Biorefinery of agricultural residues by fractionation of their components through hydrothermal and organosolv processes

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Biorefineria de residus agrícoles mitjançant fraccionament dels seus
components aplicant processos hidrotèrmics i organosolv
Biorefinería de residuos agrícolas mediante fraccionamiento de sus
componentes aplicando procesos hidrotérmicos y organosolv

RESUMEN

La producción de los residuos agrícolas más importantes en España, por su abundancia, como son la paja de cereales, los tallos de girasol, los sarmientos de vid, los tallos de algodonera, las podas de olivo, naranjo y melocotonero, y los desechos de hortalizas y otros cultivos similares, representan una cifra superior a los 50 millones de t/año. El aprovechamiento de los residuos agrícolas puede realizarse de dos maneras generales: transformando sus constituyentes sin una separación previa de los mismos (procesos de combustión, pirolisis, gasificación y licuefacción) o separando sus constituyentes, mediante fraccionamiento. La principal vía de aprovechamiento, mediante separación de los componentes, consiste en aislar las fibras celulósicas para la fabricación de papel. En los últimos tiempos este tipo de aprovechamiento ha derivado hacia la denominada biorefinería, que consiste en el fraccionamiento o separación de los distintos componentes de los materiales lignocelulósicos con el fin de aprovecharlos todos, y no sólo la celulosa para la producción de papel. Así los pasteados clásicos (como el kraft, "al sulfito" o "a la sosa") han de sustituirse por dos procesos: un tratamiento hidrotérmico que separa dos fracciones, una líquida, que contiene productos de descomposición de las hemicelulosas [oligómeros y monómeros (glucosa, xilosa, arabinosa, etc.)] que tienen diversas aplicaciones, y otra sólida, rica en celulosa y lignina; y un pasteado organosolv de la anterior fracción sólida, que da lugar a pasta y a una fracción líquida residual, de la que puede separarse lignina y otros compuestos, que pueden utilizarse en diversas aplicaciones.

Palabras clave: Residuos agrícolas, pasta, celulosa, hemicelulosa, lignina, proceso organosolv, tratamiento hidrotérmico

SUMMARY

The combined production of the most abundant agricultural residues in Spain (viz. cereal straw, sunflower stalks, vine shoots, cotton stalks, olive, orange and peach tree prunings, and horticultural and related residues) amounts to over 50 million tons per year.
Agricultural residues can be valorized by converting their components jointly (combustion, pyrolysis, gasification, liquefaction) or separately (fractionation). The most useful method for exploiting such components separately involves isolating cellulose fibres for papermaking purposes. In recent times, this valorization method has led to the development of the biorefining concept. Biorefining involves the fractionation or separation of the different lignocellulosic components of agricultural residues with a view to their integral exploitation rather than the mere use of cellulose fibre to obtain paper products. Biorefining replaces the classical pulping methods based on Kraft, sulphite and soda reagents with a hydrothermal treatment followed by organosolv pulping. The hydrothermal treatment provides a liquid phase containing hemicellulose decomposition products [both oligomers and monomers (glucose, xylose, and arabinose)] and a solid phase rich in cellulose and lignin. By contrast, the organosolv process gives a solid fraction (pulp) and a residual liquid fraction containing lignin and other useful substances for various purposes.

Keywords: Agricultural residues, pulp, cellulose, hemicellulose, lignin, organosolv, hydrothermal treatment

RESUM

La producció dels residus agrícoles més importants a Espanya, per la seva abundància, como són la palla de cereals, les tiges de gira-sol, els sarments de la vinya, les tiges de cotonera, les esporgues d'olivera, taronger i presseguer, i les restes d'hortalisses i d'altres cultius similars, representen una xifra superior als 50 milions de tones anuals. L'aprofitament dels residus agrícoles es pot realitzar de dues maneres generals: transformant els seus constituents sense cap separació prèvia dels mateixos (processos de combustió, piròlisi, gasificació i liqüefacció), o bé separant els seus constituents, mitjançant

