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# Gas conditioning in H<sub>2</sub> rich syngas production by biomass steam gasification: experimental comparison between three innovative ceramic filter candles

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## Abstract

The biomass steam gasification is a promising path to obtain hydrogen-rich syngas and to improve the global efficiency for cogeneration purposes. The present study reports the results of a campaign of steam gasification tests performed in a bench-scale gasifier (0.1 m ID) housing in its freeboard a ceramic filter, in a temperature range of 800°C – 815°C. Three new ceramic filters have been tested: (i) non catalytic candles with new support, (ii) filter candle with catalytic layer, (iii) filter candle with new integrated catalytic foam system and results were compared to those obtained in tests without candle. The volume composition of the syngas was monitored and analysed by online measurement by means of infrared – thermal conductivity detector (IR- TCD) facilities to evaluate the CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, NH<sub>3</sub> composition. The Topping Atmosphere Residue (TAR) content was evaluated by gas-chromatograph mass spectrometer (GCMS) facility; gas yield, water conversion and char conversion were also calculated from direct measurements.

The best results were obtained in the case of innovative catalytic filter in association with cycled olivine bed, obtaining gas yield equal to 1.80 Nm<sup>3</sup>/kg<sub>daf</sub> (vs 1.00 Nm<sup>3</sup>/kg<sub>daf</sub> without candle); observed to theoretical water conversion ratio equal to 0.88 (vs 0.33); H<sub>2</sub> volume content equal to 56% (vs 39%); total TAR content equal to 0.14 g/Nm<sup>3</sup> (vs 6 g/Nm<sup>3</sup>).

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## 1. Introduction

The biomass gasification allows to produce a hydrogen rich syn-gas which is usually composed by hydrogen, carbon dioxide, carbon monoxide and methane as major gas components. Nitrogen and water can be also present depending on the gasification agent as air, steam, oxygen. Beside the gas species, several non-desirable products are usually present, such as a mixture of diverse aromatic and polyaromatic compounds TAR, alkali, ammonia, solid fine particles and heavy

metal compounds [1]. These products are usually noxious for the health and the environment, but also are affecting the overall efficiency and the safety of the system. Indeed, for example, in the reformer units the catalysts might be deactivated as a consequence of carbon deposition; in the heat exchangers and turbines fouling and corrosion could represent a serious problem. For this reason an important role is played by the cleaning units, needed also for the fly ash removal, in order to reach both the environmental emission limits and the downstream units protection.

A critical issue in the gas cleaning and conditioning is the process temperature, together to the complication in the system design, in fact low temperature gas cleaning and multiple units affect the overall efficiency of the system [2-4]. Very important are also the thermodynamic efficiency and the versatility of the overall process [5]. The research efforts in the field of compact & high temperature gas cleaning systems have been increasing over the last years [6]. In respect to the low temperature systems, high temperature cleaning offers the advantage to remain above acid gas dew points, to avoid TAR condensation and to maintain the temperature more close to the requirements of the downstream catalytic units. Numerous research projects have been focused on the development of systems and materials in order to improve TAR conversion and process integration, as for example the multiple bed gasifiers and the sorption enhanced syngas reforming [7-10]. An interesting solution toward a compact and high temperature cleaning system is represented by ceramic filters inserted in the freeboard of a fluidized bed gasifier. Indeed, ceramic filters have been considered very promising devices for particles removal and many studies have been performed in recent years extensively investigating several parameters as the influence of the filters permeability on the dust cake formation, the effect of dust properties in the regeneration of the filter, the increase of the pressure drop [11-15]. In addition to the particles removal, new generations of ceramic material have been developed with a catalytic activity in order to face the problems connected to the presence of TAR by converting them at high temperature [16,17]. When catalytic candle filters are utilized in the freeboard of a fluidized bed biomass gasifier, particles removal, decomposition of TAR and ammonia are integrated with gasification in one process unit [18-22].

The aim of this work has been the evaluation of the gasification performance of different filter candles: non catalytic filter candle, filter candle with integrated catalytic layer, filter candle with integrated catalytic layer with catalytic foam. The work has been performed utilizing a gasification bench scale rig able to house a segment of a filter candle of commercial size in the freeboard. A campaign of continuous gasification tests integrated by TAR catalytic reforming and particulate abatement was performed. During each test the instantaneous gas yield and composition, TAR content, carbon conversion, pressure drop across the filter candle, have been monitored. The influence of operating parameters has been explored and the comparison with blank tests previously

performed with the same gasifier with no filter candle allowed the evaluation of filters and catalytic filters effectiveness, when located in the freeboard of the gasifier.

## **2. Experimental set-up and materials**

### **2.1 Experimental apparatus**

A scheme of the experimental apparatus is shown in figure 1 and it consists of a fluidized bed gasifier connected to the analytical tools. The reactor has an internal diameter of 0.10 m and is externally heated by a 6 kW electric furnace. The biomass is introduced into the fluidized bed from the top of the reactor vessel by means of a continuous feeder unit. The gasifying agent is fed from below the fluidized bed (steam in the case of gasification process, air in the case of the combustion/regeneration process). During the gasification test, nitrogen is used as career gas for the feedstock. The steam is generated from liquid distilled water that is fed by means of a peristaltic pump to a cylindrical stainless steel evaporator encased in a 2.4 kW electric furnace. The temperature is monitored by 5 K-type thermocouples at different points of the system (steam inlet, fluidized bed, top of the freeboard, reactor outlet, condenser system); the pressure behavior of the gasification zone and the pressure drop along the filter is monitored in real time by an analogical glass capillary system coupled to a digital system. A volumetric gas meter is employed for the measurement of the overall gas flow downstream the gasifier. A digital mass flow-meter allows monitoring and storing the flow data by means of a home-made Labview software. The home-made software also allows monitoring and storing the data from all the gas-analyzers.

In order to evaluate the performance of the different filter candles, the gasification tests have been performed keeping constant different operating conditions, such as the biomass feedstock, and the set up of the bed. Olivine is known to exhibit a favourable catalytic effect on the gasification process and is more resistant than dolomite to mechanical abrasion. For this reason, the fluidized bed has been prepared using 3 kg of olivine particles of selected size always sieved in between 200 and 425 micron, in order to obtain the desired mean diameter ( $d_{\text{Olivine}} \approx 344/350$  micron). The biomass feedstock consists of almond shells: the proximate and ultimate analysis are reported in table 1 [23]. The almond shells were crushed and sieved in between 500 and 1400 micron, in order to obtain a mean diameter close to  $d_{\text{Biomass}} \approx 1.1$  mm. The biomass feeding rate has been chosen in between  $8 \div 10$  g/min and kept constant during each test.

The gas stream coming from the gasifier goes through a couple of condensers in order to remove the water excess and the chemicals noxious for the analyzers. The former condenser is made of stainless steel and cooled with tap water; the latter one is made of three glass traps with diethylene glycol solution as refrigerant, kept at  $-20^{\circ}\text{C}$ . Different online gas analyzers (ABB IR-

TCD analyzers, modules CALDOS, URAS, LIMAS) are used for detecting in the product gas the volume fraction of: CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, NH<sub>3</sub>. In each test, the condensate fractions were recovered and weighted for the mass balance computation.

In order to obtain an analysis of the TAR, the sampling has been carried out following the standard method described in technical specification CEN/TS 15439:2006, then the samples have been analyzed by GCMS technique to identify and quantify different aromatic compounds.

At the end of each test period, the quantity of char produced by gasification was determined by the analysis of CO<sub>2</sub> and CO in the gas obtained by burning under air stream the whole carbonaceous residue trapped into the gasifier.

