PRELIMINARY DESIGN OF AN IN-SITU RESOURCE UTILIZATION (ISRU) PLANT FOR PROPELLANT PRODUCTION ON MARS: A FOCUS ON METHANATION AND SOLID OXYDE ELECTROLYSIS PROCESSES

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ABSTRACT

The work presented deals with In-Situ Resources Utilization (ISRU) systems, aimed to exploit indigenous resources on extra-terrestrial celestial bodies like planets, moons or even asteroids and comets. At the state of the art, ISRU systems encompass technologies to process soils, water, in all its aggregation states, and atmospheric gases, but since the large investments needed to develop these systems to bring them to a space-qualified level, the actual technology readiness levels (TRL) are quite low. The procession of indigenous resources leads to the production of: Life Support Fluids (LSFs), like oxygen and liquid water, to sustain a human exploration mission; Propellant, like oxygen and methane, to supply planetary ascent vehicles or exploration vehicles, such as rovers and hoppers; plastics to allow manufacturing processes. Products are obtained from in-situ resources through chemical and electro-chemical reactors. This thesis is focused on propellant production on Mars via Solid Oxide Electrolysis (SOXE) and methanation of atmospheric carbon dioxide, methanation of carbon monoxide, obtainable as a product of the SOXE process, and the exploitation of the Reverse Water Gas Shift (RWGS) reaction. A preliminary sizing of the reactors has been performed in Matlab© environment, studying the interactions among them and the interactions among the dissimilar chemical reactions occurring inside them. The design has based on an un-manned mission scenario in which propellant production is required to supply a 500 kg Mars Ascent Vehicle (MAV) to get a Circular Low Mars Orbit (CLMO) and to supply an atmospheric hopper for robotic exploration. Both the systems rely on LOX/LCH₄ propulsion technology.
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INTRODUCTION TO ISRU

The In-Situ Resource Utilization (ISRU) activities on celestial bodies beyond the Earth represent the key aspect for a stable, affordable and safety human space colonization. Even if exploitation of indigenous resources brings to many advantages, large investments are required on developing technologies.

In the “short” time of few decades, Human colonies are thought to be stable and highly self-sustained on Mars. This could be affordable only with a development of an extensive ISRU program able to provide the colonies all the basic elements needed for life. Mars seems to be a barren planet covered by the dust, but, actually, is really rich of exploitable resources. Water both in form of vapour and of ice is widely present, oxygen can be obtained from the carbon dioxide contained in the atmosphere and from water electrolysis. By the exploitation of such indigenous resources even methane and plastics can be produced.

Many studies have been performed and are currently ongoing about technological processes and ISRU systems development. Scaled systems have already been built and ready to flight. An example is the Mars Oxygen ISRU Experiment (MOXIE) on Mars 2020 Rover, a scaled oxygen producer system by Solid OXide Electrolysis (SOXE) of atmospheric carbon dioxide. Other systems designs have been done to exploit at the best the Martian resources such as LOX/LCH$_4$ engines (TRL = 6, Munk 2013) and water acquisition systems (WAVAR, Microwaving heating systems, Solar tents). Other designed systems to produce propellant from ISRU are the Sabatier-Electrolysis systems, which have been thought even to be coupled with Reverse Water Gas Shift reactors to increase the production efficiency of the process.

The main reason why ISRU programs studies and analyses have been started and upgraded is the possibility to decrease the Mass in Low Earth Orbit (MLEO) with a correspondent reduced number of heavy-lift launches from Earth (Rapp, 2016) and consequently of costs. The in-situ resources factorization could bring to other great
advantages such as the increment of the independency on Earth, in such a way that no further resources would be needed to be sent from Earth for making costs decrease, and to a better and more feasible Martian robotic and human exploration, increasing rovers’ autonomy and reducing risks for the crew’s health.

The costs reduction is of extremely importance for the future space exploration programs because of the limited budgets that governments allocate to them. This problematic has been highlighted even by a study conducted by the American National Research Council about a comparison between missions’ costs and available budgets. Results are depicted below:

![Budget-driven enhanced exploration annual cost (then-year $)](image)

*Fig. 1.1 A budget-driven pathway toward Mars (NRC, 2014)*
CHAPTER 1: RESOURCES AND STATE OF THE ART

1.1 RESOURCES

1.1.1 Water

Recent robotic missions (phoenix lander in 2008) confirmed the presence of near-surface water in the form of ice in very large amounts at high latitudes and the likely existence of water at lower latitudes in the form of hydrates or in ice in the top one meter of the regolith (Muscatello & Santiago-Maldonado, 2012).

There is a low concentration in the atmosphere (0.13%), but a massive amount of ice at the poles, especially the northern one, even concentrated in huge ice lakes near the surface.

Near the poles there is as much as water as ice within the regolith, absorbed on minerals and available from sulphates and silicates. Its concentration in the regolith is dependent on the latitude, going from 3÷8 % near the equatorial regions to >40% at 60° of latitude. The amount of water beneath the soil could be extracted via heating, with solar tents and microwaving and its chemical processing could lead to the production of elements such as H₂, O₂ and CH₄ (Moses & Bushnell, 2016).

Fig. 1.2 Water mass fraction on Mars (Credit: NASA)
In 1998, Researchers from the University of Washington designed a device called as WAVAR (Water Vapour Adsorption Reactor) aimed to extract water from the Martian atmosphere through the adsorption into Zeolite 3A (Grover, Adan-Plaza 1998). Such a device was characterized by a mass of 885 Kg and a water production rate of 3.3 Kg/sol.

1.1.2 Atmosphere

It’s an important resource of Carbon, oxygen and inert gases. Its composition is mainly carbon dioxide (95%) and small amount of inert gases such as nitrogen (2.7%) and argon (1.6%). Presence of water vapour, as previously said, is quite low (0.13%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>95.32</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.7</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.07</td>
</tr>
<tr>
<td>Water vapour</td>
<td>0.03</td>
</tr>
<tr>
<td>Neon, Krypton, Xenon,</td>
<td>Traces</td>
</tr>
<tr>
<td>Methane, Ozone</td>
<td></td>
</tr>
</tbody>
</table>

**Atmospheric pressure:** 1÷9 mbar; average: 7 mbar

*Table 1.1 Martian atmospheric composition and pressure. Data from Muscatello & Santiago-Maldonado*

The very high concentration of carbon dioxide implies the availability of a very large amount of carbon and oxygen. As what concern carbon, the atmosphere represents the principal source while instead oxygen production can rely even on the exploitation of
the water plethora discussed above. Such an exploitation could be fulfilled through two different processes. The former is a “classical” water electrolysis, while the latter is the watering of the regolith, which contains a great abundance of oxides.

Inert gases can be used for atmospheric composition in life support systems (LSS). The use of the produced oxygen is twofold: a part goes to the LSS to ensure a breathable mixture for the crew, and the other part could be stored cryogenically to be used as an oxidizer for refuelling of a possible Mars Ascent Vehicle (MAV).

1.1.3 Minerals, Ceramics and Glass

Various measurements indicate a great presence of minerals in the regolith, such as: nickel, titanium, iron, sulphur, magnesium, calcium, phosphorus, chlorine, bromine, aluminium, silicon, sodium, manganese, chromium and deuterium (Moses & Bushnell, 2016).

The Viking landers discover as the most common materials in the Martian soil Silicon dioxide (SiO$_2$) and Iron oxide (Fe$_2$O$_3$), covering respectively the 40% and the 17% of the Vikings’ soil samples.

SiO$_2$ is the basic constituent of glass and its large presence in the Martian environment is a promising base for a future Mars glass industry development. From its exploitation, many types of glass products can be obtained: from common glass to fibreglass (excellent for structures construction) and even to optical-quality glass. Concerning this last class of products, a big problematic could be introduced by the large amount of iron oxide observed. To manufacture optical-quality glass, the used sand must be iron free. The oxide can be removed by making it interact with the CO coming from the Reverse Water Gas Shift (RWGS) reaction, or from the SOXE, so to get iron and carbon dioxide as results. In this way, even iron becomes a potential resource to exploit, for example to make steel.
1.2 PREVIOUS ISRU PROCESSES

Prior to the large amounts of water resources findings, ISRU programs have focused on Oxygen production through SOXE and water electrolysis, water extraction from Martian atmosphere and on methanation by using hydrogen both transported from Earth and derived from water electrolysis. Efforts in In-situ manufacture technology to decrease the MLEO or the dependence on Earth had been poor and only in the latest years programs of development have been settled.

Only after the discovery of the water plethora beneath the surface that processing the regolith for water extraction became an engineering ISRU problem to overcome.

1.2.1 Atmospheric H₂O Extraction

As already said, before the phoenix lander mission water was thought to be obtained by condensation of the water vapour present in the atmosphere. Although its small presence, a system designed for water production rates capable to sustain a crew of eight for a mission of 600 sols has been achieved (Adan-Plaza & Glover, 1998), basing simulations and tests on the data acquired by Viking landers and orbiters and by the Mars Pathfinder. The requirements for the design of such a system, known as WAVAR, came out using as a reference the NASA Mars Reference Mission (S.J. Hoffman, 1997) and they were based on the production rate of water, system mass, system dimensions and power supply.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Restriction</th>
<th>Derived From</th>
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<tr>
<td>Net water gain</td>
<td>≥ 3.3 kg/sol</td>
<td>Mass of water needed daily over four years to make up for 600 sols of life support regenerative losses.</td>
</tr>
<tr>
<td>Average power drain</td>
<td>≤ 16 kW</td>
<td>5% of Reference Mission available power.</td>
</tr>
<tr>
<td>Footprint</td>
<td>≤ 7.5 m diameter</td>
<td>Habitat diameter is 7.5 m.</td>
</tr>
<tr>
<td>System mass</td>
<td>≤ 1200 kg</td>
<td>Reference Mission currently requires 1200 kg of seed H₂ to be launched from Earth for replacement of water lost in life support regenerative processes, assuming an H₂ boil-off rate of 0.5% per day over a 200 day Earth/Mars transit. WAVAR takes the place of this seed H₂.</td>
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Fig. 1.3 WAVAR high level requirements (Adan-Plaza & Glover, 1998)
However, even though such achievements, the developing of this technology has been put aside in favour to ISRU processes involving regolith processing and/or warming for water acquisition.

1.2.2 Life Support Fluids and Propellant Production

Production of water didn’t rely totally on exploitation of the atmosphere, in fact the previous discussed technology was thought and developed for water production for LSS only and it has never been taken under great consideration as an alternative to the chemical procession of atmospheric carbon dioxide and hydrogen of terrestrial origins.

To exploit at the best the known Martian resources, before the Phoenix mission, engineers and scientists defined four main chemical reactions to obtain rocket fuel (oxygen and methane) and water:

\[
\text{SOXE:} \quad 2 \text{CO}_2 \rightarrow 2 \text{CO} + \text{O}_2 \quad (1.1)
\]

\[
\text{CO}_2 \text{ Methanation:} \quad \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (2.1)
\]

\[
\text{CO Methanation:} \quad \text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3.1)
\]

\[
\text{RWGS:} \quad \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (4.1)
\]

Reaction (2.1) and (3.1) are exothermic reaction \((\Delta H_2 = -165 \text{ KJ/mol}; \Delta H_3 = -206 \text{ KJ/mol})\) that means no energy is needed to process them, even if an initial input is needed to start up (spontaneously starts, in presence of catalysts such as nickel or ruthenium, occur at temperatures above 250 °C). The other two reactions are endothermic, characterized respectively with standard enthalpy of reactions of \(\Delta H = 282 \text{ KJ/mol} (\Delta \text{E} = 1.33 \text{ V})\) for reaction (1.1) and \(\Delta H = 41 \text{ KJ/mol}\) for reaction (3.1). An interesting aspect that can be denoted is the fact that the superposed effect of reaction (3.1) and (4.1) is equivalent to the (2.1).

It has been designed that the hydrogen reacting in (2.1) and (3.1) should be brought from Earth. If the amount of produced water is large enough to overcome the LSS life
support fluids demand, the exceeding water could be electrolysed to produce hydrogen to send back to the Sabatier module creating, in that way, a closed loop system.

\[
\text{Electrolysis: } \quad 2 \, \text{H}_2\text{O} \longrightarrow 2 \, \text{H}_2 + \, \text{O}_2 \quad \text{(5.1)}
\]

Water electrolysis can be used not only for hydrogen production, but also to obtain oxygen in addition to (1.1). Even this chemical process is an endothermic one (\(\Delta E = 1.23 \text{ V, } \Delta H = 239 \text{ KJ/mol}\)) and it requires more energy than the Sabatier reaction could furnish, implying an energy supply system to make the process sustainable. There are two main electrolysis processes that can be adopted in a ISRU plant on Mars: the classical alkaline electrolysis and the steam electrolysis, which is performed in reactors identical to those in which SOXE is run. The former process is the most known technology to perform water electrolysis, while the TRL of the latter is at the same level of the SOXE technology.

It has even been thought to act the inverse of reaction (5.1), so to make interacting hydrogen from Earth with Oxygen resulted from SOXE, to form water (Drake, 2007). Consequently, a larger amount of hydrogen would have been required.

These reactions could be combined in many different ways to produce propellant and LSFs. Here below, a list of possible combinations thought by Zubrin et Al. (1997) can be found. An interesting prospecting, which hasn’t been considered from Zubrin in his combinations, is the possibility to inject the CO produced by SOXE into the Sabatier reaction and perform a CO methanation process to increase the water and the methane yields. He simply thought to discard the produced CO instead of exploiting it in a methanation process. Therefore, when He spoke about Sabatier reaction, He meant CO\(_2\) methanation only.

The different system trade-offs analysed by Zubrin are:

- **SOXE only**
  
  Reaction (1.1) reduce CO\(_2\) to produce CO and O\(_2\) in quantities enabling to adopt a CO/O\(_2\) mixture as rocket propellant. Although, such an engine results technically difficult requiring very high flame temperature and relatively low
specific impulse (270 s) with respect to LOX/LCH₄ engines (up to 380 s). Because of these disadvantages, it had been thought to adopt SOXE to produce oxygen only with high performing fuel such as methane transported from Earth. Since the oxygen comprises about the 80% of the LOX/LCH₄ mixture, such kind of approach resulted quite suitable and convenient for MLEO saving.

Despite of its advantages, the use of SOXE only were not seen with large enthusiasm due to the complexity of the system, low production rate and high energy requirements. With this approach, no water was produced and so it had been thought to rely on other ISRU processes to provide it.

- **Sabatier + H₂O Electrolysis (SE)**

Another possible way to obtain fuel is the adoption of a Sabatier reactor. The Sabatier reaction, as known as methanation (reaction (2.1)) is, as already said, a highly exothermic reaction and presents a very large equilibrium constant leading to reagents conversion rates higher than 90%. Methane and water obtained are separated in a condenser. Methane is liquefied and stored, whereas water is electrolysed to produce oxygen, which will be liquefied and stored, and hydrogen to feedback to the Sabatier reactor.

In 1995, thanks to the work of Zubrin et al., a complete, integrated, end-to-end, full-scale Mars in-situ propellant production unit was demonstrated.

There are two main observations concerning such a technology: the former is that, to produce oxygen and to reduce MLEO, the whole yielded water should be electrolyzed without the possibility to saving it for LSS, while the latter underline the fact that, even if hydrogen can be produced through water electrolysis, it will be always needed to bring some from Earth since the quantity obtained with electrolysis is only the half of the required to perform the Sabatier reaction. Of course, there were other options such as condensing water from the atmosphere, by using WAVAR or similar systems, and then process it or process water obtained via mining and digging regolith and permafrost. Technologies like WAVAR were too energy consumer, while the soil processing ones were too
green and there wasn’t yet the pushing effect towards this kind of technology given by the discover of the Martian water reservoirs by the phoenix lander.

The advantages of the SE system are simplicity, robustness, scalability, energy efficiency and high propellant production rate, whereas the disadvantages are the need for imported hydrogen from Earth, and the fact that the SE produces a mixture of propellant characterized by a ratio of 2/1 when the optimal mixture ratio for LOX/LCH$_4$ engines is about 3.5/1. By using only SE, the only way to reach the optimal mixture ratio was to discard part of the produced methane. This was a bad option, since part of the hydrogen brought from Earth would have been thrown away decreasing so the efficiency of the ISRU process in terms of propellant produced to hydrogen imported ratio. Nowadays, it could be thought to exploit the discarded methane for refuelling exploration rovers or hoppers.

- **SE + SOXE**
  To overcome the disadvantage, came out from the adoption of SE system only, of discarding methane to get an optimal mixture ratio, a SOXE unit has been thought to be add to the SE to increase the production of oxygen and reach the desired value of mixture ratio. The problem stayed in the too high SOXE power demand and in the scalability of the system.