fraccionament. La principal via d'aprofitament mitjançant separació dels components consisteix en aïllar les fibres cel·lulòsiques per a la fabricació de paper. En els darrers anys, aquest tipus d'aprofitament ha derivat cap a la denominada biorefineria, que consisteix en el fraccionament o separació dels diferents components dels materials lignocel·lulòsics per tal d'aprofitar-los del tot, i no només la cel·lulosa per a la producció de paper. Així, els pastaments clàssics (como el kraft, "al sulfit" o "a la sosa") s'han de substituir per dos processos: un tractament hidrotèrmic que separa dos fraccions, una líquida, que conté productes de descomposició de les hemicel·luloses (oligòmers i monòmers (glucosa, xilosa, arabinosa, etc.) que tenen diverses aplicacions, i una altra sòlida, rica en cel·lulosa i lignina; i un pastament organosolv de l'anterior fracció sòlida, que dóna lloc a pasta i a una fracció líquida residual de la que es pot separar lignina i altres compostos que es poden utilitzar en diverses aplicacions.

Mots clau: Residus agrícoles, pasta, cel·lulosa, hemicel·lulosa, lignina, procés organosolv, tractament hidrotèrmic

1. INTRODUCTION

Agricultural residues are highly abundant in Spain (particularly in the Andalusia region). The annual production of the major residues in the country (viz. cereal straw, sunflower stalks, vine shoots, cotton stalks, olive, orange and peach tree prunings, and horticultural and related residues) is estimated to exceed 50 million tons of which more than 20% is generated in Andalusia [1].

Agricultural residues consist mainly of cellulose and lignin, which jointly account for 85–90% of their dry matter content; the remaining 15–10% includes fat, wax, ash, simple sugars, starch, essential oils, pectins, gums and tannins, among other substances[2]. The body of cellulose materials present in these residues is known as "holocellulose" and includes three fractions (α-cellulose, ß-cellulose and γ-cellulose, the combination of the latter two being referred to as "hemicellulose").

Agricultural residues must inevitably be disposed of in order to avoid contamination, pest growth, occupying large expanses of land and hindering agricultural work. Residues can simply be eliminated to avoid these problems or exploited for specific components or their chemical potential energy. Obviously, the latter choice is to be preferred since, at the very least, it can reduce disposal costs or even yield some profit.

Agricultural residues can be valorized by converting their components jointly or separately.

There are various procedures for valorizing agricultural residues by transforming their components without a prior separation[3]. This requires subjecting the residues to a series of physical operations (downsizing, classification, drying, agglomeration) intended to facilitate subsequent processing. Once conditioned, the lignocellulosic materials in agricultural residues can in fact be efficiently subjected to physico–chemical and biochemical valorization treatments. The former, also known as "thermal" or "dry" treatments, involve high temperatures and require the use of sophisticated equipment operating during short processing times. On the other hand, biochemical processes use low temperatures, simple equipment and long processing times. The physico–chemical processes used in

this context include combustion to generate heat; gasification to obtain synthetic or combustion gases; pyrolysis to obtain gases, liquids, solids and various chemicals; and liquefaction to produce liquid fuels. The biochemical processes give bioalcohol (as fuel), biogas (burning gas) and single-cell protein (animal feedstuff).

Agricultural residues can be exploited by separating their components in order to obtain cellulose fibre for making pulp and paper. Also, they can be used to extract other components such as sugars or starch, which have a much lesser economic significance. Recently, however, a new trend to the integral exploitation of lignocellulosic materials (agricultural residues included) has developed and led to their "biorefining", which involves the fractionation or separation into their components with a view to their individual exploitation rather than the mere use of part of their cellulose to obtain paper with a classical (Kraft, sulphite, soda) pulping method. The fractionation of lignocellulosic materials by thermal treatment in an aqueous medium (a hydrothermal treatment) and their processing in an organic solvent (an organosolv process) have been the subject of some study[4].

The processes currently used to valorize agricultural residues fractionate their individual components in order to recover those with the highest interest. This is made difficult by the inability to efficiently isolate cellulose, hemicellulose and lignin without degrading their chemical structure. The most widely used fractionation methods are based on the following principles: dissolution of lignin in an organic solvent (an organosolv process) in order to obtain a lignin-rich liquid fraction and a cellulose-rich solid fraction that are used to produce lignin and cellulose pulp, respectively; and hydrothermal treatment, which provides a liquid fraction rich in hemicellulose degradation products mainly and a solid fraction essentially consisting of α-cellulose and lignin.

