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Electrostatic Separation as an Entry into Environmentally Eco-Friendly Dry Biorefining of Plant Materials

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Abstract

Today, most technologies used to fractionate plant materials are based on expensive chemical processes that often have negative environmental impacts by consuming water, energy, and solvents and creating large quantities of effluents. In addition, during the separation step, the major components are often partially degraded. Achieving high fractionation yields while maintaining the integrity of the macromolecular structure is a major challenge for the next generation of biomass refining processes. Electrostatic separation (ES), which enables the production of enriched fractions in compounds of interest while preserving their (native) functionalities has emerged as an eco-friendly biotechnology for the fractionation of agro-resources in dry conditions. In this review, the potential of ES in a biorefinery scheme is evaluated and the technological obstacles that still need to be overcome for its full deployment at industrial scale are identified.

Keywords: Agro-resources; Proteins; Fiber; Dry fractionation; Electrostatic separation

Highlights

- Electrostatic separation is an efficient technology for dry separation of proteins.
- Two main devices used at lab scale: tribo-electrostatic and corona belt separator.
- Their efficiency depends on the physical-chemical properties of the raw materials.
- Efficient electrostatic separation also largely depends on the milling procedure.

Introduction

Plant materials are composed of carbohydrates, proteins, lignin, ash, lipids and polyphenols. The first step in the biorefining of plant material today is separating the agro-resources (e.g., grass, straw, oil cakes, cereal grains, etc.) into its major compounds (lipids, proteins, carbohydrates, etc.) from which very rich green chemical materials can be then produced (biofuels, surfactant, resin, fiber, etc.) (Figure 1). Today, most fractionation and separation operations are based on expensive chemical processes (pulping, hydrolysis, solvent extraction, steam and ammonia explosion, ionic liquid) that are unable to isolate the main compounds (vitamin, proteins) without loss of integrity [1]. Indeed, plant materials have a robust supramolecular structure, which often requires harsh conditions to deconstruct it. In these conditions, the native functionalities of the compound are not fully preserved [2] plus the processes require large quantities of energy and water and/or solvent and the downstream purification steps required to remove the solvents have a drastic impact on the final cost of the extracted biomolecules and biopolymers. Dry fractionation processes are thus an interesting alternative to wet fractionation processes. They usually combine pretreatment, milling and physical separation to gradually deconstruct the plant materials into different tissues and/or cells [3] and to separate the fractions enriched in the compound of interest (proteins, cellulose, hemicelluloses or lignin) [4]. Electrostatic separation (ES) has been used for many years in mining and mineral processing [5,6], in the polymer industry [7,8] and for recycling metal and plastic from industrial waste [9,10]. ES recently emerged as an eco-friendly technology for sorting plant and agro-resources under dry conditions after grinding [11-13]. The principle of ES is based on the difference in electrical conductivity and/or charge between particles related to their physical-chemical composition. Charges are acquired either by turboelectric charging, i.e., when they rub against each other or against the convoying pipe, by conductive induction when in contact with an electrically charged surface, or by ionic cloud generated by a high-voltage electrical discharge. The charged particles are then separated in an electrical field. In dry biorefining of agro-resources, both are used for the electrostatic separation of plant materials (Figure 2).

Electrostatic separation technologies

Tribo-electrostatic separator: Particles are conveyed by compressed air through a charging pipe where they are tribo-charged by colliding with each other and colliding the walls of the pipe. The charging pipe is removable and the materials (stainless steel, PVC, Teflon, etc.) used to make the pipe can be adapted to optimize separation. The charged particles are then injected into a vertical separation chamber containing two high voltage electrodes, where the positively charged particles are attracted by the negative electrode and the negatively charged particles are attracted by the positive electrode (Figure 2). A particle recovery system equipped with two cyclones separates the two fractions, one containing the positively charged particles and the other the negatively charged particles. In this device, the particles are subjected to electrical forces and gravity. The conductivity of the particles, which depends on their chemical composition, their surface properties, the moisture content as well as the size, shape and density of particles, plays a major role in separation, as underlined by [14] in a theoretical study on the

