Original article

Sustainable production of Copper(I) chloride using electrolytic synthesis

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Abstract

Copper(I) chloride is a commonly used industrial chemical, with an annual production of ~165,000 tons that emits over 977,000 tons of CO_2, most of which comes from fossil fuel usage. A method to synthesize CuCl (Patent Pending) which does not require fossil fuels and can work on only renewable energy is described in this work. The process of synthesizing CuCl by the invented method involved electrolysis of an aqueous NaCl solution with a Cu anode, followed by filtration, and subsequent chemical purification by reaction with 0.1 M HCl. This work included synthesizing the CuCl by the invented method, and using a redox titration to identity the synthesized product as being CuCl with 96.7% purity. Calculations of GHG emissions for the invented and existing methods determined that the invented method emits over 2 times less greenhouse gasses than today's most common and sustainable industrial approach. In absolute terms, the effect of changing all CuCl production to the invented method would be equal to planting over 25 million trees.

Keywords

Copper(I) chloride, CuCl, Copper chloride, Electrolysis, Electrolytic synthesis, Sustainable manufacturing, Greenhouse gas, GHG, Emission, Electrochemistry

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Introduction

Copper(I) chloride is an industrially important chemical with many different uses (1, 5). The market for CuCl (also known as Cuprous chloride) generates ~ $1 billion per year (2). One of its major uses is as a catalyst in organic reactions (1); the most important reaction it catalyzes is the Sandemyer reaction, which produces chlorobenzene, an industrially important organic solvent, degreaser, and precursor to other chemicals. (1) Another major use of CuCl is as a precursor for the production of Dicopper chloride trihydroxide, which is used as a fungicide, pigment, and catalyst (7). Copper(I) chloride also has niche uses, such as a catalyst in atom transfer radical polymerization (ATRP) (1).

There are different methods to produce Copper(I) chloride, which have been employed. It was first synthesized in 1666 using a reaction of Mercury chloride and metallic copper. This method is no longer used because it is inefficient and uses toxic chemicals (3, 4). Other methods include the reduction of $CuCl_2$ via SO_2 (4), and a comproportionation reaction involving $CuCl_2$ and organic solvents (6). These and other methods release significantly more Green House Gases (GHGs) than today's common industrial approach, which involves melting copper in the presence of chlorine gas (4) (referred to in this work as the Main Industrial Method). This work also references the Copper-Chlorine Cycle (25), a method of producing hydrogen, which in theory can be modified to produce CuCl because it already forms it as an intermediate that is used soon after it is formed. It is referred to as the Theoretical Future Method because it is not in use.

Greenhouse gases (GHGs) harm the planet. By causing global warming and climate change, they endanger entire ecosystems. Droughts threaten to make agriculture impossible, densely populated coastal cities risk flooding, and these are only a part of the problem that is caused by GHG emissions. Finding a more efficient and sustainable method to produce CuCl is important because even a small improvement in efficiency, sustainability, and yield will make a sizable impact in energy use and CO_2 equivalents released due to its high demand (2). The objective of this work is to find a more sustainable way to produce CuCl.

Materials

The materials used for CuCl synthesis and purification were distilled water, sodium chloride, copper metal (part of a pre-1982 penny, which is 95% pure copper), a graphite rod, a power supply, crocodile clip wires, a timer, 0.1 M HCl, a 50 mL sidearm flask, tubing, 0.22 µm nylon membrane filter, scale, a Büchner funnel, and a 150 mL syringe. For the redox titration, the materials used were Ferric Ammonium Sulfate ($NH_4Fe(SO_4)_2$), 6 N Sulfuric Acid (H_2SO_4), Potassium Permanganate ($KMnO_4$), a burette, and a conical sidearm flask. Miscellaneous glassware, plastic apparatus and equipment were used as necessary.

Methods

Electrolysis was the potential method investigated in this study. Electrolysis is a common technique that uses electricity to introduce or change the charge on (of) atoms or ions respectively through the addition or removal of electrons. The energy required for this process is primarily dependent on the reduction potential of the various species involved and the ratio of the moles of electrons required to the moles of ions produced. The process does not necessarily require fossil fuels if clean energy from renewable sources is available, thereby making it a potentially more sustainable process.

After performing many experiments to find the correct conditions and techniques (time, voltage, NaCl concentration, extraction method, byproduct acquisition, etc.), a method of CuCl production (referred to in this work as the Proposed Method) was developed.

Synthesis and purification

The starting solution was prepared using 60 mL distilled water in which 7 g NaCl was dissolved (2 M solution). Copper metal was used as the anode and weighed before proceeding with electrolysis; graphite was used as the cathode for its non-reactive properties. A voltage of 12 V was applied for 4 hours at room temperature (25 ºC ± 3 ºC).

