ERANET-LAC PROJECT: *Production of high value bio-based products from sugar cane bioethanol industry solid and liquid wastes by low energy electrochemical treatment of effluents and pyrolysis of lignocellulosic materials using thermomagnetic catalysts*

# Conventional pyrolysis testing – influence of operating conditions

## Experimental work on conventional biomass pyrolysis

## 07/01.08.2019

| Rev. | Issue Date | Issue Description | By | Chk. | Appr. |
|---|---|---|---|---|---|
| 00 | 01.08.2019 | Experimental work on conventional biomass pyrolysis performed up to this date in Romania – influence of operating conditions on biomass pyrolysis – temperature, inert gas flow, pyrolysis time, amount of catalyst | Anca Sauciuc<br>Emese Gal | | |

# TABLE OF CONTENTS

## 1. PUROPOSE OF THE DOCUMENT

The purpose of this document is to present the experimental results obtained on conventional biomass pyrolysis performed in Romania within the ERANET-LAC project. The document contains a literature review over conventional biomass pyrolysis, details regarding the reactor types and operating conditions that have been used in literature for biomass pyrolysis, as well as the influence of each operating parameter over pyrolysis products yield and composition. The methods, materials, pyrolysis unit used on experimental work, as well as the characterization techniques for gas, liquid and solid products obtained during biomass pyrolysis are presented in details. The most important results obtained on the experimental work performed are discussed and compared with results from literature. Optimum operating conditions for conventional pyrolysis of waste biomass from bioethanol industry have been established.

## 2. LITERATURE REVIEW ON BIOMASS PYROLYSIS

### 2.1 BIOMASS AS RAW MATERIAL FOR PYROLYSIS

Energy sources are classified in two main classes – nonrenewable (coal, natural gas, petroleum, uranium and thorium) and renewable (biomass, geothermal, hydropower, solar and wind energy). The energy consumption in 2015 is presented in Figure 1.

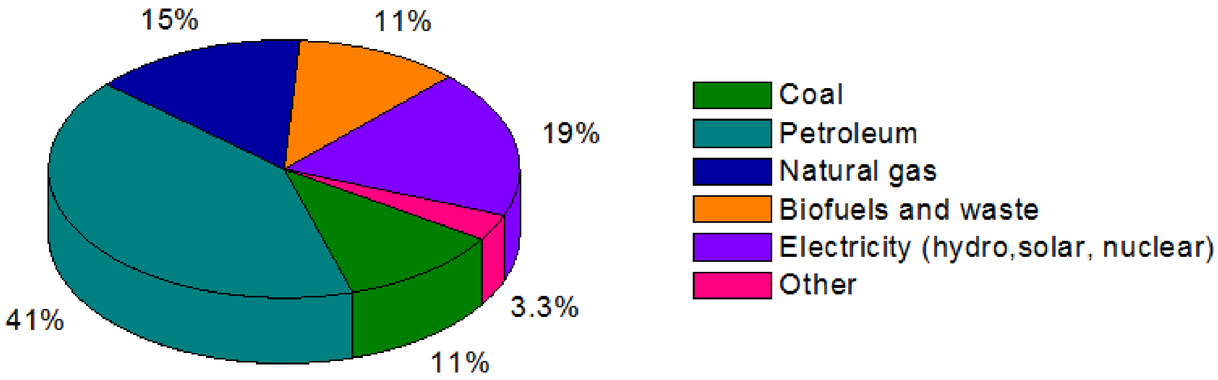


**Figure 1. World total final consumption by fuel in 2016 [1]**

The renewable resources – solar, wind, geothermal, nuclear, hydrogen and biomass have the potential to provide energy with very low or even zero emissions and it is considered that renewable energies will have a contribution to total primary energy consumption of nearly 50% by 2040. Among all renewable sources, biomass brings the highest contribution in the total energy supply (Table 1) and it is considered that by 2040 the consumption of biomass will increase with almost 60% comparative to 2010.

**Table 1. The contribution of Renewable Energy Sources (RES) to the world energy supply in 2040 [2]**

| | 2001 | 2010 | 2020 | 2030 | 2040 |
|---|---|---|---|---|---|
| Total Consumption Mtoe | 10038 | 10549 | 11425 | 12352 | 13310 |
| Biomass | 1080 | 1313 | 1791 | 2483 | 3271 |
| Large hydro | 222.7 | 266 | 309 | 341 | 358 |
| Small hydro | 9.5 | 19 | 49 | 106 | 189 |
| Wind | 4.7 | 44 | 266 | 542 | 688 |
| PV | 0.2 | 2 | 24 | 221 | 784 |
| Solar thermal | 4.1 | 15 | 66 | 244 | 480 |
| Solar thermal electricity | 0.1 | 0.4 | 3 | 16 | 68 |
| Geothermal | 43.2 | 86 | 186 | 333 | 493 |
| Marine (tidal/wave/ocean) | 0.05 | 0.1 | 0.4 | 3 | 20 |
| Total RES | 1364.5 | 1745.5 | 2694.4 | 4289 | 6351 |
| RES Contribution | **13.6%** | **16.6%** | **23.6%** | **34.7%** | **47.7%** |

A wide variety of biomass resources can be used for generation of electricity, heat, biofuels and chemicals – wood and forest residues (sawdust, barks, roots, grass), agriculture plants (grains, straw, manure, oil plants, sugar, starch and oilseed crops, lignocellulosic crops – poplar, willow, eucalyptus), aquatic plants (algae, water weed, water hyacinth, reed and rushes), residual and organic wastes from food and alcohol industries, urban organic wastes, domestic solid wastes [3-6]. The generation of energy, biofuels and biochemicals from biomass can be achieved by thermochemical technologies – combustion, pyrolysis, liquefaction, gasification, biochemical technologies – anaerobic digestion, aerobic fermentation, hydrolysis, transesterification. Among all the thermochemical processes for conversion of biomass, pyrolysis is the simplest technology to convert biomass into useful biofuels and energy. Pyrolysis is the thermochemical process which occurs in the absence of oxygen and depending on the heating rate, residence time of vapors in the reactor, operating temperature it can be:

- slow pyrolysis (operating temperature lower than 500 °C, long residence time and slow heating rate)
- moderate pyrolysis (vapor residence time 10-20 s, operating temperature 500 °C)
- fast pyrolysis (vapor residence time lower than 2 s, operating temperature above 500 °C, high heating rates, rapid quenching of pyrolysis vapors) [7,8]

In Table 2 the product distribution from different pyrolysis processes is presented.

**Table 2. Product selectivity from different pyrolysis processes of biomass [9]**

| Type | Conditions | Product distribution [%] | | |
|---|---|---|---|---|
| | | **Liquid** | **Solid** | **Gas** |
| Fast pyrolysis | ~ 500 °C, vapor residence time ~ 1 s | 75 | 12 | 13 |
| Moderate pyrolysis | ~ 500 °C, vapor residence time ~ 10-30 s | 50 | 25 | 25 |
| Slow pyrolysis | ~ 400 °C, vapor residence time ~ hours, up to days | 30 | 35 | 35 |

The advantages of biomass pyrolysis are the production of both valuable liquid and solid products – bio-oils can be directly used in combustion engines and gas turbines or after hydrogenation (for reduction of oxygenated content) in transportation sector [10]. Moreover, the liquid fraction can be used for production of various chemicals (due to the high composition – more than 300 compounds identified in bio-oil) – it has been patented the extraction of levoglucosan, aldehydes and phenolic compounds [6]. Biochar, the main component of slow pyrolysis (produce due to incomplete decomposition of organic compounds) has several applications: as fuel (substitute for coke) to provide energy, as activated carbon, as fertilizer for soils (hosting microbes, releasing nutrients and water slowly) [6]. The pyrolysis of biomass has been intensively studied from type of pyrolysis to impact of different reactors used in pyrolysis and operating conditions on product distribution [7]. A simple pyrolysis process and applications of the products obtained is shown in Figure 2.

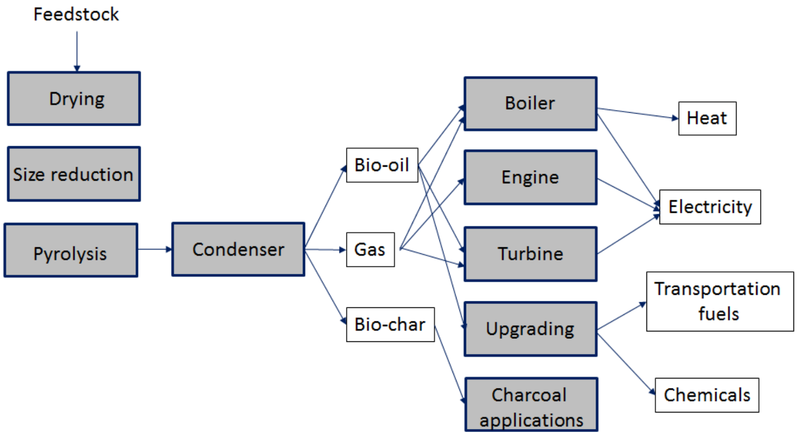


**Figure 2. Simplified process flow diagram of biomass pyrolysis [6, 7]**

It has been proved that composition of biomass along with different pyrolysis conditions and pyrolysis reactor type affects the selectivity of the products and their quality. Some of the biomass used in conventional pyrolysis are: forest pine, willow, woodchips and bark [11, 12, 13, 16], forest residues, grass [12], sawdust, seaweed and spirulina microalgae, animal waste [14], sugarcane bagasse and agricultural residues [15, 17, 19, 20], newspaper and cardboard wastes [18], sewage sludge and composted organic fines from municipal solid waste [21,22]. The properties of some of the biomass used in pyrolysis studies are listed in Table 3.

**Table 3. Biomass feedstock properties**

| | Stem wood [12] | Forest residue [12] | Bark [12] | Seaweed [14] | Spirulina [14] | Bagasse [20] | Sludge [22] |
|---|---|---|---|---|---|---|---|
| Moisture, wt% | 4.3 | 3.6 | 6.5 | 8 | 7.3 | — | |
| Volatiles, wt% | 83.3 | 80.6 | 78.4 | 54.2 | 52.2 | — | 52.8 |
| Ash, wt% | 0.3 | 2.4 | 2 | 21.9 | 10.8 | 6.5 | 32.1 |
| Fixed carbon, wt% | 15.9 | 19.5 | 19.6 | 23.9 | 36.9 | — | 15.1 |
| Ultimate analysis, % | | | | | | | |
| C | 51.3 | 51.9 | 53.5 | 29.9 | 43.3 | 42.3 | 37.3 |
| H | 6.2 | 6.2 | 6.4 | 5.05 | 7.04 | 6.3 | 5.5 |
| N | 0.1 | 0.42 | 0.4 | 1.95 | 9.06 | 0.3 | 5.67 |
| O | 42 | 39.9 | 37.7 | 41.2 | 30.1 | 44.6 | 17.94 |
| S | 0.02 | 0.024 | 0.029 | 1.74 | 0.42 | — | 1.01 |
| LHV, MJ/kg | 19.3 | 19.55 | 20.67 | — | — | — | 16.9 |
| Chem. composition, wt% | | | | | | | |
| Cellulose | 35.9 | 29.1 | 21.8 | — | — | 36.3 | — |
| Hemicellulose | 23.1 | 19.9 | 15.6 | — | — | 20.7 | — |
| Lignin | 27.2 | 31.2 | 36.5 | — | — | 22.9 | — |
| Extractives | 5.12 | 4.37 | 9.44 | — | — | 10.8 | — |

## 2.2 REACTOR TYPES USED FOR PYROLYSIS AND OPERATING CONDITIONS

The type of reactor in biomass pyrolysis will have a significant impact over product distribution and bio-oil composition. Several types of reactors have been studied for biomass pyrolysis.

### FLUIDIZED BED REACTOR

Fluidized bed reactors are well-known and extensively used in the biomass pyrolysis, having a simple construction and operation, efficient temperature control and heat transfer to biomass particles. In pyrolysis of biomass, feedstock particles mixed with hot sand are fluidized by circulating product gas. The advantages of fluidized bed reactors are very good heat/mass transfer, rapid heating of the feedstock particles and high bio-oil yield (70-75%). Catalytic pyrolysis can be also implemented in fluidized bed reactors [7, 9]. The process flow diagram of a fluidized bed reactor for biomass pyrolysis is presented in Figure 3. Charon et al. [23] used continuous fluidized bed reactor systems for fast pyrolysis of different types of biomass (hard-wood -beech wood, softwood - spruce wood and wheat straw) at 500 °C. A maximum bio-oil yields (including also water) of 74.1 wt% was achieved when softwood biomass was used as feedstock, while the biomass straw reached 58 wt% bio-oil yield (due to higher content of ash). Carboxylic acids, aldehydes and ketones are the main non-aromatic components that were identified in the bio-oil from wood and straw, while guaiacols were the main aromatic components [23].Nam et al [24] compared different reactor systems (fluidized, auger and batch reactor) for pyrolysis of rice straw biomass and reached a maximum bio-oil yield of 43 wt% when using a fluidized bed reactor for biomass pyrolysis at 500 °C.

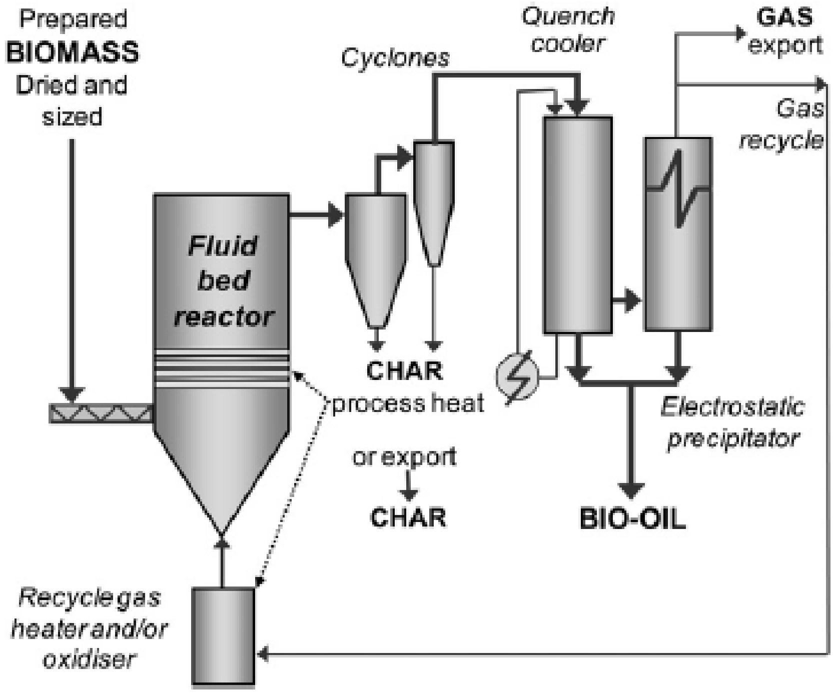


***Figure 3. Process flow diagram of a fluidized bed reactor for biomass pyrolysis [9]***

## AUGER REACTOR

Similar with fluidized bed reactor, the auger reactor is one of the most common reactors used for biomass pyrolysis (both laboratory or large scale). The auger reactor is less operationally complex, applies low carrier gas flow, is suitable for large biomass particles, making it ideal for continuous commercial applications – ABRI-Tech Canada, Lurgi-Ruhrgas Germany, Renewable Oil Intle USA are companies that produce large scale auger reactors. A typical continuous auger reactor system used for biomass pyrolysis is presented in Figure 4. It has been proved that auger reactors can also be implemented for small, portable pyrolysis systems either in distributed or decentralized processes [7, 11]. The bio-oil can reach high yields (above 70%) when the auger reactor is being used. However, the catalytic pyrolysis of biomass was less studied in auger reactor. Veses et al. [11] studied the catalytic pyrolysis of biomass in auger reactor using a mixture of sand and calcined calcite (CaO) or calcined dolomite (CaO·MgO). For these tests, biomass (forest pine wood chips, including bark) was initially dried to a moisture lower than 2 wt%, milled and sieved to a maximum size of 15 mm. Preliminary tests have been carried out at different CaO to biomass ratios: 3:1, 1:1, 1:2, 1:3 at 450 °C (N2 used as carrier gas with a flow of 5 L/min, experiments duration – 2 h). Secondary reactions with tar formation have been observed when CaO to biomass ratio was 3:1, 1:1 and 1:2, thus a low catalyst to biomass ratio of 1:3 was selected as the optimum condition. The yields of bio-oil increased slightly when CaO and CaO·MgO were used as catalysts, leading to values around 48-50 wt%. The addition of CaO and CaO·MgO in the auger reactor also improved the bio-oil properties increasing the pH and calorific value and decreasing the acidity and oxygen content (water content increased, as calcium based materials can promote dehydration reactions of the oxygenated compounds during pyrolysis). Biomass pyrolysis in an auger reactor under different operating conditions (reaction temperature, solid residence time, biomass flow rate) was also studied by Puy et al. [25]. The maximum bio-oil yield of 59% was obtained when pyrolysis was performed at 500 °C, residence time longer than 2 min.

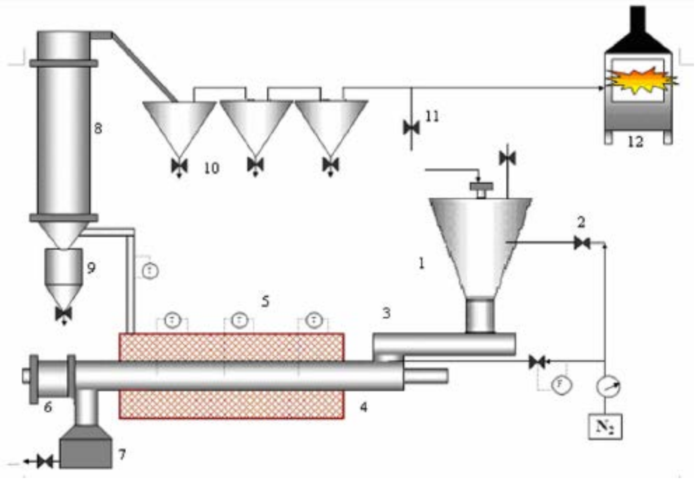


***Figure 4. Continuous auger reactor system used for biomass pyrolysis [25]***

(1) Feeding hopper; (2) nitrogen flow; (3) feeding auger conveyer; (4) auger reactor; (5) furnace; (6) reactor closure system; (7) vessle for solids; (8) condensing system; (9) liquid colecting system; (10) gas expanders; (11) gas sampling valve; (12) gas burner

### PLASMA PYROLYSIS REACTOR

This type of reactor where the heating source is supplied externally by plasma (temperature initiated in thermal plasma is between 2500-9500 °C) is in general used for syngas and char production [7].

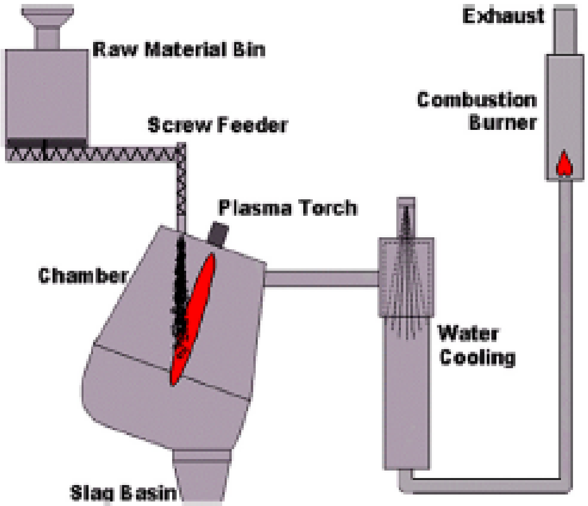


*Figure 5. Process flow for plasma pyrolysis reactor [7]*

### FIXED BED REACTOR

The fixed bed reactor is in general used for slow pyrolysis and in laboratory or bench scale tests due to the simple structure. As it can be observed in Figure 6, a carrier gas passes through the biomass bed and carries both condensable and non-condensable gasses to the condensation unit. The fixed bed reactor is also suitable for catalytic pyrolysis [7]. Le Brech et al. [26] reached 67 wt% bio-oil yield (and only 6 wt% gas yield) when a laboratory U-shape fixed bed reactor for slow pyrolysis of biomass mixture (miscanthus, douglas and oak) was used. The shape of the fixed bed reactor allowed efficient control over external mass transfer and temperature of the biomass bed, quenching char at targeted temperatures and quantification of mass balance [26].

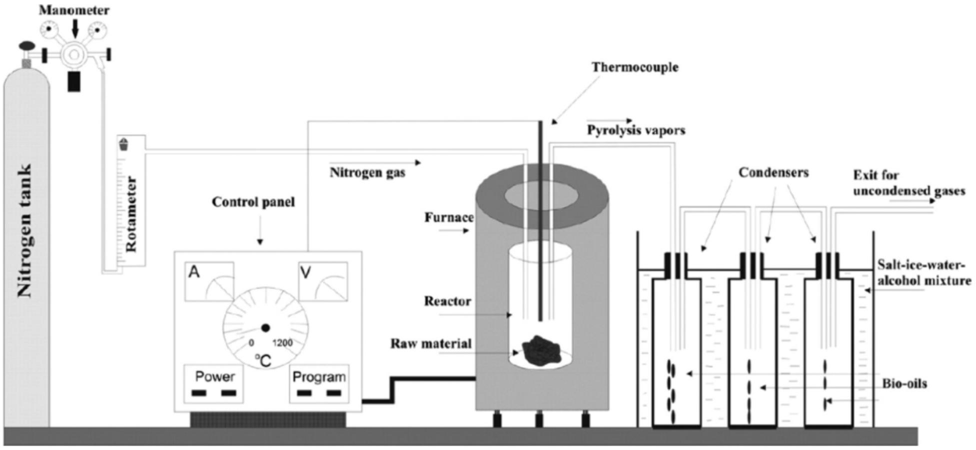


*Figure 6. Process flow diagram of a fixed-bed reactor for the pyrolysis of biomass [7]*

A simple catalytic pyrolysis lab scale unit using a fixed-bed reactor was used also by Kar et al. [27]. The fixed bed reactor had a volume of 320 $cm^3$ (140 mm length, 60 mm internal diameter) was coupled with a condensing system consisting in four traps plunged into cooling system (31 wt% $CaCl_2$ solution) as it is represented in Figure 7. Feedstock was homogenized with catalyst (ratio from 5% to 25% by weight). Pyrolysis has been performed at 375-500 °C (heating rate from room temperature to the desired operating temperature was adjusted to 10 °C/min), under nitrogen flow (100 mL/min) for 1 h.

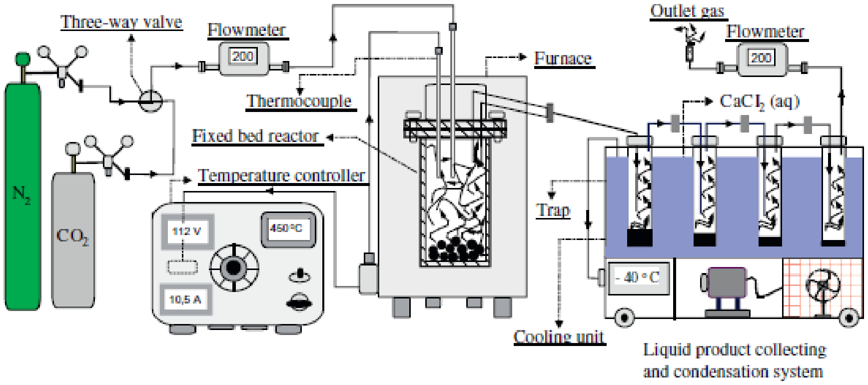


*Figure 7. Schematic diagram of a laboratory scale pyrolysis unit [27]*

Other simple representation of laboratory scale pyrolysis units are presented in Figure 8 and 9 [28, 29].

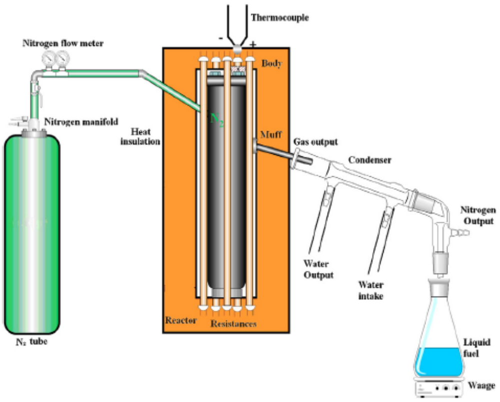


*Figure 8. Schematic diagram of fixed batch pyrolysis reactor [28]*

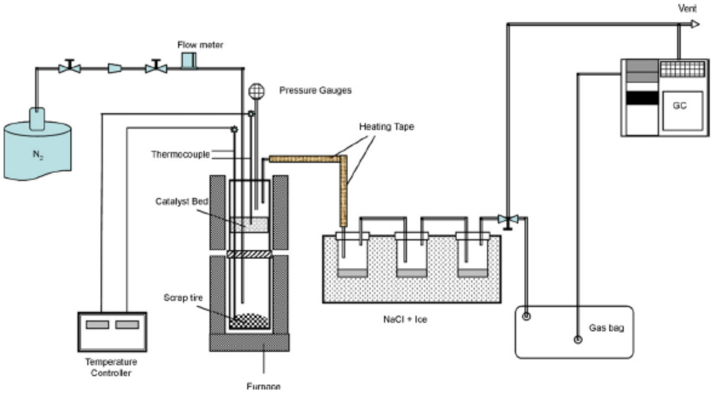


***Figure 9. Schematic diagram of fixed batch pyrolysis reactor [29]***

The properties of bio-oil produced by using different types of reactors have been presented by Papari et al. [7] (Table 4).

**Table 4. Physical and chemical properties of bio-oil produced in different pyrolysis reactor types [7]**

| Pyrolysis | Auger reactor | Fluidized bed | Fixed bed |
|---|---|---|---|
| Feedstock type | Pine wood | Softwood | Empty fruit bunches |
| Temperature, °C | 450 | N/A | 500 |
| Particle size, mm | 2-4 | N/A | 1-2 |
| Feed rate, kg/h | 1 | 0.1-5 | N/A |
| Bio-oil yield, wt% | 48.7-55.2 | 75 | 45.75 |
| Biochar yield, wt% | 17.5-19.8 | 10 | 29.05 |
| Gas yield, wt% | N/A | 8-15 | 25.02 |
| *Physical and chemical properties of bio-oil* | | | |
| Water content, wt% | 16 | 20 | 41 |
| Solid content, wt% | 0.19 | N/A | N/A |
| pH | 3.1 | 2.3 | 3.1 |
| Total acid number | 90 | N/A | N/A |
| Viscosity at 40-50 °C, cP | 60.9 | 40-200 | 1.7 |
| Density, g/cm$^3$ | 1.19 | 1.2 | 1.03 |
| HHV, MJ/kg | 21.9 | 20 | 10.49 |

## 2.3 CATALYSTS FOR BIOMASS PYROLYSIS TESTS

Catalytic pyrolysis has the major advantage of improving the property and stability of the pyrolysis oils because of cracking of the reactive species into either low molecular weight organics or gasification of some of this reactive species to carbon oxides and $C_1$ to $C_5$ hydrocarbons, leading to a pyrolysis oil with lower acidity, viscosity, oxygen content and higher heating value [6]. Catalysts used for the pyrolysis can be classified into two groups: primary catalysts and secondary catalysts. Primary catalysts are those which are mixed to the biomass before the pyrolysis. Mixing of the catalyst into the biomass can be done either by wet impregnation or by normal dry mixing. Secondary catalysts are not mixed to the biomass but they are kept in a secondary reactor located downstream from the main pyrolysis reactor [15]. For conventional pyrolysis tests, a fixed bed reactor system will be used together with a primary catalyst.

The most effective catalysts used for biomass conversion to liquids are zeolite catalysts due to their porous structure and acidic properties: .Si-SBA-15, Al-SBA-15, H-ZSM-5, H-Beta, MSN-15, MSM-15, H-Y, Al-MCM-41 [6, 14, 30]. From all the zeolites, the majority of literature showed that best results on upgrading pyrolysis oil were obtained with H-ZSM-5 catalyst.

On the other hand, some other inexpensive catalysts such as bulk metal oxides or supported sulphide/oxide and metal catalysts, mainly on alumina, have been also tested for biomass catalytic pyrolysis: CaO, CaO · MgO, NiO, $Al_2O_3$, Ni-$Al_2O_3$ [6, 11, 13, 30]. Sodium based catalysts like $Na_2CO_3$, NaOH, NaCl and $Na_2SiO_3$ have been used for biomass pyrolysis [30].

