CO₂ neutral fuels

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Summary. — CO₂ is a valuable resource, life on Earth depends on it. Rather than wasting it to the atmosphere, or burying it underground, CO₂ can be combined with water and turned into valuable chemicals and fuels, the process being powered by renewable electricity. Renewable electricity generated by wind and photovoltaics (PV) is making big strides, but is limited by ill-matched supply and demand. In addition, electricity only makes up 20% to 30% of total energy demand. Domestic heating, high temperature/pressure Industrial processes and mobility/transportation gobble up the rest. Mobility and transportation prove particularly difficult to decarbonise. Aviation is a case in point. Battery-powered aircraft are unlikely to become feasible by 2050. Hydrogen has too low an energy density and is haunted by safety issues. Current policy, therefore, is directed at bio fuels. One problem, there is not enough of it. The Fuel *vs.* Food *vs.* Flora trilemma of bio-based fuel is unlikely to gain public acceptance. By converting renewable electricity into fuel, power to molecules (P2M), two birds are killed with one stone: providing fuel for long haul transportation and enabling long-term, large-scale energy storage to cover the seasonal mismatch between supply and demand of renewable electricity. Feedstock consists of air-captured carbon or nitrogen and water. Chemically combined, it creates a liquid fuel with greatly enhanced energy density, such as kerosene or ammonia, or gaseous fuel like methane which can replace natural gas in the existing gas network. Direct air capture of CO₂ is currently being commercialised. The conversion technology of water and CO₂ by electrolysis has recently been extended to novel plasma technology, the subject of this paper. For CO₂ splitting by plasmolysis, the reduced

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electric field has been identified as the key parameter explaining and improving the energy efficiency. Energy efficiency by plasmolysis is similar to that of electrolysis, but offers advantages in energy density, upscaling and switching in response to intermittent power with no use of scarce material. A simple model explains the inverse relation between energy efficiency and particle conversion and relates input microwave power to CO₂ gas density, plasma dimension and ionisation degree, allowing design parameters for a 100 kW pilot reactor to be specified. Recycling CO₂ in combination with P2M is a game-changing technology to meet overall CO₂ emission reduction targets. It takes advantage of existing, inexpensive infrastructure for energy storage, transport and distribution. Existing internal combustion engine technology can be maintained where necessary. Close coupled to a remote solar array or an off-shore wind farm it offers a solution to decentralised renewable fuel production at the renewable electricity source.

1. – The energy transition

The next 20 years will mark a fundamental shift in the way energy is generated, stored, delivered, valued and purchased. Unlike nuclear, this energy transition will be market-driven, for governments can regulate and facilitate, industries can produce the goods, but consumer demand will ultimately decide the fate of this energy transition. This view is shared by the European Commission. Germany, pioneer in the energy transition, has added further requirements: the energy must be clean, secure and affordable. Targets for 2030 and 2050 have been set by International Agreement (UNFCCC), by the EU (RED) and by National policy [1,2]. The road to get there, however, is largely uncharted.

The driver of the energy transition is climate change. Mitigation policy is based on reduction of greenhouse gas emissions, notably CO₂ emissions from the use of fossil fuels. Currently, the rise in CO₂ emissions show signs of levelling off, see fig. 1a). The cause is attributed, not to an increased share of renewables, but to a slowing of the economy and an improved energy efficiency. What counts, however, is not CO₂ emission, it is the CO₂ concentration in the atmosphere that determines greenhouse radiative forcing. This CO₂ concentration shows no sign of levelling off, see fig. 1b). Governed by the coupling between atmosphere and ocean, it may take decades, if not centuries, before the effects of CO₂ emission reduction become tangible, ocean inertia being the rate determining factor in the climate system.

Mitigation of climate change and sustainability of System Earth call for renewable energy. Renewable energy is energy obtained real-time from our Solar System, either directly in the form of solar photons, or indirectly through wind, rain, ocean currents and waves, or driven by the moon through tides. Photosynthesis has energised the biosphere throughout geological times by converting solar photons into a finite amount of biofuel, which has allowed humankind to develop over the past million years. Bio energy derived from, for example, crops, algae, wood and bio-waste is thus renewable.

Fig. 1. – a) Global CO₂ emissions from energy use roughly flat over 2014–2016. Economic downturn and improved energy efficiency are partly responsible. Source: BP and The Economist, 17 June 2017. b) Atmospheric CO₂ concentration measured at Mauna Loa ground station. Red is monthly mean, black is seasonally corrected moving average. Source: NOAA.

Faced with a growing world population and an increasing level of consumption, bio energy is in competition with food and flora and, in any case, will not suffice to meet future world energy demand [3]. Fossilised biomass, created over several 100 million of years is resource limited and not renewable over human life span.

Alternative renewable energy sources are thus needed. Renewable energy schemes pursued to date are based on either direct conversion of solar photons into fuel, or indirectly, through the intermediate of renewable electricity. The direct conversion route, or artificial photosynthesis, mimics nature by combining solar energy conversion and fuel synthesis into one device, whereas the indirect route converts to electricity first, followed by fuel synthesis in a separate step powered by renewable electricity. Feedstock, in both cases consist of air and water. Most renewable energy sources deployed to date generate electricity, hence tailored to the indirect solar fuel production concept.

Electricity covers only about 20% to 30% of primary energy consumption, the remaining 70–80% going into low-temperature domestic heat (usually natural gas), high-temperature industrial heat (usually coal) and transportation (mainly oil). Typical CO₂ emissions produced over the various sectors are listed in table I, presented for the case of The Netherlands. It shows that CO₂ emissions are roughly equally attributed over all sectors at around 20%. Hence, in order to meet CO₂ emission reduction targets, it is paramount to shift current focus away from the electricity system towards the energy system as a whole.

The challenge is *not* how to achieve a 100% renewable electricity system, the challenge is how to transform all sectors of the economy into sustainability. Civil aviation is a case in point. The UNFCCC agreed on an overall 80–95% CO₂ emission reduction target, as compared with 1990 values, to be reached by 2050. For transportation this target has been relaxed to 60% emission reduction [4]. Aviation is exempted by a further reduced 40% sustainable fuel target in 2050, whilst ICAO, the UN civil aviation organisation, has

TABLE I. – CO₂ emissions attributed to the various sectors of the economy for The Netherlands. The Netherlands accounts for 0.5% of global CO₂ emissions, the EU for 10.5%, see also fig. 1a) for world CO₂ emission distribution.

CO ₂ emission budget	The Netherlands	0.5%
Power and lightning	electricity	26%
Low-temperature domestic heat	gas	18%
High-temperature industrial heat	coal	19%
Transport (cars, ships, airplanes)	oil	17%
Non-energy emissions (agriculture, waste, chemical feedstock)		20%
Typically CO ₂ emission distribution	20:20:20:20:20	
Source: Energy Agenda, Min. Econ. Affairs,	Dec 2016/97015	

agreed on a 50% CO₂ emission reduction by 2050 as compared with 2005 [5]. These down rated CO₂ emission targets illustrate the difficulty faced in transforming the transport sector into sustainability.

2. – Hydrogen economy

One radical option to transform the transport, heat and chemical sectors into sustainability is a hydrogen-based economy. This option has been around for a while and could be instrumental in the coupling of the electricity sector to the other sectors of the energy system. Hydrogen, however, is a highly flammable and volatile gas with a low-energy density of 0.01 MJ/ltr at ambient pressure and temperature. Also, it brittles metal containers. This limits the ability to store and transport hydrogen and to use hydrogen as an energy carrier. Combined with the high cost of producing renewable hydrogen, deployment of hydrogen as an energy carrier has been limited so far.

Several options to overcome the low-energy density problem of hydrogen are being explored, including hydrogen compression at 700 bars for storage in vehicles or at 200 bar for large scale storage in salt caverns, liquefaction at 20 K and storage in metal hydrides, Metal Organic Frameworks (MOF), Liquid Organic Hydrides (LOHC) or carbon nanotubes.

Another, attractive option is to chemically bind hydrogen to another atom, forming molecules in liquid or solid phase at ambient temperature and pressure, thereby increasing the power density by orders of magnitude. This is the case for binding hydrogen to nitrogen or carbon. Coupling hydrogen to carbon vastly increases its energy density. For example, the energy density of kerosene is 37.4 MJ/ltr, more than three orders of magnitude higher than hydrogen at ambient condition. Hydrocarbons offer a well-characterised, reliable and inexpensive solution to long-term and large-scale energy stor-

Fig. 2. – a) Wind intermittency over N-W Europe showing a large dynamic range (factor 100) on a day to day basis. Seasonal variations of a factor 2 to 3 is in phase with heat demand but not quantitatively. b) Solar PV electricity is in phase with diurnal demand, but not quantitatively with surplus during the day, shortage at night. Dramatically out of phase with renewable PV supply is seasonal heat demand over Northern EU latitudes, winter insolation being only 10% of summer whilst heat demand is up by a factor four. Courtesy Martijn Visser of Energy Academy Groningen, The Netherlands.

age and transportation, benefiting from existing infrastructure, whilst the well-qualified Internal Combustion Engine (ICE) technology remains to serve long haul transportation.

