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Techno-economic analysis of organosolv pretreatment process from lignocellulosic biomass

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1 **Techno-Economic Analysis of Organosolv Pretreatment Process from Lignocellulosic Biomass**

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6 **Abstract**

7 Lignocellulosic ethanol is a promising alternative to replace liquid fossil fuels for the transportation sector

8 in the near future. Organosolv pretreatment has been tested as a method for separating lignin from the

9 biomass and commercializing it as a biopolymer. Based on published laboratory scale data we propose a

10 feasible process flowsheet for organosolv pretreatment. Simulation of the pretreatment process provided

11 mass and energy balances for a techno-economic analysis and the values were compared with the most

12 prevalent and mature pretreatment method: diluted acid. Organosolv pretreatment required more energy,

13 578.1 MW versus 213.8 MW for diluted acid pretreatment, but resulted in a higher ethanol concentration

14 after the biomass fermentation, 11.1% compared to 5.4%. Total annual costs (TAC) calculations showed

15 advantages for diluted acid pretreatment but future improvements explored in the sensitivity analysis

16 turned into possible savings of 42.8% in the minimum ethanol selling price (MESP) for organosolv

17 pretreatment.

18

19 **Keywords:** Organosolv pretreatment, lignocellulosic biomass, process synthesis and simulation,

20 bioethanol, economic evaluation

21 **Acknowledgments**

24

1. Introduction

Oil prices fluctuation, geopolitical unrest in fossil fuel producing areas, limited known oil reserves and increasing global warming pushes humanity towards renewable fuel alternatives. High biomass availability and an established conversion process turned first generation bioethanol into a viable commercial choice in countries like United States, Brazil and China (Balat and Balat, 2009). However, the conflict between crop for fuel and crop for food caused an increase in the feedstock price, creating a lose-lose situation due to limited supply for the demand requested (Patil et al., 2008).

Having no competition with the food market, lignocellulosic feedstock represents the largest available resource for bioethanol production, commodity chemicals and green materials (Sun and Cheng, 2002). However, in order to make the sugars available for conversion, a pretreatment step is required to break the lignin barrier present on the lignocellulosic biomass. Several pretreatment methods have been tested in the past years with different degrees of success, including steam explosion, diluted acid, ammonia fiber explosion, liquid hot water and alkali pretreatments (Alvira et al., 2010; Sun and Cheng, 2002).

As the main barrier protecting the cellulose and hemicellulose from external agents, the removal of lignin can bring several advantages on the bioethanol production. A direct impact of the delignification of the biomass is the reduced energy requirements and equipment size for the later stages of the process. Furthermore, lignin is one of the responsible for the inhibitors formation that hinders the effectiveness of hydrolysis and fermentation reactions (Öhgren et al., 2007). On top of that, the possibility of separating and selling lignin co-products contribute to the plant revenue and decrease the overall product price.

Organosolv pretreatment has been known since 1940 as a pulping process to delignify the biomass and produce paper. Organosolv pretreatment relies on the solvent penetration in the biomass' pores to promote physical deconstruction of the lignocellulose structure (Zhang et al., 2016). Compared to aqueous mediums, organic solvents can increase the catalytic activity by reducing the activation energy, resulting in a higher yield for the process (Mellmer et al., 2014). Furthermore, the recovery and recycling

of the organic solvents used are simple, making the process interesting from the techno-economic point of view (Hallac et al., 2010).

Several studies have been carried out on organosolv pretreatment methods to better understand solvent choices and catalyst usage – both alone and in combination with other types of pretreatments. Araque et al. (2008) pretreated *Pinus radiata* with a mixture of acetone and water 1:1 with sulfuric acid as catalyst and obtained 99.5% of ethanol yield. Hallac et al. (2010) showed in another study that organosolv pretreatment can effectively reduce the degree of polymerization of the biomass, decrease the crystalline allomorphs of cellulose and increase the susceptibility of the feedstock to enzymatic hydrolysis. Using ethanol as solvent, Audu et al. (2012) managed to extract 67% of the initial lignin from *Typha capensis* by adding sulfuric acid as a catalyst to the process. Jang et al. (2016) investigated the effect of several organosolv pretreatment factors in the lignin recovery and enzymatic digestibility of *Liriodendron tulipifera* obtaining maximum lignin recovery of 12.9% and enzymatic conversion of 97.9%. Mesa et al. (2011) set up a two-step pretreatment process, applying organosolv pretreatment using ethanol to sugarcane bagasse previously treated with diluted acid pretreatment and obtained 9% better glucose fraction recovery when comparing to one stage diluted acid pretreatment method. In a further investigation, Mesa et al. (2016) evaluated the economic impacts of several operational conditions in the same two-step setup, achieving a cost of 1.03US\$/L of ethanol.

Many studies have been carried out on organosolv pretreatment, but mostly focused on specific conditions of the process at laboratory level. Few researchers have turned their attention to investigate the synthesis, design and process simulation of a larger scale organosolv unit. The objective of this study is to fill that gap and develop a detailed process using the conceptual and experimental works done so far as a starting point. We present the design and simulate a bioethanol production facility using the organosolv pretreatment method, including the solvent recycle and the conversion steps. Furthermore, a sensitivity analysis of several process parameters is presented to identify the most important points of the organosolv process for future process development. Finally, we compared the results obtained with published data from Larsson et al. (1999), who used a more established technology for biomass conversion: diluted acid pretreatment method.

2. Methods

2.1 Process synthesis and design

80   Significant energy is required to disrupt the lignocellulosic structure, making

81 pretreatment account for one third of the total production cost in a bioethanol plant (Mosier et al.,

82 2005).The possibility of aggregating value to lignin co-products and capital investment savings can

83 overcome the cost pressure of pretreatment methods in the overall bioethanol process, making second

84 generation bioethanol economically viable.

85   Organosolv pretreatment was proven an effective pretreatment specially for hardwood

86 and softwood biomass with a high enzymatic hydrolysis conversion rate (Pan et al., 2005). Cost, ease of

87 recovery and the ability to remove lignin are the main factors to take into account when choosing a

88 suitable solvent for the process (Zhang et al., 2016). Ethanol rises as an appropriate option for solvent in

89 the process as its low boiling point makes it simple to recover. The use of ethanol brings the potential of

90 mass integration within the process for it is the final product, reducing the costs of solvent purchase.

91 Furthermore, it has low toxicity and flammability when compared to other possible alternatives (Zhang et

92 al., 2016).