Depending on the catalysts used, the pyrolysis process can be modified by decrease of decomposition temperature of biomass, reduction of polymerization and oxygenated components, increase of decarboxylation and dehydration reactions, increase of coke formation. The effect of different catalysts in biomass pyrolysis has been described by Sharma et al [15] in Table 5.

**Table 5. The contribution of Renewable Energy Sources (RES) to the world energy supply in 2040 [2]**

| Catalyst | Biomass | Reactor | Products |
|---|---|---|---|
| ZSM-5 | Rice husk | Fluidized bed reactor with condensation and off-line gas analysis system | Oxygenated oil compounds (phenols, cresols) and gas products |
| HZSM-5 | Sawdust | Fixed bed reactor | Gas, liquid (light and heavy fraction), char |
| $ZnCl_2$, $Na_2CO_3$,$K_2CO_3$ | Cotton cocoon shell, tea factory waste, olive husk | Stainless steel cylinder reactor with electrical heated furnace | gas product (CO, $CO_2$, olefins, $H_2$, paraffins), liquid and char |
| $Cr_2O_3$, CaO, $Al_2O_3$, MnO | Rice straw, sawdust | Batch pyrolysis reactor | Gas product (CO, $CO_2$, $H_2$), water, tar char |
| Ni, Co, Ga-ZSM-5 | Wood | Tubular quartz micro-reactor and semi-continuous flow reactor | Hydrocarbons, oxygenated (phenols, cresol) and coke |

Other researches have been used different catalysts with specific properties for pyrolysis of biomass. Yathavan et al [6] used a commercial catalyst, ZSM5 from BASF catalysts LLC. The catalyst ZSM5 was calcined at 550o C for 5 hr, to convert ZSM5 into protonated form (HZSM5) and then sieved to obtain particular particle size (125 – 180 µm). The properties of the catalyst used for biomass pyrolysis: BET surface area - 115 m2 /g, Total acidity of 2.39 mmol/g. Lorenzetti et al [5] used a commercial H-ZSM-5 (SiO2/Al2O3 = 45, Zeolite Soconomy Mobil – Five, Clariant). Diameter of pores = 6 Å, surface area > 300 m2/g. Veses et al [11, 13] used for biomass pyrolysis in an auger reactor silica sand, calcined calcite and calcined dolomite, sieved in the range of 300-600 µm, as well as minerals bentonite, sepiolite, red mud. Adam et al [31] showed that Al-MCM-41 zeolyte type catalyst improved bio-oil properties. The catalyst was synthesized, with a Si/Al ratio of 20. Antonakou et al [32] also evaluated Al-MCM-41 in biomass pyrolysis for production of bio-oils and chemicals, using unmodified and modified zeolites. The unmodified Al-MCM-41 had a Si/Al ratio between 20-50, surface are between 866-972 $m^2$/g, pore volume around 1 ml/g and mesopore diameter of 35 Å. Adjaye and Bakhshi [33, 34] studied the catalytic performance of the different catalysts for upgrading of bio-oil. Among the five catalysts studied, HZSM-5 was the most effective catalyst for producing the organic distillate fraction and the least coke formation. The catalyst HZSM-5 used showed a surface area of 330 $m^2$/g, pore size 5.4 Å, Si/Al ratio 56.

Based on the literature review, the most promising catalysts that could be used in conventional and induction-heated pyrolysis tests of biomass are:

- **HZSM-5** (surface area > 300 m2/g, Si/Al ratio 45-55, pore size > 5 Å)
- **Al-MCM-41** (surface area > 800 m2/g, Si/Al ratio 20-50, pore size > 30 Å)
- **CaO** (very inexpensive)

## 2.4 INFLUENCE OF PYROLYSIS OPERATING CONDITIONS ON PRODUCTS YIELDS AND COMPOSITION

The operating conditions of the pyrolysis process can have a significant impact over the product selectivity. It has been proved that lower process temperature and longer residence time will favor the production of charcoal, high temperature and longer residence time determine the increase of gas phase, while moderate temperature and short residence time are optimum for bio-oil formation [9]. The production of the three phases produced during pyrolysis varies due to different operating conditions.

### BIOMASS TYPE

Biomass is composed in general of cellulose (25-50 wt%), hemicellulose (15-40 wt%), lignin (10-40 wt%), extractives (0-15 wt%) and small concentration of inorganic components. Depending on the composition, pyrolysis products yield can vary – cellulose and hemicellulose increase bio-oil yield, while lignin favors the production of char. In the same time, higher content of lignin can decrease the water content in bio-oil and increase its viscosity ad average molecular weight [35].

### MOISTURE CONTENT OF BIOMASS

Bridgwater [9] mentions in his review article that the biomass used as feedstock for pyrolysis should have water content lower than 10 wt% for efficient thermal conversion and in order to minimize the water from bio-oil. Moisture content can affect the heat and mass transfer processes during pyrolysis [15].

### BIOMASS SIZE

The size reduction of biomass feedstock is a high energy consumption operation, thus the capability of using large biomass particles to achieve high bio-oil yield and quality offers significant economic benefits. It has been reported that large biomass particles imply larger thermal gradient and favors secondary reactions like cracking, partial oxidation, re-polymerization, condensation which will determine the increase of char yield [15, 25].

As biomass has low thermal conductivity for a heat transfer at biomass particles it is required that biomass particles should have less than 3 mm [9]. Sharma et al [15] presented that increasing the biomass particles from 0.7 mm to 17 mm had small influence over the product yield, however increasing the particles above 17 mm determined the increase of water content in bio-oil from 40 wt% (at 17 mm particle size) to 55 wt% (at 20 mm particle size). Kan et al [35] summarized the influence of biomass particles size on the product yields in fixed bed reactor, at different operating conditions.

**Table 6. Effect of biomass particles size on pyrolysis product distribution [35]**

| Feedstock | Pyrolysis Conditions | Particle size, mm | Yield [wt%] | | |
|---|---|---|---|---|---|
| | | | **Liquid** | **Solid** | **Gas** |
| Cotton stalk | 550 °C, 7 °C/min, fixed bed | 0.225 – 0.425 | 21 | 27.5 | 31.1 |
| | | 0.425 – 0.85 | 22 | 27.8 | 30.5 |
| | | 0.85 – 1.8 | 23.8 | 27.1 | 28.6 |
| | | > 1.8 | 22.5 | 26.8 | 28.5 |
| Hazelnut bagasse | 500 °C, 10 °C/ min, fixed bed | 0.224 – 0.425 | 30.7 | 27.8 | 28.5 |
| | | 0.425 – 0.6 | 33.2 | 27.9 | 29 |
| | | 0.6 – 0.85 | 32.5 | 27.5 | 29.7 |
| | | 0.85 – 1.8 | 31.9 | 27.4 | 31 |
| Rapeseed | 550 °C, 30 °C/min, fixed bed | < 0.425 | 42.7 | 23 | 26 |
| | | 0.6 – 0.85 | 48 | 17.5 | 27.5 |
| | | 0.85 – 1.25 | 49 | 16 | 29 |
| | | 1.25 – 1.8 | 46 | 21 | 26.5 |

## REACTION TEMPERATURE

Using an U-shape fixed bed reactor for slow pyrolysis of biomass mixtures determined the increase of bio-oil yield with the increase of reaction temperature from 300 °C to 500 °C (argon was used as carrier gas – 300 NmL/min flow). The reactor was heated from 20 °C to the target temperature at a heating rate of 5 K/min. Once the target temperature was achieved, the reactor was immersed in ice-water to quench the reactions (2 min cooling time from 500 °C to 150 °C) [26]. At it can be observed in Figure 9, the yield of bio-oil and gas increased when operating temperature was increased, while char yield decreased drastically from 80 wt% (at 280 °C) to almost 30 wt% (at 500 °C).

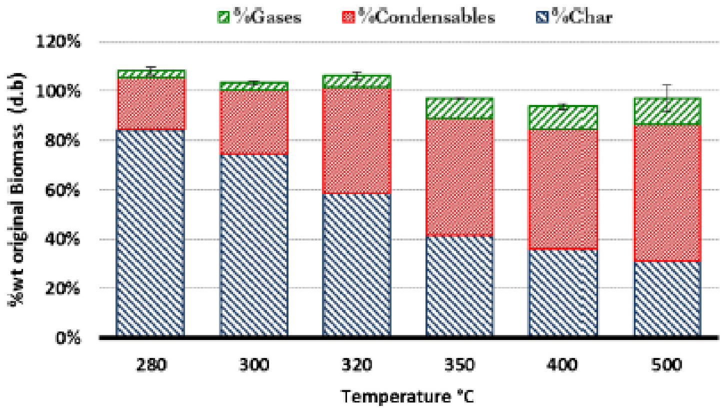


**Figure 10. Products yields from biomass pyrolysis at different operating temperatures [26]**

Puy et al. [25] studied the influence of reaction temperature in pyrolysis of biomass woodchips using an auger reactor. The pyrolysis experiments have been carried out at temperature ranging from 500 to 800 °C. Maximum bio-oil yield (58.7 wt%) was obtained at 500 °C, while at higher temperature cracking of primary components occurred. Similar results have been obtained also by Johansson et al. [12] which showed that increasing reaction temperature of pyrolysis will determine the decrease of hydrogen and oxygen content will decrease due to cracking reactions. Moreover, the content of water in bio-oil will increase. It has been observed that reaction temperature was the most important operational parameter that affected bio-oil composition [25]. Bio-oil was composed primarily from phenols (47.5%), ketones (10%), carboxylic acids (7%), aldehydes (4%), polycyclics (1%) and other organic components (0.1%). Increasing the temperature from 500 °C to 800 °C determined the increase of polycyclics content from 1% to 10.6% (higher temperature favors dehydrogenation and aromatization reactions which will determine the formation of heavier PAHs – they can a negative impact for engine combustion or for catalytic gas conversion). The increase of operating temperature in biomass pyrolysis also determined an increase of carboxylic acids, while the content of ketones and aldehydes is reduced (Figure 11).

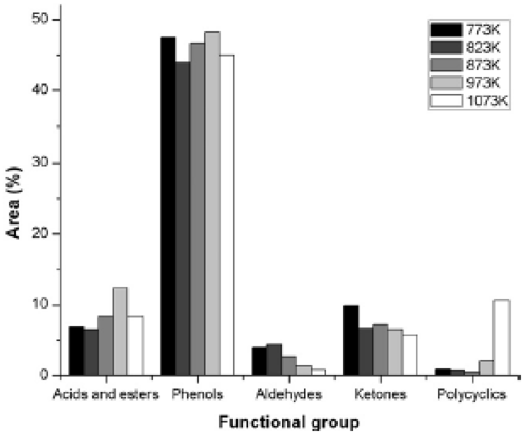


**Figure 11. Functional groups determined in bio-oil fraction obtained at different reaction temperatures of pyrolysis [25]**

Goyal et al [36] presented different research work which showed the influence of temperature over the product distribution. It has been showed that the increase of temperature will increase the oil yield up to 550 °C, while after this temperature the content of bio-oil will decrease with the increase of the selectivity for gas phase (Table 7). Also rapid heating and cooling of vapors favor bio-oil yield due to reduction of possible secondary reactions. Slow heating rate will determine the increase of char yield [12].

**Table 7. Product yield at different temperatures during slow pyrolysis [36]**

| Parameter | Yield [wt%] | | |
|---|---|---|---|
| | **Char** | **Oil** | **Gas** |
| 400 °C | 24 | 42 | 26 |
| 500 °C | 22 | 46 | 25 |
| 600 °C | 19 | 47 | 27 |
| 700 °C | 18 | 44 | 31 |

## HEATING RATE

Heating rate is a significant parameter which determined the biomass pyrolysis and product yields. Fast heating rates facilitate the decomposition of biomass and reduce mass transfer limitations and secondary reactions, leading to increase of bio-oil yield. It has been demonstrated that increasing the heating rate from 5 °C/min to 300 °C/min determined the increase of bio-oil yield from 26 wt% to 35 wt% [35]. Wu et al [16] performed a conventional pyrolysis of wood biomass (particle size 1.5 mm) in a fixed bed reactor at 520 °C, under $N_2$ flow rate of 80 mL/min and under different heating rates between 5-40 °C/min. As it is shown in Table 8, the bio-oil yield increased with the increase of heating rate from 5 °C/min to 20 °C/min from 53.9 wt% to 59.1 wt%.

**Table 8. Product yield at different heating rates during pyrolysis of wood biomass [16]**

| Parameter | Conventional pyrolysis | | |
|---|---|---|---|
| Temperature | 520 | 520 | 520 |
| Heating rate, °C/min | 5 | 20 | 40 |
| Product yield | | | |
| Char | 25.45 | 22.12 | 21.21 |
| Liquid | 53.94 | 59.09 | 58.18 |
| Gas | 20.61 | 18.79 | 20.61 |

## CARRIER GAS FLOW AND VAPOR RESIDENCE TIME

Carrier gas flow is another important parameter for biomass pyrolysis, as it helps purging the vapors formed during pyrolysis, preventing the secondary reactions that may occur during high residence time [30]. It has been proved that increasing the nitrogen flow rate, the bio-oil and gas yields are increased. The gas flow of inert through the reactor influences the residence time and the contact time of vapors with biomass char and have impact over the severity of secondary reactions and properties of bio-oil. As long the residence time of vapors, the bio-oil yield is decreasing due to cracking and polymerization reactions of vapors to gases and solids [15]. At residence time from 1 to 5 s and temperature around 250 °C tar yield is limited to around 10%, while at residence time lower than 1 s incomplete decomposition of biomass [15]. Kan et al [35] presented that by increasing the residence time from 0.2 to 0.9 s during pyrolysis of biomass bagasse at 525 °C determined an increase of bio-oil yield from 75 wt% to 57 wt%, while the yield of gas and char phases increased.

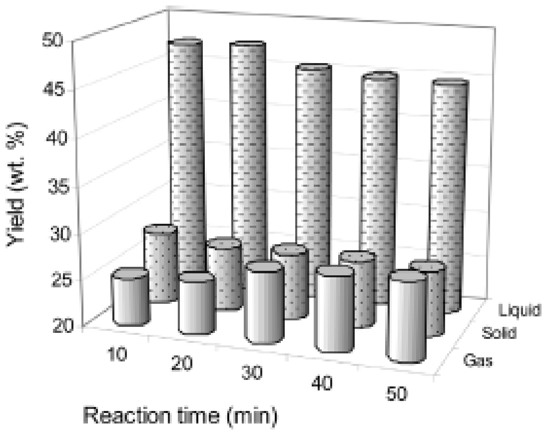


**Figure 12. Effect of reaction time over products yield in biomass pyrolysis [37]**

Acikalin and Karaca [37] performed biomass pyrolysis in a tubular reactor at 500 °C, 40 °C/min heating rate, under 250 mL/min $N_2$ flow and different reaction times between 10-50 min and showed that by increasing the reaction time, the bio-oil yield decreased from 47.4 wt% (at 20 min) to 44 wt% (after 50 min), as it can be observed in Figure 12. Moreover it has been proved that increasing the $N_2$ flow rate (from 50 to 450 mL/min) determined the decrease of residence time of the pyrolysis vapors in the reactor and condensation system, limiting the liquid yield.

## CATALYST LOADING

Pyrolysis of biomass in the presence of catalysts improves the quality of bio-oil through cracking, deoxygenation, oligomerization, cyclization, aromatization, alkylation, isomerization and polymerization. The catalyst loading together with the rest of pyrolysis operating conditions can influence the yield and composition of pyrolysis oil [38]. It has been proved that a small content of catalyst mixed with biomass particles reduced the tar formation [30]. Kabir and Hameed [38] showed that the excess of catalyst addition reduced the bio-oil production. Biomass pyrolysis at 450 °C and catalyst to biomass ratio of 1:6 were optimal conditions for production of bio-oil with high viscosity and heating value, reduced oxygen content and acidity. Rabiu et al [39] studied the influence of catalyst loading on products yield for catalyst pyrolysis of biomass at 600 °C, heating rate of 50 °C/min, N2 flow of 40 mL/min, 10 min reaction time. ZSM-5 was used as catalyst and the loading varied from 5 wt% to 25 wt% (based on feedstock amount used in pyrolysis reaction). It has been showed that bio-oil yield decreased from 40.8 wt% below 30 wt% when the catalyst loading was increased up to 25 wt%. Sebestyén et al [18, 40] reached around 50 wt% bio-oil yield when using 10 wt% HZSM-5 as catalyst on biomass pyrolysis (550 °C, 5 L/min $N_2$ flow) using a laboratory batch reactor.

A summary of operating conditions variation on biomass pyrolysis for high-grade bio-oil is presented in Table 9 [38].

***Table 9. Various conditions for catalytic biomass pyrolysis to high-grade bio-oil and chemicals [38]***

| Reactor | Time variant | Temperature | Catalyst loading $kg_{catalyst}/kg_{biomass}$ | Heating rate °C/min | Gas flow L/min | Product |
|---|---|---|---|---|---|---|
| Auger | short | 400-500 | 3:1 – 1:6 | fast | - | Bio-oil |
| | 7 min | 400-500 | 3:1 – 1:3 | fast | $N_2$, 5 | Bio-oil |
| Fixed bed | short | 350-550 | - | 10-50 | $N_2$, 0.1 | Bio-oil, gas |
| | 2.9-15.5 $h^{-1}$ | 40-650 | 90 mg | fast | $N_2$, 0.2 | Olefins |
| | 2-4 sec | 400-550 | 1:1 | fast | - | Bio-oil |
| | short | 500-600 | 1:4 | 50 | He, 20 | Bio-oil |
| | short | 600 | 10 wt% | 10 | $N_2$, 0.2 | Bio-oil |
| | short | 350-500 | - | 40 | $N_2$, 0.13 | Bio-oil |
| | 8-40 sec | 450-700 | 0-8 wt% | fast | $N_2$, 0.3 | Olefins, gas |
| | 0.03 sec | 500 | 1-10 wt% | flash | $N_2$, 0.05- | Bio-oil |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | 0.1 | |
| | 20 min | 400-600 | - | 6 | - | Bio-oil |
| | 0.5-5 sec | 400-600 | 5-10 wt% | high | He, 10 | Bio-oil |
| Fluidized | 0.15-0.9 $h^{-1}$ | 500-650 | - | fast | - | Bio-oil |
| Batch | 15-90 min | 150-400 | 5-30 wt% | fast | - | Bio-oil |

## 3. METHODOLOGY

### 3.1 FEEDSTOCK

Three biomass samples received from *Universidad del Valle, Cali – Colombia*, have been used as feedstock for first conventional pyrolysis tests. The waste biomass samples obtained from bioethanol process showed different size and moisture. The aspect of the three biomass samples is presented in Figure 13.

Press mud Powder vinasse Extraction sludge

**Figure 13. Biomass waste samples from bioethanol process**

Proximate and ultimate analyses, as well as chemical composition of the biomass samples were determined by *Universidad del Valle* (Table 10). The ultimate analyses were reanalyzed in order to compare the properties with the ones of biochar obtained during pyrolysis tests. No additional treatment was performed on biomass samples before pyrolysis.

**Table 10. Biomass feedstock properties**

| | Press mud (O1) | Powder vinasse (O2) | Extraction sludge (O3) |
|---|---|---|---|
| Moisture, wt% | 2.06 | 5.6 | 7.53 |
| Volatiles, wt% | 40.7 | 61.6 | 47.8 |
| Ash, wt% | 53.8 | 20.5 | 40.1 |
| Fixed carbon, wt% | 3.4 | 12.2 | 4.5 |
| Ultimate analysis, % | | | |
| C | 21.5 | 24.99 | 22.97 |
| H | 3.33 | 4.75 | 3.87 |
| N | 0.81 | 1.84 | 2.73 |
| O | 18.34 | 30.78 | 21.91 |
| S | 0.13 | 1.47 | 0.85 |
| LHV, MJ/kg | 7.79 | 14.45 | 8.24 |
| Chem. composition, wt% | | | |
| Cellulose | 12.8 | 12.7 | 7.5 |
| Hemicellulose | 6.5 | 8.7 | 5 |
| Lignin | 17.4 | 23 | 12.9 |

### 3.2 MATERIALS

For extraction and complete dissolution of liquid fraction obtained after pyrolysis tests Ethanol 95% and Acetone 98% were used as solvents (from Nordic Chemicals). Ethanol was used as solvent also for retaining the most volatile components produced during biomass conventional pyrolysis (in gas scrubber).

### 3.3 CONVENTIONAL PYROLYSIS UNIT

All pyrolysis tests were carried out in a batch scale reactor unit situated at the Technology Institute of Babes-Bolyai University, Cluj-Napoca. The laboratory scale pyrolysis unit (Figure 14) consists in a stainless steel reactor with 50 mm ID and 300 mm length. a cooling unit formed by four condensers and a gas scrubber, whereas first condenser cooled at room temperature to retain any biomass particles that might be driven by gas flow, second condenser cooled with ice to trap the heaviest fraction and the last two condensers are cooled with liquid nitrogen to retain the light fraction.

**Figure 14. Schematic design of batch reactor used for experimental work in Romania**

The reactor is externally heated by an electrical furnace with thermocouple and temperature controller. For all experiments, 50 g of each biomass sample was loaded directly in the reactor. For the experiments performed in the presence of a catalyst, a measured amount of catalyst was placed on top of the biomass layer. The loaded reactor was sealed and placed inside the electrical furnace. The reactor was externally heated from room temperature to target operating temperature at a heating rate of 7-8 °C/min. When temperature reached 100 °C, nitrogen flow was passed through reactor. The pyrolysis tests were performed for 2 -4 h to ensure maximum conversion of waste biomass particles. The reactor was cooled down to 100 °C under nitrogen flow and then it was allowed to reach room temperature overnight. During this time, the liquid fraction was collected in the cooling unit. After cooling, the reactor was removed from electrical furnace and material balance of the pyrolysis test was determined by measuring the amount of biochar and condensed liquid from each condenser. The liquid products were afterwards recovered by washing each condenser with ethanol and acetone. The ethanol solvent used in the gas scrubber was distilled using a rotary evaporator.

## 3.4 PRODUCT CHARACTERIZATION TECHNIQUES

### WATER CONTENT

The moisture content of biochar was established by oven drying method. according to ASTM D 4442-07.The procedure consisted in weighing a specific amount of biochar sample in a crucible and drying to constant weight at 105 °C ± 2 °C in the oven. Moisture was then calculated according to formula:

$$\%\,Moisture = \frac{m_0 - m}{m_0} \cdot 100 \qquad (1)$$

where $m_0$ represents the initial weight of sample and m represents the weight of sample after treatment.

### TOTAL SOLID CONTENT

Total solid content of biochar was determined by difference of moisture from the total of 100%.

$$\%\,Total\ solids = \left(1 - \frac{m_0 - m}{m_0}\right) \cdot 100 \qquad (2)$$

### ASH CONTENT

Ash content of biochar was determined by weighting a specific amount of biochar sample in a crucible and drying at 575 °C for 4 h. The as content was calculated according to formula:

$$\%\,Ash\ content = \frac{m_{ash}}{m_{char}} \cdot 100 \qquad (3)$$

where $m_{char}$ represents the initial weight of sample and $m_{ash}$ represents the weight of sample after treatment.

### ULTIMATE ANALYSIS

The content of C. H. N. and S in feedstock and biochar obtained after pyrolysis was determined with an elemental analyzer (Thermo EA 1222). The principle of analysis consisted in burning the organic compounds, followed by separation through chromatography column, identification and quantification of resulting gasses. For analysis, small amount of sample was wrapped in a tin sheet and introduced into the autosampler which sent the probe to the combustion chamber fluidized with oxygen and oxidation took place at 960 °C. The resulting gasses were $CO_2$, $NO_2$, $SO_2$ and $H_2O$. The carrier gas for analysis was He 6.0, while a copper electrolytic column and a TCD detector were used for separation and identification of the gasses.

### FTIR ANALYSIS

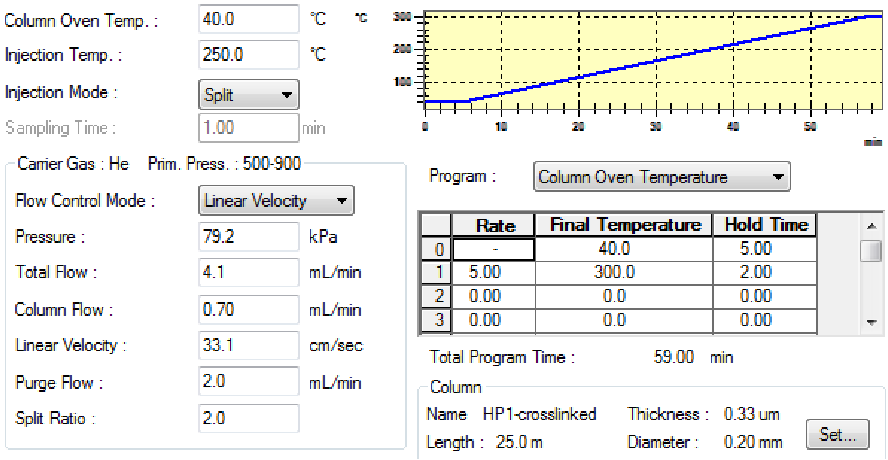
The infrared spectroscopy was used to establish the chemical structure of the waste biomass samples used in pyrolysis tests, as well as their corresponding biochar. For analysis, a Bruker Vector 22 spectrophotometer was used, with the analyzed sample incorporated in KBr pills, resolution 4 $cm^{-1}$, 20 scans and region 4000-600 cm$^{-1}$. Baseline and smooth corrections of the spectra have been done for each analysis.

## $^{13}$C-NMR ANALYSIS

The $^{13}$C-NMR spectra for determination of main organic components of pyrolysis oils were determined using a Bruker 600 MHz spectrometer. The samples were dissolved in Deuterated Acetone (CD3COCD3). The observing frequency for $^{13}$C nucleus was 150 MHz and the acquisition time 10 min.

## GC/MS ANALYSIS

The chemical composition of pyrolysis bio-oils was determined using a GC-2010 Shimadzu gas chromatograph connected to GCMS-QP2010 Plus mass spectrometer. A capillary column HP-1 (100% dimethylpolysiloxane) of 25 m with 0.2 mm ID and thickness of 0.33 µm was used for all analysis. The temperature program started from 40 °C, maintained for 5 min, and then the temperature was increased from 40 °C to 300 °C with a ramp of 5 °C/min. The temperature was maintained afterwards for 2 min. Injection temperature was set at 250 °C. Carrier gas was used He with a total flow of 4 mL/min (0.7 mL/min for the column – Figure 15). The MS was operated in electron ionization mode with 35-650 m/z range. Ion source temperature was set to 220 °C and interface temperature at 250 °C. Each peak detected was integrated and attributed to the corresponding organic compound using NIST05 library.



Column Oven Temp. : 40.0 ℃
Injection Temp. : 250.0 ℃
Injection Mode : Split
Sampling Time : 1.00 min
Carrier Gas : He    Prim. Press. : 500-900
Flow Control Mode : Linear Velocity
Pressure : 79.2 kPa
Total Flow : 4.1 mL/min
Column Flow : 0.70 mL/min
Linear Velocity : 33.1 cm/sec
Purge Flow : 2.0 mL/min
Split Ratio : 2.0

Program : Column Oven Temperature

|  | Rate | Final Temperature | Hold Time |
|---|---|---|---|
| 0 | - | 40.0 | 5.00 |
| 1 | 5.00 | 300.0 | 2.00 |
| 2 | 0.00 | 0.0 | 0.00 |
| 3 | 0.00 | 0.0 | 0.00 |

Total Program Time : 59.00 min

Column
Name HP1-crosslinked    Thickness : 0.33 um
Length : 25.0 m    Diameter : 0.20 mm

**Figure 15. GC-MS conditions used for analysis of pyrolysis bio-oil**

# 4. CONVENTIONAL BIOMASS PYROLYSIS –INFLUENCE OF BIOMASS WASTE TYPE

## 4.1 BIOMASS WASTE INFLUENCE ON PRODUCT DISTRIBUTION

For biomass waste influence over product distribution, the following operating conditions for conventional pyrolysis have been applied: operating temperature 450 °C at a heating rate of 7-8 °C/min, nitrogen flow of 50 L/h, operating time 2 h, no catalyst. The distribution of pyrolysis products (gas, liquid and solid fraction) for each biomass feedstock is analyzed in terms of their yield (wt%). Figure 16 presents the difference in pyrolysis products yields when each type of biomass waste - press mud, powder vinasse and extraction sludge – was used in conventional pyrolysis. The liquid product was divided into heavy fraction and water (collected in condenser 1) and light fraction (collected in condensers 2-4). The yield of gas products was calculated by difference from 100%. The results obtained show the significant differences between the biomass feedstock. It was observed that powder vinasse determined the formation of the lowest content of biochar (42.7%), however with the highest production of volatiles. The results are confirmed also by the proximate analysis of the raw biomass samples – powder vinasse showed the highest volatiles content (61.6 wt%) and the lowest ash content (20.5 wt%). On the other hand, extraction sludge presented the highest liquid yield (32%) with lowest gas formation (18.2 wt%). The results can be explained by the high content of water in extraction sludge (7.5 wt%) which will be seen in the high liquid heavy fraction yield (6.8 wt%) and low content of volatiles (47.8 wt%) and ash (40.1 wt%). The press mud presented the highest char yield (60.1%) due to the high content of ash (53.8%). The higher value of char yield compared with ash content for all biomass samples could suggest an incomplete decomposition of the organic phase at 450 °C.

