In-situ catalytic fast pyrolysis of poultry wastes

Ismail Cem Kantarli[1*], Stylianos D. Stefanidis[2], Konstantinos G. Kalogiannis[2],Angelos A. Lappas[2]

[1]Ege University, Ataturk Medical Technology Vocational Training School, 35100, Bornova, Izmir, Turkey.

[2] Chemical Process and Energy Resources Institute, Centre for Research and Technology Hellas, 57001 Thessaloniki, Greece

Abstract

The objective of this study was to examine the utilization of poultry waste as an energy feedstock via non-catalytic (thermal) and catalytic fast pyrolysis of poultry meal and poultry litter, initially in a fixed bed bench-scale reactor at 500 ºC. Optimum feedstock and catalyst was decided and then scaled-up in the CPERI pilot plant biomass pyrolysis unit for biomass pyrolysis. Poultry meal was more promising with respect to bio-oil yield. From the perspective of quality and quantity of bio-oil obtained from poultry meal, MgO showed a more balanced performance with good selectivity towards aliphatic hydrocarbons and an organics fraction yield of 50.9 %.Bio-oil obtained using MgO as catalyst had the highest carbon content among all bio-oils. Poultry litter was not found to be as good a candidate for fast pyrolysis as poultry meal due to its high char and low bio-oil yield.

Keywords:bio-oil, poultry wastes, catalytic upgrading, pyrolysis

1.Introduction

Environment legislation about the disposal of wastes from the poultry industry requires the proper management of these wastes. In this context, to consider poultry wastes as a potential feedstock for thermal conversion technologies can be a good alternative. Among the thermochemical conversion processes, biomass fast pyrolysis, seems to be the most emerging technology for the production of liquid oil (bio-oil), which is considered as a promising energy source. In this process, the biomass is heated under inert atmosphereusing an inert solid heat carrier at very high heating rates. The bio-oil exhibits several disadvantages such as high water and oxygen contentand needs furtherupgrading in order to improve its quality. Different approaches for upgrading of bio-oil exist in literature, including high pressure hydro-treatment [1,2], reactive pyrolysis [3], bio-oil distillation [4] and in-situ catalytic fast pyrolysis [5]. Among these approaches, in-situ catalytic fast pyrolysis of biomass might be a good alternative from the point of bio-oil quality and process economics.

In this study, non-catalytic and catalytic fast pyrolysis of poultry litter (PL) and poultry meal (PM) was carried out in a fixed bed bench-scale reactor at 500 ºC. The effect of catalyst type on product distribution, bio-oil yield and composition was investigated as the main scope. ZSM-5 and MgO were tested as candidate catalysts. The catalysts were evaluated focusing on their ability to reduce the oxygen content of the bio-oil, while maintaining the organic fraction yield at acceptable levels. The composition of the organic fraction was studied as well, in order to evaluate the catalysts' selectivity towards desirable products. The optimum feedstock and catalyst was decided and scaled-up in the CPERI pilot plant unit for biomass pyrolysis.The results obtained from non-catalytic and catalytic fast pyrolysis of PM and PL were also compared with the results obtained from non-catalytic slow pyrolysis of these feedstocks at 500 °C in a vertical fixed bed design pyrolysis reactor in Turkey.

2.Materials and Method

2.1.Materials

2.1.1. Biomass

Poultry wastes were kindly provided by CP Group, Izmir, Turkey. PM (<1 mm) was used as received, whereas PL was previously dried at room temperature and ground to <1.5 mm, then dried in a drying oven at 105 °C overnight. For characterization of PM and PL, proximate analysis (moisture content, ash content) and ultimate analysis (C, H and N content) of feedstocks were carried out. The characteristics of feedstocks are given in Table 1.

