (min)	Raffinate + bottle mass (g)	Mass difference (g)	Mass flow rate (kg/hr)
0	985.68	-	-
15	1169.91	184.23	1.11
30	1251.03	81.12	0.49
45	1384.25	133.22	0.80
60	1518.77	134.52	0.81
75	1660.29	141.52	0.85
90	1787.71	127.42	0.76
105	1945.04	157.33	0.94
120	1288.74	129.19	0.78

4. Process Model Development

The process model was developed using the Aspen Plus® process simulator, version 10, as part of the AspenOne package by AspenTech®. Under the “Property” set-up the thermodynamic model was correlated with experimental binary vapour liquid equilibrium data (VLE) obtained from literature and the selected process model developed under the “Modelling” section as described in the thesis.

4.1. Thermodynamic correlation results

The Saove-Redlich-Kwong equation of state in combination with the Kabadi Danner mixing rules (SRKKD) was the selected thermodynamic model used in this work. The thermodynamic model was correlated with VLE obtained from literature using the “Regression” function and literature experimental data for pure components were entered into the “Properties Data PURE-COMP” form.

4.1.1. Hexanal/CO_2 Results

DRS converged in 5 iterations.

Parameter	Component i	Component j	Value (SI units)	Standard deviation
PRKBV/1	HEXANAL	CO_2	-0.42	0.02
PRKBV/2	HEXANAL	CO_2	1.44E-03	6.65E-05

At 313 K:

Mole fraction	P Exp (bar	P Est (bar)	Difference	% Diff
0.682	27.3	27.15	0.15	0.5%
0.448	45.5	45.72	-0.22	-0.5%
0.278	57.4	57.74	-0.34	-0.6%
0.224	63.6	62.34	1.26	2.0%
0.135	71.8	71.20	0.60	0.8%
0.011	27.3	27.15	0.15	0.5%
0.004	45.5	45.72	-0.22	-0.5%
0.002	57.4	57.74	-0.34	-0.6%
0.001	63.6	62.34	1.26	2.0%
0.002	71.8	71.20	0.60	0.8%

At 323 K:

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.624	34.4	34.98	-0.58	-1.7%
0.512	46.2	46.05	0.15	0.3%
0.397	58.9	57.63	1.27	2.2%
0.252	73.3	73.12	0.18	0.2%
0.120	86.4	87.85	-1.45	-1.7%
0.105	88.6	87.62	0.98	1.1%
0.009	34.4	34.98	-0.58	-1.7%
0.002	46.2	46.05	0.15	0.3%
0.001	58.9	57.63	1.27	2.2%
0.003	73.3	73.12	0.18	0.2%
0.009	86.4	87.85	-1.45	-1.7%
0.020	88.6	87.62	0.98	1.1%

At 333 K:

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.601	42.1	42.61	-0.51	-1.2%
0.515	53.4	53.78	-0.38	-0.7%
0.451	64.2	63.97	0.23	0.4%
0.281	84.0	83.81	0.19	0.2%
0.154	97.1	100.00	-2.90	-3.0%
0.004	42.1	42.61	-0.51	-1.2%
0.004	53.4	53.78	-0.38	-0.7%
0.004	64.2	63.97	0.23	0.4%
0.005	84.0	83.81	0.19	0.2%
0.022	97.1	100.00	-2.90	-3.0%

4.1.2. *Trans*-2-hexenal/CO_2 Results

DRS converged in 14 iterations

Parameter	Component i	Component j	Value (SI units)	Standard deviation
SRKKIJ/1	2-HEX-01	CO_2	4.6545	0.9331
SRKKIJ/2	2-HEX-01	CO_2	-0.0143	2.91E-03

At 313 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.793	24.6	24.59	0.01	0.1%
0.658	37.2	37.44	-0.24	-0.6%
0.545	50.7	50.87	-0.17	-0.3%
0.444	61.8	61.36	0.44	0.7%
0.399	70.1	68.17	1.93	2.8%
0.316	81.6	79.73	1.87	2.3%

0.191	98.2	98.23	-0.03	0.0%
0.009	24.6	24.59	0.01	0.1%
0.004	37.2	37.44	-0.24	-0.6%
0.004	50.7	50.87	-0.17	-0.3%
0.003	61.8	61.36	0.44	0.7%
0.003	70.1	68.17	1.93	2.8%
0.004	81.6	79.73	1.87	2.3%
0.006	98.2	98.23	-0.03	0.0%

