



Optimization of the soda-ethanol delignification stage for a rice husk biorefinery



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ABSTRACT

The aim of this work was to optimize the delignification of the hemicelluloses-free fraction of rice husk to obtain fractions of lignin, cellulose, and inorganics, which could be valorized in the context of the rice husk biorefinery. The hemicelluloses were pre-extracted from the raw material by dilute sulfuric acid, and a soda-ethanol-water process was used for delignification. Two experimental designs were carried out to evaluate different ranges of the same variables (strong and light conditions), aiming to promote maximal delignification or delignify while protecting carbohydrates. The optimal delignification points were obtained using 13 and 8% of NaOH (%w/w on solid material), in a 50:50 and 54:46 ethanol:water solution. In these conditions, 94.3 and 90.1% of lignin and almost 100 and 40% of inorganics were removed from the solid, respectively. The used soda-ethanol-water process can be defined as a soda process additivated with ethanol, showing significant advantages over soda-anthraquinone process for the fractionation of lignocellulosic materials.

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1. Introduction

Through the biorefinery concept, lignocellulosic materials could be source of valuable products as fuels and building blocks for the production high value-added products as food additives, adhesives, cosmetics, and others (Barakat et al., 2013; Corma et al., 2007). These fractions can serve as viable sources of bio-chemicals with potential high-value applications. An integral fractionation of lignocellulosic materials opens the possibility of exploiting some of their main components as cellulose (Haleem et al., 2014; Zhou et al., 2010), hemicelluloses (Zhang et al., 2016), lignin (Duval and Lawoko, 2014; Kim et al., 2015; Villaverde et al., 2012; Wang et al., 2015), inorganics components (Adam et al., 2012) and substances extractives like fatty acid (José et al., 2015; Villaverde et al., 2013).

Lignocellulosic waste could also be valorized, reducing pollution and problems associated with its disposal. One of the highest advantage of the use of lignocellulosic waste is that there is not

competition with the food industry, and the economic balance is favored by obtaining high added products from a waste (Huber, 2008a).

The expanded use of renewable bio-based products and bioenergy will surely change the world economy over the coming years. Technological developments in green chemistry, chemical engineering, and biotechnologies might represent key innovations needed to start this transformation (Piergiuseppe Morone, 2016).

Rice husk (RH) is an abundant residue in the Northeast region of Argentine (provinces of Corrientes, Entre Rios, Santa Fe, Formosa, and Chaco). Rice production in Argentina reached 1,397,242 tons in 2012/13, of which about 20% was RH (Ricegrowers Association of Corrientes and Entre Rios Grain Exchange, 2013). As established in a previous work, rice husk is composed by 34.1% of cellulose, 14.6% of hemicelluloses, 19.0% of lignin, and 15.0% of inorganics (Dagnino et al., 2013). This composition agrees with that obtained by others authors (Barana et al., 2016; Hsu et al., 2010; Zhang et al., 2015).

Fractionation allows the separation of cellulose, hemicelluloses, lignin, and inorganic components, such as silica (Zhang et al., 2015). Efficient fractionation of biomass in its main components allows that all fractions can be valued for a positive economic balance (Huber, 2008b).

Nowadays, the interest on producing chemicals from renewable resources has increased and production of biofuels is one of the

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top world interests due to reduction of pollution and the use of fossil fuel sources. As consequence, researches about bioethanol production by fermentation of the sugars present in lignocellulosic raw materials became increasingly important (Demirbas, 2009).

Total or partial fractionation of different materials is possible by treatments that depend on the material and desired end products. Different methods have been investigated for the different stages, including physical, biological, chemical treatments, or their combination, using acids, alkalis, enzymes, heating, cooling, steam, pressure, decompression, microwave, fungi, and others. Treatment options and their application to various types of biomass are presented in published literature reviews (Singh et al., 2014; Taherzadeh and Karimi, 2008; Zheng et al., 2009). For example, by treating the raw material with diluted acid solutions, hemicelluloses are hydrolyzed as monomers in the liquid fraction, leaving cellulose and lignin in the solid fraction (Dagnino et al., 2013; Hendriks and Zeeman, 2009; Linde et al., 2008). Acid treatment has demonstrated to be one of most consistent methods to separate hemicelluloses as monomers in solution (Eisenhuber et al., 2013), whereas a significant fraction of lignin is solubilized in alkali treatment, with some hemicelluloses and a proportion of inorganic material (Singh et al., 2015). The use of alkaline solutions as first step seems not appropriate to obtain pure fractions. Another alternative is the use of organic solvents, which can be catalyzed with inorganic acids or bases, known as organosolv processes (Ahring et al., 2007). The organic solvent alters the bonds between lignin and hemicelluloses, so that lignin is hydrolyzed and then dissolved, being able to be retrieved in the organophilic phase (Minu et al., 2012). A combined use of organosolv process with a previous stage of dilute-acid hydrolysis allows to separate hemicelluloses and lignin in two consecutive fractionation steps. This processing could be useful to produce a pulp enriched in cellulose, avoiding the loss of potential valuable sources as hemicelluloses (Mesa et al., 2011). Organosolv process is also reported to produce a large amount of high-quality lignin that is relatively pure, primarily unaltered, and less condensed than Kraft lignin. Some organosolv processes have found a renewed interest in the last few years, mainly on the basis of second generation biorefineries, aiming at producing fuels and/or chemicals from lignocellulosic biomass. Moreover, low boiling point alcohols, mainly methanol and ethanol, seem to be the most suitable organic liquids for organosolv processes, due to their low cost and easy recovery. However, pretreatment with ethanol is safer because ethanol is less toxic than methanol (Zhao et al., 2009). Otherwise, ethanol also reduces the surface tension of the pulping liquor favoring the alkali penetration into the material structure, and lignin removal from it (Muurinen, 2000).

