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Förord

Projektet har finansierats av Energimyndigheten med 386 000 kr och av GFT, Green Fossil Technologies AB med 129 000 kr.

Innehållsförteckning

Sammanfattning

Det är mycket angeläget att minska utsläppen av koldioxid för att minska de skadliga effekterna på klimatet. Projektet PIE, Photosynthesis in Exhaust, presenterar en teori som visar hur koldioxid i avgaser kan fångas och omvandlas till bikarbonater mycket energieffektivt. Processen som bygger på utnyttjande av delar av fotosyntesen kräver i teorin ungefär 1% av bränsleenergin för att fånga all koldioxid från exempelvis kraftverk eller fartyg, under ideala tillstånd och om processen kan realiseras. Projektet har genomfört experiment som så långt visar på en koldioxidreduktion på 1-2% och samtidig ökning av syrgas med 2-4%. Ytterligare experiment med förbättrade reaktorer krävs för att bekräfta att koldioxid verkligen reduceras, men också för att fastslå att det är den föreslagna processen som aktiveras och inte den mer energikrävande normala fotosyntesen.

För implementering i praktiska applikationer krävs dessutom ytterligare arbete för att fastslå förbrukning av kloroplaster samt omhändertagande av bikarbonater.

Summary

It is very important to reduce carbon dioxide emissions in order to reduce the harmful effects on the climate. The project PIE, Photosynthesis in Exhaust, presents a theory that shows how carbon dioxide in exhaust gases can be captured and converted into bicarbonates very energy efficiently. The process, which is based on the utilization of parts of photosynthesis, requires in theory about 1% of the fuel energy to capture all carbon dioxide from, for example, power plants or ships, under ideal conditions and if the process can be realized. The project has carried out experiments that so far show a carbon dioxide reduction of 1-2% with a simultaneous increase of oxygen of 2-4%. Further experiments with improved reactors are required to confirm that carbon dioxide is actually reduced, but also to establish that it is the proposed process that is activated and not the more energy-intensive normal photosynthesis. For implementation in practical applications, additional work is also required to determine the consumption of chloroplasts and the disposal of bicarbonates.

Inledning/Bakgrund

The world's need for energy for electricity generation, heat, power and transport is largely met by fuels consisting of coal or hydrocarbons. These fuels generate carbon dioxide during combustion and by that contribute to global warming through the greenhouse effect. Due to the enormous negative effects of global warming, it is very important to be able to reduce carbon dioxide emissions by phasing out the use of carbon-based fuels or capturing carbon dioxide before it leads to negative effects. This project deals with the latter.

A patent-pending synthesis reactor was employed prior to the project and demonstrated a reduction of CO_2 in the exhaust stream of a diesel car. Those results can not entirely be explained by the energy balance of conventional photo synthesis, and one hypothesis for the project was that the abundant exhaust enthalpy and water vapor from the engine combustion was supporting the process.

The main objectives of the project were:

- Test the concept through better controlled experiments to verify a repeatable and consistent reduction of CO_2
- Theoretically explain how the process works
- Evaluate how much CO_2 that can be converted and what the byproducts consist of and how they can be handled
- Propose steps for further research of the concept

Genomförande

The project was divided into two parts. WP1 was led by Lund university, and dealt with experimental testing, using the experimental facilities at the energy laboratory at Lund university with advanced measurement systems. WP2 was led by the Royal Institute of Technology, KTH, and performed theoretical assessment through literature surveys, calculations and through participation in the assessments of the experimental data. During the project there has been frequent interactions to interpret the theoretical end experimental findings, and also to guide the next steps during the project. GFT, Green Fossil Technologies AB, initiated and has supported the experimental work but also participated in all interactions.

The experimental work was performed in three consecutives measurement campaigns due to the difficulties in establishing meaningful results and the need to build and modify equipment based on the improved understanding from the experimental and theoretical investigations. The work was delayed by the corona-pandemic, that however, from a positivistic note, provided additional time for reflections.

