

# Liquid phase pyrolysis of wheat straw and poplar in hexadecane solvent

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## **Abstract**

There is a need for replacement of fuel, especially transportation fuel, obtained from fossil resources by bio-based alternative. The thermochemical conversion is a feasible method to degrade and partially deoxygenate the natural resource lignocellulose to get bio-oils as fuel precursors. The present paper describes the liquid phase pyrolysis of wheat straw and poplar under inert atmosphere in n-hexadecane solvent. An autoclave batch reactor system was used. The influence of reaction temperature, residence time, solvent/biomass ratio and the effect of solid acid and base catalysts on the product distribution and yields were investigated. The reaction products were analyzed by means of CHNO elemental analysis, Solid Phase Micro Extraction-Gas Chromatography-Mass Spectroscopy (SPME-GC-MS), <sup>1</sup>H and <sup>13</sup>C-Nuclear Magnetic Resonance (NMR) spectroscopies. About 40-49 wt% of

lignocellulosic carbon was successfully transferred to hexadecane. The best carbon yields were achieved at 350 °C. The main extracted products were alkyl and alkoxy derivatives of phenol and furan derivatives. By comparing seven parallel experiments in presence and absence of the catalysts no or only negligible catalytic effect was observed. The effect of heterogeneous catalysts was manifested only in splitting the primarily extracted macromolecules. The carbon/oxygen mass balances suggest that the extracted compounds have relatively high residual oxygen content.

Keywords: Liquid phase pyrolysis (LPP); LPP of lignocellulose; Catalytic LPP; SPME- GC-MS; Carbon balance

Highlights:

- Degradative extraction of lignocellulose by liquid hexadecane at 350 °C.
- 40-49 wt% of the lignocellulosic carbon could be transferred to the solvent.
- Together with carbon high amount of oxygen was transferred to the solvent.
- Heterogeneous catalysts are active in splitting extracted macromolecules.
- SPME analysis of the dissolved degradation products.

## **1. Introduction**

The EU summit in 2007 endorsed 20 % as mandatory minimum share of energy from renewable sources in the overall Community energy consumption to be achieved by 2020. As part of this commitment a 10 % share of biofuels in gas and diesel fuel consumption was also approved as mandatory minimum target [1].The new RED II issued in June 2018 raises the

overall EU target for consumption of renewable energy sources to 32 % by 2030. In road and rail transport minimum of 14 % of the consumed energy is expected to be renewable [2]. The EU emphasized the significance of commercial availability and sustainability of biofuel. It is obvious that latter objective can be attained only by producing second-generation biofuels from various biomass resources and wastes. The thermochemical degradation of natural polymeric materials, such as lignocellulose, is a feasible method to obtain bio-oils of calorific value that can be fuels or fuel precursors. The most widely applied technology involves gasification to produce synthesis gas ( $\text{CO} + \text{H}_2$ ). The gas is used then to produce methanol, synthesize alkanes by the Fischer-Tropsch process, or simply generate more hydrogen applying the water-gas shift reaction [3]. Pyrolytic methods, such as, torrefaction, slow and fast pyrolysis, are also extensively used for biomass transformation to bio-oils [4,5].

Thermal degradation of lignocellulose under water gives water insoluble bio-oil. This method is usually referred to as hydrothermal liquefaction (HTL) or high-temperature carbonization (HTC) [6,7]. Water assisted liquefaction requires severe conditions, such as, 50-200 bar pressure and 250-350 °C temperature. An alternative route to process lignocellulosic materials is degradation in none-hydrogen donor organic solvent referred to as liquid phase pyrolysis (LPP) [8-13] or degradative extraction (DE) [14-16]. According to this method lignocellulosic material is treated at ~350 °C under liquid phase organic solvent and inert atmosphere at relatively low pressure (max. 20 bar). The solvent acts as a heat carrier, providing high heat transfer rate, and as media for extracting and dissolving degradation products. The method gives three types of solid materials: (i) solvent-insoluble residue, simply referred to as *residue* (ii) extract, soluble at 350 °C, but insoluble at room temperature, referred to as *deposit* (iii) extract, soluble at room temperature, referred to as *soluble*. *Gases*, mainly  $\text{CO}_2$ , and *water solubles*, non-miscible with the applied solvent, mainly  $\text{H}_2\text{O}$ , are also formed. Studies report about the use of different organic solvents, such as, mixture of n-

