Supplementary Information on Life Cycle Greenhouse Gas Emissions Analysis of the Chlor-Alkali Process and By-product Hydrogen in the United States

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Introduction

1.1. Chlor-alkali process and technology

The chlor-alkali industry mainly uses three production technologies—mercury, diaphragm, and membrane—and the use of mercury technology is diminishing because of mercury pollution. The three technologies differ in process design and energy consumption, as described in the following subsections and summarized in Figure S 1.

1.1.1. Mercury technology

The mercury process uses high-purity brine solution (with little or no metal contamination, via filtration and purification) and decomposes about 16% of the salt per passage through the mercury cells.[1,2] On the anode side, Cl_2 gas is formed and on the cathode side, sodium amalgam is formed. Subsequently, in a separate reactor (the decomposer), the amalgam is reacted with water to form hydrogen gas and caustic soda (NaOH) solution. The products from mercury technology have high purity. The chlorine generally contains almost no oxygen and can be used without further purification. The NaOH solution from the decomposer has a 50 wt% concentration, and can be directly sold as a product, either as a solution or as dried product in various shapes. Relative to the other two technologies, the mercury process requires pure brine, and operates at higher voltage and current density, and thus uses more electric energy. However, given the production of high-concentration (50 wt%) caustic, no steam is required to concentrate the caustic solution.

1.1.2. Diaphragm technology

For diaphragm technology, Cl_2 is formed on the anode side, while H_2 gas and caustic NaOH are formed on the cathode side. The anode area and the cathode area are separated by a permeable diaphragm (asbestos-based or non-asbestos-based polymers). The technology can utilize a lower-quality feedstock. The brine is purified by precipitation-filtration, and then the saturated salt (about 25%) flows into the anode compartment and through the diaphragm into the cathode compartment. The cathode effluent solution contains both product caustic soda (NaOH, about 10–12 wt%) and unreacted salt (NaCl, 15–17 wt%). The solution is evaporated to precipitate most of the NaCl, leaving 50 wt% caustic soda. The salt separated from the caustic brine can be used to make more brine as feedstock. The chlorine contains oxygen and must be purified by liquefaction and evaporation.[1] The diaphragm cell process consumes less electric energy than the mercury process but requires fuel to produce steam to concentrate the caustic brine (from 10–12 wt% to 50 wt%).

1.1.3. Membrane technology

In the membrane process, an ion-conducting membrane is used to separate the anode and the cathode. Brine solution flows through the anode compartment, where chloride ions are oxidized to form chlorine gas. The depleted brine is discharged from the anode compartment and re-saturated with salt to feed the process cell.

The sodium ions, together with water, migrate from the anode compartment through the membrane to the cathode compartment. On the cathode side, as in the diaphragm method, hydrogen gas and caustic soda are formed. The caustic soda is typically at about 32 wt% in the cell.

Meanwhile, a portion of the caustic soda solution is diluted to a concentration of approximately 30 wt% and recycled to the catholyte inlet. From the recycling loop, caustic soda is continuously removed.

The membrane cell technology needs high-purity brine feed, requiring additional purification steps. The produced caustic soda needs to be evaporated, using steam, to increase its concentration from 30–33 wt% to 50 wt%. The produced chlorine gas needs to be processed to remove oxygen by liquefaction and evaporation.

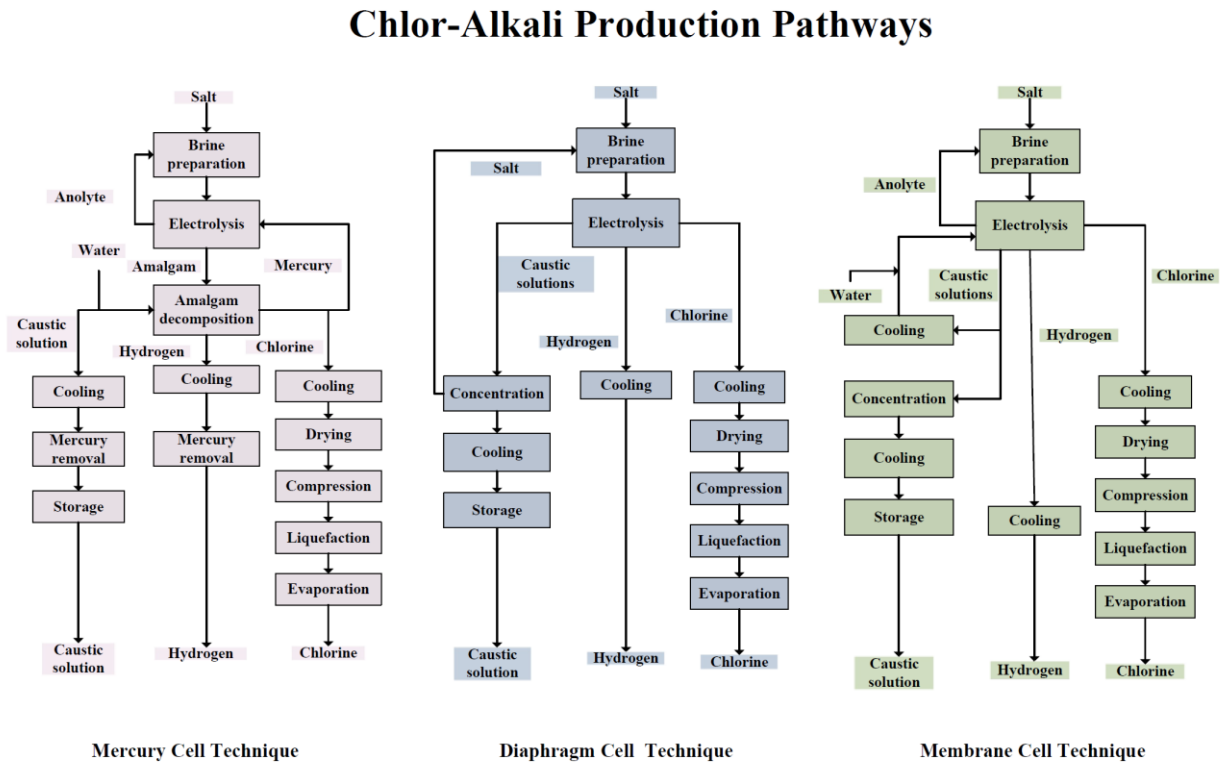


Figure S 1. Three chlor-alkali processes using different technologies (simplified from ref. 3).

1.2. Electrolysis products

In chlor-alkali plants, the brine electrolysis process produces three main products: chlorine, sodium hydroxide (or potassium hydroxide), and hydrogen. After the electrolysis process, each main product will undergo a different post treatment process. Chlorine will be processed via cooling, drying, compression, liquefaction, and evaporation, requiring both electricity (for the first four processes) and steam (for evaporation).

The main treatment for sodium hydroxide is concentration, requiring the use of steam, the amount of which varies with the aforementioned electrolysis technology.

