Silica Extraction from Organosolv Pretreated Wheat Straw

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The silica contained in biomass is generally recovered from the ashes after combustion. In this study, the main objective was the recovery of silica from wheat straw, without degrading the other biomass components. To achieve this goal, the wheat straw was first pre-treated by an acidic organosolv process to separate it into its three major components: cellulose, lignin, and hemicelluloses. The silica, due to the pre-treatment conditions, was in the cellulose fraction, from which it was extracted, under alkaline conditions. The goal was to recover pure silica with suitable particle size and BET surface area, enabling its use in various industrial applications. The extraction and precipitation steps of silica recovery were studied. After optimization, the silica extraction conditions were set at pH 9 to 10 and 85 °C and the precipitation at pH 5 to 5.5. In these conditions, up to 82% of total silica in straw was extracted with high purity, an average particle size of 4 µm, and a BET surface area of 156 m^2/g. In summary, silica can be extracted from lignocellulosic biomass, at high yield and purity, without affecting the biorefinery co-products' yields and quality.

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INTRODUCTION

Silicon (Si) is the second most abundant element in the earth's crust, after oxygen, and it accounts for approximatively 32% of the total weight of soil (Chen *et al.* 2010).

In the industrial field, silica is used as reinforcing filler in elastomers instead of carbon black (Pol and Nijman 2005; Roux 2008; Moussa 2011). The various other applications of precipitated silica are as fillers in plastics, as absorbents, as drying powder, as substrates for catalysts, and as an anticorrosion agent (Music *et al.* 2011).

Silicon is also present in biomass as three basic forms: insoluble silica, colloidal silicic acid, and silicate ions (Atik and Ates 2012). For example, nearly 90% of the silicon in rice straw is present as insoluble silica.

In most plant species, particularly those belonging to the Gramineae family, aqueous silicic acid, $Si(OH)_4$, is transported along the transpiration stream in the plant (Raven 1983), where polymerization generally occurs as a combined result with the increase of the concentration of silicic acid through transpiration. At the end of polymerization, silicon is deposited in cells and intercellular spaces, known as phytoliths (Chen *et al.* 2010). This material is a porous opal ($SiO_2 nH_2O$) (Kelly *et al.* 1991), and its morphology differs with different species in Gramineae family.

Most of the silica is concentrated inside the epidermal cells of grasses, located in the outermost layer of plant tissue. It is to a lesser degree that hypodermic and vascular

tissues can also be silicified (Piperno 1988; Motomura *et al.* 2000; Lam *et al.* 2005). This deposit, made up of phytoliths, is almost pure silica, regardless of the organic environment of the soil. Three types of cells thus constitute the epidermis: long cells, silica cells, and cork cells, arranged in parallel rows (Lam *et al.* 2005; Le *et al.* 2015).

Silica is more abundant in grasses than in wood. The silica content of a variety of agricultural residue biomasses originating from grasses is presented in Table 1 (Le *et al.* 2015). Rice straw has the highest silica content (up to 16%), and this makes it a challenge for use in industrial applications. In comparison, the silica content of wood is in the range of 0.0001 to 0.01%, with a few species having higher silica content (Torelli and Cufar 1995). Wheat straw (*Triticum aestivum* L.) has various morphologies, and its chemical composition depends on genetics, location, and growth conditions. It contains 2 to 10% silica as small crystals embedded in the straw (Pekarovic *et al.* 2006).

Table 1. Silica Content of Various Agricultural Residues

Residue	Silica (%dry matter)
Rice straw	13.0-16.0
Wheat straw	2.0-7.3
Barley straw	2.0-6.7
Sugarcane bagasse	1.9-2.4
Corn stover	0.7-2.9
Empty fruit bunches	0.4-1.2

The most common process to extract silica from plant residues is combustion (Kamath and Proctor 1998; Affandi *et al.* 2009; Okoronkwo *et al.* 2013). Rice husk, which is a major agricultural by-product from rice production, is used as a fuel in boilers. Because it produces huge amounts of silica-rich rice husk ash, many studies have been carried out on process development of silica extraction (Joglekar *et al.* 2019; Nayak *et al.* 2019; Setyawan *et al.* 2019). Pure silica has been extracted from rice husk by two steps, namely, calcination or combustion and alkaline-SiO_2 separation (Nayak *et al.* 2019). Azat *et al.* (2019) reported that rice hulk must be treated with acid before calcination to obtain pure silica (>95.6%) (Nayak *et al.* 2019; Chindaprasirt and Rattanasak 2020). Before calcination, a high concentration acid pre-treatment is also recommended for sugar cane bagasse in order to increase the quantity of silica extracted (Embong *et al.* 2016; Chindaprasirt and Rattanasak 2020). For alkaline-SiO_2 separation process, NaOH is preferred for extraction of silica with purity level above 95% (Nayak *et al.* 2019). However, due to high cost of NaOH, sodium carbonate (Na_2CO_3) has been also used to extract silica from rice husk ash with comparative efficiency.

Chen *et al.* (2010) extracted phytoliths from wheat straw by combustion and acid treatment. Okoronkwo *et al.* (2013) extracted silica from corncob ash adapting the method of Kamath and Proctor (1998), which consists of dispersing the rice hull ash in sodium hydroxide to dissolve the silica and produce a sodium silicate solution. The latter was titrated to pH 7 with sulfuric acid solution to obtain a gel at neutral pH. Then, the silica gel is aged, washed, and dried (Kamath and Proctor 1998).

