Electronic Supplementary Material (ESI) for Green Chemistry.

Achieving Absolute Sustainability Across Integrated Industrial Networks- A Case Study on the Ammonia Process†.

Nicholas Samaroo[a], Natalia Koylass[a], Miao Guo*[b], and Keeran Ward*[a]

[a]Department of Chemical Engineering, University of the West Indies, St. Augustine, Trinidad and Tobago.

[b]Department of Engineering, King's College London, Strand Campus, United Kingdom, WC2R 2LS

Telephone: 1-868-730-1980; keeran.ward@sta.uwi.edu*; +44 (0) 7726 479669; miao.guo@kcl.ac.uk*

Electronic Supplementary Information (ESI)†

1.0 Mass and Energy Balances

Table S1 below gives the plant efficiencies for viable pathways considered in the NH_3 - CO_2 integrated eco-park. Using **Equation 1 (main article)**, plant efficiencies were calculated from the input (natural gas fuel, feedstock and electricity) and output (NH_3, Urea, UAN, Mel, MeOH and purge gas fuel) flows.

Table S1: Summary of mass and energy balances for the production of 1 kg of NH_3 across eco-park design

	Unit[b]	BAU	BAU + Urea + MeOH	BAU + Urea	BAU + Urea + UAN + MeOH	BAU + Urea + UAN	BAU + Urea + Mel + MeOH	BAU + Urea + Mel	BAU + Urea + UAN + Mel + MeOH	BAU + Urea + UAN + Mel
INPUTS										
Natural gas (fuel)	**kg**	0.34	1.81	0.87	10.18	4.81	1.81	0.88	10.22	4.92
Natural gas (fuel)	**MJ[a]**	16.90	89.10	43.15	87.02	41.08	89.45	43.51	87.37	42.03
Natural gas (feedstock)	**kg**	0.63	3.57	1.14	20.58	6.61	3.57	1.14	20.58	6.61
Natural gas (feedstock)	**MJ[a]**	31.17	175.91	56.47	175.91	56.47	175.91	56.47	175.91	56.47
Process Water	**kg**	0.88	5.34	2.41	49.48	32.55	6.40	3.46	55.59	38.65
Electricity demand	**MW x 10^3**	0.02	0.69	0.55	4.35	3.54	0.75	0.61	4.69	3.88
TOTAL Duty	***MJ***	48.13	267.51	101.62	265.65	99.76	268.07	102.18	266.21	100.93
OUTPUTS										
Ammonia	**kg**	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	MJ[a]	18.60	18.60	18.60	3.22	3.22	18.60	18.60	3.22	3.22
Purge gas	**kg**	0.14	1.40	0.26	8.07	1.50	1.40	0.26	8.07	1.50
	MJ[a]	1.02	30.84	1.85	30.84	1.85	30.84	1.85	30.84	1.85
UAN	**kg**	0.00	0.00	0.00	24.45	24.45	0.00	0.00	24.45	24.45
	MJ[a]	0.00	0.00	0.00	23.05	23.05	0.00	0.00	23.05	23.05
Melamine	**kg**	0.00	0.00	0.00	0.00	0.00	0.18	0.18	1.02	1.02
	MJ[a]	0.00	0.00	0.00	0.00	0.00	0.15	0.15	0.15	0.15
Process CO_2	**kg**	1.23	0.00	1.01	0.00	5.81	0.00	1.01	0.00	5.81
	MJ	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	**kg**	0.00	1.63	1.63	0.00	0.00	1.39	1.39	0.00	0.00
	MJ[a]	0.00	8.50	8.50	0.00	0.00	7.23	7.23	0.00	0.00
MeOH	**kg**	0.00	4.92	0.00	28.41	0.00	4.92	0.00	28.41	0.00
	MJ[a]	0.00	98.05	0.00	98.05	0.00	98.05	0.00	98.05	0.00
TOTAL DUTY	***MJ***	19.62	155.99	28.96	155.16	28.12	154.87	27.83	155.32	28.28
Efficiency	***%***	40.77%	58.31%	28.49%	58.41%	28.19%	57.77%	27.24%	58.34%	28.02%

[a]Energy load calculated using the net heating value estimated from Aspen Plus.

2.0 Economic Analysis

2.1 Total Capital Investment (TCI)

For each process considered within the integrated eco-park, the total capital cost was evaluated from current process data[1-5] and scaled to capacity using the six-tenths rule[6] and inflated using the Chemical Engineering Plant Cost Indices (CEPCI)[7-10] (**Eq.1-2**). All costs were scaled to 2019 using CEPCI.

$$C_B = C_A\left(\frac{S_B}{S_A}\right)^{0.6} \tag{1}$$

$$C_2 = C_A\left(\frac{S_B}{S_A}\right)^{0.6} \times \frac{I_2}{I_1} \tag{2}$$

Where $C_{A,\ B}$ is the TCI for plant A and B respectively, $S_{A,\ B}$ is the capacity for plants A and B respectively, C_2 is the actual TCI for desired process, $I_{1,\ 2}$ are the CEPCI for the base year for the known process and the year desired respectively.

2.2 Fixed Capital Investment (FCI)

FCI was given as a function of the TCI and the working capital (WC), which was taken to be 15% of the FCI[11] by **Eq. 3-4.** ***Table S2*** gives the FCI for each viable pathway considered.

$$FCI = TCI - WC \tag{3}$$

$$FCI = \frac{TCI}{1.15} \tag{4}$$

Table S2: Overview of parameters used to calculate FCI for each scenario

Process	Existing Process TCI, C_A [$MM US]	Existing Plant Capacity, S_A [tonne/day]	Actual Plant Capacity, S_B [tonne/day]	Base Process TCI, C_B [$MM US]	CEPCI Base Year, I_1	CEPCI 2019, I_2	Actual Process TCI, C_2 [$MM US]	FCI [$MM US]
Ammonia (BAU)[2]	665	1220	1850	853.7	558.3	619.2	946.8	823.3
Ammonia/ Urea[1]	943	3610	3518	928.6	558.3	619.2	1029.9	-
Urea*	-	-	1668	-	558.3	619.2	83.1	72.3
UAN[5]	178	1106	4326	402.8	558.3	619.2	446.7	388.5
Mel[3]	350	182	180	347.9	532.9	619.2	404.2	351.5
MeOH[4]	700	4848	5027	715.4	536.4	619.2	825.8	718.1

**TCI for Urea plant was calculated by subtracting combined NH_3/Urea plant from NH_3(BAU) plant.*

2.3 Operating Cost (OPEX)

To calculate the total operating costs, utility costs (cooling water, steam, electricity and process water) were obtained from Turton et. al[12] and raw material costs (natural gas) as well as product values were based on global market trends in 2019. Electricity rates were obtained from a local supplier[13].

Operating labor costs was also calculated by establishing key unit operations within each integrated network, according to **Eq. 5- 6** from Turton et al[12] and with fixed cost allocations taken from Sinnot and Towler[11].

$$No\ of\ operators = [6.29 + (No.of\ equipment \times 0.23)]^{0.5} \tag{5}$$

$$Labour\ costs = (Approximate\ No.of\ operators \times 4.5) \times 66910 \times 1.19 \tag{6}$$

2.4 Return on Investment (ROI)

The ROI metric was utilized as an economic indicator to evaluate the economic viability of the various pathways - results given in ***Table S3***.

Table S3: Parameters utilized to calculate ROI for each pathway

Scenario	Annual Sales [$ MM US/year]	Fixed Cost [$ MM US/year]	Total Operating Cost [$ MM US/year]	ROI [%]
BAU	174	158	224	0.17
BAU + Urea + MeOH	885	312	523	19
BAU + Urea	245	174	257	3
BAU + Urea + UAN + MeOH	957	387	600	16
BAU + Urea + UAN	316	249	335	3
BAU + Urea + Mel + MeOH	927	380	593	15
BAU + Urea + Mel	287	243	328	2
BAU + Urea + UAN + Mel + MeOH	1021	456	670	14
BAU + Urea + UAN + Mel	381	318	405	3

Sample Calculation of ammonia production capacity of 1850 MTPD operational costs for 2019. Using equation 2:

$$C_{2019} = C_{2017}\left(\frac{S_{1850}}{S_{1220}}\right)^{0.6} \times \frac{619.2}{558.3}$$

Average OPEX for the natural gas ammonia production facility (C_{2017}) in accordance with literature = US $265/tonne.

OPEX for an 1850 MTPD facility in 2019: $C_{2019} = \frac{US\$265}{tonne}\left(\frac{1850}{1220}\right)^{0.6} \times \frac{619.2}{558.3}$ = US$ 377.3/tonne.

Average yearly OPEX for a 1850 MTPD plant in 2019 = $\frac{377.3}{tonne} x \frac{1850\ tonne}{day} x \frac{330\ day}{year}$ = $MM US 230.4

Average deviation in yearly OPEX from average = $MM US 4.49

Average deviation in average OPEX from average = US$7.35/tonne.

3.0 Life Cycle Impact Assessment (LCIA)

Table S4 below contains the datasets utilized from the Ecoinvent v3.4 database. For each selection, the data was aligned to reflect that of the processes within the Trinidad and Tobago energy sector as closely as possible. This was achieved by specifying heating and electricity consumption affiliated with natural gas combustion only. For nitric acid production, NO_x emissions were assumed to be negligible following selective catalytic reduction with ammonia. An economic allocation approach was chosen for each scenario based on the current market prices of the products and is shown in ***Table S5. Table S6*** gives the normalized life cycle inventory (LCI) across the various scenarios, using SimaPro v9.0.0.30 while ***Tables S7-S15*** gives the characterized environmental burdens for each impact category.

