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Sustainable hydrocarbon business based on biogenic carbon dioxide and renewable electricity

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Abstract: *The climate change forces us to shift from fossil to renewable resources. Biogenic CO_2 converted into hydrocarbons with renewable electricity can simultaneously provide us with raw materials and fuels, a positive climate impact and healthy business opportunities. Integrated CCU options benefit from energy integration, a local CO_2 source substantially reducing the CO_2 transportation costs, adjustable CO_2 purity and the possibility to utilise the produced fuels and chemicals on-site. In this paper, we examine CO_2 capture and utilisation (CCU) in formic acid production at a pulp mill, a novel CO_2 capturing concept especially suitable for biogas production as well as the potential in new CO_2 concrete curing methods.*

Keywords: power-to-product (P2X), biogenic CO_2, techno-economic feasibility, process integration

INTRODUCTION

How can we produce everyday items without fossil resources? The urgency of mitigating climate change calls for preparing for a future where fossil resources can be left untouched. To contribute to this preparation, our research group at VTT has been screening and developing sustainable CCU value chains with different carbon dioxide utilisation routes. In today's market, CCU technologies can offer a financial driver to boost the implementation of sustainable alternative technologies.

We have chosen to focus on value chains, where biogenic CO_2 originally captured by living plants through photosynthesis is the source of carbon. We assume that renewable grid electricity can provide clean energy for the chemical conversion of CO_2. A value chain in this case comprises everything from the CO_2 source to the end user, mainly: the CO_2 producing plant, other raw materials production, CO_2 capture technology, renewable electricity production, CO_2 conversion technology, CO_2 transportation, product transportation, applicable legislation and the customer.

Point sources are efficient for CO_2 capture ensuring reasonable capture costs. Matching the CO_2 source, capture and purification technology, product and plant site narrows the options down to specific integrated solutions. Developing an entire value chain as a whole early on is beneficial for early commercialisation. It also helps with consistent policymaking. We believe that our focus on biogenic CO_2 sources provides us with a solid basis for sustainable business concepts.

Our approach is to start by screening the existing CCU technology alternatives and their potential applications in the Nordic industry. As our screening criteria, we use climate benefits and sustainability, technological maturity and economics. In the process, we examine the potential value chains looking for ways to improve its feasibility or weak links. In the relatively fresh field of CCU there is still room for new innovations. A couple of our new ideas include an ejector based CO_2 capture concept for methane production and novel concrete curing methods that allow the saving of cement. For more mature technologies and their integration with the present industries, we have applied an MS Excel techno-economic assessment model. In this paper we publish also our recent results of producing formic acid at a pulp mill - a case with payback time of only a couple of years!

BACKGROUND

In this paper we examine value chains, where CO_2 in converted into something valuable. Such conversion routes can be categorised in chemical and biological conversion, and mineralisation. This conversion requires energy and its source is critical for the sustainability of CCU value chains. Other significant environmental factors include the efficiency of the entire system, origin of the other used resources, amount of CO_2 utilised and the lifetime of the product and recycling. Moreover, healthy economics and beneficial societal impacts are required.

At VTT the authors have discussed a lot about the fundamentals that would ensure the sustainability of any given CCU application and a good summary of that discussion is presented in the VTT discussion paper on carbon capture and utilisation [1]. In brief, by using only low-carbon energy in converting the CO_2 into products and utilising CO_2 from only atmospheric sources, either directly or via plants, we would have the best potential for a beneficial climate impact or even removing CO_2 from the atmosphere.

With both environmental and financial arguments in play, good legislation is needed to provide fair rules for utilising CO_2. For instance, when a fuel is combusted, biogenic and fossil CO_2 affect the climate identically. However, the benefit of biogenic fuels is currently accounted for in the EU Emissions Trading Scheme (EU ETS). Other legislation concerning CCU should consider the EU ETS, if the CO_2 source is within the EU ETS sector in order to avoid double counting of the emissions. Another aspect the future legislation should consider is the CO_2 bound in the products; with only a few years lifetime the climate effect from keeping the CO_2 from the atmosphere is marginal, but mineralisation can bind CO_2 permanently - an effect unaccounted for in the present legislation. Non-global legislation attempting to reduce emissions is also subject to possibly leaking borders in the form of relocating production plants or electricity import.