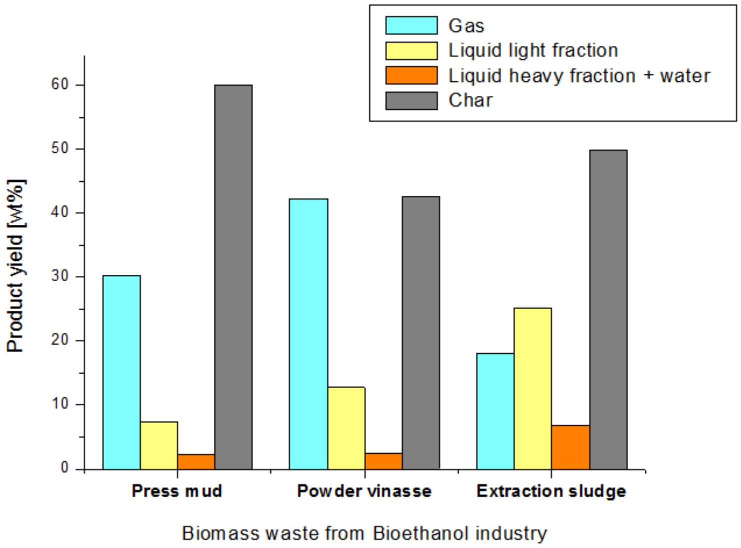


**Figure 16. Effect of biomass waste type on product distribution at 450 °C**

Similar product distributions of biomass wastes through slow pyrolysis were presented by other researches [22, 41-44]. Agar et al. [22] converted wastewater sludge and organic fines from municipal wastewater treatment plants (similar volatiles and ash content as our biomass feedstock – see Table 3) in carbon-rich char through pyrolysis in a laboratory fixed-bed reactor at 600 °C and 700 °C. The product distribution of sewage sludge at 600 °C was gas fraction 19%, liquid 33%, char 48%, while for solid organic fines the product yields at the same temperature were gas 33%, liquid 14%, char 53%. Even at 700 °C, the char yield was 45% for sewage sludge feedstock, while the gas yield increased to 29%. Williams and Besler [41] studied the influence of temperature and heating rate on the slow pyrolysis of biomass wood. The pyrolysis experiments have been performed for 2 h at temperature ranging from 300-720 °C, heating rate 5-80 K/min. The wood biomass presented moisture of 7 wt%, volatiles 92.2 wt% and ash of 0.8 wt%. At 420 °C pyrolysis temperature and 5 K/min (similar with our experimental conditions) it was obtained 29.7% char yield, oil yield 12.4 %, aqueous yield 35.9% and gas 21.5%. At higher operating temperature the char yield decreased to 23.2%, while the gas yield increased to 26.8%. Increasing the heating rate determined the decrease of oil yield and the increase of gas yield. Arni [42] obtained a product distribution of 37.6% char, 26.1% liquid and 25.1% gas from sugarcane bagasse (84 wt% volatiles, 5.9 wt% ash) by conventional pyrolysis at 480 °C, 40-50 °C/min, 1 h residence time.

The aspect of biochar and bio-oil produced from each biomass feedstock can be seen in Figure 17. All biochar samples were completely black, suggesting the decomposition of biomass (the biochar from powder vinasse was a block after cooling – it could be that heavy tar fractions remained in the char). Bio-oil obtained from extraction sludge had the darker coloration and stronger smell of ammonia (possible due to higher N content – 2.73%). On the other hand, the oil from powder vinasse showed a yellow coloration and strong smell of sulfur (S content 1.47%).


Char from Press mud


Char from Powder vinasse


Char from Extracton sludge


Oil from Press mud


Oil from Powder vinasse

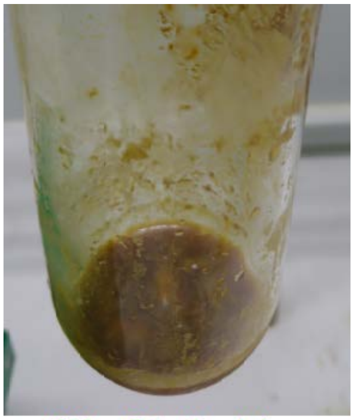

Oil from Extraction sludge

**Figure 17. Biochar and bio-oil from conventional pyrolysis of biomass waste from Bioethanol process**

## 4.2 BIOMASS WASTE INFLUENCE ON CHAR COMPOSITION AND PROPERTIES

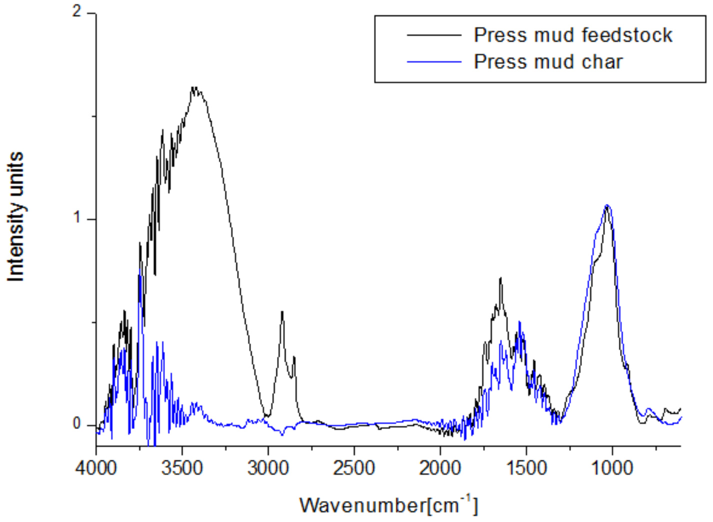
The biochar obtained after each pyrolysis test (Figure 16) was analyzed in terms of moisture content, C, H, N, S content and FTIR. The properties of the biomass feedstock and corresponding biochar samples are listed in Table 11.

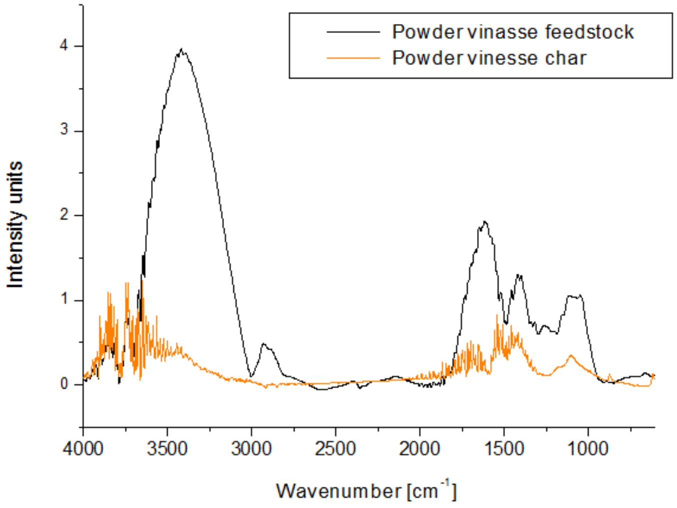
**Table 11. Proximate and ultimate analysis of char produced from each type of biomass**

| | Moisture. wt% | Ash content. wt% | C. % | H. % | N. % | S. % |
|---|---|---|---|---|---|---|
| | Press mud | | | | | |
| Feedstock | 2.06 | 53.8 | 22.308 | 3.649 | 0.896 | 0 |
| Char | 0.034 | 83.6 | 18.12 | 1.823 | 4.379 | 0 |
| | Powder vinasse | | | | | |
| Feedstock | 5.6 | 20.5 | 34.129 | 4.677 | 0.178 | 0 |
| Char | 0 | 56.5 | 38.804 | 1.639 | 1.16 | 0 |
| | Extraction sludge | | | | | |
| Feedstock | 7.53 | 40.1 | 19.567 | 3.724 | 0.909 | 0 |
| Char | 0.042 | 73.4 | 29.364 | 1.594 | 0.16 | 0 |

After pyrolysis at 450 °C for 2 h, the moisture content in all char samples decreased to almost 0%. The results are correlated also with hydrogen content which decreased in all samples after pyrolysis. Although in biomass feedstock analysis performed by Colombia partner, sulfur was detected in all samples, due to the low concentration, it was not detected in none of the samples with the system used in Romania. Nitrogen content showed high variation in the biomass feedstock and char – one explanation could be that biomass was not completely homogeneous (with particles of different size and type) which could impact N and S content. The char produced from powder vinasse was the most reach in carbon (favorable as fuel and activated carbon). The increase of carbon content after pyrolysis was observed also by Parthasarathy and Sheeba [43], Lee et al [45] due to the release of volatiles such as hydrogen and oxygen by dehydrogenation and deoxygenation.

FTIR spectra of each biomass feedstock and their corresponding chars are presented in Figure 18. Four important regions have been detected on FTIR spectra of all biomass feedstock samples: in the range of 3000-3800 $cm^{-1}$, between 2750-3000 $cm^{-1}$, a region between 1500-1800 $cm^{-1}$ and 750-1250 $cm^{-1}$. The small peak that appear at 3750-3970 $cm^{-1}$ can be related to the presence of water in all biomass samples, while the broad peaks with maximum intensity around 3420 $cm^{-1}$ can be attributed of O-H stretching from aromatic and aliphatic alcohols, in particular lignin [46]. The small peak from 2920-2930 $cm^{-1}$ is characteristic to C-H stretching of methyl and methylene groups from cellulose, hemicellulose and lignin. The peaks in the region of 1500-1750 $cm^{-1}$ correspond to C=O stretching of ketones, aldehydes, esters from hemicellulose and lignin [46, 47]. Powder vinasse shows also an intense peak at 1417 $cm^{-1}$ which is characteristic to C-H deformation of the aromatic ring from lignin. The presence of this at higher intensity in case on powder vinasse could be due to the higher content of lignin (Table 10). The peaks from 1033-1180 cm$^{-1}$ can be attributed to C-O stretching from cellulose and hemicellulose.





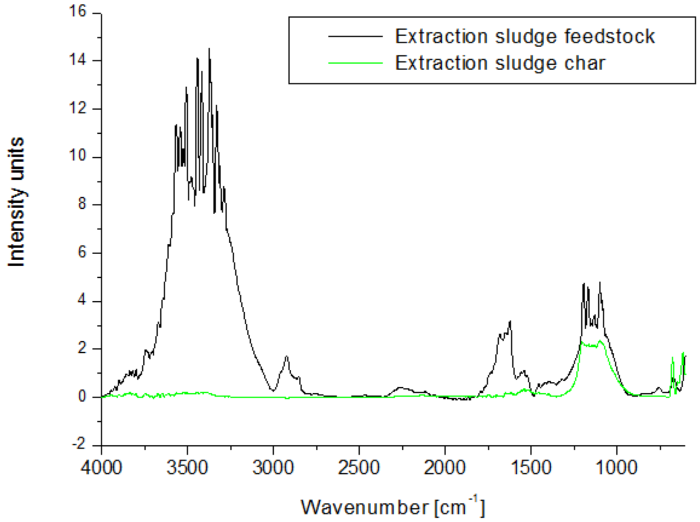
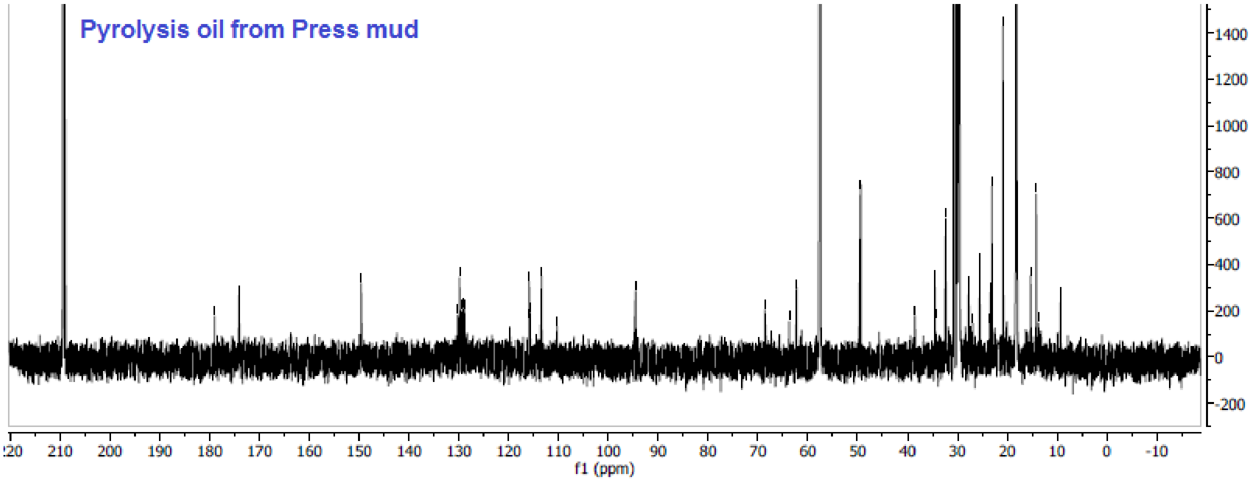


**Figure 18. FTIR spectra of biomass feedstock and biochar after conventional pyrolysis at 450 °C**

Significant changes of FTIR spectra appear in case of all char samples obtained after conventional pyrolysis at 450 °C. The OH stretching band from 3750-3970 cm$^{-1}$ decreased drastically in case of all char samples, disappearing completely in case of char from extraction sludge (with the lowest content of lignin 12.7%). The absence of the peak from 2920-2930 cm$^{-1}$ suggests the significant decomposition of the biomass material during pyrolysis [48]. If the biochar produced from press mud still show the peaks characteristic to C-O stretching at almost the same intensity as the feedstock, the other two char samples show a significant decrease of the peaks from this region, suggesting the high degradation of the organic compounds for these two biomass samples.

## 4.3 BIOMASS WASTE INFLUENCE ON PYROLYSIS OIL COMPOSITION

The functional groups from bio-oil produced from each biomass waste feedstock have been determined by $^{13}$C-NMR (Figure 19).



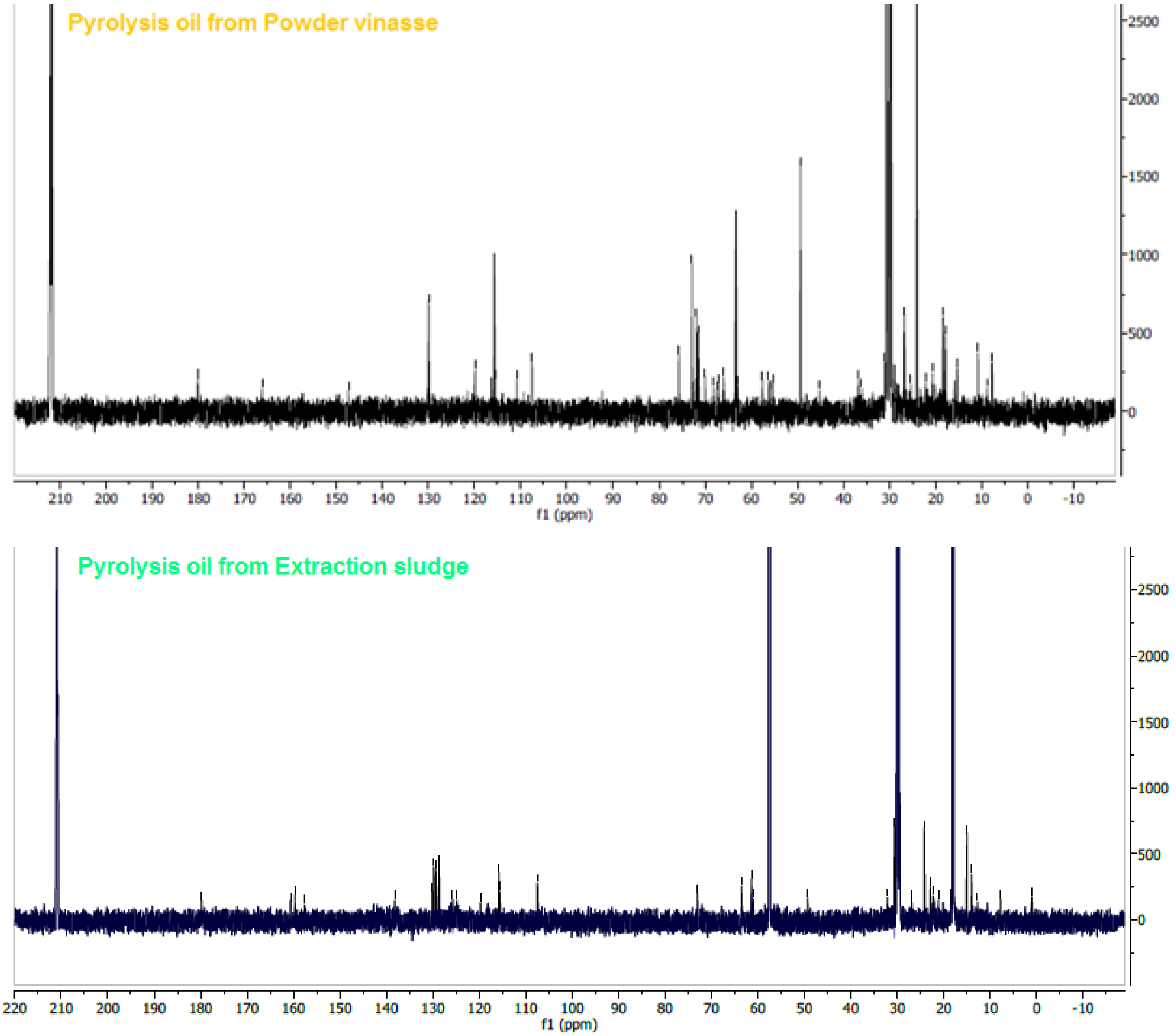


**Figure 19.** $^{13}$C-NMR spectra of bio-oil produced from different biomass feedstock

The difference in chemical composition of bio-oils can be noticed from the different peaks as well as changes of intensity of the chemical shift between 0 to 220 ppm. The peaks with the highest intensity are characteristic to the solvents used during extraction of pyrolysis oil (ethanol) and for dissolution on $^{13}$C-NMR analysis (Deuterated acetone). It has been observed that all bio-oil samples showed the peaks characteristic to aliphatic components 49.4-0.9 ppm [49] with the following differences: bio-oil from extraction sludge presents less peaks in the region of aliphatic components and the majority of the peaks are in the region 26.9-0.9 ppm which is characteristic to primary and secondary carbons [50], while bio-oil from powder vinasse and press mud show also peaks characteristic to tertiary carbons. The bio-oil from powder vinasse shows the chemical shift range at 57.5-55.3 ppm attributed to methoxyl compounds (it can be explained by the highest content of lignin in the biomass feedstock available for decomposition). The same sample presents also the largest number of peaks in the region of 94.5-60.9 ppm attributed to alcohols/carbohydrates [6, 50]. All bio-oil samples contain aromatic components (C-H at 130.2-107.5 ppm, C-C at 138.1-130.2 ppm, C-O at 160.6-147.4 ppm) and carbonyl components (possible carboxylic acids and esters due to the peaks in the region of 180.1-157.6 ppm [50]).

The bio-oils produced from each biomass waste pyrolysis were analyzed in terms of chemical composition using GC-MS technique. For this stage of our research, for each test, the oil was extracted separately from each condenser of the cooling unit and analyzed with GC-MS – the reason for analyzing separately was to observe the way the organic components condense in the cooling unit, as well as to have the possibility to identify easier the components (performing the GS-MS over the entire mixture of bio-oil could determine a wide spectrum of peaks, difficult to separate). During the GC-MS analysis of the liquid phase from each condenser, as well as solvent scrubber it has been observed:

- for all the samples, it has been observed that the liquid condensed in the line between pyrolysis reactor and condenser, as well in tube 1 and solvent scrubber, contained the peaks characteristic to phthalates (Figure 20) – the presence of this organic components is most probably due to the silicon line used to connect autoclave to condenser unit, as well as condenser unit to solvent scrubber (see Figure 14); these organic components identified were not taking into consideration in the quantity analysis of organic components produced during pyrolysis

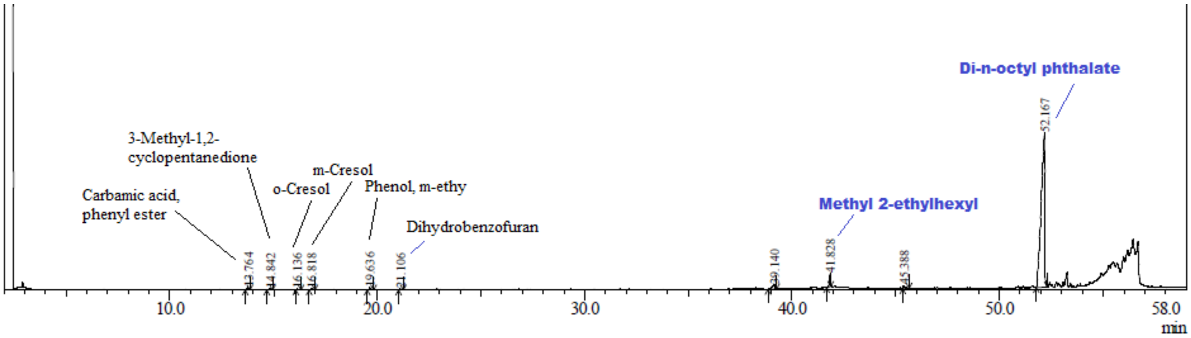


**Figure 20. GC-MS of condensed oil from line connecting pyrolysis reactor to condenser line**

- The oil collected from condenser 1 showed a high variety of organic components in case of powder vinasse and extraction sludge and less components for press mud (Table 12).

**Table 12. Composition of bio-oil collected from condenser 1 of pyrolysis unit**

| Press mud | Rel. % | Powder vinasse | Rel. % | Extraction sludge | Rel. % |
|---|---|---|---|---|---|
| Propanoic acid. 2-hydroxy-. methyl ester | **2.54** | Propanoic acid. 2-hydroxy-. methyl ester. | **2.72** | Oxalic acid. dicyclobutyl ester | **8.08** |
| 1-Hydroxy-2-butanone | **0.86** | 1-Hydroxy-2-butanone | **0.72** | Proline | **5.9** |
| Propane. 2.2-diethoxy- | **79.48** | 2-Butanone compounds | **0.27** | Oxazole. 4.5-dihydro-2.4.4-trimethyl | **3.1** |
| 2-Propanone. 1.1-dimethoxy | **0.43** | Pyrrolidine. 2-(hydroxymethyl)- | **1.21** | Hexanedioic acid. monoethyl ester | **0.36** |
| 2-Cyclopenten-1-one compounds | **4.95** | 2-Cyclopenten-1-one compounds | **3.74** | 2-Cyclopenten-1-one compounds | **4.48** |
| Furfural | **1.51** | Acetamide | **0.23** | Indolizine | **1.89** |
| 2-Propanone. 1-(acetyloxy) | **3.73** | Oxazole | **32.43** | 2-Pentanone. 4-hydroxy-4- | **3.52** |

| | | | | | |
|---|---|---|---|---|---|
| | | | | methyl- | |
| 2-Furancarboxaldehyde | **0.9** | Acetaldehyde. ethylidenehydrazone | **3.87** | Hexadecanoic acid. ethyl ester | **0.31** |
| Phenol compounds | **3.33** | Phenol compounds | **13.36** | Phenol compounds | **16.11** |
| Benzofuran. 2.3-dihydro | **0.28** | Benzofuran. 2.3-dihydro- | **1.6** | Butanenitrile. 2-methyl- | **2.52** |
| Alkanes (C12-C18) | **1.26** | Aziridine compounds | **18.39** | Aziridine compounds | **18.17** |
| Alkenes (C12-C15) | **0.27** | 1.2-Ethanediol. monoacetate | **0.47** | Alkanes (C12-C25) | **8.11** |
| Hexadecanoic acid. methyl ester | **0.15** | 2-Furanmethanol | **5.37** | Alkenes (C13-C18) | **3.47** |
| n-Hexadecanoic acid | **0.12** | Pyrazine compounds | **1.61** | 2-Furanmethanol | **12.6** |
| | | Furanone compounds | **1.32** | Pyrazine compounds | **3.90** |
| | | 1.2-Cyclopentanedione. 3-methyl | **1.94** | Others | **7.52** |
| | | Caprolactam | **1.96** | | |
| | | Others | **9.04** | | |

As it can be observed from Table 1, in general similar compounds have been obtained from all three biomass waste feedstock, however with significant differences in terms of concentration. Powder vinasse and extraction sludge showed high concentration of compounds with nitrogen (due to higher N content observed in these two samples – Table 9). The liquid obtained from Press mud showed a significant amount of 2.2-Dimethoxypropane (DMP) – the compound is in general formed from acetone and methanol at room temperature in presence of acidic environment [51]. Small amounts of 2-cyclopenten-1-one, phenol compounds, as well as alkanes C12-C18 were also observed. In case of powder vinasse, oxazole and aziridine (both with nitrogen in their structure) compounds were in the highest concentration – 50.8% together with phenol compounds (13.4%) and furanmethanol (5.4%). Although powder vinasse did not show any alkanes or alkenes, it contained significantly much higher concentration of aromatics than the liquid from press mud. Similar results have been obtained also by David et al. [19] from pyrolysis of sugarcane baggase. Extraction sludge showed the highest concentration of phenols (16.1%), aziridines and pyrazines (22.1%), furanmethanol (12.6%) together with highest content of alkanes and alkenes (11.6%).

- Heavier organic compounds have been observed on the composition of pyrolysis liquids collected in condenser 2 (Table 13).

**Table 13. Composition of bio-oil collected from condenser 2 of pyrolysis unit**

| **Press mud** | Rel.% | **Powder vinasse** | Rel.% | **Extraction sludge** | Rel.% |
|---|---|---|---|---|---|
| Phenol compounds | **31.99** | Phenol compounds | **54.61** | Phenol compounds | **49.83** |
| Oxazole. 4.5-dihydro | **6.54** | Penten-2-one compounds | **8.24** | 3-Penten-2-one. 4-methyl- | **2.02** |
| 2-Cyclopenten-1-one comp. | **7.81** | Propanoic acid. 2-hydroxy | **0.19** | Cyclopentanone | **3.12** |
| Furfural | **1.31** | 2.3-Butanediol. | **1.09** | 2-Isopropylpyrazine | **9.69** |
| 2-Pentanone. 4-hydroxy-4-methyl- | **1.7** | 2-Pentanone. 4-hydroxy-4-methyl- | **2.46** | 2-Pentanone.4-hydroxy-4-methyl- | **9.58** |

| | | | | | |
|---|---|---|---|---|---|
| 2-Propanone. 1-(acetyloxy) | **4.17** | 2-Furanmethanol | **0.5** | N-Cyano-2-methylpyrrolidine | **1.48** |
| Cyclooctane | **2.19** | 2-Propen-1-amine. N.N-bis(1-methylethyl) | **1.47** | Toluene | **2.66** |
| 2-Furancarboxaldehyde. 5-methyl- | **1.53** | Piperidine. 1.2-dimethyl- | **0.35** | 1.6-Dioxacyclododecane-7.12-dione | **1.44** |
| Benzofuran. 2.3-dihydro- | **3.09** | Benzofuran. 2.3-dihydro | **4.97** | Hexanedioic acid. ethyl.methyl es | **0.46** |
| 1.2-Cyclopentanedione. 3-methyl- | **3.74** | 1.2-Cyclopentanedione. 3-methyl | **1.88** | Indolizine | **6.11** |
| Alkanes (C13-C22) | **25.09** | Alkanes (C19-C32) | **4.29** | Alkanes (C16-C25) | **6.68** |
| Alkenes (C14-C16) | **3.19** | 2-Amino-5.6-dihydro-4.4.6-trimethyl-4H-1.3-oxazine | **4.12** | Alkenes (C16-C25) | **2.57** |
| Palmitic acid. methyl ester | **1.2** | Indole compounds | **2.29** | 1H-Indole. 3-methyl- | **1.51** |
| Hexadecanoic acid. propyl ester | **0.63** | 4-Piperidinone. 2.2.6.6-tetramethyl- | **1.03** | Others | **2.85** |
| Others | **5.81** | Thymol | **0.66** | | |
| | | Others | **11.82** | | |

For all the samples, the main components of the liquid collected from condenser 2 are phenols (due to degradation of lignin). Powder vinasse and extraction sludge showed 50% phenols, very similar results being obtained also in literature [11, 16, 19, 52, 53]. Press mud liquid contained the highest amount of alkanes (25.1%). although powder vinasse presented heavier alkenes up to C32. Higher content of ketones (aliphatic and cyclic) were formed when press mud (13.7%) and extraction sludge (14.7%) were used for pyrolysis.