Table S4: LCA dataset retrieved from Ecoinvent v3.4

Process Stream	Dataset	Year
Heating Utility	Heat, district or industrial natural gas	2013
Natural Gas Feedstock	Natural gas, low pressure	2015
Process Water	Water, deionized	2010
Electricity	Electricity, high voltage, produced	2012

Table S5: Economic approach allocation for integrated pathways

		Scenario								
	Product	**BAU**	**BAU + Urea + MeOH**	**BAU + Urea**	**BAU + Urea + UAN + MeOH**	**BAU + Urea + UAN**	**BAU + Urea + Mel + MeOH**	**BAU + Urea + Mel**	**BAU + Urea + UAN + Mel + MeOH**	**BAU + Urea + UAN + Mel**
Percent Allocation	NH_3	100.00%	10.85%	39.26%	1.74%	5.26%	10.36%	33.52%	1.63%	4.37%
	Urea	-	16.79%	60.74%	-	-	13.63%	44.09%	-	-
	UAN	-	-	-	31.33%	94.74%	-	-	29.36%	78.77%
	Mel	-	-	-	-	-	6.92%	22.39%	6.28%	16.86%
	MeOH	-	72.36%	-	66.93%	-	69.09%	-	62.72%	-

Table S6: Normalized LCI for integrated pathways (Functional unit: 1000 kg NH_3)

LCA Inventory Parameter	BAU	BAU + Urea + MeOH	BAU + Urea	BAU + Urea + UAN + MeOH	BAU + Urea + UAN	BAU + Urea + Mel + MeOH	BAU + Urea + Mel	BAU + Urea + UAN + Mel + MeOH	BAU + Urea + UAN + Mel
Inputs from Technosphere									
Natural Gas Heating (MJ)	16896.12	89097.68	43755.75	502233.46	240547.83	89450.21	44108.29	504268.07	242582.44
Natural Gas Feedstock (m^3)	39.79	224.54	72.08	1295.89	416.03	224.54	72.08	1295.89	416.03
Process Water (kg)	877.15	5339.78	2405.60	49484.94	32550.67	6397.38	3463.20	55588.77	38654.50
Electricity (MW)	0.02	0.69	0.55	4.35	3.54	0.75	0.61	4.69	3.88
Emissions to Air									
Process based CO_2 Emissions (kg)	1511.00	1671.28	1540.34	9645.60	8889.90	1671.28	1540.34	9645.60	8889.90
Process based NH_3 Emissions (kg)	-	5.68	5.68	53.92	53.92	5.98	5.98	55.67	55.67
Process based Isocyanic Acid Emissions (kg)	-	-	-	-	-	0.76	0.76	4.39	4.39
Emissions to Water									
NH_4^- (kg)	-	0.59	0.59	4.54	4.54	0.59	0.59	4.54	4.54

Table S7: Charaterised LCIA profile for BAU scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	2750.34	1511.00	1202.79	24.90	1.48	10.17
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	18.51	0.00	16.74	1.39	0.11	0.27
Ozone formation, Human health	kg NO_x eq	0.72	0.00	0.67	0.03	0.00	0.01
Fine particulate matter formation	kg PM2.5 eq	0.30	0.00	0.28	0.02	0.00	0.00
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.77	0.00	0.72	0.04	0.00	0.01
Terrestrial acidification	kg SO_2 eq	0.91	0.00	0.84	0.06	0.01	0.00
Freshwater eutrophication	kg P eq x 10^{-4}	127.58	0.00	108.13	11.45	6.52	1.48
Marine eutrophication	kg N eq x 10^{-4}	23.13	0.00	20.69	1.87	0.49	0.09
Terrestrial ecotoxicity	kg 1,4-DCB	62.61	0.00	49.49	8.40	2.76	1.96
Freshwater ecotoxicity	kg 1,4-DCB	1.70	0.00	1.48	0.16	0.04	0.02
Marine ecotoxicity	kg 1,4-DCB	2.46	0.00	2.13	0.25	0.05	0.03
Human carcinogenic toxicity	kg 1,4-DCB	3.96	0.00	3.42	0.35	0.16	0.03
Human non-carcinogenic toxicity	kg 1,4-DCB	41.23	0.00	35.58	4.10	0.98	0.56
Mineral resource scarcity	kg Cu eq	0.29	0.00	0.25	0.03	0.01	0.00
Fossil resource scarcity	kg oil eq	477.46	0.00	434.48	38.32	0.35	4.31
Water consumption	m^3	1.18	0.00	0.22	0.02	0.91	0.02

Table S8: Charaterised LCIA profile for BAU + Urea + MeOH scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	931.39	181.33	688.18	15.24	0.98	45.67
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	11.71	0.00	9.58	0.85	0.07	1.21
Ozone formation, Human health	kg NO_x eq	0.45	0.00	0.39	0.02	0.00	0.04
Fine particulate matter formation	kg PM2.5 eq	0.33	0.15	0.16	0.01	0.00	0.01
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.48	0.00	0.41	0.02	0.00	0.04
Terrestrial acidification	kg SO_2 eq	1.75	1.21	0.48	0.04	0.00	0.02
Freshwater eutrophication	kg P eq x 10^{-4}	79.82	0.00	61.86	7.01	4.31	6.64
Marine eutrophication	kg N eq x 10^{-4}	162.05	148.34	11.84	1.14	0.32	0.41
Terrestrial ecotoxicity	kg 1,4-DCB	44.06	0.00	28.32	5.14	1.82	8.78
Freshwater ecotoxicity	kg 1,4-DCB	1.05	0.00	0.85	0.10	0.03	0.08
Marine ecotoxicity	kg 1,4-DCB	1.52	0.00	1.22	0.15	0.04	0.11
Human carcinogenic toxicity	kg 1,4-DCB	2.42	0.00	1.95	0.22	0.10	0.15
Human non-carcinogenic toxicity	kg 1,4-DCB	26.05	0.00	20.36	2.51	0.65	2.53
Mineral resource scarcity	kg Cu eq	0.18	0.00	0.14	0.02	0.00	0.02
Fossil resource scarcity	kg oil eq	291.64	0.00	248.58	23.46	0.23	19.36
Water consumption	m^3	0.82	0.00	0.13	0.01	0.60	0.08

Table S9: Charaterised LCIA profile for BAU + Urea scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	1978.56	604.74	1222.89	17.71	1.59	131.63
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	21.61	0.00	17.02	0.99	0.11	3.48
Ozone formation, Human health	kg NO_x eq	0.82	0.00	0.69	0.02	0.00	0.11
Fine particulate matter formation	kg PM2.5 eq	0.86	0.54	0.28	0.01	0.00	0.02
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.88	0.00	0.74	0.03	0.00	0.12
Terrestrial acidification	kg SO_2 eq	5.33	4.37	0.85	0.04	0.01	0.05
Freshwater eutrophication	kg P eq x 10^{-4}	144.24	0.00	109.93	8.14	7.03	19.14
Marine eutrophication	kg N eq x 10^{-4}	560.82	536.76	21.03	1.33	0.52	1.17
Terrestrial ecotoxicity	kg 1,4-DCB	84.57	0.00	50.32	5.97	2.97	25.31
Freshwater ecotoxicity	kg 1,4-DCB	1.88	0.00	1.51	0.11	0.04	0.22
Marine ecotoxicity	kg 1,4-DCB	2.74	0.00	2.17	0.18	0.06	0.33
Human carcinogenic toxicity	kg 1,4-DCB	4.32	0.00	3.47	0.25	0.17	0.43
Human non-carcinogenic toxicity	kg 1,4-DCB	47.45	0.00	36.18	2.91	1.06	7.30
Mineral resource scarcity	kg Cu eq	0.33	0.00	0.25	0.02	0.01	0.05
Fossil resource scarcity	kg oil eq	525.17	0.00	441.74	27.26	0.38	55.81
Water consumption	m^3	1.45	0.00	0.23	0.02	0.98	0.23

Table S10: Charaterised LCIA profile for BAU + Urea + UAN + MeOH scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	851.41	167.83	622.10	14.11	1.45	45.92
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	10.77	0.00	8.66	0.79	0.10	1.21
Ozone formation, Human health	kg NO_x eq	0.41	0.00	0.35	0.02	0.00	0.04
Fine particulate matter formation	kg PM2.5 eq	0.39	0.23	0.14	0.01	0.00	0.01
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.44	0.00	0.37	0.02	0.00	0.04
Terrestrial acidification	kg SO_2 eq	2.33	1.84	0.43	0.03	0.01	0.02
Freshwater eutrophication	kg P eq x 10^{-4}	75.49	0.00	55.92	6.49	6.40	6.68
Marine eutrophication	kg N eq x 10^{-4}	194.49	181.85	10.70	1.06	0.48	0.41
Terrestrial ecotoxicity	kg 1,4-DCB	41.90	0.00	25.60	4.76	2.71	8.83
Freshwater ecotoxicity	kg 1,4-DCB	0.97	0.00	0.77	0.09	0.04	0.08
Marine ecotoxicity	kg 1,4-DCB	1.41	0.00	1.10	0.14	0.05	0.11
Human carcinogenic toxicity	kg 1,4-DCB	2.27	0.00	1.77	0.20	0.15	0.15
Human non-carcinogenic toxicity	kg 1,4-DCB	24.24	0.00	18.40	2.32	0.97	2.55
Mineral resource scarcity	kg Cu eq	0.17	0.00	0.13	0.02	0.01	0.02
Fossil resource scarcity	kg oil eq	266.25	0.00	224.72	21.72	0.34	19.47
Water consumption	m^3	1.10	0.00	0.12	0.01	0.89	0.08