Hydrocarbons, however, require carbon capture (CC) in order to close the carbon cycle and render the fuel cycle carbon neutral. No carbon is involved in storing hydrogen in ammonia (NH₃). Apart from the pungent smell, ammonia is characterised by low flammability, high hydrogen storage density of 17.6% by mass and 107g H₂/ltr and a high energy density of 11.5 MJ/ltr. Furthermore, ammonia is an essential element in the food chain being at the basis of fertiliser production. The fixation of nitrogen to hydrogen has allowed human population to grow without running out of food, overcoming the 19th century Malthusian dilemma of population growth outpacing food supply.

Modern ammonia plants employ steam methane reforming (SMR) to produce the hydrogen needed to react with atmospheric nitrogen under high pressure and high temperature, the Haber-Bosch process. This is an energy intensive process, and in addition, relies on fossil feedstock. Current ammonia production accounts for 1.4% of global CO₂ emission. For ammonia to become sustainable as an energy carrier both the formation process and the feedstock must become CO₂ free. Powering the process by renewable electricity and deriving hydrogen from electrolysis of water would be an option within reach of existing technology. However, it would be highly desirable to develop a less energy intensive ammonia synthesis process, mimicking nature by departing from air and water. Electro-chemistry and non-equilibrium plasma chemistry may hold the key to such nitrogen fixation pathway.

3. – Energy storage

Conversion of renewable electricity (RE) into gas or liquid fuel not only opens up a route to sustainability for these sectors, it also creates a buffer in the energy system that can handle the mismatch between renewable electricity supply and demand. This buffer

Fig. 3. – a) Gas demand [GWh/day], mainly heat, shows seasonal variation of factor 4. b) Electricity demand [GWh/day] almost flat at $\pm 10\%$ throughout the year. Courtesy Martijn Visser, Energy academy Groningen, The Netherlands.

is needed for several reasons, illustrated by figs. 2 and 3. On the supply side wind power creates large peaks and troughs in electricity generation, a dynamic range of a factor 100 between lulls and gusts in a matter of minutes is not unusual, wind power scaling with wind velocity cubed. PV displays a more predictable diurnal cycle but, obviously not matched to demand at night. Electricity overproduction during the day must be tidied over to cover night-time demand. An energy buffer acting on a short time scale of msec to days is necessary to smooth out the fast variations in the generation of renewable electricity.

Power to Heat (P2H), employing heat pumps and storage heaters to siphon off surplus electricity, may well provide a solution to cover the diurnal mismatch between RE supply and demand in domestic heating. But P2H would offer no solace in covering seasonal RE mismatch. Seasonal heat demand over Northern Europe is shown in fig. 3a), gas serving as a proxy to heat demand, again for the Dutch situation. Demand for heat in winter exceeds that of summer by a factor of four on a weekly basis. On shorter times demand is even more volatile. Electric power demand, on the other hand, is almost flat, see fig. 3b) showing a $\pm 10\%$ variation over the year. A doubling in electric power transmission to cope with seasonal heat demand variation will be costly and such grid will run idle for most of the time being massively oversized during summer. The current practise of curtailment of subsidised wind power during summer will be difficult to justify towards tax payers.

The energy supply - demand mismatch requires a buffer covering seasonal to inter-annual time scales. Existing technologies, including batteries, super capacitors, flywheels, pumped hydro and CAES (Compressed Air Energy Storage) suit the requirements of short-term energy storage, but offer no solution to large-scale seasonal and inter-annual energy storage requirements.

A third reason for an energy buffer to be included in any renewable electricity (RE) system, is that energy scenarios project a substantial surplus in electricity accumulating with increased penetration of renewable electricity in the electricity grid. The German RE scenario expects 34.5 TWh electricity surplus by 2030, increasing to 110–148 TWh

TABLE II. – *Comparison of capital investment cost per kW power transported for electricity and gas transport lines in comparable situation. Gas is a factor 20 cheaper. Source: Gas Unie, The Netherlands.*

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

Nord Stream gas pipeline: € 9/kW/100 km (Russia to Europe via Baltic).

in 2050 [6]. 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 [7]. For France, these numbers are 15 TWh for 2030 and between 44 and 91 TWh for 2050, respectively [8].

4. – Power to M

Converting renewable electricity into energy dense gaseous or liquid fuel presents a solution to long-term, large-scale energy storage. This is the Power-to-Molecules (P2M) scheme, where molecules stand for synthesised gas or liquid fuel or chemicals. P2M has the powerful ability to couple the electricity sector to the gas, the oil and the chemical sector, leading the way to CO₂ reduction of the energy system at large. Existing inexpensive infrastructure for energy storage and transport is readily available. The Dutch gas net alone unlocks a massive 550 TWh energy storage capacity. Transportation of energy by gas is more than a factor 20 cheaper than energy transport by electricity, see table II.

Currently, Europe runs about 50 pilot and demo P2G projects, about half of them in Germany, with efforts accelerating over the past years. These projects anticipate a substantial RE surplus generated in all RES scenarios by 2050 and recognise the difficulty to store and transport this surplus electricity on a large scale. The existing gas grid provides both storage and transport infrastructure that meets seasonal requirements for heat and overcomes the inherent limitations in storage of renewable electricity.

For transportation similar dilemmas are encountered. Batteries are free from carbon emission during operation. However, they suffer from low-power density compared with hydrocarbon fuel, which limits their range. Taking again the extreme example of long haul aviation: to replace the energy content of a 260 tonnes of kerosene load of an Airbus 380 at take-off, the most advanced Li-ion battery would weigh 14.000 tonnes. The plane will never take off. Long haul aviation powered by batteries is unlikely to become feasible by 2050.

Electric cars may well offer a solution to urban mobility. Both air pollution and noise will be diminished and battery charging infrastructure is relatively easy to install. Added to self-driving and ride sharing it may just cause the disruptive change the automotive

Fig. 4. – The CO₂ neutral fuel cycle of an internal combustion engine driven by hydrocarbon fuel, illustrated for the case of aviation. Sustainable aircraft grade kerosene is produced from water and air powered by renewable electricity through the splitting of CO₂, formation of syngas and Fischer-Tropsch synthesis. By recapturing the CO₂ directly from air, the CO₂ cycle has come full circle. Source: EU H2020 funded KEROGREEN project [9].

industry anticipates. However, batteries will not meet long-distance road transportation requirements, in particular not for heavy-duty lorries. The hydrocarbon powered internal combustion engine is unlikely to lose its grip on the motorways by 2050.

5. – Conversion of renewable electricity into fuel

The conversion step of electricity into fuel and chemicals is the critical step, both technically and economically. Basic research and development of cost-competitive electro-chemical solutions are subject of current R&I effort. Electro-chemical conversion is based on the electrolysis of water and CO₂ into syngas. Syngas is the key mixture around which the synthesis of hydrocarbons revolves. The process is known as Fischer-Tropsch (FT) synthesis. Both electrolysis and FT technology have been around for about 100 years. Deployment so far has been limited to strategic use in South Africa and Nazi-Germany when oil embargos threatened fuel supply. At this point in time, however, high cost and upscaling is the limiting factor to large-scale implementation.

A typical P2M-CC fuel cycle is illustrated for the case of jet powered aviation in fig. 4, borrowed from the EU H2020 funded KEROGREEN project [9]. The CO₂ neutral fuel cycle starts with renewable electricity generation. This electricity powers a microwave plasma reactor in which the CO₂ molecule is split into CO and O₂. Subsequently, the

oxygen is separated out and the CO partly converted into hydrogen by the water gas shift reaction creating syngas, a mixture of CO and H₂. Out of syngas hydrocarbons are formed by Fischer-Tropsch (FT) synthesis. The wax produced is further processed by hydrocracking to create kerosene. FT synthesised fuel at 50% blending ratio is ATSM certified as jet grade fuel. Upon combustion, CO₂ and H₂O are emitted. By recapturing the CO₂ directly from air, the fuel cycle is closed, a CO₂ neutral fuel cycle is created which does not add to the atmospheric CO₂ concentration.

Synthetic fuels, based on C-H-O compounds, usually display absorption bands in the infrared and are thus greenhouse gases (GHG). Compared with CO₂ their Global Warming Potential (GWP) maybe higher, but their relatively short atmospheric lifetime will diminish their long-term impact on global warming. For example, methane is a more potent GHG than CO₂ on a molecule by molecule basis. However, the atmospheric lifetime of methane is about 10 year, far less than the several hundred years that CO₂ stays in the atmosphere. Manmade methane emissions may result from leaking gas pipelines, estimated to amount up to 10% of total gas flow for Siberian gas transport. Methane release from the vast Siberian permafrost region may be instrumental in kick-starting climate change before CO₂ greenhouse warming takes over, a situation encountered in the Quaternary periods when ice ages and warm spells succeeded in quick succession.

On air pollution synthetic fuels meet the most stringent regulation; there is no soot because the synthesised fuels contain no aromatics, there is no sulphur because synthesis is based on H₂O and CO₂ only, and NO_x formation is lowered by tuning the ICE combustion temperature.

Carbon neutral fuels offer energy security and reduce the dependency and cost of imported fossil fuels. Feedstock consists of abundant CO₂ and H₂O, and power derives from indigenous renewable electricity. The fuel can be stored at large scale for an extended period of time, transported and distributed to customers by existing, inexpensive infrastructure, with no need to expand the electricity grid.

