# CONVENTIONAL FAST PYROLYSIS OF COATED BIOMASS AS AN ALTERNATIVE TO THE VALORIZATION OF NATURAL THERMOSET POLYMERS

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ABSTRACT: The valorization of secondary streams such as extracted tannins and lignins is a key stage in the development of lignocellulosic biorefineries. Fast pyrolysis that converts biomass into a valuable liquid product is currently of particular interest for chemical production. However, conventional fast pyrolysis of thermoset biopolymers is technically complicate. Because of feeding issues, a new coating preparative method of the *Pinus radiata* feedstock was used to process a mixture of acid isolated lignin and sawdust (LI<sub>20</sub>) using the 0.1 kg/h fast pyrolysis plant scale (FP<sub>0.1kg/h</sub>). Although a slight decrease in total liquid and organics yields was recorded when pyrolyzing LI<sub>20</sub>, we managed to feed the lignin into the FP<sub>0.1kg/h</sub> without modifying its initial design while also increasing the amount of phenolics. Experimental conditions used at the small scale (2L glass beaker and FP<sub>0.1 kg/h</sub> plant) are currently being applied to the pilot scale (100L tank and FP<sub>10kg/h</sub> plant. The lignin-coated biomass material, LI<sub>20-5kg/h</sub>, was successfully prepared at large scale showing similar physico-chemical characteristics than LI<sub>20-0.1kg/h</sub>. The preliminary results obtained from the raw biomass pyrolysis at larger scale displayed lower liquids and organics yields with a substantial increase of the pyrolytic sugar fraction that was found detrimental to bio-oil stability. Keywords: Lignin, coating, biomass, fast pyrolysis

# 1 INTRODUCTION

If biomass can be turned into a high heating value liquid through fast pyrolysis, the bio-oil is also composed of a complex mixture of organic compounds that offers a great potential to biorefinery concept development [1][2]. Urged by a need of diversifying its pool of technologies to produce renewable energy, Chile with its natural dotation of woody biomass supported the implementation of the fast pyrolysis in the country. A fast pyrolysis process using a three-stage fluidized bed reactors system with a feed capacity of 25 kg/h was developed at UDT [3]

In the past decade, the exploration and utilization of these renewable feedstocks as chemicals feedstock have also arisen; some researchers presenting the viability and feasibility of this project [4]. Lignocellulose can be pretreated and converted into chemical-enriched fractions through fast pyrolysis. In particular, lignins and tannins both polyhydroxyl aromatic compounds are considered as a potential natural phenolic source [5].

The implementation of the project aims at producing a bio-oil from lignin and tannins residues as resources for chemicals as it has been done earlier [6-7]. However, the pyrolysis processing of these natural thermoset polymers remains complicate. Indeed due to the remarkable physico-chemical properties of lignin (e.g., low bio-oil yields, low fusion point, high oxygen content...) numerous technical issues such as feeding problems due to its low fusion point, bed agglomeration and low yield of highly oxygenated liquids remain [8-9]. To overcome some of these technical issues, the same authors investigated some alternatives, the addition of CaO, the use of different bed materials [10] and finally the coating of woody biomass with lignin [11]. If the former solutions did not provide satisfactory results, the fast pyrolysis of coated biomass by lignin was successfully implemented at a small scale [11].

The present study aims at implementing a large feed capacity fast pyrolysis plant to convert isolated lignins into chemicals. To do this a series of experimental conditions previously tested at a small scale were applied to the larger scale. The study offers a comparison between small-scale results and the preliminary results

obtained from the large fast pyrolysis plant; thus showing the feasibility of the project.

## 2 MATERIALS & METHODS

## 2.1 Feedstock preparation

Pinus radiata D. Don sawdust was provided by BSQ Ltda, a forest company located in Concepción (Chile). The woody material was sieved to obtain a particle size in the range of 0.5-1.5 mm. The moisture content (MC) of the woody material was maintained at 10.4 wt.%. The acetic acid-extracted lignin (Acetosolv lignin) was prepared from the same Pinus radiata wood chips using an adaptation of the so-called Acetocell process (Berg, Fuentealba, & Salazar, 2014). The woody material was delignified using a 87 wt% acetic acid solution at 185 °C for 2 hours. The dissolved lignin was precipitated by diluting the spent pulping liquor with water. The filtered lignin was washed with water multiple times.

