

C2FUEL

Carbon Captured Fuel and Energy Carriers for an Intensified Steel Off-Gases based Electricity Generation in a Smarter Industrial Ecosystem

Deliverable

D1.1 – Specifications for the demonstrator WP1 – Specifications and demonstration setup

Project Information	
Grant Agreement n°	838014
Dates	1 st June 2019 – 31 st May 2023

PROPRIETARY RIGHTS STATEMENT This document contains information, which is proprietary to the C2FUEL Consortium. Neither this document nor the information contained herein shall be used, duplicated or communicated by any means to any third party, in whole or in parts, except with prior written consent of the C2FUEL consortium.



Document Status

Document Information

Deliverable name	C2FUEL_Deliverable D1.1 WP1_v01				
Responsible beneficiary	ENGIE				
Contributing beneficiaries	ENGIE				
Contractual delivery date	M6 – 30/11/2019				
Actual delivery date	M7 – 06/12/2019				
Dissemination level	Public				

Document approval

Name	Position in project	Organisation	Date	Visa
C. MAKHLOUFI	Coordinator	ENGIE	03/12/2019	OK
M. MAROT	Project Management Officer	AYMING	03/12/2019	ОК
P. OLIVIER	Project Management Officer	ENGIE	03/12/2019	ОК
E. FAVRE	WP LEADER	CNRS	03/12/2019	OK

Document history

Version	Date	Modifications	Authors
V1	29/11/2019	1 ST DRAFT	ENGIE
VF	30/11/2019	Final check	ENGIE



Table of content

2
3
4
4
5
5
5
5
6
6
7
7
12
12
13
15
16
18



List of figures

Figure 1. Conventional process for Formic Acid synthesis from carbon dioxide	5
Figure 2. Concept of circular economy upon which C2Fuel is built	7
Figure 3. Illustration of the filter proposed for particle separation before the CO ₂ capture in	ו the
membrane contactors (left), and inside structure of the filter (right). Filtre THE carter F	۶VC,
www.camfilfarr.fr.	8
Figure 4. Preliminary block diagram of the SOEC unit of 1 Nm ³ /h capacity	12
Figure 5. Block diagram of the CO ₂ capture unit of 1 Nm ³ /h capacity	14
Figure 6. Block diagram of the Formic Acid synthesis unit	15
Figure 7. Block flow diagram of CO ₂ hydrogenation to Formic Acid	16

List of tables

Table 1. Typical blast furnace gas composition	7
Table 2. Properties of the filter THE proposed for use upstream of the membrane c	ontactors for
CO2 capture. Filtre THE carter PVC, www.camfilfarr.fr.	8
Table 3. Summary of main impurities present in BFG, concentration range a	nd identified
purification technologies with potential for utilization in the C2FUEL pilot	9
Table 4. Commercial technologies or materials for removal of common impurities for	ound in blast
furnace gas	10
Table 5. Utility and power requirements of the SOEC unit	13
Table 6. utility and power requirements of the CO ₂ capture unit	14
Table 7. utility and power requirements of the Formic Acid synthesis unit	
Table 8. Demonstrator specifications within battery limits	16



Deliverable report

1. Executive Summary

1.1. Description of the deliverable content and purpose

The aim of this deliverable is to lay down the details relating to the overall technical design of the C2FUEL demonstrator. More specifically, this report will highlight process requirements for the production of Formic Acid through CO_2 hydrogenation. First, a thorough design of the CO_2 conditioning unit must be performed accounting for all impurities found in Blast Furnace Gas (BFG). Despite gas cleaning in a cyclone and wet gas scrubber, particles are still present in the BFG to be fed to the CO_2 capture step. Small quantities of impurities such as H_2S , COS, SO_x , NO_x , BTX, HCN, Hg, HCI and PAH's can also be present. Additionally, the purpose is to assess the site requirements at the planned scale for the demonstrator. The general methodology is based on solving mass and energy balances for the three main units of the demonstrator. By achieving complete conceptual process designs, a first estimation of site requirements and utility needs are identified to reliably define battery limits for the demonstrator.

