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# Studies on lignin extraction from rice husk by a soda-ethanol treatment: Kinetics, separation, and characterization of products

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## ABSTRACT

The delignification kinetics of lignocellulosic waste is an important tool for the study of the technical-economic viability of biorefinery processes. The aim of this work was to study the kinetic of lignin extraction by a soda-ethanol treatment of hemicelluloses-free rice husk, within the framework of a biorefinery. Additionally, the type of phenolic structures in the extracted lignin and the behavior of inorganics were evaluated. The kinetic study was carried out at 140, 150, and 160 °C, at different times between 3 and 100 min of reaction for each temperature. A first order kinetic model was adjusted to the experimental data of residual lignin in the treated solid in the fast and slow phase. The kinetic constant  $k_0$  varied from 0.021 to 0.035 min<sup>-1</sup> for 140–160 °C. The activation energies were 38.59 kJ/mol and 33.47 kJ/mol for the fast and slow phase, respectively. The inorganics components remained in the solid and the proportion of silicon increased through all treatments. About 50% of the initial lignin with 1% of inorganics was recovered by precipitation. The percentage of total OH in lignin remained high, about 8.5%, and decreased with the temperature but not with the time of the reaction.

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## 1. Introduction

The study of alternative sources of bio-based products is highly required nowadays due to the increasing concerns generated from fossil resource dependence (Asgher et al., 2014; Talebnia et al., 2010). This also generates opportunities such as the production of high-value products, for example cellulose nanocrystals (Oun and Rhim, 2016), polymers or phenolic resins from lignin (Yan et al., 2017; Naseem et al., 2016), and micro and nano silica from inorganics (Barana et al., 2016; Luo et al., 2005), among others (Barakat et al., 2013; Corma et al., 2007).

In recent years, lignocellulosic biomass has emerged as a potentially renewable resource due to its renewability and quantity. A sustainable bioeconomy based on bio-resources requires the devel-

opment and implementation of biorefinery processes, including the delignification of lignocellulosic waste. For this, the delignification kinetics is an important tool for the study of its technical-economic viability. Biorefinery concept is to utilize inedible lignocellulosic biomass to produce biofuels, cellulose, hemicellulose, lignin, and bioproducts and consists in an integrate conversion system for the production of fuels, power, heat, and/or value-added chemicals from biomasses (Menon and Rao, 2012).

To take advantage of the various components of the biomass and maximize the benefit, the fractionation of lignocellulosic into the three primary components, namely cellulose, hemicelluloses, and lignin, must be performed. Total or partial fractionation of different materials is possible by treatments that depend on the material and on the

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desired end products. Each treatment process has a different specificity on altering the physical and chemical structure of the material (Brodeur et al., 2011; Sun et al., 2016).

Rice husk (RH) is an abundant residue in the Northeast region of Argentina (provinces of Corrientes, Entre Rios, Santa Fe, Formosa, and Chaco). Rice production in Argentina reached 1,558,100 tons in 2015, of which about 20% was RH (Ministry of Agriculture and Livestock of the Argentine Nation, 2016). There are approximately 134 million tons annually available worldwide and around of 90% are burned in open air or discharged into rivers and oceans with the consequent impacts on the environment (Quispe et al., 2017). Other uses are poultry litter, nurseries for flowers, concentrated feed for animals, composting components, and solid biofuels. It was determined in previous works that the rice husk was composed of 48.7% of carbohydrates (34.1% cellulose and 14.6% hemicelluloses), 17.2% of acid-insoluble lignin, 1.8% of acid-soluble lignin, 15% of inorganics, and 8% of alcohol-water extractives (Dagnino et al., 2013).

Lignin, an only naturally available aromatic polymer, has a 3-D amorphous structure consisting of methoxylated phenylpropane structure made up in general and in particular is made up of three main units: p-coumaryl, coniferyl, and sinapyl alcohols. Studies of organosolv isolated lignin from RH *Oryza sativa* (1.024 mmol H<sub>2</sub>SO<sub>4</sub> in a distilled water-ethanol mixture 1:1 v/v; 900 rpm and 180 °C for 1 h) have shown its amorphous characteristics, and an average molecular weight between 1082 and 1366 g/mol. The typical functional groups present in the aromatic region of lignin from different rice husks are hydroxyl groups in phenolic and aliphatic structures, methyl (–CH<sub>3</sub>), methylene (–CH<sub>2</sub>–/–CH<sub>2</sub>–) and methoxy (–OCH<sub>3</sub>) groups, aldehyde in  $\alpha$ ,  $\beta$ -unsaturated aldehyde or unconjugated ketone or ester (unsaturated) aldehyde group, and ketonic and ester groups. Nevertheless, compared to other biopolymers such as starch, cellulose, hemicelluloses etc. lignin is very intricate molecule since its structure and bonding between various units varies according to plant species, age of plant, type of plant, growing conditions (temperature, humidity, soil quality, time, etc.) and, most importantly, isolation procedure employed for its extraction. (Singh and Dhepe, 2016).