A preparation method was developed to produce the coated feedstock with a uniform distribution of lignin. A solvent mixture of acetone (99.5%, Winkler) and water, four parts to one respectively, was utilized to fully dissolve the acetic-extracted lignin (up to 0.2 g/mL). A liquor to wood ratio of 8:1 was used to allow the slurry to be evenly mixed. The lignin was fully dissolved in the acetone/water mixture in 10 minutes with vigorous mixing via a mechanical stirrer. The pine powder was then added slowly over 10 minutes to ensure a uniform mixture and allowed to mix for four hours. After mixing, the sample was left in a beaker, then covered, and allowed to soak overnight for further impregnation by lignin. The sample was then placed into a pan and placed in a fume hood to allow the solvent to evaporate, and then oven dried at 45°C for 2 hrs, and finally allowed to air dry for 48 hours. The coated biomass was then sieved to the original 400-600 µm size. Pictures of coated particles were taken using a scanning electron microscope (SEM) micrograph JEOL (JSM-6010LA) equipment using a magnification range of 22-2500 with a resolution of 0.28 nm.

# 2.2 Fast pyrolysis at 0.1 kg/h

The fast pyrolysis (FP) plant (Fig. 1) can be divided into four sections: the biomass-feeding unit, the cylindrical furnace housing the bubbling fluidized bed reactor, one hot-gas filter as separation stage, and the condensation chain. The biomass-feeding unit consisted of a hopper with a screw feeder, which introduced biomass (particle size 250-2000µm) at a feed rate of 0.1  $\pm$  0.03 kg/h into the reactor. The hopper was maintained at a slight N2 overpressure (±0.02bar gauge, gas flow rate of 6 L/min) to prevent hot gas and product vapor pushing back from the reactor into the feeding system. A quartz bed was used as the heat carrier inside the reactor and fluidized using a N2 gas flow rate of 9L/min. Pyrolysis product vapors left the furnace via a heated pipe (maintained at 400°C to prevent undesired intermediate condensation) before entering the hot gas filter. The condensation chain consisted of a water-cooling tower at 4°C followed by an electrostatic precipitator set to 15 kV.

The bio-oil, product of interest, was collected from the condenser tower and precipitator and thus consisted of two single phases corresponding to the BOC and BOP fractions. The char product was recovered from the hot-filter pot, while the non-condensable gases were purged to the atmosphere. Experimental runs were duplicated at 540°C with a running time between 25 and 65 mins.

All liquid product yields ( $Y_{bio-oil}$ ,  $Y_{organics}$ , and  $Y_{pyrolytic}$  water) reported here were calculated on a dry mass basis (db, wt.%) of the initial and dried biomass feed. The bio-oil yield represents the total liquid product yield correcting for initial feed water content.

# 2.3. Fast pyrolysis at 10 kg/h

The dry sawdust (3mm) was contained in a

pressurized 2m<sup>3</sup> container and sent to the fast pyrolysis reactor through a lance (Figure 2). The biomass was discharged with a live bottom of five variable speed screw feeders into a single high-speed screw, which was also discharged into a rotary star valve and this into a pyrolysis gas (PG)-operated ejector. This latter sent the gas-solid stream to the feeding lance immersed in the fluidized bed. The pyrolysis reactor is 15cm diameter by 145cm total height, with a shallow fluidized bed of 55cm depth of silica sand (< 2mm). The fluidizing gas was preheated in a fluidized reactor (25cm diameter and 238cm height) where the PG were burnt to raise the temperature of the sand up to 550°C. An additional source of heat (electrical) was necessary to deliver the required heat for the pyrolysis reaction. The volatile residence time is estimated around 1.7s within the reactor when the combustion gas flow rate is maintained at 220L/min.

The hot pyrolysis volatiles and entrained solid particles were separated via three separation systems: an impact device (labyrintic-system), a hot cyclone and finally with a hot-filter, which were maintained at 400-420°C. The cleaned hot aerosols/vapors were condensed by ways of a water-jacketed Venturi-type spray-cooling tower and an internal water-cooled diverter cone, and finally using an electrostatic precipitator set at 15kV. An iso-paraffinic hydrocarbon liquid (Marcol N 82 purchased from Armstrong Lubricantes Ltda.) was used as direct contact quenching medium in the cooling tower.