alkanes, boiling in the temperature range of 410 and 440 °C [8,9], vacuum gasoline (VGO) that is a mixture of alkanes and aromatics, having a boiling range of 300-580 °C [10,11,13], n-hexane (bp: 69 °C) [12] and 1-methylnaphtalene (bp: 240-243 °C)[14-16].

By comparing the results of the above cited articles some general statements can be made: (i) the best temperature for LPP is ~350 °C, at lower temperatures the conversion is not high enough, at higher temperatures the condensation reactions of the primary products occur and, as a result, the amount of solid residue increases on the expense of the oily products, such as, soluble and deposit, (ii) at 350 °C the formation of oily products is finished in about 10 min, extension of contact time promotes formation of gaseous products (iii) the particle size of the feed has no effect on the process.

The product yield calculations are usually based on the CHNS elemental analysis of the product phases. It is very difficult to compare the results of the different laboratories because of the high variety of the used biomass feedstock. The used equipment setup has also great effect on the experimental results. Zhu et al. [16] reported about extremely low yields of residue (3-5 wt%), i.e., the conversion of fir sawdust, pyrolyzed in 1-methylnaphtalene at 350 °C, was almost complete [16]. The yields of the other products varied between 10-30 wt% for deposit (not soluble in the heat carrier at room temperature), 25-40 wt% for soluble (materials dissolved in heat carrier), 20-30 wt% for liquid (water soluble products) and 12-15 wt% for gases. Schwaiger et al. [8] investigated LPP of spruce wood in an n-alkane mixture, boiling in the temperature range of 410 - 440°C. The mass balance of the experiment was the following: 39 wt% of biochar (residue), 16 wt% water, non-miscible with the solvent, 26 wt% organic liquid, recovered from the solvent, 13 wt% gases, 3 wt% organics, not recovered from the solvent, and 3 wt% mass balance inaccuracy.

Various analytical methods are used to characterize the products of LPP(DE). Gas Chromatography (GC) was used to determine the gases. Functional groups of the product

molecules were identified by Fourier Transform Infrared (FT-IR) spectroscopy. Gel permeation chromatography gives information about the size distribution of molecules. NMR is able to determine the types of carbon in the product phases. With regard to further processing technology the most important characteristics are the amount of organic material transferred from the biomass to the organic solvent and the chemical composition of the transferred (extracted) material. The amount of bio-carbon transferred to the solvent can be obtained from the mass-balance of the transformation [16] or by measuring  $^{14}\text{C}$  contents using Accelerator Mass Spectrometry (AMS) [8,10,11,17], and Liquid Scintillation Counting (LSC) [17,18]. Qualitative identification of pyrolysis products is a very challenging task. The product of LPP(DE) consists of more than 100 compounds, each one in very low concentration due to the large excess of the solvent. Usually GC-MS is used for the analysis of the product molecules, but the abundance of peaks leads to overlaps and bad peak separation. In conjunction with other pyrolysis techniques (slow and fast pyrolysis, HTL) different fractionation methods were elaborated to avoid these difficulties, such as silica gel open-column chromatography [19], liquid-liquid extraction by water and organic solvents [20], or by acid-base solutions and organic solvents [21]. Solid-phase microextraction combined with GC-MS (SPME-GC-MS) was also successfully applied for qualitative analysis of lignin derived phenolic monomers [22] and for characterization of liquid products from hydrothermal liquefaction and thermal pyrolysis of biomass [23, 24]. Although main pyrolysis products or solvent molecules can saturate the SPME fiber, thus suppress the adsorption of minor products, SPME could be proposed as a fast screening method to acquire a qualitative picture of the pyrolysate composition [24].