At 323 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.812	21.6	21.17	0.43	2.0%
0.689	32.8	32.65	0.15	0.5%
0.593	41.7	41.48	0.22	0.5%
0.497	52.1	51.53	0.57	1.1%
0.370	65.9	64.16	1.74	2.6%
0.275	74.6	71.08	3.52	4.7%
0.140	89.2	83.94	5.26	5.9%
0.025	21.6	21.17	0.43	2.0%
0.004	32.8	32.65	0.15	0.5%
0.003	41.7	41.48	0.22	0.5%
0.003	52.1	51.53	0.57	1.1%
0.003	65.9	64.16	1.74	2.6%
0.003	74.6	71.08	3.52	4.7%
0.004	89.2	83.94	5.26	5.9%

At 333 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.674	30.3	29.68	0.62	2.0%
0.504	41.2	40.58	0.62	1.5%
0.402	51.0	49.92	1.08	2.1%
0.266	63.9	62.73	1.17	1.8%
0.186	70.3	74.33	-4.03	-5.7%
0.061	80.4	88.34	-7.94	-9.9%
0.007	30.3	29.68	0.62	2.0%
0.011	41.2	40.58	0.62	1.5%
0.002	51.0	49.92	1.08	2.1%
0.002	63.9	62.73	1.17	1.8%
0.002	70.3	74.33	-4.03	-5.7%
0.003	80.4	88.34	-7.94	-9.9%

4.1.3. Hexanol/CO_2 Results

DRS converged in 5 iterations

Parameter	Component i	Component j	Value (SI units)	Standard deviation
SRKKIJ/1	HEXANOL	CO_2	0.2196	5.90E-02
SRKKIJ/2	HEXANOL	CO_2	-0.0003	1.76E-04

At 293 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.3297	53.60	61.97	-8.37	-15.6%
0.5345	45.80	46.96	-1.16	-2.5%
0.7026	31.50	31.75	-0.25	-0.8%
0.7455	24.80	25.82	-1.02	-4.1%
0.8692	13.30	13.74	-0.44	-3.3%
0.9235	7.60	7.88	-0.28	-3.7%
0.0041	53.60	61.97	-8.37	-15.6%
0.0005	45.80	46.96	-1.16	-2.5%
0.0005	31.50	31.75	-0.25	-0.8%
0.0008	24.80	25.82	-1.02	-4.1%
0.0025	13.30	13.74	-0.44	-3.3%
0.0038	7.60	7.88	-0.28	-3.7%

At 303 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.2601	68.50	72.86	-4.36	-6.4%
0.3399	66.60	71.05	-4.45	-6.7%
0.4371	60.10	66.47	-6.37	-10.6%
0.5731	49.60	51.07	-1.47	-3.0%
0.5966	48.20	49.04	-0.84	-1.7%
0.7146	35.60	35.58	0.02	0.0%
0.8265	22.50	22.20	0.30	1.3%
0.8986	13.00	12.81	0.19	1.5%
0.9364	7.20	7.39	-0.19	-2.6%
0.0092	68.50	72.86	-4.36	-6.4%
0.0093	66.60	71.05	-4.45	-6.7%
0.0075	60.10	66.47	-6.37	-10.6%
0.0016	49.60	51.07	-1.47	-3.0%
0.0013	48.20	49.04	-0.84	-1.7%
0.0013	35.60	35.58	0.02	0.0%
0.0031	22.50	22.20	0.30	1.3%
0.0055	13.00	12.81	0.19	1.5%
0.0081	7.20	7.39	-0.19	-2.6%

At 333 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.1002	138.20	137.78	0.42	0.3%
0.1977	131.00	134.72	-3.72	-2.8%
0.2247	129.00	133.32	-4.32	-3.4%
0.2773	122.70	127.35	-4.65	-3.8%
0.3131	112.60	117.30	-4.70	-4.2%
0.4076	99.70	102.22	-2.52	-2.5%
0.494	89.30	89.78	-0.48	-0.5%

