CO_2 CAPTURE RESEARCH IN THE NETHERLANDS

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CO_2 capture research in the Netherlands

The global climate is changing due to human activities. This human-induced climate change is mainly caused by global emissions of carbon dioxide (CO_2) into the atmosphere. Most scientists agree that in order to mitigate climate change, by 2050, global CO_2 emissions must be reduced by at least 50% compared to their 1990 level. Fossil fuels, however, are expected to continue playing a dominant role in the world energy supply far into this century. As yet, the combined effect of improving energy efficiency and increasing the use of renewable energy (and perhaps nuclear power) cannot achieve the required reductions in CO_2 emissions. Therefore, CO_2 capture and storage (CCS) may become an important (third) option for mitigating climate change. The Dutch government has the ambition to build two large scale demonstration projects by 2015.

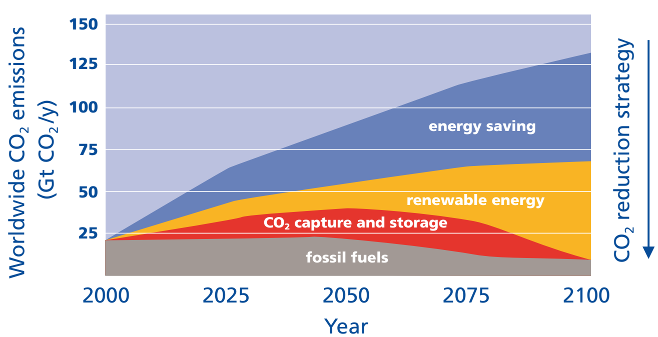


Figure 1 CCS as a third option for reducing CO_2 emissions this century (GESTCO).

The CO_2 capture and storage chain

The first step in the CO_2 capture and storage (CCS) chain is to capture and purify CO_2 generated by the combustion of fossil fuels. The next step is to compress the CO_2 to 100-150 bar. Finally, the CO_2 is transported and stored deep underground; for example, in depleted oil or gas fields.

Capturing CO_2 is not new: for almost a century it has occurred in various industrial processes, including the production of hydrogen and ammonia and the purification of natural gas. The CO_2 is usually vented to the atmosphere, as there is no economic incentive to store it. If CCS technology is to be applied on a grand scale for the new purpose of mitigating climate change, the costs of capturing CO_2 will have to be significantly reduced. The capture costs are found to be lowest at large stationary emission sources such as power plants, oil refineries and other major industrial complexes. Once CO_2 capture has become economically viable, it will be possible to apply the technology in small companies, offices and households.

Focus on CO_2 capture research

Currently, the dominant CO_2 emitters are the power and industrial sectors, which account for approximately 60% of the total global CO_2 emissions. This is why research in the Netherlands focuses on CO_2 capture at power plants. Current state-of-the-art plants with

CO_2 capture require 15-30% additional primary energy to produce the same power output as those without it. This ‘energy penalty’ makes CO_2 capture the most expensive part of the CCS chain: typically, it accounts for up to 80% of the total chain costs. The main research focus, therefore, is on reducing the energy penalty and the total costs of CO_2 capture. It is widely accepted that a 50% cost reduction relative to technologies available in 2005 is necessary and feasible.

This booklet describes the CO_2 capture research that is currently being conducted in the Dutch CATO and CAPTECH programmes (see box). These two programmes are financially supported by the Dutch Ministry of Economic Affairs under the BSIK and EOS programmes, respectively. CATO also covers important research topics that are relevant to the rest of the CCS chain, such as the available storage capacity, monitoring of stored CO_2, and public perception. Information on these topics is published on the CATO website and in booklets.

Dutch CO_2 capture research in an international perspective

The CATO and CAPTECH research portfolio covers almost the entire field of CO_2 capture technologies. Dutch CO_2 capture research is of high quality, as confirmed by an international team of experts during the CATO midterm review. Two of the three new EU projects on CO_2 capture are coordinated by Dutch research institutes, which is another indication that the Netherlands is at the forefront of CO_2 capture research.

The CATO and CAPTECH partners participate in all relevant EU capture projects, such as CASTOR, ENCAP, CACHET, NanoGLOWA, CAESAR and CESAR, as well as in several projects funded by industrial partners (for example, CCP). An overview of the projects is given at the end of this booklet. Knowledge is therefore exchanged between the Netherlands and the international community. These international projects support some of the work described in this booklet.

CATO and CAPTECH

The CATO programme comprises a high-level research and knowledge network in the field of CO_2 capture and storage in the Netherlands. CATO stands for the Dutch equivalent of ‘CO_2 capture, transport and storage’.[1] CATO covers the whole CCS chain: not only CO_2 capture but also storage, monitoring and public perception are being researched. The CATO programme ends in 2008. A follow-up programme (CATO-2) is expected to be initiated in 2009.

In the CAPTECH (CAPture TECHnology) research programme, seven Dutch consortium partners work on CO_2 capture technology. The consortium aims to identify capture technologies that will reduce power plant efficiency by less than 5 percentage points, resulting in a 50% cost reduction compared to the technology available in 2005.

The Utrecht Centre for Energy research (UCE) coordinates CATO and sub-coordinates CAPTECH, ensuring that the two programmes are strongly and directly linked and complementary to each other.

[1] Dutch: ‘CO_2 Afvang, Transport en Opslag’.

Table 1 Features of the CATO and CAPTECH programmes.

	CATO	CAPTECH
Aim and scope	Network and knowledge building for (almost) all CO_2 capture, transport and storage aspects	Capture technology development from a fundamental perspective
Size	25 M€	10 M€
Sponsor	Dutch Ministry of Economic Affairs (Bsik programme)	Dutch Ministry of Economic Affairs (EOS LT programme)
Participants	19	7
Period	2004-2008	2006-2010
Coordinated by	UCE	ECN & UCE
Post-combustion	• Coal and gas • Solvents • Membrane contactors	• Coal and gas • Advanced chemical solvents • Process development and integration • CO_2 selective membranes
Pre-combustion	• Gas • Sorbents (SERP and SEWGS) • Pd/alloy membranes	• Coal gasification • Robust sorbents and catalysts (SEWGS) • Membranes • Physical solvents
Oxyfuel	• Gas • Chemical looping (CLC) • High-temperature oxygen adsorbent (CAR)	• Gas and coal • Mixed ionic electronic conducting membrane
System integration	Economic and technical comparison of capture technologies	Multi-input-output systems and small CCS systems

Main capture processes

The various processes for capturing and purifying CO_2 (Figure 2-4) fall into three main categories: post-combustion, pre-combustion and oxyfuel combustion (which is also referred to as denitrogenated combustion).

The optimal CO_2 capture technique for a particular power plant depends on its specific characteristics; for example, the type of fuel used, the concentration of CO_2 in the flue gas, the possibility of integrating the capture processes, the space available on the plant site, the pipeline infrastructure that is in place, and the availability of adjacent sources of heat, cold and gases (for example, pure O_2). As no single technology has yet emerged as a clear winner, the Dutch CCS programmes are investigating a variety of promising capture processes.