➢ The liquid extracted from last two condensers showed a variety of components including heavy and volatiles. In liquid collected from condenser 3 there is still a significant amount of phenols

**Table 14. Composition of bio-oil collected from condenser 3 of pyrolysis unit**

| **Press mud** | Rel.% | **Powder vinasse** | Rel.% | **Extraction sludge** | Rel.% |
|---|---|---|---|---|---|
| Propane. 2.2-diethoxy | **8.26** | Propanoic acid. 2-hydroxy-. methyl ester. | **0.52** | Cyclopentanone | 1.20 |
| 2-Cyclopenten-1-one compounds | **10.49** | Penten-2-one compounds | **24.82** | Oxazole | 3.64 |
| Furfural | **5.24** | Pyrrolidine. 2-(hydroxymethyl)- | **0.41** | 3-Penten-2-one. 4-methyl | 2 |
| Propanoic acid. 2-oxo-. ethyl ester | **4.13** | 2.3-Butanediol | **1.39** | Acetaldehyde. ethylidenehydrazone | 4.56 |
| 2-Furancarboxaldehyde. 5-methyl- | **2.37** | Acetaldehyde. ethylidenehydrazone | **3.48** | 5-Hexenenitrile. 2-methyl | 4.49 |
| Carbamic acid. phenyl ester | **5.42** | 2-Cyclopenten-1-one compounds | **2.29** | 2-Pentanone. 4-hydroxy-4-methyl | 13.14 |
| 1.2-Cyclopentanedione. 3-methyl- | **3.48** | Glycine. N-(aminoiminomethyl)-N-methyl- | **1.97** | 2-Furanmethanol | 5.64 |
| Phenol compounds | **13.54** | Pentanone. 4-hydroxy-4-methyl- | **11.52** | Aziridine compounds | 4.97 |
| Larixic acid | **0.71** | 2-Furanmethanol | **2.03** | Pyrazine. 2.6-dimethyl- | 1.20 |
| Benzaldehyde. 4-methyl- | **3.83** | Aziridine. 2-(1.1-dimethylethyl)-1.3-dimethyl- | **3.81** | N-Cyano-2-methylpyrrolidine | 1.25 |

| | | | | | |
|---|---|---|---|---|---|
| Alkanes (C13-C26) | **20.85** | Pyrrole. 1-methyl-3-(1.1-dimethylethyl)- | **1.03** | 2-Cyclopenten-1-one. 3-methyl- | 1.16 |
| Alkenes (C14-C26) | **5.53** | Phenol compounds | **16.07** | 1-Heptene. 2.6-dimethyl- | 1.59 |
| Hexadecanoic acid. methyl ester | **2.52** | Pyrazine compounds | **1.28** | Phenol compounds | 15.70 |
| Octadecanoic acid. 2-propenyl ester | **0.44** | Piperidine compounds | **0.37** | Piperazine. 2.5-dimethyl-. trans | 10.93 |
| Others | **13.19** | Caprolactam | **1.20** | Pyrazole. 1.4-dimethyl | 2.73 |
| | | 2-Propen-1-amine. N.N-bis(1-methylethyl) | **3.72** | 2.2.6.6-Tetramethyl-4-piperidone | 4.39 |
| | | 4-Piperidinone. 2.2.6.6-tetramethyl- | **11.09** | Alkanes (C13-C26) | 6.51 |
| | | Benzofuran. 2.3-dihydro- | **1.36** | Alkenes (C13-C18) | 2.29 |
| | | Alkanes (C18-C28) | **1.49** | Hexadecanoic acid ester | 0.68 |
| | | Others | **9.84** | Others | 11.74 |

The liquid from press mud collected in condenser continued to show a high content of alkanes, phenols and ketones (similar as it was observed also in previous condenser). For powder vinasse the main components observed were ketones (38%), phenols (16.1%) and organic compounds bazed on nitrogen (azirides, pyrroles, piperidines, pyrazines – 17.6%). Extraction sludge showed lower content of ketones (17.5%) and phenols (15.7%) but higher amount of organic compounds with nitrogen (29.9%) and alkanes (6.5%). The liquids obtained from pyrolysis of press mud and extraction sludge seem in general heavier than the one obtained from powder vinasse (due to higher content of alkanes. they might have higher viscosity – the physical-chemical properties of pyrolysis oils will be determined for the next experiments).

**Table 15. Composition of bio-oil collected from condenser 4 of pyrolysis unit**

| Press mud | Rel.% | **Powder vinasse** | Rel.% | **Extraction sludge** | Rel.% |
|---|---|---|---|---|---|
| Acetic acid | **17.95** | 2.4.4-Trimethyl-2-oxazoline | **10.52** | 1.3-Butanediol | **2.92** |
| Toluene compounds | **14.97** | Toluene compounds | **1.27** | Toluene | **30.86** |
| Furfural | **10.96** | Furfuryl alcohol | **2.65** | 2-Pentanone. 4-hydroxy-4-methyl | **5.13** |
| Propane. 2.2-diethoxy- | **0.46** | Propanoic acid. 2-hydroxy-. methyl este | **1.06** | Phthalic acid. diethyl ester | **1.08** |
| 2-Cyclopenten-1-one | **5.31** | 2-Cyclopenten-1-one compounds | **5.34** | 1-Methyl-1-cyclopenten-3-one | **0.44** |
| Other aliphatic ketones | **0.89** | Other Aliphatic ketones | **7.11** | Other aliphatic ketones | **0.5** |
| Other aromatic ketones | **2.39** | Other aromatic ketones | **6.8** | 2.2.6.6-Tetramethyl-4-piperidinone | **2.92** |
| Benzene compounds | **5.46** | Benzene | **0.12** | Ethylbenzene | **3.66** |
| Furan compounds | **4.62** | Furan compounds | **2.87** | Furan compounds | **0.87** |
| Phenol compounds | **3.96** | Phenol compounds | **18.91** | Phenol compounds | **4.18** |
| Octadecyl vinyl ether | **2.26** | Picoline compounds | **2.16** | 2-Picoline | **2.03** |
| p-Methylbenzyl alcohol | **1.36** | Pyrazine compounds | **2.3** | Pyrazine compounds | **2.15** |

| | | | | | |
|---|---|---|---|---|---|
| 3.5-Heptadien-2-ol. 2.6-dimethyl | **1.1** | m-Xylene | **0.43** | Xylene compounds | **2.81** |
| Alkanes (C8-C28) | **14.69** | Xylenol compounds | **2.87** | Pyridine compounds | **0.57** |
| Alkenes (C7-C22) | **6.56** | 2-Methyl-2-cyclopentenone | **3.13** | 2.5-Dimethylpiperazine | **8.56** |
| Other | **7.06** | 2-Methylene-4-pentenal | **1.15** | Alkanes (C9-C27) | **9.11** |
| | | Pyridine compounds | **2.57** | Alkenes (C12-C27) | **4.63** |
| | | Cycloheptanol. 1-methyl-2-methylene- | **1.04** | Other | **17.61** |
| | | 4-(Ethylsulfanyl)-2-butanone | **0.34** | | |
| | | Alkynes (C5-C8) | **3.71** | | |
| | | Other | **21.13** | | |

It was observed that the liquid from press mud from last condenser presented a significant amount of volatiles – acetic acid and toluene (32.9%). Furfural, benzene, furan components were also in significant amount (21%). proving of the decomposition of hemicellulose. The liquid from powder vinasse still contained a significant amount of phenol compounds (18.9%). in particular phenol, phenol methoxy, phenol methyl and ethyl. In Figure 21 is presented the chromatogram of liquid obtained from powder vinasse with the identification of the peaks characteristic to phenols. A sample contained a higher content of aliphatic and aromatic ketones (19.2%) compared with the other two pyrolysis oils. Moreover the sample showed also the presence of alkynes and sulphur organic compounds (powder vinasse presented the highest content of sulfur – 1.47%). Extraction sludge showed significant amount of toluene,xylenes and benzenes (37.3%). as well as aliphatic and aromatic ketones (6%). alkanes and alkenes (13.7%).

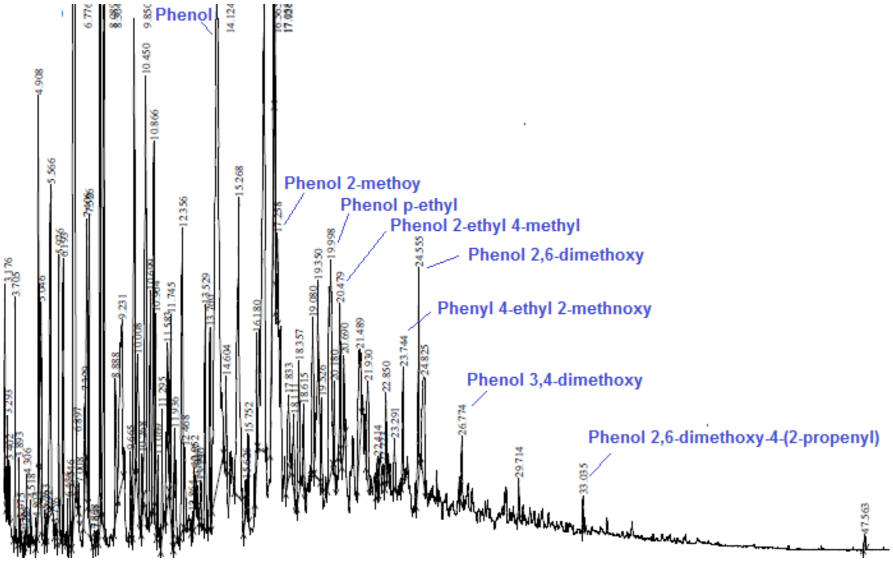


**Figure 21. GC-MS of condensed oil from powder vinasse**

After individual analysis over pyrolysis liquids samples collected from each condenser, an overall composition of the pyrolysis bio-oil for each biomass waste feedstock has been calculated based on the concentration of each component and the quantity of liquid collected from each condenser. The main components found in each pyrolysis bio-oil are listed in Table 16. As a general observation, powder vinnase determined the formation of a large variety of organic components due to thermal decomposition of the lignocellulosic compounds (with high volatiles content). More than 200 components have been identified in the liquid phases collected from each condenser, the separate GC-MS analysis being beneficial in this case. For press mud and extraction sludge the majority of organic components have been observed in all liquid phases, thus it is not necessary for the next tests each liquid phase to be analyzed individually by GC-MS. Also in case of all three biomass samples similar compounds have been identified. in particular for powder vinasse and extraction sludge (high amount of organic components with nitrogen). Press mud produced important amounts of propane alkyloxy (Propane, 2.2-diethoxy, 2-Propanone, 1.1-dimethoxy, 2-Propanone, 1-(acetyloxy)), carboxylic acids, furfural, toluene, aliphatic and aromatic phenols, as well as alkanes and alkenes. Powder vinasse showed formation of higher concentration of phenol, aliphatic and aromatic ketones as well as organic compounds with nitrogen, compared with the bio-oil produced from press mud. The bio-oil from powder vinasse show high content of aromatics and low content of hydrocarbons.

**Table 16. Overall composition of pyrolysis bio-oil obtained from different biomass feedstock**

| **Press mud** | mass % | **Powder vinasse** | mass % | **Extraction sludge** | mass % |
|---|---|---|---|---|---|
| Carboxylic acid esters | **3.02** | Carboxylic acid esters | **1.32** | Carboxylic acid esters | **2.70** |
| 1-Hydroxy-2-butanone | **0.20** | 1-Hydroxy-2-butanone | **0.12** | 5-Hexenenitrile. 2-methyl | **0.21** |
| Propane +propanone. alkyloxy- | **20.61** | 2-Cyclopenten-1-one compounds | **7.55** | 2-Cyclopenten-1-one compounds | **1.33** |
| 2-Cyclopenten-1-one compounds | **5.62** | Other Aliphatic ketones | **6.96** | Other aliphatic ketones | **0.47** |
| 2-Pentanone. 4-hydroxy-4-methyl- | **0.04** | Other aromatic ketones | **5.82** | Other aromatic compounds | **0.07** |
| 1.2-Cyclopentanedione. 3-methyl- | **0.31** | Oxazole compounds | **13.70** | Oxazoles | **0.83** |
| Other aliphatic ketones | **0.60** | Phenol compounds | **18.51** | Phenol compounds | **7.48** |
| Other aromatic ketones | **1.62** | Benzofuran. 2.3-dihydro- | **0.35** | Ethylbenzene | **2.69** |
| Furfural | **8.16** | Aziridine compounds | **3.12** | Aziridine compounds | **4.11** |
| 2-Furancarboxaldehyde | **0.40** | Furan compounds | **3.27** | Furan compounds | **3.59** |
| Phenol compounds | **5.04** | Pyrazine compounds | **2.17** | Pyrazine compounds | **2.64** |
| Benzene compounds | **4.63** | Furanone compounds | **0.21** | Piperazines | **6.80** |
| Furan compounds | **3.14** | Caprolactam | **0.37** | Piridine compounds | **0.42** |
| Benzofuran. 2.3-dihydro | **0.13** | 2-Pentanone. 4-hydroxy-4-methyl- | **0.54** | 2-Pentanone. 4-hydroxy-4-methyl- | **5.18** |
| Benzaldehyde. 4-methyl- | **0.25** | Amines | **0.29** | Indolizine | **0.44** |
| Acetic acid | **12.18** | Acetaldehyde. ethylidenehydrazone | **0.78** | Acetaldehyde. ethylidenehydrazone | **0.21** |
| n-Hexadecanoic acid | **0.03** | Piperidine compounds | **0.53** | 2.2.6.6-Tetramethyl-4-piperidone | **2.35** |

| | | | | | |
|---|---|---|---|---|---|
| Larixic acid | **0.05** | Toluene compounds | **1.03** | Toluene | **22.69** |
| Oxazole. 4.5-dihydro | **0.14** | Indole compounds | **0.02** | Butanenitrile. 2-methyl- | **0.54** |
| Cyclooctane | **0.05** | Pyrrolidine. 2-(hydroxymethyl)- | **0.21** | Proline | **1.26** |
| Toluene compounds | **10.16** | Furfuryl alcohol | **2.14** | 2-Picoline | **1.49** |
| 3.5-Heptadien-2-ol. 2.6-dimethyl | **0.75** | Picoline compounds | **1.75** | Xylene compounds | **2.06** |
| Alkanes (C12-C28) | **12.16** | Xylenol compounds | **2.32** | 1.3-Butanediol | **2.15** |
| Alkenes (C12-C26) | **4.94** | m-Xylene | **0.35** | Alkanes (C9-C27) | **8.76** |
| Others | **5.78** | Pyridine compounds | **2.08** | Alkenes (C12-C27) | **4.26** |
| | | 2.3-Butanediol. | **0.07** | Others | **15.25** |
| | | 2-Methylene-4-pentenal | **0.93** | | |
| | | Cycloheptanol. 1-methyl-2-methylene- | **0.84** | | |
| | | 4-(Ethylsulfanyl)-2-butanone | **0.27** | | |
| | | Alkynes (C5-C8) | **3.00** | | |
| | | Alkanes (C19-C32) | **0.10** | | |
| | | Benzene | **0.10** | | |
| | | Others | **19.21** | | |

On the other hand the main component of extraction sludge bio-oil was toluene (more than 22%) together with phenol compounds and organic compounds with nitrogen (azirides, piperazines, pyridines, indolizines). The content of hydrocarbons was also high for bio-oil produced from extraction sludge.

### 4.4 RECOMMENDATIONS FOR BIOMASS WASTE MIXTURE FOR NEXT CONVENTIONAL PYROLYSIS TESTS

Based on the results obtained from conventional pyrolysis of press mud, powder vinasse and extraction sludge the following observations can be concluded:

- pyrolysis at 450 °C (heating rate 7-8 °C/min), 2 h favored the production of char (42.7-60.1 % yield) for all biomass waste feedstock;
- press mud showed the highest production of biochar, but with low content of oil, while powder vinasse produced a char with almost 40% content of carbon;
- the FTIR spectra of all biochar demonstrated the significant decomposition of organic components from all biomass samples; the presence of the peaks characteristic to C-O group demonstrates still the capacity of further decomposition or organic compounds at higher temperature (the results are agreement with DSC-TGA analysis, where at 450 °C none of the biomass samples are completely decomposed);
- pyrolysis of extraction sludge determined the production of the highest amount of bio-oil and lowest amount of gas; the bio-oil produced from extraction sludge presented aliphatic compounds (in particular with primary and secondary carbons), aromatics and carbonyl compounds;
- powder vinasse showed the lowest content of char produced with a bio-oil rich in aliphatic compounds, methoxy, alcohols and carbohydrates, as well as aromatic components; this

biomass waste showed also the highest gas yield (due to high volatiles content) – the nitrogen flow set during pyrolysis could also had a negative impact over bio-oil condensation . determining the increase of gas yield – the influence of carrier gas should be determined as soon as possible in order to investigate if oil yield can be increased;

- ➢ extraction sludge can be a good feedstock for production of bio-oil and biochar. however there is the limitation in terms of the quantity produced from Bioethanol industry; From the biomass waste that is available for pyrolysis tests, extraction sludge represents around 17%, while press mud and powder vinasse are around 40%.

For the following conventional pyrolysis tests, there are three options of biomass feedstock:

- **FOR BIOCHAR PRODUCTION**:
    1. use **only Press mud** as biomass feedstock
    2. use a mixture of : **Press mud 50%, Powder vinasse 25%, Extraction sludge 25%**
- **FOR BIO-OIL PRODUCTION**:
    3. use a mixture of: **Press mud 20%, Powder vinasse 60%, Extraction sludge 20%**

Considering that powder vinasse and extraction sludge are formed from the same waste, in order to reduce a treatment step of biomass waste, only one type of feedstock should be produced (especially as both feedstock showed similar properties and pyrolysis products). As powder vinasse is easier to produce and in higher quantity, a mixture of Press mud 67% and Powder vinasse 33% could be used.

# 5. CONVENTIONAL BIOMASS PYROLYSIS –INFLUENCE OF CATALYST TYPE

## 5.1 CATALYST INFLUENCE ON PRODUCT DISTRIBUTION

Based on the previous results from Chapter 4 it has been decided that the biomass mixture to be used for the next pyrolysis tests will consist in 67% press mud and 33% powder vinasse. This mixture will be used not only for conventional pyrolysis tests, but also for induction-heated biomass pyrolysis tests.

For determining the influence of the catalysts over conventional pyrolysis of biomass waste mixture, each catalyst (ZSM-5, H-ZSM-5, CaO, Al-MCM-41) has been tested under the following pyrolysis conditions: 50 g biomass mixture (O1+O2), catalyst 5 wt%, 450 °C, atmospheric pressure, 50 L/h $N_2$ flow, 2 h reaction time. The properties of the catalysts are presented in Table 17.

**Table 17. Physical-chemical properties of catalysts used for pyrolysis tests**

| Property | **ZSM-5** | **CaO** | **Al-MCM-41** |
|---|---|---|---|
| SiO2/Al2O3 Molar Ratio | 38 | — | 25 |
| Pore Volume. cm3 /g | ≥0.25 | — | ≥0.57 |
| BET surface area. m2 /g | ≥250 | — | >633 |
| Bulk Density. g/mL | 0.72 | 3.3 | — |
| Crushing Strength. N/cm2 | ≥98 | — | — |
| Attrition. wt% | <1 | — | — |
| Appearance | Extrudates | Powder and chunks | White Powder |

Similar as in the previous tests, for each type of catalyst it was determined the yield of pyrolysis products (gas, liquid and solid fraction). The results have been compared with a pyrolysis test performed without any catalyst. As it is observed in Figure 22, In general very small differences were observed in case of product distribution when different catalyst were used for conventional pyrolysis of biomass waste mixture.

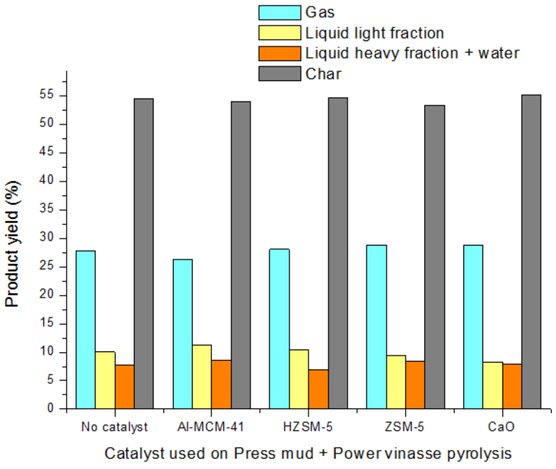


**Figure 22. Effect of catalyst type on product distribution at 450 °C, 50 L/h $N_2$ flow, 2h reaction time**

It is considered that a small amount of inorganic material mixed with biomass will reduce tar formation [30]. Antonakou et al [32] showed that using Al-MCM-41 as catalyst for biomass pyrolysis determined the increase char yield in lignocellulosic biomass pyrolysis (with increase of gas yield), but decreased the char yield for silvergrass feed. Lorenzetti et al [14] used HZSM-5 catalyst for pyrolysis of different biomass feedstocks, determining the reduction of oil yield due to the formation of water and water soluble compounds, as well as volatiles (increase of gas phase). In case of our experiments, HZSM-5 catalyst showed a slight increase of liquid yield (from 10% with no catalyst to 10.4% with catalyst) and decrease of heavy fraction + water yield with more than 10%. The non-protonated form ZSM-5 indeed showed the decrease for liquid yield (from 10% to 9.4) and increase of heavy fraction + water yield with more than 10%, as well as the increase of gas yield with almost 4%. Veses et al [11] proved also that the addition of catalysts in biomass pyrolysis did not change drastically the product distribution. Using CaO as catalyst determined the highest char yield (55.1%) with 17% decrease of bio-oil yield and the increase of volatiles to 28.7%. Based on the product distribution, it could be considered that Al-MCM-41 catalyst was the most efficient in the increase of liquid light fraction (4% increase) and heavy fraction and water (10%). Moreover the gas yield is reduced with almost 6%.

## 5.2 CATALYST INFLUENCE ON CHAR COMPOSITION AND PROPERTIES

The biochar obtained after each pyrolysis test was analyzed in terms of ash content, C. H, N, S content and FTIR. The properties of the biomass feedstock and corresponding biochar samples are listed in Table 18.

**Table 18. Proximate and ultimate analysis of char produced from each type of catalyst**

| | Ash content. wt% | C. % | H. % | N. % | S. % |
|---|---|---|---|---|---|
| No catalyst | 78 | 12.4 | 0.9 | 0 | 0 |
| Al-MCM-41 | 74.4 | 12 | 0.7 | 0.8 | 0 |
| HZSM-5 | 75.1 | 12.7 | 0.8 | 3.5 | 0 |
| ZSM-5 | 76.2 | 12.5 | 0.7 | 4.7 | 0 |
| CaO | 76.2 | 12.3 | 0.7 | 3.5 | 0 |

Press mud and powder vinasse feedstock showed significant difference of ash content when there were analyzed individually. Press mud had an ash content of 53.8wt% before pyrolysis and 83.6 wt% after conventional pyrolysis, while powder vinasse showed 20.5 wt% ash content before pyrolysis and 56.5 wt% after pyrolysis. The biochar formed from the mixture of 67% press mud and 33% powder vinasse had an ash content of 78wt%, in accordance with the previous results obtained. It was observed that ash content in biochar decreased when a catalyst was added in the reactor. The small decrease of ash content could be explained either by the variation of biomass mixture, either by a higher content of organic compounds that remained in biochar when the catalysts were used [44]. Carbon and hydrogen content in all biochar samples (with or without catalyst) did not show any significant variation. Nitrogen content in biochar samples obtained after biomass pyrolysis in the presence of ZSM-5/HZSM-5, as well as CaO catalysts showed a significant increase compared with the biochar sample obtained without a catalyst or in the presence of Al-MCM-41. Taking into consideration that nitrogen content showed high variation also in the previous pyrolysis tests (see Chapter 4.2), it could be that the high nitrogen content is no necessarily due to the presence of the catalyst, but due to incomplete homogenization of the sample.

Three samples of biomass mixture (press mud and powder vinasse) have been analyzed by FTIR (Figure 23).Similar as in case of previous FTIR analysis on biomass feedstock, it has been identified a very small peak in the region 3750-3800 cm$^{-1}$ related to the presence of water. The broad peak from 3000-3700 cm$^{-1}$ can be attributed to O-H bond, while the sharp peaks from 2850-3000 cm$^{-1}$ are related to the bending and stretching of C-H from aliphatic and aromatic ring vibration from cellulose, hemicellulose, lignin [54], The peak in the region of 1500-1800 cm$^{-1}$ corresponds to C=O stretching from hemicellulose and lignin, while the small peak from 1420 cm$^{-1}$ which is characteristic to C-H deformation of the aromatic ring from lignin [46, 47, 55]. The peak from 1030 cm$^{-1}$ can be assigned to C-O stretching vibration from polysaccharides [54, 56].

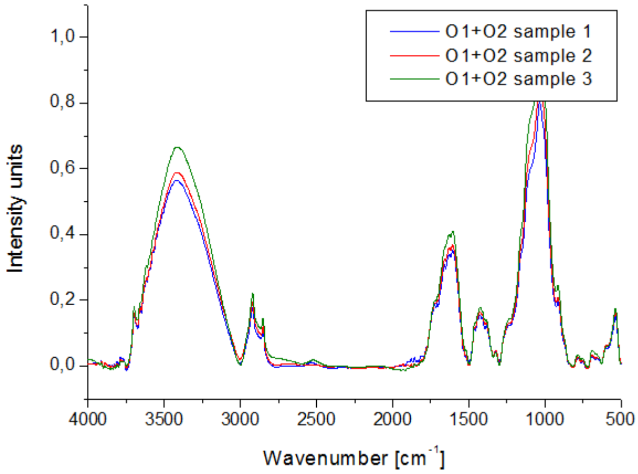


**Figure 23. FTIR spectra of biomass mixture feedstock (Press mud: O1. Powder vinasse: O2)**

The biochar from each pyrolysis test (using different catalyst) were analyzed in terms of FTIR (Figure 24). All biochar samples showed the significant reduction of the peak characteristic to O-H stretching and the disappearance of the peak associated to of C-H from aliphatic and aromatic ring, indication of the degradation of cellulose, hemicellulose and lignin. The peak characteristic to C=O stretching (1500-1800 cm$^{-1}$) reduced in intensity in case of all the biochar samples, with the increase in intensity of the peak from 1030 cm$^{-1}$ (assigned to C-O stretching). All biochars showed the presence of organic components, indicating that material can still undergo further degradation (in accordance with the proximate and ultimate analysis performed). The biochar obtained using ZSM-5 as catalyst presented the highest degradation of the organic components, showing only the peak at 1030 cm$^{-1}$ characteristic to C-O stretching vibration from polysaccharides. Based on the results presented above, ZSM-5 could represent a good candidate as catalyst for conventional biomass pyrolysis with high probability of complete degradation of organic matter (ZSM-5 showed also the lowest char yield and the highest gas yield compared with the other catalysts; a lower N2 flow might facilitate the condensation of the volatiles. with the increase of liquid light fraction yield).