Table S11: Charaterised LCIA profile for BAU + Urea + UAN scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	1497.74	467.61	900.72	13.69	2.88	112.84
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	16.49	0.00	12.54	0.77	0.21	2.99
Ozone formation, Human health	kg NO_x eq	0.63	0.00	0.50	0.02	0.01	0.10
Fine particulate matter formation	kg PM2.5 eq	0.92	0.68	0.21	0.01	0.01	0.02
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.67	0.00	0.54	0.02	0.01	0.10
Terrestrial acidification	kg SO_2 eq	6.28	5.56	0.63	0.03	0.01	0.05
Freshwater eutrophication	kg P eq x 10^{-4}	116.41	0.00	80.97	6.30	12.74	16.41
Marine eutrophication	kg N eq x 10^{-4}	568.20	549.73	15.49	1.03	0.95	1.00
Terrestrial ecotoxicity	kg 1,4-DCB	68.77	0.00	37.06	4.62	5.39	21.70
Freshwater ecotoxicity	kg 1,4-DCB	1.46	0.00	1.11	0.09	0.08	0.19
Marine ecotoxicity	kg 1,4-DCB	2.12	0.00	1.60	0.14	0.11	0.28
Human carcinogenic toxicity	kg 1,4-DCB	3.42	0.00	2.56	0.19	0.30	0.37
Human non-carcinogenic toxicity	kg 1,4-DCB	37.08	0.00	26.65	2.25	1.92	6.26
Mineral resource scarcity	kg Cu eq	0.25	0.00	0.19	0.01	0.01	0.04
Fossil resource scarcity	kg oil eq	394.96	0.00	325.36	21.08	0.68	47.84
Water consumption	m^3	2.16	0.00	0.17	0.01	1.78	0.20

Table S12: Charaterised LCIA profile for BAU + Urea + Mel + MeOH scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	895.80	173.14	659.70	14.55	1.12	47.29
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	11.33	0.00	9.18	0.81	0.08	1.25
Ozone formation, Human health	kg NO_x eq	0.43	0.00	0.37	0.02	0.00	0.04
Fine particulate matter formation	kg PM2.5 eq	0.32	0.15	0.15	0.01	0.00	0.01
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.46	0.00	0.40	0.02	0.00	0.04
Terrestrial acidification	kg SO_2 eq	1.73	1.21	0.46	0.04	0.00	0.02
Freshwater eutrophication	kg P eq x 10^{-4}	77.80	0.00	59.30	6.69	4.93	6.86
Marine eutrophication	kg N eq x 10^{-4}	154.87	141.64	11.35	10.91	0.37	0.42
Terrestrial ecotoxicity	kg 1,4-DCB	43.23	0.00	27.14	4.91	2.09	9.09
Freshwater ecotoxicity	kg 1,4-DCB	1.01	0.00	0.81	0.09	0.03	0.08
Marine ecotoxicity	kg 1,4-DCB	1.48	0.00	1.17	0.15	0.04	0.12
Human carcinogenic toxicity	kg 1,4-DCB	2.35	0.00	1.87	0.21	0.12	0.15
Human non-carcinogenic toxicity	kg 1,4-DCB	25.28	0.00	19.52	2.40	0.74	2.62
Mineral resource scarcity	kg Cu eq	0.17	0.00	0.14	0.02	0.00	0.02
Fossil resource scarcity	kg oil eq	281.02	0.00	238.30	22.40	0.26	20.05
Water consumption	m^3	0.91	0.00	0.12	0.01	0.69	0.08

Table S13: Charaterised LCIA profile for BAU + Urea + Mel scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	1710.22	516.32	1052.51	15.12	1.95	124.31
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	18.92	0.00	14.65	0.85	0.14	3.29
Ozone formation, Human health	kg NO_x eq	0.72	0.00	0.59	0.02	0.00	0.11
Fine particulate matter formation	kg PM2.5 eq	0.76	0.48	0.24	0.01	0.00	0.02
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.77	0.00	0.63	0.02	0.00	0.11
Terrestrial acidification	kg SO_2 eq	4.76	3.93	0.73	0.04	0.01	0.05
Freshwater eutrophication	kg P eq x 10^{-4}	128.28	0.00	946.16	6.95	8.63	18.07
Marine eutrophication	kg N eq x 10^{-4}	479.27	458.29	18.10	1.13	0.64	1.10
Terrestrial ecotoxicity	kg 1,4-DCB	75.96	0.00	43.31	5.10	3.66	23.90
Freshwater ecotoxicity	kg 1,4-DCB	1.65	0.00	1.30	0.10	0.05	0.21
Marine ecotoxicity	kg 1,4-DCB	2.40	0.00	1.87	0.15	0.07	0.31
Human carcinogenic toxicity	kg 1,4-DCB	3.81	0.00	2.99	0.21	0.21	0.40
Human non-carcinogenic toxicity	kg 1,4-DCB	41.82	0.00	31.14	2.49	1.30	6.89
Mineral resource scarcity	kg Cu eq	0.29	0.00	0.22	0.02	0.01	0.04
Fossil resource scarcity	kg oil eq	456.63	0.00	380.19	23.27	0.46	52.70
Water consumption	m^3	1.63	0.00	0.19	0.01	1.21	0.22

Table S14: Charaterised LCIA profile for BAU + Urea + UAN + Mel + MeOH scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	808.40	158.19	588.72	13.30	1.53	46.66
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	10.28	0.00	8.19	0.74	0.11	1.23
Ozone formation, Human health	kg NO_x eq	0.39	0.00	0.33	0.02	0.00	0.04
Fine particulate matter formation	kg PM2.5 eq	0.38	0.22	0.14	0.01	0.00	0.01
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.42	0.00	0.35	0.02	0.00	0.04
Terrestrial acidification	kg SO_2 eq	2.26	1.79	0.41	0.03	0.01	0.02
Freshwater eutrophication	kg P eq x 10^{-4}	72.60	0.00	52.92	6.12	6.78	6.78
Marine eutrophication	kg N eq x 10^{-4}	183.44	171.40	10.13	0.99	0.51	0.41
Terrestrial ecotoxicity	kg 1,4-DCB	40.55	0.00	24.22	4.49	2.87	8.97
Freshwater ecotoxicity	kg 1,4-DCB	0.93	0.00	0.73	0.08	0.04	0.08
Marine ecotoxicity	kg 1,4-DCB	1.35	0.00	1.04	0.13	0.06	0.12
Human carcinogenic toxicity	kg 1,4-DCB	2.17	0.00	1.67	0.19	0.16	0.15
Human non-carcinogenic toxicity	kg 1,4-DCB	23.22	0.00	17.42	2.19	1.02	2.59
Mineral resource scarcity	kg Cu eq	0.16	0.00	0.12	0.01	0.01	0.02
Fossil resource scarcity	kg oil eq	253.27	0.00	212.66	20.47	0.36	19.78
Water consumption	m^3	1.15	0.00	0.11	0.01	0.95	0.08

Table S15: Charaterised LCIA profile for BAU + Urea + UAN + Mel scenario (ReCiPe 2016 Midpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming	kg CO_2 eq	1260.09	388.49	754.65	11.38	2.84	102.73
Stratospheric ozone depletion	kg CFC11 eq x 10^{-5}	14.06	0.00	10.50	0.64	0.20	2.72
Ozone formation, Human health	kg NO_x eq	0.53	0.00	0.42	0.01	0.01	0.09
Fine particulate matter formation	kg PM2.5 eq	0.79	0.58	0.17	0.01	0.01	0.02
Ozone formation, Terrestrial ecosystems	kg NO_x eq	0.57	0.00	0.45	0.02	0.01	0.09
Terrestrial acidification	kg SO_2 eq	5.37	4.77	0.52	0.03	0.01	0.04
Freshwater eutrophication	kg P eq x 10^{-4}	100.57	0.00	67.84	5.23	12.56	14.94
Marine eutrophication	kg N eq x 10^{-4}	472.40	456.71	12.98	0.85	0.94	0.91
Terrestrial ecotoxicity	kg 1,4-DCB	59.96	0.00	31.05	3.84	5.32	19.75
Freshwater ecotoxicity	kg 1,4-DCB	1.25	0.00	0.93	0.07	0.07	0.17
Marine ecotoxicity	kg 1,4-DCB	1.82	0.00	1.34	0.11	0.10	0.26
Human carcinogenic toxicity	kg 1,4-DCB	2.94	0.00	2.14	0.16	0.30	0.33
Human non-carcinogenic toxicity	kg 1,4-DCB	31.79	0.00	22.32	1.87	1.90	5.70
Mineral resource scarcity	kg Cu eq	0.22	0.00	0.16	0.01	0.01	0.04
Fossil resource scarcity	kg oil eq	334.33	0.00	272.60	17.51	0.67	43.55
Water consumption	m^3	2.08	0.00	0.14	0.01	1.75	0.18

4.0 Life Cycle Contributional Analysis

The LCIA was conducted across all scenarios based on the functional unit of one (1) metric tonne of NH_3 produced per hour. The total characterized environmental effects were identified via a midpoint approach based on a cradle-to-gate life cycle. The heating utility and electricity demand were the major contributors to the environmental impacts across impact categories affiliated with natural gas extraction and combustion.

