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CO₂-NEUTRAL FUELS

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Mimicking the biogeochemical cycle of System Earth, synthetic hydrocarbon fuels are produced from recycled CO₂ and H₂O powered by renewable energy. Recapturing CO₂ after use closes the carbon cycle, rendering the fuel cycle CO₂ neutral. Non-equilibrium molecular CO₂ vibrations are key to high energy efficiency.

Renewable Energy, the need for storage

The need for energy storage arises from the fact that Renewable Energy (RE) generated is ill-matched to demand. Increasingly supply exceeds demand to the extent that it cannot be accommodated by the electricity grid, however smart. This calls for conversion into added value products, lest it be wasted by curtailment. The German RE scenario expects 34.5 TWh electricity surplus by 2030, increasing to 110-148 TWh in 2050 [1]. For the Netherlands, RE surplus is expected to amount to 1.5 TWh in 2025 (~1% total energy production), increasing to 30-55 TWh in 2050 [2]. For France, these numbers are 15 TWh for 2030 and between 44 and 91 TWh for 2050 respectively [3].

At high RE penetration scenarios foreseen by the EU 2050 Energy Roadmap, a more fundamental driver of energy storage appears; load duration curves prove incongruous to RE supply curves [4]. Only large-scale seasonal energy storage can overcome this limitation.

Energy storage comes in many shapes and sizes directed at specific power and energy requirement, each coming with their own characteristic pros and cons. One way to meet the large-scale seasonal energy storage requirement is through storage in chemical bonds. As compared with flywheels, batteries, compressed air and pumped hydro, chemicals offer higher energy density storage and are easily transported and distributed. Converting RE electricity into methane offers long-term and large-scale energy storage capacity, 552 TWh for the Dutch gas network alone. By comparison, Norway stores

approx. 15 TWh hydro power, whilst average daily European electricity production is of order 10 TWh.

Rather than strengthening the electricity grid, integration of the electricity grid with the existing EU gas grid would provide the required balancing of load and relieve the electricity grid from peak load. This is the power to gas (P2G) scheme, illustrated by Figure 1. Capital investment in electric grid expansion is avoided whilst economic advantage is gained by the fact that transportation of gas is more than a factor 10 cheaper than transport of electric energy, see Table 1. Additional routes for handling surplus RE are also shown. A profitable one is power to chemicals (P2C), through electrification of the chemical industry. Transport offers another important route for conversion of surplus renewable electricity into fuel (P2F), which may well prove essential in meeting 2050 EU transport emission targets. Case in point is long haul flight, for which there is no sustainable alternative, but for bio-kerosene, of which there is too little, being bogged down in the fuel vs food and fuel vs flora trilemma.

Economic feasibility of energy storage has been subject to various studies [1-3]. Current projections expect a business case to emerge in the 2030 timeframe. Economic advantage is gained initially by exploiting periods of low electricity price supported by government regulation, but ultimately depends on the price of carbon [5]. Currently, the Emission Trading Scheme sets too low a price on CO₂, whilst the UN principle “polluter pays” has yet to be enforced by levying a carbon tax.

CO₂-Neutral Fuels – Avenues explored

Low Carbon Energy, decarbonisation of the energy system, the common mantra of energy policymakers today, suggests no place for hydrocarbons in a future energy system, promoting hydrogen, ammonia or batteries instead. A CO₂-neutral fuel would, however, also act to stabilise carbon emissions, akin to the natural biogeochemical cycle, yet benefitting from existing infrastructure. Prerequisite is the recycling of CO₂ after use, extracting CO₂ either from flue gases or directly from ambient air to account for dispersed sources.

Nature's ability to form hydrocarbons by photosynthesis has inspired many in their quest to replicate the process and to produce synthetic fuels with high energy density that are sustainable. To date, several avenues are being explored; the direct route of solar photons into fuel including the natural and artificial approach and the indirect route through the intermediate of electricity [6]. Challenges include high energy efficiency, high energy density and throughput, use of abundantly available materials and a rapid response to intermittent supply of electricity.

