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**Lombardia & Rhein-Main towards Zero Emission:
Development and Demonstration of Infrastructure Systems for Hydrogen as an Alternative
Motor Fuel**

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Thematic Priority: Sustainable Energy Systems

Deliverable 3.6.

**OPERATIONAL EXPERIENCE AND ASSESSMENT OF THE ON-SITE H2
PRODUCTION FACILITY IN MANTOVA**

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ZEROREGIO PROJECT

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QUESTO DOCUMENTO È **RISERVATO** E DI PROPRIETÀ DI Eni S.p.A. DIV. R&M OVVERO DELLE SOCIETÀ CHE LO HANNO COMMISSIONATO. ESSO VERRÀ UTILIZZATO ESCLUSIVAMENTE PER GLI SCOPI PER CUI È STATO PRODOTTO E DISTRIBUITO E NON VERRÀ RIVELATO A TERZI SENZA PREVIA AUTORIZZAZIONE DELLA SOCIETÀ PROPRIETARIA, CHE TUTELERÀ I PROPRI DIRITTI CONTRO EVENTUALI TRASGRESSORI NELLE SEDI OPPORTUNE.

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1. PREMISES

This document is intended to provide an overview of the operational experience of the SCT-CPO H₂ production plant located inside the Eni Multifuel station in Mantova. This plant has been realised in 9 months (Oct. 2007 – June 2008) and operated for the first time on July 2009 after a quite complex procedure required for reaching the required authorisation for the construction and operation (Table 1). The description of the plant characteristics and of the first operation campaign that lasted 750 hours, has been already given in other documents^{1,2,3}. Here we will report on:

- i) the operation experience developed during the 5th year of the project by utilising the H₂ production unit in a “turn around” mode; with fast start-up, operation and shut-down cycles
- ii) the costs and energy efficiency figures of the SCT-CPO technology vs. the steam reforming technology.

Table 1.


Fact sheet related to WP3: years 2005 – 2008

June 30th, 2005:	Completion of a first PDP of the H₂ production unit (50 Nm³/h)
May 15th, 2006:	Local & Regional prescriptions for realising the multi-fuel station
Aug. 1st, 2006:	EniTecnologie merged into the Eni Group. The ZeroRegio project was assigned to the R&M Division
Sept 13st, 2006:	Issue of National prescriptions regulating the construction and operation of H₂ plants for mobility purposes
May 15th, 2007:	Final approval from Local and Regional Authorities
July 1st, 2007:	Contract assignment for realising the H₂ production unit
Sept. 15th, 2007:	Completion of a second PDP of the H₂ production unit (20 Nm³/h)
Sept. 21th, 2007:	Opening ceremony of the multi-fuel station
June 12th, 2008:	Completion on site H₂ production unit
July 16th, 2008:	Start-Up and consecutive operation (750 hours) of the SCT-CPO plant

¹ 4rd Year Activity Report (Nov. 2008)

² D 3.4.: H₂ production facility integrated with the H₂ storage, compression and distribution equipments in operation.

³ D 3.5.: Operation manual for the H₂ production unit

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2. HYDROGEN PRODUCTION PLANT OPERATION


After internal and extensive discussions it was decided to operate the H₂ production unit in a turn-around mode with short campaigns both for demonstrating the possibility of the technology to follow a variable H₂ demand and for avoiding to waste large H₂ amounts which could not be consumed by the small fleet composed by three vehicles.

Accordingly with the Comune di Mantova and with the Centro Ricerche Fiat and with Sapio an estimate was made of the H₂ consumption figures (see Tab. 2) and 5 short H₂ production campaigns were scheduled.