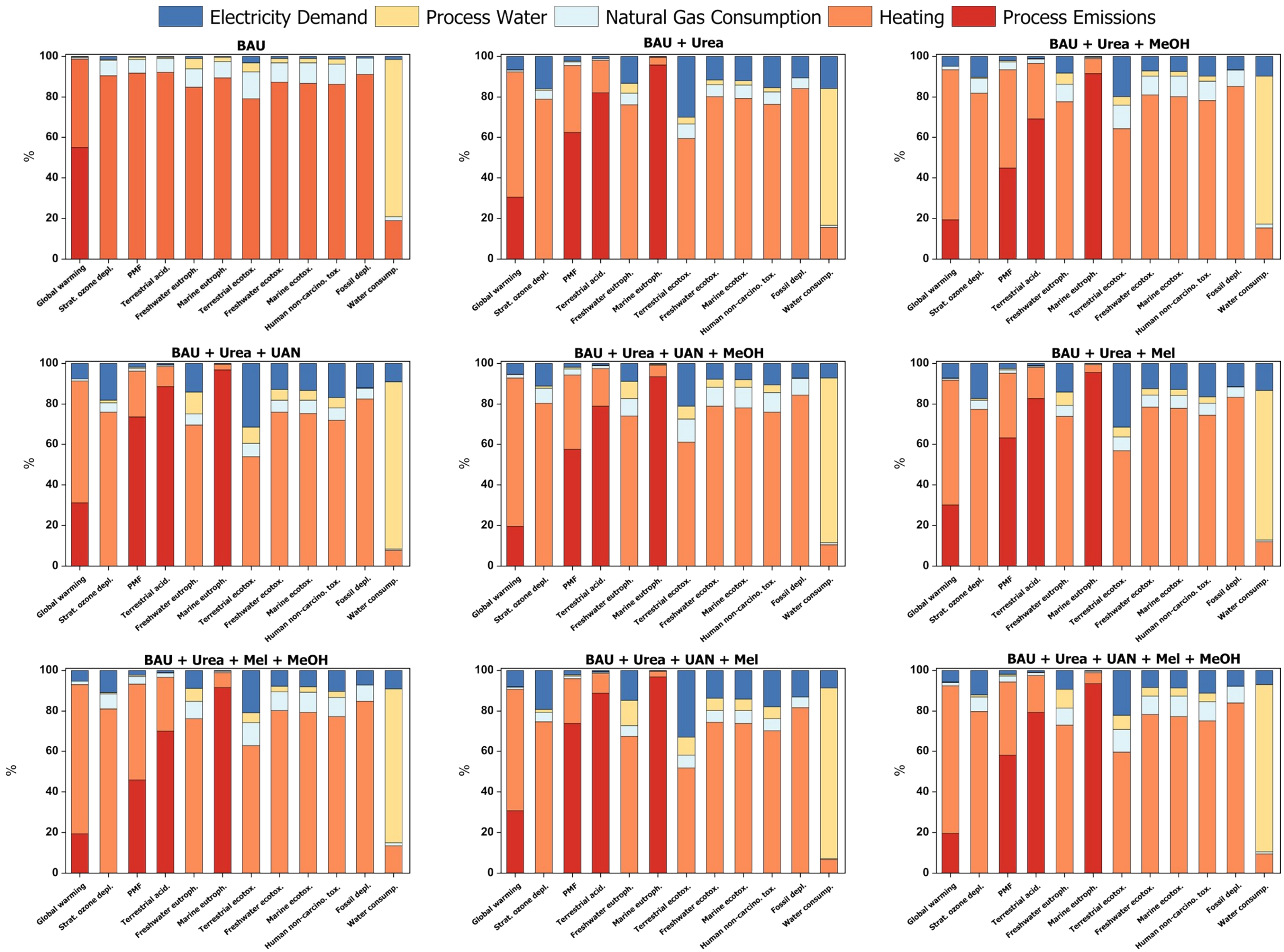

Figure S1: LCA contributional analysis for viable pathways within the NH_3-CO_2 integrated eco-park (ReCiPe 2016 Midpoint (H) V1.01).

From ***Figure S1***, the LCA contributional analysis was represented, where data across different impact categories were normalized to 100%. Heating gave the largest overall contributions to environmental burden- up to 92% across all impact categories. Significant contributions were observed for global warming (44 - 74%), stratospheric ozone depletion (75 - 90%), freshwater eutrophication (67 - 85%), terrestrial ecotoxicity (52% - 79%), freshwater ecotoxicity (74 - 87%), marine ecotoxicity (74 - 87%), human non-carcinogenic toxicity (70 - 86%) and fossil resource scarcity (82 - 91%). Environmental burdens were attributed to the release of toxic chemicals into the air, land and water courses during natural gas extraction and combustion. This was associated with steam production as well as energy needs, with natural gas combustion as the main energy source. This was especially observed across the BAU case, due to the highly energy intensive nature of the process[14].

Upon expansion of the eco-park, the prevalence of process emissions as the secondary major contributor to environmental burden became more apparent as both CO_2 and NH_3 emissions increased for added processes. This was especially observed for fine particulate matter formation (45 – 74%), terrestrial acidification (69 – 89%) and marine eutrophication (91 – 97%) impact categories. These burdens were attributed to the direct release of NH_3 into the atmosphere. With respect to process-based impacts, CO_2 emissions derived from purge gas combustion considerably increased environmental burden- noticeable for global warming (19 - 55%). Minor burden contributions were also seen from water, natural gas consumption and electricity demand (<10%) across most cases.

5.0 PB Characterization Factors

Table S16 shows the characterization factors (CF) used to align LCI entries to each Earth system in the PB-LCIA analysis.

Table S16: Data sources for determining the characterized impact scores (IMP_i).

Characterization factors (CF) used for evaluation of Impact Scores (IMP_i)[16]			
Environmental flow	**Earth System Process**	**CF**	**Unit**
CO_2	Climate Change-Energy Imbalance	3.53×10^{-13}	W yr m^2kg^{-1}
CH_4		1.59×10^{-12}	
N_2O		4.64×10^{-11}	
CO_2	Climate Change-CO_2 Concentration	2.69×10^{-11}	ppm yr kg^{-1}
CH_4		7.40×10^{-11}	
CO_2	Ocean Acidification	8.22×10^{-14}	mol yr kg^{-1}
CH_4		2.26×10^{-13}	
N_2O^a	Stratospheric Ozone Depletion	7.85×10^{-9}	W yr m^2kg^{-1}
Global P flows	Biogeochemical Flows-Phosphorus	8.61×10^{-10}	Tg P $yr^{-1}kg^{-1}yr$
Total N Flow	Biogeochemical Flows- Nitrogen	2.44×10^{-8}	Tg N $yr^{-1}kg^{-1}yr$
NO_3^-		5.51×10^{-9}	Tg N $yr^{-1}kg^{-1}yr$
Consumption of Blue Water	Freshwater Use	1×10^{-9}	km^3 m^{-3}
Global Forest Transformation	Land-System Change	1.56×10^{-12}	% m^{-2}

[a] *Converted to CFC-11 equivalent (0.0118 kg of CFC-11 equivalent per kg of N_2O) to apply CF for CFC-11*[17]

6.0 Sustainability Analysis

The normalized environmental impacts across the various scenarios are given in **Tables 17 - 19**. They highlight six impact categories, namely: global warming, stratospheric ozone depletion, freshwater eutrophication, marine eutrophication, human non-carcinogenic toxicity and fossil resource scarcity. **Tables S17 and S18** compare the BAU case with scenarios including and excluding MeOH respectively. The most environmentally sustainable networks were then selected based on minimum internal area (***Table S19***), and assessed to determine the most sustainable scenario.

Table S17: Normalized sustainability indicators for comparison of BAU case to scenarios with MeOH

Category	Scenarios				
	BAU	**BAU + Urea + MeOH**	**BAU + Urea + UAN + MeOH**	**BAU + Urea + Mel + MeOH**	**BAU + Urea + UAN + Mel + MeOH**
Global warming	100%	34%	31%	33%	29%
Stratospheric ozone depletion	100%	63%	58%	61%	56%
Freshwater eutrophication	100%	63%	59%	61%	57%
Marine eutrophication	12%	83%	100%	80%	94%
Human non-carcinogenic toxicity	100%	63%	59%	61%	56%
Fossil resource scarcity	100%	61%	56%	59%	53%
ROI (reverse score)	100%	1%	1%	1%	1%
Job creation (reverse score)	100%	39%	30%	29%	24%

Table S18: Normalized sustainability indicators for comparison of BAU case to scenarios without MeOH

Category	Scenarios				
	BAU	**BAU + Urea**	**BAU + Urea + UAN**	**BAU + Urea + Mel**	**BAU + Urea + UAN + Mel**
Global warming	100%	72%	54%	62%	46%
Stratospheric ozone depletion	86%	100%	76%	88%	65%
Freshwater eutrophication	88%	100%	81%	89%	70%
Marine eutrophication	4%	99%	100%	84%	83%
Human non-carcinogenic toxicity	87%	100%	78%	88%	67%
Fossil resource scarcity	91%	100%	75%	87%	64%
ROI (reverse score)	100%	5%	5%	8%	5%
Job creation (reverse score)	100%	58%	40%	39%	30%

Table S19: Normalized sustainability indicators for comparison of BAU case to best case scenarios

Category	Scenarios				
	BAU	**BAU + Urea + Mel + MeOH**	**BAU + Urea + UAN**	**BAU + Urea + UAN + Mel + MeOH**	**BAU + Urea + UAN + Mel**
Global warming	100%	33%	54%	29%	46%
Stratospheric ozone depletion	100%	61%	89%	56%	76%
Freshwater eutrophication	100%	61%	91%	57%	79%
Marine eutrophication	4%	27%	100%	32%	83%
Human non-carcinogenic toxicity	100%	61%	90%	56%	77%
Fossil resource scarcity	100%	59%	83%	53%	70%
ROI (reverse score)	100%	1%	5%	1%	5%
Job creation (reverse score)	100%	29%	40%	24%	30%

7.0 LCA and PB Limitations and Sensitivities

7.1 LCA Sensitivities

The cradle to gate LCA was utilized to identify the environmental impacts of the viable pathways. The analysis was performed on SimaPro using the ReCiPe midpoint approach. In conducting this assessment, a sensitivity analysis of the method was performed, comparing the selected method to ReCiPe 2016 Endpoint (H) v1.01, with scenario specific contributional analyses compared (**Tables S20 – S28**).

