

Novel Method to Systematically Resolve Global Warming by Removing CO₂ from the Air and Turning it Into Formic Acid

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Abstract

The CO₂ concentration in the atmosphere is a major problem with global warming being one of the main effects of the increased CO₂ concentration. The recapture of CO₂ from the atmosphere represents one of the most revolutionary ways of dealing with the problem. This study proposes the removal of high CO₂ concentration in the Earth's atmosphere relying on a photocatalytic conversion of CO₂ into formic acid. The use of readily available materials such as water and light makes the process easily adaptable. The study conducts an experiment on the photocatalytic conversion of CO₂ into formic acid using a RK-X reactor. Experiments conducted by the study returned 2.6g/L of formic acid achieved through the photocatalytic CO₂ conversion which can be easily restarted and adopted on a large scale basis with the right investment. The study proves that the conversion of CO₂ into formic acid is very much possible and highlights the practical applications of the process through the benefits associated with formic acid. The formic acid produced could act as a hydrogen carrier due to the formic acid's properties that make it one of the best hydrogen energy carriers hence allowing for energy from the sun to be converted and stored in chemical bonds.

Introduction

Global warming presents one of the biggest threats to planetary life. Human activity is the biggest contributor to global warming as evidenced by the 1-degree Celsius increase in global average surface temperature since 1880–1990 (pre-industrial era). This indicates a significant increase in accumulated heat with adverse climate change effects. Alarmingly, nine out of the 10 warmest years since 1880 have all occurred from 2005. The five warmest years ever recorded are also since 2015. This indicates the planet is getting significantly hotter and the effects can only get worse onwards. Addressing global warming or climate change is thereby one of the top goals as evidenced by sustainable development goals such as climate action, affordable and clean energy and sustainable cities and communities. Generally, it seems there is a genuine desire to address climate change concerns and significantly reduce the effects of global warming. Currently, efforts to address global warming focus on reducing the amount of carbon dioxide (CO₂) released into the atmosphere. Whereas the desire to cut down on the CO₂ released into the atmosphere is commendable, the effort made to make this a reality is not as impressive. With countries such as China and the United States topping the list of CO₂ emitters by country, it is easy to see why the planet keeps getting warmer. The top CO₂ emitters are predictably big industries and factories that contribute significantly to the economies of these countries. Government measures to control the amount of CO₂ released into the atmosphere may thereby not be as effective considering the contributions these companies make to their respective governments. This leaves the world in desperate need of an alternative method of resolving the global warming crisis that potentially threatens life on Earth.

One possible approach to addressing the global warming crisis is by removing CO₂ from the atmosphere and turning it into formic acid. This study focuses on this novel idea with the aim of documenting every

phase of this process, the chemist behind it, the experiments conducted and the possible practical uses for this formic acid. It analyzes how the process can be replicated from laboratory experiments to large scale implementation. The study relies purely on water, light and a catalyst (RRR) described in WO2021090038 to convert the CO₂ into formic acid. It also analyzes how the formic acid fits within the wider goal of the cleaner energy goal and hence aligning this with current sustainable development goals.

Study Objectives

The main objective for the study was to establish if photocatalytic CO₂ conversion into formic acid under the right conditions could be achieved with nothing but CO₂, water and a catalyst described in WO2021090038, when placed in a RK-X reactor.

The study also aimed to establish what the right conditions for the achievement of photocatalytic CO₂ conversion into formic acid were to allow the repeatability of the process on an even bigger magnitude.

Literature Review

Hydrogen is recognized as an excellent energy carrier placing it in high demand especially with increased concerns on finite fossil fuels. Hydrocarbons offer the most abundant sources for hydrogen especially those from the carboxylic acids' family. Formic acid (HCOOH) falls under this category and is increasingly adopted as one of the raw materials for hydrogen production mainly due to its hydrogen-bonded polymers. Mass production of formic acid to support the subsequent production of hydrogen energy is thereby the center of extensive research with promising potential for resolving the finite fossil fuels problem among others.

Research, however, indicates that the extraction of hydrogen from formic acid occurs at such a slow rate for it to be relied on for large scale production. The involvement of catalysts however allows for the hydrogen extraction from formic acid to be significantly improved. The hydrogen yield attained with the involvement of catalysts such as metals or elements within the periodic table's transition group. The involvement of these catalysts allows the process to be sped up and make it economical enough for it to be adopted on an industrial scale. Research on the best possible catalysts judging on their activation energy and reaction rates under right conditions indicate that copper (Cu) is one of the ideal catalysts for the process.