- **SE + RWGS**
  It was the most preferable solution at the time, even if any experimental work had been done to demonstrate its viability to-1997.

The RWGS in the Martian environment represents an *infinite leverage oxygen machine*, as Zubrin et al. state, combined with water electrolysis. The carbon monoxide produced by the reaction is discarded, while the water electrolyzed and the resulting hydrogen given in feedback to the reactor and the oxygen liquefied and then stored. The only reagent need to be imported is a small amount of water which is endlessly recycled, whereas the carbon dioxide is practically omnipresent in the atmosphere in a quite infinite amount.
The RWGS/electrolysis system is quite simple and very similar to the SE one. The RWGS reactor is like a Sabatier one, but with a different catalyst. The power demand is dominated by the water electrolysis subsystem, which could be in common with the SE system, since the reaction is not so endothermic. Moreover, since the required thermal power is less than the one produced by the Sabatier reaction, it could be thought to use the Sabatier to drive the RWGS reactor by a direct thermal contact. So, combining in these way SE and RWGS the net reaction produces 4 kg of methane and 16 kg of oxygen per each kg of imported H₂, fulfilling the requirement of a mixture ratio of 3.5/1.

However, this approach hide a big issue: theRWGS reaction is characterized by a low equilibrium constant that gets an asymptotic value just above the unity for temperature higher than 600 °C (Escobar, 2012) and this is a significant problem in driving the reaction to completion. An additional issue is the possibility that alternative exothermic reactions producing methane or methanol occur, avoidable by narrowly catalyse the reaction to reduce CO₂ to CO.

Possible ways out could be the overload of the reactor with CO₂ or H₂ to force the complete consumption of the other and then given in feedback to the reactor, or alternatively adopt a desiccant bed or a condenser to remove the water vapour from the reactor and drive the reaction towards right.

Figure 1.4 depict an ISRU trade tree, coming from Human Exploration of Mars: Design Reference Architecture 5.0, G.B. Drake, 2007, for LSFs and propellant production. Important to note that the Design Reference Architecture (DRA) 5.0 is the first mission concept whom took in consideration ISRU processes for water production involving soil procession. However, the large water availability on Mars wasn’t yet known and soil excavation and drying technologies were still green and at a low stage of development.
All values of $\Delta H$ and $\Delta E$ indicated above refer to standard conditions and have been taken from: Holquist, Klaus, and Nabity, *Electrochemical Carbon Dioxide Reduction with Room Temperature Ionic Liquids for Space Exploration missions*, 2016, and from Sun, Chen, Jensen, Ebbesen, Graves, Mogensen, *Thermodynamic analysis of synthetic hydrocarbon fuel production in pressurized solid oxide electrolysis cells*, International journal of hydrogen energy, November 2012, pp. 17101-17110.

1.2.3 Plastics Manufacture

Another great goal, achievable by relying on ISRU processes, is the plastics manufacture (Moses & Bushnell, 2016). The key element for plastics industries is the ethylene ($C_2H_4$), which can be obtained by modifying the ratio between carbon dioxide and hydrogen in the RWGS reaction, removing the produced water and then re-processing the remnant products in the presence of an iron-based catalyst:

Modified RWGS: $2CO_2 + 6H_2 \rightarrow 2CO + 2H_2O + 4H_2$ \hspace{1cm} (6.1)

Ethylene: $2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O$ \hspace{1cm} (7.1)
Reaction (7.1) is strongly exothermic ($\Delta H = -207$ KJ/mol. Zubrin et al., 1997) and so it could be used to drive the (6.1) too.

1.2.4 Solar Energy Exploitation

Another important resource to exploit on Mars is the solar energy. The average solar flux reaching the planet is 590 W/m$^2$ and such values of radiation still allow the adoption of solar arrays as energy converters. Previous technologies were based on Ga-As panels with efficiencies around the 20%. These low efficiency values and the continuous needs for cleaning out the dust deposited on the panels moved the attention also on nuclear power systems as energy sources. Solar energy was also thought to be used for food production in surface greenhouse cultures, but the high level of radiations and the large presence of dust in the atmosphere have brought the engineers to shift their designs to underground structures artificially illuminated.

1.3 CURRENT ISRU PROCESSES

With the confirmed existence of large water basins in the top 1 meter of the surface, the rapid evolution of technology and the enlargement of knowledge about the Red planet, new ISRU processes have been developed to reduced once more mission costs, the independence on Earth, the risks for the crew health and to increment the quality of in-situ exploration.

Criteria for the selection of one process instead of another are multiple and based on the level of technology reached, the costs for developing new processes and technologies, and on the ratio between mass of products supplied by ISRU to mission and the mass of the ISRU system brought from Earth (Rapp, 2016).

1.3.1 H$_2$O Extraction

New ISRU technologies are more focused on the exploitation of the water plethora discovered under the surface rather than to continue the path of atmospheric extraction.
through WAVAR or similar devices. The motivation could be found in the larger amount of water obtainable with the soil processing and in the increment of independency on Earth and the decrement of MLEO due to the possible replacement of the stored hydrogen brought from Earth with hydrogen obtained by electrolyzing part of the produced water.

Scientists and engineers have found many possible ways to extract water from the regolith such as drilling, digging, microwaving or heating via solar tents (Sanders & Mueller, 2015 and Ethridge & Kaukler, 2012).

Microwaving the soil has some great advantages like the absence of any regolith digging or excavation process, relatively high engineering problems since the complex mechanical operations required and since the difficulties that a frozen permafrost, as hard as granite, introduces to the regolith excavation. Another advantage is determined by the intrinsic nature of the regolith, which behaves like a good thermal insulator making appear inconvenient the adoption of a direct or solar heating strategy. The regolith insulator capabilities makes the heating process highly ineffective, because of the very slow heat flow inside of it that don’t allow the underlying regolith to get temperatures good for water extraction (Ethridge & Kaukler, 2012). Indeed, no significant work has been performed to advance the solar tents method of water extraction (Sanders & Mueller, 2015).

At the contrary, even if microwaving process presents an interesting technological path to follow, many studies have been developed about ISRU processes for water extraction involving soil excavation techniques. This kind of systems is based on three principal steps: extraction, heating, and dry soil ejection. Different excavation techniques have been thought depending on the hardness of the soil and on the form of water present in it (hydrated vs icy soil) as well as different heating methods have been taken in consideration: electrical heaters/conduction, fluidization/convection, and microwaving.

Whereas Ethridge and Kaukler focused their work on microwaves heating, Zacny and Paulsen have been focused on developing a system, whom processes the soil after the
extraction and heats it by relying on conductive heating, named Mobile In-Situ Water Extractor (MISWE). (Zacny & Paulsen, 2012). Such a system showed many advantages derived from the adopted heating technology compared to microwaving. To Zacny and Paulsen, conductive heating represents the best choice for mainly three reasons:

<<First, conductive heating can be implemented through a simple resistive heater [...] Several heaters can be used to provide distributed heating, bringing the entire mass of soil to target temperature with a minimum of wasted heat. Microwave heating, in comparison, requires waveform manipulation to avoid hot spots, or moving either the magnetron or the auger [...] This in turn would require additional actuators making system more complex. Heating of the regolith depends on absorption of the microwave energy. [...] Second, conductive heating is more flexible in its implementation, in that it can be delivered by means other than electrical power. [...] Microwave system requires electrical power and in turn, by its nature will be less efficient. [...] Third, conductive heating imposes fewer requirements on the surrounding hardware. Using a magnetron would require that the rover and interfacing components be well grounded, or else they would build up a static charge>>. (Zacny & Paulsen, 2012).

1.3.2 Life Support Fluids and Propellant Production

Processes to get LSFs (O₂ and H₂O) and propellant (O₂ and CH₄) haven’t changed significantly through the years. The ones on which previous ISRU technologies were based remain the same on which engineers rely nowadays (SOXE, Sabatier, RWGS).

Two are the mainly differences between the past and the present technologies: the first, as already said many times, born from the discovery of the undersoil water plethora that has driven to the in-situ production of hydrogen, through water electrolysis, instead of bringing it from Earth, and of oxygen, reducing the advantage of SOXE and RWGS ISRU processes, while the second difference stays in the system components and in the
resources collecting techniques evolution. TRL levels of atmospheric CO₂ processing systems and of LOX/LCH₄ engines for a MAV have reached quite high levels and they are ready to be tested and validated. A 1% scaled system for oxygen production through SOXE, MOXIE, will be sent on the Mars 2020 rover to validate and demonstrate in-situ the developed technology (Meyen, Hecht, and Hoffman, 2016). SOXE efficiency and performance have been improved and encouraging results have been obtained. Many alternative processes are under investigation and development but still at a too low TRL. An interesting alternative technology to SOXE is the electrolysis of carbon dioxide in ionic liquids that could lead to CO₂ processing at room temperatures. Room Temperature Ionic Liquids (RTILs) act as catalysts promoters which favour products formation with a lower energy cost (Holquist, Klaus, and Nabity, 2016). This kind of technology has reached TRL levels of 2-3, too low for space applications.

The research of alternatives to SOXE for Mars ISRU has not been of primary importance since, as Holquist, Klaus, and Nabity (2016) said:

<<A long duration stay on the surface of Mars provides a unique opportunity where the need for such high efficiency for O₂ recovery from CO₂ is not necessary, due to the relative abundance of CO₂ in the Martian atmosphere.>>

So, even a 50% efficient process like SOXE is well suited for ISRU purposes on Mars. Such a value of efficiency derives from the fact that only one of the two oxygen atoms composing the CO₂ molecule goes to form oxygen ions, while the other goes to form CO. Another possible advantage that such ISRU technology could lead to is the possibility to exploit oxygen, carbon dioxide and methane for fuel cells production to be, then, adopted as primary sources of energy to sustain ISRU processes and human staying on Mars in general.

1.3.3 Plastics Manufacture

Polyethylene production basic processes haven’t varied through the years, whereas the interest in exploiting such resources have increased with the discovery of the large
amount of water/ice in the soil, which leads to a larger obtainable quantity of hydrogen, and with the increasing of the 3D printing technology (Moses & Bushnell, 2016). Such a technology allows the procession of plastics or regolith without discharging material but only adding it, indeed it is also known as 3D additive manufacturing printing. Consumes could be mitigated and structural particles, items and many other useful products for exploration and for sustainability of the human presence on Mars could be obtained directly in-situ. On Earth this technology in widely used even for industrial purposes, but many upgrades are necessary to make it ready for space application: autonomous functioning and correct functioning in a reduced gravity environment represent two important aspects to develop.

1.3.4 Regolith As Radiation Shield

New ISRU technologies for habitat safety and protection against Galactic Cosmic Rays (GCR) and Space radiations focus on regolith adoption as a possible, with an extremely large in-situ availability, radiation shield. New concepts of inflatable habitats positioned underground beneath 5 meters or more the surface, via burying or exploiting already existent lava tubes, are now investigated and They became the most likable approach for human life support structures. Thermal insulation and micrometeoroid protection could be achieved too.

Inflatable structures have many advantages in terms of volume occupied in the spacecraft before the deployment and in terms of weight. In addition, such kind of habitats could be designed to adapt their shape to the chosen cave or tube. Even if preliminary computations suggest that the load provoked on the structure is almost in the same level of the one induced by the internal pressure, additional structural elements inside the habitat will prevent collapse in case of pressure loss.

An interesting aspect of inflatable habitats is the possibility to be produced even in-situ, when plastics manufacture industry will be sufficiently developed.
Other concepts for human habitats on the Moon or on Mars are based on their 3D printing by using in-situ regolith directly. Both the European Space Agency (ESA) and the National Aeronautics and Space Administration (NASA) are pushing towards this kind of technology.

Burying beneath the regolith could be an approach even for propellant and life support fluids’ tanks. This will ensure protection and, mainly, thermal insulation, a crucial aspect to maintain the products in a liquid (compulsory for propellant) or in a gaseous state. Solid state is not suitable at all for distribution systems, only in case of transportation from a locus to another or in case of stocking.

Possible alternatives to avoid water freezing could be found in the exploitation of the large amounts of perchlorates present in the soil. The freezing point could be brought down to -60° C or even to -70° C for water – Magnesium perchlorates. Another approach is to store fluids chemically or via hydrates. The water could be simply removed by heating at point of use when needed.

1.3.5 Solar Energy Exploitation

Concerning solar energy exploitation, due to the relatively low, with respect to Earth or Moon, solar heat flux on Mars and to the highly dusty environment, solar panels are not seen as the primary power generator technology. Even if new technologies have been developed on Earth and efficiencies overcome the 30%, their adoption is thought as a back-up solution in case of failure of the primary system (micro-fission nuclear reactors or Low Energy Nuclear Reactions (LENR) or even chemical reactors such fuel cells, produced exploiting in-situ resources).

1.4 ISRU SYSTEMS

Until now it has been spoken about resources available on Mars and obtainable through their factorization, and past and present ISRU technologies. A comparison between different methods of resources processing and technologies has been performed as well
as a brief introduction to the systems whom will be implemented to operate following such processes.

In this thesis work, particularly attention will be given to chemical processing systems to produce propellant as liquid oxygen (LOX) and liquid methane (LCH₄) as well as to the propeller that could use such mixture to work.

Concerning system to reduce atmospheric CO₂, many studies have been performed and technologies developed. SOXE of CO₂, RWGS and methanations are the main processes on which engineers relied the most, and many investigations and developments to reach higher levels of conversion efficiency, production rate and lower energy consumption are ongoing.

Engines based on LOX/LCH₄ propellant for a possible MAV have started to be studied in the 2000s to increase the contribution of ISRU technologies to the envelop towards less expensive, more independent and more safety missions to Mars and its far better, human and not, exploration. Nowadays re-ignitable and re-usable LOX/LCH₄ scaled engine technologies are ready to be validated and demonstrated in an operational environment.

1.4.1 Atmospheric CO₂ Processing Systems

Due to its large presence in the Martian atmosphere, CO₂ have become the best suitable resource of oxygen and carbon for O₂ and CH₄ in-situ production. The chemical and electro-chemical reactions on which scientists and engineers relied the most have already been presented in the previous paragraphs and are: CO₂ and H₂O electrolysis to produce O₂ and H₂ (Reactions (1.1) and (5.1)), methanations for CH₄ and H₂O (Reactions (2.1) and (3.1)), and the RWGS to obtain H₂O to be electrolysed or sent in the LSS (Reaction (4.1)).

1.4.1.1 Solid Oxide Electrolysis

SOXE of CO₂, adopting solid engineered ceramic Yttria-Stabilized Zirconium (YSZ) electrolytes, presents characteristics of efficiency, durability and stability greater than
other methods to fulfil the requirements on high production volumes and on a constant oxygen supply. This electro-chemical process minimizes the energy consumption operating near the theoretical efficiency limit (Hartigsen, Elangovan, and Elwell, 2016) and remains stable, with an excellent volume and phase control, even under the harsh Mars environment conditions (extreme cold, reduced gravity and dusty atmosphere). They are very important qualities that other processes, such as liquid electrolytes, nowadays don’t possess, as their phases and volumes are drastically affected by external temperatures. Even dust contamination is critical for liquid electrolytes decreasing their effectiveness.

The most advanced system based on SOXE CO$_2$ processing for in-situ oxygen production is the MOXIE system, planned to be sent on the NASA Mars 2020 rover. It’s a scaled system whose primary objective is the validation of such ISRU technology and put a first brick to an always more feasible Mars human and robotic colonization. It will enable a new class of sustainable missions by reducing the required amount of material to be brought from Earth.

The system, described by Meyen, Hecht, and Hoffman (2016), is aimed to produce oxidizer at a production rate of 1% of the needed for a return trip from Mars. It’s expected to produce about 10 g/hr of oxygen with a purity higher than 99.6 % and it’s mainly composed by three subsystems: the Carbon dioxide Acquisition and Compression (CAC), the SOXE, and the Monitor and Control System (MCS).

The CAC subsystem is aimed to draw in, through a dust filter, the Martian atmosphere by relying on a volumetric pump and pressurize it up to 1 atmosphere (important to remember that atmospheric pressure on Mars is in the order of 0.01 atm, 100 times lower than the needed). The pump volumetric efficiency is strongly affected by the value of atmospheric pressure, which varies with altitude, hour of the day, and season.