0.5451	81.80	81.43	0.37	0.4%
0.6102	68.30	67.50	0.80	1.2%
0.6843	56.40	54.68	1.72	3.1%
0.7707	40.90	39.09	1.81	4.4%
0.8598	25.50	23.89	1.61	6.3%
0.9313	12.10	11.34	0.76	6.2%
0.9596	6.00	6.01	-0.01	-0.1%
0.1002	138.20	137.78	0.42	0.3%
0.0205	131.00	134.72	-3.72	-2.8%
0.0189	129.00	133.32	-4.32	-3.4%
0.016	122.70	127.35	-4.65	-3.8%
0.0108	112.60	117.30	-4.70	-4.2%
0.0093	99.70	102.22	-2.52	-2.5%
0.0074	89.30	89.78	-0.48	-0.5%
0.006	81.80	81.43	0.37	0.4%
0.0041	68.30	67.50	0.80	1.2%
0.0032	56.40	54.68	1.72	3.1%
0.0026	40.90	39.09	1.81	4.4%
0.0033	25.50	23.89	1.61	6.3%
0.0047	12.10	11.34	0.76	6.2%
0.0102	6.00	6.01	-0.01	-0.1%

At 353 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.0808	158.80	160.55	-1.75	-1.1%
0.2463	144.90	157.09	-12.19	-8.4%
0.3301	139.70	141.88	-2.18	-1.6%
0.4026	125.50	124.74	0.76	0.6%
0.4727	109.30	108.37	0.94	0.9%
0.5526	97.60	94.44	3.16	3.2%
0.6153	83.70	79.71	3.99	4.8%
0.6371	71.30	70.02	1.28	1.8%
0.7171	61.00	57.15	3.85	6.3%
0.7765	48.30	44.88	3.42	7.1%
0.8391	33.40	31.24	2.16	6.5%
0.9155	17.40	16.14	1.26	7.2%
0.9704	6.90	6.05	0.85	12.3%
0.0808	158.80	160.55	-1.75	-1.1%
0.0214	144.90	157.09	-12.19	-8.4%
0.0132	139.70	141.88	-2.18	-1.6%
0.0083	125.50	124.74	0.76	0.6%
0.0066	109.30	108.37	0.94	0.9%
0.0044	97.60	94.44	3.16	3.2%
0.0035	83.70	79.71	3.99	4.8%
0.0023	71.30	70.02	1.28	1.8%
0.0021	61.00	57.15	3.85	6.3%
0.0026	48.30	44.88	3.42	7.1%
0.0031	33.40	31.24	2.16	6.5%
0.0051	17.40	16.14	1.26	7.2%

0.0176	6.90	6.05	0.85	12.3%

At 397 K

Mole fraction	P Exp (bar)	P Est (bar)	Difference	% Diff
0.1438	196.15	205.84	-9.69	-4.9%
0.1588	195.70	222.20	-26.50	-13.5%
0.2027	191.76	215.68	-23.92	-12.5%
0.2584	181.77	199.68	-17.91	-9.9%
0.3402	163.58	173.60	-10.02	-6.1%
0.4255	143.43	147.43	-4.00	-2.8%
0.4991	124.74	126.30	-1.56	-1.2%
0.5	124.50	125.88	-1.38	-1.1%
0.5481	111.51	112.06	-0.55	-0.5%
0.5906	100.89	100.96	-0.07	-0.1%
0.6352	86.15	87.10	-0.95	-1.1%
0.6948	70.56	71.26	-0.70	-1.0%
0.1132	196.15	205.84	-9.69	-4.9%
0.0943	195.70	222.20	-26.50	-13.5%
0.0753	191.76	215.68	-23.92	-12.5%
0.0427	181.77	199.68	-17.91	-9.9%
0.0304	163.58	173.60	-10.02	-6.1%
0.0221	143.43	147.43	-4.00	-2.8%
0.0212	124.74	126.30	-1.56	-1.2%
0.0187	124.50	125.88	-1.38	-1.1%
0.0155	111.51	112.06	-0.55	-0.5%
0.016	100.89	100.96	-0.07	-0.1%
0.0145	86.15	87.10	-0.95	-1.1%
0.0134	70.56	71.26	-0.70	-1.0%

4.2. Validation with literature and experimental data

A FLASH2 model was used to validate literature data obtained from Bejarano & del Valle (2017) and pilot plant experiments. The results were as follow:

4.2.1. Results: validation with data from Bejarano & del Valle (2017)

For the results from Bejarano & del Valle (2017), the feed was investigated at the original 0.175% organics concentration. The feed was then investigated at 101 (1.75%) and at 102 (17.5%) times the initial feed concentration to validate the accuracy of the model. The results obtained from the Aspen Plus® process simulator was as follow:

For 0.175% feed concentration:

T (ºC)	P (bar)	S/F ratio	Extract (kg/hr)	Raffinate (kg/hr)	Vapour mass fraction			
					Trans-2-hexenal	Hexanal	Hexanol	Water
50	80	5	1.21	98.79	4.12E-02	2.06E-02	8.24E-02	0.86
50	140	5	2.05	97.95	2.44E-02	1.22E-02	4.89E-02	0.91
50	80	15	3.29	3.29	1.52E-02	7.60E-03	3.04E-02	0.95
40	80	10	1.86	98.14	2.69E-02	1.34E-02	5.38E-02	0.91
60	110	5	2.23	97.77	2.24E-02	1.12E-02	4.49E-02	0.92
40	110	5	1.33	98.67	3.76E-02	1.88E-02	7.51E-02	0.87
40	110	15	3.65	96.35	1.37E-02	6.85E-03	2.74E-02	0.95
40	140	10	2.53	97.47	1.97E-02	9.87E-03	3.95E-02	0.93
60	80	10	3.01	96.99	1.66E-02	8.30E-03	3.32E-02	0.94
60	140	10	6.02	93.98	8.31E-03	4.15E-03	1.66E-02	0.97
50	140	15	5.80	94.20	8.62E-03	4.31E-03	1.72E-02	0.97
60	110	15	6.34	93.66	7.89E-03	3.94E-03	1.58E-02	0.97
50	110	10	4.14	95.86	1.21E-02	6.04E-03	2.41E-02	0.96

For 1.75% feed concentration

T (ºC)	P (bar)	S/F ratio	Extract (kg/hr)	Raffinate (kg/hr)	Vapour mass fraction			
					Trans-2-hexenal	Hexanal	Hexanol	Water
50	80	5	2.80	97.20	0.18	8.93E-02	0.36	0.38
50	140	5	3.62	96.38	0.14	6.91E-02	0.28	0.52
50	80	15	4.88	4.88	0.10	5.12E-02	0.20	0.64
40	80	10	3.46	96.54	0.14	7.23E-02	0.29	0.49
60	110	5	3.85	96.15	0.13	6.49E-02	0.26	0.55
40	110	5	2.90	97.10	0.17	8.61E-02	0.34	0.40
40	110	15	5.22	94.78	0.10	4.79E-02	0.19	0.66
40	140	10	4.11	95.89	0.12	6.09E-02	0.24	0.57
60	80	10	4.60	95.40	0.11	5.44E-02	0.22	0.62
60	140	10	7.58	92.42	6.60E-02	3.30E-02	0.13	0.77
50	140	15	7.37	92.63	6.79E-02	3.39E-02	0.14	0.76
60	110	15	7.96	92.04	6.28E-02	3.14E-02	0.13	0.78
50	110	10	5.70	94.30	8.77E-02	4.39E-02	0.18	0.69

For 17.5% feed concentration

T (ºC)	P (bar)	S/F ratio	Extract (kg/hr)	Raffinate (kg/hr)	Vapour mass fraction			
					Trans-2-hexenal	Hexanal	Hexanol	Water
50	80	5	18.71	81.29	0.27	0.13	0.53	0.06
50	140	5	19.33	80.67	0.26	0.13	0.52	0.09
50	80	15	20.76	20.76	0.24	0.12	0.48	0.16
40	80	10	19.62	80.38	0.25	0.13	0.51	0.11
60	110	5	20.28	79.72	0.25	0.12	0.49	0.14
40	110	5	18.63	81.37	0.27	0.13	0.54	0.06

40	110	15	20.94	79.06	0.24	0.12	0.48	0.16
40	140	10	19.86	80.14	0.25	0.13	0.50	0.12
60	80	10	20.47	79.53	0.24	0.12	0.49	0.15
60	140	10	23.19	76.81	0.22	0.11	0.43	0.25
50	140	15	23.07	76.93	0.22	0.11	0.43	0.24
60	110	15	24.25	75.75	0.21	0.10	0.41	0.28
50	110	10	21.29	78.71	0.23	0.12	0.47	0.18

