Deep Eutectic Solvents as pretreatment to increase Fock's reactivity under optimum conditions

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Abstract

Viscose from dissolving pulp is one of the most used fabrics in the world. However, its production involves a very hazardous compound: CS_2. Therefore, reducing its consumption is of utmost importance. In this sense, dissolving pulp can be pretreated, increasing the reactivity of the cellulose and reducing the CS_2. Deep eutectic solvents have been used in biomass pretreatment as delignifying agents since their selectivity towards lignin is high. The ones used with lignocellulosic biomass usually comprise a quaternary ammonium and an organic acid. In previous studies, the formed by choline chloride and lactic acid has excellent results among different DES. However, the optimal conditions of the treatment have not been found, which is the aim of this study. This study showed that no harsh conditions are needed to increase reactivity since temperatures below 100 ºC and time below 120 min could be used. Additionally, the study of the influence of the operating conditions led to the mathematical model of reactivity to find the optimal conditions. At the best conditions, reactivity increased to 97.97 %, with a CS_2 consumption reduction of more than 16 %.

Keywords: cellulose; deep eutectic solvents; Fock's reactivity; lignocellulosic biomass; mathematical modelling; pretreatment

Introduction

Lignocellulosic biomass (LCB) has attracted much attention in the last decade as a more environmentally compatible way to obtain energy by the production of biofuels (Borand and Karaosmanoğlu 2018) or the production of value-added chemicals (Llano et al. 2017; European Environment Agency and European Environmental Agency 2018) that might replace the ones obtained from fossil fuels (Lynam et al. 2017; Rios-González et al. 2017). Additionally, LCB can act as CO_2 sink, through the photosynthesis process (Fahriye Enda and Karaosmanoglu 2021), thus reducing net emission when biofuels are the final product.

However, these materials are not easy to manage, and some challenges must be overcome for adequate processability of the lignocellulosic material (Kumar and Sharma 2017). Thus, biomass needs a suitable pretreatment, and it can be performed by several mechanisms: Physical (Muley et al. 2019; Zhou et al. 2019), physicochemical (Arnoul-Jarriault et al. 2015), biological (Ferdeş et al. 2020) or chemical (Zhao et al. 2009; Guo et al. 2018; Wang et al. 2018; Skarpalezos and Detsi 2019).

Chemical pretreatments focus on the solubilisation of undesired components of the lignocellulosic network to avoid hindrances in the processability and increase the yield in producing the desired compounds (Geng et al. 2012). In this sense, organosolv is one of the most used techniques for the pretreatment of lignocellulosic biomass since it was first employed in the 1970s (Wei Kit Chin et al. 2020). This process characterises by the use of different organic compounds: ethanol, methanol, acetone, acetic acid, glycerol and ethylene glycol (Salapa et al. 2017; Baruah et al. 2018), and might be catalysed by the addition of acids (Pascal et al. 2019; Chotirotsukon et al. 2021), alkalis (Zhong et al. 2021; Weerasai et al. 2023) and salts (Yawalata and Paszner 2006). The role of the solvents in Organosolv process is to eliminate lignin and hemicelluloses and make cellulose more accessible to enzymatic or bacterial treatments. Additionally, one of the significant advantages of this process is that lignin is recovered raw, as organosolv lignin, and it can be further valorised into value-added bioproducts (Borand and Karaosmanoğlu 2018). However, one of the drawbacks of this technology is that harsh conditions are needed when no catalyst is used and using it can lower the conditions needed and lead to cellulose degradation (Behera et al. 2014). Recovery of the solvents is a must in this technology since large quantities of them are used, which increases the energy consumption of the global process (Teramura et al. 2016).

New solvents are being studied for their use on lignocellulosic biomass to overcome the drawbacks of other technologies. For example, Ionic liquids (IL) have been extensively studied as pretreatment of biomass as non-aqueous alternatives to organic solvents (Mora-Pale et al. 2011). IL are solvents consisting of a mixture of an anion and a cation that are liquid at room temperature (van Osch et al. 2017) which allows working with them at lower temperatures when compared with the organosolv process. They also exhibit some properties that make IL's a good option in biomass processing, such as low vapour pressure, chemical and thermal stability, non-flammability and can be tailored (Arce et al., 2020). Regarding biomass processing, these solvents have been used in the fractionation of lignocellulosic materials since they show high solubility for cellulose. Thus, dissolved cellulose can be regenerated and derivatised, depending on the application. However, IL's can fractionate the biomass by selectively removing lignin from the cellulosic network, so cellulose can be easier to process (Lee et al. 2009; Socha et al. 2014). These solvents seem to be a promising alternative for biomass processing, but some authors have pointed out some disadvantages concerning the use of IL's, such as high cost, toxicity, and environmental compatibility (Guo et al. 2018; Liu et al. 2019, 2021).

Recently, other solvents have been developed as an alternative to the ones mentioned above. These solvents are called Deep Eutectic Solvents\Systems (DES) and are mixtures of at least two components with high melting points that, when mixed at a specific ratio, become liquid and stable at room temperature. The components of the DES are Hydrogen Bond Acceptor (HBA), which usually consists of a quaternary ammonium, phosphonium or sulfonium cation, or a metal chloride, and a Hydrogen Bond Donor (HBD), which can be a carboxylic acid, alcohols, amides or sugars (Zdanowicz et al. 2018). These substances are biocompatible and available; thus, DES seem to be an interesting option regarding environmental issues, plus, they are easier to prepare when compared with IL's. In the last years, DES have been used in different areas such as metal processing (Abbott et al. 2011), biotechnology and bioengineering (Raghuwanshi et al. 2014), gas separation (García et al. 2015; Craveiro et al. 2021) or biomass processing (Majová et al. 2017). Concerning biomass processing, the use of DES presents interesting aspects, apart from the properties of DES themselves, but from the process point of view, since they can dissolve lignin with almost no cellulose losses (Francisco et al. 2012). As pretreatment of biomass, DES have been mainly used to improve cellulose processability: saccharification (Kumar et al. 2016), hydrolysis (Wahlström et al. 2016), reaction yield (da Silva Lacerda et al. 2015) or reactivity (Arce et al., 2020).