The two bio-oil fractions, BOC and BOP, were collected and stored in two separate tanks with a water-cooling jacket. The remaining non-condensables were compressed to 4bar and stored in a 2m<sup>3</sup> tank from where they were re-circulated to the pre-heating reactor.

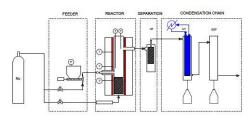
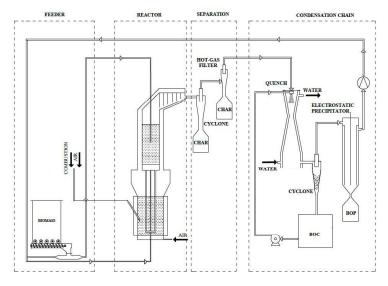


Figure 1: 0.1 kg/h capacity fast pyrolysis set-up – FP<sub>0.1kg/h</sub>



**Figure 2**: 10 kg/h capacity fast pyrolysis set-up – FP<sub>10kg/h</sub>

## 2.4. Feedstock and product analysis

Ultimate and proximate analyses were conducted on both feedstocks using respectively an elemental analyzer (Perkin Elmer 2400 Series II CHNS/O system) and a thermogravimetric analyzer (TA instruments Q500) using the ASTM E1131 standard procedure.

The lignin amount was performed using a modified NREL method which has been described elsewhere [12]. An oven-dried sample mass of 0.1g of 400µm biomass was hydrolyzed with 72wt% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich) for 2 h, then diluted to 3% before being autoclaved at 120°C for 1.5h. Hydrolysate was filtered and the liquid was analyzed by HPLC system (Agilent 1200, Agilent, Santa Clara, CA, USA) and UV-Vis spectrophotometer (Lambda XLS, Perkin Elmer, Waltham, MA, USA) for sugar and lignin analysis, respectively.

The water content of liquid fractions was determined using a Mettler Toledo V20 volumetric KF Titrator (ASTM E871) using the CombiTitrant 5 one-component reagent for volumetric Karl-Fisher titration (Merck) as titration reactant and dried methanol (max 0.003% H<sub>2</sub>O, Merck) as titration solvent.

The GC-MS analyses were performed using a Hewlett packard GC system (Model HP 6890Series) and a Hewlett packard Mass Selective detector (Model 5973). A column HP-5 60m x 0.25mm with a film thickness of 0.25 µm and operating conditions were based on following past procedures (Meng, Park, Tilotta, & Park, 2012). The heating program was an initial hold at 45°C for 4 min, followed by a ramp to 280°C at 3°C/min, and finally held at 280°C for 15min. An aliquot of 0.2g of bio-oil and 1mL of internal standard (Fluoranthene, 98%, Aldrich) were added to a 10mL volumetric flask that was completed with acetone (GC grade, Sigma-Aldrich) filtered through a 0.2µm PTFE filter (Rephile). The volume injection was 1µL and maintained by an autosampler. The mass spectrometer (MS) detector was used with a standard electron impact ionization chamber set at 70eV with a temperature of 200°C. The ions formed were separated via a quadrupole according their mass-to-charge (m/z) ratio in the range of 30-250Da. Peaks were identified by the 2008 NIST library.

Accelerated aging was performed on bio-oil samples as described by Elliott *et al.* [13]. Approximately 10g of well mixed bio-oil was placed in a sealed glass reaction tube (Ace glass) and any bubbles present were allowed to be removed. The tubes were capped, weighed and placed in a sufficiently large oven at 80°C for 24h. The vials were removed and cooled immediately in a freezer at -4°C. After cooling, they were weighed to ensure <0.1% weight loss during the aging process and stored in the freezer for future analysis.

Gel permeation chromatography (GPC) was performed to determine the severity of aging of bio-oil samples by the change in their molecular weights. Prior to analysis, the bio-oil was vigorously mixed with a vortex mixer. Approximately 20mg of the desired bio-oil fraction was fully dissolved in 1.5mL of THF (Emparta® ACS 99.5%, Merck) and filtered through a 0.2µm PTFE filter (Rephile). THF was used as the mobile phase and passed through a pre-column (Phenogel 5µ, linear mixed, 50\*7.8cm) and two columns placed in serie (Phenogel 5  $\mu$ , 10<sup>6</sup> for the first one and 10<sup>3</sup> for the second Å, 300\*7.80cm) at 35°C. Polystyrene standards (Analytical grade for GPC, Sigma) were used to generate a calibration curve to determine the molecular weights of the samples.