Campaign 1 was performed early in the project to repeat the experiments that was performed prior to the project on a diesel-fuelled passenger car. Three different reactors were tested separately, each directly attached to the tailpipe of the diesel car with the engine running at idle. The emission analyser and thermocouple was connected to the outlet of the reactor. In common for the reactors, chloroplast in the form of ground baby-spinach was injected with a handheld spray can. The differences between reactors was the number and positions of red lasers, ranging from one to three, and with a combined peak light energy of 0.14W.

The purpose of the second campaign was to investigate the performance of the original synthesis reactors using red lasers as in campaign one, but under fully controlled laboratory conditions with exhaust produced by a Pulsonex burner (see figure 1).

The third campaign used a modified synthesis reactor, guided by the theoretical findings, using four led-lights of a total 48W, with exhaust produced by a Pulsonex burner (see figure 1 and 2). This reactor used a common filter housing in which the exhaust gas was led down through a central pipe to the bottom where the exhaust gas turned upwards through a gauze for better distribution of gasses into the chloroplasts above. The led-lights were set around the transparent filter housing to better illuminate the blend of chloroplast and exhaust gasses.

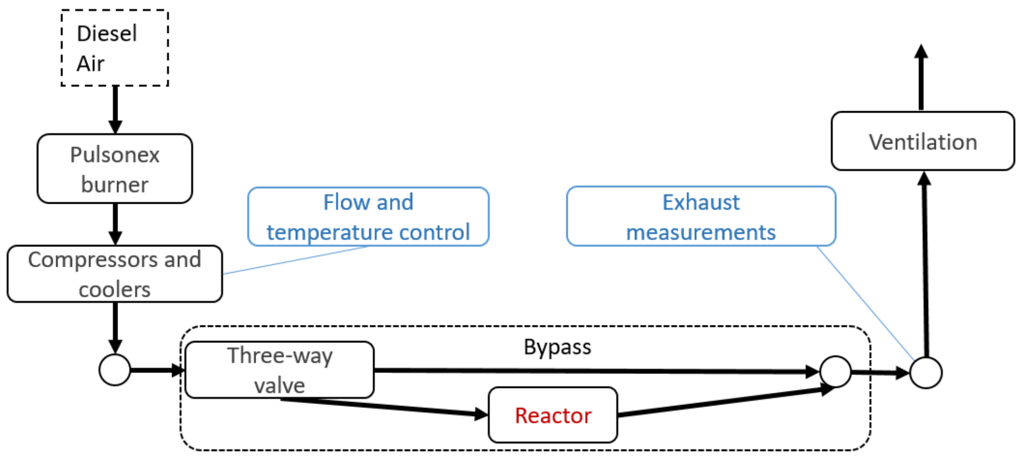


Figure 1. Layout of bench tests for measurement campaigns 2 and 3.