2. ORGANOSOLV PULPING PROCESSES

The steady growth of environmental concern in developed countries must be reconciled with their increasing demand for pulp. This need has led researchers to find alternative raw materials such as agricultural residues and also to develop new, organosolv pulping processes. Organosolv processes use sulphur-free reagents and low-output facilities to obtain high-quality pulp and paper products in high yields at a low cost. In addition, they are highly efficient in using raw materials and afford the obtainment of a number of by-products as a result[5–9].

Organosolv processes only started to challenge the supremacy of traditional chemical pulping processes after the 1970s, when they emerged as effective choices for overcoming some of their traditional problems (e.g. off odours, low yields, high pollution, large investments, and high water, energy, raw material and reagent consumption). The earliest organosolv processes were simply modified versions of previous classical processes but soon gave way to new, sulphur-free treatments. These processes posed new problems such as the difficulty of recovering the reagents and the polluting nature of the effluents. The actual usefulness of organosolv processes as alternatives to the classical processes was assessed and the former found to ensure integral exploitation of the raw material, so much so that they were regarded as the means to obtain hydrolysable cellulose, lignin phenol polymers and sugars rather

than as pulping processes proper. In the 1990s, the Kraft process still defied competition from all others; however, its environmental unfriendliness, high investment costs and low profitability on the small and medium scales fostered a search for new pulping processes not only avoiding their problems but also allowing integral use of the raw materials in order to obtain various substances of interest in addition to cellulose pulp. This is how so-called biorefining of lignocellulosic materials was born. Finally, a new line of research was started in the mid-1990s towards the efficient delignification of alternative raw materials such as agricultural residues by organosolv pulping [5, 6].

Figure 1 depicts a typical organosolv process. As can be seen, the raw material is added jointly with recycled organic solvent and the fresh solvent –which is intended to replenish any solvent lost during the recovery operation– and additives to the cooking reactor. After a preset processing time, the reactor contents are unloaded into a washer in order to separate a solid fraction (the pulp) and a liquid fraction containing the black liquor [viz. solvent plus dissolved products (lignin, mainly)] and the washing agent. Then, the liquid fraction is used to isolate lignin, sugars and the solvent, the last being recycled to the cooking reactor.
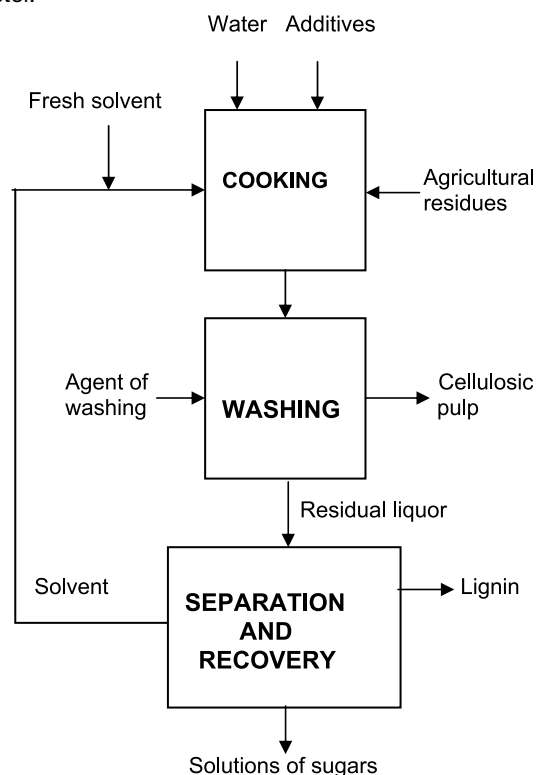

Figure 1. *Fractionation of lignocellulosic materials by organosolv processes*

The high cost of organic solvents, their difficult recover and –very often– high toxicity have fostered the use of low-molecular weight aliphatic alcohols (ethanol and methanol, mainly). These two alcohols are the oldest delignifiers; in fact, Kleinert used them separately in a 50% proportion at 195 °C in the absence of catalyst on steamed chips as early as 1974. This treatment is similar to that of the Alcell process (with ethanol), which has gained widespread acceptance. The increased use of alcohols is reflected in their being the sole organosolv reagents employed on the

pilot plant and industrial scales. Also in wide use at present are the Alcell, Organocell, ASAM (alkaline sulphite-anthraquinone-methanol), ASAE (alkaline sulphite-anthraquinone-ethanol), NAEM (alkaline-earth salt-methanol) and IDE (imprenation-disolving-ethanol) processes[5].