1.2.1. Hydrogen

For all three technologies used in the chlor-alkali process, hydrogen is co-produced from brine electrolysis with high quality (purity > 99.9 %).The co-produced hydrogen can be combusted on site to generate electricity or steam (a dominant practice), or used as a chemical reagent internally (e.g., for the production of hydrochloric acid) or on an adjacent site, or sold (e.g., for the production of ammonia, hydrogen peroxide, and methanol). The hydrogen combusted onsite could be recovered by diverting the hydrogen gas from fuel; however, additional fuel (e.g., natural gas) may be required to meet the energy demand which was supplied by the combusted hydrogen.

1.2.2. Other products from chlor-alkali plants

1.2.2.1. Hydrochloric acid (HCl)

Some plants produce hydrochloric acid via hydrogen and chlorine combustion at high temperature (2000°C). The produced HCl gas passes through a cooler with process water to produce aqueous solution.

$H_2 + Cl_2 \rightarrow 2HCl$

This reaction is highly exothermic and thus does not require a heat supply. The process requires some electricity.

1.2.2.2. Sodium hypochlorite (NaClO)

Sodium hypochlorite, commonly used for sanitizing, bleaching and water treatment, is produced by reacting diluted caustic and liquid or gaseous chlorine as shown below.

$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$

1.2.2.3. Ethylene dichloride (EDC)

EDC can be produced by direct chlorination, via reacting ethylene with chlorine in the liquid phase under mild conditions of 20–120°C and a pressure of 75 psi. The product can then be recovered and purified via distillation.

Direct chlorination:

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 + 218\ kJ/mol$

EDC can be also produced by oxychlorination, via reacting ethylene, hydrochloric acid and oxygen as shown below.

Oxychlorination:

$C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O + 238$ kJ/mol

In practice, EDC might be produced from both routes, with the first one as a standalone system and the second one integrated with the VCM reaction as shown in the next subsection.

1.2.2.4. Vinyl chloride monomer (VCM)

Vinyl chloride monomer (VCM) is produced from EDC via thermal cleavage or dehydrochlorination as shown below.

$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$ -71 kJ/mol

The co-produced HCl is used for EDC oxychlorination production. If not sufficient, supplemental HCl might be used.

2. Methodology

2.1. Data sources

2.1.1. Chlor-alkali capacity data

This study compiles comprehensive inventories of air pollutant emissions in the U.S. chlor-alkali industry (reported by facilities) and information about plant operations (electricity generation and on-site usage) and products (final products as well as intermediate products). A rigorous chlor-alkali plant list matching was conducted to ensure the same refinery coverage among emission data sets and plant product data sets, based on cross-checks of physical location, history of acquisitions and mergers, capacity, and other related factors. The capacity of individual chlor-alkali plants was obtained from various sources based on previous chlor-alkali industry studies. The capacity is presented in terms of chlorine production.

2.1.2. Chemical Data Reporting (CDR) database

Facilities report the production and use of potentially toxic substances to EPA's Chemical Data Reporting (CDR) database under the Toxic Substances Control Act. Not all data are available publicly, as some production quantities are considered confidential business information; nor are data released annually. The database is released every four years. The CDR 2012 and 2016 data (for 2011 and 2015 operation) were used in the present study to account for production quantities at U.S. chlor-alkali facilities.

2.1.3. National Emissions Inventory (NEI) Data

Criteria air pollutants (CAP) emissions information for U.S. chlor-alkali facilities is collected from the National Emissions Inventory (NEI) database. Facilities report annual emissions of CAPs, hazardous air pollutants, and other air emissions to the NEI from individual point sources. Unit-level emission sources are categorized using Source Classification Codes (SCCs), enabling emissions to be categorized by subprocess. Official

releases of NEI data occur every three years, but annual point source data are available annually from the EPA. To align with other emission and producton data, the 2011 datasets and 2016 datasets were used in this study. The facility-level CAP emissions are listed in Table S 1 below.

2.1.4. Greenhouse Gas Reporting Program (GHGRP) Data

U.S. facilities separately report annual emissions of GHGs to the Greenhouse Gas Reporting Program (GHGRP). Reporting is required for all stationary combustion emissions of CO_2, CH_4, and N_2O from industrial sources under GHGRP Subpart C. Additional reporting is required in some sectors for industry-specific emissions sources. With limited sources of GHGs, however, chlor-alkali facilities are not regulated under any additional subparts. As in the NEI case, GHG emissions are reported by unit, and include information regarding the type of fuel combusted, if applicable. The chlor-alkali facility GHG emissions are listed here, with facility total emissions in Table S 1 and facility CO_2 emission breakdown for each fuel-type combustion in Table S 2.

2.1.5. EIA-923 data for combined heat and power

Fuel consumption and electricity generation data for plants that utilize a combined heat and power (CHP) system are sourced from U.S. Energy Information Administration (EIA) reports based predominantly on the EIA-923 form. In this dataset, facilities report the quantity of fuel consumed for electricity generation as well as total fuel consumption. The difference is assumed to reflect fuel consumption for steam generation. Facilities also quantify the amount of electricity exported or resold if it is not all consumed on-site. In total, seven chlor-alkali facilities in this study were identified as using CHP through these data in one or both of the data years.

2.2. Summary of analysis approach

The steps used to obtain the energy intensity and emission intensity for facilities' individual final products are summarized in the following subsections, and details are described in Figure S 2.

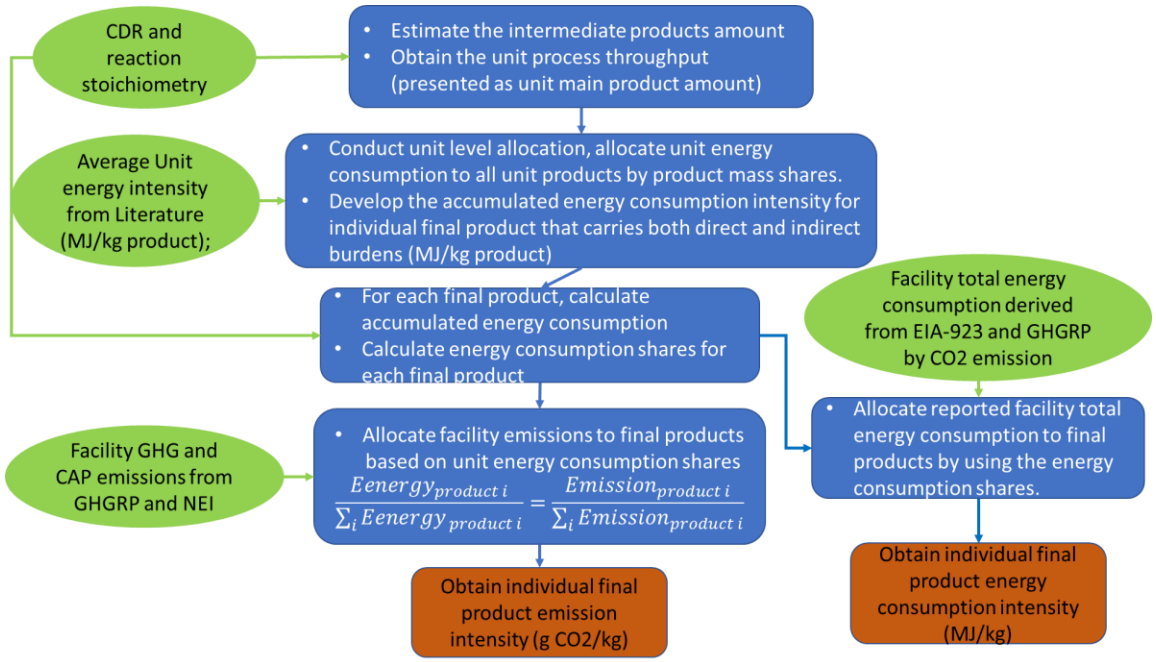


Figure S 2. Summary of data analysis steps.

