Monitoring/characterisation of stickies contaminants coming from a papermaking plant - towards an innovative exploitation of the screen rejects to levulinic acid.

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1 **ABSTRACT**

2 Recycled paper needs a lot of mechanical/chemical treatments for its re-use in the papermaking process.
3 Some of these ones produce considerable rejected waste fractions, such as "*screen rejects*", which include
4 both cellulose fibers and non-fibrous organic contaminants, or "*stickies*", these last representing a ~~weakness~~
5 ~~drawback~~ shortcoming both for the papermaking process and for the quality of the final product. Instead, the
6 accepted fractions coming from these unit operations become progressively poorer in contaminants and
7 richer in cellulose. Here, input and output streams coming from mechanical screening systems of a
8 papermaking plant using recycled paper for cardboard production were sampled and analysed directly and
9 after solvent extraction, thus confirming the abundant presence of styrene-butadiene rubber (SBR) and
10 ethylene vinyl acetate (EVA) copolymers in the output rejected stream and cellulose in the output accepted
11 one.
12 Despite some significant drawbacks, the "*screen reject*" fraction could be traditionally used as fuel for energy
13 recovery within the paper mill, in agreement with the integrated recycled paper mill approach. The waste,
14 which still contains a cellulose fraction, can be also exploited by means of the hydrothermal route to give
15 levulinic acid, a platform chemical of very high value added.
16
17 ***Keywords:*** *Screen rejects; plastic contaminants; waste incineration; energy recovery; levulinic acid.*
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1. Introduction

~~Recycling is every recovery procedure by which~~ Recycling can be defined as a recovery procedure by which waste materials are transformed into products or materials for use either in their original form or in other ones. In this context, recovered paper actually plays a very important role in the global paper industry as a very good substitute for virgin fiber pulps. Paper recovery rates continue to increase each year in North America and Europe (with the exception of 2009–2010 in Europe owing to a dip in production during the economic downturn). The American Forest & Paper Association has launched its Better Practices Better Planet 2020 initiative, establishing an ambitious goal of 70% paper recovery by 2020 (the recovery rate was 63.5% in 2010) (Bajpai, 2014). However, the use of the recycled paper is still limited by the presence of many kinds of contaminants, which can be classified according to their source (Hubbe et al., 2006), i.e. organic, inorganic and microbiological ones. The term *stickies* ~~or *bitumen*~~ is generally used to describe tacky deposits of several organic materials that mainly come from recycled paper or build up during the papermaking process. Due to the lack of an accepted classification and definition of stickies, many different classifications have been proposed. First, these organic contaminants were classified according to their physical sizes in "*macrostikies*" and "*microstickies*" (Doshi et al. 2003). ~~A possible classification of these organic contaminants is based on their different physical sizes (Doshi et al. 2003)~~. This classification defines "*macrostikies*" as solid contaminants that are retained on mesh with a diameter of about 100-150 µm and this kind of contaminants is that generally considered to monitor the removal efficiency of process units. Then, contaminants with a diameter of less than 100-150 µm ~~, but greater than 1-5 µm,~~ are defined as "*microstickies*". Microstickies can be further classified into suspended (20-100 µm), dispersed (1-2~~50~~ µm), colloidal (~~5-~~0.01-5 µm) and dissolved stickies (<0.01 µm). However, this classification by size is not enough. It is also necessary to consider the source of stickies generation. Stickies that carry over from the repulping process are termed primary stickies, whereas stickies that precipitate out of the pulp, due to changes in pH, temperature and charge, are called secondary stickies. ~~Stickies with a diameter of less than 1-5 µm are defined as stickies being mainly composed of colloids that, as a result of changes in the wet-end chemistry (i.e. temperature, pH and electric charge), are destabilized, thus forming solid deposits (Putz, 2000).~~ Stickies, ~~can fragment~~ because ~~as a consequence~~ of the mechanical operations, can fragment and give particles of smaller size ~~(from *macro* to *micro* and finally to *secondary stickies*)~~, and join again in various combinations.

From a chemical point of view, stickies include synthetic polymeric contaminants of secondary fibers, such as hot melt adhesives (typically ethylene vinyl acetate-wax hydrogenated resin acid combinations), wax and

polyethylene from coated boxes, contact adhesives (polybutylene, natural rubber, etc.), pressure sensitive adhesives (styrene-butadiene rubber (SBR), vinyl acrylates and so on) (Doshi and Dyer, 2007; Gribble et al. 2010). The heterogeneous nature of the produced wastes depends on the type of recycled paper and on the kinds of process units from which they were obtained. Therefore, the process parameters of each separation unit should be monitored and optimized in order to maximize the entire papermaking process efficiency. Starting from this statement, the rejected waste fractions should have the maximum content of contaminants and the minimum content of cellulose, respectively. On the other hand, the accepted fractions should become progressively as rich as possible in cellulose fiber up to the ~~Paper~~ paper ~~Machine~~ machine, ~~thus going on their course~~ thus becoming incorporated in the papermaking process.

Stickies represent one of the biggest problems of the paper quality control and their removal is fundamental because it prevents problems such as holes and spots in the final product and, in any case, a look that does not meet customers' requirements (Douek et al. 2003; Patrick, 2006). The presence of stickies in the ~~Paper~~ paper ~~Machine~~ machine causes plugging of wires and felts, leading to a slowing down of the water drainage of the fibrous suspension. Furthermore, mechanical problems of runnability (i.e. breakage of the sheet) may occur both in subsequent treatments (i.e. press and drying section), further lowering the process efficiency (Maher et al., 2007; Fogarty, 1993). Ultimately, all these problems are time-consuming, thus leading to higher costs for the papermaker.

The heterogeneous nature of organic contaminants trapped in recycled paper requires an integrated chemical approach for their complete characterization (Blanco et al., 2007) and for the evaluation of their subsequent alternative uses. Some of the most commonly adopted methods of analysis are reported in the literature (Doshi et al., 2000a, 2000b, 2003). Up to now, these methods have been mainly focused on the macrostickies analysis, but there is no generally accepted standardized method for microstickies determination. An interesting example for macrostickies determination is represented by the INGEDE Method 4 (INGEDE, 2011; MacNeil et al., 2010). In any case, INGEDE ~~Method 4 does not consider microstickies contribute~~ Method 4 does not consider the microstickies contribution, which represents a serious problem of the papermaking process, being the main origin of the potential deposits in the paper converting zone, mainly in the drying section (~ 70-90 wt% of the total stickies content are microstickies) (Delagoutte and Brun, 2005) and they remain as recalcitrant matter, if not effectively removed during the process. Many quantitative methods for microstickies analysis have been developed, such as UCM deposition testing (Doshi et al., 2003), the IPST (TOC) method, the "pitch-counter" method (Hamann et al., 2004; Künzel and Prinz, 2006), the PAPRICAN thermogravimetry method (Doshi et al., 2003), the TAPPI

method (Jong et al., 2006), the QCM method (Quartz Crystal Microbalance) (Goto et al., 2007), the Flow Citometry method (Wang et al., 2012).

In this context, an integrated chemical approach by solvent extraction and subsequent characterization of the extract allows the stickies analysis of all dimensions (Doshi et al., 2003, 2003b), avoiding a preliminary fractionation of the stickies and a subsequent underestimation of their content. In this sense, a lot of analytical techniques have been applied for the characterization of stickies, including Gas Chromatography/Mass Spectrometry (GC/MS), Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), Gel Permeation Chromatography (GPC) and Fourier Transform-Infrared Spectroscopy (FT-IR) (Gao et al., 2012; Sjöström and Holmbom, 1998; Zheng et al., 2002; Holbery et al., 1999; Biermann et al. 1990). In particular, Py-GC/MS has been used by many authors for the analysis of stickies and other paper additives present in pulp, deposit and paper (Kanto Öqvist et al., 2005; Odermatt et al., 2005a).

In the first part of this work, input and output (rejected/accepted) streams of mechanical coarse screening units of a papermaking plant using recycled paper for cardboard production were sampled and analysed by means of Py-GC/MS chromatography. In addition, stickies contaminants were removed from the same starting materials by means of solvent extraction and subsequently characterized by FT-IR, Py-GC/MS and GPC techniques, in order to evaluate the effectiveness of these mechanical treatments and ensure a quality control of the stock preparation process for the paperboard production.

~~Actually, according~~ According to the total quality management (TQM) and the "Define-Measure-Analyse-Improve-Control" (DMAIC) cycle, which provide the identification of the criticalities associated with the process unit operations, coarse screening unit is considered as the most critical one and it was chosen for stickies monitoring of the investigated papermaking process. ~~In fact, pulping unit~~ A pulping unit is often placed at the beginning of the cleaning process, giving an output rejected stream, which is very rich in heavy contaminants and an output accepted stream, which corresponds to the input pulp to the coarse screening units. Instead, fine screening units are foreward in the pulp cleaning process, allowing fractionation of long and short fibers and therefore working with a quite clean pulp. Furthermore, the rejected fraction of the fine screening treatment is recycled to the pulper unit, progressively enriching the starting pulp in cellulose fibers. On the contrary, coarse screening units are quite intermediate in the process of contaminants removal, thus allowing the comparison between the input screening stream (from the preceding pulping unit), with that of the output screening accept, which should mainly consist of cellulose fibers, and the output screening reject, which should be very rich in contaminants. The monitoring of these streams should allow the knowledge of

very important information for the ~~Paper~~ paper ~~Company~~ company about the efficiency of their cleaning process, thus acting in feedback on the machine parameters of the coarse screening unit.

In the second part of this work, some traditional and innovative uses of these screen rejects will be discussed. The most utilized methods of pulp and paper sludge management are land disposal, land application (composting) and energy recovery (Bajpai, 2015). Regarding the last mentioned route, many new technologies have been developed for energy recovery from waste, including pyrolysis, direct liquefaction, wet air oxidation, super critical water oxidation, steam reforming, gasification (plasma gasification, super critical gasification). Anyway, the simplest and most widely way for energy recovery remains incineration. By this route, rejects and residues in the production of brown packaging paper based on 100 % recycled paper can be used to generate 20–35 % of the energy needs of a paper mill (Menke, 2013). In order to verify this potential use, some targeted physicochemical properties of our screen rejects were evaluated, including elemental composition, heating value, moisture and ash content.