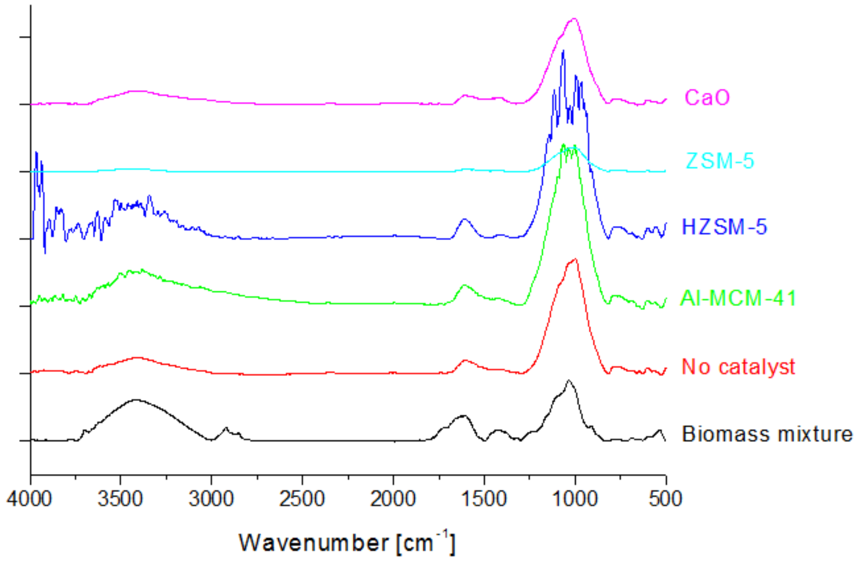
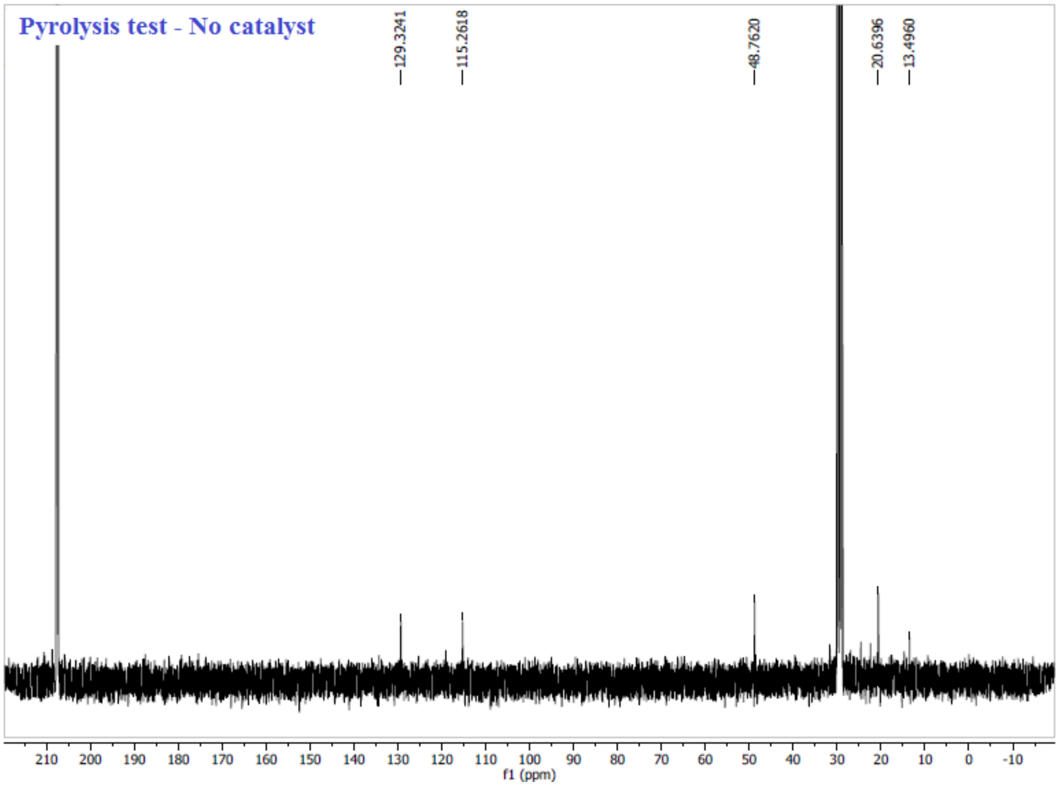
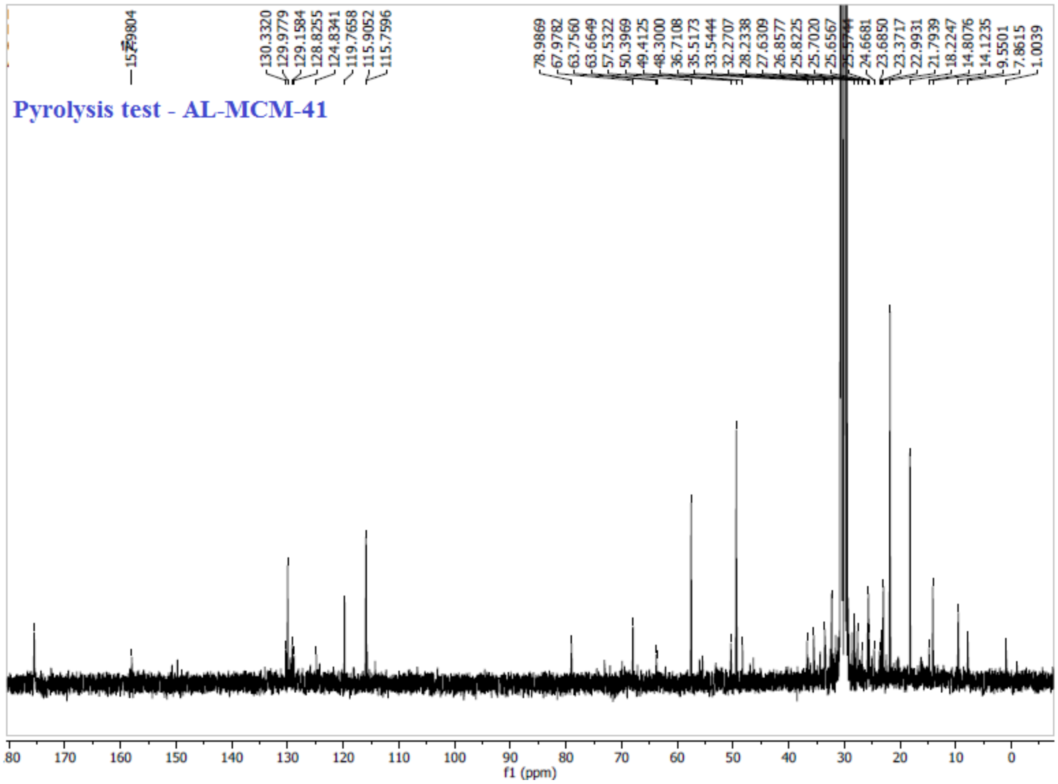


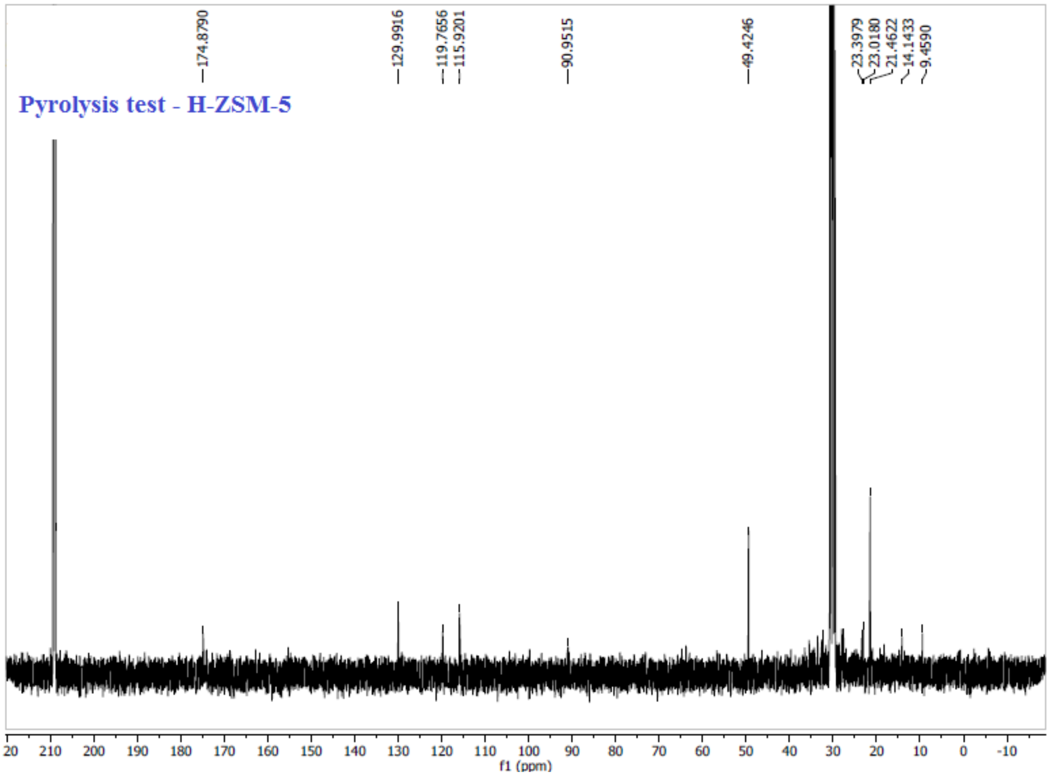
**Figure 24. FTIR spectra of biochar obtained by using different catalysts**

## 4.3 CATALYST INFLUENCE ON PYROLYSIS OIL COMPOSITION

The functional groups from bio-oil produced from each pyrolysis test, with or without catalyst have been determined by $^{13}$C-NMR (Figure 25).




Pyrolysis test - AL-MCM-41
157.9804
130.3320
129.9779
129.1584
128.8255
124.8341
119.7658
115.9052
115.7596
78.9869
67.9782
63.7560
63.6649
57.5322
50.3969
49.4125
48.3000
36.7108
35.5173
33.5444
32.2707
28.2338
27.6309
26.8577
25.8225
25.7020
25.6567
25.5744
24.6681
23.6850
23.3717
22.9931
21.7939
18.2247
14.8076
14.1235
9.5501
7.8615
1.0039
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Pyrolysis test - H-ZSM-5
174.8790
129.9916
119.7656
115.9201
90.9515
49.4246
23.3979
23.0180
21.4622
14.1433
9.4590
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

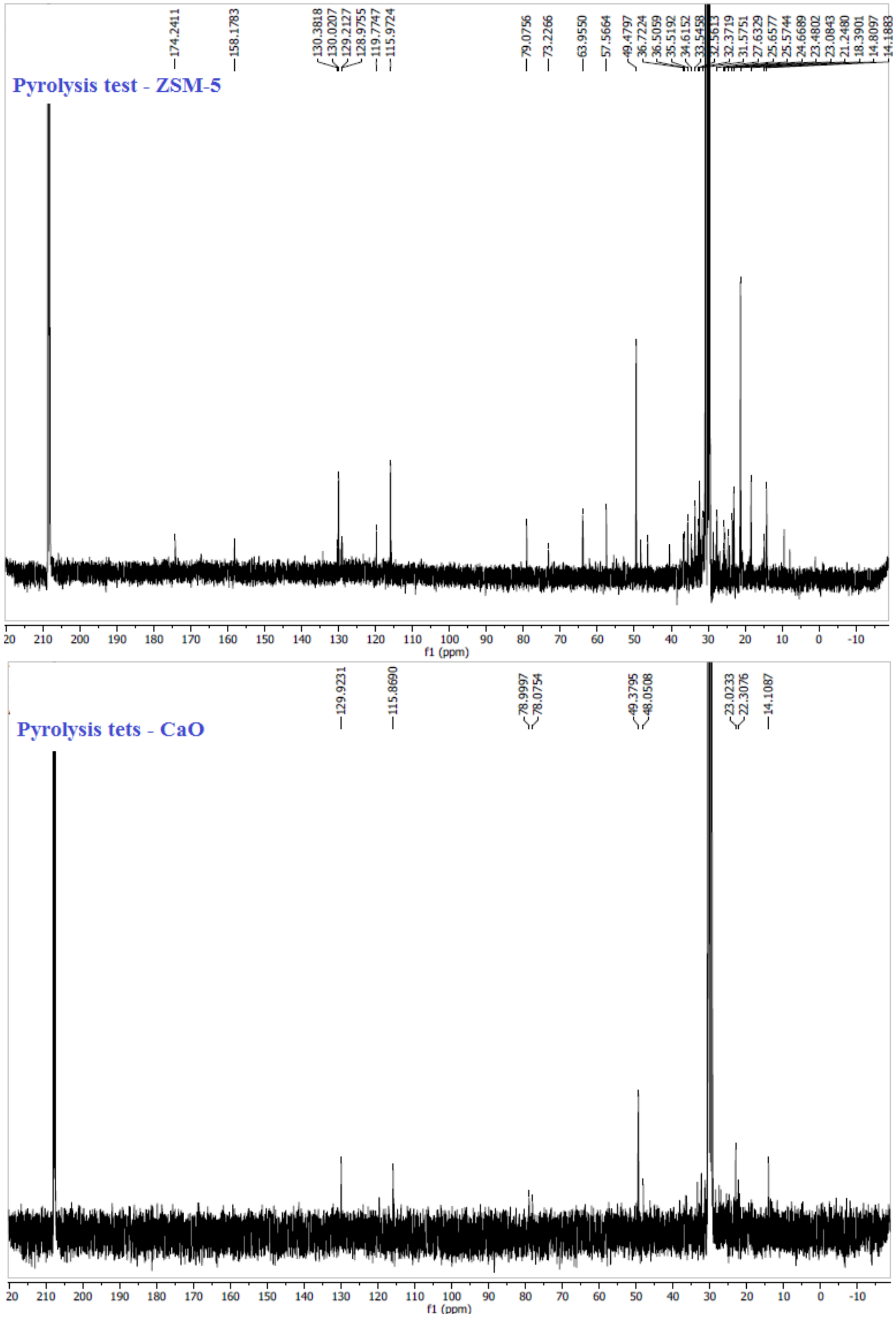


**Figure 25.** $^{13}$**C-NMR spectra of bio-oil produced using different catalyst systems**

It has been observed that when pyrolysis tests have been performed without any catalyst, the bio-oil showed the highest intensity on the peaks characteristic to aliphatic (13-48.8 ppm) and aromatic components (115.2 ppm. 129.3 ppm). The bio-oil produced when Al-MCM-41 catalyst was used as catalyst presents also peaks characteristic to methoxy components (50.4-57.5 ppm), carbohydrates (63.6-78.9 ppm) and carbonyl compounds (157.9 ppm). Similar chemical composition was observed also for bio-oil produced with ZSM-5 catalyst, while when ZSM-5 was hydrogenated as pretreatment step before pyrolysis. it has been observed peaks with lower intensity on carbonyl and aromatic components. Bio-oil obtained with CaO catalyst presented a very similar chemical composition with the one obtained without any catalyst.

For a closer look on the composition of pyrolysis liquid obtained with and without catalyst. GC-MS analyses have been performed on the liquid light fraction, as well as liquid heavy fraction. Moreover the ethanol collected from the gas scrubber from each pyrolysis experiment was also analyzed by GC-MS. The composition of the liquid collected from gas scrubber is presented in Table 19. Although the GC-MS analyses of the organic retained in ethanol scrubber can be looked only in a qualitative manner, the results demonstrate the impact of using each catalyst on the pyrolysis of press mud and powder vinasse mixture. It has been observed that the addition of catalysts decreased significantly the content of phenol components in ethanol scrubber and increased the content of benzene and cyclopentane compounds. All the catalysts increased also the content of alkanes and alkenes. In particular, Al-MCM-41 and ZSM-5 showed the highest content of alkanes and alkenes.

**Table 19. Composition of liquid from gas scrubber**

| Composition. mass% | **No catalyst** | **AL-MCM-41** | **H-ZSM-5** | **ZSM-5** | **CaO** |
|---|---|---|---|---|---|
| Cyclopentanone compounds | **8.29** | **6.06** | **10.14** | **7.01** | **10.01** |
| Cyclopentene-1-one compounds | **18.22** | **7.96** | **25.64** | **17.39** | **12.86** |
| Benzene | **0.19** | **2.86** | **7.55** | **3.41** | **10.18** |
| Naphthalene | **0.67** | **3.80** | **1.71** | **0.79** | **0.57** |
| Phenol | **11.84** | **8.46** | **9.12** | **3.56** | **6.53** |
| Benzofuran | **0.98** | **0.54** | **0.92** | **0.42** | **0.00** |
| Furan compounds | **1.26** | **0.00** | **2.49** | **0.00** | **0.64** |
| Furanone | **0.97** | **2.20** | **0.00** | **0.00** | **0.00** |
| Pyrrole | **5.60** | **2.51** | **5.60** | **0.21** | **10.77** |
| Pyridine | **2.09** | **15.56** | **0.00** | **0.00** | **0.00** |
| Pyrazine | **0.49** | **0.43** | **0.00** | **0.00** | **0.00** |
| Cyclohexene | **3.02** | **0.49** | **0.59** | **0.41** | **1.70** |
| Cyclopentanedione | **2.12** | **0.00** | **0.00** | **7.20** | **0.00** |
| Cyclobutylamine | **2.25** | **0.00** | **0.00** | **0.00** | **0.00** |
| Propanone compounds | **1.39** | **2.77** | **0.00** | **0.00** | **0.00** |
| Hexanone | **0.18** | **0.00** | **0.00** | **0.00** | **1.92** |
| Alkanes | **15.79** | **24.01** | **16.26** | **24.60** | **19.22** |

| | | | | | |
|---|---|---|---|---|---|
| Alkenes | **7.42** | **6.46** | **9.09** | **6.10** | **13.45** |
| Alkynes | **1.26** | **0.44** | **0.00** | **1.44** | **0.00** |
| Carboxylic acids | **0.58** | **0.00** | **0.00** | **9.02** | **0.00** |
| Carboxylic acids esters | **3.74** | **0.90** | **1.48** | **0.86** | **0.29** |
| Toluene | **0.00** | **0.00** | **0.00** | **0.30** | **3.22** |
| Butanedione | **0.00** | **0.00** | **0.00** | **5.97** | **0.00** |
| Alcohols | **0.28** | **0.47** | **0.00** | **0.00** | **0.69** |
| Diols | **1.22** | **0.00** | **0.00** | **0.00** | **0.00** |
| Indane | **0.00** | **0.20** | **0.00** | **0.00** | **0.00** |
| Indene | **0.30** | **0.61** | **1.76** | **1.52** | |
| Xylenes | **0.00** | **3.72** | **0.00** | **0.00** | **0.00** |
| Aziridines | **0.00** | **0.60** | **0.00** | **0.00** | **0.00** |
| Other ketones | **1.50** | **2.72** | **2.89** | **1.52** | **1.48** |
| Other aromatics | **1.44** | **0.23** | **1.61** | **0.00** | **0.00** |
| Other | **6.49** | **6.02** | **3.28** | **6.48** | **4.11** |

The liquid heavy fraction collected from 1st condenser for each pyrolysis test was analyzed by GC-MS. The results presented in Table 20 show that heavy fraction obtained from pyrolysis of press mud and powder vinasse without any catalyst contained mostly phenols, aromatic compounds (in particular cyclopentanes) and nitrogen components (pyridine, pirazines, aziridines, oxazoles). When Al-MCM-41 was used as catalyst for pyrolysis, it has been observed a significant decrease of phenols (almost 45% decrease), furans and benzenes. In the same time the content of cyclopentene compounds increased almost 8 times, ketones (propanone, butanone, pentanone) with 6 times, indicating that Al-MCM-41 favored further decomposition of heavier phenols. Similar results have been presented also by Adam et al [57] – using AL-MCM-41 (Si:Al 20) pure phenol increased with the decrease of heavier phenols. Moreover, Al-MCM-41 favored the formation of carboxylic acids. Is it considered that higher amount of organic acids has a negative impact over the engines during combustion of bio-oils (can cause severe corrosion) [57]. When H-ZSM-5 and CaO have been used as catalysts, the content of phenols decreased even more, with the increase of lighter aromatics. The decrease of phenols and increase of aromatics with H-ZSM-5 and CaO catalysts have been reported by Iliopoulou et al [58] and Mahadevan et al [59]. Higher content of nitrogen compounds have been detected in heavy fraction when both CaO and H-ZMS-5 catalysts have been used. Taking into consideration that biomass wastes showed only up to 2% N into their composition, it could be possible that these catalysts promote the interaction of the pyrolysis gas with nitrogen used as carrier gas, especially as the catalyst was placed on the top of biomass bed. For these reasons, for the next experiments it will be necessary for the catalyst to be blended with the biomass in order to avoid any possible side reactions. Moreover, the carrier gas should be changed with Argon in order to make sure that no side reaction of pyrolysis vapors will occur with carrier gas. When ZSM-5 non-protonated form was used as catalyst, it has been observed a significant increase of “desirable” hydrocarbons (alkanes and alkenes – 14.7%) and alcohols. Moreover the heavy fraction obtained with ZSM-5 showed the lowest content of aromatics (9,2 wt%).

**Table 20. Composition of liquid heavy fraction**

| Composition. mass% | No catalyst | AL-MCM-41 | H-ZSM-5 | ZSM-5 | CaO |
|---|---|---|---|---|---|
| Cyclopentene-1 compounds | **1.77** | **14.58** | **13.01** | **8.41** | **22.08** |
| Cyclopentanone compounds | **0** | **0** | **10.5** | **0** | **11.69** |
| Pyridine | **17.5** | **19.29** | **15.59** | **33.44** | **2.92** |
| Phenol | **25.56** | **14.31** | **6.02** | **6.35** | **9.81** |
| Benzofuran | **1.04** | **0.39** | **0.61** | **0.6** | **0.59** |
| Aziridines | **0** | **0.82** | **3.94** | **0** | **5.52** |
| Naphthalene | **0** | **0** | **0.14** | **0.29** | **0.23** |
| Oxazoles | **0** | **3.37** | **18.69** | **0** | **35.28** |
| Furanone | **0** | **1.59** | **1.83** | **2.7** | **0.00** |
| Furan compounds | **4.99** | **0** | **0** | **0** | **0.00** |
| Carboxylic acids | **0.79** | **2.25** | **0.33** | **8.68** | **0.00** |
| Carboxylic acids esters | **0.47** | **1.25** | **0.37** | **0.33** | **0.26** |
| Alkanes | **2.4** | **3.48** | **4** | **3.37** | **1.97** |
| Alkenes | **0.41** | **0.35** | **0.81** | **11.34** | **1.12** |
| Alkynes | **0.83** | **0** | **0** | **0** | **0.00** |
| Diols | **0** | **1.02** | **2.17** | **8.7** | **1.20** |
| Nitriles | **0.22** | **0.56** | **0.35** | **0.36** | **0.12** |
| Cyclopentanediones | **10.12** | **0** | **0** | **0** | **1.35** |
| Hexanone | **2.28** | **0** | **0** | **0** | **0.00** |
| Pyrazines | **7.23** | **0** | **0.51** | **0** | **0.00** |
| Pyrazole | **1.35** | **0** | **2.26** | **0** | **0.00** |
| 2-Hexen-1-ol. | **0** | **0** | **10.97** | **0** | **0.00** |
| Butyrolactone | **8.7** | **5.65** | **0** | **0** | **0.00** |
| Pentin-2-ol | **5.34** | **0** | **0** | **0** | **0.00** |
| Propane. 2.2-diethoxy- | **0** | **12.99** | **0** | **0** | **0.00** |
| Isocyanates | **2.97** | **0** | **0** | **0** | **0.00** |
| Propanone compounds | **0** | **8.44** | **2.48** | **0** | **0.00** |
| Butanone compounds | **0** | **2.96** | **0** | **0** | **0.00** |
| Other ketones | **0** | **1.66** | **0.79** | **0.12** | **0.60** |
| Other aromatics | **0** | **1.79** | **0** | **0.81** | **1.22** |
| Other | **6.04** | **3.29** | **4.63** | **14.51** | **4.06** |

The composition of liquid light fraction (bio-oil) determined from GC-MS analysis and the amount of liquid collected from each condenser represents more accurate and quantitative results. As a general trend, all the catalysts promoted the cracking of heavier aliphatic hydrocarbons and phenols, aromatics with the formation of lighter hydrocarbons, ketones (C3-C5 compounds), alcohols and diols, furans, benzene and toluene. All the bio-oil samples showed a small content of PAH (poly aromatic hydrocarbons – naphthalene, indene) which is beneficial for the quality of bio-oil as fuel. The lowest content of PAH was obtained with no catalyst, CaO and ZSM-5 catalyst. Al-MCM-41 favored the formation of the highest amount of bio-oil with lowest content of aliphatic hydrocarbons (16.8%), but high content of carboxylic acids (11.6%), toluene (8.6%), nitrogen components like pyridine (8.2%), oxazoles (5.4%), aziridines (2.2%). ZSM-5 and H-ZSM-5 determined the decrease of bio-oil amount and the increase of pyrolysis gas yield (suggesting a more severe cracking), however in terms of the quality, the bio-oils have higher content of aliphatic hydrocarbons (H-ZSM-5 – 23.5%), high content of pure phenol (could be valuable as chemical), toluene and benzene (in case of both catalysts) and pyridine (6.3-6.8%). The content of carboxylic acids is also significantly lower compared with the other bio-oil samples. The protonated form H-ZSM-5 shows a lower degree of cracking than ZSM-5, being more preferred as catalyst for pyrolysis tests. The lowest amount of bio-oil was produced when CaO was used as catalyst. Although the bio-oil contains a significant amount of aliphatic hydrocarbons (26.8%), the high content of carboxylic acids (13.2%) could have a negative impact if the bio-oil is used as fuel.

