

Assessment of the biomass potential of poplar wood chips from intensive plantations

Filipe Rego^a, Fátima C. Rosa^a, Abel Rodrigues^b, Ana P. S. Dias^a, Miguel Casquilho^a

^a *Instituto Superior Técnico, Lisbon, Portugal*

^b *INIAV, I. P., Oeiras, Portugal*

Abstract

In this work, poplar wood chips from intensive plantations in Portugal and Belgium for energy production were studied.

Thermogravimetry (TG) was applied for quantitative determination of lignocellulosic compounds and analysis of thermal decomposition, through the calculation of kinetic parameters. The obtained average distribution of lignocellulosic compounds was (% w/w and dry basis): 23 % of hemicelluloses, 49 % cellulose and 27 % of lignin, with 1 % ash. The useful application of TG for lignocellulosic content determination was demonstrated. The kinetic parameters were obtained using three methods, considering first order reactions. The Kissinger method obtained average values of activation energy and pre-exponential factor of, respectively, 207 kJ/mol and $6 \times 10^{25} \text{ s}^{-1}$. With FWO method, average values were, respectively, 81-301 kJ/mol and 3×10^{10} - $5 \times 10^{36} \text{ s}^{-1}$, and with KAS method, 90-306 kJ/mol and 9×10^{10} - $2 \times 10^{37} \text{ s}^{-1}$. The TG results can be useful for thermochemical conversion processes, as in pyrolysis, which was applied to the poplar chips.

Lab-scale pyrolysis at 475 °C was applied to different samples of poplar chips, and obtained average mass yield of bio-oil of 49 %. The bio-oil was analyzed with FTIR spectroscopy for content evaluation. Catalytic pyrolysis was also applied, using Na_2CO_3 , MgCO_3 , FCC catalyst and H-ZSM5. The bio-oil analysis suggests that the catalysts improved the quality of the liquid product.

Keywords: Poplar wood chips, biomass, thermogravimetry, pyrolysis, catalysis.

1. Introduction

Energy demand worldwide is constantly growing, and with it, pollutant emissions, associated with climate change. In order to reduce emissions, a change from fossil fuels to renewable fuels is needed. Biomass is a sustainable energy source and it has been mostly used in combustion (Sims et al., 2006). Other less polluting conversion processes are emerging to produce fuels from biomass: pyrolysis, gasification, anaerobic digestion, liquefaction, among others.

Wood from some specific species can be grown in an intensive plantation, called Short Rotation Coppice (SRC), and can be used sustainably for energy production (Simpson et al., 2009). Poplar trees are suitable for these plantations, since they reproduce and grow quickly, and their properties can be manipulated using genetics (Bradshaw, et al., 2000).

Characterizing poplar wood from these plantations was the objective of this study, as it is of extreme importance to the development of energy production technologies as in pyrolysis.

Thermogravimetry (TG) in an inert atmosphere was used to study the thermal decomposition of poplar wood chips from different origins and can be used as a model for the pyrolysis process, which also operates in inert conditions. From the TG and DTG (derivative thermogravimetry) data, the content of lignocellulosic material in the biomass was determined and kinetic parameters were obtained using three different methods: Kissinger, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS).

Pyrolysis in lab scale was also applied to the poplar chips, obtaining mainly a liquid product which was analyzed with FTIR spectroscopy. The use of catalysts (Na_2CO_3 , MgCO_3 , FCC catalyst and H-ZSM5) in the pyrolysis process was also studied for bio-oil upgrading. The effect of the catalysts on the quality of the bio-oil was evaluated using FTIR spectroscopy.

This work was developed in partnership with INIAV, I. P. (Instituto Nacional de Investigação Agrária e Veterinária) and the POPFULL project from the University of Antwerp.

2. Material and methods

Poplar wood chips originated from SRC plantations in Portugal (PT) and Belgium (BE). In Portugal the plantation had a 3 year cycle and in Belgium the cycle was of 2 years. The wood for the chips was cut in 2014 and belonged to 9 different genotypes of poplar. Further information about the poplar chips is presented in Table 1, Table 2 and Table 3.

Table 1: Origin of the poplar genotypes used.