The greatest shortcoming of organosolv processes are their poor performance in the production of quality paper from softwood materials –in fact, they can only compete with the Kraft process in this respect for the production of low-grade paper and board– and the potential problems encountered in pulping hardwood according to the considered species –some plant species can result in a high reject rate and poor yield, and require a large amount of refining energy or drastic bleaching.

The Alcell process, which uses ethanol in a 50 vol% proportion, is one of the best known among those using an alcohol and no catalyst[5, 10]. Its operating conditions are a temperature in the region of 195 °C, a processing time of 60 min and a liquid/solid ratio of 6:1 to 7:1. The process is especially suitable for hardwood but has provided also good results with alternative raw materials such as bagasse and cereal straw –albeit with some problems arising from the presence of large amounts of silica in both. Alcell pulp contains more α–cellulose and less hemicellulose than does Kraft pulp; by contrast, it is obtained in higher yields and loses less hemicellulose during refining. In addition, it has a lower reject rate as the likely result of the low viscosity of the mixed ethanol–water solvent facilitating access to chip fibres. The Alcell process is more economical than the Kraft process. Also, Alcell pulp is easily delignified with oxygen (the Kappa number is reduced by up to 70%) with little loss of viscosity –Kraft pulp can lose up to 50% under identical conditions. The brightness of Alcell pulp is competitive with that of conventional pulp. Also, the Alcell process gives no off-odours; produces reduced amounts of effluents and pollutants; yields by-products of a higher quality and in greater amounts; is more efficient in using raw materials; can be more readily applied to smaller amounts of raw material and implemented on a smaller scale than the Kraft process; and uses less energy than the classical process. However, it has some disadvantages. Thus, it is inapplicable to softwood, subject to increased production costs by effect of the high price of ethanol and the reagents needed to recover the target by-products, and uses more energy than the Kraft process. Some of these disadvantages, however, are offset by the additional profit resulting from by-product sales. --Hardwood can be pulped without a catalyst. Some plant species, however, require a physico–chemical pre-treatment and several cooking steps in order to ensure efficient delignification and a high yield. On the other hand, pulping softwood invariably requires using a catalyst. Thus, the patented process of Paszner and Cho uses a magnesium salt in addition to the alcohol[11]. One other pulping process involving a catalyst is that based on the sodium–bicarbonate–water system and methylanthraquinone as catalyst, which have been applied to some poplar varieties. With softwood, the yield and lignin content of the pulp can be increased relative to leafy wood by replacing the bicarbonate with oxalic acid; however, using propanol instead of ethanol leads to poorer results[5].

The MD Organocell process, which uses methanol and soda, is a complement, but not a competitor, for the Kraft process, which it can replace in countries having no Kraft pulping facilities[12]. Unlike the Alcell process, the MD Organocell process is applicable to softwood, the resulting

pulp having better strength-related properties than Kraft pulp. Also, it can be applied to mixtures of softwood and hardwood, but this requires recovering the soda in addition to the alcohol.

The Organocell process involves a second step with anthraquinone in addition to the first (methanol and soda). Typically, the operation conditions are 17–20% soda, 0.1% anthraquinone, 5–30 vol% methanol, a liquid/solid ratio of about 4:1, a temperature of 155–170 °C and a processing time of 60–120 min[10]. This process has also been applied to alternative raw materials including wheat straw and amaranth[13].

