

# Water and Carbon Dioxide

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## New Sources of Synthetic Fuels



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## EXECUTIVE SUMMARY

The depletion of fossil oil reserves, constant uncertainties as far as price is concerned, unsecured supplies and environmental pollution are among the energy problems that drive humanity in the development of alternative and more ecologically friendly fuels. In this report the production of synthetic fuels from water and CO<sub>2</sub> with the use of renewable energies is discussed. Producing fuels out of synthetic gas is a process that has been developed since the 1930s, however the development of renewable energies and technology on CO<sub>2</sub> capturing has made the idea of producing neutral CO<sub>2</sub> fuels more attractive. Firstly, the most dominant methods for the production of synthetic fuels are presented, which are hydrogenation, photocatalysis, electroreduction and biomass. Furthermore, their potential, their advantages and disadvantages, their state of development and their future possible evolution are highlighted. Afterwards, technologies for capturing CO<sub>2</sub> to supply the synthetic fuel production and possible ways of ensuring energy from renewable sources are presented along with their economical assessment and cost. In order to have a more realistic overview of the methods presented, a case study is performed, which confirms that the proposed technologies are currently not competitive in terms of efficiency and cost with the production and usage of fossil fuels. It is indispensable that research development investments should be made in this field. To conclude with, certain propositions are provided in order to drive the companies policy towards CO<sub>2</sub> recycling which could lead to a meaningful impact on CO<sub>2</sub> emissions if fuels were to be produced by direct conversion routes and in order to raise public awareness in a sense that CO<sub>2</sub> capturing will be perceived as a source of fuel production.

## Contents

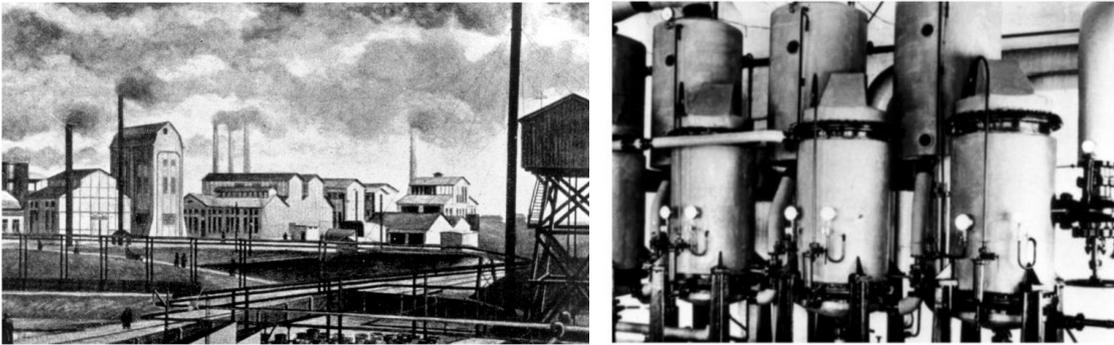
EXECUTIVE SUMMARY.....	1
1 INTRODUCTION .....	1
1.1 HISTORICAL OVERVIEW .....	1
1.2 SYNFUELS IN ENERGETIC BOARD.....	2
2 METHODS FOR SYNTHETIC FUEL PRODUCTION .....	4
2.1 HYDROGENATION.....	4
2.2 ELECTROREDUCTION .....	5
2.3 PHOTOCATALYSIS .....	7
2.4 BIOMASS.....	8
2.4.1 BIOMASS TO HYDROGEN AND SYNGAS PRODUCTION.....	9
2.4.2 ALGAL BIOMASS .....	10
3 ENERGY WATER CO2 .....	12
3.1 CO2 CAPTURE .....	12
3.1.1 POST-COMBUSTION DECARBONISATION TECHNOLOGY .....	12
3.1.2 METHODS TO CAPTURE CO2 IN DEVELOPMENT .....	13
3.2 WATER .....	14
3.3 ENERGY .....	15
3.3.1 SOLAR .....	15
3.3.2 WIND .....	16
3.3.3 NUCLEAR ENERGY.....	17
4 CASE STUDY .....	19
5 CONCLUSIONS AND PERSPECTIVE.....	20
6 REFERENCES .....	21

# 1 INTRODUCTION

## 1.1 HISTORICAL OVERVIEW

German scientists and engineers invented and developed two processes that enabled them to synthesize petroleum from their country's abundant coal supplies and to establish the world's first technologically successful synthetic liquid fuel industry.

Friedrich Bergius in Rheinau-Mannheim began the drive for energy independence with his invention and early development of high-pressure coal hydrogenation and liquefaction. Coal hydrogenation produced high quality aviation and motor gasoline. After Bergius, Franz Fischer and Hans Tropsch, invented a second process for the synthesis of liquid fuel from coal, (F-T process). This process gave high quality diesel and lubricating oil, waxes, and some lower quality motor gasoline. By the mid -1930s chemical companies had already started to industrialize synthetic liquid fuel production. However, because only coal hydrogenation produced high quality gasoline, it experienced much greater expansion than the F-T synthesis.



Picture 1.1 a) Synthetic fuel factory in Germany (1930s)

b)Reactors inside the factory

Today, there are increasing attempts to consider the CO<sub>2</sub> as a resource and a business opportunity rather than a waste with a cost of disposal (carbon taxes). Increasing amounts of low-cost and relatively pure CO<sub>2</sub> will be soon available from current and planned plants for carbon capture and storage (CCS). Therefore, CO<sub>2</sub> will be a feedstock of nearly zero (or even negative) cost for conversion to fuels and chemicals while also, companies will significantly benefit in terms of positive image.

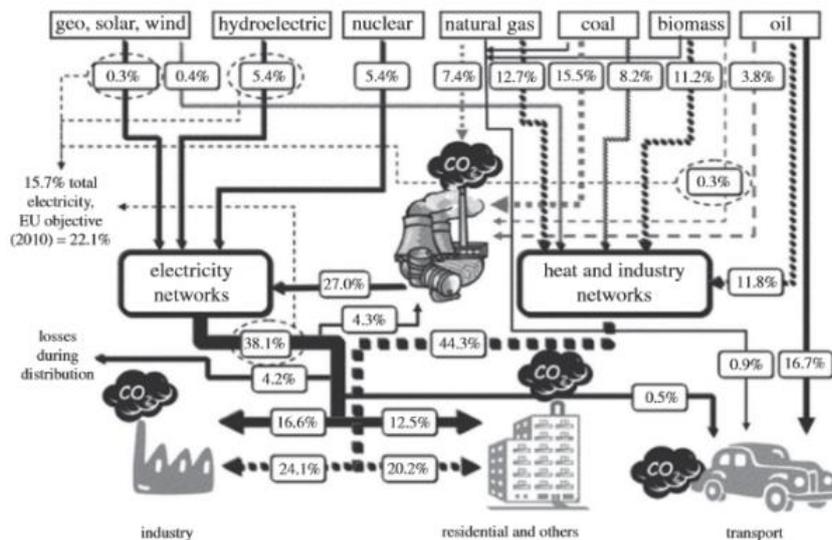
It can be roughly estimated that about 5–10% of the total CO<sub>2</sub> emissions (about 37 Gt worldwide in 2014) could be suited for production of fuels and chemicals. The actual use corresponds to a few percentage of the potential CO<sub>2</sub> suitable to be converted to chemicals. Therefore, a chemical recycling of CO<sub>2</sub> may significantly contribute to a reduction of its emissions only when the target products are components for the fuel pool. The main products of CO<sub>2</sub> conversion must be fuels to reduce CO<sub>2</sub> emissions significantly and to create great economic value. In addition, valorization of carbon dioxide emissions could be one important part of the general strategy for reducing CO<sub>2</sub> emissions and push chemical and energy companies towards a more sustainable use of the resources.