Table 1. Properties of feedstocks

Feedstock	Moisture (wt.%)	Ash (wt.%.drybasis)	C (wt.%.drybasis)	H (wt.%.drybasis)	S (wt.%.drybasis)	N (wt.%.drybasis)	O (wt.%.drybasis)
PM	6.06%	10.42%	51.59%	7.56%	0.01%	9.34%	21.08%
PL	1.64%	19.01%	38.47%	5.02%	0.00%	3.60%	33.90%

2.1.2. Catalytic materials

All catalytic materials, a ZSM-5 formulation and MgO from natural magnesite, were commercially available. Prior to the experiments, the catalytic materials were calcined at 500 °C for 3 h and stored in a desiccator. Table 2 lists all materials that were used and their properties. The materials were characterized by N_2 adsorption–desorption experiments at -196 °C for the determination of surface area (BET method), pore volume and pore size distribution (BJH method) of the samples that were previously outgassed at 250 °C for 18 h under vacuum, using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). More details about the MgO catalyst from natural magnesite can be found in the study of Stefanidis et al.[6].

Table 2. Properties of catalysts

	SSA (m^2/g)	AveragePore Size (nm)	Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Mesopore Volume (cm^3/g)	Total Acidity (μmol Pyridine/g)^1	BronstedAcidity (μmol Pyridine/g)^1	LewisAcidity (μmol Pyridine/g)^1	Total Basicity (μmol CO/g)^2	Weak / MediumBasicity (μmol CO/g)^2	StrongBasicity (μmol CO/g)^2
ZSM-5	138	4	0.108	0.037	0.071	54.6	36.5	18.1	N.D.	N.D.	N.D.
MgO	40	34.9	0.34	0	0.34	N.D.	N.D.	N.D.	147	115	32

[1] Measured by Pyridine-FTIR

[2] Measured by TPD-CO_2

2.2. Experimental method

The bench-scale in-situ fast pyrolysis experiments were carried out at 500 °C in a fixed bed reactor which was made of stainless steel 316 and heated by a 3-zone furnace. The temperature of each zone was independently controlled using temperature controllers. The catalyst bed temperature was considered as the experiment temperature, and was monitored with a thermowell. The biomass feedstock was introduced into the reactor using a specially designed piston system. A constant stream of N_2 was fed from the top of the reactor for the continuous withdrawal of the products and maintenance of the inert atmosphere during pyrolysis. The products exiting from the bottom of the reactor in gaseous form were condensed in a glass receiver submerged in a cooling bath kept at -17 °C. Non-condensable gases were collected in a gas collection system. A filter placed between the glass receiver and the gas collection system recovered any condensable gases that were not condensed in the receiver. Schematic representation of the experimental set-up is given elsewhere [5].

For the run-up of experiments, initially, the reactor was filled with 0.7 g catalyst (ZSM-5 or MgO) or silica sand for the catalytic and non-catalytic tests, respectively, and the piston was filled with either 1.5 g of poultry meal or 3 g of poultry litter. As soon as the desired reaction temperature was reached, the biomass was introduced into the reactor and the experiment began under a 100 cm^3/min nitrogen flow. At the end of the experiment (15 min), the reactor was cooled and purged for 10 min with N_2 (50 cm^3/min).

The liquid products were collected and quantitatively measured in the pre-weighed glass receiver. The pyrolytic vapors, upon their condensation in the glass receiver, formed multiple phases, which consisted of an aqueous phase, a liquid organic phase(bio-oil) and viscous organic deposits on the receiver walls. It must be noted that, two experiments under the same conditions were realized for each catalytic material (or silica sand), which differed in the collection of liquid products. At the end of first experiment, in order to collect a representative bio-oil sample for GC-MS analysis, dichloromethane was used to separate the organic phase from water phase. The bio-oil was collected as a solution and analyzed by GC-MS. After the dichloromethane solution was collected, the remaining phase in the receiver was weighed and described as the water phase. At the end of the second experiment, a sample of the bio-oil was drawn with a syringe without any solvent addition and was submitted for further analysis (carbon, hydrogen and nitrogen content) without weighing.

The gas products were collected and measured by the water displacement method.The amount of the solid residue,consisting of charcoal (biomass residue) and coke-on-catalyst formed by thermal and catalytic cracking, was weighed directly. The amount of condensable vapours recovered in the filter was also directly weighed and added to the liquid products yield.