From a different perspective, screen rejects still contain residual cellulosic fibres. Hydrothermal treatment of cellulosic biomass gives levulinic acid, a very promising platform chemical for the synthesis of resins, polymers, herbicides, pharmaceuticals and flavouring agents, plasticizers, antifreeze agents and oxygenated additives (Antonetti et al., 2015; Mukherjee et al., 2015; Raspolli et al., 2012b; Raspolli et al., 2013). The path to LA involves the dehydration of the cellulose fraction to 5-hydroxymethylfurfural (5-HMF) and the subsequent rehydration of 5-HMF to give LA and formic acid, in equimolar amounts. Overall reaction occurs in water and is acid-catalyzed (Rackermann and Doherty, 2009). LA production is cost-effective if raw starting materials are inexpensive (Raspolli et al., 2009) or, even better, at negative cost (Raspolli et al., 2012a). By this way, after LA recovery in the liquid phase, it is possible to recover a solid biochar waste, thus further postponing the combustion route and even improving the performances to give energy recovery. Clearly, our integrated "*Biorefinery*" approach is sustainable (in fact water is the only solvent and only very diluted hydrochloric acid is used) and should improve overall industrial waste management system, because it is considered as a resource/raw material rather than a waste and the amount of final waste to be managed is significantly reduced.

2. Materials and Methods

2.1. Sample, reagents and standard materials

Input pulp and rejected/accepted output streams coming from coarse screening treatments were obtained by ~~DS Smith Packaging,~~ a paper company located in Tuscany, Italy. Raw recycled paper was supplied to the ~~Paper~~ paper ~~Company~~ company by the Italian Consorzium COMIECO (National Consortium for the Recovery and Recycling of Cellulose-based Packaging), which deals with the collection, sorting, recycling and energy recovery of packaging materials.

The investigated ~~Paper~~ paper ~~Company~~ company produces corrugated cardboard. The starting recycled paper belongs to *Category II*, including unbleached and brown papers (packaging board and cardboard products) that need not satisfy optical requirements such as brightness. The acronym "*OCC*" is also used for this recovered paper grade, standing for "*old corrugated containers*". Therefore, this starting recycled paper is composed by 100 % low quality waste paper (corrugated and kraft grades) and does not need too much specific and expensive chemical treatments for contaminants removal. For greater clarity, a simplified flow-sheet of the stock preparation process adopted by the investigated ~~Paper~~ paper ~~Company~~ company, is summarized in Figure 1:

Figure 1, near at here

In the flow-sheet reported in Figure 1, recycled fiber recovery begins at the pulper, which is a large blender that pulps paper into its component fibers or clusters of fibers. During this first step, some of the more coarse contaminants are mechanically removed from the papermaking plant by a perforated plate (i.e. light plastic contaminants and cellulose fibers) and a trap for heavy contaminants (i.e. metal, glass and plastic scraps) and rejected as wastes. Instead, the accepted stock is pumped to further coarse screening treatments. These ones allow the removal/separation of contaminants of different size, shape and deformability and break down small pieces (flakes) of undisintegrated paper or pulp sheets into individual fibers (secondary disintegration or deflaking). A particular of a cylindrical screen system for coarse contaminant removal is shown in Figure 2 (Holik et al., 2013):

Figure 2, near at here

The separation principle is based on the difference of size and form of the contaminants respect to the fiber. Input dirty pulp is pushed by the rotor and screened through small holes or slots (2-5 mm for coarse screening systems) to remove non-fibrous contaminants such as metal, plastics and adhesives, that remain

176   retained inside the drum. Heise et al. (2000) have reported that 5-30 % of primary stickies may pass through

177   the screening slots. This mechanical system gives an accepted stock, richer in cellulose, which is evacuated

178   from the middle part of the equipment and sent forward to more refined mechanical treatments. Instead, the

179   rejected fraction is continuously expelled from the bottom as waste. As slot size decreases, contaminant

180   removal increases to the detriment of fibre loss (Eck et al., 1995; Lerch and Audibert, 1995). Subsequently,

181   this waste fraction is dewatered and pressed up to about 50 % of water content.

182   Regarding the rejected fraction, which is named "paper mill sludge" in the following discussion, is classified

183   by the European Legislation by the code CER 03 03 10 (EPA, 2002), that is "fiber rejects, fiber-, filler- and

184   coating-sludges obtained from mechanical separation processes". This waste is produced by the

185   investigated ~~Paper~~ paper ~~Company~~ company in a considerable quantity, e.g. 10200 tons/year (with 45-50 %

186   of moisture), corresponding ~~amounting~~ to about ~~30~~ 32 wt% of the total wastes. It comes from coarse

187   screening treatments which are quite intermediate in contaminants removal route and therefore contains a

188   cellulose fraction, but unfortunately also many plastic contaminants. This fraction is dewatered by suitable

189   sedimator/press systems to facilitate its handling and transport to landfill.

190   Regarding the waste fraction coming from the pulping step, it is classified by the code CER 03 03 07, that is

191   "rejects coming from mechanical separation processes of pulp cleaning" (EPA, 2002), mainly including metal

192   and plastic scraps and few cellulose fibers. Also this waste fraction is produced in large quantity, e.g. 28400

193   tons/year (with 68 % of moisture), corresponding to ~~about 60~~ 66 wt% of the total wastes produced by the

194   ~~Paper~~ paper ~~Company~~ company, but it was not considered in the current investigation, because it was

195   obtained upstream of the entire cleaning process of the recycled paper, thus being too rich in heavy and

196   heterogeneous gross contaminants.

197   Regarding sampling, each pulp sample was taken from the pipe line of the paperboard plant in regime of its

198   operation and was representative of the original pulp suspension. Paper mill sludge was dehydrated by the

199   ~~Paper~~ paper ~~Company~~ company for easy transport and therefore it was a solid sample. Instead, input and

200   accepted output streams were liquid, because of the high water content required by the paper production

201   process and therefore they were filtered on a G3 Gouch before the analysis. Each solid sample was dried

202   within the next 3 hours in order to avoid its biodegradation, because no biocide or fungicide was added after

203   sampling procedure.

204   Pure cellulose (microcrystalline) was obtained from Sigma Aldrich. Tetrahydrofuran and chloroform were

205   purchased by J.T. Backer and Sigma Aldrich, respectively. Hexamethyldisilazane (HMDS) was used as

206   derivatizing agent in Py-GC/MS analysis and was purchased by Sigma Aldrich.

208 *2.2. Analytical protocol*

210 For a greater clarity, inflows/outflows of the investigated coarse screening unit are reported in Figure 3,
211 together with the chosen analytical protocol (sampling/analysis):

213 Figure 3, near at here

215 The analytical methodology developed for stickies monitoring has provided the sampling/characterization of
216 coarse screening unit inflows/outflows, that is the input pulp and the rejected/accepted output streams. In
217 order to sample the streams under constant operational conditions, these ones were sampled when the plant
218 was at full speed, thus being representative of the working conditions in that time. All these ones were
219 directly analysed by Py-GC/MS chromatography. Then, stickies contaminants were gravimetrically removed
220 from the starting input/output fractions by means of $CHCl_3$ or THF solvent extraction and the resulting dried
221 extracts were subsequently characterized by Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-
222 GC/MS), Fourier Transform-Infrared Spectroscopy (FT-IR) and Size Exclusion Chromatography (GPC).

224 *2.3. Stickies extraction*

226 Stickies extraction from input pulp and rejected/accepted output fractions of coarse screening treatment was
227 performed by using a conventional laboratory Soxhlet extractor. About 3 g of the starting material, previously
228 ground in a ball-mill and dried in an oven at 105 °C for 12 hours, were put in a cellulose thimble (Whatman
229 24 mm x 80 mm) and 250 mL of the extraction solvent (THF or $CHCl_3$) were introduced in the receiving flask.
230 The extraction procedure was maintained for about 45 hours, starting from the solvent boiling. This
231 extraction time was chosen because previous experiments had proved that shorter extraction times (24 h
232 and 36 h) gave lower extraction yields, whereas longer ones (50, 60 and 70 h) did not significantly improve
233 the extraction yield. Then, the extract was concentrated by a rotatory evaporator and subsequently dried at
234 room temperature by a rotary vane oil-sealed mechanical pump. The extraction residue was dried at room
235 temperature by a rotary vane oil-sealed mechanical pump. The dried extract was weighed (up to constant
236 weight) for the gravimetric determination of the stickies, according to this formula: *Extraction Yield (wt %) =*
237 *[Dried extract (g) / dried starting material (g)] x 100.* Each experiment was repeated in duplicate and the
238 reproducibility of this analysis was within 2 %.

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2.4. Gel permeation chromatography (GPC) analysis of the extract

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The molecular weight of the extract was determined by means of gel permeation chromatography (GPC). The instrument was equipped with a HPLC Rheodyne pump with a loop of 50 µL, an oven at 35 °C WATERS 515, a detector for refractive index WATERS 2410 and a dual-beam spectrophotometer WATERS 2487. Two different HPLC columns were used for the analysis: the first one was a PL gel 5 uM MIXED-C for molecular weights less than 2 millions and the second one was a PL gel MIXED 10 M-B for molecular weights greater than 2 millions. Both columns were filled with a polystyrene-polyvinylbenzene copolymer. The eluent was chloroform, with a flow of 1 mL/min. The whole system was managed by the version 5.3.11 of the software WATERS MILLENNIUM. The calibration curve was obtained by means of the analysis of different samples of monodisperse polystyrene at known molecular weights, in the range of molecular weights of interest.

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2.5. Fourier Transform Infrared Spectroscopy (FT-IR) analysis of the extract

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FT-IR characterization of the extract was performed by a Perkin Elmer Spectrum-One spectrophotometer equipped with an attenuated total reflectance ATR apparatus. The acquisition of each spectrum has provided 12 scans in the range 4000-650 cm^{-1}, with a resolution of 4 cm^{-1}. FT-IR spectra were compared with those of the electronic library of the instrument and with ones reported in the literature.

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2.6. Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) analysis of ~~of the~~ starting materials, extracts and products of screen rejects hydrolysis

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The procedures based on analytical pyrolysis (Pyrolysis-Gas Chromatography/Mass Spectrometry, Py-GC/MS) used to investigate the stickies contaminants and products of screen rejects hydrolysis have already been described in the literature (Ribechini et al. 2011; Ribechini et al. 2012). A brief summary of the procedure follows: pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) analysis of raw materials and extracts was performed with and without the addition of the derivatizing agent, that is hexamethyldisilazane (HMDS). For the Py-GC/MS analysis, few micrograms of the sample were placed in a quartz tube (pyrolysis time: 20 s) and, in the case of the use of the derivatising agent, the starting sample was admixed with 5 µL of hexamethyldisilazane (HMDS). In both cases, the sample was pyrolysed at 550 °C. The pyrolyser (CDS Pyroprobe 5000 series) was coupled online with a 6890N GC System Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA), coupled with a 5973 Mass Selective Detector

(Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer. The pyrolyser interface was kept at 180 °C, the transfer line at 300 °C, and the valve oven at 290 °C. The mass spectrometer was operated in EI positive mode (70 eV, scanning m/z 50–650). The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at 150 °C. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5% diphenyl – 95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., J&W Scientific Agilent Technologies, USA) with a de-activated silica precolumn (2 m × 0.32 mm i.d., J&W Scientific Agilent Technologies, USA) was used. The split-splitless injector was used in split mode at 300 °C, with a split ratio between 1:10 and 1:20, depending on the sample dimensions. The injector was equipped with a glass liner (single taper, deactivated, 4 mm i.d., Agilent Technologies). The adopted chromatographic conditions were as follows: 30 °C isothermal for 8 min., 10 °C/min. up to 240 °C and isothermal for 3 min., 20 °C/min. up to 300 °C and isothermal for 30 min. The carrier gas (He, purity 99.9995 %) was used in the constant flow mode at 1.0 mL/min. Peak assignation was based on comparison with analysed reference compounds and materials, with library spectra (The National Institute of Standards and Technology library mass spectra, NIST 1.7) and on the interpretation of mass spectra. The stickies were identified by comparing their mass spectra with those reported in the Wiley and the NIST libraries, as well as in the literature.

