Electronic Supplementary Material (ESI) for Green Chemistry.

System-level analysis and life cycle assessment of CO_2 and fossil-based formic acid strategies

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APPENDIX

A. Process simulation

With the conventional process, this study deals with the FA production process using CO_2 and H_2 as raw materials. To establish mass and energy balances for CO_2-based FA production, it was simulated by Aspen Plus Process Simulator and detailed process flowsheet (Fig. A.1) and stream data (Table A.1) as follows:

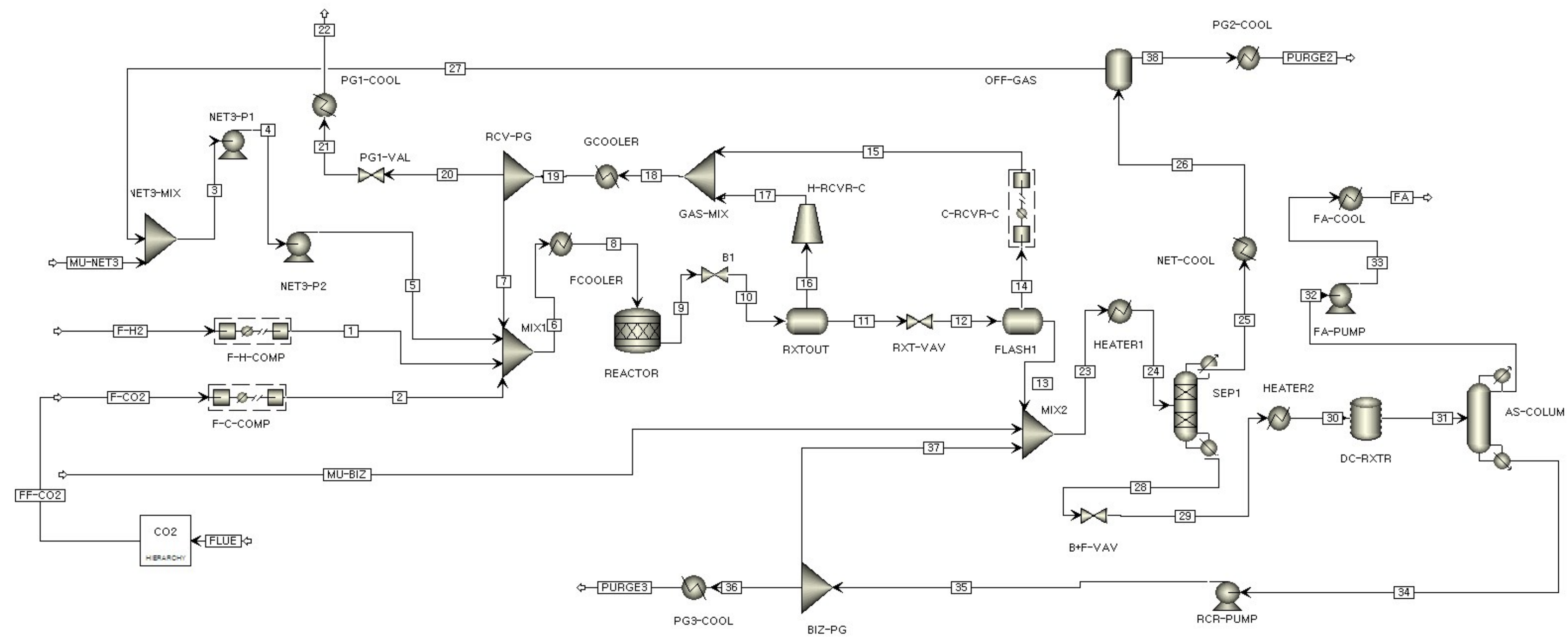


Fig. A.1 Detailed process flowsheet of CO_2-based FA production

Table A.1 Detailed stream data of CO_2-based FA production

		MU-NET3	F-H2	F-CO2	MU-BIZ	27	5	PURGE3	35	37	6	7	20
Mass flows	[kg/hr]	-	-	-	-	-	-	1.3	1,344.8	1,343.5	44.9	44.9	0.5
FA	kg/hr	-	-	-	25.0	-	-	25.0	24,968.6	24,943.6	-	-	-
BIZ	kg/hr	41.0	-	-	-	4,216.1	4,257.1	-	-	-	4,375.0	118.0	1.2
NET3	kg/hr	-	-	4,401.0	-	29.3	29.3	-	-	-	6,122.7	1,692.5	17.1
CO2	kg/hr	-	201.6	-	-	0.0	0.0	-	-	-	624.1	422.5	4.3
H2	kg/hr	298.2	298.2	298.2	298.2	313.2	321.3	298.2	387.1	387.1	302.4	313.2	313.2
Temperature	K	1.0	30.0	1.0	1.0	1.0	180.0	1.0	1.0	1.0	180.0	180.0	180.0
Pressure	bar	101.2	2.0	44.0	124.2	100.3	100.3	114.3	114.3	114.3	22.7	9.1	9.1
Enthalpy	MW	-	-	-	-	-	-	1.3	1,344.8	1,343.5	44.9	44.9	0.5

		19	9	11	16	13	14	23	28	25	38	32
Mass flows	[kg/hr]	45.4	4,548.9	4,538.7	10.3	4,503.6	35.1	5,847.1	5,847.1	-	-	4,502.2
FA	kg/hr	-	-	-	-	-	-	24,968.6	24,968.6	-	-	0.0
BIZ	kg/hr	119.2	4,375.0	4,349.6	25.5	4,255.9	93.7	4,255.9	-	4,255.9	39.9	-
NET3	kg/hr	1,709.5	1,816.0	991.1	824.9	106.5	884.6	106.5	-	106.5	77.2	-
CO2	kg/hr	426.8	426.8	10.9	415.9	0.0	10.9	0.0	-	0.0	0.0	-
H2	kg/hr	313.2	313.2	313.2	313.2	293.2	293.2	334.2	451.2	451.2	313.2	329.7
Temperature	K	180.0	180.0	130.0	130.0	1.0	1.0	1.0	1.0	1.0	1.0	0.2
Pressure	Bar	9.1	28.3	58.3	5.7	62.3	37.6	94.4	93.9	98.1	54.3	46.0
Enthalpy	MW	19	9	11	16	13	14	23	28	25	38	32

In the CO_2-based FA production, H_2 and CO_2 must be supplied at high pressure for reaction. Compressors are used to compress CO_2 and H_2 and feed them to the reactor. A simple diagram and specifications are shown in Fig. A.2 and Table A.2, respectively.

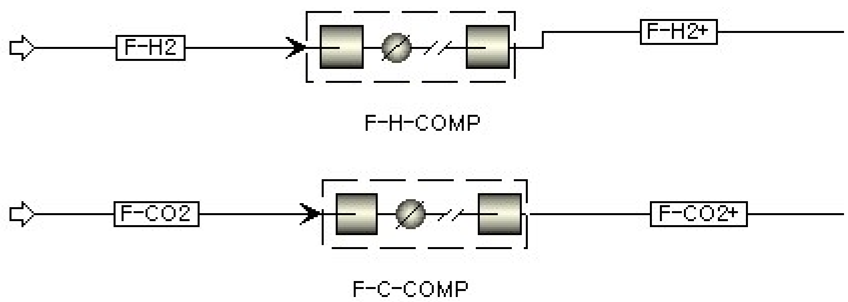


Fig. A.2 Diagram of two compressors in the CO_2-based FA production

Table A.2 Specification of two compressors in the CO_2-based FA production

	F-H-COMP	F-C-COMP
Number of stages	3	6
Discharge pressure from last stage (bar)	180	180
Net work required (kW)	192.6	481.4

FA is produced according to the reactor yield, assuming that CO_2, H_2, and Net3 are reacted under high-pressure reactor while temperature and pressure are constant.

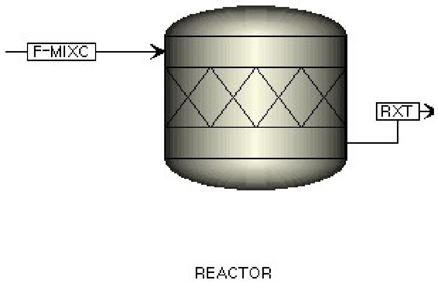


Fig. A.3 Diagram of the reactor in the CO_2-based FA production

Table A.3 Detailed flow data of the reactor in the CO_2-based FA production

		F-MIXC	RXT
Mass Flows	kg/hr	11,167	11,167
FA	kg/hr	45	4,549
BIZ	kg/hr	-	-
NET3	kg/hr	4,375	4,375
CO2	kg/hr	6,123	1,816
H2	kg/hr	624	427
Temperature	C	40	40
Pressure	bar	180	180

The FA-Net3 adduct is generated after producing FA using CO_2, H_2, and Net3. Since FA and Net3 have an azeotropic point, it is difficult to separate them, so we use 1-n-butylimidazole to separate Net3 and FA. This separated Net3 is recovered for reuse, and the distillation column is used to separate the remaining FA and 1-n-butylimidazole.