On one hand Organosolv technological application have proven to be possible, since many pulp mills operate under this pulping process. Considering production costs, the biggest differences from DES or IL delignification are the operational conditions and the chemicals used. On one hand, chemicals used for organosolv are cheap and available, however higher temperatures are required in comparison (180 ºC for 120 min)(Dornelles et al. 2021). On the other hand, DES and IL do not require such harsh conditions, generally around 100 ºC for about 60 min is enough (Kalhor and Ghandi 2019; Meeuwes 2020). Furthermore, IL compounds are more expensive than DES constituents (van Osch et al. 2017). Nonetheless, the biggest concern in these processes is the technological availability.

Nowadays, dissolving pulp is the primary source of high purity cellulose and is the raw material for the production of a wide range of cellulose derivatives such as viscose fibres, cellulose esters and ethers (Llano et al. 2018). The main use of dissolving pulp (70 % of the total demand) is the production of viscose fibres (Kumar and Christopher 2017). Reactivity plays a vital role in the viscose process. It measures the ability of chemicals to dissolve cellulose to be transformed into viscose, a form of regenerated cellulose obtained by the xanthation of cellulose. This process uses CS_2 to dissolve cellulose, a very harmful substance whose use should be reduced as much as possible, which can be possible by increasing reactivity. DES can increase reactivity, but the best conditions of the process have yet to be found. Thus, this research aims to optimise the use of DES based on a previous study that employed four different Choline Chloride (ChCl)-based DES (Arce et al., 2020).

Based on the study mentioned before, a DES consisting of ChCl and Lactic Acid (LA) was optimised to find out the best operating conditions for the pretreatment of dissolving pulp: temperature, reaction time and DES to cellulose ratio were chosen as the independent variables. Reactivity was the main control parameter. However, α-cellulose and viscosity were also considered, to maintain cellulose quality. So, the influence of the operating conditions was analysed, and a mathematical model of the process was obtained, which was later used to optimise the process. There is a lot of uncertainty regarding the influence of DES and dissolving pulp, because no other than the authors of this paper have tried to increase Fock's reactivity through DES. This article is the result of a collaboration with a pulp mill interested in increasing Fock's reactivity and reducing CS2 consumption and the manageability will be studied further in time.

Material and methods

Pulp conditioning and DES treatment

The raw material used in this study is acid sulphite dissolving pulp from a pulp mill in northern Spain (Sniace). Pulp characteristics were: Fock's reactivity, 81.3 %; alfa-cellulose, 89.1 %; viscosity, 467 mL/g. Pulp conditioning was performed to facilitate the contact between DES and pulp. Pulp was soaked and stirred in water to reach a pulp consistency of 4 %, based on the methodology by (Majová et al. 2017). To calculate the water added, initial moisture content was analysed by drying pulp in an oven/furnace until constant weight for 24 h at 105±1 ºC. Pulp moisture content was 7.8 %.

As stated before, based on previous studies, DES used in this article is a mixture of ChCl and LA. The mole ratio for the composition of DES was (1:9) ChCl:LA and reactants were weighed, mixed and heated at 80 ºC until a clear liquid was formed according to (Arce et al., 2020). Finally, pulp and DES were put together in a flask and a water bath at the desired temperature (30, 50 or 80 ºC). When the treatment was finished, the pulp was washed with tap water until the pH of the washing wastewater was nearly 7, similar to tap water. Initial pH of wastewater was between 4 and 5. Finally pulp was ready to be analysed.

Response variables: analytical procedures

To analyse the influence of the DES treatment, the following pulp quality parameters were considered: Fock's reactivity, alfa-cellulose and intrinsic viscosity, which are of utmost importance in the viscose industry. In this section, the analytical procedures are explained. All the analyses were performed in triplicates.

Fock's reactivity

Fock's reactivity measures the quantity of pulp that the CS_2 can dissolve. It also gives an idea of the accessibility of the pulp. This analysis's methodology is shown in the article by (Tian et al. 2014) . 0.5 g of oven-dried (o.d.) sample were weighed and introduced into an Erlenmeyer. 50 mL of sodium hydroxyde (NaOH) solution at 9 % were added and stirred for 15 min in a water bath at 19 ºC and 250 rpm. After stirring, 1.3 mL of carbon disulphide (CS_2) was carefully added to the Erlenmeyer and immediately sealed with parafilm to prevent CS_2 from evaporating. After 3 hours of stirring at 250 rpm, water was added until the weight was 100 g, and the sample was transferred to a falcon recipient. It was then centrifuged for 15 min at 5000 rpm to obtain two phases: the undissolved cellulose in the bottom and the dissolved sample in the supernatant. After separation, 10 mL of supernatant was transferred to an Erlenmeyer flask and 3 mL of H_2SO_4 at 20% was added to regenerate the dissolved cellulose. This solution was left to degas in a fume hood for 15-20 h.

Then, 20 mL of 68 % sulphuric acid (H_2SO_4) was added to the solution to ensure an acidic media and the solution was stirred at 250 rpm for 1 hour. When the sitting time was met, 10 mL of potassium dichromate ($K_2Cr_2O_7$) 1/6 M were added to the solution, and it was then reflux boiled for an hour to oxidise the cellulose and left to cool in a water bath and diluted until a final volume of 100 mL. Finally, 40 mL of the sample were titrated with sodium tiosulphate ($Na_2S_2O_3$), adding 5 mL of 10 % potassium iodide (KI) and using starch as an indicator. The volume of $Na_2S_2O_3$ spent was noted, and reactivity, noted as dissolved cellulose (DC), was calculated using the following equation (eq. 1):

$$DC(\%) = \frac{\left[v_1 \cdot c_1 - \left(v_2 \cdot c_2 \cdot \frac{100}{40}\right) \cdot \frac{1}{6}\right] \cdot M \cdot \frac{1}{4} \cdot \frac{100}{10.4}}{m} \cdot 100 \qquad \text{(eq. 1)}$$

Where M is the molecular weight of glucose, v_1 and c_1 are the volume and concentration of $K_2Cr_2O_7$, v_2 and c_2 are the volume and concentration of $Na_2S_2O_3$, and m is the mass of the sample.

