IN-SITU CATALYTIC FAST PYROLYSIS OF POULTRY WASTES

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Outline

- Introduction
- Materials
- Methods
- Results and discusions
  - Catalytic fast pyrolysis results
- Conclusion

POULTRY INDUSTRY AND POTENTIAL WASTES

- According to the Food and Agriculture Organization of the United Nations (FAO), poultry account for over 80% of all livestock (FAO, 2015a).
- The poultry industry produced approximately **23 billion poultry** in 2013 all over the world (FAO, 2015b).
- Today, poultry are mostly raised in large farms.

✓Poultry industry produces two types of wastes:

1. **Poultry meal:** is made from ground, rendered, clean parts of poultry carcasses and can contain bones, offal, undeveloped eggs, and in few cases, feathers, that are unavoidable in the processing of the poultry parts.
2. **Poultry litter:** is a mix of poultry excreta, spilled feed, feathers, and bedding materials resulting from intensive poultry production.

- ➢ Environment legislation about the disposal of wastes from the poultry industry requires the proper management of these wastes.

MANAGEMENT OF POULTRY WASTES

- Due to the intensive poultry farming, **poultry litter** raise serious concerns about treatment and disposal. It is traditionally used as fertilizer, but potential environmental problems such as spread of pathogens [1] and emission of greenhouse gases and odorous compounds are reported due to its overuse as fertilizer [2].
- **Poultry meal** was used in formulated animal feed, but today it can be only used in formulated pet feed according to EU Regulation 1774/2002 (European Community, 2002).
- Therefore, the poultry industry is facing difficulties in the proper treatment of surplus poultry litter and meal and seeking an alternative technology for the utilization of these wastes.

- In this context, to consider **poultry wastes** as a **potential feedstock** for **thermal conversion technologies** can be of great interest both economically and environmentally.
- Among the thermochemical conversion processes, **biomass fast pyrolysis** seems to be the most emerging technology for the production of liquid oil (**bio-oil**).

Bio-oil is considered to be a very promising biofuel / bioenergy carrier, as

✓ it can be easily transported,

✓ burned directly in thermal power stations or in gas turbines and

✓ utilized into a conventional petroleum refinery for the production of higher quality light hydrocarbon fuels [3].

Disadvantages of Bio-oil

- Bio-oil usually presents several disadvantageous characteristics, such as
  - ✓ High water and oxygen content,
  - ✓ corrosiveness,
  - ✓ instability under storage and heating conditions,
  - ✓ immiscibility with petroleum fuels,
  - ✓ high acidity,
  - ✓ high viscosity,
  - ✓ low calorific value;
  - ✓ all these become the primary obstacles for its direct application as a fuel [3].

Upgrading of Bio-oil

➢Different approaches for upgrading of bio-oil exist including

✓ high pressure hydro-treatment [4, 5]

✓reactive pyrolysis [6]

✓bio-oil distillation [7] and

✓**catalytic fast pyrolysis of biomass** [8]**.**

➢ Catalytic fast pyrolysis of biomass might be a good alternative from the point of bio-oil quality and process economics.

Catalytic fast pyrolysis

➢Catalytic pyrolysis of biomass takes place under the same conditions as thermal fast pyrolysis, with the difference being that pyrolysis vapors come in contact with a solid catalyst prior to their condensation.

➢The specific function of various catalysts can alter the product yields and selectivity.The catalytic reactions that take place on the catalyst's surface enhance the removal of oxygen in the form of CO_2, CO and H_2O, thus leading to the formation of a bio-oil with tailored composition and improved properties.

➢Several types of microporous (e.g. zeolites: Y, ZSM-5, Mordenite and Beta) and mesoporous (e.g. MCM-41, MSU, SBA-15) materials have been studied as catalysts for biomass pyrolysis or for the upgrading of bio-oil.

Objectives

The main purpose of this study was to convert poultry wastes into bio-oil by catalytic fast pyrolysis.

The specific objectives were to:

1. to investigate the effect of catalyst type (ZSM-5 and MgO) on product distribution, bio-oil yield and composition
2. to evaluate the catalysts' ability to reduce the oxygen content of the bio-oil, while maintaining the bio-oil yield at acceptable levels (catalyst screening)
3. to evaluate the catalysts' selectivity towards desirable product

Elemental, Proximate and Component Analysis of Poultry Wastes

	Proximate analysis, (wt.%)		Component analysis, (wt.%)	
	Moisture	**Ash**	**Protein**	**Oil**
PM	6.1	10.4	59	16
PL	1.64	19.0	23	N.D.

