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# Comparison of direct and staged pyrolysis of the ligno-cellulosic biomass with the aim of the production of high added value chemicals from bio-oil

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## Abstract
This work presents a comparative study of direct and staged pyrolysis of softwood (500/200) and hardwood (315HD) for the production of bio-oil with the aim to enhance the selective production of high added value molecules. The experiments were conducted in a fixed bed reactor under nitrogen flow rate. The effect of temperature is investigated between 250- 550°C and maximum bio-oil yields of 49.8% at 450°C for 315HD and 45.5% at 500°C for 500/200 were obtained. The staged pyrolysis was carried out at 250°C, 350°C and temperature at which a maximum yield of bio-oil in direct pyrolysis. The temperatures of the first two steps were previously determined by TGA analysis of the biomass so as to target the selective degradation of hemicelluloses and cellulose. The overall yields of bio-oil obtained by staged pyrolysis were lower than those obtained by direct pyrolysis for both biomasses. In the first stage, the produced bio-oil is rich in phenolic and furan derivatives and the gaseous fraction is rich in $CO_2$. In the second one, the rest of the bio-oil is produced and the gas produced contains mainly CO and $CO_2$. In the last stage, only a production of CO, $CO_2$ and $CH_4$ is observed.

*Keywords*: Wood, Direct pyrolysis, Staged pyrolysis, bio-oil, Pre-separation, Added value molecules.

## 1. Introduction
Pyrolysis was used in numerous works for the valuation of the ligno-cellulosic biomass [1-10]. It consists in decomposing the organic matter under the influence of the heat in an inert atmosphere to produce non condensable gas, bio-oil and bio-char. Three types of pyrolysis (slow, fast and flash) allow the orientation of the process towards the production of one of the three types of products of pyrolysis according to the conditions of the processing. Due to the crisis of 1973, many research groups are involved in the development of reactor technologies for the production of bio-oils [1-11]. Indeed, bio-oil represents an alternative for the fossil fuels. However, its application as fuel remains limited because of its higher heating value (17 MJ/kg) which represent only 45% of that exhibited by fossil fuels due to its strong moisture content (30 %) and its wealth in oxygenated compounds. However, these compounds represent a real source for the chemical industry. Indeed, the oil of pyrolysis includes more than 300 valuable oxygenated compounds such as furans, ketones, phenols and esters [11,13]. Dynamotive process has developed the organic lime from the reaction of carbonyl groups and the phenols provided from bio-oil fraction with the lime form salts of calcium [12]. Pyrolyticlignins find applications in resins synthesis [14]. Furthermore, certain phenolic compounds are known for their insecticidal and fungicidal effects. Several works studied the effect of the temperature of pyrolysis on the production and the quality of bio-oil from various types of biomass [12-15]. The characterization of oil by conventional analytical methods such as FTIR and the GC/MS shows a complex mixture including compounds with lower molecular weight such as monomers, rearranged moieties and fragmented derivatives coming from the three macro-components of the biomass. The separation of the constituents of the oil is a difficult and complex process [16]. Among classical separations, distillation cannot be applied due to the polymerization of the aromatic core obtained from the lignin degradation. Extractive and chromatographic methods can be applied [17-23] even if they present the drawback of a strong solvent consumption.

To limit the economic impact of the difficult separation of the bio-oil constituents, a staged pyrolysis in temperature can be applied. Starting from ligno-cellulosic biomass, this process uses the temperatures of the macro-components degradation [14]. Hemicellulose tends to degrade in the range of temperature between 200-300°C to give mainly furan derivatives such as furfural or 2-methylfuran and possibly acetic acid. Cellulose decomposes between 300°C and 400°C to give mainly levoglucosan, acetic acid and hydroxyacetaldehyde while the lignin degrades in a wide interval of temperature (150°C-600°C) to give pyrolytic lignin and phenol derivatives. It was notable that hemicellulose and cellulose present a fast degradation in a range of narrow temperature. Furthermore, the wide interval of temperature of lignin degradation gives a rise to an overlapping domain of the decomposition of the three macro-components of the biomass [24]. For that purpose, different parameters impact the process. The control of the heating velocity, the choice of the temperature and residence time of the biomass are necessary for selective pyrolysis of macro-components and thus for selective production of chemicals having high added value. Moreover, due to the origin of the biomass, several types of cellulose, hemicellulose and lignin have different temperatures of degradation for the same macro-component. Thermogravimetric analysis (TGA) allows the determination of the real temperatures of the degradation of hemicellulose and cellulose, and this method is widely used for the characterization of the lignocellulosic biomass [25].
In the concept of the orientation towards a selective chemicals production, the use of biomass in the presence of additives can be applied. For example, impregnation of cellulose by $H_3PO_4$ showed an increase of the production of furfural and levoglucosenone while starting from xylan, furfural, 3-methyl-2-cyclopenten-1-one,3,4-dihydroxy-2-methoxy-2H-pyran,4-hydroxy-5,6-dihydro-2H-pyran-2-one are observed [26]. The demineralization of the biomass by acid washing allows the increase in production of levoglucosan [27].
To simplify the separation plan of pyrolysis bio-oil, a staged process in the temperatures of degradation of macro-components can be applied for the production of chemicals having high added value. This method was applied for the study of the production of the phenolic compounds from the vacuum pyrolysis of the bark and the sapwood of the birch. Treatment was led on five stages of temperatures of 200-550°C [28]. The first one begins at 200°C then the temperature rose by 75°C in the second and the third and by 100°C for the last two stages. The study showed that the staged pyrolysis favors the formation of phenol derivatives for temperature ranging from 275°C to 350°C.Methylguaiacol, ethylguaiacol, guaiacol, 4-propenylsyringol, phenol and catechol reach their maximal yields in this range of temperature (275-350°C). Between 350°C and 450°C, the pyrolysis ends and phenols are converted into catechols by dimethylation of the methoxy groups. The comparison of direct and staged pyrolysis for the production of phenols revealed a yield of added value compounds that is twice greater for the staged pyrolysis [28]. Recently, treatment in two stages was applied for the pyrolysis of the pine in Auger reactor and the biomass was preprocessed in temperatures between 270°C to 370°C before being increased at 500°C. The results showed that the pretreatment of the biomass at lower temperatures than 270°C does not affect the yield of products in comparison with the direct pyrolysis at 500°C excepted that the total yield of furfuryl alcohol and sugars such as arabinose and fructose increases. For preprocessing carried out at equal or higher temperatures than 300 °C, the total yield of bio-oil remains lower than that one obtained by direct pyrolysis. Total yield of glycolaldehyde produced from cellulose fragmentation increases as well as that of the methanol which reaches themaximumof production between 290°C and 320°C, what is explained by the acceleration of the reactions involving the polycondensation of the lignin during thermal pretreatment [29].
In this work we investigate the direct and staged pyrolysis of hard and soft wood in a fixed bed reactor for comparison of the bio-oil production and to examine the possibility of pre-separation of the constituents because of the selective decomposition of the macro-components (hemicellulose, cellulose and lignin) according to the temperature.

## 2. Experimental details

*2.1Biomasses*

Wood of beech and pine are used to represent soft and hard wood, respectively. The biomasses were supplied in the form of powder the trade name of which are 315HD and 500/200, respectively with a particle size ranging between 50 and 600 µm.

*2.2. Elementary and ultimate analysis of the biomasses*
Several physico-chemical analyses were made to characterize the biomasses. The percentages of total carbon, hydrogen, nitrogen and sulphur were found by dry combustion and the oxygen was calculated by the complement at hundred of the sum of the percentages. The composition in cellulose, hemicelluloses and lignin was determined by extraction by neutral and acid detergent fibers using Van Soest method [30].

