THE REVALUATION OF SOLID WASTE FROM THE GOAST TANNING

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ABSTRACT

To highlight the LIFEGOAST project's attention to sustainability, the entire production cycle of the leather supply chain was taken into account. Therefore, besides developing a new metal-free tanning technology, the LIFEGOAST project pointed attention to the requalification of solid wastes derived from it. In this work, the solid waste coming from the leather shaving process was considered. The approach chosen is that of pyrolysis. The pyrolysis aimed at obtaining biochar that could be used for the formulation of new materials. Pyrolysis is a thermal process conducted at high temperatures in the absence of oxidizing agents, which involves the decomposition of organic material with the consequent formation of a solid fraction (biochar), a condensable fraction (biooil) and a gaseous fraction (biogas). Within the LIFEGOAST project, the goal was to maximize the yield in the solid fraction (biochar) by selecting appropriate operating conditions. In this context, the biochar obtained from LIFEGOAST leather shaving has shown promising characteristics for its application as a soil conditioner, anode for lithium batteries, replacement of aggregates in cementitious materials and production of activated carbon and last but not least as a biocharms.

Kaywords: LifeGoast, solid waste, pyrolysis, biochar, new materials.

1. Introduction

Solid waste generated by the municipal and industrial sectors is a major problem worldwide due to issues associated with collection, transportation, treatment, and disposal (Velusamy2020). The recycling and re-use of solid waste represent a great opportunity in terms of resource-saving, environmental protection, and economic development.

Tanning process from raw hides to finished leather is very complex, which takes several steps and generates substantial quantities of solid and liquid wastes.

At present, over 85 % of the world's leather production processing is chrome tanned (Yang2020). Consequently, large amounts of chromium-containing shaving wastes need to be treated. The major concern about the management of this kind of solid waste is ascribed to chrome content, which makes the conventional disposal methods, such as landfilling and incineration, not practicable (Rosu2018). Therefore, many efforts have been made in recent

decades for promoting eco-friendly/alternative leather production, and more effective waste management. Since GOAST leather processing is 100% organic, no heavy metals will be present in the shaving waste as well, so it can be easier recyclable than chromium-tanned shaving waste. In this scenario, our study concerned the treatment of solid waste deriving from the skin shaving from, tanning processes in the leather industry. Pyrolysis could be considered one of the possible approaches for the treatment of solid wastes from the tanning (Jiang2016). Pyrolysis is a thermal process conducted at high temperatures in the absence of oxidising agents, which involves the decomposition of organic material with the consequent formation of a solid fraction, a condensable fraction, and a gaseous fraction (Hasan2021). The solid fraction, called biochar, has some interesting properties, such as high specific surface area, porous structure, surface functional groups, and high mineral content (Sashidhar2019). Moreover, these properties can be modified through an appropriate activation treatment (Salimi2022).

Therefore, biochar thanks to its physical, and chemical properties can find different applications such as soil amendment, support for catalysts, absorbent material, supercapacitors, filler in polymeric and cementitious composites (Giorcelli2019; Legan2022).

In this study, the attention was focused on the valorisation of GOAST shaving waste by the pyrolysis approach, with the aim of creating new synergies with other industries by placing new materials on the market. Moreover, an exhaustive investigation of the physical activation process using steam and CO_2 to design activated carbons from LIFE GOAST biochar was carried out. The aim was the comparison of both activation agents on carbon properties at the same reaction conditions. Several reaction parameters were investigated such as temperature, time, total flow, and amount of activation agent. The work moved to the study of potential applications of GOAST-biochar and activated carbons. Different application fields such as anode for lithium ions batteries (LIBs), catalytic support, filler for asphalt, and replacement of sand in concrete were investigated. Herein, the discussion of results related to the application as anode for LIBs and support for heterogeneous catalysis are reported. The results achieved reveal that pyrolysis represents a promising approach for the valorisation of the GSW by its conversion into carbonaceous materials.