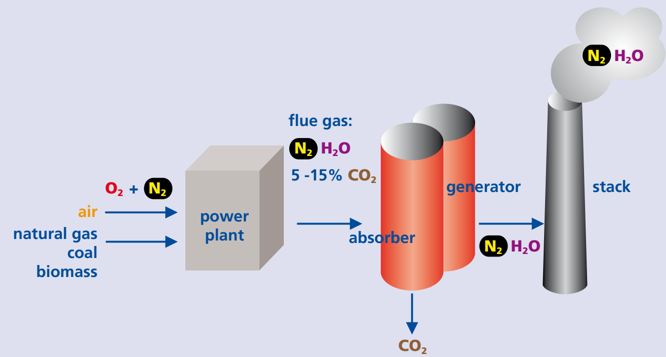


Figure 2 Schematic diagram of post-combustion capture.

Post-combustion capture

In conventional power plants the fuel is combusted with air, which results in a flue gas with a CO_2 concentration of 5-15 volume percent. Separation of the N_2-diluted CO_2 from the flue gas is referred to as post-combustion capture.

For post-combustion capture, chemical or physical solvents, sorbents or membranes can be used. State-of-the-art supercritical pulverised coal-fired power plants typically have an efficiency of 45%. Implementation of current post-combustion CO_2 capture technology with a 10 percentage point energy penalty will lower this to 35%, resulting in a 25% increase in energy input. For natural gas combined-cycle power plants, efficiencies are approx. 58% without, and approx. 50% with, CO_2 capture. The main advantages of post-combustion capture are the relatively low costs of retrofitting existing power plants for CO_2 capture, and the fact that the CO_2 capture does not adversely affect power plant reliability. The main disadvantage is the high energy consumption of CO_2 capture.

Pre-combustion capture

Combustion of fossil fuel in air results in a low CO_2 concentration in the flue gas because of the high N_2 concentration in the air. One way to prevent this N_2 dilution is to remove the carbon from the fuel before it is combusted. For this purpose, the fuel is transformed into syngas: a high-temperature mixture of H_2 and CO. After cooling, the CO reacts with H_2O to form H_2 and CO_2 (water-gas shift reaction). The result is a gas stream mainly consisting of H_2 and CO_2, with some contaminants.

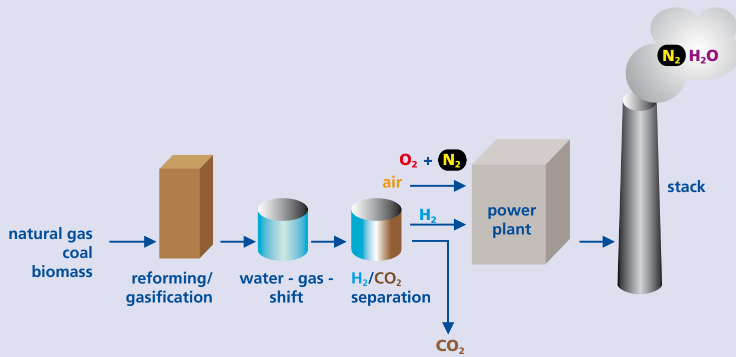


Figure 3 Schematic diagram of pre-combustion capture.

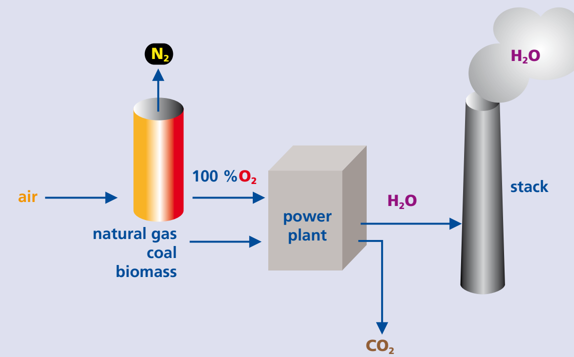


Figure 4 Schematic diagram of oxyfuel combustion capture.

Membranes, solid sorbents and solvents are used to remove the CO_2. After its removal and purification, nearly pure H_2 is combusted. The high pressure and concentration of the CO_2 makes pre-combustion capture more efficient than post-combustion capture; the energy penalty is lower. A state-of-the-art coal gasifier (IGCC) has an efficiency of approx. 49%. With CO_2 capture, this is reduced to approx. 43%. The higher efficiency of pre-combustion capture is its main advantage. The disadvantages are the high investment costs for IGCC installations and the need for expensive pure O_2.

Oxyfuel combustion capture

Another way to prevent N_2 dilution and directly produce a CO_2rich flue gas is to combust the fuel in pure oxygen. This is the idea behind oxyfuel , a contraction of 'oxygen' and 'fuel', combustion. O_2 is extracted from the air and the pure O_2 is used to combust the fuel, producing mainly CO_2 and H_2O. After condensation of the steam, a highly concentrated CO_2 stream is obtained. The efficiencies of oxyfuel combustion are 36% for coal-fired power plants and 48% for natural gas-fired power plants — figures which are comparable to those for post-combustion capture. The main advantages are the relatively low costs of retrofitting existing power plants for oxyfuel combustion and the absence of CO_2 capture materials (e.g. solvents, sorbents and membranes). The main disadvantage is the need for expensive pure O_2.

Gas separation methods

1. Membranes

Membranes are materials that selectively allow molecules to pass through. A major challenge in designing membranes is to make them highly selective while maintaining a high mass transfer rate. Membranes are made of polymers, ceramics or metals; the choice of material depends on process conditions including the working pressure, the temperature, and the presence of contaminants. The membranes are in the form of flat sheets, tubes, capillaries or hollow fibres.

Phase contactors are membranes that can separate a gas from a liquid and allow molecules to move from the gas to the liquid and vice versa. Phase contactors are not selective to the type of molecule, only on the phase in which it occurs. An example is the membrane that lines human lungs, where the air can contact the blood to exchange CO_2 and oxygen.

2. Sorbents

Sorbents (known as solvents when in the liquid phase) are materials that easily bind CO_2. Changing the pressure or temperature releases the initially captured CO_2 in a high concentration. The sorbent can then be re-used. This regeneration of the sorbent costs energy and is the main cause of the energy penalty in capturing CO_2. The challenge is to create sorbents that can be regenerated with little energy input, yet bind CO_2 effectively. Another topic of interest is the degradation and production costs of sorbents. The amount of CO_2 per unit volume of sorbent is also an important research topic, as this determines the size of the installation and thus the overall investment costs.

3. Cryogenic distillation

By cooling a gas stream to sufficiently low temperatures, one of the gaseous compounds, for example CO_2 or O_2, will liquefy. This liquid can then be easily separated from the remaining gases. Although no chemicals are needed, the cooling requires large amounts of energy or a nearby cold source.