The test campaign was performed using three different types of filters hosted in the freeboard of the reactor:

- Non catalytic candle: Al<sub>2</sub>O<sub>3</sub> based hot gas filter candle of new improved candle support type with an Al<sub>2</sub>O<sub>3</sub> outer membrane.
- Catalytic candle: catalytically activated Al<sub>2</sub>O<sub>3</sub> based hot gas filter candle of new improved candle support type with an Al<sub>2</sub>O<sub>3</sub> outer membrane, where a MgO – NiO catalytic layer system was applied.
- Catalytic candle with catalytic foam: catalytically activated Al<sub>2</sub>O<sub>3</sub> based hot gas filter candle of new improved candle support type with an Al<sub>2</sub>O<sub>3</sub> outer membrane and with an integrated catalytic ceramic foam, where a MgO – NiO catalytic layer system was applied on the filter support and a MgO – Al<sub>2</sub>O<sub>3</sub> – NiO based catalytic layer system was applied on the integrated catalytic ceramic foam.

All the filters were characterized by: outer diameter equal to 0.06 m; inner diameter equal to roughly 0.040 m (except the catalytic candle with catalytic foam, id= 0.015 m); total length equal to roughly 0.45 m, a filtering length equal to roughly 0.40 m. An example of a filter candle (before to be used) is shown in figure 3.

## **2.2 Experimental conditions**

The tests have been performed on filter candles of three different types, as indicated above. In each gasification test, the gasifier was first heated up to 800°C using air as fluidizing agent, then the biomass was fed at constant rate once the system was stabilized under steam and nitrogen flow (roughly 7 minutes). The nitrogen flow was set in order to obtain the desired superficial filtration velocity. The water flow was set in order to obtain the desired steam to biomass ratio. The actual average water flow rate was also verified weighting the feed tank before and after each test. The detailed gasification conditions are reported in table 2.

In all cases, the gasifier was previously heated up to 800°C using air, then the gasification was performed under steam and nitrogen flow.

## **2.3 Results and discussion**

### **2.3.1 Pressure drop**

The pressure drop across the filter candle was measured with two pressure probes inserted in the reactor through its head, with the tips placed in the regions inside and outside the candle, respectively, and connected to a digital manometer (Lab DMM, Bit02, DFP) and an analogical glass capillary system. During the gasification runs, the pressure drop was monitored as function of time; the gas flow and the temperature were evaluated by means of on-line measurements. In the case of the non catalytic candle, as can be seen in Figure 4, the pressure drop increase was almost constant during the whole gasification time, close to 0.14 cmH<sub>2</sub>O/min, whereas in the case of the catalytic candles, without and with foam, the corresponding value of 0.06 cmH<sub>2</sub>O/min was observed. During tests the temperature was about 800 °C, the face filtration velocity was about 90-100 m/h and the syngas flow, shown in figure 5, was in the range 20 - 30 l/min depending on the gasification performance.

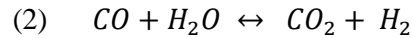
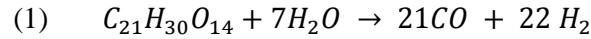
The higher rate of pressure drop increase observed with no catalytic candle (NC) could be explained by considering that tests with the catalytic candles are less affected by accumulation of carbonaceous compounds in the reactor. In fact, after gasification tests, by burning these deposits and measuring the volume fraction of carbon monoxide and carbon dioxide in the exit gas stream, it was found that the average carbonaceous residuals were about 47, 48 and 70 g/kg<sub>biomass-daf</sub> (with a fluctuation of 30%) in the case of catalytic candle, catalytic candle with foam and non catalytic candle, respectively. These results will be discussed in the next paragraph.

### **2.3.2 Gasification results**

All gasification runs showed better performance in respect to the case without candle (examined in a previous test campaign: see [21]), as reported in table 3. The main difference is observed in the hydrogen percentage in the product gas. In the case of filter candles, the hydrogen content has been detected in a range in between 49% - 57%, being the minimum related to the non catalytic candle and the maximum related to the catalytic candle with catalytic foam, vs 39% in the tests with no candle.

The water conversion has been evaluated from the collected condensate and compared with the theoretical value. The theoretical value of the water conversion has been evaluated under the hypothesis of thermodynamic equilibrium at the operating conditions of test, i.e. under the

hypothesis of total conversion of the biomass (with no residuals of hydrocarbons and char) and the chemical equilibrium of the water gas shift reaction. Taking into account the elemental analysis of the biomass (from which the biomass raw molecular formula can be expressed as  $C_{21}H_{30}O_{14}$ ), the reactions are:

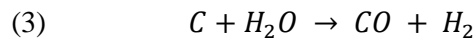


For each run, the theoretical water conversion depends on the steam to biomass ratio (water input) and on the reaction temperature (influencing the equilibrium point of the water gas shift - WGS reaction, i.e. the equation 2).

As before, the best results are obtained with the catalytic candle with integrated catalytic foam. In fact, the mean value of the observed water conversion is equal to about 25% in the case of no catalytic candle while it increases to 33% in the case of the catalytic candle (with a maximum of 37%) and it reaches the value of 37% in the case of the catalytic candle with integrated catalytic foam (with a maximum of 42%).

Together to the hydrogen increase, when runs with filter candles are compared to the case without candle, it can be observed a decrease in the volume percentage of all remaining gas components. It is worth stressing that, even if the volume percentage decreases, in the case of  $H_2$ , CO and  $CO_2$  the moles per  $kg_{\text{biomass-daf}}$  of biomass increase due to the TAR reforming (more noticeably in the catalytic cases). The trend is different for the methane yield, decreasing both in volume composition and moles/ $kg_{\text{biomass-daf}}$  (from 10% to 2% vol and from 4.5 to 1.6 mol/  $kg_{\text{biomass-daf}}$ , respectively, in case of absence of the filter candle and in case of the best catalytic conversion obtained with the catalytic filter candle with integrated catalytic foam).

The increased reaction rate for the WGS reaction (reaction 2) due to the catalytic effect of Ni metal in the catalytic filter candle could explain the lower residual carbon (and thus lower pressure drops) observed in paragraph 2.3.1. In fact the WGS reaction converts CO that is a product specie for the steam gasification of char (reaction 3).



Because the CO is removed by WGS, the reaction 3 is shifted and further carbon can be converted during the process. This could explain the lower residual carbon measured after tests with catalytic filter candles. In fact the particulate matter that forms the cake deposited to the outer surface of the candle, and responsible of the pressure drop increase during the process, is mainly composed of ashes and not converted carbon. If the carbon conversion in the cake increases, the

cake thickness would result smaller or much more porous. As consequence, the pressure drops would be lower, as observed.

In general, as expected, the most interesting results are related to the use of the catalytic filter integrated with catalytic foam. In this case, in relation to other filters, higher percentage of hydrogen, smaller percentage of methane, higher water conversion, smaller content of TAR have been observed in the product gas as reported in table 3 and figure 6. In addition, using a catalytic candle (with or without foam) a remarkable decrease of the ammonia content has been observed, as can be seen in figure 7.