## 1.2 SYNFUELS IN ENERGETIC BOARD

The recent drop in world oil, natural gas and coal prices has turned energy into a very dynamic sector that raises uncertainty in terms of sustainability. Despite the low prices in the fossil-fuel, global investment in the renewable-based power was not affected, reaching \$270 billion of investments (according to International Energy Agency, 2015).

Renewable technologies are becoming increasingly cost competitive in numerous countries around the globe. However, public support schemes are still required to support deployment in many others. Renewables-based power generation capacity is estimated to have increased by 128GW in 2014, of which 37% is wind power, almost one-third solar power and more than a quarter, hydropower.

In several countries, nuclear energy is an important part of the electricity production. In 2013, the world's 392 GW of installed nuclear capacity accounted for 11% of electricity production, mostly in OECD countries. The use of nuclear energy has prevented the release of 56 Gt of CO<sub>2</sub> since 1971, equivalent to almost two years of global emissions at current rates (IEA, 2014). Further deployment of nuclear energy is stated government policy in many countries, and 74 GW of capacity was under construction by end-2014 (almost 40% in China).



Picture 1.2 Primary energy sources and their ultimate secondary energy outlets

For 2010 oil, coal and gas supplied almost 90% of the global energy needs (Z. Jiang et al). Although the situation has changed in the recent years, fossil fuel still remains the most important energy source. This is attributed to several facts, advantages and conveniences that come along with this energy form. First of all, they are widely spread and accessible in various forms, almost, all around the globe. Second, human kind has learned how to use them effectively to provide energy for a myriad of application at every scale. Finally, there is no other energy form and fuel that can subsidize fossil fuels in a large scale for transportation as they are portable and contain a considerable amount of stored chemical energy.

In order to overcome the growth in both, population (and therefore, in energy demand) and in hydrocarbons production costs, the liquid synthetic fuels appear as the most practical solution as they are easy to transport and store.

## 2 METHODS FOR SYNTHETIC FUEL PRODUCTION

There are many methods to produce synthetic fuels. In this report, four processes will be presented: Hydrogenation, Electro-reduction, Photocatalysis and Biomass.

### 2.1 HYDROGENATION

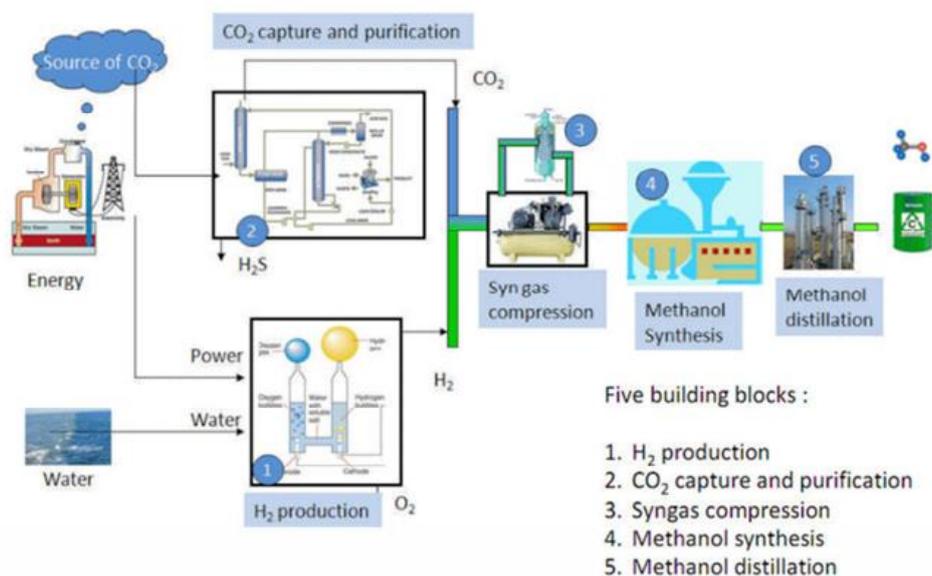
In this process, different products are generated (methanol, ethanol, DME, formic acid and hydrocarbons) through the chemical reaction between H<sub>2</sub> and CO or CO<sub>2</sub>. There are two main processes of hydrogenation, the direct hydrogenation which occurs in only one chemical reaction between CO<sub>2</sub> and H<sub>2</sub> and the indirect hydrogenation which has an additional intermediary step to convert CO with H<sub>2</sub> reaction.

#### DIRECT HYDROGENATION

The direct hydrogenation is completed in one step, which is the reaction of the H<sub>2</sub> directly with the CO<sub>2</sub>. For example, the following reactions describe the methanol and methane production by direct hydrogenation of CO<sub>2</sub>:

- Formic acid       $\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$
- Methanol         $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
- Methane          $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

In the following figure, methanol production in one step through a catalytic reactor fed by H<sub>2</sub> and CO<sub>2</sub> is presented. The water is a product of the reaction as well as the ethanol, thus it is necessary to separate them by distillation.



Picture 2.1 Schematic representation of the hydrogenation process to produce CH<sub>4</sub>

The main advantage of this method is the fact that the reaction is made in one step and it is less exothermic than the hydrogenation of the CO, ensuring an easier control of the temperature. Along the main drawbacks if this process is the water-methanol separation requisite and necessity of CO<sub>2</sub>/H<sub>2</sub> compression. In order to apply this method, it is necessary to develop more efficient catalysts and less sensible to CO<sub>2</sub> purity.

## INDIRECT HYDROGENATION

This method involves two main steps represented in the following reactions:

- Carbone Monoxide       $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$       RWGS
- Methanol                 $\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$       Synthesis of methanol
- Hydrocarbons           $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$       Fischer-Tropsch

The first step is the reverse water-gas shift (RWGS) to obtain CO. It is carried out by injecting CO and H<sub>2</sub> (in excess) in a RWGS reactor. The water is separated from the CO before the methanol synthesis, which makes the water extraction easier.

The combination of the CO produced with H<sub>2</sub> results in synthesis gas (or syngas) formation, more suitable for methanol or hydrocarbons production through the methanol synthesis or the Fischer-Tropsch (FT) reactions.

The RWGS reactors are used in an industrial scale in order to adjust the H<sub>2</sub>/CO ratio of syngas but this operation is not well developed starting only from CO<sub>2</sub> and H<sub>2</sub>. For this reason, the research projects are focusing in the RWGS reaction.

The Fischer-Tropsch synthesis has a low selectivity, leading to a wide range of products (olefins, paraffins, oxygenates) depending on the operating conditions (pressure, temperature), the H<sub>2</sub> / CO ratio of the input syngas (around 2) and the catalyst used.

Although the present method makes the extraction of the water easier thanks to the RWGS, it is more complex than the direct hydrogenation (higher CAPEX) while the combination of H<sub>2</sub> with the CO is also more exothermic. The FT allows producing high quality fuels (energy density similar to fossil fuels, high C number, low sulfur content) which can be incorporated or substitutable for fossil fuels.