When the various processes and technologies are combined, a matrix of possible CO_2 capture routes can be determined (see Table 2 below). The routes currently being researched in the Netherlands are highlighted in orange. This booklet describes the activities on CO_2 capture carried out by the partners in the CATO and CAPTECH programmes. When CATO and CAPTECH started (in 2004 and 2006, respectively), these programmes combined almost all research on CO_2 capture in the Netherlands. Recently, activities have started at other research centres including the NUON energy company, Delft University of Technology and Groningen University. These activities are expected to become part of the follow-up to the CATO programme. Recently the Dutch Ministry of Economic Affairs has also provided 10 million euros for each of three pilot projects. These are described at the end of the booklet.

Table 2 The broad portfolio of Dutch research on CO_2 capture, arranged according to process and technology.

Capture method	Post-combustion processes	Pre-combustion processes	Denitrogenation
Membranes	Phase contactors. Polymeric, ceramic, metal or carbon membranes	Phase contactors. CO_2/H_2 separation: ceramic, polymeric or palladium membranes	O_2-conducting membranes
Solid sorbents	Hydrotalcites, lime carbonation	Hydrotalcites, dolomite, zirconates	O_2 adsorbents
Solvents	New solvents, process design	New solvents, process design	O_2 absorbents
Cryogenic distillation	CO_2 liquefaction	CO_2 liquefaction, O_2 liquefaction	O_2 liquefaction

Progress in post-combustion capture

Solvents

The classical method of capturing CO_2 at relatively low concentrations is by chemical absorption and desorption, whereby flue gas flows through the chemical solvent (often amines), which absorbs the CO_2. The solvent, loaded with CO_2, is then heated or depressurised in order to remove the CO_2, after which it can be re-used for the same purpose. In the Netherlands, research on amine solvents for chemical absorption is currently being conducted by Shell, Procede, TNO and the University of Twente.

Fundamental understanding

One of the main objectives of the research is to understand better how the solvents interact with CO_2, so that more efficient solvents can be developed for CO_2 absorption processes. At the University of Twente, the effects of functional groups (such as amine, acid and alcohol groups) and chain-branching within the solvent molecular structure are being studied, with particular focus on CO_2 capture properties such as absorption capacity, regeneration energy and reaction kinetics. Results so far indicate that some functional groups, for example CH_3 and NH_2, increase the CO_2 absorption capacity, whereas other functional groups, for example ketones and esters, decrease it. A second area of study is fundamental research on precipitating CO_2 absorption liquids.
Procede is developing an integrated computer model that relates the molecular structure of solvents to the efficiency and economics of CO_2 capture plants. The computer model simulates the behaviour of mixtures of chemical solvents (for example, amines), physical solvents, and mixtures of physical and/or chemical solvents with the flue gas. It uses easily measurable parameters – such as acidity, molecule size and vapour-liquid-equilibrium (VLE) – to estimate the optimal solvent mixture for specific CO_2 capture plant designs. This computer model represents a breakthrough in solvent development, as the optimal solvent can be estimated, reducing the amount of experimental testing.

One interesting result is that adding small amounts of accelerator can reduce the column heights of both the absorber and the regenerator – and thereby the investment cost of the gas treatment plant – by as much as 30%. This potential improvement is significant because improvements to absorbers usually have negative impacts on the regenerator. In addition to providing a greater understanding of the principles that underlie the absorption process, the software integrates reactor configurations and other unit operations as required for

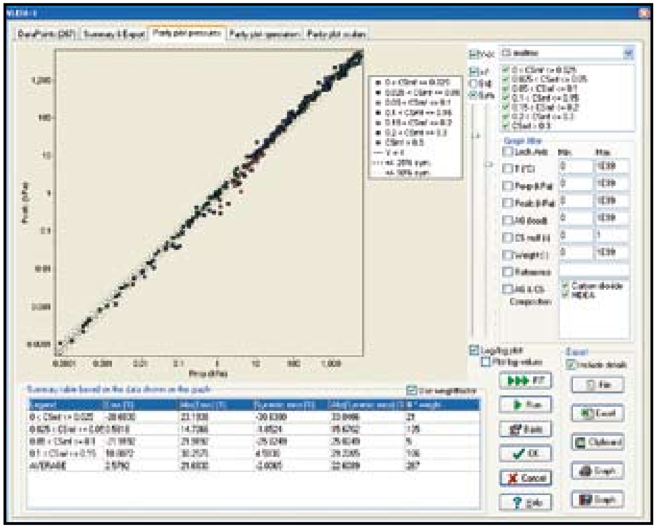


Figure 5 Screen dump of computer model Pro2Sim (Procede).

Figure 6 Amine Screening Apparatus (Shell).

the design of gas treatment plants. Alternatively, the software can be used to evaluate the data produced in pilot plant testing. This software tool can be further developed by integrating a costing tool.

Solvent testing

In addition to developing new solvents from a fundamental perspective, Procede, Shell, TNO and the University of Twente have developed test methods and facilities to benchmark solvents.

Procede performs standardised measurements of vapour-liquid-equilibrium, reaction kinetics, heat of reactions, and gas-liquid contactor solvent matching. Their facilities allow measurements of all kinds of gas-liquid combinations, including flue gas, syngas and natural gas, at atmospheric pressure, 35 bar and 70 bar. In addition to CO_2, virtually all kinds of gas components that commonly occur in flue gas can be measured; for example, COS, H_2S, NH_3, mercaptans, SO_x, NO_x, H_2 and CO.

Shell measures various characteristics; for example, oxidative stability, corrosion, heat of reaction, aging, and energy consumption for ab-/desorption. Shell has also built a bench-scale unit that can be operated continuously with well-integrated absorber and regenerator columns. With this unit, the energy efficiency of various solvents can be measured to a high degree of accuracy. The measured values,

after a correction for the energy loss, approximate closely to the reported values in existing CO_2 capture units. In addition, potential technical problems with newly developed solvents can be discovered and solved by running them in the unit, thus avoiding unnecessary mistakes in a pilot or demonstration plant, and saving time and money in the development of new solvents.

TNO provides testing methods for measuring oxidation, corrosion, eco-toxicity, aging, and energy consumption for desorption. Promising solvents are tested in large facilities under realistic conditions for prolonged periods of time. The largest installation is the pilot plant on the Maasvlakte (see box CATO CO_2 Catcher). With these test facilities, both quick scanning and detailed testing of solvents can be performed in the Netherlands.