Genotype	Origin
AF2 (PT)	Hybrid <i>P. canadensis</i>
AF8 (PT)	Hybrid <i>P. generosa</i>
Bak (BE)	Hybrid <i>P. trichocarpa</i> x <i>P. maximowiczii</i>
Bra (BE)	Species <i>P. nigra</i>
Eil (BE)	Hybrid <i>P. canadensis</i>
Gri (BE)	Triple hybrid <i>P. deltoides</i> x (<i>P. trichocarpa</i> x <i>P. deltoides</i>)
Hee (BE)	Hybrid <i>P. canadensis</i>
Ska (BE)	Hybrid <i>P. trichocarpa</i> x <i>P. maximowiczii</i>
Wol (BE)	Species <i>P. nigra</i>

Table 2: Proximate analysis (% m/m) of the poplar chips.

Genot.	M	VM	FC	A
AF2	35,4	48,4	15,2	1,0
AF8	29,1	61,7	8,5	0,7
Bak	40,3	52,7	6,2	0,8
Bra	39,1	50,6	9,1	1,2
Eil	41,7	50,6	6,7	1,0
Gri	36,3	48,5	14,4	0,8
Hee	36,8	54,7	7,5	1,0
Ska	37,9	54,3	6,9	0,9
Wol	39,3	51,3	8,3	1,1

M: Moisture; VM: Volatile Matter; FC: Fixed Carbon; A: Ash.

Table 3: Elemental analysis (% m/m) and calorific values (MJ/kg) of the poplar chips.

Genot.	C	H	O	N	HHV	LHV
AF2	46,5	5,4	47,0	1,1	16,1	15,0
AF8	50,6	5,9	42,4	1,1	19,7	18,5
Bak	48,9	6,1	44,5	0,5	17,8	16,5
Bra	48,6	6,1	44,9	0,4	18,4	17,1
Eil	49,2	6,2	44,3	0,3	18,7	17,4
Gri	49,7	6,2	43,8	0,3	17,7	16,4
Hee	49,2	6,2	44,1	0,5	19,0	17,7
Ska	48,4	6,1	45,3	0,2	17,8	16,5
Wol	48,3	6,1	45,2	0,4	19,1	17,8

HHV: High Heating Value; LHV: Low Heating Value.

TG analysis was applied to pulverized samples (30-70 mg) of the 9 poplar genotypes on a NETZSCH STA 409 PC thermobalance in an inert atmosphere of nitrogen (15 L/min) and 5 different linear heating rates: 10, 20, 30, 40 and 50 °C/min. Analysis started at 30 °C and ended at 1100 °C.

Deconvolution was applied to the DTG results for determining lignocellulosic content using 4 symmetric gaussian-type curves

considering 4 groups of pseudo-components: water and extractives, hemicellulose, cellulose and lignin. Optimization of the deconvolution curves was done using *Microsoft Excel Solver*, minimizing the difference (root mean squared error and maximum error) between the experimental DTG curve and the curve composed of the sum of the 4 deconvolution curves (“theoretical” curve). For adjustment of the parameters of the gaussian-type individual curves (a , amplitude, b , position, and c , width at half of the maximum height, in Eq. 1), values of decomposition temperatures of lignocellulosic components from the literature were used (Blasi, 2008).

$$a \exp \left[- \left(\frac{T-b}{c} \right)^2 \right] \quad (1)$$

Kinetic parameters were obtained using model-free methods: Kissinger method (Eq. 2), FWO isoconversional method (Eq. 3) and KAS isoconversional method (Eq. 4) (Vyazovkin, et al., 2011).

$$\ln \left(\frac{\beta}{T_{\max}^2} \right) = - \frac{E_a}{RT_{\max}} + \ln \left(\frac{AR}{E_a} \right) \quad (2)$$

$$\ln(\beta_i) = -1,052 \left(\frac{E_{a,\alpha}}{RT_\alpha} \right) + \ln \left(\frac{A_\alpha E_{a,\alpha}}{g(\alpha)R} \right) - 5,331 \quad (3)$$

$$\ln \left(\frac{\beta_i}{T_\alpha^2} \right) = - \frac{E_{a,\alpha}}{RT_\alpha} + \ln \left(\frac{A_\alpha R}{g(\alpha)E_{a,\alpha}} \right) \quad (4)$$

Lab-scale pyrolysis was applied to approximately 5 g of pulverized and fractionated (710 μm) samples of chips of the 9 genotypes. The arrangement of the equipment can be seen in Figure 1, with a vertical fixed-bed reactor consisting of a column with diameter of approximately 1,8 cm and height of 53,6 cm. A fine layer of glass wool was placed in the bottom of the reactor,

to support a filling of an inert solid (carborundum, SiC). On top of the filling, another fine layer of glass wool was inserted, to support the biomass sample.