Right after the pump there is a small volume, called *plenum*, to help buffer the SOXE from any pressure spikes from the pump.
The flow gets the SOXE, after being pre-heated, where the CO\textsubscript{2} electro-chemical reduction could start at a temperature of 800°C (1073 K). The SOXE is arranged in stacks, which are constituted by cells. Cells are the base unit and each of them contains an oxygen permeable electrolyte sandwiched between a cathode and an anode. The cells are connected in series in the stack and, since the voltage is applied across it, they feel the same current intensity, but the voltage drop across each cell varies depending on its electrochemical resistance. The oxygen production rate in a cell is dependent on the current intensity felt and so, each cell is characterized by the same production rate.
The CO$_2$ flows over the cathode where the reduction process occurs and CO molecules and O$^{2-}$ ions are formed. Then, thanks to the potential applied, the ions pass through the YSZ ceramic electrolyte towards the anode to be oxidized, obtaining O$_2$ molecules.

The unprocessed CO$_2$ and the produced CO are exhausted, of course, via a different duct with respect to oxygen. Since MOXIE is only a scale system aimed to demonstrate the technology for carbon dioxide reduction in the operational environment, the products and the unprocessed atmospheric gas are vented into the Martian atmosphere instead of being collected or addressed towards other ISRU systems as it would happen with a full scale and fully operative ISRU system.

The inlet and the outlet gas state, the pump health and the electrochemical process information are monitored, sent in feedback and controlled by the MCS thanks to the numerous sensors along the system.

![MOXIE flow chart](image)

**Fig. 1.7** MOXIE flow chart (the MOXIE team, 2016)

**1.4.1.2 Sabatier and RWGS Reactors**

The most detailed studies about methanation and RWGS processes to exploit in a ISRU plant on Mars have been conducted by Dr. Robert Zubrin of Pioneer Astronautics from
1993 to 1998. In literature nods concerning such kinds of systems can be found (i.e. Muscatello & Santiago-Maldonado) but not as detailed as Zubrin’s works. Rapp, in his analysis about the NASA space exploration program (2016), speaks about the possibility to exploit the Sabatier and the RWGS reactions to reduce the required MLEO for Mars missions, and in addition proposes a solution on which Zubrin hadn’t worked: the possibility to perform the processes in the same reactor exploiting a transition zone in which both occur, which will be the way this work will follow.

Fig. 1.8 Methanation system scheme (Zubrin et al. 1997)

The scheme designed by Zubrin et al. based on Sabatier and electrolysis process is depicted in figure 1.8. The CO\textsubscript{2} is acquired from the atmosphere and pass through a flow control section that filters the stream from dust and control the mass flow rate to inject in the reactor. The gas is preheated also exploiting the heat released by the exiting products through a heat exchanger before entering the reactor, in which the process is performed. A Sabatier reactor is very simple, and usually is a cylinder filled with a fixed catalytic bed through which the mixture flows and reacts. Just after the reactor, the products released their heat to the inlet stream and goes towards an ulterior cooling stage where water condenses and is separated by methane. This is possible thanks to
the lower methane liquefaction point with respect the water one. The water is then alkaline electrolysed and hydrogen is sent back to the Sabatier reactor, while the oxygen is liquefied, releasing is heat to the liquefied stored hydrogen that goes to be methanized, and then stored. The same process occurring at the produced oxygen is reserved for the methane after being separated by the water.

The scheme is practically the same even for the methane and oxygen production system exploiting the RWGS reaction (figure 1.9), but instead of producing methane and water, the reactor produces water and carbon monoxide. The flow follows the same path described in the previous system until the water condenser unit, where the separation among products occur. The water is electrolysed as described before and the oxygen collected, while the remained CO, CO$_2$ and H$_2$ pass through a dryer, re-pressurised and sent in feedback to the reactor. To avoid the recirculation of the produced CO, a gas separating membrane could be adopted to separate CO from the other gases to be then vented.

Fig. 1.9  Oxygen production system through RWGS (Zubrin et al. 1997)
1.4.1.3 Criticalities

The presented systems show different critical aspects concerning:

- Storage of hydrogen and products;
- Reactions efficiency.

Criticalities concerning the storage process are related to the large power demand to store H\(_2\) and propellants. It’s not compulsory to store cryogenically the hydrogen brought from Earth because it isn’t required to be at its liquid form to be processed in the reactors, but an analysis on boil-off and leakage is required to understand which kind of storage process is better. Contrary with respect to hydrogen, oxygen and methane must be stored cryogenically at very low temperatures to be maintained at the liquid phase. This increases the power demand and the complexity of the storage system, that can be set on surface as a plant’s subsystem or sited directly on the vehicle that will use the propellant.

The most important criticalities considered in this thesis work are those regarding the efficiency of the processes. In the reactors, not only the desired reactions occur, but also side reactions that exploit the same reagents and products of the principal ones are performed. The most dangerous side reactions can occur in all the seen reactors are those leading to carbon deposition. Such a phenomenon is very dangerous for the reactions correct proceeding because solid carbon goes to “poison” the catalysts and, in the case of the SOXE, the cathode porous material inhibiting therefore the processes. To avoid this critical process, the reactors operative conditions in terms of temperature and pressures must be selected in order to prevent the side reactions occurrence.

The principal carbon depositing processes occurring during methanations, RWGS and SOXE are:

\[
\text{Boudouard: } \quad 2\, CO \rightarrow C(s) + CO_2 \quad (8.1)
\]

\[
\text{CH}_4 \text{ Cracking: } \quad CH_4 \rightarrow 2\, H_2 + C(s) \quad (9.1)
\]
The Boudouard reaction at standard pressure presents high rate of deposition between 450 ÷ 650 °C, but with the increasing of pressure the range of temperature shifts towards 725°C and reaction rates increases, but other side reactions occur too and consumed all the deposited carbon, decreasing the total deposition process. Methane cracking, at the contrary, occurs at temperature between 600 ÷ 750 °C, becoming totally inconsistent at 800°C. The increment in pressure favours the reverse reaction leading to a solid carbon consumption process.

1.4.2 LOX/LCH₄ Engines

Propulsion systems based on hydrocarbons are considered a high-priority technology to develop to fulfil the top technical challenge of a new, performant, less toxic and cheaper propulsion system. Systems based on LOX/LCH₄ mixtures are one of the most interesting solutions presenting the above characteristics and they have all the potential, in a long-term perspective, to cover a wide range of applications, from launcher main stages up to small thrusters. An ulterior advantage this technology leads is the possibility to reduce the costs and the dependency on Earth of a Moon/Mars exploration mission, where propellant could be produced in-situ and not brought from Earth. This helps to overlap also problems related to propellant storage for long time periods in a harsh environment as the interplanetary space is.

NASA and Agenzia Spaziale Italiana (ASI) have invested many funds in developing such a technology awarding contracts with local industries and research centres (NASA with Aerojet and Northrop Grumman industries, whereas ASI with Centro Italiano Ricerche Aerospaziali (CIRA) and AVIO Spa).

NASA based the project design on previous demonstrated non-toxic Reaction Control Engines (RCE), whom exploited LOX/Ethanol and LOX/LH₂ propellants, developed during the NASAs 2nd Generation Reusable Launch Vehicle/Next Gen Launch Technology Program – Auxiliary Propulsion Project (2000-2004). In the 2005-2010 timeframe, the NASA Propulsion and Cryogenics Advanced Development Project (PCAD) conducted
numerous in-house experiments on LOX/LCH₄ RCE. NASA is still developing the technology and recently it has focused on Additive Manufacturing Demonstration (AMD) engines (Brown et al., 2016). Other projects involved in technology demonstrations are the Cryogenic Fluid Management Project (CFMP), Morpheus, Evolvable Cryogenics (eCRYO) Project and the Cryogenic Propellant Storage and Transfer (CPST) project.

All those works led to the development and to the maturation of two main application for LOX/LCH₄ propulsion systems, such as RCE and pressure/pump fed main engines.

1.4.2.1 RCEs

Concerning RCEs, Aerojet successfully designed, tested and demonstrated a reaction control engine capable to meet the specifics given by NASA and even exceeding them. The specifics were:

- 317 s vacuum specific impulse;
- 4 lb s minimum impulse bit;
- 80 ms electrical pulse width;
- 25000 valve cycles;
- Ignition and operation over a range of inlet conditions including liquid and gaseous propellants.

Such an engine was called Aerojet 100-lbf LOX/LCH₄ RCE and were provided to NASA 5+2 units to be tested. The Northrop Grumman industry, whom was primarily based on previous hypergolic propellant engines works, delivered a single pre-prototype unit, the Northrop Grumman Pre-Prototype 100-lbf RCE, that was tested in vacuum conditions at their test facility fulfilling, in turn, the given requirements. (Brown et al., 2016).
1.4.2.2 Main Engines

About LOX/LCH₄ main engines a lot of work has been done by NASA and it has been distributed in two main research areas:

- Pressure-fed main engines: ~ 6000 lbₗ (26 kN) class
- Pump-fed (throttleable) main engines: ~ 25000 lbₗ (111 kN) class

ATK/XCOR and KT Engineering (KTE) were initially funded to conduct LOX/LCH₄ pressure-fed main engine workhorse demonstration efforts, but due to the evolving technology demonstration requirements, contract options hadn’t been exercised and NASA funded Aerojet to develop the work. The specifics given to Aerojet were:

- 5500 lbₗ thrust, 355 s vacuum specific impulse;
- 90% rated thrust within 0.5 s;
- Total of 24 restarts;
- Operation over a range of inlet conditions from gas to liquid for start.

Aerojet delivered to NASA the Aerojet 5500 lbₗ LOX/LCH₄ Main engine to demonstrate and test both sea-level and altitude performances. Results showed the engine got all the
requirements except the 355-s vacuum specific impulse, presenting an average value of 348 s with an expansion ratio of 150:1. However such a value had been considered sufficiently near the goal, being within 2% of it.

Recently NASA is pursuing additively manufactured regenerative cooled LOX/LCH₄ engine concepts. The work is underway and initial hot fire testing has verified injector stability and has successfully demonstrated the 3D concept.

From the side of pump-fed main engines, PCAD project conducted efforts aimed to demonstrate LOX/LH₂ throttleable main engines. Only in recent years, due to the always increasing interest in future Mars exploration missions, NASA started to think about LOX/LCH₄ architectures and demonstrate additively manufactured engine components and systems operation. In March 2016, an additively manufactured LOX/LCH₄ Turbo-Pump has been successfully demonstrated. Development of other components and system-level test-bed demonstrations are planned for the next future (Brown et al., 2016).

Even Italy, as already mentioned, is investing in LOX/LCH₄ engines technology with the Italian National Propulsion Program HYPROB-BREAD, aimed at designing, manufacturing and testing a Launch & Recovery Element (LRE) demonstrator of 30 kN thrust class based on a liquid methane cooler reliant regenerative cooling system. The objective of the project is to increase the TRL of the technology by testing and demonstrating it in relevant facilities such as CIRA HYPROB-PLUS and FAST2 AVIO-ASI. The final configuration of the demonstrator has successfully passed the Detailed Design Review (DDR) milestone and currently is in the manufacturing phase. Intermediate technological breadboards have already been developed, manufactured and tested (Salvatore et al., 2016). Preliminary firing tests had been conducted in the end of the 2016.
CHAPTER 2: SYSTEM REQUIREMENTS AND ARCHITECTURE

DEFINITION

2.1 SYSTEM REQUIREMENTS

In the past years, many studies had been conducted to estimate the amount of life support fluids and propellant needed for a human mission to Mars and the obtained results had become useful in listing requirements for ISRU technologies design and in the evaluation of the advantage, mainly in MLEO saving, that those systems might bring.

The most considered results are the ones coming from the analysis of the NASA’s Design Reference Architecture, a mission design for the Mars human exploration continuously updated through the years by NASA engineers, and reported in Table 2.1.

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<tr>
<td><strong>O₂ for LSS</strong></td>
<td>3.6 Tons</td>
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<tr>
<td><strong>O₂ for MAV</strong></td>
<td>22.5 ÷ 30 Tons</td>
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<tr>
<td><strong>CH₄</strong></td>
<td>7.5 ÷ 10 Tons</td>
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</table>

*Table 2.1 LSFs and propellant requirements from DRA*

These quantities are for a 600 day mission for a crew of 6 members adopting a MAV to ascent from the Martian surface relying on a LOX/LCH₄ propulsion system working at a mixture ratio of 4:1 and from them requirements on ISRU systems can be extracted in terms of production rate (Table 2.2).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O₂ for LSS</strong></td>
<td>6 kg/day</td>
</tr>
<tr>
<td><strong>O₂ for MAV</strong></td>
<td>37.5 ÷ 50 kg/day</td>
</tr>
<tr>
<td><strong>CH₄</strong></td>
<td>12.5 ÷ 16.7 kg/day</td>
</tr>
</tbody>
</table>

*Table 2.2 LSFs and propellant requirements from DRA*
In the present work, we will focus on sizing a system able to withstand, in terms of production rates, the propellant demand coming from a mission scenario that sees a production system supplying fuel to:

- a 500 kg MAV for unmanned transfers from the Martian surface to a Circular Low Martian Orbit (CLMAO) where it will be docked by a space station orbiting the Red planet. The orbit is thought to be just outside the atmosphere.
- A hopper capable to transfer exploration vehicles, such as landers and rovers, to an angular distance of 120° from the lift-off point and return. The Curiosity rover stats will be taken as a reference for the hopper payload.

Important to note that the oxygen production will be aimed only to fulfil the propellant requirements without caring about any kind of LSFs demand.

The *rocket equation*, as known as the *Tsiolkowsky equation*, is adopted to compute a preliminary estimation of the propellant needs to get the CLMAO. The parameters adopted are:

<table>
<thead>
<tr>
<th>Orbit radius [km]</th>
<th>Required ΔV [m/s]</th>
<th>Dry mass [kg]</th>
<th>Specific impulse [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>3418</td>
<td>500</td>
<td>317</td>
</tr>
</tbody>
</table>

The required velocity variation is simply the velocity acquired by the MAV to orbit on the desired CLMAO. Very simple orbital mechanics equations have been exploited to get its value, but they won’t be showed herein this work due to their extremely high triviality. The mass ratio is the ratio between the system’s dry mass and the propellant mass; its value has been computed by reversing the Tsiolkowsky formula. LOX/LCH4 engines state of the art has been considered for the specific impulse choice.
Considering a mixture ratio of 4:1, even if Zubrin in his works indicate 3.5 as the optimal value (1997), the results can be recapped as follow:

<table>
<thead>
<tr>
<th>Propellant mass [kg]</th>
<th>Oxidizer mass [kg]</th>
<th>Fuel mass [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8644</td>
<td>6915</td>
<td>1729</td>
</tr>
</tbody>
</table>

*Table 2.4 MAV propellant requirements*

Even for the hopper the Tsiolkowsky equation results quite helpful. To simplify the computations as much as possible, three phases are taken in consideration: the vertical lift-off, the horizontal cruise to get the target point and the return. The hopper’s engine is still a LOX/LCH4 one and the parameters adopted in the computation are:

<table>
<thead>
<tr>
<th>Cruise altitude [km]</th>
<th>Max angular distance [rad]</th>
<th>Payload mass [kg]</th>
<th>Mass ratio [-]</th>
<th>Specific impulse [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2/3 π</td>
<td>900</td>
<td>0.15</td>
<td>317</td>
</tr>
</tbody>
</table>

*Table 2.5 Tsiolkowsky equation parameters for hopper*

Knowing the equatorial radius of Mars, the maximum angular distance the hopper can cover back and forth could be expressed in meters instead of radians by only multiply it by the Martian equatorial circumference and divide by $2\pi$. The results are summarized in table 2.6.

<table>
<thead>
<tr>
<th>Max distance [km]</th>
<th>Propellant mass [kg]</th>
<th>Oxidizer mass [kg]</th>
<th>Fuel mass [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3556.5</td>
<td>2690</td>
<td>2152</td>
<td>538</td>
</tr>
</tbody>
</table>

*Table 2.6 Hopper propellant requirements*

Putting all together, the total demand of propellant to achieve the mission objectives is:
<table>
<thead>
<tr>
<th>Propellant mass [kg]</th>
<th>Oxidizer mass [kg]</th>
<th>Fuel mass [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11334</td>
<td>9067</td>
<td>2267</td>
</tr>
</tbody>
</table>

*Table 2.7 Total demand of propellant*

Since an unmanned scenario has been considered, there is not a big criticality and a real constraint on the time needed to fill the propellant tanks. Of course, faster the ISRU system will be and greater will be the exploration vehicles transfers or the ascents towards the CLMAO.