**Table 21. Composition of liquid light fraction**

| Composition. mass% | **No catalyst** | **AL-MCM-41** | **H-ZSM-5** | **ZSM-5** | **CaO** |
|---|---|---|---|---|---|
| Acetaldehyde, ethylidenehydrazone | 0.08 | 0.00 | 0.00 | 0.26 | 0.84 |
| Propen-1-amine | 1.17 | 1.53 | 0.71 | 1.65 | 2.58 |
| Cyclopentanone compounds | 15.69 | 5.95 | 4.90 | 1.96 | 2.43 |
| Cyclopentene-1-one compounds | 9.65 | 3.72 | 6.08 | 3.69 | 4.33 |
| Pentanone compounds | 0.46 | 4.93 | 2.04 | 0.74 | 4.83 |
| Furan compounds | 0.42 | 3.35 | 2.37 | 0.61 | 0.80 |
| Phenol | 11.46 | 8.83 | 10.51 | 7.87 | 3.90 |
| Toluene | 0.00 | 8.66 | 8.99 | 10.23 | 7.57 |
| Oxazoles | 0.21 | 5.38 | 1.50 | 5.21 | 2.28 |
| Cyclopentanediones | 0.30 | 0.65 | 1.73 | 1.33 | 0.94 |
| Aziridines | 0.91 | 2.17 | 2.92 | 2.26 | 1.44 |
| Benzene compounds | 4.49 | 3.14 | 9.22 | 11.92 | 5.43 |
| Naphthalene | 0.14 | 0.91 | 1.29 | 0.73 | 0.18 |
| Carboxylic acids | 0.05 | 11.63 | 5.81 | 3.74 | 13.12 |
| Carboxylic acids esters | 4.21 | 1.25 | 0.30 | 2.11 | 2.47 |
| Alkanes | 27.44 | 12.46 | 19.29 | 13.54 | 15.67 |
| Alkenes | 7.81 | 3.62 | 4.16 | 3.29 | 10.88 |
| Alkynes | 0.00 | 0.81 | 0.05 | 0.03 | 0.28 |
| Pyridine | 1.90 | 8.20 | 6.31 | 6.87 | 5.32 |
| Creatine | 0.00 | 0.00 | 0.98 | 1.44 | 0.27 |
| Pyrazines | 0.00 | 0.27 | 0.00 | 0.17 | 0.12 |
| Pyrazole | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 |

| | | | | | |
|---|---|---|---|---|---|
| Pyrrole | 0.00 | 0.00 | 0.20 | 0.57 | 2.11 |
| Piperidine | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 |
| Proline | 0.00 | 0.00 | 0.10 | 0.00 | 0.00 |
| Pyrrolin | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Pyrrolidine | 0.03 | 0.00 | 0.00 | 0.64 | 0.00 |
| Picoline | 0.00 | 0.71 | 0.00 | 0.00 | 0.00 |
| 2-Hexen-1-ol, | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Butyrolactone | 0.49 | 0.34 | 1.47 | 1.99 | 0.00 |
| Propen-1-amine | 1.17 | 1.53 | 0.71 | 1.65 | 2.58 |
| Cyclohexen-1-one compounds | 0.07 | 0.25 | 1.01 | 1.31 | 0.00 |
| Furanone | 0.08 | 0.18 | 0.00 | 1.22 | 0.00 |
| Indene | 0.00 | 0.00 | 1.42 | 0.00 | 0.00 |
| Benzofuran | 0.17 | 0.07 | 0.35 | 0.12 | 0.00 |
| Caprolactam | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Alcohols | 0.39 | 0.70 | 0.63 | 0.15 | 0.00 |
| Diols | 2.99 | 0.00 | 0.23 | 2.01 | 0.07 |
| Nitriles | 0.24 | 0.49 | 0.25 | 0.29 | 0.88 |
| Acetaldehyde, ethylidenehydrazone | 0.08 | 0.00 | 0.00 | 0.26 | 0.84 |
| Propanone compounds | 0.06 | 0.00 | 0.00 | 0.49 | 0.95 |
| Butanone compounds | 0.00 | 0.00 | 0.00 | 0.00 | 0.16 |
| Other ketones | 0.33 | 0.96 | 0.90 | 1.61 | 0.62 |
| Other aromatics | 1.31 | 2.93 | 1.86 | 3.03 | 2.33 |
| Other | 7.44 | 5.94 | 2.40 | 6.88 | 7.21 |

## 4.4 RECOMMENDATIONS FOR CATALYST FOR NEXT CONVENTIONAL PYROLYSIS TESTS

Based on results presented above, the following observations can be concluded:

- Al-MCM-41 catalyst was the most efficient in the increase of liquid light and heavy fraction and water; the char and gas yield have been reduced compared with the pyrolysis experiment without any catalyst; however the product yields were not significantly affected neither by the other catalysts; ZSM-5 showed the lowest char yield with the increase of gas yield, indicating a more severe cracking; the protonated form H-ZSM-5 showed less severe cracking, showing higher content of liquid and less gas yield compared with ZSM-5; CaO showed the lowest liquid yield from all the catalysts;
- biochar obtained when catalysts have been used in pyrolysis tests showed lower ash content and significantly higher nitrogen content (for H-ZSM-5, ZSM-5 and CaO), being an indication that organic components remained in the char (possible also as the catalyst was placed on the top of the biomass bed); These results have been proved also by FTIR analysis;
- The biochar obtained using ZSM-5 as catalyst presented the highest degradation of the organic components, when analyzed by FTIR. ZSM-5 could represent a good candidate as catalyst for

conventional biomass pyrolysis with high probability of complete degradation of organic matter; lower N2 flow might facilitate the condensation of the volatiles. with the increase of liquid light fraction yield;

- The GC-MS analysis of liquid from gas scrubber showed that the addition of catalysts decreased significantly the content of phenol components and increased the content of benzene and cyclopentane compounds. All the catalysts increased also the content of alkanes and alkenes (In particular, Al-MCM-41 and ZSM-5); the analysis of liquid from gas scrubber demonstrates that part of organic components (aliphatic hydrocarbons, aromatics, nitrogen compounds) are not condensed on the condensation system most probably due to the high carrier gas flow;
- The composition of bio-oil by GC-MS showed that all the catalysts promoted the cracking of heavier aliphatic hydrocarbons and phenols, aromatics with the formation of lighter hydrocarbons, ketones (C3-C5 compounds), alcohols and diols, furans, benzene and toluene. Moreover, all the bio-oil samples presented small content of PAH, which could be beneficial if the bio-oil is used as fuel; Al-MCM-41 determined bio-oil with low content of aliphatic hydrocarbons, but high content of carboxylic acids, toluene, nitrogen components (pyridine, oxazoles, aziridines). The protonated form H-ZSM-5 showed lower degree of cracking than ZSM-5 with higher content of aliphatic hydrocarbons, pure phenol, toluene, benzene and pyridine; the bio-oil from CaO contained significant amount of aliphatic hydrocarbons and carboxylic acids;

Based on the results, we are considering the following recommendations:

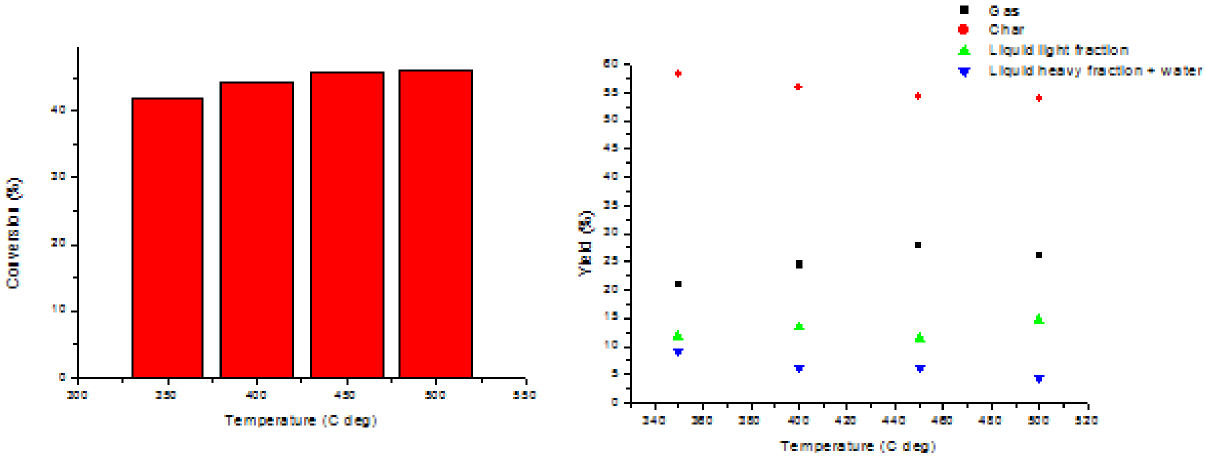
- conventional pyrolysis tests could be performed without any catalyst, as the products yields does not change significantly and the bio-oil contains desirable compounds in order to be used as fuel;
- any of the studied catalysts promotes further decomposition of the heavier hydrocarbons; ZSM-5 and CaO show the lowest bio-oil yield, with high content of carboxylic acids; these two catalysts could be used in case there is interest in obtaining valuable chemicals from conventional pyrolysis of biomass wastes – toluene and benzene for ZSM-5, carboxylic acids, alkanes and alkenes for CaO;
- Al-MCM-41 and H-ZSM-5 are more suitable for production of higher bio-oil yield suitable as fuel; as Al-MCM-41 is economically significantly more expensive than H-ZSM-5 (and the bio-oil yield is only with 8% higher than in case of H-ZSM-5), the next conventional tests could be performed using H-ZSM-5 catalyst (which will decompose phenols and heavier aromatics to lighter fractions); As all the catalysts presented high content of nitrogen components into bio-oil composition, as well as biochar, the carrier gas will be changed with Argon and catalyst will be mixed with the biomass.

## 6. CONVENTIONAL BIOMASS PYROLYSIS –INFLUENCE OF OPERATING CONDITIONS

### 6.1 INFLUENCE OF OPERATING TEMPERATURE OVER CONVENTIONAL BIOMASS PYROLYSIS

For the determination of operating conditions over product distribution and composition, the same biomass mixture as in Chapter 5 has been used: 67% press mud and 33% powder vinasse. For all tests H-ZMS-5 has been used as catalyst, based on the previous results. For operating temperature variation the following temperatures have been tested: 350 °C, 400 °C, 450 °C, 500 °C, while the rest of the conditions have been kept constant: 50 g biomass mixture , catalyst 5 wt%, atmospheric pressure, 50 L/h Ar flow, 2 h reaction time.

The biomass conversion and pyrolysis products yield (gas, liquid and solid fraction) with temperature variation are presented in Figure 26. As it can be observed, the increase of temperature favored the conversion of biomass, with an increase with more than 10% of conversion from 350 °C to 500 °C. The maximum conversion was achieved at 500 °C (46.06%), although the conversion at 450 °C was with only 1% lower, meaning that biomass mixture is fully converted at 450 °C pyrolysis temperature. Regarding product distribution, the increase of operating temperature determined the decrease of biochar and liquid heavy fraction, with the increase of gas and liquid light fraction. The liquid light fraction and gas yields increased with almost 25% each from 350 °C to 500 C, while the heavy fraction yield decreased with 51%. Although as a general trend biochar yield decreased, even at 500 °C biochar yield was 53.9% due to the high content of ash present in the feedstock (Table 11). Similar results have been obtained also by Brech et al [26] when the yield of bio-oil and gas increased when operating temperature was increased from 300 C to 500 C, while char yield decreased drastically.



.

**Figure 26. Effect of temperature over conversion and product yield on biomass conventional pyrolysis**

Demirbas and Arin [60] showed that biochar yield decreased from 97% to 49% while the gas and liquid yields increased (for bio-oil the increase was from 0% to 35%) when temperature was increased from 235 °C to 410 °C. They also suggested that for a maximization of bio-oil yield biomass pyrolysis should be performed at low temperature with high heating rate, while for a high biochar production the pyrolysis should be performed at low temperature and heating rate. In case of our conventional pyrolysis tests, the heating rate could not be varied, due to the limitation of the electrical furnace. For all the experiments the heating rate was around 7-8 °C/min which could have favored the low bio-oil yield and high biochar content.

The biochar obtained after each pyrolysis test with operating temperature variation was analyzed in terms of C. H, N, S content and FTIR. The properties of the biomass feedstock and corresponding biochar samples are listed in Table 22.

**Table 22. Proximate and ultimate analysis of char produced during operating temperature variation**

| | C. % | H. % | N. % | S. % |
|---|---|---|---|---|
| Feedstock | | | | |
| Biochar at 350 °C | 21,31 | 1,37 | 0,26 | 0,68 |
| Biochar at 400 °C | 21,15 | 1,05 | 0 | 0,96 |
| Biochar at 450 °C | 21,65 | 0,87 | 0,06 | 0,22 |
| Biochar at 500 °C | 21,78 | 0,69 | 0,24 | 0,51 |

Increasing the operating temperature of conventional pyrolysis determined the increase of carbon content and decrease of hydrogen content. Similar results have been reported also by Al-Wabel et al [61] who considered the increase of carbon content with temperature due to increasing degree of carbonization. On the other hand the decrease of hydrogen content can be attributed to the clavage and cracking of weaker bonds in biochar structure with release of volatiles [43, 45, 61, 62]. Weber and Quicker [63] presented a clear representation of carbon and hydrogen content of biochar obtained from woody biomass pyrolysis with temperature variation (Figure 27). Compared with the previous results on elemental analysis, it can be observed a significant lowering of nitrogen content in biochar samples. There results could prove the beneficial effect have argon as inert gas, eliminating the risk of secondary reactions between nitrogen and organic compounds formed during pyrolysis with the possibility to conserve the nitrogenous compounds in biochar.

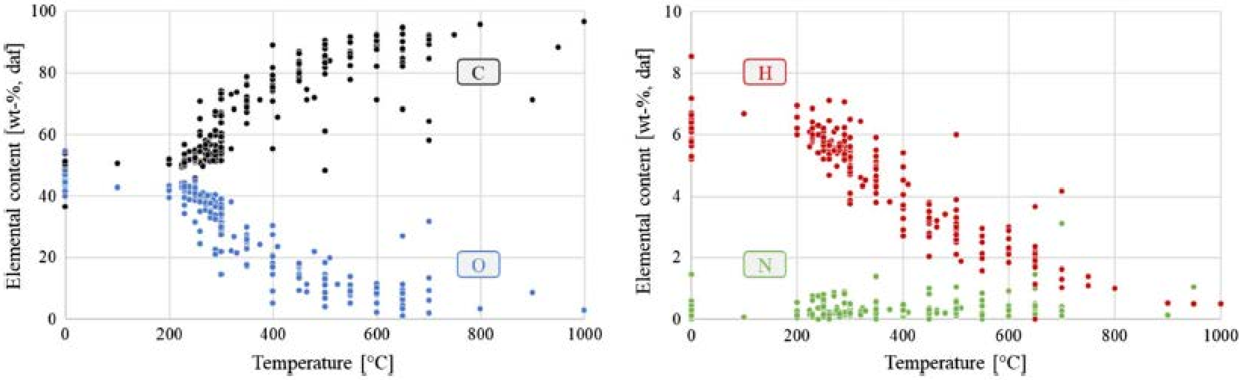
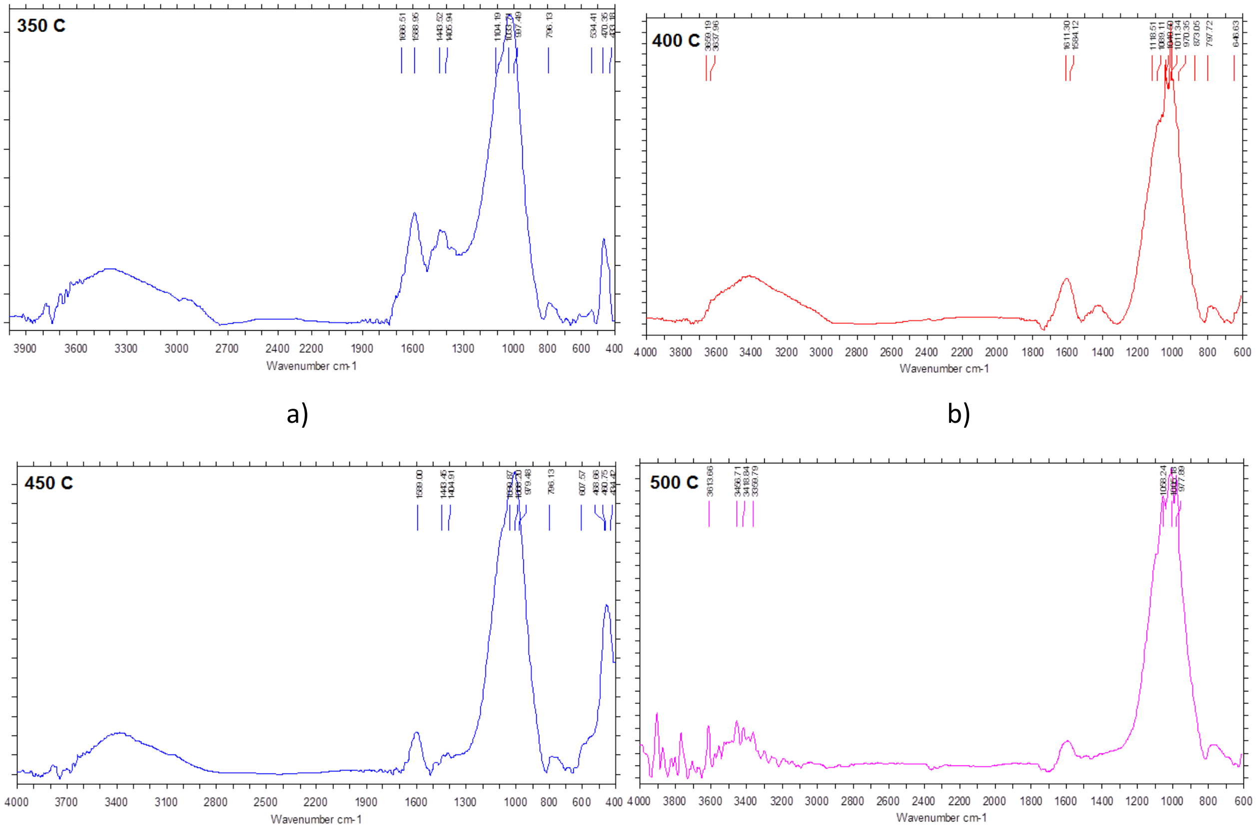


**Figure 27. Elemental analysis of biochar from biomass with operating temperature variation [63]**

The biochar from each pyrolysis test performed with temperature variation were analyzed in terms of FTIR (Figure 28). The O-H stretch peak from 3700-3000 $cm^{-1}$ gradually decreased with increasing of operating temperature, the peak being nearly absent at 500 °C, indication of the acceleration of dehydration reaction and ignition loss of OH group in biomass [61, 62]. The peak at 3000-2800 $cm^{-1}$ characteristic to C-H stretch vibration has been completely reduced with the increase of operating temperature. Similar, the C=O stretching vibration band from 1700-1500 $cm^{-1}$ characteristic to ketones, carboxylic acids and aldehydes [64] decreased in intensity with the increase of pyrolysis temperature. Only the peaks at 1100-1000 $cm^{-1}$ assigned to C-O stretching and the small peak at 800 $cm^{-1}$ characteristic to aromatic stretching vibration [64, 65] remained at the same intensity even at higher temperature – the peaks could suggest the presence of cellulosic and lingocellulosic constituents [61]that are not decomposed even at 500 °C.



a)

b)

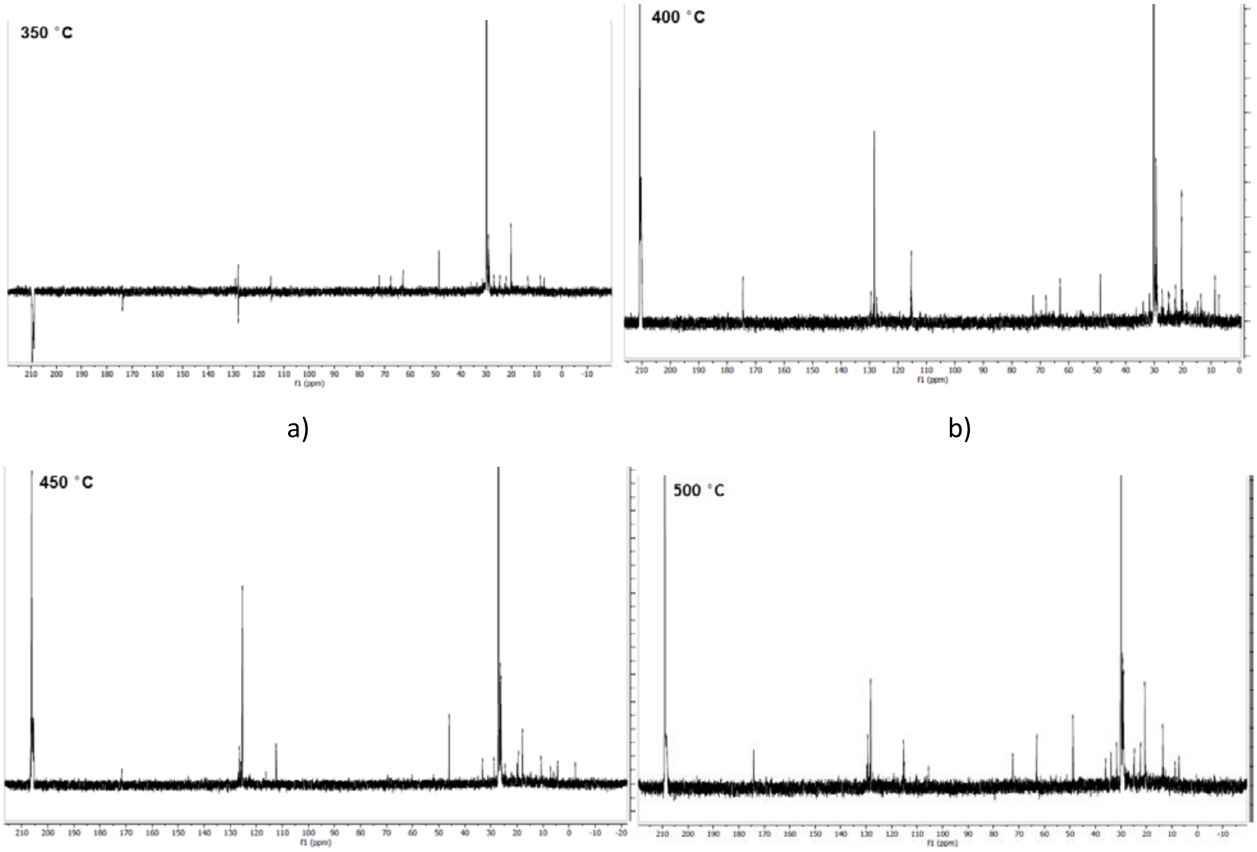
c)

d)

**Figure 28. Biochar FTIR with operating temperature variation**

a) biochar obtained at 350 °C; b) biochar obtained at 400 °C; c) biochar obtained at 450 °C; d) biochar obtained at 500 °C;

The functional groups from bio-oil produced from each pyrolysis test with temperature variation have been determined by $^{13}C$-NMR (Figure 29). The samples of bio-oil have been collected from the last condenser of the cooling system. Comparing the results, it has been observed that bio-oil at 350 °C contains in particular aliphatic compounds (mostly primary and secondary carbons) at 7-29 ppm, small intensity peaks between 62-72 ppm which suggest the presence of methoxy/hydroxyl compounds and between 115-129 ppm suggesting the presence of aromatics [49, 50]. On the other hand with th increase of operating temperature it has been observed the increase of aliphatic compounds (0-50 ppm) and aromatics (112-129 ppm). The bio-oil obtained at 500 °C shows also the presence of carbohydrates due to the presence of peak at 105 ppm. Moreover, starting with 400 C pyrolysis temperature, the bio-oil shows the presence of carboxylic acids and/or esters due to the peaks in the area of 171-174 ppm [50].



a) b)

c) d)

**Figure 29. $^{13}$C-NMR spectra of bio-oil produced during operating temperature variation**

a) bio-oil obtained at 350 °C; b) bio-oil obtained at 400 °C; c) bio-oil obtained at 450 °C; d) bio-oil obtained at 500 °C

A more details composition of light and heavy condensates obtained during conventional pyrolysis at different operating temperature has been determined by GC-MS analysis.

## 6.2 INFLUENCE OF INERT GAS FLOW OVER CONVENTIONAL BIOMASS PYROLYSIS

For these pyrolysis tests it has been used the following operating conditions: 50 g biomass mixture, catalyst 5 wt%, 500 °C, atmospheric pressure, 2 h reaction time, while argon flow varied at 18 L/h Ar flow, 36 L/h Ar flow, 50 L/h Ar flow, 60 L/h Ar flow. The conversion and product yield results are presented in Figure 30.

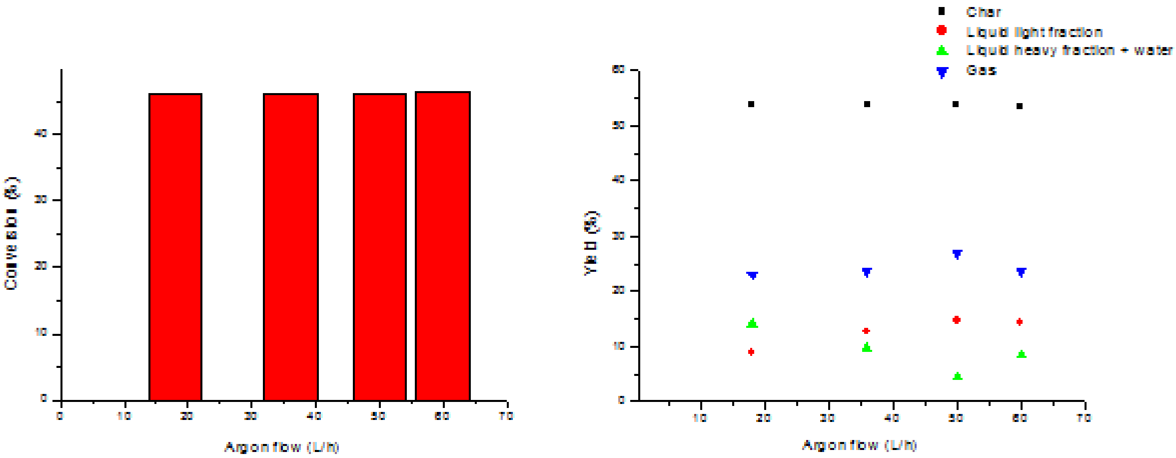


**Figure 30. Effect of gas flow over conversion and product yield on biomass conventional pyrolysis**

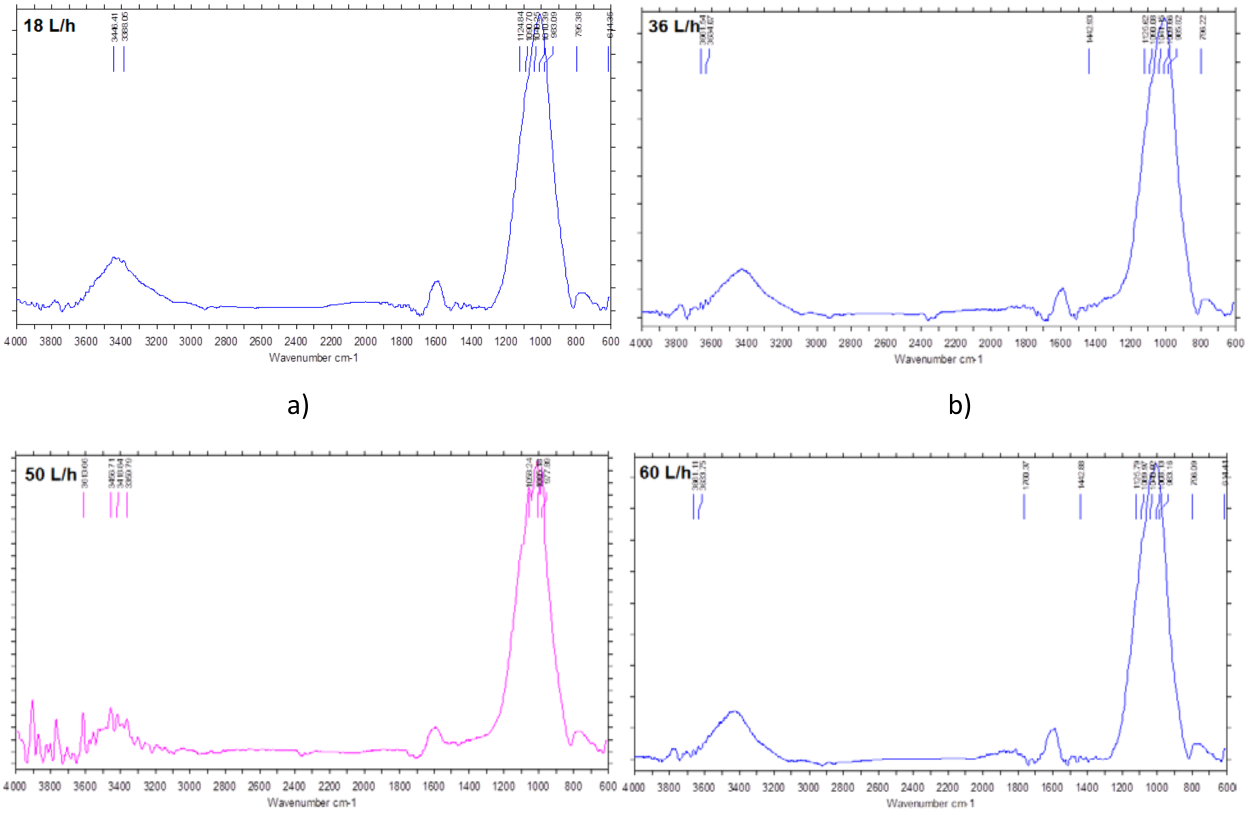
It has been observed that argon gas flow did not have any influence over conversion which maintained around 46% for all experiments. The biochar yield was neither affected by the variation of argon gas flow, in case of all the experiments that yield of biochar was between 53.6-53.9%. It has been observed that with the increase of argon flow, the gas yield as well as light liquid yield increased, while the content of liquid heavy fraction decreased. The higher inert gas flow facilitated fast removal of the pyrolysis gasses from the reactor, avoiding any polycondensation reactions. In the same time higher inert gas did not allow the condensation of the liquid fraction in the first two condensers from the cooling system, condensation being done mostly in condensers 3 and 4 and ethanol scrubber – this could explain higher content of liquid light fraction and lower liquid heavy fraction when 50-60 L/h argon flow was employed. At lowest argon flow – 18 L/h it was able to catch all the light and heavy condensates in the cooling system (with the maximum overall yield of 23.1%) and to reduce gas yield to 23%. When the gas flow was reduced to 18 L/h the majority of organics condensed in the first and second condensers (with the first condenser being attributed to liquid heavy fraction), thus the heavy condensate yield increased significantly to 14.1%. Considering the ability to condense most of the organic components released from pyrolysis into the first two condensers, it has been decided to use for the next pyrolysis tests 18 L/h as optimum argon flow, regardless the characteristics of biochar and bio-oil. Based on review of several researches on biomass pyrolysis, Tripathi et al [30] indicated that even low gas flow rate is sufficient to carry most of the vapors out of the reactor, resulting in high biochar yield. Guedes et al [66] demonstrated that depending on the residence time in reactor, the pyrolysis vapors can suffer secondary reactions of thermal cracking, repolymerization and recondensation of the char residue, determining the decrease of bio-oil yield, thus a fast removal of the vapors can minimize secondary reactions. Moreover it has been observed that bio-oil yield increased with the increasing of gas flow up to a point, after that limit higher gas flow did not affect the yield. Depending on the reaction type and size, even biomass type the optimum gas flow will vary. It has been also considered that high temperature in longer residence time is suitable for production of oxygen-free bio-oil.