The high stability of CO₂ is one of the main reasons that resolving the CO₂ emission crisis has proven to be such a challenge. The high stability of CO₂ means that for any transformation to occur energy must be applied. Some of the conditions required for any transformation include high temperatures, extremely reactive reagents and energy derived from photons. One natural process offers inspiration on how to achieve CO₂ transformation with readily available products namely photosynthesis. Plants convert CO₂ into oxygen with the help of naturally occurring light through photocatalytic conversion. Inspiration from this process can thereby be used to replicate CO₂ conversion into another product including formic acid.

Initial studies on photocatalytic reaction as reported by Inoue et al. indicate that photocatalytic reduction of CO₂ in an aqueous suspension of a semiconductor can form methanol, methane, formaldehyde and formic acid. This has since influenced the direction of research on the photocatalytic mechanism of CO₂ conversion using various semiconductors. A critical part of the process is the adsorption of CO₂ since the high anti-bonding orbital of gas-phased CO₂ is what determines its need to be adsorbed on the surface for photocatalytic reduction can be achieved. Water plays an important part in the reaction as the water environment has the potential to change the adsorption configuration and reaction energies of CO₂ photoreduction. Monitoring the water environment thus becomes a critical part of the process due to its influence on the reaction.

Some of the biggest impediments to adopting hydrogen as a clean fuel lie in its storage and transportation. Two options exist for this either through physical or chemical storage. For physical storage, the hydrogen is stored in the diatomic molecular form in closed containers at low temperatures and high pressures or through cryo-compression. The chemical storage method on the other hand sees the hydrogen stored in the chemically bonded form instead of the molecular form used in the former. This is achieved through suitable molecules with higher hydrogen content that can release the hydrogen efficiently provided with the right conditions either through a catalytic or non-catalytic process. These include metal hydrides, hydrazine, metal borates, sodium borohydride and formic acid among others. Formic acid has been identified as one of the more ideal owing to properties such as it is non-toxic, liquid at room temperature, high density and normal handling conditions. It is these properties that have driven scientists to continued research on how to explore the use of formic acid in storage and transportation of hydrogen especially on a large scale basis.

Methodology

A total of 6 experiments were then conducted and observed to study the effectiveness of converting CO₂ into formic acid using light, water and the RRR catalyst. The catalyst used for the experiments was made as a fulvic acid derivatives by IOI Investment Zrt. The RRR catalyst is a silver complex as described in WO2021090038. Balint Analytics Engineering, Research and Service Provider Ltd determined the formic acid content of the aqueous solutions of the following samples: RK-X11, RK-X12, RK-X13, RK-X14, RK-X1, RK-X2, RK-X3, RK-X4.

Experiment #1

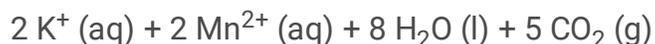
A Schott DURAN 1000 cm³ glass bottle was filled with aqueous carbonic acid solution freshly prepared from 950 cm³ of distilled water. A SodaStream soda water automaton was used during the preparation of the aqueous carbonic acid solution.

Exactly 20.00 mg of RRR catalyst was added to the solution obtained, and after sealing the glass bottle, it was shaken until the dissolution of the catalyst. The initial pH of the solution was 4.2, the endpoint pH was 3.0. The pH of the reaction mixture was measured with a digital pH meter and a Dosatest pH indicator strip. The glass jar was exposed to natural sunlight. The reaction mixture was under the influence of full daylight for 14 days [end of experiment: 16.07.2019]. The onset of the reduction reaction is indicated by the appearance of a semicircular Tyndall phenomenon. The samples were identified as RK-X11 and RK-X12.

The progress of the reaction was monitored by measuring the pH of the reaction mixture and the amount of potassium permanganate and bromine used up by the sample of the reaction mixture.

Two observations were carried out to confirm that aqueous carbonic acid solution was converted to formic acid.

Potassium permanganate reacts with the formed formic acid according to form the below reaction equation: $5 \text{HCOOH (aq)} + 2 \text{KMnO}_4 \text{ (aq)} + 6 \text{H}^+ \text{ (aq)} \rightarrow$



Observation: The reaction mixture decolorizes the potassium permanganate solution.