1.2. Brief description of the state of the art and the innovation breakthroughs

As the share of renewable sources continues to increase in the energy mix, hydrogen storage has become a palpable issue now more than ever. Currently, several solutions are under investigation so as to measure their potential as hydrogen carriers. Amongst those, Formic Acid stands out as a suitable way and a promising solution to both store and transport hydrogen. Formic Acid, or FA, is the simplest carboxylic acid and it already has several industrial applications. The purpose behind using FA as a hydrogen carrier is to take advantage of existing infrastructure to easily store and transport hydrogen. With this in mind, there is still a significant number of technological and economical challenges to overcome before this concept can be brought to daylight as a feasible solution.

In today's industry, Formic Acid is produced following a Methyl Formate hydrolysis process. Usually, syngas recovered from gasification units is used to produce Methyl Formate in an intermediate step before reacting the latter with water to produce FA and Methanol in the final stage. This route, while technologically mature and economically optimized throughout the years of its existence, has the major flaw of relying on carbon monoxide as a reagent. Besides, it also suffers from high energy consumption related to CO and steam generation needs.



Figure 1. Conventional process for Formic Acid synthesis from carbon dioxide (adapted from [1])

A first alternative to this conventional process would be to produce FA through carbon dioxide hydrogenation. This path requires the use of solvents (generally strong bases) to increase catalyst

H2020 Grant Agreement N° 838014 – C2FUEL D1.1: Specifications for the demonstrator



activity. The downside is the need of additional separation steps to recover homogenous catalyst and/or break FA-solvent/FA-water azeotropes which drastically decreases the process overall efficiency. In order to avoid complex separation phases and substantial catalyst losses, some advanced alternative strategies could be considered. Notably, a possible improvement could be achieved with the use of pH-controlled catalysts that can precipitate at a known range of pH values, thus allowing the recovery of catalyst in solid form. However, the control of pH implies the continuous use of base/acid solutions to switch the pH value, hence impacting the operating cost of the process. Another option is to use heterogenous catalysts in structured reactors. While this solves catalyst recovery related issues, the need of downstream purification units still stands. Furthermore, so far, heterogenous catalysts has shown lower activity and lesser selectivity towards FA formation than their homogeneous counterparts.

The second route considers the electroreduction of carbon dioxide. In an electrochemical reactor, CO_2 is reduced to FA among other components (mainly H₂ and CO). The clear advantage in this process is the direct formation of FA without H₂ intermediate production. Here, catalyst selectivity is of paramount importance as it dictates the Faradic Efficiency of the electrochemical cell. Reducing cell potential is an another issue that can be solved by enhancing Membrane-Electrode Assembly (MEA) performance. Carbon dioxide concentration at the electrode surface is identified as the main limiting factor for achieving both high selectivity and production rate. This lack of mass transport can be solved by improving reactor design. Usually, to increase both membrane conductivity and catalyst selectivity, solvents are added on each sides of the reactor. Thus leading to further separation steps to purify the final product. In the current demonstrators, reactor efficiency was assessed to reach around 15% per pass. To increase the overall efficiency, reactants are usually recycled back to the reactor after intermediate separation steps.

1.3. Corrective action (if relevant)

Not relevant here.

1.4. IPR issues (if relevant)

Not relevant here.



2. Deliverable section 1 – CO₂ pre-treatment requirements

2.1. CO₂ captured from off-gases

The C2FUEL project is built on the concept of circular economy: the main goal is to demonstrate at industrial-relevant scale the conversion of captured CO_2 from carbon intensive off-gases in chemical energy carriers (i.e. formic acid and dimethyl ether). The overall target is to avoid the emission of 2.4 million tCO₂ per year, by its reutilisation.



Figure 2. Concept of circular economy upon which C2Fuel is built

The CO₂ is captured from a blast furnace gas (BFG), produced by the steel factory and used in the DK6 power plant to generate electricity. The typical BFG composition is shown in Table 1.

	Raahe (Finland) [2]	Ghent (Belgium) [3]	Undisclosed (France) [4]	Dunkirk (France) [5]				
Main gases (%vol.)								
CO ₂	22.1	22.5	23.70	23.40				
CO	23.1	24.43	25.15	23.5				
N ₂	45.1	48.46	46.7	48.9				
H ₂	5.3	3.38	4.45	4				
O ₂	0.2	0.62 (Ar+O ₂)	-	0.2				
H ₂ O	4.3	-	-	-				

Table 1. Typica	l blast furnace	e gas compos	sition
-----------------	-----------------	--------------	--------