Phase contactor reactors

Another method of reducing the size of the absorber reactors, and thus potentially the costs, is to use phase contactors. Phase contactors hold the liquids in place, while allowing the gases to pass through. They can be used for both absorption and regeneration. During absorption, the flue gas flows along the contactor. The CO_2 passes through the contactor into the absorption liquid, where it is absorbed. Although the contactor is not selective to the other gases, only minimal quantities of them pass through it, because the liquid is saturated with the non-CO_2 gases from the flue gas (Figure 7). During regeneration, the loaded liquid solvent is on one side of the membrane, with a partial vacuum on the other side. The absorbed

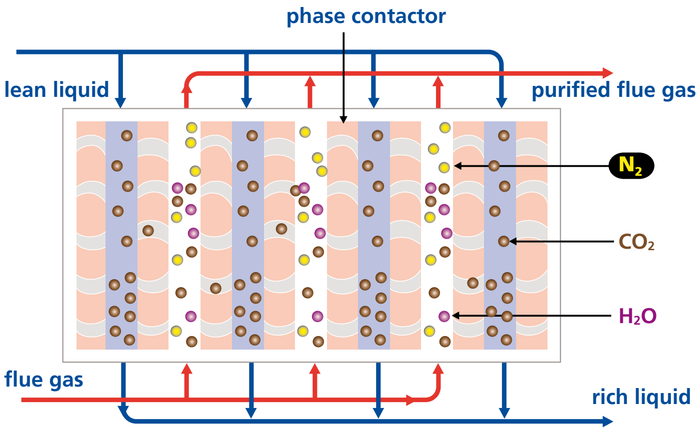


Figure 7 The working principle of a phase contactor (TNO).

CO_2 diffuses from the solvent, through the membrane and into the vacuum. The benefit of this method is that the solvent can remain under high pressure, avoiding the need for re-pressurisation. This results in a significant reduction of the energy requirements of the CO_2 capture unit.

TNO has a long tradition of research on phase contactor capturing (or membrane-gas absorption) processes, and has been developing a CO_2-absorbing liquid suitable for such processes. This highly stable solvent, CORAL, a mixture of amino acids, alkali salt and amines, has been under development since the 1990s. Currently, TNO aims to deliver a proven CO_2 capture process concept and to improve and develop CO_2 capture solvents suitable for phase contactor reactors. TNO's membrane module design is based on its in-house know-how

CATO CO_2 Catcher

A major achievement in post-combustion capture R&D is the CATO CO_2 Catcher pilot plant at the E.ON coal-fired power plant on the Maasvlakte (Rotterdam harbour area). This pilot plant is used to test solvents and phase contactors under real industrial conditions. The Membrane-Gas Absorption unit captures CO_2 from a side stream of the flue gas from one of the existing coal-fired power plants on the Maasvlakte (EFM2). The pilot plant captures about 250 kg of CO_2 per hour, comparable to 0.4 MWe from a full-scale coal-fired power plant. This size is considered to be an optimal balance between flexibility and learning from scaling factors. The pilot plant can test conventional amine solvents, as well as the new concept of phase contactors.

Figure 8 Minister Cramer opening the CATO CO_2 Catcher.

on desalination membranes. The main issue here is to design phase contactors that can be produced on a large scale at low costs. Flat sheets seem most promising for this purpose. Models have been developed to optimise the configuration based on mass transfer. Fundamental research is being conducted in cooperation with the Russian Academy of Sciences and Dutch universities. By using these phase contactors, the column size of the absorber can be reduced by more than 50%. The research aims to improve manufacturing techniques and the connections between the membranes and the reactors.

Figure 9 Selective membrane module: new, after 10 months, after cleaning (KEMA).

Membrane separation

The second method of capturing CO_2 from flue gases is membrane separation of CO_2 from the other gases. In this process, the membrane allows only CO_2 to permeate, resulting in a pure CO_2 stream. KEMA, the University of Twente and several other international partners are collaborating in the EU project NanoGLOWA (coordinated by KEMA), which aims to remove CO_2 using various nano-structured membranes. The research ranges from membrane development, through module and process design, to analysis of CO_2 capture power plants using these membranes. The project is a continuation of a Dutch EET project (SenterNovem), in which KEMA and the University of Twente successfully developed hollow-fibre membranes and modules for the removal of water vapour from flue gases. The developed membranes underwent long-term field tests (>5000 hours) under real flue-gas conditions at a power plant at Borsele (in the Netherlands). The results demonstrated the long-term stability and durability of this membrane process, thereby confirming that CO_2 capture using membranes has great potential.

KEMA is now transferring that knowledge to the Dutch energy sector. The focus is on developing membrane performance diagnostics, as well as development of a reliable membrane module for application in existing and new plants. Fouling experiments in the power plant showed serious fouling, but also the possibility of in-situ cleaning with water. The experiments were repeated at KEMA under simulated flue gas conditions in order to assess in detail the effect of the fouling on the membranes. In the past two years, five different membranes – three organic polymer membranes, a ceramic membrane, and a carbon-based membrane – have been developed. Their potential for CO_2 removal is currently being evaluated.

Progress in pre-combustion capture

Most of the research on pre-combustion capture in the Netherlands is conducted by ECN. The research focuses on efficiently converting all the fuel to H_2 and CO_2, and then separating these two gases. A hydrogen membrane reactor removes the H_2, while a sorption-enhanced reactor (SER) removes the CO_2, resulting in highly efficient conversion of fuel to hydrogen.

Hydrogen membrane reformer

The H_2 membrane reformer is basically three reactors in one: it combines the steam-reforming reaction ($CH_4+H_2O \rightleftharpoons CO+3H_2$), the water-gas shift (WGS) reaction ($CO+H_2O \rightleftharpoons H_2+CO_2$) and H_2 separation by simultaneously using different catalysts and an H_2-selective membrane (Figure 10). The catalysts enhance the reforming and WGS reactions. As the H_2 is removed from the

Chemistry of pre-combustion capture

Reforming/gasification reaction: fuel(C)+H_2O+$O_2 \rightleftharpoons CO+H_2+CO_2$
Water-gas shift reaction: $CO+H_2O \rightleftharpoons H_2+CO_2$
(low conversion at high temperatures)

The water-gas shift reaction is an equilibrium reaction. By removing one of the products on the right side of the equation, the conversion factor increases. Note that there is a temperature conflict in achieving a high conversion rate for the reaction.

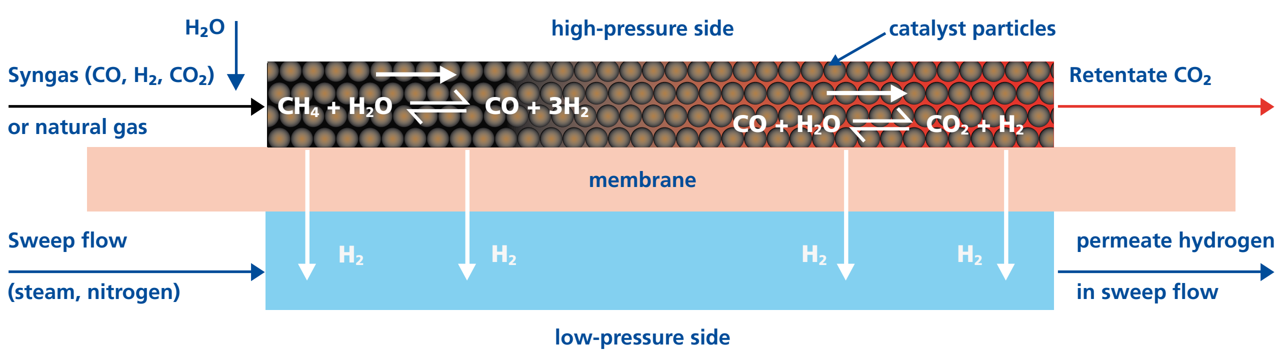
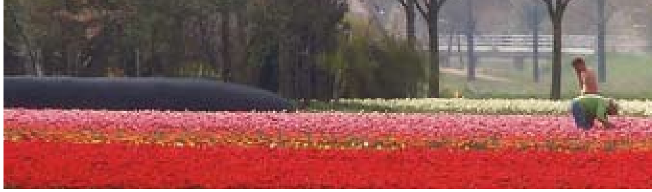