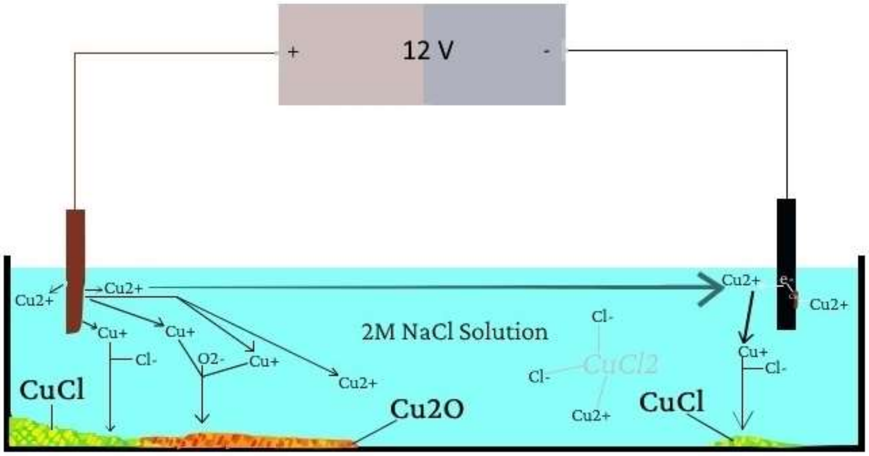

Figure 1. The process of CuCl production used involves electrolysis with a copper anode, graphite cathode, and sodium chloride solution. When water is electrolyzed with a copper anode, the anode partially dissolves, producing both Cu^{2+} and Cu^{+}. In the presence of the aqueous NaCl solution, the Cu^{+} ions will react with the Cl^{-} ions and precipitate out as CuCl. Unlike CuCl, $CuCl_2$ is water soluble, so the Cu^{2+} ions will not precipitate out. Some of the Cu^{2+} may be anticipated to be reduced to Cu^{+} or Cu (s) at the cathode.

The potential reactions along with their reduction potentials (where available from the literature) are presented below (all ions are in aqueous solution). It can be seen that the generation of O_2 gas at the anode is thermodynamically favored over the generation of Cl_2 gas. The generation of Cu^{+2} is thermodynamically favored over that of Cu^{+1} at the cathode. However, since there is a large overpotential applied of 12 V, a mixture of products is possible depending on the kinetics and equilibrium conditions of any given reaction. For example, the low K_{sp} of CuCl (see Discussion); coupled with the relative thermodynamic unfavorability of oxidation of Cl^{-} in the presence of H_2O may favor Cu^{+1} consumption into the formation of CuCl before it can be converted to Cu^{+2}

$Cu^{+1} + e- \rightarrow Cu_{(s)}$	+0.52 V
$Cu^{+2} + 2e^{-} \rightarrow Cu_{(s)}$	+0.34 V
$Cu^{+2} + e^{-} \rightarrow Cu^{+1}$	+0.15 V
$Cl_{2(g)}+2e^{-} \rightarrow 2Cl^{-}$	+1.36 V
$O_{2(g)} + 4H^{+} + 4e^{-} \rightarrow 2H_2O_{(l)}$	+1.23 V
$2H^{+} + 2e^{-} \rightarrow H_{2(g)}$	0.00 V
$Na^{+} + e^{-} \rightarrow Na_{(s)}$	-2.71 V

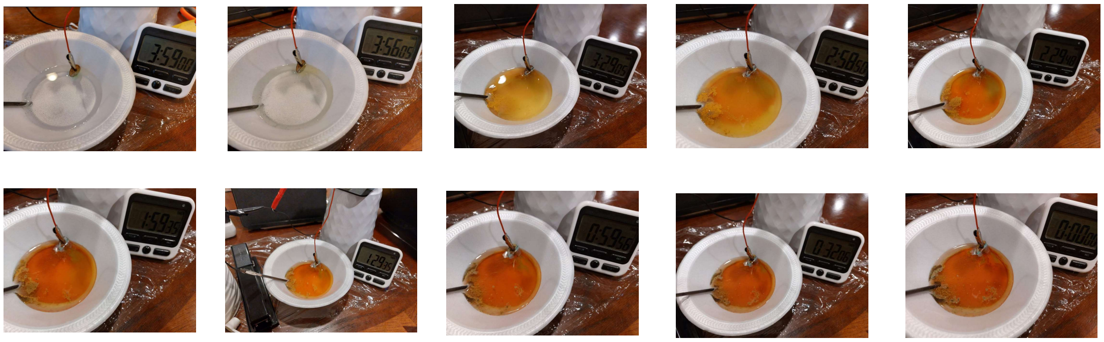

Figure 2. The progression of CuCl electrolytic synthesis over the course of four hours. Top left to bottom right: 1 minute, 4 minutes, 30 minutes, 1, 1.5, 2, 2.5, 3, 3.5 and 4 hours.

After 4 hours, a mixture of two different precipitates was observed - one light green, located predominantly near the anode with some near the cathode; and the other, colored orange, spread fairly evenly throughout the electrolyte solution and in a mixed state with the green precipitate in places (see Figure 2). Based on color, solubility in water, and reaction with dilute HCl, the green and orange precipitates were identified as CuCl and Cu_2O respectively. The electrolyzed contents were vacuum filtered using a 0.22 μm nylon membrane filter immediately after the electrolysis ended, and the un-electrolyzed copper was weighed. The solid retained on the filter was removed and placed into 50 mL of 0.1 M HCl in order to dissolve $CuCl_2$ impurities and react with the Cu_2O byproduct to form more CuCl. (Cu_2O + 2 HCl -> 2 CuCl + H_2O). After stirring the mixture for 30 minutes and waiting for the precipitates to turn a uniform light green color, signifying a complete reaction, the supernatant was removed by vacuum filtration (using the same filter type), and the product was dried.

Figure 3. Progression of CuCl extraction after electrolysis, and purification. Top left to bottom right: Filtration of precipitate mixture, Precipitates separated from water, Before HCl reaction (0 minutes), During HCl reaction (10 minutes), During HCl reaction (20 minutes), During HCl reaction (40 minutes), Filtration of product, Product on filter before drying, Dried product on filter.