## 2.2 ISRU PLANT ARCHITECTURE

In the previous chapter, the CO and CO\textsubscript{2} methanation processes, the RWGS and the CO\textsubscript{2} and H\textsubscript{2}O electrolyses turned out has the most suitable chemical reactions to exploit the Martian in-situ resources for propellant production for a new generation of LOX/LCH\textsubscript{4} rocket engines.

It appears quite trivial even before any analysis that the methanation processes, due to the similarity in terms of species involved and to their moderate exothermal nature, can occur in the same reactor. It’s also obvious that the CO methanation and the RWGS, by looking at their combined effect as shown before, will occur preferably in the same reactor despite their different nature. If the RWGS could be thought to be driven in the same reactor in which methanations occur due to its low endothermicity, the same could not be expected for the electrolysis processes, which are characterized by elevated levels of endothermicity. The numbers of the reactors in the system is influenced even by the choice of which kind of water electrolysis perform: the classical alkaline water electrolysis, or the higher temperature steam electrolysis.

In this section, a preliminary architecture of the whole plant will be defined, analysing and comparing various aspects of the reactions and their mutual influence inside a reactor.
2.2.1 Reactors Definition

In the following section the behaviour of the reactions with operative conditions will be investigated, highlighting the differences among the reactions and leading eventually to a definition of the number and of the type of reactor required in the system.

There are numerous aspects to investigate for each reaction, and, in this work, a particular attention has been given to the dependency on the operative temperature, strictly related to the exothermic or endothermic nature of the reactions. An exothermic process is strongly disadvantaged if operated at elevated temperatures, totally the opposite of what happen with an endothermic one.

The pressure dependency has not been considered as a dominant parameter on which base a comparison among the processes because of the small range of values that pressure could take, limited by the power required to pump the atmospheric gas from the extremely low pressure level existent on Mars. On Earth, where problems led by power requirements are inexistent, this dependency acquires the same weight of the one on temperature. Indeed, by looking at the Le Chatelier principle, a pressure increment favour the methanation reactions because the gaseous moles of the products are less than the ones of the reagents, and this explains why on Mars the gases are pumped at least up to 1 atmosphere and not left at ambient pressure. As what concern the electrolysis process is the contrary, but since the products are brought away from the reaction site, the equilibrium is always shifted in favour to the reaction. Furthermore, a higher pressure is preferred because it limits the electrodes and the electrolyte poisoning by carbon deposition processes.

The parameter through which the behaviour with temperature can be studied is the equilibrium constant $K_{eq}$. It indicates how much a reaction is favoured or not: if it’s high it means a favoured reaction, on the other hand, if it’s low it means a not favoured reaction. Its computation is simply performed by exploiting the thermodynamics’ second principle and the definition of the Gibbs free energy.
2.2.1.1 Methanations and RWGS Analysis

For a generic chemical reaction,

\[ aA + bB \leftrightarrow cC + dD \]  

(7)
driven at temperature \( T \), the variation of the Gibbs free energy of the system can be computed as:

\[ \Delta G = \Delta H - T\Delta S \]  

(8)

Where \( \Delta H \) and \( \Delta S \) are respectively the variations of the enthalpy and the entropy of the system, computed as the difference between the sum of the products quantities and the sum of the reagents ones.

Expanding the terms of equation (8), it is possible to rewrite the variation of the Gibbs energy in other terms:

\[ \Delta G = \Delta G^0 + R_u T \ln(Q) \]  

(9)

Where \( Q \) represents the reaction quotient, \( R_u \) the universal gas constant and the apex \( ^0 \) stands for “standard conditions”.

From the study of the chemical equilibrium, that won’t be proposed here, turns out that the variation of the Gibbs free energy at equilibrium is null, and the reaction quotient becomes equal to the equilibrium constant leading to the following relation:

\[ \Delta G^0 = -R_u T \ln(K_{eq}) \]  

(10)

That can be simply reversed, obtaining:

\[ K_{eq} = \exp\left(-\frac{\Delta G^0}{R_u T}\right) \]  

(11)

The results for the methanation processes and for the RWGS can be observed in figure 2.1. It turns out immediately that the methanation processes are largely dependent on temperature conditions, and such a dependency could be easily seen in the large difference, in terms of order of magnitude, between the equilibrium constants at 473 K
and their values at 1473 K. Roughly speaking, it gets a value of $10^{15}$ for CO methanation and $10^{11}$ for the other methanation process. It appears quite clearly that low operative temperatures would be preferred to favour the methane production. Observing the trend of the RWGS equilibrium constant, it can be noted that the reaction is favoured by the increment of temperature, but even at elevated temperature conditions its value gets very large orders of magnitude staying always around the unity. The difference between the values at 473 K and the one at 1473 K is very narrow related to the ones listed before for the methanations ($10^3$).

The differences between the results is explained with the large exothermicity level of the methanations with respect to the lower endothermicity level of the RWGS: higher is the level of exo/endothermicity and higher is the dependency of the process on temperature.

The RWGS is preferred to be driven in the same reactor of the CO methanation process because, as already seen, their combined effect results equivalent to the CO$_2$ methanation’s. The main advantage of such a coupling is the increment of water production and so an increment on the oxygen production too. Concerning the hydrogen required to perform the RWGS, any problem of consumption arises because it could be fully recovered from water electrolysis. Therefore, it can be thought to drive the reactions in the same reactor, adopting a temperature condition for which the RWGS equilibrium constant stays near the unity and meantime the methanations’ ones can be maintained at large values.
2.2.1.2 Electrolysis Processes Analysis

The analysis will be subdivided in two parts: the former concerning the CO2 and the steam SOXE processes; the latter focused on alkaline electrolysis.

In the electrochemistry, things are slightly different but the concepts remain the same. The only thing changed with respect to classical thermochemistry is the computation of the Gibbs free energy that becomes:

$$\Delta G = nF\Delta E$$  \hspace{1cm} (12)

Where \( n \) is the moles of electrons needed to the reduction process at the cathode, \( F \) is the Faraday’s constant (96485 C/mol) and \( \Delta E \) is the Nerst potential. In this way, following the same considerations as before, the expression of the equilibrium constant of the reaction becomes:

$$K_{eq} = \exp\left(-\frac{nF\Delta E^0}{RT}\right)$$  \hspace{1cm} (11)

The term \( \Delta E^0 \) is also called as equilibrium potential.
Computing $K_{eq}$ for the CO$_2$ and steam electrolysis processes, the results in figure 2.2 have been gotten. As expected, the electrolysis process is favoured with the increment of operative temperature due to its endothermic nature. The difference in magnitude of the equilibrium constant between the selected temperature range borders is in the same order of the previously seen for methanation processes, but in opposite sign. It appears clear that the reaction must be performed in conditions of temperature as high as possible. From the literature (Meyen, Ni, Redissi, Becker, and many others) appears as the production rates increase as the temperature increases, because they are strictly related to the value of the current intensity that flows through the cells of the stacks, which is in turn dependent on both the equilibrium potential and the area specific resistance (ASR) of the cells. These last quantities decrease with temperature letting the current intensity as well as the production rate increase. Of course, for the operative temperature selection, it must be taken into account also a limiting value due to structural and efficiency reasons. All the performed studies agree to consider $800 \div 1100$ K as an optimal reference temperature range in which the performance of the YSZ electrolyte gets its maximum, and this is reflected even on the overall system performance. Such an elevated temperature does not favour the methanation and so different reactors working at different conditions are required.
The theoretical formulation for the alkaline electrolysis is the same presented for the solid oxide electrolysis processes. The main difference from the previous analysis is that the considered temperature range is obviously stricter and narrower (0 °C or 273 K) due to the necessity to operate with liquid water. From the results the equilibrium constant value appears lower than for steam electrolysis and this because of the lower operative temperature, but its variation with temperature present the same trend. Years of applications suggest an operative range of 40 °C (313 K). It’s preferred to avoid operative temperature next to 100 °C to avoid partially evaporation of the water to electrolyze.

If this type of electrolysis is chosen, due to the totally different working temperatures, it will be assured, without performing any behaviour analysis, that a specific reactor, dissimilar from the others, will be required to drive the reaction.
2.2.1.3 Considerations about Water Electrolysis

As already said, the choice of a water electrolysis process rather than the other has a profound influence on the system architecture. From a first sight, the alkaline electrolysis seems the less suggestable solution since, for sure, a specific reactor would be required for it, but it’s not sufficient to discard completely this solution. A comparison between the processes is needed.

Observing the comparison in table 2.8, new considerations come out. It’s true that the SOXE process don’t need a dedicated reactor and it can be driven in the same of the CO2 electrolysis (co-electrolysis process), but the concurrence of both the reactions at the cathode side in presence of a Ni-based catalyst leads to undesired side reactions such as the RWGS or the methanations (due to the presence of the methane in the inlet flow). At the SOXE operative temperature condition, the RWGS is exothermic, while the equilibrium constant of the methanations is negative and so the inverse reaction is favoured. Therefore, there would be a conversion of water and methane into hydrogen and carbon monoxide, which are products on the cathode side of the main reactions,
leading to a decrement in the efficiency of the cell. A lower operative temperature, in such a way to obtain low values of equilibrium constant for those two kind of side reactions, near the 700°C can be adopted, but entering in this way in the carbon deposition temperature range due to methane cracking and Boudouard reactions. The nominal working condition in this range of temperature, implies a maintenance service to the system that means a supplementary robotic system, to add to the plant, aimed to substitute the cell every time it will be saturated of deposited carbon. Of course, this condition is preferred to be avoided containing therefore the complexity and the cost of the system.

To avoid such kind of problems, the water steam coming from the Sabatier reactor can be separated from the other products and then sent to the SOXE reactor, where no methanation processes will occur as well as any carbon deposition. The big issue is the separation of the water steam from the remnant. The only solution is to condense the water to be re-heated before being electrolyzed as steam, but this would require an ulterior energy consumption that in the case of alkaline electrolysis wouldn’t be needed.

An intrinsic fundamental advantage of the alkaline process is that it works better at atmospheric pressures rather than at more elevated ones, working at higher efficiency levels and producing high purity products (Gotz et al., 2016). This is probably the most important advantage of this method since the necessity to contain the pressure level in the system. With the adoption of this technology, there would be the assurance to work at the best condition for the water electrolysis reactor despite the relatively low pressure allowable.

A last aspect to discuss is the greatest disadvantage of the alkaline electrolysis: the electrolyte solution corrosiveness. In alkaline electrolyses, aqueous alkaline solutions are used as electrolyte. They are highly corrosive and this leads to the necessity of a general overhaul of the system every 7-12 years, but in the last years the technology level has been further developed and the period between two maintenance cycles can increase (Gotz et al., 2016). Such a larger period before any kind of maintenance is a
positive aspect: it means that the system could work for years without problems and the decennial overhaul can be planned with a further mission on Mars.

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Alkaline electrolysis | • Well known technology  
                     | • Available even for large plant size  
                     | • Lower system costs  
                     | • Higher selectivity of inlet reagents  
                     | • Large lifetime  
                     | • Optimal for low pressure conditions | • Higher energy requirements  
                     | • Electrolyte solution is corrosive  
                     | • Minutes to hour to restart  
                     | • A specific reactor is required |
| SOXE             | • High electrical efficiency  
                     | • Lower energy requirements  
                     | • A specific reactor is not compulsory | • Technology in development  
                     | • Possible electrode poisoning  
                     | • Inlet reagent selectivity not possible  
                     | • More expensive system  
                     | • Fast material degradation |

Table 2.8 Water electrolysis processes comparison

The maintenance issue is present in the SOXE too. Omitting the carbon deposition effects on the cells, the elevated temperatures lead to a more rapid degradation with respect to one caused by corrosion in the alkaline technology, making necessary a substitution of the cells in less than few years. Of course, this is a CO₂ electrolysis problem too and a maintenance system must be always considered to ensure its good behaviour in time even if the steam electrolysis will not be chosen. Nowadays, researchers are investigating the entity of the degradation and the period after which the cells must be replaced. The MOXIE subsystem, that will fly in 2020 on Mars, will be very helpful in this research giving feedback data directly “from the court” to analyse.
2.2.1.4 Architecture Selection

From the previous analyses, 3 main scenarios result (figure 2.4):

- Scenario (A): A reactor in which the methanations and the RWGS reaction occur to produce methane and water steam. The outlet flow is cooled and the water is condensed and then electrolyzed in an alkaline solution. The CO$_2$ electrolysis is run in a separate reactor and the produced CO is sent in input to the Sabatier reactor.

- Scenario (B): Also in this case, there is a reactor in which methanations and the RWGS occur. The outlet flow is not cooled, but is sent directly in the SOXE reactor where the co-electrolysis process can occur. The products will be sent back to the Sabatier reactor, except for the produced oxygen.

- Scenario (C): Is the same architecture as before, but before to be injected in the SOXE reactor, the outlet flow from the Sabatier is cooled and water is condensed. Then, is re-heated and steamed to be sent in input to the SOXE reactor to perform the co-electrolysis process.

The selection of the system architecture depends on which type of water electrolyses will be performed. After a critical analysis, performed in the previous section, about advantages and disadvantages that characterize the different electrolysis methods and about the effects they cause on the entire system, the alkaline electrolysis has been selected. The main reasons that have brought to this decision are:

- The reliability deriving from the deep knowledge of the process and the technologies to run it;
- The optimum functioning at Earth atmospheric pressure conditions;
- The large lifetime of the cell;
- The avoidance of unwanted side reactions in the reactors.

Therefore, the architecture that the system will present will be based on scenario (A).
2.2.2 System Flow Chart

After the definition of the numbers of reactors to design and the reactions to drive in them, a preliminary scheme of the system architecture can be proposed taking as reference the already existent systems (from Zubrin’s Sabatier reactor design and the Moxie system design).

The simplest scheme representing the system functioning is a closed-loop system, characterized by an input, an output and a feedback line. The input refers to the reagents to provide to the reactors, the output refers to the products and the feedback line is mainly representing the hydrogen and the carbon monoxide reutilization. The aim of this work is to maximize the level of the loop closure, in terms of H₂ and CO reutilization, to minimize the resources brought from Earth and consequently maximize the MLEO savings.
The real flow chart is much more complex, and the system is decomposed in all its sublevels in order to highlight the various interaction among themselves and to understand the basic functioning and the logic behind the work. For our purposes, a scheme of intermediate complexity and detail, figure 2.5, is appropriate to describe the system working principles.

![Simplified closed-loop system](image1)

**Fig. 2.5  Simplified closed-loop system**

The system functioning begins with the acquisition and the filtration of atmospheric CO₂ by a volumetric pump that draws it through a dust filter and compresses the flow up to the desired pressure condition. In the chart only one acquisition block appears, but it could be that more than one pump/filter subsystem will be needed due to mass flow rate demands or due to power requirements. After the inlet, there will be two CO₂ flows

![System flow chart](image2)

**Fig. 2.6  System flow chart**
directed one towards the CO₂ electrolysis reactor and one towards the reactor where methanations and RWGS occur, which in the chart has been called “Sabatier reactor” for brevity reasons.

After the electrolytic process, the produced O₂ pass through a heat exchanger and the CO is sent to the Sabatier reactor to be then methanized. The heat extracted from the oxygen is used to pre-heat the incoming CO₂ before entering the stacks.

The same occurs after the Sabatier process: the outflowing CH₄, H₂O and the unreacted H₂ pass through a heat exchanger. The flow continues towards a water condenser, where water is liquified and sent to the H₂O electrolysis unit, while methane and hydrogen enter in a methane liquefier. After that, the methane is stored and the unreacted H₂ is sent in feedback to the Sabatier reactor. Of course, an initial quantity of hydrogen is needed as an input to the reactor and it must be brought from Earth (with cryogenic storage or as liquid water to be then electrolysed).

The water electrolysis gives O₂ and H₂ as outputs. The former is sent to the oxygen liquefier and then stored, whilst the latter is sent in feedback to the Sabatier reactor too.

As it happens for the inlet reagents of the CO₂ electrolysis reactor, even those in input to the Sabatier one are pre-heated by means the heat extracted from the outlet elements and, if necessary, from apposite heaters.

2.2.3 Level of Loop Closure

As already mentioned, the level of the loop closure is quantified as the level of H₂ reutilization. The recycled H₂ can be unreacted hydrogen outflowing the Sabatier reactor, or the one produced by water electrolysis. A preliminary estimation of the difference between the needed and the recycled hydrogen can be performed only looking at the involved chemical reactions.

For what concern the consumed hydrogen, a look must be given at the Sabatier reactor and at the reactions driven in there. It has already seen that the combined effect of the CO methanation and the RWGS process is equivalent to the CO₂ methanation, therefore,
the total products/reagents balance of the reactor says that 2 moles of water are produced per each 4 moles of hydrogen reacted.