From Figure S 2, the key information required to conduct the analysis is intermediate and final product amount, unit-level energy usage, facility total energy consumption (fuel & electricity), and total CO_2 emissions. The following subsections discuss in detail how this key information is derived.

2.3. The determination of EDC production for two pathways

Some products, such as EDC, can be and often are produced from two different pathways: chlorination and oxychlorination. These two pathways use different amounts of energy; thus the individual EDC production amount from each pathway needs to be identified, using the approach described below. The CDR database provides the amount for each intermediate product and each net output, which helps identify the pathway. Assume X moles of EDC are formed via chlorination and Y moles are formed via oxychlorination, and Z moles of EDC are cracked to produce VMC:

X: $C_2H_4+Cl_2 \rightarrow$EDC

Y: $C_2H_4+2HCl+0.5O_2 \rightarrow EDC+H_2O$.

Z: EDC→ VCM+ HCl

Thus, the Z value is known via the amount of final net product of VCM (a kg):

Z=a/MW[VCM]

In addition, the Y value can be derived from the internal HCl consumption (intermediate HCl [b kg] minus the final net HCl amount [c kg]):

MW(HCl) × (2Y – Z) =b – c, then Y=(MW[HCl] – (b – c) + Z)/2

Then X can be derived by subtracting the Y amount from the intermediate EDC amount [d kg]:

MW[EDC]×X= d – Y×MW[EDC]

3. Reported data on amounts of chlor-alkali plant products

3.1. Chlor-alkali plant emission data

Table S 1. Chlor-alkali plants' GHG (kg/yr) and CAP emissions (kg/yr) reported in GHGRP and NEI for years 2011 and 2016.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Year	**2011 (kg)**						
CO_2	1,309,013,000	3,675,410,000	169,721,294	448,892,400	36,529,520	34,556,667	13,596,300
CH_4	24,240	288,090	3,030	81,200	652	-	-
N_2O	2,420	27,147	2,144	4,575	461	-	-

NOx	1,107,439	-	-	1,627	27,197	39,707	42,819
PM_{10}	268,221	-	-	1,643	27,649	639	2,497
$PM_{2.5}$	256,825	-	-	1,201	24,038	630	2,158
SOx	3,520	-	-	10	459	3,962	647
VOC	165,071	-	-	5,837	3,154	681	934
CO	820,038	-	-	1,366	33,554	9,521	14,318
Year	**2016 (kg)**						
CO_2	1,136,836,200	3,621,785,900	173,535,946	458,183,300	27,139,300	33,168,900	18,196,900
CH_4	20,630	367,900	3,098	56,340	510	650	-
N_2O	2,063	25,655	2,192	3,412	51	69	-
NOx	998,988	-	2,087	1,681	23,578	70,788	-
PM_{10}	144,695	-	159	1,647	7,521	3,502	-
$PM_{2.5}$	117,055	-	159	1,205	4,705	3,502	-
SOx	2,416	-	13	10	474	2,776	-
VOC	109,123	-	115	7,008	1,343	2,359	-
CO	807,162	-	1,753	1,412	3,944	24,902	-

Table S 2. Chlor-alkali plants' CO_2 emissions for each fuel combustion reported in GHGRP for years 2011 and 2016.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Year	**2011**						
Assorted Oil ($kg\ CO_2$)	-	50,319,000	-	341,700	-	-	-
Coal ($kg\ CO_2$)	-	-	-	-	-	-	-
Diesel ($kg\ CO_2$)	-	-	-	24,700	-	1,004,542	-
Fuel Gas ($kg\ CO_2$)	-	1,328,928,500	-	320,901,000	-	-	-
Natural Gas ($kg\ CO_2$)	1,285,287,000	2,207,549,300	169,721,294	24,093,000	36,529,520	33,552,125	18,196,900
Other ($kg\ CO_2$)	-	-	-	-	-	-	-
Total combustion CO_2 emission ($kg\ CO_2$)	1,285,287,000	3,586,796,800	169,721,294	345,360,400	36,529,520	34,556,667	13,596,300
Flare ($kg\ CO_2$)	23,726,000	88,613,200	-	103,532,000	-	-	-
Total ($kg\ CO_2$)	1,309,013,000	3,675,410,000	169,721,294	448,892,400	36,529,520	34,556,667	13,596,300
Year	**2016**						
Assorted Oil ($kg\ CO_2$)	-	49,650,100	-	1,656,700	-	-	-
Coal ($kg\ CO_2$)	-	-	-	-	-	-	-
Diesel ($kg\ CO_2$)	-	-	-	-	-	964,200	-
Fuel Gas ($kg\ CO_2$)	-	1,321,045,900	-	112,291,700	-	-	-
Natural Gas ($kg\ CO_2$)	1,094,877,900	2,129,942,900	173,535,946	252,270,300	27,139,300	32,204,700	18,196,900
Other ($kg\ CO_2$)	-	-	-	10,984,100	-	-	-
Total combustion CO_2 emission ($kg\ CO_2$)	1,094,877,900	3,500,638,900	173,535,946	377,202,800	27,139,300	33,168,900	18,196,900
Flare ($kg\ CO_2$)	41,958,300	121,147,000	-	80,980,500	-	-	-

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Total (kg CO_2)	1,136,836,200	3,621,785,900	173,535,946	458,183,300	27,139,300	33,168,900	18,196,900

3.2. Chlor-alkali plants' product amounts reported in CDR database

The plant product amounts reported in the CDR database are shown below.