The optimum feedstock and catalyst was decided and scaled-up in the CPERI medium-scale pilot plant unit for biomass pyrolysis. Poultry meal and ZSM-5 was chosen for the scale-up study as feedstock and catalyst, respectively.The reactor was a fluidized bed reactor loaded with 150 g of the ZSM-5 catalyst formulation.Biomass was fed continuously from a feed hopper into the hot catalyst bed at a rate of 5 g/min for 20 min. A total of 100 g of biomass were catalytically pyrolyzed at each run. The catalytic pyrolysis temperature was 500 °C, followed by a catalyst regeneration cycle carried out at 650 °C and in the presence of oxygen in order to burn off the solid products in the reactor. More details about the medium-scale experimental setup and procedure can be found in the study of Stefanidis et al. [7].

Slow pyrolysis experiments were also carried out in a vertical fixed bed design pyrolysis reactor in Turkey. In a typical run, 50 g of feedstock was placed into the reactor. The system was heated to 500 ºC at a heating rate of 5 ºC min^{-1}, and held at this temperature for 1 h. The volatile products were swept by nitrogen gas with a flow rate of 25 mL min^{-1} from reactor to collection flasks cooled with ice where the liquid products were condensed in the traps and then weighed after separation. The non-condensable volatiles (gases) were vented to the atmosphere. The solid residue (biochar) was weighed and biochar yield was calculated.

2.3. Analysis methods

The water content of the bio-oil sample(organic phase only) obtained by pilot-scale fast pyrolysis was determined by Karl–Fischer titration (ASTM E203-08). The carbon, hydrogen and nitrogen content of all bio-oil samples were determined with an elemental CHN LECO-628 analyzer. Bio-oil composition was analyzed using an Agilent 7890A/5975C gas chromatograph-mass spectrometer system (Electron energy 70 eV; Emission 300 V; Helium flow rate: 0.7 cc/min; Column: HP-5MS 30 m × 0.25 mm ID × 0.25 μm). The NIST05 mass spectra library was used for the identification of the compounds found in the bio-oil.

3.Results and discussion

3.1.Product yield distribution

Product yield distribution (wt.% on biomass) obtained from bench-scale slow pyrolysis, bench-scale fast pyrolysis, and pilot-scale fast pyrolysis of PM are given in Figure 1. It is obvious that each catalytic material seems to affect the product yields to a different extent. For PM, the highest liquid (64.6 wt.%) yield was achieved in the bench scale catalytic run with ZSM-5 and the highest bio-oil yield (61.3 wt.%) was achieved in the non-catalytic runs.The use of catalysts in fast pyrolysis led to a decrease in bio-oil yield with a simultaneous increase in water phase yield. The comparison of water phase yield from catalytic pyrolysis with that of non-catalytic run shows the dehydration effect of catalyst. In pilot-scale run with ZSM-5, the liquid and bio-oil yields were lower, while the gas and solid yields were higher in comparison with bench scale runwith ZSM-5. It should be noted that the PM was not run in pilot plant as received. It was oily and it would stick on the walls of the feed hopper. In order to make it less sticky, it was submerged into hexane for 2 days and then the hexane was removed by vacuum filtration and by drying at 80 °C for another 2 days. This pre-treatment resulted in about 19% weight loss of the initial feedstock, which was attributed to the removal of the oils in the poultry meal with the hexane. Therefore, the removal of oils from poultry meal seems to be the main reason for less liquid and organic phase yields in pilot scale run.