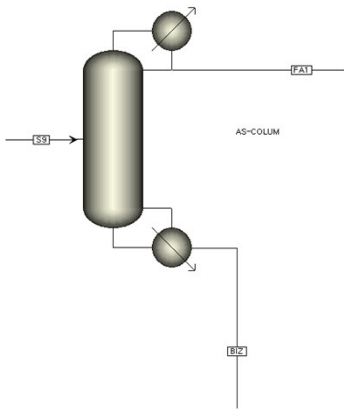


Fig. A.4 Diagram of the column in the CO_2-based FA production

Table A.4 Specification of the column in the CO_2-based FA production

Calculation type	equilibrium
Number of stages	10
Condenser	Total
Distillater rate	97.82 kmol/hr
Reflux rare	195.64 kmol/hr
Condender heat duty	-3052.02 kW
Reboiler heat duty	230.27 kW

Table A.5 Detailed flow data of the column in the CO_2-based FA production

		S9	BIZ	FA
Mass Flows	kg/hr	30815.64	26313.41	4502.23
FA	kg/hr	5,847	1,345	4,502
BIZ	kg/hr	24,969	24,969	0
NET3	kg/hr	-	-	-
CO2	kg/hr	-	-	-
H2	kg/hr	-	-	-
Temperature	C	185	114	25
Pressure	bar	0.200	0.200	1.013

To evaluate the environmental impacts of each representative subprocess in the CO_2-based FA production, we divide into four sub-stages: Compression; Reaction; Net3 recovery; FA purification and 1-n-butylimidazole recovery.

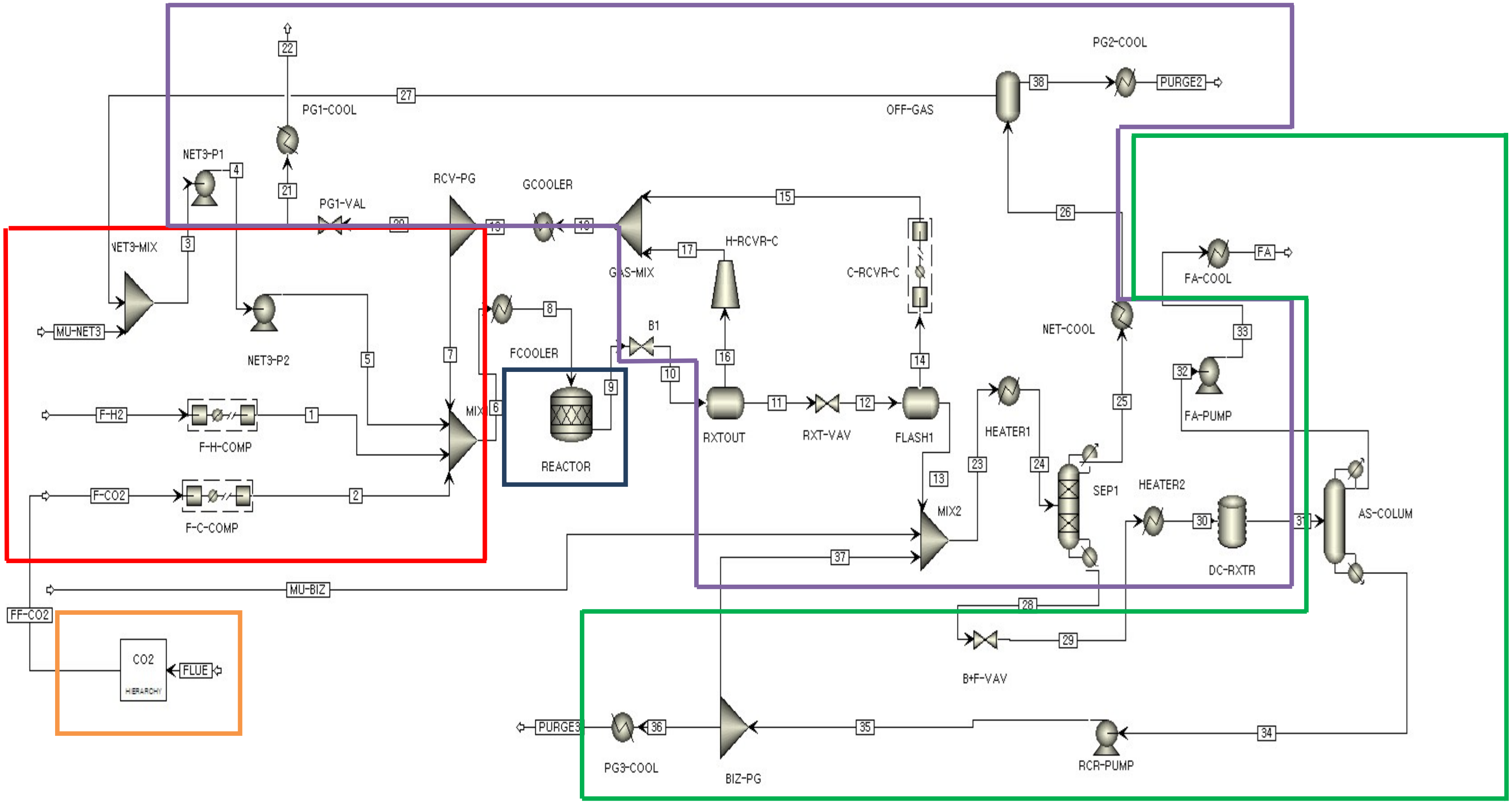


Fig. A.5 Process flowsheet of CO_2-based FA production with sub-processes (red line: compression stage; blue line: reaction stage; purple line: Net_3 recovery stage; green line: FA purification and 1-n-butylimidazole recovery; orange line: CO_2 capture)

The four stages are represented by boxes, and the correlation and usage of materials and energy used in each stage are expressed as the process flow chart.