Alkali or acid treatments have demonstrated to be promising fractionating methods in biorefinery processes (Li et al., 2016). Moreover, the combination of dilute-acid hydrolysis with an organosolv process allows the separation of hemicelluloses and lignin in two consecutive fractionation steps. This could be useful to produce a pulp enriched in cellulose, avoiding the loss of hemicellulosic components produced in the delignification process. It has been demonstrated in a previous work that the extraction of lignin is not efficient when untreated rice husk is used (Dagnino et al., 2017; Mesa et al., 2011). This finding agrees with others studies. For example, Sarwar found that the pulp produced from pre-extracted rice straw showed improved drainage resistance, delignification, and less degradation of cellulose (Jahan et al., 2012). Dilute sulfuric acid pre-hydrolysis before an organosolv treatment demonstrated to have a favorable effect on delignification (Brosse et al., 2010). However, when the first step is performed at high severity the removal of lignin might be hindered by lignin re-polymerization through the formation of a carbonium ion intermediate, which promotes the formation of new linkages of  $\beta$ - $\beta$ ,  $\beta$ -1 and  $\beta$ -5 types (Li and Lundquist, 2000). Treating the material with adequate chemicals in a sequential biorefinery processing allows obtaining cellulose and lignin fractions of higher added value than the currently available industrial ones (Vallejos et al., 2015). Organosolv processes are also reported to produce large amounts of high-quality lignin that is relatively pure (Yáñez-S et al., 2014). The acid treatment also might increase the accessibility, allowing a more efficient delignification (Shatalov and Pereira, 2012). Lignin separation (delignification) is one of the most important chemical processes in a biorefinery. Therefore the delignification kinetics is an important tool for its technic-economic viability. This information could allow designing an optimal reactor that ensures optimum conversion and product high quality. The chemical heterogeneity of lignin, i.e. various types of structural elements and linkages with different stability within a non-linear polymer, causes the kinetic heterogeneity during the chemical processing (Shatalov and Pereira, 2005).

This work presents the kinetic study of the lignin extraction of hemicellulosic-free rice husk based on the concentration of the remaining lignin in the treated solid after a soda-ethanol-water treatment. Additionally, it was measured the OH variation in the extracted lignin and the evolution of inorganics throughout the overall process to evaluate their quality modifications due to the different treatment conditions.

## 2. Materials and methods

### 2.1. Raw materials and supplies

Rice husks (*Oryza sp*, *epagri* variety), was provided by a local industry (rice processing in the of Chaco province, Argentina). The raw material (RH) was milled to a size smaller than 10 × 1 mm in a grinder at 22,000 rpm. The milled material was stored in a closed container at room temperature until further use.

### 2.2. Treatments

The kinetics of delignification of the soda-ethanol (SodEt) treatment of hemicelluloses-free rice husk was determined.

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). Then, this hemicelluloses-free RH was treated with a SodEt process (NaOH 8% on od material and 54:46 ethanol:water relation) agreeing with the optimized treatment explained in a previous work (Dagnino et al., 2017). The SodEt delignification process was carried out in an 180 ml AISI 316 stainless steel reactor, heated in a bath of silicon, in a proportion of 10% solids (liquor:solid ratio of 10:1). After the reaction time, the reactor was placed in a cold-water bath. At the end of the treatments, the liquid–solid mixtures were filtered by a 100 mesh screen and the treated solids were washed with distilled water to eliminated residual liquor over the solid, then with 20 ml of 0.25 mol/l NaOH solution for removed any condensed lignin and finally thoroughly with distilled water again. The solids were cooled to 4 °C until characterization (determination of the concentrations of lignin and inorganics). Lignin was separated from the liquid fraction by precipitation, as described in Section 2.3.

The kinetic study was carried out at 140, 150, and 160 °C, at different times (3, 15, 30, 40, 50, 60, 80, and 100 min) of fractionations. A separate trial was performed for each time and temperature.