Considering the water electrolysis process, the obtained moles of $\text{H}_2$ are equal to the moles of inlet water and so the ratio between the recovered hydrogen and the reacted one becomes 0.5. So, exploiting such kinds of reactions half the reacted hydrogen can be recovered by the system.

The things may change considering an ulterior input to the system: indigenous water. With that, the production of hydrogen by water electrolysis increases, reducing the ratio between recovered and exploited hydrogen and increasing the level of closure of the system. The difficulty stays in the development of a technology capable to furnish the indigenous water to the system. In this thesis, any indigenous water supply will be considered in such a way to evaluate only the performance of combined Sabatier/electrolyses system.

2.3 REACTORS ARCHITECTURE AND POSSIBLE TRADE-OFFS

In this section, the analysis of the system will go deeper to a subsystem level to investigate and analyse the reactors architectures and the possible trade-offs on their design.

2.3.1 $\text{CO}_2$ Electrolysis Reactor

Section 1.5.1 has already described the architecture and the functional analysis of a classical SOXE cell, taking the MOXIE system as a reference. The Reactor was presented as an ensemble of stacks made by multiple cells in which the electrolysis reaction take place. All the cells are fed with pressurized atmospheric $\text{CO}_2$ and put in series in the stacks. Therefore, the current intensity is the same in each cell, while the potential drops depend on the values of ASR.
Each cell present three layers of porous materials overlapped one to each other: the cathode where reduction occurs, the electrolyte through which the $O^{2-}$ ions diffuse, under the effect of the applied potential, and the anode where oxygen molecules are formed consequently to the oxidation reaction. The layers are respectively made by Ni/YSZ, YSZ and LSM-YSZ and, usually, the cathode is many times thicker than the other two (3÷5 times). LSM is an acronym that stays for Lanthanum-Strontium-Manganese oxide ($\text{MnO}_3$).

The most important characteristic of the electrolyte material is the pores mean radius: in order to let flow only the $O^{2-}$ ions towards the anode, the average dimension of the electrolyte’s pores must be as larger as enough to let the ions pass, but, at the same time, as smaller as enough to block the passage of the CO and $\text{CO}_2$ molecules.

2.3.1.1 Alternatives and Trade-offs

There are many alternatives and trade-offs in the design of a SOXE system to be considered. They can be grouped in dissimilar categories dependently on which aspect of the reactor they influence at the most:

- Alternatives concerning reactor geometry;
- Alternatives concerning the effectiveness of the process;
Alternatives concerning the processes involved.

Considering the first type of alternatives, two main cells’ geometry had been investigated through the years:

- Tubular cells;
- Planar cells.

The former type of cells consists in YSZ tubes coated with porous platinum electrodes but most of the works has been done on more compact and potentially rugged flat geometries (Rapp, 2016). Such planar cells can present circular or rectangular shape, they can be ensembled in stacks to get the desired production values and represent the most practical solution for SOXE cells’ geometry.

A possible trade-off that can be considered and has a significant impact on the process effectiveness is the choice of the catalyst. Ni-based catalysts have been already cited as the best suited catalyst for this process and all the authors in literature agree with that. The fact is that, if the reactor works in the carbon deposition range dictated by the Boudouard reaction that goes from 450 to 600 °C, this kind of catalysts promote the carbon deposition too and this is one of the reasons why the CO₂ SOXE process is performed at higher temperatures. However, researchers have studied many other catalysts to allow operations in carbon deposition temperature ranges without promote it, finding Ruthenium-based catalysts suitable for the process. The disadvantage deriving from their use is the decrement in the catalytic effectiveness and so in the efficiency of the system.

About involved processes, an interesting alternative has been already described and analysed in the previous sections regarding the water electrolysis processes and consists in considering the possibility to drive both the electrolysis reactions in the same reactor (Co-electrolysis). Obviously, the water would be in the form of steam. At the cathode surface, due to the reduction reactions, would be present H₂ and CO₂, which could react to give more H₂O and CO through the RWGS. On this alternative, a large number of
experimental tests have been conducted and model developed (Ni, 2011; Menon et al., 2014; Ebbesen & Mogensen et al., 2012; Redissi & Bouallou, 2013; Hartvigsen, 2009; to cite a few) and much further work has to be done to understand completely and in a better way the behaviour of the processes involved and their mutual effects. RWGS seems to act in favour of the steam electrolysis rather than the CO₂ one, because the water production increases the reagent concentration at the cathode for steam electrolysis, while the CO one increases the products concentration at the cathode sorting the opposite effect for the CO₂ SOXE process.

However, as said before, a water alkaline electrolysis reactor is foreseen to be present in the system architecture instead of performing a co-electrolysis process in the SOXE reactor. Therefore, a trade-off on the type of reactions occurring in the reactor is not considered for real in the modelling process.

2.3.2 Sabatier Reactor

The Sabatier is a very simple reactor composed by a cylinder in which a fixed Nickel-catalytic bed is set. The flow diffuses into the bed where reactants interact with the catalyst particles and reactions occur.

![Fig. 2.8 Scheme of a simple fixed bed reactor (Froment, 2011). The section marked as “1” is the reactor filled with catalyst, while the section “II” is the pre-heater before the inlet.]

Despite their apparent simplicity, Sabatier reactors designs require the investigation of a large number of aspects dependent on the reactions and on the operative conditions.
in which they are driven. The most common alternatives and trade-offs in the reactor definition are on:

- The reactor internal design;
- The flow pattern;
- The catalyst particles dimensions;

2.3.2.1 Alternatives and Trade-offs

Alternatives concerning the reactor internals, all related to the operative conditions, mainly in terms of temperature, exist and are aimed to maintain the reactor conditions in the optimal range. The various internal design options are aimed to improve the rate and uniformity of heat removal in the reactor. For exothermic processes, the temperature could rise at values prohibitive for the reactor itself or for the equilibrium conditions, the selectivity or even for the catalyst stability. From this considerations that arises the necessity to remove the generated heat from the reactor. There are principally two ways to act:

- Subdividing the reactor in more stages and between each stage put a heat exchanger to cool the flow (multibed reactors). The put in action of such kind of solution requires an optimal study to set the optimal parameters to get the desired yields.
- Adopting a multitubular geometry: If the heat flux to remove is too high as well as the needed number of intermediate beds, the solution could be the cooling by means a constant heat exchange among the flow and numerous small tubes containing recirculating molten salts that in turn give off their heat to a boiler.

Here below a depiction of both kind of reactors can be found:
Fig. 2.9 Representation of a multibed reactor architecture. (A) represents the simplified scheme, while in (B) can be appreciated the real architecture of a multibed adiabatic reactor for NH₃ synthesis (Froment, 2011)

Fig. 2.10 Ammonia synthesis reactor with multitubular heat exchangers

In addition to the internal design trade-offs, alternatives on the type of flow pattern to consider can be investigated:

- Plug flow;
- Radial flow.
The plug flow is the “classical” flow pattern adopted in each preliminary reactor design. The flow is pumped into the reactor and gets a longitudinal envelop depending only on the longitudinal coordinate. The velocity across any cross-section perpendicular to the reactor axis is assumed to be constant, avoiding therefore the modelling of the viscous effects near the boundaries of the reactor through the boundary layer equations.

If the pressure drop across the bed is too large, it can be thought to adopt a radial flow pattern to decrease it and thus to enhance the recycle compressor capacity. In that case, the flow does not present only a longitudinal envelop but also a radial one, depending on the distance from the center of the reactor.

Another way to control the pressure drop across the bed is performing a trade-off on the size of the catalyst particles and consequently on the porosity and on the density of the bed. Larger particles mean smaller pressure drop, and so it can be assumed to adopt larger particles in region where a limitation of the pressure drop is needed, and smaller particles in the other regions.
CHAPTER 3: MODELLING

After having given a look at the entire system architecture and then at the reactors’ one and after having listed and analysed the various possible trade-offs in the reactors architecture design, the modelling of the chemical reactions is the next step. The modelling terminology in this work is intended in computing the output of the reactors finding the physical-mathematical links to the inputs.

3.1 SOXE REACTION MODELLING

The SOXE is a very complex electro-chemical process. Its modelling requires excellent knowledges in electro-chemistry, fluid dynamics and numerical computations. Since most of the works on this technology is of experimental nature, literature is very poor in detailed theoretical mathematical approaches. An ulterior reason for this lack of models can be found also in the extreme complexity of the electro-chemistry and thermodynamics behind the reaction.

Nevertheless, 4 different approaches have been emerged from literature:

- Zero-dimensional electro-chemical model;
- One-dimensional thermal-fluid model;
- Quasi-Two-dimensional thermal-fluid model;
- Two-dimensional thermal-fluid model;

Descriptions of these models are given in Ni (2010), in Menon et al. (2014), and in He, Li & Birgersson (2012) works.

To understand and evaluate the reactor production capabilities and the process modelling, a complex model, such as the latter presented above, may be too heavy and specific. The quasi-2D model is quite complex too and it can find a better use in a further and deeper analysis on diffusivity inside the cathode, the electrolyte and the anode as a support to experimental works. Therefore, to evaluate the system performances, it has been thought to adopt the Zero-D electro-chemical model, because, despite of its
simplicity with respect the other two methods, it can be considered specific and
accurate enough to model the system in a proper way.

The 1D thermal-fluid model has also been investigated to understand the effects of the
variation of CO₂ and CO compositions along the cell and to compare the results with the
more generic method as the former is.

3.1.1 Zero-dimensional Electro-Chemical Model

This model redaction has been based on the previously developed electro-chemical
model for steam electrolysis and consider all the irreversible losses in the process, in
terms of activation, concentration and ohmic overpotentials. It’s a simple model based
on nominal operative conditions and is useful to predict and estimate the functioning
and the production level of the system.

The first step consists in considering not the only net reaction that has been seen in the
previous chapters but even the two semi-reactions of reduction and oxidation occurring
respectively at the cathode and at the anode side.

\[
\text{Reduction: } \quad CO_2 + 2 \, e^- \rightarrow CO + O^{2-} \quad (14)
\]

\[
\text{Oxidation: } \quad O^{2-} \rightarrow \frac{1}{2} O_2 + 2 \, e^- \quad (15)
\]

From the reactions, an important observation that can’t be possible to do by looking
only at the net electrolysis reaction is the number of electrons needed to reduce one
mole of carbon dioxide, 2. Changing the point of view, it can be said that 4 moles of
electrons are needed to oxidize a mole of oxygen.

Since the extremely high ionic conductivity of the YSZ electrolyte, all the electrons are
ionically transferred (Meyen et al, 2016) and this can allow a real time monitoring of
oxygen production rate. If \( J \) is the current density across the cell, the oxygen molar
production rate per cell, measured in [mol/m²/s] is:

\[
\dot{n}_{O_2} = \frac{J}{4 \, F}
\]
While the consumption rate of CO\textsubscript{2} will be the double because only the half of the electrons moles are involved in its reduction, and it will be the same (in modulus) of the CO production rate.

In order to measure an electrons current flow, an electrical potential \( V \) has to be applied across the cell and its value must take into account even for the overpotential losses. It can be written as:

\[
V = \Delta E + \eta_{tot}
\]

\[
\eta_{tot} = \eta_{con,a} + \eta_{con,c} + \eta_{act,a} + \eta_{act,c} + \eta_{ohmic}
\]

Where \( \Delta E \) is the already seen Nerst potential, and \( \eta_{con} \), \( \eta_{act} \) and \( \eta_{ohmic} \) are respectively the concentration, the activation and the ohmic overpotentials. The subscripts \( a \) and \( c \) stand for anode and cathode.

In the previous chapter an expression for the Nerst potential has already been done. Expanding the expression of the reaction quotient a direct correlation with the envelop of the reaction is found:

\[
Q = \frac{[CO][O_2]^{0.5}}{[CO_2]} = \frac{p_{CO}p_{O_2}^{0.5}}{p_{CO_2}}
\]

\[
\Delta E = \Delta E^0 + \frac{R_u T}{2 F} \ln \left( \frac{[CO][O_2]^{0.5}}{[CO_2]} \right)
\]

The values between the square brackets indicates the concentrations of the reagent and the products, while \( p_i \) stand for partial pressures. Of course, since any molecule of oxygen is present at the cathode side and, vice versa, any molecule of CO\textsubscript{2} or CO is present at the anode, the concentrations are referred to the side in which the species are present.

For the estimation of the equilibrium potential, a linear correlation between its value and the temperature exists for a temperature range that goes from 600 to 1200 K (Ni, 2011):
\[ \Delta E^0 = 1.1043 - 0.00045 (T - 800) \]

A problem is encountered in the computation of the overpotentials: the existent formulations are dependent on the current intensity value, which in turn is dependent on the applied voltage. It appears clear that the needed voltage to be applied can’t be computed with the above formula, but it turns out as an independent variable to be set. The only information gotten is the minimum value that it can take to allow a current flow in the cell: since losses are strictly positive quantities, the applied potential must be categorically larger than the equilibrium one. \( \eta_{tot} \) value can be computed reversing the formula.

Since the computation of the current intensity requires the knowledge of, at least, the activation overpotentials, an alternative way is needed. Meyen & the MOXIE team propose a computation that is based on the modelling of an ASR model for the cell dependent only on the electrolyte mean temperature and through this get the current density by means a simple Ohm’s law. The disadvantages of such a solution is the difficulty to model in a proper way the ASR before testing, because it encompasses a variety of information about electrode kinetics, gas diffusion, local variations in flow, temperature and current density. The ASR is modelled as:

\[ \text{ASR}(T) = \text{ASR}_{ref} - 0.463 + 3.973 \times 10^{-5} \exp \left( \frac{10300}{T} \right) \]

Once obtained it, all the factors needed to compute the current density are defined and the computation can go on:

\[ J = \frac{(V - \Delta E)}{\text{ASR}} \]

The \( \text{ASR} \) is expressed in \([\Omega \cdot \text{mm}^2]\), \( V \) and \( \Delta E \) in \([\text{V}]\) and so \( J \) results expressed in \([\text{A/mm}^2]\).

The results that can be obtained with this model are the most optimistic with respect the other because the evolution of the flow along the reactor is not considered,
therefore neither the production of CO at the cathode, which surely affect in a negative way the process, reducing the oxygen production rate.

3.1.2 One-Dimensional Thermal-Fluid Model

The 1D flow model was presented by Menon (et al.) for a SOXE for syngas production exploiting H₂O and CO₂ electrolysis, making necessary an arrangement for a CO2 electrolysis process only. The main difference with respect to the previous model is the consideration of the flow envelop along the reactor and its effect on the electro-chemical process in the modelling procedure.

The model is quite simply and does not consider any diffusion process since it computes the behaviour of the flow only along the cathode surface. A plug flow pattern is considered characterized by a constant pressure along the reactor. The governing equations are the ones coming from the Navier-Stokes set except for the momentum equation that has not been considered, since the hypothesis of a null pressure gradient in the reactor. In addition to them, a mass balance equation per species and an equation of state for the mixture are set.

Continuity: \[
\frac{d(\rho u)}{dx} = S_m
\]

Energy: \[
\frac{d(\rho c_{p,mix} u T)}{dx} = 0
\]

Component mass balance: \[
\frac{d(u[X]_i)}{dx} = S_i
\]

Equation of state: \[
\frac{dp}{dx} = -\frac{P}{RT^2} \frac{dT}{dx} - \frac{P}{R^2T} \frac{dR}{dx}
\]

Where:

- \(x\) is the reactor coordinate, [m];
- \(\rho\) and \(u\) are the density [kg/m³] and the velocity [m/s] of the flow;
- \([X]_i\) are the species molar concentrations, [mol/m³/s];
• $C_{p,\text{mix}}$ is function of temperature and of species molar concentrations and is the mixture specific heat [J/kg/K];
• $S_m$ is the source term [kg/m$^3$/s] in the continuity equation and can be written as the difference between the mass production rate of CO and the mass reduction rate of the CO$_2$:

$$S_m = \dot{M}_{\text{CO}} - \dot{M}_{\text{CO}_2} = \frac{J}{2Fd_c} (M_{\text{mol,CO}} - M_{\text{mol,CO}_2})$$

• $S_i$ are the source term [mol/m$^3$/s] in the component mass balances and their values are equal in module for both the species:

$$S_{\text{CO}} = -S_{\text{CO}_2} = \frac{J}{2Fd_c}$$

The modelling is completed with the electro-chemical formulation seen in the Zero-D model to compute all the quantities depending on the molar composition of the flow over the cathode, $J$ included.

For more specific details about the resolution scheme of the set of ordinary differential equations see section 2.3 of this chapter.