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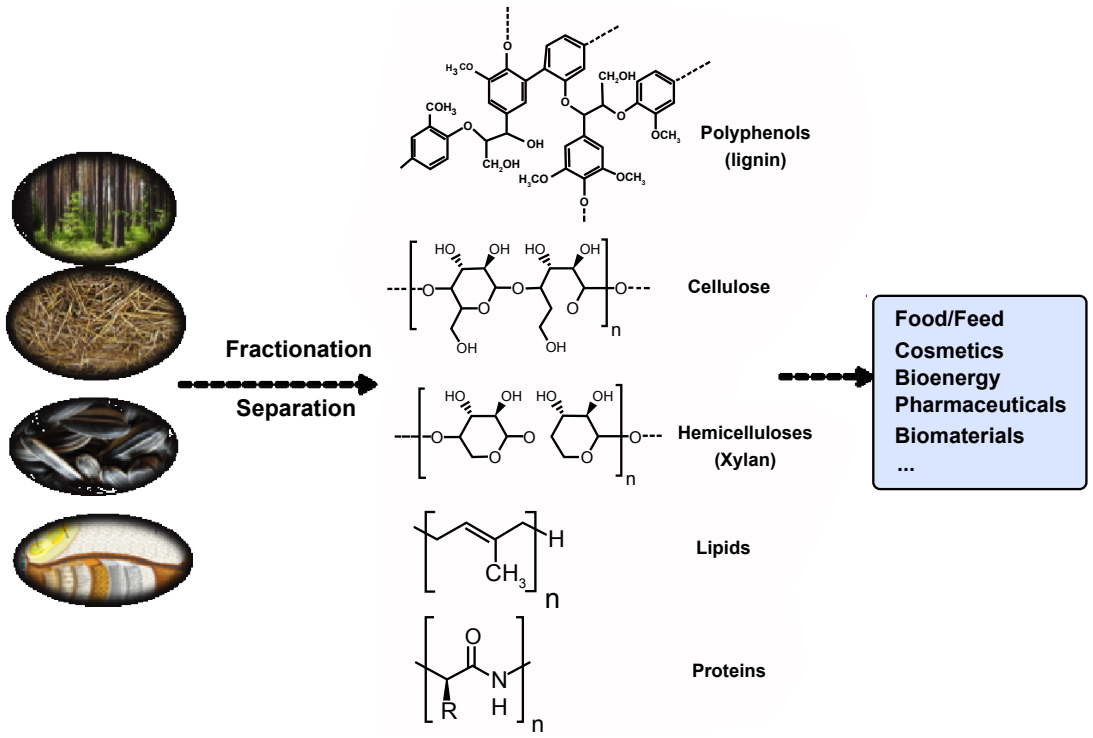

Figure 1: Plant biorefining and chemical structure of biopolymers.

ES of a gluten-starch mixture. Compared to the traditional free fall electrostatic separators used in the mineral industry, the specificity of devices used for the separation of plant materials is that the particles are in a laminar airflow thereby making it possible to control the motion of small particles of plant origin, which are much lighter than mineral particles.

Belt-corona separator: The belt-corona separator can be seen as a smaller scale version of the drum electrostatic separator frequently used at industrial scale in the plastics and minerals industries. Particles are deposited on a grounded conveyor. They are charged by corona discharge, induction or contact electrification prior to separation. The conducting particles rapidly lose their charge in contact with the ground conveyor, while the poorly or non-conducting particles, which lose their charge more slowly, are attracted to the rotor surface by the image force of their surface charge (Figure 2) [13,15,16]. The ratio of the electrical forces to the gravity forces, which is related to the mass of a particle, their shapes and their compositions, mainly govern the separation of the particle and the efficiency of the system.

Potential of electrostatic separation in an agro-resources biorefinery scheme

Plant biomass materials such as wood, oil cakes, cereal grain, corn, etc., are structurally organized as a multilayer composite containing epidermal, parenchyma, sclerenchyma and vessel tissues, which include different botanical compounds and have different properties. As the efficiency of an electrostatic separator is based on differences in the electrical properties of particles to be separated, the choice of a milling technology depends on the mechanical properties of the plant material and is a crucial way to increase the difference between particles originating from different tissues [17,18]. It is also important to bear in mind that the efficiency of the electrostatic separation (discussed below) can never be greater than the efficiency of the milling technique used to dissociate plant materials.