#### 3 RESULTS & DISCUSSION

#### 3.1 Feedstock characterization

The initial characterization of the feedstocks was important to appreciate the efficiency of the coating method and the possible chemical and/or physical changes. The compositional analysis showed in Table I indicates that the lignin content was increased systematically and effectively. The starting biomass contained 32.78 wt% of native lignin, which was increased to 38.30 wt% corresponding approximatively to an increase of 17% in mass in the coated material, LI<sub>20</sub>. The moisture content remained constant for all samples between 3.97% and 5.24 wt% meaning the samples were effectively dried prior to being pyrolyzed. Although both ash content of virgin biomasses are low, 0.92 and 0.55 wt% for Pine and the isolated lignin respectively, a slight increase in ash content was observed for the coated preparations, 0.82 wt% for LI<sub>20</sub> and 1.49 wt% for LI<sub>20</sub>-10kg/h. This result was attributed to the impurities present in the acetone solvent used during the preparation.

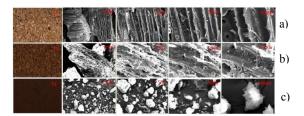
**Table I:** Compositional and physico-chemical properties of feedstocks.

|                              | Pine                          | LI20-0.1kg/h | LI <sub>20-10kg/h</sub> | Lignin     |  |  |  |
|------------------------------|-------------------------------|--------------|-------------------------|------------|--|--|--|
| MC                           | 5.24                          | 3.97         | 4.94                    | 4.74       |  |  |  |
|                              | $\pm 1.37$                    | $\pm 1.08$   | ±3.03                   | $\pm 0.72$ |  |  |  |
| Compo                        | Compositional analysis (wt.%) |              |                         |            |  |  |  |
| Lignin                       | 32.78                         | 38.30        | 38.57                   | 97.19      |  |  |  |
|                              | $\pm 0.74$                    | $\pm 0.47$   | $\pm 1.90$              | $\pm 0.29$ |  |  |  |
| AIR                          | 32.23                         | 37.67        | 37.89                   | 95.11      |  |  |  |
|                              | $\pm 0.72$                    | $\pm 0.45$   | $\pm 1.87$              | $\pm 0.17$ |  |  |  |
| ASL                          | 0.55                          | 0.63         | 0.68                    | 2.08       |  |  |  |
|                              | $\pm 0.02$                    | $\pm 0.02$   | $\pm 0.02$              | $\pm 0.12$ |  |  |  |
| Ultimate analysis (db, wt%)  |                               |              |                         |            |  |  |  |
| C                            | 48.18                         | 48.55        | 40.57                   | 65.98      |  |  |  |
|                              | $\pm 0.92$                    | $\pm 0.20$   | $\pm 0.54$              | $\pm 0.11$ |  |  |  |
| Н                            | 5.61                          | 5.76         | 5.46                    | 5.52       |  |  |  |
|                              | $\pm 0.10$                    | $\pm 0.37$   | $\pm 0.26$              | $\pm 0.38$ |  |  |  |
| N                            | 0.07                          | 0.07         | 0.06                    | 0.11       |  |  |  |
|                              | $\pm 0.02$                    | $\pm 0.02$   | $\pm 0.01$              | $\pm 0.01$ |  |  |  |
| O                            | 49.74                         | 46.64        | 55.18                   | 30.22      |  |  |  |
|                              | $\pm 0.84$                    | $\pm 0.30$   | $\pm 0.75$              | $\pm 0.54$ |  |  |  |
| Proximate analysis (db, wt%) |                               |              |                         |            |  |  |  |
| VM                           | 94.70                         | 84.25        | 83.66                   | 59.58      |  |  |  |
| FC                           | 4.38                          | 14.93        | 14.85                   | 39.87      |  |  |  |
| AC                           | 0.92                          | 0.82         | 1.49                    | 0.55       |  |  |  |

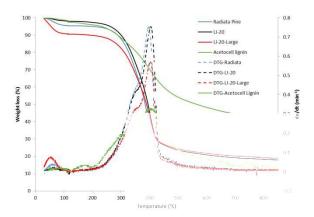
The scanning electron microscopy (SEM) images of the longitudinal and transversal sections of coated particles (Figure 3) confirm the deposit of extracted lignin particles onto the surface of pine biomass and into its pores; thus providing an even coating over the entire surface.