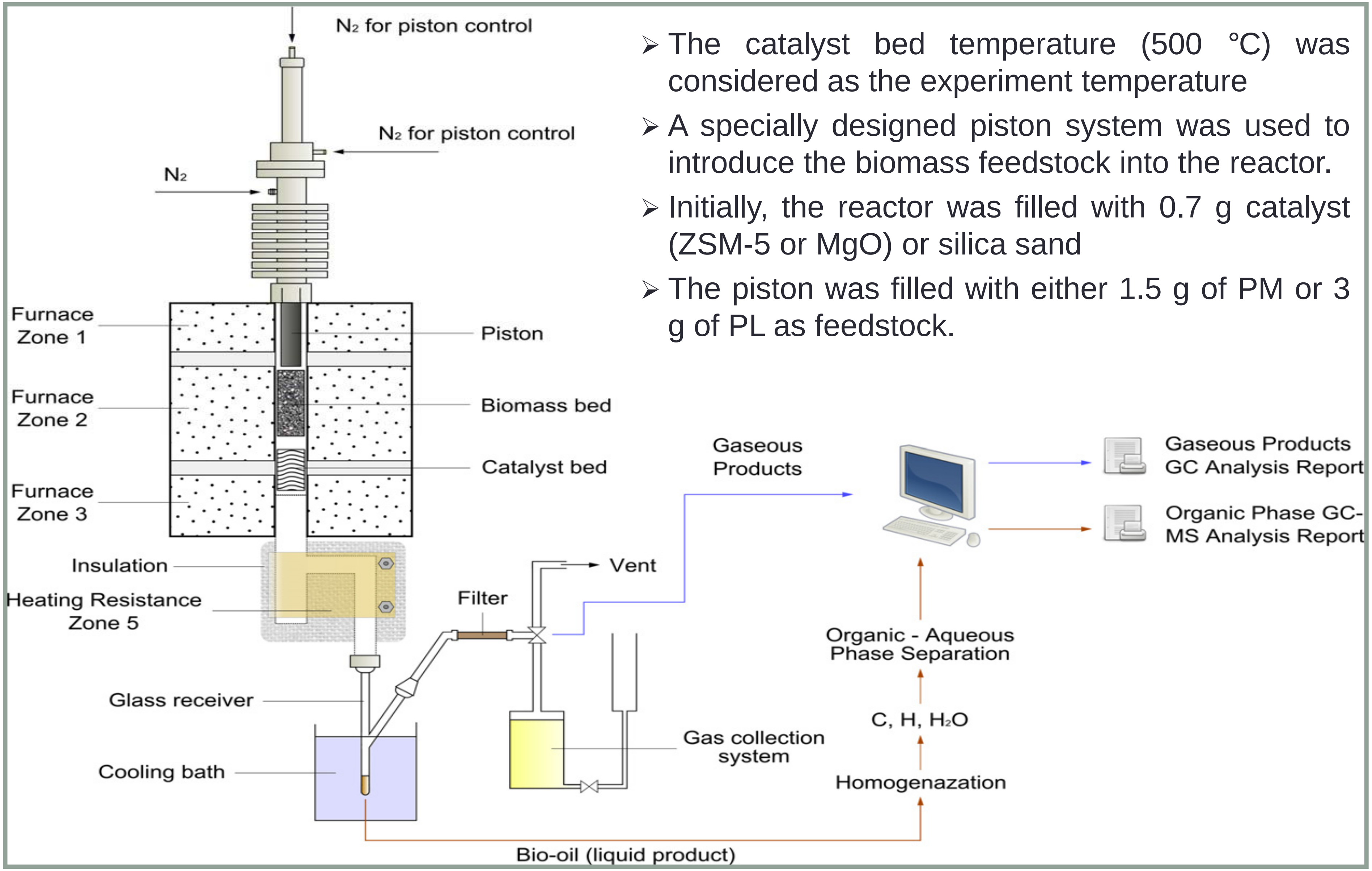
	Elemental analysis, (wt.%)				
	C	**H**	**N**	**S**	**O***
PM	51.6	7.6	9.3	0.0	21.1
PL	38.5	5.0	3.6	0.0	33.9

