Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Decision making with deterministic judgment of urea production with various hydrogen sources: technical, economic, and environmental aspects

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1. Process modeling

This work covered the comprehensive analysis including technical, economic, and environmental aspects, simultaneously, for urea production with different types of hydrogen (H_2) based on the process modeling results using Aspen Plus®. Table S1 shows the main flow results for urea production process modeling including the ammonia synthesis section.

Table S1. Main flow results of renewable urea production

	H_2	N_2	1	2	3	4
Temperature/ °C	25.000	25.000	24.761	172.992	120.000	235.069
Pressure/ bar	10.000	10.000	10.000	30.000	30.000	60.000
Molar Vapor Fraction	1.000	1.000	1.000	1.000	1.000	1.000
Molar Liquid Fraction	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flows/ kmol hr^{-1}	214.298	71.394	285.692	285.692	285.692	285.692
Mole Fractions						
H_2	1.000	0.000	0.750	0.750	0.750	0.750
N_2	0.000	1.000	0.250	0.250	0.250	0.250
NH_3	0.000	0.000	0.000	0.000	0.000	0.000
CO_2	0.000	0.000	0.000	0.000	0.000	0.000

H_2O	0.000	0.000	0.000	0.000	0.000	0.000
$(NH_2)_2CO$ (Urea)	0.000	0.000	0.000	0.000	0.000	0.000
NH_2COONH_4 (Ammonium carbamate)	0.000	0.000	0.000	0.000	0.000	0.000
O_2	0.000	0.000	0.000	0.000	0.000	0.000

(Continuous)

	5	6	7	8	9	10
Temperature/ °C	240.000	364.538	360.000	461.714	480.000	332.291
Pressure/ bar	60.000	100.000	100.000	150.000	150.000	50.000
Molar Vapor Fraction	1.000	1.000	1.000	1.000	1.000	1.000
Molar Liquid Fraction	0.000	0.000	0.000	0.000	0.000	0.000

Mole Flows/ kmol hr^{-1}	285.692	285.692	285.692	285.692	285.692	460.342
Mole Fractions						
H_2	0.750	0.750	0.750	0.750	0.750	0.693
N_2	0.250	0.250	0.250	0.250	0.250	0.230
NH_3	0.000	0.000	0.000	0.000	0.000	0.075
CO_2	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.002
$(NH_2)_2CO$ (Urea)	0.000	0.000	0.000	0.000	0.000	0.000
NH_2COONH_4 (Ammonium carbamate)	0.000	0.000	0.000	0.000	0.000	0.000
O_2	0.000	0.000	0.000	0.000	0.000	0.000

(Continuous)

	11	12	13	14	15	16
Temperature/ °C	605.451	480.000	931.265	948.607	948.609	100.000
Pressure/ bar	150.000	150.000	150.000	150.000	150.000	150.000
Molar Vapor Fraction	1.000	1.000	1.000	1.000	1.000	1.000
Molar Liquid Fraction	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flows/ kmol hr^{-1}	460.342	460.342	339.589	334.912	334.911	334.911
Mole Fractions						
H_2	0.693	0.693	0.406	0.390	0.390	0.390
N_2	0.230	0.230	0.135	0.130	0.130	0.130
NH_3	0.075	0.075	0.457	0.478	0.478	0.478
CO_2	0.000	0.000	0.000	0.000	0.000	0.000

H_2O	0.002	0.002	0.002	2.497E-03	2.497E-03	2.497E-03
$(NH_2)_2CO$ (Urea)	0.000	0.000	0.000	0.000	0.000	0.000
NH_2COONH_4 (Ammonium carbamate)	0.000	0.000	0.000	0.000	0.000	0.000
O_2	0.000	0.000	0.000	0.000	0.000	0.000

(Continuous)

	17	18	19	Purge	20	21
Temperature/ °C	20.000	22.634	20.000	20.000	20.000	351.011
Pressure/ bar	5.000	5.000	5.000	5.000	5.000	50.000
Molar Vapor Fraction	0.000	0.0123	1.000	1.000	1.000	1.000
Molar Liquid Fraction	1.000	0.988	0.000	1.00E-10	1.00E-10	0.000

Mole Flows/ kmol hr^{-1}	9991.520	10326.431	218.319	43.664	174.650	174.650
Mole Fractions						
H_2	0.000	0.0127	0.599	0.599	0.599	0.599
N_2	0.000	4.202E-03	0.199	0.199	0.199	0.199
NH_3	0.000	0.0155	0.198	0.198	0.198	0.198
CO_2	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	1.000	0.968	4.788E-03	4.788E-03	4.788E-03	4.788E-03
$(NH_2)_2CO$ (Urea)	0.000	0.000	0.000	0.000	0.000	0.000
NH_2COONH_4 (Ammonium carbamate)	0.000	0.000	0.000	0.000	0.000	0.000
O_2	0.000	0.000	0.000	0.000	0.000	0.008

(Continuous)

	22	23	24	25	26	CO_2
Temperature/ °C	100.000	20.000	21.976		20.000	100.000
Pressure/ bar	50.000	5.000	146.000	146.000	146.000	138.274
Molar Vapor Fraction	1.000	0.000	0.000		0.000	1.000
Molar Liquid Fraction	0.000	1.000	1.000		1.000	0.000
Mole Flows/ kmol hr^{-1}	174.650	10108.112	10108.112		10108.112	65.000
Mole Fractions						
H_2	0.599	2.429E-07	2.429E-07		2.429E-07	0.000
N_2	0.199	5.221E-08	5.221E-08		5.221E-08	0.0594
NH_3	0.198	0.0116	0.0116		0.0116	0.000
CO_2	0.000	0.000	0.000		0.000	0.922