6. – Electro chemistry

Electro-chemical conversion of H₂O and recently CO₂ is traditionally based on alkaline electrolyzers. The technology is commercially available. Power density is low (0.1 W/cm²) which means sizable plant lay-out. Proton Exchange Membrane (PEM) electrolyzers are at early commercial stage and show higher energy efficiency and power density (1 W/cm²), allowing more compact sized equipment and up-scaling to MW level within reach [10]. However, PEM employs an expensive membrane and noble metal electro-catalysts, *i.e.* platinum and iridium, resulting in cost and sustainability issues. Degradation causes limitations to membrane operational life time.

Solid Oxide Cells (SOC) are at the R&D stage and offer higher energy efficiency and power density (~ 5 W/cm²) at high operating temperature (700–800 °C) and pressure (50 bar) to produce hydrogen at over 80% energy efficiency. Recently, syngas (H₂-CO) was produced in a SOC in one step co-electrolysis of CO₂ and H₂O [11, 12]. Upscaling of SOC is hampered by cell degradation and stack lifetime. The physics and chemistry

at the triple phase boundary layer between gas reactant, electrode and catalyst is poorly understood [13]. Both alkaline and SOC do not respond well to intermittent renewable electricity.

7. – Plasma chemistry

Plasma-chemical conversion or plasmolysis increases the power density and consequent productivity by more than an order of magnitude compared with SOC. Electro-chemical conversion is a surface process taking place at the gas-electrode interface. By contrast, plasma chemical conversion is a volume process and hence scales with dimension cubed rather than dimension squared of a surface process. Combined with high gas flow rates, upscaling to high CO production rates at 100 kW power level is feasible. Plasma chemical conversion does not employ scarce materials and a plasma responds instantly to intermittent input power.

The plasma eases conditions for splitting CO₂ through vibrational excitation of the molecules, not through direct electron impact dissociation, electron dissociative attachment or through heating of the gas [14, 15]. As a consequence, vibrational temperature exceeds the translational and the rotational temperatures, the CO₂ gas is in a thermodynamic non-equilibrium state. The CO₂ gas is weakly ionised —only one in 10⁵ molecules is ionised— and is relatively cold, similar to a fluorescent lamp. The energy to produce the plasma is a relatively small fraction in the energy balance.

By tuning the electron energy distribution function EEDF, energy is directed mainly at the CO₂ vibrational degree of freedom, not to translational or rotational energy. A non-equilibrium condition is created whereby the vibrating molecules impart vibrational energy on each other, ratcheting up vibrational energy of one molecule at the expense of others, ultimately breaking the CO₂ molecular bond. Most effective in vibrational dissociation is the CO₂ asymmetric stretch mode, stretching the O atom away from the CO part of the linear CO₂ molecule. This mode is excited most effectively by relatively low energy electrons in the range of 0.4–2 eV [16].

Dissociation to CO proceeds in two steps: first one molecule CO and one atomic oxygen O are formed at 5.5 eV dissociation energy. Subsequently, the atomic oxygen reacts with another excited CO₂ molecule to form a second CO at 0.3 eV net energy, yielding a net enthalpy H for the production of one CO molecule $H = 5.8/2 = 2.9$ eV. This is much lower than direct electron dissociation and lower than the > 7 eV required for an electron induced Franck-Condon transition [15]. The loss of vibration energy by vibrational-translational relaxation is reduced by cooling the gas, notably for the asymmetric stretch mode [17]. Low gas temperature ($T_0 < 1000^\circ\text{C}$) also prevents the reverse CO₂ forming reaction from taking place. Low temperatures are obtained by supersonic expansion of the gas through a nozzle.

7.1. Plasma experiments. – CO₂ plasmolysis experiments are conducted in an microwave powered reactor equipped with a cylindrical quartz flow tube of length 124 mm and 26 mm diameter, placed on axis of the RF cavity [18, 19]. The CO₂ gas is injected

tangentially at the entrance of the reaction chamber to create a vortex gas flow aimed at stabilising the plasma by creating a radial pressure and temperature gradient. Gas composition measurements are based on quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES). Gas pressure is measured at the entrance and at the exit of the reaction chamber. A typical plasma discharge is shown in fig. 5b) [20-22].

Experimental results show production rates of 7.5 slm CO at 200 mbar pressure at a CO₂ gas flow rate of 75 slm. The energy efficiency η , defined in sect. 11, reaches 60% at 3 kW microwave power (915 MHz) absorbed. The CO₂ to CO conversion ratio is relatively low at 10% for safety reason. However, conversion ratio CO₂ to CO is shown to scale linearly with RF power and inversely with gas pressure to reach 70%, see fig. 5c) and fig. 12. A typical CO spectrum is shown in fig. 5d). Linear scaling of CO concentration with power is confirmed by CO line strength measurement.

7.2. *Plasmolysis vs. electrolysis.* – The effectiveness of plasma against electro chemistry is illustrated by comparing the physical size of the plasma reactor itself with an SOC electrolyser producing the same amount of O₂ flux. Plasma O₂ production rate per kW input power is 1.25 slm O₂, which corresponds to $0.93 \cdot 10^{-3}$ mole O₂/s. At typical SOC transport of 1 A/cm² this requires about 358 cm² SOC surface area (Faraday constant $1/4 F$ to account for transport of 2 double negatively charged O atoms). By contrast, the surface area surrounding the plasma is about 30 cm². Hence, plasma productivity is up by a factor 10 by volume compared with SOC electro-chemical conversion for the same surface envelope.

The relevant parameter in achieving high vibrational excitation and subsequent high energy efficiency and conversion, turns out to be the reduced electric field E/n , see sect. 10 and subsect. 14.2. Although known from theoretical studies [23], these experiments show direct experimental evidence for the first time [21]. CO₂ molecules are vibrational excited by low energy electrons in the range of 1 eV where the reaction rate peaks at about 10^{-8} cm³/s. This is achieved by adjusting the mean free path of plasma electrons accelerated in the externally applied RF electric field E and tuning the neutral particle density n to obtain $E/n \sim 10^{-16}$ V cm². Current CO₂ plasmolysis development is directed at optimisation of the reduced electric field E/n and reduction of the CO₂ gas temperature, both aiming at an increased energy efficiency.

7.3. *Plasma modelling.* – Computational studies support the experimental effort to improve energy efficiency and CO yield. This modelling requires detail knowledge of the plasma physics and the plasma chemistry, referring to a large number of chemical reactions with vibrational excited cross-sections largely unknown. Models of the reaction kinetics developed so far contain only crude approximations. At DIFFER a zero-dimensional computational model for CO₂ plasma dissociation is being developed based on a Monte Carlo solution of the Boltzmann equation for electrons and ions and a hybrid discrete-continuum model for vibrational up pumping [24]. Employing a fast computational solver, the vibrational and non-equilibrium electron energy distributions are computed in the presence of molecular and atomic carbon and oxygen species.

Fig. 5. – a) Schematic of the 30 kW 915 MHz plasmolysis reactor for CO₂ splitting. Microwave power absorbed creates a stable plasma column at a pressure of 200–500 mbar, contained within a cylindrical quartz tube of length 12.4 cm and 26 mm diameter. CO₂ gas injected tangentially at the entrance of the tube creates a vortex flow to stabilise the plasma and is expanded at the exit by a nozzle to cool the gas. Diagnostics include Optical Emission Spectroscopy and Quadrupole Mass Spectrometry. b) High-density contracted CO₂ plasma driven by microwave power at 3 kW absorbed and a CO₂ gas flow rate of 75 slm (Type II discharge). The blue light emitted is from the CO 3rd positive bands, see panel d) Combined with the C₂ Swan band it produces an intense white light. Enthalpic energy efficiency reached is 50–60% while conversion ratio ranges from 10% to 70% scaling with power. c) Linear scaling of CO₂ conversion with input microwave power. The conversion ratio of CO₂ to CO is the determining factor in system productivity and cost. Drawn lines are stoichiometric fits to CO and O₂ ratio. d) A typical CO spectrum at high density (Type II) operation mode. Left are the 4th positive singlet and 3rd positive and 5B triplet CO bands. Between 400 and 650 nm the CO Ångström and triplet system is observed together with an upcoming C₂ Swan band emission at high gas density. All CO lines observed result from direct excitation by plasma electrons.

8. – Gas separation

A major challenge is the separation of O_2 from the CO_2 , CO , O_2 gas mixture produced by plasmolysis of CO_2 . Notably the separation of the oxygen molecule from the nearly equally sized CO molecule, with kinetic diameters of 0.346 nm and 0.376 nm, respectively, is not trivial. Various schemes have been considered, based on paramagnetic properties of oxygen, cryogenic distillation and membranes. The membrane scheme includes polymeric membranes, MOFs, ceramic microporous membranes, mixed ion electron conducting membranes and electrochemical oxygen pumps.

The latter, considered here, is a solid oxide cell (SOC), similar to that used in high-temperature fuel cells and electrolyzers. It consists of a thin electrolyte sandwiched between two oppositely biased electrodes, one of these usually providing mechanical support. An SOC operates in the temperature range 700 to 800 °C where the material becomes conductive to negatively charged oxygen ions. If the SOC is operated as an electrolyser, the plasma electrode displays high electro-catalytic activity in reducing CO_2 . If the SOC is operated as an oxygen selective pump it suppresses the back reaction of CO by the electrochemical O_2 reduction reaction and transport of ionic oxygen away from the electrode surface into the electrolyte.