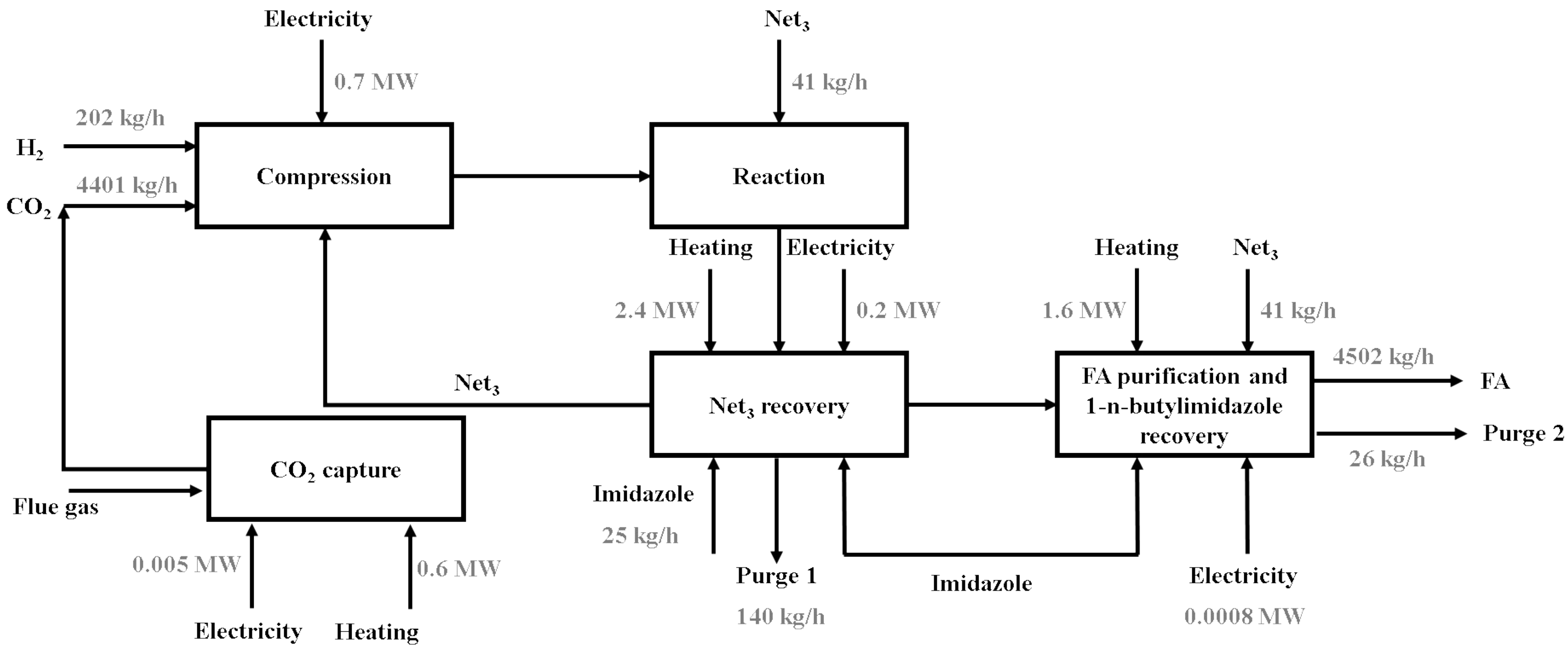


Fig. A.6 Process flow chart of CO_2-based FA production

The calculations for input and output materials at each step are shown in Table A.6.

Table A.6 Detailed input/output data of the CO_2-based FA production

	Input [kg/hr]					Output [kg/hr]				
	FA	1-n-butylimidazole	Net_3	CO_2	H_2	FA	1-n-butylimidazole	Net_3	CO_2	H_2
Compression	44.9	0.0	4375.0	6122.7	624.1	44.9	0.0	43.75.0	6122.7	624.1
Reaction	44.9	0.0	4375.0	6122.7	624.1	4548.9	0.0	4375.0	1816.0	426.8
Net_3 recovery	5892.4	24968.6	4375.0	1816.0	426.8	5892.4	24968.6	4375.1	1816.0	426.8
FA purification and 1-n-butylimidazole recovery	5847.1	24968.6	0.0	0.0	0.0	5847.1	24968.6	0.0	0.0	0.0
CO_2 capture	0.0	0.0	0.0	6122.7	0.0	0.0	0.0	0.0	6122.7	0.0

In order to evaluate the environmental impact of each stage, we used the equivalent ratio of the materials and energy used in each stage and the amount of CO_2 emitted, compared to the total amount of FA produced in the CO_2-based FA production.

Table A.7 Detailed data for FA production from CCU processes (values per kg pure FA)

	Input				Output
	H_2 [kg/ kg_{FA}]	CO_2 used [kg/kg_{FA}]	Electricity [kWh/kg_{FA}]	Steam [kWh/kg_{FA}]	CO_2 emission [kg/kg_{FA}]
Compression	0	0	0.158589	0.02264	0
Reaction	0.045	1.359936	0	0	0.403
Net_3 recovery	0	0	0.046252	0.533992	0
FA purification and 1-n-butylimidazole recovery	0	0	0.000178	0.349307	0
CO_2 capture	0	0	0.001051	0.1338	0

B. LCA data and results

SimaPro software was used to evaluate fossil-based and CO_2-based FA productions and. Ecoinvent 3 database was used, and the sources for the use of raw materials and utilities are shown in Table B.1.

Table B.1 Considered LCA data sets

Product	Name of data set	Database
Electricity	Electricity from natural gas by using the conventional power plant [KR]	SimaPro
Electricity	Electricity from blast furnace gas by using the power plant [KR]	SimaPro
Electricity	Electricity from biogas by using the power generation plant with gas engine [KR]	SimaPro
Electricity	Electricity from hard coal by using the hard coal power plant [KR]	SimaPro
Electricity	Electricity from hydropower technology by using the run-of-river power plant [KR]	SimaPro
Electricity	Electricity from nuclear technology by using the pressure water reactor [KR]	SimaPro
Electricity	Electricity from oil by using the oil power plant [KR]	SimaPro
Electricity	Electricity from photovoltaic technology by using the open ground photovoltaic plant [KR]	SimaPro
Electricity	Electricity from wind technology by using the wind turbine [KR]	SimaPro
Electricity	Electricity from the wood chip by using the power generation plant [KR]	SimaPro
Heat	Heat from the natural gas by using the combined cycle power plant [KR]	SimaPro
Heat	Heat from BFG by using the power plant [KR]	SimaPro
Heat	Heat from the biogas by using the heat generation plant with gas engine [KR]	SimaPro
Heat	Heat from the hard coal by using the heat generation plant [KR]	SimaPro
Heat	Heat from the oil by using the heat generation plant [KR]	SimaPro
Heat	Heat from the wood chip by using the heat generation plant [KR]	SimaPro
CO	CO from partial combustion of heavy heating oil [RoW]	SimaPro
H_2	H_2 from chor-alkali electrolysis technology by using membrane cell [RoW]	SimaPro
H_2	H_2 from the naphtha cracking technology [RoW]	SimaPro
H_2	H_2 from chor-alkali electrolysis technology by using mercury cell [RoW]	SimaPro
H_2	H_2 from steam reforming technology	SimaPro

The environmental assessment of the two processes of the FA production (conventional process vs. CCU process) was conducted. Fig. B.1 shows the values for 18 environmental impact factors as shown in Fig. 3 in the main text. The value for a process with a large value is substituted for 100%, and the ratio to the value is presented in Fig. B.1.

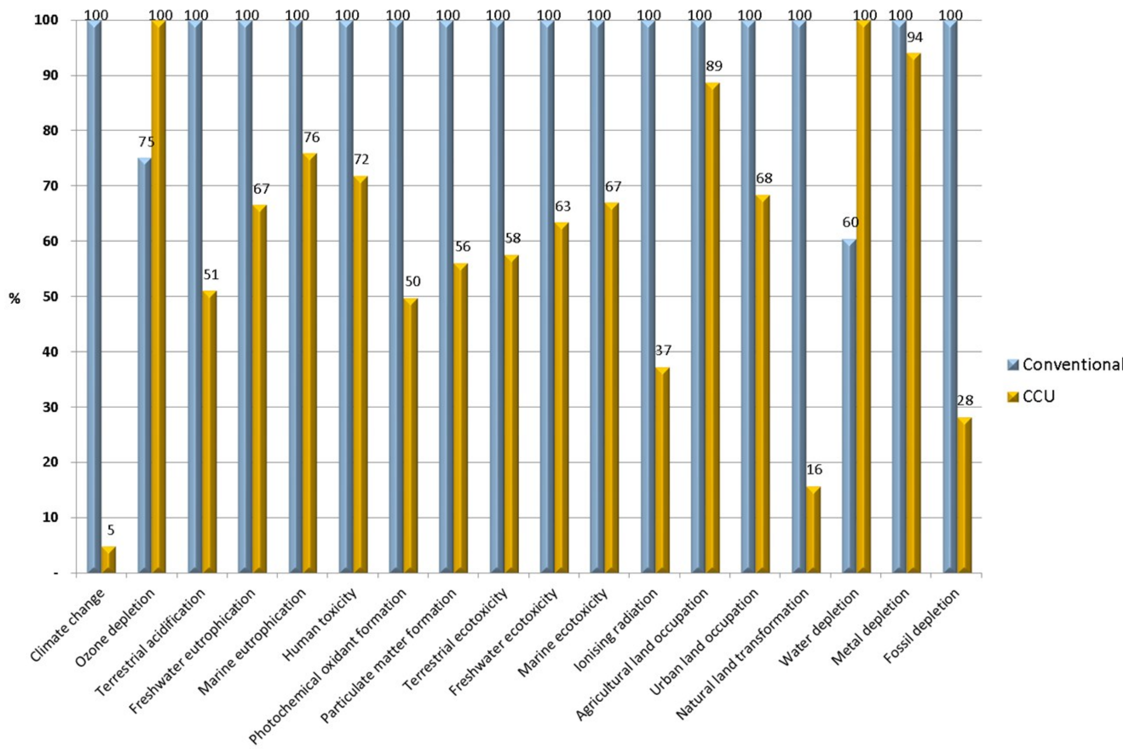


Fig. B.1 Comparison of environmental impact assessment results for two processes.