Materials and Methods

Pyrolysis and equipment set up

The pyrolysis process was carried out by a laboratory-scale prototype plant (Carbolite custom model EVT 12/450B). The pyrolysis was performed in a fixed bed quartz tube equipped with a porous septum connected to the quenching system through a heated outlet pipe (ca. 200°C) to prevent condensate build-up. The quenching system consisted of a series of glass condensers, cooled at 0°C in an ice bath, for collecting the condensable fraction. The output of the condenser was directly connected to the GC-TCD injector for the gas analysis. The furnace temperature was controlled using an electrical heater and a PID temperature controller. N-type thermocouples were used to measure both temperatures of the furnace and the quartz tube reactor. The desired inert gas flow (N_2) was set using a Brooks mass flow controller. The schematically pyrolysis plant is reported in figure 1

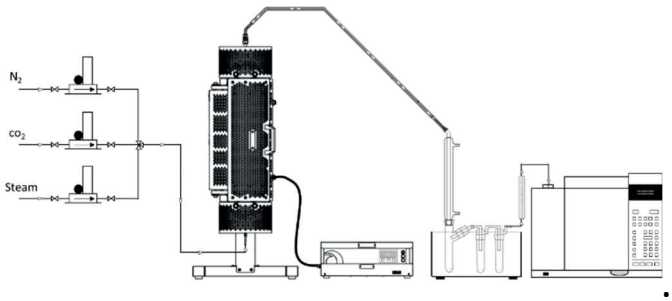


Fig 1. Custum pyrolysis plant[8]

In a typical run 50 g of GOAST-shaving waste, previously dried and sieved, was treated. The pyrolysis was performed under nitrogen flow of 100 mL/min at 700°C with a heating rate of 5°C/min, and residence time of 30 minutes.

The obtained biochar was labelled as GOAST-Biochar.

Physical activation process and applications

The activation process was conducted in the same plant used for pyrolysis treatment (Carbolite custom model EVT 12/450B). In a typical run, approximately 10g of GOAST-biochar was placed into the reactor. The investigation has been conducted by studying the effect of reaction parameters, such as temperature, residence time, amount of activation agent and inert flow rate.

The following reaction conditions have been investigated:

Temperature from 600°C to 800°C

Amount of activation agent from 50% to 70%

Residence time from 60 min to 240 min

Flow rate of N_2 from 30 mL/min to 100 mL/min

The surface area and pore volume analysis were performed by nitrogen physisorption measurements using a Micromeritics Tristar II Plus absorptiometer (MICROMERITICS USA). The elemental analysis (C, H, N, S) was carried out by UNICUBE organic elemental analyser (Elementar), and the oxygen content was calculated by difference.

The heavy metals content was performed using ICP-OES (Perkin Elmer 5300DV) Surface functional groups were investigated by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) using a Perkin Elmer Frontier FT-IR spectrometer.

The samples were labelled as shown in the following example:

C 70 2. 6-100

Where

C: CO_2, S: Steam; 70: % of AA; 2: Time (h); 6: Temperature; 100: Total Flow

For battery application, biochar was then physically activated by steam and CO_2 flow at 800 ° C under 57 vol. % steam / N_2 mixture for 4 hours, with a total gas flow of 160 mL / min.

For catalytic applications, biochar was physiscally activated by steam flow at 850°C, heating rate 10°C/min for 3 hours, H_2O: N_2=1:1 flow of 100 mL/min.

Results and Discussion

1. *Study of activation process on GOAST-biochar*

Through the activation process it is possible to change the physical / chemical properties of the biochar depending on the final application. For this purpose, the biochar LIFEGOAST has been activated under appropriate conditions and is applied in the anode area for batteries (Pejman2022) and in the catalytic support area (Longo2022).

Several reaction parameters were investigated such as temperature, time, total flow, and amount of activation agent. The results demonstrated that GOAST- biochar is a suitable carbonaceous precursor to produce activated carbons. Indeed, the activation process allowed us to obtain carbon materials with high surface area (up to 830 m^2/g), high content of surface functional groups, and a good order degree.

Nitrogen physisorption analysis was used to monitor the influence of activation agent on the porosity and surface area of the GOAST-biochar and activated carbons. Indeed, the Biochar porosity comes from the spaces between crumpled carbon sheets, which can be improved by an activation process that enlarge the volume of pores and cause a micro-meso-macro hieratical porous structure.

The results are reported in Table 1 and Figure 2 (a, b, c, d).