H_2O	4.788E-03	0.988	0.988		0.988	0.0103
$(NH_2)_2CO$ (Urea)	0.000	0.000	0.000		0.000	0.000
NH_2COONH_4 (Ammonium carbamate)	0.000	0.000	0.000		0.000	0.000
O_2	0.000	0.000	0.000		0.000	8.10E-03

(Continuous)

	27	28	29	Urea
Temperature/ °C	167.000	161.000	161.000	161.000
Pressure/ bar	141.000	141.000	141.000	141.000
Molar Vapor Fraction	0.000	2.360E-05	0.000	0.0946
Molar Liquid Fraction	1.000	1.000	1.000	0.905

Mole Flows/ kmol hr^{-1}	10057.482	10114.719	10049.215	65.504
Mole Fractions				
H_2	2.441E-07	2.427E-07	0.000	3.748E-05
N_2	3.840E-04	3.818E-04	0.000	0.0590
NH_3	1.161E-04	1.155E-04	0.000	0.0178
CO_2	2.118E-04	2.106E-04	0.000	0.0325
H_2O	0.993	0.994	1.000	0.000
$(NH_2)_2CO$ (Urea)	0.000	5.659E-03	0.000	0.874
NH_2COONH_4 (Ammonium carbamate)	5.748E-03	5.716E-05	0.000	8.826E-03
O_2	5.236E-05	5.206E-05	0.000	8.039E-03

2. Economic assessment

All cost functions that can calculate for each investment items regarding renewable urea production were presented.

$C_{Cap} = C_{Ref} \times \left(\frac{A_a}{A_b}\right)^n \times \left(\frac{I_a}{I_b}\right)$ where n is a cost exponent, I is the CEPCI, and A is the attribution of equipment	Equation S1
$C_F = 2.47 \times 9.832 \times (F_g)^{0.8}$ where F_g is the feed rate (kg s^{-1}) of gas into flash drum	Equation S2
$C_C = 8650 \times \left(\frac{W_{cp}}{\eta_{cp}}\right)^{0.82}$ where W_{cp} is compressor power (hp) and η_{cp} is the compressor efficiency (%)	Equation S3
$log_{10}C_p^0 = K_1 + K_2log_{10}(A) + K_3[log_{10}(A)]^2$ where C_p^0 is equipment cost, A is feed flow rate or duty, K values are used in correlation	Equation S4
$C_u = 1.6917 \times 8000 \times 3600 \times M_u$ where M_u is mass flow rate (kg s^{-1}) for urea synthesis	Equation S5
$CRF = \frac{a(1+a)^n}{(1+a)^n - 1}$ where n is the project period and a is a discount rate	Equation S6
$C_R = C_{H_2} \times F_{H_2} \times MW_{H_2} + \left(C_{CO_2} - CD_{CO_2}\right) \times F_{CO_2} \times MW_{CO_2} + C_{N_2} \times F_{I}$	Equation S7

where F is feed flow rate (kmol h^{-1}) from process simulation results, MW is molecular weight (kg $kmol^{-1}$), C_{CO_2} is cost of CO_2 capture (74 \$ ton^{-1}) [1], and CD_{CO_2} is cost of CO_2 credit (29.6 \$ ton^{-1}) [2], C_{N_2} is cost of N_2 (0.01 \$ kg^{-1})[3].	

3. Environmental assessment

For environmental assessment, the respective values of CO_2 emissions according to H_2 production technology from many works of literature were used to assess the carbon footprint analysis of renewable urea production. Table S2 indicates the amount of CO_2 emissions of H_2 production technology.

Table S2. Carbon dioxide emissions of hydrogen production technology

Hydrogen (H_2) production technology	Carbon dioxide (CO_2) emissions/ $kgCO_2eq$ $kg\text{-}urea^{-1}$	Ref
Steam methane reforming (SMR)	2.20	[4]
SMR	2.04	[5]
SMR	1.72	[6]
SMR	2.03	[7]
SMR	1.91	[8]
SMR	1.86	[9]
SMR	2.04	[10]
SMR	1.90	[11]
SMR	2.02	[12]

SMR	1.99	[13]
SMR with carbon capture storage (CCS)	1.44	[4]
SMR with CCS	1.29	[6]
SMR with CCS	1.11	[14]
SMR with CCS	1.18	[15]
Coal gasification (CG)	2.88	[4]
CG	3.23	[4]
CG	1.96	[16]
CG	1.99	[17]
CG	1.96	[18]
Methane pyrolysis	1.50	[4]
Methane pyrolysis	1.23	[19]

Methane pyrolysis	1.27	[20]
Methane pyrolysis	1.06	[21]
Methane pyrolysis	1.08	[22]
Wind electrolysis	0.91	[4]
Wind electrolysis	0.93	[5]
Wind electrolysis	0.92	[6]
Wind electrolysis	0.83	[7]
Wind electrolysis	0.89	[19]
Wind electrolysis	0.95	[23]
Wind electrolysis	0.92	[18]
Solar electrolysis	1.02	[4]
Solar electrolysis	1.44	[5]

Solar electrolysis	1.07	5
Solar electrolysis	1.03	6
Solar electrolysis	1.04	6
Solar electrolysis	0.86	7
Solar electrolysis	1.14	17
Solar electrolysis	1.03	17
Solar electrolysis	1.03	23
Solar electrolysis	1.07	18
Water electrolysis, diaphragm cell	0.92	7
Water electrolysis, membrane cell	0.92	7
Water electrolysis, mercury cell	0.93	7
High temperature electrolysis	1.03	11