### 3.2 METHANATIONS AND RWGS MODELLING

The methanation and the RWGS reaction modelling consists in an easier task rather than the electrolysis one, also because of the simpler physics and chemistry behind the reactions.

The modelling process has been split in two phase:

• The chemical kinetics modelling, based both on theory and on experimental results of Xu & Froment (1989), and of Parlikkad et al. (2012) mainly;
• The reactor modelling, performed by using the “Chemical reactor Analysis & Design” manual by Froment, Bischoff & De Wilde (2011) as a fundamental base.
Before entering deeper in the fluid flow characterizations and in kinetics formulations, it’s retained that a brief overview about steps to consider during any catalytic reaction and catalysts properties is quite helpful to then understand in a better way the models.

### 3.2.1 Overview About Catalytic Processes

Catalytic processes are often really complex and aim to decrease the activation energy of specific reactions without modifying their final net results. With the decrement of the activation energy the probability that two molecules, with energy as high as or higher than such an energetic level, collide increases, incrementing also the velocity of the reaction. Poorly speaking, catalysts are needed to increase the production/consumption rate of the reactions.

Considering fixed bed catalytic reactors, as like as the Sabatier one, the particles of catalysts are held in place and don’t present any relative motion with respect to a fixed reference frame. The flow occupies the interstitial spaces among the particles and diffuse through them. The reactions occur basically into the catalyst particles.

In metal catalysts, the metal is usually dispersed onto a high-area metal oxide, that in turn could be dispersed in a second carrier oxide such as vanadia supported on titania, or made in a large area oxide. Carriers are generally pressed into shapes or extrudes into pellets.

In Rawlings & Ekerdt (2012), a list of principal steps to consider in any catalytic reaction is given:

- Transport of reactants and energy from the bulk fluid up to catalyst pellet exterior surface;
- Transport of reactants and energy from the external surface into the porous pellet;
- Adsorption, chemical reaction, and adsorption of products at the catalytic sites;
- Transport of products from the catalyst interior to the external surface of the pellets;
• Transport of product into the bulk fluid.

An important consideration, to which pay attention, is that the coupling of transport process with chemical reactions can induce concentration and temperature gradients within the pellet, between the surface and the fluid, or both.

The main characteristic properties of catalysts, exploited in the following models, are:

• Pellets diameter, $d_p$ (for fixed bed reactors can range from 0.3 to 0.7 cm);
• Pellets density, $\rho_p$ [kg/cm$^3$];
• Void fraction (or porosity), $\varepsilon$ [dimensionless units]. It’s defined as the volume of voids per volume of reactor and is the result of the product between the density of the pellet particle and the pore volume. The pore volume is a function of the catalyst preparation method and can range from 0.1 to 1 cm$^3$/g.

The pellets diameter is of extremely importance for the Reynolds number and the friction coefficient computation to valued the pressure drop along the reactor, while the latter two are very suitable properties to allow to switch from reaction rates in terms of moles per particle volume per second to reaction rates in terms of moles per reactor volume per second.

The basic principles about catalytic processes have been presented, so now it becomes possible to present the chemical kinetics and the reactor modelling.

3.2.2 Chemical Kinetics

The modelling of the chemical kinetics is of extreme importance to understand the behaviour of the reactions in time and in space. They depend strongly, and obviously, on the type of catalyst adopted, on the operative conditions and on the concentrations of the reagents in the reactor.

The model is the one deriving from the experimental test of Xu & Froment in 1989. They ran it in a laboratory catalytic test facility equipped with an autoclave and using a proprietary nickel based industrial catalyst. The resulting rate expressions are:
\[ r_{\text{CMM}} = -\frac{k_{\text{CMM}}}{p_{H_2}^{2.5}} \left( \frac{p_{\text{CH}_4}p_{H_2O} - p_{\text{CO}p_{H_2}^3}}{K_{\text{CMM}}} \right) \text{DEN} \]

\[ r_{\text{WGS}} = \frac{k_{\text{WGS}}}{p_{H_2}^2} \left( \frac{p_{\text{CO}p_{H_2O} - p_{\text{CO}_2p_{H_2}^4}}}{K_{\text{WGS}}} \right) \text{DEN}^2 \]

\[ r_{\text{CDM}} = -\frac{k_{\text{CDM}}}{p_{H_2}^{3.5}} \left( \frac{p_{\text{CH}_4}p_{H_2O}^2 - p_{\text{CO}_2p_{H_2}^4}}{K_{\text{CDM}}} \right) \text{DEN} \]

\[ \text{DEN} = 1 + p_{\text{CO}}K_{\text{CO}} + p_{H_2}K_{H_2} + p_{\text{CH}_4}K_{\text{CH}_4} + p_{H_2O}K_{H_2O}p_{H_2}^{-1} \]

Where:

- \( r_j \) is the reaction rate of the reaction \( j \) per unit volume of reactor, [mol/s/kg\text{cat}];
- \( k_j \) is the intrinsic reaction rate constant of reaction \( j \), [variable units];
- \( K_j \) is the equilibrium constant of reaction \( j \), [variable units];
- \( p_i \) is the partial pressure of species \( i \), [bar];
- \( K_i \) is the adsorption coefficient of species \( i \), [bar];
- \( \text{CMM}, \text{WGS} \) and \( \text{CDM} \) subscripts stand for Carbon Monoxide Methanation (CMM), Water Gas Shift (WGS) and Carbon Dioxide Methanation (CDM).

\( k_j \) and \( K_i \) can be computed with the following exponential formulas:

\[ k_j = k_j^0 \exp \left( -\frac{E_j}{R_uT} \right) \]

\[ K_i = K_i^0 \exp \left( -\frac{\Delta H_i}{R_uT} \right) \]

Where:

- \( k_j^0 \) and \( K_i^0 \) are pre-exponential factors;
- \( E_j \) is the activation energy for the chemical reaction, [J/mol];
- \( \Delta H_i \) is the heat of adsorption of component \( i \), [J/mol].
The rates dependency on species concentration is clearly evident by those expressions: considering stable operative conditions, if the concentrations of products are low, the equilibrium is shifted towards right and the reaction is favoured with a positive reaction rate, but if, on the other hand, the reagents concentrations are too low, the equilibrium is shifted towards left favouring the backward reaction and presenting a negative reaction rate.

An ulterior step in the kinetics modelling is the definition of production/consumption rates of the chemical species in the reactor as a function of the reaction rates. The formulation is very simple and it's weighted basing on the stochiometric coefficients that species present in the various reactions:

\[ r'_i = \sum_{j=1}^{3} \alpha_{ij} \eta_j r_j \]

\( \alpha_{ij} \) indicates the stochiometric coefficient of species \( i \) in the reaction \( j \), while \( \eta_j \) represent the effectiveness factor of reaction \( j \) and it's strictly correlated with the transport resistance in the reactor.

Once the kinetics have been modelled, the modelling of the behaviour and the evolution of the flow along the reactor can be faced.

### 3.2.3 1D Flow

Following the logics presented in the previous chapter, the first approach to the reactor modelling is to consider a 1D flow along an adiabatic reactor, neglecting all radial variations and considering only the ones along the longitudinal axis. Instead of using the classical Navier-Stokes governing equations in the full model, Darcy’s law is applied to govern the momentum transport for the porous flow field.

There exist two main models for 1D flow:

- The pseudo-homogeneous 1D model, which considers only transport by plug flow in the axial direction and catalyst is not considered explicitly;
• The heterogeneous 1D model, which considers the transport by plug flow again, but distinguishes between conditions in the fluid and in the solid and so it exploits different conservation equations for fluid and catalyst, taking in consideration even the effects transport resistance.

The model on which researchers have mostly based their work is the pseudo-homogeneous model due to its higher simplicity and to its tendency to lead towards results that are less optimistic that the ones given by the heterogeneous model. From an engineering point of view, these two reasons are fair enough to drive the choice of the model towards the former method, since that for a preliminary study such a model is better than a more complex and optimistic one to get an estimation of the reactions behaviour and of the productivity levels.

3.2.3.1 Pseudo-homogeneous Model

As said before, this is the most common model adopted by researcher in previous works. The principal difference with the heterogeneous one is the neglecting of any transport resistance and so the characteristic to have a constant effectiveness factor along the reactor.

It has already said that the governing equations are for what concerning the overall mass balance and the energy equation the ones resulting from Navier-Stokes, while, for the definition of the pressure drop, Darcy’s law has been adopted instead of the Navier-Stokes momentum equation. In addition to them, even a component mass balance equation for each species in the reactor have been set as it happened for the 1D thermal-fluid model for SOXE modelling.

Important to note that in the energy equation does not appear any term of external heat transfer since the reactor is considered adiabatic.

Continuity: \[
\frac{d(\rho u)}{dx} = 0
\]
Pressure Drop: \[
\frac{dp}{dx} = -f \frac{\rho u^2}{dp}
\]

Energy: \[
\frac{d(\rho C_{p,\text{mix}} u T)}{dx} = Q_{\text{rxn}}
\]

Component mass balance: \[
\frac{d(u[X]_i)}{dx} = r_i \rho_p (1 - \varepsilon)
\]

Where:

- \(\rho\) and \(u\) are the density and the velocity of the bulk flow;
- \(f\) is the friction factor that can be computed as:
  \[
  f = \frac{1 - \varepsilon}{\varepsilon^3} \left(1.75 + 150 \frac{(1 - \varepsilon)}{Re_p}\right)
  \]

\(Re_p\) and \(\varepsilon\) are the Reynolds number and the bed porosity. Their expressions are:

\[
\varepsilon = 0.38 + 0.073 \left(1 + \frac{(d_r - 2)^2}{(\frac{d_r}{dp})^2}\right)
\]

\[
Re_p = \frac{\rho u d_p}{\mu_{\text{mix}}}
\]

- \(d_r\) is the reactor diameter, [m];
- \(Q_{\text{rxn}}\) is the heat released (or adsorbed) by the reactions and can be written in the following form:

\[
Q_{\text{rxn}} = \sum_{j=1}^{3} (-\Delta H_{\text{rxn},j}) r_j \rho_p (1 - \varepsilon)
\]

\(\Delta H_{\text{rxn},j}\) are the enthalpies of reaction. The expression of \(Q_{\text{rxn}}\) can be re-written pre-multiplying by the effectiveness factor \(\eta\) to simulate a transport resistance.
variation, but Parlikka et al. (2012) highlight how this method lead to wrong results very different to the heterogeneous model, and so $\eta$ has been considered always unitary.

- $[X]_i$ are the species molar concentrations, [mol/m$^3$/s];
- $C_{p,mix}$ and $\mu_{mix}$ are function of temperature and of species molar concentrations and are, respectively, the mixture specific heat [J/kg/K] and the mixture dynamic viscosity [Pa·s]. They have been computed by the own species properties adopting a weighted criterium basing on their molar fractions. The values of viscosity of the single species have been computed by following the directions on “The properties of gases and liquids” (Poling, Prausniz & O’Connell, 2004). The coefficient to compute the species’ specific heats have been taken from “Mechanics and Thermodynamics of Propulsion” (Hill & Peterson, 1991).

To complete the system of equations, an equation of state for the flow and the variations of the mixture specific heat and gas constant are missing. The former, adopting the perfect gas hypothesis, expresses the relation among the variation of the flow density and the variations of the temperature, the pressure and the gas constant.

$$\frac{dp}{dx} = \frac{1}{RT} \frac{dp}{dx} - \frac{P}{RT^2} \frac{dT}{dx} - \frac{P}{R^2 T} \frac{dR}{dx}$$

The latter two, have been obtained by considering the specific heat and the gas constant as composite functions:

$$R = R \left( M_{mol,mix}([X_{CO}], [X_{H_2}], [X_{CH_4}], [X_{H_2O}], [X_{CO_2}]) \right)$$

$$C_{p,mix} = C_{p,mix} \left( T, ([X_{CO}], [X_{H_2}], [X_{CH_4}], [X_{H_2O}], [X_{CO_2}]) \right)$$

The variations will take the form of:

$$\frac{dR}{dx} = \frac{dR}{dM_{mol,mix}} \sum_{i=1}^{5} \left( \frac{dM_{mol,mix}}{d[X_i]} \frac{d[X_i]}{dx} \right)$$
\[
\frac{dC_{p,\text{mix}}}{dx} = \frac{dC_{p,\text{mix}}}{dT} \frac{dT}{dx} + \sum_{i=1}^{5} \left( \frac{dC_{p,\text{mix}}}{d[X_i]} \frac{d[X_i]}{dx} \right)
\]

The system is now composed by 11 ordinary differential equations in 11 unknowns and it could be integrated by relying on Runge-Kutta methods. To solve the system, the MATHWORKS’ software MATLAB has been used.

The problem arisen from the integration of this system of equations is the explicit dependency on the variation of species concentrations in the reactor of the gas constant and of the temperature (through \(C_{p,\text{mix}}\)) variation expressions. This wouldn’t be a problem if the concentrations variations wouldn’t depend on their values, but they do and this leads to the necessity to rewrite the equations in such a way to cancel out those dependencies. To avoid such a non-smart procedure, a while MATLAB cycle can be set:

- The computational flow enters the cycle with an initial value of gas constant and of temperature variations errors;
- The equations are solved in the following order:
  - Gas constant variation;
  - Temperature variation;
  - Pressure variation;
  - Density variation;
  - Velocity variation;
  - Molar concentrations variations;
- \(R\) and \(T\) variations are then recomputed with the obtained \([X_i]\) variations and compared with their initial values to compute the relative error between them.
- If the relative errors are larger than a threshold (set as 1% in this work), the cycle is repeated entering with the just obtained values and new ones are recomputed.
and compared with them, otherwise the solutions are accurate enough and the ode solver can proceed with the next step of the integration. Obviously, for the first iteration the initial value of the errors will be for sure higher than the threshold.

![System solution flow chart](image)

Fig. 3.1  System solution flow chart

3.3  DESIGN PARAMETERS

In this section, a look at the effects of the main parameters and the independent variables to set in the design of the reactors will be given.

3.3.1  SOXE Reactor

The principal variables to “play” with in the design of the SOXE reactor are:

- Operative temperature and pressure;
- Applied electric potential;
- Inlet mixture velocity;
- Inlet mixture composition.

Many of these, like operative temperature and pressure, the applied potential and the specific mass flow rate, are strictly related to the system power budget and performance capability of the volumetric pump in the acquisition block. Since a space system is considered, this strictly relation with the system power budget acquires much more
importance because to guarantee very high levels of power, required costs and mass reach important levels too.

The selection of the operative temperature and pressure is extremely important, because they largely affect the efficiency of the system in terms of oxygen production rate and in terms of power requirements. An analysis about the possible effects to consider in their selection can be seen in Table 4.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Low</th>
<th>Elevated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>• Lower productivity</td>
<td>• Higher productivity</td>
</tr>
<tr>
<td></td>
<td>• Higher energy demand</td>
<td>• Lower energy demand</td>
</tr>
<tr>
<td></td>
<td>• Carbon deposition</td>
<td>• No carbon deposition</td>
</tr>
<tr>
<td></td>
<td>• Lower thermal control</td>
<td>• Higher thermal control</td>
</tr>
<tr>
<td></td>
<td>• Lower degradation</td>
<td>• Higher degradation</td>
</tr>
<tr>
<td>Pressure</td>
<td>• Lower productivity</td>
<td>• Higher productivity</td>
</tr>
<tr>
<td></td>
<td>• Carbon deposition inhibited</td>
<td>• Carbon deposition</td>
</tr>
<tr>
<td></td>
<td>• Lower energy required</td>
<td>• Higher energy required</td>
</tr>
</tbody>
</table>

Table 4.1 Effects of operative temperature and pressure on the system performances

Before analysing the different combined effects deriving from the operative conditions selection, it is retained important to specify that for elevated pressure is meant 1 atm and for low pressure is meant Martian atmospheric pressure (0.01 atm), while for low temperature is intended 600 ÷ 700 °C and for elevated is intended all the values over that range.

The effects of temperature levels on the SOXE process has already been investigated during the comparison between the water electrolysis methods in previous sections, but a brief recall will be given:

- Low temperature values:
  They favour the carbon deposition, and so the electrolyte and the cathode poisoning, through Boudouard reaction, decreasing therefore the efficiency of the system and bring it towards a slowly degeneration leading to a cell
replacement necessity. Other effects caused by lower temperatures are the decrement of the oxygen productivity consequently to the increment of the cell resistance to the ions diffusivity and of the equilibrium potential, which its trend is inversely proportional to the temperature one, due to the endothermic nature of the reaction. To maintain the same level of production presented for higher temperatures, the required potential to apply across the stacks must increase, increasing in turn the required power. Against those negative effects, two positive ones are present: the former is that lower temperatures require lower thermal control to maintain the operative condition; and the latter is that with lower temperatures the material inside the cells are subjected to lower thermal stress and degradation diminishes.