In this study, the utilities required for FA production are satisfied by a power plant using natural gas. Three case studies (2, 3, and 4) were conducted to evaluate and compare the environmental impacts of changes in raw materials and technologies that produce utilities. First, the results of case 2, in which heat is produced and supplied using natural gas when the raw materials are changed to produce heat (BFG, biogas, hardcoal, oil, and wood chip) in the conventional process, are shown in Fig. B.2.

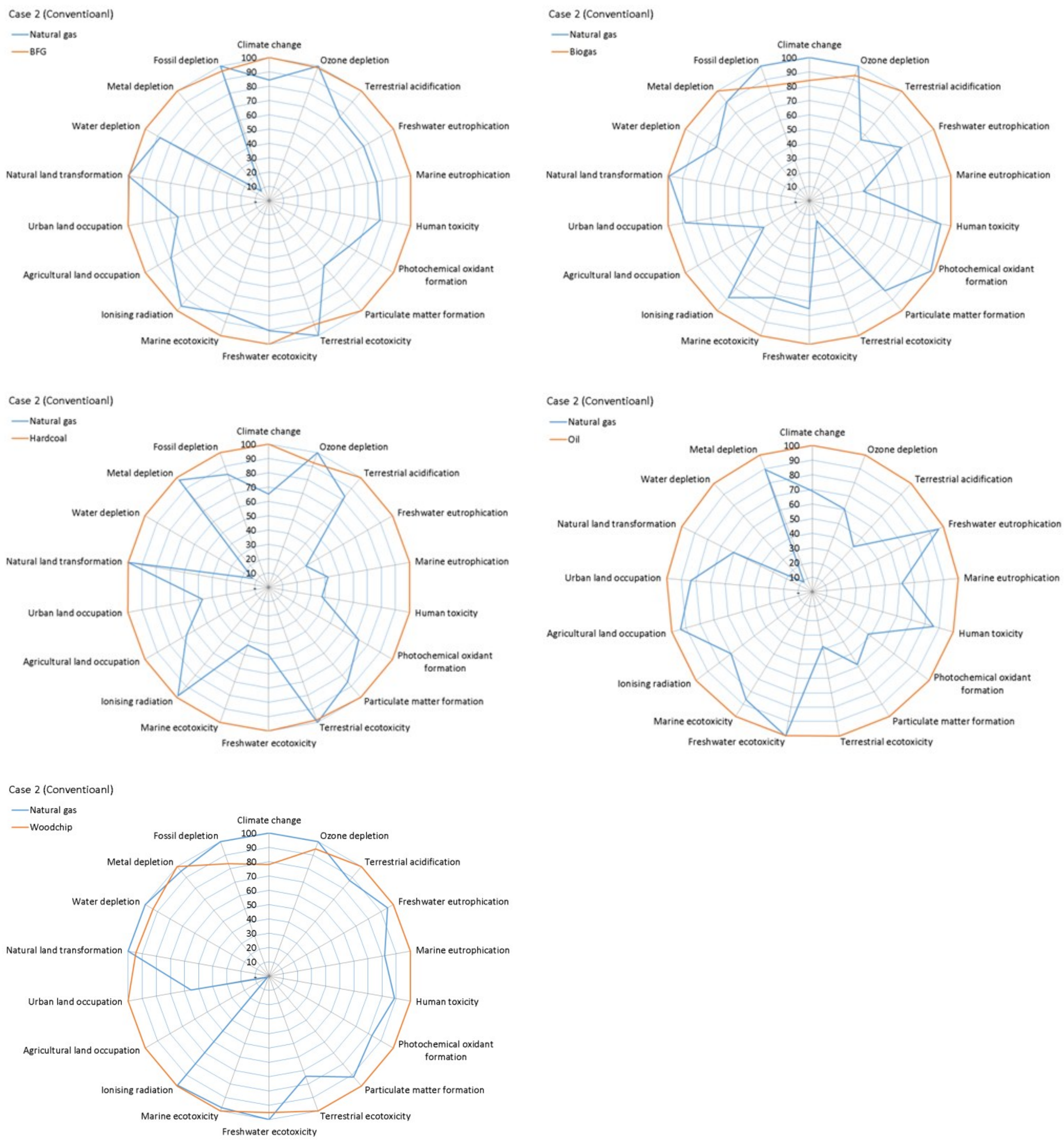


Fig. B.2 Comparison of environmental impact assessment results for conventional process in case 2.

Like the conventional process, the environmental impacts of changes in raw materials and technologies that produce utilities in CCU process are shown in Fig. B.3.

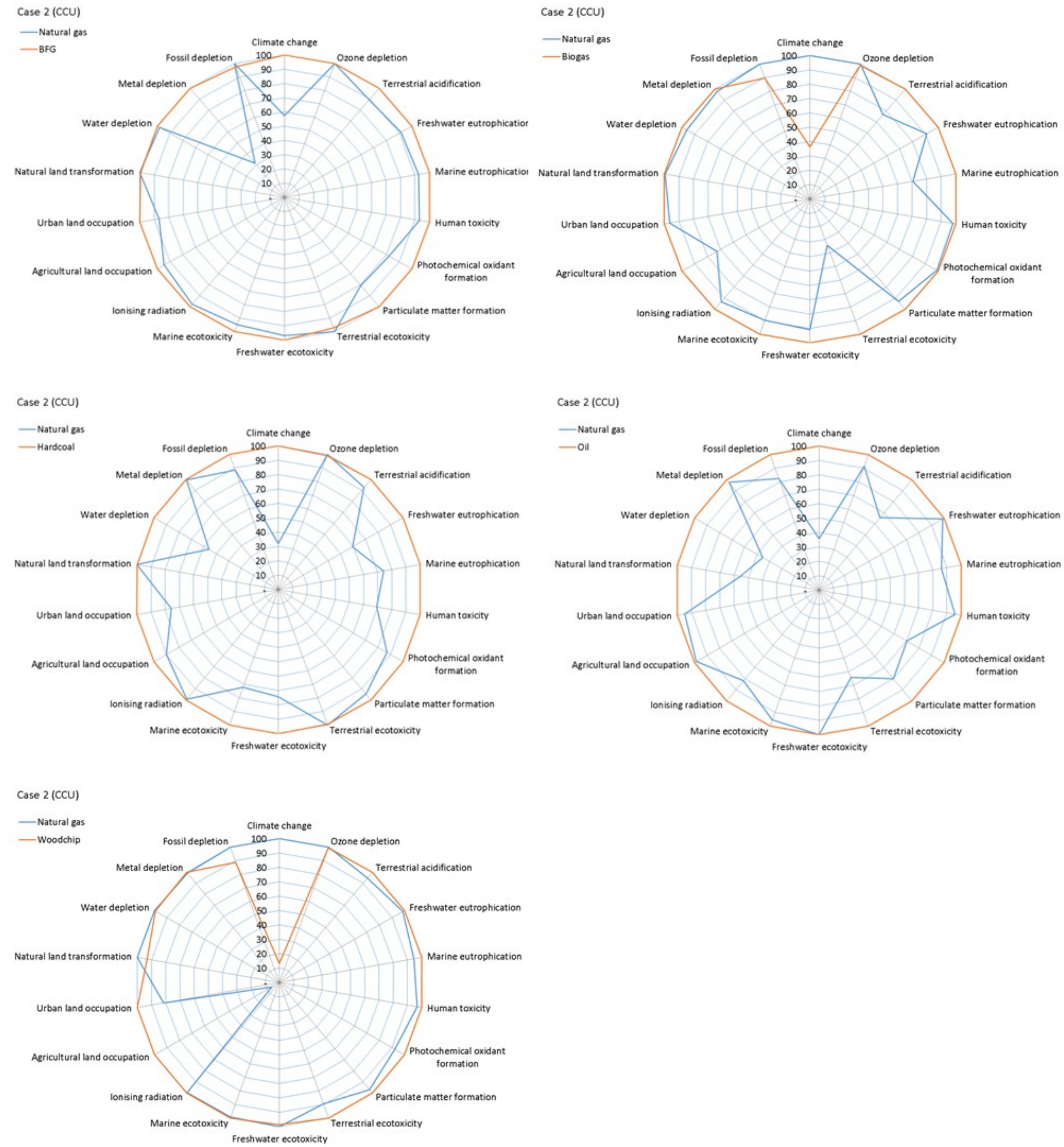
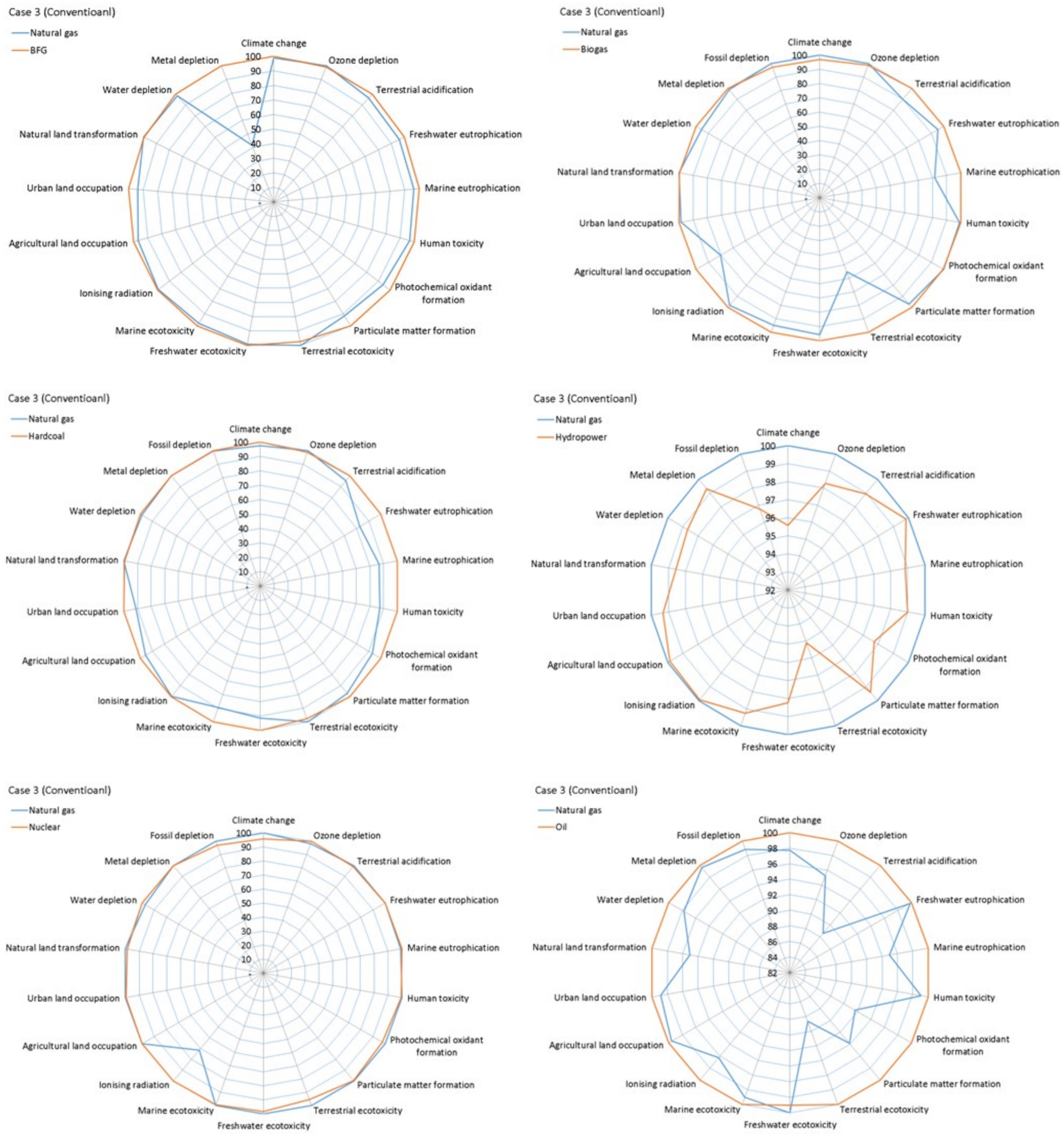