High temperature electrolysis	1.03	[5]
Nuclear high temperature electrolysis	0.90	[4]
Nuclear high temperature electrolysis	1.02	[6]
Cu-Cl cycle	0.89	[6]
Nuclear high temperature electrolysis	0.86	[24]
Nuclear conventional electrolysis	0.87	[24]
Cu-Cl cycle	0.97	[25]
Cu-Cl cycle	0.96	[26]
Cu-Cl cycle	0.95	[26]
Nuclear electrolysis	0.89	[26]
Nuclear high temperature electrolysis	0.87	[26]
Cu-Cl cycle	0.90	[23]

S-I cycle	0.87	[23]
Nuclear high temperature electrolysis	1.03	[23]
Cu-Cl cycle	1.51	[27]
Cu-Cl cycle	1.68	[28]
Cu-Cl cycle	1.69	[11]
S-I cycle	0.87	[11]
S-I cycle	1.08	[29]
Cu-Cl cycle	2.07	[18]

4. Analytic hierarchy process

Fig. S1 – S6 represent the results of the analytic hierarchy process (AHP) for 30 selected cases in terms of weighted values as well as priority. Each of the figures indicates that priorities result in different types of H_2.

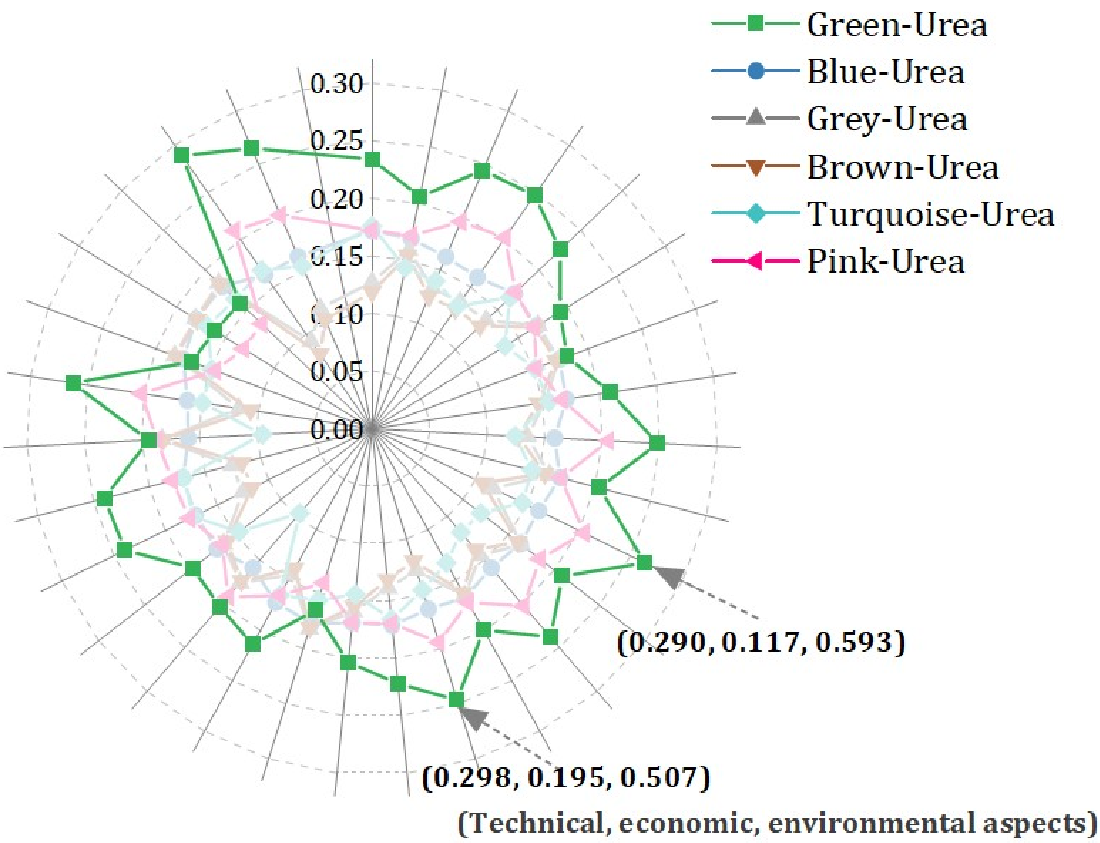

Fig. S1. AHP results for 30 selected cases in terms of weighted values with green urea