Since first generation biorefineries mainly focused on starch for the production of bioethanol, the competition with human feeding has led the research and industry to rather focus on non-food lignocellulosic raw materials. To be economically attractive, cellulose-to-ethanol processes need to adopt an integrated approach and to valorize as much material as possible. These processes, in addition to carbohydrates, also aim at isolating lignin in good yields and purity, for high added-value applications (Duval and Lawoko, 2014). However, the organosolv processes without additional catalysts usually require high reaction temperatures (160–200 °C) to produce sufficient delignification of lignocellulosic biomass (Jang et al., 2016). The use of sodium hydroxide as catalyst during ethanol pretreatment greatly improves ethanol selectivity respect to lignin by improving the delignifying ability of ethanol (Marton and Granzow, 1982).

Once separated, the components can be processed to obtain different products. For example, oligomers and glucose can be obtained by the enzymatic hydrolysis of cellulose and they can finally be fermented to produce bioethanol (Dagnino, 2012). Huijgen et al. applied a three stages treatment to fractionate wheat

straw, using an aqueous pretreatment to hydrolyze hemicelluloses into monomeric sugars, then an organosolv ethanol-water delignification, and finally, an enzymatic hydrolysis of cellulose. The authors showed that the aqueous pretreatment prevented degradation of hemicelluloses in the subsequent step (organosolv process) and that the enzymatic digestibility of the solid material after organosolv delignification was improved by prehydrolysis from 49 to 80% (Huijgen et al., 2012). Furthermore, Wildschut et al. evaluated the organosolv process without pretreatment, obtaining a partial separation of the components i.e., a solid constituted by cellulose, hemicelluloses, and lignin, and a liquid containing xylose and lignin, without referring to inorganic components, possibly because they were not significant in the raw material (Wildschut et al., 2013).

The aim of this work was to optimize the delignification of the hemicelluloses-free fraction of rice husk. The soda-ethanol-water process was used to obtain fractions of lignin, cellulose, and inorganics, which could be valorized in the context of the rice husk biorefinery. The soda process is the most suitable and historically used for grasses. The addition of ethanol facilitates the removal of the hydrolyzed lignin, given its chemical affinity. Preliminary tests were conducted using variants of soda and ethanol delignification to have a basis for comparison. Two experimental designs were carried out to evaluate different ranges of the same variables (strong and light conditions), aiming to promote maximal delignification or delignify while protecting carbohydrates.

2. Materials and methods

2.1. Raw materials and supplies

Rice husks (RH), *epagri* variety, was provided by a local industry (rice processing in the of Chaco province, Argentina). The raw materials were milled (mill-colter grinder, 22000 rpm) to a size less than 10×1 mm. The milled material was stored in a closed container at room temperature until further use.

2.1. Characterization of raw materials and reaction products

Preparation of the samples was carried out following the procedure "Preparation of samples for compositional analysis," NREL/TP-510-42620. Determination of total solids and moisture was made according to NREL/TP-510-42621, using the method of convection oven. Extractable substances in water and ethyl alcohol were evaluated as specified in NREL/TP-510-42619. Inorganics were determined in the solid sample free of extractives according to the procedure specified in NREL/TP-510-42622. The composition of structural carbohydrates and lignin in biomass was carried out according to procedure NREL/TP-510-42618. Structural carbohydrates and sugars were quantified by high resolution liquid chromatography (Waters HPLC System), with an Aminex-HPX87H (BIO-RAD) chromatographic column using the following conditions: 4 mM H₂SO₄ as eluent 0.6 ml/min, 35 °C, using a refractive index detector for the quantification of sugars and a diode array detector for the quantification of degradation products.

2.2. Fractionations

2.2.1. Acid pretreatment

Hemicelluloses-free RH was obtained by diluted acid fractionation. The original RH was pretreated with a sulfuric acid solution 0.3%w/v, at 152 °C, according to the optimized process for RH detailed in a previous work (Dagnino et al., 2013). In this process, the original RH is mixed with the acid solution; the mixture is placed in the reactor and heated with steam at 152 °C (5 atm vapor

pressure). After 33 min of reaction, the heating is stopped and the solid is separated from the liquid.

2.2.2. Preliminary trials

A series of chemical fractionations were accomplished to select the most suitable conditions. The following preliminary treatments were applied: (a) soda-antraquinone, (b) ethanol-water, (c) ethanol-water catalyzed with acid, and, (d) ethanol-water catalyzed with alkalis (sequences and conditions are exposed in Table 1). These tests were conducted over the original raw material and over the acid pretreated RH (hemicelluloses-free RH). Levels of variables to be used in the optimization designs were selected by selecting the most suitable fractionation conditions (Table 2). All fractionations were carried out in a 180 ml AISI 316 stainless steel reactor, heated in a bath of silicon at 160 °C for 60 min, in a proportion of 10% solids, without agitation. This relatively simple equipment produces results which are easily scalable to higher volumes. Time to maximum temperature was about 25 min. After the reaction time, the reactor was placed in a cold water bath.

After all treatments, the liquid-solid mixtures were filtered by a 100 mesh screen and the pretreated solids were washed repeatedly with distilled water to remove the remaining solution. The solids were cooled to 4 °C until characterization. Lignin, carbohydrates and inorganics concentrations were determined in the solid fraction.

2.2.3. Optimization of the delignification process

Response surface methodology (RSM) is conformed by a collection of mathematical and statistical techniques. It is usually used for modeling and analyzing systems in which a response of interest is influenced by several variables, allowing the optimization of the processes (Montgomery and Runger, 2002). A central composite design is the most commonly used response surface designed experiment, composed by a factorial design with center points plus axial points (also called star points) to estimate curvature. The design allows the optimization of all parameters in the mathematical model with a relatively small number of tests (Montgomery, 1991).