Dust content in the BFG was measured to be 22-24 mg/Nm³ in 2010 by external companies for DK6, results of these measurement campaigns were transmitted to ENGIE. Due to the change on regulation in 2013 [14], the dust content in current emissions should be \leq 10 mg/Nm3 as reported by Thieffry [6], however no data after 2010 on dust content has been transmitted to ENGIE. Size distribution of the particles in the BFG after wet scrubbing (cleaned gas) is also not available. Thieffy [6] assumes a distribution of 0.1 -20 µm based on size distribution of particles separated before the wet scrubber. The necessity for a measurement campaign is to be determined. Based on the estimated BFG flowrate of 5 Nm³/h, a dust content of 10 mg/Nm³ and 25 mg/Nm³ leads to 50 and 125 mg/h of dust to be removed. These flowrates for a 3000 h operation would amount to 150 and 375 g of dust respectively to be collected during the pilot operation.

Implementation of technologies such as cloth filtration in baghouses or wet electrostatic precipitators seems not feasible at the scale of the pilot based on open literature from vendors. The utilization of filters such as absolute filters, HEPA/THE filters for dust removal in the C2FUEL pilot has to be checked with manufacturers and vendors to evaluate the life of the filter under the above conditions of dust concentration and determine if an appropriate selection and design of the filtration step allows for an effective continuous operation of the unit for 3000h. For later scale-up of the technology to a commercial size, the use of filters has to be evaluated, implementing instead an additional technology such as wet electrostatic separators after the wet scrubber could be the way to go if it is shown that the dust content in the BFG is too high for direct utilization in the CO2 capture step. Information gathered on the impact of dust content in the CO2 capture step to be obtained during operation of the pilot will help to determine the needs for dust separation during scale-up.

The filter presented Figure 3 has been proposed by CNRS for particle removal before the CO_2 capture step. THE (or HEPA) filters are able to retain at least 99,97% of the particles with a diameter superior or equal to 0,3 μ m.



Figure 3. Illustration of the filter proposed for particle separation before the CO_2 capture in the membrane contactors (left), and inside structure of the filter (right). Filtre THE carter PVC, <u>www.camfilfarr.fr</u>.

Properties of the filter are given in the following Table:

Table 2. Properties of the filter THE proposed for use upstream of the membrane contactors for CO₂ capture. Filtre THE carter PVC, <u>www.camfilfarr.fr</u>.

Reference	Model	Dimensions (ØxH) mm	Uranine efficiency	Uranine coefficient	Media surface m ²	Flowrate/ΔP m ³ /h/Pa	Thread	Joint	Mass kg
3203.01.00	30 m³/h	140x190	> 99,98%	CE>5000	0,49	30/200 20/120 10/40	Ø 61,6 pas 2,5	Neoprene 5 mm	0,745



3204.01.00	50	160x218	> 99,98%	CE>5000	0,75	50/250	Ø 61,6	Neoprene	1,2
	m ³ /h					30/130	pas	5 mm	
						20/80	2,5		

Concerning gas impurities, Table 3 presents a summary of the concentration range of the impurities in BFG and the suggested purification technologies that could be implemented in the C2FUEL pilot.

Table 3. Summary of main impurities present in BFG, concentration range and identified purification technologies with potential for utilization in the C2FUEL pilot.