During the experimental campaign with the catalytic filters, it was noticed the influence of “time on test” (aging) of the olivine bed on the gasification performance. In fact, the tests revealed the influence on the gasification process of the *age* of the olivine bed: the longer the bed age, the better the gasification results are. In figure 8a), 8b) and 8c) the gas yield, the experimental to theoretical ratio of the water conversion and the experimental to theoretical ratio of the hydrogen production are reported as a function of the age status of the bed for tests performed by catalytic candles with foam. It can be seen that, keeping the same conditions for the biomass feeding rate and the steam to biomass rate, the tests with used olivine bed are characterized by better gasification performance. The effect could be related to the accumulation into the olivine bed of the biomass ash, and/or deposition of a more catalytically active layer on the outer surface of the olivine particles as shown in a recent literature study [24] . A catalytic activity of the biomass ashes has been observed in earlier studies for the oxidation of  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{HCN}$  [25] . In the case of the present work, the ashes are not leaving the reactor during the gasification tests, due to the filtering action of the candles, increasing the bed content of the alkaline metals associated to the biomass feedstock. An EDX analysis has been performed on the olivine bed which allowed to evaluate the presence in the bed of several elements and to confront the differences in bed composition at different time. The analysis have been performed on the fresh olivine and on the olivine employed for the gasification process after the combustion step (figures 9 and 11). In the figure 10 is shown the EDX analysis performed on the intermediate step, i.e. after the gasification but before the combustion, on the char residuals. In figures 9, 9a) and 9b) the EDX pattern, the SEM image and the elements mapping of the fresh olivine are shown, where can be seen the typical olivine pattern. In figures 10, 10a), 10b) the same measures are shown for the char residuals, where it is stressed the presence of carbon and several alkaline metals. In the last figures 11, 11a) and 11b) on the olivine bed after gasification and successive combustion, the absence of carbonaceous substances and the presence of alkaline metal, as potassium, confirms the presence of the ash remaining after combustion.



### **3. Conclusion**

An experimental campaign has been performed to study the performance of different type of catalytic filter candles when employed for the steam biomass gasification, using a compact gasifier able to house the filter in the reactor freeboard.

Concerning the pressure drop during the gasification process, the filters had different behaviors during the different tests and a general increasing trend during gasification can be recognized, coherent with the increase of the output gas volume. In the case of the non catalytic filter candles, the rate of increase of pressure drop always showed higher values with respect to the catalytic filters.

Concerning the gasification tests, all runs showed better performance in respect to the case without candle (examined in a previous test campaign). The main difference is observed in the hydrogen percentage in the product gas. In the case of filter candles, the hydrogen content has been detected in a range in between 49% - 57%, being the minimum related to the non catalytic candle and the maximum related to the catalytic candle with catalytic foam, vs 38% in the tests with no candle. In general, the best performance of the catalytic candle with integrated catalytic foam is proven, also for what concerning the water conversion, the TAR content and the ammonia decomposition.

### **4. Acknowledgment**

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### **Figure list**

Figure 1: schematic view of the bench scale gasification system.

Figure 2: details of the reactor vessel and the candle housing.

Figure 3: example of filter candle (non catalytic type)

Figure 4: Pressure drop through the non catalytic candle: NC; catalytic candle:CC; catalytic candle with foam: CF.

Figure 5: Syngas flow with no catalytic candle: NC; catalytic candle: CC; catalytic candle with foam: CF.

Figure 6: TAR content

Figure 7: Ammonia content

Figure 8: Gas yield - a), experimental water conversion on theoretical water conversion ratio -b), experimental hydrogen production on theoretical hydrogen production - c).

Figure 9: EDX pattern, a) SEM image and b) elements mapping of the fresh olivine

Figure 10: EDX pattern, a) SEM image and b) elements mapping of the char after gasification

Figure 11: EDX pattern, a) SEM image and b) elements mapping of the olivine bed after gasification and successive combustion.

### **Table list**

Table 1: Biomass proximate and ultimate analysis (see [23])

Table 2: Test conditions on different candles

Table 3 - Catalytic candle with and without foam and non catalytic candle performances in respect to the case without candle.

**Table 1: Biomass proximate and ultimate analysis (see [23])**

Proximate analysis	%wt/wt	Elemental	Composition % wt/wt (dried at 105°C)
Dry matter	92.3	C	48.9
Ash	1.1	H	6.2
Volatile matter	71.7	N	0.18
Fixed carbon	19.5	O <sup>a</sup>	43.5
		Cl	0.029
		S	0.026

$$^a \%O = 100 - (\%C + \%H + \%N + \%Cl + \%S + \%ash)$$

**Table 2: Test conditions on different candles**

	non catalytic candles	catalytic candles	catalytic candles with foam
Number of tests	5	5	5
Range of total gasification [h]	3-5	3-6	3-5
Biomass feed rate, g/min	10	10	10
Range of steam flow rate, g/min	8-9.7	8-9	8-9.6
Range of steam to biomass, g/min	1.1-1.2	1-1.2	0.9-1.1
Range of nitrogen flow rate, l/min	10-11.3	10-11.1	10-11.4
Range of filtration velocity m/h	92-112	94-101	95-114
Range of bed temperature °C	800-806	800-805	800-815

**Table 3 - Catalytic candle with and without foam and non catalytic candle performances in respect to the case without candle.**

Candle	None	Non catalytic	Catalytic	Catalytic & foam			
	best - value	Mean value	Best value	Mean value	Best value		
Gas yield [Nm <sup>3</sup> (dry N <sub>2</sub> free)/kg daf]	<b>1</b>	1.4	<b>1.4</b>	1.6	<b>1.8</b>	1.7	<b>1.8</b>
H <sub>2</sub> [%vol (dry gas, N <sub>2</sub> free)] (H <sub>2</sub> [mol/kg <sub>daf</sub> ])	<b>39</b> <b>(17.4)</b>	50.2 (31.4)	<b>51.5</b> <b>(32.2)</b>	53.8 (38.4)	<b>55.5</b> <b>(44.6)</b>	55 (41.7)	<b>57</b> <b>(45.8)</b>
CO <sub>2</sub> [%vol (dry gas, N <sub>2</sub> free)] (CO <sub>2</sub> [mol/kg <sub>daf</sub> ])	<b>26</b> <b>(11.6)</b>	24.3 (15.2)	<b>22.5</b> <b>(14.1)</b>	22.3 (15.9)	<b>21.5</b> <b>(17.3)</b>	21.4 (16.2)	<b>20</b> <b>(16.1)</b>
CO [%vol (dry gas, N <sub>2</sub> free)] (CO [mol/kg <sub>daf</sub> ])	<b>24</b> <b>(10.7)</b>	18.8 (11.7)	<b>18</b> <b>(11.2)</b>	19.4 (13.8)	<b>18</b> <b>(14.5)</b>	20.5 (15.5)	<b>20</b> <b>(16.1)</b>
CH <sub>4</sub> [%vol (dry gas, N <sub>2</sub> free)] (CH <sub>4</sub> [mol/kg <sub>daf</sub> ])	<b>10</b> <b>(4.5)</b>	6.6 (4.12)	<b>5.5</b> <b>(3.44)</b>	4.5 (3.21)	<b>3</b> <b>(2.41)</b>	3.5 (2.65)	<b>2</b> <b>(1.60)</b>
Water conversion [%]	<b>16</b>	24.9	<b>25.2</b>	33	<b>37.4</b>	36.8	<b>42.4</b>