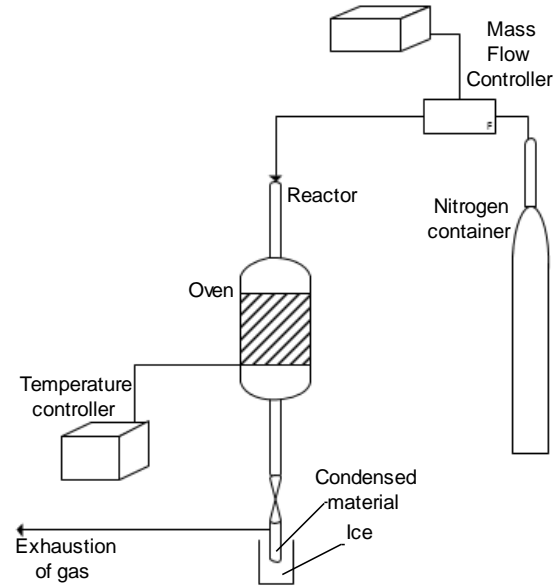


Figure 1: Representation of the equipment used for lab-scale pyrolysis experiments.

The pyrolysis experiments were performed to the 9 genotypes at a temperature of 475 °C for 15 minutes. For comparison, pine wood bark was pyrolysed at a temperature of 475 °C. Pyrolysis was also applied to a mixture of the 9 poplar genotypes, at different temperatures: 425, 475 and 500 °C. Finally, catalytic pyrolysis using 4 different catalysts (Na_2CO_3 , MgCO_3 , FCC catalyst and H-ZSM5) was applied to the mixture at a temperature of 500 °C. A 1:10 ratio of sample mass and catalyst mass was used.

Solid product (bio-char) from pyrolysis was removed from the reactor and weighed. The liquid product was extracted with acetone and methanol from the inert solid in the reactor and dried in a rotary evaporator, obtaining the bio-oil. After weighing, this product was analyzed with FTIR spectroscopy for quality evaluation. The gas products (including inert

gas) were evacuated to the outside of the lab and its quantity was obtained by difference.

3. Results

3.1. Thermogravimetry

TG analysis yielded results in the form of listed data and graphic form, of mass loss in function of temperature (TG) and rate of mass loss in the function of temperature (DTG).

3.1.1. Lignocellulosic content

For determining the content of hemicellulose, cellulose and lignin, the results of the TG analysis using a heating rate of 30 °C/min were used.

The graphical results of the optimization of the deconvolution curves can be seen in Figure 2, corresponding to the DTG results for the genotype Gri.

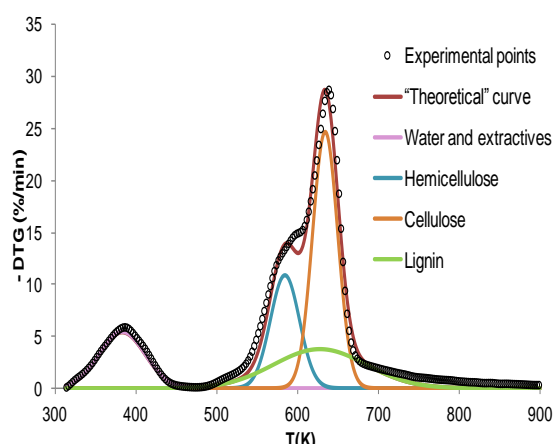


Figure 2: DTG experimental curve, “theoretical” curve and deconvolution curves (genotype Gri).

After optimization, the areas beneath each deconvoluted curve, corresponding to a pseudo-component, were integrated using the analytical integral (I) of the Gauss function (Eq. 5).

$$I = a c \left[\operatorname{erf} \left(\frac{b}{c} \right) \right] \sqrt{\pi} \quad (5)$$

After determining the total area beneath the curve composed of the sum of the individual curves, the proportion of the individual curves is calculated and can be corresponded to the percentage of each component in the volatized material of the sample. The non-volatized material in the end of the TG analysis is composed of fixed carbon and ash. The fixed carbon originates mainly from the lignocellulosic material and this part of the content has to be taken into account for determining the total of the percentage of lignocellulosic components in the sample. After calculating the proportions of the components in the volatized material, these proportions were considered as the same in the non-volatized part of the sample and the percentages of lignocellulosic components in the residue of the TG analysis could be obtained. Thus, total percentage of components in the sample was determined by the sum of the percentage in the volatized part and the percentage in the non-volatized part. The total percentages (dry mass basis) of the lignocellulosic components in the sample are presented in Table 4. The sum of the percentages with the ash contents in Table 2 yields 100 %.