Separation and concentration of proteins and fiber in oil cake biomass: The production of concentrated proteins with low fiber and anti-nutritional components from oilseed meal or oil cake for their valorization as animal feed is challenging. Indeed, they generally contain substantial amounts of fiber (sunflower meal contains about 50% w/w of fiber) and high concentrations of phenolic and lignin compounds, which reduce protein solubility and give the final product undesirable organoleptic characteristics. In this context, [12,19,20] investigated the potential of ES using a corona drum electrostatic separator (corona-ES) with sieving-wind sifting separation and ultrafine milling coupled with tribo-ES, respectively [19]. sorted de oiled milled oilseeds into different fractions using an apparatus generally called a “purifier” that exploits differences in the size and density of particles. The sorted fractions are then separated electrostatically, and these authors obtained 2 to 2.5 times more fiber rich and 1.1 more protein rich fractions than the original fraction. In the process developed by [12,20], sunflower oil cakes (SOC) and rapeseed oil cakes (ROC) were milled into an ultrafine powder (UFM: ultra-fine milling) centrifugally using a 0.25 mm screen. The milled raw material (F_0) was then continuously introduced into a pilot electrostatic separator and sorted into two fractions named F^+ and F^- according their positive or negative charge. The F^+ and F^- fractions also differed in color linked to their composition (Table 1 and Figure 3). For SOC biomass, the negatively charged fraction (F^-) was seen to be 5 times richer in lignin, 3 times richer in glucose and 2.5 times richer in hemicelluloses than the positively charged fraction (F^+), while the latter was 9.5 times richer in protein. In the case of ROC biomass (Table 1 and Figure 3), an increase in lignin content from 16% (F_0) to 39% was observed after the second fractionation step (F^+). Protein content also increased from 37% for (F_0) to 50% in F^+ and with only

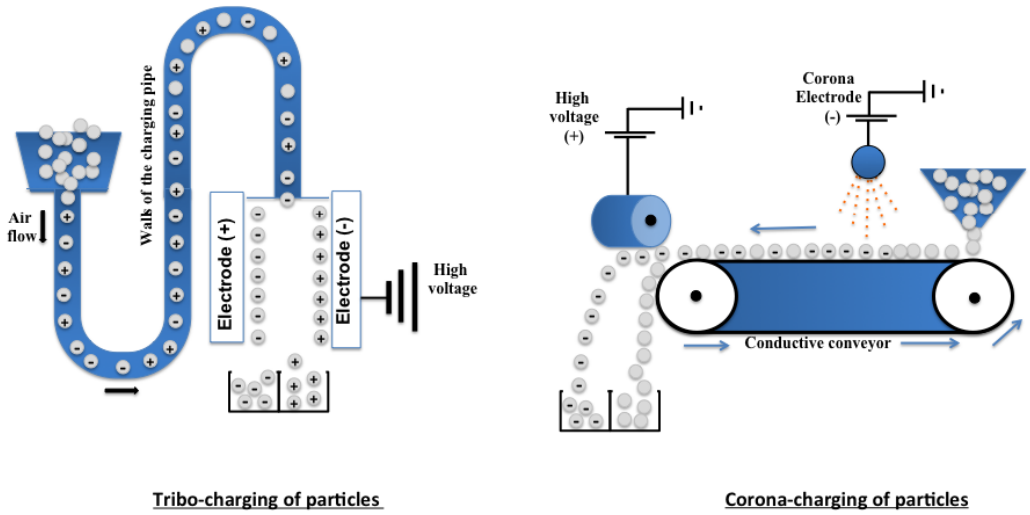

Figure 2: Schematic diagram of electrostatic separation technologies.

7% of lignin (Table 1). This technology can thus separate two original fractions in the biomass, the first fraction rich in proteins that can be used as feed/food ingredients, and the second fraction rich in fiber. In a biorefinery scheme, it would be logical to consider using the fraction poor in protein but with high fiber, phenolic and lignin content for other applications such as biofuel, chemicals and materials production.

Electrostatic separation in cereal processing: Bran produced by milling wheat grains contains high nutritional value components in the different layers and tissues. By combining cryogenic or ambient milling with a tribo-ES step in the same device as described above, [21,22] fractionated wheat bran to break down bran tissues to isolate their sub-cellular constituents (cell walls rich in fiber versus cell content rich in micronutrients). Hemery et al observed that the ultrafine bran obtained after cryogenic milling contained more composite particles than ultrafine bran produced by milling at ambient temperature. The authors thus suggested performing tribo-ES on an ultrafine bran sample obtained by ambient milling, in which the bran tissues are more efficiently dissociated. The biochemical compositions listed in Table 1 underline the contrast between the positively charged "F^{+}" and negatively charged fraction "F^{-}" linked to the histological origins of the particles. As previously observed for oilseed meals, the fiber rich particles in the pericarp were more abundant in the negatively charged fractions "F^{-}", and aleurone cell walls (β-glucans and arabinoxylans) and loose protein containing material from the aleurone and endosperm was more abundant in the positively charged fraction "F^{+}".