The ReCiPe Endpoint Hierarchist version 1.01 / World method comprised 12 impact categories; global warming, human health (Climate change (HH)), global warming, terrestrial ecosystems (Climate change (eco)), stratospheric ozone depletion (strat. ozone depl.), fine particulate matter formation (PMF), terrestrial acidification (terrestrial acid.), freshwater eutrophication (freshwater eutroph.), marine eutrophication (marine eutroph.), terrestrial ecotoxicity (terrestrial ecotox.), freshwater ecotoxicity (freshwater ecotox.), marine ecotoxicity (marine ecotox.), human non-carcinogenic toxicity (human non-carcino. tox.) and fossil resource scarcity (fossil depl.). Comparing **Figures S1 and S2**, the impact categories examined for both midpoint and endpoint methods gave similar results (not exceeding sensitivity threshold of 1%) towards the characterization of environmental burden for all scenarios. Thus, the characterization model was not a factor of sensitivity for evaluating the environmental profiles across integrated networks.

Furthermore, insights into the allocation approach used to attribute burdens to co-products was investigated for the BAU + Urea + UAN+ Mel + MeOH case. As shown in **Figure S3**, economic allocation gives the lowest fraction of environmental burdens across all categories to ammonia production, with mass allocation increasing the burden by 11.6% and energy allocation by 57.9%. Although economic allocation was used in this particular study in accordance with past research[18 - 20], these results illustrate the limitations of the underlying allocation approach on assessing environmental profiles and informing decision-making.

Table S20: Characterized LCIA profile for BAU scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALYx10^{-6}	2552	1402	1116	23.10	1.37	9.44
Global warming, Terrestrial ecosystems	species.yrx10^{-8}	770.17	423.08	336.84	6.98	0.41	2.85
Stratospheric ozone depletion	DALYx10^{-8}	9.82	0.00	8.88	0.74	0.06	0.14
Fine particulate matter formation	DALYx10^{-6}	190.61	0.00	174.66	12.87	2.06	1.02
Terrestrial acidification	species.yr x10^{-9}	192.30	0.00	177.00	12.94	1.17	0.89
Freshwater eutrophication	species.yr x10^{-10}	85.44	0.00	72.41	7.67	4.37	0.99
Marine eutrophication	species.yr x10^{-13}	39.38	0.00	35.22	3.18	0.83	0.15
Terrestrial ecotoxicity	species.yr x10^{-11}	71.43	0.00	56.46	9.59	3.15	2.23
Freshwater ecotoxicity	species.yr x10^{-10}	11.77	0.00	10.28	1.10	0.27	0.12
Marine ecotoxicity	species.yr x10^{-11}	25.89	0.00	22.41	2.64	0.57	0.27
Human non-carcinogenic toxicity	DALYx10^{-6}	9.41	0.00	8.12	0.94	0.22	0.13
Fossil resource scarcity	USD2013	170.38	0.00	155.09	13.68	0.07	1.54
Water consumption, Human health	DALYx10^{-8}	260.90	0.00	49.47	5.20	202.20	3.95

Table S21: Characterized LCIA profile for BAU + Urea + MeOH scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALYx10^{-6}	864.32	168.28	638.61	14.14	0.91	42.38
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	26.08	5.08	19.27	0.43	0.03	1.28
Stratospheric ozone depletion	DALYx10^{-8}	6.21	0.00	5.08	0.45	0.04	0.64
Fine particulate matter formation	DALYx10^{-4}	2.07	0.93	0.99	0.08	0.01	0.05
Terrestrial acidification	species.yr x10^{-9}	370.66	256.51	101.45	7.92	0.77	4.01
Freshwater eutrophication	species.yr x10^{-10}	53.46	0.00	41.43	4.70	2.89	4.45
Marine eutrophication	species.yr x10^{-13}	276.16	252.83	20.15	1.95	0.55	0.69
Terrestrial ecotoxicity	species.yr x10^{-11}	50.28	0.00	32.30	5.87	2.08	10.03
Freshwater ecotoxicity	species.yr x10^{-10}	7.26	0.00	5.88	0.67	0.18	0.53
Marine ecotoxicity	species.yr x10^{-11}	16.02	0.00	12.82	1.62	0.38	1.20
Human non-carcinogenic toxicity	DALYx10^{-6}	5.94	0.00	4.65	0.57	0.15	0.58
Fossil resource scarcity	USD2013	104.07	0.00	88.73	8.38	0.05	6.91
Water consumption, Human health	DALYx10^{-8}	182.78	0.00	28.30	3.19	133.58	17.71

Table S22: Characterized LCIA profile for BAU + Urea scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALYx10^{-6}	1836.07	561.20	1134.82	16.43	1.48	122.15
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	55.41	16.93	34.25	0.50	0.04	3.69
Stratospheric ozone depletion	DALYx10^{-8}	11.46	0.00	9.03	0.53	0.06	1.85
Fine particulate matter formation	DALYx10^{-4}	5.39	3.37	1.78	0.09	0.02	0.13
Terrestrial acidification	species.yr x10^{-8}	113.55	92.82	18.03	0.92	0.13	1.16
Freshwater eutrophication	species.yr x10^{-9}	9.66	0.00	7.36	0.55	0.47	1.28
Marine eutrophication	species.yr x10^{-13}	955.78	914.83	35.81	2.26	0.89	1.99
Terrestrial ecotoxicity	species.yr x10^{-11}	96.51	0.00	57.40	6.82	3.39	28.90
Freshwater ecotoxicity	species.yr x10^{-10}	13.05	0.00	10.45	0.78	0.29	1.53
Marine ecotoxicity	species.yr x10^{-11}	28.74	0.00	22.79	1.88	0.61	3.46
Human non-carcinogenic toxicity	DALYx10^{-6}	10.83	0.00	8.26	0.66	0.24	1.67
Fossil resource scarcity	USD2013	187.41	0.00	157.68	9.73	0.08	19.93
Water consumption, Human health	DALYx10^{-7}	32.28	0.00	5.03	0.37	21.78	5.11

Table S23: Characterized LCIA profile for BAU + Urea + UAN + MeOH scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALYx10^{-5}	79.01	15.57	57.73	1.31	0.13	4.26
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	23.84	4.70	17.42	0.40	0.04	1.29
Stratospheric ozone depletion	DALYx10^{-8}	5.71	0.00	4.59	0.42	0.06	0.64
Fine particulate matter formation	DALYx10^{-5}	24.59	14.17	9.03	0.73	0.20	0.46
Terrestrial acidification	species.yr x10^{-9}	494.49	390.27	91.71	7.33	1.15	4.03
Freshwater eutrophication	species.yr x10^{-10}	50.56	0.00	37.45	4.35	4.29	4.47
Marine eutrophication	species.yr x10^{-13}	331.46	309.93	18.22	1.80	0.81	0.69
Terrestrial ecotoxicity	species.yr x10^{-11}	47.81	0.00	29.20	5.43	3.09	10.08
Freshwater ecotoxicity	species.yr x10^{-10}	6.74	0.00	5.32	0.62	0.26	0.53
Marine ecotoxicity	species.yr x10^{-11}	14.86	0.00	11.59	1.50	0.56	1.21
Human non-carcinogenic toxicity	DALYx10^{-6}	5.53	0.00	4.20	0.53	0.22	0.58
Fossil resource scarcity	USD2013	94.99	0.00	80.21	7.75	0.07	6.95
Water consumption, Human health	DALYx10^{-8}	244.88	0.00	25.58	2.95	198.53	17.81

Table S24: Characterized LCIA profile for BAU + Urea + UAN scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALYx10^{-4}	13.90	4.34	8.36	0.13	0.03	1.05
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	41.94	13.09	25.22	0.38	0.08	3.16
Stratospheric ozone depletion	DALYx10^{-8}	8.75	0.00	6.65	0.41	0.11	1.59
Fine particulate matter formation	DALYx10^{-5}	58.15	42.82	13.08	0.71	0.40	1.14
Terrestrial acidification	species.yr x10^{-9}	1331.87	1179.79	132.78	7.12	2.28	9.90
Freshwater eutrophication	species.yr x10^{-9}	7.80	0.00	5.42	0.42	0.85	1.10
Marine eutrophication	species.yr x10^{-13}	968.37	936.92	26.38	1.75	1.62	1.70
Terrestrial ecotoxicity	species.yr x10^{-11}	78.47	0.00	42.28	5.27	6.15	24.77
Freshwater ecotoxicity	species.yr x10^{-10}	10.14	0.00	7.70	0.60	0.53	1.31
Marine ecotoxicity	species.yr x10^{-11}	22.32	0.00	16.78	1.45	1.11	2.97
Human non-carcinogenic toxicity	DALYx10^{-6}	8.46	0.00	6.08	0.51	0.44	1.43
Fossil resource scarcity	USD2013	140.88	0.00	116.14	7.52	0.14	17.08
Water consumption, Human health	DALYx10^{-8}	478.45	0.00	37.04	2.86	394.78	43.76