Overall, the extraction of precipitated silica starts with the combustion of the plant material to obtain ash, and this is dispersed in sodium hydroxide to obtain silicate solution, before being acidified with a mineral acid (*i.e.*, sulfuric acid) (Hsieh *et al.* 2009). Precipitation is carried out under alkaline conditions; the type of agitation, precipitation time, temperature, and pH can affect the properties of the silica (Kamath and Proctor 1998; Aujla *et al.* 2007; Dewati *et al.* 2018). The overall reaction is given in the following formula:

$$(SiO_2)_x(Na_2O)_y,nH_2O + yH_2SO_4 = xSiO_2 + yNa_2SO_4 + (y+n)H_2O \qquad (1)$$
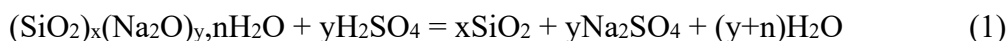
Silica can also be recovered from pulping black liquors; silica is precipitated by lowering the pH of the liquors (Aujla *et al.* 2007; Atik and Ates 2012; Minu *et al.* 2012). In fact, during straw pulping in alkaline media, part of the silicon derivative content is solubilized as silicates. When the alkalinity, *i.e.*, pH, of black liquor is reduced, the silicate ion and a part of the organic material in the liquor agglomerate to a colloidal form. When the pH is sufficiently low, it solidifies as amorphous silica and organic matter. The solidified matter can be separated from the liquor by filtration or centrifugation. The first aim of this study was to provide a method for silica extraction from lignocellulosic plant material without degrading the other major constituents, *i.e.* cellulose, lignin, and hemicelluloses. To achieve this goal, the biomass was first fractionated into its main components, using the acidic organosolv pre-treatment process, developed by CIMV (Benjelloun-Mlayah *et al.* 2006; Snelders *et al.* 2014). This pre-treatment can isolate the silica in one of the fractions in order to simplify its recovery, without affecting the biorefinery's products.

Among the different raw material treated by this organosolv process, wheat straw has been used as reference because it is the most abundant biomass feedstock among agricultural residues in Europe (Kim and Dale 2004). It mainly consists of cellulose (28 to 39%), hemicellulose (23 to 24%), and lignin (16 to 25%), but considerable levels of ash (6.4 to 9.7%) are also present (Carvalheiro *et al.* 2009).

The other purpose of this work was to obtain a silica from wheat straw, having characteristics (purity, particle size) enabling its use in various types of industries such as elastomers, chemicals, adhesives, and cosmetics. To this end, after the silica location in the different fractions that were obtained from wheat straw pre-treatment (ICP-MS and SEM-FEG/EDX analyses), an extraction step was implemented on the silica-rich fraction. The two key steps of silica recovery, namely, extraction and precipitation, were optimized.

In silica recovery, parameters such as temperature, precipitation time and pH, influence its properties (Joni *et al.* 2020). The effect of pH on the quality of the silica (granulometry, purity) was studied. The isolated silica has been characterized by different techniques including field emission gun-scanning electron microscopy coupled with energy dispersive-ray spectroscopy (SEM-FEG /EDX), laser granulometry, and BET surface area analyses.

EXPERIMENTAL

Material

The raw material was wheat straw (*Triticum aestivum* L.) from Hauts-de-France (France). Its chemical composition is given Table 2.

Table 2. Chemical Composition of Wheat Straw

Component	% Relative to the Dry Matter of Wheat Straw
Glucan[a]	33.08
Xylan[a]	19.58
Arabinan[a]	2.40
ASL[a]	2.59
AIL[a]	18.64
Klason lignin[a]	21.23
Acetates[a]	1.98
Minerals	6.51
Proteins	2.91
[a] Values obtained by NREL protocol: Determination of structural carbohydrates	

Methods

Wheat straw pre-treatment

The straw was crushed to obtain appropriate length (5 to 15 cm) and then treated by the acidic pre-treatment process at pilot scale (Compiègne, France) (Fig. 1).
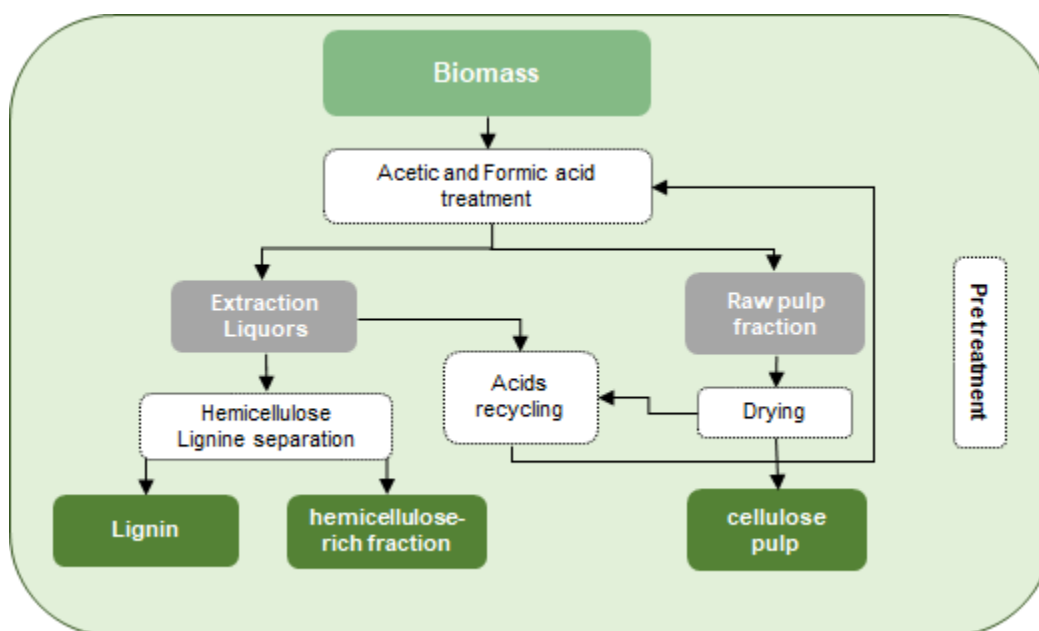
Fig. 1. Organosolv pre-treatment process block diagram