Table S 3. Chlor-alkali plants' net and intermediate product amounts reported in CDR for year 2011.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Net products							
Chlorine	-	-	32,370,204	58,123,579	172,824,342	133,599,985	14,693,016
Sodium hydroxide	380,110,858	810,490,969		298,947,630	196,982,065	91,563,444	61,093,522
Hydrogen	9,596,951	1,799,872	682,406	7,454,475	5,052,763	4,217,078	413,584
Hydrochloric acid	9,525,451	75,870,123	8,374,232	734,074	-	12,401,774	35,458,719
Sodium hypochlorite	-	12,526,649	-	-	-	16,342,045	-
VCM	635,030,073	713,595,994	-	417,663,361	-	-	-
Intermediate data reported in CDR							
Chlorine	358,338,398	763,452,431	32,370,204	284,700,765	179,373,072	163,158,277	49,169,471
Sodium hydroxide	403,697,689	853,148,388	-	309,030,338	205,294,756	111,322,586	61,093,522
HCl Hydrochloric acid	18,143,716	719,262,812	8,374,232	20,632,172	-	13,830,955	35,458,719
Sodium hypochlorite	-	13,185,946	-	-	4,719,404	16,342,045	-
EDC Ethylene dichloride	1,016,048,117	1,573,714,149	-	629,599,205	-	-	-

VCM Vinyl chloride	635,030,073	713,595,994	-	417,663,361	-	-	-
Potassium hydroxide			65,033,844			97,781,900	

Table S 4. Chlor-alkali plants' net product and intermediate product amounts reported in CDR for year 2016.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Net products							
Chlorine	-	-	19,439,155	-	146,852,072	137,101,853	49,964,187
Sodium hydroxide	332,425,961	930,072,603	-	300,574,091	165,271,732	79,498,413	60,344,618
Hydrochloric acid	8,393,014	9,453,388	620,078	7,687,087	4,136,678	81,000	1,407,030
Sodium hypochlorite	8,330,484	71,952,088	17,090,000	2,018,144	-	14,075,798[a]	48,007,978
Ethylene dichloride	-	9,202,505	-	-	-	18,547,936	-
Vinyl chloride	15,867,588	571,633,434	-	-	-	-	-
Potassium hydroxide	555,365,567	678,891,700	-	596,873,552	-	-	-
Intermediate products							
Chlorine	313,384,855[b]	868,883,616	41,413,891	289,983,172	146,852,072	163,626,045	49,964,187
Sodium hydroxide	353,053,825[b]	979,023,792	-	309,197,557	170,685,629	109,164,352	60,344,618

Hydrochloric acid	15,867,588 [b]	548,310,554	19,947,632	17,573,034	-	-	48,007,978
Sodium hypochlorite	-	9,248,748	-	-	-	18,547,936	-
EDC Ethylene dichloride	888,584,907 [b]	1,691,719,435	-	914,683,983	-	-	-
VCM Vinyl chloride	555,365,567[b]	678,891,700	-	596,873,552	-	-	-
Potassium hydroxide	-	-	70,105,422	-	-	105,284,232	69,785,586

[a] Estimated from 2011 data. [b] No CDR data for year 2016; the product data were derived from CDR 2011 by using the ratio of electricity change from 2011 to 2016.

3.3. Chlor-alkali plants' co-generation data

Table S 5. Chlor-alkali plants' co-generation data reported in EIA-923 for years 2011 and 2016.

Year		2011			2016		
		C_1	C_2	C_3	C_1	C_2	C_3
Plant capacity (MT)		410,000	740,000	40,000	408,000	736,000	40,000
Co-generation		Yes	Yes	Yes	Yes	Yes	Yes
Total Cogen electricity	Electricity (GJ)	6,111,418	14,948,939	1,198,681	5,503,471	13,649,742	1,225,623
Import elec	Electricity (GJ)	86,584	1,014,239	-	57,974	-	
Station use	Electricity (GJ)	108,202	311,396	30,139	111,352	299,711	30,817
Facility use	Electricity (GJ)	5,656,320	15,395,018	567,993	4,946,735	13,350,031	554,499
Export elec	Electricity (GJ)	433,480	256,763	656,371	503,359	-	671,124
F_{onsite}		93.5%	100.0%	47.9%	91%	98%	46%
Total Cogen	Fuel (GJ)	22,316,877	31,917,487	3,016,248	20,012,337	27,348,001	3,084,041
for Electricity	Fuel (GJ)	11,143,517	30,469,086	642,898	7,241,113	19,223,111	657,347
for Steam	Fuel (GJ)	11,173,360	1,448,402	2,373,351	12,771,224	8,124,830	2,426,694

Cogen efficiency (%)[a]		27.4%	46.8%	39.7%	29.6%	49.9%	39.7%

[a]The efficiency is calculated as the total generated electricity divided by the total fuel consumption.

4. Processed data for chlor-alkali plants

4.1. Calculated chlor-alkali plants' energy use allocated to all products at unit level, by using process energy use data from the literature

Table S 6. The accumulated unit energy consumption intensity for the final products, derived from individual process energy consumption intensity from the literature.

	Electricity (MJ/kg product)			Fuel (MJ/kg product)		
Technology	Diaphragm	Membrane	Mercury	Diaphragm	Membrane	Mercury
Cl_2	5.702	5.368	6.788	0.927	0.927	0.927
NaOH	4.717	4.383	5.803	4.860	1.849	0.367
H_2 without compression	4.504	4.170	5.590	0.367	0.367	0.367
H_2 with compression	10.696	10.362	11.782	0.367	0.367	0.367
HCl	6.869	6.535	7.955	0.912	0.912	0.912
NaClO	5.916	5.536	7.149	3.516	1.705	0.814
EDC by chlorination	4.330	4.090	5.108	2.695	2.695	2.695
EDC by oxychlorination from HCl by H_2 and Cl_2	5.165	4.919	5.966	4.322	4.322	4.322
EDC by oxychlorination from HCl by VCM	0.100	0.100	0.100	3.650	3.650	3.650
VCM from EDC by chlorination	7.158	6.778	8.391	6.179	6.179	6.179
VCM from EDC by oxychlorination from HCl from H_2 and Cl_2	8.482	8.092	9.750	8.756	8.756	8.756
VCM from EDC by oxychlorination from EDC-VCM	0.458	0.458	0.458	7.692	7.692	7.692
KOH	3.943	3.559	4.841	4.797	1.785	0.304

5. Calculated results for chlor-alkali plants

5.1. Calculated intermediate-product amounts

Table S 7. Calculated chlor-alkali plants' intermediate products for year 2011 (kg/yr).

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Utilization rate	88%	104%	101%	114%	110%	73%	51%
H_2 from electrolysis	10,094,039	21,505,702	1,140,945	8,019,740	5,052,763	4,596,008	1,385,056
Cl_2 from electrolysis	358,338,398	763,452,431	40,503,534	284,700,765	179,373,072	163,158,277	49,169,471
NaOH from electrolysis	403,697,689	853,148,388	-	309,030,338	205,294,756	111,322,586	61,093,522
EDC cracked for VCM	1,005,887,636	1,130,336,054	-	661,578,765	-	-	-
Net HCl consumption	8,618,265	643,392,689	-	19,898,099	-	1,429,181	-
HCl used for EDC production from oxychlorination	379,475,828	1,060,132,750	-	263,813,502	-	-	-
EDC chlorination-using Cl_2	501,416,515	135,999,872	-	271,824,730	-	-	-
EDC by oxychlorination from HCl by H_2 and Cl_2	11,687,784	872,546,250	-	26,985,093	-	-	-
EDC by oxychlorination	502,943,818	565,168,027	-	330,789,382	-	-	-