Table S25: Characterized LCIA profile for BAU + Urea + Mel + MeOH scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALY x 10^{-6}	831.29	160.68	612.19	13.50	1.04	43.89
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	25.09	4.85	18.47	0.41	0.03	1.32
Stratospheric ozone depletion	DALY x 10^{-8}	6.01	0.00	4.87	0.43	0.04	0.66
Fine particulate matter formation	DALYx10^{-5}	20.32	9.36	9.58	0.75	0.16	0.48
Terrestrial acidification	species.yr x 10^{-9}	367.70	257.85	97.25	7.57	0.88	4.15
Freshwater eutrophication	species.yr x 10^{-10}	52.10	0.00	39.72	4.48	3.30	4.60
Marine eutrophication	species.yr x 10^{-13}	263.92	241.41	19.32	1.86	0.63	0.71
Terrestrial ecotoxicity	species.yr x 10^{-11}	49.33	0.00	30.97	5.60	2.38	10.38
Freshwater ecotoxicity	species.yr x 10^{-10}	7.03	0.00	5.64	0.64	0.20	0.55
Marine ecotoxicity	species.yr x 10^{-11}	15.51	0.00	12.29	1.55	0.43	1.24
Human non-carcinogenic toxicity	DALY x 10^{-6}	5.77	0.00	4.45	0.55	0.17	0.60
Fossil resource scarcity	USD2013	100.27	0.00	85.06	8.00	0.05	7.16
Water consumption, Human health	DALY x 10^{-8}	201.33	0.00	27.13	3.04	152.82	18.34

Table S26: Characterized LCIA profile for BAU + Urea + Mel scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALY x 10^{-6}	1587.06	479.15	976.71	14.03	1.81	115.36
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	47.89	14.46	29.48	0.42	0.05	3.48
Stratospheric ozone depletion	DALY x 10^{-8}	10.04	0.00	7.77	0.45	0.07	1.75
Fine particulate matter formation	DALYx10^{-5}	47.87	30.28	15.28	0.78	0.27	1.25
Terrestrial acidification	species.yr x 10^{-9}	1009.76	834.29	155.16	7.86	1.55	10.91
Freshwater eutrophication	species.yr x 10^{-10}	85.91	0.00	63.36	4.66	5.78	12.10
Marine eutrophication	species.yr x 10^{-13}	816.80	781.08	30.82	1.93	1.10	1.88
Terrestrial ecotoxicity	species.yr x 10^{-11}	86.69	0.00	49.40	5.82	4.17	27.29
Freshwater ecotoxicity	species.yr x 10^{-10}	11.46	0.00	8.99	0.67	0.36	1.44
Marine ecotoxicity	species.yr x 10^{-11}	25.24	0.00	19.61	1.61	0.75	3.27
Human non-carcinogenic toxicity	DALY x 10^{-6}	9.54	0.00	7.11	0.57	0.29	1.57
Fossil resource scarcity	USD2013	162.93	0.00	135.71	8.31	0.09	18.82
Water consumption, Human health	DALY x 10^{-8}	362.32	0.00	43.29	3.16	267.67	48.21

Table S27: Characterized LCIA profile for BAU + Urea + UAN + Mel + MeOH scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALY x 10^{-6}	750.18	146.80	546.32	12.34	1.42	43.30
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	22.64	4.43	16.49	0.37	0.04	1.31
Stratospheric ozone depletion	DALY x 10^{-8}	5.45	0.00	4.35	0.39	0.06	0.66
Fine particulate matter formation	DALYx10^{-5}	23.71	13.79	8.55	0.69	0.21	0.47
Terrestrial acidification	species.yr x 10^{-9}	478.80	379.80	86.79	6.91	1.21	4.09
Freshwater eutrophication	species.yr x 10^{-10}	48.62	0.00	35.44	4.09	4.54	4.54
Marine eutrophication	species.yr x 10^{-13}	312.63	292.12	17.24	1.70	0.86	0.70
Terrestrial ecotoxicity	species.yr x 10^{-11}	46.27	0.00	27.63	5.12	3.28	10.24
Freshwater ecotoxicity	species.yr x 10^{-10}	6.44	0.00	5.03	0.59	0.28	0.54
Marine ecotoxicity	species.yr x 10^{-11}	14.20	0.00	10.97	1.41	0.59	1.23
Human non-carcinogenic toxicity	DALY x 10^{-6}	5.30	0.00	3.97	0.50	0.23	0.59
Fossil resource scarcity	USD2013	90.35	0.00	75.91	7.31	0.07	7.06
Water consumption, Human health	DALY x 10^{-8}	255.29	0.00	24.21	2.78	210.20	18.09

Table S28: Characterized LCIA profile for BAU + Urea + UAN + Mel scenario (ReCiPe 2016 Endpoint (H) V1.01)

Impact category	Unit	Total	Process Emissions	Heating	Natural Gas Consumption	Process Water	Electricity Demand
Global warming, Human health	DALY x 10^{-6}	1169.34	360.52	700.30	10.55	2.64	95.33
Global warming, Terrestrial ecosystems	species.yrx10^{-7}	35.29	10.88	21.13	0.32	0.08	2.88
Stratospheric ozone depletion	DALY x 10^{-8}	7.46	0.00	5.57	0.34	0.11	1.44
Fine particulate matter formation	DALYx10^{-5}	49.71	36.73	10.96	0.59	0.40	1.03
Terrestrial acidification	species.yr x 10^{-9}	1140.44	1012.02	111.25	5.91	2.25	9.01
Freshwater eutrophication	species.yr x 10^{-10}	67.35	0.00	45.43	3.50	8.41	10.00
Marine eutrophication	species.yr x 10^{-13}	805.10	778.40	22.10	1.45	1.59	1.55
Terrestrial ecotoxicity	species.yr x 10^{-11}	68.42	0.00	35.42	4.38	6.07	22.55
Freshwater ecotoxicity	species.yr x 10^{-10}	8.66	0.00	6.45	0.50	0.52	1.19
Marine ecotoxicity	species.yr x 10^{-11}	19.07	0.00	14.06	1.21	1.10	2.70
Human non-carcinogenic toxicity	DALY x 10^{-6}	7.25	0.00	5.09	0.43	0.43	1.30
Fossil resource scarcity	USD2013	119.24	0.00	97.30	6.25	0.14	15.55
Water consumption, Human health	DALY x 10^{-8}	462.74	0.00	31.04	2.38	389.49	39.84

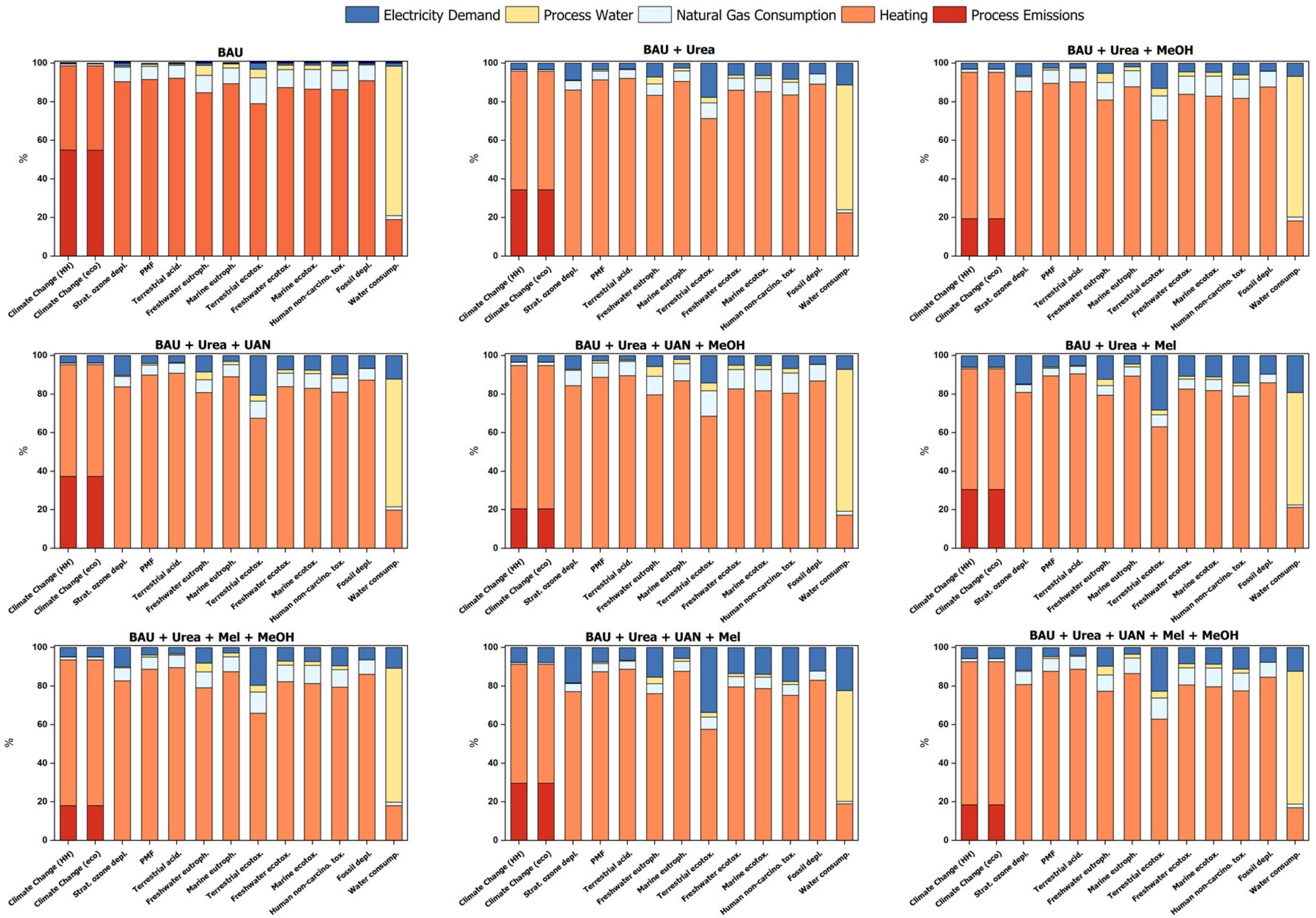

Figure S2: LCA contributional analysis for viable pathways within the NH_3-CO2 integrated eco-park (ReCiPe 2016 Endpoint (H) v1.01)