Dynamic measurements combined with the proximate analyses indicated that the significant weight loss registered for LI<sub>20-10kg/h</sub> between 25 and 105°C corresponds to the moisture and residual solvent evaporation (Figure 3). When considering the thermal stability, Pine, LI<sub>20-0.1kg/h</sub> and LI<sub>20-10kg/h</sub> remained quite similar both starting to degrade at 180°C, whereas the initial degradation temperature of the isolated lignin was 126°C (Figure 4). The maximum temperature of degradation also varied shifting towards higher temperatures from 399°C for the pine to 405°C for both coated materials. This result was found in accordance

with the well-known slow decomposition of lignins over a broad temperature range [14-15] between 126-850 °C for this study (Figure 3).



**Figure 3**. SEM photos of a) Pine, b) LI<sub>20</sub> and c) Acid-extracted lignin powder.



**Figure 4**. TG and DTG curves of raw and coated materials at 100 °C/min.

## 3.2 Fast pyrolysis yields

The preparation of coated feedstock allowed the fast pyrolysis of technical lignin lowering the bio-oil yields from 52.3 wt.% for pine to 46.2 wt.% for LI<sub>20</sub> with FP<sub>0.1kg/h</sub> (Table II). This result represents a significant improvement regarding the low yields and technical issues obtained in the case of lignin [9]. The yield of organics decreased from 37.84 wt% to 31.11 wt% when the isolated lignin was added, while the pyrolytic water yield increased from 4.96 wt% to 11.27 wt% (Table 2); thus indicating that the presence of the isolated lignin affects the chemistry of pyrolysis by promoting the dehydration reactions. The drastic pyrolysis mechanistic changes were attributed to the presence of the fine and impermeable layer formed by the melted isolated lignin; thus preventing the release of pyrolysis volatiles [11].

Preliminary results obtained at large scale indicate that the FP<sub>10kg/h</sub> plant achieved significantly lower total liquid and organic yields, 45.2 wt% and 33.2 wt% when pine was pyrolyzed (Table II). The decrease in yields could be attributed to the enrichment of the 'neutral" atmosphere with CO2 and CO inside the fast pyrolysis reactor due to the use of combusted gases as fluidizing gas. Indeed, CO and CO2 have been shown to negatively affect both total liquid and oil yields [16]. In addition, the increasing scale entails the inevitable loss of products, which could have an important role on the final yields [17]. Moreover, the presence of the long piping line between separation and condensation devices increases the homogeneous vapours/aerosols residence time and thus increasing the probability of secondary reactions to occur, promoting the gas formation [17].

**Table II:** Yields of fast pyrolysis products for  $FP_{0.1~kg/h}$  and  $FP_{10kg/h}$  at  $540^{\circ}C$ .

|                      | FP <sub>0.1kg/h</sub> |                  | FP <sub>10kg/h</sub> |
|----------------------|-----------------------|------------------|----------------------|
|                      | Pine                  | $LI_{20}$        | Pine                 |
| Y <sub>bio-oil</sub> | 52.32± 3.96           | 46.24± 7.00      | 45.2±10.8            |
| Yorganics            | 37.84± 3.72           | 31.11± 1.41      | 33.2±9.1             |
| Ypyrolyticwater      | $4.96 \pm 0.51$       | $11.27 \pm 0.06$ | 4.3±1.1              |

#### 3.3 Bio-oil characterization

## 3.3.1 Aging of fast pyrolysis bio-oil fractions

The initial BOC and BOP collected from the FP<sub>10kg/h</sub> were both dark-brown liquids. After the accelerated aging at 80 °C, a significant amount of brown solid was formed for both fractions. This observation was corroborated by the increase of the average molecular weight after aging, which was particularly pronounced for the BOP fraction (Table III).