In the present study we show the results obtained by LPP(DE) of wheat straw (WS) and poplar (PP). The use of n-hexadecane heat carrier/solvent is advantageous because it is liquid at room temperature and, therefore, it is relatively easy to separate the soluble and

deposit product phases, moreover, it does not contain aromatics allowing easier identification of phenolic monomers extracted from lignocellulose. Previous studies showed that homogeneous basic catalysts [25,26] or supported metal catalysts [12,27] can enhance the depolymerization of the lignin component of biomass. In our study the effect of heterogeneous solid acid and base catalysts on the LPP(DE) were tested. Besides of elemental analysis, NMR and SPME-GC-MS methods were used to analyze the products of the lignocellulose LPP(DE) process.

## **2. Materials and methods**

### *2.1 Materials*

The 0.5-2 mm fraction of air-dried wheat straw (WS) and poplar (PP) were used in LPP(DE) process. The organic solvent was n-hexadecane (95 %, Alfa Aesar, the impurities were C<sub>16</sub>-alkane isomers). The effect of solid acid catalysts was tested by using hydrogen-form Amberlyst<sup>®</sup>15 (Sigma-Aldrich), Nafion<sup>®</sup> NR50 (Sigma-Aldrich), H-Beta (Si/Al=15, Süd-Chemie AG) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CK-300, Ketjen). As basic catalyst MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide, produced from Mg,Al-Layered Double Hydroxyde (LDH) by calcining at 550 °C for 5 h, was used. The synthesis of Mg,Al-LDH is reported elsewhere [28]. The characteristics of the catalysts are summarized in Table 1.

### *2.2 Experimental procedure*

The LPP(DE) experiments were carried out in a 500 mL stainless steel autoclave (H-ION Research, Development and Innovation Ltd., Hungary) equipped with a magnetically-

coupled stirrer (Parr Instrument Company) (Fig. S1). The reactor was equipped with a dip tube, a purge valve, rupture disc, pressure transducer and a thermocouple placed in a thermowell. At the bottom of the autoclave a four-membered set of stainless filter plates (10, 25, 53 and 100  $\mu\text{m}$  openings) was located. The autoclave reactor was connected to a stainless steel reservoir (500 mL) *via* a valve. In a typical experiment, 20 g of lignocellulose and 200 ml of n-hexadecane was put in the reactor, then the reactor was purged with He (99.999 %; Linde) several times and sealed at 0.2 MPa He pressure. The reactor was heated up then to the desired temperature (usually 350 °C) at a rate of  $\sim 5$  °C/min and 60 rpm stirring speed. Temperature and pressure profile of one of the experiments is shown in the Supporting Material (Fig. S3). The effect of reaction temperature and residence time on the conversion was examined between 275-375 °C and 0-120 min, respectively. The influence of catalyst loading was tested adding 2, 5, or 10 g of  $\gamma$  Al<sub>2</sub>O<sub>3</sub> to a mixture of 20 g of lignocellulose and 200 ml of n-hexadecane. In order to check the effect of biomass-to-solvent ratio a comparative experiment was made using of 20 g lignocellulose and 100 ml of hexadecane. When the planned time of heat treatment expired the valve at the bottom of the autoclave reactor was opened to allow the solvent to pass together with extracted material through the filter plates to the reservoir. The filter plates retained the solid material (residue) in the reactor autoclave. The temperature of the reservoir was set to 140 °C. When the autoclave reactor cooled down also to 140 °C the low boiling point products, steam and gases were distilled out from the reservoir by opening the purge valve. Differences between liquid phases with and without distillation step are shown on Fig. S4. The distillate was cooled to room temperature using a Liebig-type stainless steel condenser. The condensed and gaseous fractions were separated. The gas was passed through a gas-meter to get its amount and collected in a gas bag. The residue was thoroughly washed with n-hexane, and it was allowed to dry at ambient conditions. The dried matter was treated in oven at 110 °C for 24 h. Soluble

and deposit phases were separated when the reservoir cooled from 140 °C down to room temperature. The soluble was stored in a capped bottle at room temperature. The deposit was dissolved from the reservoir by acetone then the acetone was left to evaporate. In order to remove adsorbed n-hexadecane, the deposit was washed with n-pentane several times and stored at room temperature. GC-MS and Simulated Distillation measurements proved that there is no serious degradation of solvent during the LPP(DE) experiments (See Fig. S5 and Chromatogram S4 in Supporting Material).