One other widely use organosolv process is ASAM, which combines the action of soda, sulphite, anthraquinone and an alcohol. The process uses a chemical load of 15–25% soda, an alkali (Na_2SO_3/NaOH/Na_2CO_3) proportion of 85:15–70:30, 0.05–0.1% anthraquinone, 15–30 vol% methanol, a liquid/solid ratio of 3:1 to 5:1, temperatures of 170–180 °C and processing times of 60–150 min[10]. The results are similar to those of the Kraft process in terms of paper strength and to those of the sulphite process as regards brightness. The ASAM process has some advantages over the Alcell and Organocell processes (e.g. Alcell paper has better breaking length, however). Also, Alcell pulp is comparable to Kraft pulp in many respects, uses the same types of facilities and reagents as the sulphite process –in addition to dedicated equipment to recover methanol–, and provides cleaner, brighter raw pulp[14]. However, it has some disadvantages such as the need for high pressures and temperatures, larger capital investments and greater amounts of sodium sulphite; and more complicated reagent recovery, which requires a methanol recovery system and an appropriate unit to convert sulphides into sulphites[5].

The ASAE process is a variant of the ASAM process which replaces methanol with ethanol. Its optimum operating conditions for pulping pine wood, for example, are 20% sulphite, 50% ethanol and a processing time of 150 min at a high temperature. The resulting yield, viscosity, brightness and mechanical properties are all better –breaking length excepted– than those of Kraft pulp[15]. This process has been applied to alternative raw materials (cotton stalks[16]).

Although the ASAM, ASAE and Organocell processes are efficient in delignifying both hardwood and softwood, they are confronted with the difficulty of recovering the reagents, which is as complex as in the Kraft process and even more so than in the Alcell process. On the other hand, these processes release no sulphur compounds and are thus more environmentally benign than the Kraft process. Finally, the resulting pulp is brighter and amenable to bleaching with a totally chlorine-free (TCF) sequence.

The NAEM process is suitable for both softwood and hardwood, as well as for sugarcane bagasse. It uses methanol as solvent and an alkaline-earth salt as catalyst, and produces pulp with a small Kappa number and moderate viscosity. An appropriate post-cooking treatment, however, allows yield, viscosity and various other properties to be improved in relation to Kraft pulp. In fact, the outcome of the NAEM process clearly surpasses those of various others (ethanol, soda–ethanol, phenol–hydrochloric acid, cresol, ester, ASAM)[5]. There have been some NAEM trials at high pressures[17].

The IDE process involves three consecutive steps (impregnation with concentrated sodium carbonate, cooking with ethanol and extraction with an ethanol–water mixture) and

has so far been applied to both hardwood and softwood, as well as to cereal straw and other alternative raw materials[5, 18, 19].

Other organic solvents widely used for cooking purposes include low-molecular weight organic acids, which are the basis for the Acetocell, Milox and Formacell processes.

The Acetocell process uses acetic acid in combination with hydrochloric or sulphuric acid as catalyst[20]. It is suitable for both hardwood and softwood, and also for bagasse and annual plants. Some variants use acetic acid–water, acetic acid–carbon dioxide or acetic acid–water–carbon dioxide mixtures under supercritical conditions[21]. The process has also been applied to alternative raw material such as rice straw at atmospheric pressure[22].

Pulping hardwood with formic acid has the advantage of a low solvent cost and the ability to use of low pressures and temperatures[23]. The acid has been used to cook various alternative raw materials[24, 25]. The Milox process uses peroxyformic acid, which forms spontaneously upon mixing formic acid in an 80% proportion with hydrogen peroxide[25]. This process is especially effective for delignifying birch wood in three steps: treatment with peroxyformic acid at 80 °C, treatment with formic acid at 100 °C and bleaching with hydrogen peroxide to achieve 90% ISO brightness[26]. The mechanical properties of the resulting pulp are essentially identical with those of Kraft pulp; softwood, however, provides poorer results with the Milox process. The greatest shortcoming of this process is that distilling the reaction mixture to recover the solvent provides an azeotrope containing a 78% concentration of formic acid, which is inadequate for recycling. The Milox process has been applied to bagasse, rice straw and other alternative plants[27–30] in addition to wood raw materials.