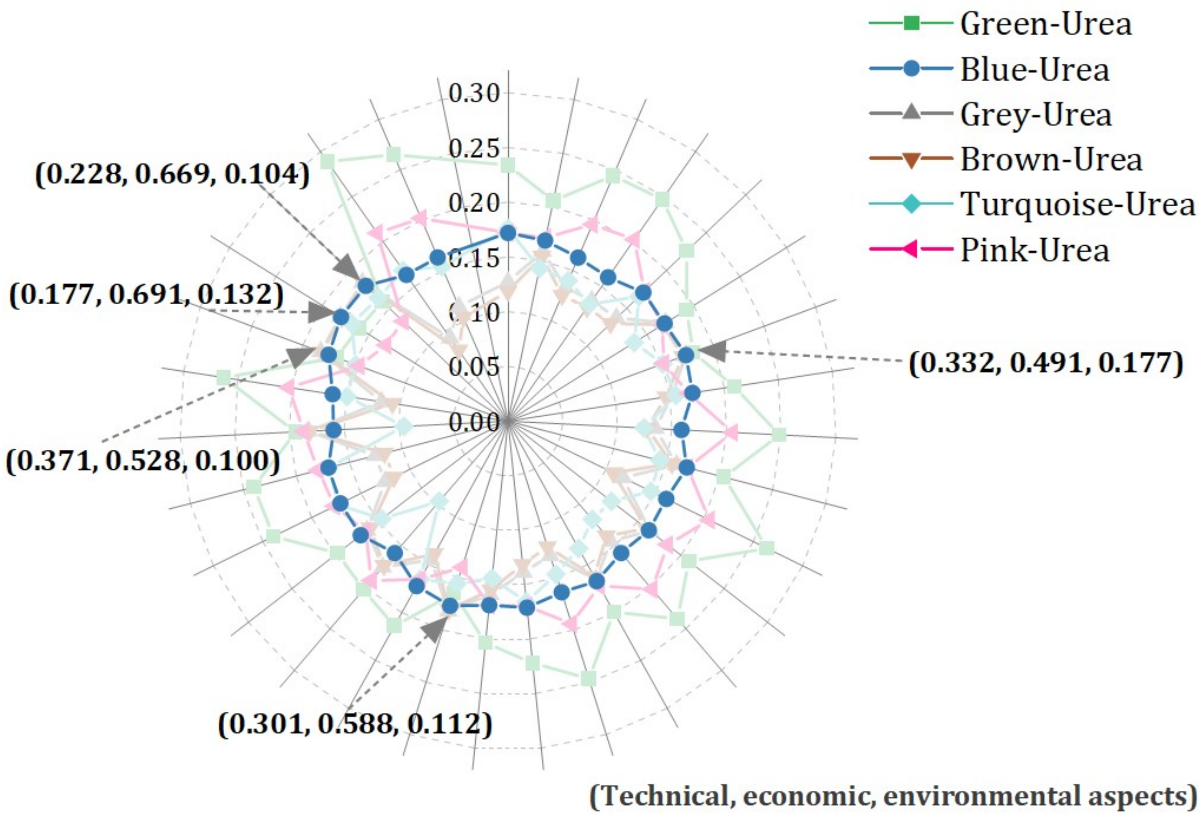

Fig. S2. AHP results for 30 selected cases in terms of weighted values with blue urea

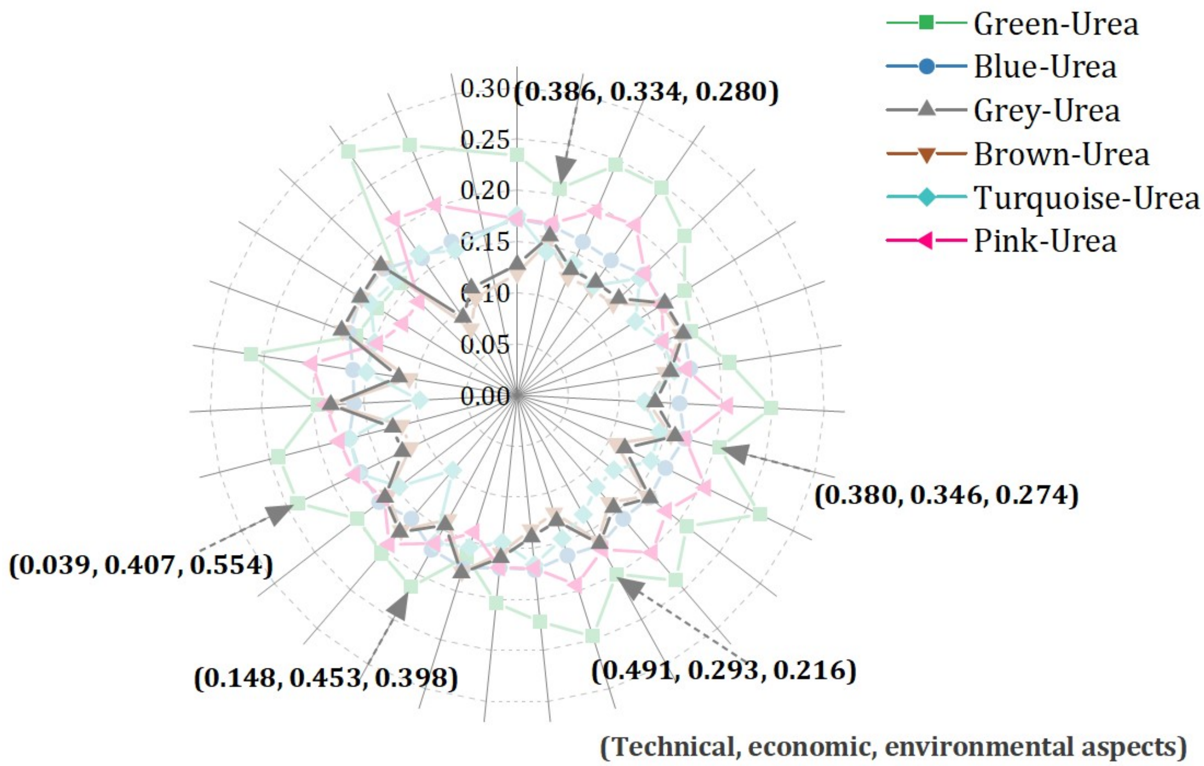

Fig. S3. AHP results for 30 selected cases in terms of weighted values with grey urea