### *2.3 Analysis of reaction products*

The carbohydrate contents of lignocellulosic materials were analyzed according to the modified method reported by Sluiter et. al. [29]. The samples were ground to < 1 mm particle size and dried at 40 °C for 1 day. The samples were treated in a two-step acid hydrolysis with 72 % H<sub>2</sub>SO<sub>4</sub> for 2 h at room temperature, and then with 4 % H<sub>2</sub>SO<sub>4</sub> for 1 h at 121 °C. The obtained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, xylose, and arabinose) of the filtered supernatants were analyzed with high-performance liquid chromatography using an Agilent 1260 system with a Hi-Plex H column at 65 °C. An eluent of 5 mM H<sub>2</sub>SO<sub>4</sub> was used at a flow rate of 0.5 mL min<sup>-1</sup>. The solid residues obtained after washing were dried at 105 °C until a constant weight. The dried residues consisted of acid-insoluble organics and acid-insoluble ash. The amounts of acid-insoluble ash were determined by incinerating the sample at 550 °C for 5 h until the sample weight was constant [30]. The Klason lignin content was calculated by subtracting the acid-insoluble ash content from the acid-insoluble residue content. All experimental data were determined using three replicates.



The raw materials and solid products (residue and deposit) were analyzed by elemental analysis by Vario EL III instrument, Elementar Analysensysteme GmbH, Germany, in carbon, nitrogen and hydrogen mode. The amount of formed gases was measured with Ritter TG 05 drum-type gas meter. Gas phase products were analyzed by Perkin-Elmer Autosystem XL GC-FID-TCD, 30 m, 0.32 mm Carboxen 1006 PLOT column. Water and water soluble products were analyzed by Shimadzu 2010*plus*-QP2010SE GC-MS, 30 m, 0.32 mm, 0.25  $\mu\text{m}$  ZB-WAX Plus column. The SPME- GC-MS measurements were performed on Shimadzu 2010-QP2010 GC-MS by using 65  $\mu\text{m}$  PDMS/DVB, Fused Silica 24 Ga SPME fiber and Rxi-5 Sil MS 30m, 0.25 mm, 0,25  $\mu\text{m}$  column. Before every individual analysis, the fibers were conditioned in the GC injector for 30 min at 250  $^{\circ}\text{C}$  for cleaning. 0.5  $\text{cm}^3$  of the sample was placed in a 20  $\text{cm}^3$  glass vial, containing a magnetic stirrer and sealed using a PTFE-coated silicone rubber septum. In next step the vial was thermostated in water bath ( $T=80\text{ }^{\circ}\text{C}$ ) for 10 min. Then the fiber was immersed in the headspace of the samples for further 10 min. After 10 min the fiber was stabbed directly through the GC septum and left there for 1 min. The best sampling conditions were determined by sampling from liquid and headspace and by varying the injection time (3 sec, 1 min, 3 min). The corresponding chromatograms are presented in the Supporting Material.

NMR experiments were carried out on a Varian NMR System spectrometer operating at the  $^1\text{H}$  frequency of 400 MHz. Solution state spectra were recorded with a 5 mm inverse detection tunable dual-broadband  $\{^1\text{H}-^{19}\text{F}\}/\{^{31}\text{P}-^{15}\text{N}\}$  probe equipped with Z-gradient. The samples were dissolved in  $\text{CD}_2\text{Cl}_2$  and deuterated acetone. The measurements were carried out on 25  $^{\circ}\text{C}$  with 4 s of acquisition and 20 s repetition time. Chemical shifts were referenced to the solvent peaks. Samples were thermally equilibrated 30 min before the acquisition. Solid state spectra were recorded with a Chemagnetics 4.0 mm narrow-bore double resonance T3 probe. The spinning rate of the rotor was 8 kHz in all cases. For the one-dimensional  $^{13}\text{C}$