Table 4: Lignocellulosic content (% m/m and dry basis) in the samples of poplar genotypes.

Genot.	Hemicellulose	Cellulose	Lignin
AF2	26,0	49,7	23,3
AF8	23,3	47,9	28,0
Bak	18,5	52,4	28,2
Bra	23,0	46,5	29,1
EII	24,4	48,1	26,4
Gri	24,4	47,8	26,9
Hee	22,6	50,2	26,1
Ska	19,9	49,1	30,0
Wol	23,9	47,8	27,0
Average	22,9	48,9	27,2

Values of lignocellulosic content are according to values from the literature, for example (Sannigrahi, et al., 2010), lignocellulosic content obtained from chemical methods (% m/m and dry basis) in several poplar genotypes was: 16,6-23,2 % for hemicellulose, 42,2-49,0 % for cellulose and 21,4-29,1 % for lignin. There are, however, some limitations to the method used in this work, owing to the considerations applied: deconvolution could have been done with other non-symmetrical curve types for improved approach to the kinetic mechanisms; the residual mass (besides ash) is not likely to have the same proportion of lignocellulosic material as the volatilized part of the sample; and ash content is probably higher than the values in Table 2, resulting in a decrease in the final results. Application of chemical methods for the determination of lignocellulosic proportions in the poplar chips analyzed in this work would have given the possibility for better confirming the results obtained with thermogravimetry.

Besides the limitations (which the chemical methods for content determination also have, in other forms), TG analysis was found useful for determining the percentages of lignocellulosic components in biomass.

3.1.2. Kinetic parameters

For the calculation of kinetic parameters, data from TG analysis at the 5 heating rates were used. With Kissinger method, temperature corresponding to the maximum rate of mass loss was used in order to develop the linear relationship of the method. An example of the application of Kissinger method (genotype AF8) can be seen in Figure 3.

Activation energy and pre-exponential factor were obtained, respectively, from the slope and intercept and their values are in Table 5, as well as the correlation coefficient.

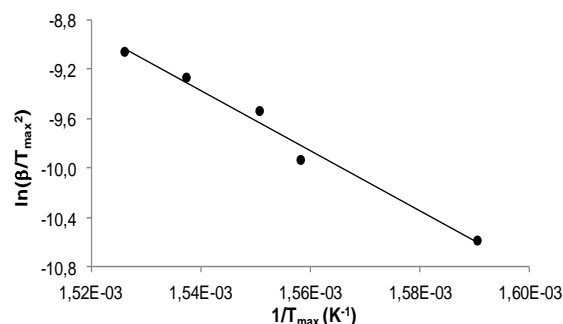


Figure 3: Graphical application of Kissinger method to genotype AF8.

Table 5: Kinetic parameters obtained with Kissinger method.

Genot.	E_a (kJ/kg)	A (s^{-1})	R^2
AF2	108,2	$1,2 \times 10^9$	0,775
AF8	203,4	$4,8 \times 10^{16}$	0,983
Bak	232,8	$2,2 \times 10^{19}$	0,983
Bra	250,4	$5,7 \times 10^{20}$	0,922
Ell	204,4	$1,1 \times 10^{17}$	0,825
Gri	175,2	$2,8 \times 10^{14}$	0,941
Hee	189,9	$6,0 \times 10^{15}$	0,978
Ska	319,9	$5,4 \times 10^{26}$	0,869
Wol	181,7	$8,3 \times 10^{14}$	0,967
Average	207,3	$6,0 \times 10^{25}$	-

Comparing with the results from a study applied to poplar chips (Slopiecka, et al., 2011), the obtained values are lower than the ones from that study ($153,9$ kJ/mol and $3,5 \times 10^{10} s^{-1}$), probably due to the lower heating rates applied (2, 5, 10 and 15 °C/min). Activation energies are, however, in agreement (except for AF2 and Ska) with activation energies for cellulose decomposition (195-286 kJ/mol) (Blasi, 2008), which is the component mainly responsible for the maximum rate of mass loss.