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
from HCl by VCM							
EDC chlorination-using Cl_2	49.3%	8.6%	0.0%	43.2%	0.0%	0.0%	0.0%
EDC by oxychlorination from HCl by H_2 and Cl_2	1.2%	55.4%	0.0%	4.3%	0.0%	0.0%	0.0%
EDC by oxychlorination from HCl by VCM	49.5%	35.9%	0.0%	52.5%	0.0%	0.0%	0.0%
HCl produced from H_2 and Cl_2	18,143,716	719,262,812	8,374,232	20,632,172	-	13,830,955	35,458,719
NaClO	-	13,185,946	-	-	4,719,404	16,342,045	-
KOH	-	-	65,033,844	-	-	97,781,900	-
Remaining H_2	9,596,951	1,799,872	911,514	7,454,475	5,052,763	4,217,078	413,584
NaCl coproduced with NaClO	-	10,354,065	-	-	3,705,841	12,832,344	-
HCl for EDC from H_2 and Cl_2	8,618,265	643,392,689	-	19,898,099	-	-	-
HCl coproduced from EDC cracking to VCM	370,857,563	416,740,060	-	243,915,403	-	-	-
HCl for EDC from H_2 and Cl_2	2.3%	60.7%	0.0%	7.5%	0.0%	0.0%	0.0%
HCl coproduced from EDC cracking to VCM	97.7%	39.3%	0.0%	92.5%	0.0%	0.0%	0.0%

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
VCM	635,030,073	713,595,994	-	417,663,361	-	-	-

Table S 8. Calculated chlor-alkali plants' intermediate products for year 2016 (kg/yr).

2016	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Utilization rate	77%	118%	104%	116%	90%	74%	101%
H_2	8,827,742	24,475,595	1,166,588	8,168,540	4,136,678	3,579,000	2,722,317
Cl_2	313,384,855	868,883,616	41,413,891	289,983,172	146,852,072	163,626,045	96,642,267
NaOH	353,053,825	979,023,792	-	309,197,557	170,685,629	109,164,352	60,344,618
EDC cracked for VCM	879,699,058	1,075,364,453	-	945,447,706	-	-	-
Net HCl consumption	7,537,104	476,358,467	2,857,632	15,554,890	-	4,020,371	-
HCl used for EDC production from oxychlorination	331,870,595	872,831,220	-	364,129,045	-	-	-
EDC chlorination-using Cl_2	438,513,826	508,016,822	-	420,865,141	-	-	-
EDC by oxychlorination from HCl by H_2 and Cl_2	10,221,552	646,020,386	-	21,094,988	-	-	-
EDC by oxychlorination from HCl by VCM	439,849,529	537,682,227	-	472,723,853	-	-	-

2016	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
EDC chlorination-using Cl_2	49.3%	30.0%	0.0%	46.0%	0.0%	0.0%	0.0%
EDC by oxychlorination from HCl by H_2 and Cl_2	1.2%	38.2%	0.0%	2.3%	0.0%	0.0%	0.0%
EDC by oxychlorination from HCl by VCM	49.5%	31.8%	0.0%	51.7%	0.0%	0.0%	0.0%
HCl produced from H_2 and Cl_2	15,867,588	548,310,554	19,947,632	17,573,034	-	-	48,007,978
NaClO	-	9,248,748	-	-	-	18,547,936	-
KOH	-	-	70,105,422	-	-	105,284,232	69,785,586
Remaining H_2	8,393,014	9,453,388	620,078	7,687,087	4,136,678	3,579,000	1,407,030
NaCl co-produced with NaClO	-	7,262,440	-	-	-	14,564,487	-
HCl for EDC from H_2 and Cl_2	7,537,104	476,358,467	-	15,554,890	-	-	-
HCl coproduced from EDC cracking to VCM	324,333,491	396,472,753	-	348,574,154	-	-	-
HCl for EDC from H_2 and Cl_2	2.3%	54.6%	0.0%	4.3%	0.0%	0.0%	0.0%
HCl coproduced from EDC cracking to VCM	97.7%	45.4%	0.0%	95.7%	0.0%	0.0%	0.0%
VCM	555,365,567	678,891,700	-	596,873,552	-	-	-

5.2. Calculated chlor-alkali facility energy consumption

Table S 9. Chlor-alkali plants' total energy consumption (GJ/yr) in 2011, derived from CO_2 emission.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Utilization rate	88%	104%	101%	114%	110%	73%	51%
Assorted Oil	-	696,528	-	4,730	-	-	-
Coal	-	-	-	-	-	-	-
Diesel	-	-	-	352	-	14,330	-
Fuel Gas	-	23,764,302	-	5,738,449	-	-	-
Natural Gas	25,556,909	43,895,360	3,016,248	479,070	649,194	667,157	323,391
Other	-	-	-	-	-	-	-
Total fuel with carbon content	25,556,909	68,356,190	3,016,248	6,222,601	649,194	681,487	323,391
Potential H_2 for use as fuel	1,151,634	215,985	109,382	894,537	606,332	506,049	49,630
Total fuel consumption including H_2	26,708,543	68,572,174	3,125,630	7,117,138	1,255,526	1,187,537	373,021

Table S 10. Chlor-alkali plant's energy consumption in 2016, derived from CO_2 emission.

2016 Fuel consumption (GJ/yr)	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No

Utilization rate	77%	118%	104%	116%	90%	74%	101%
Assorted Oil	-	687,269	-	22,932	-	-	-
Coal	-	-	-	-	-	-	-
Diesel	-	-	-	-	-	13,755	-
Fuel Gas	-	23,623,343	-	2,008,034	-	-	-
Natural Gas	21,770,775	42,352,219	3,084,041	5,016,194	539,643	640,365	323,391
Other	-	-	-	222,563	-	-	-
Total fuel with carbon content	21,770,775	66,662,830	3,084,041	7,269,723	539,643	654,119	323,391
Potential H2 for use as fuel	1,007,162	1,134,407	74,409	922,450	496,401	429,480	168,844
Total fuel consumption including H2	22,777,937	67,797,237	3,158,451	8,192,174	1,036,045	1,083,599	492,235

Table S 11. The fuel shares.

Fuel Shares	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Year	**2011**						
Assorted Oil	0%	1%	0%	0%	0%	0%	0%
Coal	0%	0%	0%	0%	0%	0%	0%
Diesel	0%	0%	0%	0%	0%	1%	0%
Fuel Gas	0%	35%	0%	81%	0%	0%	0%
Natural Gas	96%	64%	97%	7%	52%	56%	87%
Other	0%	0%	0%	0%	0%	0%	0%
H_2	4%	0%	3%	13%	48%	43%	13%
Total fuel consumption including H2	100%	100%	100%	100%	100%	100%	100%
Year	**2016**						
Assorted Oil	0%	1%	0%	0%	0%	0%	0%
Coal	0%	0%	0%	0%	0%	0%	0%
Diesel	0%	0%	0%	0%	0%	1%	0%
Fuel Gas	0%	35%	0%	25%	0%	0%	0%
Natural Gas	96%	62%	98%	61%	52%	59%	66%
Other	0%	0%	0%	3%	0%	0%	0%
H_2	4%	2%	2%	11%	48%	40%	34%
Total fuel consumption including H2	100%	100%	100%	100%	100%	100%	100%

5.3. Calculated chlor-alkali plants' unit energy demand

Table S 12. Estimated chlor-alkali plants' process electricity use for year 2011 (GJ/yr) used in unit energy consumption estimation.