CP MAS (cross-polarization magic angle), 4-6000 transients were recorded with SPINAL-64 decoupling with a strength of 83 kHz and 2 ms of contact time with 5 s of recycle delay. The temperature of all the measurements was 20 °C. Adamantane was used as external chemical shift reference (38.55 and 29.50 ppm). The 90° pulse lengths were 3 μs for both the proton and the carbon channels.

### 3. Results

The elemental composition and contents of structural carbohydrates, lignin and ash are shown in Table 2. The scheme of the reactor system and separation of different reaction products is presented in Fig. 1. The carbon and oxygen mass balances were calculated based on the carbon/oxygen content of different phases. The sum of the carbon/oxygen content of gases (mainly CO, CO<sub>2</sub> and CH<sub>4</sub>), water, water solubles (mainly acetone, acetic acid, methanol and methyl acetate) and residue was subtracted from carbon/oxygen content of raw biomass. The result of this operation gives the mass of carbon/oxygen elements present in the deposit and soluble phases. The carbon yield is calculated as ratio of carbon content of extracted phase (sum of carbon contents of deposit and soluble phases) and the carbon content of the feed. The calculation scheme is shown in Supporting Material (Fig. S2). The Table 3 shows the effects of catalysts on the LPP(DE) process of WS samples. The standard deviation values were calculated from the results of seven parallel experiments (Table S1–S4). In case of Amberlyst and Nafion catalysts the experiments were made at a temperature, whereon the catalyst structure was still thermally stable, i.e., at 120 and 280 °C, respectively. The Amberlyst catalyst is very strong acid, but no conversion was detected at 120 °C in its presence in the LPP(DE) system (results not shown). The Nafion catalyst was used at 280 °C. From the first two rows of Table 3 we can conclude that the amount of extracted carbon is

slightly higher in the presence of catalyst, i.e. the carbon yield increased from 40.00 to 42.92 %. The other measurements, listed in Table 3, were carried out at 350 °C. The lowest carbon yield was obtained with the H-BEA zeolite. In accordance with the low carbon yield high amount of gas was formed. In case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and hydrotalcite (HT) no catalytic effect could be observed. Nevertheless, in the light of the standard deviation of the measurements the catalytic effect is questionable. The results of seven parallel measurements with WS,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/WS and HT/WS are shown on Fig. 2A. Results obtained at different catalyst loadings are presented in Table 4. In case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/WS conversions no systematic variation of results is observable. The highest carbon yield (46.61 %) in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/PP system was achieved by 2 g catalyst loading. At higher catalyst loadings (5 and 10 g) the amount of residue was found to become higher (~4.8 g), resulting in a drop of carbon yield from 47 to 41 %. Effect of reaction temperature on the LPP(DE) of poplar is shown in Table 5. The results show that by raising of temperature from 275 to 350 °C, the yield of biological carbon, extracted by the solvent continuously grows from starting 19-20 % to 46-49 %. It can also be noticed that the gas evolution is always higher at higher temperatures. At 375 °C the amount of the residue phase is higher (4.62-4.66 g) compared to the values at lower temperatures (4.08-4.34 g at 350 °C). In harmony with above described results regarding to overall carbon yield no significant catalytic effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be observed. However, the amount of deposit, which is a heavy organic product, is always lower in the catalytic reaction, indicating that the catalyst takes part in the splitting of dissolved large molecules. Table 6 shows the effect of residence time on product distribution at 350 °C for WS and PP samples. In general for both samples is valid that by increasing the residence time amount of residue and gas phases increases, resulting in a lower carbon yield. In catalytic reactions the effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is expressed in a somewhat higher gas evolution and in a lower amount of deposit. Results obtained with different solvent/biomass ratios are given in Table 7. Decreasing the

solvent/biomass ratio from 10/1 to 5/1 results in the decrease of the extracted biological carbon yield and increase of deposit phase.