Impurities	Emission limit in France (ppm)	Concentration range in BFG from open literature (mg/Nm³)	Concentration range in BFG from direct measurements from Explor Air's 2013 report communicated by DK6 (mg/Nm ³)	Suggested separation technique for C2FUEL pilot based on preliminary evaluation of commercial alternatives
H ₂ S		40 – 116 (mg/Nm ³) 26 – 76 (ppm vol.)	12 – 45 (mg/Nm ³) 8 – 30 (ppm vol.)	H ₂ S scavengers such as Sulfatreat [®] or DS series or impregnated activated carbons
COS		40 – 120 (mg/Nm ³) 15 – 45 (ppm vol.)	52 – 97 (mg/Nm ³) 19 – 36 (ppm vol.)	COS scavengers such as Filsorb S 201 or impregnated activated carbons
SOx	200 mg/Nm ³ (SO ₂) [6]	2.6 (mg/Nm ³) ^a 0.9 (ppm vol.)	Not measured	Reach lower concentrations (<1 ppm) is difficult and may not be necessary Alternatively SO _X traps based on basic metallic oxides
NOx	100-200 mg/Nm³ [6]	2.1 (mg/Nm ³) ^b 1 (ppm vol.)	Not measured	Reach lower concentrations (<1 ppm) is difficult and may not be necessary Alternatively NO _X traps based on basic metallic oxides
BTX (Total) Benzene Toluene Xylenes		411 ^c (mg/Nm ³) 100 (ppm vol.) Not specified Not specified	Not detected ^d Not detected Not detected Not detected	Activated carbon adsorbents such as Durasorb® BTX
HCN		0,24 (mg/Nm ³) 0.2 (ppm vol.)	Not measured	Carbon molecular sieves such as Carbosieve® S-III or activated carbon
Hg		3.2x10 ⁻³ (mg/Nm ³) 0.0009 (ppm vol.)	Not measured	Reach lower concentrations may not be necessary. Activated carbon bed impregnated with sulfur such as NORIT® or a mixed-metal oxide such as Durasorb® HG
HCI PAH's	10-25 mg/Nm ³ [6] 0.01-0.1 mg/Nm ³ [6]	0,2-8 (mg/Nm ³) 0.1-5 (ppm vol.) 4000 ° (mg/Nm ³) 700 (ppm vol.)	Not measured Not measured	Chloride guards such as FCR-71/91 or Puraspec® PAH's can be condensed and separated as a liquid with a gas cooler or use of activated carbons

H2020 Grant Agreement N° 838014 – C2FUEL D1.1: Specifications for the demonstrator



- a. Assuming molar mass of SO₂ (64 g/mol)
- b. Assuming molar mass of NO₂ (46 g/mol)
- c. Assuming molar mass equimolar mix (92 g/mol)
- d. Comparatively high maximum concentrations of Benzene (517 ± 5) and of Toluene (2360 ± 24) were measured in 2010 [7].
- e. Assuming mol mass of 128 g/mol for PAH's (Naphtalene molar mass)

Because of the relative small flowrate of the BFG to be treated, ~5 Nm3/h, and the low concentration of impurities to be removed, due to indirect purification done at the wet scrubber, adsorption seems the more adapted alternative to implement in the C2FUEL pilot. For later scaleup, adsorption and absorption technologies seem to the most appropriate again because of the low level of impurities in the BFG. For implementation in the C2FUEL pilot, a multi-layered adsorption bed composed of chosen adsorbents targeting each specific impurity to be removed could be installed for thorough removal of the impurities removal by adsorption. Similar to the impact of particles, information gathered on the impact of impurities in the CO2 capture step to be obtained during operation of the pilot will help to determine the needs for separation during scale-up. Table 4 presents a non-exhaustive list of the main commercial technologies identified for removal of each impurity.

H ₂ S		
Technology	Product (Company)	Website
Activated	GC Sulfusorb	https://generalcarbon.com/activated-carbon/
carbon	Plus (General	
	Carbon	
	Company)	
Impregnated	Desorex®	https://www.donau-carbon.com/?lang=en-US
activated carbon	(Donau Carbon)	https://www.combatach.do/alticlehia/Olana.au
activated carbon	activated	nttps://www.carbotecn.de/aktivkonie/?lang=en
	carbons	
	(CarboTech)	
Iron-oxide-	Sulfatreat®	https://www.slb.com/well-production/production-
based	(Schlumberger)	chemicals/sulfatreat-h2s-removal-and-treatment/hydrogen-
adsorbents		sulfide-removal-from-gas
Zinc-oxide or	DS-series (Dorf	https://www.dorfketal.com/industry-solutions/catalysts-and-
mixed metal	Ketal)	adsorbents/sulphur-guard-catalysts
oxides		
Bioreactor	Sulfothane™	https://www.veoliawatertechnologies.com/fr/produits/sulfot
	(Veolia)	hane
Absorption-	LO-CAT®	http://www.merichem.com/LO-CAT-Flexible-H2S-
oxidation	(Merichem)	Removal-Process
COS		1
Technology	Product (Company)	Website
Hydrolisis-	COSWEET™	https://www.axens.net/product/process-
amine	(IFP)	licensing/20132/cosweet.html
separation		
Hydrolisis-	Puraspec®	https://matthey.com/products-and-services/chemical-
adsorption	(JM)	processes/absorbents/cos-removal
metal oxides		

Table 4. Commercial technologies or materials for removal of common impurities found in blast furnace gas.