The bromine in the bromine water reacts with formic acid according to the below reaction equation: $\text{HCOOH (aq)} + \text{Br}_2 \text{ (aq)} \rightarrow + 2 \text{Br}^- \text{ (aq)} + 2 \text{H}^+ \text{ (aq)} + \text{CO}_2 \text{ (g)}$

Observation: The reaction mixture decolourises the bromine water.

Test results for solutions RK-X11 and RK-X12 in [mg/L] units

Laboratory code	Sample code	Sample preparation commenced (test ended)	Quantity of formic acid
19-735/1	RK-X11	25.07.2019	11.1
19-735/2	RK-X12	25.07.2019	11.0

Table 1.

Experiment #2

Using 200 mg/L RRR catalyst and winter sunlight for 14 days [end of experiment: 01.01.2020], in a 50 litres LABFREEZ VGR-50DL PYREX 3.3 glass reactor. The samples were identified as RK-X13 and RK-X14.

Test results for solutions RK-X13 and RK-X14 in [mg/L] units

Laboratory code	Sample code	Sample preparation commenced (test ended)	Quantity of formic acid
20-10/2	RK-X13	15.01.2020	179.0
20-10/3	RK-X14	15.01.2020	176.0

Table 2.

Experimental details in 2022 with the photoreactor (RK-X)

To determine the parameters for the very first CO₂ – formic acid conversion, a photoreactor (RK-X) was used.

Reactor parameters (RK-X)

Height: 500 mm

Outer diameter: 100 mm

Inner diameter: 90 mm

Height (top and bottom fittings): 40 mm

Gross Volume: 2670 cm³

Net Volume: 2100 cm³

Volume (lighting fitting): 570 cm³

Volume (Gas): 400 cm³

Volume (Liquid): 1700 cm³

Lighting: LED 0.702 A (231 lux, 626 nm, 17 W – 48 W)

Experiment #3

The RK-X reactor was filled with 1700 cm³ of distilled water and RRR catalyst (300 mg/L) was dissolved. Fully saturated water with carbon-dioxide (CO₂) was created in the reactor (constant pressure indicated that the water is fully saturated). The reactor was charged to 5 bar with carbon-dioxide (CO₂) gas. Then the lights were switched on and left the reaction go until pressure in the reactor reduced to 1 bar. The sample was identified as RK-X1.

Amount of reacted CO₂ (n) = 0.01613582 mol

Calculated concentration = 0.01613582 mol*46/1700 cm³ = 436.62 mg/L

Measured concentration (RK-X1): 301 mg/L

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Experiment #4

Procedure was followed as described of Experiment #3. The sample was identified as RK-X2.

Amount of reacted CO₂ (n) = 0.01613582 mol

Calculated concentration = 0.01613582 mol*46/1700 cm³ = 436.62 mg/L

Measured concentration (RK-X2): 313 mg/L

Experiment #5

Procedure was followed as described of Experiment #3. The sample was identified as RK-X3.

Amount of reacted CO₂ (n) = 0.0645433 mol

Calculated concentration = 0.0645433 mol*46/1700 cm³ = 1746.46 mg/L

Measured concentration (RK-X3): 1650 mg/L

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Experiment #6

In Experiment #6 the procedure of Experiment #3 was applied twice. The procedure of Experiment #3 was followed and when the pressure dropped to 1 bar, the reactor was recharged with carbon-dioxide to 5 bar

and the reaction was carried on until the pressure dropped to 1 bar again. The sample was identified as RK-X4.

Pressure (Δp) = 8 bar (2x4 bar)

Amount of reacted CO₂ (n) = 0.1290865 mol

Calculated concentration = 0.1290865 mol*46/1700 cm³ = 3492,93 mg/L

Measured concentration (RK-X4): 2600 mg/L

Test results for formic acid using RK-X photoreactor in [mg/L] units

Laboratory code	Sample code	Sample preparation commenced (test ended)	Quantity of formic acid (mg/L)
22-68/4	RK-X1	03.02.2022	301
22-68/2	RK-X2	03.02.2022	313
22-68/6	RK-X3	07.02.2022	1650
22-68/8	RK-X4	11.02.2022	2600

Table 3.