Renewable Energy Directive II of the EU [2] is being finalised as we write this article. This directive is going to play an essential role in which kind of CCU concepts are going to be possible business cases and the drafts currently under discussion vary greatly in their content.

METHODS

The objective of our work is to find and develop sustainable CCU value chains. In our work, we have used specific screening criteria and MS Excel based techno-economic analyses as well as thermodynamic modelling for estimating the potential of novel concrete curing methods. Our screening criteria includes:

- good environmental impact with biogenic CO_2, renewable electricity and large CO_2 utilisation potential,
- technological maturity and
- economic evaluation based on market size and product value.

For more than a decade by now, few companies have been developing CO_2 curing methods for the construction industry [3–5]. During our work we found e.g. that there could be great unutilised potential in curing concrete with CO_2, which we assessed with thermodynamic modelling. Concrete is conventionally made of cement, water and aggregate. Portland cement and water can form a flowing mixture that does not change its volume during hardening. The hardening occurs due to the hydration reaction resulting in calcium hydroxide and calcium-silicate hydrates. Much effort has been devoted to reducing the cement content, but the optimal water/cement ratio has remained. Introducing CO_2 curing may change this, because CO_2 is able to react with the primary and secondary hydration reaction products. In this study, we have made a thermodynamic model of CO_2 cured concrete. Our model simulates a concrete structure manufactured in a way that allows the cement paste to expand. The thermodynamic model predicts then the stable phases and their volumes. The result is a theoretical optimum based on the thermodynamic equilibrium, which indicates the potential of such a set-up, where the cement paste may freely expand. This may not necessarily be achieved in practice, because of possible kinetic restrictions. Data for the modelling was retrieved from CEMDATA, Nagra/PSI, Thermoddem, Thermochimie and OECD-NEA databases. The elemental composition of Annläggninscement (CEMI) with a water-cement ration of 0.5 and varying dosage of CO_2 in normal temperature and pressure were used for modelling the CO_2 curing of concrete. This technology design would be especially suitable for concrete elements or concrete products, not ready-mixed concrete

Another idea that we developed is a novel ejector based CO_2 capture and utilisation system for both thermal and biological methane. We studied the new technology was studied with an MS Excel model for ejector behaviour, reaction and solubility balances. The system is presented in Figure 1.

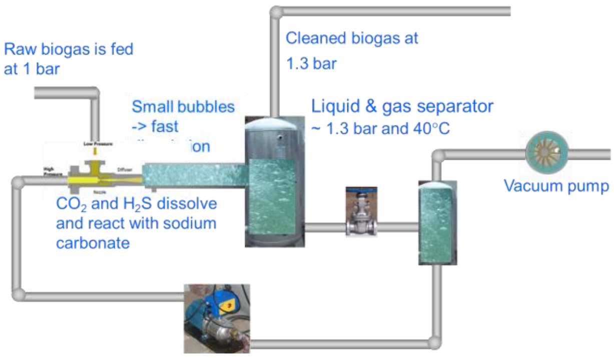


Figure 1. A schematic drawing of the novel CO_2 capturing concept, when CO_2 is separated for use outside the process.

The concept is based on employing an aqueous solution of sodium carbonate and bicarbonate solution in order to improve the solubility of CO_2. Instead of a conventional adsorption column a liquid-gas ejector is used, which results in faster dissolution of CO_2 and smaller and cheaper process equipment. A concentrated stream of CO_2 can be obtained by regeneration of the sodium carbonate solution under vacuum at 40 °C, so that only a low temperature heat compensating for the energy needed for evaporating water is needed. In addition, two cases where the captured CO_2 was converted together into methane using hydrogen from water electrolysis either by biological or thermal process were studied.