Fig. B.3 Comparison of environmental impact assessment results for CCU process in case 2.

Second, the results of case 3, in which electricity is produced and supplied using natural gas when the raw materials are changed to produce electricity (BFG, biogas, hardcoal, hydropower, nuclear, oil, photovoltaic, wind power and wood chip) in the conventional process, are shown in Fig. B.4.



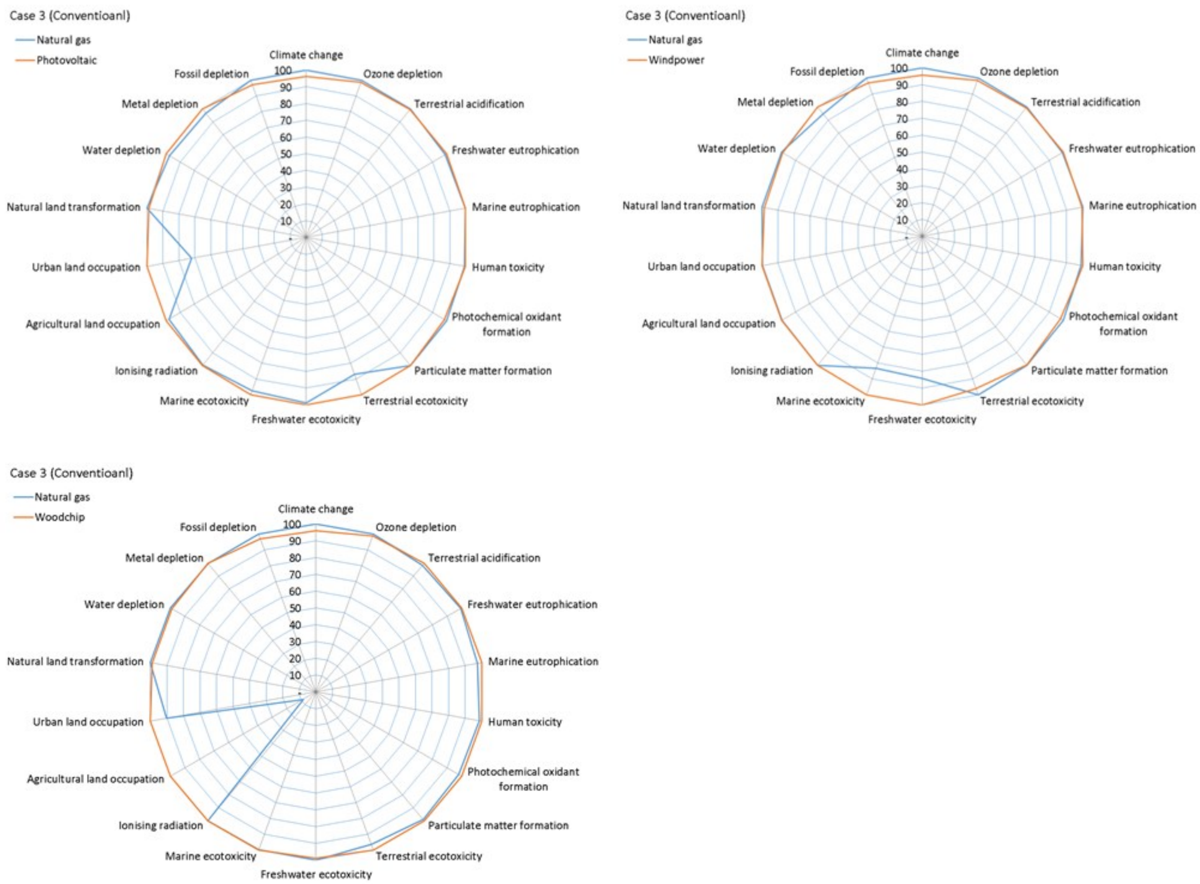
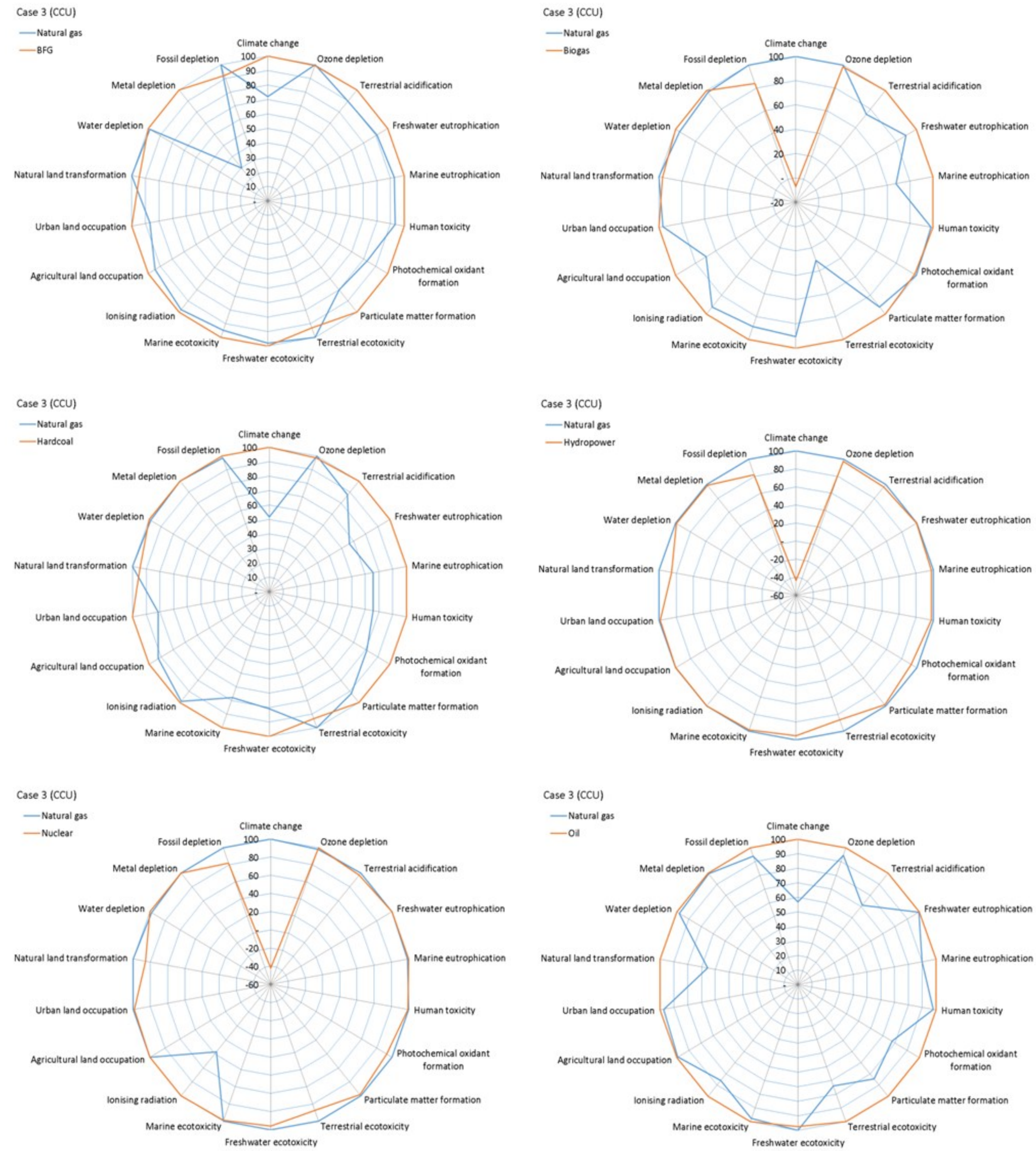