Soda-ethanol-water process was optimized following two scenarios: design A (carried out in severe conditions), seeking maximum delignification, and defined on the base of results obtained in the preliminary trials and supported by the literature (de Carvalho et al., 2014); and design B (in light conditions), looking for the least components degradation. The optimization of the selected fractionation process was carried out through two Central Composite Experimental Designs (A and B), both with two replicas

of the center point, varying sodium hydroxide concentrations and the ethanol: water proportion (EtOH:H₂O):

- A.) NaOH: 9.0–17 g/l of solution (9.0–17%OD NaOH) and EtOH: H₂O proportion: 46:54 to 60:40.
- B.) NaOH: 1.9–8.0 g/l of solution (1.9–8.0%OD NaOH) and EtOH: H₂O proportion: 26:74 to 54:46.

Coded and real values are shown in Table 3. Results were analyzed using multivariate analysis of variance (ANOVA). Statistical analysis was performed by Statgraphics software at 95% level of significance.

3. Results and discussions

3.1. Preliminary trials

Initial RH (RH₀) was composed of 48.7% of carbohydrates (34.1% cellulose and 14.6% hemicelluloses), 17.2% of acid-insoluble lignin (AIL), 1.8% of acid-soluble lignin (ASL), 15% of inorganics (In), and 8% of alcohol-water extractives.

Results of preliminary experiences are shown in Table 1.

Lignin content in RH treated with dilute acid, ethanol-water and soda-antraquinone decreased from 17.2% to 13.5%, 15.0% and 5.2% on oven dry weight of RH₀ (OD RH₀), respectively. Delignification with dilute acid and with ethanol-water (also acidic by autohydrolysis) was not significant, agreeing with which was obtained by other authors (Ang et al., 2013). This was possible due to the presence of waxes and gums on the surface of the RH that hinder the entry of reagents (Jahan and Rahman, 2012).

On the other hand, an important removal of lignin was achieved with the soda-antraquinone process. Yields of the acid, soda and organosolv processes were 52%, 55%, and 73%, respectively. These data confirm that the organosolv treatment without catalysis barely access to the rice husk matrix. Trial 5 (ethanol-water delignification of RH₀ with alkaline catalyst), shows that the alkaline catalyzed process reduced lignin content from 15.0 to 6.2%OD RH₀.

The lowest lignin content in the solid (1.8%OD RH₀) was produced by the acid pretreatment followed by the soda-antraquinone process. However, as an alternative to the use of anthraquinone, promising results were obtained by acid pretreatment followed by alkaline organosolv (2.5%OD RH₀).

To better study the soda-ethanol-water system (from now on, SodEW), the experimental design included the raw material (RH original and RH pretreated with acid), NaOH concentration (0, 2 and 10%), and ethanol:water ratio (0:100 and 50:50) as independent variables. Results are shown in Table 2.

Table 1
Acid-insoluble lignin (AIL) remaining in the solid after different rice husk treatments (preliminary trials).

Trial	Treatment conditions*	AIL (%OD)	AIL (%OD RH ₀)
1	RH ₀ (without treatment)	19.0	19.0
2	RH ₀ + EtOH:H ₂ O 50:50; 160 °C; 60 min	20.5	15.0
3	RH ₀ + Acid pre-hydrolysis (p-h RH)	26.0	13.5
4	RH ₀ + EtOH:H ₂ O 50:50; 2% NaOH; 160 °C, 60 min	12.2	6.2
5	RH ₀ +10% NaOH; 0.1%AQ; 160 °C; 60 min	9.5	5.2
6	p-h RH + EtOH:H ₂ O 50:50; 1% H ₂ SO ₄ ; 160 °C, 60 min	19.0	7.7
7	p-h RH + EtOH:H ₂ O 50:50; 2% NaOH; 160 °C, 60 min	12.2	5.6
8	p-h RH + EtOH:H ₂ O 50:50; 160 °C, 60 min	13.4	4.6
9	p-h RH + EtOH:H ₂ O 50:50; 2% H ₂ SO ₄ ; 160 °C, 60 min	13.8	4.6
10	p-h RH + EtOH:H ₂ O 50:50; 10% NaOH; 160 °C, 60 min	8.2	2.5
11	p-h RH + 10% NaOH, 0.1%AQ; 160 °C, 60 min	6.1	1.8

RH₀: Initial rice husk.

AIL (%OD): Acid-insoluble lignin, treated solid base.

AIL (%OD RH₀): Acid-insoluble lignin, oven dry weight on RH₀ base.

Acid pre-hydrolysis conditions: 0.3%*v/v* H₂SO₄; 150 °C; 33 min.

* 10% solids.

Table 2

Acid-insoluble lignin (AIL) remaining in the solid after the preliminary tests of the soda-ethanol-water process applied to rice husk (RH).

Acid Pretreatment	Yes						No					
	0:0	0:0	0:0	50:50	50:50	50:50	0:0	0:0	0:0	50:50	50:50	50:50
EtOH:H ₂ O (%)	0:0	0:0	0:0	50:50	50:50	50:50	0:0	0:0	0:0	50:50	50:50	50:50
NaOH (%)	0	2	10	0	2	10	0	2	10	0	2	10
AIL (%OD RH ₀)	13.5	12.5	5.8	4.6	5.6	2.5	19.0	16.9	5.2	13	6.2	6.3

RH₀: Initial rice husk.AIL (%OD RH₀): Acid-insoluble lignin, oven dry weight on RH₀ base.