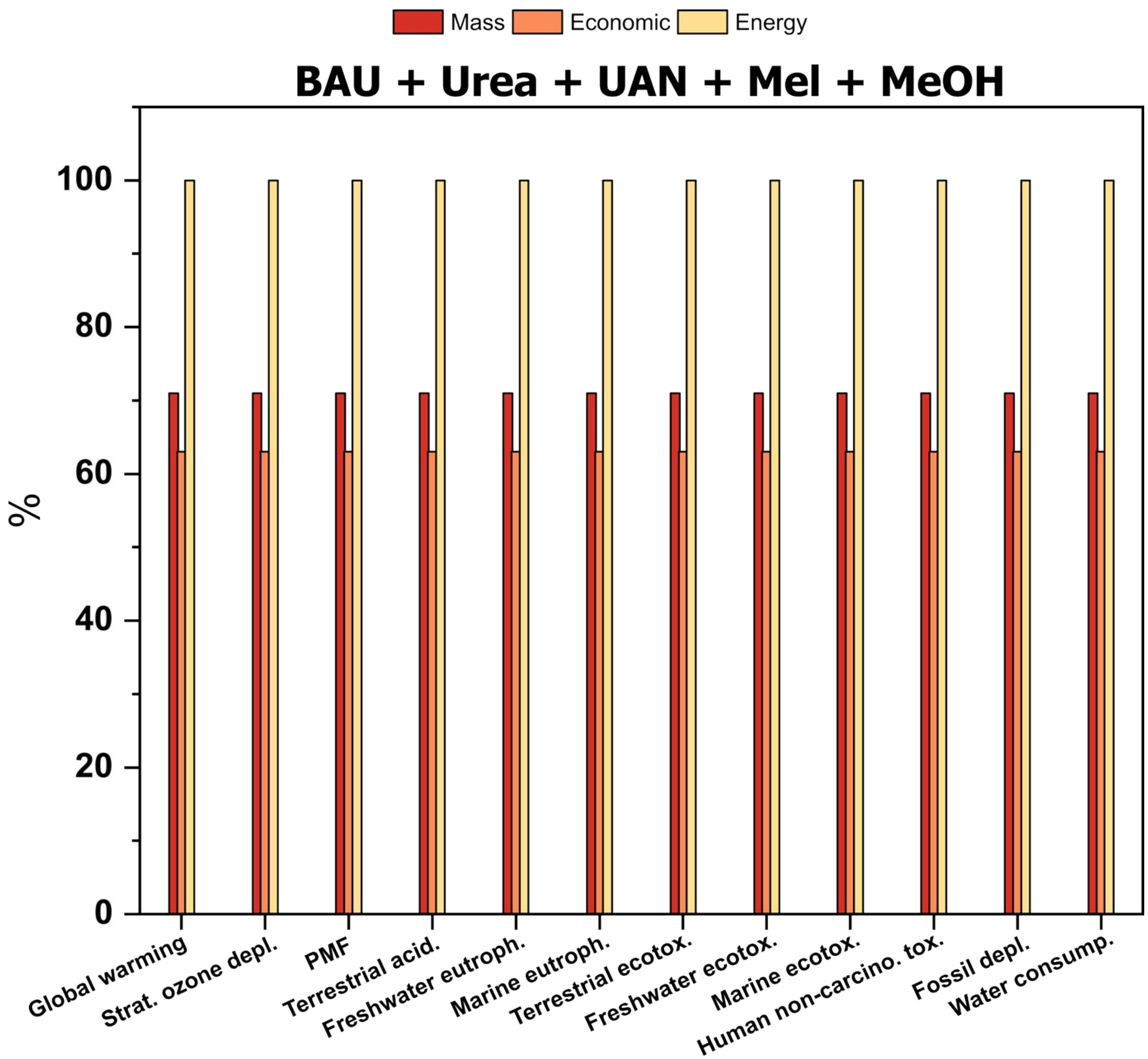

Figure S3: Sensitivity of the LCA methodology (ReCiPe 2016 Midpoint (H) v1.01) of the BAU + Urea + UAN + Mel + MeOH scenario relative to the allocation approach.

7.2 Limitations in PB Framework

- The software used to quantify burdens for the PB-LCIA analysis (Ecoinvent database v3.4 on SimaPro v9.0.0.30) has not been updated to reflect the current global industrial policies with respect to halon, HCFC and CFC use[21]. However, in alignment with work by Algunaibet et al.[17], the burden associated with N_2O was considered by converting the N_2O contributions to a CFC-11 equivalent. Consequently, the transgression for each scenario was determined solely based on the N_2O contributions while halon, HCFC and CFC were excluded given that legislation has restricted the utilization of these specific chemicals with respect to fire extinguishers etc.
- Due to lack of reliable data with respect to land utilization among process industries in Trinidad and Tobago, impacts associated with land system change was neglected from our study.
- Presently, there is no best practice which guides how the share of the safe operating space should be assigned. Furthermore, some sensitivity exists in the selection of sharing principle where one principle can show adherence to the designated share for a given PB while others report transgressions[22]. Acknowledging the lack of guidance in the allocation of shares and with limited availability of global data to consider other sharing principles (such as an egalitarian approach), a status quo approach was considered in this case study[22, 23].

8.0 MeOH Process Description

8.1 MeOH Process Description

Aspen Plus® V10 was used to simulate the MeOH process using the process design from our previous work[24]. The model consisted of front end and back end models. Peng- Robinson was selected as the thermodynamic model for all units except for the distillation columns which were modelled using the Vanlaar thermodynamic model. A brief process description is given here.

8.1.1 Front End

Natural gas, steam and combustion air were fed as raw materials for steam methane reforming with captured CO_2 from the ammonia process[25] being blended with the feedstock and syngas to increase MeOH conversion[26 - 29]. Heavy carbon fractions (C_2H_6 and C_3H_8) were converted to CH_4,

CO, CO_2 and H_2 in the pre-reforming section according to **Eq. 7 – 10** subsequent to steam reforming **Eq. 9 and 11**. Synthesis gas was then utilized within the back-end model for MeOH production. Heat duties for reforming were met directly using natural gas combustion. The two-stage waste heat recovery implemented consisted of the hot effluent synthesis and flue gases being used for steam generation and to maintain distillation duties.

$$C_2H_{6(g)} + 2H_2O_{(g)} \rightarrow 2CO_{(g)} + 5\,H_{2(g)} \qquad \Delta H^\circ = 346.64\frac{kJ}{mol} \tag{7}$$

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \qquad \Delta H^\circ = 498.95\frac{kJ}{mol} \tag{8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^\circ = -41.1\frac{kJ}{mol} \tag{9}$$

$$CO + H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^\circ = -205.91\frac{kJ}{mol} \tag{10}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^\circ = 205.91\frac{kJ}{mol} \tag{11}$$

8.1.2 Back-end

MeOH synthesis was achieved using two fixed bed tubular reactors arranged in a parallel configuration. Reaction kinetics from Vanden Bussche and Froment[30] were considered for MeOH synthesis (**Eq. 12 and 13**).

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^\circ = -41.2\frac{kJ}{mol} \tag{12}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^\circ = 41\frac{kJ}{mol} \tag{13}$$

A final MeOH purity of 99.99% was achieved by distillation of the recovered crude MeOH in a topping and refining column.

9. Estimation of Scenario Specific Production Rates

Scenario specific production rates were estimated based on functional unit (FU) indicators taken from industrial data[25,31] and literature sources[32-36] (**Table S29 and S30**). Firstly, the production rates of ammonia, UAN and Mel were retrieved from industrial sources relevant to the Trinidad and Tobago energy sector. From here, production rates for nitric acid (NA), ammonium nitrate (AN) and Urea were estimated from mass balancing in order to meet the raw material needs for UAN and Mel. MeOH flows were estimated based on Aspen Plus simulations in an effort to utilize all remaining CO_2.