	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	Micropore Area (m^2/g)	V_{tot} (cm^3/g)
S701.8	275	390	331	0.16
S702.8	564	784	616	0.31
S703.8	731	1087	747	0.46
S704.8	831	1204	752	0.55
S702.8-100	269	385	322	0.16
S702.8-230	361	504	411	0.20
S702.8-330	564	784	616	0.31
S702.6	85	136	104	0.04
S702.7	309	428	360	0.17
S702.8	564	784	616	0.31
S502-8	244	357	303	0.15
S602.8	306	448	372	0.18
S702.8	564	784	616	0.31
C701.8	254	365	288	0.15
C702.8	474	714	548	0.28
C703.8	619	895	656	0.34
C704.8	611	934	511	0.36
C702.8-100	420	599	468	0.24
C702.8-230	443	641	457	0.25
C702.8-330	474	714	548	0.28
C702.6	n.d	n.d	n.d	n. d
C702.7	n.d	n.d	n.d	n.d
C702.8	474	714	548	0.28
C502.8	337	509	370	0.20
C602.8	403	586	426	0.23
C702.8	494	714	548	0.28

Table 1. Surface properties of STEAM (blue) and CO_2 (yellow) activated biochar

As expected, the features of activated carbons in terms of surface area and pore distribution were strongly influenced by reaction parameters and activation agents. For both activation agents, increasing the residence time, temperature, total rate flow and amount of activation agent, the surface area increases too. Comparing the two activation agents, it is worth noting that the activation process using steam led to higher surface area and pore volume.

Elemental analysis was used to detect the influence of the activation agent on the chemical composition of the GOAST-biochar at respective reaction conditions tested. The results are reported in Table 2.

Also in this case, the chemical composition of activated carbons was strongly influenced by reaction parameters and activation agents. Focusing the attention on the effect of time, it is possible to note as the steam have higher carbonization degree (lower H/C) than CO_2 samples suggesting that the carbon structure is more aromatic and carbonaceous. As regards the O/C ratio, for both steam and CO_2 samples it increases with time increasing. This can be ascribed to formation of O-containing functional groups on the carbons surface. Moreover, it's interesting to note that CO_2 samples present higher N/C and S/C ratios than steam samples with the time increasing. This aspect could be related to the less oxidizing strength of CO_2 molecule compared with water molecule. This suggests that the N and S atoms could be inside the polyaromatic structure of carbons.

FTIR was used to qualitatively analyse the functional groups on the carbon surface after the activation process. The results are reported in Figure 3

Even though the activated samples show a similar IR profile to the pristine biochar, it is possible to observe some differences in the wavenumber range from 2300 cm^{-1} to 800 cm^{-1}, which is typical of surface functional groups and component oxygen species of the structural network. Overall, the samples activated using steam showed higher content of oxygen functional groups than samples activated using CO_2. Concluding, this study demonstrates as leather- shaving waste is a suitable carbonaceous precursor to produce activated carbons. Furthermore, by defining the treatment parameters and selecting the activation agent, it is possible to modulate the morphological and chemical properties of the resulting activated carbons.

It's worth noting that the activation process using CO_2 led to obtaining activated carbons with high content of heteroatoms (nitrogen and sulfur) making them attractive in the field of batteries and supercapacitors and catalysis.