Qualitative determination of compounds formed in catalytic LPP(DE) of WS was performed by SPME-GC-MS analysis. The products are systematized by retention times and sorted in three groups, such as aliphatics, cyclopentanone and heterocyclic compounds, simply referred to as cyclic compounds, and phenol derivatives. (Table 8). The aliphatics are acids, ketones, hydroxy-ketones and esters. The heterocyclic compounds are furans and furan derivatives. The main phenolic components, formed from splitting of lignin, are 2-methoxyphenol, 4-ethylphenol, 2-methoxy-4-methylphenol, 2,6-dimethoxyphenol etc. The cumulated peak areas based on the Total Ion Chromatograms (TIC) of different compound groups are 4-7 % for aliphatics, 15-28 % for cyclic compounds, and 68-81 % for phenol derivatives (Fig. 3). It should be mentioned that the SPME-GC-MS analysis of deposit samples did not result in meaningful chromatographs, since the vapor pressure of macromolecules, dissolved in acetone was very low in the headspace to be efficiently sampled for SPME-GC-MS.

It is more complicated to set up an oxygen mass balance. The complete results of seven parallel experiments by using PP are shown in Fig. 2B and Supporting Material, Table S5. Average of the results showed that from 9.77 g of oxygen in 20 g of raw material 1.35 g remained in the residue, 0.51 g evolved as a gas and 0.63 g as water and water soluble materials. That means that 2.53 g of oxygen is removed from PP and 7.24 g is transferred to soluble phase.

Fig. 4 shows the  $^{13}\text{C}$  CP MAS spectra of WS and of its deposit after 50 min LPP(DE) at 350 °C. Spectra (Fig. 4a) of WS is dominated by the cellulose/hemicellulose signals (55-110 ppm). Typical lignin signals (aromatic, carboxylic and other aliphatic groups) have only small intensity accordingly to the composition of the WS. After a heat treatment the peaks

ascribed to the carbon atoms in cellulose/hemicellulose completely disappeared indicating the decomposition of polysaccharides. On the spectrum of the deposit three different regions could be distinguished (Fig. 4b). The signals from 0-60 ppm were attributed to aliphatic groups connected to aromatic compounds. The sharp signals in this region indicate the presence of solvent (n-hexadecane) and its decomposition products in the deposit phase. These signals have a much larger intensity on the direct polarization spectrum indicating their higher mobility, thus weak cross polarization efficiency (spectrum not shown). It should be noted that after LPP(DE) the products from cracking of n-hexadecane were always detected in a small amount (~1 %). The broad signal from 100 to 160 ppm is attributed to polycondensed aromatic structures. In both regions signals of ether (C-O-C) and hydroxyl (C-OH) groups are also present (40-60 and 140-160 ppm). The peaks associated with the carbonyl groups (C=O) in aldehyde or ketone functional groups appear in region of 190-220 ppm. Fig. 5 shows <sup>1</sup>H NMR spectra of the soluble (mixed with CDCl<sub>2</sub>) and deposit (dissolved in acetone-d<sub>6</sub>) phases. The spectrum of the soluble is very similar to the spectrum of the n-hexadecane, because of the great excess of solvent. Peaks at 5.0 and 5.8 ppm are associated with C=C double bonds in aliphatic olefins formed in cracking reaction of n-hexadecane. Signals of small molecular weight products appear on the spectra, but the determination of their exact structure and size were not possible due to low concentration. Small molecular aromatic compounds (6.4-7.8 ppm), O –containing etheric functional groups (3.4-4 ppm) and no hetero atom containing aliphatic signals (below 2.8 ppm) can be identified. The deposit phase consists of from low-molecular weight fraction (~10 %) and from high-molecular weight fraction, which has a polycondensed aromatic structure, with attached methyl- and ethyl chains and with ether and hydroxyl functional groups. Narrow signals can be attributed to the small molecular fraction, while the very broad to the polycondensed fraction both in the aromatic and in the aliphatic region.