### 2.3. Lignin separation from the liquid fraction

Lignin was precipitated from the liquid fraction of SodEt process by acidification (Mussatto et al., 2007). The liquor was diluted with distilled water (dilution factor 1:2), then heated to 50 °C in a water bath, stirring at 10 rpm. Subsequently, the mixture was acidified with 5%v/v of a sulfuric acid solution until pH 3, and it was immediately cooled in a water bath at room temperature. The precipitated lignin was filtered with vacuum in a Buchner funnel and it was dried at room temperature in a desiccator for 24 h. The lignin was characterized by total solids and moisture, inorganics content, and OH phenolic content. The percentage of recovered lignin was determined by gravimetric analysis, according to the equation: %AIL liquor: (g AIL recovered/g AIL in free-hemicelluloses RH) \* 100.

**Table 1 – Acid insoluble lignin (AIL) and yields vs. time of the applied soda-ethanol (SodEt) process.**

Time [min]	140 °C			150 °C			160 °C		
	Yield [%]	AIL [%OD RH <sub>0</sub> ]	Removed AIL (%)	Yield [%]	AIL [%OD RH <sub>0</sub> ]	Removed AIL (%)	Yield [%]	AIL [%OD RH <sub>0</sub> ]	Removed AIL (%)
3	89.25	10.77	43.32	87.15	10.07	47.02	84.70	8.78	53.78
15	88.98	8.75	53.96	79.61	7.65	59.76	74.74	6.73	64.57
30	75.14	7.30	61.59	76.14	5.90	68.95	68.69	3.23	83.02
40	68.83	5.08	73.28	70.99	4.05	78.69	63.89	2.68	85.88
50	67.51	4.39	76.88	63.04	3.33	82.45	63.31	2.22	88.34
60	64.82	3.43	81.95	62.84	2.68	85.89	57.12	1.79	90.58
80	64.54	2.99	84.27	62.91	1.89	90.03	57.00	1.71	90.99
100	61.56	2.11	88.91	60.83	1.83	90.37	54.05	1.62	91.47

#### 2.4. Characterization of raw materials and reaction products

Solids (unpretreated and pretreated raw material) were characterized by total solids and moisture using the convection oven method (NREL/TP-510-42621). Lignin in biomass was determined according to procedure NREL/TP-510-42618. Inorganics were determined in solids samples according to the procedure NREL/TP-510-42622. For the determination of acid-insoluble ash, a sample is dry-ashed and the residue is treated with hydrochloric acid. The insoluble residue is filtered, washed, and weighed. The acid insoluble ash is mostly composed of silica or silicates, (TAPPI standard T244). Phenolic hydroxyl groups were quantified by UV spectroscopy, based on the absorption difference of phenolic units in neutral and alkaline solutions at 300 and 360 nm (Zakis, 1994).

### 3. Results and discussion

#### 3.1. Kinetic of the optimized soda-ethanol (SodEt) process

The reaction rate of the SodEt delignification process was determined by treating the acid pretreated RH in the optimal conditions found in a previous work, at different reaction times up to 100 min (Dagnino et al., 2017).

Delignification kinetics was assessed through the change in the residual lignin content in pulps, expressed as acid insoluble lignin %AIL. Results of the characterization of the treated solids are shown in Table 1. All the results were expressed as oven dry weight percentage referred to the raw material and symbolized as [%OD RH<sub>0</sub>].

The increase in the percentage of lignin removal along time was considered for the definition of the kinetics of delignification and to estimate its parameters. The fast phase and the slow phase can be clearly distinguished by the change of the slope, almost vertical in the fast step and almost horizontal in the slow step. To find the rate constant, measurements at several temperatures during two pulping runs were accomplished. Lignin removal increased with time between the ranges: 43.3–88.9, 47.0–90.4, and 53.8–91.5%, for 140, 150 and 160 °C, respectively. At 160 °C the extraction was substantial up to 50 min, with a delignification of 90%, but after that only 3.1% additional was extracted. At 150 °C the extraction might be continued 30 min more than at 160 °C, to increase about 8.0% between 50 and 80 min. The reaction at 140 °C might be continued to 100 min or more before the extraction stabilized. The rapid reaction was probably because rice straw is a porous structure with pores much larger than those of the woody plants, thus, ensuring the penetration of the cooking liquor

and a rapid delignification reaction (Ho et al., 2011). Additionally, the abundance of *p*-hydroxyphenylpropane units and free phenolic groups in monocots leads to fast removal of the first large portion of lignin, assigned to the initial fraction (Shatalov and Pereira, 2005).