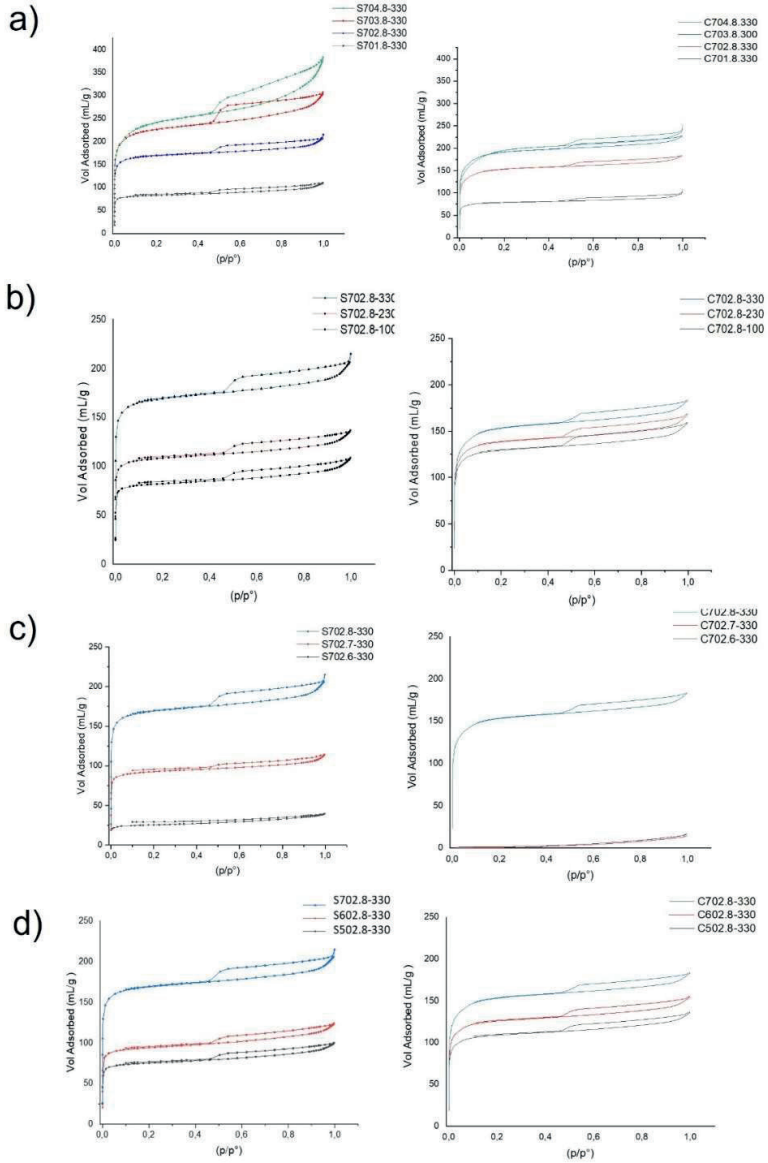


Figure 2. Effect of residence time on surface area (a), effect of total flow rate on surface area (b), effect of temperature on surface area (c), and effect of amount of activation agent on surface area (d)

	N [%]	C [%]	H[%]	S[%]	O [%]	H/C	O/C	N/C	S/C	Ash [%]	HHV (MJ/ kg)
T77-Biochar	11.0	71.6	1.8	1.1	5.7	0.025	0.08	0.15	0.015	8.8	24.1
S701	6.7	70	1.4	0.8	12.3	0.020	0.18	0.10	0.012	8.8	22.5
S702	4.4	72	1.3	0.7	12.8	0.018	0.18	0.06	0.010	8.8	23.4
S703	4.6	72.9	1.1	0.6	11.7	0.016	0.16	0.06	0.009	9.0	23.6
S704	1.8	64.7	1.0	0.5	23.1	0.016	0.36	0.03	0.008	9.0	19.3
S702-100	6.1	72.4	1.3	0.8	10.6	0.019	0.15	0.08	0.011	8.8	23.6
S702-230	5.4	71.7	1.5	0.8	11.8	0.021	0.16	0.08	0.011	8.8	23.6
S702.6	9.0	70.2	1.8	1.2	9.0	0.026	0.13	0.13	0.017	8.8	23.4
S702.7	7.5	72.5	1.4	1.1	8.6	0.020	0.12	0.10	0.015	8.8	23.9
S502	7.1	73.1	1.7	0.9	8.4	0.023	0.11	0.10	0.012	8.8	24.5
S602	6.0	72.3	2.1	0.8	10.0	0.030	0.14	0.08	0.011	8.8	24.9