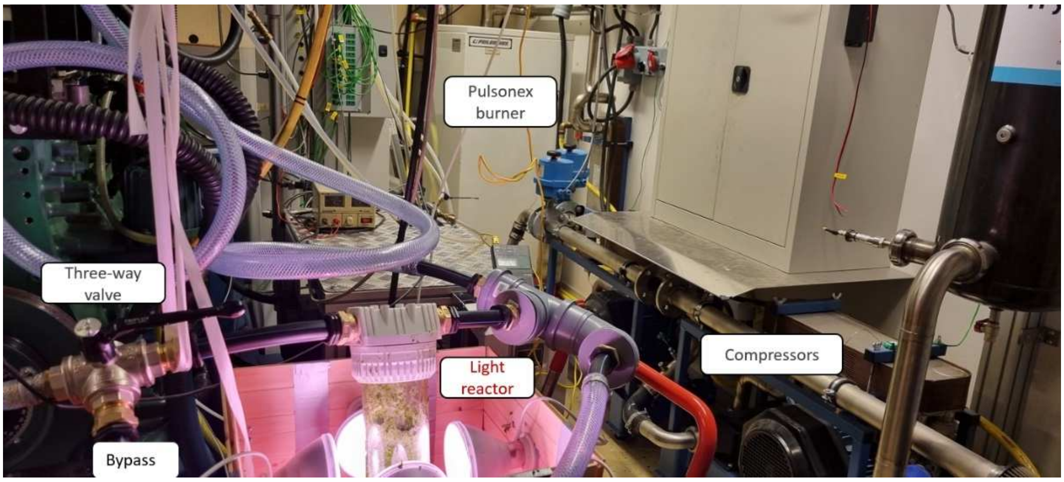


Figure 2. Layout of bench tests for measurement campaigns 2 and 3, but with the led-lights for campaign 3. The led-light provide primarily light in the red band of 660 nm and the blue band of 450 nm.

The two laboratory test campaigns used a Pulsonex burner and a compressor/cooler unit to provide very stable exhaust properties. A three-way valve was used to allow quick shifts between leading exhaust through the reactor or through the bypass, to be able to determine any difference in exhaust gas composition from the burner and from the reactor. While the system worked with slight over-pressure of exhaust gas, efforts were still made to check and avoid potential risks of air entering into the system, that would lead to erroneous results.

For all experiments the emissions were measured using an AVL Ama i60 emissions analyser for CO_2, CO, HC, NOx, O_2. All temperatures were measured with type K thermocouples. The exhaust gas flow for the laboratory tests was measured using a Testo 416 small vane anemometer. For all laboratory tests the exhaust composition from the Pulsonex burner was very stable. The response time from starting the burner to stable conditions took less than a minute, and the measurement response time while shifting the three-way valve was within a few seconds.

The typical sequence for the laboratory tests were

1. Fill reactor with chloroplast (ground plant material)
2. Start burner and bypass exhaust gas until stable exhaust conditions are recorded
3. Start the light sources and turn the three-way valve to lead the exhaust gas through the reactor. At the first time after filling the reactor the reactor is full with air, which needs to be displaced with exhaust gas. The initial measurements thus provide a dip of CO_2 while the air in the reactor is displaced.
4. Repeatedly turn the three-way valve to run the exhaust gas through the bypass or through the reactor to get repetitions of the measurements. For each repetition: 1) measure the bypassed exhaust composition 2) measure the exhaust composition from the reactor 3) and again measure the bypassed exhaust composition. The reactor is not touched in between, so there should not be any air left inside. The measurements while bypassing provides the exhaust composition from the Pulsonex burner while the measurements while flowing the reactor provides the gas composition after the reactor.

By this sequence it is possible to isolate the effect from the reactor on the exhaust gas composition, while the bypass measurements before and after, makes sure to record any drift in the measurements that could lead to errors in analysis.

The sequence was repeated for alternations of reactors or amount of chloroplast.

Resultat

Experimental findings

Measurement campaign 1

The purpose of this campaign was to repeat the experiments that was done prior to this project. The same car and same reactor were used. The conclusion from campaign 1 is that the variation of exhaust CO_2 from the diesel engine car is much greater than the effect of activating the reactor. The conclusion can be explained by that diesel engines at any given engine speed controls load by varying fuel amount, while air amount is more or less constant. This leads to a strong correlation between load, lambda value and amount of CO_2 in the exhaust. The used passenger car continuously adjusted load at constant idle speed to accommodate passenger compartment air conditioning and generator control (battery charging), which could not be turned off, and led to a strong variation of exhaust CO_2. It was thus not possible to confirm the results from the experiments that had been done prior to this project, or confirm any conclusive reduction of CO_2.