At the experimental scale, the filter was dried in a microwave (1480 Watts, 40 seconds) and the product was left on it for weighing because the quantity produced was so small that any losses would significantly impact measurements. The filter with the dried product on it was weighed, and after the product was removed the filter was weighed again. The empty filter weight was subtracted from the initial filter weight to get the yield. The mass of the product was determined to be 0.840 g.

Figure 4. The final product (scraped off filter after weighing).

Identification

The product was identified using an oxidation-reduction; or redox; titration, which is a widely used method of measuring the concentration of a dissolved substance amenable to being reduced or oxidized. Two solutions were made, the first with 2.5 g $NH_4Fe(SO_4)_2$ in 25 mL of 6 N H_2SO_4, and the second with $KMnO_4$ in water diluted to 0.1 M. The product was dissolved in the sulfuric acid solution and then titrated with the 0.1 M potassium permanganate solution until the color changed from green to brown.

During the titration, Fe^{3+} was reduced to Fe^{2+} by the Cu^{+} in acidic medium, which in turn was oxidized to Cu^{2+} according to the following equation:

$$Cu^{+} + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$$

Then the Fe^{2+} was oxidized back to Fe^{3+} by Mn^{7+} in acidic medium, which in turn was reduced to Mn^{2+} according to the following equation:

$$MnO_4^{-} + 8H^{+} + 5Fe^{+2} \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

Multiplying the first equation by 5 and adding to the second equation yields the effective ionic equation, 1 mole of MnO_4^{-1} is hence required to neutralize 5 moles of Cu^{+}.

$$MnO_4^{-1} + 8H^{+} + 5Cu^{+} \rightarrow 5\ Cu^{+2} + Mn^{+2} + 4H_2O$$

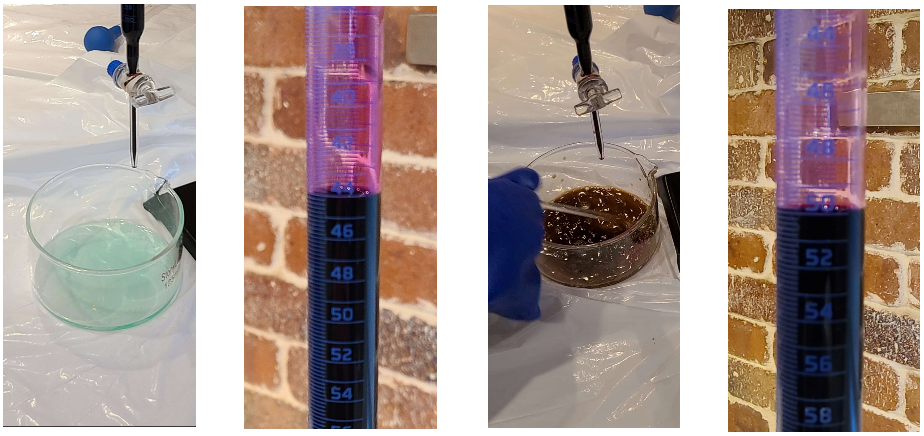

Figure 5. The initial and final analyte colors and titrant volumes. Left to right: Dissolved sample before titration, Initial $KMnO_4$ volume in burette, Dissolved sample at endpoint of titration, Final $KMnO_4$ volume in burette.

Results

Identification

5.8 mL of the potassium permanganate solution was used to titrate 0.297 g of the sample. 5.8 mL of 0.1 M $KMnO_4$ solution is equal to $5.8*10^{-4}$ mol. The mole ratio of Cu^+ to Mn^{7+} is 5:1, so $5.8*10^{-4}$ was multiplied by 5 to obtain $2.9*10^{-3}$ mol Cu^+ (equal to the amount of CuCl moles). $2.9*10^{-3}$ multiplied by 99, the molar mass of CuCl, is equal to 0.2871 g. To determine the purity of CuCl in the sample, 0.2871 (the calculated mass of CuCl) was divided by 0.297 (the mass of the sample). (0.2871/0.297=0.967). The calculated purity of CuCl in the sample is 96.7%. (42).

GHG emission calculations for the different methods

To compare GHG emissions* from the Proposed Method with the emissions from other methods of producing CuCl, extensive research was conducted on the emissions from each reaction and raw materials used in four different methods and the total CO_2 equivalent emissions were calculated. The methods compared were reduction of $CuCl_2$ with SO_2, comproportionation in acetone, the Main Industrial Method (direct combination of molten Cu metal with Cl_2 gas), and a version of the Copper-Chlorine Cycle (25) (which is an emerging method of hydrogen production) modified to produce Copper(I) Chloride (referred to as the Theoretical Future Method because it does not exist today).

GHG emission using the Proposed method

The Proposed Method has five major sources of GHG emissions: the raw materials copper, sodium chloride, and hydrochloric acid, and the processes of electrolysis and filtration. Below is the calculation for each source.

Copper production emits 4.1 g CO_2 per gram Cu (8), and 30% of copper is recycled (9) meaning copper acquisition emits an average of 2.9 g CO_2 per gram Cu (4.1*0.7=2.9 g). During the testing of the Proposed Method, 0.786 g of copper was oxidized from the anode to produce 0.840 g of CuCl. Thus, the amount of copper needed to produce 1g of CuCl by the Proposed Method is 0.936 g (0.786/0.84), accordingly, 2.7 g CO_2/g CuCl in this method comes from copper (0.936*2.88=2.7 g CO_2).