SOC composed of perovskite electrode material and an Yttria stabilized Zirconia (YSZ) electrolyte have shown remarkable properties that can be fully exploited in oxygen gas separation. They act as an oxygen extractor and a barrier to other species in gas mixtures when subjected to electrical potential gradients. Issues include the oxidation of CO by gaseous or lattice oxygen at the hot plasma electrode surface in competition with desired catalytic reduction of CO_2 at that surface. Furthermore, chemo-mechanical compatibility of electrode-electrolyte materials and negative oxygen ion conductivity are key parameters. The reaction kinetics of oxygen reduction $O_2 + 4e^- \rightarrow 2O^{2-}$ at the plasma electrode is influenced by both the plasma sheath electric field and the externally applied voltage across the SOC membrane. Both compete in pulling electrons out of the plasma electrode interface.

8.1. Perovskite membranes. – Lanthanum-based perovskite membranes yield superior oxygen flux values for oxygen separation. State-of-the-art materials for solid oxide fuel cells are based on an electrolyte of Yttria stabilized Zirconia (YSZ) and a Ni/YSZ cermet fuel electrode. The oxygen electrode is a $La_{0.85}Sr_{0.15}MnO_{3\pm\delta}$ (LSM) or $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF) perovskite that forms a good combination with YSZ or GDC (gadolinium-doped ceria). The Ni/YSZ fuel electrode displays excellent catalytic properties for fuel oxidation and good current collection, however, carbon deposition and poor redox cycling degrades performance. Furthermore, electrolysis of H_2O and/or CO_2 oxidises the Ni leading to NiO/YSZ which is a poor conductor and therefore not suitable for the important functionality of current collection, hence Ni/YSZ cannot be employed in our case. Current research concentrates on alternative redox stable perovskites.

One candidate material is $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ since it has comparable electrochemical performance as the Ni/YSZ cermet and is redox stable [25-27]. This material

Fig. 6. – Voltage distribution of the plasma across the plasma sheath and across the solid oxygen membrane. An externally applied electric field across the membrane transports the negative oxide ions to the oxygen electrode. Plasma-activated CO_2 , CO , O_2 molecules, radicals, atoms and plasma electrons incident on the plasma electrode and subjected to the plasma sheath electric field influence the electro-chemistry at the plasma perovskite interface, synergistically boosting CO formation and oxygen transport.

will be the starting point for the development of an efficient plasma electrode which will be inactive for CO oxidation and will exhibit oxygen separation fluxes upon mild polarization. On the oxygen side, state of the art material LSCF or LSM in combination with YSZ or GDC will be used, while YSZ will be the electrolyte.

8.2. Plasma electrochemical interaction. – Novel is the presence of plasma adjacent to the SOC cathode, see fig. 6. The plasma leads to activated species including vibrational and electronically excited molecules and atoms, radicals, ions and electrons. This will activate the chemistry at the plasma electrode interface. In addition, the positively charged plasma and the polarisation of the SOC will enhance reactivity. Preliminary hybrid plasma-SOC experiments conducted at the Tokyo Institute for Technology indicate that synergism occurs between a SOC membrane and a plasma-activated CO_2 gas, lowering the SOC operating temperature to $600^\circ C$ and improving conversion ratio as compared with pure electrolysis [28,29].

8.3. Two SOC design concepts. – Two SOC design concepts are being explored, one based on flat membranes employing heritage from Fuel Cell technology, the other based

Fig. 7. – Schematic of the oxygen separator module based on planar membranes arranged at the plasma exit in hexagonal geometry. The oxygen outlet is indicated in blue. Detail on the right hand side shows the membrane assembled into a cell. Indicated are the perovskite plasma electrode (red), electrolyte (yellow) and the oxygen electrode (green). This membrane sandwich is mechanically supported by the castellated metal surface also serving as oxygen gas transport conduit. The SOC Cell is equipped with current feed through connected to the plasma and oxygen electrodes, respectively.

on capped tubular membranes which offer intimate plasma to SOC coupling [30,9]. Requirements include gas tight separation of oxygen to plasma compartment and Galvanic isolation of the electrodes. Tubes are thermo-mechanically more stable and benefit from proven metal jointing technology. If failed, they can be individually replaced. The main issue is the fabrication of tubular membranes and their current collection. Here, the planar membrane concept offers advantage. The deposition of thin layers is simpler than for tubular membranes. Commercial Fuel Cell technology is predominantly based on the fabrication of planar membrane cells and their integration into stacks, offering a well proven technology. A conceptual design is shown in fig. 7.

At the typical plasma conditions discussed, 1.25 slm O_2 needs to be transported out of the plasma per kW power input, corresponding to 0.93×10^{-3} mole/sec. The membrane surface area required is 358 cm^2 at a typical SOC current density of 1 A/cm^2 , taking account a 4 times Faraday constant to account for $2O^{2-}$ ion transport. This figure forms the basis of membrane surface area specification of the O_2 separator.

Computational studies carried out at DIFFER assist in development of new perovskite material for the efficient separation of O_2 from the plasma CO_2 , CO , O_2 gas mixture and associated atoms, radicals, ions and electrons [31]. The strategy is to use high-throughput computation based on *ab initio* quantum chemical computation to study the performance of variant perovskite materials. Density Function Theory (DFT) can effectively approximate the electron distribution that governs fundamental physical material properties. DFT calculations will be carried out using the *Vienna Ab Initio Simula-*

Fig. 8. – Alternative scheme to oxygen separation: replace by proton feed. This option does away with the water gas shift and CO purification units, however, adds a water electrolyser unit.

tion Package (VASP) [32]. Computation is directed at newly doped quinary perovskite electrodes, that are expected to perform better than the existing electrode materials such as $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) [33, 34].

8.4. *Alternative to oxygen separation.* – A proton conducting cell [30] is employed as an alternative to oxygen separation, see fig. 8. In this approach water electrolysis occurs at the oxygen electrode and is followed by injection of protons into the plasma electrode. This is expected to lead to selective water formation at the plasma electrode interface through oxygen reduction. The intermediate operation temperature of proton conducting SOC (500–600 °C) is expected to reduce the kinetics of the undesired back reaction of CO oxidation to CO₂ at the plasma electrode. If CO oxidation kinetics dictate a further lowering of the operation temperature, the scenario of employing commercial PEM electrolyzers becomes an option. These electrochemical cells operate in the temperature range of 20–200 °C, however, at the expense of costly and less-sustainable noble metals needed for the electrode materials.

9. – Basic parameters

In order to understand the plasma chemistry of CO₂ dissociation it is useful to gain insight into the characteristic time and length scales of the weakly ionised CO₂ plasma and its interaction with the driving electro-magnetic field. This includes collision times

and mean free paths for the CO₂ gas and for the plasma constituents. For the plasma, the electric shielding distance (Debye length), plasma frequency and electro-magnetic wave dispersion add to pertinent time and length scales. Some simplified considerations will provide an order of magnitude ordering of the relevant processes.

9.1. The CO₂ molecule. – Carbon dioxide is a linear molecule exhibiting 4 vibration and 2 rotation oscillation modes: the symmetric stretch mode ($\nu, 0, 0$), the asymmetric stretch mode ($0, 0, \nu$) and two bend modes ($0, \nu, 0$) in two perpendicular directions, hence 9 degrees of freedom in total including translational motion. The radius of a CO₂ molecule is $a_0 = 0.116$ nm (the equilibrium C-O distance). The electron dissociation energy of CO₂ is $D = 5.451$ eV, the cross-section reaches a max 10^{-16} cm² above 30 eV. Similarly, the cross-section for dissociative ionisation and formation CO⁺ starts at 25 eV reaching a max 0.39×10^{-16} cm² at ~ 90 eV electron energy. The ionisation energy of CO₂ is 13.777 eV, reaching a maximum at an electron energy ~ 100 eV [17].

9.2. Spectrum of CO₂. – The absorption/emission spectrum of CO₂ vibration-rotation modes is situated in the IR, see the HITRAN database [35]. The fundamental of the asymmetric mode is found at $\lambda = 4.24\text{--}4.28$ μm (750 THz, $\tau = 14$ fs, $h\nu = 0.29$ eV) with an absorption cross-section of 1.4×10^{-17} cm²/molecule. Overtones are found at $\lambda = 2.68\text{--}2.78$ μm and $\lambda = 2.0\text{--}2.02$ μm . The fundamental of the bend mode is at $\lambda = 14.9\text{--}15$ μm with cross-section 5×10^{-18} cm²/molecule. The symmetric mode has no IR transition (no dipole).

Electronic excitations in the eV range produce optical emission of the molecules involved [36]. The CO₂ term scheme, representing the electronic energy levels, is given by [37]. As it turns out, there is no emission of CO₂ in the UV visible. Only in the far UV 140–160 nm some weak absorption bands exist. Emission of CO₂⁺ exist for the transitions $A^2\Pi_u > X^2\Pi_g$ at 393.3–438.4 nm and $B^2\Sigma_u^+ > X^2\Pi_g$ at 218.9–226.8 nm [36]. These emissions have not been observed in our experiments.

9.3. Emission spectra of CO, C₂, O, O₂ reaction products. – These spectra, by contrast, exhibit emission spectra in the UV-visible. The CO molecule energy diagram is given in [38]. In our experiments, the UV 4th positive singlet system $A^1\Pi > X^1\Sigma^+$ (200–250 nm) and 3rd positive and 5B triplet system $b^3X^+ > a^3\Pi$ (260–390 nm) have been identified. In the visible, the Ångström singlet $B^1\Sigma^+ > A^1\Pi$ and the Triplet system $d^3\Pi > a^3\Pi$ (400–650 nm) are also observed. A shift from 3rd and 4th positives to the Ångström and Triplet system is observed at high gas pressure. The plasma turns from pale blue (Type I) to intense white (Type II).