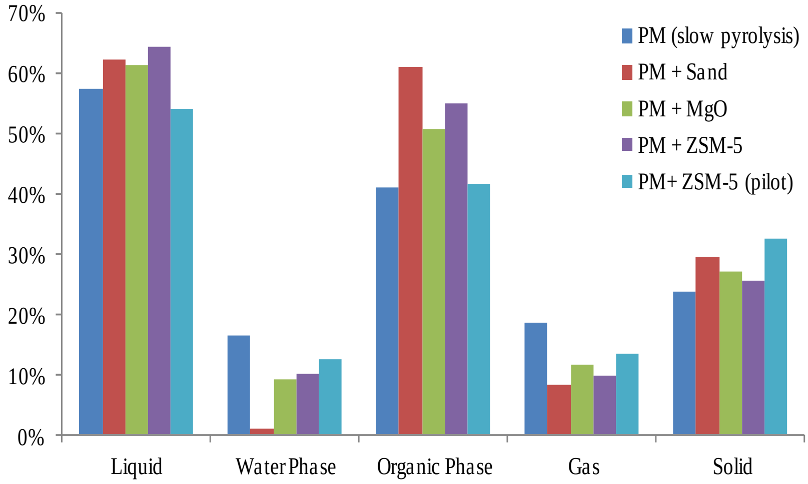


Figure 1. Product yield distribution obtained from bench-scale slow pyrolysis, bench-scale fast pyrolysis, and pilot-scale fast pyrolysis experimental runs (wt.% on biomass) with PM.

Product yield distribution (wt.% on biomass) obtained from bench-scale slow pyrolysis, and bench-scale fast pyrolysis of PL are given in Figure 2. For poultry litter, the highest liquid (42.3 wt.%) yield was achieved in the non-catalytic runs and the highest bio-oil yield was achieved with MgO (28.2 wt.%). The use of MgO increased the organic phase yield and decreased the water phase yield.

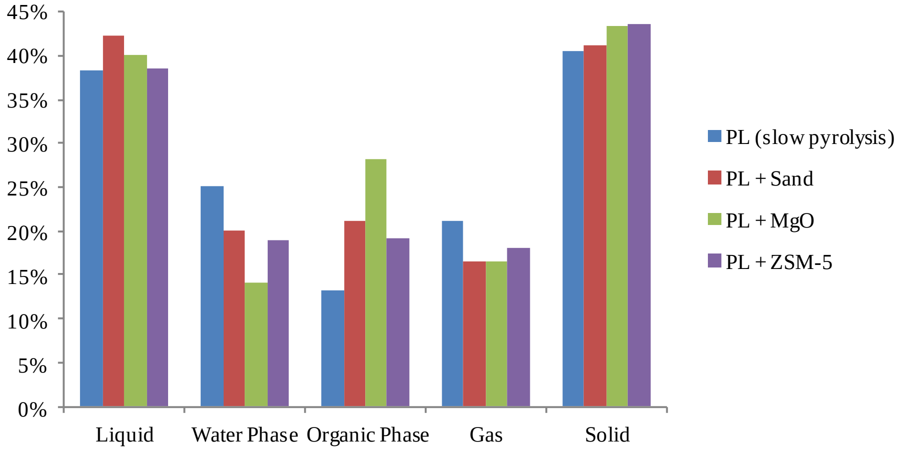


Figure 2. Product yield distribution obtained from bench-scale slow pyrolysis and bench-scale fast pyrolysis experimental runs (wt.% on biomass) with PL.

Figure 3 presents CO_2, CO and other gas yields for each catalyst used. The main gaseous products were CO_2 and CO. CH_4 was also detected, as well as other light hydrocarbons, mainly C_2–C_6 light hydrocarbons, particularly for PM. Compared to the non-catalytic run, ZSM-5 increased the gas yield from PL, which was noticeable as an increase in both CO and CO_2 yield. Acidic catalysts were reported to have the tendency to favor CO production in the study of Stefanidis et al.[5].This tendency of the acidic catalyst was very significant in the pilot scale pyrolysis of PM using ZSM-5 catalyst. In case of in-situ pyrolysis of PM, MgO increased the gas yield, which was mainly noticeable as an increase in CO_2 yield and light hydrocarbons. The increase in $CO_2$was attributed to the conversion of acids in the pyrolysis vapors to ketones via ketonization reactions, which release CO_2 and are catalysed in the presence of basic catalysts. The ketonization of acids over basic catalysts has previously been reported in the literature [8-10].

