

Conventional pyrolysis testing – influence of catalysts

Experimental work on conventional biomass pyrolysis

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1. PUROPOSE OF THE DOCUMENT

The purpose of this document is to present the experimental results obtained so far 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 so far are discussed and compared with results from literature.

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.

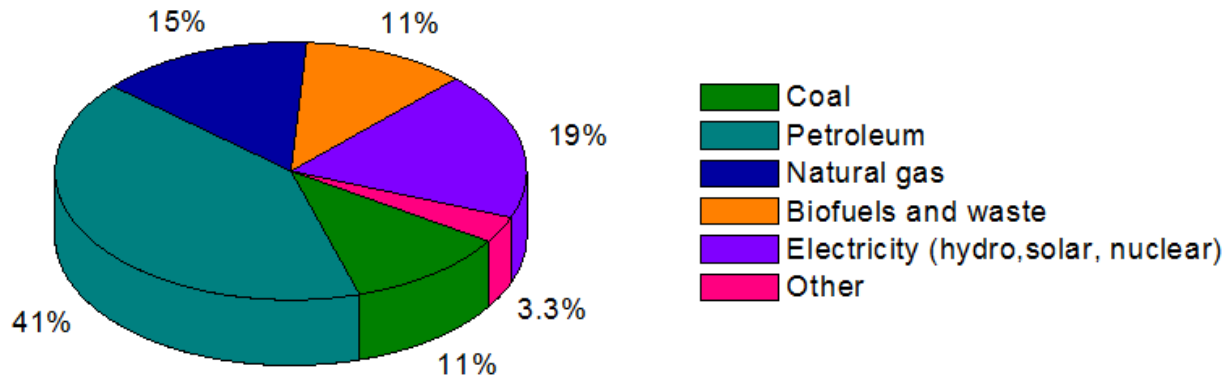


Figure 1. World total final consumption by fuel in 2016 [1]

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]. Bio-char, 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.

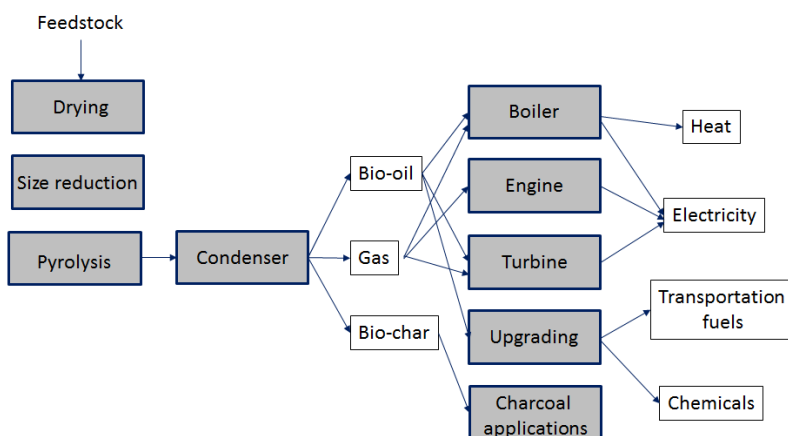


Figure 2. Simplified process flow diagram of biomass pyrolysis [6, 7]

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.

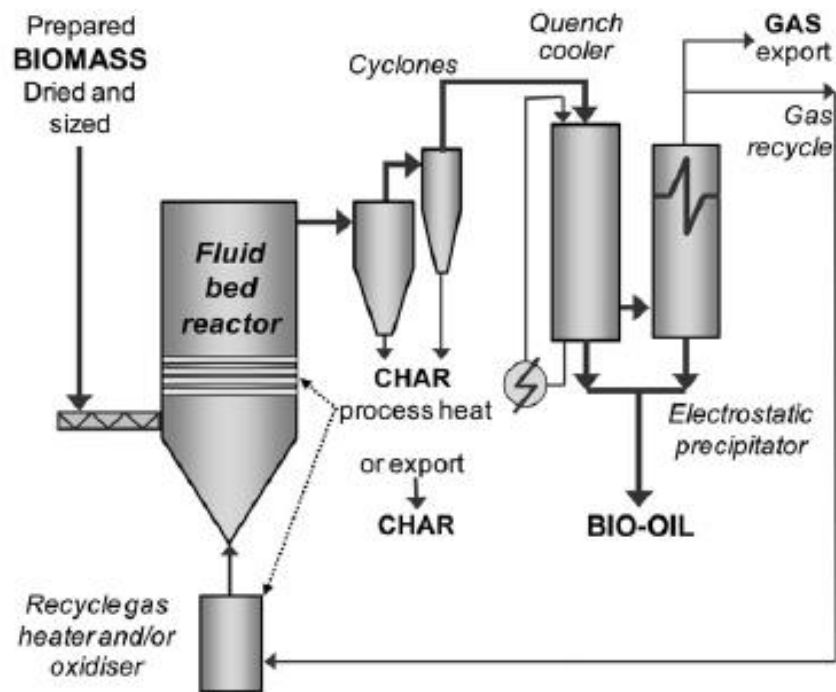


Figure 3. Process flow diagram of a fluidized bed reactor for biomass pyrolysis [9]

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-Ruhrigas 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.

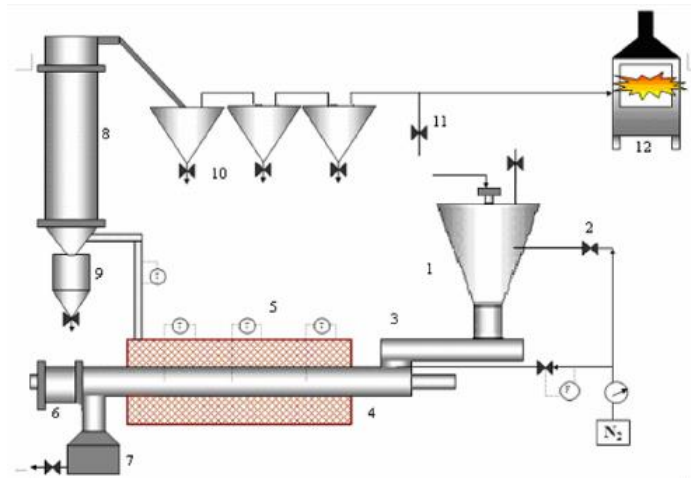


Figure 4. Continuous auger reactor system used for biomass pyrolysis [25]

(1) Feeding hopper; (2) nitrogen flow; (3) feeding auger conveyer; (4) auger reactor; (5) furnace; (6) reactor closure system; (7) vessele 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].