93   The organosolv process requires a high temperature in the pretreatment reactor (160°C -

94 250°C) for effective delignification of the biomass(Zhao et al., 2009). However, the use of acid as a

95 catalyst in the process makes possible a reduction in reactor temperature and the total residence time of

96 the process (Zhang et al., 2016). The ethanol concentration in the solvent also impacts biomass

97 delignification: low ethanol concentrations promote acid-catalyzed cleavage in the lignin linkages,

98 fragmenting the lignin molecules and increasing their solubility, whereas high ethanol concentrations

99 solubilize the lignin molecules without fragmentation. Hallac et al. (2010) tested different ethanol

100 concentrations in a high lignin content biomass and achieved the best result combining delignification and

101 hydrolysis conversion by using an ethanol concentration of 50% (w/w).

102   In this work, Aspen Plus v8.0 was used to set up a plant processing 88,500 kg per hour of

103 dry biomass, similar to values used by Humbird et al. (2011) and Aden and Foust (2009). The selected

104 biomass was spruce, a softwood tree from the Pinaceae family. The dry matter biomass composition was

105 45% glucan, 22% xylan, 28% lignin, 3% acetate and 2% ash (Wingren et al., 2003). Furthermore, to

106   represent more closely the real feedstock, we considered that 20% of moisture content was present in the

107   biomass, adding up to 106,200 kg/h of processed raw material. The NRTL (non-random two-liquid)

108   property method was used in the simulations and components in Aspen's native databanks were used

109   whenever possible, otherwise properties from the National Renewable Energy Laboratory - NREL report

110   were used instead (Humbird et al., 2011).

111   *2.1.1 Process setup for organosolv pretreatment*

112   Figure 1 presents the flowsheet setup used for organosolv pretreatment. The setup was

113   based on previously published experimental and theoretical works (Hallac et al., 2010; Mesa et al., 2011;

114   Pan et al., 2005). It is important to mention that, although hemicellulose can be separated from the

115   biomass by organosolv pretreatment (Pan et al., 2005; Zhang et al., 2016), we chose to co-ferment those

116   sugars to increase the ethanol yield of the process. The wood chips at the processing plant are pre-

117   steamed to 130°C (ST1) and afterwards mixed with 50% (w/w) ethanol solution in a solvent:dry biomass

118   ratio of 5:1. Sulfuric acid is added as a catalyst to the process in a total of 1.75% (w/w) to dry weight

119   biomass. The pretreatment reactor (R1) operates at 180°C and 27.2 atm of pressure, with a total residence

120   time of 40 minutes. After the cooking time, the pressure is released and the pretreated material is filtered

121   (F1) to obtain one solid rich (PULP) and one liquid rich stream (LIQ). The solid stream, also called pulp

122   stream, is rich in cellulose and goes through a two stage washing step. In the first step (W1) the pulp is

123   washed with the same ethanol (50/50) solvent, in a ratio of 2:1 to the pulp weight stream in order to

124   recover some of the solvent and the remaining ethanol organosolv lignin (EOL) that are still present in the

125   solid fraction. The second stage of the washing process (W2) is done with water to recover the remaining

126   solvent present in the pulp stream, in a ratio of 2:1. After the washing process the pulp is sent to the

127   mixing tank (T1) prior to hydrolysis and fermentation. As no literature data was available regarding the

128   washing step, we considered that all the solvent soaked in the solid fraction was recovered in the washing

129   step, which is a conservative way for process evaluation in that the energy required for the solvent

130   recovery is maximized.

131   The liquid stream from the pretreatment reactor is rich in lignin, hemicellulose and solvent. The

132   stream is flashed (FL1) to initially recover part of the solvent used in the process. The bottom stream

133   (S11) from the flash operation is mixed with the solvent and water used in the washing steps of the pulp

134   stream and more water (S24) is added to precipitate the lignin in the precipitation tank (P1). The material

135   is filtered (F2) to recover the lignin (EOL) and the liquid stream (S25) is sent to a distillation column (C1)

136   to recover the remaining solvent as distillate (S26). The amount of ethanol organosolv lignin was

137   obtained from the literature where the same conditions as the simulated process were used (Hallac et al.,

138   2010). The bottom product of the column is rich in hemicellulose and the acid catalyst and needs to be

139   neutralized prior to the hydrolysis and fermentation steps. Acetic acid formed in the pretreatment reactor

140   and sulfuric acid are neutralized with ammonia (S31). Part of the water is removed from the stream by an

141   evaporator (FL2) and the remainder of the liquid fraction is mixed with the pulp stream in the mixing tank

142   (T1). The solids content is adjusted to 20% (w/w) and sent to the hydrolysis (R3) and fermentation (R4)

143   steps.
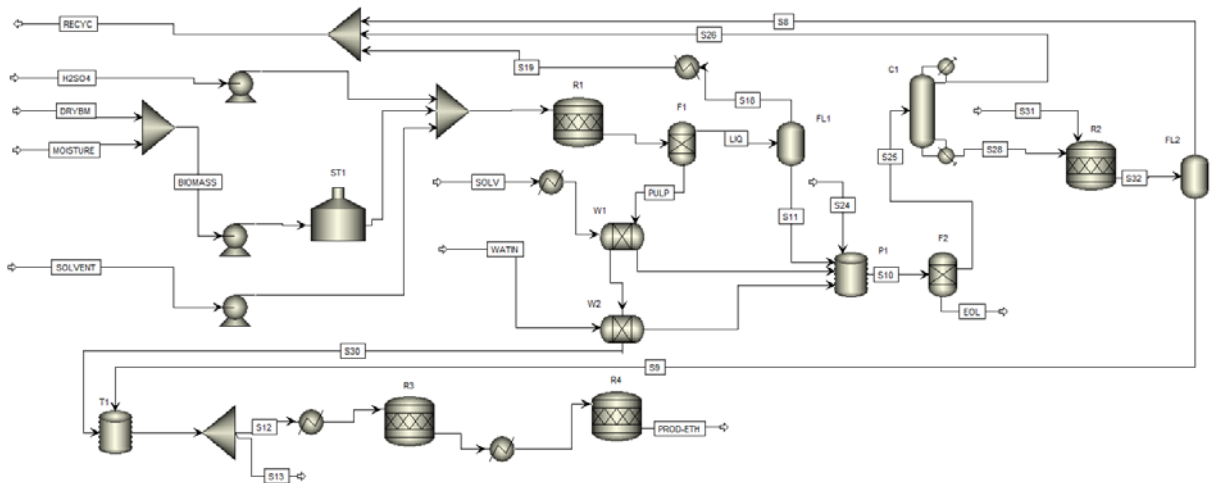
144
145   **Fig. 1** Flowsheet setup for organosolv pretreatment