A first order kinetic model was adjusted to the experimental data of residual lignin in the treated solid. Even if delignification is a second-order process, it can be treated as a pseudo-first-order reaction in most cases, knowing that the obtained first-order rate constant will depend on sodium hydroxide concentration. The reaction rate was expressed by the equation:

$$-d(\text{AIL})/d(t) = k_0 [\text{AIL}] \quad (1)$$

Where,

$-d(\text{AIL})/d(t)$  = Rate of delignification

$k_0$  = Kinetic constant

$[\text{AIL}]$  = AIL [%OD RH<sub>0</sub>]

In models like that of Eq. (1), the effect of alkali concentration on the reaction rate is usually taken into account through the kinetic constant (Santos et al., 1997). The alkali charge in the initial phase is usually consumed in the hydrolysis of acetyl side groups associated with hemicellulose polymers (Sjöström, 1981), but they are absent in this material, and in the bulk phase, the consumption of alkali for lignin dissolution is low.

By integrating Eq. (1):

$$\ln[\text{AIL}] = -k_0 t + \ln[\text{AIL}_0] \quad (2)$$

Where,  $[\text{AIL}_0]$  = Initial concentration of AIL

The natural logarithm of the AIL [%OD RH<sub>0</sub>] was plotted for all temperatures tested in function of reaction time in two stages, the fast phase, between 0 and 50 min and the slow phase, initiating in 50 and finishing when the delignification stopped, according to the temperature tested (50–60 min for 160 °C; 50–80 min for 150 °C and 50–100 min for 140 °C).

Sometimes the delignification process is considered to happen in three stages: initial, bulk, and residual (Kim et al., 2006; Shatalov and Pereira, 2005), where the residual phase consists in the cleavage of carbon-carbon linkages in lignin with degradation of carbohydrates. Other authors report only two phases, an initially fast one and an ulterior slow reaction (Area et al., 2009; Lourenço et al., 2012). In this study, the second option was used (two-step reaction), because the reaction was stopped before the last step to prevent carbohydrates loosing. Simplified models like Saeman's model (Saeman, 1945), are not suitable for delignification due to the complexity of the reactions, as consequence of the chemical

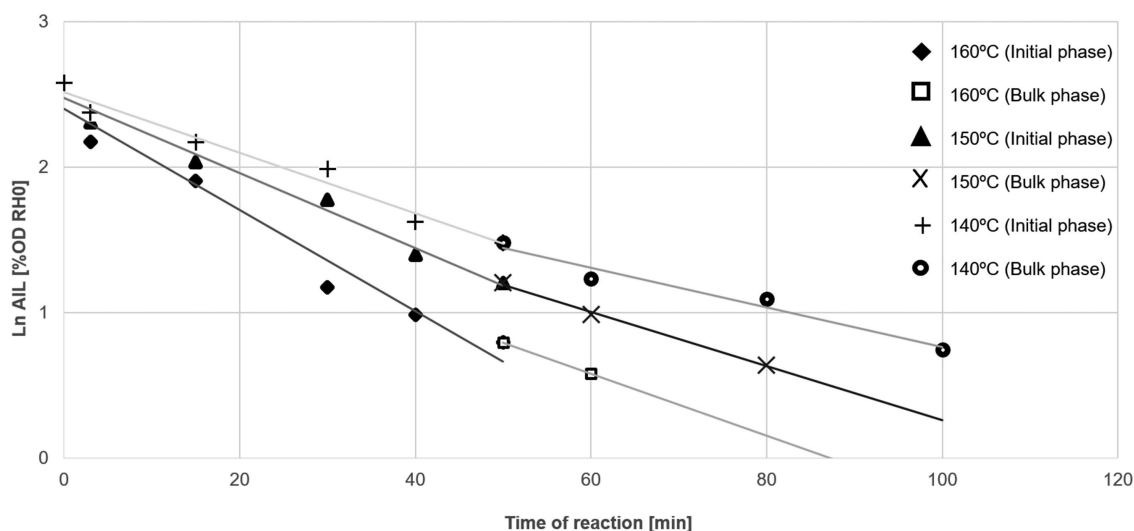


Fig. 1 – Kinetics of the soda-ethanol delignification reaction applied to hemicellulosic-free RH.

Table 2 – Regression equations ( $\text{Ln} [\text{AIL}] = -k_0 \cdot t + \text{Ln} [\text{AIL}_0]$ ) of Ln [AIL] vs. time in initial and bulk phase of the SodEt process.