For the techno-economic assessment of formic acid production at a pulp mill we used an hourly optimisation model based on the work in the NeoCarbon Energy project [6] for MS Excel. It takes into account mass and energy balances and efficiencies. The model as well as the results for the bio-SNG, methanol and formic acid cases at a sawmill and wastewater treatment plant were reported earlier at EUBCE 2017 [7]; the work on the polyols production case is still on-going. The data for the pulp mill is based on an IEAGHG report [8] scaled to the Äänekoski pulp mill that has a production volume of 1 300 000 ADt/a. The here examined formic acid production process is presented in Appendix A and is based on [9]. The process consists of an electrolyser, a synthesis unit and separation, solvent stripping and distillation units. The key parameters of the process are presented in Table 1. For the particular pulp mill case the formic acid production was scaled so that the oxygen from the electrolyser was enough to cover the consumption at the pulp mill. This led to an electrolyser size of 32.5 MWe.

Table 1. Key parameters of the formic acid production process.

TABLE 1	Formic acid (TRL 3-5)
Reaction	**$CO_2 + H_2 \rightarrow HCOOH$**
Synthesis efficiency ($LHV_{product}/LHV_{H2}$)	55%
Inputs:	
Electricity, MW_e	1
CO_2, kg/h	282
Outputs:	
Product, $MW_{LHV, dry}$	0.37
Heat, MW	0.7
Steam, MW	-0.95

Given the net steam consumption of the process and by-production of oxygen in the electrolyser, a pulp mill would be a suitable environment for formic acid production, since low cost steam is available and there is use for the oxygen in the pulping process. Moreover, if an investment in CO_2 capture is considered, there would be multiple uses for the CO_2 in addition to formic acid production. Notable in this process is also the technology readiness level 3-5 according to [9], which is still some steps from being commercially available. In addition, direct electrochemical utilisation of CO_2 for formic acid production has also been studied [10]. We prepared two different market scenarios for the analysis: an optimistic and a conservative estimate. The most important market parameters for each case are listed in Appendix B.

RESULTS AND DISCUSSION

Concept screening

The first results from concept screening revealed us that there were hundreds of research projects either on-going or finished even in a single CCU project database with the applications touching multiple industry sectors. [11] However, only few technologies were applied in semi-commercial or commercial for instance in greenhouses, mineralisation, power-to-fuels, power-to-chemicals or polymers production.

Narrowing down from the vast amount of possible value chains to examine we began to search within the biomass treating industries that produce biogenic CO_2 emissions. Many of those processes were also familiar to us already and are of major importance in the Nordic. This would allow close collaboration with the companies and should be helpful in getting new business up and running. These included the pulp and paper sector, chemicals production, combined heat and power production, biogas production and wastewater treatment. After consideration, we excluded algae cultivation and greenhouses from our scope because we wanted to aim for concepts utilising larger amounts of CO_2. Some of the near term applications for greenhouses and pulp mills were also examined in a collaboration research project [12] giving reason to leave them with less attention in our work.

Finally we selected methane, methanol, formic acid and polyols production considering a sawmill, a pulp mill, a biogas plant or a wastewater treatment plant as integration environments for closer techno-economic analysis. The latest complete results, formic acid production at a pulp mill are presented later in Figure 2. In addition, we investigated two novel ideas regarding CO_2 curing concrete and CO_2 capturing from biogas production.

Potential of CO_2 curing concrete with novel methods

Results from the thermodynamic modelling of CO_2 cured concrete are presented in the Appendices C and D. In Appendix C the modelled volumes of solids are shown. The y-axis shows the total volume of solids at equilibrium. The chemical composition at equilibrium varies with increasing mass percentage of CO_2 added per binder (cement), as shown on the x-axis. Largest increase in the volume of solids has been reached by adding about 40 wt-% of CO_2 per binder leading to the largest potential in saving cement by up to 26 wt-%. This would probably be the current optimal amount of adding CO_2, because savings in cement consumption would be a major economic driver. The modelled pH is still at around 12 with 40 wt-% of CO_2 added. With higher dosages of CO_2 the pH would drop significantly and may not be enough to protect possible steel reinforcements from corrosion. Appendix D shows that the amount of CO_2 bound in the concrete increases linearly until reaching a maximum at 0.51 t CO_2 per t of cement, which is well aligned with estimated maximum of ~0.5 t CO_2 /t of cement-based material presented in [13].