It is obvious from the comparison of slow pyrolysis with in-situ fast pyrolysis that slow pyrolysis yielded less liquid and bio-oil, while it yielded more water phase and gas. Since the pyrolysis vapors had a residence time of less than 1 sec in the reactor and were rapidly cooled during in-situ fast pyrolysis[5], they yielded more bio-oil.

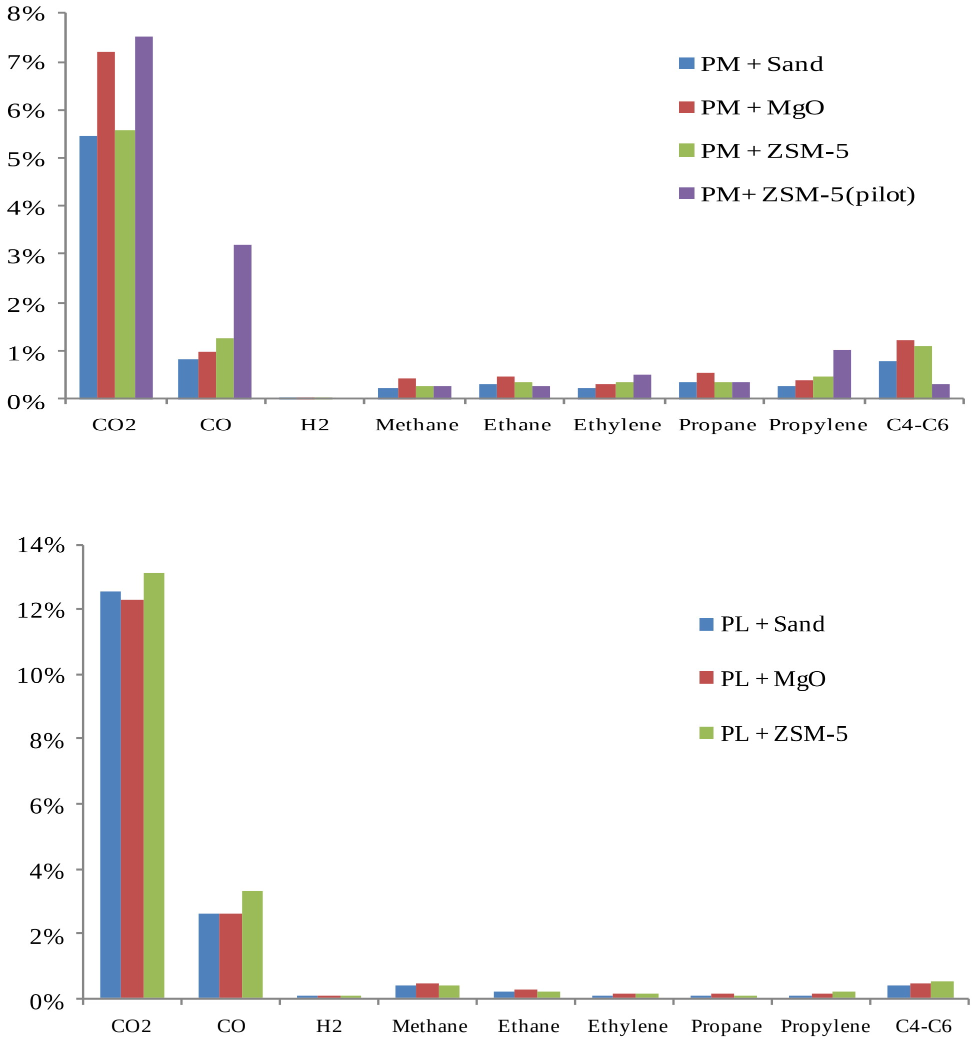
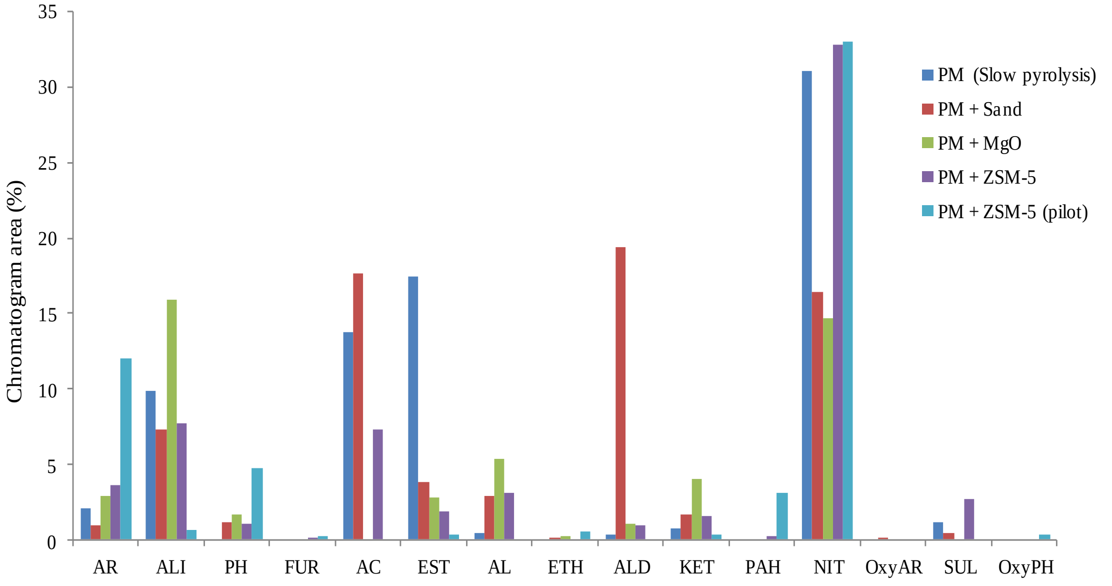