Table 2. Comparisons between Scheduled H₂ consumption & production features during year 2009

	H₂ Cons.	(kg)	H₂ Prod.	(kg)
	Scheduled	Accomplished	Scheduled	Accomplished
April	36.5	13.9	45.0	40.0(20)
May	27.8	3.6	50.0	
June	30.6	20.4	0.0	
July	36.6	32.9	50.0	40.0
Aug	0.0	20.0	0.0	
Sept	34.6	15.5	45.0	
Oct	43.2	6.3	50.0	40.0
Nov.	17.3	6.7	0.0	
Sum	242.4	119.2	240.0	120.0

For each campaign a 5 days procedure was define for completing the entire start-up, operation and shut-down cycles for H₂ refilling of Sapio storage system (40 kg). The procedure hereafter described had been successfully validated through 3 campaigns carried out during the 5th year of project. Indeed the reduction of the number of the H₂ production campaigns from 5 to 3 was determined by the reduction of the H₂ consumption figures as described in Tab. 1. It is here noted that the five day operation cycle included two days in which the plant was prepared for the start-up and for remaining unattended for 3 months period

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without being operated. Indeed without these long intervals between the three operation campaigns the entire start-up, production & shut-down cycles would have been completed in 3 days.

Table 3

Fact sheet related to WP3: year 2009

April-May 2009: cyclic operation of the SCT-CPO plant

July 2009: cyclic operation of the SCT-CPO plant

Oct. 2009: cyclic operation of the SCT-CPO plant

Timing of the turn - around operation mode

Day 1.	Start-up of the utilities	3 h
	Start-up of the Combustor	7 h
	SCT-CPO Reactor Preheating	4 h
Day 2.	Start-up of the SCT-CPO reactor and achievement of stationary conditions (O₂/C = 0.60 v/v S/C = 0.50 v/v – P = 16 barg)	4 h
	Start-up of the WGS	2 h
	Start-up of the PSA	2 h
	Analysis of H₂ samples	2 h
Day 3.	Refilling of the storage system	30 h (40 kg of H₂)
Day 4.	Shut-Down of the unit	3 h (24 hrs cooling of the refractory)
Day 5.	Battery limits blinding	

2.1 Day 1

Utilities start-up: cooling water circuit, air compressor for instrument and process air production, demineralised water package. Duration: 3 hours (08:30 – 11:30).

Process skids leak test: check process skids are proper tightened. Duration: 8 hours (09:00 – 17:00).


Thermal combustor: refractory lining is heated up to 800°C with 100°C/h ramp through methane and air control. Duration: 8 hours (11:30 – 19:30).

SCT-CPO reactor heating: CPO reactor is heated up to 350°C. Duration: 12 hours (19:30 – 07:30).

2.2 Day 2

DS reactor start-up: feeding natural gas. Duration: 0,5 hours (07:30 – 08:00).

SCT-CPO reactor start-up: reaction ignition and steady state at 15 barg. Duration: 6 hours (08:00 –

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14:00).

HTS reactor start-up: feeding CPO outlet stream and steady state at 14,5 barg. Duration: 2 hours (14:00 – 16:00).

PSA start-up: feeding HTS outlet stream and steady state at 13,5 barg. Duration: 2 hours (16:00 – 18:00).

PSA off-gas to thermal combustor: feeding PSA off-gas to the burner. Duration: 0,5 hours (17:00 – 17:30).

H₂ analysis and sampling: continuous analysis of pure H₂ from PSA through micro GC and off-line sampling for CO analysis (< 0,3 ppm) in San Donato Milanese labs.

H₂ refilling of Sapio storage bottles: feeding pure H₂ from PSA (around 1,5 kg/h) to Sapio storage bottles. Duration: 30 hours (18:00 – 24:00 day after).

2.3 Day 3

H₂ refilling of Sapio storage bottles: completion of refilling operation. Duration: 30 hours (18:00 day before – 24:00).

2.4 Day 4

PSA shut-down: stop feeding HTS outlet stream and purge of the unit with N₂. Duration: 1 hour (08:00 – 09:00).

HTS reactor shut-down: stop feeding SCT-CPO outlet stream. Duration: 0,5 hours (09:00 – 09:30).

SCT-CPO reactor shut-down: stop feeding reactant streams, depressurisation and purge of the reactors (CPO and HTS) with N₂. Duration: 3,5 hours (09:30 – 13:00).