The Formacell process uses a mixture of acetic acid, water and formic acid[31]. Its application to beech, pine and poplar wood provides pulp with a small Kappa number. The process has been used with alternative raw materials[29, 30]. Acetic acid containing sulphuric acid and a phenol has provided good results with birch wood[32]. Finally, the Formacell process has also been implemented with supercritical mixtures of acetic acid, carbon dioxide and water[21].

Dimethylformamide has been increasingly used since recently in the pulping of alternative raw materials[33–35].

Some high-boiling organic solvents such as ethanolamines and ethyleneglycols[6] are especially interesting in this context as they can be used under milder (Kraft-like) conditions than the previous alcohols and organic acids. These cooking solvents have so far been applied to empty fruit bunches (EFB)[36,37], rice straw[38], olive prunings[39, 40], vine shoots[41, 43] and cotton stalks[42].

Other organic solvents including phenols, glycols, esters, acetone, ammonia, amines, formamide, dimethylformamide and dioxane have also been used in organosolv processes. For example, rice straw has been cooked with phenol, acetic acid, formic acid, formaldehyde and acetone[6].

3. HYDROTHERMAL PROCESSES

One of the ways of fractionating lignocellulosic materials is by hydrothermal treatment or autohydrolysis, which facilitate depolymerization of hemicellulose (see Fig. 2, that also includes an organosolv pulping and the solvent recovery). These hydrothermal processes provide an aqueous fraction of hemicellulose containing xylo-oligosaccharides and monosaccharides (xylose, glucose, arabinose)[44–46],

and a solid residue consisting largely of cellulose and lignin amenable to pulping. The solid reside can be pulped with a classical or organosolv procedures. The latter have the advantage that they additionally facilitate the isolation of lignin and its use as a source for a wide variety of chemicals, some with a high added value[4, 47–49].

Hydrothermal treatments can be implemented in various ways. One especially interesting method is steam explosion: following autohydrolysis, the raw material is subject to abrupt depressurization in order to evaporate water contained in its fibres and facilitate disaggregation of the lignocellulose matrix[47].

Hemicellulose undergoes autohydrolysis at temperatures above 150–250 °C in an aqueous medium. Under these conditions, the autoionization of water produces protons that act as catalysts for the autohydrolysis process by attacking acetyl groups present in ester form in hemicellulose heteropolymers and causing the release of acetic acid as a result. The acid provides up to one million times more protons than water; therefore, water protons contribute very little to the hydrothermal treatment once the acid is formed. In addition to completely or partially dissolving hemicellulose, the process causes its efficient transformation into oligosaccharides and monosaccharides with a variety of potential uses.

Other less significant reactions occurring during the treatment include the formation of compounds such as furfural from pentoses and 5-hydroxymethyl-2-furfural (HMF) from hexoses; production of carbon dioxide by decomposition of carboxyl groups in uronic acids; condensation of unstable molecules acting as reaction intermediates; decomposition, under drastic conditions, of acid-sensitive products such as furfural or HMF into formic and levulinic acids; and condensation of various substances with lignin[50-52].

An autohydrolysis treatment has some advantages over acid hydrolysis, namely: greater operational simplicity; a reduced environmental impact as a result of the absence of acid neutralization sludge; and the ability to subject the resulting suspension to abrupt depressurization (steam explosion) in order to disaggregate the lignocellulose matrix and facilitate subsequent processing with a view to the obtainment of cellulose pulp[47].

Hydrothermal treatments can be performed over a wide temperature range. The outcome is influenced by temperature, time, solid concentration and particle size[47]. The temperature is always higher than 100 °C, below which no autohydrolysis occurs. Favouring depolymerization of hemicellulose requires establishing an appropriate upper limit for this variable. Thus, in a weakly acidic medium, ether bonds in lignin start to break at 160–180 °C, whereas α-cellulose depolymerization starts above 210 °C. The operating time can range from a few seconds to several hours. When using a relatively high temperature, the heating time (heating ramp) used to reach the target operating temperature can be very important. In some cases, the heating time can be much longer than the operating or reaction time; by contrast, the cooling time is comparatively short (the cooling rate is in the region of 30 °C/min) and has little influence on the results. The solid concentration (or solid–liquid ratio) typically ranges from 2 to 40 g water/g lignocellulosic material, but is usually set at about 10 g/g. A high solid–liquid ratio facilitates extraction of hemicellulose but is costly; on the other hand, a low ratio can initially be economical but subsequently result in impaired diffusion and transfer of the reaction products. Also, a small particle size facilitates hydrothermal treatment but requires milling, which raises energy expenses. Typically, laboratory treatments use particles 0.5–1.0 cm in size, and industrial and pilot-plant treatments chips of several centimetres. The study of the ¡influence of particle size on the process has been considered by some authors(50-52).