Adsortion	Filsorb S201	https://www.dorfketal.com/industry-solutions/catalysts-and-				
metal oxides	(Dorf Ketal)	adsorbents/cos-removal-catalyst				
SO _x and NO _x						
Technology	Product (Company)	Website				
Activated	Activated	https://ieaghg.org/docs/General_Docs/OCC2/Presentation				
carbon beds	carbon	<u>s/OCC2%20-</u>				
for SO _x and	process	%20Near%20Zero%20Emissions%20CPU%20-				
NO _X (under	(Praxair)	%20Sept%202011%20-%20no%20animation.pdf				
development)		https://www.go.com/power/stoom/ogoo/cov.control.ufgd				
desulfurization	(GE)	mips.//www.ge.com/power/steam/aqcs/sox-control-wigu				
for SO_{γ}	(OL)					
Selective	SCR (Dürr	https://www.durr-meatec.com/en/products/exhaust-gas-				
catalytic	Megtec)	and-air-pollution-control/catalyticnon-catalytic-				
reduction for	J ,	processes/selective-catalytic-reduction/				
NO _X						
Dust removal	CataFlex™	https://cdn2.hubspot.net/hubfs/2115834/CAMPAIGNS/Cat				
+ selective		aflex/CataFlex.pdf				
catalytic						
NO_{x} trans by	NAC (JM)	https://matthey.com/products-and-services/emission-				
chemical		control-technologies/mobile-emissions-control/nox-				
adsorption		adsorber-catalysts				
HCN						
Technology	Product	Website				
L hardwark and a	(Company)					
Hydrolysis	CUS/HUN	<u>nttps://www3.wipo.int/wipogreen-</u>				
Teactions	corporation)					
Adsorbent	Carbosieve S-	https://www.sigmaaldrich.com/catalog/product/supelco/101				
(CMS)	III (Merck)	84?lang=fr®ion=FR				
BTX						
Technology	Product	Website				
	(Company)					
Activated	Durasorb BTX	https://catalysts.bast.com/files/literature-library/Gas-				
Combination of	SeparSIV [™]	https://www.uop.com/processing-solutions/gas-				
adsorbents -	(UOP)	processing/technologies/dew-pointing-and-dehydration/				
TSA						
Hg						
Technology	Product	Website				
Sulphur-	(Company)					
imprograted	(Company) Norit® Darco®	http://www.cabotcorp.com/solutions/applications/flue-gas-				
Impregnated	(Company) Norit® Darco® (CABOT)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal				
activated	(Company) Norit® Darco® (CABOT)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal				
activated carbon	(Company) Norit® Darco® (CABOT)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal				
activated carbon Modified	(Company) Norit® Darco® (CABOT) HgSIV™	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/				
activated carbon Modified molecular	(Company) Norit® Darco® (CABOT) HgSIV [™] (UOP)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/				
Activated activated carbon Modified molecular sieves Mixed metals	(Company) Norit® Darco® (CABOT) HgSIV [™] (UOP)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/				
Activated carbon Modified molecular sieves Mixed metals sulphides	(Company) Norit® Darco® (CABOT) HgSIV [™] (UOP) Puraspec [™] (JM)	http://www.cabotcorp.com/solutions/applications/flue-gas- treatment/mercury-removal https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://www.uop.com/uop-hgsiv-adsorbent-dryer-units/ https://watthey.com/products-and-services/chemical-processes/absorbents/mercury-removal-absorbents				



Mixed metal oxides adsordents	Dursorb [™] HG	https://catalysts.basf.com/files/literature-library/Gas- Treatment-Brochure.pdf
HCI	·	
Technology	Product (Company)	Website
Doped Aluminas adsorption	Puraspec [™] (J M)	https://matthey.com/en/products-and-services/chemical- processes/absorbents/chloride-guards
Doped Aluminas adsorption	FCR 71/91 (Dorf Ketal)	https://www.dorfketal.com/industry-solutions/catalysts-and- adsorbents/chloride-guard-catalysts
PAH's		
Technology	Product (Company)	Website
Activated carbon adsorption	Activated carbon (DESOTEC)	https://www.desotec.com/en/carbonology/carbonology- cases/removing-pahs-flue-gas

3. Deliverables section 3 – Process conceptual design

3.1. High temperature electrolysis unit

In the C2FUEL demonstrator, hydrogen is produced through high temperature electrolysis. Solid Oxide Cells (SOE) has been extensively developed as a low-carbon, efficient energy production through SOFC application. However, significant progress has been made throughout the recent years for the operation of SOE in electrolysis mode according to the reactions described below. Indeed, compared to other low temperature water electrolysis technologies, high temperature favours reaction kinetics and ohmic resistance which is expected to reduce power consumption.