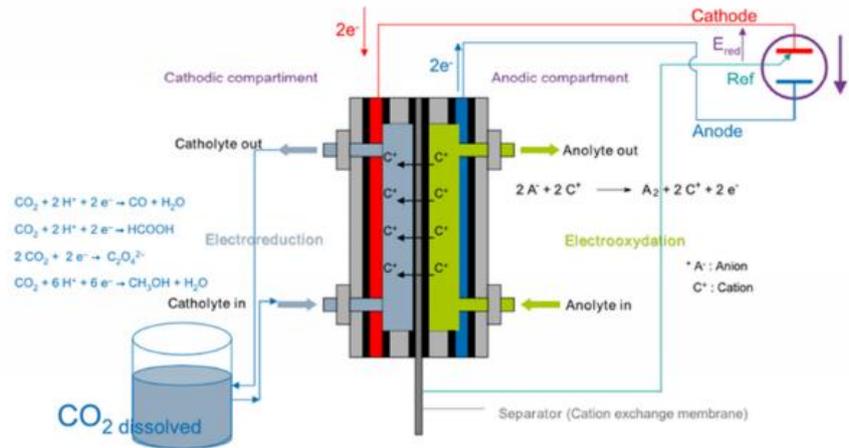
As well as the direct method, this process requires an improvement in the knowledge of the catalysts both for the RWGS and the FT reaction, regarding their stability over the time, the impact that the impurities can cause them. Specially, for the FT reaction for which the selectivity is very important.

This method has been implemented at an industrial scale in Germany as it is described in the introduction and in South Africa as well. A good example of a developing project is the pilot plant of Audi in Dresden, Germany where 160 l/d of “e-diesel” is produced with an overall process efficiency of around 70%.

## 2.2 ELECTROREDUCTION

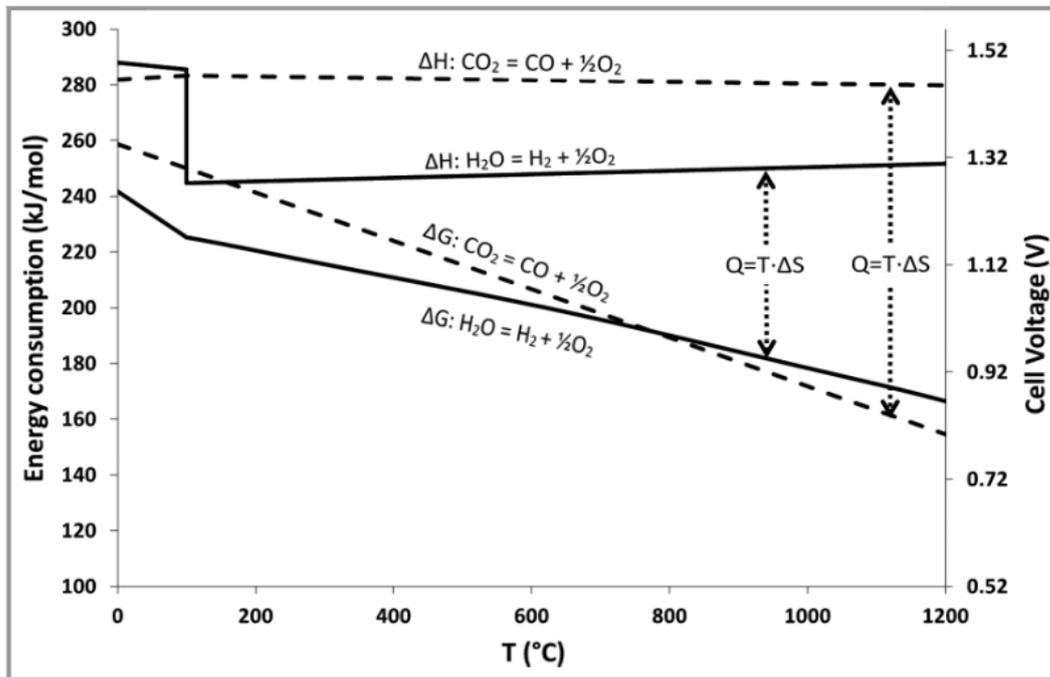
This method addresses the electrochemistry reduction or electrolyse of CO<sub>2</sub>. This process can be performed in two ways. To be more specific:

- ❖ The electrolyte at high temperature: In this procedure water and CO<sub>2</sub> are put together at high temperature (700 – 800°C), producing a mixture of CO and H<sub>2</sub> (synthetic gas). This mixture can be transformed to fuel by F-T reaction or to alcohol. This method requires a lot of energy and heat to activate the CO<sub>2</sub> molecule.
- ❖ The electrolyte at environmental temperature in electrocatalytic cells: In this method, the electrons are provided by electric energy and the H<sub>2</sub> by oxidation of a non anodic acid directly in the reactor, or by acidification (HCL reaction).



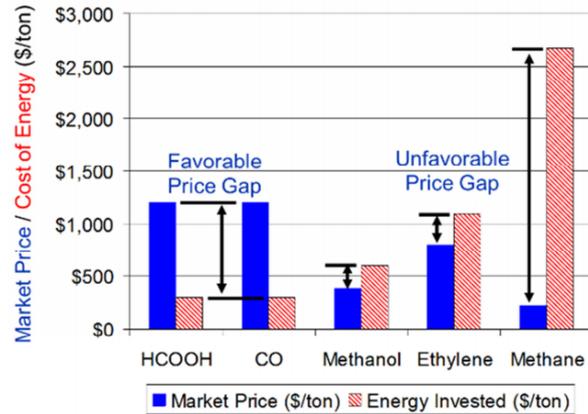
Picture 2.2 CO2 electroreduction

The efficiency of the electrolyte is the ratio between the current (or number of electrons) used to perform the reaction desired, and the total current invested in the electrolyte. The energy consumption of the electrolysis process depends, nevertheless, on temperature and pressure. The thermodynamic properties are plotted in Pic 2.3 as a function of temperature for the H<sub>2</sub>-H<sub>2</sub>O and CO-CO<sub>2</sub> systems from 0 degC to 1200 degC at standard pressure. It shows that the Gibbs free energy change (DG) for the reacting system decreases with increasing temperature, while the product of temperature and the entropy change (TDS) increases. Therefore, for reversible operation, the electrical work requirement decreases with temperature, and a larger fraction of the total energy required for electrolysis (DH) can be supplied in the form of heat (Nguyen and Blum, 2014).



Picture 2.3 Temperature dependency of energy demand of H<sub>2</sub>O and CO<sub>2</sub> reactions

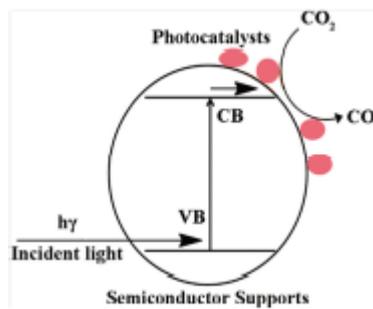
Formic acid and carbon monoxide are less expensive products and more profitable because they require less energy (Pic 2.4).