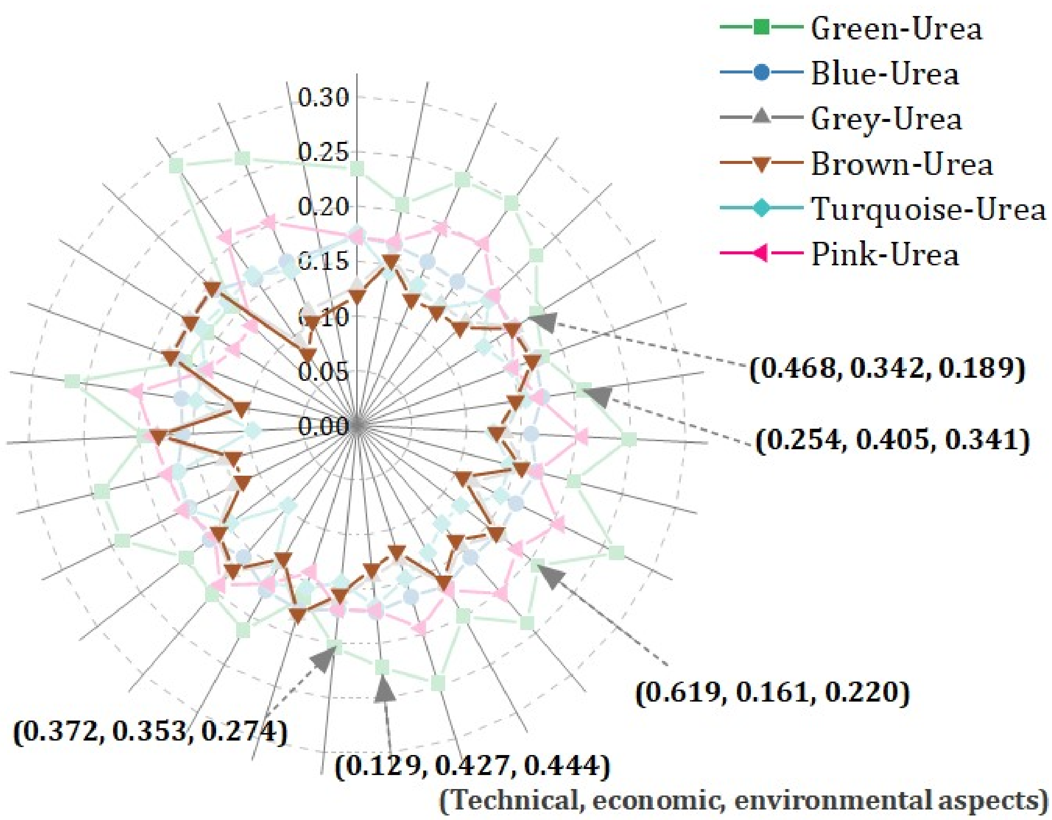

Fig. S4. AHP results for 30 selected cases in terms of weighted values with brown urea

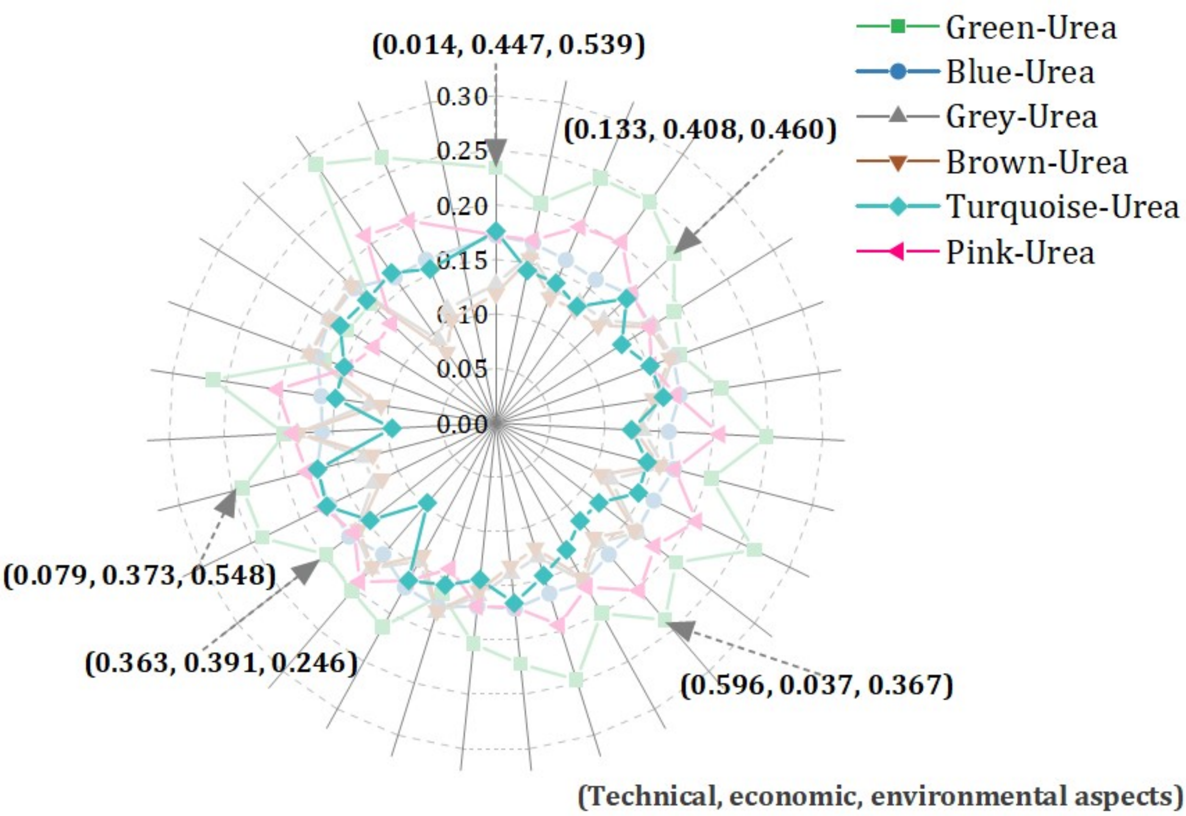

Fig. S5. AHP results for 30 selected cases in terms of weighted values with turquoise urea