Figure01

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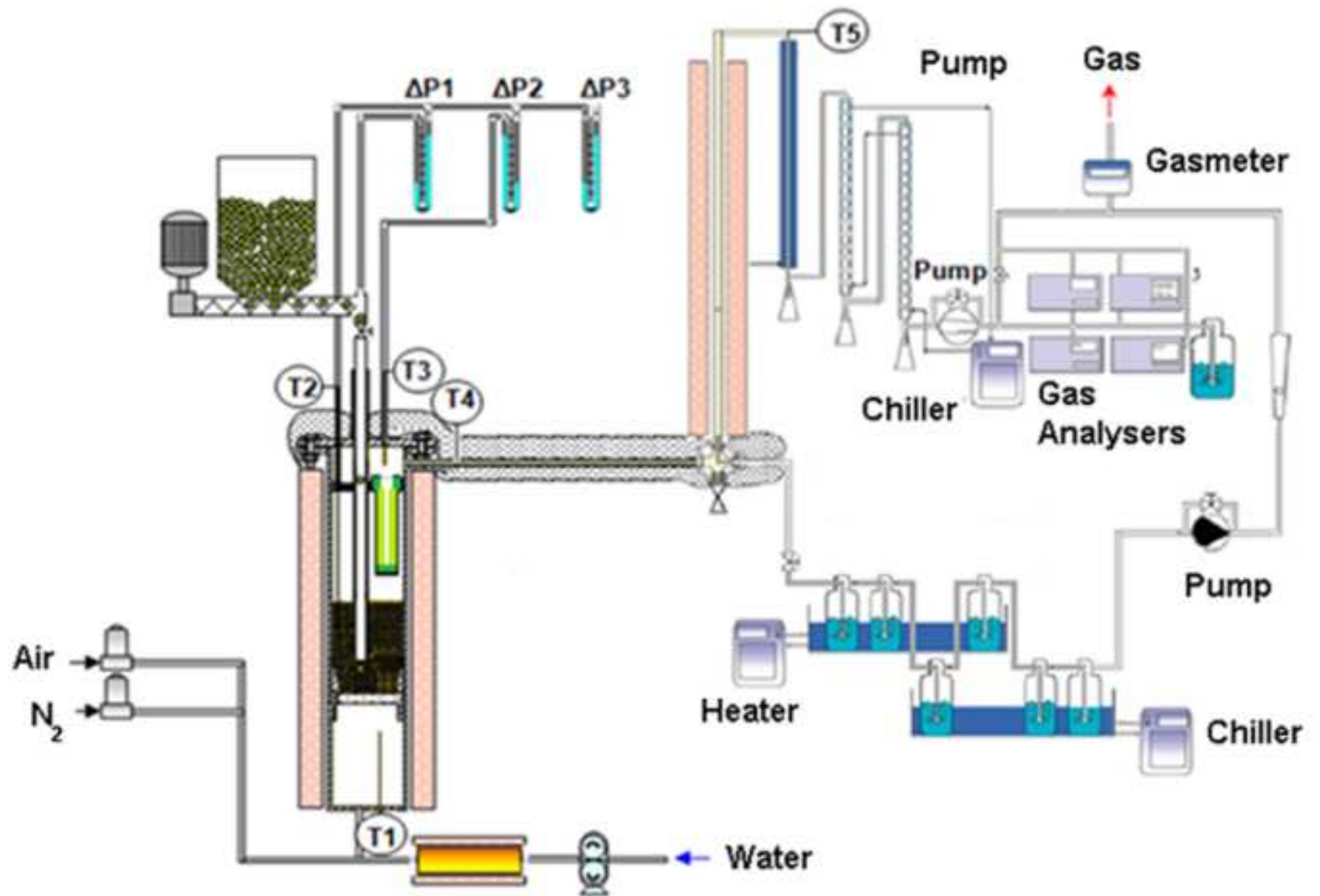


Figure02  
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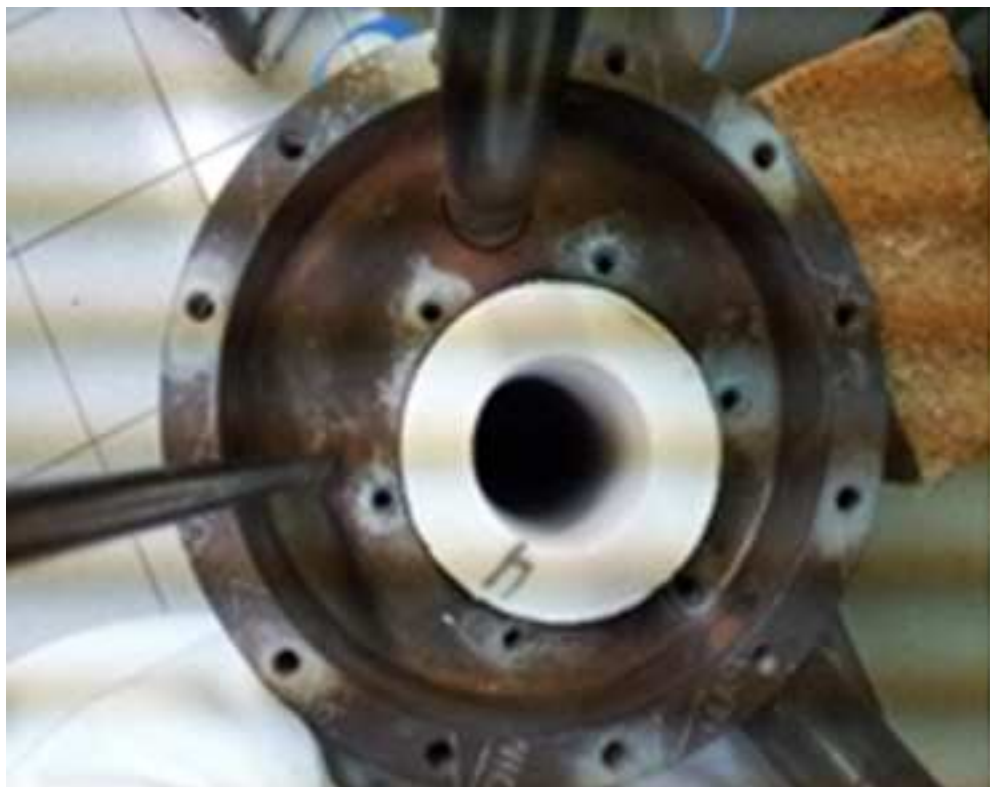


Figure03

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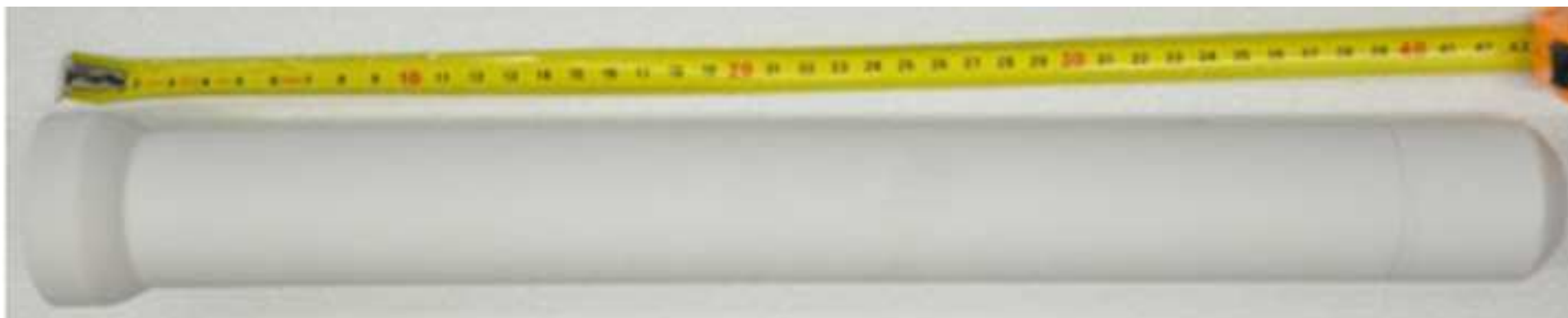