Discussion

The most significant takeaway from the experiment was that it is possible to achieve photocatalytic conversion of CO₂ into formic acid through the RK-X reactor. Even more importantly, the process can be scaled up. The 50 mmol/h CO₂ conversion achieved in the 2L photocatalytic reactor means that in 2m³ reactor we can achieve the kilo range formic acid production. The ability to significantly increase and improve on the level of photocatalytic CO₂ conversion using the results from the study's prototype is the most critical part of the study. It offers endless opportunities for the application and utilization of the formic acid and subsequently hydrogen energy as discussed in the literature review section. The readily available materials for this process and its ability to be restarted easily make it a viable option for addressing the CO₂ concentration problem as well as addressing other pressing problems such as the finite fossil fuel challenge as well as the need to adopt interplanetary life.

Application of Photocatalytic CO₂ Conversion

Experiments conducted on the RK-X reactor and their promising results indicate a potential to achieve this on an even grander scale. With the right investment in the photocatalytic conversion process inorganic carbon can be converted to organic carbon on a large-scale basis. This is significant in the practical application of the process to the modern world. The formic acid produced through photocatalytic conversion from the RK-X reactor will not only help in the reduction of CO₂ concentration in the atmosphere, but also applied to resolve other global problems.

Hydrogen Energy Production

One of the challenges facing humanity in the 21st century is the potential threat to fossil fuel exhaustion. It is estimated that the world will run out of fossil fuels in this century due to the rate of consumption of these fuels being significantly greater to their formation rates. The expanding population and increased reliance on these fuels around the globe have significantly contributed to this reality. As a result, shifting to renewable sources of energy is no longer a matter of preference but one of need failure to which the world as we know will grind to a halt once the fossil fuel is exhausted. This study proves that the photocatalytic process of converting CO₂ into formic acid can come in handy in breaching the gap in energy needs.

Hydrogen energy has been touted as the future of energy with regions such as Europe aiming to shift towards hydrogen energy fully by 2030. Although it is still a relatively new renewable energy resource and hence at the initial phase of research and advancement, the potential it holds makes it highly attractive in resolving the renewable energy problem across the globe. The high energy efficiency, economic competitiveness and overwhelming social and environmental benefits associated with hydrogen energy make it the ideal energy for the future[1]. However, a viable hydrogen energy carrier is needed if hydrogen energy is to be adopted on a large scale. Formic acid's qualities such as the high volumetric capacity (53 g H₂/L), low toxicity and flammability in ambient conditions make it one of the most promising hydrogen energy carriers[2]. The photocatalytic conversion of CO₂ in the air to formic acid on a large scale as evidenced in the study's experiments will thus not just be about lowering the CO₂ concentration in the atmosphere, but also resolving the renewable energy problem.

Interplanetary Life

This study also presents itself as potentially critical in resolving the challenge of interplanetary life. Presently, Mars is the most likely destination for humans in terms of planet colonization with continuous research on how life on Mars can be achieved. This is of course informed by the awakening realization that human civilization will could be significantly weakened if a momentous event were to occur. The results of the study prove that this process can be replicated in Mars and solve one of the problems in the planet by producing hydrogen energy enough to power civilization on the planet. Recent discoveries reveal

the presence of water in ice form on Mars. Additionally, Mars' atmosphere is 96% CO₂ meaning that the components needed (water, sunlight and CO₂) for the RK-X process can be readily found in Mars. The conversion of the abundant CO₂ in the atmosphere to formic acid as per the study's process would thus come in handy in reducing CO₂ concentration in the atmosphere as well as producing much needed hydrogen energy to power activities and possibly life on the planet. Although this process needs to be perfected on Earth first being replicated in Mars, it is highly promising that it can be useful in the resolution of some of the pressing challenges related to Mars colonization. The byproduct from the formation of formic acid is oxygen which can also be used to produce oxygen which is in extremely scarce levels on Mars at just 0.2%. The low concentration of oxygen levels on Mars means that animals including humans cannot inhale oxygen naturally as on Earth hence artificial production of oxygen is needed to support life. This makes the photocatalytic CO₂ conversion process even more important on Mars due to its bypass product.