Picture 2.4 Temperature dependency of energy demand of H<sub>2</sub>O and CO<sub>2</sub> reduction reactions

### 2.3 PHOTOCATALYSIS

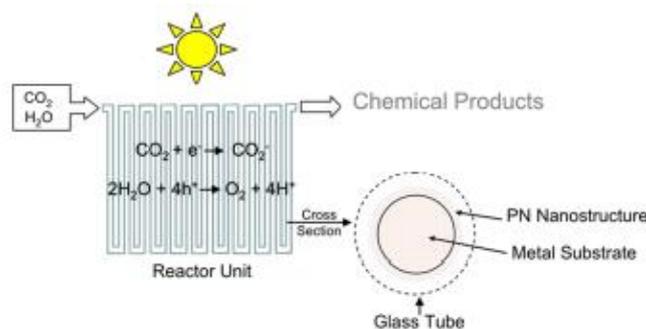
This method is similar to photosynthesis natural process, but with the help of inorganic photo catalysers. The objective is to convert CO<sub>2</sub> and water to obtain high added value products via catalysers, generally semiconductors, which are activated by a light irradiation. The light irradiation, which is a function of its wave length, will permit the catalyser to generate a pair of electron-hole who will launch chemical reactions.



Picture 2.5 Interaction between CO<sub>2</sub> and solar light to produce CO

The photo catalysis operates directly on both water and CO<sub>2</sub> (dissociation of water and reduction of CO<sub>2</sub>).

In the figure below, the photo catalysis principle is presented. A mix of water and CO<sub>2</sub> is injected in a reactor permitting the reduction of CO<sub>2</sub>, the dissociation of water and the formation of the products needed. This reactor is made of tube fiberglass with a photocatalyser, in one of which, the CO<sub>2</sub> – water mixture is circulated. The fiberglass tubes are enlightened by a light source, which in our case is the sun.



Picture 2.6 Photocatalysis process

Advantages:

- The use of the sunlight as principle energy source.
- No need of H<sub>2</sub> source.

Disadvantages:

- Very low efficiency (around 1%)
- Big space

It is important to remark that this method is in early development stage, as it has been performed only at a laboratory scale.

## 2.4 BIOMASS

Biomass appears as an attractive source for the production of fuels and chemicals due to its versatility, renewable nature and low environmental impact. In the near term biomass is the most likely renewable organic substitute to petroleum. Biomass is a renewable material containing appreciative quantities of hydrogen, oxygen and carbon and it is available from a wide range of sources.



Picture 2.7 Biomass lifecycle

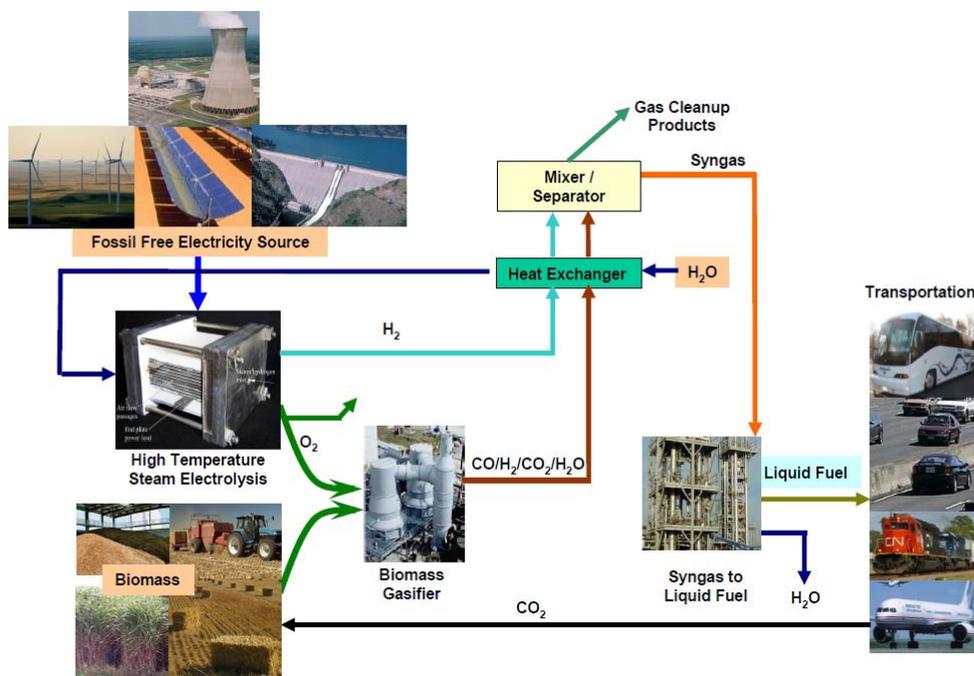
Biomass resources available to be converted into energy are classified into 4 categories:

- Energy crops
- Agricultural residues and waste
- Forestry wastes and residues
- Industrial and municipal wastes

The available energy production processes from biomass can roughly be divided into two general categories: thermochemical and biological processes. Pyrolysis, gasification, reforming and combustion are the four thermochemical processes and direct biophotolysis, indirect biophotolysis, biological water gas shift reaction, photofermentation and dark fermentation are the five biological processes.

## 2.4.1 BIOMASS TO HYDROGEN AND SYNGAS PRODUCTION

For hydrogen and syngas production, the current biomass technologies include : pyrolysis, gasification, reforming (most studied) and combustion.



Picture 2.8 Generation of syngas from biomass and fossil free electricity

### PYROLYSIS

Parameters as temperature, heating rate, residence time and type of catalyst used in the process are very important. More specific, high temperature, high heating rate and long time volatile phase residence are required in order to increase gaseous products and especially hydrogen. Fast pyrolysis is considered mainly for hydrogen production. It is a high temperature process, in which biomass is heated rapidly in the absence of air, to form vapour and subsequently condensed to dark brown mobile bio-liquid. The products of pyrolysis can be found in all phases but the gaseous product is more interesting due to its potential as a source of hydrogen fuel.

For hydrogen production of biomass the price is in the range of 3 - 7 US/ liter depending on the facility size and biomass type. For comparison, the costs by wind electrolysis systems and PV – electrolysis systems are 8 and 15 US/liter respectively.

### GASIFICATION

It is a renewable alternative that has the potential to decrease CO<sub>2</sub> emissions. It is an old thermo-chemical conversion technology with a change of the chemical structure of the biomass at 800 - 1000 C in the presence of a gasifying agent. The promotion of steam reforming reactions is enabled and thus it consists another method of producing a H<sub>2</sub> rich gas from biomass. Air has been widely used as the oxygen source of the gasification.

For the production of hydrogen and syngas with gasification, the temperature is the most influential factor. Increasing the temperature resulted in increase in gas yield and more hydrogen production. Particle size is another factor that affects the gasification process, therefore carbon conversion efficiency and hydrogen yield increase with decreasing particle size.

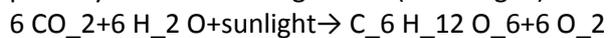
## STEAM REFORMING

It is performed in low temperatures in the presence of catalysts. The metal components have a significant influence in performance and distribution of gaseous products but the formation of coke and catalyst deactivants must be controlled. In this process, the substrate is reacted with steam in the presence of a catalyst to produce hydrogen, carbon dioxide and carbon monoxide. The reform process involves mainly the breakdown of hydrocarbons in the presence of water, water gas shift, producing hydrogen. Furthermore, carbon monoxide is turned into methane.