Figure04

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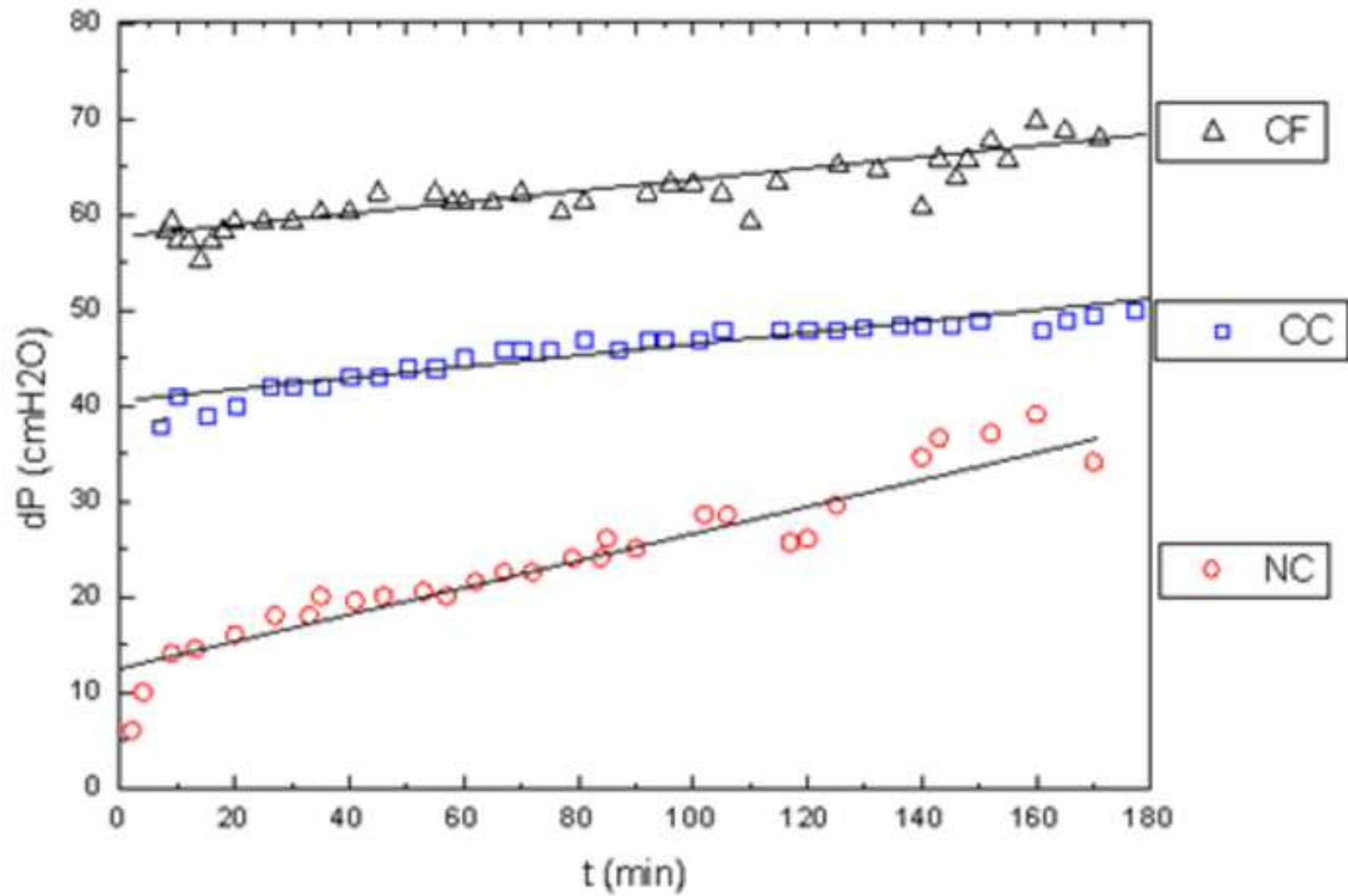


Figure05  
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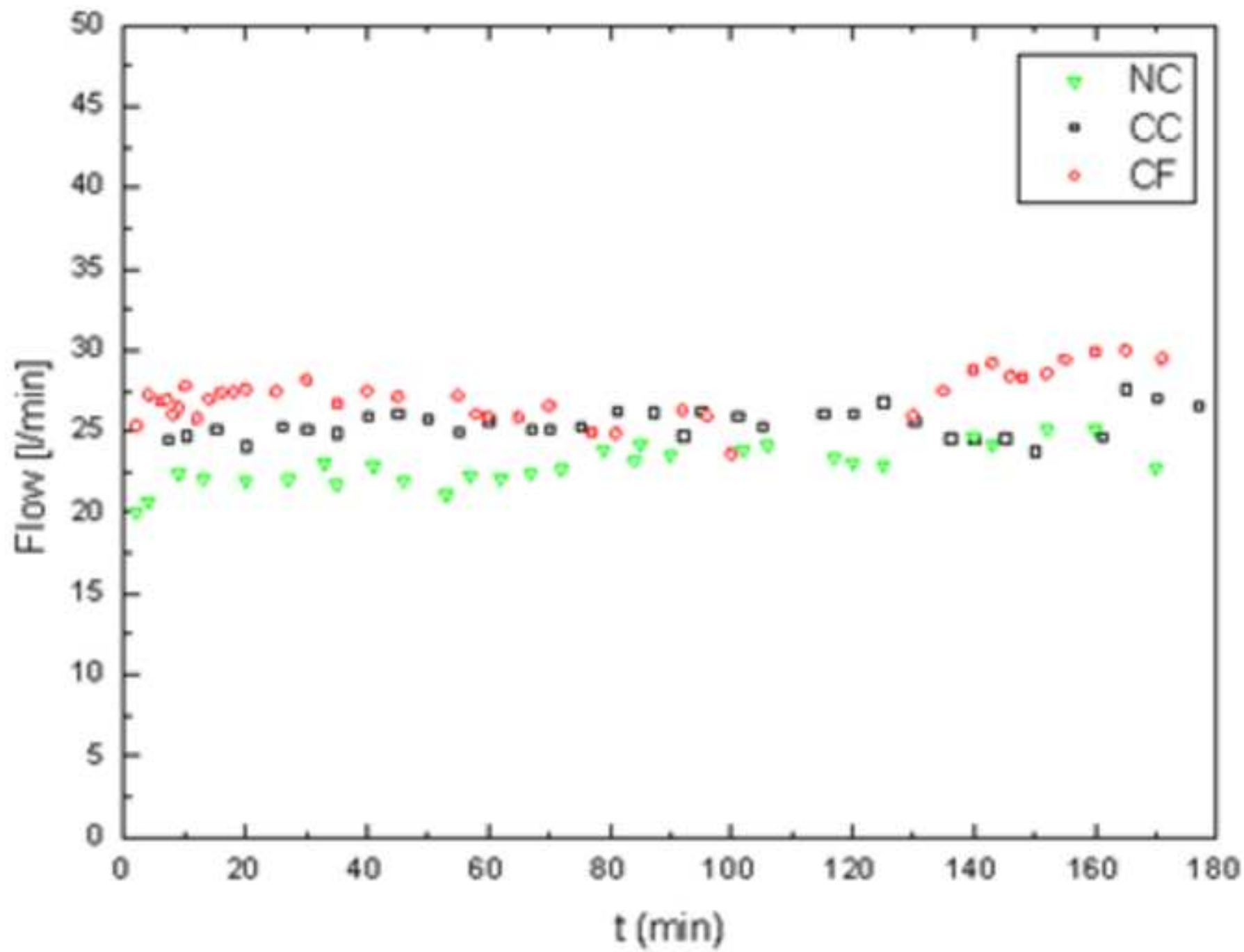