*2.3 Characterization of the biomasses by TGA*
The thermal characteristics of both types of wood were determined by TGA. The analysis was led to a maximal temperature of 900°C with 30 mg of wood with a heat velocity of 100°C / min under a nitrogen flowrate of 50 ml/min in a device SETRAM TGA 92 1618.

*2.4 Description ofthe experimental set-up*
Pyrolysis tests were carried out in an installation provided with a fixed bed reactor (Figure 1). The reactor is made of stainless steel and is cylindrical body of 50 cm in length and 3.2 cm in diameter in which the bed of biomass is placed. A mass flow meter allows to fixe in all the tests a flowrate of 50 L/h of nitrogen that is preheated at 350°C at the inlet of the reactor and then warmed by a vertical tubular oven (Nabertherm) at the required temperature. A thermocouple allowing the temperature measurement of the particles of biomass is inserted in the fixed bed. Bio-oil is collected in a series of three condensers cooled in a water bath at room temperature. The remaining gases cross filters of silica gel and activated carbon then two on-line gas filters before arriving to the µGC (SRA 3000) to be analyzed and quantified.

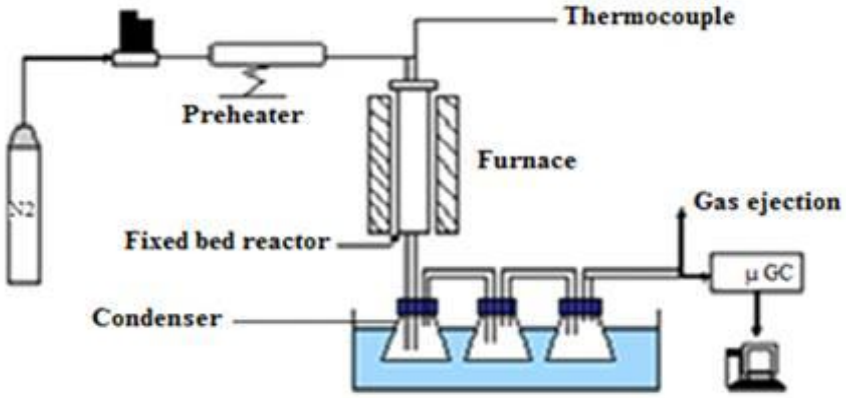



**Figure1:** Experimental set up

*2.5 Influence of thetemperature on the products of pyrolysis*
The experiments were carried outat 250, 300, 350, 400, 450, 500 and 550 °C. The reactor was beforehand warmed with a heat velocity of 60 °C/min and it was maintained at the final temperature during one hour. The recovery of bio-oil was realised at ambient temperature. Pyrolysis gases were continuously analyzed by the µGC with an interval of two minutes. The bio-char was withdrawn at the end of pyrolysis and weighed for the mass balance assessments. For some tests of the staged pyrolysis, the bio-char wasrecoveredafter each stage and was analyzed so as to determine the fraction converted of each macro-component in each stage.

*2.6 Stagedpyrolysis of the biomass*
This part is devoted to determine the influence of the temperature on the yield and the pre-separation of bio-oil. 20 g of biomass with a particle diameter ranging between 200 and 315 µm was previously dried at 105°C during 12 hours. The experiments were led at three temperature levels during one hour for every stage. In the first stage, the pyrolysis takes place at 250°C and the bio-char obtained is then used at 350°C in the second stage and finally at the temperature giving the maximal production of bio-oil for each biomass in direct pyrolysis. The first two levels of temperature correspond to the beginning of degradation of hemicellulose and cellulose, respectively [31]. Both two levels of temperature were detectedfrompreliminaryTGA tests. The mass balance assessment of every stage is established from the bio-oil recovered in the condenser, the bio-char and the analyzed gases by

µGC. For some tests, the bio-char was recovered after each stage and was analyzed so as to determine the fraction converted of each macro-component in each stage.

*2.7 Mass balance assessments*

The mass balance assessment of every experiment is defined by the sum of the yields corresponding to the final bio-char, cumulated bio-oil and gas produced during all the stages. The percentage of each product is expressed with regard to the initial mass of the biomass. The yield of bio-oil is determined from the difference of the mass of the empty and full condensers. Gases were mainly constituted of $CO_2$, CO, $CH_4$ and $H_2$ and were analyzed by µGC (SRA 3000). The yield of every gas was calculated by digital integration of its molar flowrate over the duration of one hour corresponding to each stage.

*2.8 Determination of water content*

The water content in bio-oil was determined by Karl-Fischer titration (Metler Toledo C30) using hydranalcoulomat E as titrant. To ensure the accuracyof the results, every analysis was repeated three times.

*2.9 Analysis of bio-oil by IR*

For the chemical characterization of bio-oil, the analysis was carried out by an infrared spectrometer (Nicolet impact 400) to determine the functional groups present in the bio-oil. A droplet of the bio-oil was placed on a KBr pellet. Samples were analyzed in a range of wavenumber between 400 and 4000 $cm^{-1}$.

*2.10 Analysis of bio-oil by GC/MS*

1 µl of every sample of bio-oil was diluted in the acetone in a vial of 1 ml. The injection is automatically made in a thermo scientific chromatograph trace GC Ultra by using Split mode. A Thermo-5ms SQC30m*0.25mmID*0.25µm column was used for compound identification; helium was employed as carriergas at a flowrate of 1mL/min.The temperature was fixed at 110 °C during 1 minute then ramped at 1°C/min to 130°C and maintained during 2 minutes and then ramped at 10°C/min to 300°C and held for further 10 minutes.

## 3. Results and discussion

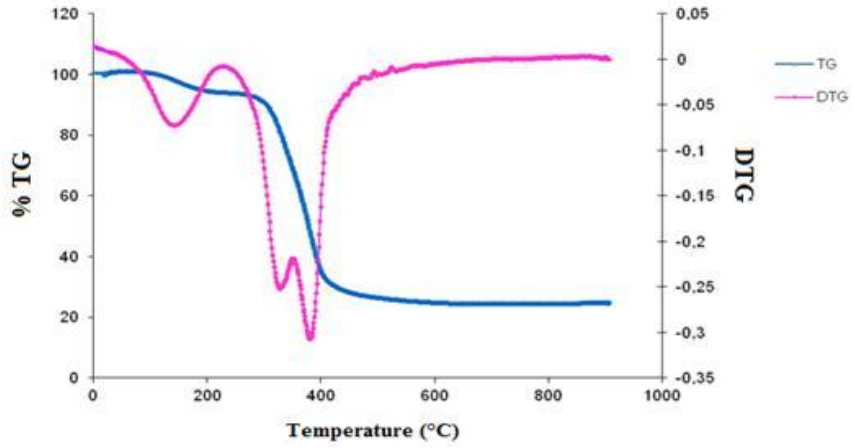
*3.1 Elementary analysis of the biomasses*

The results of elementary analysis of the biomasses presented in Table 1 show a slight difference in the elementary composition. The content in carbon is 2 % superior for 315HD while oxygen and mineral content are higher for the biomass 500/200. Carbon, oxygen and hydrogen are distributed in the biomass in the form of hemicellulose, cellulose and lignin. The biomass 315HD contains more hemicellulose and cellulose than the biomass 500/200 and lignin content is twice as big in the biomass 500/200.