The analysis of variance indicated that NaOH concentration and ethanol:water ratio produced significant variations on acid-insoluble lignin concentration (*p* values: 0.03 and 0.02, respectively), whereas the effect of the acid pretreatment resulted in the limit of significance (*p*-value: 0.051).

The statistical test of multiple ranges showed that the means of residual lignin concentration differ in trials with and without ethanol (0:0 and 50:50), and also with low and high NaOH charge (0 and 2% vs. 10%).

Based on the foregoing results, pretreatment with dilute acid (Dagnino et al., 2013) followed by a SodEW process seems to be the most advantageous choice for rice husk extraction of hemicelluloses and lignin. This sequence has other benefits, as fast reaction, lower NaOH charge than the conventional soda process, anthraquinone elimination, and the possibility of ethanol recovery and reuse (Zhao et al., 2009). Chromatographic and spectroscopic characterization demonstrated that a combined acidic-alkaline treatment enhanced the degradation of the lignin-carbohydrates complexes, releasing lignin and hemicelluloses in higher yields and purity than alkaline treatment only (Barana et al., 2016).

In the above described scheme, the first acid stage extracts hemicelluloses in the form of monomers (mainly xylose) and the alkaline ethanol medium produces delignification, leaving a solid rich in cellulose (Huijgen et al., 2012). Xylose in the liquid fraction of the first stage could be recovered to produce different byproducts (Zhang et al., 2016) and lignin dissolved in the liquid fraction of the second stage can be precipitated by dilution and acidification (Vallejos et al., 2011).

Organosolv pretreatment with ethanol produces ethanol organosolv lignin, which has structural properties such as low molecular weight, high purity, and narrow molecular weight distribution. Condensation reactions are quite limited due to the presence of organic solvents, and therefore these lignins have a structure more similar to native lignin than that of those extracted by other industrial processes. Organosolv lignins increase their phenolic functionality as result of the acidolytic or alkaline cleavage of aryl ether linkages. Being also sulfur-free, they represent a good source for polymer applications (Vallejos et al., 2011). Moreover, some investigations indicated that the enzymatic hydrolysis had best result by the utilization of soda-ethanol-water pretreatment than others with only soda-water or ethanol (Kruyenskiski et al., 2015).

3.2. Optimization of the soda-ethanol-water process

The concentration of residual lignin and inorganics in the solid pretreated with acid and delignified by the SodEW process are shown in Table 3.

3.1.1. Optimization of SodEW process in severe conditions (design A)

Lignin concentrations varied from 5.18 to 1.88% OD RH₀, when medium values of NaOH and low and medium of EtOH were applied, respectively (Table 3, trials A1 to A10). Standard deviation of the replicas in the center point for acid-insoluble lignin (AIL) was 0.033%.

Table 3

Central Composite Designs A and B for the optimization of the soda-ethanol-water process applied to hemicelluloses-free rice husk: variables and percentages of residual and removed acid-insoluble lignin (AIL) and inorganics (In).

Trial	Treatment combinations (tc)				AIL (%OD RH ₀)	In (%OD RH ₀)	Removed AIL (%)	Removed In (%)	Yield (%OD RH ₀)
	NaOH		EtOH						
	Cv	%	Cv	%					
A1	-1	10	-1	48	3.30	8.54	82.62	43.08	62.03
A2	1	16	-1	30	2.63	4.61	86.18	69.25	53.51
A3	-1	10	1	58	4.88	8.13	74.30	45.79	70.35
A4	1	16	1	30	3.63	4.32	80.90	71.20	52.16
A5	-1.41	9	0	53	4.20	9.34	77.91	37.75	60.56
A6	1.41	17	0	30	4.22	3.37	77.78	77.52	52.39
A7	0	13	-1.41	46	5.18	5.69	72.71	62.07	58.96
A8			1.41	60	3.08	7.23	83.77	51.79	49.73
A9			0	53	1.94	6.74	89.79	55.07	49.27
A10					1.88	8.14	90.09	45.75	57.63
B1	-1	2.8	-1	30	5.80	9.66	69.47	35.61	87.06
B2	1	7.1	-1	30	4.08	9.01	78.51	39.92	57.42
B3	-1	2.8	1	50	5.05	9.00	73.40	40.03	65.96
B4	1	7.1	1	50	4.35	10.50	77.09	30.03	66.51
B5	-1.41	1.9	0	40	7.55	12.64	60.29	15.72	84.39
B6	1.41	8	0	40	4.02	10.82	78.83	27.87	66.15
B7	0	5	-1.41	26	5.80	11.26	69.48	24.91	74.77
B8			1.41	54	5.32	10.57	71.99	29.52	67.58
B9			0	40	4.34	9.18	77.17	38.82	61.88
B10					4.47	9.05	76.45	39.65	63.41

Cv: Coded variables.

AIL (%OD RH₀): Acid-insoluble lignin, oven dry weight on RH₀ base.In (%OD RH₀): Inorganics, oven dry weight on RH₀ base.