The pre-treatment organosolv process uses a mixture of acetic acid and formic acid (Benjelloun-Mlayah *et al.* 2006) to fractionate the wheat straw. After 3.5 h at 105 °C and at atmospheric pressure, lignin and hemicelluloses are dissolved in the acid medium. The remaining solid, mainly composed of cellulose, is delignified by using peracids to remove the residual lignin. The delignified pulp is deacidified by drying and washed.

The liquid part, *i.e.* the acidic liquor, is then separated into lignin and hemicellulose fraction (Benjelloun-Mlayah *et al.* 2011; Benjelloun-Mlayah *et al.* 2019).

This process yields approximately 50% cellulose pulp, 25% hemicellulose-rich fraction, and 22% lignin fraction (named Biolignine™) (Snelders *et al.* 2014).

Silica location in feedstock and products

Wheat straw and the three fractions obtained after pre-treatment, *i.e.*, C5 sugar syrup, Biolignine^{TM} and cellulose pulp, were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) and FEG-SEM/EDX to identify and locate the silica contained in these fractions and within leaf tissues. ICP-MS analyses were performed with an ICP-MS iCAP™ RQ equipment (Thermo Fisher Scientific, Courtabœuf, France). The samples were calcined (84 h at 600 °C). The ash obtained was mineralized overnight on a hotplate at 90 °C in the presence of concentrated acids (nitric and hydrofluoric) before being analysed. FEG-SEM/EDX analyses were performed with a JEOL microscope (JSM7100F model, JEOL (Europe), Croissy-sur-Seine, France) equipped with an X-Max SDD X-ray detector 50 mm^2 (Oxford Instruments, Gometz-la-Ville, France). The samples were plated with gold before analysis.

Silica extraction

Silica was extracted from the pulp in alkaline conditions for 60 min at 85 °C. The pH range of 9 to 12 was adjusted with 12% NaOH solution. The pulp was washed until it reached pH 7 to obtain purified cellulose, alkaline washing effluents, containing silica and residual organic material (*i.e.*, lignin). The alkaline effluents were concentrated to 12 to 15% dry matter.

Silica precipitation

Tests were carried out on the alkaline concentrated effluents obtained after the extraction step by lowering the pH to 5 to obtain the maximum silica precipitate (Minu *et al.* 2012). The effluent pH was lowered using acetic acid (1 wt%) recycled from the pre-treatment organosolv process.

The precipitate was collected by centrifugation using a basket centrifuge (Rousselet-Robatel, model RC30VxR). The basket is made of polyamide with a mesh of 1 to 5 µm. The precipitate was washed sequentially with a ratio H$_2$O/effluent of 1/1, repeated three times.

Silica characterization

FEG-SEM/EDX analyses were performed with a JEOL microscope (JSM7100F model, JEOL (Europe), Croissy-sur-Seine, France) equipped with an X-Max SDD X-ray detector 50 mm^2 (Oxford Instruments, Gometz-la-Ville, France).

Particle size distributions were determined by wet and dry laser diffraction using a Mastersizer 3000 and Mastersizer 2000, respectively (Malvern Instruments, Malvern, U.K.).

BET surface area analysis and BJH pore size and volume were determined using a Belsorp-max model (MICROTRAC MRB France, Eragny-sur-Oise, France) after a preheating at 90 °C for 2 h (adsorbat: nitrogen).

RESULTS AND DISCUSSION

Silica Location in the Pretreatment Fractions

After CIMV organosolv pre-treatment, the wheat straw was separated into three fractions: delignified pulp, Biolignine™, and hemicelluloses-rich fractions. The yields were as follows (% on dry straw mass): 24.82% Biolignine^{TM}, 25.02% hemicelluloses, and

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50.16% delignified pulp. The ash content in wheat straw was 4.77% (% on dry mass). The distribution of ash and silica is given in Table 3.

Table 3. Ashes and Mineral Content in the Organosolv Pre-treated Fractions

	Biolignine™	Hemicelluloses	Delignified Pulp
Ashes*	2.97	53.35	43.68
Si**	14.98	2.32	82.69
K**	0.20	99.53	0.27
Ca**	8.04	86.16	5.80
* % on total ashes in pre-treated fractions of straw			
** % on total inorganic element in pre(treated fractions of straw			

During the wheat straw pre-treatment, the inorganic compounds were not totally extracted, and more than 40% of the total ash was retained in the cellulose fraction (Table 2). The rest, which was solubilized in the organic acid media, was recovered in the hemicellulose fraction.

However, silica was not extracted during the wheat straw pre-treatment, and almost all the silica was contained in the cellulose fraction (82.69% of total silica). This result is explained by the acidic conditions of the pre-treatment, which are not favorable to silica solubilization; in fact, silica is extremely alkali soluble and weakly soluble in acid media (Pekarovic *et al.* 2006; Okoronkwo *et al.* 2013; Nayak *et al.* 2019; Setyawan *et al.* 2019). Its behavior during the pre-treatment is different from other inorganics such as calcium and potassium that were almost completely recovered in the hemicellulose fraction (Table 2).