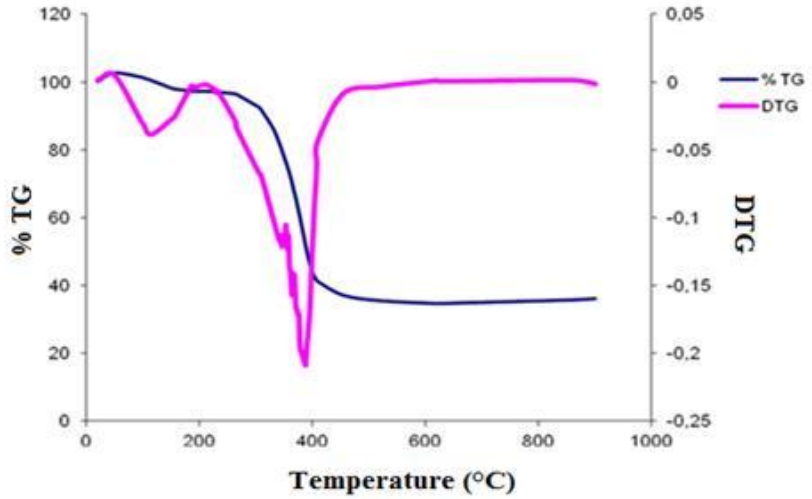
*3.2 TG analysis*

In Figure 2 are presented the results of the TGA where can be observed the same trend of degradation for both biomasses but with a loss of different mass. A loss of considerable mass is observed for both biomasses in the temperature interval between 250°C and 400°C and a slowing down is noticed between 400°C and 600°C. Between 600°C and 900°C, the mass loss stabilizes at 80 % in the case of the biomass 315HD and 60 % for the biomass 500/200. DTG curves of both biomasses present three peaks of degradation.

The first phase of mass loss corresponds to the evaporation of the humidity at around 100°C. The degradation of hemicellulose, which is the most unstable constituent and the least resisting one takes place at 250 °C and the mass loss is around 70 % for the biomass 315HD and 50 % for the biomass 500/200. The third peak corresponds to the decomposition of the cellulose and occurs at 400°C. Indeed, the decomposition of the cellulose requires more energy than for the hemicellulose because of its high degree of polymerization [32]. Lignin presents a wide range of temperature of decomposition between 150 and 500°C [31] justifying the absence of the peak of degradation of the lignin on TG and DTG curves for both biomasses. The difference of the behaviour of both biomasses during the thermogravimetric analysis is due to the lignin content, which is
higher in the biomass 500/200: indeed, the lignin reduces the biomass decomposition because of its rigidity and its resistance [33-36].




(a)

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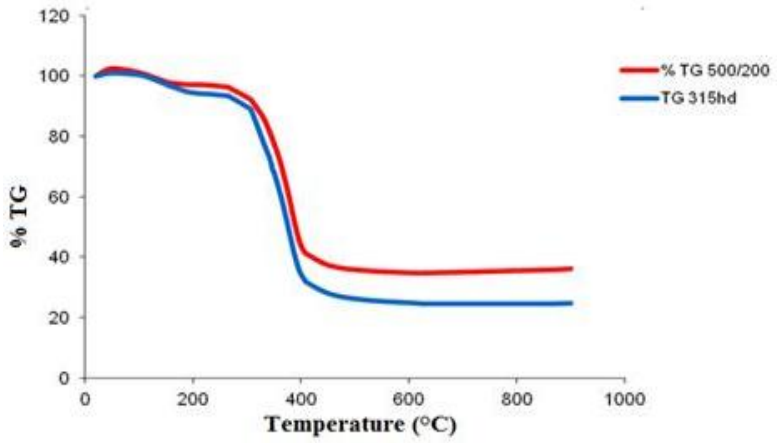



(c)

**Figure 2:** TGA curves with temperature increase velocity of 100°C/min, (a) 315HD, (b) 500/200, (c) comparison of ATG of 315HD and 500/200

*3.3 Effect of thetemperature on the yield on the products of pyrolysis*

Figure 3 shows the influence of the temperature on the yields of products in direct pyrolysis. Both biomasses tend to decompose to give bio-oil and gas. The primary decomposition of the biomass gives mainly chemical

compounds stemming from the fragmentation of macro-components forming the biomass. For both biomasses, the bio-oil yield increases with the temperature until a maximal yield of 49.8 % at 450°C and 45.5 % at 500°C for the biomasses 315HD and 500/200, respectively. The biomass 315HD gives more bio-oil at lower temperature in comparison with the biomass 500/200. This behaviour difference in pyrolysis is due to the difference in macro-components content in the biomasses. Indeed, the biomass 315HD contains more cellulose and hemicellulose which tends to degrade quickly to give more bio-oil in comparison with the biomass 500/200 which contains higher lignin content (Table 1). Beyond the temperatures of maximal production of bio-oil, an increase of gas yield is observed due to the side reactions of cracking of the condensable vapours and some gasification of the char [37]. These side reactions are of heterogeneous and homogeneous nature. Boroson.[38] explained that at temperature higher than 450°C, the char plays the role of a catalyst for the cracking of the condensable vapours. This heterogeneous catalysis takes place on the surface of the microporous char. Another type of reaction is the cracking of the condensable vapours of low molecular weight which reduces the yield of bio-oil. The secondary decomposition of the condensable vapours can take place inside or outside the particles.