Intrinsic viscosity

This analysis is performed according to the ISO 5351, 2010 standard. First, 0.25 gr of o.d. sample was weighed and stirred with 25 mL of deionised. Then, 25 mL of cupriethylenediamine (CED) was added to the recipient and stirred again. Afterwards, the recipient was capped, ensuring air was not inside, and stirred at 250 rpm for 30 min. The sample was put in a water bath at 25 ºC for 15 min. Finally, effusion time through a viscosimeter was measured and used to calculate viscosity. It should be noted that the sample needed for the analysis depends on the value of the expected viscosity. In these experiments, the expected viscosity range is between 401 and 650 mL/g.

α-cellulose

The main component of dissolving pulp and the primary precursor for viscose production is α-cellulose. Therefore, this value needs to be assessed and controlled. Its value should be >90 % to be considered suitable for viscose production. This analysis is performed according to TAPPI T 203 cm-99 (1999).

Before the analysis was performed, a blank analysis should be performed. It takes the same steps as a regular analysis but uses less quantity of reactants. To perform the blank analysis, 12.5 mL of 17.5 % NaOH were mixed with 12.5 mL of deionised water (H_2O) at 25 ºC. Then, 10 mL of $K_2Cr_2O_7$ 0.5 N and 50 mL of high-purity H_2SO_4 were added. The mixture was left to cool for 15 min, and 50 mL of H_2O was added and put in tap water to cool. Finally, it was titrated with 0.1 N Mohr's salt($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) using ferroin as an indicator. The volume of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was taken as Vb.

For the sample analysis, 1.6 ± 0.1 g oven-dried moisture content was also needed. Pulp samples were weighed and extracted with 75 mL of 17.5 % NaOH and stirred for 30 min at 300 rpm. 25 mL of 17.5 % NaOH and 100 mL of deionised water were added to the suspension left in a water bath at 25 ºC, for another 30 min. Then, the sample was filtrated under vacuum, and 25 mL of the filtrated was mixed with 10 mL $K_2Cr_2O_7$ and, carefully, 50 mL of 96% H_2SO_4. The sample was left to room temperature for 15 min, and

50 mL H_2O was added to the solution and left in a water bath. Finally, it was titrated under the same conditions as the blank analysis.

α-cellulose content was obtained using the following equation (eq. 2).

$$Alfa - cellulose\ (\%) = 100 - \frac{6.85 \cdot (EB_1 - V) \cdot 2}{25 \cdot mass \cdot CS} \qquad \text{(eq. 2)}$$

CS_2 consumption reduction

The objective of increasing Fock's reactivity is to reduce CS_2 when pretreated with DES. To estimate CS_2 consumption reduction, the method published by (Arce et al. 2020) was used. Considering Fock's reactivity as a reaction yield of xanthation and α-cellulose content of the pulp, the theoretical quantity of fibre (TF) can be obtained using (eq. 3).

$$TF\ (\%) = \frac{alfa - cellulose\ (\%) \cdot Reactivity\ (\%)}{100} \qquad \text{(eq. 3)}$$

Using the stoichiometric value of CS_2 required for the xanthation phase, 23.5 % w CS_2/w cellulose (Gondhalekar et al. 2019), CS_2 consumption can be calculated by (eq. 4).

$$CS_2 (\%) = \frac{\alpha - cellulose\ (\%) \cdot 23.5}{100} \qquad \text{(eq. 4)}$$

CS_2 consumption needs to be calculated also considering the quantity of theoretical fibres in the sample. Therefore, the ratio CS_2/TF was measured and called the ratio of consumption per fibre (RCF) as follows in (eq. 5).

$$RCF = \frac{CS_2\ (\%)}{TF\ (\%)} \qquad \text{(eq. 5)}$$

Experimental design

Based on previous work, the best DES mixture for the pretreatment of dissolving cellulose is composed of choline chloride and lactic acid (ChCl:LA) at 1:9 mole ratio (Arce et al., 2020). In this work, a Box-Behnken design (BBD) was applied for cellulose pretreatment optimisation. A Three-level-three-variable BBD based on response surface methodology (RSM) was carried out. RSM is a combination of mathematical and statistical methods widely used to optimise chemical reactions and the interactive influences between individual factors (Song et al. 2018).

The levels of the factors are shown in Table 1. Each factor coded as X_1 (DES to cellulose ratio, in w/w), X_2 (temperature, in ºC), and X_3 (time, in min) was varied over three levels between -1 and +1 at the determined ranges.

The number of assays was determined following (eq. 6). As seen in Table the BBD does not contemplate any experiment where all factors simultaneously reach the maximum level (+1) (Gil 2020).

$$N = 2k \cdot (k - 1) + n_c \qquad \text{(eq. 6)}$$

Where k is the level number, and n_c is the number of central points. In this case, k and n_c are equal to three, and the total number of assays resulted in 15.

Table 1. Factors and levels of the BBD-RSM design.