2.7. Chemical characterization of the starting screen rejects

Regarding the air dried sample, umidity moisture content was determined through UNI EN 15414-3:2011 method, by heating the sample in a TGA equipment at 105 °C under nitrogen flow, up to constant weight. Ash content was estimated at 550 °C following the UNI EN 15403:2011 procedure.

Elemental analysis (C, H, N and O) was performed according to the official UNI EN 15407:2011 method. Carbon and hydrogen contents were determined by infrared spectroscopy and nitrogen by thermal conducibility. Lastly, oxygen content was calculated by difference: O (%) = 100 (%) – C (%) – H (%) – N (%). Sulfur content was determined by the UNI EN 15408:2011. The sample was firstly heated under argon/water vapor flow and secondly burned under oxygen/water vapor flow. The fumes were bubbled through a solution of hydrogen peroxide where the SO_2 was oxidized to sulfuric acid. The recovered solution was analyzed by ion chromatography to quantify the content of sulphates.

Higher Heating Value (HHV) was performed according to UNI EN 15400:2011 procedure, by using an automatic LECO AC 500 calorimeter. This method involves the combustion of sample at constant volume

(HHV$_v$) and temperature (25 °C), in a thermostated water bath. The calorimeter was previously calibrated by the combustion of a certified reference of benzoic acid, thus obtaining the "*effective heat capacity*" (ε) of the instrument. Then, 0.5 g of sample were weighed in a quartz crucible and put in the calorimeter. Calorimeter was closed, the oxygen (25-30 atm) was introduced and the combustion was started. By measuring the temperature change (θ) of the thermostated water bath, it was possible to directly obtain the HHV parameter, and correcting this value for heat losses to the mass of the container, heat conduction through the container wall, and heat losses to the surroundings of the device.

Instead, lower heating value (LHV) was obtained by taking into account H, C, N and O contents. This parameter is expressed at constant pressure (LHV$_P$), by taking into account small volume changes that occur in the calorimeter as a result of the combustion, according to the equation:

$$LHV_P = HHV_V - 218.3 * H\ (\%) + 6.15 * H\ (\%) - 0.8 * [O\ (\%) + N\ (\%)].$$

All the above considered parameters are expressed on "*as-received*", "*air-dried*" and "*oven-dried*" basis, by taking into account the ASTM D 3180-12 method.

Lastly, mMicroelements (trace heavy metals) and macroelements were determined according to the UNI EN 15411 and UNI EN 15410 method, respectively. The elements were determined by Inductively Coupled Plasma Mass Spectrometry (ICP- MS) after digestion of the sample with acqua regia in a microwave oven. Three independent replicates were performed and blanks were measured in parallel.

Lastly, thermogravimetric analysis (TGA) was carried out by heating the samples from room temperature up to 900 °C at a rate of 20 °C/min, under a 40 mL/min flow of nitrogen or air. Both TGA (weight loss as a function of temperature) and DTG (rate of mass loss as a function of temperature) curves were acquired during each experiment. The analyses were performed in duplicate.

2.8. Catalytic experiments of screen rejects conversion to levulinic acid

Hydrolysis experiments were carried out by means of a mono-mode microwave reactor (CEM Discover S – Class System), in a 80 mL vessel containing a Teflon stir bar. The reactor was closed and purged with three cycles of vacuum-nitrogen and the sealed system was irradiated up to the set-point temperature by employing a fixed ramping time. At the end of each experiment, the reactor was rapidly cooled to room temperature by means of air which was blown directly on the surface of the reactor and a small amount of

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the reaction mixture was filtered on a 0.2 μm Whatman filter, properly diluted with water and analysed by HPLC. A Perkin Elmer Flexar Isocratic platform, equipped with a differential refractive index detector, was used for this analysis. 20 μL of sample were loaded into a Polypore CA column (4.6 mm x 220 mm x 10 μm) and eluted with a 0.5 mM H_2SO_4 at a flow rate of 0.1 mL/min. The column was maintained at 60 °C and the calibration was carried out by using a commercial LA sample. LA yield based on the weight of screen rejects was calculated as: *Yield in LA (wt%) = [LA recovered after hydrolysis (g) / dried screen rejects (g)] x 100*. The analysis was carried out in duplicate and the reproducibility of this analysis was within 3 %.

3. Results and discussion

3.1. Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) analysis of the raw materials

The streams of the raw materials coming from the papermaking plant were directly characterised by means of pyrolysis gas chromatography mass spectrometry (Py-GC/MS). Figure 4 shows the results obtained:

Figure 4, near at here

All the obtained pyrograms show a similar composition but it is possible to observe important differences in the quantitative profile of the various samples. In particular, the analytical pyrolysis demonstrates that in the rejected output stream, the abundance of the pyrolysis products is higher than in the other two streams. In detail, the abundant presence of styrene and smaller amounts of α-methylstyrene and 1,3-butadiene highlights the presence of ~~Styrene~~ styrene-~~Butadiene~~ butadiene ~~Rubbers~~ rubbers (SBR) (Tsuge et al., 2011), those last ones being copolymers which are found as pressure sensitive adhesives (PSA) in recycled paper (i.e. packaging tapes and/or labelling), indicating that at room temperature they adhere to a surface upon application of pressure (Brockmann et al., 2005). Going on the discussion about the pyrolysis products, derivatives such α-methylstyrene have evolved from those volatile radicals which have been produced by the β-scission of the PS chain end deriving from SBR copolymers (Kusch et al., 2013). At this level of investigation, the pyrograms reported in Figure 4 show that the rejected output stream was particularly enriched in styrene, ~~thus indirectly confirming the effectiveness of the investigated mechanical treatment for the contaminants removal~~ as expected, due to the presence of the mechanical treatment for the contaminants removal.

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365 Subsequently, the on-line silylation derivatization by means of hexamethyldisilazane (HMDS) and the

366 subsequent analyses by means of pyrolysis gas chromatography mass spectrometry (Py-GC/MS) were

367 performed on the same raw materials. The derivatization reaction by HMDS leads to unambiguous

368 identification of contaminants and improves conventional direct Py-GC/MS technique. In fact, it involves the

369 conversion of non-volatile polar compounds such as acids, alcohols, amines, and phenols or thermally

370 sensitive compounds into related less polar silylated derivatives, which are more volatile than starting

371 compounds. Extracted ion chromatogram of m/z 204 (fragment ion typical of trimethylsilylated compounds

372 obtained from the pyrolysis of polysaccharides such as the cellulose) was used to monitor the presence of

373 cellulose in the investigated streams. Figure 5 shows an enlargement of the extract ion chromatogram of m/z

374 204, where the presence of cellulose is evident.

375

376   Figure 5, near at here

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378 The pyrograms uniquely confirm the presence of cellulose in the investigated streams. In fact, dehydrated

379 glucose comes from side group elimination of adsorbed water on cellulose, which occurs at low pyrolysis

380 temperatures (200-300 °C), without significant depolymerization of the cellulose skeletal structure

381 (Moldoveanu, 1998). Then, Figure 5 shows the presence of 1,6-anhydro-*D*-galactopyranose and

382 levoglucosan, which are evolved as a result of cellulose depolimetization reactions, that is chain scissions by

383 transglycosidation and retroaldolization, which occur at higher pyrolysis temperatures (>300 °C)

384 (Moldoveanu, 1998). Taking the peak of 1,6-anhydro-*D*-galactopyranose as that of reference for cellulose

385 detection and monitoring, it is possible to state that, as expected, the accepted output fraction has been

386 enriched in cellulose and, on the contrary, the rejected output fraction has been impoverished in it, due to the

387 presence of mechanical unit operation for the contaminants removal. This is a further indirect confirmation of

388 what previously stated, that is the effectiveness of the investigated mechanical unit operation for the

389 contaminants removal.

390 In addition, the analytical pyrolysis carried out in the presence of HMDS evidenced the presence of acetic

391 acid, which could be evolved from adhesive EVA copolymers (Klemchuk et al., 1997). This statement will be

392 deepened in the following paragraphs.

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394 *3.2. Stickies extraction*

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396 Stickies extraction from both input pulp and rejected/accepted output fractions of coarse screening unit was

397 performed by using a conventional Soxhlet apparatus. $CHCl_3$ and THF were chosen for this purpose,

398 because of their good solvent ability towards stickies contaminants (Biermann and Lee, 1990; MacNeil et al.,

399 2006). The results of the gravimetric ~~analysis~~ analyses are reported in Figure 6:

400

401   Figure 6, near at here

402

403 For the same stream, $CHCl_3$ and THF extraction yields are very similar. Furthermore, extraction yield

404 considerably increases from ~ 6 wt% in the input pulp up to ~ 17 wt% in the rejected output stream. This

405 result~~s~~ seems to confirm the effectiveness of the screening treatment in contaminants enrichment and

406 recovery in the output waste fraction. However, extraction yield slightly decreases from ~ 6 wt% in the input

407 pulp up to ~ 5 wt% in the accepted output stream. From this point of view, the screening unit operation

408 seems not very efficient, but the ~~Paper~~ paper ~~Company~~ company does not have special optical and

409 mechanical paper quality needs, because it produces coarse corrugated cardboard and a stickies content of

410 ~ 5 wt% in the accepted output fraction is still allowed. At the level investigation of the present study and

411 under the assumptions made regarding the extraction time (see Section 2.3), these achieved extraction

412 yields correspond to the total recovery of stickies, that means a removal efficiency of 100%. Further work is

413 in progress in order to tune up a standard methodology to compare our standardized removal efficiencies

414 with those reported in the literature, especially based on physical separation, which are evaluated respect to

415 a standard method (generally solvent extraction). In particular, the removal efficiency depends on many

416 variables, first of all the nature of the starting material and its composition. Moreover, the design of the

417 screening sequence also affects to great extent how the stickies are removed: for example if the stages are

418 organized in cascade or in feed-forward mode. Definitely, the contaminants are effectively concentrated in

419 the waste stream thanks to the dewatering (pressing) step rather than to the screening operation. With the

420 current adopted screening technology, delays in the papermaking production should be expected, that is a

421 lower plant efficiency of the ~~Paper~~ paper ~~Company~~ company. In order to further lower the contaminants

422 content in the accepted output stream, other in-series screening units and mechanical treatments (such as

423 deflaking units and/or cleaners) could be included in the papermaking plant.