The C₂ Swan band has been observed in the same spectral interval (430–620 nm) as the CO Ångström and Triplet bands, showing further decomposition of CO₂ to carbon taking place.

Molecular oxygen O₂ has a number of absorption and emission bands in the vis-NIR range, notably the oxygen absorption bands at 680–690 nm and 760–764 nm and the emission band at 1.27 μm [35]. These lines are outside the spectral range (< 725 nm) of

the OES spectrometer, hence not observed in our experiments. Unfortunately, also the 680 nm oxygen line is not observed.

Atomic oxygen lines $^3D^0$ and $^5D^0 > ^5P$ around 615 nm are observed in the measured spectrum. These small peaks are only measurable in the high-reduced E -field condition. At low reduced E -field the Swan band outshines them. Atomic oxygen spectral lines could elucidate their vibrational origin, deriving either from the $O(^1D)$ state or the lower energy $O(^3P)$ dissociation branch of CO_2 . The $O(^1D) 2p^4$ transition to ground state $O(^3P)$ has an emission at 636 nm, whilst $O(^3P)3s$ to $O(^3S)$ has an emission at 844.7 nm [39]. Unfortunately, these lines could not be identified from our measurements.

In conclusion, the CO molecule produced in the CO_2 dissociation process is in the $X^1\Sigma^+$ singlet ground state. Hence, no electronic emission representing this state is available. Atomic oxygen produced is either in the ground state $O(^3P)$ or in the excited state $O(^1D)$. A transition from the excited singlet D level to the ground state would reveal its origin. The line corresponding to $^1D \rightarrow ^3P$ at 630 nm has not been observed. Similarly, transitions $^5S^0$ and $^3S^0$ to the 3P ground level at wavelength 130 and 135 nm, respectively, would produce tell-tale signs, but are not within spectral range of the spectrometer and anyway are blocked by absorption in air. Hence, all CO and O lines observed result from direct excitation by plasma electrons and not from vibrational excited CO_2 energy levels.

9.4. The microwave field. – The electro-magnetic field in the cylindrical cavity is in the TM_{010} mode, hence the electric field maximises on-axis to which it is aligned. A typical electric field strength on axis of the RF cavity calculated by COMSOL is $E = 27 \text{ kV/m}$ @ 915 MHz and $P_{\text{RF}} = 3 \text{ kW}$ [19]. The distance travelled by an electron accelerated in vacuum by this E -field during the half cycle $\tau = 0.546 \text{ ns}$, is $s = 1/2(eE/m)t^2 \sim 720 \mu\text{m}$. By contrast, CO_2^+ ions move only 9 nm, remaining essentially stationary during RF-field oscillation. The speed acquired by electrons in this half cycle ($v = at$) becomes $v = 2.6 \times 10^6 \text{ m/s}$, equivalent to an energy of $\sim 20 \text{ eV}$.

The de Broglie wavelength $\lambda = h/p$ of a 20 eV electron is 0.28 nm, hence of the size of the CO_2 diameter (0.232 nm). Above this energy, the electrons start seeing individual atoms, rendering them ineffective for excitation of molecular vibration.

9.5. Electron- CO_2 gas collisions. – The cross-sections of vibrational excitation of a CO_2 molecule by electrons at around 1 eV electron energy is of order $\sim 10^{-16} \text{ cm}^2$ for all modes, dominated by the asymmetric stretch mode. The cross-section for the asymmetric mode peaks at 0.4 eV and drops characteristically as $\sigma \approx 1/v$ with increasing energy [17]. This implies a constant collision frequency for the asymmetric stretch mode over the range from 0.5 to over 30 eV electron energy.

Considering the total collision cross-section for electrons in CO_2 , $\sigma_{\text{tot}} \sim 10^{-15} \text{ cm}^2$, the mean free path $\lambda_{\text{tot}} = 1/n\sigma_{\text{tot}}$ at low pressure Type I discharge (1 mbar) is $\lambda_{\text{tot}} \sim 370 \mu\text{m}$, *i.e.* $\lambda_{\text{tot}} \approx s$ at low pressure Type I discharge and the electron is able to gain relatively high energy between collisions.

TABLE III. – Characteristic time scales and lengths of the electron neutral CO₂ gas interaction.

P mbar	τ_{exc} fs	τ_{vib} fs	τ_{tot} ps	τ_{ev} ps	τ_{nn} ns	λ_{nn} μm	λ_{ev} μm	λ_{tot} μm	s μm
1	0.39	14@	62	12E3	130	50	74E3	370	720@
100		$\lambda = 4.2 \mu\text{m}$	6	62	1.3	0.5	37	3.7	$E = 27 \text{ kV/m}$

At high-pressure Type II discharges ($> 100 \text{ mbar}$), the situation is very different since $\lambda_{\text{tot}} \approx 4 \mu\text{m}$ and therefore $\lambda_{\text{tot}} \ll s$, *i.e.* the electron is never able to pick up speed between collisions. At less than 1/100 of the RF cycle, the electron is knocked off-course by collision with a CO₂ molecule. A constant drift velocity establishes with $v_{\text{D}} \approx E\lambda \approx E/n$, where the proportionality factor is the electron mobility defined as $\mu = e/(mv)$.

The interaction time of an electron with a CO₂ molecule $\tau_{\text{exc}} = 2a_0/v_e = 0.39 \text{ fs}$ for a 1 eV electron ($v_e = 5.93 \times 10^5 \text{ m/s}$), is much faster than the vibration time $\tau_{\text{vib}} = 14 \text{ fs}$ ($\sigma = \pi/4a_0^2 \approx 10^{-16} \text{ cm}^2$). Hence, the molecule can be regarded as frozen during the inelastic electron collision; the Frank-Condon principle applies. The electron acts as a clapper ringing the CO₂ molecular bell.

The electron neutral collision time follows from the total cross-section averaged over the electron velocity distribution $\tau_{\text{etot}} = 1/n\langle\sigma_{\text{tot}}v_e\rangle$ yielding $\tau_{\text{tot}} = 6 \text{ ps}$ at $p = 100 \text{ mbar}$ and 1 eV electron energy. Similarly, for the excitation of the asymmetric vibration mode the electron collision time becomes $\tau_{\text{ev}} = 60 \text{ ps}$ at $p = 100 \text{ mbar}$, both much smaller than the RF oscillation time.

The mean free path for inter-molecular CO₂-CO₂ collision at 300 K is $\lambda_{\text{nn}}[\text{m}] = 4.5 \times 10^{-5}/p [\text{mbar}]$. At a pressure of 1 mbar (Type I discharge) this yields a mean free path $\lambda_{\text{nn}} = 50 \mu\text{m}$. At a pressure of 100 mbar $\lambda_{\text{nn}} = 0.5 \mu\text{m}$. This path length results in a collision time with $T_{\text{gas}} = 300 \text{ K}$ ($v_{\text{th}} = 378 \text{ m/s}$) of $\tau_{\text{nn}} = \lambda_{\text{nn}}/v_{\text{th}} = 130 \text{ ns}$ at 1 mbar and $\tau_{\text{nn}} = 1.3 \text{ ns}$ at 100 mbar. These times become a factor 3 shorter at $T_{\text{gas}} = 3000 \text{ K}$ and another factor 5 at a pressure of 500 mbar, more typical for the Type II discharge. Hence, typical n - n collision times of Type II discharges are $\tau_{\text{nn}} < 0.1 \text{ ns}$, *i.e.* shorter than the oscillation period. The interaction time of two CO₂ molecules is $\tau_{\text{int}} = 4a_0/v_{\text{th}} = 1.2 \text{ ps}$, *i.e.* slow compared with the vibration oscillation time. Interacting molecules are locked together for some 100 vibrations.

Results on characteristic times and mean free path calculations are summarised in table III, leading to the following ordering in time and length scales pertaining to the CO₂ plasma discharge:

$$\tau_{\text{exc}} \ll \tau_{\text{vib}} \ll \tau_{\text{int}} \ll \tau_{\text{etot}} \ll \tau_{\text{ev}} \ll \tau_{\text{nn}} \ll \tau_{\text{osc}}.$$

Inter-molecular energy exchange acts on a time scale much longer than the electron-molecule collision time scale. However, electrons are light and not very effective in transferring energy to molecules. When two CO₂ molecules collide the energy exchange is a factor $2M/m \sim 10^5$ larger and, albeit less frequent (factor 20 to 5000), neutral-neutral collisions dominate the rate of energy transfer between molecules.

Once the CO₂ molecule is vibrational excited in the ground state $^1\Sigma^+$ by high rate electron impact, it needs to climb the vibration energy ladder in order to overcome the dissociation threshold energy of 5.5 eV. The necessary energy derives from the kinetic energy of intermolecular CO₂-CO₂ collision. Energy is transferred in high-energy vibration modes at points where the nuclear coordinates of the different molecular energy levels match according to the Frank-Condon principle. This VV exchange process populates the higher 1B_2 vibration energy levels of the CO₂ molecule. It is the limiting factor in the rate of dissociation [15]. Thus, CO₂ molecular bells, gently but repeatedly twanged by electrons, chime in unison until occasionally crashing into each other, transferring sufficient energy to ring overtones. Overtones of sufficiently high energy break the bell.