Fig. B.4 Comparison of environmental impact assessment results for conventional process in case 3.

Like the conventional process, the environmental impacts of changes in raw materials and technologies that produce electricity in CCU process are shown in Fig. B.5.



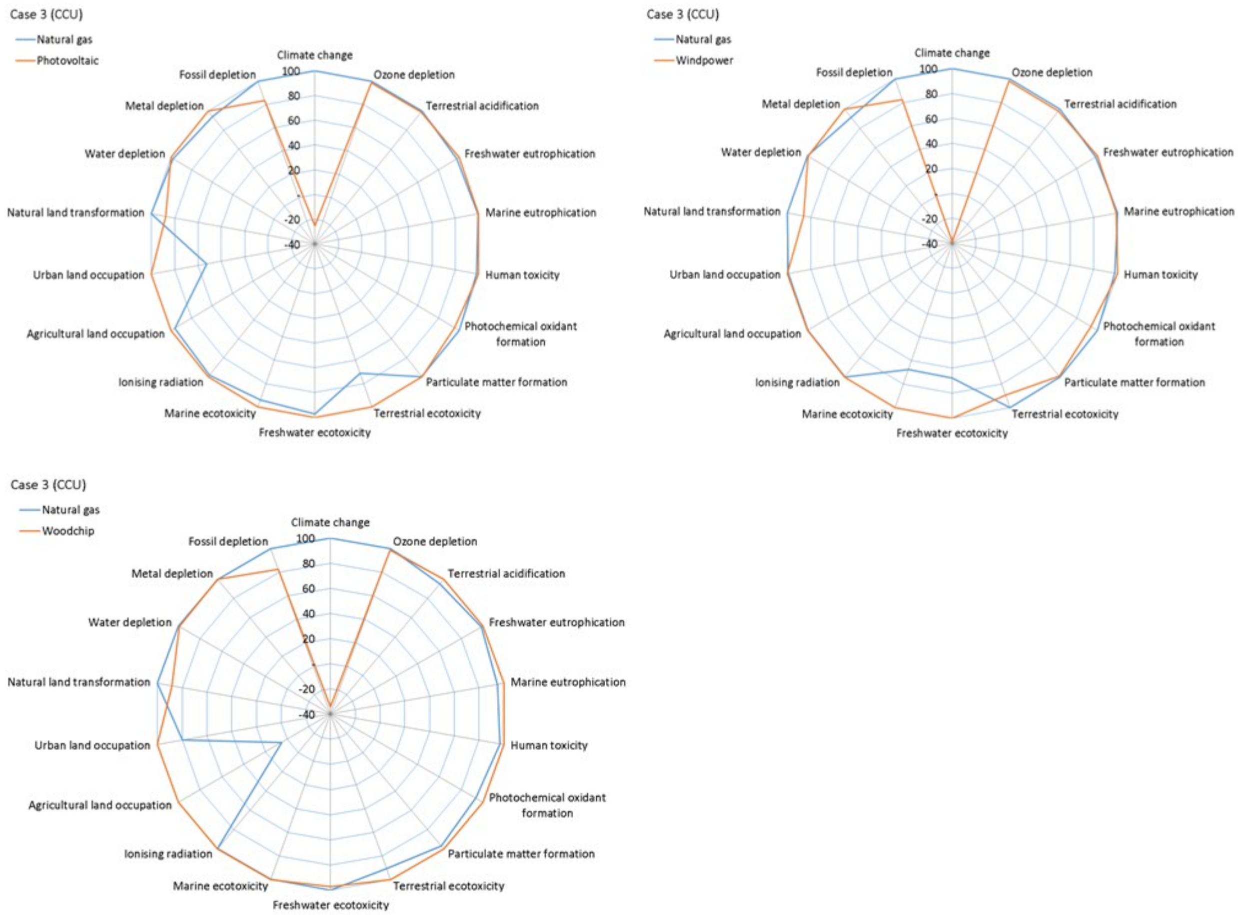


Fig. B.5 Comparison of environmental impact assessment results for CCU process in case 3.

In the last case study, we selected raw materials and technologies which had the best environmental factors by the results of case 2 and 3. Also, the environmental impact was applied to the process of producing FA by using selected raw materials and technology. The results of this case study (case 4) were compared with the results of an environmental impact assessment using natural gas only (case 1).

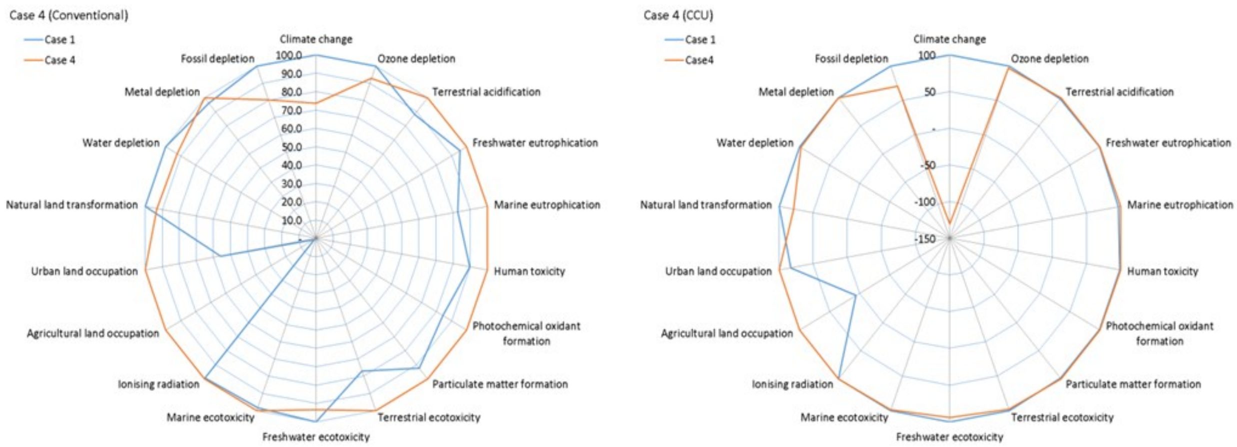


Fig. B.6 Comparison of environmental impact assessment results for two processes in case 4.