424 Taking into account the data of the extraction yields and those related to the input/output streams, the latter

425 which were provided by the ~~Paper~~ paper ~~Company~~ company, it is possible to obtain the unit mass balance of

426 the screening unit, as depicted in Figure 7:

427

428   Figure 7, near at here

429

430   The above figure shows that the input pulp fraction contains 4.5 wt% of stickies, the weight ratio between

431   accepted and rejected output fractions is 70/30 and the percentages of stickies in these flows are 3.2 wt%

432   and 3.5 wt%, respectively. On the basis of the unit mass balance, if an input pulp flow of 100 Kg/h is

433   considered (flow A), a water input flow of 36.8 Kg/h (flow B), an accepted output fraction of 95.7 Kg/h (flow

434   C) and a rejected output one (flow D) of 41 Kg/h are calculated. These last two flows (C and D) contain an

435   amount of solid equal to 3 kg/h and 1.4 kg/h, respectively. Considering these data and the experimental

436   extraction yields reported in Figure 6, on the basis of the input pulp flow (A), it is possible to recover a

437   stickies flow of 0.26 Kg/h, whereas, after the sedimator/press unit (E), an amount of 0.24 Kg/h is obtained. At

438   first sight, this result could not seem interesting but it is necessary to highlight that the last amount comes

439   from the flow (E), which is 30 wt% of the input pulp flow and corresponds to a percentage of 31.9 wt%

440   respect to solids. In fact, comparing (A) and (E) flows in the same conditions, which means without the

441   output flow division, it is possible to recover in the first one a stickies amount of 0.26 Kg/h, as previously

442   reported, whereas in the second one an amount of [(0.24*100)/31.9] = 0.75 Kg/h. These data underline that

443   the recovery of the stickies after the sedimator/press unit becomes about 3 times (0.75/0.26 = 2.88) higher

444   than that achieved in the input pulp flow, pointing out the good efficiency of the entire mechanical treatment

445   (screening system + sedimator/press unit) for the contaminants removal. The ascertained enrichment of the

446   press filtrate in stickies evidences the difficulty of the re-use of this fraction into the papermaking process. In

447   fact, the paper company has already tried to include this waste fraction into the process itself, but the quality

448   of the obtained final cardboard was not acceptable, in terms of both mechanical and optical properties.

449   Definitely, with the current adopted technology, this stream must be managed as a waste.

450   In principle, these extractable contaminants should contain not only sticky adhesives but also (few) residual

451   lignin derivatives and other extractive components (fatty acids and their esters or resin acids), these last

452   compounds being present in the starting wood. In the next paragraph, GPC, FT-IR and Py-GC/MS

453   characterization of these extracts will be discussed.

454

455   *3.3. Gel permeation chromatography (GPC) characterization of stickies and Fourier Transform-Infrared*

456   *Spectroscopy (FT-IR) characterization of the extract*

457

Gel permeation chromatography (GPC) and FT-IR characterization of the THF and CHCl$_3$ extracts coming from screen rejects were carried out in order to get information about the nature, the molecular weights and polydispersities of the polymeric contaminants. Both CHCl$_3$ and THF extracts appeared to be dark-brown resinous solids. GPC analyses reveal that CHCl$_3$ and THF extracts were composed mainly of non-cross-linked ~~high~~low molecular weight polymers, ~~which were~~ variously polydispersed, showing molecular masses of 36217 and 37124 for CHCl$_3$ and THF extracts respectively (M_n = 21173 and 22112 for CHCl$_3$ and THF extracts respectively; M_w = 43514 and 44212 for CHCl$_3$ and THF extracts respectively) characterized by a polydispersity index of 2.0 and 2.2 for CHCl$_3$ and THF extracts respectively. FT-IR analysis, acquired using ATR technique which is the best one to directly acquire IR spectra of these tacky compounds, reveals the presence of ethylene vinyl acetate (EVA) copolymers by the comparison among the FT-IR spectrum of the CHCl$_3$ extract (Figure 8) and those reported in the literature (Pouchet, 1985).

~~Gel permeation chromatography (GPC) of the THF and CHCl$_3$ extracts coming from the rejected output stream was carried out in order to evaluate the molecular weights and polydispersities of the polymeric contaminants. The results are reported in Table 1:~~

~~Table 1, near at here~~

~~Above similar results suggest that CHCl$_3$ and THF extracts were composed mainly of non-cross-linked high molecular weight polymers, which were variously polydispersed.~~

~~*3.4. Fourier Transform-Infrared Spectroscopy (FT-IR) characterization of the extract*~~

~~CHCl$_3$ and THF extracts appeared to be dark-brown resinous solids. ATR technique was the best one to directly acquire IR spectra of these tacky compounds. The comparison among the FT-IR spectrum of the CHCl$_3$ extract (Figure 8) and those reported in the literature (Pouchet, 1985) has uniquely confirmed the presence of ethylene/ vinyl acetate (EVA) copolymers:~~

Figure 8, near at here

Regarding the band assignments, it is possible to observe the typical absorption bands of the polyvinyl acetate (Naranjo et al. 2008). In detail, both the carbonyl band at about 1730 cm^{-1}, due to the C=O stretching

490 of the acetate group and the bands at about 1230 cm^{-1} and at 1020 cm^{-1}, due to the C-O stretching of the

491 ester group, unequivocally confirm the presence of the acetate group (Scheirs, 2000). Some typical

492 absorption bands of methyl and of methylene bending (scissors) are evident, in particular at 1375 cm^{-1} and at

493 1440 cm^{-1}, respectively. All these statements were confirmed also for the THF extract. EVA copolymers are

494 generally used as thermoplastic hot melt adhesives in the paper and packaging industry (on packaging

495 machines which erect and seal packages, on folding machine gluers, for cigarette paper), for sticky labels

496 (address labels), in book binding (adhesive binding) and for the manufacture of hygienic products (baby

497 diaper). In addition to these uses, EVA adhesives are used also in the corrugated paperboard process,

498 keeping together its different layers and for labelling in the converting section.

499 On the other hand, regarding SBR, these ones were identified by Py-GC/MS analysis of the raw materials

500 but are not clearly visible by the FT-IR technique because their absorption bands were hidden by those of

501 EVA, which are far more intense. This statement was confirmed by the evaluation of the FT-IR spectrum (in

502 ATR mode) of a SBR copolymer of reference, which was included in the electronic library of the instrument.

503 Also the solid residues recovered at the end of the extraction procedures were properly dried under vacuum

504 at room temperature and characterised by means of FT-IR spectroscopy. The FT-IR spectrum of the solid

505 residue recovered after CHCl$_3$ extraction is reported in Figure 9, together with that of the commercial

506 microcrystalline cellulose:

507

508   Figure 9, near at here

509

510 The perfect match between the spectral pattern of the solid residue recovered after CHCl$_3$ extraction and that

511 of the pure commercial cellulose confirms the cellulose-like nature of the extraction residue. Stickies

512 extraction has released the hydroxyl functionalities of the cellulose fraction, which gives the typical

513 broadband stretching at about 3300 cm^{-1}. Moreover, the band at 1022 cm^{-1}, which is due to the vibration of

514 the C-O-C pyranosidic ring of cellulose units, was found. There are also two distinctive absorption bands, the

515 first one at 1160 cm^{-1} (C-O stretching and OH bending) and the second one at 895 cm^{-1} (C-O-C stretching of

516 β-(1$\rightarrow$4) glycosidic bond) (Ciolacu et al., 2011). The same statements were also confirmed for the solid

517 residue recovered after THF extraction. So, stickies contaminants were previously attached to the cellulose

518 structure, not allowing its further recovery by means of simple mechanical treatments. Ultimately, this paper

519 mill sludge has really to be considered as a waste material.

520

17

3.54. Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) characterization of the extract

The characterization of CHCl$_3$ and THF extracts by means of Py-GC/MS was performed, thus identifying the contaminants contained in the paper mill sludge extracts. The first pyrolysis experiments were performed without the use of the derivatising agent. Figure 10 shows the pyrogram of the CHCl$_3$ extract:

Figure 10, near at here

The above pyrogram confirms the presence of all pyrolysis products which were previously identified in the raw materials. In addition, hexadecanoic and octadecanoic acids (palmitic and stearic acid, respectively) were detected, coming mainly from SBR pyrolysis (Sarkissian, 2007) but also from fatty acids that could be still present in the lipophilic extractives of the starting wood material (Silverio et al., 2007). All these statements were confirmed also for the THF extract.

Subsequently, the on-line silylation derivatization by means of hexamethyldisilazane (HMDS) and the subsequent analyses by means of pyrolysis gas chromatography mass spectrometry (Py-GC/MS) were performed. Figure 11 shows the pyrogram of the CHCl$_3$ extract:

Figure 11, near at here

The above pyrogram immediately evidences the abundant presence of acetic acid, which is evolved by mild thermal degradation of EVA ester groups (Klemchuk et al., 1997). Also in the pyrogram of HMDS derivatized sample, styrene and indene were found, further confirming the presence of SBR copolymers. The presence of hexadecanoic and octadecanoic acids (palmitic and stearic acid, respectively) was due to the presence of SBR copolymers, as previously stated (Sarkissian, 2007) or to residual extractives. Lastly, dehydroabietic acid (DHA) was found, being a resin acid used in the production of wood pulp and common in paper mill effluents.