Even though the results of the modelled potential in binding CO_2 were as expected, the possible savings in cement use were surprisingly high. It means that if such a process can be developed, where the concrete is allowed to expand during its CO_2 curing, the savings could be of immense significance for the industry. Such enabling modifications in the curing process might include a closed CO_2 environment, a higher water content and CO_2 gas injection from multiple points. The suggested process is best suitable for manufacturing concrete elements and other concrete products, where the curing may already happen in a closed CO_2 atmosphere. The process could enable the use of belite cement, allowing to reduce cement kiln temperatures further decreasing the emissions. If the process would be applied to all of the Finnish concrete element and product manufacturing with an estimated cement consumption of 1,100,100 t/a [14], about 286,000 t/a cement could be saved and bind permanently some 330,000 t CO_2/a when cured with possible further emission reductions from fuel savings. Since the specific process is not known yet, further economic analysis would include great uncertainties. Nevertheless, given the potential in developing such a new CO_2 curing process, the authors encourage further experimental research on the subject.

Ejector concept for CO_2 capture and methanation

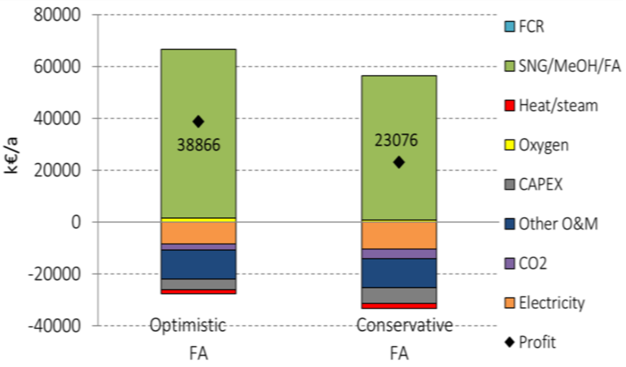
Preliminary techno-economic calculations show that the concept could reduce the capital cost of CO_2 separation from biogas by at least 30 % and during 2018-2019 VTT will demonstrate the concept experimentally. Especially biological methanation of CO_2 could be significantly enhanced by using the novel ejector based concept. The main advantages include pressurising CO_2 with hydrogen obtained from electrolysis and enhancing mass transfer between aqueous phase and gas phase resulting in speeding up the process.

In addition, CO_2 could be captured and used elsewhere more efficiently with lower CAPEX cost compared to standard processes such as water washing, amine scrubbing, membrane processes and equal or lower operating costs. The method is especially suitable for cases where the CO_2 should be removed from biogas or another gas to a low level and where the obtained CO_2 should contain a low level of methane which is a powerful greenhouse gas and no residues of chemicals like amines. Biomethane production is therefore one very suitable application candidate.

These promising results led us to applying for a patent for the novel ejector based concept.

Formic acid

Figure 2 presents the latest complete results of our techno-economic analyses: formic acid production at a pulp mill.



	Optimistic FA	Conservative FA	
Profit	38 866	23 076	k€/a
EBIT	40 645	25 617	k€/a
EBIT DA	43 036	29 033	k€/a
Payback time	1.2	2.6	years
Pre-tax IRR	90 %	42 %	
LCOP	0.28	0.35	€/kg

Figure 2. Techno-economic analysis of formic acid production at a pulp mill.

The columns present the income and expenditure of the formic acid plant in each market scenario. Nearly all of the income comes from the formic acid production, only a fraction from selling the oxygen. This is specific for the formic acid case, where the main product has a high price. Most of the expenses are related to electricity purchases as well as catalyst and solvent consumption (Other O&M), but the CAPEX is also significant if the market assumptions are conservative. Nevertheless, as highlighted with the red boxes, in both market scenarios the process seems to be very profitable with a payback time of only a couple of years and a decent levelised cost of product leaving operating margin for future businesses. This means that the process deserves further development, to get rigid experimental proof in an industrial scale. One specific research topic could be to optimize CO_2 purification for the biogenic CO_2 captured at the mill, hence the current catalytic processes require very high purity levels regarding sulfur for instance.

CONCLUSIONS

We aimed at finding new sustainable business in producing materials for everyday items without fossil resources. We found numerous possible CCU routes connecting with practically all fields of industries. Single value chains may be profitable, but finding these is a challenge. The market is not ready yet, so learning about the specific barriers regarding each value chain is important. Perhaps due to these weak links in some value chains, CCU appears to be a hot topic, but only up to demo scale and only few businesses were found readily operating. Moreover, the most profitable cases may have disadvantages in technological maturity or market size.