- Elevated temperature values:
  Boudouard reaction is inhibited at such elevated temperatures, therefore the carbon deposition process can be considered avoided and the longevity of the cell increased. The equilibrium potential and the resistance to the ions diffusivity decrease and so the oxygen productivity is larger and the power demand is lowered. The negative aspects are the opposite of the positive one caused by low temperatures: higher thermal control is needed and due to higher temperature levels, the degradation of the cell materials is accentuated.

Those just presented are the temperature induced effects considering a constant pressure condition, but what are the combined effects?

- Low temperature & Low pressure:
  There are three main effects induced by a low-pressure condition: an inhibition of the carbon deposition processes, because lowering the pressure the inverse reaction of the Boudouard is favoured and therefore the carbon reacts with CO₂ to reproduce CO molecules. This because a decrement of pressure favours the reaction that produce more gaseous species, in this case: the reverse Boudouard reaction; contrary to what happen for the Boudouard, the electrolysis process is
favoured in terms of efficiency but the production levels will be lower; at last, the pump required power to pressurize the gas decreases because the variation of pressure to give to the flow decreases. The superposed effects of low pressures and temperatures are translated in reduced carbon deposition, less energy required to the volumetric pump and to the thermal control but large energy required by the process and low productivity.

- Elevated temperature & Low pressure:
  The combined effects between elevated temperatures and low pressures result in: Carbon deposition avoided; less energy demanded to the volumetric pump and to perform the process; higher energy required for thermal control and higher degradation; There is only one conflict between low pressure and elevated temperatures: the lower productivity due to low pressures values that goes against the higher productivity due to elevated temperatures.

- Low temperature & Elevated pressure:
  Elevated pressure levels favour the carbon deposition, require more power to the pump, but ensure a higher productivity. The combined effects with low temperatures are very negative: large carbon deposition; large power demand to the pump and to perform the process; and the conflict about productivity levels. Of course, there are also positive aspects such as lower thermal control and reduced degradation.

- Elevated temperature & Elevated pressure:
  The combined effects of these two conditions leads to a high productivity level, to the avoidance of carbon deposition (due to elevated temperatures), and to lower energy demand to perform the process. The drawbacks are a higher energy demand to the volumetric pump, higher thermal control and more accentuated degradation.

The pressure and the temperature levels in the reactor, in addition, strongly affect the structural design and the sealing of the reactor itself. Higher the temperature and the
pressure are, stricter the sealing and the structural robustness requirements will be. It’s also because of these reasons that the pressure level is limited to 1 atmosphere.

Another interesting variable, that affects the performance of the system is the applied potential. If the conditions in the reactor are maintained stable and only the applied potential could vary, an increment of the current intensity and so of the production rate will be recorded consequently to an increment of the potential, but, since the required power can be computed as the product between the potential and the current through the cell, there will be an increment of the power demand too. An important consideration can be done on the minimum value that this potential could take. If from one hand it doesn’t present any theoretical upper boundary, from the other hand the applied voltage must be greater than the equilibrium potential to guarantee a current flux into the cells. The equilibrium potential, indeed, is also known as “open circuit voltage”.

The other performance influencing variables are the inlet gas velocity and the inlet mixture composition: the inlet gas velocity greater effects are caused to the downstream flow. As the velocity increases, as the distribution of CO$_2$ along the cathode surface is homogeneous with a consequently decrement of the Nerst potential and an increment of the current density, as it can be seen in Ni, 2009.

Always from Ni’s works, it could be appreciated how a greater presence of CO$_2$ at the inlet section increases the performances of the system because of the decrement of the Nerst potential due to the high concentration of reagent at the cathode surface. Operating the SOXE on Mars is great advantage because of the planetary atmospheric composition that is for the 96% CO$_2$.

### 3.3.2 Sabatier Reactor

In the design of the Sabatier reactor, the variables that can play an important role and that affect the most the performances of the process are:

- Operative temperature and pressure;
- Inlet mixture composition;
- Inlet mixture velocity;
- Density of the catalytic bed and catalyst particle dimensions;

The effects of the temperature on the reaction have been partially descripted by the previous analyses on the equilibrium constants and on the side reactions occurring consequently to the injection of the Sabatier outflow into SOXE reactor to perform a co-electrolysis process. In this section, they will be recalled and deeper investigated.

Since the exothermic nature of the methanation reactions, elevated temperatures don’t favour the processes and cause a profound decrement in their equilibrium constant values. At the contrary, the endothermic RWGS reaction results favourite in such conditions. Therefore, in order to achieve a greater quantity of water production per hydrogen reacted in the reactor, the temperature level must be larger enough to promote RWGS but not so larger to inhibit methane and water formation by methanations. Of course, it’s not just a matter of temperature, but also of inlet concentrations. If the temperature level is too low to favour the RWGS, but the concentrations of H$_2$ and CO$_2$ are much larger than those of H$_2$O and CO, the process is tent to occur because the reaction quotient proceeds towards the rightward direction.

Even the pressure level induces effects on the process behaviour: Gao, Wang et al. performed an interesting study about CO and CO$_2$ methanations and the pressure effects on them, coming at the conclusion that higher is the pressure and higher is the carbon deposition inhibition in the optimal operative temperature range. They found out that at atmospheric pressure the deposition process is highly favoured between a temperature range that goes from 450 to 750 °C presenting a maximum at 600 °C, while increasing the pressure the deposition decreases and the maximum point shifts towards higher temperatures. The shifting process occurs towards the limiting value of 750 °C, reached in proximity of 15 atmosphere condition. After such values, any carbon deposition occurs at all.
Other effects, in addition to those previously mentioned, of the inlet mixture composition have been investigated by researchers (Gao et al., 2011; Parlikkad et al., 2012) and results suggest that CO₂ methanation is inhibited by the CO in the reactor and that with the increasing of the CO₂/CO ratio, the “active reactive” volume of the reactor, intended as the volume from the inlet up to the point in which the reactions take place, increases. Such a volume is influenced by the inlet velocity too: more the stream is faster and more the volume increases. This phenomenon could be a positive effect to limit the temperature levels in the reactor until a certain velocity value, and then, if the flow is too fast, this could become a negative phenomenon because the reactions could don’t have the time to occur.

Other variables and parameters that could cause an effect on the reactor performances are the characteristics of the catalyst bed. Higher is its density and higher results the reaction effectiveness, but also the reactor temperature and the catalyst degradation as well as the pressure drop across the bed.
CHAPTER 4: SIMULATIONS SETTINGS AND RESULTS

In this chapter, in first place, the verification of the models seen in chapter 3 will be presented comparing the obtained results with the expectations using specific sets of parameters defined to investigate the models in various aspects. Then, it will be shown the followed simulation scheme to get the conclusive results and, at last, considerations about them.

4.1 MODELS VERIFICATION

The verification process will be a parametric study in which the main variables that affect the performance of the reactor, listed in section 3.1 of chapter 3, will be led to vary over determinate ranges of values to test the answer and the behaviour of the system.

4.1.1 SOXE Model

To verify the SOXE reactor models, the behaviours of current density, Nerst potential and ASR are analysed and compared with the results in literature.

4.1.1.1 Zero-Dimensional Model

The zero-dimensional model, as already said, allow the estimation of the production rate basing only on the upstream flow conditions knowledge. The results obtained with this method must be considered optimistic with respect the real obtainable values, because any diffusive resistance inside the porous materials have been taken into account as well as any change in species compositions over the cathode, which is a very important phenomenon that could inhibit the reaction and cause a decrement in the oxygen production. The concentrations variation could only decrement the production rate because if the production of CO at the cathode is considered, the molar fraction of CO$_2$ decrease and so decrease also the effectiveness of the process with a consequently current intensity drop.
The range of values in which the performances have been investigated are listed in table 4.1 and have been selected to simulate possible system operative conditions. Any parametric study on initial stream velocity is performed because of the independency of the production rate on it in the Zero-D model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000 ÷ 1300</td>
<td>[K]</td>
</tr>
<tr>
<td>Applied potential</td>
<td>1 ÷ 2</td>
<td>[V]</td>
</tr>
<tr>
<td>CO₂/CO inlet ratio</td>
<td>0.2 ÷ 0.99</td>
<td>[--)</td>
</tr>
</tbody>
</table>

*Table 4.11 Parameters variations for Zero-D model verification*

What is expected is a decrease of the Nerst potential with temperature and inlet mixture ratio increment, with a consequently larger oxygen production. Another expected effect is the decrement of the ASR with temperature, reflecting the improved ionic conductivity of the electrolyte. No ASR variations should be registered for inlet mixture ratio and applied potential changes, since it depends only on the electrolyte temperature. The current density will present a dependency on temperature, deriving from the Nerst potential dependency on it, and one due to the applied potential: the more the applied potential increases and the more the current density will be higher.

The results of the verification are presented in the following charts and, compared with the ones obtained by Meyen & the MOXIE team, the behaviour of the investigated quantities follows completely the expectations, confirming the correct modelling of the system. Due to the simplicity of the ASR experimental expression, its independency on the applied potential appears quite trivial to see and so any verification analysis on it has been shown.
Fig. 4.1  Current density variation with temperature and applied potential

Fig. 4.2  Nerst potential variation with temperature and inlet mixture ratio
4.1.1.2 One-Dimensional Thermal-Fluid Model

The model was presented as an evolution of the previously mentioned Zero-dimensional one, with the difference that, in addition to the only electro-chemistry modelling, it also considers the thermal-fluid evolution of the gaseous stream along the cell to take into
account the variations of the species concentrations due to the reaction occurrence. A direct consequence is the variation of the Nerst potential as well as the current density along the cell.

The expected result is an increment of the Nerst potential and therefore a decrement of the current density along the reactor due to an increasing CO molar fraction due to the envelop of the reaction. The expected Nerst potential variation will be dependent on the inlet mixture velocity too, because higher will be the stream velocity and higher will be the homogeneity of CO\textsubscript{2} distribution on cathode surface, diminishing the Nerst potential and increasing the current density. An interesting dependency that doesn’t appear in the Zero-Dimensional model is the indirectly one of the Nerst potential on the applied voltage: the applied voltage influences the current density, which in turn influences the CO production rate that goes directly to influence the Nerst potential. Therefore, an increment of the applied voltage will lead to an increment of the CO molar fraction in the reactor and consequently to an increment of the Nerst potential too. In conclusion, the model can be considered less optimistic than the Zero-Dimensional one, because, even with high speed flows, a little decrement in the production rate will be always measured along the cell.

The parameters varied in the verifications and the ranges in which they have been varied can be found in table 4.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000 ÷ 1300</td>
<td>[K]</td>
</tr>
<tr>
<td>Applied potential</td>
<td>1 ÷ 2</td>
<td>[V]</td>
</tr>
<tr>
<td>CO\textsubscript{2}/CO inlet ratio</td>
<td>0.2 ÷ 0.99</td>
<td>[--]</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>0.1 ÷ 5</td>
<td>[m/s]</td>
</tr>
</tbody>
</table>

Table 4.2 Parameters variations for One-D model verification

The CO\textsubscript{2}/CO inlet ratio, \(x_r\), is defined in such a way that:
\[
\begin{align*}
[X_{CO_2}] &= [X_{TOT}] \cdot xr \\
[X_{CO}] &= [X_{TOT}] \cdot (1 - xr)
\end{align*}
\]

The results respect the previsions and present an interesting aspect to analyse: after a transition phase, where the molar mixtures vary, with a rate dependent on the mixture velocity, the dynamics of the system become more stable and the Nerst potential tends to an asymptotic value, due to the stabilization of the species molar concentrations. This is a simply consequence of the fact that much more CO is produced at the cathode and much more the molar fraction of CO$_2$ diminishes causing a decrement on the reaction quotient.

Interesting to note is the effect of the inlet velocity on the system: faster the stream is and more the solution is closer to the Zero-dimensional one. Therefore, it could be said that the Zero-D solution is the theoretical asymptotic solution of the 1D model, characterized by an infinite inlet velocity.

![CO$_2$ molar concentration variation with inlet velocity and axial location](image-url)

*Fig. 4.5* CO$_2$ molar concentration variation with inlet velocity and axial location
Fig. 4.6  CO molar concentration variation with inlet mixture ratio and axial location

Fig. 4.7  Nerst potential variation with inlet velocity and axial location
Fig. 4.8  Current density variation with temperature and axial location

Fig. 4.9  Nerst potential dependency on the applied potential. The other variable parameters are kept fixed.
4.1.2 Sabatier Reactor – 1D Pseudo-Homogeneous Model

The verification procedure will be performed following the same path adopted for the SOXE models: the main influencing parameters will be varied and performances studied and commented. The main variable parameters have been listed in section 3.2 of chapter 3 and are the inlet temperature, the inlet mixture composition and the inlet mixture velocity and the catalyst bed characteristics and they are varied in the ranges of value listed in table 4.3. Important to say is that the variation of the catalytic bed density is expressed as a variation in the bed porosity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>423 ÷ 923 K</td>
<td></td>
</tr>
<tr>
<td>CO₂/CO inlet ratio</td>
<td>0.2 ÷ 0.99</td>
<td>[-]</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>0.1 ÷ 5 m/s</td>
<td></td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.1 ÷ 0.7 %</td>
<td></td>
</tr>
</tbody>
</table>

*Table 4.3 Parameters variations for One-D pseudo-homogeneous model verification*

In this case, the inlet mixture ratio is defined to obtain:

\[
\begin{align*}
[X_{CO_2}] &= \left( [X_{TOT}] - [X_{H_2}] \right) \cdot x_r \\
[X_{CO}] &= \left( [X_{TOT}] - [X_{H_2}] \right) \cdot (1 - x_r)
\end{align*}
\]

Since the overall performance of the reactor is dependent on the proceeding of 3 different process, the estimations of the production and of the system behaviour becomes more difficult than for SOXE models. It’s expected that for the lowest values of inlet temperature, the processes won’t occur in an effective way, while for a range of temperatures that goes from 500 ÷ 700 K the effectivity of the process is expected to increase. For the most elevated inlet temperature values, the effectiveness is estimated to diminishes again. With variations of the CO₂/CO inlet ratio, the active reactive volume is expected to vary, as observed from Parlikkad et al., depending on the products
concentration in the reactor: if any water is given in input to the reactor, the equilibrium of the CO\textsubscript{2} methanation is much more favoured than the CO methanation one because of its dependency on the inverse of the water molar concentration square, therefore an increasing of the inlet mixture ratio will correspond to a decreasing of the active reactive volume. The active reactive volume will be, for sure, affected even by the inlet velocity value: faster stream will result in larger active reactive volume. The affection on results by the variation in the bed porosity is expected to be an inversely behaviour of the active reactive volume.

The model can be subjected to other 2 verifications:

- The respect of the continuity equation presenting a constant mass flow rate across the reactor;
- The respect of the perfect gas law during all the process.

The results are shown in the following figures.

\textit{Fig. 4.10} Reactor temperature variation with inlet temperature and axial location
Fig. 4.11 CH$_4$ yield variation with inlet temperature and mixture ratio

$CH_4$ molar concentration vs Bed porosity vs Axial location

Fig. 4.12 CH$_4$ concentration variation with inlet temperature along the reactor
The predicted trends have been respected: From figure 4.10 and 4.11 can be appreciated what has been previously said about the reaction affection by the inlet temperature value: under and above certain thresholds, depending on mixture composition, the reaction does not occur. The fact that the temperature threshold varies, is strictly correlated with the active reactive volume variation due to mixture composition changes. In figure 4.12 and 4.13, also the effects of inlet velocity and bed porosity on the active reactive volume are evident.
For what regard the 2 additional verifications, the results are given in figure 4.14 and 4.15. The mass flow rate varies with inlet conditions, but remains constant across the reactor. On the other hand, the perfect gas law results always respected, with a maximum error of $10^{-5}$ possibly due to uncertainties introduced by the solver and by the procedure to solve the set of ordinary differential equations explained in section 2.3.1 of chapter 3.

### 4.2 SIMULATIONS FLOW DEFINITION

In this section, the logics adopted to perform the simulation is explained. The difficulty in designing the system is the dependency on the inlet CO of the Sabatier reactor that must be furnished by the SOXE subsystem. The simulation flow that has been followed was aimed to ensure the productivity levels of $O_2$ and $CH_4$ required to the system.