With the same Dascalescu et al, [21] explored the potential of using a belt-corona separator to separate a mixture of aleurone and bran. The two fractions resulting from the process were respectively a non-conductive fraction attracted by the electrode, which was 20 times richer in bran, and a conductive fraction not attracted by the electrode, which was almost 4 times richer in aleurone Remadnia et al.

Similarly, although in fact [23] were studying the separation of a synthetic mixture of 50% peel and 50% gluten originating from wheat grains, they showed that separation was more efficient when the particles were charged by induction, with 23% of peel recovered in the conductive fraction and 53% of gluten in the non-conductive fraction. The separation was hypothesized to be related to the big difference in particle size: small particles of gluten being attracted by the electrode because of their low mass, whereas big particles of peel remained on the conveyor belt because of their weight.

Electrostatic separation in lignocellulosic biomass biorefinery: Barakat and Chuetor [4,24] investigated the efficiency of tribo-ES technology on the fractionation of wheat straw (WS) and rice straw (RS), respectively. In the case of wheat straw, fluorescence microscopy and morphology analyses revealed differences in microstructure between the positively "F^{+}" and the negatively charged fractions "F^{-}". The "F^{+}" fraction appeared to be crumblier and to contain homogeneous small particles, whereas the "F^{-}" fraction contained more heterogeneous long fibrous particles (Figure 4). These differences were linked to the different histological origins of the particles, confirmed by their physical-chemical properties and the composition of the different fractions (Table 1). Once again, the "F^{+}" and "F^{-}" fractions of the wheat and rice straw were also shown to have differ biochemical properties (Table 1). The "F^{+}" fraction was richer in cellulose than the "F_0" and negatively charged "F^{-}" fractions. The negatively charged "F^{-}" fractions were rich in lignin; hemicellulose (and hence in arabinoxylan) and ash compared to positively charged "F^{+}" fractions (Table 1). The authors also demonstrated that UFM/tribo-ES could separate the crystalline from amorphous cellulose polymers. They reported that the negatively charged "F^{-}" fractions exhibited higher CrI compared to the F.

raw material and to the positively charged fraction (Table 1) studied the effect of coupling TES [4] and enzymatic hydrolysis on the production of biofuels. After ES, the wheat straw and rice straw fractions were hydrolyzed with an enzyme cocktail (Figure 5) shows that the positively charged "F^{+}" fractions produced the maximum glucose yield with respectively, 254 and 203 mg glucose g^{-1} obtained from the "F_2^{+}" and "F_2^{+}" fractions of wheat straw compared only to 130 mg glucose g^{-1} from the original "F_0" fraction, whereas the maximum yield of glucose from rice straw was respectively, 250 and 222 mg glucose g^{-1} from the "F_2^{+}", "F_1^{+}" fractions. These results clearly show that ES technology can used to isolate enzymatic accessible biomass without using water and chemical pretreatment.