In our work we learned that the most important factors for the economic feasibility include:

- electricity price and main product price,
- integration possibilities in heat and steam connections,
- utilising CCU by-products and end products on-site,
- matching the concentration and purity of available CO_2 and utilised CO_2,
- avoiding CO_2 transportation and
- large scale (in relation to the CCU field).

Formic acid production at a pulp mill appears to be a good business opportunity with a payback time between 1-3 years, as long as the process can be proven in an industrial scale. The value of the product is high, but the relevant market size is limited. New CO_2 concrete curing methods could enable the permanent binding of CO_2 and lead to savings in cement consumption by up to 26 %, but such a process is yet to be developed in practice. However, the global climate impact could be vastly positive. The novel ejector based concept for CO_2 separation could be especially beneficial in biogas upgrading, where the capital costs could be decreased by up to 30 %.

We believe that if in the coming years the formic acid CCU process can gain enough experimental validation in larger scales, it could be a significant alternative in the global formic acid market. In a couple of years time the promising modelled results from new concrete CO_2 curing methods can be proven experimentally, allowing the design of a pilot plant. For the ejector concept, lab-scale experimental work is planned for 2018-2019 and a pilot is foreseeable in the 2020's.

In the coming years the supply chains would change: our carbon feedstock would be local bio-waste rather than overseas imported fossil resources. As the change progresses, the supplier countries may as well adopt the new, more sustainable processes allowing them too to increase their standard of living, while eventually leaving the fossil carbon untouched.

These and other CCU technologies will have an essential role enabling us to eventually live without using fossil resources, but for the time being many conventional value chains still lack a valid sustainable alternative. When facing such great challenges one might consider acting on those processes first, that provide us with sustainable alternatives for our basic needs: food, shelter, water, clothing and energy.

Despite its important role in a sustainable future society, CCU has had only moderate, but lately growing, interest in Finland. We found this in our social network analysis, workshops and discussions with the Finnish companies. We believe that demos and pilots as well as the media about them are important to wake more interest and gain credibility. According to our accumulated knowledge, future research efforts should be aimed at demonstrating few of the most promising technologies with intact value chains in a large enough scale, so that the commercialisation could take place soon after.