9.6. Plasma parameters. – The degree of ionisation is a critical parameter in the dissociation of CO₂ for being the source of electrons that are instrumental in vibrational excitation and subsequent dissociation. The relaxation efficiency η_{VT} is defined as the fraction of vibration energy going into dissociation over the fraction going into translation energy [15]. Thus, relaxation efficiency η_{VT} must be high for effective dissociation. It increases with the degree of ionisation in the discharge at fixed energy input. At an input energy of $E_v = 0.5$ eV per molecule CO₂ and an ionisation degree $n_e/n_0 = 10^{-6.5}$ the relaxation efficiency $\eta_{VT} = 40\%$. This increases to $\eta_{VT} = 80\%$ for ten times higher ionisation degree $n_e/n_0 = 10^{-5.5}$. At a neutral density $n_0 = 5.38 \times 10^{18} \text{ cm}^{-3}$ (pressure of 200 mbar) and an electron density $n_e = 1.7 \times 10^{13} \text{ cm}^{-3}$, a relaxation efficiency $\eta_{VT} = 80\%$ is reached. In RF discharges, the energy efficiency peaks at $E_v = 0.8\text{--}1$ eV [15]. Optimum energy efficiency for CO₂ dissociation is reached at $E_v = 0.5$ eV and an ionisation degree $n_e/n_0 \sim 10^{-5}$.

Since the degree of ionisation is important for efficient dissociation of CO₂, plasma parameters add to characteristic time and length scales relevant to the activation system. These parameters include Coulomb collisions, Debye length and plasma frequency.

Coulomb collision times vary as $(m^{1/2}T^{3/2})/n$. Hence, at low electron temperature and high plasma density these times become remarkably short, nearing neutral collision times. Times for electrons relate to times for ions as $\tau_e = (m_e/m_i)^{1/2}\tau_i$. Hence, electron-electron collision times are a factor 3.5×10^{-3} shorter than CO₂ ion-ion collision times. On the other hand, collision times between electrons and ions are approximately equal to the electron-electron collision times: $\tau_{ei} = 2\sqrt{2}\tau_{ee}$. Thus, the following ordering in Coulomb times results: $\tau_{ee} \approx \tau_{ei} \ll \tau_{ii}$, showing that electrons relax by mutual collision much faster than ions. As shown before, Coulomb collisions do not play a role in plasma thermalisation, the plasma is electron-neutral collision dominated.

Coulomb collision times are calculated from the Spitzer formula, including a weak dependence on the Coulomb logarithm $\ln \Lambda$, varying from 7 to 15 in the parameter range considered. The Coulomb logarithm represents the screening of a test particle by the plasma at distances greater than the Debye length, yielding small angle scattering as the dominant collision mechanism,

$$\tau_{ei} = 3(2\pi)^{3/2} \left\{ \varepsilon_0^2 m_e^{1/2} T_e^{3/2} \right\} / \left\{ n_i (Ze^2)^2 \ln \Lambda \right\}.$$

TABLE IV. – *Electron-ion Coulomb collision times τ_{ei} vs. electron temperature and ion density.*

n_i	$T_e = 0.1 \text{ eV}$	$T_e = 1 \text{ eV}$	$T_e = 10 \text{ eV}$	$T_e = 100 \text{ eV}$
10^{18} m^{-3}	$\tau_{ei} = 1.3 \text{ ns}$	$\tau_{ei} = 32 \text{ ns}$	$\tau_{ei} = 840 \text{ ns}$	$\tau_{ei} = 23 \mu\text{s}$
10^{19} m^{-3}	$\tau_{ei} = 0.15 \text{ ns}$	$\tau_{ei} = 3.6 \text{ ns}$	$\tau_{ei} = 92 \text{ ns}$	$\tau_{ei} = 2.5 \mu\text{s}$

Results of the Coulomb collision time τ_{ei} and τ_{ii} calculation are shown in table IV and table V, respectively.

Hence, electron-ion Coulomb collision times are longer than electron neutral collision times, even for a cold, dense plasma. Also, the Coulomb collision times are longer than the RF oscillation time. Only collisions with neutrals play a role, the plasma is neutral collision-dominated, but essentially collision-free for electron and ion collisions mutually.

The Coulomb collision mean-free path follows from $\lambda = v_{th}\tau$ with $1/2 mv_{th}^2 = kT$. For the same temperature $\lambda_{ee} = \lambda_{ii}$. Results are shown table VI.

For low T_e and high density the mean free path becomes of order plasma dimension. Otherwise, no Coulomb collision takes place inside the plasma volume.

The Debye length is given by $\lambda_D = \sqrt{(\epsilon_0 kT)/(ne^2)}$. Results are tabulated in table VII.

For most conditions the Debye screening length is $< 10 \mu\text{m}$, *i.e.* small compared with the plasma dimension. For a collisional plasma the skin depth becomes the relevant parameter, depending on the plasma resistivity.

The number of particles in a Debye sphere is given by $N_D = 4/3\pi\lambda_D^3 n_e$. Results are tabulated in table VIII. Hence, at low T_e there are very few particles contained in a Debye sphere in this type of plasma.

Plasma frequency is defined as $\omega_{pe}^2 = n_e e^2 / \epsilon_0 m_e$. Results are tabulated in table IX.

The RF frequency (915 MHz) is lower than the plasma frequency. Hence, the wave cannot propagate. The wave can propagate when collisions are included. The plasma permittivity $\epsilon(\omega) = 1 - \omega_{pe}^2 / \omega^2 \{1 - i\nu/\omega\}$ contains the factor $i\nu/\omega$, where ν is the electron neutral collision frequency. Since this ratio is generally larger than 1, the electric field in the RF cavity is displaced by the plasma.

9.7. Plasma chemistry. – The reaction proceeds in two steps, starting with CO_2 in the $^1\Sigma^+$ ground state, excited by electron impact to low-level vibrational energy [15]:

TABLE V. – *Ion-ion Coulomb momentum transfer-time τ_{ii} .*

n_i	$T_i = 0.1 \text{ eV}$	$T_i = 1 \text{ eV}$
10^{18} m^{-3}	$\tau_{ii} = 287 \text{ ns}$	$\tau_{ii} = 9.1 \mu\text{s}$
10^{19} m^{-3}	$\tau_{ii} = 32 \text{ ns}$	$\tau_{ii} = 1 \mu\text{s}$

TABLE VI. – Mean free path $\lambda_{ee/ii}$ Coulomb interaction.

n_i	$T_e = 0.1\text{ eV}$	$T_e = 1\text{ eV}$	$T_e = 10\text{ eV}$
10^{18} m^{-3}	$\lambda_{ee/ii} = 238\text{ }\mu\text{m}$	$\lambda_{ee/ii} = 13.8\text{ mm}$	$\lambda_{ee/ii} = 1.5\text{ m}$
10^{19} m^{-3}	$\lambda_{ee/ii} = 27.5\text{ }\mu\text{m}$	$\lambda_{ee/ii} = 2.1\text{ mm}$	$\lambda_{ee/ii} = 0.17\text{ m}$

The higher CO₂ vibrational energy level 1B_2 is reached by molecular V-V relaxation. Activation energy is lowered by a non-adiabatic singlet 1B_2 to triplet 3B_2 spin transition. This happens at the point where energy level and molecular distance of the O=CO bond coincide. It allows molecular break-up at minimum 5.5 eV energy, leaving CO and O formed in the ground electronic state.

The atomic oxygen radical produced follows up by a second reaction with abundantly available CO₂ producing one more CO molecule at 0.3 eV net energy, additional energy being freed by recombination of atomic oxygen into molecular oxygen at 5.2 eV:

The three-body recombination reaction of atomic oxygen to O₂ has a much lower rate coefficient as compared with the reaction with CO₂. The two reactions in succession yield a net enthalpy for the production of one CO molecule $H = 5.8/2 = 2.9\text{ eV}$, the limiting stage being reaction (1).

10. – Reduced electric field

Electrons gain energy by the applied electric field and are scattered by CO₂ molecules that can be considered stationary (Lorentzian gas). A steady-state electron drift sets up with velocity v_D proportional to the applied electric field with proportionality constant μ_e , the electron mobility. The velocity acquired between collisions is $v_D = (eE/m_e)\tau_{en}$, where $\tau_{en} = (n_0\sigma_{en}v_D)^{-1}$ is the collision time. Combination yields the energy U_e gained by electrons between collisions

(3)

$$U_e = 1/2\,m_e v_D^2 = 1/2\,eE/(n_0\sigma_{en}) = 1/2\,eE\lambda_{en},$$

TABLE VII. – Debye length λ_D .

n_e	$T_e = 0.1\text{ eV}$	$T_e = 1\text{ eV}$	$T_e = 10\text{ eV}$
10^{18} m^{-3}	$2.35\text{ }\mu\text{m}$	$7.45\text{ }\mu\text{m}$	$23.5\text{ }\mu\text{m}$
10^{19} m^{-3}	$0.75\text{ }\mu\text{m}$	$2.35\text{ }\mu\text{m}$	$7.45\text{ }\mu\text{m}$

TABLE VIII. – *Number of particles N_D in a Debye sphere.*

N_D	$T_e = 0.1 \text{ eV}$	$T_e = 1 \text{ eV}$
10^{18} m^{-3}	54	1720
10^{19} m^{-3}	17	550

where λ_{en} is the electron neutral mean free path. This expression yields a relation between electron energy and the reduced electric field:

$$(4) \quad U_e = e/(2\sigma_{\text{en}})\{E/n_0\}.$$

This expression permits calculation of the reduced electric field for a given electron energy. For example, the cross-section for vibrational excitation of the CO_2 asymmetric stretch mode peaks at an electron energy of 0.4 eV where the cross-section is $\sigma_{\text{en}} = 1.8 \times 10^{-16} \text{ cm}^2$ [16]. Substitution yields $E/n_0 = 1.4 \times 10^{-16} \text{ V cm}^2$ for the reduced electric field value, where vibrational excitation by electrons is maximum. This value corresponds with Russian theory [15].