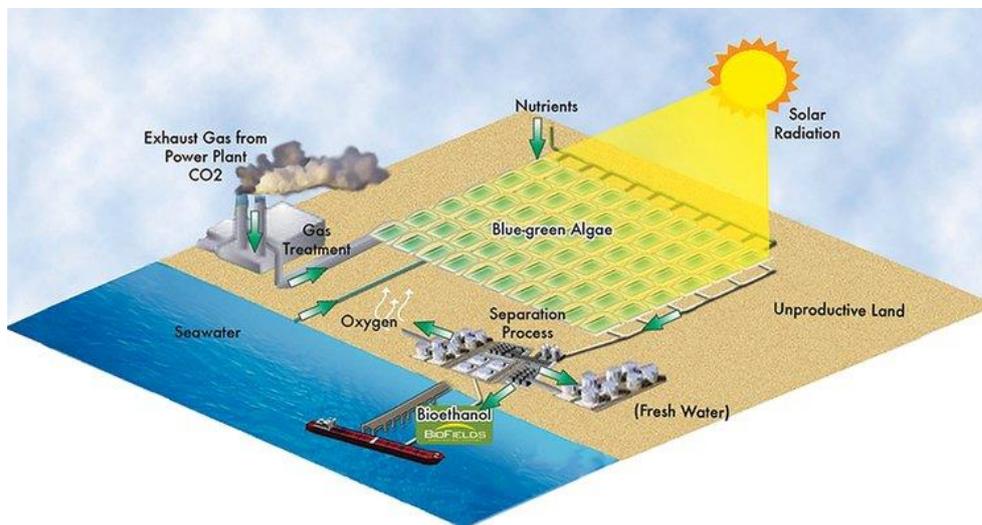
Biomass is renewable, abundant and easy to use. Over the life cycle, net CO<sub>2</sub> emissions is nearly zero due to the photosynthesis of green plants. The thermochemical pyrolysis and gasification methods for hydrogen and syngas production are economically viable, while the cost for hydrogen production with biomass pyrolysis is more competitive than the costs by electrolysis systems.

### 2.4.2 ALGAL BIOMASS

Photosynthesis is the largest scale CO<sub>2</sub> conversion process, since it is present in all plants and photosynthetic microorganisms (microalgae). Sunlight powers the CO<sub>2</sub> conversion reaction:



The integration of chemicals and energy production in large scale industrial algal biofarms has led to the “algal biorefinery” concept. On life cycle algae appear to have larger environmental impacts, energy use, and greenhouse emissions (in harvesting and processing) compared to conventional crops, regardless of cultivation method. Algae perform favourably only in total land use and eutrophication potential, however, algae cultivation performs poorly with respect to water consumption.



Picture 2.9 Algal biofarm

Over 150 companies worldwide are involved in algal biofuels, including some major companies.

In terms of CO<sub>2</sub> consumption a total of 1.8 tons of CO<sub>2</sub> is needed in order to produce 1 ton of algal biomass, while nitrogen and phosphorus nutrients are also needed. The estimated costs to produce algae oils and algae biodiesel today range between 3 and 10 (dollars) per gallon in ponds and 6-12 (dollars) per liter in photobioreactors.

The most practical approach to integrate algal fuels with the existing infrastructure would be to subject the algal oils to the same refining steps as petroleum, either alone or as a mixture with petroleum. This would produce a fuel identical to petroleum derived fuels and eliminate separate process and logistics chains for raw and transesterified oils. Further, by allowing a ready fit of the new fuel into existing infrastructure and eliminating the need for biofuel – specific engine modifications, the economics of use and marketability would be greatly enhanced.

Wijffels and Barbosa, in their outlook paper on microalgal biofuels indicated that at least 10 -15 years are necessary for the development of sustainable and economically viable process for the commercial production of biofuels from algal biomass.

It is necessary to reduce production costs and energy requirements, while maximizing lipid productivity and increasing the biomass value by making use of all algal biomass components. The use of wastewater and/or plant emitted CO<sub>2</sub> besides improving LCA and possibly producing clean water, also improves the economics of the system.

Thus, even if current state in development of algal carbon capture at large emitter sites indicates an economic cost that is still too high, there are signals of fast scientific and technological development in this area, including improvements in :

- Photobioreactor design
- Harvesting and processing technologies
- Photosynthetic efficiency, productivity, compatibility with concentrated CO<sub>2</sub> streams and tuning to desired end product by genetic engineering

The production of algal biofuels is limited by the availability of suitable land resources, access to CO<sub>2</sub> and water. Estimates of future algal biofuel production vary significantly. A report from Pike Research note that 180 million liters of algal biofuels may be produced worldwide annually by 2020. More optimistic assessment from the Algal Biomass Organization (ABO) indicate 18000 million liters of algal biofuels per year by 2022.

If algal biofuels could be successfully commercialized, the preliminary calculations indicate that 10 to 40 million tons of CO<sub>2</sub> could be utilized by the producing 0.8 billion gallons of biodiesel( 2.2 million gallons/day) using microalgae.

## 3 ENERGY WATER CO<sub>2</sub>

### 3.1 CO<sub>2</sub> CAPTURE

Various aspects and components of the CCS process chain have been researched over the past 15 year. The research has revealed that CCS can be a valuable part in the portfolio of technologies to reduce CO<sub>2</sub> emissions. Both capture and transport of CO<sub>2</sub> can be done using technologies which are commercially available. For instance, CO<sub>2</sub> separation technologies are commonplace in the oil and gas industry. There is a need to adapt and optimise these separation technologies for CCS.

The contribution of capture to the overall cost is around 75%, so CO<sub>2</sub> capture determines the cost of the CCS route. The production costs of electricity will increase by over 50%. This shows that cutting the costs of capture is one of the most important issues in making the option acceptable to the energy industry.

CO<sub>2</sub>-capture processes or decarbonisation technologies can be divided into three main categories or general process routes:

- Post-combustion processes
- Pre-combustion processes
- Denitrogenation processes.

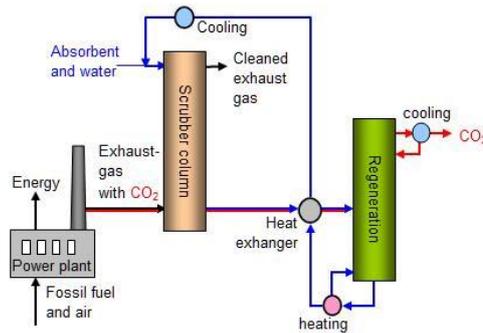
These process categories are applicable to both fossil fuel and biomass based energy conversion processes (power plants and industrial plants). The process details will however be different for each type of fuels, and each type of energy conversion process. In addition to this, for coal based energy conversion processes, the sulphur content of coal is an item which impacts on the design, operation and costs of decarbonisation processes. This also applies for situations where bottom fuels, such as petcoke or asphalt are used.

The post-combustion process is the most used and the cheaper one. Therefore, a more detailed overview of this method will be presented.

#### 3.1.1 POST-COMBUSTION DECARBONISATION TECHNOLOGY

The process route is ideally suitable for conventional power station, the fuel is mixed with air and burnt. Power is produced by gas turbines and/or steam turbines. Post-combustion decarbonisation consists of two main process steps: an energy conversion step during which power is produced, followed by a CO<sub>2</sub> separation process in which a concentrated stream of CO<sub>2</sub> is produced.