FEG-SEM/EDX analyzes were carried out on the delignified pulp fraction to observe the minute structure of plant bodies and the silica location (Fig. 2(a), (b), (c)).
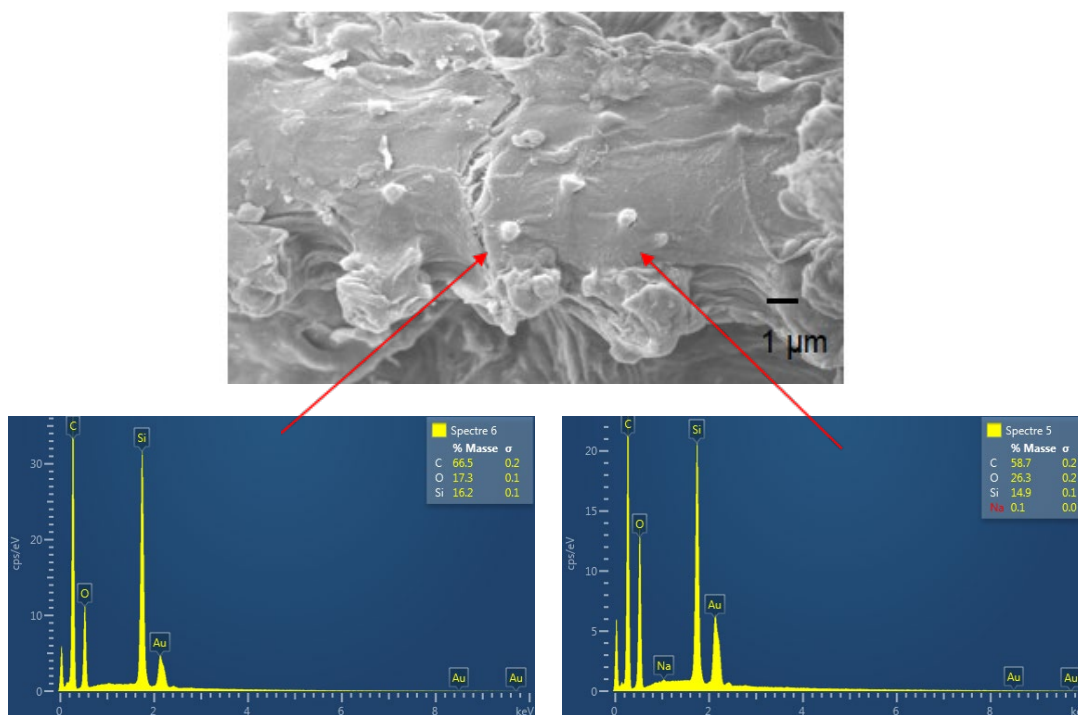

Fig. 2(a). FEG-SEM of wheat straw delignified pulp (x3,5-5.0 kV)
Fig. 2(b), (c). EDX spectra

As shown in Fig. 2, silica was located in the wheat straw epidermal cells, in accordance with previous studies (Sahebi *et al.* 2015). Among annual plants, wheat (*Triticum* spp.) absorbs a large amount of silicon (Si), 50 to 150 kg Si ha⁻¹. Monosilicic acid or orthosilicic acid (H_4SiO_4) are the Si forms that are absorbed by plant roots. Consequently, Si accumulates in the epidermal tissue.

Silica Extraction

Preliminary test

The preliminary alkaline extraction of silica was carried out at pH 11 to 12, using sodium hydroxide solution. The cellulose fraction and alkali washing effluents were recovered. As shown in Table 4, ICP-MS analyses revealed that the cellulose fraction contained only traces of silica (25 mg/kg). The delignified pulp held 82.69% of the silica contained in the wheat straw and the alkaline extraction makes it possible to extract 99.61%.

Table 4. ICP-MS Analyses of the Cellulose Fraction before and after Silica Extraction

Mineral	Delignified Pulp (mg/kg on DM)	Delignified Pulp after Silica Extraction (mg/kg on DM)
Ca	369	1410
K	26	71
Mg	23	< 61
Na	49	69
S	40	81
Si	6468	**25**

Minu *et al.* (2012) isolated the silica and the lignin from the black liquor by precipitation, lowering the pH using dilute sulfuric acid (2%, v/v) and, thereby, making silica and lignin insoluble. The initial pH of the alkaline was pH 12 to 14. As they noted in their study, there was no substantial precipitation up to pH 8. As the pH value was reduced from pH 8 to pH 5, there was a gradual increase in the weight of the precipitate and the maximum quantity of the precipitate was obtained at pH 5. For these reasons, these preliminary extraction and precipitation steps were carried out using the following operating conditions. The alkaline effluent was first concentrated to 12 to 15% dry matter, then the pH was lowered to 5 to 5.5 by adding acetic acid solution to precipitate the silica. The precipitate was collected by centrifugation using a basket centrifuge and then filtered and washed to remove the soluble impurities. The product was dried at 100 °C, before being analyzed by FEG-SEM/EDX, sieve and surface area analyses (Fig. 3, Table 4).

FEG-SEM/EDX analysis

The analyses showed that the product obtained was almost pure silica (traces of calcium). The washing step was effective; no residual sodium hydroxide from the alkaline extraction step was detected. However, FEG-SEM analyses showed heterogeneity in silica particles size. To determine the average size of these particles, a sieve analysis by dry laser diffraction was conducted. Surface area was determined because these parameters are important for silica applications. The results of these analyses are presented in Table 5.