The biochar obtained after each pyrolysis test with argon flow variation was analyzed in terms of C. H, N, S content and FTIR. The properties of the biomass feedstock and corresponding biochar samples are listed on Table 23.

**Table 23. Proximate and ultimate analysis of char produced during Argon gas flow variation**

| | C. % | H. % | N. % | S. % |
|---|---|---|---|---|
| Feedstock | | | | |
| Biochar at 18 L/h | 21,38 | 0,89 | 0 | 0,24 |
| Biochar at 36 L/h | 19,38 | 0,81 | 0 | 1,21 |
| Biochar at 50 L/h | 21,78 | 0,69 | 0,24 | 0,51 |
| Biochar at 60 L/h | 22,10 | 0,74 | 0,33 | 0 |

The results of elemental analysis show no correlation between the increase of Argon flow rate and the composition of biochar. The content of carbon and hydrogen showed variation with the increase of gas flow rate demonstrating that in case of our pyrolysis tests even 18 L/h might be a sufficient high flow that will carry the organics out from reactor without affecting the quality of the biochar.



a)

b)

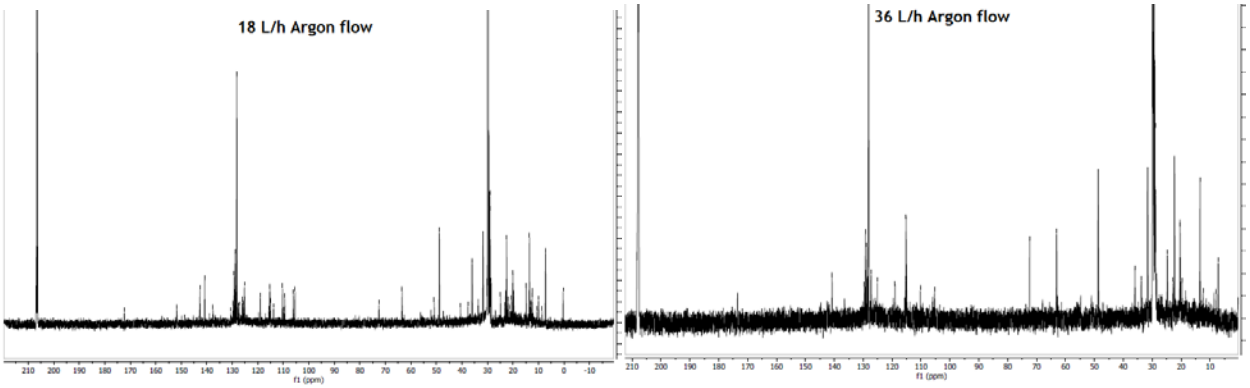
c) d)

**Figure 31. Biochar FTIR with gas flow rate variation**

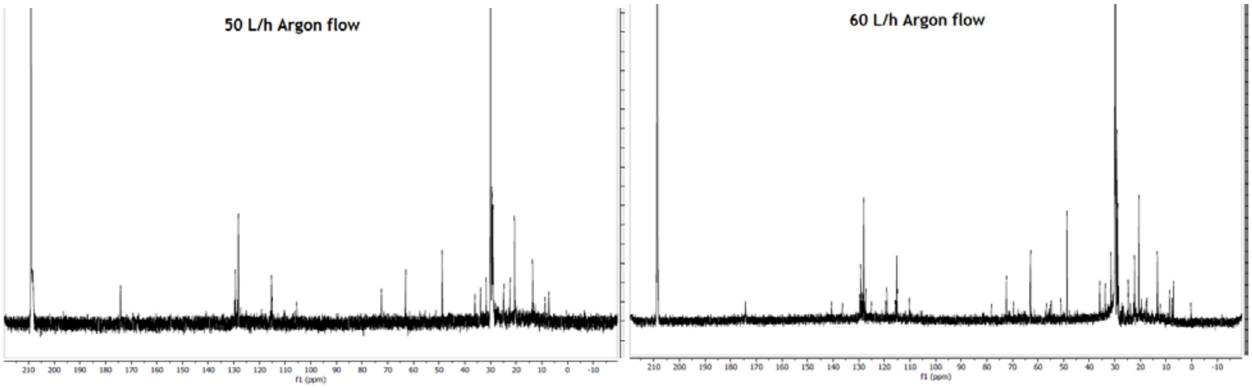
a) biochar obtained at 18L/h; b) biochar obtained at 36 L/h; c) biochar obtained at 50 L/h; d) biochar obtained at 60 L/h

The previous results on elemental analysis over biochar samples are supported also by FTIR analysis (Figure 31) which show that the composition of biochar did not changed with the increase of gas flow rate. In all biochar samples it has been observed the `peak between 3600-3200 cm$^{-1}$ characteristic to O-H stretching group, the small peak between 1700-1500 cm$^{-1}$ for C=O stretching, the large peak at 1250-960 cm$^{-1}$ of C-O-C group related to ether linkage present in carbohydrates derivates and the absorbance at 795 indicating the presence of aromatic hydrocarbons [67, 68].

The functional groups from bio-oil produced from each pyrolysis test with gas flow rate variation have been determined by $^{13}$C-NMR (Figure 32). At low Argon flow rate (18-36 L/h) it has been observed higher concentration of aliphatic compounds (0-50 ppm) and significant amount of aromatics (110-151 ppm), in particular in the bio-oil sample obtained at 18 L/h. The same sample it has been observed a clear presence of carbohydrates (105-109 ppm). A small peak around 173 ppm characteristic to carbonyl - carboxylic acids and/or esters [50] has been observed in all bio-oil samples. The bio-oil sample obtained with the highest gas flow 60 L/h show also the presence of methoxy from lignin due to the presence of peaks in the region 51-56 ppm. It could be possible that due to the high flow, the heavier components have been carried, condensing in the last condenser of the cooling system. Based on the $^{13}$C-NMR results the bio-oil samples obtained when lower gas flow rate was employed show more potential for formation of valuable organic compounds.



a) b)



c) d)

**Figure 32. $^{13}$C-NMR spectra of bio-oil produced during gas flow variation**

a) bio-oil obtained at 18 L/h; b) bio-oil obtained at 36 L/h; c) bio-oil obtained at 50 L/h; d) bio-oil obtained at 60 L/h

## 6.3 INFLUENCE OF CATALYSTAMOUNT OVER CONVENTIONAL BIOMASS PYROLYSIS

From the previous results presented on Chapter 5 it has been considered that HZSM-5 is the most suitable catalyst for the conventional pyrolysis of the biomass wastes. In order to determine the influence of the catalyst amount over biomass pyrolysis several tests have been performed – the following conditions have been applied 50 g biomass mixture, 500 °C, atmospheric pressure, 18 L/h Argon gas flow, 2 h reaction time, with catalyst amount varying – 5wt%, 10 wt%, 15 wt%, 20 wt% (from the mass of biomass introduced in the reactor). From Figure 33 it has been observed that maximum conversion of biomass was obtained when 20 wt% catalyst was employed (46.18 %), however a very similar conversion was obtained also when only 5 wt% catalyst was used for biomass pyrolysis. The results show that in case of our waste biomass samples (it has high amount of ash >40wt% and low content of cellulose, hemicellulose and lignin) the catalyst amount did not have an influence over conversion, but mostly on the product yield. Increasing the amount of catalyst mixed with biomass seemed to increase the liquid light fraction and decrease of liquid heavy fraction and gas yield – the higher content of catalyst facilitated the cracking of heavy hydrocarbons leading to light condensable components [69]. At 20wt% catalyst amount the maximum light condensate yield have been obtained (light 14.8%, total liquid yield 26.7%). High liquid yield (light + heavy 26.9%) has been obtained also when 10wt% catalyst has been used. Moreover at this content of catalyst it has been obtained the lowest gas yield (18%) and a char yield above 55%. Even though the light liquid yield at 10wt% catalyst was with 16% lower than the one obtained at 20wt%, from the economical perspective as ZSM-5 is quite expensive it can be considered more appropriate to use lower amount of catalyst 10wt% mixed with waste biomass from bioethanol industry for conventional pyrolysis – although the conversion might be a little reduced (up to 3% lower), it can be obtained a high liquid yield (more heavy components) and low gas yield. Tripathi et al [30] considered that a small amounts of catalyst mixed with the biomass can reduce the tar formation, enhancing the liquid yield while the gas and char yield are decreased. Balasundram et al [70] obtained similar results using a HZSM-5 catalyst modified with Cerium – increasing the amount of catalyst determined the increase of bio-oil yield by promoting the acid-catalyzing cracking of biomass components – hemicellulose, cellulose, lignin.

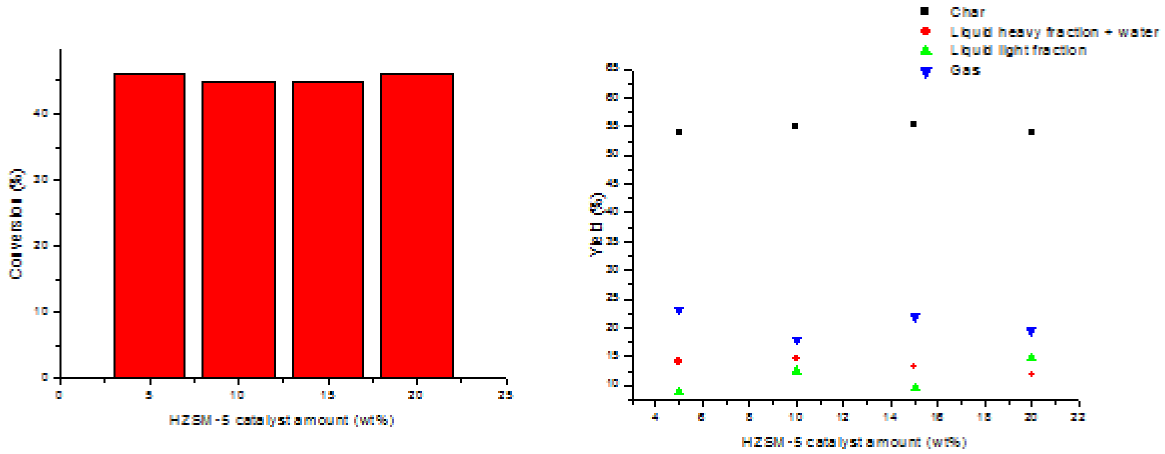


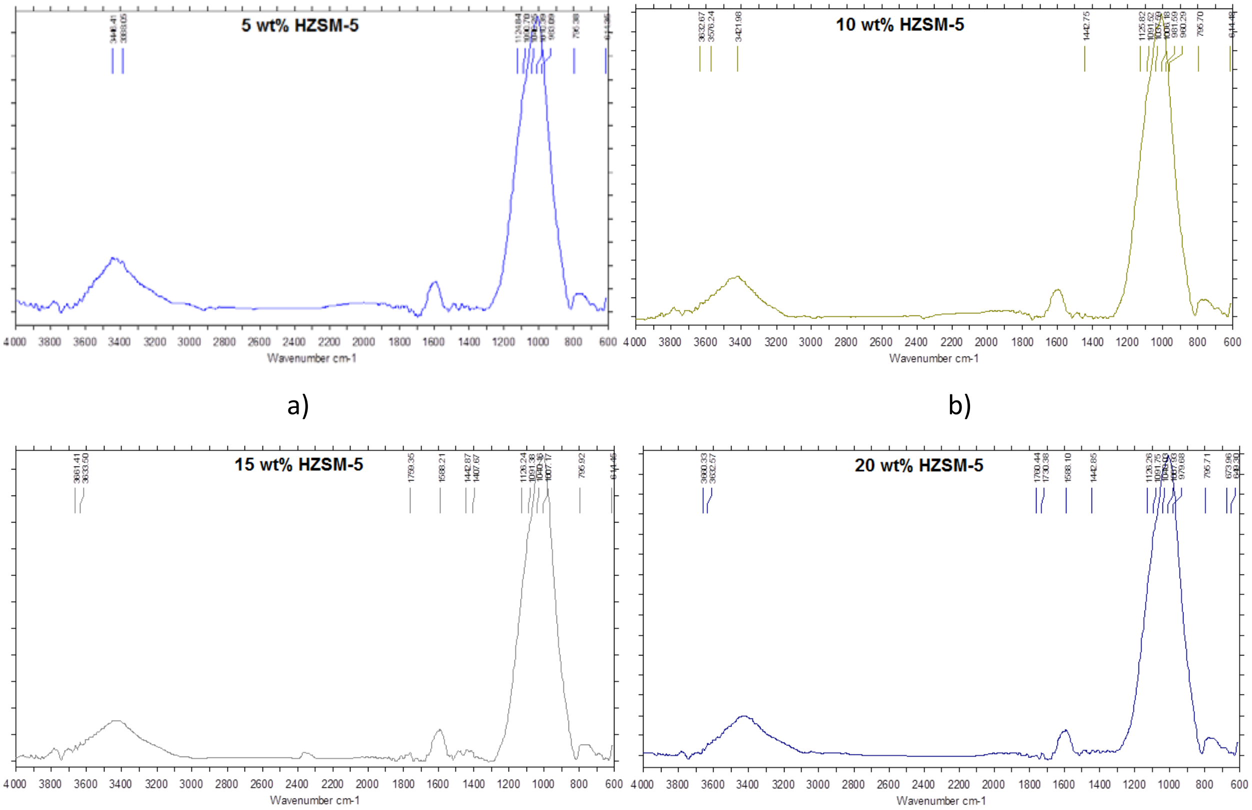
**Figure 33. Effect of catalyst amount over conversion and product yield on biomass conventional pyrolysis**

The biochar obtained after each pyrolysis test with HZSM-5 catalyst amount variation was analyzed in terms of C. H, N, S content and FTIR. The properties of the biomass feedstock and corresponding biochar samples are listed on Table 24. As it can be observed, the content of carbon seems to increase with the increase of catalyst amount, probably due to additional cracking reactions for decomposition of cellulose, hemicellulose and lignin. On the other hand the increase of carbon content is not as relevant, especially as in case of biochar obtained with 10wt% HZSM-5 catalyst showed the lowest carbon and hydrogen content. Sulfur content seemed not to be influenced as well by the amount of catalyst present in reactor. Only in case of nitrogen content the amount of catalyst in the biomass mixture seemed to have a clear influence – the nitrogen content increased gradually with catalyst amount. The catalyst might favor the conservation of nitrogen inside the complex structures of biomass that are resistant to heating and not easily volatilized [61].

**Table 24. Proximate and ultimate analysis of char produced during catalyst amount variation**

| | C. % | H. % | N. % | S. % |
|---|---|---|---|---|
| Feedstock | | | | |
| Biochar at 5 wt% HZSM-5 | 21,38 | 0,89 | 0 | 0,24 |
| Biochar at 10 wt% HZSM-5 | 20,00 | 0,67 | 0,15 | 0,58 |
| Biochar at 15 wt% HZSM-5 | 22,35 | 0,87 | 0,36 | 0 |
| Biochar at 20 wt% HZSM-5 | 22,33 | 0,87 | 0,56 | 0 |

When biochar samples have been analyzed by FTIR (Figure 34) it has been observed that the spectra looked very similar for all the samples – except for the sample at 5wt% HZSM-5 which showed higher intensity for the band at 3200-3600 cm-1 (O-H stretching vibration), the rest of the biochar samples showed lower intensity of the band in this region, suggesting a further decomposition of aromatic and aliphatic alcohols, in particular lignin [46]. The FTIR results prove that the conventional pyrolysis of biomass waste from bioethanol industry using can be performed in the presence of at least 10wt% HZSM-5 catalyst. From this amount above, the catalyst has no influence over the composition of the biochar. A more significant influence should be observed in the composition of bio-oil.



a) b)

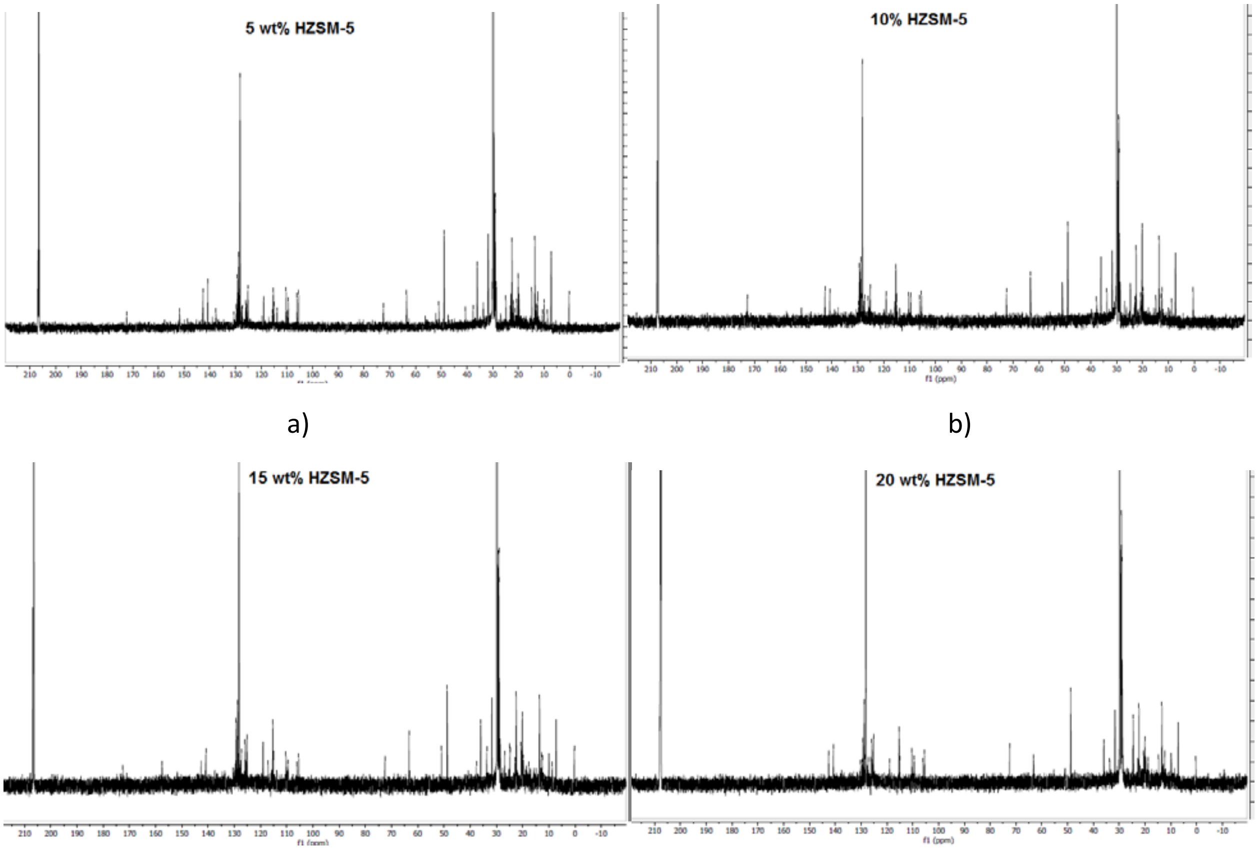
c) d)

**Figure 34. Biochar FTIR with catalyst amount variation**

a) biochar obtained at 5 wt% HZSM-5; b) biochar obtained at 10 wt% HZSM-5; c) biochar obtained at 15 wt% HZSM-5; d) biochar obtained at 20 wt% HZSM-5

The difference in chemical composition of bio-oils obtained at different catalyst amount used in biomass pyrolysis has been determined by $^{13}$C -NMR and GC-MS analysis. In case of $^{13}$C –NMR (Figure 35), for all samples it has been observed the presence of short aliphatics (in the region 0-28 ppm) and long and branched aliphatic components (in the region 28-55 ppm). All samples presented as well two peaks around 63 ppm and 72 ppm which could be characteristic to alcohols, ethers or methoxy compounds (carbohydrates) [71]. The bio-oil sample obtained with 5 wt% HZSM-5 showed more peaks in the region

105-142 ppm assigned to aromatics, while the bio-oil sample obtained with 20 wt% catalyst showed the lower number of peaks in this area, demonstrating the further decomposition of organic components from biomass when larger amount of catalyst is introduced in reactor. Moreover, compared with the other samples, the bio-oil obtained with 20 wt% catalyst did not show any peak around 175 ppm characteristic to carboxylic acids or esters [71]. For all the samples, the large peak at 210 ppm is attributed to the acetone solvent used to extract bio-oil samples from cooling system.



a)

b)

c)

d)

**Figure 35. $^{13}$C-NMR spectra of bio-oil produced during catalyst amount variation**

a) bio-oil obtained at 5 wt% HZSM-5; b) bio-oil obtained at 10 wt% HZSM-5; c) bio-oil obtained at 15 wt% HZSM-5; d) bio-oil obtained at 20 wt% HZSM-5

## 6.4 INFLUENCE OF OPERATING TIME OVER CONVENTIONAL BIOMASS PYROLYSIS

Last parameter to be tested was the reaction time of conventional pyrolysis. As from the preliminary tests it has been established that 1 h reaction time is not sufficient for decomposition and condensation of all pyrolysis products. Thus is has been considered a minimum 2 h reaction time for biomass pyrolysis. The conditions applied for these tests have been: 50 g biomass mixture, 10 wt% HZSM-5 catalyst, 500 °C, atmospheric pressure, 18 L/h Argon gas flow, and reaction time of 2 h, 3 h or 4 h. Higher conversion was achieved when longer reaction time was employed. The maximum conversion was achieved after 4 h reaction time – however the increase was with only 3%, suggesting that high conversion is achieved even in shorter reaction time (possible due the biomass wastes which have been alreay subjected to extraction of organic matter). With the increase of reaction time it has been observed that heavy condensate yield decreased while the light condensate yield increased – maximum 15.3% was achieved after 4 h (with 23% more that the light condensate obtained after 2 h reaction time). Longer operation time favored the secondary reactions as carbonization, cracking of tars and formation of lighter organic fraction [66]. The gas yield increased also, but with only 5%.

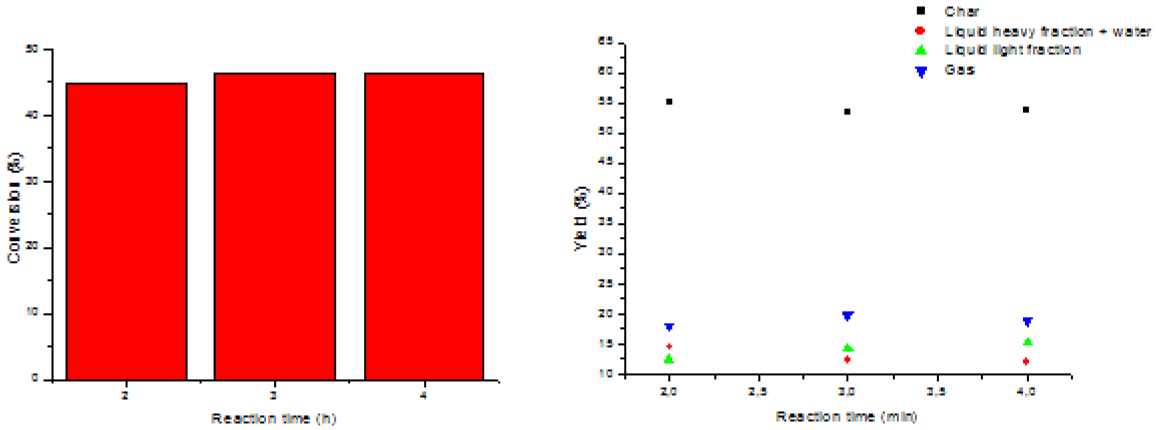


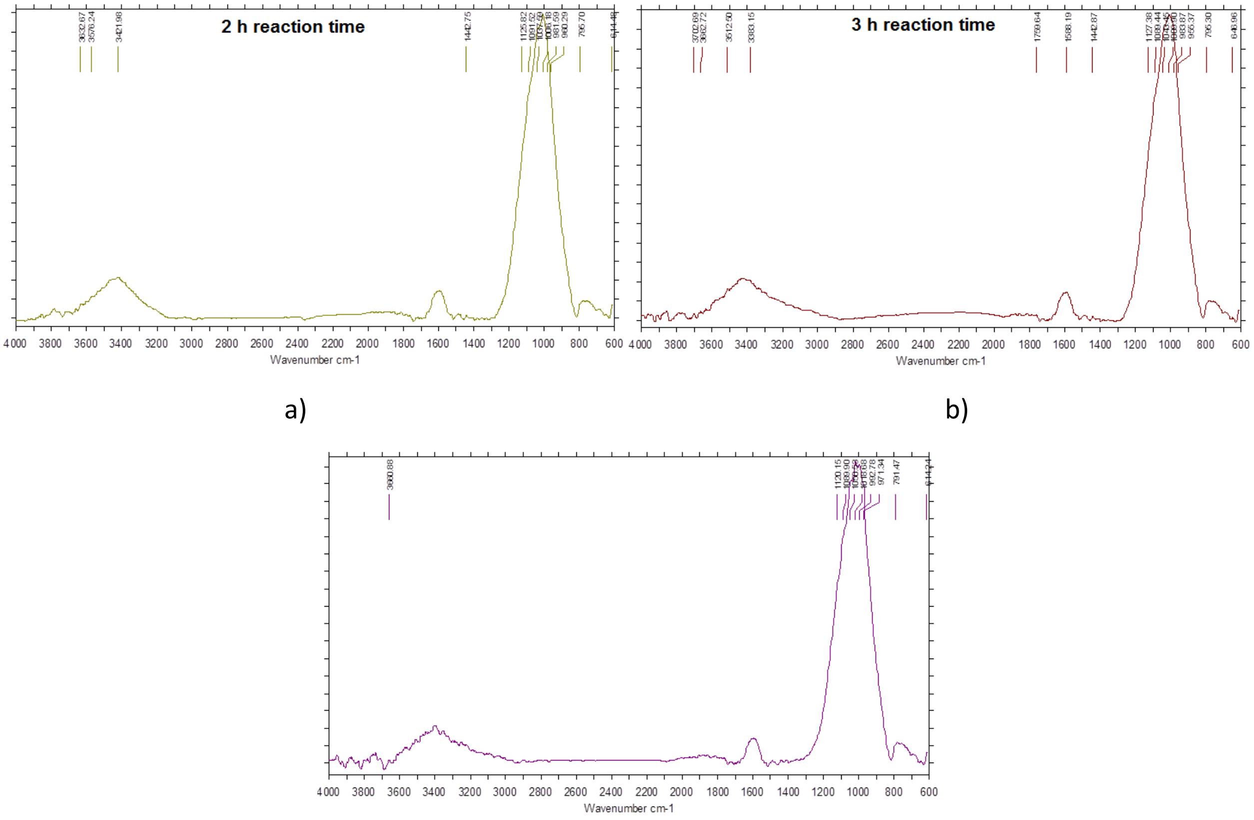
**Figure 36. Effect of reaction time over conversion and product yield on biomass conventional pyrolysis**

Analyzing the biochar obtained from each test with different reaction time (Table 25), it has been observed that carbon content in biochar has the tendency to increase with increasing of reaction time. The results could be explained by the increasing degree of carbonization with time [61, 62]. On the other hand, neither hydrogen nor nitrogen content shows a clear trend with the increase of pyrolysis reaction time.