Through collisions the electrons randomise and, albeit non-Maxwellian, could be assigned a temperature. Since $U_e = 3/2kT_e$ the expression for the reduced electric field yields

$$(5) \quad kT_e = e/(3\sigma_{\text{en}})\{E/n_0\}.$$

Hence, a linear relation exists between electron temperature and reduced electric field, which is useful in relating measured plasma parameters to the reduced electric field. The above expression differs from [15] by a numerical factor, which takes into account inelastic energy loss during electron randomisation.

11. – Energy efficiency for CO_2 splitting

Energy efficiency is defined as $\eta = H/E_{\text{CO}}$, where $H = 2.9 \text{ eV}$ is the minimum net enthalpy required for the production of one CO molecule from CO_2 input gas flow and E_{CO} is the actual energy expended per CO molecule produced. Measured is E_v , the energy input per incoming CO_2 molecule, which is proportional to input power P_{RF} over gas flow rate Q or $E_v \approx P_{\text{RF}}/Q$. The fraction of CO_2 converted into CO is $\alpha = [\text{CO}]_{\text{out}}/[\text{CO}_2]_{\text{in}}$. Since the input energy E_v is distributed over CO_2/α molecules to

TABLE IX. – *Plasma frequency as a function of plasma density.*

n_e	$\nu_{\text{pe}} = 8.967\sqrt{n_e}$
10^{18} m^{-3}	$\sim 9 \text{ GHz}$
10^{19} m^{-3}	$\sim 28 \text{ GHz}$

produce one CO molecule, it holds that $E_v = \alpha E_{co}$. Since both α and E_v are amenable to measurement, the energy efficiency η becomes expressed in measured quantities:

$$(6) \quad \eta = CQ/P_{RF} = \alpha H/E_v.$$

Here, C is a constant of numerical factors, in this case $C = 1.93 \times 10^2$ at 300 K. The conversion factor α is determined experimentally from mass analysis of the exit gas stream and supported by spectral line strength measurement. Measured values of η *vs.* E_v are plotted in figs. 11, 12 and 13 applying eq. (6).

12. – Plasma particle balance

Plasma is created by electron ionisation of the CO₂ gas and lost by ambipolar diffusion up to the sheath edge where the ions reach the Bohm velocity. The Bohm velocity is a result of the overriding need for plasma neutrality, which requires fluxes of ions and electrons out of the plasma to be equal. Equating production and loss, the steady-state particle balance is obtained. Since production by ionisation is a volume process and loss by diffusion a surface process, the gas density n_0 and the plasma radius R , are coupled parameters:

$$(7) \quad 2v_B = n_0 \langle \sigma_{ion} v \rangle R \approx \sqrt{(E/n)}$$

here $v_B = \sqrt{2kT_e/m_i}$ is the Bohm velocity and $\langle \sigma_{ion} v \rangle$ the ionisation rate averaged over the electron velocity distribution, whilst use is made of eq. (5) to relate electron temperature to the reduced electric field. The ionisation rate increases proportionally with the reduced electric field. This expression shows the plasma discharge radius to contract with increasing gas pressure. This phenomenon has been observed experimentally in the transition of going from Type I discharge at low pressure (1 mbar), see fig. 9, to Type II discharge at high pressure (100 mbar), see fig. 5b).

Put differently, the loss of the plasma can be expressed in a plasma electron containment time τ_e as

$$(8) \quad \tau_e \sqrt{(E/n)} \approx R.$$

Hence, increasing electron containment—which is good because ionisation is energetically expensive—lowers the reduced electric field for fixed plasma radius and thereby increases energy efficiency.

The energy balance yields an expression for the electron density n_e

$$(9) \quad P_{RF} = n_e \Sigma_i n_0 \langle \sigma_i v \rangle \Delta \varepsilon_i V,$$

where σ_i represents vibration, excitation and ionisation cross-sections summed, causing an electron energy loss $\Delta \varepsilon_i$, V is the volume of the discharge. The above equations

Fig. 9. – Typical Type I discharge with nozzle placed at the entrance of the discharge, characterised by 1 mbar pressure. After expansion striations are visible indicating shock fronts, a tell-tale sign of supersonic flow.

yield basic gas discharge parameters. Typically, the plasma density is in the range 10^{18} – 10^{19} m^{-3} , ionisation degree 10^{-6} to 10^{-5} and electron temperature in the range 1 to 10 eV.

13. – Vortex flow

Gas is injected tangentially at the entrance of the cylindrical reaction chamber through a small orifice where it accelerates and expands. A strong spiralling gas flow is established along the chamber wall, causing a radial pressure and temperature gradient to build up. This type of flow has been exploited in the Ranque-Hilsch cooling machine [40,41]. In our case it provides stability of the plasma discharge.

In axial direction, flow is directed through a nozzle after which the gas expands and cools. When the exit pressure is low enough this flow reaches a maximum, called choked flow. Under this condition, in the throat of the nozzle, the gas velocity reaches the speed of sound c_s or Mach $M = 1$. Beyond, the velocity increases and becomes supersonic at the exit of the reaction chamber leading to shock waves to form, see fig. 9. At these sonic gas speeds the vortex rotates at high frequency, 300000 r.p.m. is not unusual. The resulting centrifugal acceleration typically reaches $10^6 g$ at the wall of the reactor vessel.

Assuming $M = 1$ in the throat of the nozzle, *i.e.* choked flow, the gas velocity equals the speed of sound. The gas flow velocity v_F follows from $nv_F O = F$, *i.e.* $v_F = F/nO = (kT/p)(F/O)$, assuming an ideal gas. For $v_F = c_s$ to hold, the relation between temperature and gas pressure becomes: $kT = \gamma/m_i(pO/F)^2$, where $\gamma = (i + 2)/i = 11/9 = 1.222$, the number i being the 9 degrees of freedom of the CO_2 molecule. Converting F from particles/sec to slm, using $F = N_A F_{\text{slm}}/(60 * 24) \text{ s}^{-1}$ yields $T = 6.93 * 10^6 \{pO/F_{\text{slm}}\}^2$. As a consequence, at constant flow, the gas pressure scales $p \sim 1/\sqrt{T}$. The pressure is seen to increase linearly with power; hence the gas temperature T increases with power. Gas temperature values ranging between $T = 500^\circ\text{C}$ and 3000°C have been calculated in this way.

Fig. 10. – The CO 3rd positive triplet band is shown to increase linearly with gas pressure, consistent with CO production rates.

14. – Experimental results

Three types of discharge have been investigated at constant input CO₂ gas flow rate of 11.1 slm:

Type I gas expansion nozzle, 10 mm diameter is placed at the entrance of the cavity expanding the gas into the discharge. Typical gas pressure 1 mbar is characterised by high $E/n \sim 100 \times 10^{-16} \text{ V cm}^2$. Typical energy efficiency $\eta = 15\%$ is found constant with power and particle conversion α increases linearly with power. OES shows dominance of 3rd and 4th positive CO bands to increase linear with power.

Type II gas expansion nozzle is placed at the exit of the cavity freely expanding the converted gas stream. The high-pressure 200 mbar gas discharge is characterised by low $E/n \sim 10^{-16} \text{ V cm}^2$. The discharge diameter contracts with higher pressure in accord with eq. (7), see fig. 5b). Typical energy efficiency $\eta = 35\%$ increases by reducing power. Particle conversion increases with power from 10% upward. The OES is dominated by the CO Ångström and CO Triplet system, see fig. 5d), whilst the Swan system reveals carbon.

Type III exit nozzle diameter has been increased in steps from 5 mm, to 10 mm, to 26 mm diameter. This type of discharge is characterised by an intermediate reduced electric field regime $E/n \sim 10 \times 10^{-16} \text{ V cm}^2$. Intermediate energy efficiencies result.

In order to increase energy efficiency, Type II high-gas-flow experiments are repeated at increased gas flow rate of 75 slm and 3 kW absorbed power, reaching record high energy efficiency $\sim 50\%$ albeit at low conversion fraction 10%, as expected from eq. (6). Power density is typically 45.5 W/cm^3 . At 200 mbar the CO output flow becomes 20 A/cm^2 equivalent.

Fig. 11. – Energy efficiency and particle conversion in terms of energy E_v per incoming CO₂ molecule obtained from variation of RF power. Data are constrained by stoichiometric fit, taking the O₂ data as reference for not suffering from cracking products produced inside the QMS.

Fig. 12. – shows energy efficiency and particle conversion in terms of energy E_v [eV/mol] per incoming CO₂ molecule, obtained from variation of gas flow rate extending the data range of fig. 11. Conversion ratios of 70% are reached at reduced energy efficiency. A stoichiometric constrained fit is applied.