The method used to produce sodium chloride for industrial purposes is solar evaporation (10), which releases on average $4*10^{-2}$ g CO_2 per gram (11). The Proposed Method uses 7 g of NaCl to produce 0.840 g CuCl, meaning 8.3 g (7/0.84) are needed to produce 1 g CuCl. In total

0.3 g CO_2/g CuCl comes from sodium chloride ($4*10^{-2}*8.3=0.3$ g CO_2).

Renewable energy sources emit ~50 grams of CO_2 per kWh of power (12). The Proposed Method uses $2.54*10^{-3}$ kWh (12V, $5.3*10^{-2}$ A, 4h) to produce 0.840 g CuCl, meaning $3.0*10^{-3}$ kWh is needed to produce 1 g of CuCl. The total emissions from electrolysis are 0.1 g CO_2/g CuCl ($3.0*10^{-3}*50=0.15$ g CO_2).

30% (9.45 M) HCl production emits 1.2 g CO_2 per gram (13). 50 mL of 0.1 M HCl are used for the production of 0.840 g CuCl, which equates to 0.5 g of 30% HCl (1.2 g/mL), or 0.6 g per gram CuCl (50*(0.1/9.45)*(1/0.840)). This emits 0.8 g CO_2/g CuCl (0.63*1.2=0.8 g CO_2).

Filtration uses 0.5 Kwh/m^3. Therefore, filtration of 60 mL of electrolysis solution is calculated to use 3 X 10^{-5} Kwh of power and hence emit 0.0015, or ~0 g CO_2.

Therefore, the Proposed Method emits [2.7 g + 0.3 g + 0.1 g + 0.8 g + 0 g] = 3.9 g CO_2/g CuCl.

However, the Proposed Method also results in byproducts and unreacted reagents that can be collected and utilized. Because of this, the CO_2 that would have been emitted from manufacturing the byproducts and unreacted reagents should be subtracted from the total value. The byproducts formed are $CuCl_2$ and H_2 gas, and the unreacted reagent left over is NaCl. Hydrogen is formed at the cathode from reduction of water, and $CuCl_2$ is formed from the Cu^{2+} ions in solution. The $CuCl_2$ and unreacted NaCl can be separated by saturating the solution with NaCl to precipitate out $CuCl_2$. The resulting saturated NaCl solution can be reused by mixing with water to create a 2 M solution, the $CuCl_2$ can be packaged and sold like the main product, and the hydrogen can be burned with no emissions to generate some of the electricity to be used for electrolysis. A calculation of the emissions to be subtracted from the total follows.

$CuCl_2$ is produced by the reaction of $CuCO_3$ and HCl (14).

$$CuCO_3 + 2\,HCl \rightarrow CuCl_2 + CO_2 + H_2O$$

1 g ($7.4*10^{-3}$ mol) of $CuCl_2$ requires 0.9 g $CuCO_3$ and 0.3 g HCl. The reaction itself also releases 0.3 g CO_2/g $CuCl_2$. $CuCO_3$ production emits 2.0 g CO_2/g (13), meaning that producing 0.9 g would emit 1.8 g CO_2 (0.9*2). 30% HCl Production emits 1.2 g CO_2/g (13), meaning production of the equivalent of 0.3 g pure HCl would emit 1.1 g CO_2. In total, $CuCl_2$ production emits 3.3 g CO_2/g (0.3 g+ 1.2 g+ 1.0 g = 3.3 g).

GHG emissions from NaCl production were already calculated earlier and emissions from hydrogen were not included since not enough is produced in the Proposed Method for any meaningful difference to be achieved by subtracting emissions from it.

As stated earlier, the Proposed Method uses 0.786 g Cu and produces 0.840 g CuCl. Based on the percent by mass of Cu in CuCl, 0.147 g of Cu remains in solution as $CuCl_2$. Based on the percent by mass of Cu in $CuCl_2$, 0.3 g of $CuCl_2$ are formed. The total mass of chlorine in 0.840 g CuCl and 0.3 g $CuCl_2$ is 0.5 g. The mass of chlorine in 7 g of NaCl is 4.3 g, meaning that 3.7 g of it (4.2 g - 0.5 g) is left unreacted. Based on the percent by mass of Cl^- in NaCl, there are 6.1 g of unreacted NaCl left. The GHG emission coefficients for $CuCl_2$ and NaCl were found earlier. Multiplying 6.1 by $4*10^{-2}$ and 0.3 by 3.3 results in a total value of 1.3 g CO_2/g CuCl saved by extracting byproducts and unreacted reagents (1.0 g +0.3 g). Subtracting 1.3 g from the calculated value for total GHG emissions per gram (3.9 g) results in 2.6 g. Thus, the total GHG emissions from CuCl production by the Proposed Method are equal to 2.6 g CO_2/g CuCl.