Assay N°	**DES-cellulose ratio** w/w	**Temperature** °C	**Time** min
1	0	1	1
2	1	0	-1
3	0	-1	0
4	-1	0	0
5	1	0	1
6	-1	1	0
7	1	1	0
8	0	-1	1
9	-1	0	1
10	-1	-1	0
11	0	1	-1
12	1	-1	0
13	0	0	0
14	0	0	0
15	0	0	0

Factors	**Levels**		
	-1	0	1
X_1: ratio (w/w)	1:1	10.5:1	20:1
X_2: T (°C)	30	55	80
X_3: t (min)	30	105	180

The data obtained from the BBD experiments were analysed by Stat Graphics Centurion XVII.II software and a statistical model with response surface curves were given. The model was described by a second-order regression equation eq.7.

$$Y = b_0 + \sum b_i \cdot X_i + \sum b_{ii} \cdot X_i^2 + \sum b_{ij} \cdot X_i \cdot X_j \qquad \text{(eq. 7)}$$

Where Y is the response variable, also called dependent variables, in this case, Y_1 reactivity (%), Y_2 cellulose content (%), and Y_3 intrinsic viscosity (mL/g); X_i and X_j are the i, jth independent variables, in this case, X_1 ratio (w/w), X_2 temperature (°C), and X_3 time (min); b_0 is the offset term (constant); b_i is the coefficient of the linear parameter X_i; b_{ii} is the coefficient of the quadratic parameters X_i^2; and b_{ij} is the coefficient of the interaction parameters X_i and X_j.

Analysis of variance (ANOVA) was conducted to assess the adequacy of the response surface model and the significance of independent variables and interaction parameters in the model.

Results

Influence of the individual effects

Figure 2 shows the effect of the independent variables (temperature, ratio DES:biomass and time) on reactivity, α-cellulose, and viscosity.

As can be seen from figure 2, increasing temperature increases the reactivity and reduces the alfa-cellulose content. Therefore, increasing temperature enhances the effect of DES. It should be noted that the reduction of cellulose does not mean it is destroyed; the effect is that acidic DES catalyse the cleavage of glycosidic bonds of cellulose (Mnasri et al. 2022). This effect is specially enhanced because lignin content in dissolving cellulose is low. Plenty of literature states that DES selectively dissolves lignin over cellulose. 95.5 % of lignin dissolution using microwave-assisted DES extraction of cocoa beans was reached in the literature (Mao et al. 2023). Other authors used DES treatment to isolate lignin from bamboo biomass. Some authors found a maximum dissolution ratio of 91.32 % and an increase of nearly 45 % in cellulose (Zhang et al. 2023). Others found that ChCl-derived DES can dissolve lignin and starch with a negligible solution of cellulose (Francisco et al. 2012; Kumar et al. 2016; Tan et al. 2018; Yiin et al. 2023). In the current study dissolving pulp is used, which shows mid-to-high crystalline behavior around 80% based on XRD experiments. In a previous study by the same authors, using the same raw material, it was demonstrated that acidic ChCl-based DES shows negligible solubility of cellulose even with low lignin content (Arce et al., 2020). As a result, considering the effect of temperature, it is recommended to operate at temperatures below 55 ºC, because higher temperatures reduced cellulose content below 90 %.

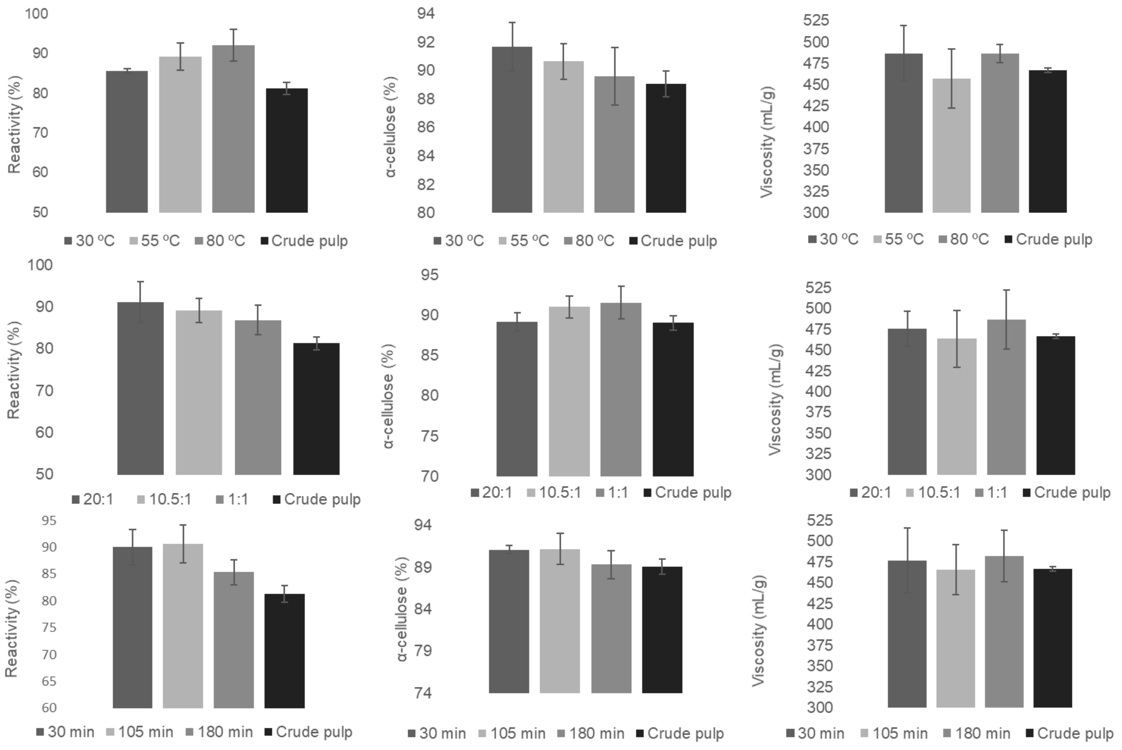

Figure. 2 Results of the quality pulp response variables as a function of the individual independent variables. From top to bottom: Temperature, DES ratio and time.