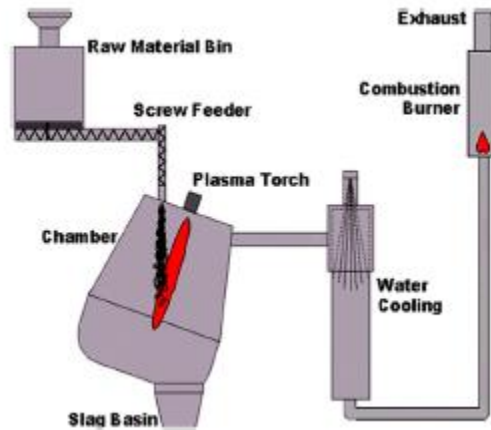


Figure 5. Process flow for plasma pyrolysis reactor [7]

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].

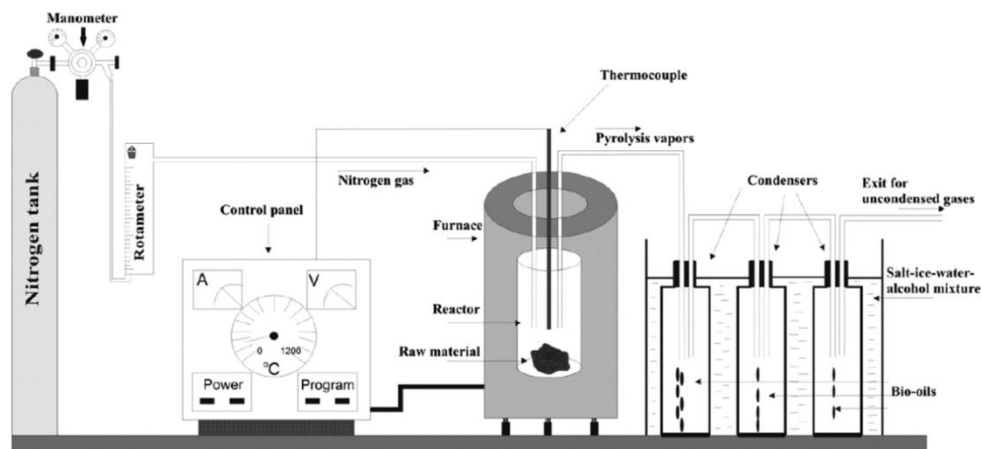


Figure 6. Process flow diagram of a fixed-bed reactor for the pyrolysis of biomass [7]

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 cm³ (140 mm length, 60 mm internal diameter) was coupled with

a condensing system consisting in four traps plunged into cooling system (31 wt% CaCl₂ 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.

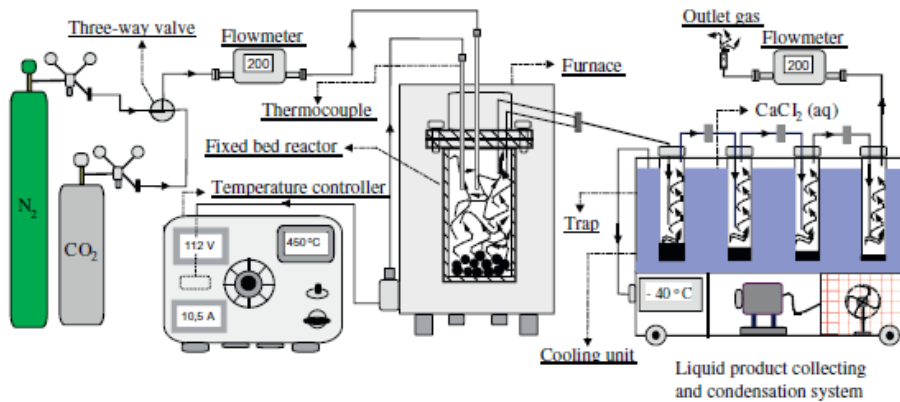


Figure 7. Schematic diagram of a laboratory scale pyrolysis unit [27]

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

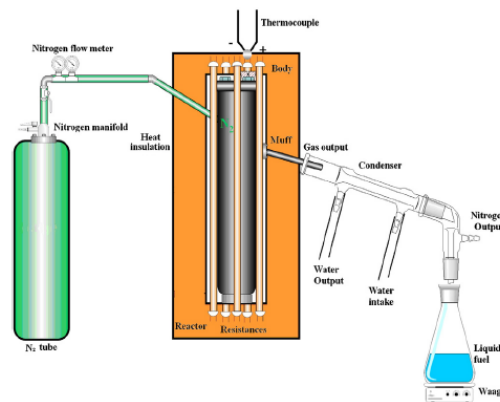


Figure 8. Schematic diagram of fixed batch pyrolysis reactor [28]

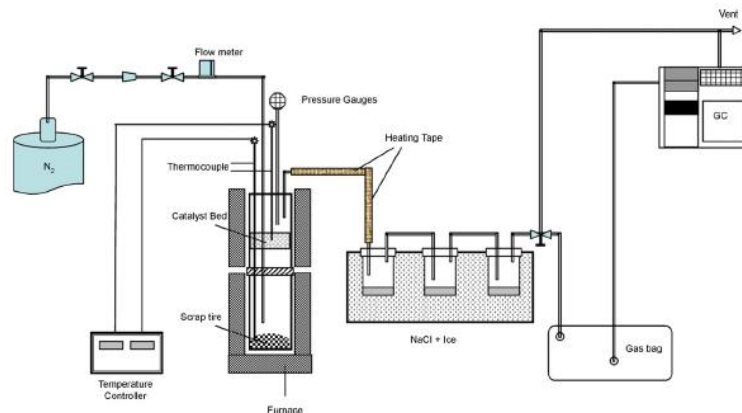


Figure 9. Schematic diagram of fixed batch pyrolysis reactor [29]

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
Bio-char yield, wt%	17.5-19.8	10	29.05
Gas yield, wt%	N/A	8-15	25.02
<i>Physical and chemical properties of bio-oil</i>			
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 C₁ to C₅ 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, Al₂O₃, Ni-Al₂O₃ [6, 11, 13, 30]. Sodium based catalysts like Na₂CO₃, NaOH, NaCl and Na₂SiO₃ 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 ₂ CO ₃ , K ₂ CO 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 ₂ O ₃ , CaO, Al ₂ O 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 m²/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 m²/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:

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- **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 and 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).