Energimyndigheten

Measurement campaign 2

Campaign 2 used the same reactors and light sources as in campaign 1 but in a much better controlled environment (see figure 1). The laboratory setup provided very stable conditions of flow, exhaust gas composition and lambda value, and temperature. The variation of CO_2 during any period of measurement stayed within 0.1%, while a drift over a period of three hours was less than 1%. Mean values were for CO_2 11.3%, O_2 5.3%, CO 15 ppm, NOx 28 ppm and THC 7 ppm. Lambda stayed at 1.3, while the flow was 19 m3/h, and the temperature 23° C. No clear reduction of CO_2 could be observed for any of the combinations of reactors/lasers that were tested. The main reason for the lack of CO_2 reduction was later understood to be insufficient light energy of the lasers.

Measurement campaign 3

After the second campaign the theoretical investigations concluded that there was no evidence suggesting that exhaust enthalpy could support the photosynthesis beneficially. So, this particular hypothesis of the project did not hold. There is nothing wrong with the hypothesis that photosynthesis can be used with artificial lights to reduce CO_2, but the energy needed to do so is unlikely to come from exhaust enthalpy.

The continued theoretical investigations thus revealed that the light energy in the red lasers was much too low to convert any meaningful amounts of CO_2. Further it was also concluded that the useful wavelength spectra coincided with that of led lights (red band of 660 nm and blue band of 450 nm), that indeed are commonly used today for indoor cultivation of plants. In preparation for the third measurement campaign the reactor was modified to carry four led lights of 12W each (total 48W) that also provides a wider exposure to the chloroplast in the transparent reactor, compared to the shallow beams from the lasers previously used.

Campaign 3 used the modified reactor with the led-lights and the main layout as in figures 1 and 2. Once again the setup provided very stable conditions. The variation of CO_2 during any period of measurement stayed within 0.1%, while a drift over a couple of hours mounted to about 1%. Mean values were for CO2 11.3%, O_2 5.3%, CO 18 ppm. NOx and HC were not measured this time, due to temporarily malfunction of those two channels of the analyzer. Considering the same levels of CO_2, O_2 and CO as previous investigations, it is likely that Lambda stayed at 1.3. The flow was 19 m3/h and the temperature 25° C.

The results show a consistent and repeatable 0.9% reduction of CO_2 and an O_2 increase of about 2% (figure 3 and table 1). Different amounts of chloroplast were investigated: in the first test of the campaign, with a high amount of chloroplast, a reduction of 2.4% CO_2 was observed (figure 4 and table 2). Since this measurement was performed at the first exposure of exhaust, after filling the reactor with chloroplast, there is a larger uncertainty for this specific measurement due to need to displace the air inside the reactor with exhaust. That specific result could be correct, but there is a higher risk of remaining air inside the reactor influencing the results, compared to the other experiments.

	Bypass	Active	Bypass	Active	Bypass	Active	Bypass
In temp [°C]	25.4	25.4	25.4	25.4	25.4	25.4	25.4
CO2 [%]	11.25	11.17	11.27	11.17	11.27	11.22	11.29
CO [ppm]	19.6	18.2	18.2	18.2	18.3	18.3	18.1
O2 [%]	5.21	5.37	5.25	5.40	5.24	5.35	5.26

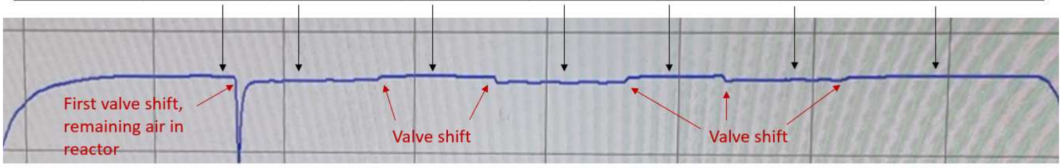
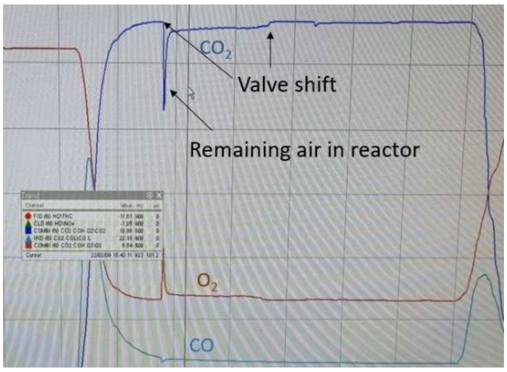