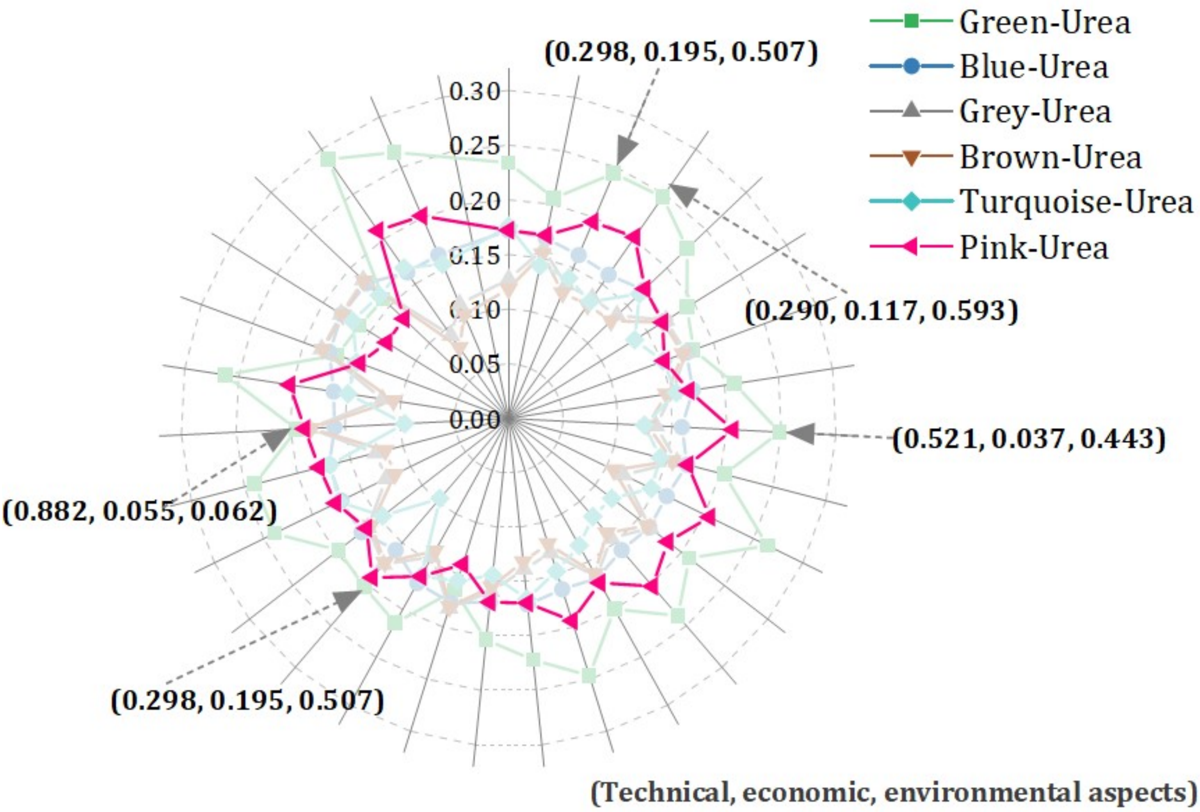

Fig. S6. AHP results for 30 selected cases in terms of weighted values with pink urea

5. **Fitted line plot for various H_2 production costs.**

Fig. S7 – S12 shows a fitted line plot for various H_2 production costs. Based on this fitted line plot for H_2 production cost results, the unit urea production cost hat relies on H_2 pries was estimated as follows.

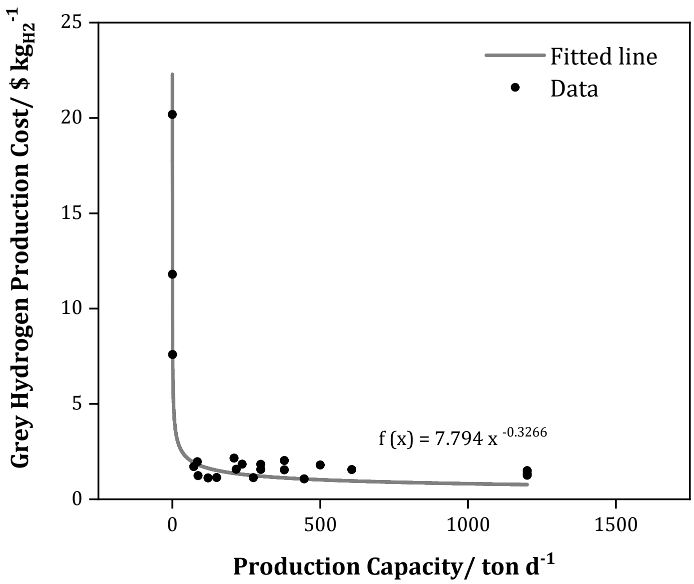

Fig. S7. Fitted line plot for grey hydrogen production cost.