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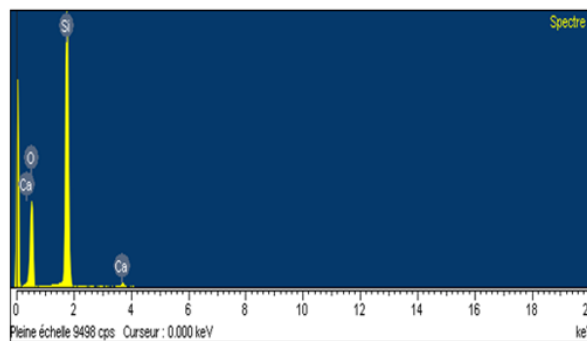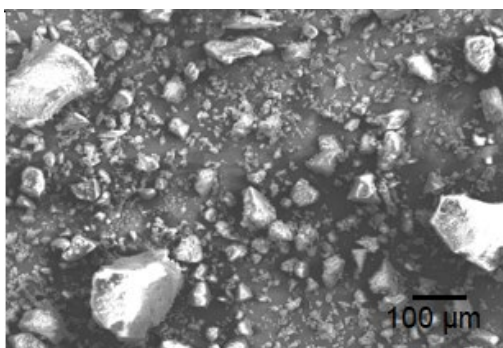
Element	Atomic %
O	66.37
Si	33.03
Ca	0.60

Fig. 3(a). FEG-SEM of silica obtained from CIMV process (alkaline extraction at pH 11-12) (x100-10.0kV)
Fig. 3(b). EDX spectra

Table 5. Silica Sieve and Surface Area Analyzes (Extraction at pH 11 to 12)

	D (0.5) (µm)	BET Surface Area (m^2/g)	Adsorption Total Pore Volume of pores (cm^3/g)	BJH Adsorption Cumulative Pore Volume of pores (cm^3/g)	BJH Adsorption Average Pore Diameter (nm)
Precipitated silica	123	413.5	1.25	1.21	11.07

Dry laser diffraction analysis of the silica demonstrated a silica particle median diameter (D (0.50)) of 123 µm. As previously mentioned, the characteristics silica produced from wheat straw must fit those of precipitated silica. The requirements for particle size of the silica depend on the application. In the rubber industry, for instance, the primary reinforcing fillers to produce rubber articles are precipitated silica and carbon black. The silica particle size for this application is of the order of a few micrometers (< 20 µm). Regardless of the application (plastics, paints, oral care, cosmetics, *etc*.), the size characteristics of commercial precipitated silicas must be less than 30 µm.

The BET surface area and pore volume are important because these parameters influence the mechanical, thermal, and chemical behavior of the porous materials, which are of significance for industrial applications (Wongmanerod *et al.* 2001). The commercial precipitated silica used as reinforced filler for rubber, paints or pesticides industries, range from 35 to 240 m^2/g. Furthermore, Ubukata *et al.* (2010) reported that silica formed from wheat straw by chemical pulping with H$_2$SO$_4$, followed by combustion of the residue at 500 °C, has a BET surface area of 291 m^2/g, a pore volume of 0,398 cm^3/g, and an average pore diameter of 2,7 nm. The silica surface analyses are presented in Table 4. Its BET surface area (413.5m^2/g), greater than that of silica obtained by a conventional process (291 m^2/g), gives it the possibility to be used in many applications including adhesives, plastics, sealants, and coatings (Bartunek *et al.* 2018). However, the total pore volume is almost three times that of silica from a conventional extraction process (resp. 1.25 and 0.398

cm^3/g), which gives it a much larger available porous volume. The BJH adsorption cumulative pore volume value was close to the total pore volume value (1.21 and 1.25, respectively), which gives it a mesoporous character, confirmed by the median pore diameter, which is 11.07 nm. As regards the surface characteristics (BET surface area), the silica obtained seems to comply with industrial specifications. However, this measure is to be taken with caution because it shows the total available surface of the particles and thus brings together the internal and external surfaces. Hence, if a material is very porous, this value does not accurately reflect the specific surface. Moreover, the morphology of silica grains is heterogeneous (Fig. 3a).

In summary, under the conditions tested, it was possible to extract more than 80% of the silica contained in the wheat straw (Table 2). However, the physical characteristics of the silica obtained are not optimal. In order to obtain silica with higher performances, the extraction conditions have been optimized.

Optimization of Silica Extraction

Silica in plant material is easily extracted as silicate because it is in a soluble amorphous form in alkaline conditions (Hsieh *et al.* 2009). This extraction step requires dissolution of the silica contained in the cellulose. Silica dissolves in concentrated sodium hydroxide solutions (Greenberg 1957). Because silica is a polycondensation polymer of silicic acid $Si(OH)_4$, the solubilization of silica is caused by depolymerization (Le *et al.* 2015) into silicic acid according to the reverse reaction as follows:

$$SiO_{2(s)} + 2H_2O_{(l)} \leftrightarrows Si(OH)_{4(aq)} \tag{2}$$

This reaction is spontaneous in water, but it is catalyzed both in alkaline and acidic conditions. At alkaline pH it is initiated by nucleophic attack of OH^- on silicon to increase its coordination number and weakening the underlying Si-O bonds. This is followed by breakage of a Si-O bond. Repeating this step results in release of free $Si(OH)_4$, which can adsorb on the silica surface, retarding further dissolution. Preventing repolymerization of silicic acid is therefore a key aspect in inducing silica solubilization. At pH > 9, silicic acid is totally deprotonated, preventing recondensation.

Dissolution of silica involves several silicate species, including the presence of oligomers. The process starts by combining two molecules of $Si(OH)_4$ to form $Si_2O_7H_6$ with a siloxane bond (Si-O-Si), and the formation of dimers can increase as pressure and temperature increase (Zotov and Keppler 2002; Manning 2004; Tossell 2005; Fertani-Gmati and Jemal 2011). The dimer can be linked to other $Si(OH)_4$ to form higher order oligomers, and those having more than 3 atoms of Si can move into cyclic structures or into more complex forms leading to an infinite variety of polymers. The dominant species depend strongly on experimental conditions.