The ratio of DES to biomass was studied as well. As seen in the previous figure, increasing the DES:biomass (w/w) ratio increases reactivity and reduces the alfa-cellulose content. When the temperature increases to 80 ºC, the highest value for reactivity is obtained. However, α-cellulose is the lowest. The reduction in α-cellulose content shows that using higher values for the operating conditions degrades cellulose, so reaction points are created. These reaction points increase the accessibility for the chemicals and, thus, the reactivity. These results agree with the previous study by previous studies. Increasing the DES:biomass (w/w) ratio from 5:1 to 20:1 increased reactivity, alfa-cellulose and viscosity (mL/g) when compared to the untreated pulp (Arce et al., 2020). Other authors also proved the reactivity increase produced when bamboo dissolving pulp was treated with ChCl:LA. Other authors found an increase from 40 % to about 55 % in reactivity (Duan et al. 2023a).

Time has a similar effect on the pretreatment of pulp. In the range of the reaction time studied, intermediate times (105 min), reactivity increases (from 81.3 % to 90.6 %). Increasing reaction times to 180 min reduces reactivity compared to the results at 105 min. This effect is also observed in α-cellulose content. Considering the mild conditions for the pretreatment regarding time and temperature, it can be said that this process is not energy intensive. As a result, energy demand for the process would be acceptable. Viscosity is not influenced by any of the operating conditions proposed in this study. However, the values obtained for the pulp are between an acceptable range (400-450 mL/g) to be considered for viscose production (China National Standard Press 2010). Thus, even though the lowest value for viscosity is obtained in the intermediate range for time and temperature, it is still high enough to be considered for viscose purposes.

Regarding viscosity, there is an initial increase when considering all the variables. The reason for the increase is attributed to the selectivity that DES present towards delignification, since eliminating lignin leads to cellulose release, which increases viscosity shown in the evolution of α-cellulose content. Viscosity then decreases for the intermediate values of the independent variables, this is an indicative of cellulose degradation (Carvalho et al. 2000; Johansson and Germgård 2008), and this also can be seen on the cellulose tendency which is decreasing. However, there is a sudden increase in the viscosity at the most severe conditions (80ºC, 20:1 g DES: g biomass, 180 min), even though α-cellulose still decreases. Authors attribute this phenomenon to the release of hemicellulose. Whenever lignin content reaches a minimum value, DES starts to degrade α-cellulose which increases pentosan content which can soften the viscosity reduction due to cellulose degradation (Arce et al., 2020). Additionally, in that study, viscosity also increased when the ratio DES to biomass was 20:1.

Other studies have used DES to increase accessibility of cellulose on other biomasses (Ruesgas-Ramón et al. 2017; Zdanowicz et al. 2018; Husanu et al. 2020; Mnasri et al. 2022). Some authors have used ammonium thiocyanate and urea DES to increase biomethane production from corn stover. Specifically, biomethane production was increased by 48 % when biomass was pretreated at a 1:2 biomass:DES ratio and 100 ºC and 60 min (Olugbemide et al. 2021).

As seen from the previous results, it can be said that DES treatment increases pulp quality for viscose purposes since reactivity is increased without compromising alfa-cellulose content. Furthermore, viscosity changes are within limits considered for good-quality viscose.

Mathematical modelling and statistical analysis

The analysis of the individual effects led to the obtention of the coefficients used for the mathematical modelling (Table 2).

Table 2. Coefficients of the mathematical adjustment for each dependent variable and ANOVA table.

DES treatment factors	**Y_1: Reactivity**			**Y_2: α-cellulose**			**Y_3: Viscosity**		
	b_{ij}	**F-Ratio**	**p-values**	**b_{ij}**	**F-Ratio**	**p-values**	**b_{ij}**	**F-Ratio**	**p-values**
Intersection	76.24	-	-	89.48	-	-	656.11	-	-
X_1:ratio	-0.14	12.07	0.018	-4.01E-03	7.34	4.23E-02	-11.09	0.32	0.596
X_2:temperature	0.25	27.66	0.003	5.49E-02	5.61	6.41E-02	-4.98	0	0.988
X_3:time	0.11	14.3	0.013	5.91E-02	4.13	9.77E-02	-0.46	0.07	0.798
X_1X_1	-4.59E-03	0.21	0.667	-8.28E-03	1.38	2.94E-01	0.23	2.25	0.194
X_1X_2	7.01E-03	3.65	0.114	1.79E-04	0	9.47E-01	3.59E-02	0.41	0.552
X_1X_3	7.37E-04	0.36	0.573	4.25E-04	0.24	6.42E-01	3.51E-02	3.5	0.120
X_2X_2	-1.09E-03	0.57	0.485	-2.43E-04	0.06	8.21E-01	5.10E-02	5.25	0.071
X_2X_3	-6.85E-04	2.18	0.200	-6.76E-04	4.29	9.32E-02	-9.72E-03	1.86	0.231
X_3X_3	-5.30E-04	10.79	0.022	-1.82E-04	2.57	1.70E-01	3.15E-03	1.62	0.260
Statistical data									
Number of experiments	15			15			15		
R^2	93.44			83.45			73.9341		
R^2-adjusted	81.65			53.8			27.015		
Sum-Square errors	15.1825			14.3786			3578.1		
p-value	0.017			0.13			0.32		
Standard error	1.74			1.22			13.8956		
Total d.f	14			14			14		
Model d.f	9			9			9		
Error d.f	5			5			5		

Pareto plots are obtained using the p-values from the mathematical model. P-values determine whether the factor considered significantly influences the variable observed. If p-values are lower than 0.05, the factor has a significant effect with a 95 % confidence level. Additionally, the effects with a p-value higher than 0.05 can be eliminated from the final equation, thus simplifying the mathematical expression. Pareto plots are shown in Figure 3.