3.65. Traditional versus innovative exploitation possibilities of the screen rejects: energy recovery Evaluation of some targeted energetic properties of the screen rejects versus hydrothermal conversion of the cellulose fraction into levulinic acid

18

On the basis of the technology adopted by the considered paper company, a combustion unit for the energy recovery is not present and therefore screen reject stream is simply landfilled. Anyway, energy recovery by incineration could represent the main traditional and immediate exploitation possibility of the screen rejects. In order to verify the feasibility of this application, some targeted physico-chemical properties of the screen rejects were evaluated, including elemental composition, heating value, moisture and ash content. The obtained data are summarized in Table 2 1:

Table 2 1, near at here

Energy content of the as-received screen rejects is well in agreement with that reported by CEPI for the same kind of waste (CEPI, 2011). Furthermore, energy content of the "*as-received*" rejected screens is high, thanks to the significant amount of plastics and fibres (which affects positively the heating value) and to the quite low ash content (which should affect negatively the heating value). Elemental composition and moisture data of the screen rejects are different from those of mechanical/biological sludges, but rather similar with those of deinking sludges (Clarke and Guidotti, 1995; Gavrilescu, 2008), despite the much more higher ash content in this last case (~50 wt%), which leads to a much more lower heating value (~2800 KJ/Kg). However, the high moisture content of the screen rejects adversely affects the heating value, thus requiring significant energy consumption for water removal. The preliminary water The complete water removal leads to a drastic increase of the energy content (Table 2 1), but it is not economically advantageous because it adds further processing costs. This is the main limit for the optimal use of this kind of waste as solid fuel for energy recovery. However, the direct combustion of the "as-received" waste (58 % moisture), which is recovered after the press unit, could be the best choice for energy valorization, if the plant itself is integrated with the energy generation unit.

The use of the screen rejects for energy recovery within an incineration plant has to take into account air emissions. In this sense, in order to minimize environmental pollution from screen rejects incineration, heavy metal loading must meet the law requirements (Alvarenga et al., 2015). This is something that requires consideration when using these wastes (as sludge) for composting and agricultural/land application purposes (Alvarenga et al., 2015). Starting from this statement, a preliminary investigation of macro- and micro-elements content in the screen rejects was carried out. The results of these analyses are reported in Table 3 2 and Table 4 3, respectively:

19

583   Table 3̶ 2, near at here

584   Table 4̶ 3, near at here

585

586   Table 3̶ 2 shows that screen rejects contain firstly calcium, which is due to the precipitated calcium

587   carbonate, and secondly silica and aluminum, those ones being the main components of kaolin. These

588   mineral constituents are commonly used during the papermaking process in the formulation of fillers and

589   coating pigments. Screen rejects heavy metal concentrations reported in Table 4̶ 3 are very low and in

590   addition these are below the limits required by both the "*EU ECO Label for Soil Improvers*" (Commission

591   Decision 2006/799/EC) and the "*Proposed Limit Values for Compost*" (Saveyn and Eder, 2014), except for

592   copper, whose content is lower than that of primary and secondary sludges (Integrated Pollution Prevention

593   and Control IPPC, 2001). The copper content is probably due to blue pigments of printing inks which contain

594   phthalocyano-compounds. Anyway, screen rejects contain lower amounts of heavy metals compared, for

595   example, to municipal solid waste. So, the flue gas treatment system suitable for municipal solid waste

596   incineration plants can be easily applied to sludge incineration process to comply with the regulations set on

597   heavy metals emissions.

598   In order to complete the thermal characterization of the screen rejects, thermogravimetric analysis was

599   carried out and the obtained TG and DTG curves are reported in Figure 12:

600

601   Figure 12, near at here

602

603   The above TG and DTG graphs show a similar behavior of the screen rejects under nitrogen and air, despite

604   thermal degradation steps under air are better defined. Taking into account the thermal degradation of the

605   screen rejects under nitrogen atmosphere, three steps are detected. The first one, which occurs up to about

606   100 °C, is due to the moisture loss of the starting sample. Then, the second one is in the range between 200

607   and 400 °C, including mainly the decomposition of paper fibers, and, to a lesser extent, of sticky

608   contaminants. This temperature range is well in agreement with those reported by Wang et al. (2012) for old

609   newspapers (ONP) and mixed office wastepaper (MOW), under the same working conditions. In all these

610   cases, this thermal degradation step is not much more wider respect to that of the clean pulp board and

611   wood fibers, which occurs between 300 and 400 °C, suggesting that the stickies loading in these wastes is

612   not excessively high (Wang et al., 2012). The last degradation step occurs at a higher temperature, between

613   700 and 800 °C, being due to the decomposition of $CaCO_3$ filler into CaO and CO_2.

3.76 Hydrothermal conversion of the cellulose fraction of the screen rejects into levulinic acid

After having investigated the possible traditional use of the screen rejects, these ~~wastes~~ ones were used as starting materials for the production of levulinic acid (LA), a very high-value platform chemical, by means of acid-catalyzed hydrolysis. The reaction mechanism is reported in Figure 13:

Figure 13, near at here

In order to evaluate this innovative exploitation ~~opportunity~~ possibility, ~~some preliminary~~ hydrolysis tests were carried out in a microwave (MW) reactor, by using water as the only green solvent, dilute ~~HCl~~ hydrochloric acid as catalyst, and the optimization of ~~optimizing~~ the main reaction parameters, that is concentration of the acid catalyst, solid/liquid ratio of the reaction mixture, and hydrolysis temperature/time ~~and concentration of the acid catalyst~~ was performed. The appropriate choice of the reaction conditions has been done starting from the previously published results obtained from the conversion of herbaceous and waste biomasses into LA (Antonetti et al., 2015, Raspolli Galletti et al., 2012a). In this sense, it was found that acid concentration and reaction temperature/time were the main reaction parameters to be carefully optimized for LA production. In greater detail, an increase of the acid concentration favours the LA production, but it is necessary to find a compromise, in order to minimize the problems of plant corrosion and ensure process sustainability. On this basis, different concentrations of hydrochloric acid were tested, in the range between about 0.5 and 3 wt%. Regarding the appropriate reaction temperature, LA is certainly obtained under thermodynamic control, and therefore it is certainly necessary to adopt high temperatures, in the range 160–190 °C (Antonetti et al., 2015). Anyway, when dilute hydrochloric acid concentrations, short reaction times and high temperatures are adopted, the hydrothermal process could still be considered as a mild one and therefore sustainable. Formulation and reaction conditions adopted in our previous work (Antonetti et al., 2015) have been used again in a preliminary test with the screen rejects, in order to qualitatively detect the presence of LA in the hydrolyzate solution, thus immediately demonstrating the possibility of using screen rejects for this new purpose. Py-GC/MS chromatography was adopted for the analysis of the hydrolyzate solution, and the obtained pyrogram is reported in Figure 14:

Figure 14, near at here

21

In the above pyrogram, unsaturated and saturated carboxylic acids and aromatic derivatives are identified. In more detail, the abundant presence of LA is clearly confirmed, thus further encouraging the optimization of the screen rejects hydrothermal conversion. Furthermore, some simple phenolic derivatives have been identified, which come from the partial depolymerization of the lignin fraction of the starting screen rejects. The absence of residual carbohydrates in the pyrogram is a clear evidence of the complete degradation/conversion of these precursors, under the adopted harsh reaction conditions, in particular reaction temperature.

Starting from these promising preliminary results, the effect of the acid concentration on the LA production was studied more in depth in the MW reactor, by performing hydrolysis reactions with HCl in the range between about 1 and 3 wt%, by adopting harsh reaction conditions, e.g. reaction temperature and time, which were certainly appropriate for LA production, e.g. 190 °C and 20 minutes, respectively. The results of the acid concentration effect on LA yield are reported in Table 4.

Table 4, near at here

On the basis of the above data, it is possible to state that these screen rejects could be advantageously converted into LA, with acceptable ponderal yields. Anyway, organic contaminants hamper the cellulose fraction conversion and this justifies the lower LA yields respect to those obtained by using other waste biomasses (Raspolli et al., 2012) or, even better, more "cleaner" lignocellulosic ones (Antonetti et al., 2015; Rivas et al., 2016; Rivas et al., 2015). The above data show that a significant improvement in LA yield has occurred in test E_4, which corresponds to the best acid concentration already adopted in our previous work on giant reed conversion (Antonetti et al., 2015). In detail, at lower acid concentrations (Table 4, Tests E_1-E_3), the LA yields are still too low, whilst at higher concentrations (Table 4, Tests E_5-E_8), only mild increases in LA yield occur, to the detriment of greater corrosion problems from a plant-based perspective. Therefore, acid concentration equal to 1.6 wt% could be chosen for the versatile optimal conversion of these different kinds of biomasses into LA, thus minimizing the problems of plant corrosion, at the same time ensuring the entire process sustainability.

After having found the optimal acid concentration for LA production, the effect of the reaction temperature and time was investigated and also these parameters were optimized. The results obtained from temperature optimization are reported in Figure 15.

22

676   Figure 15, near at here

678   The above figure confirms that screen rejects conversion into LA needs of a careful temperature optimization,

679   allowing the optimal LA production at about 190 °C. In fact, milder reaction conditions don't allow the

680   complete solubilization/conversion of the C6 carbohydrates into LA, whilst harser ones do not significantly

681   improve the yield, confirming that thermodynamic control for LA production has been reached. On this basis,

682   temperature represents the main reaction parameter to be carefully monitored and optimized. In the case of

683   screen rejects conversion, this temperature range must not be lower than 160-170 °C, which is in agreement

684   with the results reported in our previous work on giant reed conversion (Antonetti et al., 2015).

685   Instead, the results obtained from reaction time optimization are reported in Figure 16.

687   Figure 16, near at here

689   The above data confirm that temperature is the main parameter to be optimized by the MW approach, whilst

690   the gain obtained by the reaction time optimization is rather modest, beyond a certain determined limit. The

691   high LA yields evidenced in Figure 15 and Figure 16 were favored by the fast heating and cooling protocol

692   under the microwave irradiation procedure (ramping heating/cooling time equal to 10 minutes), which can be

693   reproduced only with greater difficulty under conventional heating protocols.

694   Lastly, the effect of the solid loading on LA yield was studied and optimized. This parameter is very important

695   from an industrial perspective, having a strong impact on the productivity of the same plant. Anyway, this

696   parameter cannot be indefinitely enhanced, because a too much high solid loading leads to an inefficient

697   solubilization of the C6 carbohydrates and, as a consequence, to their worse conversion into LA. Starting

698   from this statement, some hydrolysis experiments were carried out by changing the solid loading of the

699   starting formulation, keeping constant the previously optimized reaction variables. Also the amount of

700   recovered solid residue was monitored in each test. The obtained results are reported in Table 5.

702   Table 5, near at here

704   The above data show that it not advatageous to enhance too much the solid loading of the formulation, this

705   choice leading to an evident worsening in LA yield (Table 4, tests E_10-E_12). This is due to the inefficient

706   diffusion of the acid catalyst and solvent into the biomass, which is degraded to hydrolysis residue, rather

than being advantageously converted into LA. In fact, the amount of the hydrolysis residue increases up to about 40 wt% by increasing the solid loading, thus further confirming that formulation adopted in test E_4 is the best for the hydrothermal conversion of the screen rejects into LA.