The steps to follow to get a preliminary design of the reactors were:

- Optimization of the Sabatier reactor in order to maximize the methane yielding;
- Optimization of a SOXE cell to maximize the Oxygen production;
- Definition of a reactor size and computation of the number of reactors needed to get the required methane production yield;
The same must be done with the SOXE reactor: definition of a cell geometry and a stack architecture and then, dissimilarly from the Sabatier reactor, two different computations must be performed:

- The former is about the number of stacks needed to reach the required oxygen production rate, taking in consideration also the water produced by the Sabatier reactor as an oxygen source for the system;
- The latter is the computation of the stacks needed to feed the Sabatier reactor to get its optimal working condition.

After the computations, the two resulted numbers have been compared and the solution representing the larger number of required cells has been taken as the best suited for the system.

4.2.1 Notes on optimization procedure

The optimization process is aimed to search for a stable equilibrium point of a given function with respect to the main parameters on which its value is dependent the most, that is they are aimed to find the minimum of such function. There are several types of optimization procedures, based on different algorithms and different concepts, that could search for local or absolute minimum points. The processes that search for local minimum points are called constraint minimization processes, where, as can be deduced from the name, the solutions found must respect some given constraints, while the ones searching for absolute minimums are known as unconstrained minimization processes. It could be that the functions of a problem to minimize are more than one, leading to a multi-objective optimization, in which a trade-off must be performed to get a solution that satisfies the objectives.

If it has been required a function maximization, like in this case, it could be simply thought to minimize the opposite function.

Since the optimization of SOXE and Sabatier reactors were two unrelated problems, the procedure followed to get a solution resulted simplified. In addition, a further
simplification has been added by the fact that both the problems were a single-objective optimization. In other words, the optimization procedures were aimed to pursue a maximization of only one function, that was, respectively, the methane and the oxygen productions rate. The variable parameters are the same led to vary in the verification of the models.

The mathematics behind the procedure is the *Lagrange multipliers method*. For a detailed description, see: Trench, 2013. The method has been implemented on Matlab© in the *fmincon* function, that receives in input the function to minimize, as known as objective function, the variable parameters, the ranges in which they are varied and the linear and not linear constraints that the solutions must respect. As output, it gives the magnitude of the optimal parameters to get the optimal solution and its value.

4.2.2 *Definition of the Variable Parameters Ranges*

The bounds of the parameters variation ranges have been set to guide the optimizations to find solutions with specific characteristics.

4.2.2.1 *SOXE Reactor*

Concerning the SOXE optimization, the considered variable parameters were:

- Operative temperature;
- Inlet mixture composition;
- Applied potential;
- Inlet stream velocity;

The range of values in which they could vary has been set in order to evaluate only possible working conditions, avoiding, therefore, useless-extra-computations. Basing on the various considerations made in all the previous sections of the thesis, the ranges has been selected as:
Inlet temperature | 1000 ÷ 1173 [K]
---|---
$\text{CO}_2/\text{CO}$ inlet ratio | 0.5 ÷ 0.99 [--]
---|---
Applied potential | 1 ÷ 1.4 [V]
---|---
Inlet velocity | 0.1 ÷ 10 [m/s]

Table 4.4 Allowable ranges of parameters variation for SOXE optimization

The temperature range has been selected to avoid carbon deposition and high materials degradation zones. The applied potential has been chosen to allow a current flow through the cell, but, at the same time, limited to avoid carbon deposition zones. The inlet velocity has been selected to analyse different regimes of mass flow rate. Low values of inlet mixture ratio have been investigated to simulate a recirculation process.

4.2.2.2 Sabatier Reactor

To optimize the production rate of the Sabatier reactor, the solution is to study the system response to the variation of the main variables that affect the reactions, which are:

- Inlet temperature;
- Inlet molar composition;
- Inlet stream velocity.

The bed porosity has been decided to be kept fixed since the minimal impact shown with respect the other variables.

The ranges in which the effects of those variables have been measured can be found in table 4.5 and have been selected, as above, in such a way to examine only possible working conditions, discarding the unrealistic ones, and are:
Inlet temperature \(500 \div 700\) [K]

\(0 \div 0.99\) \([-\]

Inlet velocity \(0.1 \div 10\) [m/s]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>(500 \div 700) [K]</td>
</tr>
<tr>
<td>(\text{CO}_2/\text{CO}) inlet ratio</td>
<td>(0 \div 0.99) [-]</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>(0.1 \div 10) [m/s]</td>
</tr>
</tbody>
</table>

Table 4.5 Variable parameters ranges

The inlet temperature range has been selected to investigate the region related to higher productivities, the inlet velocity range has been set to analyse different regimes of mass flow rate as occurred for SOXE, while the inlet mixture ratio has been studied for the possible values: from a reactor only exploiting the CO coming from the SOXE to a condition in which only atmospheric carbon dioxide is processed.

### 4.3 RESULTS

#### 4.3.1 SABATIER

The results obtained for the Sabatier reactor, as expected from the trends previously analysed, have confirmed the maximum methane production rate have been obtained in the narrow range of temperatures between \(500 \div 600\) K, precisely at 561 K. The value of inlet mixture ratio is 0, because it has been resulted that the presence of \(\text{CO}_2\) in the reactor inhibits the CO methanation resulting in a smaller amount of methane yield. The SOXE reactor will have to guarantee the required CO flux. The better functioning in CO2 absence condition, can be explained with the following reasoning: the absence of CO2 in the inlet stream put at disposition of the CO methanation all the amount of hydrogen supplied; when CO methanation occurs, water is produced, but water and CO are the products of the RWGS reaction which is so induced to act at the reverse to produce reagents such as \(\text{CO}_2\) and \(\text{H}_2\), but these, in turn, are reagents of the \(\text{CO}_2\) methanation that can occur to increase the production of methane. The only unwanted thing is the decrement of the water production due to the WGS, but since its low reaction rate this decrement appears limited. Concerning the inlet velocity, is obvious that the maximum
production rate results for faster streams, because of the higher flow rate in the reactor. Higher velocities lead to the increment of the active reactive volume because the time the particles have to react is smaller and so the percentage of unreacted reagents increase, but the presence of a recirculating system make this problem totally negligible. The solution resulted present an active reactive volume equal to the reactor volume, this because the reactions are highly exothermic and temperature increase in a large way, but if temperatures increase too much the reactions become unfavourite and so the optimal condition for an adiabatic reactor like the one studied, to don’t present such a decrement in the methane productivity, is to present such an active reactive volume equal to the reactor one.

The optimal inlet parameters resulted are:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>561</td>
<td>[K]</td>
</tr>
<tr>
<td>CO₂/CO inlet ratio</td>
<td>0</td>
<td>[--]</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>3.5</td>
<td>[m/s]</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.51</td>
<td>[%]</td>
</tr>
</tbody>
</table>

*Table 4.6 Sabatier optimal parameters*

Computing the production and consumption rates of elements adopting the same reactor geometry and the same Ni-based catalyst adopted from Parlikkad (table 4.7), the obtain results can be seen in table 4.8.
Diameter 0.1 [m]
Length 1 [m]
Catalyst density 1700 [kg/m³]
Catalyst particles diameter 0.005 [m]

Table 4.7 Reactor and catalyst characteristics

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ inlet flow rate</td>
<td>77.4</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>CO inlet flow rate</td>
<td>361.1</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>H₂ outlet flow rate</td>
<td>45.3</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>CO outlet flow rate</td>
<td>156.5</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>CH₄ production rate</td>
<td>93.9</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>H₂O production rate</td>
<td>78.9</td>
<td>[kg/day]</td>
</tr>
</tbody>
</table>

Table 4.8 Production rate results

In the figures below the behaviour of temperature, pressure and concentrations can be appreciated as well as the consideration about active reactive volume and variation in concentrations due to the different reactions.
Fig. 4.16  Methane production rate

Fig. 4.17  Water production rate
Fig. 4.18 CO conversion along the reactor

Fig. 4.19 Species molar fractions along the reactor
With those kind of results, the time needed to get the desired amount of CH₄ to supply to the MAV and the hopper, 2267 kg, is 25 days. In those 25 days, the amount of produced oxygen and hydrogen from water electrolysis are, respectively, 1753 kg and 219 kg. The required amount of hydrogen and of carbon monoxide required from the
reactor can be computed as a difference among the mass at the inlet and the one at the outlet section, and they are: 32.1 kg/day of hydrogen and 204.6 kg/day of CO. As a result, the required amount of hydrogen is 802.5 kg in 25 days and so the net amount of hydrogen to be brought from Earth is 583.5 kg per each 25 days on Mars.

4.3.2 SOXE

By looking at the behaviour of the cell performances, monotonic trends of the current intensity, and so of the oxygen production rate, with the parameters variation have been noted. This fact implied an enormous saving of time because the optimal operativity condition have been computed by only observing the influences acted on the production rate by the variable parameters:

- Observing the operativity temperature induced effect, the best adoptable value in the range is the most elevated;
- The same occurs for the applied voltage and for the inlet mixture ratio.

Therefore, by adopting the Zero-dimensional model, the optimal oxygen production rate and the parameters to get it are:

<table>
<thead>
<tr>
<th>Inlet temperature</th>
<th>1173 [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CO inlet ratio</td>
<td>0.99 [-]</td>
</tr>
<tr>
<td>Applied potential</td>
<td>1.4 [V]</td>
</tr>
<tr>
<td>O₂ production rate</td>
<td>52.7 [kg/m²/day]</td>
</tr>
</tbody>
</table>

*Table 4.9 Zero-D model optimal parameters and maximum production rate*

For the One-dimensional model the trends are the same, but in addition to the Zero-D one, the effect of the inlet velocity must be considered. From the effects caused on the Nerst potential observed in figure 4.7 and from the previous considerations, is easily seen that, even in this case, the maximum production rate is obtained for the maximum
velocity possible. Of course, such a condition does not allow the total CO₂ consumption in the reactor, but since its huge abundancy in the Martian atmosphere, the fact is not considered a problem at all. Therefore, the optimal production rate and the optimal conditions for 1D model are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>1173</td>
<td>[K]</td>
</tr>
<tr>
<td>CO₂/CO inlet ratio</td>
<td>0.99</td>
<td>[--]</td>
</tr>
<tr>
<td>Applied potential</td>
<td>1.4</td>
<td>[V]</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>10</td>
<td>[m/s]</td>
</tr>
<tr>
<td>Average current density</td>
<td>6057</td>
<td>[A/m²]</td>
</tr>
<tr>
<td>CO₂ average consumption rate</td>
<td>119.3</td>
<td>[kg/m²/day]</td>
</tr>
<tr>
<td>CO average production rate</td>
<td>75.9</td>
<td>[kg/m²/day]</td>
</tr>
<tr>
<td>O₂ average production rate</td>
<td>43.4</td>
<td>[kg/m²/day]</td>
</tr>
</tbody>
</table>

Table 4.10 One-D model optimal parameters and maximum production rate

Fig. 4.22 Oxygen production rate along the reactor
Fig. 4.23 Molar fractions at the cathode

Fig. 4.24 Current density along the reactor
Defined the maximum production rate, an estimation of the cells geometry can be done. It has been thought to adopt a cell geometry like the one of the MOXIE system:

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Rectangular cells</th>
<th>[--]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Area</td>
<td>0.0025</td>
<td>[m²]</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>5⋅10⁻⁶</td>
<td>[m]</td>
</tr>
</tbody>
</table>

Table 4.11 SOXE cells characteristics

The production per cell can be computed and, looking at the required propellant to produce, an estimation of their number can be performed as well as the number of stacks, taking as an example the moxie system with stacks made by 11 cells. For the computation, only the 1D model has been taken into account because of its higher vicinity to the real performances. To take under consideration is also the CO production required to perform the methanation processes inside the Sabatier reactor. From the results of the Sabatier reactor came out that the desired methane production has been reached in 25 days and in those days 1753 Kg of oxygen are produced via electrolysis of the obtained water, reducing the demand on the oxygen production by SOXE, which
become of 7314 kg. Meanwhile, the consumption rate of CO has been computed as 204.5 kg/day. Considering, as a limiting time to produce the required oxygen mass, 25 days of continuable production, the resulting number of cells is 1885, that can't be divided by 11 and so it has been decided to group the cells in stack of 13, obtaining a need for 145 stacks. Considering, on the other hand, the amount of CO to produce to supply the Sabatier reactor, the total number of cells results 1078, a quantity largely inferior to the one obtained from the previous computation. Therefore, looking at the obtained results, the chosen architecture consists in 1885 cells grouped in 145 stacks. The required electrical power to supply at the SOXE plant can be computed as the product of the current intensity across the cell and the voltage applied multiplied by the number of cells. The Power required results to be 21.2 W/cell and so 275.6 W/stack and globally 39.962 kW.

<table>
<thead>
<tr>
<th>Required O₂ mass</th>
<th>292.6</th>
<th>[kg/day]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required CO mass</td>
<td>204.5</td>
<td>[kg/day]</td>
</tr>
<tr>
<td>Operative time window</td>
<td>25</td>
<td>[day]</td>
</tr>
</tbody>
</table>

Table 4.12 System production requirements

<table>
<thead>
<tr>
<th>Number of cells</th>
<th>1885</th>
<th>[-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of stacks</td>
<td>145</td>
<td>[-]</td>
</tr>
<tr>
<td>Power required</td>
<td>39.962</td>
<td>[kW]</td>
</tr>
</tbody>
</table>

Table 4.13 System architecture and electrical power demand

The amount of produced CO in excess can be discarded through a flow rate regulation valve.
CHAPTER 5: CONCLUSIONS

5.1 Conclusions and Results

During this work problems of chemical, thermal-fluid and electro-chemical nature have been faced to model the plant. Due to the large number of variables involved in the design of the reactors, many have been the aspects to consider and to analyse and this is why it has been decided to exploit an optimization approach.

The obtained results define a time window of 25 days to produce the required propellant to supply at the MAV and at the hopper and this is a very nice value because every 25 days, or even less if the MAV is not used, a new exploration mission can be performed by relying on transportation of exploration rovers at very large distances via hopper.

Analysing deeply the results of the Sabatier reactor, it comes out that they are less optimistic with respect the expectations for what concern the hydrogen recirculation: instead of reach recirculation values of 0.5, intended as the ratio between recovered hydrogen and reacted hydrogen, the system works with a recirculation level of 0.375.

This value could be increased in two ways:

- Considering a Sabatier reactor with a temperature control system to maintain the reactor at an optimal temperature for the process, avoiding too elevated temperatures that result counter-productive;
- Processing water coming from another ISRU system source. In this way, the production of hydrogen via water electrolysis would result independent from the Sabatier reactor performance and, theoretically, unitary recirculating levels could be reach, reducing the amount of hydrogen brought from Earth at zero.

For what concern the SOXE reactor, the obtained production rates are comparable with the expected values. A consideration that must be made is the fact that no carbon dioxide is required in input to the Sabatier reactor, but the flow outgoing the SOXE is not completely CO but it is 45% CO₂. The solutions to this problem could be:
• Adoption of the same separation membrane cited by Zubrin et al. to separate
the two species, but with an increasing of complexity of the system.
• Performing an optimization of the overall system and not 2 different
optimizations, where the inlet mixture composition of the Sabatier reactor is
directly the outflow of the SOXE reactor, without the necessity to separate the
gases and to discard the CO in excess.

5.2 Limits and Further Developments

The limits of this work can be found in the thermal-fluid modelling of the reactors. The
limits of the 1D pseudo-homogeneous model to model the dynamics of the Sabatier
reactor are mainly two:

• The absence of any distinction between conditions in the flow and in the bed
side. The results can be more accurate and the influence of the catalytic bed on
the reaction can be better understood and described. An improvement in this
sense could be the adoption of the Heterogeneous models, briefly discussed in
chapter 3.
• Any radial description of the fluid is given. Introducing a 3D model of the reactor,
with the fluid presenting both axial and radial variations, a better understanding
of the reaction can be obtained as well as more accurate results.

Further developments on this system may encompass:

• The design of a reactor that is no more adiabatic, but that presents a thermal
control system to control the inner temperature to look for higher production
rates;
• Laboratory tests on catalysts performances to improve the kinetics modelling or
to improve carbon deposition inhibition or increase the catalyst degradation
threshold.

For what concern the SOXE reactor modelling, the limit stay in the absence of any
consideration about the diffusion process inside the porous cathode that could bring to
a better modelling of the production rates. A quasi-2D model of a SOXE cell allows even the computation of the temperature variation inside the electrolyte layer, causing a variation in the ASR of the cell and so in the production levels.

Further developments on this system could be focused on modelling the deposition of carbon on the cathode side that could cause the poisoning of the catalyst and the decrement of the production rate.
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