GHG emissions using SO_2 reduction

The SO_2 reduction method involves the reaction of $CuCl_2$ with SO_2 in water.

$$2CuCl_2 + 2H_2O + SO_2 \rightarrow 2CuCl + 2HCl + H_2SO_4$$

For every gram of CuCl, this requires 0.3 g of SO_2 (because of the 2:1 mole ratio of SO_2 and CuCl), which is produced directly from burning fossil fuels and emits 551.9 g CO_2/g (15-18). Hence, 176.6 g CO_2/g CuCl are emitted from SO_2 production alone. The remaining emissions come from the production of $CuCl_2$, which is used as the copper source in this reaction rather than copper metal. $CuCl_2$ is produced by the reaction of $CuCO_3$ and HCl (14).

$$CuCO_3 + 2\ HCl \rightarrow CuCl_2 + CO_2 + H_2O$$

1 g of $CuCl_2$ requires 0.9 g $CuCO_3$ and 0.3 g HCl. The reaction itself also releases 0.3 g CO_2/g $CuCl_2$. $CuCO_3$ production emits 2.0 g CO_2/g (13), meaning that producing 0.9 g would emit 1.8 g CO_2 (0.9*2). 30% HCl production emits 1.2 g CO_2/g (13), meaning production of the equivalent of 0.3 g pure HCl would emit 1.1 g CO_2 (0.3*1.2/0.3). In total, $CuCl_2$ production emits 3.2 g CO_2/g as calculated from (0.3 g +1.8 g +1.1 g). 1.3 g $CuCl_2$ are needed for the reaction, hence $CuCl_2$ production for this method emits 4.4 g CO_2/g CuCl. Adding the emissions from SO_2 and $CuCl_2$, the SO_2 reduction method emits 181.0 g CO_2/g CuCl.*

GHG emissions using comproportionation in acetone

The comproportionation method uses 5 mL of acetone per $2*10^{-3}$ g $CuCl_2$ and $1*10^{-3}$ g Cu ($3*10^{-3}$ g CuCl) (19). This would mean that 1.7 L of acetone are required to produce 1g CuCl. This alone emits 3384.4 g CO_2 because acetone production emits 2.6 g CO_2/g (20), and combined with the other sources of emissions ($CuCl_2$ and Cu Metal, described above), the total for this method is 3387.5 g CO_2/g CuCl.*

GHG emissions using the Main Industrial Method

The Main Industrial Method has four major sources of GHG Emissions*: copper production, chlorine production, copper melting, and natural gas production.

Copper production emits 4.1 g CO_2 per gram Cu (8), and 30% of copper is recycled (9) meaning copper acquisition emits an average of 2.9 g CO_2 per gram Cu (4.1*0.7=2.9). The calculation assumes 100% yield, meaning 0.6 g Cu is used to produce 1 g of CuCl (based on the Cu % by mass in CuCl), accordingly, in the Main Industrial Method 1.8 g CO_2/g CuCl originates from copper (0.6*2.9=1.8 g).

Chlorine production emits 2.1 g CO_2 per gram (21). The calculation assumes 100% yield, meaning 0.4 g Cl are used to produce 1 g of CuCl (based on the Cl % by mass in CuCl). In total 0.8 g CO_2/g CuCl comes from chlorine (2.1*0.4=0.8 g).

In the Main Industrial Method, 3.3 g CO_2/g CuCl comes from the acquisition and burning of natural gas. Based on its specific heat and heat of fusion, copper requires 615.1 Joules of energy per gram to melt it (assuming 100% efficiency in heating). Assuming 100% yield, the Main Industrial Method uses 0.6 g Cu to produce 1 g CuCl (based on the Cu % by mass in CuCl), meaning 393.6 J (0.6*615.1) are needed to melt it. 1 cubic foot of natural gas can be burned to produce $1.1*10^6$ J of energy (22). Burning 1 cubic foot of gas emits $5.5*10^{-2}$ kg of CO_2 (23). This means 0.02 ($393.6/1.1*10^6*5.5*10^{-2}*1000=0.02$), or ~0 g CO_2 are emitted from melting copper. Natural gas extraction emits 8.4 g of CO_2 per megajoule (24). It was calculated that 393.6 Joules of energy from natural gas are used in the Main Industrial Method to produce 1 g of CuCl, meaning 3.3 g CO_2 (8.4*390.6/1000=3.3 g) are emitted from natural gas acquisition. Therefore, the total GHG can be calculated as (1.8 g +0.8 g +0 g +3.3 g) = 5.9 g CO_2/g CuCl.

Heat loss and impurities increase the emissions of the listed steps of the Main Industrial Method, however their extent is unknown. Due to the lack of information, it is also unknown if there are more GHG-emitting steps in it. Notwithstanding the high likelihood of their existence, all the unknown emissions in the Main Industrial Method are not counted in this calculation. In total, the Main Industrial Method emits > 5.9 g CO_2/g CuCl.