Post-combustion capture is designed to retrieve the CO<sub>2</sub> diluted in the combustion flue gas. The challenge of this occasion is to develop a CO<sub>2</sub> separation process at an acceptable energy penalty and costs. The main technical difficulty is precisely the weak concentration of CO<sub>2</sub> in these gases, but it is nevertheless the one that is most frequently adopted because it can be integrated into existing facilities without calling for major modifications. The most common process is CO<sub>2</sub> capture by solvents, generally amines, but other processes are being examined that involve the calcium cycle and cryogenic separation. The former uses solvent-based capture, solvent is then heated, thereby releasing CO<sub>2</sub> and producing free CO<sub>2</sub> solvent again for recycling. Commercially available chemical solvents are primary, secondary and tertiary amines and also alkaline salt solution. Important parameters in the selection of chemical solvents are the CO<sub>2</sub>-loading capacity to result in low absorption liquid flow rates and the reaction rate, as this will determine the size of the equipment and the heat requirement for regeneration which dominates the operating costs.



Picture 3.1 Principle of post-combustion

### ECONOMIC CASE STUDY

The case of a coal power plant of 600MWe will be used as reference. Without capturing CO<sub>2</sub>, the plant rejects 750kg of CO<sub>2</sub> per MWh produced. The cost of 1MWh is around 38€. By capturing CO<sub>2</sub>, the electricity production is reduced at 480MWe and the cost increases around 65€. The inflation is around 27€. But capture system will avoid the emission of 635kg of CO<sub>2</sub> per MWh. If we divide 27€ per 0,635, we obtain a cost of 40€ per ton of CO<sub>2</sub> avoided.

### 3.1.2 METHODS TO CAPTURE CO<sub>2</sub> IN DEVELOPMENT

In Canada, they developed a wall of fans to capture the CO<sub>2</sub> in the atmosphere. The atmosphere contains around 400ppm of CO<sub>2</sub>.



Picture 3.2 CO<sub>2</sub> capturing pilot plant

With this method, one ton of CO<sub>2</sub> per day can be captured. The cost of one complete installation is 200 Million of \$.

In the USA, they focus on capturing the CO<sub>2</sub> from the sea as CO<sub>2</sub> is very soluble in water, and its concentration in the ocean is about 140 times higher than that in the air. The process has not been scaled up, but the technology and challenges are similar to reverse osmosis desalination, making the method attractive and mainly possible. The lifetime of membranes operated in seawater is also unknown, but again, membrane desalination of seawater shows that the problem can be overcome by using techniques like polarity reversal to remove scale formation. This process doesn't require material inputs of acids or bases, they are generated internally by electricity, and it is non-polluting, only the original seawater is discharged, minus the CO<sub>2</sub>. The process consumes 242 kJ per mole of CO<sub>2</sub>.

Applying the capital, operating expense, and cost of energy assumptions made by the Navy researchers and using Navy nuclear electricity at 7.0 c/kWh, a carbon capture cost of about \$114

per tonne CO<sub>2</sub> is estimated. The Navy estimated the capital cost of the carbon capture process at \$16m for a 715 tCO<sub>2</sub> per day plant. Unfortunately no further explanation and analysis is provided to justify this cost, so it is possible that the CO<sub>2</sub> capture cost is underestimated.

## 3.2 WATER

In this report, water is chosen as the source of H<sub>2</sub> that must be supplied in order to perform the methods for the syngas production presented above. Therefore, the water must be fresh water. All projections of the future suggest that with the growth of population, along with the increase of fuel request, the demands of food and water will increase too.

It is considered that it will be difficult and expensive to produce synfuels in global scale while being in direct competition with drinking water. It was estimated, that the quantity of water to produce gasoline, is about 1liter of water for 1 litre of gasoline. Only in the USA, around 500 billion litres of gasoline are consumed each year. This means that our water reservoir has to be enormous in order to be able to meet this demand. Therefore, sea water desalination is suggested in order to solve this problem.

Due to relatively high energy consumption, the costs of desalinating sea water are generally higher than the alternatives (fresh water from rivers or groundwater, water recycling and water conservation). However, alternatives are not always available and rapid overdraw and depletion of reserves is a critical problem worldwide. Quoting Christopher Gasson, of Global Water Intelligence, "At the moment, around 1% of the world's population are dependent on desalinated water to meet their daily needs, but by 2025, the UN expects 14% of the world's population to be encountering water scarcity. Unless people get radically better at water conservation, the desalination industry has a very strong future indeed."

The single largest desalination project is Ras Al-Khair in Saudi Arabia, which produced 1,025,000 cubic meters per day in 2014. A minimum energy consumption for sea water desalination of around 1 kWh/m<sup>3</sup> has been determined, excluding pre-filtering and intake/outfall pumping. The process of water desalination can be simplified by using excess heat from electricity generation for another task. The advantage of dual-purpose facilities is that they can be more efficient in energy consumption, thus making desalination a more viable option. Eight nuclear reactors coupled to desalination plants are operating in Japan alone, making Nuclear-powered desalination might be economically attractive on a large scale.

In 2013 the costs of desalinating sea water (infrastructure, energy, and maintenance) were in the range of US\$0.40 to \$1.00 per cubic metre. However, more than half of the total cost of desalination comes directly from energy cost, and since energy price is very volatile, any calculated cost of desalination is only as cost effective as the energy price at the time of calculation. Factors that determine the cost for desalination include the capacity and type of facility, location, feed water, labour, energy, financing, and disposal concentration. To improve the efficiency of the desalination pressure, temperature, and brine concentrations are controlled. Technology improvements have cut the cost of desalination in half in the past decade.

According to the Environmental Protection Agency (EPA), water intake structures cause adverse environmental impact by pulling large numbers of fish and shellfish or their eggs into an industrial system. Alternative intake types which avoid this environmental impact include beach wells, but they require more energy and higher costs, while having a limited output. In the outflow, Brine is denser than seawater due to higher solute concentration. However, the ocean bottom and life is at

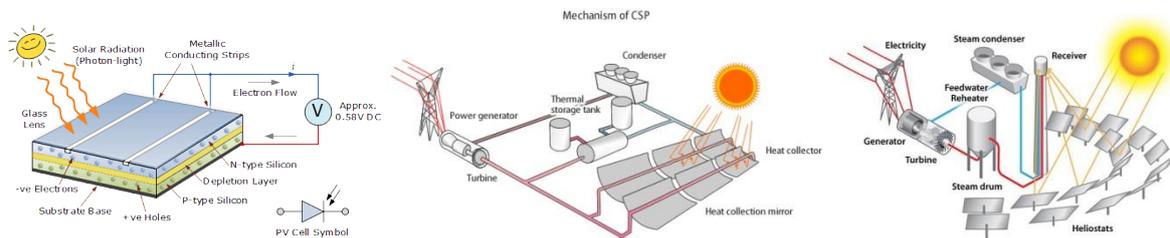
risk because the brine sinks and remains there long enough to damage the ecosystem, a problem that can be minimized by careful reintroduction.

### 3.3 ENERGY

#### 3.3.1 SOLAR

Every hour the sun beams into Earth more than enough energy to satisfy global energy needs for an entire year. The United Nations Development Programme, in the World Energy Assessment of 2000, found that the annual potential of solar energy was in the magnitude of 1,575–49,837 exajoules (EJ). This quantity is several times larger than the total world energy consumption, which was 559.8 EJ in 2012. Technological developments and research are performed in order to harness the sun's energy and make it useable. Today, the technology produces less than one tenth of one percent of global energy demand.