~~Despite these drawbacks, our approach is feasible~~ On the basis of the overall analysis of the obtained results, it is possible to state that screen rejects can be exploited for the LA production, especially taking into account ~~because of~~ the negative-cost of the starting material. Furthermore, screen rejects could be directly used in ~~the~~ a LA dedicated Biorefinery plant, e.g. "as-received", thus avoiding ~~expensive~~ additional drying procedures. ~~Combustion~~ By this route, the combustion is moved after LA recovery, being carried out on the solid residue ~~of~~ recovered after the hydrolysis reaction. This residue is a carbonaceous charred material, which ~~and~~ could be better used for energy recovery, thus closing the entire Biorefinery cycle of the waste material, and at the same time meeting the requirements of Wwaste Mmanagement Ppolicy.

4. Conclusions

The characterization of the input/output streams of the screening unit of a papermaking plant has showed ~~that~~ an ~~real~~ ~~clearly~~ evident enrichment of contaminants in the output rejected stream ~~has occurred~~, due to the accumulation/pressing unit located in the output rejected stream, rather than to the mechanical operation of sieving of the screening unit. Analytical pyrolysis of the screen rejects coming from a papermaking plant has demonstrated that output rejected stream is very rich in organic contaminants, mainly ethylene vinyl acetate (EVA) and styrene-butadiene rubber (SBR) copolymers. Definitely, output screen rejects represent an abundant waste fraction of the papermaking plant and must be exploited, in agreement with the waste management policy. Plastic contaminants trapped in the screen rejects could be ideally removed from the waste into valuable oil/wax products by a traditional thermal pyrolysis route. However, the pyrolysis of this kind of waste is not still (unfortunately) economically advantageous on industrial scale, because of the low cost of the styrene monomer. Therefore, main immediate exploitation route of the screen rejects remains energy recovery by incineration. In this sense, this waste has interesting physicochemical properties, except the moisture content, which is unfortunately high. Furthermore, heavy metal content screen rejects are below those limits required by the European Legislation, except for copper. Anyway, flue gas treatment system suitable for municipal solid waste incineration plants can be easily applied to sludge incineration process to comply with the regulations set on heavy metals emissions.

Lastly On the other hand, screen rejects contain a residual cellulose fraction, this latter finding innovative and promising applications in thermochemical conversion processes, such as the hydrothermal one for the recovery of high value-added platform chemicals, e.g. 5-hydroxymethylfurfural or such as levulinic acid. The optimization of the reaction starting from screen rejects was carried out and the best ascertained LA yield amounted to about 7 wt%, on dry basis. Despite this value is lower than those obtained by using lignocellulosic biomass, the re-use of screen rejects for this purpose is strongly encouraged by the Waste Management Policy, because of the negative value of this waste material, which should otherwise be destined for landfill. Furthermore, By this way by our new approach, it is possible to move the combustion after the levulinic acid recovery, being carried out on the same solid residue of the hydrolysis residue. This solid residue new waste material represents a deoxygenated "coal-like" material, and could be more effectively used as fuel for energy recovery, thus allowing the closing of the Biorefinery cycle of the entire waste material.

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975

976 **Table 1**: Results of the GPC analysis of the CHCl₃ and THF extracts coming from the investigated screen
977 rejects.

Extract	Mₙ	Mᵥ	PM	Polydispersity Index
CHCl₃ extract	21173	43514	36217	2.0
THF extract	22112	44212	37124	2.2

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979

980 Table 21: Physicochemical properties of interest for the use of screen rejects as solid fuel.

Physicochemical Properties	~~Rejected screens~~ Screen rejects (as-received)	~~Rejected screens~~ Screen rejects (air dried)	~~Rejected screens~~ Screen rejects (oven dried)
Higher heating value, [KJ/Kg]	7320	16705	17620
Lower heating value, [KJ/Kg]	5385	15430	16410
Moisture (%)	58.5	5.2	-
Ash, (%)	4.4	10.1	10.7
C, (%)	18.3	41.7	44.0
O (%)	16.2	37.2	39.2
H, (%)	2.4	5.4	5.7
N, ~~(%)~~ [mg/kg]	~~0.15~~ 1500	~~0.35~~ 3500	~~0.35~~ 3500
S [mg/kg]	359	820	865
~~O, (%)~~	~~16.21~~	~~37.17~~	~~39.17~~

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985 Table 32: Macro-elements composition in screen rejects (mean ± standard deviation, n = 3). Results are
986 reported on dry matter basis (g kg⁻¹ DM).

Al	Ca	Fe	Na	Si
4.6 ± 0,.2	34.9 ± 2,.5	1.1 ± 0.1	0,7 ± 0.1	8,1 ± 0.1

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993 Table 43: Micro-elements (heavy metal) composition in screen rejects (mean ± standard deviation, n = 3).

994 Results are reported on dry matter basis (mg kg^{-1} DM).

As	Ba	Cd	Cr	Hg	Ni	Pb	Cu	Se	Sn	Tl	Zn
<1	71 ± 30.6	<1	39 ± 0.7	<0.05	19 ± 2.1	8 ± 0.1	26 ± 1.8	<1	7 ± 1.2	<1	65 ± 7.5

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997 Table 4: Optimization of screen rejects conversion into LA in the MW reactor, as a function of hydrochloric

998 acid concentration. Formulation and operating conditions: 1.63 g screen rejects, 23.3 g water. Reaction

999 temperature = 190°C, ramping time = 10 minutes, reaction time = 20 minutes.

Test	HCl concentration (wt%)	LA yield (wt%)
E 1	0.4	1.5
E 2	0.8	3.1
E 3	1.2	5.2
E 4	1.6	6.8
E 5	2.0	6.9
E 6	2.4	7.2
E 7	2.8	7.4
E 8	3.2	7.5

1000

1001
1002
1003 Table 5: Optimization of screen rejects conversion into LA in the MW reactor, as a function of the starting

1004 solid loading. Formulation and operating conditions: 23.3 g water, 1.6 wt% HCl. Reaction temperature =

1005 190°C, ramping time = 10 minutes, reaction time = 20 minutes.

Test	Screen rejects (g)	LA yield (wt%)	Recovered hydrolysis residue (wt%) [a]
E 9	0.81	6.5	35.5
E 4	1.63	6.8	35.1
E 10	2.43	4.8	38.0
E 11	3.24	3.5	39.2
E 12	4.05	2.4	40.1

1006 [a] The amount of recovered hydrolysis residue was evaluated respect to the starting dry screen rejects.

1007

Captions for Figures

Figure 1: Flow-sheet of the stock preparation process adopted by the investigated ~~Paper~~ paper ~~Company~~ company for the removal of contaminants from OCC recycled paper.

Figure 2: (Left) Particular of a cylindrical screen system for coarse screening. (Right) Cylindrical screen with opened housing, showing the cylindrical screen and the foil rotor.

Figure 3: Analytical protocol for sampling/characterisation of the stickies contaminants in the investigated paperboard production plant.

Figure 4: TIC pyrograms of the not-derivatized raw materials. [B, black] Input pulp stream; [A, blue] accepted output stream; [C, red] rejected output stream.

Figure 5: Extracted ion chromatogram of m/z 204 (fragment ion typical of trimethylsilylated pyrolysis products obtained from cellulose). [B, black] Input pulp stream; [A, blue] accepted output stream; [C, red] rejected output stream.

Figure 6: Gravimetric determination of $CHCl_3$ and THF extractable compounds from the screening unit streams. Reagents and operating conditions: 3.0 g of dried starting material, 250 mL of extraction solvent, extraction time = 45 hours. The extraction yield was calculated as: *Extraction yield (wt %) = [dried extract (g) / dried starting material (g)] x 100.*

Figure 7: Mass balance of screening unit operation of the investigated ~~Paper~~ paper ~~Company~~ company. Note *: Reported extraction yields are referred to $CHCl_3$ extraction experiments.

Figure 8: FT-IR spectrum of the $CHCl_3$ extract. The FT-IR spectrum was acquired by ATR mode.

Figure 9: Comparison between the FT-IR spectrum of the solid residue recovered after $CHCl_3$ extraction [black] and that of commercial microcrystalline cellulose [blue].

Figure 10: Pyrogram of stickies contaminants. Not-derivatized $CHCl_3$ extract. Note * = Contaminants contained in the analytical blank.

Figure 11: Pyrogram of stickies contaminants. HMDS derivatized CHCl$_3$ extract. Note * = Contaminants contained in the analytical blank.

Figure 12: Yield in LA (wt %) as a function of the hydrolysis temperature (left) and time (right) with HCl (1.6 wt%). The Yield is calculated as: *Yield in LA (wt %) = LA recovered after reaction (g) / dried screen rejects (g)] x 100*. Reagents and operating conditions for temperature-dependent experiments: 1.62 g screen rejects, 23.3 g water, 0.93 mL HCl 37 wt%, hydrolysis time = 20 minutes, ramping time = 10 minutes. Reagents and operating conditions for time-dependent experiments: 1.62 g screen rejects, 23.3 g water, 0.93 mL HCl 37 wt%, hydrolysis temperature = 190 °C, ramping time = 10 minutes. Hydrolysis experiments were performed in a CEM discover S-Class MW reactor.

Figure 12: Weight loss (%) TG and derivative weight loss (%/°C) DTG of the investigated screen rejects, under nitrogen and air atmosphere.

Figure 13: Synthesis of levulinic acid in the presence of HCl catalyst from screen rejects.

Figure 14: Py-GC/MS chromatogram of the aqueous phase recovered after hydrolysis of the screen rejects in the MW reactor (Table 4, Test E_4). Formulation and operating conditions: 1.63 g screen rejects, 23.3 g water, 1.6 wt% HCl. Reaction temperature = 190 °C, ramping time = 10 minutes, reaction time = 20 minutes.

Figure 15: Yield in LA (wt%) as a function of the hydrolysis temperature. The yield is calculated as: *Yield in LA (wt%) = [LA recovered after reaction (g)/dried screen rejects (g)] x 100*. Formulation and operating conditions: 1.62 g screen rejects, 23.3 g water, 1.6 wt% HCl. Ramping time = 10 minutes, reaction time = 20 minutes.

Figure 16: Yield in LA (wt%) as a function of the hydrolysis time. The yield is calculated as: Yield in LA (wt%) = [LA recovered after reaction (g)/dried screen rejects (g)] x 100. Formulation and operating conditions: 1.62 g screen rejects, 23.3 g water, 1.6 wt% HCl. Reaction temperature = 190 °C, ramping time = 10 minutes.