	N [%]	C [%]	H[%]	S[%]	O [%]	H/C	O/C	N/C	S/C	Ash [%]	HHV (MJ/ kg)
T77-Biochar	11.0	71.6	1.8	1.1	5.7	0.025	0.08	0.15	0.015	8.8	24.1
C701	8.2	73.7	1.7	1.4	6.2	0.023	0.08	0.112	0.019	8.8	24.9
C702	7.5	67.8	1.8	1.6	12.5	0.026	0.18	0.110	0.023	8.8	22.2
C703	7.5	67.9	1.8	1.7	12.4	0.026	0.18	0.110	0.024	8.8	22.3
C704	5.9	55.3	2.0	2.7	25.4	0.037	0.46	0.106	0.049	8.8	16.6
C702-100	7.2	68.3	1.8	1.4	12.6	0.026	0.18	0.10	0.021	8.8	22.4
C702-230	7.2	65.7	1.7	1.4	15.2	0.026	0.23	0.11	0.021	8.8	21.1
C702.6	9.8	69.8	1.6	1.3	8.6	0.023	0.12	0.14	0.019	8.8	23.0
C702.7	9.7	70.3	1.4	1.2	8.6	0.020	0.12	0.14	0.017	8.8	22.9
C502	7.7	69.8	1.9	1.5	10.3	0.028	0.15	0.11	0.022	8.8	23.4
C602	7.7	69.3	1.9	1.5	10.9	0.028	0.16	0.11	0.021	8.8	23.1