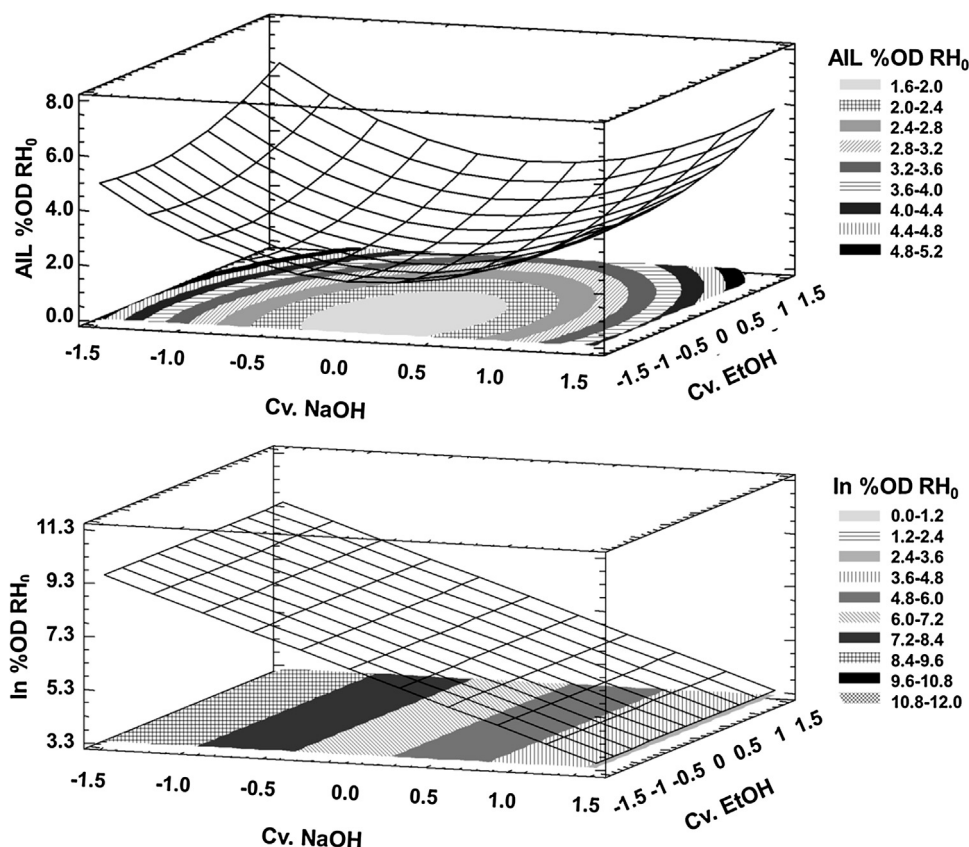


Fig. 1. Response surface of models obtained in conditions A. (a) Minimization of acid insoluble lignin (AIL) in the pretreated solid; (b) Minimization of inorganics (In) in the pretreated solid.

The contours of the response surface for AIL content (%OD RH₀) in the pretreated solid are shown in Fig. 1a.

Fig. 1a shows a minimum and two zones of relatively high concentration of AIL remnant in the pretreated solid. Best delignification of rice husk by the SodEW process (90.1% of AIL removal or 1.9%OD RH₀), was attained with 13% NaOH and 50:50 of EtOH:H₂O.

Extreme conditions produce an ineffective AIL removal, although in all cases 80% of AIL removal was exceeded. Similar results were obtained in the preliminary tests (Table 2) with AIL values of 5.6 and 2.5%OD RH₀ with the application of 2 and 10% of NaOH, respectively.

As AIL concentration is expressed as percentage on dry basis solid, it increased due to the loss of another structural component (cellulose). Therefore, at high NaOH concentrations (right area of Fig. 1a) AIL% in the solid seems to be high, surely due to cellulose degradation, that occurs when it is heated with dilute solutions of sodium hydroxide at temperatures around 170 °C (Knill and Kennedy, 2003). This hypothesis also applies to process yield, which decreases from 62% to 50% approximately (Table 3) in processes with low and high charges of NaOH, respectively.

It is also possible that an increased measure of AIL might be produced by pseudo-lignin formation. Pseudo-lignin involves different compounds that in the experimental determination resemble native lignin, but are related with the degradation of glucose to 5-(hydroxymethyl)-2-furaldehyde (HMF), levulinic acid, formic acid, and/or various phenolic compounds (Rasmussen et al., 2014).

ANOVA analysis indicated that both variables (EtOH:H₂O and NaOH) showed significant effect ($p < 0.05$) on AIL removal in the studied range and their interaction was significant too. The optimum calculated conditions were 13% NaOH (midpoint) and 50:50 ethanol:water (-0.8 as coded variable). The regression equation of

the fitted model (coded variables) is:

$$\text{AIL}(\% \text{ODRH}_0) = 3.7 - 0.5 * \text{NaOH} + 1.1 * \text{EtOH} + 2.3 * \text{NaOH}^2 + 0.6 * \text{EtOH}^2 \quad (1)$$

This adjusted model accounts for 99.7% of the variability of residual acid-insoluble lignin.

To determine an eventual influence of pH decrease on delignification on the end of the treatment, fresh liquor was added at 60 min of reaction. After additional 20 min, the percentage of residual lignin in the solid decreased by 31%. Up to this point the pretreated solid had been washed with distilled water, so another trial involved washing with 0.25N NaOH, producing 39% of additional lignin removal. These similar results indicate a possible reprecipitation of lignin by cooling. It was then decided to wash the pretreated solid with alkali to facilitate lignin extraction, resulting in a decrease of the processes yields.

Inorganics (In) decreased from 15.0% (initial content in RH₀) to 3.37% and 9.34% with the highest and lowest concentration of NaOH, respectively (Fig. 1 b). Standard deviation of the replicas in the center point for inorganics was 0.237. Only NaOH concentration resulted significant on inorganic compounds removal. The regression equation of the fitted model, accounting for 87% of inorganics variability, was:

$$\% \text{In} = 6.5 - 2.0 * \text{NaOH} \quad (2)$$

Inorganics solubilization is due to the formation of soluble silicates which remain with dissolved lignin in the spent liquor.