Although conceptually attractive, the direct conversion route has a long way to go to reach useful efficiencies. Indirect conversion technology already produces fuel at an order of magnitude higher energy efficiency. For example, photo-voltaically driven electrolyzers produce hydrogen at about 20% overall efficiency. Employing the reverse water gas shift reaction to create syngas, followed by Fischer-Tropsch reaction to produce liquid hydrocarbon fuel, reaches an overall energy efficiency of 10% [7].

Electro-chemical conversion traditionally is based on alkaline electrolyzers. Recently, Polymer Electrolyte Membrane (PEM) electrolyzers have shown higher energy efficiency and density, but scarce platinum is employed as a catalyst at the cathode. Still higher energy efficiency, power density and output pressure go with Solid Oxygen Electrolyser Cells (SOEC), operating at high temperature

	Power: BritNed	Gas: BBL
Length	260 km	230 km
Investment	600 M€	500 M€
Capacity	1 GW	20 GW
Specific investment costs	€ 230 /kW/100km	€ 11 /kW/100km

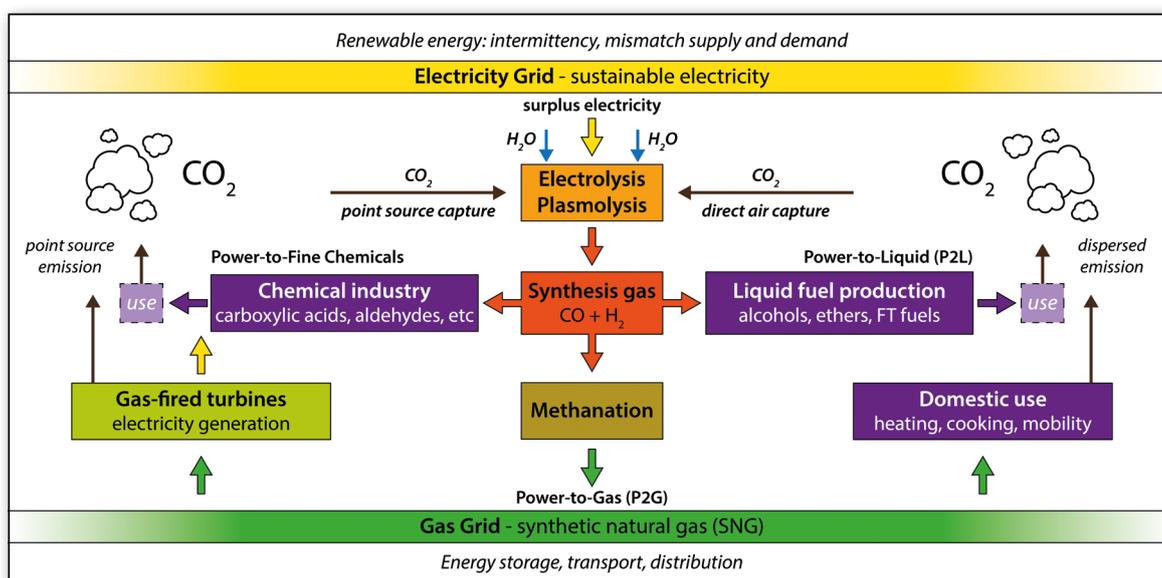
Source: GasUnie, the Netherlands.
Ref.: Nord Stream gas pipeline from Russia to Europe via Baltic: € 9 /kW/100km

(700-800°C) and pressure (50 bar) to produce hydrogen at over 80% energy efficiency. Recently, SOEC produced syngas in one step by co-electrolysis of CO₂ and H₂O [8]. Issues include life time and degradation of the electrodes at high current density. The fuel cathode is made of porous nano structured Ni/YSZ (Y₂O₃ stabilised ZrO₂), the electrolyte layer consists of YSZ (Yttria stabilised Zirconia) and the oxygen anode is a porous SrO doped LaMnO₃ (LSM/YSZ). The electrode-electrolyte interface layer is key to performance. Recently, perovskites, including LSCF (Lanthanum Strontium Cobalt Ferrite) and SSC (Samarium Strontium Cobalt) have shown promising stable high current density performance [9].