Until now, we have carried out the environmental evaluation based on the total amount of materials and energy of two processes that produce FA. In order to evaluate the environmental impacts of the subprocess in CO_2-based FA production, we divided it into four stages and carried out an environmental impact assessment.

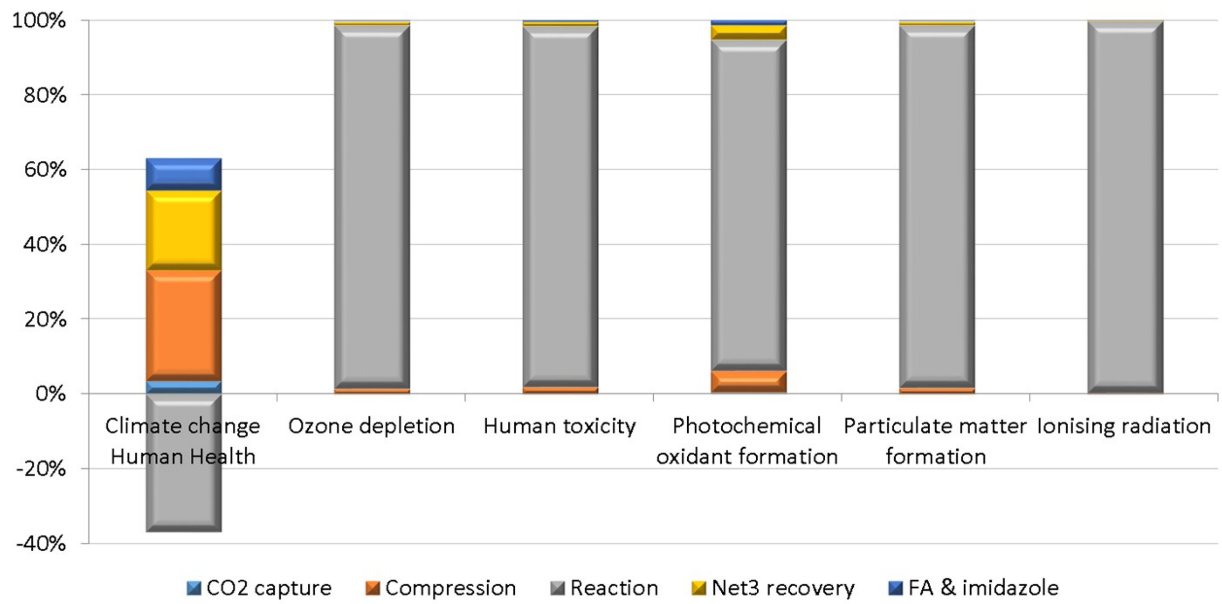


Fig. B.7 Comparison of environmental impact assessment results for sub-processes in CO_2-based FA production.

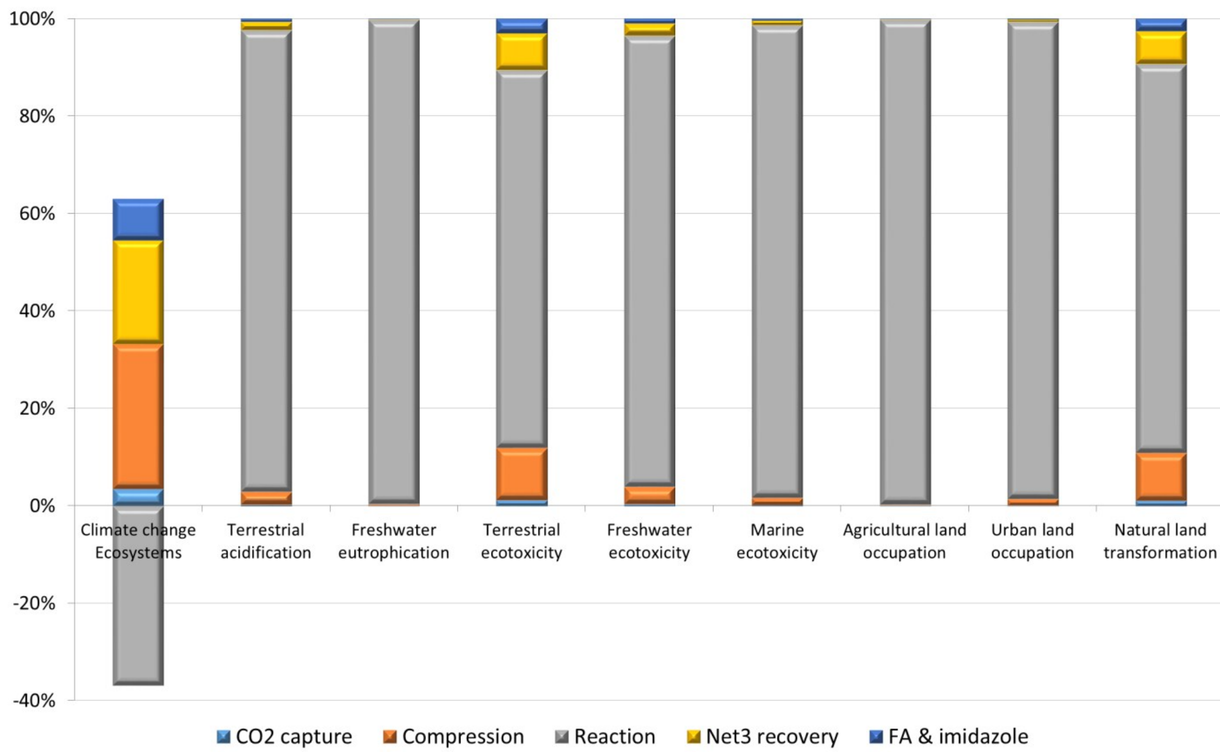


Fig. B.8 Comparison of environmental impact assessment results for sub-processes in CO_2-based FA production.

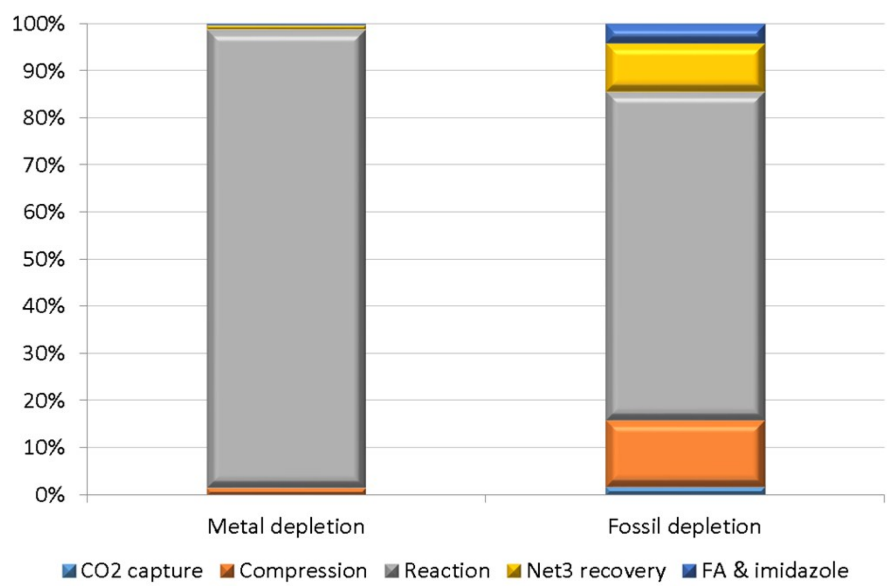


Fig. B.9 Comparison of environmental impact assessment results for sub-processes in CO_2-based FA production.