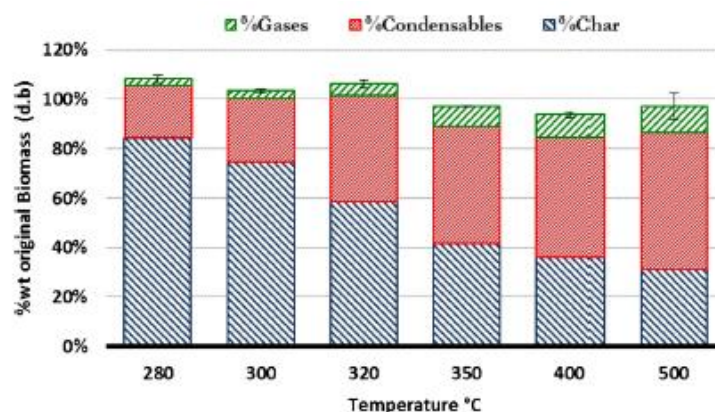
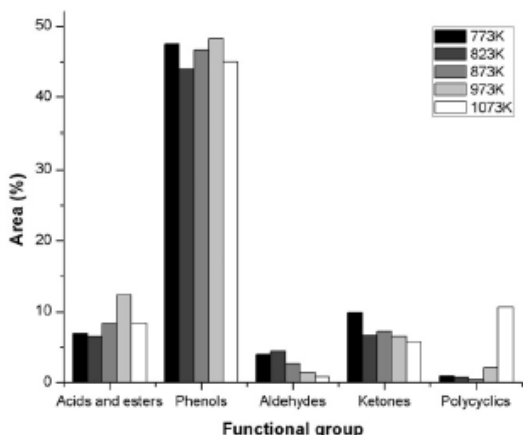


Figure 10. Products yields from biomass pyrolysis at different operating temperatures [26]

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

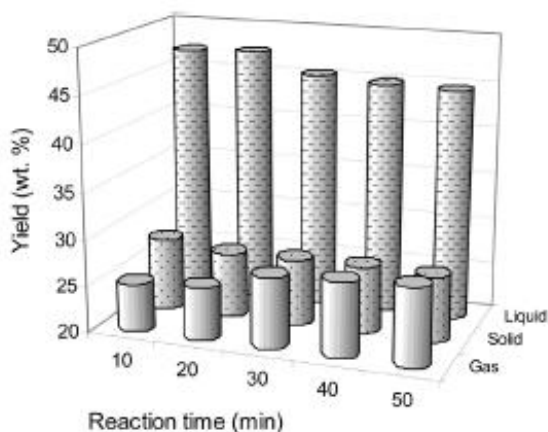
wt% [35]. Wu et al [16] performed a conventional pyrolysis of wood biomass (particle size 1.5 mm) in a fixed bed reactor at 520 °C, under N₂ flow rate of 80 mL/min and under different heating rates between 5-40 °C/min. As it is shown in Table 8, the bio-oil yield increased with the increase of heating 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 N₂ 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 N₂ 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. Rabiou 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 N₂ 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- 0.1	Bio-oil
	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	-
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.



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 bio-char 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 450 °C at a heating rate of 7-8 °C/min. When temperature reached 100 °C, nitrogen flow of 50 L/h was passed through reactor. The pyrolysis tests were performed at 450 °C for 2 h to ensure maximum conversion of waste biomass particles. The reactor was cooled down to 100 °C under nitrogen flow of 50 L/h 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 bio-char 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 bio-char was established by oven drying method. according to ASTM D 4442-07. The procedure consisted in weighing a specific amount of bio-char sample in a crucible and drying to constant weight at $105 \pm 2 \text{ }^\circ\text{C}$ in the oven. Moisture was then calculated according to formula:

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

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 bio-char was determined by difference of moisture from the total of 100%.

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

ASH CONTENT

Ash content of bio-char was determined by weighting a specific amount of bio-char sample in a crucible and drying at $575 \text{ }^\circ\text{C}$ for 4 h. The ash content was calculated according to formula:

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

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 bio-char 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 $960 \text{ }^\circ\text{C}$. 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 bio-char. 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 $4000\text{-}600\text{ cm}^{-1}$. Baseline and smooth corrections of the spectra have been done for each analysis.

¹³C-NMR ANALYSIS

The ¹³C-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 ¹³C 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.

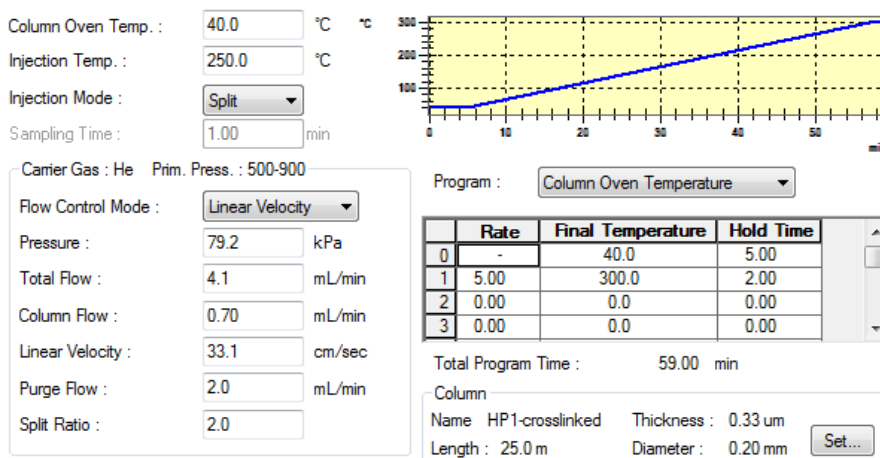


Figure 15. GC-MS conditions used for analysis of pyrolysis bio-oil

4. CONVENTIONAL BIOMASS PYROLYSIS –INFLUENCE OF BIOMASS WASTE TYPE

4.1 BIOMASS WASTE INFLUENCE ON PRODUCT DISTRIBUTION

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 bio-char (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.