146   *2.1.2 Process setup for diluted acid pretreatment*

147   Diluted acid pretreatment was simulated according to the methods described by Larsson

148   et al. (1999). In their work they also used spruce as the biomass for the process, however the feedstock

149   composition was slightly different: cellulose (43.4%), xylan (4.9%), lignin (28.1%), mannan (12.0%),

150   galactan (1.8%), arabinan (1.1%) and extractives (1.0%) with a moisture content of 57%. For simulation

151   purposes we grouped all the hemicellulose sugars, i.e. galactan, mannan, arabinan and xylan into the

152   xylan composition following the guidelines of the NREL group (Humbird et al., 2011). Therefore the

153   final biomass composition consists of cellulose (43.4%), xylan (19.8%), lignin (28.1%) and extractives

154 (1.0%) with the remaining 7.7% considered as ash and acetate. The flowsheet setup for the diluted acid

155 process is presented in Figure 2.

156   The process starts by mixing the biomass with diluted sulfuric acid at 2.4% (w/w) and

157 incubated at room temperature. The biomass is preheated to 100°C and then fed to the pretreatment

158 reactor operating at 210°C. In the referenced paper there was no indication on the operating pressure and

159 solids loading of the pretreatment reactor, as a simulation alternative we used the same values as the

160 NREL report (Humbird et al., 2011), 5.5 atm and 30% of solids loading. At the discharge of the reactor, a

161 flash operation (FL1) separates some of the volatile inhibitors formed (S5), such as acetic acid and

162 furfural. Following the flash, a filtration process (F1) separates the liquid fraction and the solid fraction.

163 The pH of the liquid fraction is adjusted by adding calcium hydroxide and any resulting precipitate is

164 removed by centrifugation. The streams were then mixed and had their solids level adjusted to 20 % prior

165 to the hydrolysis and fermentation section.
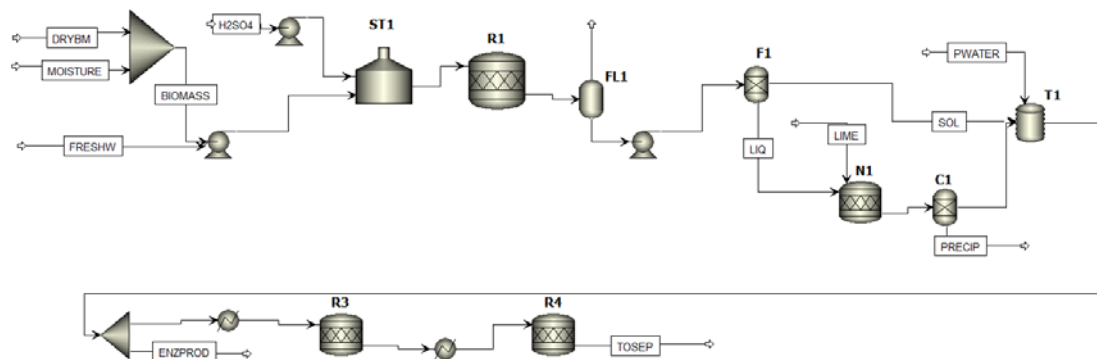
166

167 **Fig. 2** Flowsheet setup for diluted acid pretreatment

168 *2.1.3 Hydrolysis and fermentation*

169   For the sake of comparison we used separate hydrolysis and fermentation (SHF) method

170 for bioethanol conversion, the same method employed in the NREL analysis. 10% of the biomass from

171 the conditioning tank was diverted to in-situ enzyme production (S13) while the remaining (S12) was

172 cooled to 48°C and sent to the hydrolysis reactor (R3). Cellulase was added at 20mg/g cellulose,

173 providing 90% cellulose to glucose conversion (Humbird et al., 2011). Passed 84h of the reaction, the

174 slurry was further cooled and sent to the fermentation reactors (R4) where *Zymomonas mobilis* was

7

175 added. The initial inoculum level was 10% volume and the fermentation required 36h of residence time.

176 Finished the fermentation reactions, the products are ready to be sent to separation and purification areas.

177 *2.1.4 Product separation*

178 Although the main objective of this study is to evaluate the main bottlenecks for the

179 development of the organosolv pretreatment method in an industrial level, a product separation stage was

180 included and analyzed for the best case scenario to provide a more realistic final ethanol price. The

181 separation process is presented in Figure 3. Initially, the fermentation broth is vented to remove part of

182 the carbon dioxide present in the stream and the resulting stream is sent to the beer well tank. From the

183 beer well the broth is directed to the beer column where 3 streams are separated. The top product stream

184 is rich in carbon dioxide and contains around 3% (w/w) of ethanol. This carbon dioxide rich stream is

185 mixed with the fermentation vent and sent to a vent scrubber, where water is added on a counter-flow

186 configuration to recover the ethanol present in the vapour phase. The effluent stream from the vent

187 scrubber is sent back to the beer well. The bottom product of the beer column contains the non reacted

188 and dissolved solids, which can be dried and burned for energy production. Finally, a side stream is

189 drawn from the beer column containing ethanol at 40% (w/w) and 99.5% of the total ethanol entering the

190 column. The side stream is sent to the rectifying column where it is purified to the near azeotropic point

191 and directed to the molecular sieves. The two molecular sieves units work on offset cycles, meaning that

192 while one unit is adsorbing the water from the stream the other is regenerating. Two streams leave the

193 molecular sieves, ethanol product at 99.5% (w/w) and low concentration ethanol, that is sent back to the

194 beer well.
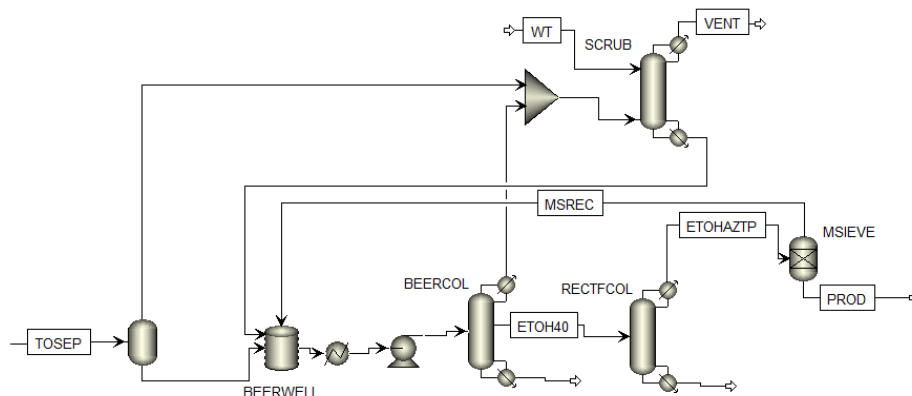
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196   <mark>**Fig. 3** Flowsheet setup for product separation and purification.</mark>