4.2.2. Results: validation with experimental pilot plant data

Results obtained from the Aspen Plus® process simulator for the previously described experiments (2 parameters investigated) was as follow:

Compound	**Mass flow rate (kg/hr)**		
	Feed	**Vapour**	**Liquid**
	40ºC, 70 bar and S/F ratio 5		
Hexanal	1.47E-02	1.47E-02	5.39E-09
***Trans*-2-hexenal**	5.82E-02	5.82E-02	1.85E-08
Hexanol	4.93	4.93	6.91E-06
Water	95.00	0.70	94.30
Total	100.00	5.70	94.30
	50ºC, 100 bar and S/F ratio 5		
Hexanal	1.47E-02	1.47E-02	2.45E-09
***Trans*-2-hexenal**	5.82E-02	5.82E-02	5.63E-09
Hexanol	4.93	4.93	2.47E-06
Water	95.00	1.84	93.16
Total	100.00	6.84	93.16

4.3. Multicomponent phase behaviour

The FLASH2 model previously validated were used to investigate the multicomponent phase behaviour for the apple aroma concentrate obtained from industry. The range of parameters investigated were as follow:

Temperature (ºC)	40 – 60
Pressure (bar)	80 – 140
S/F ratio	5 – 15

4.3.1. Results: at a constant S/F ratio of 5

Temperature (°C)	Pressure (bar)	Separation Factor		
		Organics/water	Hexanal+*trans*-2-hexenal/water	Hexanal+*trans*-2-hexenal/hexanol
40	80	1.54E+08	5.26E+08	3.41
	100	2.22E+08	5.67E+08	2.56
	140	1.61E+08	4.08E+08	2.53
50	80	3.80E+07	2.00E+08	5.25
	100	8.83E+07	4.08E+08	4.62
	140	8.06E+07	3.73E+08	4.63
60	80	1.21E+07	7.34E+07	6.06
	100	2.14E+07	1.34E+08	6.24
	140	4.18E+07	6.25E+08	14.93

4.3.2. Results: at constant temperature, 40°C

Pressure (bar)	S/F	Separation Factor		
		Organics/water	Hexanal+*trans*-2-hexenal/water	Hexanal+*trans*-2-hexenal/hexanol
80	5	1.54E+08	5.26E+08	3.41
	10	1.54E+08	5.24E+08	3.42
	15	1.53E+08	5.24E+08	3.42
100	5	2.22E+08	5.67E+08	2.56
	10	2.22E+08	5.68E+08	2.55
	15	2.22E+08	5.68E+08	2.55
140	5	1.61E+08	4.08E+08	2.53
	10	1.62E+08	4.08E+08	2.53
	15	1.62E+08	4.08E+08	2.53

5. Process layout considerations

The counter-current fractionation column was to be retrofitted to a current process layout. Albeit multi-component phase behaviour indicating a near perfect separation, the model is not accurate in its predictability of experimental data. Thus, further optimisations of this model were investigated to obtain the best-suited layout for the fractionation of the apple aroma concentrate. Two process layouts were considered, because other layouts did not improve product quality nor yield. The layouts considered was as follow:

5.1. Consideration 1: CC fractionation with n number of stages

The investigation was carried out at the following parameters:

Temperature (°C)	40
Pressure (bar)	80

S/F ratio	5 – 40
Number of stages	1 – 3

The results were as follow:

For single stage (1 FLASH2 unit)