Theoretical and experimental optimums were 1.6% of residual AIL (equivalent to 91.6% AIL removal) and 1.1% of residual AIL (94.3% of AIL removal), respectively. Strong treatment conditions

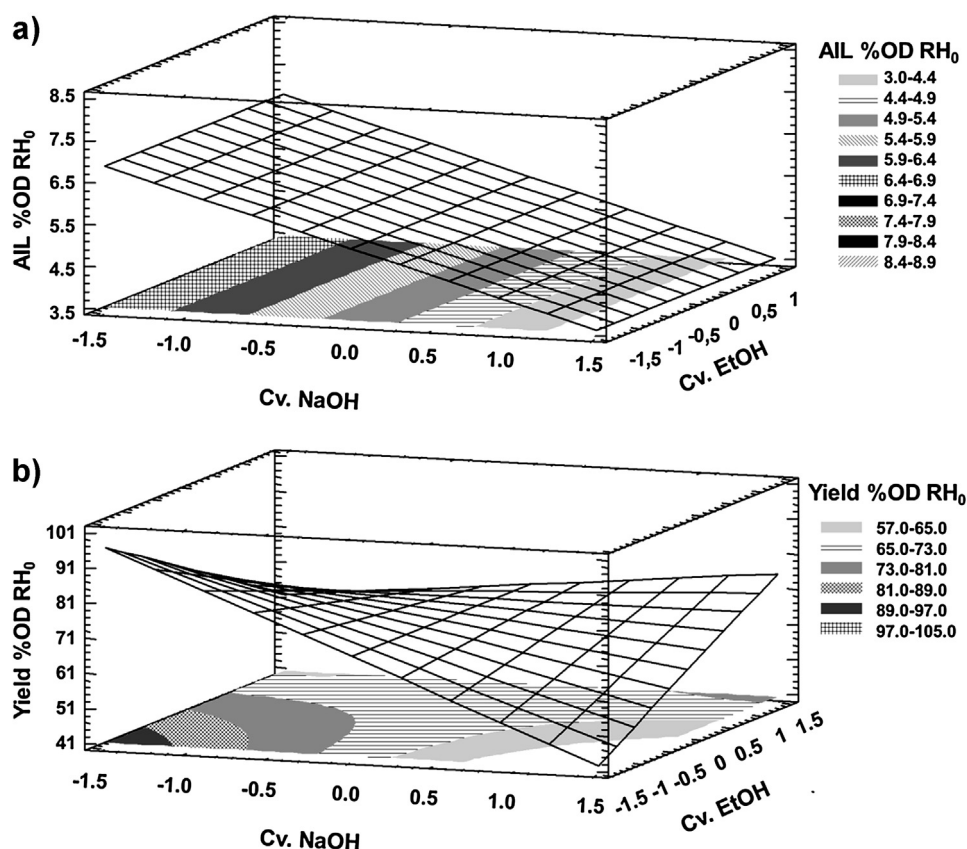


Fig. 2. Response surface of models obtained in conditions B. (a) Minimization of acid insoluble lignin (AIL) in the pretreated solid; (b) Maximization of the process yield.

(A) produced high lignin extraction, but carbohydrates were highly degraded, which is not advantageous for bioethanol production. The pretreated solid contained more than 91% of cellulose, 6.1% of lignin and 2.9% of inorganics, but about 23% of the carbohydrates were degraded to formic acid and 30% to other degradation products (being detected in the spent liquor by HPLC analysis). These degradation products could be the responsible of the pseudo lignin formation in the so-called strong conditions.

3.1.2. Optimization of SodEW process in light conditions (design B)

Lignin contents varied from 4.02 to 7.55%OD RH₀ at medium values of EtOH and low and high values of NaOH, respectively, as shown in Table 3 (trials B1 to B10). Standard deviation of acid-insoluble lignin (AIL) replicas in the center point was 0.77%.

Best delignification (AIL removal) of rice husk by the SodEW process in B conditions was 80.5% (3.7%OD RH₀ remaining in the solid). The optimum is located at 8% NaOH and 54:46 ethanol:water (both at -1.41 as coded values), (Fig. 2a). Unlike treatment under severe conditions, ANOVA analysis and contour plot of the response surface for AIL content in the pretreated solid (%OD RH₀) showed that AIL% only depends of NaOH concentration, whereas EtOH does not have an important effect in the studied range (Fig. 2a). The regression equation of the fitted model in coded variables, which accounts for 67.0% of the variability of residual acid-insoluble lignin, is:

$$\text{AIL}(\% \text{ODRH}_0) = 5.2 - 1.1 * \text{NaOH}(3) \quad (3)$$

Inorganic compounds in the solid decreased from 15.0% (initial content in RH₀) to 9.0% (maximal removal of 40%), showing that inorganics are not significantly removed when working in light conditions.

Yield was affected by NaOH and by the interaction between NaOH and EtOH:H₂O (Fig. 2b). The obtained regression equation of the fitted model in coded variables is:

$$\begin{aligned} \text{Process yield}(\% \text{OD}) = & 69.2 - 6.9 * \text{NaOH} \\ & + 7.5 * \text{NaOH} * \text{EtOH} : \text{H}_2\text{O} \end{aligned} \quad (4)$$

It is clearly seen that residual lignin is minimal when soda charge is maximum for any value of ethanol (Fig. 2a), and yield is also minimum when the soda charge is maximum (Fig. 2b). However, yield increases to maximum EtOH proportion (interaction), which means that carbohydrates loss decreases in these conditions.

The desirability function approach is the most popular method for the multi-response optimization problem. It is defined as the combined response that optimizes the response variable desired, maximizing or minimizing other response variables, simultaneously. The contour plot for the minimization of AIL content in the pretreated solid and the maximization of the process yield (equations 3 and 4) is shown in Fig. 3. The shape of the curves is the result of NaOH-ethanol interaction.