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity (MT)	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
VCM production process	190,509	214,079	-	125,299	-	-	-
PVC production process							
EDC chlorination	120,340	32,640	-	65,238	-	-	-
EDC oxychlorination	51,463	143,771	-	35,777	-	-	-
NaClO process	-	807	-	-	289	1,000	-
HCl from H_2 and Cl_2	21,772	863,115	10,049	24,759	-	16,597	42,550
Electrolysis of NaCl	3,454,382	6,809,996	-	2,539,531	1,600,008	894,291	438,592
Brine prep	-	-	-	-	-	-	-
Cl_2 post-process	440,326	938,130	49,771	349,840	220,414	200,489	60,419
NaOH post-process	98,332	207,809	-	75,273	50,006	27,116	14,881
H_2 post-process	62,814	133,828	7,100	49,906	31,443	28,601	8,619
Electrolysis of KCl, brine prep	-	-	485,232	-	-	561,081	-
KOH post-process	-	-	15,841	-	-	23,818	-
Potential H_2 elec compression for export	59,424	11,145	5,644	46,158	31,287	26,112	2,561
Total estimated elec demand from	4,439,940	9,344,176	567,993	3,265,624	1,902,159	1,752,992	565,062

unit process, without H_2 export							
Total estimated elec demand from unit process, with H_2 export	4,499,364	9,355,321	573,637	3,311,782	1,933,445	1,779,104	567,623
EIA-923 reported facility electricity use	5,656,320	15,395,018	567,993				

Table S 13. Estimated chlor-alkali plants' process electricity use for year 2016 (GJ/yr).

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
Year	**2016**						
VCM production process	166,610	203,668	-	179,062	-	-	-
PVC production process							
EDC chlorination	105,243	121,924	-	101,008	-	-	-
EDC oxychlorination	45,007	118,370	-	49,382	-	-	-
NaClO process	-	563.19	-	-	-	1,135.13	-
HCl from H_2 and Cl_2	19,041	657,973	23,937	21,088	-	-	57,610
Electrolysis of NaCl	3,021,030	7,750,442	-	2,586,650	1,309,920	864,200	472,088
Brine prep	-	-	-	-	-	-	-
Cl_2 post-process	433,833	1,203,024	-	379,942	209,739	134,141	74,151

NaOH post-process	76,334	211,642	10,088	70,634	35,770	39,856	23,540
H_2 post-process	54,934	152,310	7,260	50,832	25,742	22,272	16,941
Electrolysis of KCl, brine prep	-	-	496,138.41	-	-	595,344.73	389,961
KOH postprocess	-	-	17,076.23	-	-	25,645.06	16,998.32
Potential H_2 elec compression for export	51,970	58,535	3,840	47,598	25,614	22,161	8,712
Total estimated elec demand from unit process, without H_2 recovery	3,922,032	10,419,916	554,499	3,438,597	1,581,171	1,682,593	1,051,289
Total estimated elec demand from unit process, with H_2 recovery	3,974,002	10,478,451	558,338	3,486,196	1,606,786	1,704,755	1,060,002
EIA-923 reported facility electricity use	4,946,735	13,350,031	554,499				

Table S 14. Estimated chlor-alkali plants' process fuel use for steam generation for year 2011 (GJ/yr).

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
VCM process	1,212,907	1,362,968	-	797,737	-	-	-
EDC chlorination	1,017,876	276,080	-	551,804	-	-	-
EDC oxychlorination	1,878,405	5,247,657	-	1,305,877	-	-	-

NaClO	-	2,308	-	-	825.90	2,859.86	-
HCl from H_2 and Cl_2	-	-	-	-	-	-	-
Electrolysis from NaCl,	-	-	-	-	-	-	-
Brine preparation	283,446	603,891	32,038	225,198	141,884	129,058	38,893
Cl_2 post-process	200,670	427,533	22,681.98	159,432.43	100,449	91,368.63	27,534.90
NaOH post-process	1,813,801	1,264,199	-	457,922	304,207	164,958	90,529
H_2 post-process	-	-	-	-	-	-	-
Electrolysis from KCl	-	-	-	-	-	-	-
KOH post-process	-	-	-	-	-	144,894	-
Estimated total fuel demand for steam use	6,407,105	9,184,636	54,720	3,497,971	547,365	533,139	156,957
CO_2-derived fuel use for steam generation	25,556,909	68,356,190	3,016,248	6,222,601	649,194	681,487	323,391

Table S 15. Estimated chlor-alkali plants' process fuel use for steam generation for year 2016 (GJ/yr).

	C_1	C_2	C_3	NC_1	NC_2	NC_3	NC_4
Plant capacity	410,000	740,000	40,000	250,000	165,000	220,000	100,000
Co-generation	Yes	Yes	Yes	No	No	No	No
VCM process	1,060,748	1,296,683	-	1,140,028	-	-	-
EDC chlorination	890,183	1,031,274	-	854,356	-	-	-
EDC oxychlorination	1,642,759	4,320,515	-	1,802,439	-	-	-
NaClO	-	1,610.44	-	-	-	3,245.89	-
HCl from H_2 and Cl_2	-	-	-	-	-	-	-

Electrolysis from NaCl	-	-	-	-	-	-	-
Brine preparation	247,887	687,287	32,758	229,377	116,160	129,428	76,444
Cl_2 post-process	175,496	486,574.82	23,191.78	162,390.58	82,237.16	91,630.59	54,119.67
NaOH post-process	1,586,260	1,450,721	-	458,170	252,923	161,760	89,419
H_2 post-process	-	-	-	-	-	-	-
Electrolysis from KCl	-	-	-	-	-	-	-
KOH post-process	-	-	-	-	-	156,011	103,409
Estimated total fuel demand for steam use	5,603,333	9,274,665	55,950	4,646,761	451,320	542,075	323,391

5.4. Resultant energy consumption of individual final products of chlor-alkali facilities

Table S 16. Energy consumption shares of final products for chlor-alkali facilities with CHP.