Plasma-chemical conversion or plasmolysis increases the power density by more than an order of magnitude compared with SOEC [10-12]. High gas flow rates allow upscaling to high CO production rates at MW level. No scarce materials are employed and a plasma rapidly responds to intermittency. The plasma eases conditions for splitting CO₂ through vibrational excitation of the molecules. Such plasma is weakly ionised - only one in 10⁵ molecules is ionised - and relatively cold, similar to a fluorescent lamp. The energy to produce the plasma is a relatively low factor in the energy balance.

To close the fuel cycle and render it CO₂ neutral, CO₂ emitted must be recaptured after use of the hydrocarbon produced, from point source initially (fossil fired power, cement, steel plants), from the atmosphere eventually to account for dispersed CO₂ emissions (cars, ships, planes).

◀ **Table 1:** Comparison of capital investment cost per kW power transported for electricity and gas transport lines from the Netherlands to the UK in comparable situation. Gas is a factor 20 cheaper. Source: Dutch Gas Unie.



◀ **FIG. 1:** Power to Gas (P2G) scheme converting Renewable Electricity (RE) into synthetic gas or liquid fuel (P2F) or chemicals (P2C). Syngas (H₂, CO₂) is the central element from where methane, Fischer-Tropsch fuel or other chemicals are formed. After use, the CO₂ emitted is captured and recycled in order to render the fuel cycle CO₂ neutral. The critical element, both technically and economically, is the splitting of water and CO₂ into syngas.

Alternatively, CO₂ may be captured from the ocean taking advantage of the higher concentration. Both, direct air and ocean CO₂ capture plants are not linked to emission sites; plants may be sited anywhere around the globe. Research challenges include the development of energy efficient materials to capture and desorb CO₂, including ionic liquids [13, 14].

Carbon capture and utilisation (CCU) will close the carbon fuel cycle, however, raises the question of scale and cost of the carbon capture plants. For example, a direct air capture plant is similar in size to a concurrent wind farm producing the electricity required to convert the CO₂ captured into fuel. This implies non-trivial infrastructure. Cost on the other hand, often seen as an impediment to carbon capture, is an order of magnitude lower than the cost of splitting CO₂ or H₂O, hence not a cost driver at system level.

Plasmolysis - the physical picture

A plasma offers advantages in CO₂ splitting including high energy density and high gas throughput with scope for upscaling. A microwave discharge creates the plasma and accelerates the electrons which vibrationally excite the CO₂ molecules by a slight touch (max. cross section at 0.4 eV) like a clapper ringing a bell. The CO₂ molecules, whilst chiming away, occasionally bang into each other, exciting overtones thereby ratcheting up vibrational energy of one molecule at the expense of others. Eventually, this leads to breaking the CO₂ molecular bond at 5.5 eV energy, releasing a CO molecule and oxygen atom. This oxygen radical is put to good use by reacting with another CO₂ molecule producing a second CO molecule at 0.3 eV energy. The net energy expended per CO produced is thus lowered to 2.9 eV, much smaller than the dissociation energy of 5.5 eV and the 7 eV or more electron energy required for vibronic excitation of CO₂ by Franck-Condon transition.

This process directs energy along a path where it is most effective in dissociation, rather than heating the gas: it exploits a non-equilibrium process where vibrational energy exceeds the translational and rotational energy. Vibrational up pumping under non-equilibrium conditions is a robust process based on the asymmetric stretch bond of the CO-O potential well. Pioneered by the Russians during the cold war, this scheme is reported to reach energy efficiencies of over 80% [10-12]. The only snag: results have never been reproduced in the West.

Worse, details of the non-equilibrium vibrational kinetics have never been verified experimentally.