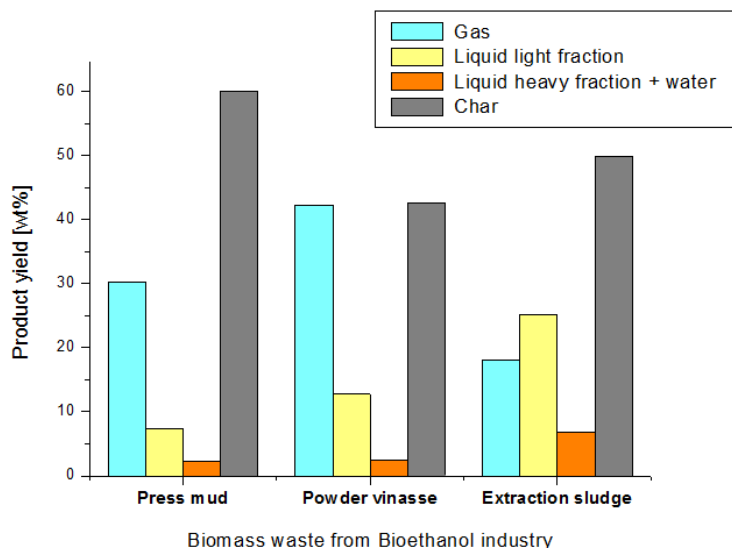


Figure 16. Effect of biomass waste type on product distribution at 450 °C

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 bio-char and bio-oil produced from each biomass feedstock can be seen in Figure 17. All bio-char samples were completely black, suggesting the decomposition of biomass (the bio-char 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%).



Figure 17. Bio-char 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 rich 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.

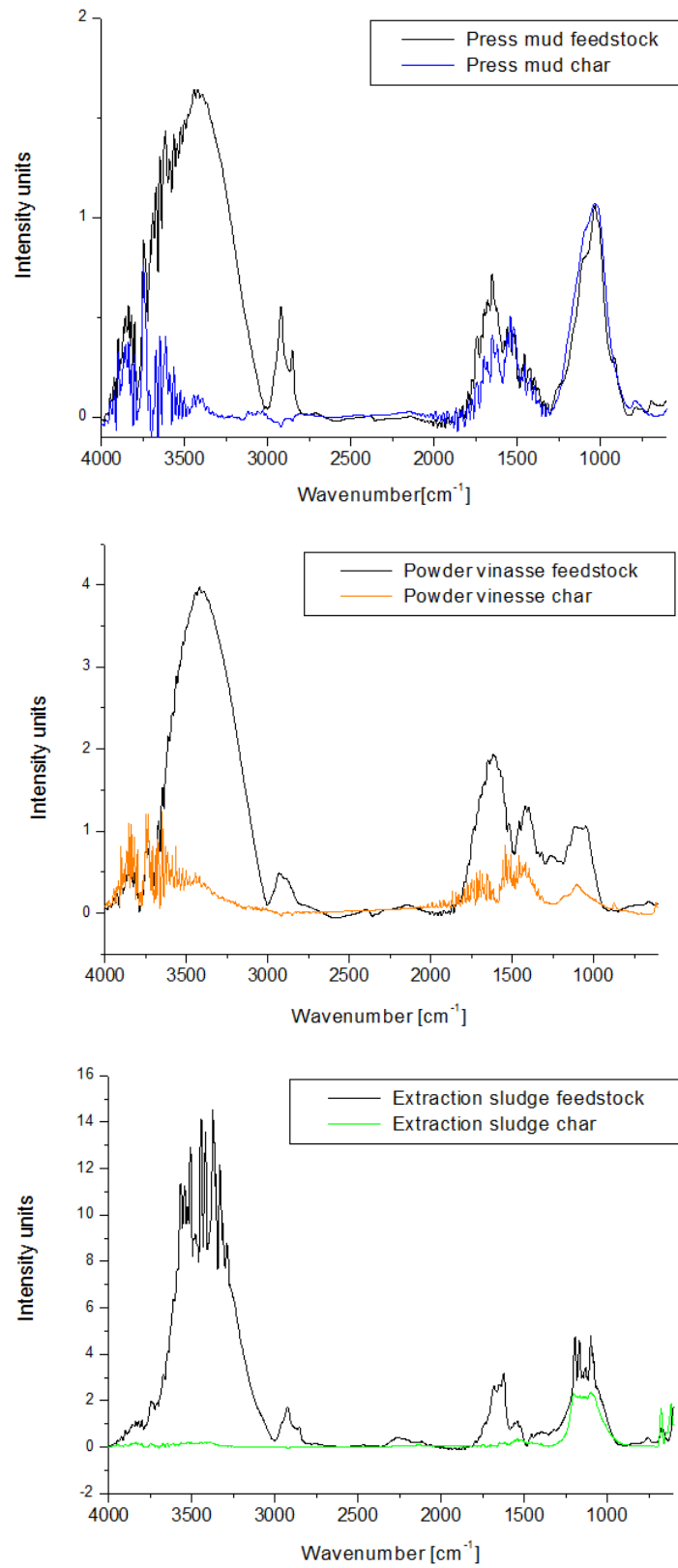
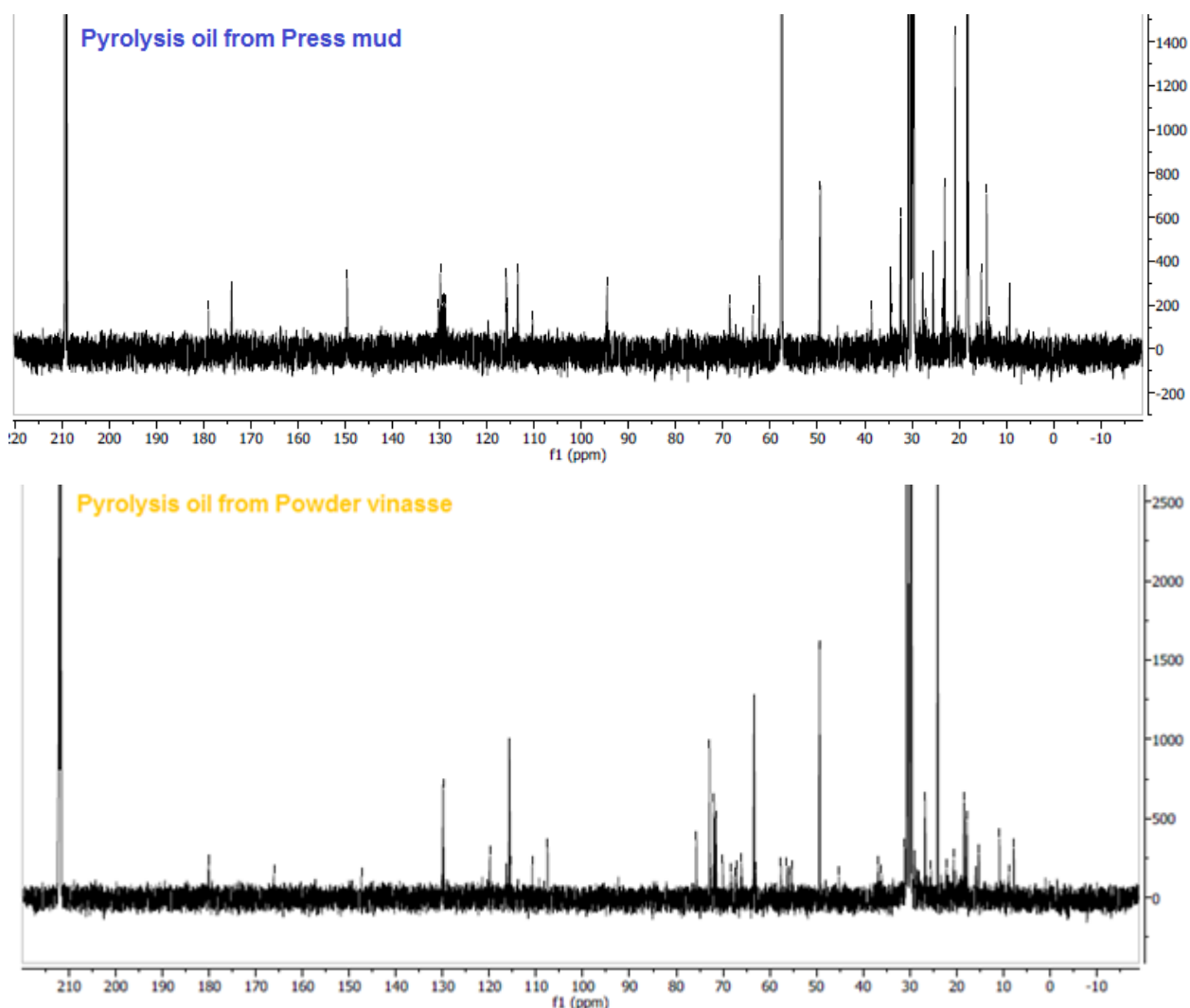