FWO and KAS isoconversional methods were used to obtain values of activation energies, corresponding to several values of growing conversion. Examples (genotype Ska) of the graphical linear correlation for these methods can be seen in Figure 4 and Figure 5.

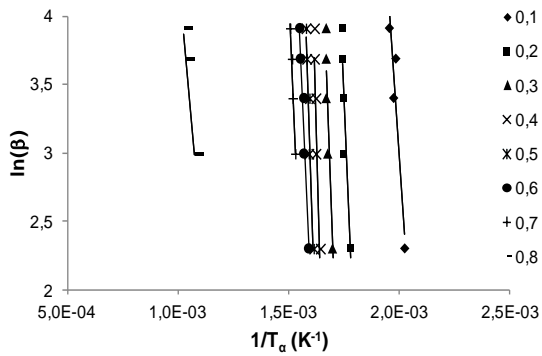


Figure 4: Graphical application of FWO method to genotype Ska.

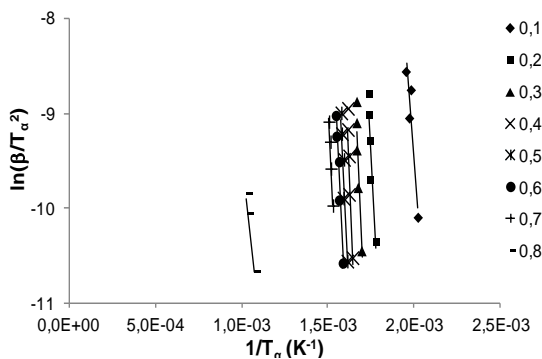


Figure 5: Graphical application of KAS method to genotype Ska.

Some points were rejected in order to obtain a better correlation coefficient. For some genotypes, kinetic parameters could not be calculated for some values of conversion, due to poor correlation coefficient or due to conversion not reaching values of 0,8 and/or 0,7. Activation energy values were obtained from the slope of the linear correlation, and pre-exponential factor values were obtained from the intercept, assuming first order reactions ($g(\alpha) = -\ln(1-\alpha)$). Results can be seen graphically in Figure 6 and Figure 7, respectively, for FWO and KAS method.

With FWO method, average values were, respectively for activation energy and pre-exponential factor, 80,5-301,1 kJ/mol and $3,1 \times 10^{10}$ - $4,8 \times 10^{36} \text{ s}^{-1}$, and with KAS method, 89,6-306,0 kJ/mol and $8,5 \times 10^{10}$ - $2,4 \times 10^{37} \text{ s}^{-1}$.

Activation energy values obtained (except some values belonging to genotypes Ska and

Wol) are comparable with the results from a work studying the application of FWO and KAS methods to poplar chips (Slopiecka, et al.,2011): 107,9-209,5 kJ/mol and 105,0-209,9 kJ/mol, respectively.

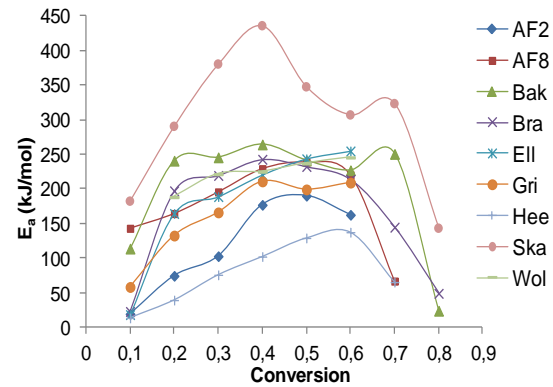


Figure 6: Activation energy evolution with conversion for FWO method.

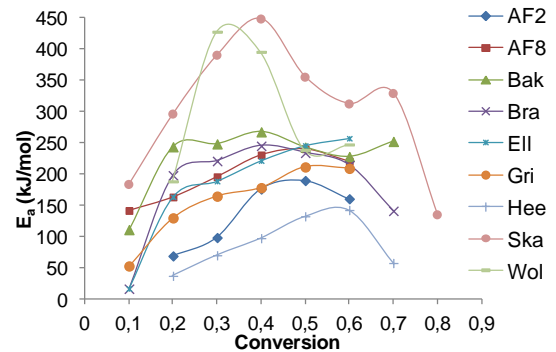


Figure 7: Activation energy evolution with conversion for KAS method.