In the meantime, the hydrogen energy produced with the formic acid can be used to power rocket fuels and facilitate research. The production of stored energy also allows for the storage of sun's energy within chemical bonds. Hydrogen can then be used to power up planetary life in Mars without the risk of environmental hazards that would disrupt the planet's atmosphere as has been the case with Earth. It would thereby be creating a more environmental-friendly planet to support human life.

Conclusion

The photocatalytic CO₂ conversion into formic acid analyzed, experimented, and successfully achieved at 2.6g/L in the study is one of the more impressive feats for modern chemistry. This is not only for its potential contribution to addressing the high CO₂ concentration in the atmosphere leading to global warming, but also for the other applications of the formic acid produced. Studies reveal that other approaches to carbon capture and reuse emit more carbon dioxide than they capture with 32 out of 40 technologies tested falling under this category. This indicates that modern efforts to reduce CO₂ concentration through CO₂ capture are not as advanced as often thought, and hence the need to give this technology even more attention and investment. The success exhibited by the experiments conducted as well as the significantly little time taken to achieve this CO₂ conversion justify the need for bigger experiments to test the large scale and commercial adaptation of this prototype.

The RK-X photocatalytic CO₂ conversion into formic acid represents the future of addressing global warming and finite fossil fuel problems. This chemical process is informed by legit chemical processes and tried out on competent laboratories with results backing the theory of formic acid formation. Future studies should now be conducted that aim to replicate the results of the study on a larger scale.

Significant resources are however needed for such experiments, but the study's results should be enough justification.

References

1. Ed Hawkins et al., "Estimating Changes In Global Temperature Since The Preindustrial Period", *Bulletin Of The American Meteorological Society* 98, no. 9 (2017): 1841–1856, doi:10.1175/bams-d-16-0007.1.
2. "Top 10 Warmest Years On Record", *Climatecentral.Org*, Last modified 2020, <https://www.climatecentral.org/gallery/graphics/top-10-warmest-years-on-record>.
3. Thomas Frohlich and Liz Blossom, "China, US: These Countries Produce The Most CO2 Emissions", *Usatoday.Com*, Last modified 2019, <https://www.usatoday.com/story/money/2019/07/14/china-us-countries-that-produce-the-most-co-2-emissions/39548763/>.
4. Samuel Eshorame Sanni et al., "Strategic Examination Of The Classical Catalysis Of Formic Acid Decomposition For Intermittent Hydrogen Production, Storage And Supply: A Review", *Sustainable Energy Technologies And Assessments* 45 (2021): 101078, doi:10.1016/j.seta.2021.101078.
5. National Research Council et al., *Carbon Management: Implications For R&D In The Chemical Sciences And Technology* New York: National Academic Press, 2001.
6. Chao Peng et al., "Perspective: Photocatalytic Reduction Of CO2 To Solar Fuels Over Semiconductors", *The Journal Of Chemical Physics* 147, no. 3 (2017): 030901, doi:10.1063/1.4985624.
7. Chao Peng et al., "Perspective: Photocatalytic Reduction Of CO2 To Solar Fuels Over Semiconductors", *The Journal Of Chemical Physics* 147, no. 3 (2017): 030901, doi:10.1063/1.4985624.
8. Ashish Kumar Singh, Suryabhan Singh and Abhinav Kumar, "Hydrogen Energy Future With Formic Acid: A Renewable Chemical Hydrogen Storage System", *Catalysis Science & Technology* 6, no. 1 (2016): 12–40, doi:10.1039/c5cy01276g.
9. Jukka Hietala et al., "Formic Acid", *Ullmann's Encyclopedia Of Industrial Chemistry*, 2016, 1–22, doi:10.1002/14356007.a12_013.pub3.
10. Paulo Emilio V. de Miranda, *Science And Engineering Of Hydrogen-Based Energy Technologies* New York: Elsevier Science, 2018.
11. Jacques Amouroux et al., "Carbon Dioxide: A New Material For Energy Storage", *Progress In Natural Science: Materials International* 24, no. 4 (2014): 295–304, doi:10.1016/j.pnsc.2014.06.006.
12. Kiane de Kleijne, Steef V. Hanssen, Lester van Dinteren, Mark A.J. Huijbregts, Rosalie van Zelm, Heleen de Coninck "Limits to Paris compatibility of CO2 capture and utilization", *One Earth, Review: Vol 5, Issue 2, P168-185 (2022) DOI: <https://doi.org/10.1016/j.oneear.2022.01.006>*