Figure 18. FTIR spectra of biomass feedstock and biochar after conventional pyrolysis at 450 °C

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 bio-char 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 ¹³C-NMR (Figure 19).



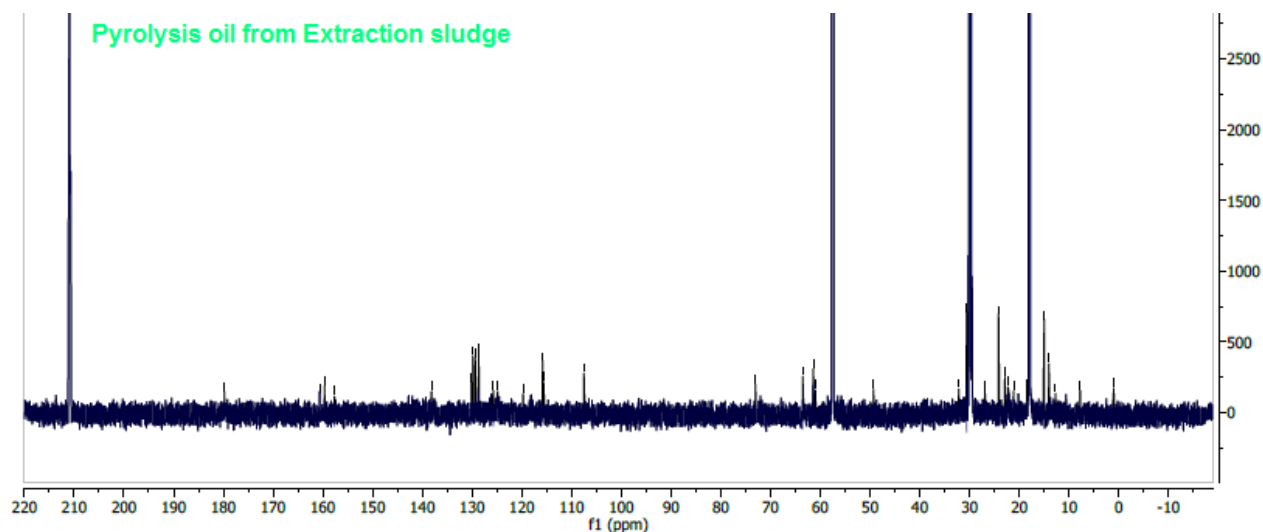


Figure 19. ¹³C-NMR spectra of bio-oil produced from different biomass feedstock

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 ¹³C-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

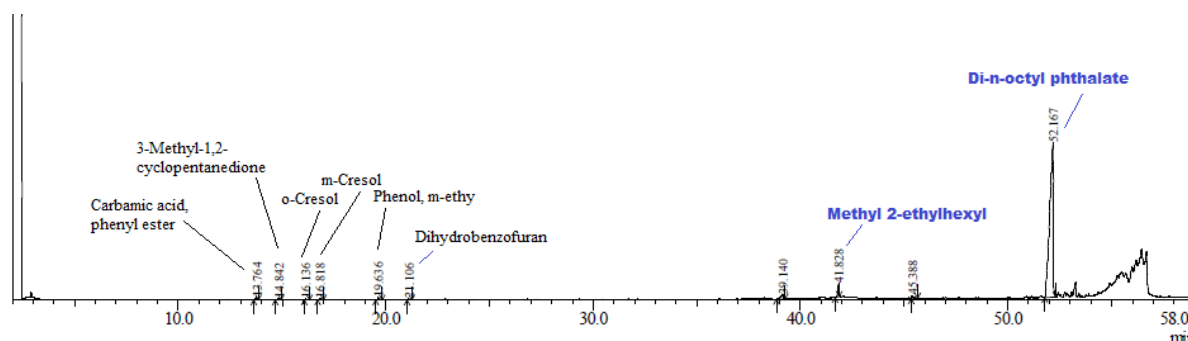


Figure 20. GC-MS of condensed oil from line connecting pyrolysis reactor to condenser line

- 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-methyl-	3.52
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-Ethandiol. 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 based 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-pental	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%).