Figure 1

| Re-pulping | → | Coarse screening unit | → | Fine screening unit | → | Thickening | → | Refining |

Light & heavy contaminants *rejected*

Paper mill sludge *rejected*

Addition of chemicals

Paper Machine
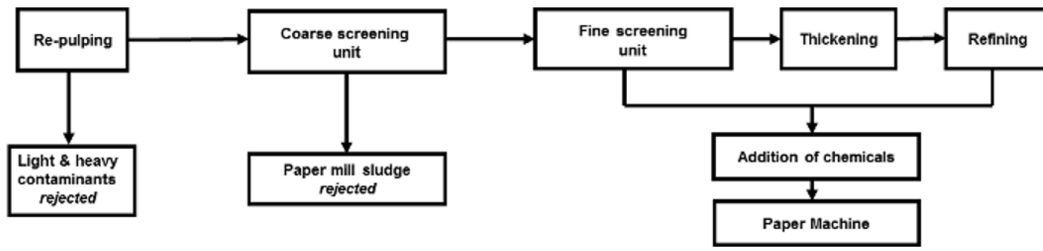
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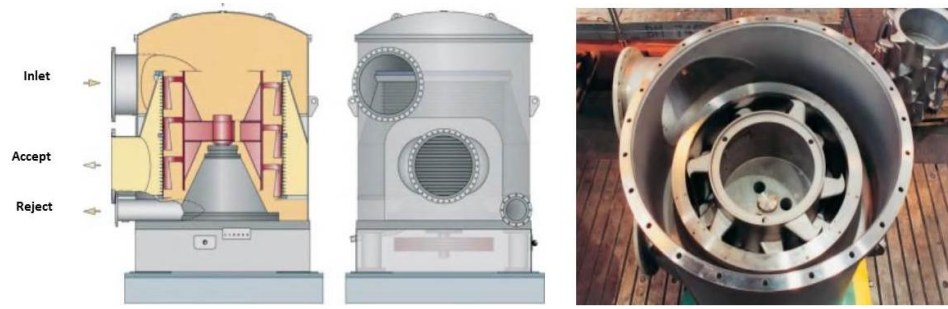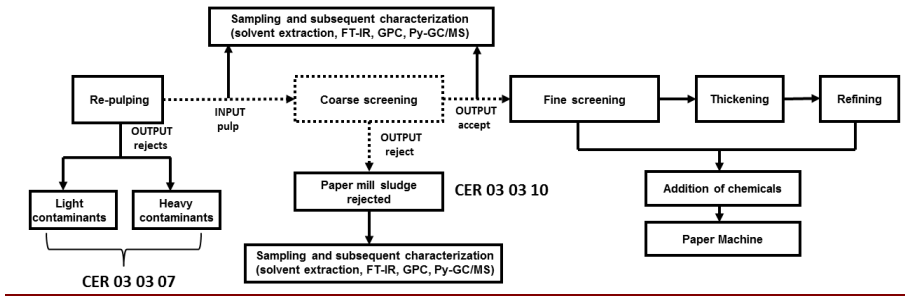1097
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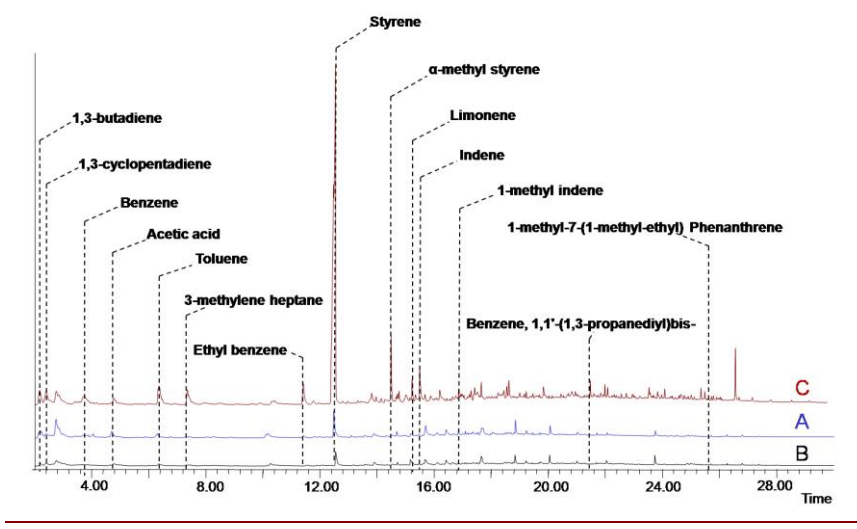1099
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Figure 2

Inlet

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1144   <u>Figure 3</u>

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                      ┌─────────────────────────────────────────────┐
                      │   Sampling and subsequent characterization  │
                      │   (solvent extraction, FT-IR, GPC, Py-GC/MS)│
                      └─────────────────────────────────────────────┘

    ┌───────────┐                 ┌ ─ ─ ─ ─ ─ ─ ─ ┐    OUTPUT   ┌──────────────┐   ┌─────────────┐   ┌──────────┐
    │ Re-pulping│ ···INPUT···▶    │ Coarse screening│  ··accept··▶│Fine screening│─▶│  Thickening │─▶│ Refining │
    └───────────┘     pulp        └ ─ ─ ─ ─ ─ ─ ─ ┘             └──────────────┘   └─────────────┘   └──────────┘
       │ OUTPUT                            │ OUTPUT                     │
         rejects                             reject                     ▼
       │                                   │                    ┌──────────────────┐
   ┌───┴────┐                        ┌──────────────┐           │ Addition of      │
   ▼        ▼                        │ Paper mill   │  CER 03 03 10 │ chemicals     │
┌───────┐┌───────┐                   │ sludge       │           └──────────────────┘
│ Light ││ Heavy │                   │ rejected     │                    │
│contam.││contam.│                   └──────────────┘                    ▼
└───────┘└───────┘                          │                    ┌──────────────┐
   └────┬────┘                       ┌─────────────────────────┐ │ Paper Machine│
   CER 03 03 07                      │ Sampling and subsequent │ └──────────────┘
                                     │ characterization        │
                                     │(solvent extraction,     │
                                     │ FT-IR, GPC, Py-GC/MS)   │
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Figure 4

1209 Figure 5

1239 <u>Figure 6</u>

1269 <u>Figure 7</u>

Input water flow
Flow B

Input pulp flow → **Coarse Screening** → Output accepted stream

Flow A
100 Kg/h
4.5 wt % of stickies
Extraction yield 5.9 % *

Flow C
3.2 wt % of stickies
Extraction yield 4.7 % *

Output rejected
stream
Flow D
3.5 wt % of stickies

weight ratio
flow C/flow D
= 70/30

Press Unit

Final output rejected flow
Flow E
50 wt % of stickies
Extraction yield 16.8 % *
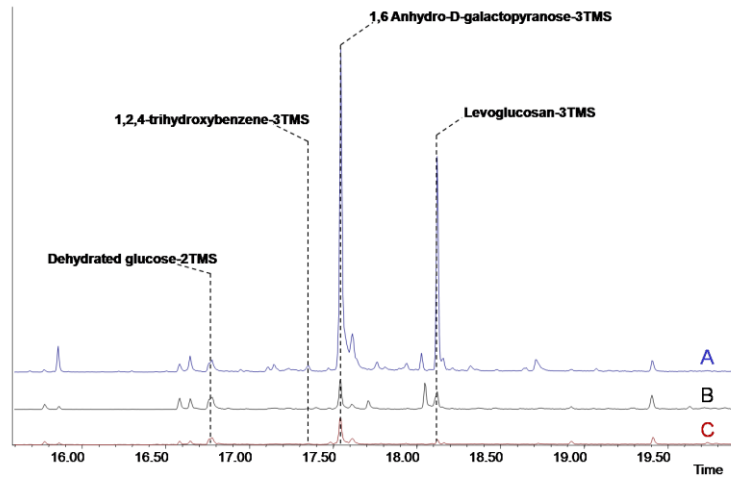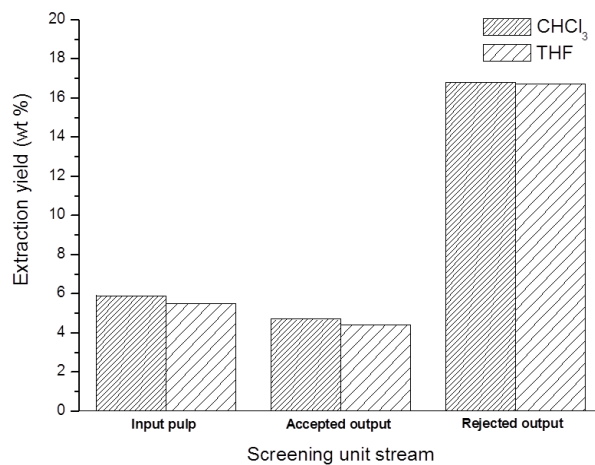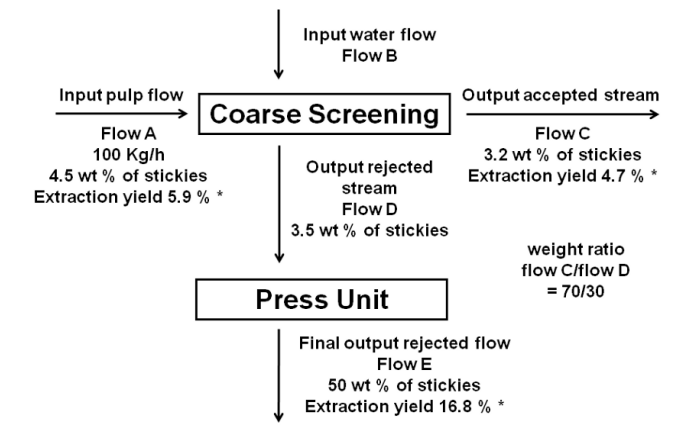
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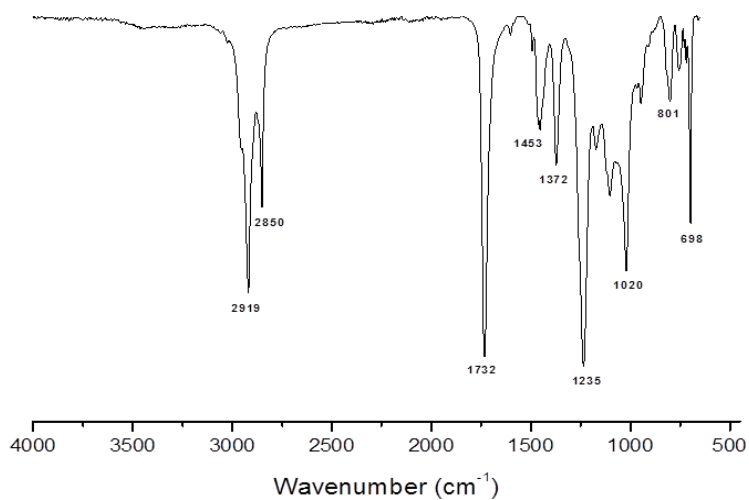
Figure 8