**Table 25. Proximate and ultimate analysis of char produced during reaction time variation**

| | C. % | H. % | N. % | S. % |
|---|---|---|---|---|
| Feedstock | | | | |
| Biochar at 2 h | 20,00 | 0,67 | 0,15 | 0,58 |
| Biochar at 3 h | 26,38 | 1,11 | 1,12 | 0 |
| Biochar at 4 h | 24,26 | 1,01 | 1,02 | 0 |

No influence over the composition of biochar could be seen when the samples were analyzed by FTIR (Figure 37). All samples showed a very similar spectrum consisting of large peak at 3700-3300 cm$^{-1}$ assigned to O-H stretching vibration (hemicellulose and cellulose), the band around 1600 cm$^{-1}$ attributed to C=O stretching (based on other researches this band can be also assigned to aromatic C=C stretching [72]), large bands between 1125-955 cm$^{-1}$assigned to C-O stretch from organic alcohols, esters, as well as C=C ring stretching from lignin (the high intensity of these bands could be due to the higher temperature required to break down all lignin components - from TGA of raw materials at 600 C the entire organic mass is reduced) and the band at 795 cm$^{-1}$ characteristic to aromatics. Based on the elemental and FTIR analysis, it can be concluded that the composition of biochar is not affected by reaction time. However, longer time will be beneficial for further decomposition of complex structures, in particular the one from lignin, with the increase of carbon content in biochar.



a)

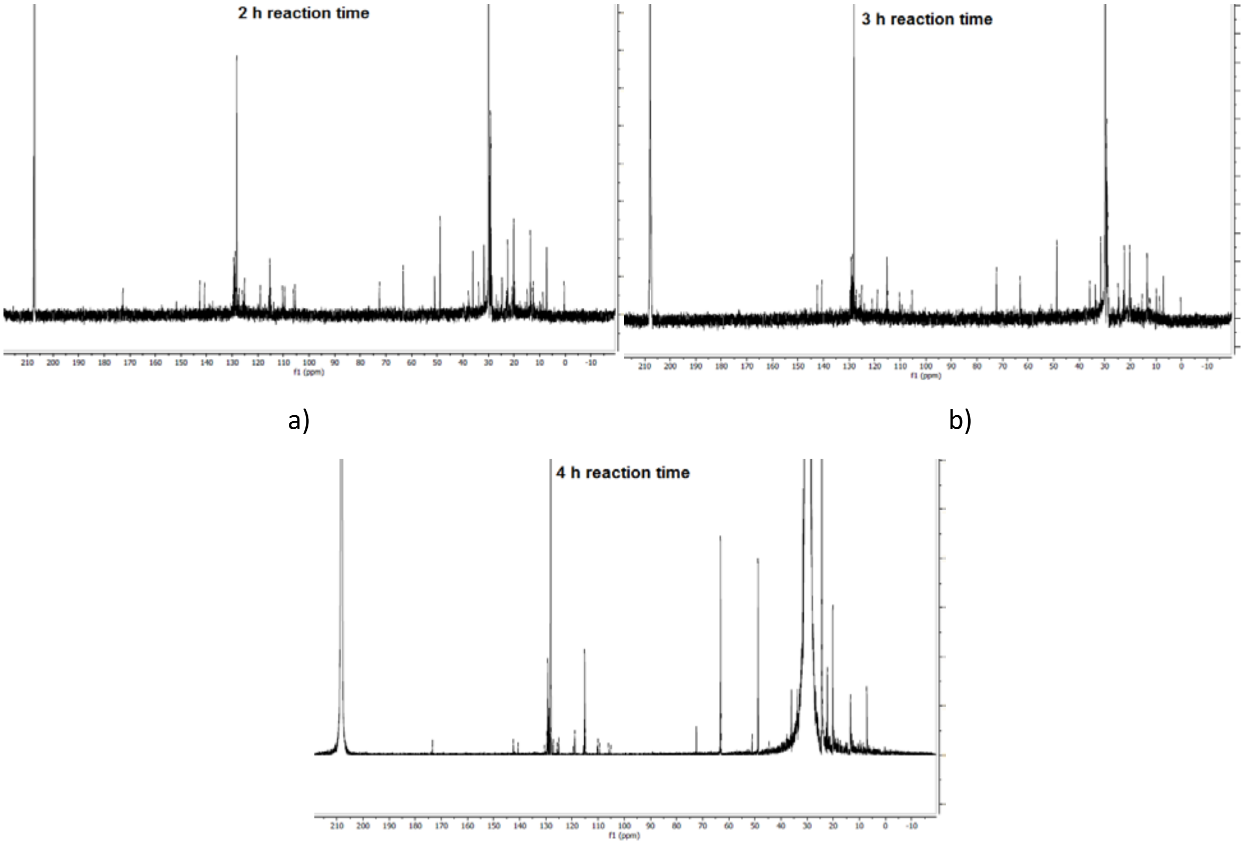
b)

c)

**Figure 37. Biochar FTIR with pyrolysis reaction time variation**

a) biochar obtained after 2 h reaction time; b) biochar obtained after 3 h reaction time; c) biochar obtained after 4 h reaction time

The composition of bio-oil samples produced at different reaction time for conventional pyrolysis have been analyzed in terms of $^{13}$C-NMR analysis. All samples presented a variety of peaks in the region of 0-50 ppm characteristic to short and long or branched aliphatic components, with a significant increase of these components after 4 h reaction time (Figure 38 c), suggesting a further decompositions of complex organic components (lignin) when pyrolysis is performed for longer time. The same bio-oil sample presented also high intensity peaks in the area 63-72 ppm assigned to alcohols, ethers and carbohydrates [71, 73, 74]. The bio-oil samples after 2 h and 3 h present as well the peaks in this region, however the intensity of the peaks is lower, suggesting lower content of these organic components. Similar observation can be withdrawn also for the peak at 127 ppm – the intensity of the peak increased gradually with time, suggesting an increase of concentration for aromatics. The bio-oil after 4 h pyrolysis shows clear indication of the presence of carbonyl compounds (possible carboxylic acids and esters) due to the peaks at 173 ppm. A more detailed composition of bio-oil samples is detected with GC-MS analysis.



a) b)

c)

**Figure 38. $^{13}$C-NMR spectra of bio-oil produced during pyrolysis reaction time variation**

a) bio-oil obtained after 2 h reaction time; b) ) bio-oil obtained after 3 h reaction time; c) ) bio-oil obtained after 4 h reaction time

## 6.4 OPTIMUM OPERATING CONDITIONS FOR CONVENTIONAL BIOMASS PYROLYSIS

Based on the results presented in the previous subchapters, the optimum operating conditions for conventional pyrolysis of biomass wastes from bioethanol industry are:

- biomass mixture: 67% press mud, 33% powder vinasse
- operating temperature: 500 °C
- catalyst type: zeolite HZSM-5
- catalyst amount: 10 wt% HZSM-5 (based on biomass sample used in reaction)
- Argon gas flow: 18 L/h
- reaction time: 4 h

- atmospheric pressure

With these operating conditions a maximum conversion of 48% was achieved, with a selectivity: 52% biochar, 27.8% pyrolysis liquid (with 15.7% light condensate and 12.1% heavy condensate) and 20.2% gas. Biochar obtained with optimum operating conditions show a composition of: 23.3% C, 1.1% H, 1,6% N and 0% S. The composition of bio-oil presented in Table 26 show high content of propanedione – 17.7 wt%, cyclopentanone compounds – 9.5 wt%, benzene compounds – 17.5 wt%, phenol compounds – 11.1 wt%, alkanes C8-C29 – 11.2 wt%, alkenes C11-C29 – 3wt%, furan compounds – 7.2 wt% and nitrogen compounds – 11 wt%.

**Table 26. Chemical composition of bio-oil obtained with optimum operating conditions for biomass conventional pyrolysis**

| Compound | Mass% |
|---|---|
| Acetic acid | 0,82 |
| Acetoxyacetone | 0,83 |
| Propane, 1-nitro- | 0,23 |
| Propanal, 2-oxo- | 17,71 |
| 2-Propanone, 1-hydroxy- | 0,30 |
| 2-Butanone | 2,45 |
| Butanal, 3-methyl- | 0,27 |
| Butyrolactone | 1,11 |
| 1-Pentene, 4,4-dimethyl- | 0,68 |
| Furan, 2-methyl- | 1,04 |
| Furan, 2,5-dimethyl- | 1,53 |
| 2-Furancarboxaldehyde | 3,35 |
| 2-Furancarboxaldehyde, 5-methyl- ( | 1,27 |
| Pyridine | 0,58 |
| Pyridine, 4-methyl- | 0,68 |
| Aziridine, 2-isopropyl-1,3-dimethyl-, trans- | 8,00 |
| Aziridine, 2-(1,1-dimethylethyl)-1,3-dimethyl- | 1,00 |
| Acetaldehyde, ethylidenehydrazone | 0,70 |
| 2-Pentanone, 4-hydroxy-4-methyl- | 0,15 |
| 2,5-Dimethylcyclopentanone | 0,44 |
| Cyclopentanone | 0,47 |
| Cyclopentanone, 2-methyl- | 2,22 |
| Cyclopentanone, 2,4-dimethyl- | 0,28 |
| 2-Cyclopenten-1-one | 0,60 |
| 2-Methyl-2-Cyclopenten-1-One | 3,20 |
| 3-Methyl-2-Cyclopenten-1-One | 0,63 |
| 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 0,68 |
| 2,3-Dimethyl-2-cyclopenten-1-one | 1,00 |

| | |
|---|---|
| **1,3-Cyclohexanedione** | 0,29 |
| **Benzene** | 0,85 |
| **Benzene, methyl-** | 4,93 |
| **Benzene, ethyl-** | 1,32 |
| **Benzene, 1,4-dimethyl-** | 4,66 |
| **Benzene, 1,2,4-trimethyl-** | 2,79 |
| **Benzene, 1-ethyl-3-methyl-** | 1,74 |
| **Benzene, 4-ethyl-1,2-dimethyl-** | 0,64 |
| **Benzene, butyl-** | 0,22 |
| **Benzene, 1,2,3,4-tetramethyl-** | 0,09 |
| **Benzaldehyde, 4-methyl-** | 0,28 |
| **Phenol** | 4,14 |
| **Phenol, 2-methyl-** | 1,36 |
| **Phenol, 3-methyl-** | 1,16 |
| **Phenol, 4-methyl-** | 0,30 |
| **Phenol, 2-methoxy-** | 0,46 |
| **Phenol, 4-ethyl-** | 2,28 |
| **Phenol, 4-ethyl-2-methoxy-** | 0,82 |
| **Phenol, 2,6-dimethoxy-** | 0,34 |
| **4-Vinyl-2-methoxy-phenol** | 0,17 |
| **6-Vinyl-2-methoxy-phenol** | 0,12 |
| **1H-Indene, 2,3-dihydro-5-methyl-** | 0,14 |
| **Naphthalene** | 0,10 |
| **Naphthalene, 1-methyl-** | 0,24 |
| **Naphthalene, 2-methyl-** | 0,18 |
| **Hexadecanenitrile** | 0,70 |
| **Hexadecanoic acid, methyl ester** | 0,33 |
| **Hexadecanoic acid** | 0,75 |
| **Alkanes C8-C29** | 11,20 |
| **Alkenes C11-C29** | 2,99 |
| **Other** | 3,25 |

## 7. EXPERIMENTAL WORK AFTER TERMINATION OF THE PROJECT IN ROMANIA

Due to valuable results that have been obtained on conventional pyrolysis tests performed in Romania under Romanian National Authority for Scientific Research and Innovation (CCCDI – UEFISCDI 20/09/2019) the team from Romania will continue the research investigation in this area after termination of the project by:

- further investigation of the quality of biochar (obtained with optimal operating conditions for conventional pyrolysis) by several analysis: ICP, BET, SEM-EDX.
- further investigation of the quality of bio-oil (obtained with optimal operating conditions for conventional pyrolysis) by several analysis: viscosity, density, flash point, sulfur and water content, elemental analysis, calorific value, distillation, content of PAH.
- as the partners from Panama are still under investigation of induction-heated biomass pyrolysis, we will investigate the characteristics of biochar and bio-oil produced during these tests: for biochar – elemental analysis, FTIR, ICP, BET, for bio-oil: C-NMR, GC-MS; the results obtained will be compared with the ones obtained during biomass conventional tests.
- dissemination of all results in at least 2-3 articles.

## 8. ADMINISTRATIVE MILESTONES ON ERANET-LAC PROJECT (ROMANIA)

- Funding agreement with UEFSCDI: Signed on August 24th. 2017 (Original budget: 121236 EURO)
- Funding in 2017 – Original budget: 14182 EURO. Accepted budget: 14182 EURO
- Funding in 2018 – Original budget: 81363 EURO. Accepted budget: 72522 EURO
- Funding in 2019 – Original budget: 32882 EURO. Accepted budget: 32882 EURO
- Report 1 "Scope of work for conventional biomass pyrolysis experiments"– December 12th. 2017
- Financial Audit 1 – December 15th. 2017
- Report 2 – due to December 2018
- Financial Audit 2 – due to December 2018
- Technical presentation of ERANET-LAC project ROMANIA – May 2019
- Internal reports to the partners. including the present one:
  - Report no. 1 - Characterization of raw materials used in pyrolysis tests: June 15th. 2017
  - Report no. 2 - Catalysts for pyrolysis tests: June 15th. 2017
  - Report no. 3 - Scope of work for conventional biomass pyrolysis experiments in Romania: December 5th. 2017
  - Report no. 4 - Conventional pyrolysis testing – influence of biomass feedstock. August 12th. 2018
  - Report no. 5 - Conventional pyrolysis testing - influence of catalyst. November 19th. 2018
  - Report no. 6 – Annual report of ERANET-LAC project ROMANIA 2018
  - Report no. 7 - Conventional pyrolysis testing - operating conditions. August 30th 2019
  - Report no.8 – Final report ERANET-LAC project ROMANIA 2019

# 9. REFERENCES

[1] International Energy Agency. Key World Energy Statistics 2017. pp.34
https://www.iea.org/publications/freepublications/publication/KeyWorld2017.pdf

[2] European Renewable Energy Council. Renewable Energy Scenario to 2040 – Half of the global energy supply from renewables in 2040
http://www.censolar.es/erec2040.pdf

[3] H. An. W.E. Wilhelm. S.W. Searcy. ***Biofuel and petroleum-based fuel supply chain research: A literature review***. Biomass and Bioenergy 35 (2011) 3763-3774

[4] H.L. Chum. R.P. Overend. ***Biomass and renewable fuels***. Fuel Processing Technology 71 (2001) 187-195

[5] M.de Wit. A. Faaij. ***European biomass resource potential and costs***. Biomass and Bioenergy 34 (2010) 188-202

[6] B. Yathavan. ***Conventional and catalytic pyrolysis of pinyon juniper biomass***. Master of Science. Utah State University. Logan. Utah. 2013

[7] S. Papari. K. Hawboldt. ***A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models***. Renewable and Sustainable Energy Reviews 52(2015)1580–1595

[8] L. Qiang. L. Wen-Zhi. Z. Xi-Feng. ***Overview of fuel properties of biomass fast pyrolysis oils***. Energy Conversion and Management 50 (2009) 1376–1383

[9] A.V. Bridgwater. ***Review of fast pyrolysis of biomass and product upgrading***. Biomass and bioenergy 38 (2012) 68-94

[10] A. Demirbas. ***Present and Future Transportation Fuels***. Energy Sources. Part A: Recovery. Utilization and Environmental Effects 30. No. 16 (2008) 1473-1483

[11] A. Veses. M. Aznar. I. Martínez. J.D. Martínez. J.M. López. M.V. Navarro. M.S. Callén. R. Murillo. T. García. ***Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts***. Bioresource Technology 162 (2014) 250–258

[12] A.C. Johansson. H. Wiinikka. L. Sandström. M. Marklund.O.G.W. Öhrman. J. Narvesjö. ***Characterization of pyrolysis products produced from different Nordic biomass types in a cyclone pilot plant***. Fuel Processing Technology 146 (2016) 9–19

[13] A. Veses. M. Aznar. J.M. López. M.S. Callén. R. Murillo. T. García. ***Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials***. Fuel 141 (2015) 17–22

[14] C. Lorenzetti. R. Conti. D. Fabbri. J. Yanik. ***A comparative study on the catalytic effect of H-ZSM5 on upgrading of pyrolysis vapors derived from lignocellulosic and proteinaceous biomass***. Fuel 166 (2016) 446–452

[15] A. Sharma. V. Pareek. D. Zhang. ***Biomass pyrolysis—A review of modelling. process parameters and catalytic studies***. Renewable and Sustainable Energy Reviews 50(2015)1081–1096

[16] C. Wu. V.L. Budarin. M.J. Gronnow. M. De Bruyn. J.A. Onwudili. J.H. Clark. P.T. Williams. ***Conventional and microwave-assisted pyrolysis of biomass under different heating rates***. Journal of Analytical and Applied Pyrolysis 107 (2014) 276-283

[17] M.R. Islam. M.N. Islam. ***Fixed bed pyrolysis of sugarcane bagasse for liquid fuel production***. Proceedings of the International Conference on Mechanical Engineering (2003). 1-5

[18] Z. Sebestyén. E. Barta-Rajnai. J. Bozi. M. Blazso. E. Jakab. N. Miskoczi. Z. Czegeny. ***Catalytic pyrolysis of biomass and plastic mixtures using HZSM-5 zeolite***. Energia Procedia 105 (2017) 718-723

[19] G.F. David. V.H. Perez. O.R. Justo. M. Garcia-Perez. ***Effect of acid additives on sugarcane bagasse pyrolysis: Production of high yields of sugars***. Bioresources Technology 223 (2017) 74-83

[20] F.L. Mendes. V. L. Ximnes. M.B.B. de Almeida. D.A. Azevedo. N.S. Tessarolo. A. de Rezende Pinho. ***Catalytic pyrolysis of sugarcane bagasse and pinewood in a pilot scale unit***. Journal of Analytical and Applied Pyrolysis 122 (2016) 395-404

[21] E. Agrafioti. G. Bouras. D. Kalderis. E. Diamadopoulos. ***Biochar production by sewage sludge pyrolysis***. Journal of Analytical and Applied Pyrolysis 101 (2013) 72-78

[22] D.A. Agar. M. Kwapinska. J.J. Leahy. ***Pyrolysis of wastewater sludge and composted organic fines from municipal solid waste: laboratory reactor characterization and product distribution***. Environmental Science and Pollution Research. 2018

[23] N. Charon. J. Ponthus. D. Espinat. F. Broust. G. Volle. J. Valette. D. Meier. ***Mechanism-technique characterization of fast pyrolysis oils***. Journal of Analytical and Applied Pyrolysis 116 (2015) 18–26

[24] H. Nam. S.C. Capareda. N. Ashwath. J. Kongkasawan. ***Experimental investigation of pyrolysis of rice straw using bench-scale auger. batch and fluidized bed reactors***. Energy 93 (2015) 2384-2394

[25] N. Puy. R. Murillo. M.V. Navarro. J.M. Lopez. J. Rieradevall. G. Fowler. I. Aranguren. T. Garcia. J. Bartroli. A.M. Mastral. ***Valorization of forestry waste by pyrolysis in an auger reactor***. Waste Management 31 (2011) 1339–1349

[26] L. Brech. L. Jia. S. Cisse. G. Mauviel. N. Brosse. A. Dufour. ***Mechanism of biomass pyrolysis studied by combining a fixed bed reactor with advanced gas analysis***. Journal of Analytical and Applied Pyrolysis 117 (2016) 334–346

[27] Y. Kar. ***Catalytic pyrolysis of car tire waste using expanded perlite***. Waste Management 31 (2011) 1772–1782

[28] C. Ilkiliç. H. Ayden. ***Fuel production from waste vehicle tires by catalytic pyrolysis and its application in a diesel engine***. Fuel Processing Technology 92 (2011) 1129–1135

[29] N.A. Dũng. A. Mhodmonthin. S. Wongkasemjit. S. Jitkarnka. ***Effects of ITQ-21 and ITQ-24 as zeolite additives on the oil products obtained from the catalytic pyrolysis of waste tires***. Journal of Analytical and Applied Pyrolysis 85 (2009) 338–344

[30] M. Tripathi. J.N. Sahu. P. Ganesan. ***Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review***. Renewable and Sustainable Energy Reviews 55 (2016) 467–481

[31] J. Adam. M. Blazsó. E. Mészáros. M.l Stöcker. M.H. Nilsen. A. Bouzga. J.E. Hustad. M. Grønli. G. Øye. ***Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts***. Fuel 84 (2005) 1494–1502

[32] E. Antonakou. A. Lappas. M.H. Nilsen. A. Bouzga. M. Stöcker. ***Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals***. Fuel 85 (2006) 2202–2212

[33] J.D. Adjaye. N.N. Bakhshi. ***Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts***. Fuel Processing Technology 45 (1995) 161-183

[34] Z. Qi. C. Jie. W. Tiejun. X. Ying. ***Review of biomass pyrolysis oil properties and upgrading research***. Energy Conversion and Management 48 (2007) 87–92

[35] T. Kan. V. Strezov. T.J. Evans. ***Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters***. Renewable and Sustainable Energy Reviews 57 (2016) 1126–1140

[36] H.B. Goyal. D. Seal. R.C. Saxena. ***Bio-fuels from thermochemical; conversion of renewable resources: A review***. Renewable and Sustainable Energy Reviews 12 (2008) 504–517

[37] K. Açikalin. F. Karaca. ***Fixed-bed pyrolysis of walnut shell: Parameter effects on yields and characterization of products***. Journal of Analytical and Applied Pyrolysis 125 (2017) 234–242

[38] G. Kabir. B.H. Hameed. ***Recent progress on catalytic pyrolysis of lignocellulosic biomass to high grade bio-oil and bio-chemicals***. Renewable and Sustainable Energy Reviews 70 (2017) 945–967

[39] S.D. Rabiu. A. Auta. A.S. Kovo. ***An upgraded bio-oil produced from sugarcane bagasse via the use of HZSM-5 zeolite catalyst***. Egyptian Journal of Petroleum (2017)

[40] Z. Sebestyén. E. Barta-Rajnai. J. Bozi. M. Blazsó. E. Jakab. N. Miskoczi. J. Sója. Z. Czégény. ***Thermo-catalytic pyrolysis of biomass and plastic mixtures using HZSM-5***. Applied Energy 207 (2017) 114-122

[41] P.T. Williams. S. Besler. ***The influence of temperature and heating rate on the slow pyrolysis of biomass***. Renewable Energy 7 (1996) 233-250

[42] A.A. Arni. ***Comparison of slow and fast pyrolysis for converting biomass into fuel***. Renewable Energy 124 (2018) 197-201

[43] P. Parthsarathy. K.N. Sheeba. Generation of fuel char through biomass slow pyrolysis. Energy Sources. Part A: Recovery. Utilization and Environmental Effect (2017) 599-605

[44] F. Ronsse. S. van Hecke. D. Dickinson. W. Prins. ***Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions***. GCB Bioenergy 5 (2013) 104-115

[45] Y.Lee. P.R.B. Eum. C. Ryu. Y.K. Park. J.H. Jung. S. Hyun. ***Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1***. Bioresource Technology 130 (2013 345-350

[46] F. Xu. J. Yu. T. Tesso. F. Dowell. D. Wang. ***Quantitative and qualitative analysis of lignocellulosic biomass using infrared techniques: A mini-review***. Applied Energy 104 (2013) 801-809

[47] C.M. Popescu. M.C. Popescu. C. Vasile. ***Characterization of fungal degraded lime wood by FT-IR and 2D IR correlation spectroscopy***. Microchemical Journal 95 (2010) 377-387

[48] C. Guizani. M. Jeguirim. S. Valin. L. Limousy. S. Salvador. ***Biomass chars; the effect of pyrolysis conditions on their morphology. structure. chemical properties and reactivity***. Energies 10 (2017) 1-18

[49] R.M. Happs. K. Lisa. K.R Ferrell. ***Quantitative 13C NMR characterization of fast pyrolysis oils***. Royal Society of Chemistry 6 (2016) 102665-102670

[50] N. Hao. H. Ben. C.G. Yoo. S. Adhikari. A.J. Ragauskas. ***Review of NMR characterization of pyrolysis oils***. Energy Fuels 30 (2016) 6863-6880

[51] Patent CN103772167A. ***Preparation method of 2.2-dimethoxypropane*** (2014)

https://patents.google.com/patent/CN103772167A/en

[52] C.P. Hsu. A.N. Huang. H.P Kuo. ***Analysis of the rice husk pyrolysis products from a fluidized bed reactor***. Procedia Engineering 102 (2015) 1183-1186

[53] K.H. Khor. K.O. Lim. Z.A. Zainal. ***Characterization of bio-oil: A by-product slow pyrolysis of oil palm empty fruit bunches***. American Journal of Applied Sciences 6 (2009) 1647-1652

[54] G.E. Acquah. B.K. Via. O.O. Fasina. L.G. Eckhardt. ***Rapid quantitative analysis of forest biomass using fourier transform infrared spectroscopy and partial least squares regression***. Journal of Analytical Methods in Chemistry (2016) 1-10

[55] S. Dolinska. I. Znamenackova.M. Lovas. J. Briancin. V. Cablik. ***Characterization of various biomass waste***. 15th International Conference on Environmental Science and Technology. Rhodes. Greece. 2017.

[56]F. Wilson. P. Tremain. B. Moghtader. ***Characterization of biochars derived from pyrolysis of biomass and calcium oxides mixtures***. Energy Fuels 32 (2018) 4167-4177

[57] J. Adam. M. Blazsó. E. Mészáros. M. Stocker. M.H. Nilsen. A. Bouzga. J.E. Hustad. M. Grønli. G. Øye. ***Pyrolysis of biomass in the presence of Al-MCM-41 type catalyst***. Fuel 84 (2005) 1494-1520

[58] E.F. iliopoulou. S.D. Stefanidis. K.G. Kalogiannis. A. Delimitis. A.A. Lappas. K.S. Triantafyllidis. ***Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite***. Applied Catalysis B: Environmental 127 (2012) 281-290

[59] R. Mahadevan, R. Shakya, S. Neupane, S. Adhikari, ***Physical and chemical properties and accelerated aging test of bio-oil from in situ catalytic pyrolysis in a bench-scale fluidized-bed reactor***, Energy Fuels 29 (2015) 841-848

[60] A. Demirbas, G. Arin, ***An overview of biomass pyrolysis***, Energy Sources 24 (2002) 471-482

[61] M.I. Al-Wabel, A. Al-Omran, A.H. El-Naggar, M. Nadeem, A.R.A. Usman, ***Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes***, Bioresource Technology 131 (2013) 374-379

[62] K.H. Kim, J.Y. Kim, T.S. Cho, J.W. Choi, ***Influence of pyrolysis temperature on physicochemical properties of biochar***, Bioresource Technology 118 (2012) 158-162

[63] K. Weber, P. Quicker, ***Properties of biochar***, Fuel 217 (2018) 240-261.

[64] S. Kumar, D. Pattnaik, S.K. Bhuyan, S.C. Mishra, ***Influence of temperature on pyrolysis of biomass***, IOP Conf. Series: Materials Science and Engineering 338 (2018) 1-6

[65] D. Ozcimen, A. Ersoy-Mericboyu, ***Characterization of biochar and biooil samples obtained from carbonization of various biomass materials***, Renewable Energy 35 (2010) 1319-1324

[66] R.E. Guedes, A.S. Luna, A.R. Torres, ***Operating parameters for bio-oil production in biomass pyrolysis: a review***, Journal of Analytical and Applied Pyrolysis 129 (2018) 134-149

[67] M. Bardalai, D.K. Mahanta, ***Characterization of biochar produced by pyrolysis from Areca Catecha dust***, Materials Today: Proceedings 5 (2018) 2089-2097

[68] J. He, V. Strezov, R. Kumar, H. Weldekidan, S. Jahan, B.H. Dastjerdi, X. Zhou, T. Kan, ***Pyrolysis of heavy metal contaminated Avicennia marina biomass from phytoremediation: Characterizaztion of biomass and pyrolysis products***, Journal of Cleaner Production 234 (2019) 1235-1245

[69] A.P. Soares Dias, F. Rego, F. Fonseca, M. Casquilhho, F. Rosa, A. Rodrigues, ***Catalyzed pyrolysis of SRC poplar biomass. Alkaline carbonate and zeolite catalysts***, Energy 183 (2019) 1114-1122

[70] V. Balasundram, N. Ibrahim, R.M. Kasmani, R. Isha, M.K.A. Hamid, H. Hasbullah, R.R.Ali, Catalytic upgrading of sugarcane bagasse pyrolysis vapours over rare metal (Ce) loaded HZSM-5. Effect of catalyst to biomass ratio on the organic compounds in pyrolysis oil, Applied Energy 220 (2018) 787-799

[71] C.A. Mullen, G.D. Strahan, A.A. Boateng, **Characterization of various fast-pyrolysis bio-oil by NMR spectroscopy**, Energy & Fuels 23 (2009) 2707-2718

[72] M. Jouiada, N. Al-Nofeli, N. Khalifa, F. N. Benyettouc, L.F. Yousef, **Characteristics of slow pyrolysis biochars produced from Rhodes grass and fronds of edible date palm**, Journal of Analytical and Applied Pyrolysis 111 (2015) 183-190

[73] H. Ben, F. Wu, Z. Wu, G. Han, W. Jiang, A.J. Ragauskas, A comprehensive characterization of pyrolysis oil from softwood barks, Polymers 11 (2019) 1-13

[74] A. Majid, I. Pihillagawa, Potential of NMR spectroscopy in the characterization of nonconventional oils, Journal of Fuels (2014) 1-7