Moreover, the silica is precipitated after being extracted. This process comprises four stages taking place, almost instantly, one after the other:

1. Formation of primary nanoscale particles (2 to 40 nm) of a very short lifespan (Schlomach 2004; Eur.com. 2006) (Fig. 4)

2. Immediate regrouping of these particles based on covalent bonds (Ten Brinke 2002; Schlomach 2004; Noguera *et al.* 2015), to form non-dissociable aggregates (100 to 500 nm) under standard conditions (Eur.com. 2006)

3. These aggregates bond electrostatically (Van der Waals interactions) to form agglomerates of 0.2 to 30 μm (Ten Brinke 2002). Electrostatic bonds, while weaker

than covalent bonds, cannot be broken from normal use; breaking these bonds requires the use of a dispersant (Eur.com. 2006)

4. These clusters of particles themselves form macroscopic objects (hydrogen bonding) which the size can reach the millimeter: the granules.

For instance, it is in this form of macroparticles that silica is introduced into elastomers (Boudimbou 2011). During rubber compounding, due to the high energy involved, the granules or micropearls of the precipitated silica are broken down, again turning into the afore mentioned agglomerates with dimensions between 0.2 and 30 μm. Due to the high mechanical energy applied to rubber, these agglomerates may be broken down and transformed into aggregates, some of which are nanometric in size (their dimension ranges between 100 and 500 nm).

Considering these observations, the pH is an essential parameter of the dissolution/ extraction of silica. Thus, the main species present in aqueous solution at low pH is monomeric, while up to hexameric species are formed in solution at pH greater than 10 (Fertani-Gmati and Jemal 2011). Therefore, silica extraction was tested at lower pH (9-10). Wet sieve analysis was performed on the silica obtained under these conditions to compare it with that obtained at pH 11 to 12.
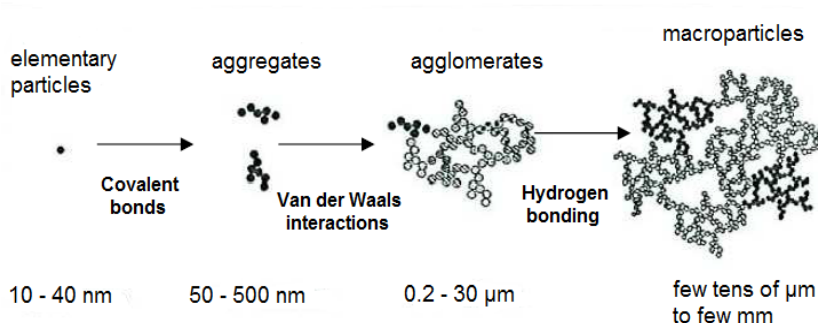

Fig. 4. Representation of particle organizational levels constituting the precipitated silica

Particle size distribution by wet laser diffraction

Wet laser diffraction was used to analyze the particle size of silica extracted at pH 9 to 10. The results are summarized in Table 6. Lowering the pH of the silica extraction step considerably reduces the median diameter of the silica particles; the $D_v(50)$ value fell from 19.3 to 0.057 μm (pH 11 to 12 and pH 9 to 10, resp.).

Table 6. Silica Sieve Analysis (Wet Laser Diffraction) Comparison between Dispersion Methods and pH Silica Extraction

	pH 11 to 12	pH 9 to 10
Dv(50)	19.3 μm	0.0571 μm

Particle size analysis by wet laser diffraction shows that pH of the extraction step has a great influence on the particle size of the silica. Therefore, the influence of the pH of silica extraction was compared with those obtained after extraction at pH 1 to 12 and at pH 9 to 10, using the analyses described below.

Laser diffraction analysis

The silica particles size average was 4 µm (Fig. 5), which was much lower than that found for silica obtained on the first test, *i.e.*, 123 µm. The silica obtained at pH 9 to 10 was soft and powdery, as talc, while the one obtained at higher pH was rough. These results are consistent with the observations cited above (Fertani-Gmati and Jemal 2011), namely that a wide variety of polymers is formed in solution for pH>10, while at lower pH values, the main species present are monomeric (H_4SiO_4 (aq), $H_3SiO_4^-$, and $H_2SiO_4^{2-}$). This could explain the significant difference between the two silicas; at pH 9 to 10, less hexameric species or oligomers are formed than at pH 11 to 12. Introducing less soda in the second test could induce a decrease in bridges. Thus, the medium should contain smaller oligomers, which would promote the production of finer silica after the precipitation step.
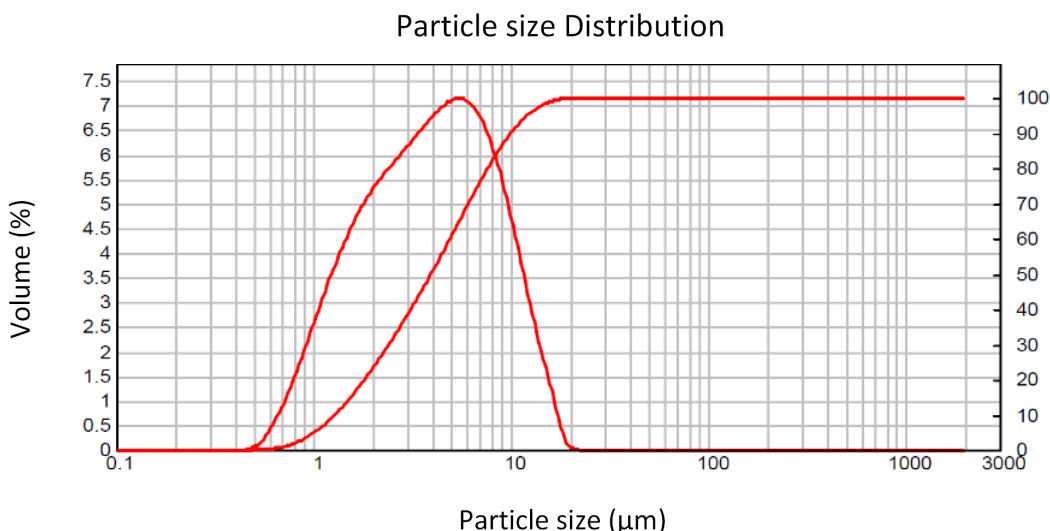