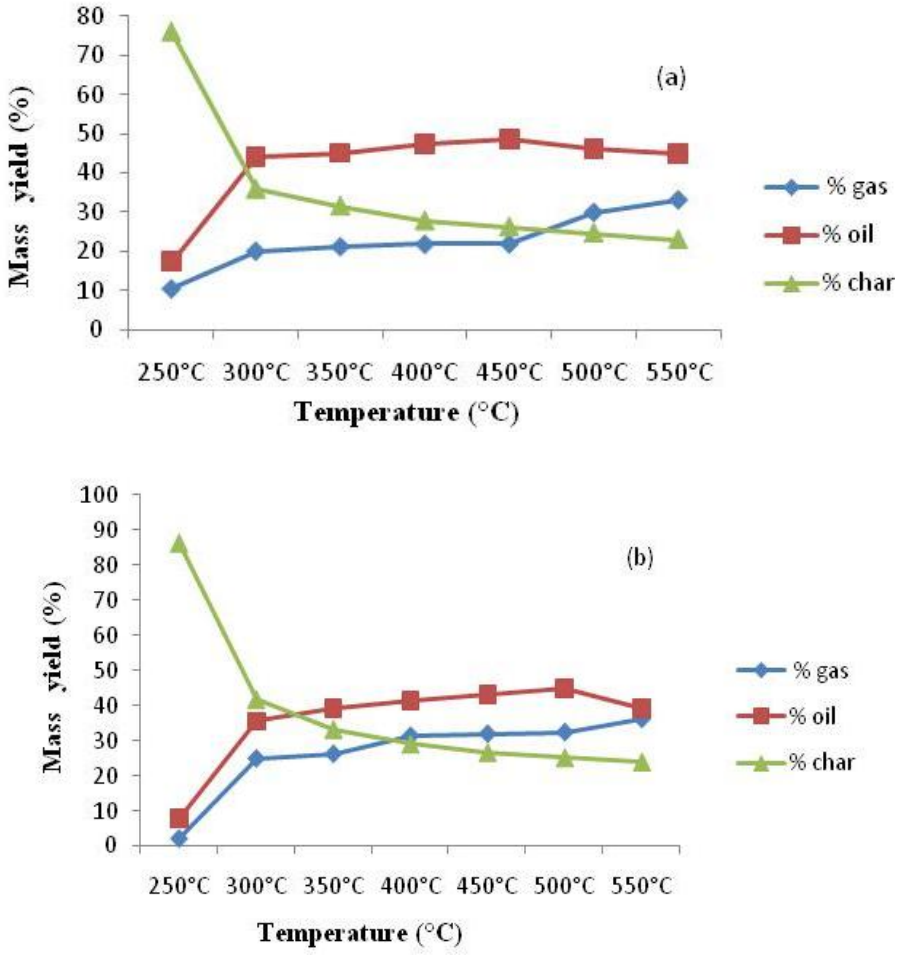



**Figure 3:** Influence of the temperature on the yield of the products of pyrolysis (a) 315HD, (b) 500/200

*3.4 Influence of the temperature on the production of gases*

Figure 4 presents the mass fraction of every gas according to the temperature. Produced gases are essentially $CO_2$ and CO, with small amounts of $CH_4$ and $H_2$. In the temperature range 250°C-350°C, due to the reactions of primary decomposition of the biomass, produced gases are exclusively $CO_2$ and CO. The $CO_2$ produced at this range of temperature is ascribed to the decarboxylation reaction of O-acetyl groups linked to the xylan in the hemicellulose and to series of complex reactions of decomposition of cellulose to produce a substance with relatively simple composition and lower degree of polymerization, named active cellulose. Shafizadeh [39] explained that during the biomass pyrolysis in the interval of temperature 200°C- 280°C, the formation of dehydro-cellulose is accompanied by a production of $CO_2$ and CO. These results are in agreement with those

obtained by different groups [40-42]. In this range of temperature, the biomass 315HD gives yields in $CO_2$ and in CO higher than those of the biomass 500/200 due to the strong hemicelluloses and cellulose content in the biomass 315HD (Table 1).

**Table 1**: Elementary analysis of biomasses 315HD and 500/200

| **Element** | **315HD** | **500/200** | **Analysismethod** |
|---|---|---|---|
| % Hemicellulose | 24.49 | 16.1 | Van Soest method |
| % Cellulose | 55.22 | 50.68 | Van Soest method |
| % Lignin | 12.29 | 24.22 | Van Soest method |
| % Moisture | 7.56 | 7.3 | Gravimetry |
| Dry material | 91.70 | 91.70 | Gravimetry |
| Mineral matter | 0.44 | 1.09 | |
| Elemental analysis (%) | | | |
| C | 49 | 47.1 | Dry combustion |
| H | 6.67 | 6.8 | Dry combustion |
| O | 44.14 | 46 | Calculation |
| N | 0.078 | 0.04 | Dry combustion |
| S | < 0.1 | <0.1 | Dry combustion |

A remarkable decrease of the $CO_2$ production is observed with the increase of temperature for both biomasses due to the side reactions which become intensified with the temperature. Wen and Dutta [43] propose several secondary reactions such as the reaction of the char with the $CO_2$ which occurs during the primary degradation of the biomass. $H_2$ production does not exceed 2-5% for both biomasses and production of $CH_4$ (10%-15%) is observed from 400°C for the biomass 315HD and 500°C for the biomass 500/200.

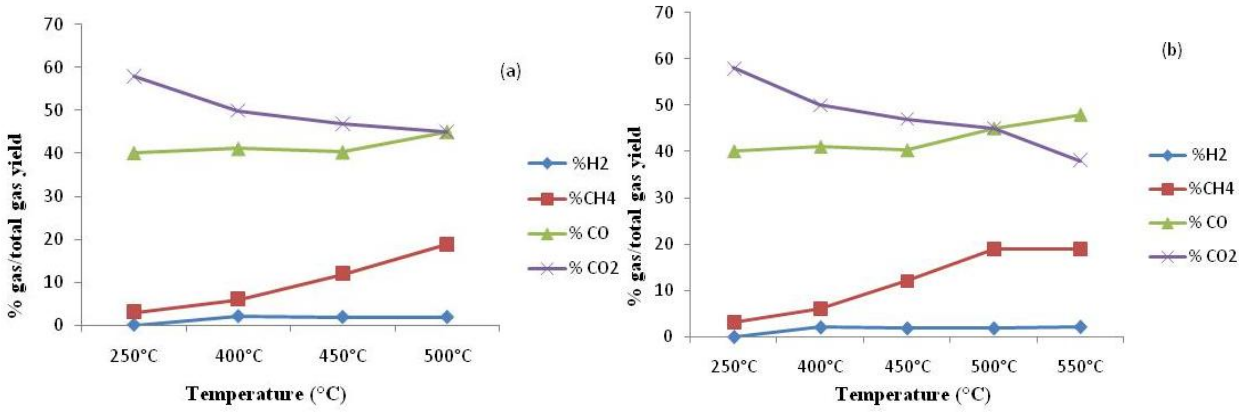



**Figure 4:** Influence of the temperature on the gases production from wood pyrolysis (a) 315HD, (b) 500/200

*3.5Characterization of bio-oil*

*3.5.1 Water content*

Figure 5 shows an increase of the water content in bio-oil with the temperature of pyrolysis for both biomasses and a maximal water content of 33 % is reached. The presence of the water is due to the degradation of cellulose and hemicelluloses. For the first one, reactions of dehydration, polycondensation and cross linking afforded acetic acid, formaldehyde and furan derivatives [43-46]. For the second one, mechanism of decomposition furnishes mainly the furfural [46]. Chiwat [45, 46] explained that a water molecule is formed from two groups OH during the cellulose reticulation.

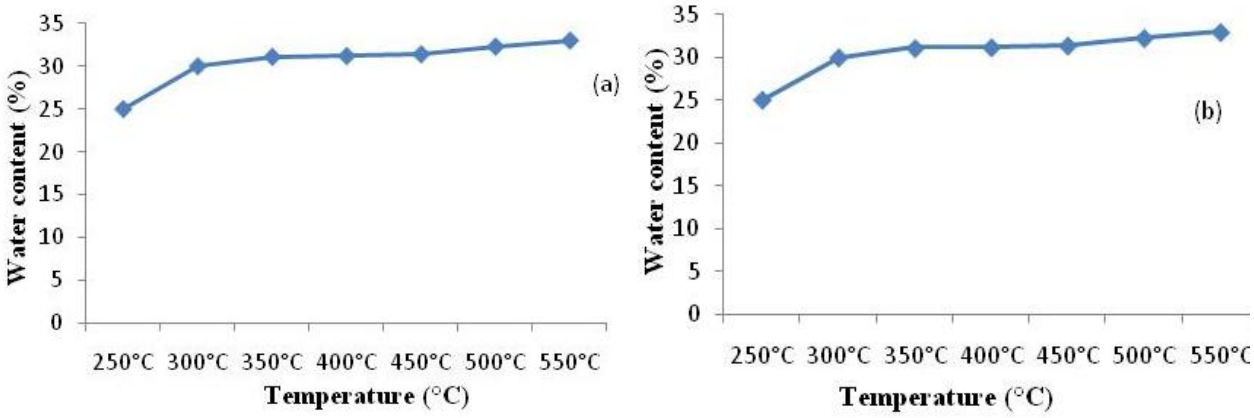



**Figure 5:** Water production with the temperature (a) 500/200 (b) 315HD

*3.5.2 IR spectroscopy analysis*

With the aim of a material valuation, the physico-chemical analyses were made on oil produced at various temperatures. Bio-oil produced at different temperatures presents the same characteristic bands in the infrared domain (Figure 6). A wide band of strain is observed between 3200 $cm^{-1}$ and 3600 $cm^{-1}$ and is attributed to the hydroxyl groups of phenols and alcohols [47]. A band of absorption of low intensity appearing between 2800 $cm^{-1}$ and 3000 $cm^{-1}$ is attributed to the aliphatics C-H stretching vibration. A strong band is observed at 1713 $cm^{-1}$ which represents the C=O double bond of aldehydes and ketones. Peaks at 1500 and 1514 $cm^{-1}$ are those of aromatic bonds C=C double bonds. Peaks between 1043 $cm^{-1}$ and 1224 $cm^{-1}$ represent the carbon-oxygen single bond of secondary alcohols.