Figure 3. Gas product yields for non-catalytic and catalytic experimental runs (wt.% on biomass)

Figure 4 presents the qualitative composition of the bio-oil obtained from GC–MS analysis. The identified compounds were classified into15 groups: aromatic hydrocarbons (AR), aliphatic hydrocarbons (ALI), phenols (PH), furans (FUR), acids(AC), esters (EST), alcohols (AL), ethers (ETH), aldehydes(ALD), ketones (KET), polycyclic aromatic hydrocarbons (PAH), nitrogen containing compounds (NIT), benzene rings with oxygenated substitutes excluding phenolics (OXYAR), sulphur containing compounds (SUL) and phenolics with oxygenated substitutes, such as guaiacols, syringols and catechols (OXYPH). Aromatic hydrocarbons, aliphatic hydrocarbons and alcohols are considered desirable products for biofuel production. Phenols and furans are considered as high added value chemicals. Acids, on the other hand, are considered undesirable, since they are responsible for the corrosiveness of the bio-oil. Ketones and aldehydes are also considered undesirable, since they are responsible for the instability of the bio-oil during transport and storage. Ethers, esters andoxygenates in general reduce the heating value of the bio-oil and PAHs and nitrogen compoundsare detrimental for environmental reasons, so their existence in bio-oil is not desired [5].