Figure06

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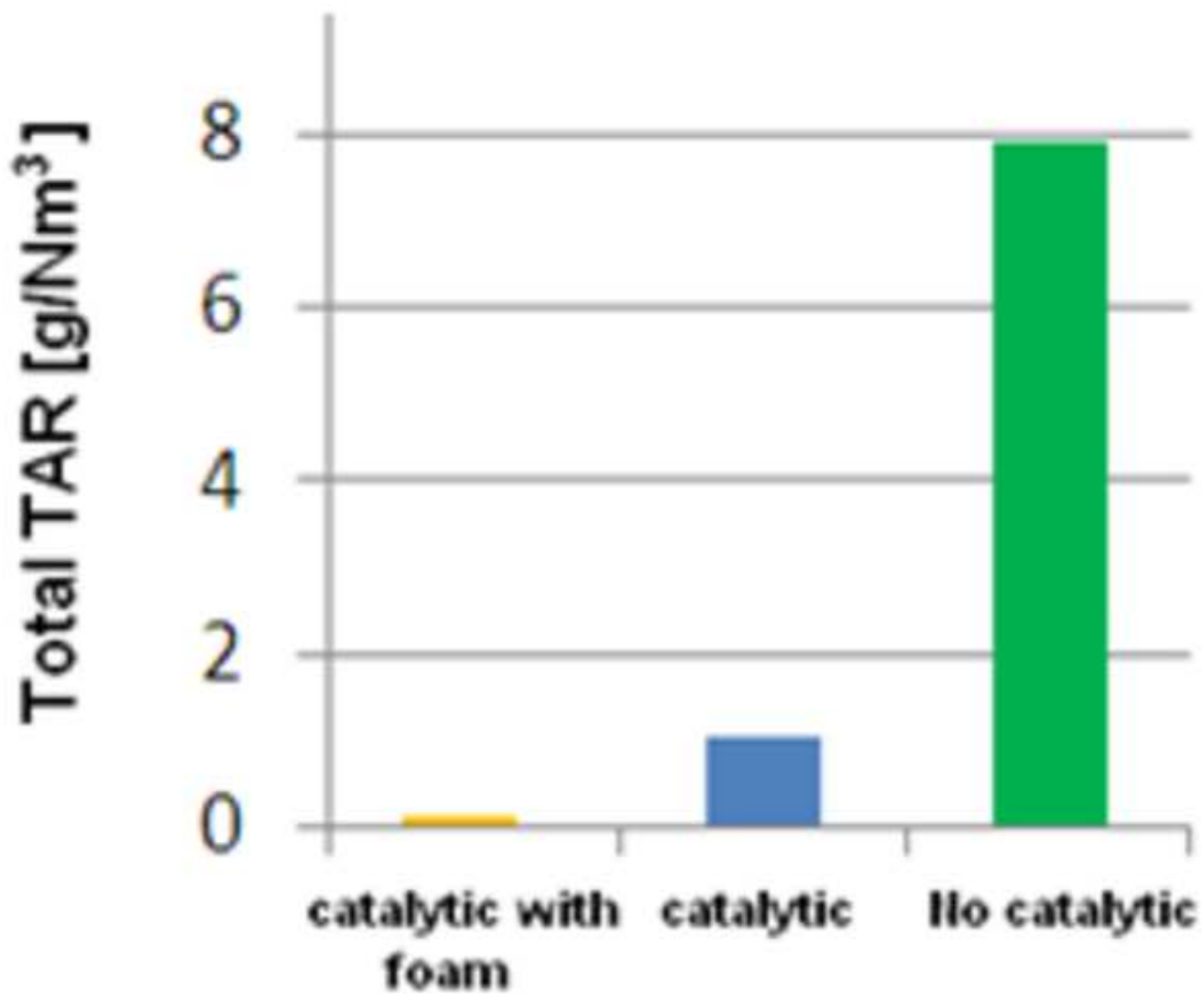


Figure07

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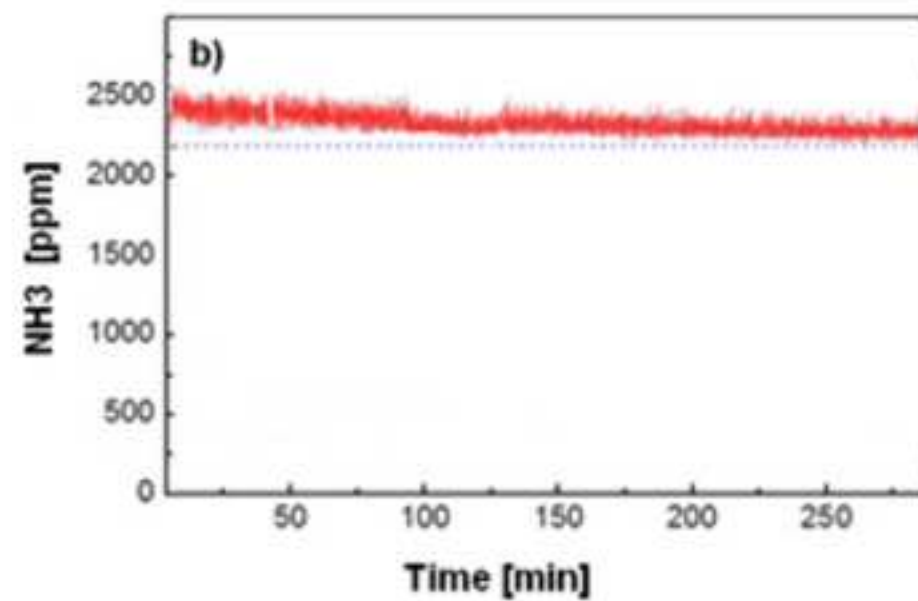
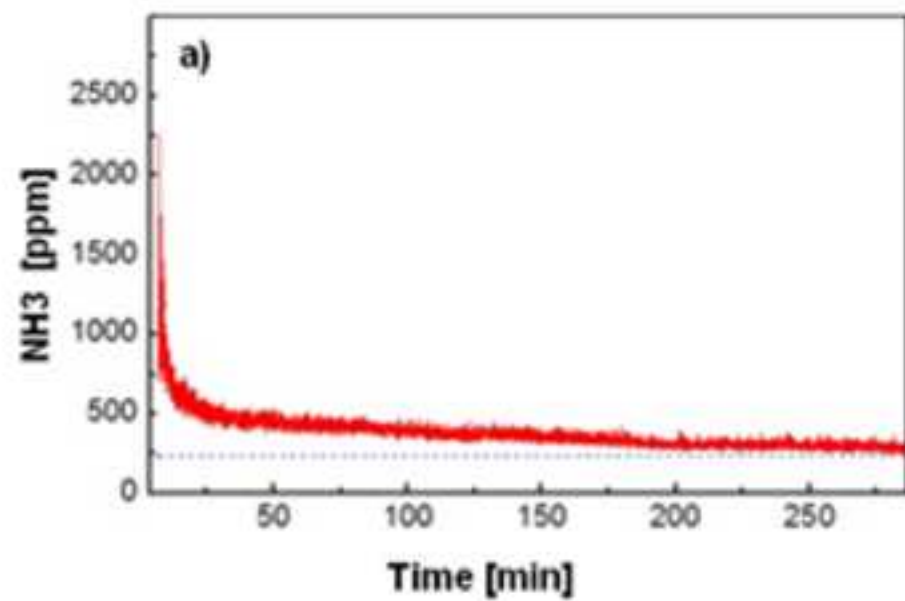