Fig. 13. – Energy efficiency η for CO production increases by lowering the energy E_v per incoming CO_2 molecule.

Increasing the input microwave power P_{RF} at constant flow rate Q shows an approximate linear increase in particle conversion ratio $\alpha = aP_{\text{RF}}$ for all types of discharge, see fig. 5c). Since $E_v/H \sim P_{\text{RF}}/Q$, where E_v is the energy expended per incoming CO_2 molecule expressed in units of H , the minimum enthalpy, it follows that $\alpha \approx (E_v/H)Q$. Since the energy efficiency $\eta = H/E_{\text{co}} = \alpha(H/E_v) \approx P_{\text{RF}}(H/E_v) = Q$, it follows that at constant flow rate the energy efficiency is constant with power. In reality there are deviations to linearity of conversion ratio, which explains that calculated energy efficiencies show a slight increase at low power.

Fig. 14. – Lowering the reduced electric field E/n is key to increased energy efficiency η (left) but goes at the expense of the conversion fraction α , consistent with E_v values below the dissociation energy (right).

The CO emission line strength is shown to increase linearly with RF power, confirming the QMS data, see fig. 10. Similarly, with gas pressure the line strength is seen to increase linearly.

14'1. Energy efficiency. – Plotting CO conversion data as a function of input power, fig. 5c) and similar for gas flow variation, in terms of specific energy E_v per CO₂ molecule yields figs. 11 and 12. The typical energy efficiency 50% obtained reduces with increase of power, whilst the conversion to CO increases linearly with power.

14'2. Reduced electric field. – The electric field has been calculated by Comsol Multiphysics simulation program [19]. The vacuum field strength on axis of the cavity is $E[\text{V/cm}] = 4.965\sqrt{P_{\text{RF}} [\text{W}]}$. Since the microwave frequency is much lower than the cut-off plasma frequency, power is absorbed by e-n collisions in the plasma. At the plasma density considered the E -field skin depth still penetrates the plasma on axis, albeit at reduced strength. These aspects have been ignored in the E estimate.

Results are collated in figs. 13 and 14. The trend suggests that higher efficiencies may be obtained at lower E/n values. Here, conflicting requirements on sustaining the gas discharge requiring $T_e > 1 \text{ eV}$ and low E/n values requiring $T_e < 1 \text{ eV}$ need to be accommodated, suggesting decoupling of requirements necessary. This may be achieved by a double humped electron energy distribution function (EEDF). Energy efficiency goes up with decreasing energy E_v per incoming CO₂ molecule, whilst particle conversion goes down. This result is consistent with eq. (6) and is tantamount to saying that the available energy per input CO₂ molecule needs to be concentrated in one out of many CO₂ molecules in order to accumulate sufficient energy to attain the net 2.9 eV dissociation energy.

REFERENCES

- [1] United Nations Framework Convention Climate Change, http://unfccc.int/paris_agreement/items/9485.php.
- [2] RED 2009/28/EC, <https://ec.europa.eu/energy/en/consultations/preparation-new-renewable-energy-directive-period-after-2020>.
- [3] MOHR A. and RAMAN S., *Energy Policy*, **63** (2013) 114; SEARLE S. Y. and MALINS C. J. Proc. 20th Eur. Bio. Conf. & Exh., Milan, Vol. **53**, (2012).
- [4] A European Strategy for Low-Emission Mobility SWD(2016) 244 final, Brussels, 20.7.2016 COM(2016) 501 final.
- [5] UN International Civil Aviation Organisation, http://www.icao.int/Meetings/a39/Documents/Resolutions/a39_res_prov.en.pdf.
- [6] BMU Leitstudie 2012 by DLR, IWES, IFNE.
- [7] GROND L. J. *et al.*, DNV-KEMA report GCS 13.R.23579 (2013), www.energieia.nl/docs/P2G_ECN_2014.pdf.
- [8] E&E Consultants, Etude portant sur l'hydrogene et la methanation comme procédé de valorisation de l'électricité excédentaire, Hespul, Solagro (2014).

- [9] KEROGREEN, EU H2020 funded project 763909 “*Production of Sustainable aircraft grade Kerosene from Water and Air powered by Renewable Electricity through the splitting of CO₂, formation of Syngas and Fischer-Tropsch synthesis*” by DIFFER, KIT, VITO, HyGear, CerPoTech and INERATEC, see <https://www.differ.nl/network/kerogreen>.
- [10] CARMO M., FRITZ D. L., MERGEL J. and STOLTEN D., *Int. J. Hydrogen Energy*, **38** (2013) 4901.
- [11] JENSEN S. H., SUN X., EBBESEN S. D., KNIBBE R. and MOGENSEN M., *Int. J. Hydrogen Energy*, **35** (2010) 9544.
- [12] ZHENG Y., WANG J., YU B., ZHANG W., CHEN J., QIAO J. and ZHANG J., *Chem. Soc. Rev.*, **46** (2017) 1427.
- [13] IRVINE J. T., NEAGU D., VERBAEKEN M.C., CHATZICHRISTODOULOU C., GRAVES C. and MOGENSEN M. B., *Nature Energy*, **1** (2016) 15014.
- [14] LEGASOV V. A. *et al.*, *Dokl. Akad. Nauk.*, **238** (1978) 66, *Sovj. Phys. Dokl.*, **23** (1978) 66.
- [15] RUSANOV V. D., FRIDMAN A. A. and SHOLIN G. V., *Sov. Phys. Usp.*, **24** (1981) 447, *Usp. Fiz. Nauk.*, **134** (1981) 185.
- [16] ITIKAWA Y., *J. Phys. Chem. Ref. Data*, **31** (2002) 749.
- [17] AZIZOV R. I., VAKAR A. K., ZHIVOTOV V. K., KROTOV M. F., ZINOV’EV O. A., POTAPKIN B. V., RUSANOV A. A., RUSANOV V. D. and FRIDMAN A. A., *Sov. Phys. Dokl.*, **28** (1983) 567.
- [18] LEINS M. *et al.*, 31th Int. Conf. Phen. in Ionized Gases, Granada (2013).
- [19] LEINS M., Thesis, Ch 2.3.2 (2010), Universität Stuttgart.
- [20] GOEDE A. P. H. and VAN DE SANDEN M. C. M., *Europhys. News*, **47**, issue No. 3 (2016) 22, <http://dx.doi.org/10.1051/epn/2016304>.
- [21] GOEDE A. P. H. *et al.*, *EPJ Web of Conferences*, **79** (2014) 01005, DOI:10.1051/epjconf/20147901005.
- [22] GOEDE A. P. H., *Joint EPS-SIF International School on Energy*, edited by CIFARELLI L. and WAGNER F. (SIF, Bologna) 2015, pp. 357-380, ISBN 978-88-7438-094-7.
- [23] NIGHAN W. L., *Phys. Rev. A*, **2** (1970) 1989.
- [24] DIOMEDE PAOLA, DIFFER communication.
- [25] TSAMPAS M. N. *et al.*, *Cat. Sci. Techn.*, **5** (2015) 4884, <http://dx.doi.org/10.1039/C5CY00739A>.
- [26] SAPOUNTZI F. M. *et al.*, *Solid State Ionics*, **277** (2015) 65, <http://dx.doi.org/10.1016/j.ssi.2015.05.003>.
- [27] VERNOUX P. *et al.*, *Chem. Rev.*, **113** (2013) 8192, <http://dx.doi.org/10.1021/cr4000336>.
- [28] TAGAWA Y. *et al.*, *Kagaku Kogak Ronbunshu*, **37** (2011) 114.
- [29] TUN L. L., MATSUURA N. and MORI S., *22nd Int. Symp. Plasma Chemistry* (2015) p. O-15-3.
- [30] TSAMPAS MIHALIS, DIFFER Internal Communication.
- [31] SULEYMAN E. R., DIFFER Internal Communication.
- [32] KRESSE G. and FURTHMULLER J., *Phys. Rev. B*, **54** (1996) 11169, DOI:10.1103/PhysRevB.54.11169.
- [33] TAO S. and IRVINE J. T. S., *Nat. Mater.*, **2** (2003) 320, DOI:10.1038/nmat871.
- [34] YUE X., ARENILLAS A. and IRVINE J. T. S., *Faraday Discuss*, **190** (2016) 269, DOI:10.1039/C6FD00001K.
- [35] HITRAN (2004) Harvard Smithsonian, Cambridge, <http://vpl.astro.washington.edu/>.
- [36] PEARSE R. W. B. and GAYDON A. G., *The Identification of Molecular Spectra*, 4th edition (Chapman and Hall) 1976, pp. 109–112.
- [37] HERZBERG G., *Spectra of Polyatomic Molecules*, Vol. **III** p. 503, CO²⁺ energy diagram.

- [38] HERZBERG G., *Molecular Spectra and Molecular Structure*, Vol. **1** *Spectra of Diatomic Molecules*, 2nd edition, p. 452.
- [39] HERZBERG G., *Atomic Spectra and Atomic Structure* (Dover books) 2010, p. 163.
- [40] LIEW R., ZEEGERS J. C. H., KUERTEN J. G. M. and MICHALEK W. R., *Phys. Rev. L*, **109** (2012) 054503.
- [41] LIEW R., ZEEGERS J. C. H., KUERTEN J. G. M. and MICHALEK W. R., *Exp Fluids*, **54** (2013) 1416.