197   *2.2 Economic analysis*

198   The factorial method using the parameters defined by Towler and Sinnott (2008) was

199 used for the capital costs calculations. Correction factor due to fluid-solid process was applied in the

200 analysis. Furthermore, factors corresponding to equipment erection, piping, instrumentation and control,

201 electrical installations, civil costs, structural and building costs, design and engineering and contingency

202 costs were also considered (Towler and Sinnott, 2008). <mark>All prices reported in the manuscript are in U.S.</mark>

203 <mark>dollars.</mark>

204   Table 1 shows the values used for variable costs calculations. Utilities and chemicals

205 costs were obtained from the literature and corrected to 2014 prices (Turton et al., 2009). Equipment costs

206 were corrected using CEPCI 2014 index of 576.1. Total annual cost (TAC) was calculated by dividing the

207 total capital cost (CC) by the years for return of investment (n), defined as 5, and adding to that the annual

208 value of the variable costs, composed by utilities cost (UC), chemicals cost (ChemC) and raw material

209 cost (RM), as shown in the Equation 1 below:

210     $$TAC = \frac{CC}{n} + UC + ChemC + RM \quad (1)$$

211   Table 1: Feedstock, chemicals and utilities prices.

Input	Price
Spruce	67.13 US$/ton
Calcium Hydroxide	0.07 US$/kg
Sulfuric Acid	0.085 US$/kg
Ammonia	0.30 US$/kg
Water	0.40 US$/ton
Vapour – Hot utility	16.50 US$/GJ
Cool water – Cold utility	0.35 US$/GJ
Electricity	16.8 US$/GJ

212

213   We calculated the fixed capital investment (FCI), the variable operating costs and the

214 fixed operating costs to compute the discounted cash flow rate of return (DCFROR) and to obtain the

215 minimum ethanol selling price (MESP). Fixed operating costs were estimated based on literature and

216   cover labor salary costs, labor burden (90% of total salaries) and property insurance (0,7% of FCI)

217   (Humbird et al., 2011). We considered the plant operational life as 30 years, running 7920h per year, with

218   the remaining hours as downtime and programmed maintenance stops. The internal rate of return was set

219   at 10% and taxes at 35%. Internal Revenue Service Modified Accelerated Cost Recovery System (IRS-

220   MACRS) was used as the depreciation method. Working capital was defined as 5% of FCI and the

221   construction period was 3 years. The plant did not need external financing and once the construction was

222   finished the plant was fully functional. The considerations used for the calculations of MESP were based

223   on previously published papers (Humbird et al., 2011). For the MESP calculation, we did not use the

224   isolated lignin as a co-product nor burned it for the co-generation of energy to the process. The MESP

225   was obtained by iterating the net present value (NPV) until its value equaled zero, where NPV is defined

226   as follows:

227    $$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \quad (2)$$

228   With n being the period, t the number of time periods, i is the internal rate of return and CF_n is the net

229   cash flow in the period n.

230   *2.3 Sensitivity analysis*

231   Several process parameters can impact the final performance of the plant. Future

232   technological scenarios and their effects on plant performance and economics were investigated. All

233   changes made in the sensitivity analysis were based on previously published research results (Aden and

234   Foust, 2009; Gnansounou and Dauriat, 2010; Humbird et al., 2011). We analyzed the changes in raw

235   material, chemicals and utilities costs, utilities consumption, solvent usage, amount of acid catalyst

236   utilized, solvent ratio (fraction of ethanol to water), the effects of temperature in the pretreatment,

237   hydrolysis and fermentation reactors, the effect of pressure in the pretreatment reactor, the conversion in

238   the pretreatment, hydrolysis and fermentation reactors and the solids loading in the hydrolysis reactor.

239   Each process and economical variable was changed individually while all the others were kept constant.

240   The effect of those changes in the TAC and MESP was investigated and discussed in more details at

241   section 3.

3. Results and Discussion

From the initial 88,500 kg/h of spruce feedstock, simulation results show that the product stream from organosolv pretreatment yields 25,084.5 kg/h of ethanol, of which 300 kg/h is due to incomplete recovery of solvent ethanol used in the pretreatment process, as seen on column S9 from Table 2. The ethanol productivity represents around 75% of the total theoretical ethanol yield possible and was obtained with a total energy consumption of 598.6 MW, equivalent to 23.9 kW/kg of ethanol. Furthermore, organosolv pretreatment consumed 147,480 kg/h of water in the total process and was able to recycle nearly 99.9% of the ethanol used as solvent. Detailed values for the most important streams can be seen in Table 2, such as the amount of solvent recovered in the first flash operation (S18), in the solvent distillation column (S26) and in the evaporator unit (S8). Streams S18, S26 and S8 need to be balanced to reach the desired solvent concentration, and the remaining of the water can be sent to the waste water treatment. Moreover, from Table 2 we can also observe the amount of unreacted solids in the production streams, that can be further burned to produce energy for the process.

Table 2: Mass balance for organosolv pretreatment.