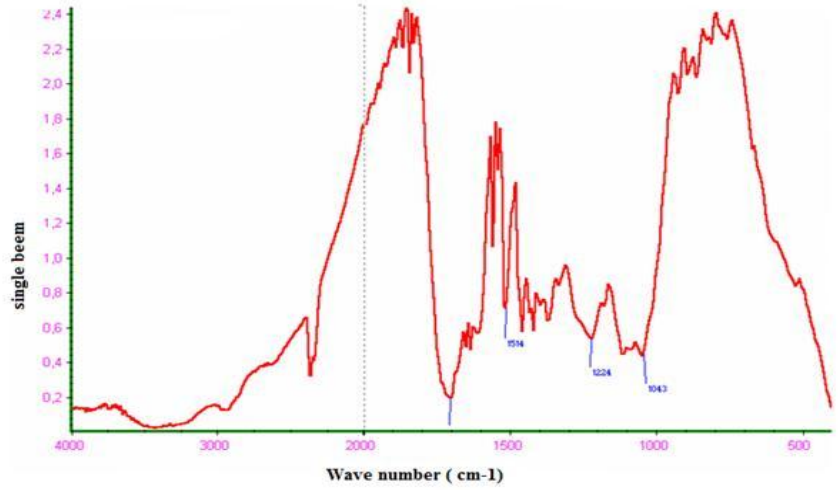



**Figure 6:** IR spectrum of the bio-oil obtained by pyrolysis of 315HD at 450°C

*3.5.3 Identification of chromatographic peaks*

The chemical composition of bio-oil is very complex [48, 49] and the use of a single analytical method is generally not sufficient for bio-oil characterization because of the diversity of the chemical compounds. The GC /MS (Figure 7) was used for the detection of the typical compounds of the pyrolysis of the ligno-cellulosic biomass. The identification of CG / MS peaks (Table 2) was realized by the software Xcalibur with the probability of more than 95 %. The acid character of produced bio-oil is due to the strong content in by-products of furan stemming from hemicellulose decomposition and more exactly from the depolymerisation of the xylan units. The pentose dehydration mechanism for furfural formation has not been generally accepted by all the community and a clear consensus should be reached on this important issue (cyclic versus acyclic intermediates) [50, 51].

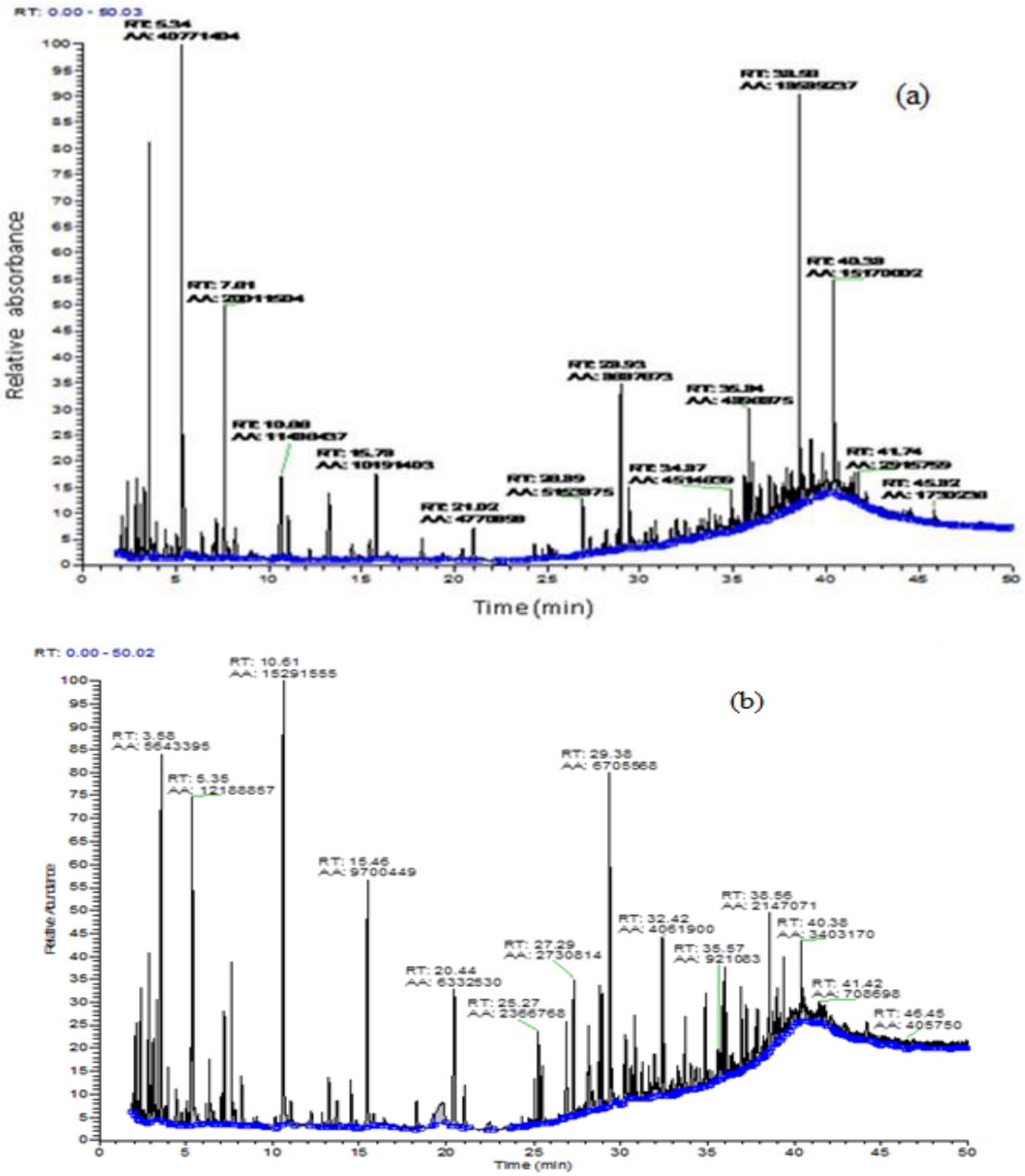



**Figure 7:** Chromatogram of bio-oil (a) 500/200 at 500 °C, (b) 315HD at 450°C

Furfural is a typical product found in the bio-oil and the study of thermal formation mechanism of furfural was discussed by Shafizadeh*et al.*[52]. It is shown that the addition of zinc chloride improve the formation of furfural during hemicellulose pyrolysis. The furfural is produced from the cleavage of the bond between oxygen and C-5 and ring forming between C-2 and C-5 position on the xylan unit. Two new plausible mechanisms are proposed for the production of furfural by [53, 54] for the thermal decomposition of hemicellulose units during pyrolysis. The first is a ring-opening reaction of the depolymerised xylan unit through the cleavage of the hemi-acetal bond (between oxygen and C-1 on the pyran-ring), followed by the dehydration between the hydroxyl groups on C2and C5 position. The second one is the cleavage of the 1, 2 glycosidicbond between the xylan unit and 4-O-methylglucuronic acid unit, followed by the ring-opening reaction and rearrangement of the 4-O-methylglucuronic acid accompanied by the elimination of $CO_2$ and methanol. The furan can be also formed from the decomposition of the cellulose units at high temperature. This mechanism is in competition with the formation of levoglucosan [32, 55]. GC / MS analysis showed a strong presence of the phenol derivatives the

origin of which is the degradation of lignin which consists of two types of aromatic units: guaiacyl and syringyl. The distribution of these units differs according to the wood type. Soft wood such as the biomass 500/200 contains the units of guaiacyl only however, both units are present in hard wood [14], what can affect the behaviour of wood during the pyrolysis. Both bio-oils contain furan derivatives as furfural, 2, 5 dimethyl furan, furfuryl alcohol produced from the decomposition of hemicelluloses and cellulose.