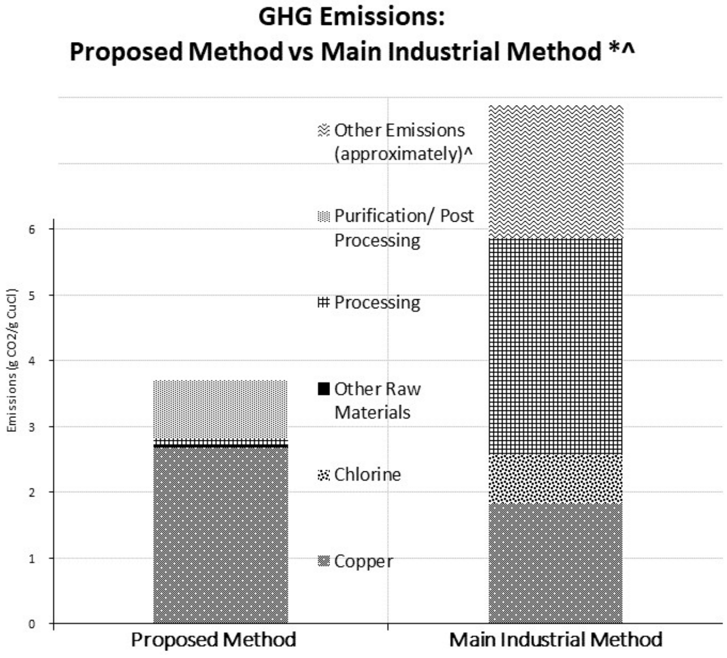

Figure 6. GHG Emissions By Source*: Main Industrial Method^ vs Proposed Method (not counting byproduct recovery). *Emissions from comparable sources not counted. ^Due to the lack of information about the Main Industrial Method, this calculation assumes 100% efficiency in heating and 100% yield, does not include emissions from the purification process, etc. which means that emissions from the Main Industrial and Theoretical Future Methods may be greater than those calculated above.

Thus, the Main Industrial Method (5.9 g CO_2/g CuCl) emits ~ 2.3 times the GHGs as the Proposed Method (2.6 g CO_2/g CuCl). The SO_2 Reduction Method and the Comproportionation Method emit orders of magnitude more GHGs than both the Main Industrial Method and the Proposed method.

GHG emissions using the Theoretical Future Method

The Theoretical Future Method consists of the following reactions:

$$H_2O_{(g)} + 2CuCl_{2(s)} \rightarrow Cu_2OCl_{2(s)} + 2HCl_{(g)}$$
$$2Cu_2OCl_{2(l)} \rightarrow 4CuCl_{(l)} + O_{2(g)}$$

The first reaction takes place at 400 °C (26) and the second reaction takes place at 530 °C (26). There are three major sources of emissions in this method* - Copper(II) chloride and two instances of heating - as well as one byproduct that can be utilized (HCl) (26), which will be factored into the calculation in the same way that $CuCl_2$ was in the Proposed Method.

Copper(II) chloride emissions were calculated in the Proposed Method section and are equal to 3.3 g CO_2/g. 1.4 g are used, hence the total emissions from CuCl are 4.4 g CO_2/g CuCl.

As of today, industrial processes are usually heated with natural gas (27), which emits significantly more GHGs than renewable energy sources, however, because this is an emerging method that might be used in the future, the emissions from heating are calculated assuming that renewable energy sources are used for electric heating. The following calculation thus represents the lowest possible emissions from this method. To produce 1 g of CuCl, the Theoretical Future Method requires 0.1 g H_2O and 1.4 g $CuCl_2$ to be heated to 400 °C, and 1.1 g Cu_2OCl_2 to be heated from 400 ºC to 530 °C. In total, 800.5 J are needed (273.4 J for $CuCl_2$, 141.4 J for H_2O, 72.42 J for Cu_2OCl_2 (28), 110 J for CuCl melting, and 203.4 J for H_2O vaporization). 800.5 J is equal to $2.2*10^{-4}$ kWh. Renewable sources of energy emit 50 g CO_2/kWh, meaning that the heating process emits 0.01, or ~0 g CO_2/g CuCl.

Gaseous HCl production emits 0.9 g CO_2/g (13), and the Theoretical Future Method produces 0.4 g HCl for every gram of CuCl. This means that total emissions are reduced by 0.3 g CO_2/g CuCl (0.9*0.4). The total emission therefore is calculated as (4.4 g +0 g -0.3 g=4.1 g CO_2 /g CuCl).

Since this method is not yet operational, it is impossible to accurately calculate heat loss. In this calculation, heat loss is assumed to be zero, however in reality, emissions from heat loss and similar sources would significantly increase total emissions. In total, according to this calculation the Theoretical Future Method emits > 4.1 g CO_2/g CuCl.*

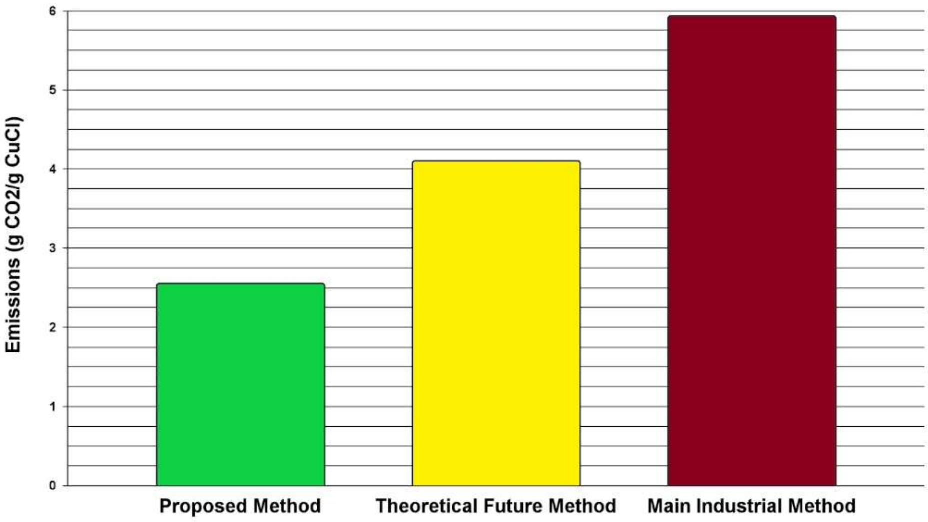

Figure 7. GHG Emissions*: Proposed Method *vs* Theoretical Future Method^ *vs* Main Industrial Method^. *Emissions from comparable sources not counted. ^Due to the lack of information about the Main Industrial Method and the Theoretical Future Method, this calculation assumes 100% efficiency in heating and 100% yield, does not include emissions from the purification process, etc. which means that emissions from the Main Industrial and Theoretical Future Methods in reality are significantly higher than calculated above.