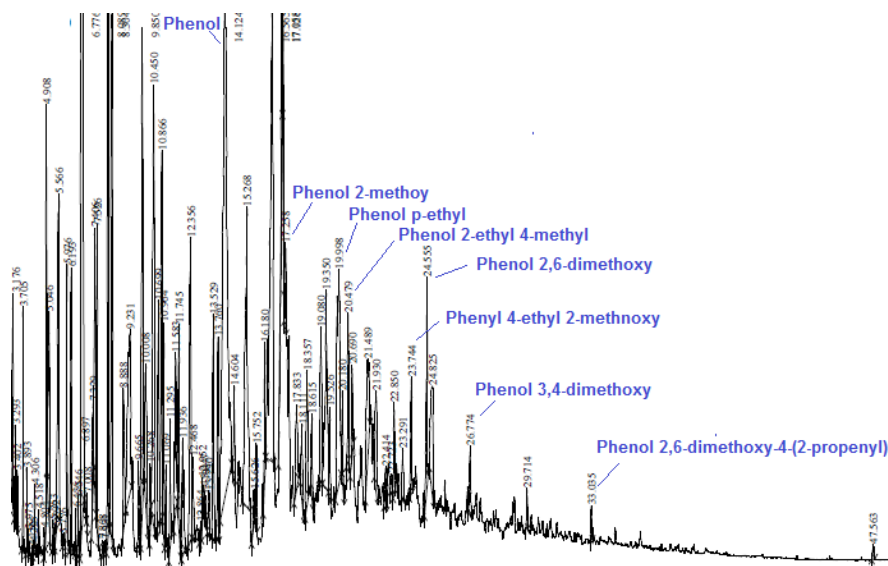


Figure 21. GC-MS of condensed oil from powder vinasse

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 bio-char, but with low content of char, while powder vinasse produced a char with almost 40% content of carbon;
- the FTIR spectra of all bio-char 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 of 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 bio-char. 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 BIO-CHAR 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 N₂ 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
SiO ₂ /Al ₂ O ₃ Molar Ratio	38	—	25
Pore Volume. cm ³ /g	≥0.25	—	≥0.57
BET surface area. m ² /g	≥250	—	>633
Bulk Density. g/mL	0.72	3.3	—
Crushing Strength. N/cm ²	≥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.

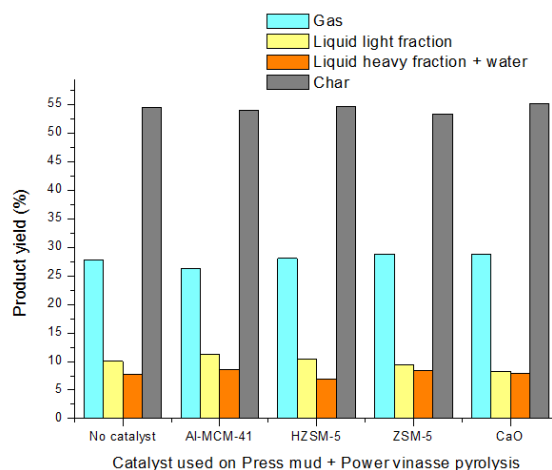


Figure 22. Effect of catalyst type on product distribution at 450 °C, 50 L/h N₂ flow, 2h reaction time

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 bio-char 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 bio-char 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 bio-char when the catalysts were used [44]. Carbon and hydrogen content in all bio-char samples (with or without catalyst) did not show any significant variation. Nitrogen content in bio-char 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 bio-char 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 $3750\text{--}3800\text{ cm}^{-1}$ related to the presence of water. The broad peak from $3000\text{--}3700\text{ cm}^{-1}$ can be attributed to O-H bond, while the sharp peaks from $2850\text{--}3000\text{ cm}^{-1}$ 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 $1500\text{--}1800\text{ cm}^{-1}$ 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].

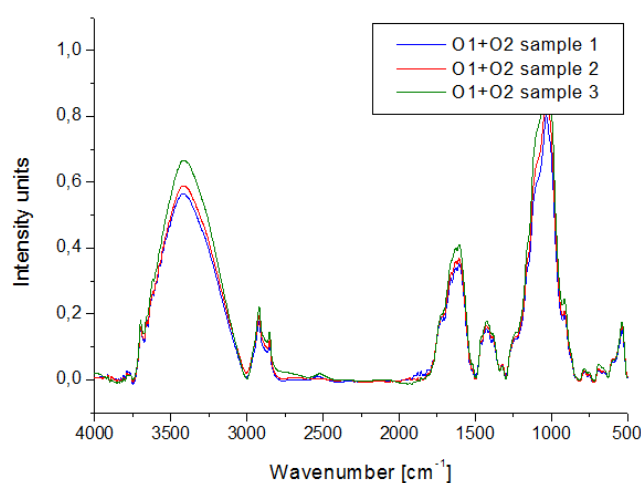


Figure 23. FTIR spectra of biomass mixture feedstock (Press mud: O1. Powder vinasse: O2)

The bio-char from each pyrolysis test (using different catalyst) were analyzed in terms of FTIR (Figure 24). All bio-char 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 ($1500\text{--}1800\text{ cm}^{-1}$) reduced in intensity in case of all the bio-char samples, with the increase in intensity of the peak from 1030 cm^{-1} (assigned to C-O stretching). All bio-chars showed the presence of organic components, indicating that material can still undergo further degradation (in accordance with the proximate and ultimate analysis performed). The bio-char 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).