	Wheat bran (WB)			Sunflower oil cake (SOC)			Wheat straw (WS)			Rice Straw (RS)			Rapeseed oil cake (ROC)		
	F_0	F^-	F^+	F_0	F^-	F^+	F_0	F^-	F^+	F_0	F^-	F^+	F_0	F^-	F^+
D50 (µm)	54.9	88	26.5	69.5	77.2	24.2	81.9	95.7	62.9	64.8	72.7	56.1	89.7	127	78.8
Glucose	14.8	5.5	19.8	17.6	24.3	7.7	45.4	40.8	58.4	49.8	40.3	59.4	8.3	14.4	4.4
Lignin	-	-	-	21.2	39.4	7.5	21.5	21.3	17.7	13.8	17.4	9	16.2	17.4	9
Proteins	15.4	6.7	19.5	30.8	5.1	48.9	-	-	-	-	-	-	37	39.4	7.2
Hemicelluloses	40.9	53,0	35.8	10.8	13.3	5.5	29.1	32.6	21.7	22.5	26.2	22.7	15.6	22.7	7.2
Ash	7.1	4	7.6	6.2	4.2	8.6	4.5	5.2	2.6	13.8	16.1	8.9	6.3	5.3	6.1
***p-CA**	0.15	0.1	0.19	0.03	0.03	0.03	4.02	3.21	5.22	-	-	-	0.05	0.06	0.04
***SA**	0.27	0.2	0.24	-	-	-	-	-		-	-	-	0.38	0.21	0.44
***FA**	5.04	3.5	6.49	0.07	0.09	0.04	0.13	0.15	0.08	-	-	-	0.13	0.16	0.11
***di-FA**	1.02	1.9	0.64	0.02	0.04	0	0.13	0.11	0.16	-	-	-	0.03	0.05	0.02
***VA**	-	-	-	0.05	0.1	0.01	-	-	-	63.7	68.3	56.7	-	-	-
CrI	-	-	-				54.9	60.4	52.3	63.7	68.3	56.7	37.6	43.2	34.1
CrI: crystallinity; FA ferulic acid, di-FA: di-ferulic acids, SA: syringyl acid; p-CA: p-coumaric acid; VA: Vanillic acid. *(µg/mg)															

Table 1: Biochemical composition of the tribo-separated fractions from different substrates.