In summary, the Proposed Method was found to be the most sustainable, emitting ~ 2.6 g CO_2/g CuCl. The Theoretical Future Method was found to emit > 4.1 g CO_2/g CuCl, and the most polluting of the three – the Main Industrial Method – was found to emit > 5.9 g CO_2/g CuCl.

Discussion

Calculation of the theoretical yield of CuCl upon electrolysis

Measurement of the current with an ammeter (AstroAI Multimeter TRMS 4000) before electrolysis did not register a stable reading, fluctuating ~0.04 Amperes. The initial weight of the copper metal before electrolysis was 2.032 g. After the electrolysis was completed the non-electrolyzed weight of the remaining copper metal was 1.246 g. Therefore 0.786 g was electrolyzed (oxidized). 1 mole electrons are required to oxidize 1 mole copper per the equation $Cu_{(s)} \rightarrow Cu^{+1} + e^{-1}$. Then, using Faraday's equation for electrolysis

$$\frac{0.04C}{1s} \text{x}\ 4h\ \text{x} \frac{60min}{1h} \text{x} \frac{60s}{1min} \text{x} \frac{1 molelectrons}{96500C} \text{x} \frac{1 mol\ Cu}{1 mol\ electrons} \text{x} \frac{63.55 gCu}{1 molCu} = 0.38 \text{ g}$$

Hence the theoretical yield of electrolyzed Cu should be 0.38 g. Using a mole ratio of Cu^{+1} to Cl^{-1} of 1:1, 0.38 g of Cu^{+1} requires 0.21 g Cl^{-1}. Hence the theoretical yield of CuCl is 0.59 g. If, on the other hand, 100% $CuCl_2$ was formed, the theoretical yield can be calculated as 0.8 g. 100% $CuCl_2$ yield would amount to a 0.1 M solution (0.786 g in 60 mL). $CuCl_2$ is soluble in water to the extent of 5 M. Hence, the filtration step immediately after electrolysis would have filtered out the Cu in the form of soluble $CuCl_2$ without any material remaining on the filter paper. However, the fact that the precipitate deposited on the filter paper; after purification with 0.1 M HCl and drying was identified to be > 95% CuCl (see Figure 8, the "Identification" in "Results") implied that the current measured was incorrect. Therefore, for all other calculations in this paper – including those to calculate GHG -, a value of 0.053 A was used, based on a theoretical yield of Cu^{+1} of 0.5 g and hence a theoretical yield of CuCl of 0.78 g.

Calculation of CuCl lost when placed and stirred with 0.1 M HCl

In an effort to reduce the Cu^{+2} species and purify CuCl, the precipitate from electrolysis – which contained CuCl, Cu_2O, and small amounts of $CuCl_2$ – was placed in 50 mL 0.1 M HCl. The K_{sp} of CuCl is 1.2×10^{-6}, but the solubility of CuCl in 0.1 M HCl is significantly greater due to the formation of a $[CuCl_2^-]$ complex - of the order of 9.4×10^{-3} M - according to standard equilibrium ICE calculations using the equilibrium constant for the reaction:

$$CuCl + Cl^- \rightarrow CuCl_2^- \qquad K_{eq} = 1.04 \times 10^{-1}$$

This represents 0.03 g CuCl dissolved in 50 mL 0.1 M HCl which represents 0.03/0.84 = 3.6% of CuCl yield loss to the 0.1 M HCl. Hence, the purification step with 0.1 M HCl is anticipated to lose 3.6% of the yield of CuCl obtained from electrolysis.

Theoretical Justification of product formed

In the Proposed Method, the only elements present in the electrolysis reaction are Cu, Na, Cl, H, and O, meaning the only salts that theoretically could have formed (disregarding reduction potentials) are CuCl, $CuCl_2$, CuH, CuO, Cu_2O, $Cu(OH)_2$, NaCl, NaH, NaOH, and Na_2O.

However, NaH and Na_2O could not have formed because they quickly react with water to form NaOH (37,39). Since the water was filtered before the precipitate was added to HCl, the product was not water soluble. This therefore excludes $CuCl_2$, NaCl, and NaOH (31,36,38).

No elements are present in HCl that were not present in the previous solution, however possible salts can still be excluded based on reactions with or solubility in HCl. Cu_2O and CuH could be excluded because they react with HCl to form CuCl (32,34), and $Cu(OH)_2$ and CuO could be excluded because they react with HCl to form $CuCl_2$ (33,35), which dissolves (31) and is removed with the supernatant during filtration. As a result, this left CuCl as the only possible compound that could be formed in this process (Figure 8). Also see 'Identification' in the Results section.