Streams	DRYBM	BIOMASS	PTINLET	LIQ	PULP	S18	WTR-S24	S10	EOL	S25	S26	NH3-S31	NEUT-S32	S8	S9	S30	DEV-S13	S14	PROD-ETH
Temperature (°C)	25	25	35.9	131.1	131.1	**85**	25	64.9	64,9	64.9	**78.3**	25	95	**100.5**	100.5	28.5	97.5	45	32
Pressure (atm)	1.0	1.0	27.2	5.0	5.0	**1.0**	1.0	1.0	1,0	1.0	**1,0**	1,0	1.0	**1.0**	1.0	1.0	1.0	1,0	1.0
Mass Vapor Fraction	0	0	0	0.206	0	**1**	0	0	0	0	**0**	1	0	**1**	0	0	0	0	0.084
Mass Solid Fraction	1	0.833	0.161	0.004	1	**0**	0	0.003	0	0.003	**0**	0	0.004	**0**	0.009	1	0.206	0.206	0.089
Component flowrate (kg/h)																			
CELLULOSE	39825	39825	39825	0	28223	**0**	0	0	0	0	**0**	0	0	**0**	0	28223	2822	25401	1219
XYLAN	19470	19470	19470	0	3037	**0**	0	0	0	0	**0**	0	0	**0**	0	3037	303	2733	546
LIGNIN	24780	24780	24780	0	18585	**0**	0	0	0	0	**0**	0	0	**0**	0	18585	1858	16726	16726
ACETATE	2655	2655	2655	0	0	**0**	0	0	0	0	**0**	0	0	**0**	0	0	0	0	0
ASH	1770	1770	1770	1770	0	**0**	0	1770	0	1770	**0**	0	1770	**0**	1770	0	177	1593	1593
ETHANOL	0	0	221250	221250	0	**138333**	0	132767	13	132753	**127187**	0	5566	**5230**	336	0	33	302	25084
WATER	0	17700	239066	238133	0	**54838**	65500	398344	398	397946	**14086**	0	383859	**219895**	163964	0	16396	147567	144857
GLUCOSE	0	0	0	12832	0	**0**	0	12832	0	12832	**0**	0	12832	**0**	12832	0	1283	11549	1701
XYLOSE	0	0	0	14991	0	**0**	0	14991	0	14991	**0**	0	14991	**1.5**	14990	0	1499	13491	2304
XYLOSE OLIGOMER	0	0	0	467	0	**0**	0	467	0	467	**0**	0	467	**trace**	467	0	46	421	420
GLUCOSE OLIGOMER	0	0	0	13	0	**0**	0	13	0	13	**0**	0	13	**0**	13	0	1	12	1140
SOLUBLE LIGNIN	0	0	0	6195	0	**0**	0	6194	4460	1734	**0**	0	1734	**1**	1733	0	173	1560	1560
GLYCEROL	0	0	0	0	0	**0**	0	0	0	0	**0**	0	0	**0**	0	0	0	0	199
CELLOBIOSE	0	0	0	29	0	**0**	0	29	0	29	**0**	0	29	**0**	29	0	3	26	321
O2	0	0	0	0	0	**0**	0	0	0	0	**0**	0	0	**0**	0	0	0	0	34
CO2	0	0	0	0	0	**0**	0	0	0	0	**0**	0	0	**0**	0	0	0	0	23674
NH3	0	0	0	0	0	**0**	0	0	0	0	**0**	1250	40	**38**	2	0	0.2	1.8	1.8
SULFURIC ACID	0	0	1548	1548	0	**trace**	0	1548	0	1548	**0**	0	0	**0**	0	0	0	0	0
ACETIC ACID	0	0	0	2655	0	**285**	0	2369	0	2369	**trace**	0	0	**0**	0	0	0	0	0
HMF	0	0	0	9	0	**trace**	0	9	0	9	**0**	0	9	**trace**	9	0	1	8	8
FURFURAL	0	0	0	623	0	**223**	0	399	0	399	**trace**	0	399	**353**	45	0	4	41	41
AMMONIUM ACETATE	0	0	0	0	0	**0**	0	0	0	0	**0**	0	3041	**0**	3041	0	304	2737	2737
AMMONIUM SULFATE	0	0	0	0	0	**0**	0	0	0	0	**0**	0	2086	**0**	2086	0	208	1877	1877

256   Diluted acid on the other hand, produced 16,202.5 kg/h of ethanol, approximately 34.6%

257   less when compared to organosolv pretreatment. The fraction of the theoretical ethanol yield achieved by

258   diluted acid pretreatment in the process corresponded to 49.2%, showing that diluted acid pretreatment is

259   not recommended for high lignin content biomass. The formation of lignin droplets and considerable

260   amounts of inhibitors is a known fact when using diluted acid pretreatment in softwood biomass,

261   hampering the biomass overall conversion yield as stated by several authors (Brodeur et al., 2011;

262   Larsson et al., 1999; Tengborg et al., 1998). However, considering the amount of energy spent per mass

263   unit of ethanol produced, diluted acid pretreatment of softwood utilized 13.2 kW/kg of ethanol, 55% of

264   the value obtained for the organosolv pretreatment. In total, diluted acid required 213.8 MW of energy,

265   64% less than the organosolv pretreatment, as no recycle was used to recover the acid in the process.

266   Table 3 shows detailed values for electricity, hot utilities, cold utilities, water and

267   chemicals used in the processes. Limitations due to heat and mass transfers require that the biomass has a

268   low solids loading in the processes. To decrease the solids fraction, water is used as solvent for the diluted

269   acid pretreatment, whereas a mixture of ethanol and water is employed for the organosolv method. The

270   direct consequence of the biomass dissolution in the processes is that the demand of water in diluted acid

271   doubles the amount required for the organosolv process. However, to be economically feasible,

272   organosolv pretreatment needs to recover the solvent used in the process, greatly increasing its energy

273   demand. Figure 4 shows that the solvent recovery section represents more than 70% of the utilities

274   requirement for the organosolv process. The solvent distillation column and the evaporator unit, simulated

275   as a flash 2 separator, need 92.4MW and 108.8MW of hot utilities, respectively, and are the main energy

276   sinks of the process. Furthermore, in the organosolv pretreatment, a high amount of cold utility is

277   necessary to condense the solvent back to its liquid form, whereas for diluted acid there is no such

278   requirement as, in our case, the water is not recycle back to the process.

279   Table 3: Summary of process data.

	Organosolv	Diluted Acid
Ethanol Productivity (kg/h)	25,084.5	16,202.5
Ethanol concentration (%w/w)	11.1	5.4
Electricity (kW)	476.5	82.9
Hot Utilities (kW)	331,279.8	149,708.2
Cold Utilities (kW)	266,850.0	64,057.5

Total Energy (MW)	598.6	213.8
Energy (kW)/kg of Ethanol	23.9	13.2
Water consumption (kg/h)	147,480.0	391,000.0
Chemicals consumption	1,550 kg/h H2SO4	5,328 kg/h H2SO4
	1,250 kg/h NH3	3,084 kg/h Lime