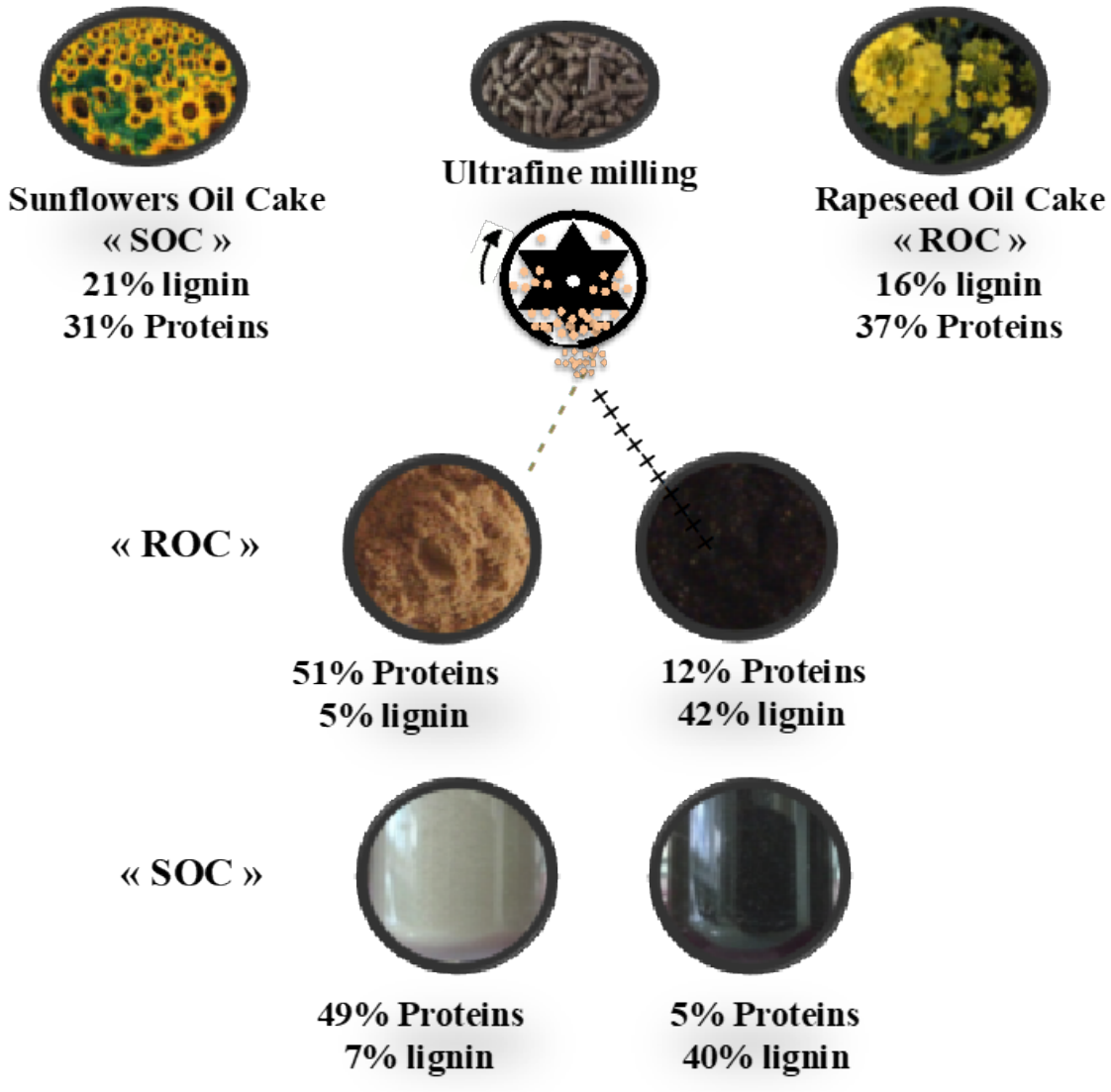

Figure 3: Electrostatic fractionation of sunflower oil cake “SOC” and rapeseed oil cake “ROC” for the extraction and concentration of proteins.

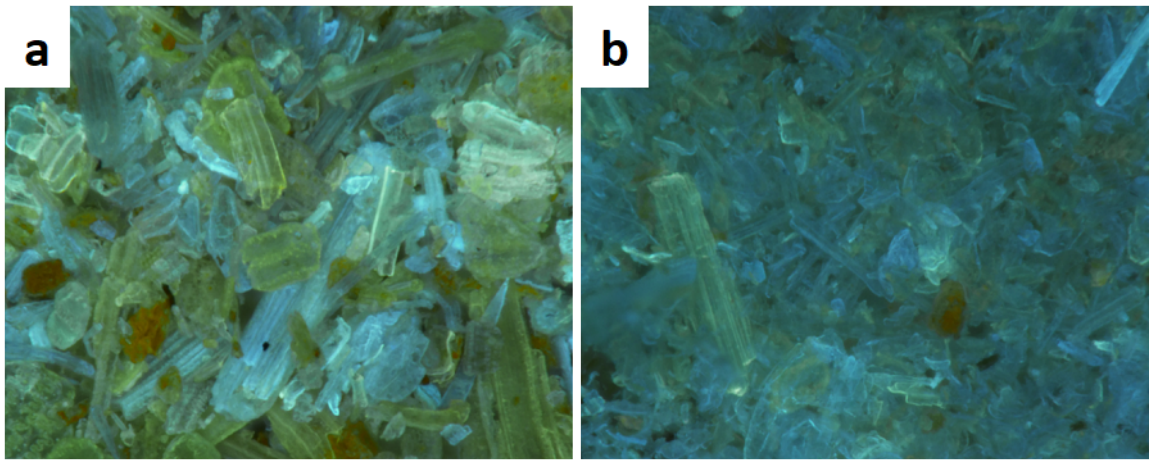

Figure 4: Micrographic and morphology of WS after ES, a) negatively charged fraction (F^-) and b) positively charged fraction (f^+).