It is possible to absorb solar energy by means of photovoltaic cells or solar panels which are made of semiconductor materials (Pic 3.3). When sunlight hits the cells, it knocks electrons loose from their atoms. As the electrons flow through the cell, they generate electricity. On a much larger scale, solar thermal power plants employ various techniques to concentrate the sun's energy as a heat source. The heat is then used to boil water to drive a steam turbine that generates electricity in almost the same process as coal and nuclear power plants, supplying electricity for thousands of people. In another technique, long troughs of U-shaped mirrors focus sunlight on a pipe of oil that runs through the middle. The hot oil then boils water for electricity generation. Furthermore, moveable mirrors that focus the sun's rays on a collector tower, where a receiver sits, are used. Molten salt flowing through the receiver is heated to run a generator.



**Picture 3.3 Methods of capturing solar energy a) photovoltaic cells b) thermal power plant c) concentrating solar power tower plant**

Solar energy is certainly an inexhaustible fuel source that is pollution and often noise free. The technology to harness it, is versatile. For example, solar cells generate energy for far-out places like satellites in Earth orbit and cabins deep in the Rocky Mountains as easily as they can power downtown buildings and cars. However, solar energy doesn't work at night without a storage device such as a battery, and cloudy weather can make the technology unreliable during the day. Solar technologies are also very expensive and require a lot of land area to collect the sun's energy at rates useful to lots of people.

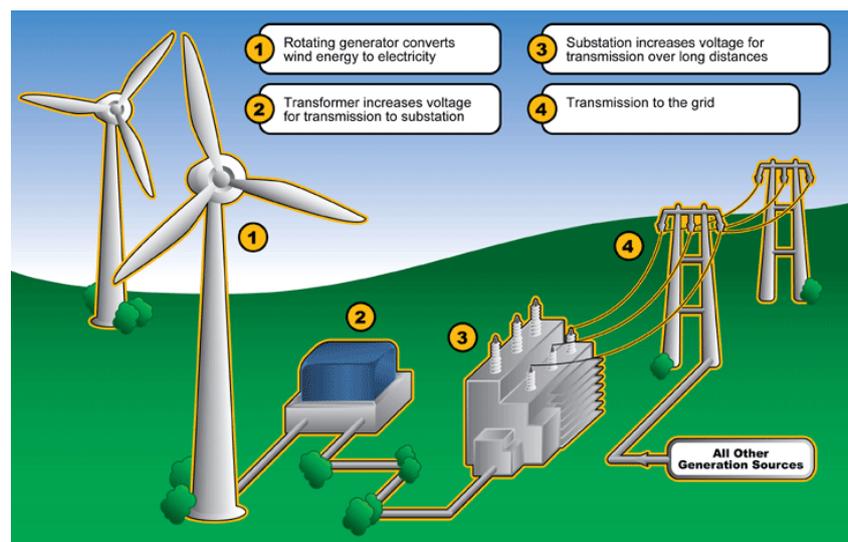
Despite the drawbacks, solar energy use has surged at about 20 % a year over the past 15 years, thanks to rapidly falling prices and gains in efficiency. Japan, Germany, and the United States are major markets for solar cells. With tax incentives, solar electricity can often pay for itself in five to ten years.

In 2000, the United Nations Development Programme, UN Department of Economic and Social Affairs, and World Energy Council published an estimate of the potential solar energy that could be used by humans each year that took into account factors such as insolation, cloud cover, and the land that is usable by humans. The estimate found that solar energy has a global potential of 1,575–49,837 EJ per year

### 3.3.2 WIND

Wind is a form of solar energy as it is caused by the uneven heating of the atmosphere by the sun and is modified by the irregularities of the earth's surface, and rotation of the earth. The terms "wind energy" or "wind power" describe the process by which the wind is used to generate mechanical power or electricity. Wind turbines convert the kinetic energy of the wind into mechanical power which can be used for specific tasks (such as grinding grain or pumping water). Alternatively, a generator can convert this mechanical power into electricity to power homes, businesses, schools, etc.

Wind turbines are often grouped together (hundred individual wind turbines distributed over an extended area) into a single wind power plant (Pic 3.4) also known as a wind farm, and generate electrical power. Electricity from these turbines is fed into a utility grid and distributed to customers, which is the case for conventional power plants as well.



Picture 3.4 Wind power plant

Onshore wind is an inexpensive source of electricity, competitive or cheaper, in many places, than coal or gas plants. Offshore wind is steadier and stronger than on land. Also, offshore farms have less visual impact, but construction and maintenance costs are considerably higher. Small onshore wind farms can feed some energy into the grid or provide electricity to isolated off-grid locations.

Wind energy is a source of clean, non-polluting electricity (no air pollutants or greenhouse gases),. According to the U.S. Department of Energy, in 1990, California's wind power plants offset the emission of more than 2.5 billion pounds of carbon dioxide, and 15 million pounds of other pollutants that would have otherwise been produced. It would take a forest of 90 million to 175 million trees to provide the same air quality.

Even though the cost of wind power has decreased dramatically in the past 10 years, the technology requires a higher initial investment than fossil-fueled generators. Roughly 80% of the

cost is the machinery, with the balance being site preparation and installation. If wind generating systems are compared with fossil-fueled systems on a "life-cycle" cost basis (counting fuel and operating expenses for the life of the generator), wind costs are much more competitive with other generating technologies. This is because there is no fuel to purchase and the operating expenses are minimal.

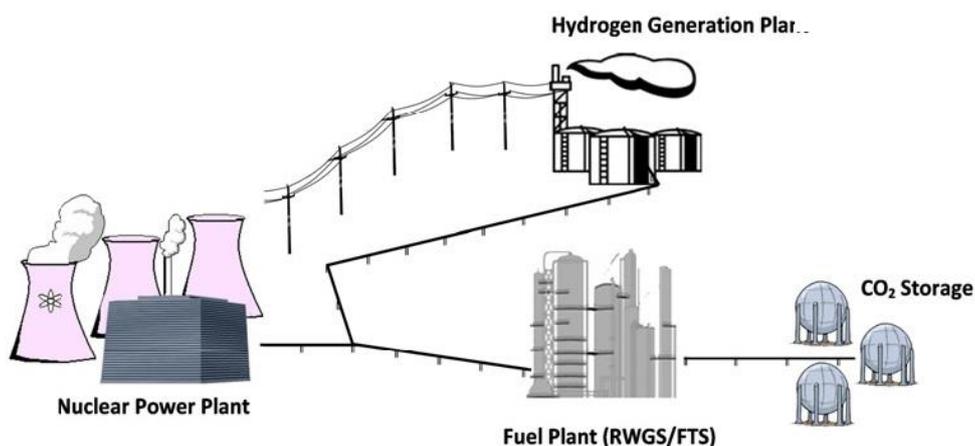
The major challenge of using wind as a source of power is that it is intermittent and does not always blow when electricity is needed. Wind cannot be stored (although wind-generated electricity can be stored), and not all winds can be harnessed to meet the timing of electricity demands. Furthermore, good wind sites are often located in remote locations far from areas of electric power demand (such as cities). Finally, wind resource development may compete with other uses for the land, and those alternative uses may be more highly valued than electricity generation. However, wind turbines can be located on land that is also used for grazing or even farming.