Table S29: Scenario specific raw material mass balances[1]

	Product Flows				
Normalized Input flows taken from Literature	**Urea FU - 1 kg**	**UAN FU - 1 tonne**	**AN FU - 1 kg**	**NA FU - 1 kg**	**Mel FU - 1 kg**
NH_3 kg	**0.497[35,36]**	**0.3[34]**	**0.219[33]**	**0.294[32]**	-
Urea kg	-	**327.7[34]**	-	-	**1.389[32]**
NA kg	-	-	**0.812[33]**	-	-
AN kg	-	**425.7[34]**	-	-	-
CO_2 kg	**0.733[35,36]**	-	-	-	-
Scenario Specific Mass Balance					
Production flows tonne/day	**1667.65**	**4326[31]**	**1841.58**	**1495.36**	**180[31]**
NH_3 tonne/day	**828.82**	**1.298**	**403.306**	**439.636**	-
Urea tonne/day	-	**1417.63**	-	-	**250.02**
NA tonne/day	-	-	**1495.36**	-	-
AN tonne/day	-	**1841.58**	-	-	-
CO_2 tonne/day	**1222.388**	-	-	-	-

[1]Specified flows recorded in **bold**, calculated raw material flows recorded in **blue,** calculated product flows recorded in **red.** Reference to literature is given as superscript.

Sample Calculations: Overall mass balance on UAN.

Based on the normalized input flows for UAN, approximately 327.7 kg Urea/tonne UAN and 425.7 kg AN/tonne UAN is required.

Total Urea required for UAN based on UAN production rate =
$$\frac{327.7\ kg\ Urea}{tonne\ UAN} x \frac{4326\ tonne\ UAN}{day} x \frac{1 tonne}{1000\ kg} =$$ **1417.63 tonne/day.**

Total AN required for UAN based on UAN production rate =
$$\frac{425.7\ kg\ AN}{tonne\ UAN} x \frac{4326\ tonne\ UAN}{day} x \frac{1 tonne}{1000\ kg} =$$ **1841.57 tonne/day.**

Table S30: Overall mass balances for full inclusion of all processes: BAU + Urea + UAN+ Mel +MeOH

Material Flows	Produced	Used	Excess	Comments
NH_3 tonne/day	**1850[25]**	**1673.06**	**176.94**	In alignment with the aim of our study, NH_3 is produced alongside Urea, UAN, Mel and MeOH, in accordance with the operations of the Trinidad and Tobago Energy sector[31].
Urea tonne/day	**1667.65**	**1667.65**	**0**	BAU + Urea : Urea production = 1667.65 tonne/day BAU + Urea + Mel: Urea production = 1417.63 tonne/day
NA tonne/day	**1495.36**	**1495.36**	**0**	All NA used to produce UAN.
AN tonne/day	**1841.578**	**1841.578**	**0**	All AN used to produce UAN.
CO_2 tonne/day	**2250**	**2250**	**0**	Excess CO_2 quota of 1027.612 tonne/day exported to MeOH[24]. Total production rate for MeOH supporting full utilization = 5027 tonne/day
Mel tonne/day	**180**	**0**	**180**	-
UAN tonne/day	**4326**	**0**	**4326**	-

9.0 References

1. S. O. Santos, G. Collodi, G. Azzaro and N. Ferrari, *Techno-economic evaluation of HYCO plant integrated to Ammonia/Urea or Methanol production with CCS*, IEA Greenhouse Gas R&D Programme. Report number 2017-03, 2017.
2. T. Brown, *Ammonia plant cost comparisons: Natural gas, coal, or electrolysis?*, https://ammoniaindustry.com/ammonia-plant-cost-comparisons-natural-gas-coal-or-electrolysis/, (accessed January 2020).
3. Chemicals Technology, *QAFCO Melamine plant*, https://www.chemicals-technology.com/projects/qafcoplant/, (accessed January 2020).
4. U. Turaga, *Small-scale methanol technologies offer flexibility, cost effectiveness*, http://www.gasprocessingnews.com/features/201510/small-scale-methanol-technologies-offer-flexibility,-cost-effectiveness.aspx, (accessed January 2020).
5. W. Conroy, *Poland's ZAP to build 365000 tonne/year nitric acid plant,* https://www.icis.com/explore/resources/news/2017/04/25/10100367/poland-s-zap-to-build-365-000-tonne-year-nitric-acid-plant/, (accessed May, 2020).
6. R. W. Whitesides, *Process equipment cost estimating by ratio and proportion*, https://www.pdhonline.com/courses/g127/g127content.pdf, (accessed January 2020).
7. Economic Indicators. *Chem. Eng.,* 2010, **117(4)**, 80.
8. Economic Indicators. *Chem. Eng.,* 2016, **123(4)**, 96.
9. Economic Indicators. *Chem. Eng.*, 2017, **124(6)**, 80.
10. Economic Indicators. *Chem. Eng.*, 2019, **126(4)**, 60.
11. R. K. Sinnott and G. Towler, *Coulson & Richardson's Chemical Engineering: Chemical Engineering Design*, Elsevier, 2019.
12. R. Turton, J. A. Shaeiwitz, D. Bhattacharyya and W. B. Whiting, *Analysis, Synthesis, and Design of Chemical Processes*, Prentice Hall, 2018.
13. Trinidad and Tobago Electricity Comission, *Summary of electricity rates,* https://ttec.co.tt/default/wp-content/uploads/2015/08/Tariffs.pdf, (accessed January 2020).
14. A. Makhlouf, T. Serradj and H. Cheniti, *Environ. Impact Assess. Rev.*, 2015, **50**, 35-41.

15. M. A. Ahmadi, in *Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs*, ed. A. Bahadori, Gulf Professional Publishing, 2018, DOI: https://doi.org/10.1016/B978-0-12-813027-8.00009-6, pp. 269-290.
16. M. W. Ryberg, M. Owsianiak, K. Richardson and M. Z. Hauschild, *Ecol. Indic.*, 2018, **88**, 250-262.
17. I. M. Algunaibet, C. Pozo, Á. Galán-Martín, M. A. J. Huijbregts, N. Mac Dowell and G. Guillén-Gosálbez, *Energy Environ. Sci.*, 2019, 12, 1890-1900.
18. D. F. Rodríguez-Vallejo, G. Guillén-Gosálbez and B. Chachuat, *ACS Sustainable Chem. Eng.,* 2020, **8 (8)**, 3072 - 3081.
19. S. Farzad, M. A. Mandegari, M. Guo, K. F. Haigh, N. Shah and J. F. Görgens, *Biotechnol. Biofuels*, 2017, **10**, 87.
20. A. Durkin, I. Taptygin, Q. Kong, M. F. M. Gunam Resul, A. Rehman, A. M. L. Fernández, A. P. Harvey, N. Shah and M. Guo, *ChemistryOpen*, 2019, **8 (6)**, 668 - 688.
21. François, *Halon 1301 emissions in petroleum, gas and uranium datasets*, https://www.ecoinvent.org/support/ecoinvent-forum/topic.html?&tid=279, (accessed December 2019).
22. M. W. Ryberg, M. Owsianiak, J. Clavreul, C. Mueller, S. Sim, H. King and M. Z. Hauschild, *Sci. Total Environ.*, 2018, **634**, 1406-1416.
23. A. González-Garay, M. S. Frei, A. Al-Qahtani, C. Mondelli, G. Guillén-Gosálbez and J. Pérez-Ramírez, *Energy Environ. Sci.*, 2019, **12**, 3425-3436.
24. C. Jaggai, Z. Imkaraaz, K. Samm, A. Pounder, N. Koylass, D. P. Chakrabarti, M. Guo and K. Ward, *Green Chem.,* 2020, **22**, 4279-4294
25. S. Sadeek, T. Lee Chan, R. Ramdath, A. Rajkumar, M. Guo and K. Ward, *Chem. Eng. Res. Des.*, 2020, **158**, 177-192.
26. S. Reddy, M. Bhakta, J. Gilmartin and J. Yonkoski, *Energy Procedia*, 2014, **63**, 1407 1414.
27. G. Leonzio, Processes, 2018, **6(3)**, 20.
28. I. L. Wiesberg, J. L. de Medeiros, R. M. B. Alves, P. L. A. Coutinho and O. Q. F. Araújo, Energy Convers. Manage., 2016, **125**, 320-335.
29. G. Collodi, G. Azzaro, N. Ferrari and S. Santos, Energy Procedia, 2017, **114**, 122-138.
30. K. M. Vanden Bussche and G. F. Froment, J. Catal., 1996, **161(1)**, 1-10.

31. Ministry of Energy and Energy Industries – UAN & Melamine, http://www.energy.gov.tt/our-business/lng-petrochemicals/petrochemicals/uan-malamine/ (accessed June 2020).
32. H. Althaus, M. Chudacoff, S. Hellweg, R. Hischier, N. Jungbluth, M. Osses and A. Primas, *Life cycle inventories of chemicals data v2.0*, Swiss Centre for Life Cycle Inventories, Ecoinvent Report No. 8, v2.0, 2007.
33. Kongshaug G., *Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production. Hydro Agri Europe, Norway*. EFMA Seminar on EU Legislation and the Legislation Process in the EU relative to Fertilizer, Prague, 1998.
34. EFMA, *Best available techniques for pollution prevention and control in the european fertilizer industry - Production of urea and urea ammonium nitrate*, Belgium, 2000.
35. T. Nemecek and T. Kägi, *Life cycle inventories of agricultural production systems v2.0*, Swiss Centre for Life Cycle Inventories, Ecoinvent Report No. 15, v2.0, 2007.
36. J. Davis, *Life cycle inventory (LCI) of fertiliser production : fertiliser products used in Sweden and Western Europe*, SIK Institutet för livsmedel och bioteknik, Göteborg, Sverige , 1999.