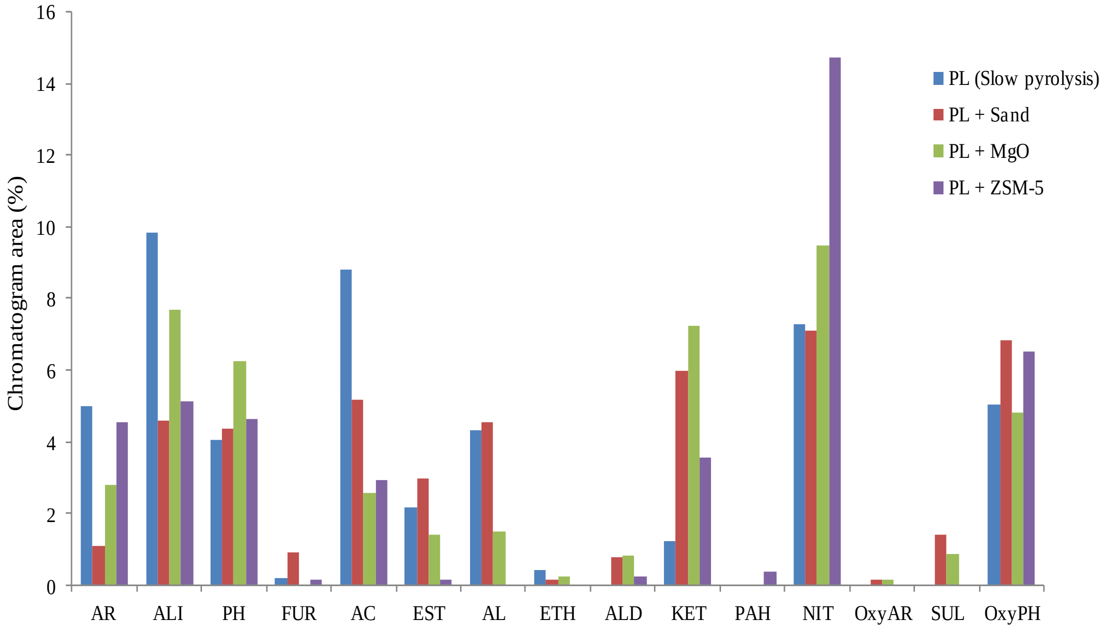


Figure4. Chemical composition of the organic fraction (peak area %).

If bio-oils obtained by bench-scale catalytic fast pyrolysis are examined, particularly MgO was found to be effective in reducing the undesirable compounds, particularly the acids and aldehydes concentration and effective to an extent in reducing nitrogen containing compounds concentration providing a bio-oil with upgraded characteristics. It can be said that the acids present in the thermal bio-oil were transformed into aliphatic hydrocarbons due to the decarboxylation reactions favoured by the MgO. The ZSM-5 on the other hand did not significantly increase aliphatic hydrocarbons, since it favours aromatization and cracking reactions that lead to smaller molecular weight compounds [11]. The bio-oil obtained from the pilot-scale fast pyrolysis with ZSM-5 had higher aromatic content, but lower alcohol and aliphatic content in comparison with that obtained from bench-scale catalytic flash pyrolysis with ZSM-5. The amount of PAHs is high in this bio-oil probably due to aromatization–polymerization reactions.

It must be noted that half of the compounds in the bio-oil produced in the presence of MgO as catalyst could not be identified. MgO was very selective towards aliphatic hydrocarbons production. In comparison with the non-catalytic fast pyrolysis bio-oil, it had a higher aromatic and alcohol content, too. On the other hand, the reason of increase in ketones content was attributed to the ketonization of acids over basic catalyst. Overall, MgO had a more balanced performance with good selectivity towards aliphatic hydrocarbons and an organic phase yield of 50.9 wt.%.

On the other hand, the bio-oils obtained from poultry litter by either slow pyrolysis or non-catalytic or catalytic fast pyrolysis were considered low-quality bio-oil, since it contained undesired compounds such as acids and ketones, although they contained aliphatics and aromatics as well. The use of catalysts increased the amount of aromatics and aliphatics and decreased the amount acids and ketones. However, it must be noted thathalf of the compounds in bio-oil produced from poultry litter could not be identified.

3.3. Elemental composition of the bio-oil

Table 4 presents the elemental composition of the bio-oil obtained by slow pyrolysis, non-catalytic or catalytic fast pyrolysis and pilot-scale fast pyrolysis. For PM, the non-catalytic fast pyrolysis bio-oil had the lowest carbon content (67.2%) among all of the bio-oils obtained. The addition of catalytic materials resulted in an increase of the carbon content of the bio-oil. In fast pyrolysis runs, an increase in C content was observed with both MgO and ZSM-5 catalysts. C content of the bio-oil from the pilot-scale pyrolysis of PM with ZSM-5 was as high as that obtained from bench-scale fast pyrolysis of PM with MgO. On the other hand, for PL, non-catalytic pyrolysis bio-oil has a C content of 71.9 %, which was significantly increased to 82.9 % with the use of ZSM-5 as catalyst.