Figure08

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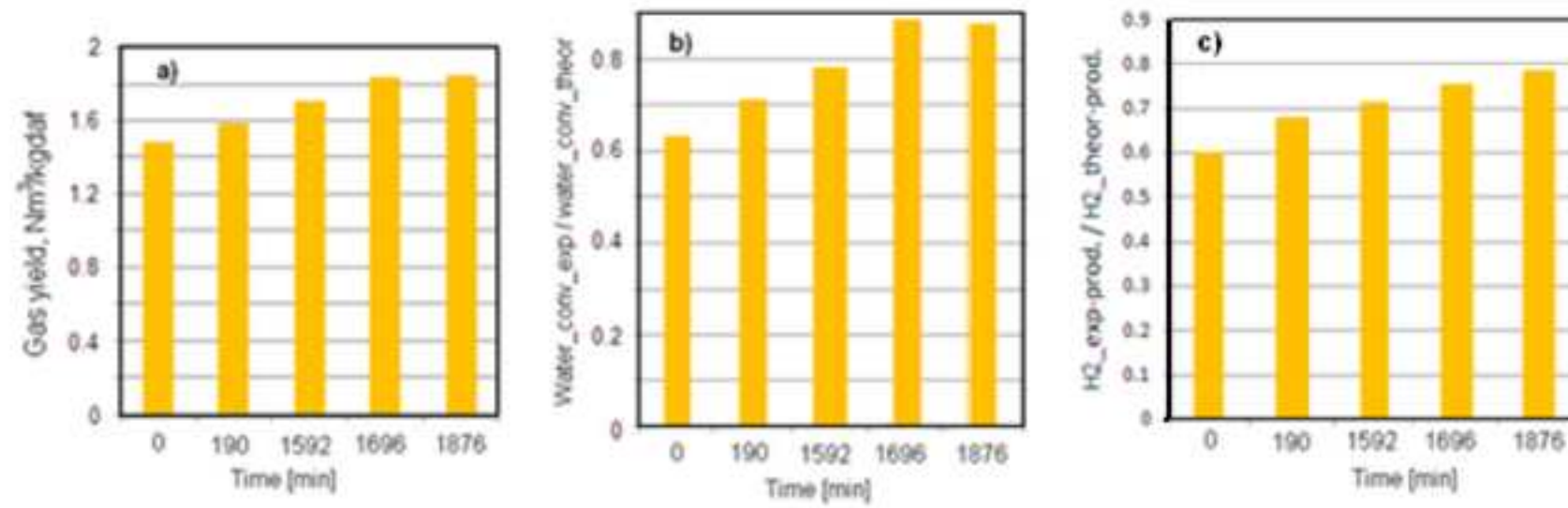


Figure09

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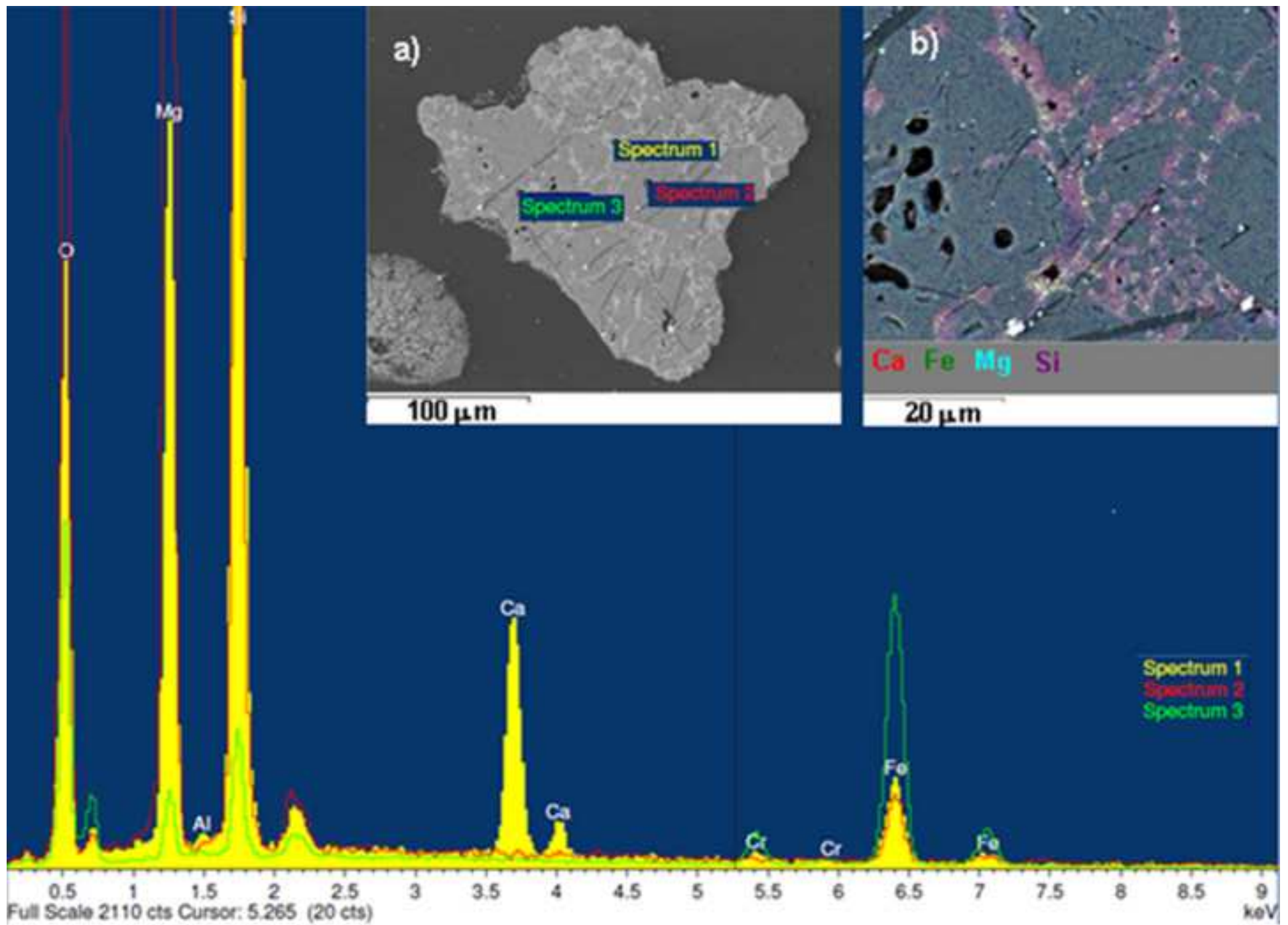