Temp. [°C]	Initial phase			Bulk phase <sup>a</sup>		
	$-k_0$ [ $\text{min}^{-1}$ ]	$\text{Ln} [\text{AIL}_{0i}]$	$R^2$	$-k_0$	$\text{Ln} [\text{AIL}_{50b}]$	$R^2$
140	0.021	2.514	0.97	0.014	2.121	0.96
150	0.026	2.476	0.98	0.019	2.124	0.99
160	0.035	2.402	0.96	0.021	1.859	0.99

<sup>a</sup> Bulk phase: 50–60 min for 160 °C; 50–80 min for 150 °C and 50–100 min for 140 °C.

heterogeneity of lignin as compared with sugars. The typical plot of residual lignin content (logarithmic scale) versus time for ethanol-alkali delignification is shown in Fig. 1.

The regression equations obtained in each phase are shown in Table 2. The slope of the straight line represents the kinetic constant  $k_0$  valid for the SodEt process in the studied conditions. The rate of reaction (and  $k_0$  value) increases with the increase of temperature in the first phase and this rate is very fast since ethanol-water mixtures provide rapid and complete impregnation of the lignocellulosic material because its transport is governed by surface tension differences, allowing the fast transport of the cooking agents to the reaction sites inside the solid. This effect eliminates the need for a separate impregnation step and decreases substantially the overall cooking duration. Moreover, phenolic hydroxyl groups are ionized under alkaline pulping conditions, along with a substantial percentage of the aliphatic hydroxyl groups and some C–H bonds. The basicity of compounds should change with temperature so when the temperature increases, reaction rates generally increase due to additional vibrational energies imparted to the bonds. In addition, due to the breakdown of hydrogen bonds, hydroxide ion should be less solvated and, thus, more reactive as the temperature increases (Dimmel and Gellerstedt, 2010). The fast phase was considered between 0 and 50 min, whereas the slow phase varied with the temperature of reaction according to the time in which the reaction was considered as finished. For example, at 160 °C the percentage of removed AIL in the slow phase achieved to 90.6% at 60 min and delignification became minimum hereinafter, so it was considered that the reaction was completed at that time. At this temperature, the reaction becomes very slow so the slow reaction at 160 °C was considered to happen between 50 and 60 min. On the contrary, at 140 °C removed AIL was

76.9% in the fast phase, achieving a maximal value of 88.9% at the end of the slow phase (similar to that obtained at 160 °C and 50 min, Table 1). At 150 °C the reaction seems to stop after 80 min.

The kinetic constant  $k_0$  increased with the temperature of reaction and the obtained values were similar to those found by others authors. For example, Ho et al. found a  $k_0$  of  $0.0224 \text{ min}^{-1}$  (period 0–90 min) and a value of  $0.0089 \text{ min}^{-1}$  (period of 90–210 min) treating rice husk with tetrahydrofurfuryl alcohol/HCl (0.020HClmol/l at 140 °C), (Ho et al., 2011).

The temperature dependence of the delignification rate constants for each lignin fraction, expressed as activation energy ( $E_a$ ), was found from the logarithmic form of the Arrhenius equation:

$$\text{Ln } k = \text{Ln } A - E_a/RT \quad (3)$$

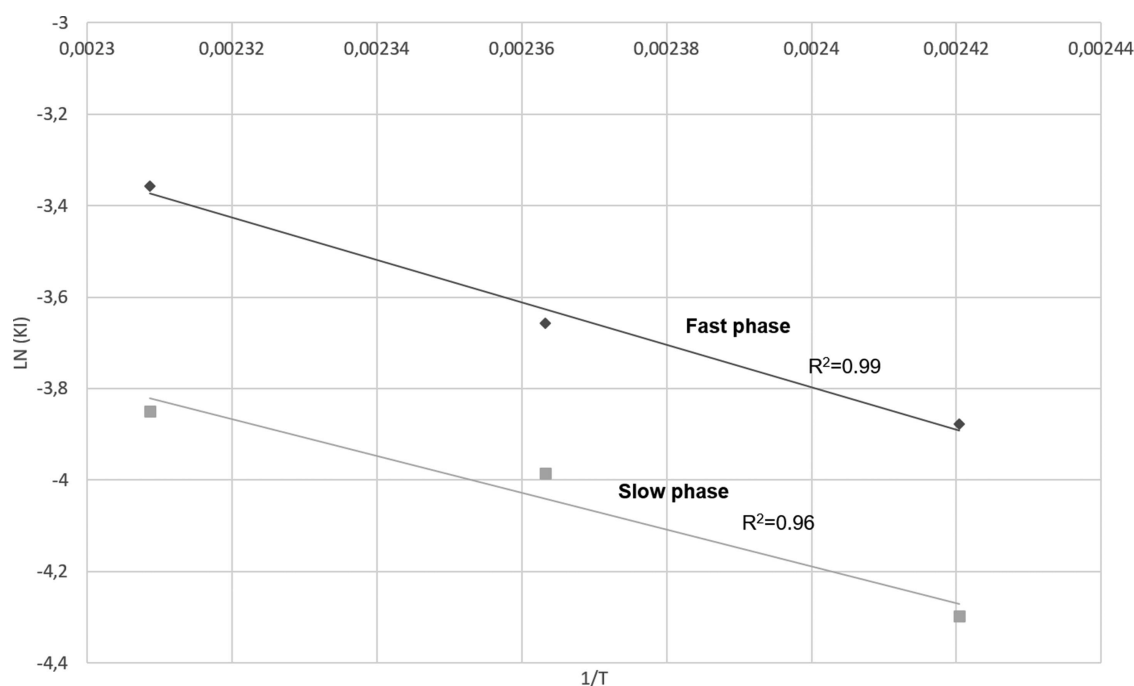
Where,

- A is the Arrhenius constant;
- R is the universal gas constant (8.314 J/mol °K);
- T is the absolute temperature.

The Arrhenius plot is presented in Fig. 2.

An activation energy of 38.59 kJ/mol ( $R^2:0.99$ ) for the fast phase and of 33.47 kJ/mol ( $R^2:0.96$ ) for the slow phase (50–60 min for 160 °C; 50–80 min for 150 °C and 50–100 min for 140 °C) can be estimated from the plot of  $\text{Ln } k$  against  $1/T$ . The  $E_a$  of the fast phase is lower than that found by others authors. For example, in the case of the organosolv delignification (alkali charge 25% as NaOH) of *Arundo donax* L. the  $E_a$  was 64.58 kJ/mol (Shatalov and Pereira, 2005) and it was of  $E_a$  of 84 kJ/mol and 70 kJ/mol using 35 and 70% of ethanol, respectively, for the organosolv delignification of a hardwood (Macfarlane et al., 2009). The activation energy found by Ho





**Fig. 2 – Logarithm of the delignification rate constant vs.  $1/T$  for the fast and slow phases in the delignification of RH free of hemicelluloses.**

et al. treating rice husk with tetrahydrofurfuryl alcohol/HCl was 26.5 kJ/mol, very similar to that of this work (Ho et al., 2011).

The removal of inorganic components did not show a variation with temperature and with time, remaining relatively constant with a value around 32.6%, so the kinetic study of the inorganic variation in the pretreated solid was not performed. However, the variation of its chemical composition was an interesting issue.

The percentage of inorganics increased through all stages, because of the extraction of the different biomass components. For example, it was 18.8% OD in the original rice husk, 24.3% OD in the free-hemicelluloses rice husk, and 33.0% OD after the delignification stage. This behavior indicates the permanence of inorganics in the solid through all the treatments. Moreover, the proportion of acid insoluble ash (silica or silicates) present in the inorganics varied from 93.6% in the  $RH_0$  to 99.7% in the free hemicelluloses RH. It was observed a little diminution in the SodEt RH with a proportion of acid-insoluble ash of 98.7%, maybe due to the presence of small quantities of Na.

### 3.2. Lignin separation from the liquid fraction

The percentage of lignin recovered by precipitation from the liquid fraction is shown in Fig. 3.

The percentage of AIL recovered from the liquor increases with time and temperature according to the results obtained in the lignin removal from the solid. The %AIL recovered varied between the ranges: 7.4–44.0, 11.5–50.0, and 12.0–52.7% for 140, 150 and 160 °C, respectively.

In Fig. 3 can be observed that the AIL recovered from the liquor increases rapidly up to 50 min (fast phase) and then stay practically constant (slow phase). The highest amount of lignin precipitated was 52.7% OD of lignin in the free-hemicelluloses RH and 70% OD of lignin present in the spent liquor obtained at 160 °C and 100 min. The yield of %AIL recovered is relatively higher than the obtained by Barana et al. in samples

of rice husk lignin (29, 46 and 51% of yield according to different extraction conditions) and in samples of *Arundo donax* (43 to 53% of yield obtained according to different extraction conditions) (Barana et al., 2016), but relatively lower to the obtained for Mussatto et al. that achieved a removal of 81.43% from of a black liquor produced by soda pulping of brewer's spent grain (Mussatto et al., 2007).

The proportions of inorganics in lignins were very low. They varied from 0.55%, 0.51% and 0.48%–1.77%, 1.59% and 1.04% at 160 °C, 150 °C and 140 °C, respectively. These results are according with the low removal of inorganics from the SodEt treated solid.