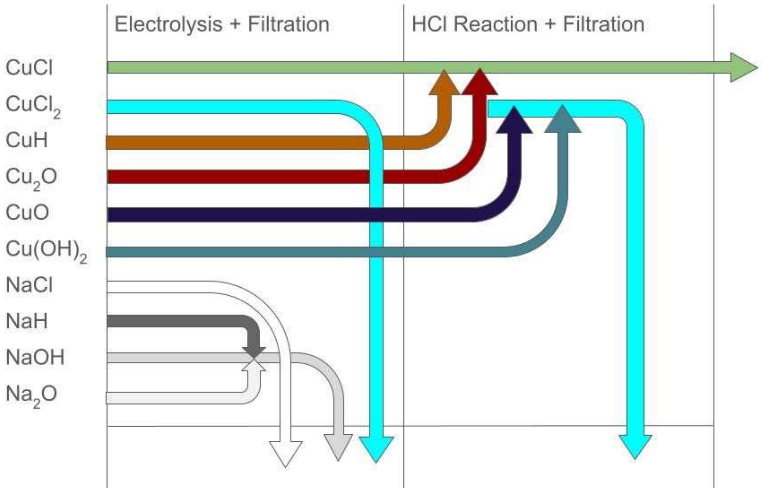

Figure 8. Flowchart illustrating the way that all possible salts would behave in the process and that the only possible product is CuCl. (An arrow ending on the bottom means that the salt is filtered out, an arrow ending in another arrow means that the salt reacts to become a different compound).

GHG emission calculations for comparable, offsite and/or product/method agnostic processes

At the industrial level, multiple changes could be made from the experimental procedure, which was not fully optimized due to resource limitations. The drying method would most likely be different – unlike the experiments, minor (non-proportional) losses are not expected to be significant at large scale, so the product could be spread out to dry faster. Additionally, drying could use solar or waste heat as they emit no additional GHGs and can be retrofitted into current manufacturing processes to use at large scale. The GHG emission calculations are meant to accurately represent emissions from industrial production using the Proposed Method, rather than from the experiments. Therefore, emissions from unit operations or factors that would be product agnostic and hence similar across methods on a per-gram crystalline product basis; on a large scale; such as drying, mixing, or pneumatic or hydraulic pressure creation for pumping and filtration; among others; are presumed to be similar across all the methods studied; as are emissions from comparable peripheral off-site operations such as logistics, transport and warehousing.

Rationale for chosen process

In order to lower GHG emissions from the Proposed method to only 2.6 g CO_2/g CuCl, multiple factors were considered. One of the biggest sources of emissions in this method was HCl, meaning that its use had to be reduced by as much as possible. This was achieved by conducting experiments with progressively smaller quantities of HCl in the purification step until a minimal amount for the reaction to take place reasonably quickly was reached. By reducing the volume used from 90 mL to 50 mL, total emissions were reduced by ~0.6 g CO_2/g CuCl, which is close to 25%. Also, NaCl was used rather than HCl in the solution for electrolysis since its production emits far less GHGs than does a solution of HCl (12, 14). Using NaCl afforded additional advantages. Significantly greater concentration of NaCl could be used when compared with HCl because concentrated HCl dissolves CuCl (1), and unreacted NaCl can be recovered more easily than can unreacted HCl. Since over half of the chloride ions are left unreacted, the recovery of NaCl reduces emissions by a significant amount. Another way in which emissions were reduced was by carefully selecting the precipitate extraction method. Experiments with boiling away the water were conducted, and although they were successful, the boiling alone released more GHGs than the rest of the process combined. Filtration was chosen as the method of extraction, although it was slower than boiling, it emitted negligible GHGs when compared to boiling, thereby reducing total emissions further.

Perspectives and scale up to Industrial capacity

0.05 amps produces ~0.8 g of CuCl in 4 hours ($2.4*10^{-3}$ KWh). 165000 tons of CuCl are produced per year (see the Conclusion section), which is equivalent to 450 tons per day. This will require 1350 MWh per day. If solar energy is utilized, with a 6-acre farm generating 1 MWh per hour (43), or 12 MWh per day, 676 acres of solar panels (along with batteries to enable 24/7 operation) would be enough to meet the electrolysis requirement for the Proposed Method to produce all the Copper(I) Chloride that is used worldwide.

Although today large-scale electrolysis with renewable energy might be difficult to implement, the renewable power sector is quickly growing. According to the International Energy Agency, "Global renewable power capacity is now expected to grow to 7300 GW over the 2023-28 period…Solar PV and wind account for 95% of the expansion, with renewables overtaking coal to become the largest source of global electricity generation by early 2025" (40). The cost of renewable energy is also dropping quickly, for example the price of solar PV modules halved in 2023 alone (40). This creates the potential for electrolysis to be viable not only because of sustainability, but also cost effectiveness. According to S&P Global, electrolysis is already one of the fastest growing areas for new investments (41).

Limitations

This research was limited by a number of factors, the most important of which was the lack of equipment. A number of useful experiments were unable to be conducted, which necessitated more time to develop alternatives with simpler equipment which could be performed at home or in some cases in the high school laboratory. Other limitations included part-time involvement and finances.

Conclusion

The experiments conducted in this research provided evidence for the hypothesis that electrolytic synthesis of CuCl is possible, and led to the development of a method of Copper(I) chloride production which uses electrolysis followed by purification. The proposed method was found to emit ~ 2.6 g CO_2/g CuCl, less than half that emitted by the currently used Main Industrial Method.

This work is an attempt to contribute to mitigating the Greenhouse Gas – primarily CO_2 – emission challenge facing the planet. Considering that ~ 165000 tons of CuCl are produced every year (based on market size (2) and bulk prices (29)), if the Proposed Method is implemented at large scale so as to replace the Main Industrial Method, global greenhouse gas emissions would be reduced by > 550000 tons per year, which is equivalent to planting > 25.5 million trees (30).

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Note

The method presented in this manuscript is Patent Pending.

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