Year	**2011**			**2016**		
	C_1	C_2	C_3	C_1	C_2	C_3
Plant capacity	410,000	740,000	40,000	410,000	740,000	40,000
Co-generation	Yes	Yes	Yes	Yes	Yes	Yes
Utilization rate	88%	104%	101%	77%	118%	104%
Electricity						
Cl_2	-	-	33.1%	-	-	20.9%
NaOH	40.3%	38.0%	-	40.3%	40.5%	-
H_2	2.3%	0.2%	1.3%	2.3%	1.0%	1.2%
HCl	1.5%	5.2%	10.3%	1.5%	4.7%	22.1%
NaClO	-	0.7%	-	-	0.5%	-
EDC	0.9%	16.4%	-	0.9%	17.8%	-
VCM	55.0%	39.5%	-	55.0%	35.5%	-

KOH	-	-	55.3%	-	-	55.8%
Steam						
Cl_2	-	-	50.8%	-	-	33.3%
NaOH	29.2%	16.2%	-	29.2%	19.1%	-
H_2	0.1%	0.0%	0.4%	0.1%	0.0%	0.4%
HCl	0.1%	0.7%	12.9%	0.1%	0.7%	28.7%
NaClO	-	0.2%	-	-	0.2%	-
EDC	0.9%	20.9%	-	0.9%	22.8%	-
VCM	69.7%	62.0%	-	69.7%	57.2%	-
KOH	-	-	35.9%	-	-	37.6%
Electricity + Steam						
Cl_2	-	-	34.7%	-	-	22.0%
NaOH	33.7%	27.1%	-	33.7%	30.3%	-
H_2	1.0%	0.1%	1.2%	1.0%	0.5%	1.2%
HCl	0.7%	3.0%	10.5%	0.7%	2.8%	22.6%
NaClO	-	0.5%	-	-	0.3%	-
EDC	0.9%	18.6%	-	0.9%	20.2%	-
VCM	63.7%	50.7%	-	63.7%	45.8%	-
KOH	-	-	53.6%	-	-	54.2%

Table S 17. Energy consumption shares of final products for chlor-alkali facilities without CHP.

	NC_1	NC_2	NC_3	NC_4	NC_1	NC_2	NC_3	NC_4
Plant capacity	250,000	165,000	220,000	100,000	250,000	165,000	220,000	100,000
Co-generation	No	No	No	No	No	No	No	No
	2011				**2016**			
Utilization rate	114%	110%	73%	51%	116%	90%	74%	101%
Electricity								
Cl_2	9.8%	50.0%	41.0%	13.5%	-	50.7%	43.4%	23.4%
NaOH	41.3%	47.2%	25.5%	46.0%	37.4%	46.6%	21.8%	24.6%
H_2	2.4%	2.8%	2.5%	0.7%	2.3%	2.8%	0.1%	1.3%
HCl	0.2%	-	4.7%	39.8%	0.4%	-	5.5%	27.7%
NaClO	-	-	5.4%	-	-	-	6.4%	-
EDC	-	-	-	-	-	-	-	-
VCM	46.3%	-	-	-	60.0%	-	-	-
KOH	-	-	20.9%	-	-	-	22.9%	23.1%
Steam								
Cl_2	1.5%	30.0%	23.1%	8.6%	-	30.7%	23.9%	13.9%
NaOH	15.5%	69.7%	35.1%	71.0%	11.7%	68.9%	31.0%	34.4%
H_2	0.1%	0.3%	0.3%	0.1%	0.1%	0.3%	0.0%	0.1%
HCl	0.0%	-	2.1%	20.3%	0.0%	-	2.5%	13.1%
NaClO	-	-	5.4%	-	-	-	6.2%	-
EDC	-	-	-	-	-	-	-	-
VCM	82.9%	-	-	-	88.2%	-	-	-
KOH	-	-	34.0%	-	-	-	36.4%	38.5%
Electricity + Steam								
Cl_2	5.4%	45.5%	36.8%	12.5%	-	46.3%	38.8%	21.2%
NaOH	27.6%	52.2%	27.8%	51.3%	22.6%	51.5%	24.0%	26.8%
H_2	1.2%	2.3%	2.0%	0.6%	1.0%	2.2%	0.0%	1.0%
HCl	0.1%	-	4.1%	35.6%	0.2%	-	4.7%	24.3%

NaClO	-	-	5.4%	-	-	-	6.4%	-
EDC	-	-	-	-	-	-	-	-
VCM	65.7%	-	-	-	76.2%	-	-	-
KOH	-	-	24.0%	-	-	-	26.1%	26.6%

6. Allocated energy use and emission results for chlor-alkali plants

6.1. Energy consumption shares for final products relative to facility total energy consumption

By using the unit energy consumption intensity information from the literature, the accumulated energy consumption intensity for each final product is derived, as shown in Table S 6. For each facility, given the various facility configurations, the energy consumption shares for individual final products are calculated from the following equation, as shown in Table S 19.

$$Energy\ Share_{Product\ i}(\%) = \frac{Energy\ intensity_{product\ i} \times Mass_{\ product\ i}}{\sum_i Energy\ intensity_{product\ i} \times Mass_{\ product\ i}}$$

Table S 18. Facility energy consumption in year 2016, allocated to final products on the basis of the total energy of electricity and steam.

	Product							
Facility ID	Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
C_1	-	33.7%	1.0%	-	0.7%	-	0.9%	63.7%
C_2	-	30.3%	0.5%	-	2.8%	0.3%	20.2%	45.8%
C_3	22.0%	-	1.2%	54.2%	22.6%	-	-	-
NC_1	-	11.7%	0.1%	-	0.0%	-	-	88.2%
NC_2	30.7%	68.9%	0.3%	-	-	-	-	-
NC_3	23.9%	31.0%	0.0%	36.4%	2.5%	6.2%	-	-
NC_4	13.9%	34.4%	0.1%	38.5%	13.1%	-	-	-

6.2. Allocated energy use and emissions for H_2 venting scenario

Only one Non-CHP and one CHP facility (i.e., NC_4 and C_3, respectively) vent H_2 in our analysis.

Table S 19. On-site electricity and fuel consumption allocated to final products for Non-CHP facilities with H_2 venting scenario.

Facility ID	Year	Fuel type	Products' electricity/fuel use (MJ/kg)							
			Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
NC_4	2011	Electricity	5.37	4.38			6.54			
		Fuel	1.89	3.76			1.86			
NC_4	2016	Electricity	5.04	4.38		3.56	6.21			
		Fuel	0.90	1.85		1.79	0.88			

Table S 20. CHP facilities with H_2 venting scenario on-site fuel consumption allocated to final products.

Facility ID	Year	Products' fuel use (MJ/kg)							
		Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
C_3	2011	25.94			19.94	30.40			
	2016	27.62			21.24	32.38			

The emissions allocated to individual products for the hydrogen venting scenario are provided below.

Table S 21. Non-CHP chlor-alkali facilities' emission burden for H_2 venting scenario.

Facility ID	Year	NERC Region	CO_2 emissions (kg/kg)							
			Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
NC_4	2011	MRO	1.04	0.95	0.00		1.25			
	2016		0.95	0.89	0.00	0.74	1.16			

Table S 22. CHP chlor-alkali facilities' emission burden for H_2 venting scenario.

Facility ID	Year	CO_2 emissions (kg/kg)							
		Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
C_3	2011	1.36		0.00	1.04	1.59			
	2016	1.43		0.00	1.10	1.68			

In comparison to the exporting scenario, we observe that there is little to no difference between the emissions for all the products except H_2. No burdens are allocated to H_2 when it is vented. However, the amount of H_2 that is produced and eventually vented is significantly smaller compared to the other products, resulting in an insignificant increase in emission burdens for other products. However small, CHP facility C_3 has enough H_2 production (which is vented) to create a slight observed increase in emission burden.

6.3. Allocated energy use and emissions for H_2 exporting scenario

When the same grid electricity (i.e., U.S. mix) is chosen for each facility, the emissions for NC_4 aren't significantly different from those of other facilities.