Figure 10 Working principle of a H_2 membrane reactor (reformer and water-gas shift (ECN)).



reactor, more of the fuel is converted, and thus more H_2 and CO_2 is produced, than in normal power plants. The reactor consists of tubular palladium-silver membranes (Pd/Ag) filled with the catalysts. At ECN, Pd/Ag membrane development focuses on improving the fabrication procedures (including the manufacturing of membrane supports), increasing the reproducibility of membrane manufacturing, and upscaling. This has resulted in the commercial production of membranes of up to 60 cm in length. Reformer experiments with a single membrane tube under realistic conditions have shown that Pd/Ag membranes enhance the reforming reaction at temperature of 600°C and elevated pressures. Under these conditions, the conversion rate of natural gas is increased to 80-85%. Even higher temperatures (600-650°C) would further increase the conversion rate, but the Pd/Ag membranes are not (yet) suitable for such temperatures. In addition to the membrane tubes that have so far been developed, several membrane reactor concepts have been evaluated for the membrane reformer. Special attention has been given to various heat input methods.

The main advantage of this technology is that it is a continuous process and does not require sorbent regeneration. Membranes for water-gas shift and reformer reactors have been extensively tested with H_2/N_2 gas mixtures and in simulated feed gases. Under relevant process conditions, the membranes performed satisfactorily in term of flux, stability and separation factors. They will soon undergo further testing under relevant process conditions at ECN's Process Development Unit (PDU) for membrane reactor testing.
Ongoing testing of single membrane-tube reactors for both reforming and water-gas shift reactions is affirming the following working principles of hydrogen membrane reactors:

- Parallel reaction and H_2 separation;
- Equilibrium shift towards high conversions according to Le Chatelier's principle;
- WGS reaction at increased temperatures;
- Reforming at decreased temperatures.

Sorption-enhanced reformer

Like the H_2 membrane reformer, the sorption-enhanced reformer (SER) is a three-in-one reactor: it combines the reforming and WGS reactions and CO_2 absorption by simultaneously using different catalysts and CO_2 sorbents. In a SER, absorbers remove the CO_2 from the reaction zone. Since hydrotalcites (see box Hydrotalcites)

Figure 11 Palladium-silver membranes (Pd/Ag) filled with catalysts (ECN).

have emerged as the most promising absorbers, ECN and Utrecht University has conducted extensive research on them.
However, in-depth experiments and reactor modelling have shown that at elevated pressure, temperatures of 600-700°C are needed to achieve methane conversion greater than 85%. These temperatures are well above the maximum operating temperature of hydrotalcites, which lose their CO_2 capture capacity at temperatures above 500°C. Therefore, experimental and modelling work is continuing, with the aim of finding other CO_2-sorbent materials that work in a SER at the given temperatures and pressures. Currently, calcium oxide is the most likely candidate, although there is some concern about its stability. Initial durability tests at atmospheric pressure show encouraging results, though further durability tests at elevated pressures are needed to confirm them.

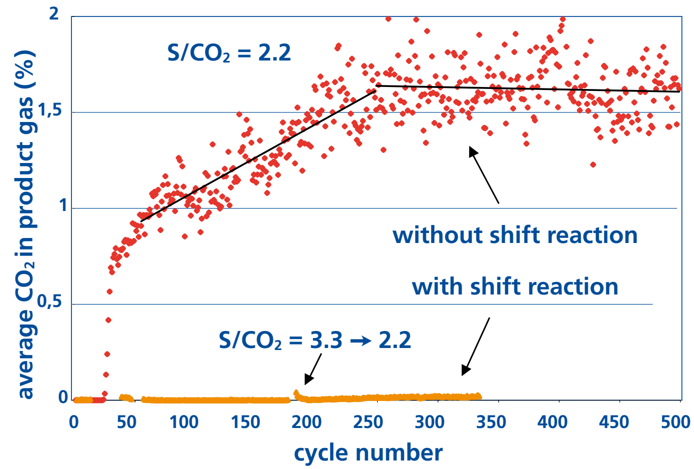


Figure 12 CO_2 slip during SEWGS experiments (ECN).

Sorption-enhanced water-gas shift

Testing of the sorption-enhanced reformer revealed numerous problems when the three different reactions were combined. Therefore, the sorption-enhanced water-gas shift (SEWGS) combines only the WGS reaction and CO_2 absorption. In a separate reactor, natural gas or coal is converted to syngas at high temperatures. In the SEWGS, H_2 is formed and CO_2 is simultaneously captured. The SEWGS operates at much lower temperatures than the 3-in-1 SER process, significantly extending the lifetime of the sorbents.

ECN's results with mixtures of catalysts and hydrotalcites in a single reactor seem promising. The CO in the syngas is converted to CO_2, which is almost immediately absorbed by the hydrotalcites in the column. Once the sorbents are saturated with CO_2, the reactor is regenerated.

The regeneration is achieved by stopping the syngas flow and reducing the pressure in the reactor. The CO_2 desorbs from the absorbents and a pure CO_2 stream is obtained. The problem with this method is that the syngas flow has to be repeatedly interrupted (batch processing). Under the EU-CACHET programme, ECN has recently built an array of six identical reactors, each in a different stage of the absorption-regeneration cycle. By accurately controlling the flows of these six reactors, a continuous process can be achieved. Tests are now being done to validate laboratory-scale experiments and to optimise the absorption-regeneration cycle. Although the

principle of using multiple reactors in different stages is widely used in industry, experimental work is needed to verify whether the SEWGS can be operated in such a continuous process.

Figure 13 Test unit of multi SEWGS reactor (ECN).

Hydrotalcites: size does matter

In Utrecht University's Inorganic Chemistry and Catalysis group, extensive research is being conducted to gain a fundamental understanding of hydrotalcites (HTs); in particular, the relationship between CO_2 absorption and the size of the HTs. HTs are clay minerals consisting of magnesium-aluminium oxide. HTs are promising CO_2 absorbents, as they are cheap to manufacture and have a low regeneration energy penalty. However, their CO_2 uptake is only moderate and they have poor mechanical strength. Use of the currently available HTs in a CO_2 capture plant would therefore require large reactors and special treatment of the HTs because of their low mechanical strength. A promising approach is to support the HTs on carbon nanofibres (CNF). This may improve the CO_2 absorption capacity per unit mass of HTs by at least a factor of 10. The current hypothesis is that this factor is related to a lattice disorder in the HTs that is higher for the supported HTs. The average size of HTs on CNF is 20 nm, compared to 200 nm (typically) for normal HTs. Another benefit of using CNF support is the increased mechanical strength due to the carbon nanofibres. The Utrecht University group aims to understand the fundamentals (for example, the kinetics of the oxides' CO_2 absorption capacity), thereby enabling more accurate prediction of the behaviour and CO_2 sorption properties of HTs.