Fig. 5. Silica sieve analysis (alkaline extraction at pH 9-10)

As noted previously, the precipitated silica had a spontaneous tendency to agglomerate (Fig. 4). The laser diffraction analysis revealed a maximum size of the silica particles, which themselves consist of smaller particles. To examine the detailed structure of the precipitated silica, FEG-SEM/EDX analysis was performed.

FEG-SEM/EDX analysis

The silica obtained during the preliminary extraction step at pH 11 to 12 or at pH 9 to 10 is quasi-pure (traces of calcium). The SEM images of silica particles of these two tests show huge differences (Figs. 3 and 6). For the first test, these particles had heterogeneous sizes and forms, and there were clusters with diameters up to 200 µm (Fig. 3). In contrast, the silica obtained at the lowest pH had regularly shaped particles, with diameters of a few hundred of nanometers.

As noted above, the precipitated silica was composed of elementary particles (size 5 to 40 nm), which coalesced and formed aggregates ranging in size between 50 and 500 nm (Fig. 4). The aggregates in turn were grouped to give agglomerates with size ranging from 0.2 to 30 µm. These agglomerates themselves formed macroscopic objects called macro particles, which size can reach the millimeter. Thus, the precipitated silica at pH 9 to 10 had an average agglomerates size of 4 µm. These agglomerates themselves consisted for the most part of aggregates of 400 nm.
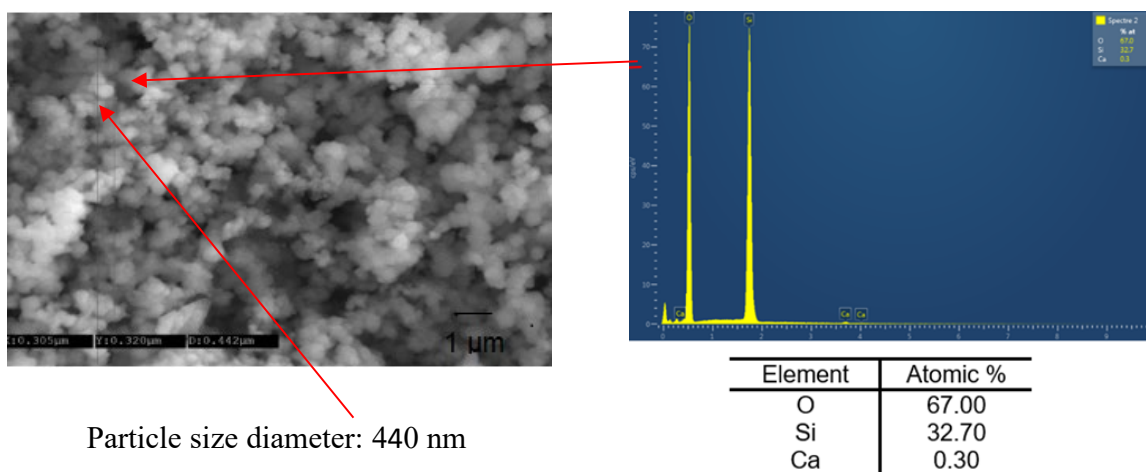

Particle size diameter: 440 nm

Element	Atomic %
O	67.00
Si	32.70
Ca	0.30

Fig. 6(a). FEG-SEM of silica extracted at pH 9-10 from cellulose fraction (x12,000-10.0kV)
Fig. 6(b). EDX spectra

Throughout the dissolution/extraction step of silica, reduction of the pH would allow the formation of smaller species of silicate (Fertani-Gmati and Jemal 2011) and stop this spontaneous coalescence at the "agglomerate stage".

Surface area analysis

Surface area measurements were conducted as a final comparative analysis of the two silicas, as presented in Table 7. Similar to the silica obtained at pH 11 to 12, the structure of that obtained at pH 9 to 10 was mesoporous (BJH Adsorption cumulative pore volume of pores value was 0.28 for a total pore volume value of 0.30). Though these two silicas also had a median pore diameter very close, it was not the same for the other three parameters. For the finest silica (4 µm average particle size), the BET surface area was lower than that of silica larger particle size (123 µm average particle size), 155.9 and 413.5 m^2/g, respectively. This is contrary to what can be expected but can be explained by the fact that these two silicas had cumulative BJH adsorption pore volumes of pores very distant (1.21 and 0.28 cm^3/g for, respectively, Silica 1 and Silica 2). The difference between these two values means that the first silica (pH 11 to 12) was much more porous than the second one (pH 9 to 10). The BJH adsorption cumulative pore volume of pores corresponds to the volume of nitrogen (adsorbent used for these analyses) that fills mesopores. This observation is important because the manner that this silica will react as filler in elastomers is unpredictable.