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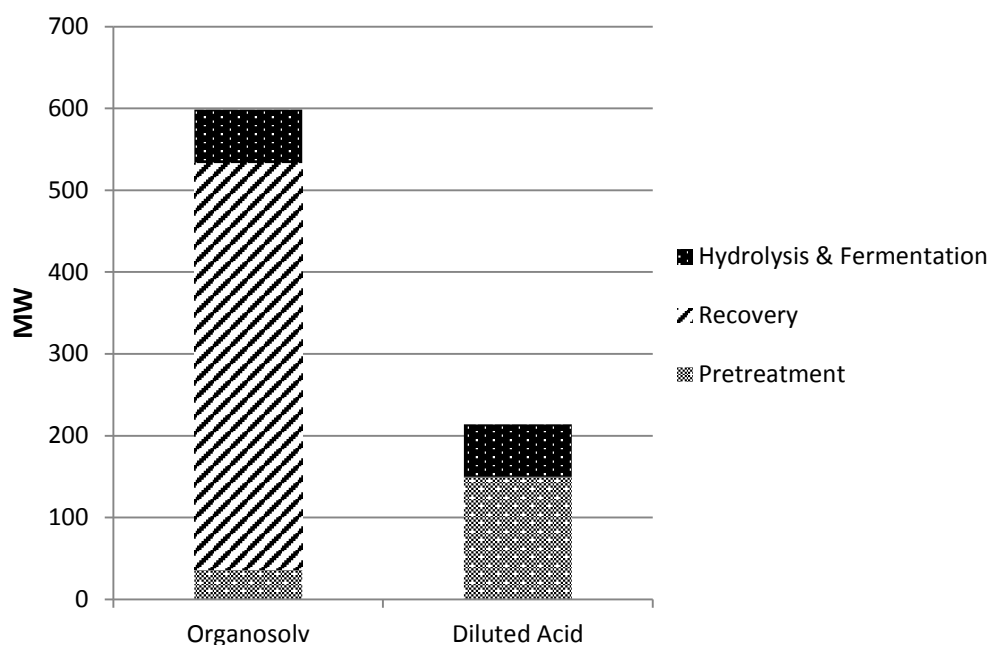
281

282 **Fig. 4** Energy consumed (MW) in each process section

283 *3.1 Economic evaluation*

284 Diluted acid is a relatively simple process, with no recycles or washing steps, however,

285 the equipment costs are considerably higher due to increased chances of corrosion in the process and the

286 requirements for special materials (Kumar et al., 2009). Equipment costs including hydrolysis and

287 fermentation series of batch reactors account for nearly 135.1 million dollars for diluted acid

288 pretreatment, whereas for organosolv pretreatment represent approximately 113 million dollars, 16.3%

289 less. Tables 4 and 5 show the major equipment costs for organosolv and diluted acid pretreatments.

290 Table 4: Major equipment costs for organosolv pretreatment.

Equipment	Type	Cost (Million US$)
ST1	Pre-steamer	2.44
R1	Jacketed agitated reactor	6.02

Equipment	Type	Cost (Million US$)
R2	Jacketed agitated reactor	5.54
F1	Plate and frame filter	2.45
F2	Plate and frame filter	1.06
FL1	Flash tank	4.16
FL2	Flash tank	2.54
C1	Distillation column	1.69
P1	Precipitation tank	0.68
T1	Mixing tank	5.58

291

292 Table 5: Major equipment costs for diluted acid pretreatment.

Equipment	Type	Cost (Million US$)
ST1	Pre-steamer	7.42
R1	Jacketed agitated reactor	5.12
N1	Jacketed agitated reactor	1.80
FL1	Flash tank	4.45
F1	Filter	1.31
T1	Mixing tank	4.10

293

294   Combining the capital costs and the variable costs of the processes result in a total annual

295 costs (TAC) of 243.18 million U.S. dollars per year for organosolv pretreatment. The main contribution to

296 the TAC comes from the total utilities costs required for the process, accounting for 158.74 million U.S.

297 dollars per year, i.e. 65% of total annual costs. Table 6 shows the breakdown of the TAC for organosolv

298 and diluted acid pretreatment. The feedstock cost in organosolv pretreatment is responsible for 19% of the

299 total share, whereas for diluted acid it represents 28.7%. The lower consumption of utilities for diluted

300 acid translates into a lower TAC and, therefore, increases the total share of the biomass on it. On the other

301 hand, chemical costs and equipment costs are lower for organosolv pretreatment, as less amount of acid is

302 required in the process.

303 Table 6: TAC breakdown for the pretreatment processes.

	Organosolv (Million US$)	Diluted Acid (Million US$)
Feedstock	47.05	47.05
Hot Utilities	155.85	70.43
Cold Utilities	2.66	0.64
Electricity	0.23	0.04
Water	0.47	1.24
Sulfuric Acid	1.12	3.59
Ammonia	2.97	-
Lime	-	1.71

Annualized Capital Costs	32.82	39.21
TAC	243.17	163.91

304

305   Considering the aspects presented in section 2.2 and taking into account the ethanol

306   productivity of both pretreatments, it is possible to calculate the minimum ethanol selling price for the

307   processes. Organosolv pretreatment resulted in a MESP of 1.228 US$/kg of ethanol, whereas diluted acid

308   pretreatment showed a MESP of 1.248 US$/kg of ethanol. Although diluted acid had a considerable lower

309   value on the total annual costs, the ethanol productivity from softwood by diluted acid pretreatment

310   counterbalanced the difference for the minimum ethanol selling price. Figure 5 shows the main

311   contributions for the MESP in both organosolv and diluted acid pretreatments. It can be observed that

312   utilities cost plays an important role in the final ethanol price for both organosolv pretreatment and

313   diluted acid, more precisely 65.8% and 44.4% of the MESP, respectively. It is important to highlight as

314   well the higher share of the feedstock and equipment capital costs in the MESP for the diluted acid

315   pretreatment, with values of 29.4% and 18.5%.
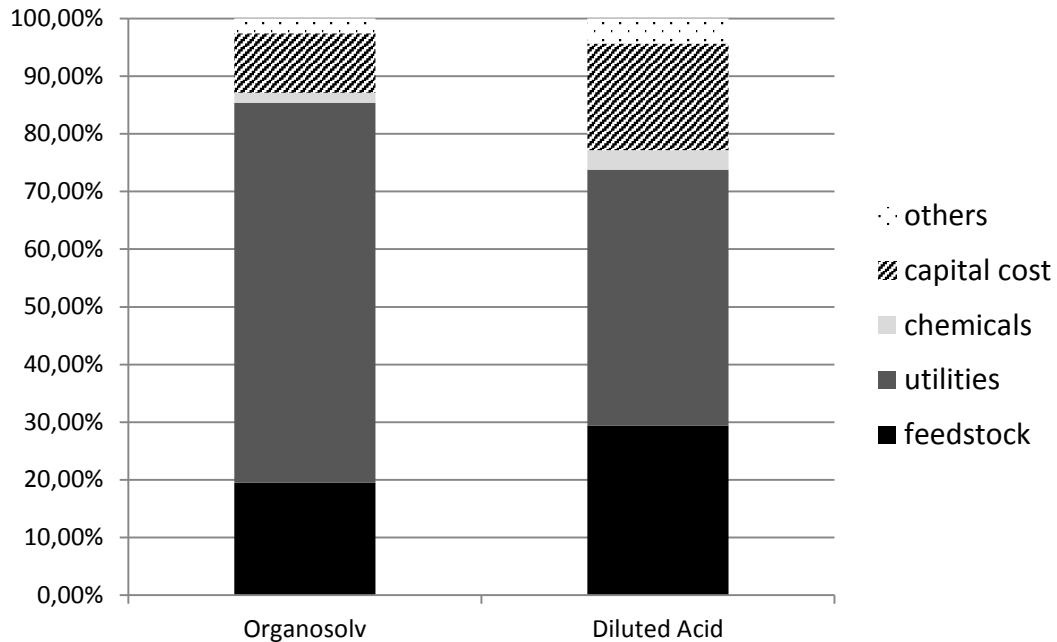
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317   **Fig. 5** MESP contributions from each pretreatment method