Recently, researchers at the Dutch Institute for Fundamental energy Research (DIFFER) together with colleagues at the University of Stuttgart Institute for Interfacial Research and Plasma processes (IGVP) have explored the route to CO₂ neutral fuels [15]. The IGVP microwave plasma facility (915 MHz, 30kW) coupled to a cylindrical cavity creates an axial electric field sufficiently high (~10 kV/m) for ignition and maintenance of the CO₂ plasma, see Figure 2. The electric field may be regarded as stationary because electron neutral collisions and plasma processes occur on much shorter time scale (<< 1ns) in comparison with the oscillation period. The CO₂ gas is injected tangentially at the entrance of the cylindrical reaction chamber creating a vortex gas flow. Flow rates are up to 75 standard ltr/min, gas pressures in the range 200-800 mbar. A nozzle expands the gas to supersonic speed causing the gas to cool. A cold gas is needed to prevent vibrational relaxation into translational energy [12].

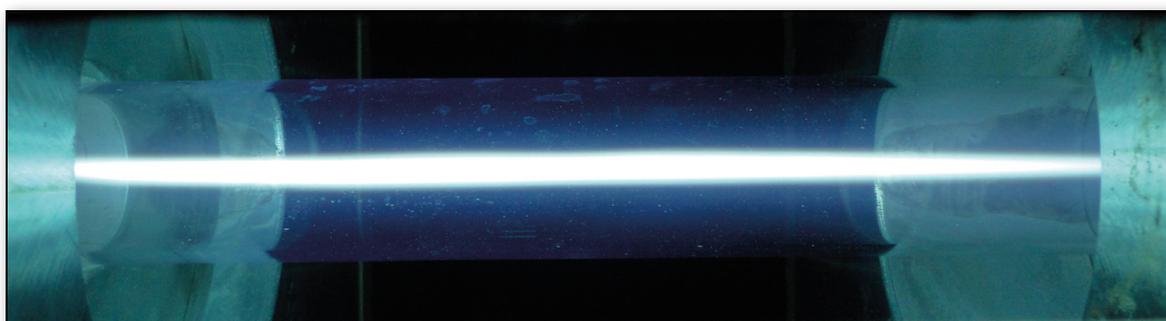
Experimental results

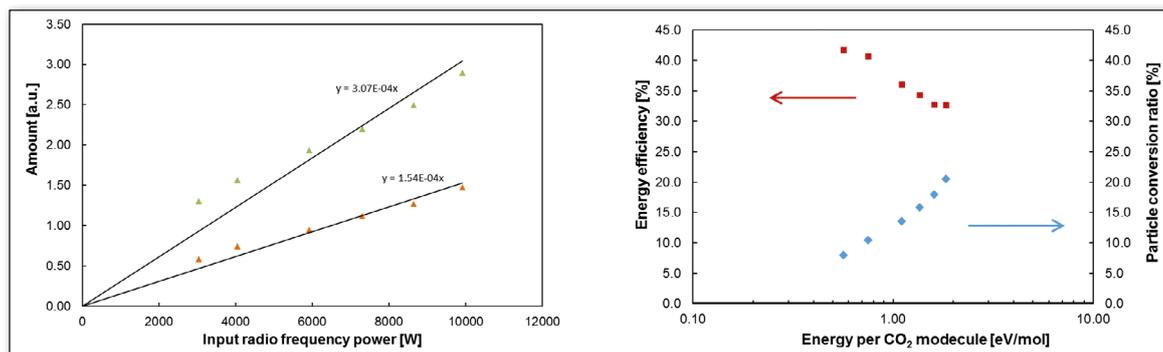
Gas composition measurements are carried out by quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES) which reveal the particle conversion ratio to increase linearly with RF power, whilst highest energy efficiency is reached at low RF power, see Figure 3.

Optical emission spectroscopy (OES) provides complementary information on the plasma dissociation process. UV-visible light emitted by the plasma is observed through a slit in the microwave cavity shown in Figure 2, collected and guided by fibre optics to a commercial spectrometer with spectral range 175-725 nm at ~ 2 nm resolution, sufficient to resolve the electronic bands, but not the vibration-rotation fine structure. Reaction products CO and O₂ exhibit emission spectra in the UV-visible. This is not the case for CO₂ where only some weak absorption bands in the far UV 140-160 nm exist.