DS reactor shut-down: stop feeding natural gas and purge of the reactor with N₂. Duration: 1 hour (11:00 – 12:00).

SCT-CPO reactor cooling: natural ventilation cooling to ambient temperature. Duration: 1 day (13:00 – 13:00 day after).

Thermal combustor shut-down: stop of the unit. Duration: 1 hour (13:00 – 14:00).

Thermal combustor cooling: natural ventilation cooling to ambient temperature. Duration: 1 day (14:00 – 14:00 day after).

Utilities shut-down: stop of cooling water circuit, air compressor and demineralised water package. Duration: 3 hours (14:00 – 17:30).

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2.5 Day 5

Battery limits blinding: production plant mechanically disconnected at battery limits. Duration: 3 hours (14:00 – 17:00).

3. OPERATIONAL EXPERIENCE ASSESSMENT

The operation procedure described in the previous paragraph had been developed during the first campaign (July – August 2008) and successfully adopted according to the proposed schedule during the following runs. The use of such procedure together with ease of operation of the production plant (after the detailed commissioning performed before the first start-up, no problem arose during all the campaigns) led to the successful completion of all the 5 days long campaigns in terms of quantity and quality (fuel cell grade) of produced hydrogen. Figure 1 includes the composition of the feed, syngas, shifted syngas and produced H₂ streams.

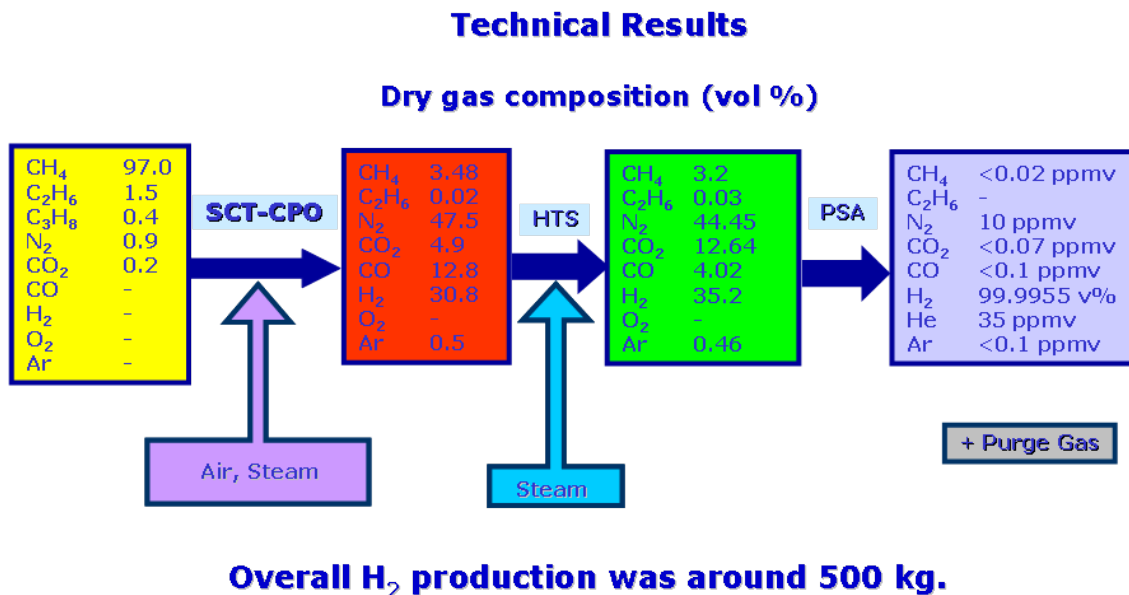



Figure 1. Compositions of the feed, syngas, shifted syngas and produced H₂ streams.