Solvent-to-feed ratio	5	10	15	20	30	40
0.30%						
Total (solvent-free)	1.15	1.99	2.84	3.68	5.36	7.05
Total Organics concentration	0.27	0.15	0.11	0.08	0.06	0.04
Water concentration	0.73	0.85	0.89	0.92	0.94	0.96
Total yield	1%	2%	3%	4%	5%	7%
Total recovery of organics	100%	100%	100%	100%	100%	100%
10%						
Total (solvent-free)	11.21	11.89	12.71	13.55	15.22	16.90
Total Organics concentration	0.89	0.84	0.79	0.74	0.66	0.59
Water concentration	0.11	0.16	0.21	0.26	0.34	0.41
Total yield	11%	12%	13%	14%	15%	17%
Total recovery of organics	100%	100%	100%	100%	100%	100%
50%						
Total (solvent-free)	51.06	52.24	53.57	55.12	56.49	57.90
Total Organics concentration	0.98	0.96	0.93	0.91	0.89	0.86
Water concentration	0.02	0.04	0.07	0.09	0.11	0.14
Total yield	0.51	0.52	0.54	0.55	0.56	0.58
Total recovery of organics	1.00	1.00	1.00	1.00	1.00	1.00
90%						
Total (solvent-free)	3.22	7.52	11.51	15.22	22.07	28.41
Total Organics concentration	0.57	0.60	0.62	0.65	0.70	0.73
Water concentration	0.43	0.40	0.38	0.35	0.30	0.27
Total yield	0.03	0.08	0.12	0.15	0.22	0.28
Total recovery of organics	0.02	0.05	0.08	0.11	0.17	0.23

For two stages (2 FLASH2 units)

Solvent-to-feed ratio	5	10	15	20	30	40
0.30%						
Total (solvent-free)	1.15	1.99	2.84	3.68	5.36	7.05
Total Organics concentration	0.27	0.15	0.11	0.08	0.06	0.04
Water concentration	0.73	0.85	0.89	0.92	0.94	0.96
Total yield	1%	2%	3%	4%	5%	7%
Total recovery of organics	100%	100%	100%	100%	100%	100%
10%						
Total (solvent-free)	11.21	11.89	12.71	13.55	15.22	16.90
Total Organics concentration	0.89	0.84	0.79	0.74	0.66	0.59
Water concentration	0.11	0.16	0.21	0.26	0.34	0.41

Total yield	11%	12%	13%	14%	15%	17%
Total recovery of organics	100%	100%	100%	100%	100%	100%
50%						
Total (solvent-free)	51.06	52.24	53.57	55.12	56.49	57.90
Total Organics concentration	0.98	0.96	0.93	0.91	0.89	0.86
Water concentration	0.02	0.04	0.07	0.09	0.11	0.14
Total yield	0.51	0.52	0.54	0.55	0.56	0.58
Total recovery of organics	1.00	1.00	1.00	1.00	1.00	1.00
90%						
Total (solvent-free)	3.31	7.93	12.34	16.43	23.61	29.90
Total Organics concentration	0.55	0.56	0.57	0.59	0.64	0.69
Water concentration	0.45	0.44	0.43	0.41	0.36	0.31
Total yield	0.03	0.08	0.12	0.16	0.24	0.30
Total recovery of organics	0.02	0.05	0.08	0.11	0.17	0.23

For three stages (3 FLASH2 units)

Solvent-to-feed ratio	5	10	15	20	30	40
0.30%						
Total (solvent-free)	1.15	1.99	2.84	3.68	5.36	7.05
Total Organics concentration	0.27	0.15	0.11	0.08	0.06	0.04
Water concentration	0.73	0.85	0.89	0.92	0.94	0.96
Total yield	1%	2%	3%	4%	5%	7%
Total recovery of organics	100%	100%	100%	100%	100%	100%
10%						
Total (solvent-free)	11.21	11.89	12.71	13.55	15.22	16.90
Total Organics concentration	0.89	0.84	0.79	0.74	0.66	0.59
Water concentration	0.11	0.16	0.21	0.26	0.34	0.41
Total yield	11%	12%	13%	14%	15%	17%
Total recovery of organics	100%	100%	100%	100%	100%	100%
50%						
Total (solvent-free)	51.06	52.24	53.57	55.12	56.49	57.90
Total Organics concentration	0.98	0.96	0.93	0.91	0.89	0.86
Water concentration	0.02	0.04	0.07	0.09	0.11	0.14
Total yield	0.51	0.52	0.54	0.55	0.56	0.58
Total recovery of organics	1.00	1.00	1.00	1.00	1.00	1.00
90%						
Total (solvent-free)	3.32	8.01	12.59	16.94	24.32	30.44
Total Organics concentration	0.55	0.55	0.55	0.57	0.62	0.68
Water concentration	0.45	0.45	0.45	0.43	0.38	0.32
Total yield	0.03	0.08	0.13	0.17	0.24	0.30
Total recovery of organics	0.02	0.05	0.08	0.11	0.17	0.23