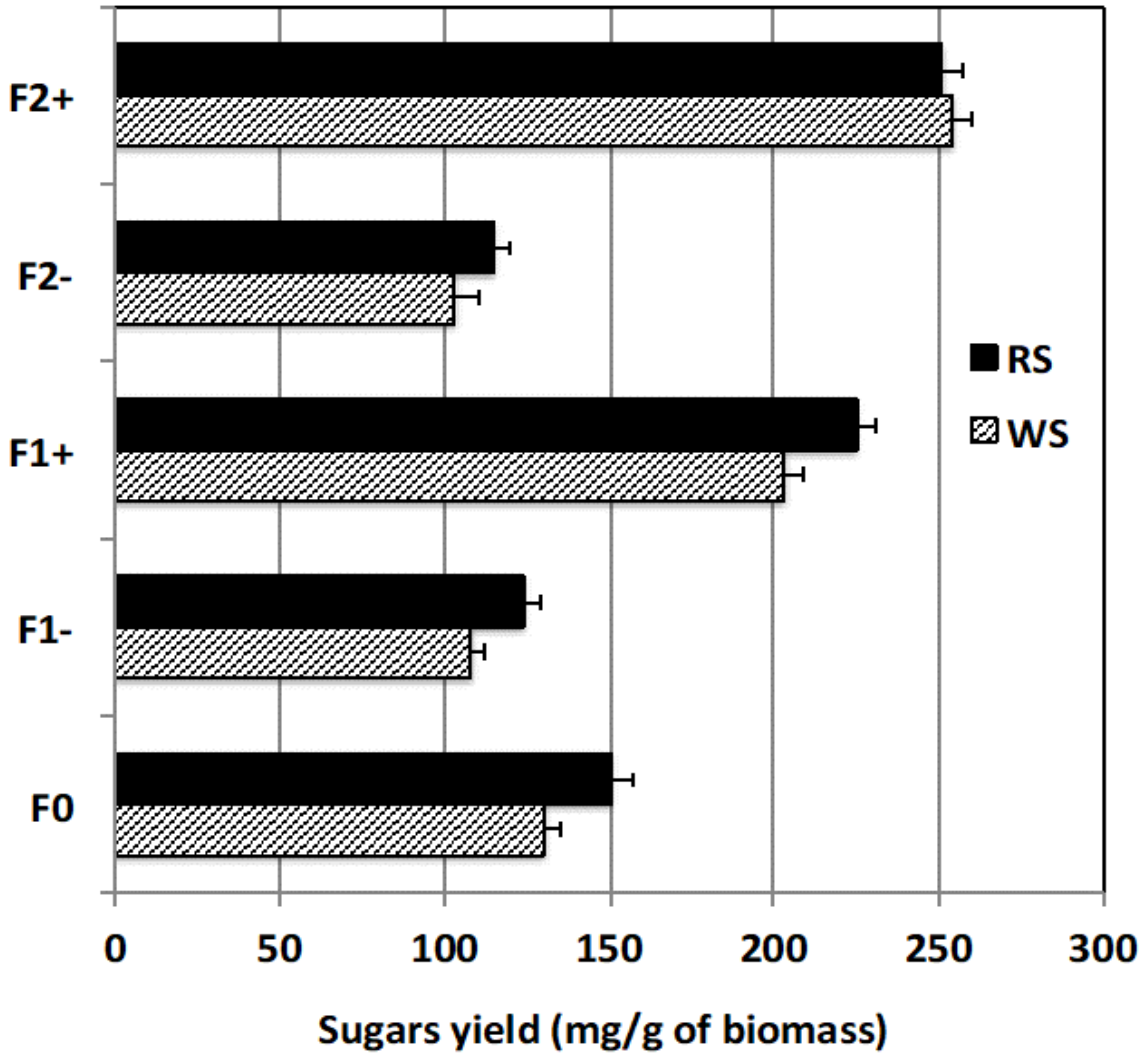

Figure 5: Glucose yields after enzymatic hydrolysis of different electrostatic fractions (Barakat et al. 2015 and Chuetor et al. 2015). RS: rice straw; WS: wheat straw.

Discussions/Conclusion: Challenges for Tomorrow

Both the corona separator and tribo-electrostatic separator have demonstrated their potential for the production of different fractions of plant biomass with highly contrasted fiber, protein and cellulose contents at laboratory semi pilot scale. They both use the difference in the composition of the different particles for separation. However, in tribo-electrostatic separation, the difference in the charges acquired by the particles during the charging step linked to their surface composition enables separation, whereas in the corona separator, separation is controlled by the dielectric conductivity of the particle, which depends on bulk composition, among other things. The physical properties of the particles including size, density, and shape also play a key role since the separation process is dynamic and the particles are in motion. These different factors explain why the two technologies do not result in the same separation of the same raw materials. Consequently, the choice of one technology over the other requires a good understanding of the raw material concerned and of its properties, while bearing in mind that efficient mechanical deconstruction of biomass prior to ES is also a crucial step to optimize separation. Although electrostatic separation technology is commonly used at an industrial scale in mining and in the recycling of electronic waste, it has not yet been used for the separation of biomass and organic waste, which contain smaller more plastic particles that are also lighter than mineral particles. From the standpoint of process ability, only particles measuring between 0.6 and 1.2 mm can be separated with existing industrial scale corona separators. Fine powders can theoretically be separated in a tribo-electrostatic separator but some obstacles have been identified for such particles, for example, the need to ensure the regular input and conveyance of fine particles of plant origin, the risk of explosion in presence of an electrostatic field, agglomeration and clogging effects. Consequently, technological improvements are still required to enable implementation at an industrial scale.

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