Optimal conditions correspond to the area of high concentration of both variables (+1.41 as coded values). Theoretical values at this conditions were 74% of process yield and 3.7% of residual lignin in the solid, whereas experimental values in the same conditions were 57.1% of process yield and 1.8% of AIL (90.1% of AIL removal). A pretreated solid with approximately 70.3% of cellulose, 5.7% of insoluble lignin and 24% of inorganics was obtained. Degraded carbohydrates in spent liquor accounted for 22% of in the form of formic acid. Results were better than expected, since lignin removal reached 90% and carbohydrates degradation was about half of that obtained in strong conditions. Time of reaction should also be evaluated to reduce the degradation of carbohydrates. For

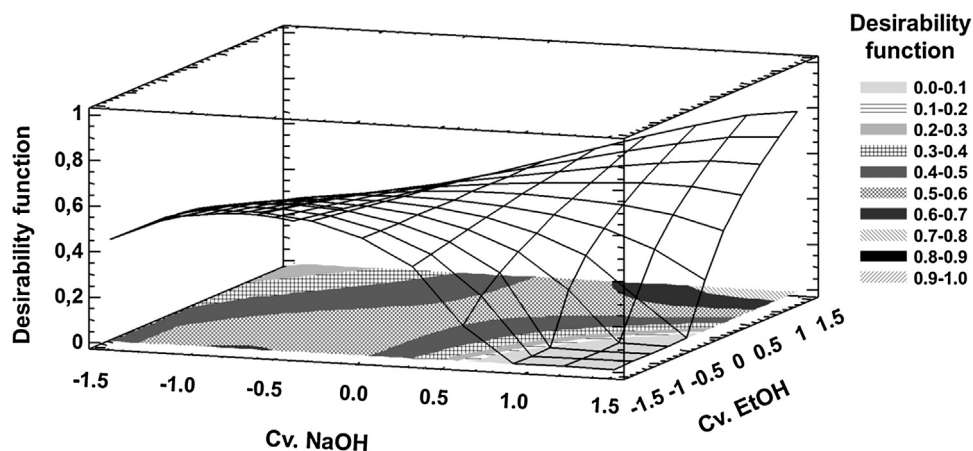


Fig. 3. Response surface of the desirability function from models obtained in conditions B (minimization of acid insoluble lignin (AIL) in the pretreated solid and maximization of process yield).

example, for sugarcane bagasse, de Carvalho et al. have found that using 15% NaOH charge, 25% ethanol at 195 °C, maximal retention of glucans and xylans was obtained at the lowest retention time of their design (90 min). Under these conditions, the glucans and xylans remaining in the pulp after cooking were of 69.0 and 41.7%, respectively (de Carvalho et al., 2014) (Fig. 4).

Residual AIL obtained by other authors using organosolv treatments and different raw materials were in most cases superior to those of this work (Table 4), except for a treatment of wheat straw using an acid catalyzed organosolv process at 179 °C for 30 min, resulting in AIL removal of 98% (de la Torre et al., 2013) and the treatment of cardoon (*Cynara cardunculus*) with peroxyformic acid at 80 °C and 90 min, with an AIL removal of 94.1%.

Most authors used higher times and temperatures than those used in this work, but soda concentrations were inferior in all cases. Nevertheless, the high NaOH concentration used for high AIL removal is offset with the reduction of consumed energy as result of low temperatures and times of reaction. Sustainable chemistry is focused on the design of products and processes that minimize the use and generation of hazardous substances. The analysis of the efficiency of chemical reactions is based on a series of parameters, through which the extent of the impact of the reactions can be assessed, by specifying the used resources and the generated waste by unit of produced mass (García Calvo-Flores, 2009). Van Aken et al. have developed a semi-quantitative analysis tool for the evaluation of the quality of a reaction based on economic and ecological

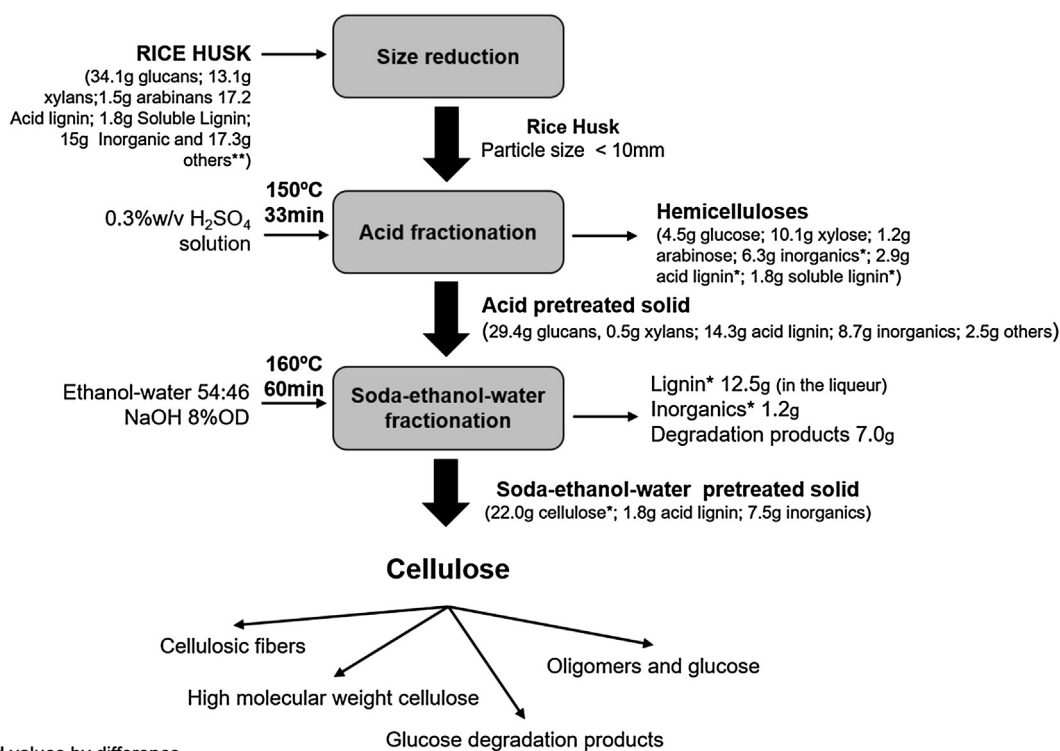


Fig. 4. Flow sheet and mass balance for a proposed rice husk biorefinery, with sequential acid and soda-ethanol-water fractionation, to obtain hemicelluloses, lignin, and a solid fraction composed mostly of cellulose.