Sensitivity analysis for optimum conditions

For the sensitivity analysis the following range of parameters was investigated:

Temperature (°C)	40 – 80
Pressure (bar)	70 – 110

The results were as follow:

T (°C)	P (bar)	Mass flow rate (kg/hr)			
		Water	**Hexanol**	**Hexanal**	***Trans*-2-hexenal**
40	70	0.67	0.30	9.01E-04	3.56E-03
40	80	0.85	0.30	9.01E-04	3.56E-03
40	90	1.25	0.30	9.01E-04	3.56E-03
40	100	1.17	0.30	9.01E-04	3.56E-03
40	110	1.16	0.30	9.01E-04	3.56E-03
50	70	0.95	0.30	9.01E-04	3.56E-03
50	80	1.04	0.30	9.01E-04	3.56E-03
50	90	1.23	0.30	9.01E-04	3.56E-03
50	100	1.63	0.30	9.01E-04	3.56E-03
50	110	1.98	0.30	9.01E-04	3.56E-03
60	70	1.36	0.30	9.01E-04	3.56E-03
60	80	1.42	0.30	9.01E-04	3.56E-03
60	90	1.54	0.30	9.01E-04	3.56E-03
60	100	1.74	0.30	9.01E-04	3.56E-03
60	110	2.06	0.30	9.01E-04	3.56E-03
70	70	1.95	0.30	9.01E-04	3.56E-03
70	80	1.97	0.30	9.01E-04	3.56E-03
70	90	2.04	0.30	9.01E-04	3.56E-03
70	100	2.18	0.30	9.01E-04	3.56E-03
70	110	2.40	0.30	9.01E-04	3.56E-03
80	70	2.76	0.30	9.01E-04	3.56E-03
80	80	2.73	0.30	9.01E-04	3.56E-03
80	90	2.76	0.30	9.01E-04	3.56E-03
80	100	2.86	0.30	9.01E-04	3.56E-03
80	110	3.01	0.30	9.01E-04	3.56E-03

5.2. Consideration 2: Recycle of extract

For the recycle of the vapour (i.e., extract), three stages was considered due to the absence of organics in liquid phase albeit it comprising insignificant quantities for less stages. The process layout was investigated at a variation in the split fraction at 40°C, 70 bar and S/F ratio of 5. The results were as follow:

Split fraction	Vapour mass fraction			
	Water	**Hexanal**	***Trans*-2-hexenal**	**Hexanol**
0.1	0.845	9.005E-04	3.563E-03	3.016E-01
0.2	0.845	9.006E-04	3.563E-03	3.017E-01
0.3	0.845	9.006E-04	3.563E-03	3.017E-01
0.4	0.845	9.006E-04	3.563E-03	3.017E-01
0.5	0.845	9.006E-04	3.563E-03	3.017E-01
0.6	0.845	9.006E-04	3.563E-03	3.017E-01
0.7	0.845	9.006E-04	3.563E-03	3.017E-01
0.8	0.845	9.006E-04	3.563E-03	3.017E-01
0.9	0.845	9.006E-04	3.563E-03	3.017E-01

The predictability of the FLASH2 was further investigated with a FLASH3 model for the multicomponent phase behaviour to investigate the accuracy of the model. The results obtained through the use of the “Sensitivity Analysis” using the Aspen Plus® process simulator was as follow:

T (ºC)	P (bar)	Mass flow rate (kg/hr)			
		Water	**Hexanol**	**Hexanal**	***Trans*-2-hexenal**
40	70	0.68	0.30	9.01E-04	3.56E-03
40	80	0.85	0.30	9.01E-04	3.56E-03
40	90	-	-	-	-
40	100	-	-	-	-
40	110	-	-	-	-
50	70	0.96	0.30	9.01E-04	3.56E-03
50	80	1.05	0.30	9.01E-04	3.56E-03
50	90	1.24	0.30	9.01E-04	3.56E-03
50	100	1.65	0.30	9.01E-04	3.56E-03
50	110	0.00	0.00	0.00E+00	0.00E+00
60	70	1.38	0.30	9.01E-04	3.56E-03
60	80	1.44	0.30	9.01E-04	3.56E-03
60	90	1.55	0.30	9.01E-04	3.56E-03
60	100	1.76	0.30	9.01E-04	3.56E-03
60	110	2.07	0.30	9.01E-04	3.56E-03
70	70	1.98	0.30	9.01E-04	3.56E-03
70	80	1.99	0.30	9.01E-04	3.56E-03
70	90	2.07	0.30	9.01E-04	3.56E-03
70	100	2.21	0.30	9.01E-04	3.56E-03
70	110	2.42	0.30	9.01E-04	3.56E-03
80	70	2.80	0.30	9.01E-04	3.56E-03
80	80	2.76	0.30	9.01E-04	3.56E-03
80	90	2.79	0.30	9.01E-04	3.56E-03
80	100	2.89	0.30	9.01E-04	3.56E-03
80	110	3.04	0.30	9.01E-04	3.56E-03