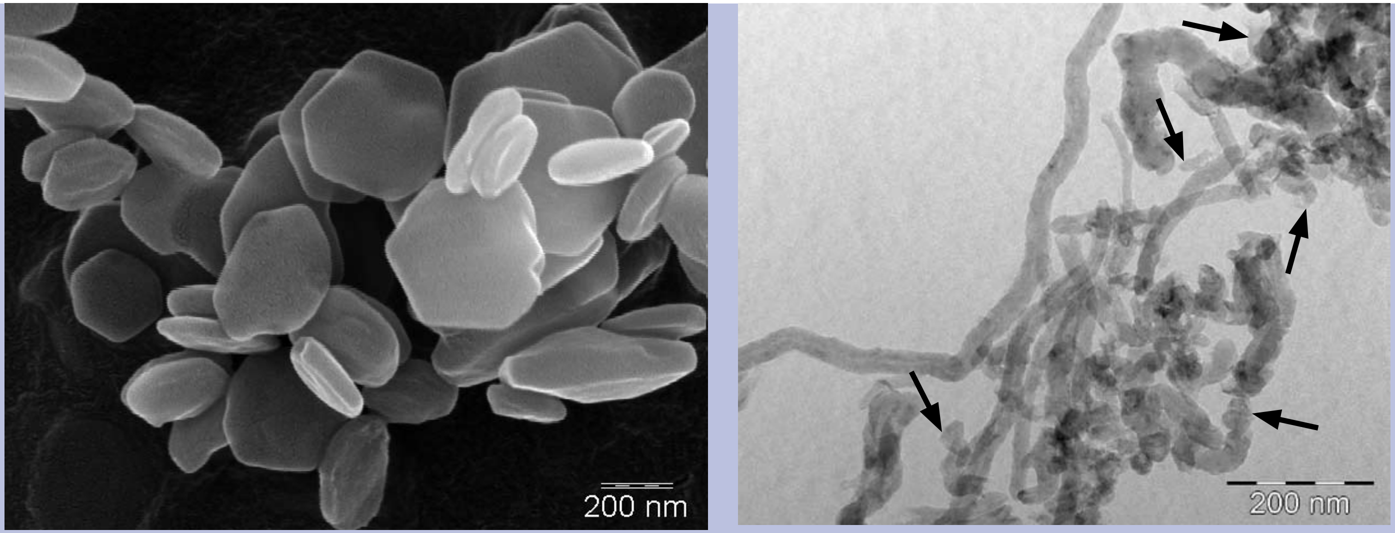


Figure 14 Electron micrographs of conventional hydrotalcites (left) and small hydrotalcites supported on carbon nanofibres (right). Arrows indicate HT platelets (Utrecht University).

Progress in oxyfuel combustion

Conventionally, fuel is combusted in air, which contains 80% N_2. The CO_2 concentration in the flue gas is therefore only 5-15 volume percent. Such low CO_2 concentrations make it difficult to remove CO_2 (post-combustion capture). Oxyfuel uses pure O_2, thereby avoiding N_2 dilution. This can be accomplished either by removing the N_2 from the air prior to combustion or by feeding the oxygen to the fuel indirectly. Both options are currently being investigated in the Netherlands.

Removing the N_2 from the air is commonly achieved by cryogenic cooling (air separation). At very low temperature (-196°C), N_2 liquefies and can be separated from the oxygen (O_2). This process is very energy-intensive (0.25-0.30 kWh/kg O_2). In order to reduce the energy requirement, ECN is developing ceramic membranes that selectively allow the O_2 to pass but not the N_2, eliminating the need for cryogenic cooling. The problem with current membranes is their low mass-transfer rate and their unsatisfactory long-term stability. ECN and KEMA are jointly analysing which system configurations are most promising for incorporation of this technology.

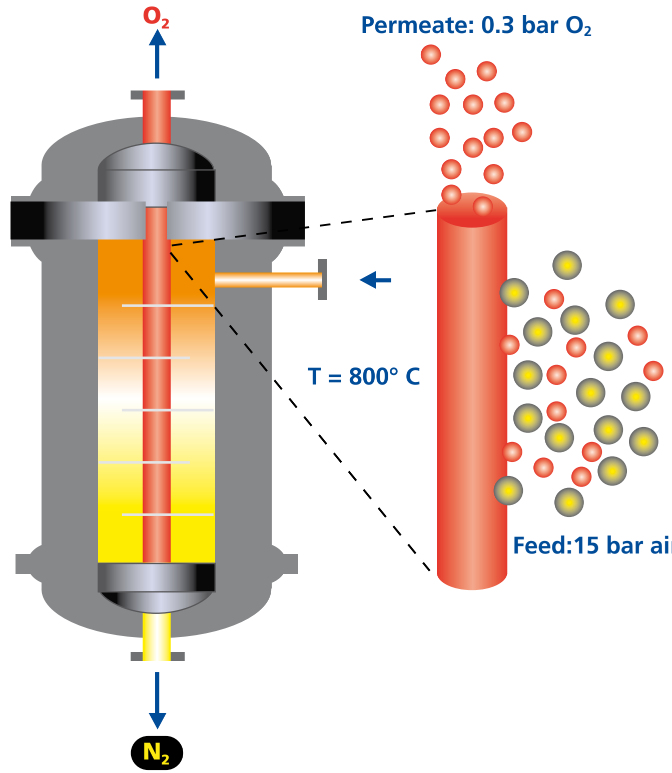


Figure 15 Working principle air separation with a perovskite membrane (ECN).

Chemical looping

TNO and the University of Twente are investigating chemical looping, an advanced oxyfuel combustion process. Chemical looping consists of two steps. In the first step, pressurised air (at 20 bar) is pumped into a reactor containing metal particles. The oxygen in the air oxidises the metal particles, generating heat. The heated air is expanded in a turbine and generates electricity. In the second step, fuel passes through the reactor, where it reacts with the oxidised metals,

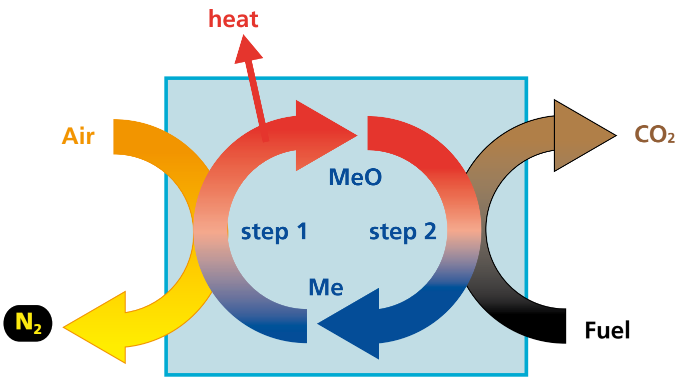


Figure 16 Working principle chemical looping reactor (TNO).