The use of drastic operating conditions causes hemicellulose to be dissolved to a large extent and hence unwanted products (furfural, HMF) to be produced in high proportions. This requires controlling a number of operating variables in order to maximize the content in hemicelluloses of the liquid fraction with a view to producing monosaccharides (xylose, glucose, arabinose) or oligosaccharides –both of which are desirable products– while minimizing the formation of degradation products. The use of appropriate conditions allows 60–85% of the total amount of hemicellulose in the raw material to be recovered as oligosaccharides and monosaccharides. The proportion of oligosaccharides invariably surpasses that of monosaccharides and often accounts for more than one half of the initial hemicellulose content. The inability to quantitatively recover sugar oligomers and monomers in the liquid fraction is a result of the presence of degradation reactions (e.g. the formation of furfural and HMF), which develop to an extent dependent on the particular operating conditions and varying widely for the same raw material[53–55].

The ability of hydrothermal treatments to provide delignifiable solid residues in addition to the liquid fraction affords the additional production of cellulose pulp by integrating the recovery of sugar by-products with pulping –as well as with lignin recovery if an organosolv process is used[50-54].

The liquor remaining after the autohydrolysis of lignocellulosic materials consists largely of oligosaccharides and monosaccharides; by appropriate transformation, separation and purification, these sugars can be used in various fields, namely: agriculture (growth boosters and accelerators); animal (pet, fish) feeding; medicine (prevention and treatment of gastrointestinal diseases, and treatment of osteoporosis, otitis and hair and skin problems); human nutrition (reinforced foodstuffs, special food for antiobesity diets, symbiotic foods containing microorganisms in addition to nutritional principles with healthy effects)[47].

Hydrothermal treatments have been applied to various types of agricultural residues including sunflower stalks[51], vine shoots[53], legumes[54, 55] and rice straw[56].

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Agricultural residues

Water → **HYDROTHERMAL TREATMENT** ← Heat

↓

SEPARATION → Liquid fraction (Hemicelluloses)

↓ Solid fraction

Solvent → **ORGANOSOLV PULPING** ← Heat

↓

RECOVERY AND SEPARATION

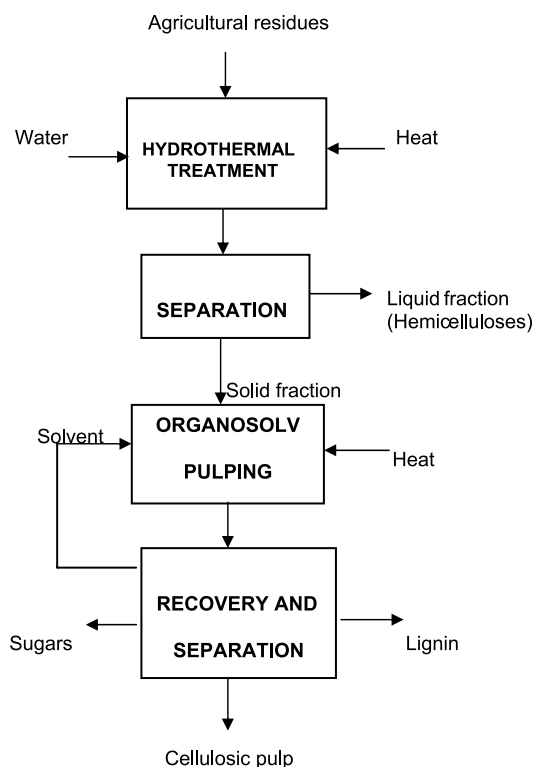Sugars ← ↓ → Lignin

↓

Cellulosic pulp

Figure 2. *Fractionation of lignocellulosic materials by hydrothermal and organosolv processes*