6. Economic evaluation

An economic evaluation was performed on the full CO2 recycle process for the optimum process layout (single FLASH2) for the energy consumption. The parameter selected for each process unit was as follow:

Unit	Conditions
Cooler (heater)	14.27^{o}C and 50 bar
Pump	70 bar discharge pressure
Heater (heater)	40°C and 70 bar
Column (FLASH2)	40°C and 70 bar
Heater after column (heater)	50°C and 70 bar
Separator (FLASH2)	40°C and 50 bar

The CO2 recycle process represented the process in the pilot plant described in Chapter 3 of this study. The units were interlinked based on that layout. The energy consumption for each unit obtained from the Aspen Plus® process simulator is shown below:

Unit	Energy (W)
Cooler	-7.65E+06
Heater	6.37E+06
HX after col	2.36E+03
Column	42.10
Separator	2.53E+06
Pump	950.16

The energy consumption presented in this work was based on MJ/kg product. The energy consumption was further evaluated based on the CO2 recycled into the process based on the units that had the largest energy consumption and the results were as follow:

Recycle fraction	Energy (W)		
	Cooler	Separator	Heater
0.05	-3.44E+07	1.01E+07	2.55E+07
0.1	-1.66E+07	5.06E+06	1.27E+07
0.15	-1.06E+07	3.37E+06	8.50E+06
0.2	-7.67E+06	2.53E+06	6.37E+06
0.25	-5.88E+06	2.02E+06	5.10E+06
0.3	-4.69E+06	1.69E+06	4.25E+06
0.35	-3.84E+06	1.45E+06	3.64E+06
0.4	-3.21E+06	1.27E+06	3.19E+06
0.45	-2.71E+06	1.13E+06	2.83E+06
0.5	-2.31E+06	1.01E+06	2.55E+06

Appendices

Gas chromatography coupled with Mass Spectroscopy (GC-MS) analysis results

All GC-MS analysis was carried out on a Thermo TSQ 8000 coupled to a Thermo Trace 1300 GC. The headspace of the samples was analysed with a PDMS/DVB/Carboxen SPME fibre (grey). The analysis was done as follow:

- For hexanal: 200 µl of sample was pipetted into 5 ml MQ water and then extracted with 2 ml diethyl ether.
- For trans-2-hexenal: 20 µl of the samples for 01, 02 and FEED was pipetted into 5 ml MQ water and then extracted with 2 ml diethyl ether. While for samples 03 – 08, 200 µl of sample was pipetted into 5 ml MQ water.
- For hexanol: 20 µl of the samples for 01, 02 and FEED was pipetted into 5 ml MQ water and then extracted with 2 ml diethyl ether. While for samples 03 – 08, 200 µl of sample was pipetted into 5 ml MQ water.

Sample number	**Sample Description**	**Concentration (mg/g)**		
		Hexanal	***Trans*-2-hexenal**	**Hexanol**
FEED sample		0.834	1.631	42.997
01	Extract from exp 1	19.711	60.106	929.505
02	Extract from exp 2	4.650	2.804	56.359
03	Average raffinate exp 1	0.355	0.762	46.553
04	Average raffinate exp 2	0.156	not detected	12.328
05	Steady state evaluation of raffinate at 30 min exp 1	0.326	not detected	12.893
06	Steady state evaluation of raffinate at 45 min exp 1	0.172	not detected	13.362
07	Steady state evaluation of raffinate at 60 min exp 1	0.257	not detected	14.234
08	Steady state evaluation of raffinate at 75 min exp 1	0.229	not detected	11.131