UV-spectroscopic methods for the determination of phenolic hydroxyl groups in lignin are based on the wavelength shift between ionized and protonated phenolic hydroxyl groups. The intensities of the absorbances in the ionization difference spectrum are proportional to the content of phenolic hydroxyl groups. The method is based on the difference in absorption at 300 and 360 nm between phenolic units in neutral and alkaline solutions. The content of ionizing phenol hydroxyl groups can be quantitatively evaluated by comparing the values of substances studied at certain wavelengths to the values of the respective model compounds (I, II, III, IV types), as shown in Fig. 4 (Lin and Dence, 1992; Vallejos et al., 2011).

The phenolic hydroxyl content determined for the lignins obtained by precipitation from the liquid fraction of the applied SodEt process are presented in Fig. 5. In this figure, it can be observed the great preponderance of the structure I, least reactive (due to the absence of carbonyl groups). For the same reason, the next main structure is III. In addition, it is noted the effect of temperature, as the total OH concentration decreases from 8.91% at 140 °C to 8.05% at 160 °C. On the contrary, the time of the reaction did not show a significant effect in the percentage of OH.

The phenolic OH content in lignins is very variable and depends on the type of process used for its extraction. For example, Schorr et al. found higher phenolic hydroxyl contents in Kraft lignins (5.23–8.24%) than in pyrolytic (4.04%)

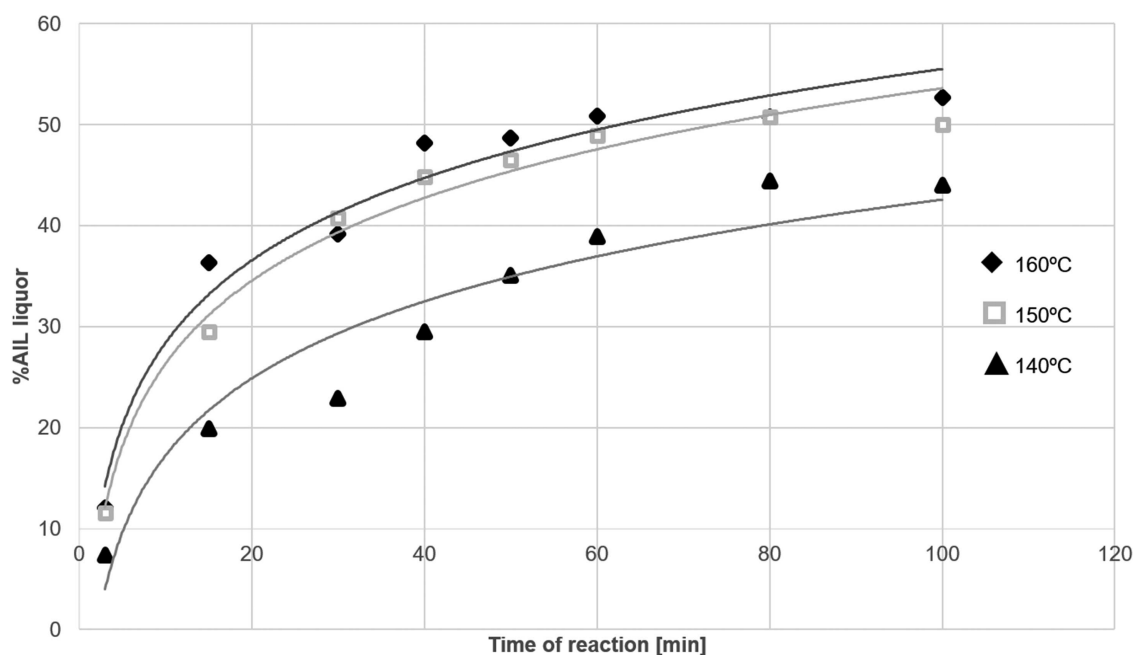


Fig. 3 – Percentage of lignin recovered from the liquor by precipitation.

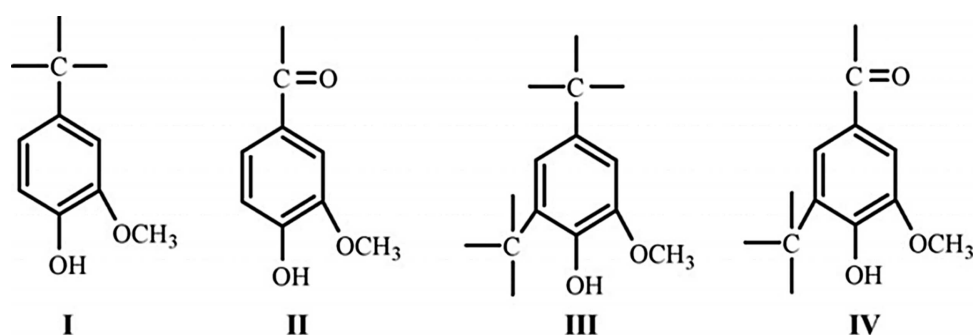


Fig. 4 – Types of phenolic structures determined by the UV method (Zakis, 1994).