**Table 2**: Chemical compositions of bio-oil produced from 315HD and 500/200

| **Retention time** | **Compound** |
|---|---|
| 1.95 | Furfural |
| 2.14 | Furfuryl alcohol |
| 2.18 | 2,5-dimethylfuran |
| 2.22 | 5-furfuraldehyde |
| 2.33 | 1,4 benzenediol |
| 2.42 | Phenol |
| 2.54 | 2-acetyl-5-methylfuran |
| 2.86 | Corylon |
| 2.99 | Cyclohexane-1,4-dione |
| 3.58 | 4-methoxyphenol |
| 3.72 | 2-methoxyphenol |
| 4.63 | p-xylene |
| 5.34 | 2 methoxy-4methylphenol |
| 5.71 | ethyl but-2-enoate |
| 6.89 | 2,4-dimethoxytoluene |
| 7.20 | 3-methylcetechol |
| 10.61 | 2, 6-dimethoxyphenol |
| 13.72 | Vanillin |
| 15.78 | 2-methoxy-4-(1-propenyl) phenol |
| 20.44 | 3-hydroxy-4,5-dimethoxybenzaldehyde |
| 25.27 | 2,3,4-trimethoxybenzaldehyde |
| 27.09 | Syringaldehyde |
| 28.78 | 3, 4, 5-trimethoxybenzaldehyde |
| 29.33 | Diphenylmethane |
| 32.42 | ND |
| 38.56 | fluorene |

The relative absorbance of furan derivatives is more important in the bio-oil produced from 315 HD than 500/200 due to the presence of high lignin content. Indeed, the interaction between lignin and hemicelluloses led to the decrease of furan derivatives and C-O containing compounds, including various aldehydes and ketones [56]. The product of the primary decomposition of the lignin are mainly composed by 2-methoxyphenol, 2 methoxy -4-methylphenol, 2,6 dimethoxyphenol,syringaldehyde and 2,3,4 trimethoxybenzaldehyde resulting from the primary decomposition of lignin units. The bio-oil produced from 500/200 (Figure 7.b) is mainly formed by 2 methoxyphenol and 2 methoxy -4-methylphenol. The major difference between bio-oils lies on the 2,6dimethoxyphenol (syringol), 4-hydroxy-3,5dimethoxybenzaldehyde (syringaldehyde), guaiacol (2-methoxyphenol) and trimethoxybenzaldehyde content. The lignin of the biomass 315HD decomposes to produce mainlysyringol (2, 6 dimethoxyphenol), guaiacol 2-methoxyphenol) and the 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) due to the decomposition of coniferyl and sinapyl alcohol of the lignin. The relative absorbance of the syringol (2,6dimethoxyphenol) in bio-oil produced from 500/200 (Figure 7 a) is less important than the relative absorbance of the bio-oil produced from 315HD (Figure7 b) due to the lack of syringyl units in the lignin of the biomass 500/200.

*3.6 Stagedpyrolysis*

*3.6.1 Effect of staged pyrolysis on the product yields*

In the first stage both biomasses are pyrolysed at 250°C during one hour. Table 3 shows the results of the staged pyrolysis with which were compared those of direct pyrolysis. In the first stage the major product is the solid residue with a yield of 76.1 % and 86.22 % for the biomasses 315HD and 500/200, respectively. The yield of the bio-oil produced from the major decomposition of hemicellulose are 14.25% and 7.05% for 315HD and 500/200, respectively with a poor production of gas ( 3.52% for 315HD and 6.52% for 500/200) composed mainly by $CO_2$ and CO. In the second stage, the solid residue produced at 250°C is pyrolysed at 350°C during one hour. The yield of the solid residue decreases from 76 % to 32.5 % for the biomass 315HD and from 86.22% to 33.65% for the biomass 500/200.

During this stage, an intense volatilization of the biomass is observed and the yield of the bio-oil reaches 26.5 % for the biomass 315HD and 30.8 % for the biomass 500/200. The production of gas in also intensified due to the decomposition of the cellulose and lignin.

The solid residue produced in the second stage is a matrix of products of decompositions of the cellulose, hemicellulose and lignin .The pyrolysis of the solid residue at the temperature of maximal production of bio-oil in the direct pyrolysis shows a production of a very poor yield of bio-oil for both biomasses. The pyrolysis in this step is oriented to the production of coke and gas. The comparison between the mass balance of direct and staged pyrolysis shows a decrease in yield of bio-oil in the staged pyrolysis. The results of bio-oil yield in the conditions of direct and staged pyrolysis are in agreement with those of De Wild [31] who realized a staged pyrolysis on the hard and soft wood in Auger reactor in the conditions of conventional pyrolysis.

**Table. 3:** Comparison of products of both biomasses obtained by direct and staged pyrolysis (a) 500/200, (b) 315 HD

| **mass (%)** | **250°C (1)** | | **250°C-350°C (2)** | | **350°C-Tmax (3)** | | **1+2+3** | | **Direct pyrolysis** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **(a)** | **(b)** | **(a)** | **(b)** | **(a)** | **(b)** | **(a)** | **(b)** | **(a)** | **(b)** |
| **$CO_2$** | 2.17 | 5.26 | 14.88 | 12.20 | 1.48 | 2.10 | 18.53 | 19.56 | 17.11 | 17.25 |
| **CO** | 1.35 | 1.33 | 7.28 | 7.66 | 4.94 | 2.89 | 13.57 | 11.88 | 9.86 | 5.4 |
| **$CH_4$** | 0 | 0 | 0.057 | 0.74 | 0.56 | 0.62 | 0.61 | 1.36 | 2.62 | 3.55 |
| **$H_2$** | 0 | 0 | 0.01 | 0.25 | 0.04 | 0.006 | 0.05 | 0.26 | 0.004 | 0.018 |
| **Bio-oil** | 7.05 | 14.25 | 30.8 | 26.64 | 0.6 | 0.1 | 38.45 | 40.99 | 45.5 | 49.8 |
| **Char** | 86.22 | 76.1 | 33.65 | 32.5 | 26.1 | 25.15 | 26.16 | 25.15 | 25.05 | 26.4 |
| **Gas** | 3.52 | 6.59 | 22.23 | 20.85 | 7.02 | 5.61 | 32.76 | 33.06 | 29.59 | 26.21 |
| **total %** | 96.79 | 96.94 | 86.68 | 79.99 | 33.72 | 30.86 | 97.37 | 99.2 | 100.1 | 102.4 |