318   *3.2 Sensitivity analysis*

319   A sensitivity analysis was done to investigate the effects of future technological

320   improvements for organosolv pretreatment and how they affect the TAC and the MESP of the process.

321   Several process improvements and prices fluctuations were evaluated regarding their impacts on

322   economic aspects of the process, as shown in Table 7. Cases 1 to 7 are related to costs and general

323   chemicals consumption in the process, and reflect directly in the TAC and MESP calculations, whereas

324   cases 8 to 15 are related to technological process improvements. For those cases new simulations were

325   performed considering the parameter values showed in Table 7. For all the cases evaluated, the process

326   variables were kept constant and adjustments were made when necessary to maintain the hydrolysis solids

327   loading at 20% (except for case 15) and inhibitors and ethanol level below 0.14% (w/w).

328   In the first category, cases 1 to 7, the solvent usage was the most important factor for reducing the

329   final MESP for organosolv pretreatment. A reduction in 5% of total solvent usage caused a decrease of

330   4.32% in the minimum ethanol selling price due to energy savings in the pretreatment reaction section

331   and in the solvent recovery section. The second most significant process parameter in this category was

332   the solvent ratio (ethanol to water percentage in the solvent). A 5% increase in the amount of ethanol

333   fraction in the solvent reduced the total MESP in 3.91%, whereas a decrease in 5% of the ethanol fraction

334   in the solvent caused an increase of 15.23% in the MESP. The change observed was mostly due to the

335   difference in the specific heat capacity, i.e. more ethanol in the solvent used means that less energy is

336   required for the recovery, since ethanol boiling point is lower than water. Furthermore, according to

337   Zhang et al. (2016) an increase in the ethanol fraction can improve the delignification process and provide

338   even further savings for the process.

339   Table 7: Parameters evaluated and impacts on TAC and MESP.

Parameter changed		min	Baseline	max	unit	TAC (Million US$/year)					MESP (US$/kg)				
						min	(%) change	Baseline	max	(%) change	min	(%) change	Baseline	max	(%) change
Raw material Cost	case 1	63.77	67.13	70.49	US$/ton	240.82	-0.97	243.18	245.53	0.97	1.216	-0.98	1.228	1.240	0.98
Chemicals Cost	case 2	different for water and sulfuric acid				243.10	-0.03	243.18	243.26	0.03	1.227	-0.08	1.228	1.228	0.00
Utilities Cost	case 3	different for each utility				235.24	-3.26	243.18	251.11	3.26	1.187	-3.34	1.228	1.268	3.26
Utilities Consumption	case 4	446.43	469.93	493.43	MW	235.24	-3.26	243.18	251.11	3.26	1.187	-3.34	1.228	1.268	3.26
Solvent Usage	**case 5**	**420,000.0**	**442,500.0**	**465,000.0**	**kg/h**	**232.78**	**-4.28**	**243.18**	**253.93**	**4.42**	**1.175**	**-4.32**	**1.228**	**1.282**	**4.40**
Solvent Ratio [a]	**case 6**	**45.0**	**50.0**	**55.0**	**%**	**280.02**	**15.15**	**243.18**	**233.83**	**-3.84**	**1.415**	**15.23**	**1.228**	**1.180**	**-3.91**
Acid catalyst Usage [b]	case 7	1.5	1.75	2.0	%	242.88	-0.12	243.18	243.09	-0.04	1.226	-0.16	1.228	1.227	-0.08
PT temperature change	case 8	170.0	180.0	190.0	°C	243.17	0.00	243.18	243.17	0.00	1.228	0.00	1.228	1.228	0.00
PT pressure change	case 9	25.5	27.2	28.5	atm	243.18	0.00	243.18	243.18	0.00	1.228	0.00	1.228	1.228	0.00
Hyd temperature change	case 10	42.0	45.0	48.0	°C	243.18	0.00	243.18	243.18	0.00	1.228	0.00	1.228	1.228	0.00
Ferm temperature change	case 11	30.0	32.0	34.0	°C	243.18	0.00	243.18	243.17	0.00	1.228	0.00	1.228	1.228	0.00
PT conversion [c,d]	case 12	-3.0	-	3.0	%	240.15	-1.24	243.18	260.71	7.21	1.217	-0.90	1.228	1.311	6.76
Hyd conversion [c,e]	case 13	-3.0	-	3.0	%	243.16	-0.01	243.18	243.19	0.01	1.250	1.79	1.228	1.206	-1.79
Ferm conversion [c,f]	case 14	-3.0	-	3.0	%	243.17	0.00	243.18	243.18	0.00	1.269	3.34	1.228	1.189	-3.18
Hyd Solids loading	**case 15**	**-3.0**	**20.0**	**3.0**	**%**	**227.14**	**-6.59**	**243.18**	**251.64**	**3.48**	**1.146**	**-6.68**	**1.228**	**1.271**	**3.48**

340
341   PT: Pretreatment
342   Hyd: Hydrolysis
343   Ferm: Fermentation
344   a: ethanol to water
345   b: acid to dry biomass w/w
346   c: Variations of -3% and +3% in the conversion of the products of interest
347   d: Glucose, xylose and soluble lignin for pretreatment
348   e: Glucose and xylose for hydrolysis
349   f: Glucose and xylose to ethanol for fermentation

350   The effects on the TAC and MESP for cases 8-15 are less direct, being mostly due to

351 changes in the overall yield of the process and/or an indirect effect on the process' utilities consumption.