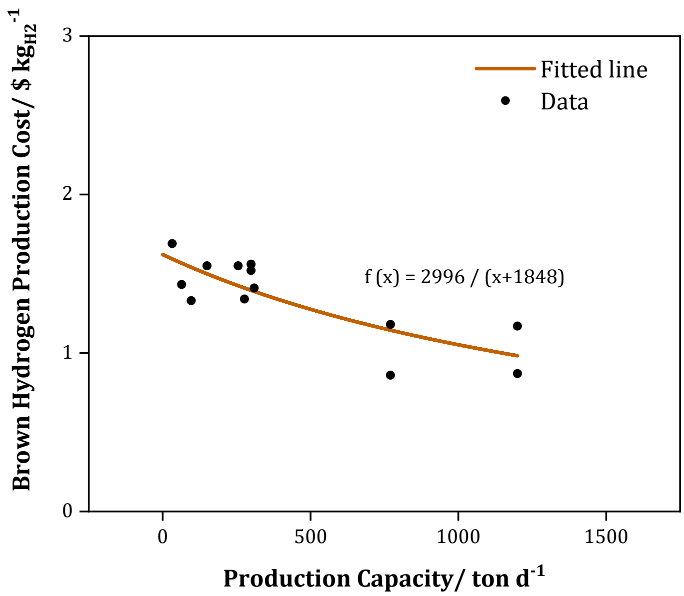

Fig. S8. Fitted line plot for brown hydrogen production cost.

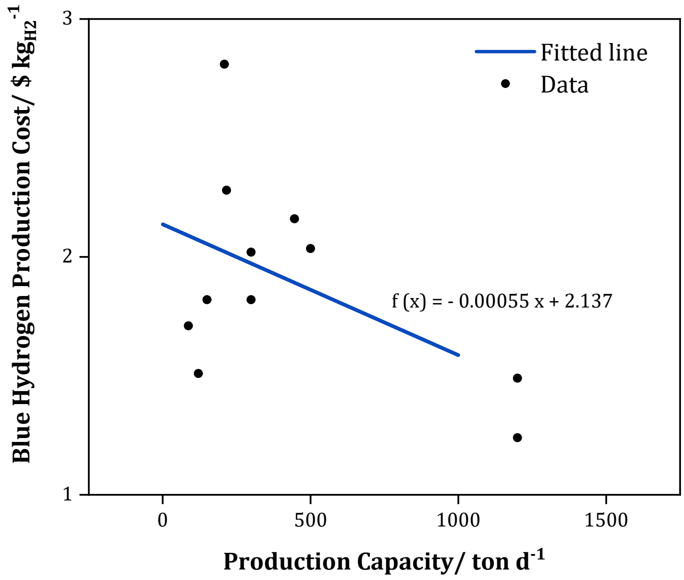

Fig. S9. Fitted line plot for blue hydrogen production cost.

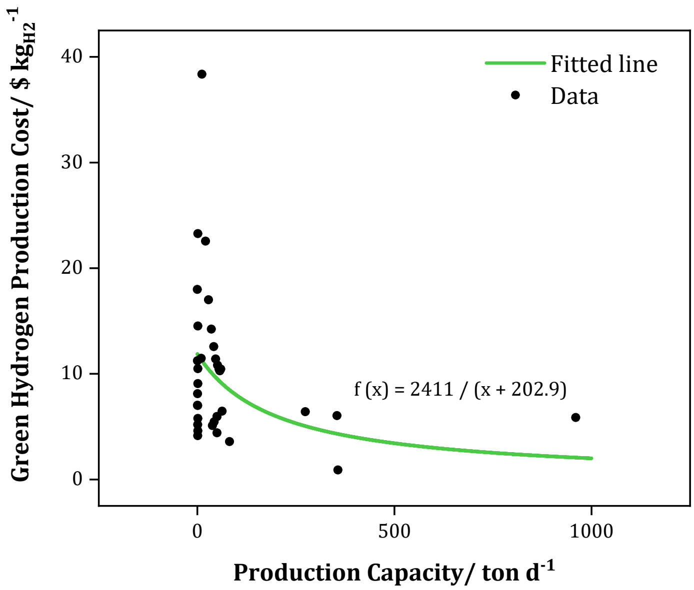

Fig. S10. Fitted line plot for green hydrogen production cost.

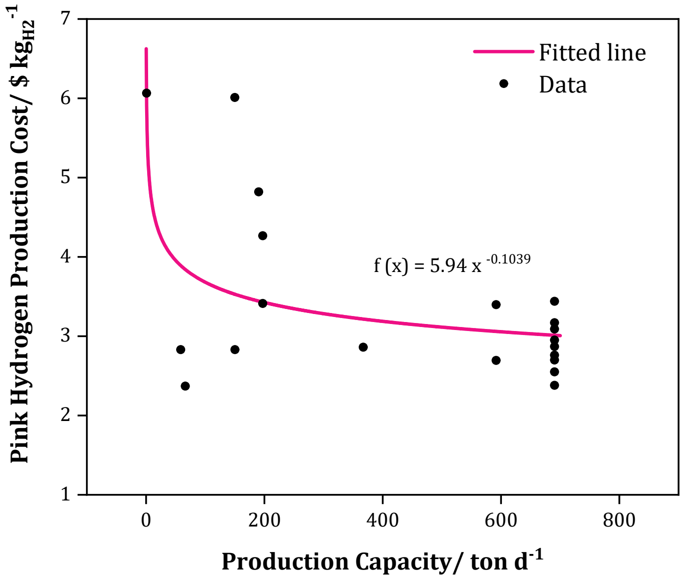

Fig. S11. Fitted line plot for pink hydrogen production cost.