The aging index also indicates that the BOP aged more severely than the BOC fraction; thus indicating that the BOP composition including both pyrolytic lignin and sugar fractions is more unstable [13,18-19]

**Table III:** Accelerated aging results for BO<sub>10kg/h</sub> produced from pine.

|            |      | Fresh       | Aged |
|------------|------|-------------|------|
| AI (%)     | BOC: | 7.6<br>31.6 |      |
|            | BOP: |             |      |
| Mw (g/mol) | BOC: | 402         | 453  |
|            | BOP: | 367         | 504  |
| Mn (g/mol) | BOC: | 257 232     |      |
|            | BOP: | 217         | 252  |
| PD         | BOC: | 1.57        | 1.95 |
|            | BOP: | 1.70        | 2.00 |

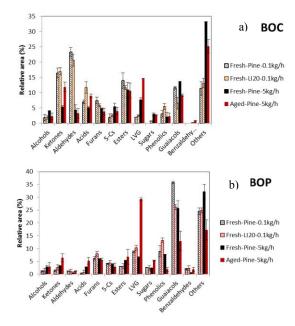
## 3.3.2 GC-MS results

Despite detecting only a portion of the bio-oil composition [20], the relevant chromatographic peaks were combined by chemical families to visualize changes between the relative functional group distribution with increasing amount of technical lignins. The organics were classified into thirteen groups including alcohols, ketones, aldehydes, acids, furans, compounds with a ring of 5 carbons (5-Cs), esters, anhydrosugars, phenolics, guaiacols, benzaldehydes and others (Figure 3). The fraction recovered from the first condensation stage (BOC) either by indirect cooling contact for FP<sub>0.1 kg/h</sub> or spray-cooling for FP5kg/h contains many light oxygenated compounds (Figure 3a). The tarry phase collected from the second condensation stage via an electroprecipitator (BOP) contains a large oxygenated aromatic portion that is partially composed of phenolics and guaiacols (Figure 3b). Although GC/MS only detects the volatiles and monomeric phenolics and not dimers, trimers, tetramers, it was observed that the addition of lignin affected the chemical composition of BOC and BOP fractions from FP<sub>0.1kg/h</sub> (Figure 5a-b). Indeed, a significant increase in the phenolics accompanied with the decrease in guaiacols was observed. This is not surprising, as the formation of monomeric phenolic compounds via free radical reactions has been often reported during the pyrolysis of isolated and native lignins [21-22]. Finally, the levels of acids in BOC were noticeably increased with the addition of lignin.

When considering the  $BO_{10kg/h}$  fractions, the results revealed the presence of alkanes and naphthalene in the

first condensation stage (BOC<sub>10kg/h</sub>); thus confirming the contamination of the bio-oil by the current mineral oil used, which reduced viscosity, 14.5 cSt at 40°C, and lower boiling point, 182 °C, differ from those of traditional mineral oils used (31 cSt at 40 °C and 205 °C). Lower content of light oxygenated compounds, ketones and aldehydes, were measured in BOC<sub>10kg/h</sub> when compared to the composition of BOC<sub>0.1kg/h</sub>. This result combined with the higher LVG and sugars content in BOC<sub>10kg/h</sub> could indicate that the pyrolysis reaction carried at large scale was not complete. In the case of the BOP fraction, the lowest guaiacols and phenols contents detected in addition to LVG and sugars could corroborate the incomplete pyrolysis; thus suggesting that the use of combusted fluidized gas is likely to provide a less stable bio-oil.

After accelerated aging, the levels of light organics (ketones and acids) and LVG measured in both BOC 10kg/h and BOP 10kg/h were significantly increased, whereas guaiacols level was reduced. This result confirms that the significant portion of sugar-derived products was transported in an aerosol state phase, which was efficiently collected by the electoprecipitator system and is suspected to promote the aging of bio-oil.



**Figure 5:** Relative area distribution of products detected by GC-MS in a) BOC and b) BOP.

# 3.3.3 Key compounds

match The determination of absolute concentration of key organics involved into the biomass pyrolysis was also carried out. The selection of the key compounds was based on previous studies that described in detail the pyrolysis mechanisms of major polymers that composed the lignocellulosic biomass (i.e., hemicelluloses, cellulose and lignin) [23,24,25]. As a result levoglucosan (LVG), acetol (ACe) and glycoaldehyde (GA) were selected to follow the cellulose pyrolysis, while phenol, phenol, 4-methyl and phenol, 2-methoxy-4-methyl were chosen as lignin-derived products.

A substantial increase in pyrolytic water and acetic acid was measured with the addition of the isolated lignin, which shows that the presence of this latter affected the chemistry of pyrolysis by promoting the dehydration reactions.