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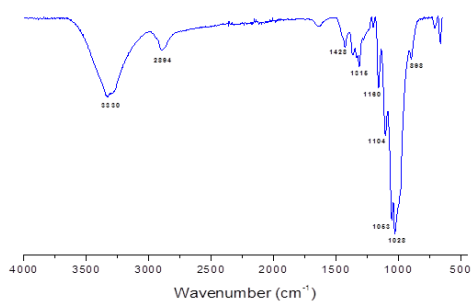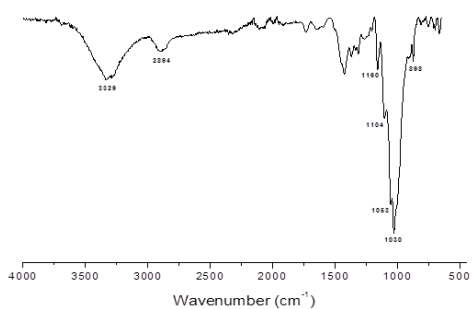
Figure 9

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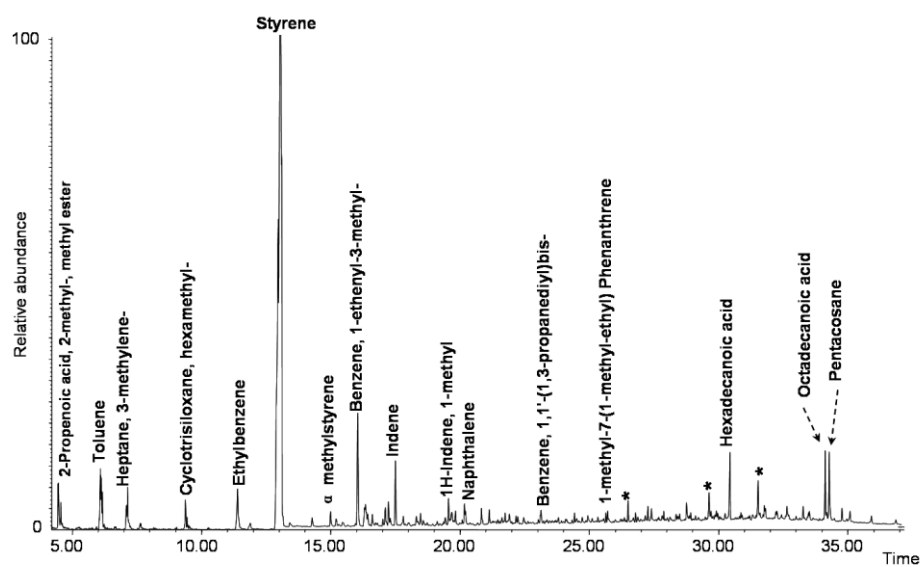
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1386 <u>Figure 11</u>
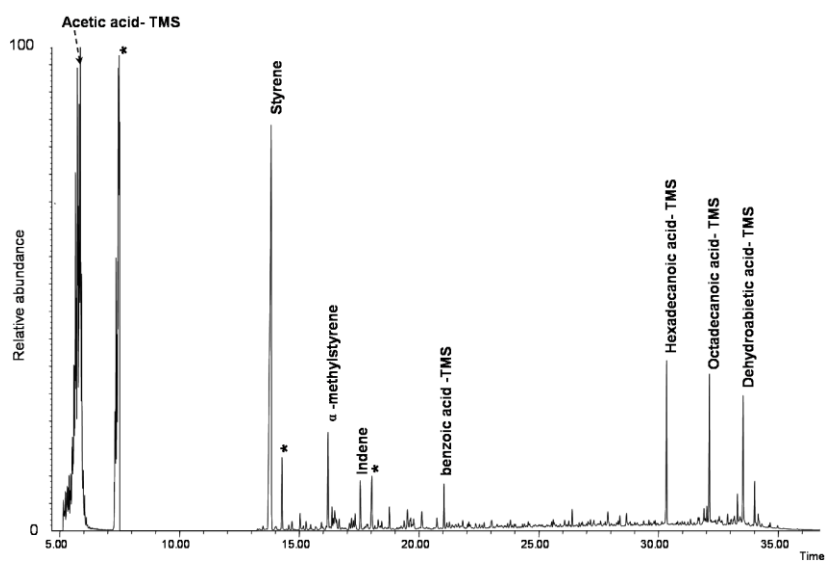
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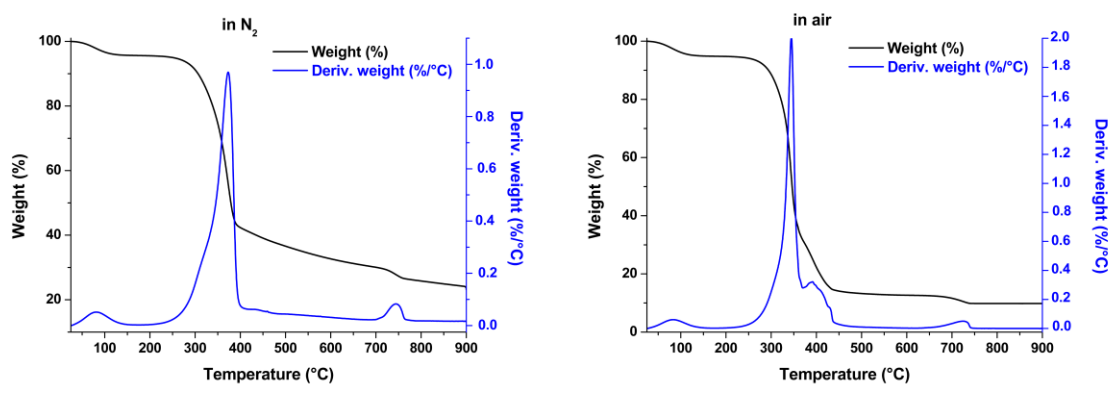
Figure 12

1446 Figure 13

concentration of HCl acid
solid/liquid ratio
T and time

Glucose   5-Hydroxymethylfurfural (5-HMF)   Levulinic acid (LA)
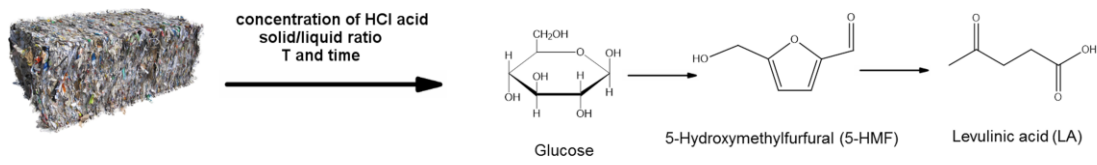
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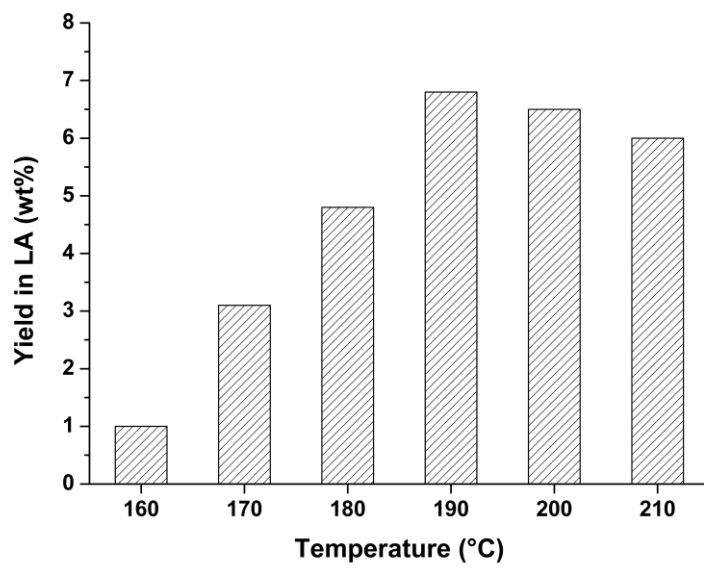
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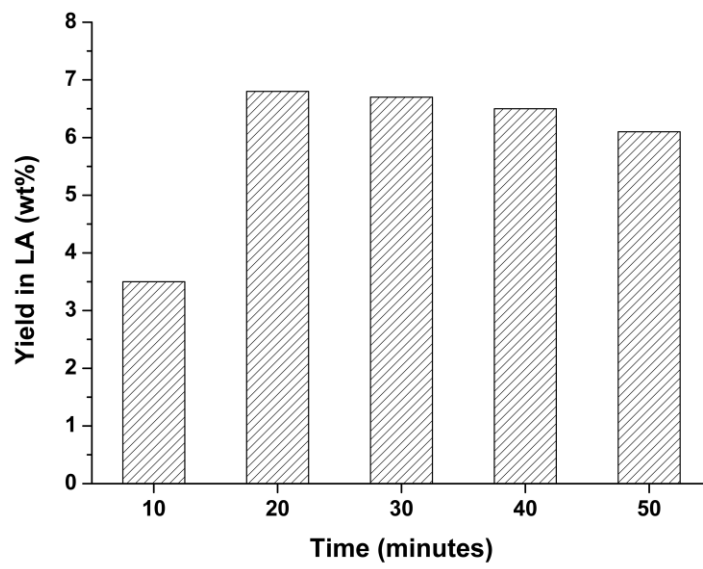
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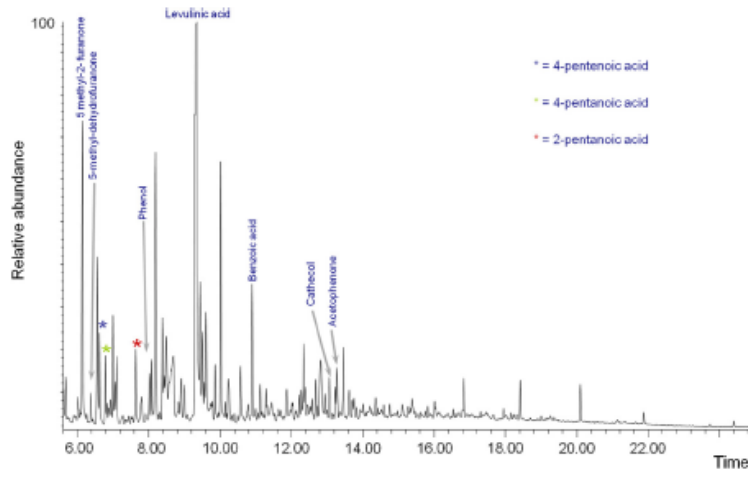
Figure 14

1513 Figure 15

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Figure 16

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