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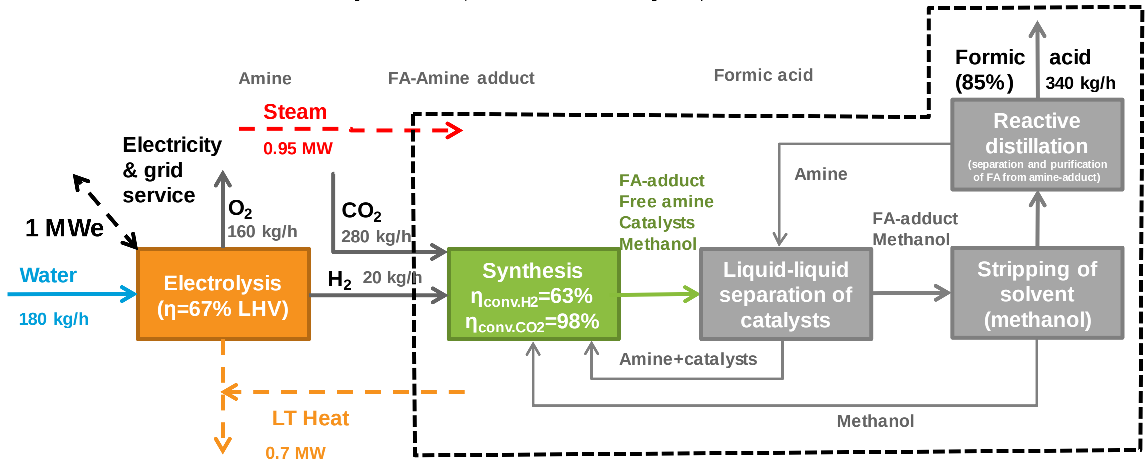
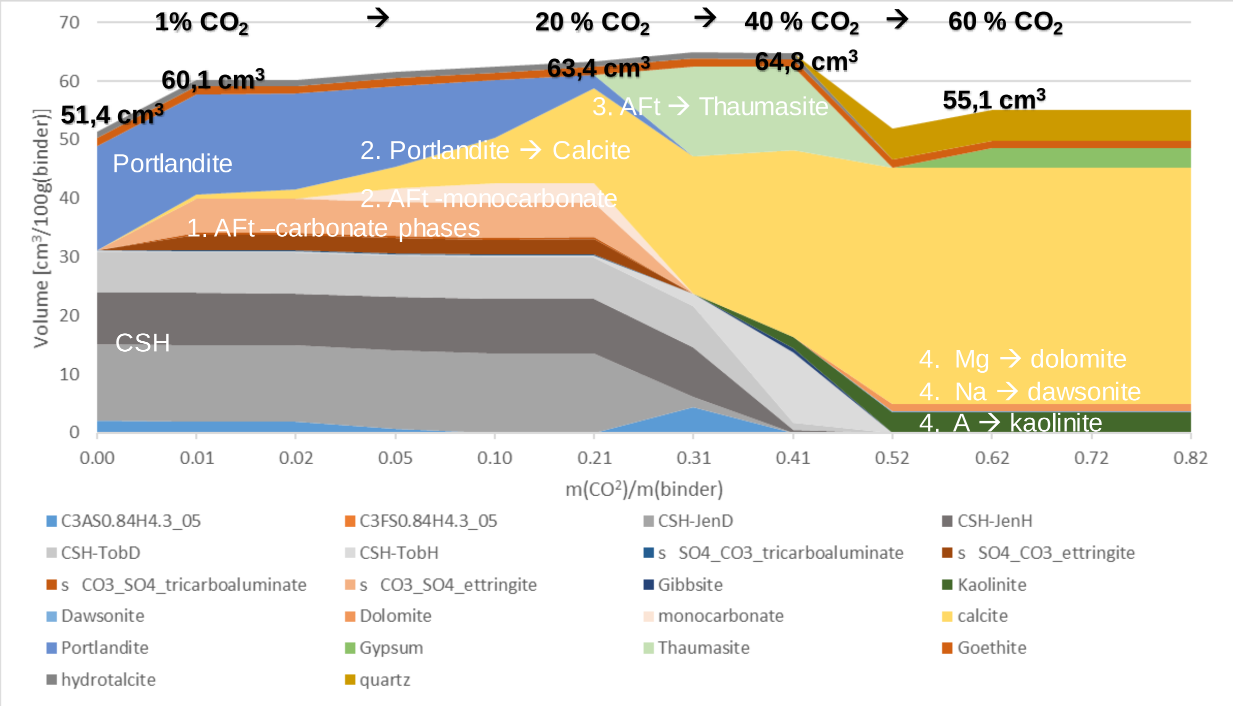
APPENDIX A: Formic acid synthesis (1 MWe electrolyser).



APPENDIX B: Assumed market parameters for formic acid production at a pulp mill.

	Optimistic scenario	Conservative scenario
Products	Formic acid 700 €/t	Formic acid 600 €/t
Electricity spot price scenario	• Finland 2016 · 80% (avg. price 25.6 €/MWh) • Extra price variation ±30%	• Finland 2016 (avg. price 32.0 €/MWh)
Electricity transmission + net taxes	2 €/MWh (only net tax)	2 €/MWh (only net tax)
FCR scenario	-	-
CO_2 capture+purification	30 €/t_{CO2}	50 €/t_{CO2}
O_2 utilisation	Avg 34 €/t_{O2} (decreased electricity demand + other PSA OPEX 5 €/t + PSA CAPEX 20 €/t)	Avg 16 €/t_{O2} (decreased electricity demand + 5 €/t for other PSA OPEX)
Heat utilisation	0 €/MWh	0 €/MWh
Cost of steam	Avg 6.5 €/MWh	Avg 8.1 €/MWh
Investment subsidy	30%	0%

APPENDIX C: Modelled volumes of solids in CO_2 cured concrete.



APPENDIX D: Modelled amount of CO_2 bound in the concrete