At fuel electrode:	$H_2O + 2e^{\scriptscriptstyle -} \rightarrow H_2 + O^{2 \scriptscriptstyle -}$
At air electrode:	$O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^{-}$

The C2FUEL project is a unique opportunity to investigate SOECs at system level in order to take advantage of the demonstrated high efficiency at stack level to enhance the energy efficiency at system level. To operate the SOEC stack at nominal power, several Balance of Plant (BOP) components need to be integrated to the system. Figure 4 shows the general layout of the system.



Figure 4. Preliminary block diagram of the SOEC unit of 1 Nm³/h capacity

Version: V1 Dissemination level: Public



First, water is purified to prevent damaging the SOE cells. Water purification also decreases the amount of heat required by the steam generator. Considering the demonstrator small scale, all heat requirements are provided electrically as shown in the bock diagram of the unit. On the other side of the SOEC stack, sweeping air is filtered and heated to the SOEC operating temperature set at 700°C. Electric-power supply includes a rectifier unit converting the alternating current (AC) to direct current (DC) required for the SOEC stack operation.

Saturated hydrogen gas is recovered at the outlet of the SOEC stack. It is then cooled and purified to remove contained water and protect downstream compressor. Afterwards, high purity hydrogen is compressed to 15 bar and stored for later use. On the anode side, sweeping air including oxygen is vented after an intermediate heat recovery step.

Lastly, mass and energy balances applied to the SOEC unit as hereby described, provide a preliminary estimation of the utility and power requirements to produce 1 Nm³/h of pure hydrogen at 15 bar. Thus, the energy efficiency of the SOEC unit is estimated at **71.5%** on HHV basis.

Table 5. Othery and power requirements of the OOEO unit					
Parameter	Value	Unit			
Max power 3×400VAC 50HZ	7.85	kW			
Nominal power	4.89	kW			
Stack power	2.83	kW			
Tap water	63.5	l/day			
Cooling Water at 15°C	0.54	m ³ /day			
Air	182.7	m ³ /day			
H ₂ production	23.7	Nm³/day			

Table 5. Utility and power requirements of the SOEC unit

3.2. Carbon dioxide capture unit

According to the proposed process scheme (Figure 5), the BFG gas is sent to a membrane gas absorber in which the simultaneous transfer of species between two phases is occurring: the gas phase and the absorbing solvent. A typical solvent used for CO_2 capture is Monoethanolamine (MEA). In this unit, CO_2 is transferred from the gas to the liquid phase, therefore a stripping process is required to recover the CO_2 from the solvent. Both the absorption and the stripping processes are limited by equilibrium, as a result, the CO_2 so captured might contain small amounts of both the BFG gases and the solvent used in the contactor.

The membrane gas contactor and stripper should be designed in a way that no further feed pretreatment and purification is needed before the reactor. Therefore, the information here presented is necessary for a proper design of these units. The previous section of this report has focused on the pre-treatment requirement of the BFG before entering the CO_2 capture unit. The main purpose of this section is to assess the utility and power requirements of the capture unit provided that the gas composition meets the specifications of the membrane contactor. H2020 Grant Agreement N° 838014 - C2FUEL



D1.1: Specifications for the demonstrator



Figure 5. Block diagram of the CO₂ capture unit of 1 Nm³/h capacity

The preliminary conceptual design of the CO_2 capture unit is provided in Figure 5. At the inlet of the capture unit, the already solid and sulfur free BFG gases enter to the membrane contactor where the liquid absorbent captures the CO_2 , rendering it rich absorbent. A washing section placed on the top of the absorber allows for component recovery. The rich absorbent is pumped to a heating section and then to the stripper, in which CO_2 is stripped from the absorbent. In order to separate de CO_2 from the absorbent liquid, the later comes in contact with water vapor, which is obtained through partial evaporation of the liquid absorbent in the reboiler. The heat applied to the reboiler is provided by an electric heater. A pre-condenser is added to this section in order to increase enthalpy and solvent recovery. The relatively warm lean absorbent is then sent to the condenser, in which it is cooled by the rich absorbent, to finally enter to the absorber to close the loop. Once the CO_2 is separated from water in the condenser, it is ready to be brought to the compression section, in which the CO_2 is delivered at suitable storage conditions. The produced CO_2 is lastly stored at 15 bar for later use in the synthesis section.