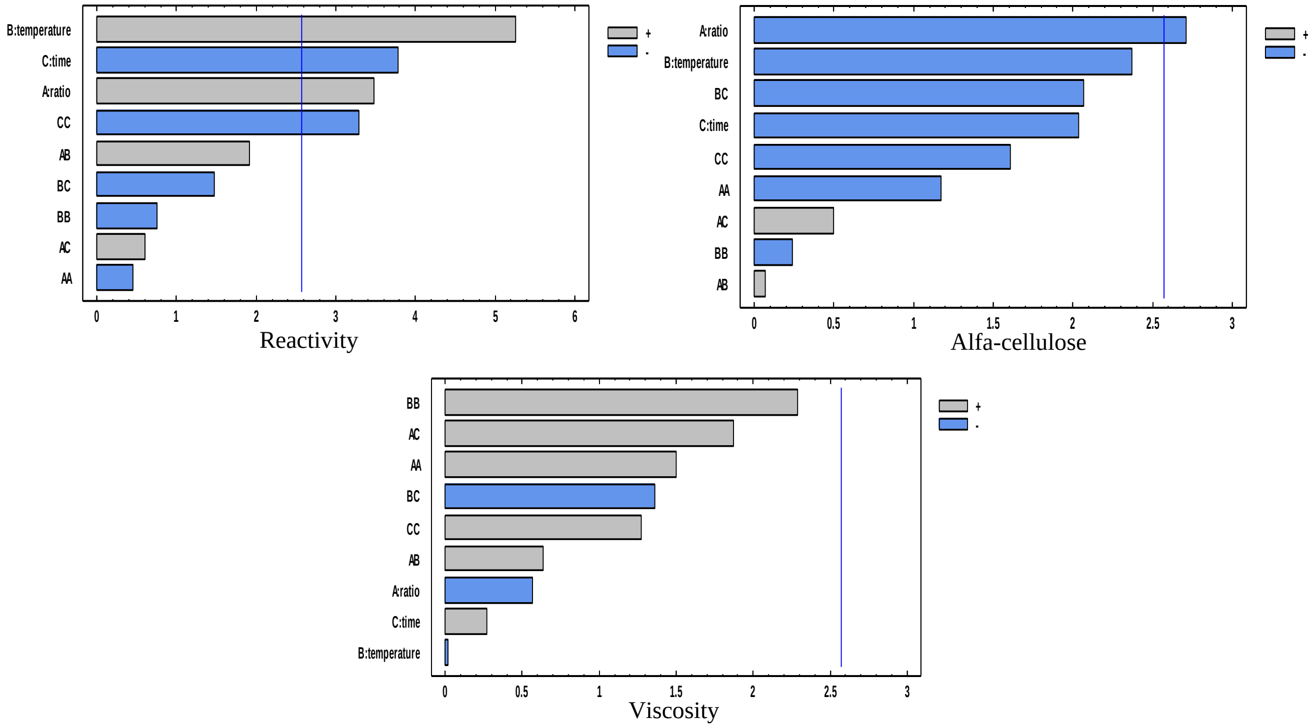

Figure. 3 Pareto plots for the three pulp quality parameters.

Using eq. 2 and the coefficients in Table 1, it was possible to build a mathematical expression to predict pulp quality. This expression considers the influence of the lineal and quadratic factors. From the pareto plots, some factors could be eliminated from the mathematical expression, p>0.05. However, all the factors were considered to observe the model's accuracy and the errors. The parity plots determined the model's accuracy, representing the modelled, real values, and confidence bands. They allow to identify how close to the real values are the modelled values. Figure 4 shows the parity plots for each quality parameter.