### 3.3.3 NUCLEAR ENERGY

CO<sub>2</sub> recycling to produce carbon based fuel can be a potential mechanism to reduce CO<sub>2</sub> emission and put us on the path to a carbon-neutral energy system. The CO<sub>2</sub>-to-fuel integrating the heat from nuclear plant technology could lead towards the sustainable development in the long term as nuclear energy has a low CO<sub>2</sub> footprint. CO<sub>2</sub> to fuel has been usually considered coupled to renewable sources such as wind power. However, in France for example, where 78% of electrical power is provided by nuclear reactors, without any new nuclear power plant construction, the emission of several millions tons of CO<sub>2</sub> could be avoided by using a CO<sub>2</sub> to fuel technology to adjust the electricity produced by nuclear energy to the electricity grid demand. This will not only mitigate CO<sub>2</sub> emissions but could also increase nuclear economic competitiveness.

There are already two different designs discussed for the production of DiMethyl Ether (DME) from CO<sub>2</sub>, H<sub>2</sub> and nuclear power. The first one is with current nuclear reactors, using solely electrical energy to transform CO<sub>2</sub> into fuel but with the idea to use the conversion of CO<sub>2</sub> to fuel as a fluctuating energy demand to complete the grid electricity demand. The second one will directly be coupled to the under schedule new nuclear reactor SFR (sodium fast reactor). Heat can be provided by this reactor up to a temperature of 500°C.

Synthetic fuel from CO<sub>2</sub> as electrical "storage" Hydrogen can already be produced from water using pem or alkaline electrolysis. CO<sub>2</sub> and hydrogen can then be transformed to various synthetic fuels (methanol, ethanol, diesel...).



Picture 3.5 Nuclear power plant and Synfuel production

The process design is based on 3-step reactor network consisting of a Reverse Water Gas Shift (RWGS) reactor, a methanol (MeOH) synthesis reactor and a dehydration reactor of MeOH to DME. Next step is the conversion of syngas, after condensing water, to methanol. Finally, the methanol is dehydrated into DME in the third reactor.

Supposing that all this extra electricity generation is used for synthesis fuel generation, it is estimated that 5 to 10 million tons of CO<sub>2</sub> could be saved, as this DME did not anymore require to be produced from fossil sources.

## 4 CASE STUDY

For this case study, the annual gasoline consumption of France will be used as reference. The consumption is estimated around 7,8 Mt per year. By performing the necessary mathematical and chemical calculations, to produce 1l of synthetic fuels we will need :

- 1 liter of water
- 3,5 kg of CO<sub>2</sub>
- Additional acids and additives, depending of the fuel we want.

10 000 Ml of water and 35 Mt of CO<sub>2</sub> is needed for this case study.

The price of feedstock needed to produce 1 liter of synthetic fuel will be calculated:

The price of 1 liter of water is approximately 0,5€/m<sup>3</sup>.

By checking the Frenchs' companies annual CO<sub>2</sub> emissions, it is deduced that the total amount of CO<sub>2</sub> we need can be captured with just 9 plants.

Arcelormittal Atlantique Et Lorraine Site De Dunkerque	59381 Dunkerque	Sid�rurgie, m�tallurgie, coke	12 300 000 000
Celsa France- Acierie Atlantique	64340 Boucau	Sid�rurgie, m�tallurgie, coke	11 000 000 000
Arcelormittal Fos	13776 Fos-sur-Mer	Sid�rurgie, m�tallurgie, coke	7 920 000 000
Gdf Suez Thermique France - Centrale dk6	59951 Dunkerque	Energie	3 940 000 000
Raffinerie De Normandie	76700 Harfleur	P�trole et gaz	2 780 000 000
Edf - Up Cordemais	44360 Cordemais	Energie	2 580 000 000
E.On - Centrale Emile Huchet	57500 Saint-Avoid	Energie	1 980 000 000
Raffinerie De Port-J�r�me / Gravenchon	76330 Notre-Dame-de-Gravenchon	P�trole et gaz	1 980 000 000
Naphtachimie	13117 Martigues	Chimie et parachimie	1 700 000 000
		Total	46 180 000 000

The cost of CO<sub>2</sub> capture, compression, and transport is around 60€/ton, whereas the cost of CO<sub>2</sub> for 1 liter of synthetic fuel is around 0,21€. However, the most expensive part is the process to transform the feedstock (CO<sub>2</sub>+H<sub>2</sub>O) into fuel.

The transformation to hydrogen costs 10€/kg, the required energy is 33,5 kWh/kg, and 111g of hydrogen are needed. Optimistically, a cost of 5€/kg will be presumed, resulting in around 1,7€ to produce this 111g of hydrogen, included the energy of the electrolysis transformation.

As a result: CO<sub>2</sub> + H<sub>2</sub> = 1,91€ for feedstock only.

Regarding the process to transform it into fuel, a lot of process already exist and the cost of production is very high. Currently, the cost for 1 barrel of synthetic fuel is around 200€. The main problem is the cost of the feedstock. Consequently, for the future development and industrialization, the cost of CO<sub>2</sub> and H<sub>2</sub> have to be decreased to obtain synthetic fuel economically viable.

## 5 CONCLUSIONS AND PERSPECTIVE

Having conducted a thorough research on the topic of sunfuels production it is easy to conclude that there are several industrial groups and scientific teams that are working individually for the same cause. As a result, too many methods are being developed or are optimized in an effort to ensure the sustainability of sunfuel production from new and renewable sources. However, uniting all the scientific groups and people in a community and allowing them to work under a common project with the same cause would certainly be more productive and efficient. By identifying which method is more promising to give a better efficiency in terms of synfuel production and by concentrating the research and development on that method, the desired results is more likely to be achieved and in a shorter time margin.

Furthermore, at the current technological point, it is obvious that the balance in the market is unfavourable at the moment for the methods presented compared to fossil fuels alternatives that are currently used. This is because there are several costs involved for the processes which raise the cost of production significantly while the efficiency of most of the methods are still not so high enough to allow them to be implemented in large scale production. Therefore, massive RND investments and the well identified road map to faster, cheaper, easier and greener fuels from synthetic gas should be encouraged. In order to achieve that, incentives should be given and regulations should be proposed. Companies, especially, should be motivated to drive their policy towards CO<sub>2</sub> recycling which could lead to a meaningful impact on CO<sub>2</sub> emissions if fuels were to be produced by direct conversion routes. This could be achieved by granting taxation reductions to the companies or even be subsidized form the government. Moreover, regulations should be proposed in order to enforce companies to follow this policy on this matter.

Moreover, the public awareness should be raised an the point of view should be changed in order CO<sub>2</sub> capturing to be seen as a source of fuel production and not as a waste that comes with a disposal cost. The societal push to reduce CO<sub>2</sub> emissions will open new opportunities for a sustainable, resource efficient chemical and energy industry that considers CO<sub>2</sub> as an abundant, renewable, economic and green carbon feedstock. CO<sub>2</sub> mitigation made by CO<sub>2</sub> recycling into fuels is towards the development of lower carbon economies and by raising the public awareness on that matter will push companies towards that direction in order to retain a better and greener image. At this point, it should be mentioned that all of the methods presented in this report should be approached with a more rigorous and economic and lifecycle assessment before implemented for large scale production. Analysing and assessing the methods might reveal that there is a big amount of uncertainty involved, concerning the feedstocks for the production in the future. Important aspects to consider for the future that influence the feedstock significantly are the expected trend in CO<sub>2</sub> prices and the environmental needs and conditions.

To conclude with, the current data and analysis concerning the production of synfuels from CO<sub>2</sub>, water and renewable sources are underlying factors that synfuels are not the solution to the energy issues but it can certainly be a part of it that can prove advantageous on many fields.

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