Figure 17 The chemical looping reactor (TNO).

resulting in reduced metal particles and a flue gas mainly containing H_2O and CO_2. The reduction of the metals requires energy, which is supplied by oxidising the fuel. The cycle is then repeated. The flue gas is condensed, resulting in a pure CO_2 stream. A major drawback of chemical looping is that the reactor temperature must be kept much lower than in a conventional gas turbine (800-1200°C rather than 1350°C) because, otherwise, the metal particles would melt together (sinter). Unfortunately, running at this lower temperature significantly degrades the turbine efficiency. By burning a small amount of natural gas downstream from the chemical looping reactor, the temperature of the heated air can be raised to levels comparable with those in conventional gas turbines. Although this increases the efficiency, it lowers the CO_2 capture fraction. The net result is that chemical looping can achieve an efficiency of 50-55%. The obvious advantage is the high efficiency when CO_2 capture is included. The main disadvantages are the need for a second reactor and the fact that this technology is still in an experimental stage. Thus, chemical looping can be regarded as the next generation of capture technology.

TNO is studying active metals trapped in a membrane at 1100°C and up to 30-35 bar. The University of Twente is studying fixated metals in a particle bed. Both institutes have constructed small-scale reactors to demonstrate the principles. These reactors will provide experimental data to validate computer models and enable the development of process controls to regulate the temperature and pressure, making the process suitable for power-generation applications.

Progress in system analysis and implementation of CO_2 capture

System integration analysis brings together all the information provided by the CATO and CAPTECH programmes in order to analyse, compare and evaluate potential energy conversion processes with CO_2 capture from the broad perspective of sustainability.

KEMA has been analysing the feasibility of retrofitting CO_2 capture units into existing coal-fired power plants in the Netherlands by 2020. This company is also designing new coal-fired power plants to make them 'capture ready', allowing implementation of CO_2 capture with fewer changes. This is achieved by modifying the layout of the steam turbine and making necessary improvements to the flue gas cleaning technology. KEMA has also been looking into non-technical issues concerning CCS in the power sector; for example, regulations, public acceptance, and transport of CO_2. Procede, in cooperation with Shell and KEMA, has analysed potential waste-heat utilisation for amine-based post-combustion capture.

The Utrecht University's Copernicus Institute extensively analyses energy systems with CO_2 capture. A recent dissertation includes an extensive review and comparison of a variety of CO_2 capture technologies from technical and economic viewpoints and for various timeframes in the future. It compares the cost of electricity (COE) for a number of state-of-the-art and advanced CO_2 capture technologies

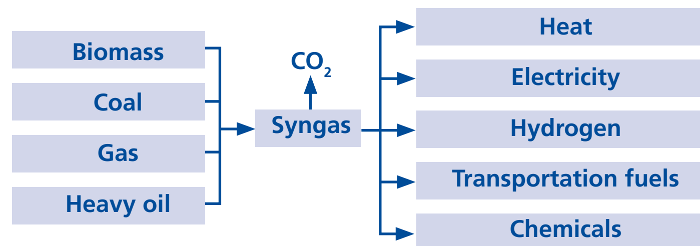


Figure 18 Multi-input, multi-output concept (Utrecht University).

and finds that COEs are increased by 25-50% for state-of-the-art technologies and 15-35% for advanced technologies. Another important finding is that small-scale CCS may become economically competitive in the future. Membrane reactors for hydrogen fuel production may enable cost-effective CCS at a scale smaller than 10 MW H_2 output, if thin and highly stable membranes can be cheaply manufactured. Solid oxide fuel-cell (SOFC) technology may also enable low-cost CCS at scales of 20 MWe. This is of particular interest to the Netherlands, as the Dutch energy system is characterized by a relatively high share of decentralized cogeneration of heat and power (CHP) in industry (40%).

Several research projects are underway at the Copernicus Institute. The first project is investigating the techno-economic performance of multi-feedstock (e.g. natural gas, coal and biomass), multi-product (e.g. electricity, H_2 fuel and chemicals) chemical plants with CO_2 capture. The high feedstock flexibility and the diversity of the products enables the chemical plant to adjust rapidly to market fluctuations, maximising its profitability.

The second project is to determine the future prospects of capturing CO_2 from smaller emission sources in the period up to 2030. The aim is to find cost-effective CO_2 capture options by studying advanced small-scale CO_2 capture technologies (e.g. solid oxide fuel cells and membrane reactors) and small-scale emission sources with conditions suitable for CO_2 capture. This project is also investigating cost-effective CO_2 transport for small-to-medium emission sources, which is considered one of the bottlenecks for small-scale CCS. Preliminary results indicate that CO_2 can be captured economically from industrial combined heat and power plants as small as 100 MWe that are operated under part-load conditions. These costs are comparable to CO_2 capture costs for 400 MWe natural gas-fired power plants.

The third project is investigating how deploying CCS can contribute effectively to a Dutch strategy for mitigating climate change. The approach is to analyse the Dutch energy system with CCS over time. This project is examining various aspects, including the effect of future H_2 fuel demand on CO_2 capture potential, and the spatial and temporal implications of a CO_2 transport infrastructure that may limit capturable CO_2 emission sources. The first article published by the project team indicates how important the timing of CCS deployment is to the future course of CO_2 emission mitigation in the Netherlands. One interesting conclusion is that in order to achieve a 20% and a 50% reduction of CO_2 emissions in 2020 and 2050 respectively (compared to the 1990 level), new coal-fired power plants without CCS should not be built at all, or only in a limited number.

The fourth research project focuses on the environmental impacts of CCS. A life-cycle assessment of a coal-fired power plant with post-combustion CO_2 capture shows that CCS substantially reduces the greenhouse gas emissions per kWh. However, some important environmental trade-offs were also found which may partially offset the environmental benefit of CCS. The aim of another study was to inventorise and assess the impact that implementing CO_2 capture technologies (including pre- post- and oxyfuel combustion capture) in the power sector would have on transboundary air pollution levels in 2020. The inventory presents ranges for emission factors of SO_2, NO_x, particulate matter, volatile organic compounds and ammonia for various energy conversion technologies with and without CO_2 capture.

Table 3 Dutch involvement in CO_2 capture projects.