Operating personnel was also a key factor for the success of the operation of the plant. Initial extensive training was given about technology know-how, production plant design criteria and safety issues of Mantova site. During the first campaign, operating personnel was made up of 8 operators in shift (24 hours per day, 7

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days per week) coordinated by operators' chief and vice-chief. The expertise of the operators developed during the first campaign together with detailed operating procedure led to the reduction of the operating personnel to 4 operators in shift and an operators' chief in the following campaigns. Subsequently during year 2009 a detailed engineering work was developed for allowing operation of the plant with a remote control. This remote operation procedure was not implemented due to the reduction of the number of the production campaigns.

4. SCT-CPO vs. SR: COSTS AND EMISSIONS


An analysis had been carried out about the comparison of SCT-CPO and SR technologies assuming large scale and centralised H₂ production and decentralised small scale H₂ production. For the large scale H₂ production it was also examined the possibility of removing the CO₂ (Carbon Capture) associated with plant operations. This analysis considered the results obtained during the Mantova experience and the knowledge developed on SR and SCT-CPO during an intensive and broad Eni R&D project devoted to the development of energy efficient and economic H₂ production technologies⁴.

The main results of this extensive analysis that has been developed in co-operation with main Industrial companies commercialising leading H₂ production technologies are highlighted in the following Table 4 (noteworthy the costs of this analysis have not been included in the project budget).

Tab. 4	SCT-CPO 55,000 Nm ³ /h	SCT-CPO + CC 55,000 Nm ³ /h	SCT- CPO 310 Nm ³ /h	SR 55,000 Nm ³ /h	SR + CC 55,000 Nm ³ /h	Unit
Specific capacity	165040	165040	930	165040	165040	kW(H2)
Annual op. hours	8400	8400	8000	8400	8400	h/y
Lifetime	15	15	15	15	15	Y
Annual H ₂ prod.	1,386,333,480	1,386,333,480	7,813,880	1,386,333,480	1,386,333,480	kWh(H2)/y
Output H ₂	1000	1000	1000	1000	100	1 kWh
Specific H ₂ cost without fuel and	0,53	0,68	4,61	0,86	1	SCT-CPO / SR



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electricity costs						
Specific CO ₂ emissions	3,01	0,10	4,20	3,00	1	SCT-CPO / SR

It is also noted that the data have been produced with procedures analogous to those adopted by the TRIAS project⁵ and have been normalised with respect to the large scale SR case in which the CO₂ emissions have been captured. It is also noted that these CO₂ emissions can be almost completely captured by utilising the SCT-CPO technology but not in the SR technology. In this last case the CO₂ emissions (ca. 40% of the total CO₂ emissions) associated to the heating furnace cannot be avoided.

From the table it appears that for large scale H₂ production, the costs not including fuel and electricity costs, are largely in favour of the SCT-CPO technology. This result is not only related to the strong reduction of capital cost but also to the reduction in operation & maintenance costs that are a consequence of the technological simplicity and easy operability of SCT-CPO. In many situations the inclusion of fuel and electricity costs would not alter these comparisons. However their inclusion in the table would complicate the analysis behind the scope of the present document. Indeed SCT-CPO has a much wider flexibility on feedstock composition compared to SR and can utilise low cost hydrocarbons but also compounds produced from bio-mass. For the same reason the CO₂ emission penalisation cost have not been included but it is clear that in case of CO₂ taxation and when sequestration the CO₂ would be feasible, the SCT-CPO advantage would be dramatically increased.

The table also show that the costs and CO₂ emissions related to H₂ production in small scale SCT-CPO plants⁶ are increased with respect to the costs of H₂ production in large scale plants. However the Table does not include the H₂ transportation costs from the centralised production units into the multi-fuel delivery stations.

⁵ http://www.transport-research.info:8080/web/projects/project_details.cfm?id=35677&page=results

⁶ The small scale plant considered in the technical economical analysis has a capacity of 310 Nm³/h of pure H₂ this capacity is much higher than the capacity of the ZeroRegio plant (20 Nm³/h of pure H₂) that has been downsized considering the small H₂ consumption of the three vehicles fleet and in order to avoid a waste of H₂. However this small capacity has been considered unrealistic for real application in the mobility sector.