352 For these cases, the hydrolysis' solids loading showed the most impact on the final MESP of the process,

353 a decrease of 6.68% from the initial value when the hydrolysis was carried with 23% solids loading

354 instead of 20%. An increase in solids loading means that less water needs to be cooled prior to the

355 conversion section, furthermore it also increases the ethanol concentration in the product stream, which

356 according to da Silva et al. (2016) can provide savings in the downstream purification process. The effect

357 of the parameters evaluated as a percentage of the variation on the MESP can be seen in Figure 6.
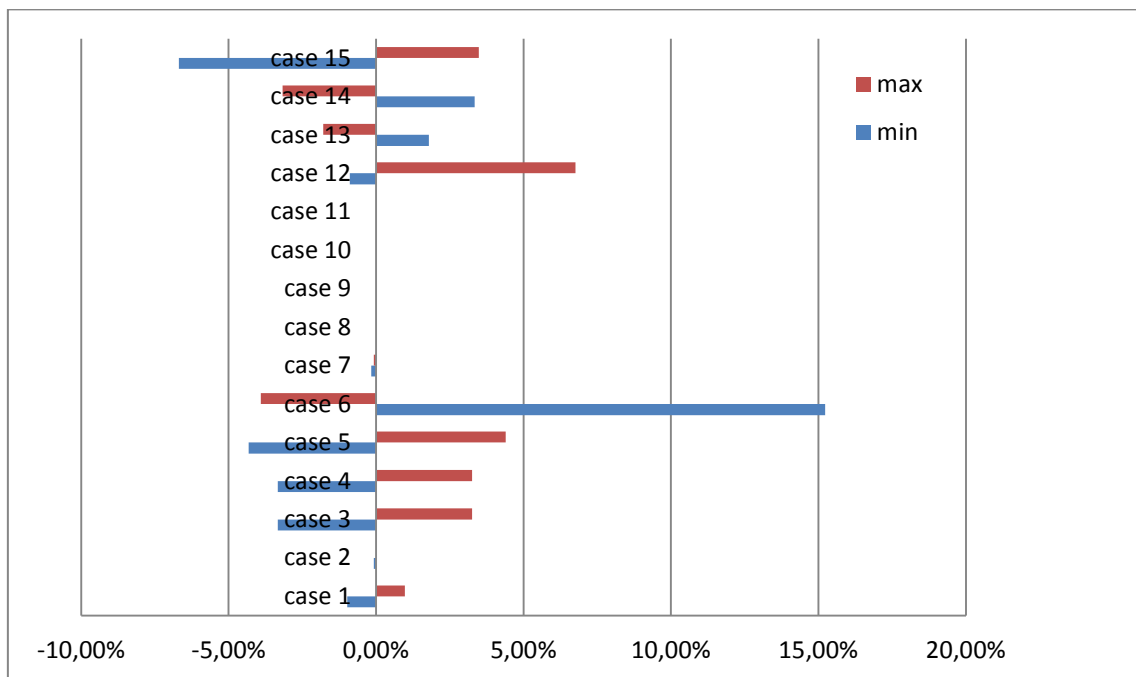
359 **Fig. 6** MESP fluctuation with parameters changes

360   Contrary to expectations, changes in the pretreatment temperature, pretreatment pressure,

361 hydrolysis temperature and fermentation temperature did not affect the MESP or TAC. For the

362 pretreatment parameters, savings in the energy consumption in the reactor meant more energy spent in the

363 flash and solvent recovery. For the hydrolysis and fermentation processes, changes in the temperature

364 resulted in savings in one reactor, but were balanced with more spending in the other.

365   Considering the evaluated cases, a future best case scenario was also investigated. In this

366 scenario we considered a plant five times bigger, resulting in an economy of scale for the total capital

367 investment and raw material cost of 5%. The new plant was set to operate 8316 hours per year for a

368 period of 40 years, instead of 7920 hours and 30 years period as the previous calculations. Furthermore,

369 we assumed an increase in the pretreatment, hydrolysis and fermentation effectiveness and a decrease in

370 the overall utilities consumption and solids loading for hydrolysis and fermentation due to improvements

371 in mass and energy transfers in the process' equipment. The sensitivity analysis indicated that ethanol to

372 water solvent at 55/45 (w/w) and solvent usage of 4.75:1 solvent to dry biomass ratio achieved the best

373 results, therefore, those values were chosen for the new simulation. The internal rate of return was fixed

374 at 5% and taxes at 30%, in contrast with 10% and 35% from the initial cases, respectively. The long term

375 scenario provided a final MESP 0.702 US$/kg of ethanol, a value 43.3% lower than the diluted acid

376 counterpart and represented a reduction of 42.8% from the initial organosolv process.

377 In order to get closer to future real results of the production costs and thus the product

378 price, a product separation area, as described on section 2.1.4, was included in the calculations. The

379 addition of the separation stage in the process raised the fixed capital investment of the process by 10%

380 and the total utility costs by 27.4%. The new MESP obtained was 0.857 US$/kg of ethanol. Comparing to

381 other published data, the value was 16.8% lower than the reported by Mesa et al. (2016), confirming that

382 the improvements proposed can indeed make the process more competitive. However, Humbird et al.

383 (2011) obtained a MESP of 0.720 US$/kg of ethanol utilizing corn stover pretreated with diluted acid and

384 Piccolo and Bezzo (2009) using acid catalyzed steam explosion on hardwood achieved 0.811 US$/kg of

385 ethanol, showing that there is still work to be done before the commercial application of the organosolv

386 process for bioethanol production.

387 **4. Conclusions**

388 Organosolv pretreatment requires higher energy consumption than diluted acid

389 pretreatment. However, the organosolv process uses less water, and enables savings in equipment costs

390 and better usage of the biomass. Much work still has to be done on energy saving mechanisms, especially

391 during solvent recovery stage, to make the process more competitive. Furthermore, ethanol productivity,

392 25,084.5 kg/h, and concentration, 11.1%, represent the biggest benefits of organosolv pretreatment when

393 comparing to diluted acid pretreatment, which gives 16,202.5 kg/h and 5.4% respectively. The increased

394 amount of ethanol produced and the more efficient removal of lignin translate into a higher ethanol

concentration in the products (pretreatment output) stream, meaning more savings potential in the downstream purification process. Additionally, compared to other methods for softwood biomass, organosolv pretreatment is one of the most preferable methods. Furthermore, additional development of organosolv pretreatment are expected to reduce solvent usage, create higher solids loading in hydrolysis and increase the ratio of ethanol in the solvent. When simulated, these changes revealed some promising results, with savings of 43.3% in the MESP compared to the most commonly employed diluted acid pretreatment method using softwood as biomass.

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