Table 2. Elemental analysis of STEAM (blue) and CO_2 (yellow) activated samples

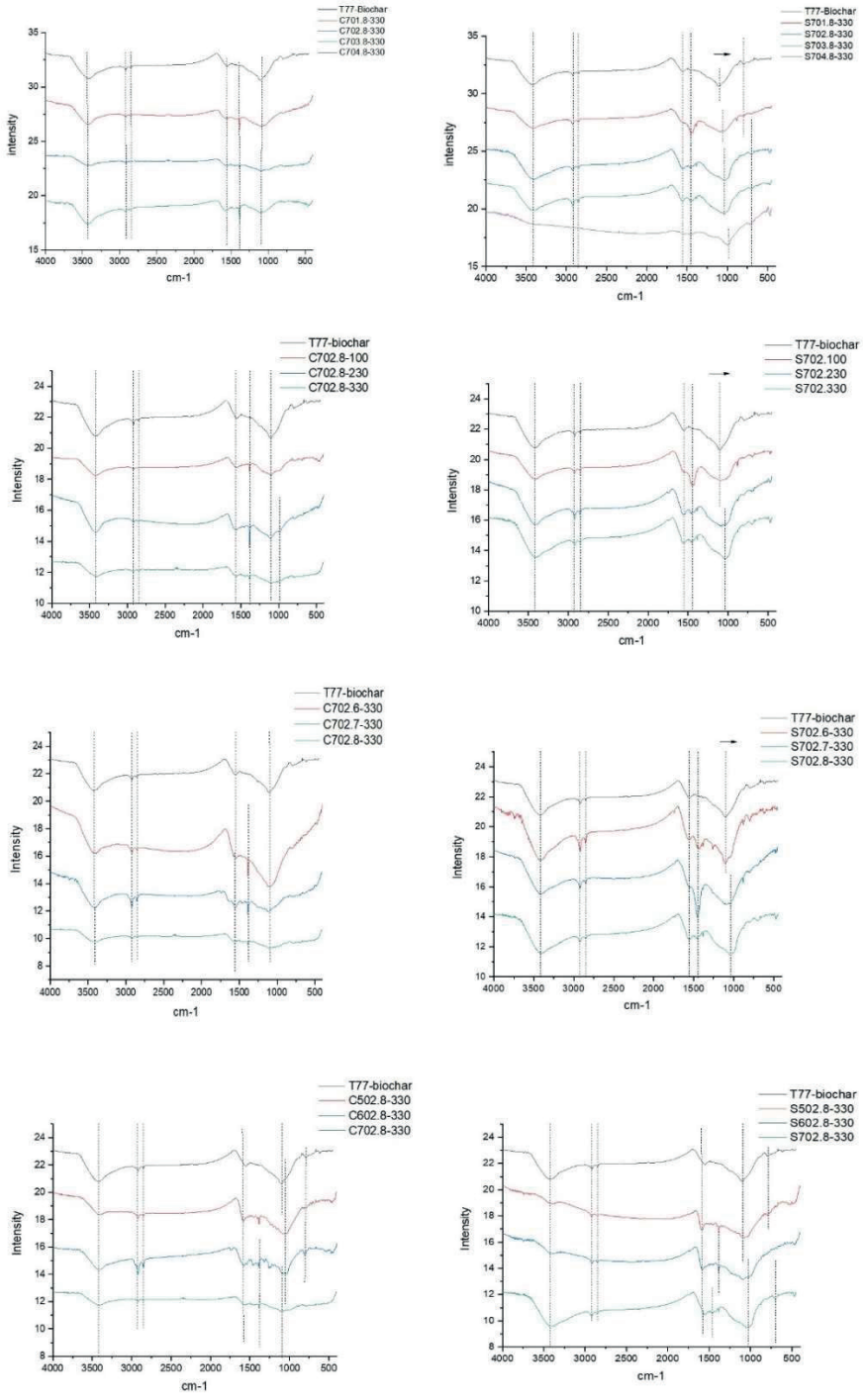


Figure 3. Effect of residence time on functional groups (a), effect of total flow rate functional groups (b), effect of temperature functional groups (c), and effect of amount of activation agent functional groups (d).

2. Results of GOAST carbons applications

As previously highlighted the LIFEGOAST Biochar and relative activated carbons are being tested in different fields, such as anode for lithium ions batteries (LIBs), catalytic support, filler for asphalt, and replacement of sand in concrete.

• *N-doped porous carbon from leather solid waste for application in sustainable lithium batteries*

Lithium-ion batteries (LIBs) are considered as the most popular energy storage system for portable electronic

devices and transportation applications. However, LIBs still face several challenges, particularly in electrodes' capacity, stability, and cost, which play a crucial role in a battery efficiency. Although the conventional electrode such as graphite as the anode part in commercial batteries possesses several advantages, it could not meet the future needs of the battery industry. The graphite has a limited theoretical gravimetric capacity of 372 mAh g^{-1}, poor diffusion kinetics of lithium, and it relies heavily on fossil fuel-based precursors and harsh or energy-intensive synthesis. In this scenario, biochar (solid fraction of pyrolysis process) represents an attractive alternative either from an economic or electrochemical point of view. For this purpose, in collaboration with Istituto Italiano di Tecnologia (IIT) we carried out a study on the application of the carbons obtained from Goast shave waste (GSW) to design anode for half-cell and full- cell Lithium-ion batteries. The results showed that the spontaneous presence of heteroatoms such as N and S in the GSW, together with the high surface area, the electrochemical response of the activated carbons resulted in a high initial specific capacity of 1520 and 2063 mAh g^{-1} at 0.1 A g^{-1} for the electrodes activated with steam (LSW-ACS) and CO_2 (LSW-ACC) in lithium- metal half-cells, respectively. Furthermore, the steam-activated electrode demonstrates a specific discharge capacity of 735 mAh g^{-1} after 1000 charge and discharge cycles at 0.5 A g^{-1}(Salimi2022).

• *GSW-derived activated carbon as catalytic support*

The GOAST-biochar were also tested as support for heterogeneous metal-based catalysts comparing their performance with carbons obtained from other biomasses. The catalysts were tested for 5-hydroxymethylfurfural (HMF) hydrogenation to 1-hydroxy-2,5-hexanedione (HHD). HHD is a valuable building block that can be used as an intermediate for production of several other fruitful target chemicals such as triols, pyrroles, and cyclopentanone derivatives with extensive applications in surfactants, solvents, pharmaceuticals, and polymers. The catalyst supported on GOAST carbon exhibited high catalytic activity leading to a 90 % of conversion and yield in HHD under the reaction conditions tested. The catalyst also gave a promising performance compared to catalyst reported in literature and tested in the same reaction. It's worth noting that this study is the first example of applying carbon materials from leather solid waste in the catalysis field. The data about the applications of LIFEGOAST carbons were comprehensively reported and discussed in the work of Longo et al. (2022).

Conclusion

Concluding, the investigation conducted by UNIVE researchers revealed that the pyrolysis treatment can be considered an effective approach for valorising leather solid waste. The main findings of the applications investigated are promising and could have implications for other industrial sectors by placing new materials in the market.

Acknowledgements

The LIFE GOAST team would like to acknowledge the EC for fundings (LIFE16 ENV/IT/000416) and the single partners for the remarkable job carried out since the beginning of the project. Special thanks should be done to *GSC Group spa*, *Conceria Pasubio*, *Medio Chiampo*, *Ca'Foscari University of Venice and Istituto Italiano di Tecnologia (IIT).*

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Note