*3.6.2 Analysis of macro-compounds in the solid residue*

Few works concerned the chemical composition of the solid residue which is approached, generally, only by its structure and its porosity with the aim of applications as adsorbing or for its use for the combustion. Indeed, the chemical composition of the solid residue differs according to the temperature of the pyrolysis. The analysis of the macro-component content in the solid residue after each stage of the pyrolysis (Figure 8) shows changes of its morphological structure because of both dehydration and depolymerisation of the cellulose. At 250°C, the cellulose content decreases by 36 % compared with its initial content (Table 1) in the biomass, lignin content decreases by 67 % while hemicellulose is almost completely converted. Yields of bio-oil are 14.25 % for the biomass 315HD and 7.05 % for the biomass 500/200. Indeed, at this temperature level, a series of complicated reactions occurs to form active cellulose. On the other hand, hemicellulose is mostly converted to produce condensable volatiles and gas. The decrease of the lignin content is due to the primary decomposition ofthe lignin. Even if there is an overlap in the degradation of the three macro-components, the degradation of hemicelluloses remains the most active. In the second stage (350°C), the deoxygenation of both biomasses becomes intensified to form bio-oil and gas, what results in a solid residue rich in carbon in the form of sheet of graphene which increases with the temperature [57]. Pilon et al. [58] were interested in the chemical composition of the solid residue produced from biomass at 300, 400 and 500 °C by the slow pyrolysis. The chemical

characterization of the solid residue was made by extraction with dichloromethane by using soxhlet apparatus. The results showed the presence of chemical compounds bearing various functional groups, due to the recombination and re-condensation in the solid during the ejection of the volatile matter. The solid produced at 300 °C contains alcanes stemming from the pyrolysis of the extractible which begins at 200°C. The identified compounds are essentially phenols. The domain of temperature (350°C-450°C) is the one of the active decomposition of the lignin the composition of which is a hetero-polymer constituted by guaiacyl unit in the case of soft wood such as the biomass 500/200 and by syringyl and guaiacyl in the case of hard wood 315HD. According to the analysis of the solid residue produced in the second stage of the pyrolysis, quasi-total lignocellulosic destruction of fibbers leads to the formation of residues essentially formed by lignin units such as guaiacol and syringol of which the high-temperature pyrolysis higher than 400°C promotes the formation of the coke and gases such as $CH_4$. The mechanism of the production of gases is explained by the homolysis of the O-$CH_3$ bond followed by a rearrangement by iso-substitution to form aromatic methyl [59, 60], what can explain the formation of gases to the detriment of bio-oil in the third stage of the pyrolysis.

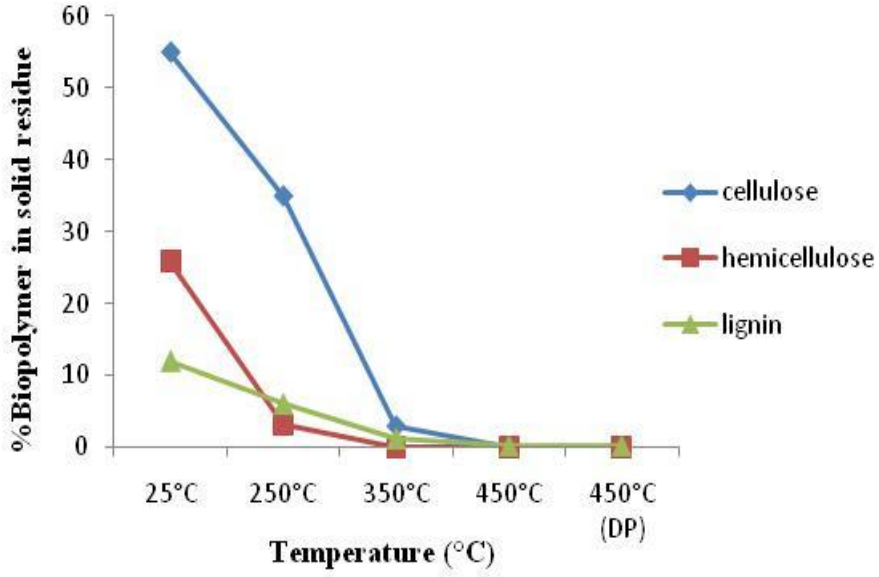



**Figure 8:** Influence of the staged pyrolysis on the macro-components content in the solid residue of the biomass 315HD

*3.6.3 Gas analysis during staged pyrolysis*

Previous researchers have found the gas composition from the pyrolysis of biomass macro-components. Figure 9 shows that in the first stage (250°C) both biomasses produce more $CO_2$ than CO which is due to the decarboxylation of the acetyl side chain present in hemi-cellulose [43,44] and to the primary decomposition of lignin which generates a low amount of volatiles in the first stage with more $CO_2$ generated than CO .The gas analysis results at stage 2 showed a dominance of $CO_2$ and CO which is due to the degradation of the cellulose and the lignin (Figure 8) to form mainly furan derivatives and phenolic compounds. In stage 3, the gas composition is mainly constituted of CO, $CH_4$ and a low content in $H_2$; The origin of these gases is associated with the secondary reactions stemming from the decomposition of compounds adsorbed on the solid residue or by the direct reaction of the solid with gases of pyrolysis such as the steam or the hydrogen for the production of the CO [37]. It can also be due to the pyrolysis of residual lignin content in the matrix of the solid residue obtained in the second stage.

*3.6.4 GC/MS analysis of bio-oil produced by staged pyrolysis*

Figure 10 presents the CG/FID analysis of the bio-oils obtained by the staged pyrolysis of the biomass 500/200. In the first stage, the products of degradation of hemicelluloses are mainly detected as the furan derivatives (furfural,furfuryl alcohol, 2.5-dimethylfuran and 5-furfuraldehyde) and also phenolic compounds as (phenol, 2,6 dimethoxytoluene,3,4,5-trimethoxybenzaldehyde) which refer to the beginning of the degradation of the lignin due to its wide interval of temperature degradation.