Observing activation energy evolution with conversion, the variation is due to the complex behavior of thermal decomposition of the various components of the biomass, through competitive and dependent reactions, as was expected (Strezov, et al., 2003).

The methods used, although not reproducing the exact mechanisms of thermal decomposition, were found to be useful for determining kinetic parameters.

3.2. Lab-scale pyrolysis

3.2.1. Product yields

The range of product yields of the pyrolysis applied to the 9 different poplar genotypes can be seen in Table 6.

Table 6: Yields (% m/m) of pyrolysis of poplar genotypes.

	Biochar	Biooil	Gas
Yield	20,04-25,92	43,03-51,91	26,20-36,93
Average	21,50	48,75	29,75

Relatively small variability was found in the yields, in agreement with the also relatively small variability in the lignocellulosic contents determined, which originate the pyrolysis products. However, there are many sources of error, for example, from the extraction of the liquid product from the reactor, the drying of the solvents used for extraction, and, finally, the weighing of the bio-oil.

Pyrolysis was also applied to a mixture of the chips of the 9 genotypes, at different temperatures. Yields can be verified in Table 7. Also presented in Table 7 are the yields from pyrolysis applied to pine wood bark.

Table 7: Yields (% m/m) of pyrolysis applied to a mixture of poplar chips and to pine bark.

T (°C)	Bio-char	Bio-oil	Gas
425	22,50	30,09	47,41
475	21,24	25,07	53,69
475 (repetition)	21,58	35,82	42,60
500	20,46	52,95	26,59
475 (pine bark)	41,75	36,75	21,50

Pyrolysis at 425 and 475 °C obtained bio-oil with a lower yield than expected (from the yields from the genotypes, Table 6). Assuming sample conditions are approximately the same between the experiments, pyrolysis temperature, heating rate and residence time are the experimental conditions that can influence the product yields. Since bio-char yields are within the expected values, it can be

postulated that pyrolysis temperature did not influence the yields significantly. Fluctuations in the temperature control could have altered the heating rate, originating the yields presented. Residence time in the reactor is related to the removal of the gas phase, which is controlled by the inert gas flowing through the column. Fluctuations in the inert gas flow controller or leaks in equipment connections could have altered the inert gas flow and the residence time, and consequently, the product yields observed. The experimental conditions related to the sample are, for example, granulometry, which can lead to deficient packing of the sample in the reactor.

On the other hand, yields from pyrolysis at 500 °C are according to expected: the higher temperature breaks down and volatilizes more molecules, diminishing the solid product and increasing liquid product.

The pyrolysis applied to pine bark resulted in yields according to the nature of the biomass used: bark has high lignin content (Rowell, et al., 2005), and lignin is the main contributor to solid product (Van de Velden, et al., 2010), which represented the highest yield. Comparing with the poplar wood chips, which have less lignin content, the bark yielded almost double the proportion of bio-char.

Catalytic pyrolysis was applied to the mixture of poplar chips, at a temperature of 500 °C, using 4 different catalysts: Na₂CO₃, MgCO₃, FCC catalyst and H-ZSM5. Yields from these experiments can be seen in Table 8.

Table 8: Yields (% m/m) of catalytic pyrolysis applied to a mixture of poplar chips.

Catalyst	Bio-char	Bio-oil	Gas
Na ₂ CO ₃	20,90	43,40	35,70
MgCO ₃	17,10	35,10	47,80
FCC	18,47	48,76	32,77
H-ZSM5	20,18	39,54	40,28

Products yields from the catalytic pyrolysis obtained lower proportions of bio-oil comparing with the non catalyzed pyrolysis. Bio-char yields are also lower, although not as significantly as the bio-oil yields. The results obtained are in agreement with the goal of the catalytic pyrolysis: favoring cracking reactions of molecules into compounds of lower molecular weight, as well as reactions of deoxygenation (Wang, et al., 2014). These reactions originate more volatile material that adds to the gas products, diminishing solid and liquid yields. The reactions of catalytic upgrading also improve the energetic quality of the liquid product.

In particular, $MgCO_3$ and H-ZSM5 catalysts obtained the lowest yields of bio-oil, which could be an indicator that these were the catalysts with the best performance in upgrading the bio-oil. FTIR spectroscopy was applied to the bio-oils for quality evaluation.