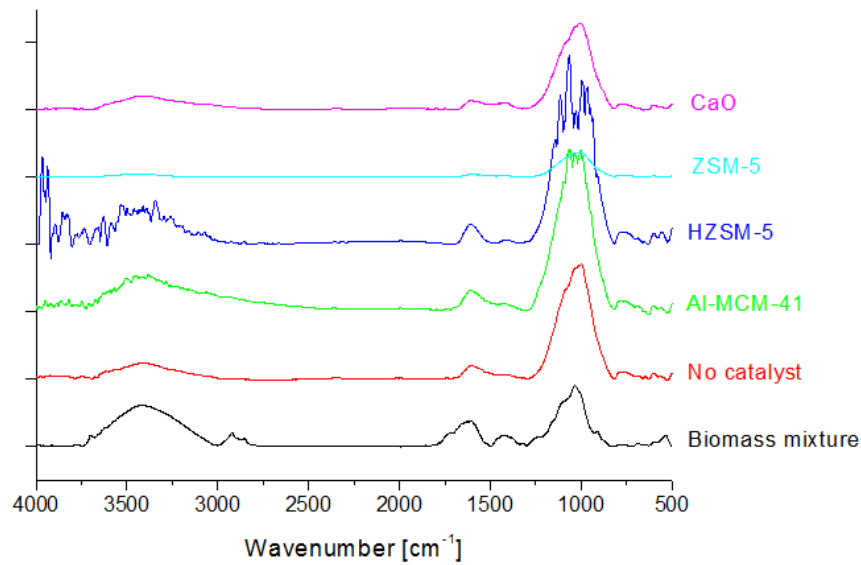
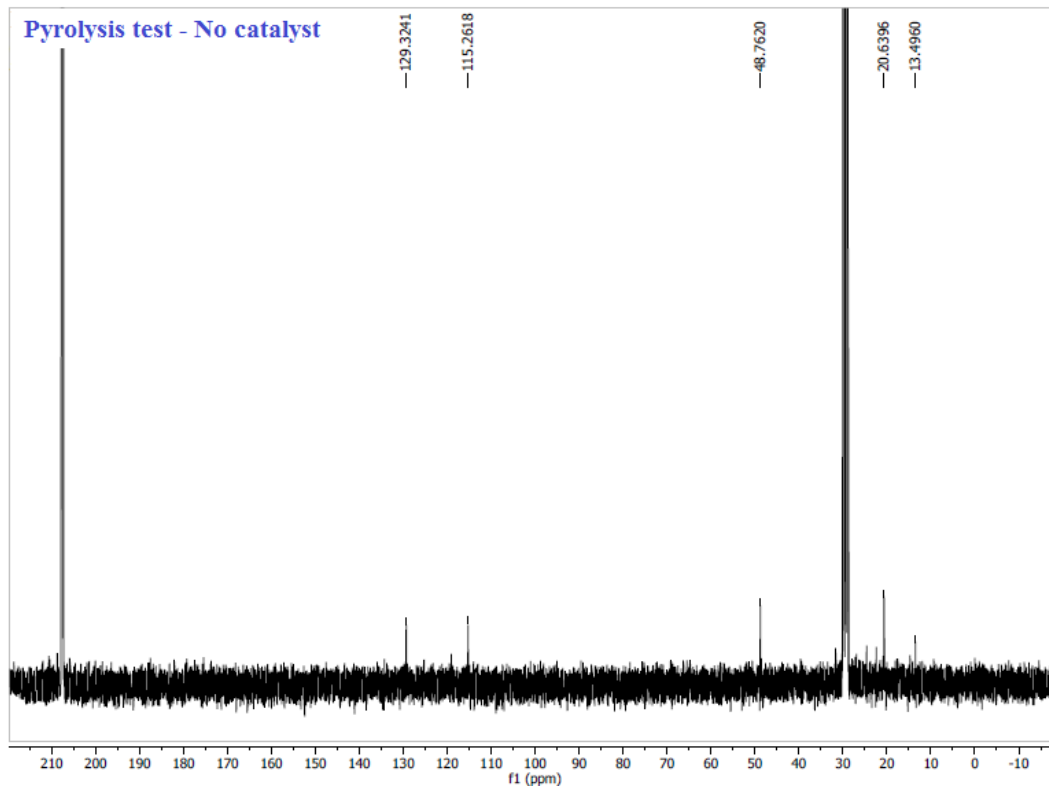
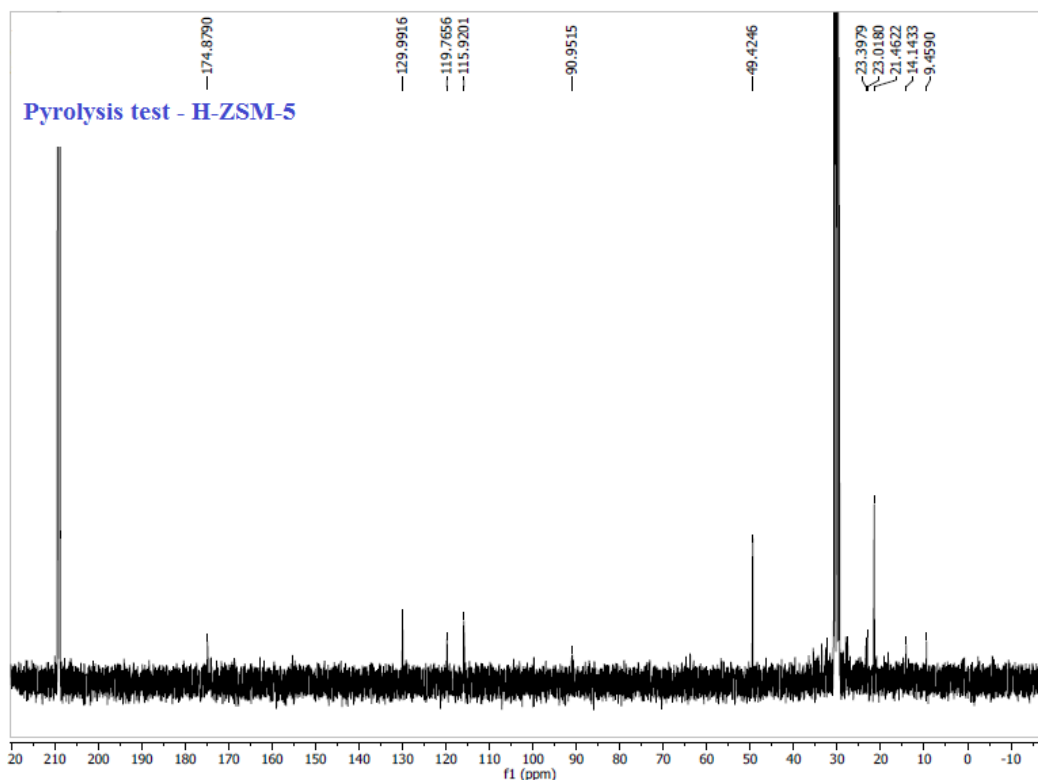
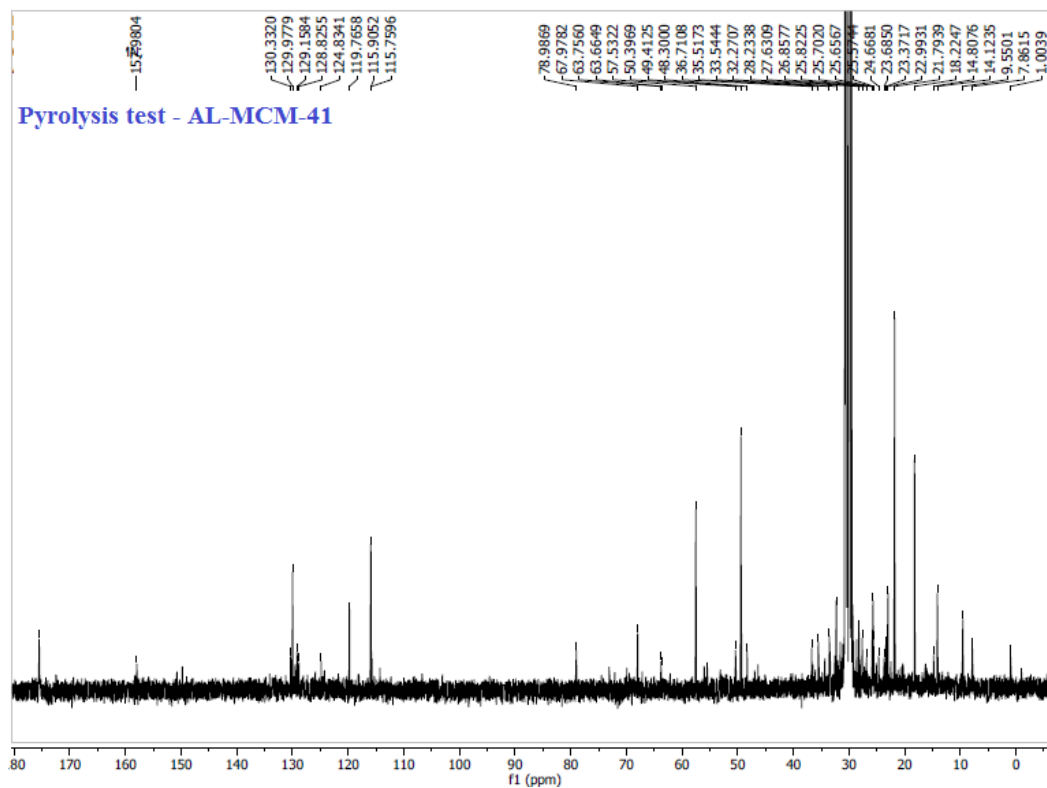