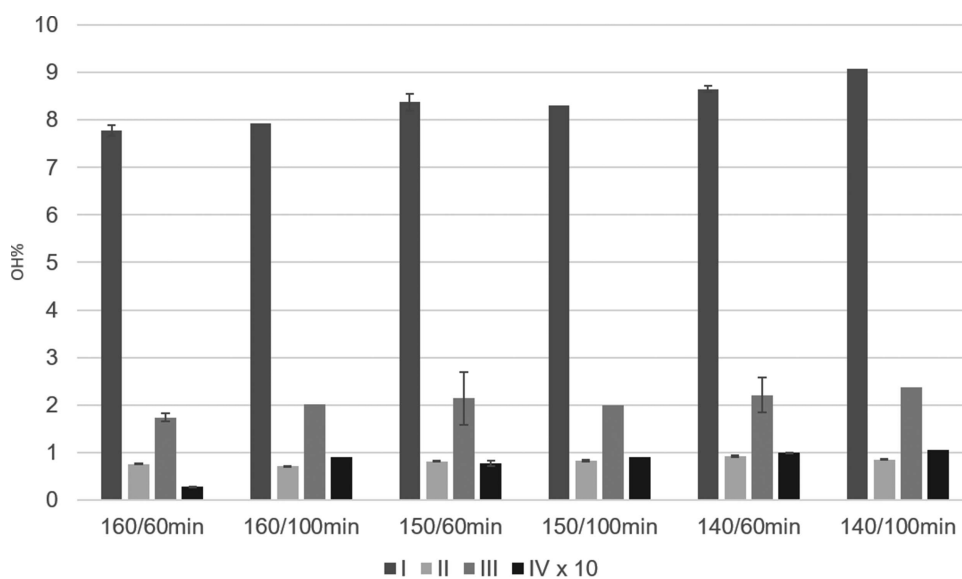


Fig. 5 – Phenolic hydroxyl contents of lignins obtained by precipitation from the liquid fraction of the applied SodEt process.

or Soda lignins (4.88%). Relatively milder pulping conditions did not allow for extensive fragmentation through cleavage of ether linkages. Moreover, the phenolic hydroxyl content of softwood Kraft lignin (5.79–8.24%) was higher than that of hardwood Kraft lignin (5.23%) (Schorr et al., 2014).

The percentage of OH obtained in this work are higher than those obtained by others authors in similar processes. In the case of the characterization of lignins precipitated from acid ethanol–water fractionation of bagasse, the authors found that total OH in the extracted lignin was 6.45% (OHI: 0.82; OHII:

0.82; OHIII: 1.51; OHIV: 0.00) (Vallejos et al., 2011) whereas it was 2.11% for soda lignin obtained from alfa grass (OH I + III: 1.97; OH II + IV: 0.14) (Nadji et al., 2009).

#### 4. Conclusions

The lignin extraction of hemicellulosic-free rice husk increased with temperature and time. The maximal lignin removal was 91.7% at 160 °C during 100 min. A first order kinetic model was adjusted to experimental data of residual lignin in the treated solid in the fast and slow phases. The kinetic constant  $k_0$  increased with the temperature of reaction and the values 0.021, 0.026, 0.035 min<sup>-1</sup> were obtained for 140, 150 and 160 °C, respectively, being similar to those found by others authors.

The activation energy, valued as the temperature dependence of the delignification rate constants for each lignin fraction, found were 38.59 kJ/mol for the fast phase and of 33.47 kJ/mol for the slow phase.

The inorganic components in the solid pretreated did not show a great variation either with temperature nor with time and the proportion of inorganics increased compared with the original rice husk. The inorganic components remained in the solid through all the applied treatments and the proportion of silicon present in the inorganics increases too.

The maximal percentage of lignin recovered by precipitation from the liquid fraction of the applied SodEt process was 52.7% of the lignin present, containing 1% of inorganics.

The SodEt processes generated a high percentage of OH structures. The total OH concentration decreased from 8.91% at 140 °C to 8.05% at 160 °C, but the time of the reaction did not show a significant effect on the percentage of OH.

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