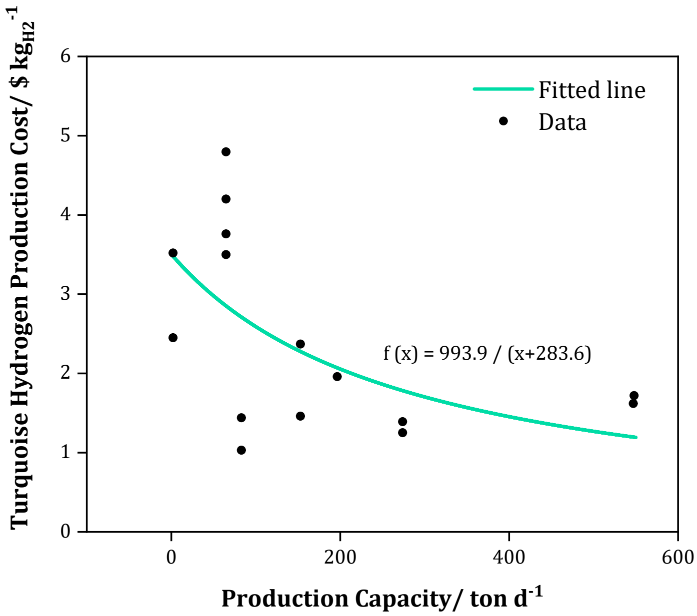

Fig. S12. Fitted line plot for turquoise hydrogen production cost.

References

1 E. S. Rubin, J. E. Davison and H. J. Herzog, *International Journal of Greenhouse Gas Control*, 2015, **40**, 378–400.

2 R. Chauvy, L. Dubois, P. Lybaert, D. Thomas and G. De Weireld, *Applied Energy*, 2020, **260**, 114249.

3 A. Ebrahimi, M. Meratizaman, H. A. Reyhani, O. Pourali and M. Amidpour, *Energy*, 2015, **90**, 1298–1316.

4 B. Parkinson, P. Balcombe, J. F. Speirs, A. D. Hawkes and K. Hellgardt, *Energy Environ Sci*, 2019, **12**, 19–40.

5 V. Utgikar and T. Thiesen, *International Journal of Hydrogen Energy*, 2006, **31**, 939–944.

6 R. Bhandari, C. A. Trudewind and P. Zapp, *Journal of Cleaner Production*, 2014, **85**, 151–163.

7 F. Suleman, I. Dincer and M. Agelin-Chaab, *International Journal of Hydrogen Energy*, 2016, **41**, 8364–8375.

8 F. Kerscher, A. Stary, S. Gleis, A. Ulrich, H. Klein and H. Spliethoff, *International Journal of Hydrogen Energy*, 2021, **46**, 19897–19912.

9 S. Sadeghi, S. Ghandehariun and M. A. Rosen, *Energy*, 2020, **208**, 118347.

10 A. Ozbilen, I. Dincer and M. A. Rosen, *International Journal of Hydrogen Energy*, 2011, **36**, 11321–11327.

11 A. Ozbilen, I. Dincer and M. A. Rosen, *Journal of Cleaner Production*, 2012, **33**, 202–216.

12 E. Cetinkaya, I. Dincer and G. F. Naterer, *International Journal of Hydrogen Energy*, 2012, **37**, 2071–2080.

13 Y. Khojasteh Salkuyeh, B. A. Saville and H. L. MacLean, *International Journal of*

Hydrogen Energy, 2017, **42**, 18894–18909.

14 F. Kerscher, A. Stary, S. Gleis, A. Ulrich, H. Klein and H. Spliethoff, *International Journal of Hydrogen Energy*, 2021, **46**, 19897–19912.

15 Y. Khojasteh Salkuyeh, B. A. Saville and H. L. MacLean, *International Journal of Hydrogen Energy*, 2017, **42**, 18894–18909.

16 R. Bhandari, C. A. Trudewind and P. Zapp, *Journal of Cleaner Production*, 2014, **85**, 151–163.

17 S. Sadeghi, S. Ghandehariun and M. A. Rosen, *Energy*, 2020, **208**, 118347.

18 E. Cetinkaya, I. Dincer and G. F. Naterer, *International Journal of Hydrogen Energy*, 2012, **37**, 2071–2080.

19 F. Kerscher, A. Stary, S. Gleis, A. Ulrich, H. Klein and H. Spliethoff, *International Journal of Hydrogen Energy*, 2021, **46**, 19897–19912.

20 B. J. Leal Pérez, J. A. Medrano Jiménez, R. Bhardwaj, E. Goetheer, M. van Sint Annaland and F. Gallucci, *Int J Hydrogen Energy*, 2021, **46**, 4917–4935.

21 J. Dufour, D. P. Serrano, J. L. Gálvez, J. Moreno and C. García, *International Journal of Hydrogen Energy*, 2009, **34**, 1370–1376.

22 B. Parkinson, M. Tabatabaei, D. C. Upham, B. Ballinger, C. Greig, S. Smart and E. McFarland, *International Journal of Hydrogen Energy*, 2018, **43**, 2540–2555.

23 A. Ozbilen, I. Dincer and M. A. Rosen, *International Journal of Hydrogen Energy*, 2011, **36**, 11321–11327.

24 M. R. Giraldi, J. L. François and D. Castro-Uriegas, *International Journal of Hydrogen Energy*, 2012, **37**, 13933–13942.

25 A. E. Karaca, I. Dincer and J. Gu, *International Journal of Hydrogen Energy*, 2020, **45**, 22148–22159.

26 Y. Bicer and I. Dincer, *International Journal of Hydrogen Energy*, 2017, **42**, 21559–21570.

27 A. Ozbilen, I. Dincer and M. A. Rosen, *Journal of Cleaner Production*, 2012, **33**, 202–216.

28 A. Ozbilen, I. Dincer and M. A. Rosen, *Journal of Cleaner Production*, 2012, **33**, 202–216.

29 W. C. Lattin and V. P. Utgikar, *International Journal of Hydrogen Energy*, 2009, **34**, 737–744.