Table 7. Surface Area Analyses of the Precipitated Silica

	BET Surface Area (m^2/g)	Adsorption Total Pore Volume of pores (cm^3/g)	BJH Adsorption Cumulative Pore Volume of pores (cm^3/g)	BJH Adosrption Average Pore Diameter (nm)
Silica - pH 11-12	413.5	1.25	1.21	11.07
Silica - pH 9-10	155.9	0.30	0.28	8.23

BET Surface area serves as a measure of the total available surface area of the silica particles (both their inner surface and their outer surface). The BET surface area value of Silica 2 better reflects its specific surface and complies with industrial requirements.

Integration of Silica Extraction Process in the Biorefinery

The silica extraction process can be integrated in the Biorefinery developed by CIMV, valorizing a waste effluent and increasing the value of the products (Fig. 7).

- The cellulose fraction, obtained after wheat straw pre-treatment is dried, washed and repulped.
- Soda is added to achieve the extraction of silica at pH 9 to 10, at 85°C for 60 min.
- The washed pulp is pressed and hydrolyzed to produce cellulosic glucose for ethanolic fermentation. The resulting alkaline effluent contained solubilized silica.
- After concentration of the alkaline effluent, the silica is precipitated at pH 5 by addition of recycled acid stream from the pre-treatment process.
- Silica is then recovered after centrifugation and washing.

The separation process is carried out using a simple and low-cost system with minimal chemical and operating requirements. Therefore, by developing an efficient and integrated silica extraction step, valuable products, *i.e.*, cellulose, lignin, hemicellulose, and silica, can be produced from wheat straw in sustainable biorefinery.
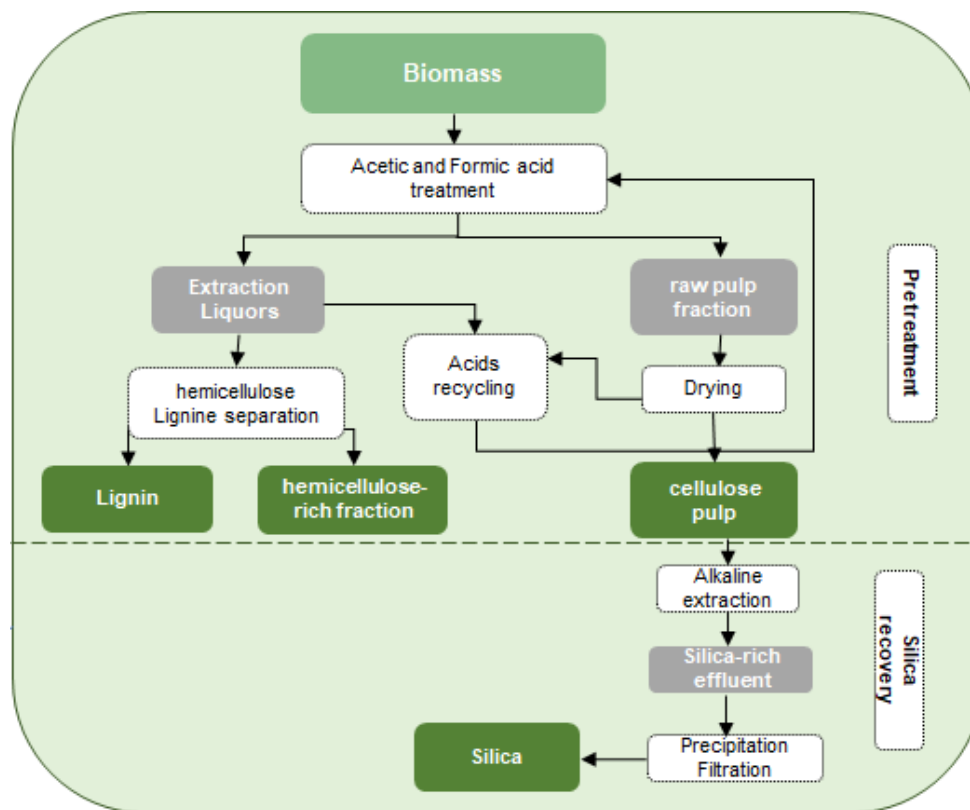
Fig. 7. Biorefinery process-Block diagram integrating the silica recovery

CONCLUSIONS

1. This work developed a method for silica extraction from wheat straw without degrading the other compounds contained in the plant material such as cellulose, lignin, and hemicelluloses. Therefore, silica recovery step was implemented after the pre-treatment of the biomass. The recovery was integrated into the organosolv pre-treatment process.

2. Silica was located in the cellulose fraction obtained after wheat straw fractionation. A preliminary alkaline extraction test was conducted at pH 11 to 12. High yield of pure silica was obtained but having a very porous and heterogeneous structure. In addition, the average particle size range is too wide (123 µm) for any field of use.

3. The pH of the extraction has a great influence on the quality of the silica. In order to optimize the extraction step, alkaline extraction was performed at a pH lower than the preliminary test, *i.e.*, 9 to 10. The silica obtained is mesoporous and has a BET surface area of 156 m^2/g. The average particle size is 4 µm, which mostly consist of 400 nm aggregates. Adjusting the pH of the alkaline extraction step from 11 to 12 to 9 to 10 greatly improved the silica characteristics.

4. The acidic organosolv pre-treatment process allows the fractionation of the lignocellulosic biomass leading to separate it into the three major compounds *i.e.* cellulose, lignin, and hemicelluloses. In this study, an additional silica extraction step was integrated, leading to the recovery of a fourth compound, silica, increasing the economic viability of the process and its sustainability.

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