Figure10  
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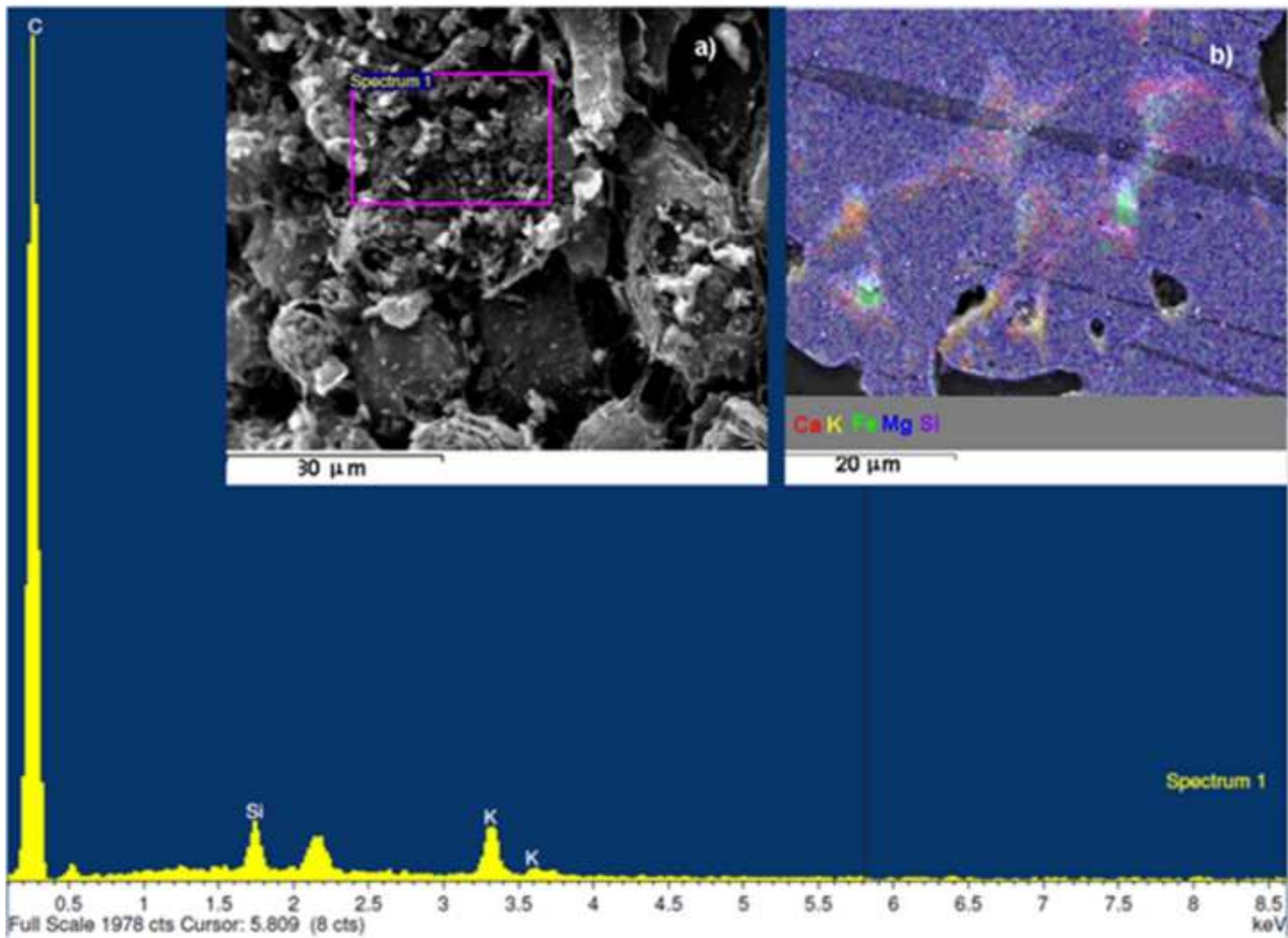
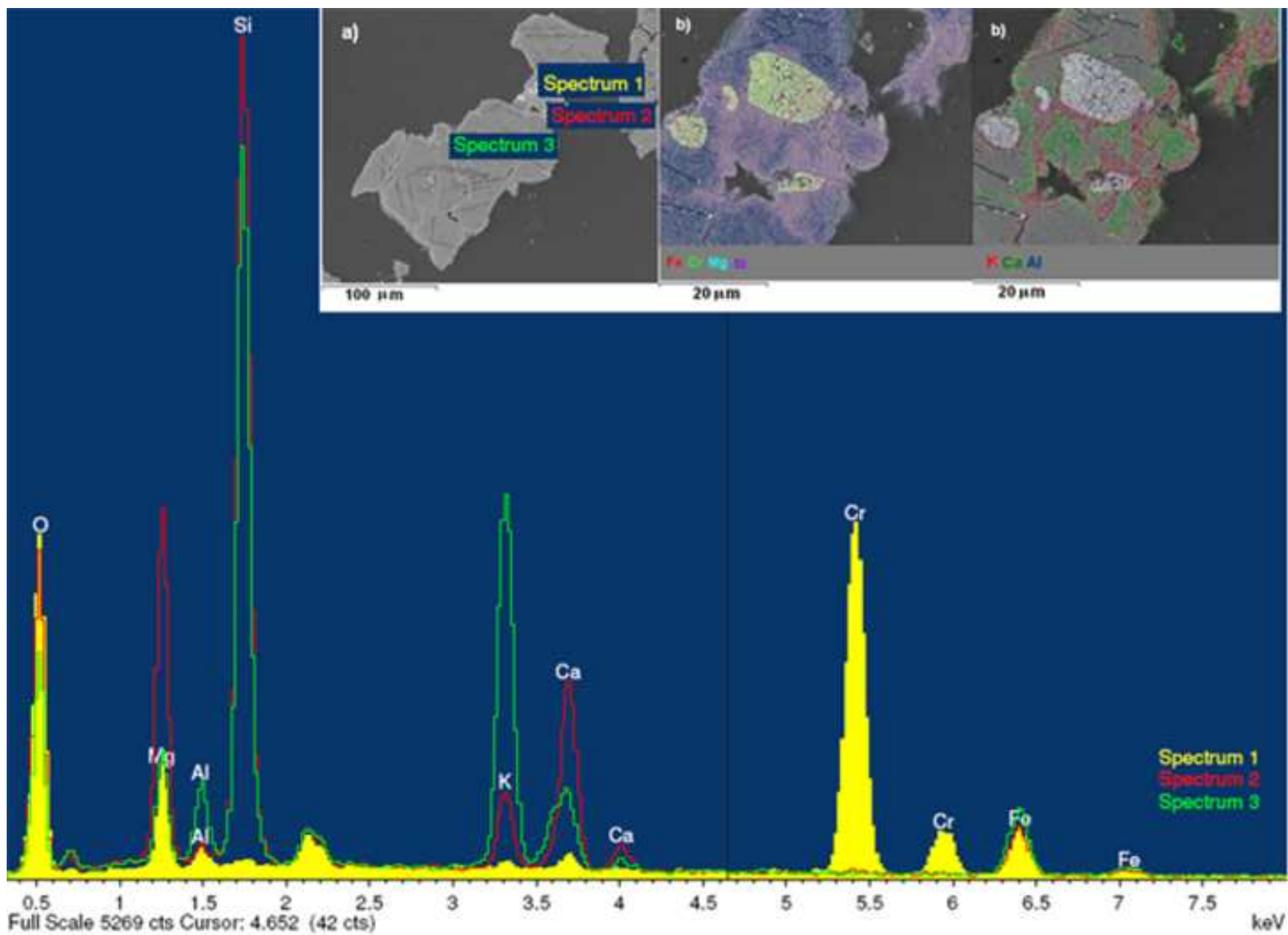


Figure11  
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## Highlights

- Gas conditioning in H<sub>2</sub> rich syngas production by biomass steam gasification.
- Three innovative ceramic filter candles are experimentally compared.
- Hydrogen content close 56% in the product gas is achieved.
- Gas yield equal to 1.80 Nm<sup>3</sup>/kgdaf and good water conversion are obtained.
- Optimal performance of catalytic candle integrated with catalytic foam is proven.