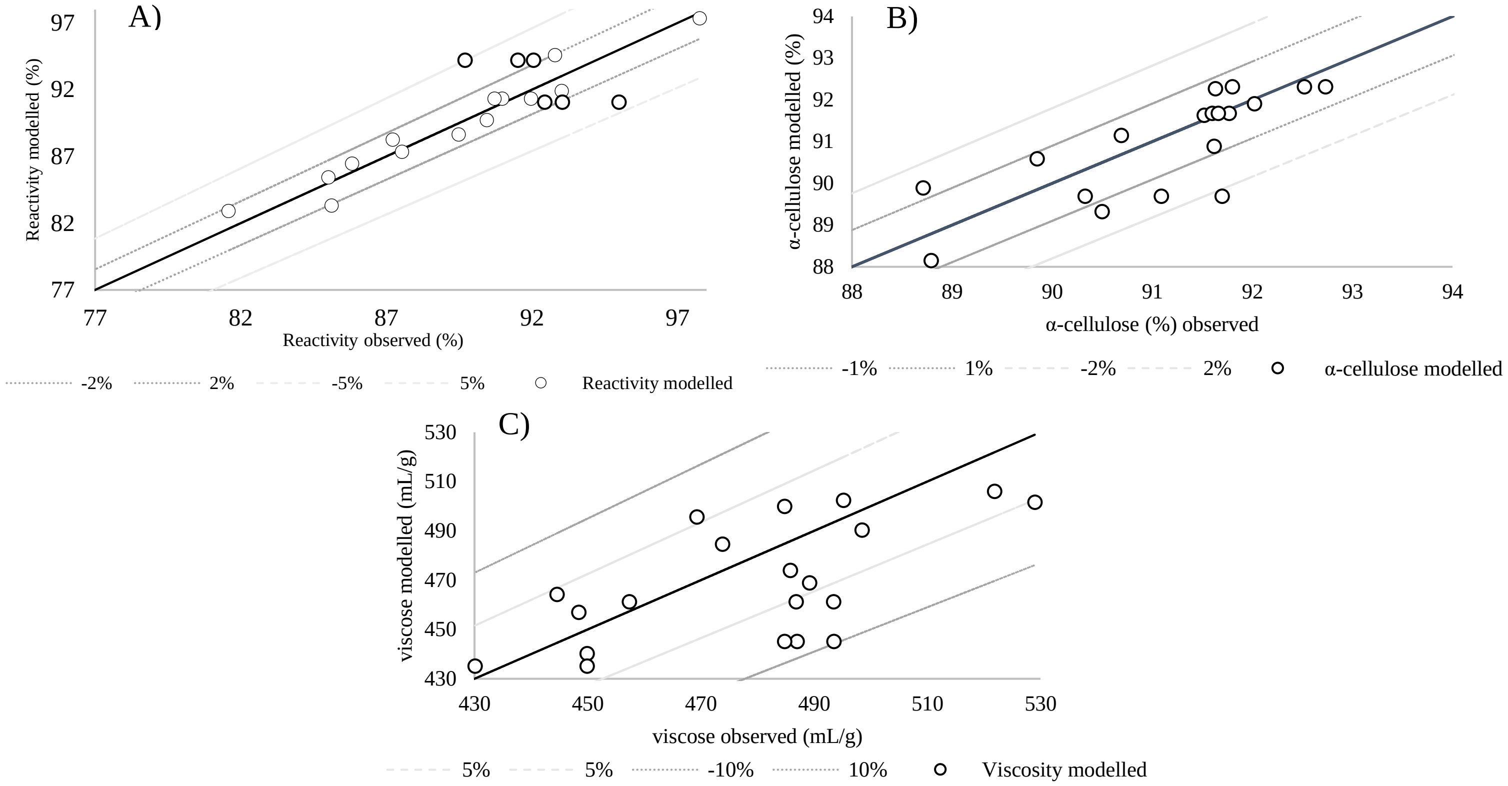

Figure. 4 Parity plots: relationship between predicted to empirical values for: Reactivity; A) , α-cellulose; B) and viscosity; C)

Using parity plots also helped to validate de model. In these graphs 6 additional values from previous experiments were added, the conditions of the experiments were the same regarding time and temperature, 60 s and 60 C, respectively, and the DES to biomass ratio were 20:1 and 5:1. Parity plots showed good fit with the experimental results, especially with reactivity and α-cellulose. In most of the cases, the error was not above 5 %. Regarding reactivity, 66.7 % of the values had lower error than 2 % and 90 % of the values were below 5 % error. 70 % of α-cellulose modelled values were below 1 % error, but 95 % of the values were below 2% error. Viscosity-modelled values were the most inaccurate with 66.7 % of the values below 5 % error and 100 % of the values below 10 % error. Furthermore, in order to observe the if the model is predictive, a one-way ANOVA test was performed using the modelled and the real values obtained. If the p-value is lower than 0.05 it can be said that the model is predictive. As a result, it was obtained that p-values for reactivity and alfa cellulose were 0.022 and 0.0022 respectively. However, viscosity p-value was 0.13, which states that it cannot be used to predict viscosity values.

After the most influential operational conditions have been analysed, it is possible to build response surface graphs. These graphs represent the values of the dependent variable vs the two most affecting independent variables. They allow the observation of the most appropriate values of the independent variables for optimum region values of the dependent variable (Figure 5).

The optimal region for α-cellulose is for a lower ratio and temperature. At around 30 ºC and 1:1 biomass to DES ratio, α-cellulose value is slightly lower than 93 %. This region agrees with the reactivity trend shown before. Reducing α-cellulose content reflects the glucose chain's degradation, leading to a higher accessibility of the reaction spots, thus increasing reactivity. Viscosity trend agrees with those found for the other quality pulp parameters. There is a region between 12 and 20 biomass-to-DES ratio and 30 and 90 min, where viscosity is reduced to 430 mL/g. However, increasing time from 90 to 140 min, viscosity reaches values around 460 mL/g, which are high enough to be considered suitable for viscose purposes. This variation in the viscosity values is explained by the reduction in α-cellulose content since cellulose chains become shorter than before the treatment.

Reactivity-wise, when compared to time and temperature, the region with the highest reactivity is between 0 to 90 min and temperature between 70-80 ºC. Under these conditions, it reaches 94 %. On the other hand, lower temperatures (30 ºC) lead to a reactivity of 84 %. Thus, the temperature should be kept between 70-80 ºC and residence time not higher than 120 min.

Other studies showed similar trends after DES treatment of pulp. Duan et al. (2023) found a comparable decrease in pulp viscosity, from 700 mL/g to 350 mL/g, and an increase in Fock's reactivity, from 40 % to 85 %. It should be noted that in this study, DES performance was coupled with microwave treatment (Duan et al., 2023). Another study found cellulose degradation using another carboxylic acid, reaching a maximum of 25 % cellulose removal and 45 % hemicellulose removal, associated with the decrease in intrinsic viscosity (Wang et al. 2022).