#### 4. Discussion

The essential purpose of LPP(DE) process is to transfer biological carbon from lignocellulosic material to an organic liquid, which is a heat carrier and solvent for extracting degradation products. Regarding further processing the chemical composition, i.e. nature of the extracted molecules (aliphatic, aromatic), and the number of carbon and oxygen atoms in the molecules, are most important. A petrochemical feedstock, which needs further hydroprocessing looks to be advantageous heat carrier/solvent because the extract could be simply co-processed by the solvent. However, if the composition of the feedstock is very complex the identification of the extracted molecules in the dilute solution is almost impossible. Thus a real petrochemical feedstock is not suitable solvent if the process is subject of scientific research. In our experiments n-hexadecane was used as solvent that is beneficial regarding the analytical procedure. The results listed in Table 3 and 4 suggest that heterogeneous catalysts have only little effect on the carbon yield and product selectivity. The statistical analysis of seven parallel experiments supports this statement. Moreover, the share of different product groups is very similar to that of the blank experiment with WS (Fig. 3). It is known that mineral acids, such as sulfuric and hydrochloric acid can enhance the bio-oil production by fragmentation of lignin [31,32]. In present study heterogeneous (solid) acidic/basic catalysts were used. The results suggest that the solid-solid interaction between catalyst and substrate is not intimate enough to promote the acid catalyzed scission of lignin intralinkages. Moreover, the non-aqueous media does not favor the acid/base catalyzed reactions. Still, the results of GC-MS-SPME measurements show that the amount of phenol derivatives, is the highest in the product (68-81 %). But it must be mentioned that the adsorption/desorption equilibrium on SPME fiber can enrich some analytes in the sample. In

the head space analyses the fiber adsorbent gets in equilibrium with the vapor phase having a composition different of that of the liquid phase. Moreover, TIC values, given by the GC-MS are not directly proportional with the concentration of a component even in the thus obtained sample. As a consequence, the quantitative conclusions about the composition of the soluble fraction can be drawn in a very broad sense only. The main extracted products are alkyl and alkoxy derivatives of phenol and furan derivatives. It is obvious that the phenol derivatives stem from lignin molecules and that the other molecules, the cyclic compounds, containing five or six carbon atoms, and the shorter oxygenates, are products of cellulose/hemicellulose decomposition. As biofuel components or precursors phenol derivatives are more appropriate than the other extracted molecules due to their higher C/O atom ratio. In view of carbon balances the results of present study are similar to that obtained in LPP(DE) of spruce wood in semibatch reactor by using heat carrier having boiling point in the range of 410 and 440 °C. The corresponding data of our study and those determined for spruce wood are 52 vs. 59 wt% for the residue, 43 vs. 28 wt% for the soluble, and 5 vs. 8 wt% for the gas. [8]. Our results in comparison to those of ref [8] are: 52 vs. 59 wt% for the residue, 43 vs. 28 wt% for the soluble and 5 vs. 8 wt% for the gas. It must be mentioned that by using of high boiling point heat carrier the separation of residue and soluble phases is not possible, so some amount of extractable biological carbon remains in the residue. The LPP(DE) experiments performed with 1-methylnaphthalene showed very high conversion. The amount of the residue for the fir sawdust and rice straw were only 3 and 19 wt%, respectively [15,16]. Similar elemental composition was obtained for the residue (biochar) independently of the used solvent and reaction system. In the present study the residue of poplar after a near to 0 minute residence time at 350 °C contains 69.0 wt% carbon, 4.7 wt% hydrogen and 26.3 wt% of oxygen. Using 1-methylnaphthalene solvent in similar experiment Zhu [16] et al found 74.0 wt% carbon, 5.1 wt% hydrogen and 20.6 wt% oxygen, while Schwaiger [8] et al. found 75.3 wt% carbon, 5.2

wt% hydrogen and 20.6 wt% oxygen. As the elemental analysis of the residue is the easiest task and the results of different laboratories are very similar. It seems rational to think that the differences in the determined amounts of the other phases stem from the different separation techniques and calculation methods applied. Regarding solvent/extract co-processing the C/O ratio of the extract, to be processed is most important. The difficulties of quantitative separation and collection of water-containing phases and the exact measurement of organic oxygen make the oxygen balance less accurate than the accuracy of the carbon balance. Anyhow, the oxygen balance is good enough to suggest that the extract still contains unfavorably high amount of oxygen.