Figure 24. FTIR spectra of bio-char obtained by using different catalysts

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 ¹³C-NMR (Figure 25).





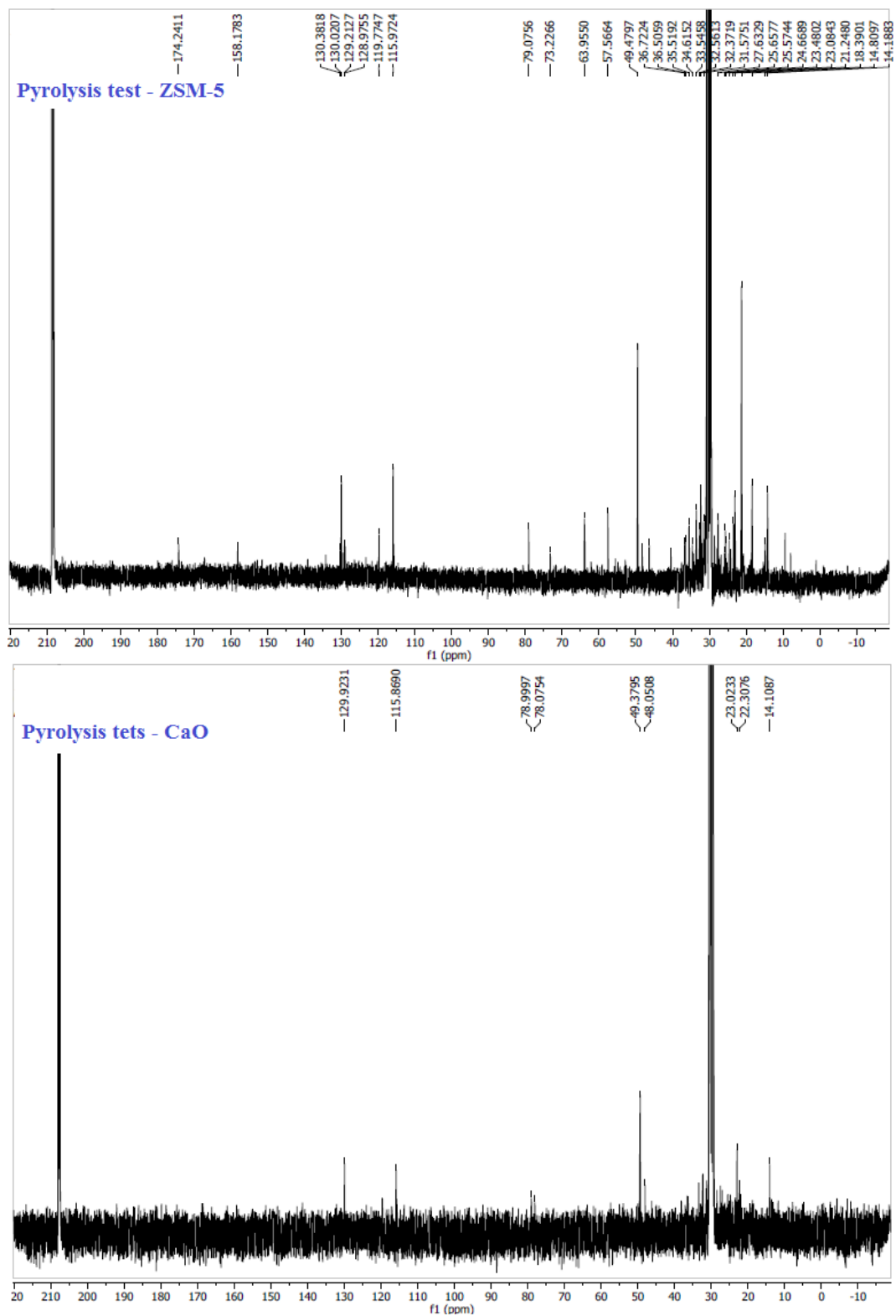


Figure 25. ¹³C-NMR spectra of bio-oil produced using different catalyst systems

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-ZSM-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
Pyrrrolin	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;
- bio-char 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 bio-char 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 bio-char, the carrier gas will be changed with Argon and catalyst will be mixed with the biomass.

6. CONVENTIONAL PYROLYSIS TESTS UNDER EXECUTION

The following activities are under execution:

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*

- finalize the agreement with subcontractor for pyrolysis gas analysis
- preliminary tests for pyrolysis gas sampling
- commissioning GC-FID chromatograph
- pyrolysis tests – use of Ar as carrier gas – repeat tests with Al-MCM-41 and H-ZSM-5; evaluation of temperature. N2 flow. catalyst content. operation time;

7. 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
- 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
- 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

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