The CO emission line strength (3rd positive, 5B triplet) is shown to increase linearly with RF power, confirming the QMS data. Similarly, the line strength is seen to increase linearly with gas pressure. These results are consistent with a power balance model, showing electronic excitation to be linearly proportional to microwave power

► FIG. 2: CO₂ plasma discharge at 3 kW absorbed power at 500 mbar pressure and 75 standard ltr/min gas flow rate





◀ FIG. 3: left panel: Production of CO and O₂ by plasmolysis of CO₂ as a function of absorbed microwave power. The drawn lines are constrained by the stoichiometry of CO and O₂ products. Right panel: Energy efficiency and particle conversion in terms of energy E_v per incoming CO₂ molecule. Particle conversion increases with power whilst energy efficiency reaches highest value at low power.

and neutral gas density, consistent with electron excitation of CO in the sigma singlet ground state.

The reduced electric field E/n (n is neutral gas density) has been identified as the key parameter controlling energy efficiency [15]. An ancient concept in plasma physics, it expresses the potential drop an electron experiences in between collisions and is typically $\sim 10^{-16}$ Vcm². Lowering the reduced electric field enhances the energy efficiency, albeit at the expense of conversion ratio. Through randomisation E/n is proportional to the electron temperature. Thus, a low electron temperature plasma ($T_e \sim 1$ eV) is favoured from the viewpoint of energy efficiency, however, leads to conflicting requirements between ionisation degree which requires higher electron temperature. This suggests that optimum conditions may be reached by decoupling plasma formation from dissociation by a two stage plasma reactor or by shaping the electron energy distribution function (EEDF) with a bump in the high energy tail. Similarly, the reduced electric field can be shown to scale inversely with electron containment time, offering another route to high efficiency, in addition to control of the EEDF under non-equilibrium conditions.

Challenges ahead

Having demonstrated the splitting of CO₂ into CO and O₂ by plasmolysis, the next step is to separate the effluent gas stream into its constituent parts. Following that, methane and higher order hydrocarbons must be formed selectively at high efficiency. Oxygen pumping membranes, such as electrically driven SOEC or pressure driven MIEC (Mixed Ionic Electron Conducting) are a first try. Exothermic water gas shift or parallel electrolytic hydrogen production creates syngas, the central element from which traditional chemical pathways lead to P2G, P2C and P2L, or in short P2X.

Outlook

CO₂-neutral fuels based on synthetic hydro-carbons and recycled CO₂ offer advantage over hydrogen, ammonia and batteries in that infra structure is readily available, whilst the high energy density fuel allows long haul transport to remain feasible. Here plasmolysis is featured as an energy efficient means to split the CO₂ molecule into CO and O₂. Cold weakly ionised CO₂ plasma electrons serve to vibrational excite CO₂ molecules into a thermal non-equilibrium state

conducive to dissociation. The scheme offers advantages over electrolysis in power density, upscaling to megawatt level, instant response to intermittent renewable electricity and no use of scarce materials.

The EU Energy System is undergoing profound change. Rather than concentrating on the energy source, a system approach is needed which includes energy storage and the recycling of waste. A number of challenges remain in the conversion of CO₂ back into hydrocarbons. Direct conversion of solar photons into fuel and the indirect route via renewable electricity require understanding at the basic research level. Technical challenges include upscaling and system response to intermittent power. To date, P2X energy storage is not economically feasible - that is not unless the cost of waste recycling, be it CO₂ or radioactive, is factored into the price of fossil fuel and nuclear power... ■

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Adelbert Goede worked on the European fusion machine JET from 1975 to 1988. From 1988 to 2008 he worked on the European Space Agency Envisat as Co-Principal Investigator of the SCIA-MACHY instrument measuring global greenhouse gas distributions from space. In 2006 he returned to energy research picking up on a proposition of his 1975 PhD thesis on off-shore wind energy.



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