Figure 3 and table 1. Results from test 3 in campaign 3 with a medium amount of chloroplast and with several repetitions



	Bypass	Active reactor	Bypass
In temp [°C]	25.4	25.4	25.4
CO2 [%]	11.24	10.98	11.25
CO [ppm]	25.3	22.1	22.1
O2 [%]	5.21	5.54	5.25

Figure 4 and table 2. Results from test 1 in campaign 3 with the largest amount of chloroplast.

Potential error sources

As already discussed - air trapped within or leaking in to the system would lead to lower values of CO_2 being recorded. To reduce this risk the system was run with slight over-pressure.

We don´t anticipate any relevant errors in the analysers.

Another issue to consider is that CO_2 could have been dissolved in the humid plant slurry for other reasons than photo chemical conversion. This would not be a measurement error, per se, but rather an interpretation error of the results. What could speak against this potential error is that the measurements recorded an increase in O_2 parallel to a reduction of CO_2.

Theoretical findings

The aim of the project is to capture carbon dioxide in exhaust gases with the help of a solution containing plant parts that are activated with light. The goal has been to use low-intensity light and thereby use a low amount of energy. If this is possible, carbon dioxide generated in a combustion process (to create physical work) could be captured using a smaller amount of energy than that extracted.

This can only happen in two ways 1) energy generated in the combustion that is not used for physical work creates a driving force for carbon dioxide uptake 2) the process for carbon dioxide uptake requires significantly less energy than that generated in the combustion.

We have conducted literature studies and minor calculations to investigate these two possibilities. To begin with, we describe the energy needs in photosynthesis. If we disregard losses, photosynthesis requires about 50% of the energy generated by the combustion of completely deoxygenated hydrocarbons. Since an internal combustion engine has an efficiency of less than 50% [Tunér 2016], this could not be used to capture carbon dioxide and at the same time generate net energy. If the remaining energy from the combustion could be used, a certain net surplus could be generated in theory. An example here is CHP plants, where both heat and power are generated with up to 85% efficiency [Breeze 2018]. Given the expected losses in all parts of the process in a practical application, a net energy surplus is still of low likelihood.

Furthermore, the photo systems, where the energy conversion in plants takes place, are very specific for the absorption of light in the visible spectrum. It is very unlikely that heat, which mainly affects the translational, rotational and vibrational movements of the molecules, could be converted into an excitation, the process by which an electron absorbs energy to move to a higher energy level. This process is central to photosynthesis as the movement of an electron generates a positive charge that can be used to oxidize water to oxygen, and a negative charge that can be used to reduce carbon dioxide (via NADP + to NADPH). Thus, it does not seem reasonable either from an energy balance perspective or from a molecular perspective that the first alternative should work.

The second alternative is that with the help of light we can activate processes that require less energy, and which allow carbon dioxide to be taken up from the exhaust gases. Carbon dioxide has relatively low solubility in neutral water. To improve the uptake of carbon dioxide, plants have a process in the chloroplasts where light is used to generate a pH gradient across the cell membranes [Biochimica 1975]. This leads to a pH of about 8 in the stream outside the chloroplast membrane and a pH of about 6 inside the chloroplast. At pH 8, carbon dioxide is easily absorbed in the form of bicarbonate [Front 2021]. Given that this process can be activated without the rest of the photosynthesis working, carbon dioxide uptake should be possible with low-intensity light. The energy required to generate a pH gradient of two pH units (6 and 8) is only 11.4 kJ / mol if we assume $\Delta G = RT\ln(\Delta conc)$. If each hydroxide generated is used to form bicarbonate, the process requires only 1/40 of the energy to take up one equivalent of carbon dioxide through full photosynthesis. It could thus be a possible process to be able to reduce the amount of carbon dioxide in exhaust gases with the help of low-intensity light, since then only about 1% of the energy (50% / 40) in the fuel is needed to absorb all the carbon dioxide.