Parameter	Value	Unit
Max power 3×400VAC 50HZ	17.98	kW
Nominal power	15.40	kW
BFG	102.6	Nm ³ /day
Cooling Water at 15°C	5.39	m³/day
MEA makeup stream	0.014	l/day
H ₂ O makeup stream	30.97	l/day
CO ₂ production	24.00	Nm ³ /day
Flue gas	78.56	Nm ³ /day

Table 6	. utility	and po	wer re	quireme	nts of	the	CO ₂	capture	unit

Similarly to the SOEC unit, heat and mass balances were applied to this unit to estimate overall process requirements. Table 6 provides the type and value of each utility according to the preliminary design. Most of the required electric power is expected to come from the reboiler of the stripping unit. Solvent and water makeup streams are evaluated according to the assumed net losses that occur in the condensation step. Flue gas composition is assumed to be identical to the BFG entering the capture unit, barring the CO₂ content captured downstream.



3.3. Formic Acid synthesis unit

Carbon dioxide hydrogenation to Formic Acid is an endergonic reaction with a positive free energy, therefore it is not possible to carry out the reaction without provoking a shift in thermodynamic equilibrium (partially due to CO_2 thermodynamic stability and less reactive nature).

 $CO_{2 (g)} + H_{2 (g)} \rightarrow HCOOH(l)$ $\Delta G^{\circ} = 32.9 \text{ kJ/mol}; \ \Delta H^{\circ} = -31.2 \text{ kJ/mol}; \ \Delta S^{\circ} = -215 \text{ J/mol}. \text{ K}$

To improve the enthalpy of reaction, a trialkylamine base is usually added leading to a negative free energy value (e.g. the addition of NH_3 leads to a value of -9.5 kJ/mol). Besides, the dissolution of the gases enhances the entropy of reaction (e.g. dissolution of CO_2 and H_2 leads to a free energy value of -35.4 kJ/mol [8], [9]). Nonetheless, the separation step(s) and isolation for pure Formic Acid from amine-based processes are complicated and energy-consuming motivating the exploration for alternative solutions.

In the C2FUEL project it is envisaged to resort to a process intensification strategy in order to overcome the mass transfer limitation associated with CO_2 hydrogenation reaction. This strategy relies on two novel technologies which are developed for this specific application : the Spinning Disc Reactor (SDR) for Formic Acid synthesis and the membrane separator for the product purification step.

The outstanding heat and mass transfer properties of the spinning disc technology combined with its versatility to integrate separation processes, e.g. extraction, membranes, and to have electrode functionality, make it a universal solution for processes in which mass transfer and/or heat transfer are the rate limiting steps [10]–[12]. For the CO₂ hydrogenation, a high kinetic reaction rate can be matched with a high mass transfer rate towards catalyst particles deposited on the rotor and on the stator wall.

Separation through membranes is an interesting alternative considering the lower temperature requirement and the attractive cost. Other conceivable technologies for water/formic acid separation could include pervaporation, capillary distillation or diffusion distillation.



Based on this preliminary conceptual design, it is expected to significantly reduce the number of required process steps in contrast with the conventional process presented earlier in Figure 1. As shown in Figure 6, produced hydrogen and carbon dioxide enter the unit at 15 bar where they are mixed with a polar solvent which enables a higher concentration of CO₂ in the liquid phase. The gas/liquid mixture is then preheated to reach the required inlet temperature of the Spinning Disc



H2020 Grant Agreement N° 838014 – C2FUEL D1.1: Specifications for the demonstrator

Reactor. Unreacted gases are separated from the solvent/product phase and are recycled back to the inlet of unit. The product rich phase is preheated before entering the membrane separation apparatus which delivers a 85% pure Formic Acid product. Other required utilities alongside with electric power are recapped in Table 7.