**Table IV:** Concentration (wt.%, bio-oil) of key coumpounds in fresh and aged bio-oils.

|          | FP <sub>0.1 kg/h</sub> |           | $FP_{10kg/h}$ |       |
|----------|------------------------|-----------|---------------|-------|
|          | Pine                   | $LI_{20}$ | Pine          |       |
|          | Fresh                  | Fresh     | Fresh         | Aged  |
| WC BOC:  | 47.0                   | 55.3      | 34.94         | 37.59 |
| BOP:     | 5.2                    | 7.3       | 25.12         | 33.06 |
| GA BOC:  | 9.30                   | 5.86      | 4.15          | 1.94  |
| BOP:     | 2.21                   | 2.21      | 0.48          | 1.20  |
| AA BOC:  | 3.95                   | 3.19      | 3.39          | 3.91  |
| BOP:     | 2.77                   | 3.33      | 1.85          | 3.53  |
| ACe BOC: | 4.13                   | 2.72      | 3.42          | 3.36  |
| BOP:     | 1.3                    | 1.70      | 1.06          | 1.72  |
| FU BOC:  | 0.12                   | 0.11      | 0.14          | 0.08  |
| BOP:     | 0.29                   | 0.46      | 0.25          | 0.12  |
| LVG BOC: | 0.28                   | 0.19      | 3.13          | 3.24  |
| BOP:     | 6.00                   | 7.77      | 2.72          | 6.00  |
| Ph BOC:  | 0.03                   | 0.07      | 0.27          | 0.13  |
| BOP:     | 0.16                   | 0.38      | 0.18          | 0.04  |
| pCR BOC: | 0                      | 0         | 0.25          | 0.08  |
| BOP:     | 0.1                    | 0.21      | 0.08          | 0     |
| G BOC:   | 0.07                   | 0.02      | 0.11          | 0.03  |
| BOP:     | 0.6                    | 0.55      | 0.33          | 0.05  |

Glycolaldehyde (GA), often referred in the literature as the most abundant aldehyde identified in the bio-oil, was present in large quantities in fresh bio-oils (4.15-9.30 wt%). After accelerated aging, the levels of GA and lignin-derived products (Ph, p-CR and G) decreased. Similar results were previously reported indicating the ability of GA to self-polymerize and/or react with phenols (pyrolytic lignin) through condensation reactions under strong acidic conditions and/or react with carboxylic acids through esterification reactions. The decrease of furfural content after aging also indicated its non-negligible reactivity during the aging process. High levels of acetic acid were observed after aging. A surprising increase in LVG after aging indicated that anhydrosugars, precursor compounds of the LVG, were further degraded during the aging process highlighted; thus confirming the important role of the pyrolytic sugar phase during the aging process [19].

## 4 CONCLUSIONS

The lignin content of *Pinus Radiata* was effectively increased from 32.78% to 38.30% using a new biomass coating preparation technique. Although the LI<sub>20-10kg/h</sub> contains residual trace of solvent, the thermal degradation behavior for the raw and coated materials remained quite similar. The coated biomass was successfully fed into the small-scale fast pyrolysis plant. Slight decreases in both liquids and organics yields accompanied with the increase of pyrolytic water, indicated that the presence of isolated lignin content was affecting the pyrolysis chemistry. This result was confirmed by the GC-MS analyses that displayed a beneficial increase of the phenolic fraction. The preliminary results with respect to the scale-up of the fast pyrolysis resulted in lowering both liquids and organics yields. The high levels of LVG and sugars measured were mainly attributed to the nature of fluidizing gases leading to incomplete pyrolysis. The accelerated aging of bio-oil fractions confirmed the

important role of both pyrolytic lignin and sugars fractions. More research data is required for assessing the role of technical lignin on the large-scale fast pyrolysis and the economic and sustainability aspect of the process.

## 5 ABBREVIATIONS

A: Aged

AA: Acetic acid

AC: Ash content

ACe: Acetol

AI: Aging Index

AIL: Acid-insoluble lignin

AIR: Acid-insoluble residue

BOC: Bio-oil collected by condensator

BOP: Bio-oil collected by precipitator

F: Fresh

FC: Fixed carbon

FP: Fast pyrolysis

FU: Furfural

G: Guaiacol

GA: Glycoaldehyde

LVG: Levoglucosan

MC: Moisture content

Mw: Molecular weight

Mn: Number average of molecular weight

pCR: p-cresol

PD: Polydispersity

PG: Pyrolysis gas

Ph: Phenol

VM: Volatile matter

WC: Water content

Y: Yield

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# 8 LOGO SPACE