Table 4
Bibliography reports of acid insoluble lignin obtained by different organosolv treatments applied to various raw materials.

Raw material	Time (min)	T (°C)	Reagents	Residual AIL (%)	Comments	Reference
Whet Straw	90	210	EtOH 50% w/w	7.2 (84% removal)	Milled whet straw	Wildschut et al. (2013)
	90	190	EtOH 60%w/w + 15 mM H ₂ SO ₄ catalyst	6.8 (84% removal)	Milled whet straw	
	60	200	EtOH 60%w/w	5.4 (64.2% removal)	Acid pretreated whet straw	Huijgen et al. (2012)
	30	180	EtOH 50–80%w/w, 0.01N HCl catalyst	5.8 (94.2% removal)	–	de la Torre et al. (2013)
	120	170	Acetone 80%w/w + 0.01 N HCl catalyst	2.2 (97.8% removal)	–	
Yellow poplar	10	160	Ethanol 50%w/w + 1 % H ₂ SO ₄ catalyst	2.7 (88.2% removal)	–	Kim et al. (2015)
Sugarcane bagasse	180	140	Ethanol 50%w/w + 0.01g AQ catalyst	5.8 (68.2% removal)	–	Yu et al. (2015)
	120	160	Ethanol 50%v/v + 0.5 g/L H ₂ SO ₄ catalyst	4.51 (77.3% removal)	–	Area et al. (2009)
	20	195	Ethanol 30%w/w + 3% NaOH catalyst	25% w/w in pretreated solid (yield not reported)	Acid pretreated sugarcane bagasse	Mesa et al. (2011)
Grass	90	160	Ethanol 60%	10.8% w/w in pretreated solid (yield not reported)	Organosolv and ultrafiltration	González-Alriols et al. (2010)
Miscanthus x giganteus	180	Boiling point	Acetic acid + 0.1% HCl	Maximal delignification: 1.3 (95% removal)	–	Villaverde et al. (2010)
Bamboo (Phyllostachys acuta)	120	101	Three steps: 88% formic acid 60 min + 3% H ₂ O ₂ 80 °C 60 min + 101 °C 60min	2.9 (88.8% removal)	–	Li et al. (2012)
Cardoon (Cynara cardunculus)	90	80	80% Formic acid + 5% H ₂ O ₂	1.0 (94.1% removal)	–	Ligero et al. (2008)
Rice Straw	150	60	Ethanol 75%v/v + 1% H ₂ SO ₄ catalysis	8.9 (60% removal)	–	Amiri et al. (2014)
Rice husk	180	200	1,4-butanediol 80%	4.4 (89.5% removal)	Acid pretreated rice husk	Zhang et al. (2015)
Rice husk	60	160	Ethanol 54% + 8% NaOH	1.8 (90.1% removal)	Acid pretreated rice husk	This work

parameters (Van Aken et al., 2006). A total of 6 parameters influencing the quality of the reaction conditions were established (yield, price of reagents, catalysts and solvents, safety, handling, temperature/time, processing and purification). The eco-scale value of these parameters can be obtained by the assignation of points, using an online form (<http://www.ecoscale.org/>). The ideal process has an eco-scale value of 100. In this case, using ethanol and NaOH as reagents and 160 °C of temperature for 60 min, the eco-scale value obtained for the SodEW process was 80, which can be considered as a good value to separate 90.1% of AIL from the raw material. Moreover, the used soda-ethanol-water process can be defined as a soda process additivated with ethanol more than an ethanol process catalyzed with alkali. In this sense, this process is advantageous over the soda-anthraquinone process.

3.3. Mass balance of rice husk processing by acid pretreatment ± SodEW

A flow sheet and a mass balance for 100 g RH₀ of the optimized acid pretreatment earlier followed by the SodEW process (model B in this work) are shown in Fig. 3.

The cellulose obtained as residual solid has several applications, like a source of glucose for bioethanol production. It could be fermented along with the glucose and xylose extracted in the diluted acid pretreatment.

The developed scheme of fractionation has shown to produce a residual solid rich in cellulose for further hydrolysis and fermenta-

tion, allowing also hemicelluloses, lignin, and inorganics separation for other uses.

4. Conclusions

A combined treatment of dilute acid for hemicelluloses removal followed by a soda-ethanol-water treatment for lignin extraction was applied to rice husk based on the biorefinery concept. The optimization of the delignification step was carried out, and the optimal delignification point in each studied scenario was obtained using 13 and 8 NaOH (%w/w on solid material) in 50:50 and 54:46 ethanol:water solutions, respectively. Maximal removals of lignin from the solid were 94.3 and 90.1%, and 100 and 40% of inorganics in each scenario, respectively. Optimal delignification point to avoid carbohydrates degradation was defined as 8%w/w NaOH in a 54:46 ethanol:water solution. In those conditions, lignin removal reached 90% and degraded carbohydrates accounted for about half of those produced in strong conditions which could be due to EtOH presence, which prevents carbohydrates loss from the solid.

The used soda-ethanol-water process can be defined as a soda process additivated with ethanol, showing significant advantages over soda-anthraquinone process for the fractionation of lignocellulosic materials.

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