Parameter	Value	Unit
Max power 3×400VAC 50HZ	0.51	kW
Cooling water at 15°C	1.07	m ³ /day
Solvent makeup stream	8.70	l/day
Formic acid production	36.34	l/day

Table 7. utility and power requirements of the Formic Acid synthesis unit

3.4. Demonstrator specifications

The C2FUEL demonstrator aims to produce 85% pure Formic Acid by combining 1 Nm³/h high purity hydrogen produced through high temperature electrolysis with 1 Nm³/h of high purity carbon dioxide directly captured form a steel factory Blast Furnace Gas. The 3 unites were predesigned to assess the power and utility requirements. Figure 7 and Table 8 provide an overall review of these requirements.



Figure 7. Block flow diagram of CO₂ hydrogenation to Formic Acid

The demonstrator is expected to consume around 26 kW of electric power during start-up mode (i.e. max electric power). During nominal operation, the demonstrator consumes around 21 kW to produce 36 l/day of 85% pure Formic Acid. This translates to a specific consumption of approx. 17 kWh/kg of Formic Acid. A significant share of the electric power is consumed by the CO₂ capture unit (namely the boiler) and the electrolysis unit. Other noticeable utilities required by the demonstrator include cooling water and solvent makeups that are required to continuously operate the unit.

Parameter	Value	Unit
Electricity 3×400 VAC 50HZ	26.3	kW
Nominal Power	20.8	kW
Specific consumption	16.8	kWh/kg.FA

Fable 8. Demonstrato	r specifications	within	battery	limits





Formic Acid product	36.3	l/day
H ₂ O	94.5	l/day
H ₂	23.7	Nm ³ /day
CO ₂	24.0	Nm ³ /day
Air	182.7	m ³ /day
Blast Furnace Gas	102.6	Nm ³ /day
MEA make-up	0.014	l/day
FA Solvent make-up	8.70	l/day
Flue gas	78.6	Nm ³ /day
Cooling water @15°C	7.00	m ³ /day



Bibliography

- [1] G. Fachinetti, « (54) PROCESS FOR PREPARING FORMIC ACID », p. 20.
- [2] A. Arasto, E. Tsupari, J. Kärki, E. Pisilä, et L. Sorsamäki, « Post-combustion capture of CO2 at an integrated steel mill – Part I: Technical concept analysis », *International Journal of Greenhouse Gas Control*, vol. 16, p. 271-277, août 2013.
- [3] G. Thieffry, « Procédé alternatif pour l'épuration des fumées de hauts fourneaux. Thèse présenté pour l'obtention du grade de docteur de l'Université de Lorraine. Spécialité Génie des procédés, des produits et des molécules. » LRGP.
- [4] M. Dreillard, P. Broutin, P. Briot, T. Huard, et A. Lettat, « Application of the DMXTM CO2 Capture Process in Steel Industry », *Energy Procedia*, vol. 114, p. 2573-2589, juill. 2017.
- [5] « AMF Energy Department. Steel gases specifications for powerplant gas consumption. ».
- [6] « Arrêté du 26 août 2013 relatif aux installations de combustion d'une puissance supérieure ou égale à 20 MW soumises à autorisation au titre de la rubrique 2910 et de la rubrique 2931. https://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000027995928 ».
- [7] Explor Air, « Suivi qualitatif et quantitatif d'un gaz issu de hauts fourneaux et de cokerie. SOCOR AIR DK6 Dunkerque. » sept-2010.
- [8] P. G. Jessop, Takao. Ikariya, et Ryoji. Noyori, « Homogeneous Hydrogenation of Carbon Dioxide », *Chem. Rev.*, vol. 95, nº 2, p. 259-272, mars 1995.
- [9] N. Onishi *et al.*, « Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid », 2018.
- [10]M. Meeuwse, «Rotor-Stator Spinning Disc Reactor», PhD Thesis, Eindhoven University of Technology, 2011.
- [11]M. M. de Beer, J. T. F. Keurentjes, J. C. Schouten, et J. van der Schaaf, « Intensification of convective heat transfer in a stator-rotor-stator spinning disc reactor », *AIChE J.*, vol. 61, n° 7, p. 2307-2318, juill. 2015.
- [12]F. Visscher, J. van der Shaaf, M. de Croon, et J. C. Schouten, « Liquid-liquid mass transfer in a rotorstator spinning disc reactor », présenté à AIChE Annual Meeting, 2011.