3.2.2. FTIR analysis of bio-oils

Firstly, the bio-oils from the pyrolysis at 475 °C applied to the different genotypes were analyzed. The corresponding FTIR spectra can be seen in Figure 8.

Analysing the spectra, it can be verified that relatively small variability is found between the bio-oils from the different genotypes, in agreement with the also small variability of the lignocellulosic contents in the different genotypes, which originate the bio-oils.

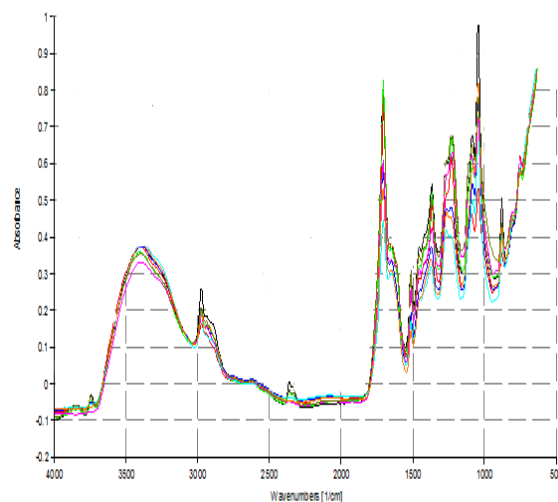


Figure 8: FTIR spectra for bio-oils obtained from pyrolysis at 475 °C to poplar genotypes.

Classes of compounds in the bio-oil were identified from the spectra, according to the wavenumbers that correspond to certain functional groups (Yorgun, et al., 2015).

Alkanes, aliphatic and aromatic compounds are present, as indicated by the absorbance at the ranges of wavenumbers of 3050-2800 cm^{-1} and 1475-1350 cm^{-1} , corresponding to C-H vibrations. Alkenes are also present due to absorbance at the ranges of 1645-1500 cm^{-1} and 1150-1000 cm^{-1} , from C=C and C-H (bending) vibrations. The range 1150-1000 cm^{-1} has a very noticeable peak.

Oxygenated compounds are present in the form of aldehydes, ketones, carboxylic acids, phenolic compounds, esters, ethers, alcohols and water, from absorbance at the wavenumber ranges of 3500-3200 cm^{-1} (O-H), 1750-1650 cm^{-1} (O=H), 1300-1150 cm^{-1} and 900-675 cm^{-1} (C-O). Particularly, at the range of 1750-1650 cm^{-1} (O=H), a strong peak is noticeable.

The bio-oils from the catalytic pyrolysis at 500 °C were also analyzed in order to evaluate the effect of the catalysts used. The bio-oil of the non catalyzed pyrolysis of the mixture of poplar chips was also analyzed for

comparison. FTIR spectra of these bio-oils can be seen in Figure 9. Arbitrary units were used so as to provide better visual comparison.

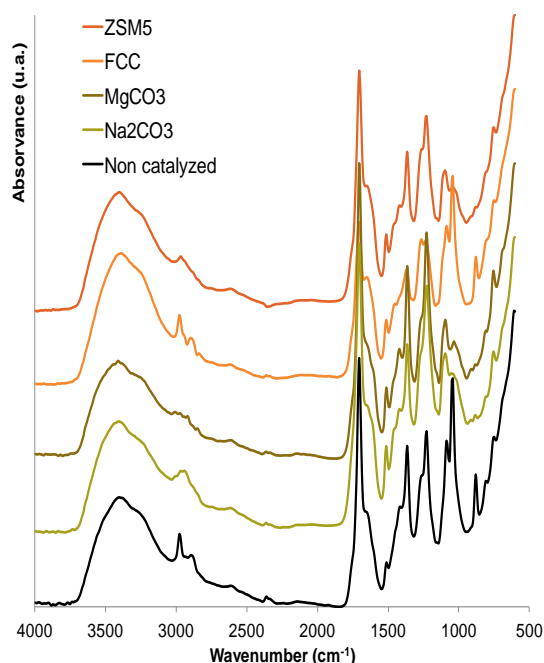


Figure 9: FTIR spectra for bio-oils obtained from pyrolysis at 500 °C to the mixture of poplar chips.

The spectrum belonging to the bio-oil from the non catalyzed pyrolysis of the mixture of poplar chips was found to be representative of the spectra of the bio-oils in Figure 8, due to the resulting absorbance being approximately the same. Since catalyzed pyrolysis was applied to the mixture of poplar chips, comparison of bio-oil qualities from catalyzed pyrolysis and non catalyzed pyrolysis can be done.