Diskussion

The presented theory for converting CO_2 into bicarbonates, using chloroplast and light, with very high energy efficiency is a promising one. According to ideal theory only about 1% of the power system fuel energy would be needed to reduce all CO_2. In a practical application one must, however, expect much lower efficiency in the conversion of CO_2 to bicarbonates. For CHP systems where the fuel to power and heat efficiency may approach 85% there is likely still leverage for overall system efficient capture and conversion of CO_2. The use of sustainable electro-fuels or biofuels could lead to heat and power systems with net negative CO_2 emissions.

The experiments demonstrated a consistent and repeatable reduction of CO_2 of on average 1%. This is far from the theoretical potential, and not satisfactory evidence of CO_2 reduction through photosynthesis processes. Still it is a positive indication to explore the idea further.

During the project, lessons were learned about suitable light sources and relevant energy levels to run those. It was also discovered that the current reactor design, although providing some CO_2 reduction, is insufficient in providing conditions where chloroplast, water, exhaust and photons are perfectly exposed to each other everywhere. During the measurements it was observed how exhaust gases created paths through the water/chloroplast mixture and more or less bypassing them without exposure. The led-lights were placed outside the transparent reactor thus also limiting exposure of light to chloroplast at the periphery of the reactor and not to chloroplast further inside.

Considering the mentioned limitations, the recorded 1-2% reduction of CO_2 is not unreasonable, and that new investigations should exploit our findings to design reactors that can provide much improved conditions for better mixing of chloroplast, water, exhaust while fully exposed to photons. It´s a matter of maximizing light surface area versus volume, and inspiration for improved reactor designs can be found from process industry and waste water treatment devices.

Coming back to the great potential with the proposed theory - one of the questions that was raised during the project was whether the process indeed stops at the formation of potassium and sodium bicarbonates, or continues to the much more energy consuming process of full photosynthesis from CO_2 to sugars and starches. While there were preparations to analyze pH to determine the byproducts of the process, the low conversion rate of CO_2 made the analysis of the remains in the reactor inconclusive. Further work is needed to answer the question of the composition of the byproducts and also how those should be removed and used.

Regarding mass flows, each kg of converted CO_2 leads to about two kg of bicarbonates. To remove the bicarbonates a continuous stream of recirculated water leading to a condenser could be one option. In theory there would be no need to replace the chloroplast, but it is uncertain how many hydroxide-equivalents the chloroplast can generate before it loses its function. To be able to determine whether a commercial system could be practical and cost efficient, the handling of bicarbonates and chloroplast needs to be understood.

The current effect of the project is inconclusive. Additional efforts have been made during the project, since one of the original hypothesis had to be rejected, while the new and promising theory is not yet proved experimentally.

Suggestions for further research

Renewed experiments are needed to confirm or reject this project findings. Before performing new experiments, an improved reactor design is needed. To realize a better reactor design, suitable process-industry experts should be consulted and the theoretical basis evaluated together. Some ideas have already been raised above. The goal should be to achieve a much stronger CO_2 reduction consistently, and to be able to analyze the biproducts to determine if bicarbonates are formed, to prove the proposed theory.

With the above achieved successfully, a more solid estimation of the potential process can be done. That would provide more information of the energy efficiency potential, and ultimately ideas of operational costs. The separation of biproducts and their potential use will require specific research.

During the project the members discussed suitable sources of chloroplast. Baby spinach is one such source, and was used in the experiments, but there are eukaryotic algae and cyanobacteria that are better suited [The plant 2015, PNAS 2016]. An assessment of such would also be needed.

Finally, the engineering for practical applications will likely require substantial efforts.

The project group is positive to the concept, and determined to investigate it further to prove or disprove it fully.

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