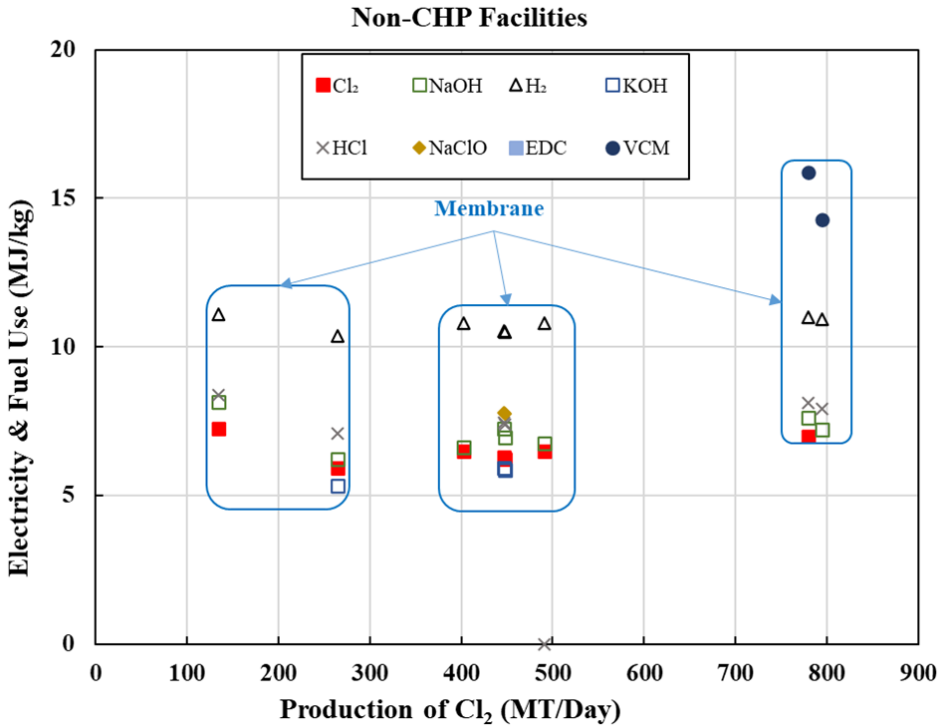


Figure S 3. Electricity and fuel use for non-CHP facilities for years 2011 and 2016.

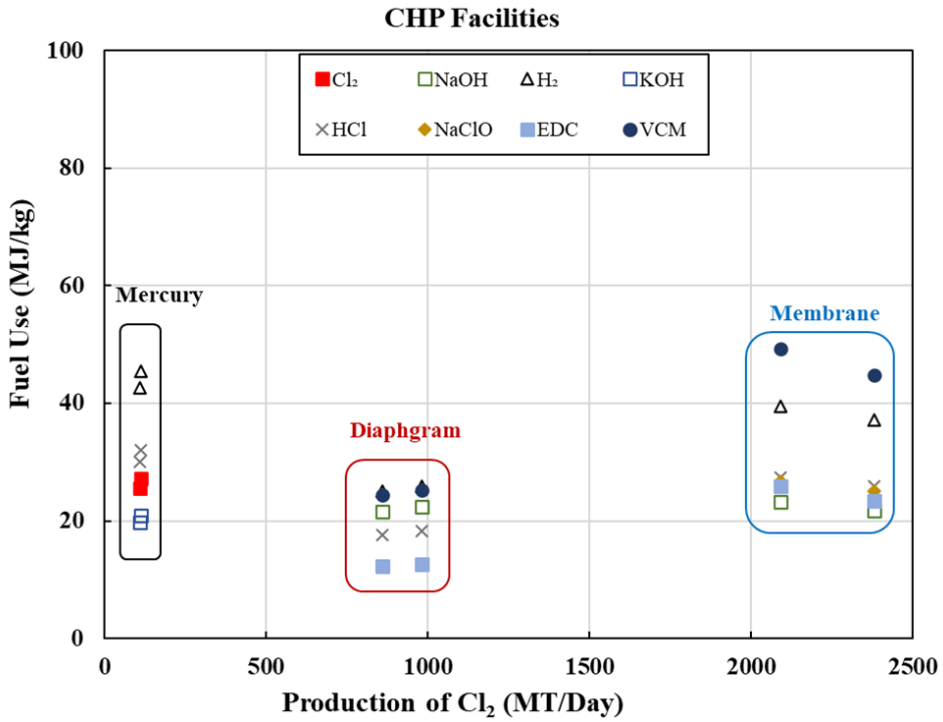


Figure S 4. Fuel use for CHP facilities for years 2011 and 2016.

*Table S 23. WTG emission burden allocated to non-CHP plants using U.S. grid mix electricity.**

Facility ID	Year	CO_2 emissions (kg/kg)							
		Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
NC_1	2011	0.81	0.80	1.39		0.96			1.81
NC_2		0.77	0.71	1.38					
NC_3		0.73	0.74	1.34	0.59	0.88	0.84		
NC_4		0.78	0.73	1.38		0.93			
NC_1	2016		0.78	1.46		0.99			1.70
NC_2		0.76	0.69	1.38					
NC_3		0.73	0.71	1.35	0.59	0.88	0.84		
NC_4		0.71	0.67	1.32	0.56	0.86			

*The carbon intensity for the U.S. mix is 0.41 kgCO2/kWh.

The emissions for NC_1, NC_2, and NC_3 slightly increase for all individual products because the U.S. mix is slightly more carbon-intensive than SERC.

*Table S 24. WTG emission burden allocated to CHP plants: Electricity export credits provided by displacing U.S. grid mix electricity.**

Facility ID	Year	CO_2 emissions (kg/kg)							
		Cl_2	NaOH	H_2	KOH	HCl	NaClO	EDC	VCM
C_1	2011		1.32	1.52		1.07		0.75	1.72
C_2			1.40	2.39		1.66	1.61	1.61	3.16
C_3		1.33		2.21	1.02	1.56			
C_1	2016		1.29	1.49		1.04		0.73	1.69
C_2			1.30	2.24		1.55	1.51	1.46	2.87
C_3		1.40		2.33	1.08	1.64			

*The carbon intensity for the U.S. mix is 0.41 kgCO2/kWh.

References

1. Lee D-Y, Elgowainy A, Dai Q. Life cycle greenhouse gas emissions of hydrogen fuel production from chlor-alkali processes in the United States. *Applied Energy.* 2018;217:467–479.

2. U.S. Environmental Protection Agency. 2012 and 2016 CDR Data. *Chemical Data Reporting*, https://wwwepagov/chemical-data-reporting/access-cdr-data. 2021.

3. Brinkmann T, Giner Santonja G, Delgado Sancho L, Schorcht F, Roudier S. *Best available techniques (BAT) reference document for the production of chlor-alkali: Industrial Emissions Directive 2010/75/EU (integrated pollution prevention and control).* Joint Research Centre, Institute for Prospective Technological Studies, Publications Office; 2014.