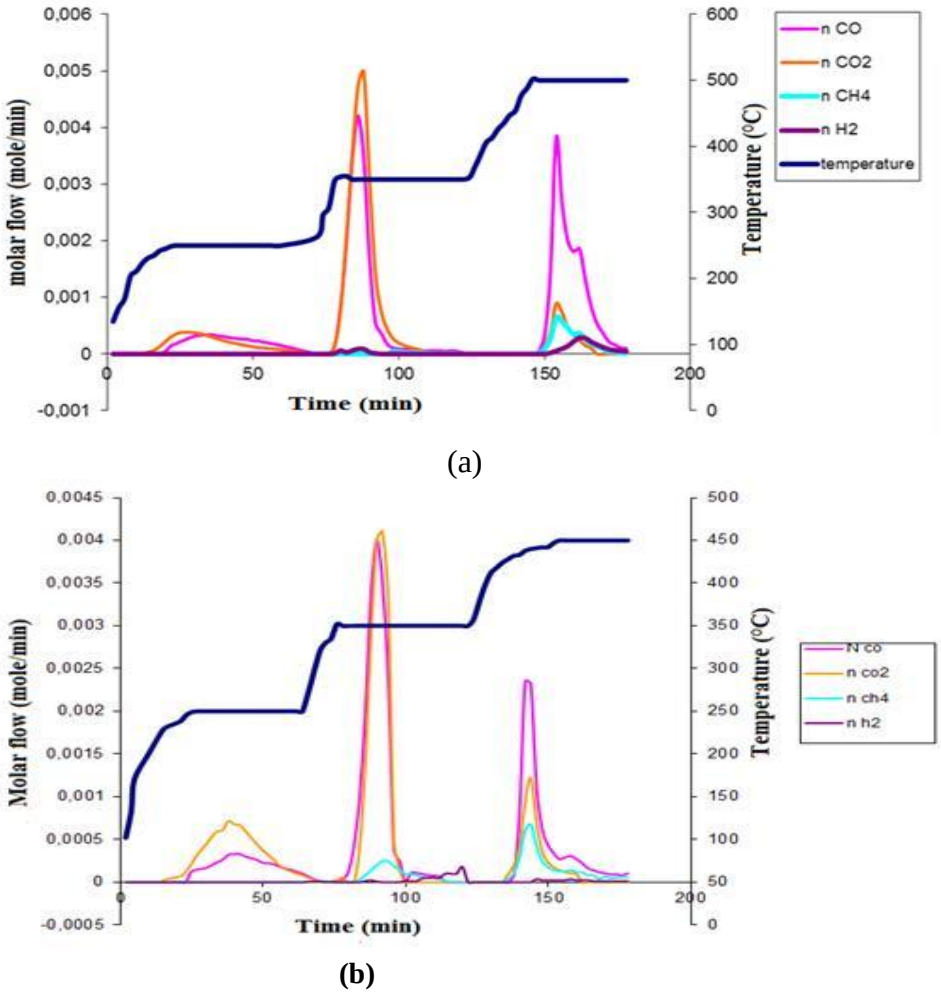
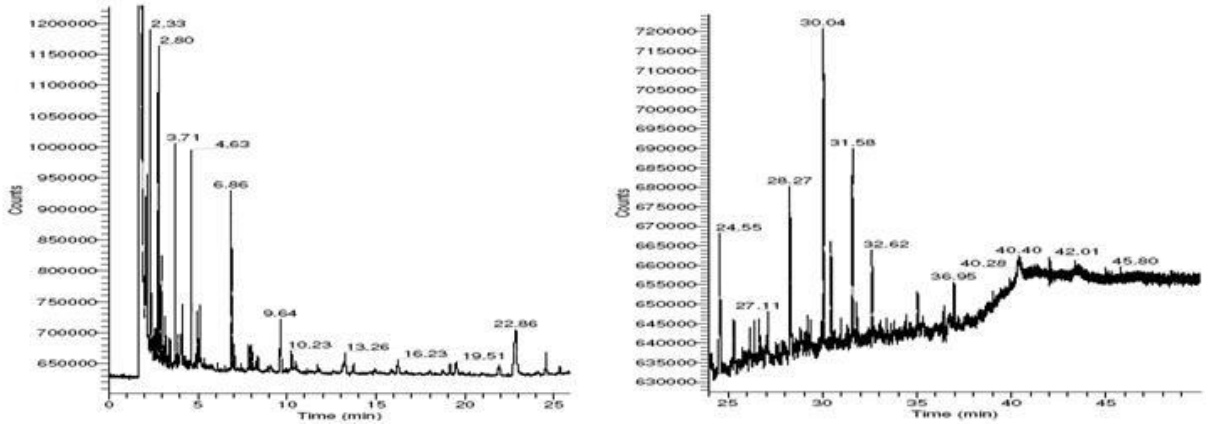


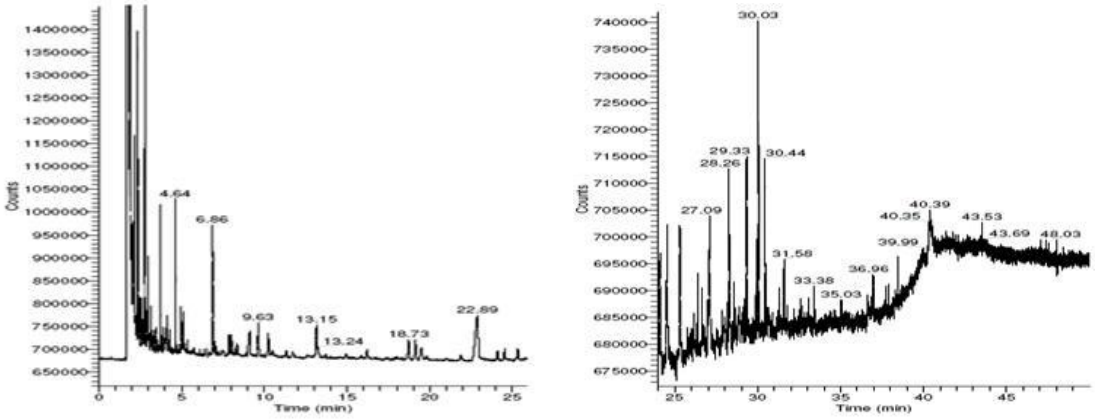

**Figure 9:** Production of gases during the staged pyrolysis of the biomasses (a) 500/200,(b) 315HD

In the stage 2, the abundance of the furan derivatives resulting from the decomposition of the cellulose mechanism [52] is observed. The intensity of phenolic compounds increases and a peaks oftrimethoxybenzaldehyde isomers (1,2,3-trimethoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde) and 4-hydroxy-3,5-dimethoxybenzaldehyde) appeared, what is explained by the intensification of the reactions of decomposition of the cellulose and the lignin (Figure 8). In the third stage, the absence of the peaks of the isomers of trimethoxybenzaldehyde is observed. The presence of small amount of 4-methoxy phenol, p-xylene is assigned to secondary decomposition of the residue obtained in the second stage constituted mainly by the lignin.

**Step 1:**



**Step 2**




**Step 3**

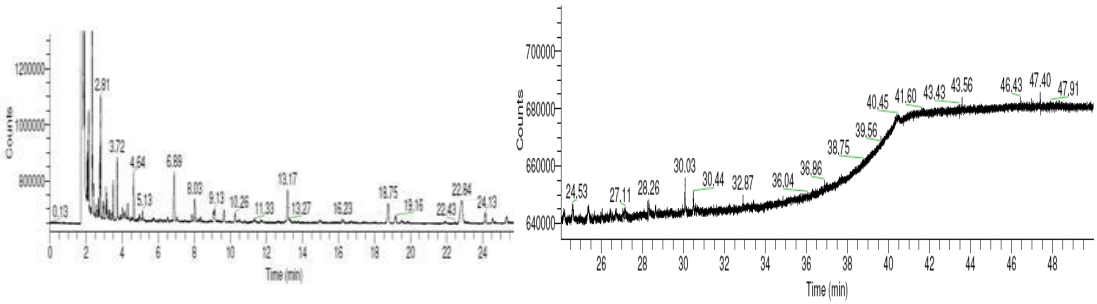



**Figure 10:** GC / FID analysis of the fractions of oil obtained by staged pyrolysis of the biomass 500/200

## Conclusion

Biomasses 315HD and 500/200 were used to represent the hard and soft wood, respectively. The effect of the temperature on the production of bio-oil pyrolysis was examined by the direct and staged pyrolysis. The study revealed a higher bio-oil yield in the case of the direct pyrolysis of the hard wood because of its lower lignin content which is considered as a limiting factor for the lignocellulosic biomass degradation. The comparison of bio-oil yields in direct and staged pyrolysis showed a higher production in the direct pyrolysis for both biomasses. However, the staged pyrolysis can constitute an interesting way for the preconcentration of added value chemicals. For the better selective degradation of macro-components, a pre-treatment at temperatures lower than 250°C should be applied to reduce the cellulose degradation. Otherwise the choice of biomass is an important criterion for the production of chemicals. To improve the production of furan derivatives, it is suggested to use biomasses with low lignin content to reduce the overlap in the temperature degradation of the macro-components.

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