Table B.2 Non-normalized environmental impacts for the FA of sub-processes in kg product

	Unit	CO_2 capture	Compression	Reaction	Net3 recovery	FA production and 1-n-butylimidazole recovery
Climate change	kg CO2 eq	0.012811	0.110894	-0.13744	0.079993	0.031686
Ozone depletion	kg CFC-11 eq	8.91E-10	7.74E-09	4.64E-07	5.57E-09	2.20E-09
Terrestrial acidification	kg SO2 eq	9.79E-06	9.83E-05	0.003557	6.47E-05	2.40E-05
Freshwater eutrophication	kg P eq	1.19E-07	1.54E-06	0.00042	8.77E-07	2.86E-07
Marine eutrophication	kg N eq	3.81E-07	4.19E-06	0.000208	2.62E-06	9.27E-07
Human toxicity	kg 1,4-DB eq	0.000742	0.00746	0.396226	0.004909	0.001819
Photochemical oxidant formation	kg NMVOC	1.37E-05	0.00014	0.002141	9.13E-05	3.35E-05
Particulate matter formation	kg PM10 eq	3.31E-06	3.39E-05	0.002159	2.21E-05	8.11E-06
Terrestrial ecotoxicity	kg 1,4-DB eq	6.91E-07	6.05E-06	4.39E-05	4.33E-06	1.71E-06
Freshwater ecotoxicity	kg 1,4-DB eq	5.04E-05	0.000451	0.011646	0.000319	0.000124
Marine ecotoxicity	kg 1,4-DB eq	1.79E-05	0.000171	0.010985	0.000116	4.39E-05
Ionising radiation	kBq U235 eq	2.79E-05	0.000265	0.081582	0.00018	6.87E-05
Agricultural land occupation	m2a	6.25E-06	7.58E-05	0.024888	4.48E-05	1.51E-05
Urban land occupation	m2a	4.63E-06	0.000106	0.007781	4.64E-05	1.04E-05
Natural land transformation	m2	1.47E-06	1.34E-05	9.05E-05	9.34E-06	3.61E-06
Water depletion	m3	2.08E-05	0.000169	0.015909	0.000127	5.15E-05
Metal depletion	kg Fe eq	5.81E-05	0.000661	0.042814	0.000405	0.000141
Fossil depletion	kg oil eq	0.004811	0.041613	0.203051	0.030033	0.0119

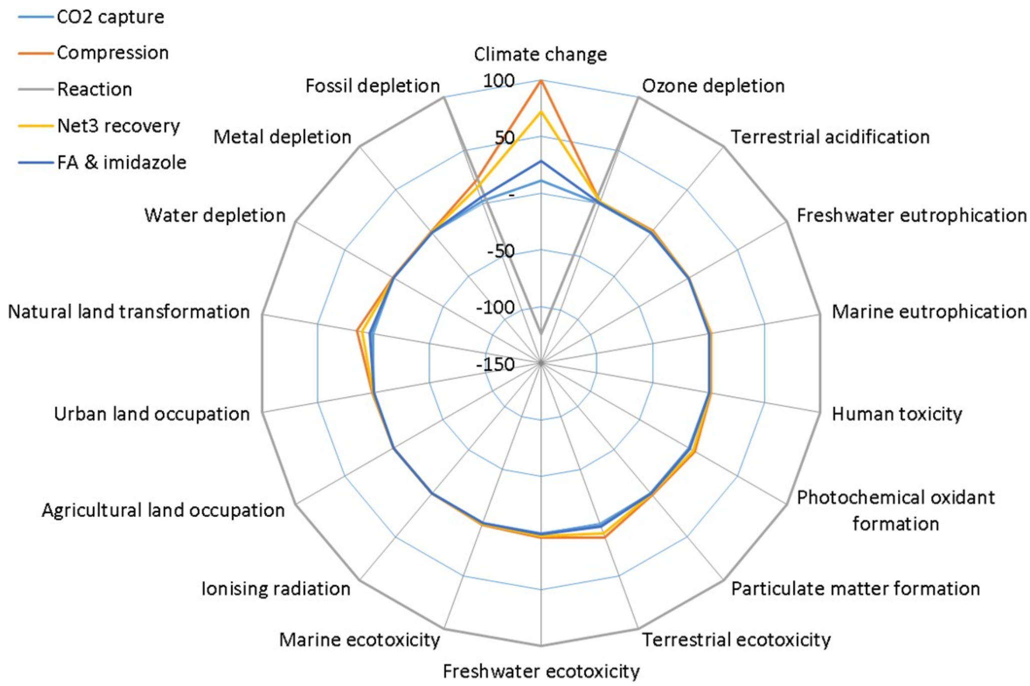


Fig. B.10 Comparison of environmental impact assessment results for four sub-stages in CO_2-based FA production.

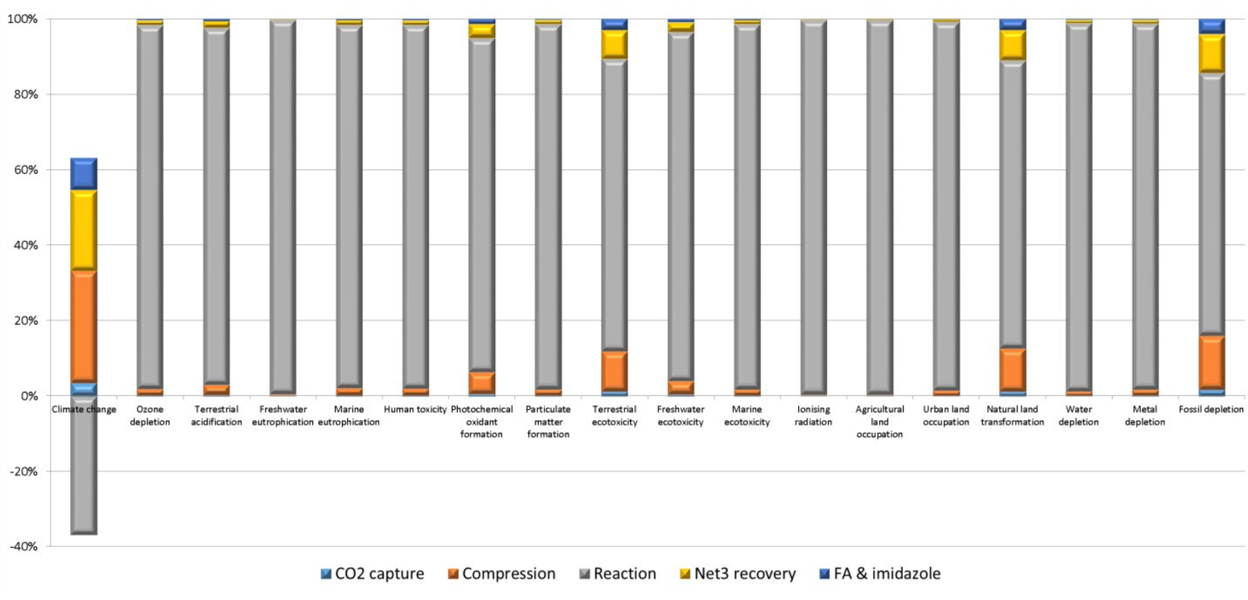


Fig. B.11 Environmental profile of 1 kg of formic acid showing relative proportions of each of the 18 impact categories.

C. Catalyst information

In CO_2-based FA production, with homogeneous promoter, the low-molecular-weight amine NR_3 is quantitatively converted into amine FA adduct ($HCOOH$-NR_3) with an acid-amine molar ratio (AAR) > 1.33.[1] To increase AAR and solve difficulty of catalyst separation, a heterogeneous catalyst supported metal was investigated to produce them. By employing a metal catalyst (i.e., commercial AUROlite catalyst consisting of gold supported on titania), the direct formation reaction of amine FA adduct took place with high AAR (1.715) and the catalyst was stable without deactivation.[1] By using AUROlite catalyst, FA is more producible, but the drawback of this procedure remains the separation of NR_3 to make pure FA.

We calculated the price based on the catalyst composition. The results are shown in Table C.1.

Table C.1 Datails of AUROlite catalyst cost

	Unit	Au[2]	TiO_2[3]
Composition	wt%	1	99
Material cost	US$/kg	8,632	3
Catalyst cost	US$/kg	90	

Reference

1. D. Preti, C. Resta, S. Squarcialupi and G. Fachinetti, *Angewandte Chemie*, 2011, **123**, 12759-12762.
2. Au catalyst price, (https://www.kitco.com/charts/historicalgold.html) (accessed 05/05/2019).
3. TiO2 catalyst price, https://www.indmin.com/Article/3826556/TiO2-prices-hold-steady-market-reaches-equilibrium.html (accessed 05/05/2019).