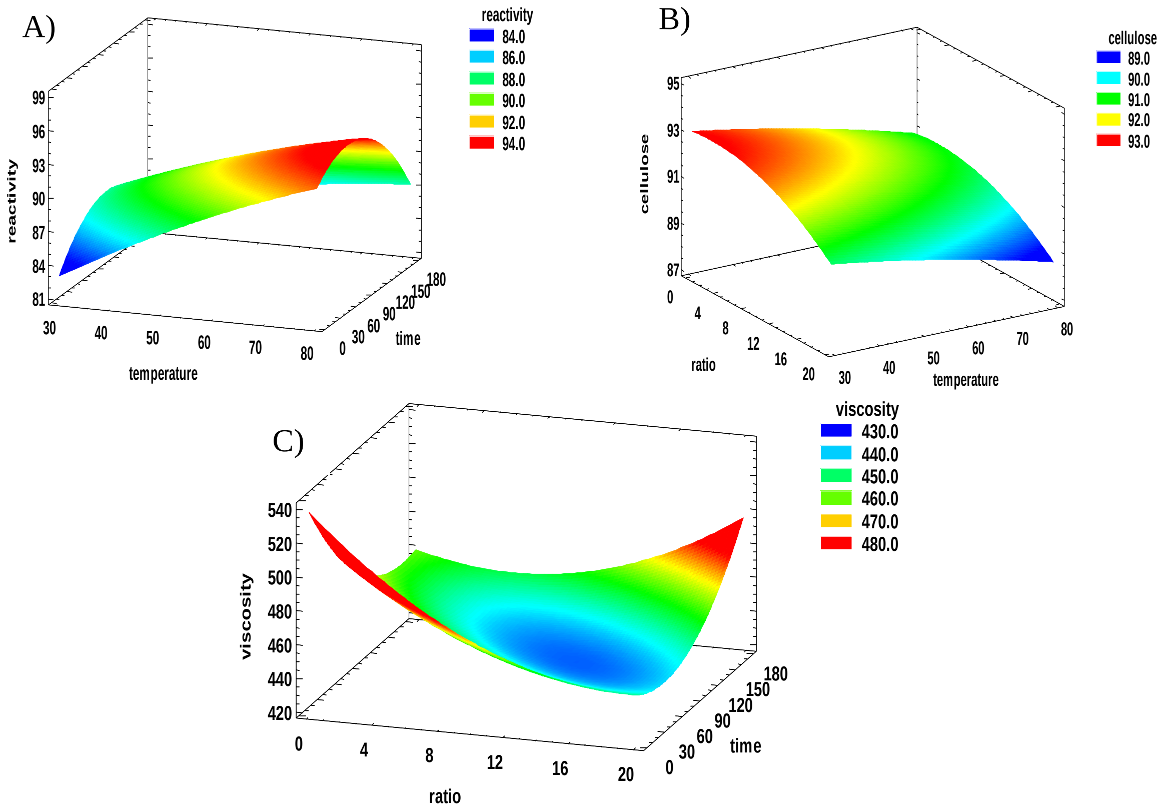

Figure. 5 Response surface graphs of the quality pulp parameters: Reactivity; A) , α-cellulose; B) and viscosity; C).

Optimal conditions and results compared with other biomass resources.

Based on the individual effects and considering the mathematical modelling and the response surface graphs, the optimal conditions within the study range were obtained. Each one of the response variables has its optimum, as shown in Table 3.

Table 3. Optimal conditions for each of the measured quality pulp parameters.

Response variable	Optimum value	Experimental conditions		
		T (ºC)	t (min)	ratio
Focks' reactivity (%)	97.97	80	66	1:20
Alfa-cellulose (%)	93.05	30	110	1:2
Intrinsic viscosity (mL/g)	537.9	30	180	1:20

In general, low temperatures of 30 ºC and times between 110-180 min favour alfa-cellulose content and intrinsic viscosity. In the case of reactivity, temperatures must be higher at around 80 ºC for no more than one hour. Under these conditions, some cellulose fibres were destroyed, so alfa-cellulose content and viscosity decreased. These results are in accordance with the previous study by Arce et al. (2020), where the highest reactivity of 93.70 % was found at 60 ºC for 60 min at a ratio of 1:20, reducing the CS_2 consumption of 15.83 % in the viscose process. Thanks to the Box-Behnken statistical analysis, 16.16 % of CS_2 can be saved.

Xie et al. (2021) treated pine biomass with benzyltrimethyl-ammonium and formic acid at 150 ºC, and the hemicellulose decreased by 6 %, whereas lignin decreased by 19.9 %. Another research found that using DES mixtures with acids such as proline/lactic acid, proline/malic acid, or glycine/malic acid, the best delignification occurs, reaching values of 15 % (Zdanowicz et al. 2018). The same study highlighted using choline chloride with oxalic acid removing 58 % lignin in wheat straw. Chen et al. (2020) tested holocellulose removals in herbal wastes using choline chloride and p-coumaric acid. Jiang et al. (2020) treated thermomechanical cellulose pulp (not as pure as used in this work) and demonstrated that the best delignification occurs at the highest temperature tested (90 ºC) with choline chloride and oxalic acid which promotes lignin hydrolysis.

Finally, Table 4 shows the optimal values combining all the effects and parameters together.

Table 4. Optimal conditions for the whole process.

Response	Optimized	Prediction	Min Value	Max value	Objective
Reactivity	yes	94.14	90	97	Max
Cellulose	yes	91.78	90	92	Max
Viscosity	yes	500	450	500	Max
Conditions: DES to biomass ratio: 9.31; Temperature 80 C; time 35.25 min					

Conclusions

This work studied the pretreatment of dissolving pulp using DES (ChCl:LA) to increase its reactivity. The effect of the operating conditions: time, temperature and ratio on cellulose properties was evaluated to assess its availability. The study shows that mild conditions, below 50 ºC and 105 min, are enough to increase the reactivity of dissolving pulp, making this process not energy intensive. Additionally, it does not reduce viscosity significantly, meaning cellulose quality is not compromised. The pareto plots confirmed these effects using Statgraphics software, which also showed that reactivity was affected by all the operating conditions studied.

Furthermore, it was possible to build an equation to predict the evolution of reactivity within the conditions studied with reasonable accuracy. The mathematical modelled allowed the optimisation of the process focusing on reactivity: time = 80 min, temperature = 66 ºC and reactants ratio = (1:20) (biomass-to-DES). Under these conditions, reactivity reached 97.7 %, leading to a CS_2 usage reduction above 16 %. Additionally, it was found that DES can be used as pretreatment with several kinds of lignocellulosic biomass, such as pine biomass, wheat straw, herb wastes and corn residues.

Ethics approval and consent to participate.

The reported manuscript did not involve human participants, human data or human tissue.

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Consent for publication

All co-authors agree to submit the manuscript.

Availability of data and materials

All data used in this manuscript has been obtained by the authors and co-authors.

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Competing Interests

There is no conflict of interest to declare.

Author contributions

Conceptualisation; T. Ll, Data curation; A. W, T. Ll and C. A, Formal analysis; T. Ll and C. A, Investigation; C. A, T. Ll and A. W, Methodology; C. A Project administration; A.C, Resources; A. C and T. Ll Software; T. Ll and A.W, Supervision; C. A, A. C and T. Ll, Validation; A.C Visualisation; C.A and T. Ll Roles/Writing-original draft; C.A and T. Ll Writing-review & editing: A. C.

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