It has been demonstrated that the prolonged reaction times and high temperatures (more than 350 °C) are disadvantageous in view of carbon yield, due to the condensation reactions between primarily formed product molecules [16]. Our results support these findings (Tables 5 and 6). The amount of residue phase is higher if the reaction temperature and/or the residence time of the reactant is higher. It is also interesting that at higher temperatures (325-375 °C) and at higher residence times (30-120 min) the amount of deposit is always lower, if catalyst is present in the reactor, indicating that the catalyst causes to occur the scission of the larger molecules of this phase. As it was mentioned, high excess of solvent makes the analysis of the LPP(DE) products difficult. Results listed in Table 7 suggests that by decreasing the solvent/biomass ratio this problem can not be mitigated, because lower amount of the solvent promotes polymerization of the extracted molecules resulting in an increased amount of residue and deposit phases.

## **5. Conclusions**



Liquid phase pyrolysis of ground lignocellulose, obtained from wheat straw and poplar, were carried out in n-hexadecane solvent under inert atmosphere. About 40-49 wt% of biological carbon was transferred into the solvent. Dissolved molecules were identified by SPME-GC-MS method and sorted in three groups, such as aliphatic, cyclopentanone and heterocyclic compounds, and phenol derivatives. The cumulated peak areas based on the Total Ion Chromatograms showed that the share of phenolic components is 68-81 %. However, the carbon/oxygen balance calculations suggested that relative to the amount of transferred biological carbon high amount of organic oxygen were transferred to the solvent. The solid acid or base catalysts were of negligible effect on the product distribution and yield of liquid phase pyrolysis.

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## Figure legends

Fig. 1. The sketch drawing of the reactor system and method for separation of different reaction products.

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Fig. 2. Carbon yields in the liquid phase pyrolysis (LPP) of wheat straw (WS) without catalyst, and in presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and hydrotalcite catalysts, 20 g WS, 200 ml hexadecane, 2 g catalyst, 350 °C, 0 min residence time(A) and oxygen balance in LPP of poplar at 350 °C, 0 min residence time (B) The shown results are average of the seven parallel measurements listed in Tables S1-S4 in Supporting Material

Fig. 3. The cumulated peak areas based on the Total Ion Chromatograms (TIC) of different compound groups of wheat straw determined by SPME GC-MS method. Samples were collected from headspace at 80 °C, 10 min, injection time 1 min at 250 °C.

Fig. 4. Solid state <sup>13</sup>C CP-MAS NMR spectra of wheat straw (a) and deposit (b).

Fig. 5. Solution state <sup>1</sup>H NMR spectra of Soluble in CDCl<sub>2</sub> (a) and deposit in acetone-d<sub>6</sub> (b).

Table legends

Table 1: Physicochemical properties of the catalysts.

Table 2: The cellulose, hemicellulose, and the lignin content of the biomass samples analyzed by the modified method of Sluiter et al.[27,28 ]

Table 3: The effect of solid catalysts on the carbon balance and carbon yield of liquid phase pyrolysis of wheat straw

Table 4: The effect of the catalyst loading on the carbon balance and carbon yield of liquid phase pyrolysis

Table 5: The effect of the temperature on the carbon balance and carbon yield of liquid phase pyrolysis of poplar in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Table 6: The effect of residence time on the carbon balance and carbon yield of liquid phase pyrolysis

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Table 7: The effect of the biomass-to-solvent ratio on the carbon balance and carbon yield of liquid phase pyrolysis

Table 8: Effect of catalysts on the product distribution in liquid phase pyrolysis of wheat straw determined by SPME-GC-MS method