Oxygen was removed from the pyrolysis vapors mainly in the form of CO_2 as well as CO and H_2O and this resulted in the subsequent reduction of the total liquid and bio-oil yields due to the transfer of carbon in the gas products, the formation of water and the formation of coke deposits on the catalyst surface. It is therefore expected, that as more oxygen is removed from the liquid organic fraction, less liquid organic products will be collected. This trend can be observed for PM in bench-scale fast pyrolysis runs as shown in Figure 6. MgO produced the most deoxygenated bio-oil and the lowest bio-oil yield at the same time. It must be noted that pilot-scale pyrolysis of PM with ZSM-5 produced the most deoxygenated bio-oil.

Table 4. Elemental composition of the produced bio-oils (wt.% on organic phase).

	Carbon	Hydrogen	Nitrogen	Oxygen[1]
Poultry Meal (slowpyrolysis)	71.41%	10.01%	9.22%	9.36%
Poultry Meal + Sand	67.22%	10.23%	8.90%	13.65%
Poultry Meal + MgO	74.70%	11.02%	9.51%	5.77%
Poultry Meal + ZSM-5	72.25%	10.50%	9.75%	7.30%
Poultry Meal + ZSM-5 (pilot)	74.5%	8.3%	11.5%	5.7%
PoultryLitter (slowpyrolysis)	73.10%	8.61%	7.88%	10.42%
PoultryLitter + Sand	71.88%	7.42%	N.D.	N.D.
PoultryLitter + MgO	71.97%	8.26%	8.07%	11.7%
PoultryLitter + ZSM-5	82.85%	7.64%	4.92%	4.59%

[1] Determined by difference
N.D. not determined

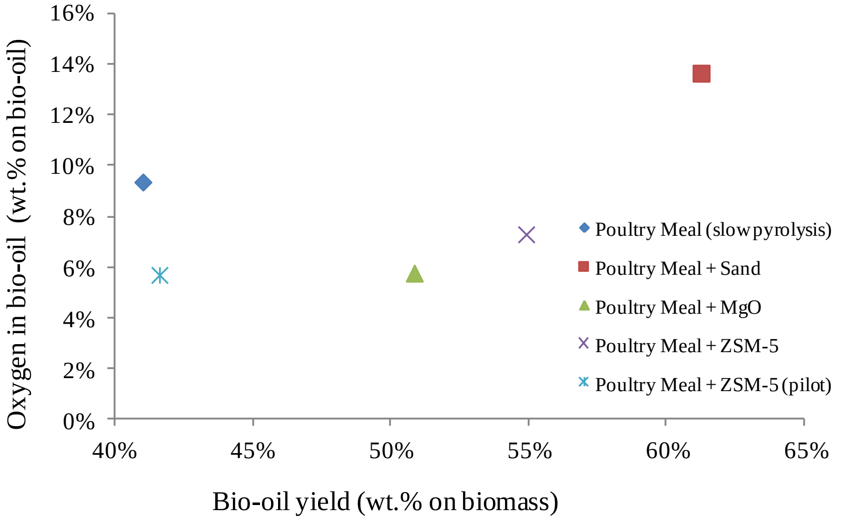


Figure 6. Bio-oil yield versus oxygen content in the bio-oil.

4. Conclusion

In this work, the potential of utilizing poultry wastes,poultry meal and poultry litter, as feedstock for the production of a liquid energy carrier via catalytic pyrolysis was investigated. Pyrolysis of poultry waste, particularly poultry meal, gave high yields of bio-oil, but it was of very low quality because of the unusually high nitrogen content (compared to lignocellulosic feeds). The catalysts reduced the oxygen content of the bio-oils and also reduced some undesirable compounds, but according to the elemental analyses, the nitrogen content remained high. Therefore, even the catalytic bio-oils can be problematic and further research is needed to improve their quality in order to be considered for energy purposes.

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