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Transiciones microestructurales inducidas por cizalla en sistemas acuosos de un tensioactivo catiónico tipo esterquat

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RESUMEN

Se presenta un estudio basado en técnicas reológicas y de microscopía electrónica de barrido de bajas temperaturas (cryo-SEM) sobre los cambios de microestructura provocados por el flujo en cizalla de dispersiones acuosas de un tensioactivo catiónico tipo esterquat. Se comparan micrografías de cryo-SEM y las respuestas bajo cizalla oscilatoria de dispersiones sin y con cloruro de calcio. Esta última no presenta zona de comportamiento viscoelástico lineal, apuntando su respuesta no lineal a un fenómeno de estructuración inducida por cizalla. Ensayos transitorios de inicio al flujo, entre 0,1s^{-1} y 2000s^{-1}, confirman que se producen aumentos de viscosidad más acusados con el tiempo de flujo a medida que aumenta la velocidad de cizalla. La técnica de cryo-SEM apoya que los resultados transitorios se deben a que un exceso de energía mecánica provoca transiciones de bicapas de tensioactivo a vesículas. Diferentes ensayos reológicos realizados en serie avalan la naturaleza irreversible, en la escala de tiempo de esta investigación, de las transiciones microestructurales inducidas por cizalla. Se demuestra que a pesar de la presencia de cloruro de calcio (0,1%), la aplicación de una velocidad de cizalla excesiva puede dar lugar a la aparición de respuestas viscoelásticas lineales significativas.

Palabras clave: Reología, viscoelasticidad, tensioactivos cationicos, esterquats

SUMMARY

This paper deals with a rheological and microstructural (cryo-SEM) characterization of shear-induced microstructure transitions in aqueous dispersions of an esterquat cationic surfactant. Cryo-SEM micrographs and oscillatory shear results of systems containing or not calcium chloride are compared. The addition of calcium chloride precluded the occurrence of significant viscoelastic properties and the estimation of the linear viscoelastic range. The non-linear oscillatory response pointed to the occurrence of incipient shear-induced build-up phenomena. Start-up flow tests between 0.1s^{-1} and 2000s^{-1} showed that the increase of viscosity with shear time was more marked as shear rate was increased. Cryo-SEM observations supported that build-up results in transient flow were due to an excess of mechanical energy, which resulted in transitions from surfactant bilayers to vesicles. Several series of rheological tests were carried out to demonstrate that shear-induced microstructure transitions were irreversible in the time scale of this investigation. Despite the addition of calcium chloride (0.1% wt), the shear-induced dispersion of vesicles may provoke the onset of significant linear viscoelasticity.

Keywords: Rheology, viscoelasticity, cationic surfactants, esterquats

RESUM

Es presenta un estudi basat en tècniques reològiques i de microscòpia electrònica d'escombratge de baixes temperatures (cryo-SEM) sobre els canvis de microestructura provocats pel flux en cisalla de dispersions aquoses d'un tensioactiu catiònic tipus esterquat. Es comparen micrografies de cryo-SEM i les respostes sota cisallament oscil·latòri de dispersions sense i amb clorur de calci. Aquesta darrera no presenta zona de comportament viscoelàstic lineal, apuntant la seva resposta no lineal a un fenomen d'estructuració induïda per cisallament. Assaigs transitoris d'inici al flux, entre 0,1s-1 y 2000s-1, confirmen que es produeixen augments de viscositat més acusats amb el temps de flux a mesura que augmenta la velocitat de cisallament. La tècnica de cryo-SEM recolza que els resultats transitoris es deuen a que un excés d'energia mecànica provoca transicions de bicapes de tensioactiu a vesícules. Diferents assaigs reològics realitzats en sèrie avalen la naturalesa irreversible, a la escala de temps d'aquesta investigació, de les transicions microestructurals induïdes per cisallament. Es demostra que, tot i la presència de clorur de calci (0,1%), l'aplicació de una velocitat de cisallament excessiva pot donar lloc a l'aparició de respostes viscoelàstiques lineals significatives.