In general, all of the catalysts had some effect of bio-oil upgrading. In the case of alkanes, alkenes, aliphatics and aromatics, absorbance in the range of 3050-2800 cm^{-1} (C-H) was diminished by MgCO_3 and H-ZSM5, FCC catalyst affected the range of 1475-1350 cm^{-1} (C-H bending) and in the range of 1150-1000 cm^{-1} (C-H bending), a decrease of absorbance was observed,

especially with MgCO_3 , Na_2CO_3 and H-ZSM5. These results indicate that the catalysts favored cracking reactions.

In the case of oxygenated compounds, the range of 3500-3200 cm^{-1} (O-H) had a decrease in absorbance with the catalyst MgCO_3 , the peak at 1750-1650 cm^{-1} (C=O) diminished with FCC catalyst, the range 1300-1150 cm^{-1} (C-O stretching and O-H bending) decreased in absorbance with FCC and H-ZSM5 catalysts, and absorbance at the range of 900-675 cm^{-1} (O-H bending) had a general decrease, especially noticeable with H-ZSM5, MgCO_3 and Na_2CO_3 .

Hence, catalyst application in pyrolysis has a positive effect on reactions such as cracking and deoxygenation, upgrading the quality of the bio-oil.

4. Discussion and conclusion

Results from this work allowed the characterization of poplar wood chips, in terms of composition, thermal decomposition, pyrolysis yields (non catalyzed and catalyzed) and quality of bio-oil obtained from pyrolysis.

Thermogravimetry was shown to be a simple and method for determining lignocellulosic material proportions in biomass (averages (m/m) of 23 % hemicellulose, 49 % cellulose and 27 % lignin), obtaining results in agreement with traditional chemical methods. Determination of kinetic parameters also showed acceptable results and the complex thermal degradation of biomass in inert atmosphere was confirmed.

The lab-scale pyrolysis experiments were able to obtain bio-oil as the major product, with an average yield of 49 % (m/m) at 475 °C. Catalytic pyrolysis for bio-oil upgrading was also applied and FTIR spectra indicated that

the catalysts used (Na_2CO_3 , MgCO_3 , FCC catalyst and H-ZSM5) had a positive effect on bio-oil energetic quality, through the favoring of cracking and deoxygenation reactions.

Future studies should be conducted, analyzing, for example, influence of temperature, granulometry and catalyst application in pyrolysis. Comparison with biomasses other than poplar wood chips should also be performed, as well as applying other energetic conversion processes, as in gasification and liquefaction.

5. References

- Blasi, Colomba Di. 2008. Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science*. 2008, Vol. 34, 47-90.
- Bradshaw Jr., H. D., et al. 2000. *Emerging model systems in plant biology: Poplar (Populus) as a model forest tree*. Washington, 2000.
- Sannigrahi, Poulomi, Ragauskas, A. and Tuskan, G. 2010. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioproducts and Biorefining*. 2010, Vol. 4, 209-226.
- Simpson, James, et al. 2009. *IEA Bioenergy Task 30 Technical Review No. 3: Environmental benefits associated with short-rotation woody crops*. Paris: International Energy Agency, 2009.
- Sims, Ralph, et al. 2006. Energy crops: current status and future prospects. *Global Change Biology*. 2006, Vol. 12, 2054-2076.
- Slopiecka, Katarzyna, Bartocci, Pietro and Fantozzi, Francesco. 2012. Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. *Applied Energy*. 2012, Vol. 97, 491-497.
- Strezov, V., Moghtaderi, B. and Lucas, J. 2003. Thermal study of decomposition of selected biomass samples. *Journal of Thermal Analysis and Calorimetry*. 2003, Vol. 72, 1041-1048.
- Van de Velden, M., et al. 2010. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy*. 2010, Vol. 35, 232-242.
- Vyazovkin, S., et al. 2011. *Thermochemical Acta. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*. 2011, Vol. 520, 1-19.
- Wang, Y., et al. 2014. Catalytic fast pyrolysis of lignocellulosic biomass. *Chem. Soc. Rev.* 2014, Vol. 43, 7594.
- Yorgun, S. and Yildiz, D. 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *Journal of Analytical and Applied Pyrolysis*. 2015, Vol. 114, 68-78.
-