	Consortium partner	Programme/ sponsors	Research topics(CO2 capture part only)
		Dutch projects	
CATO	ECN, KEMA, Shell,TNO, UTwente, UU, UCE	Bsik	Sorbents, solvents, membranes, systems integration
CAPTECH	ECN, KEMA, Shell, TNO, UTwente, UU, UCE, Procede	EOS-LT	Sorbents, solvents, membranes, systems integration
C-CLEAR	ECN	EOS-LT	Pre-combustion, sorbents
CATHY	ECN	EOS-LT	Catalysts membrane and sorbent reactors
		International projects	
ENCAP	TNO, UTwente	EU-FP6	Pre-combustion and denitrogenation
CASTOR	TNO, UTwente	EU-FP6	Post-combustion capture, storage
CAPRICE	TNO	EU-FP6	Post-combustion capture, membranes
CACHET	ECN, Shell	EU-FP6	Sorbents and membranes for pre-combustion
GCEP	ECN	Exxon, GE et al.	Advanced membrane reactors
Dynamis	TNO	EU-FP6	Preparing the ground for Hypogen
CCP1-CCP2	Shell	Oil companies	Membranes, sorbents
NanoGLOWA	KEMA, UTwente	EU-FP6	Membranes for CO_2 removal
CAESAR	ECN	EU-FP7	Pre-combustion
CESAR	TNO	EU-FP7	Post-combustion
DECARBit	TNO, Shell, TUD, NUON	EU-FP7	Pre-combustion: benchmarking, capture, turbine, denitrogenation.

UKR pilot projects

In addition to subsidising the CAPTECH and CATO research programmes, the Dutch Ministry of Economic Affairs has provided 10 million euros for each of three pilot projects. These were selected from proposals submitted under the Unique Opportunities Scheme (UKR, Unieke Kansen Regeling), which is part of the Energy Transition (EnergieTransitie) project. The three pilot projects are briefly described below:

Oxyfuel

For several years, SEQ International BV (SEQ) has been working on a Zero Emission Power Plant (ZEPP) concept. The basic principle of this technology is that the fuel is combusted with pure oxygen in a combustion chamber. Then steam is produced by injecting water. The steam is fed to a high temperature turbine to produce electricity. Suitable steam turbines, operating at 1100-1200°C for high efficiency, are expected to be available by 2013.

With steel manufacturers CORUS and other partners, a CCS project feasibility study is now underway at the CORUS blast furnaces and steelmill in IJmuiden. If economic feasibility is demonstrated, a pilot project will capture and store approximately one megatonne of CO_2 per year. In the context of this project, 'CCS' stands not only for 'CO_2 capture and storage' but also 'climate clean steel'.

CO_2 capture through coal gasification

Nuon Energy Sourcing and the Delft University of Technology (TU Delft) are cooperating in this project to test CO_2 capture at the Willem Alexander coal gasification plant in Buggenum. If successful, the technology will be scaled up for application at the new Magnum multi fuel power plant to be built near the Eemshaven seaport. Substantial reductions in CO_2 emissions can be achieved by gasifying biomass along with the coal and capturing CO_2 from the resulting gas stream. A special feature of this gasification technology is that the CO_2 is captured before the power generation stage, which should result in lower energy loss.

Cryogenic CO_2 capture

Enecogen and the Province of Zuid-Holland are collaborating in this project. Enecogen intends to build an 840-megawatt natural gas-fired plant on the Maasvlakte (Rotterdam harbour area), adjacent to the planned LionGas liquefied natural gas (LNG) terminal. Enecogen plans to capture CO_2 and apply the cryogenic principle, whereby LNG is supplied at an extremely low temperature. The 'cold' produced while heating the LNG can be used to freeze CO_2 for storage. The plant is scheduled to begin producing power in 2011. Originally, it was hoped that the CO_2 capture facility would be fully operational by 2013. However, thorough calculations led the project to conclude that cryogenic CO_2 capture is not yet economical feasible.

CATO[2] and CAPTECH participants working on CO_2 capture

Utrecht University

The Utrecht University Copernicus Institute organised the first worldwide CCS conference in 1992. Its research focuses mainly on system analysis, energy scenarios, transition and risk. The Inorganic Chemistry and Catalysis group researches synthesis, characterisation and performance of solid catalysts. Their main aim is a fundamental understanding of the relationship between structure and catalytic function on atomic and mesoscopic scales. Contact: Wim Turkenburg

ECN

The Energy research Centre of the Netherlands (ECN) is the country's largest research institute in the field of energy. The Hydrogen & Clean Fossil Fuels unit focuses on pre-combustion CO_2 capture. Their expertise is in developing separation-enhanced reactors (membranes and sorbent technology). They also research low-energy production of pure oxygen in membranes. Contact: Daniel Jansen

UCE

The Utrecht Centre for Energy research (UCE) at Utrecht University initiates, acquires and manages national and international energy research projects. It conducts research on energy efficiency, renewable energy sources and carbon capture and storage. Its work ranges from fundamental research to support for policymakers. The UCE also coordinates the CATO programme. Contact: Erik Lysen

Shell

Shell has a long tradition of work on gas treatment and coal gasification. Their main area of interest is solvent development for both post-combustion and pre-combustion. Contact: Frank Geuzebroek

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[2] Only the participants working on CO_2 capture are mentioned here.

KEMA

KEMA is a commercial enterprise specialising in high-grade technical consultancy, inspection, testing and certification. KEMA supports clients concerned with the supply and use of electrical power and other forms of energy. Their expertise is in integrating various kinds of capture technology in energy-conversion concepts, such as post-combustion capture, pre-combustion capture, oxyfuel (AZEP) and chemical looping. They also test and develop membranes for CO_2 separation. Contact: Theo Bosma

PROCEDE

Procede is a small-to-medium company, a spin-off of the University of Twente. They have a long history of work on gas treatment (CO_2 removal and desulphurisation). Their expertise is in applying theoretical knowledge to engineering practice. Contact: Sjaak van Loo

University of Twente

The University of Twente is an entrepreneurial research university. It provides education and research in areas ranging from public policy studies and applied physics to biomedical technology and chemical engineering. Areas of focus relevant to CO_2 capture include process and contactor development, and mass transfer accompanied by chemical reactions in multiphase systems, on which the University has done more than 25 years of fundamental work. Contact: Wim Brilman

TNO

TNO's mission is to apply scientific knowledge with the aim of strengthening the innovative power of industry and government. The Science and Industry unit focuses on post-combustion capture and chemical looping combustion (oxyfuel). TNO is an expert on membrane gas absorption and can test solvents for various properties under differing conditions. Contact: Lodewijk Nell

The Netherlands offers a wide variety of high-quality facilities and opportunities for CO_2 capture research, in areas ranging from fundamental understanding to large-scale testing. During the CATO midterm review, an international team of experts confirmed the high quality of CO_2 capture research in the Netherlands. Another indication that the Netherlands is at the forefront of CO_2 capture research is the fact that two of the three new EU projects on CO_2 capture are coordinated by Dutch research institutes. In addition to detailed know-how on CO_2 capture, high-level knowledge on storage and system analysis is also present in the Netherlands. The Dutch government has the ambition to build two large scale demonstration projects by 2015.

CO_2 capture is the main cost factor in the whole CO_2 capture and storage chain. Unfortunately, the technology is still too expensive to be implemented full-scale. To reduce the costs of avoiding CO_2 emissions, more research is needed — at both fundamental and large-scale demonstration levels.

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