Catalytic Materials

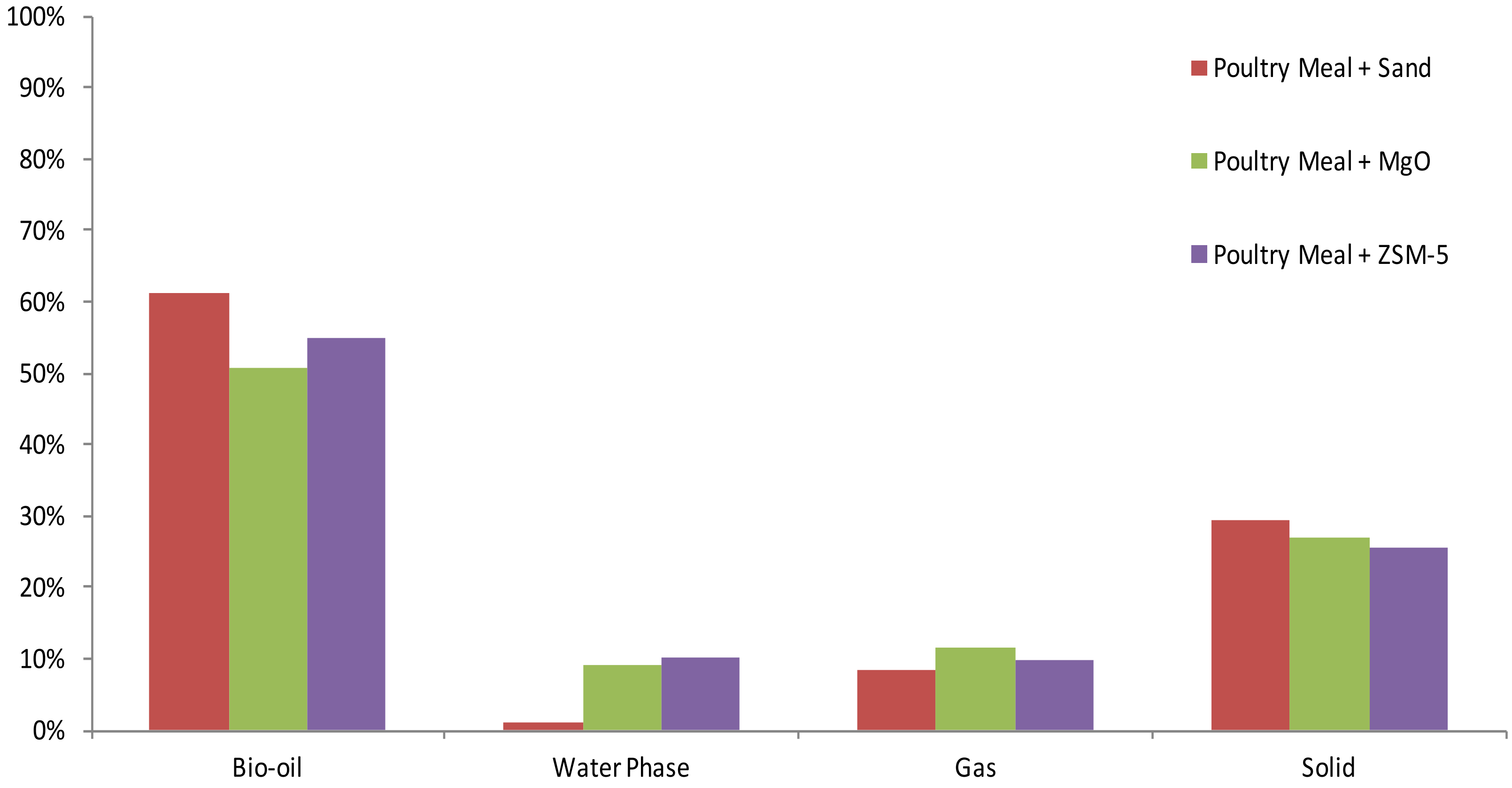
	ZSM-5	MgO
Average Pore Size (nm)	138	40
Average Pore Size (nm)	4	35
Pore Volume (cm^3/g)	0.11	0.34
Micropore Volume (cm^3/g)	0.04	0
Mesopore Volume (cm^3/g)	0.07	0.34
Total Acidity (µmol Pyridine/g)[1]	54.6	N.D.
Bronsted Acidity (µmol Pyridine/g)[1]	36.5	N.D.
Lewis Acidity (µmol Pyridine/g)[1]	18.1	N.D.
Total Basicity (µmol CO/g)[2]	N.D.	147
Weak / Medium Basicity (µmol CO/g)[2]	N.D.	115
Strong Basicity (µmol CO/g)[2]	N.D.	32

Catalytic Fast Pyrolysis Experiments

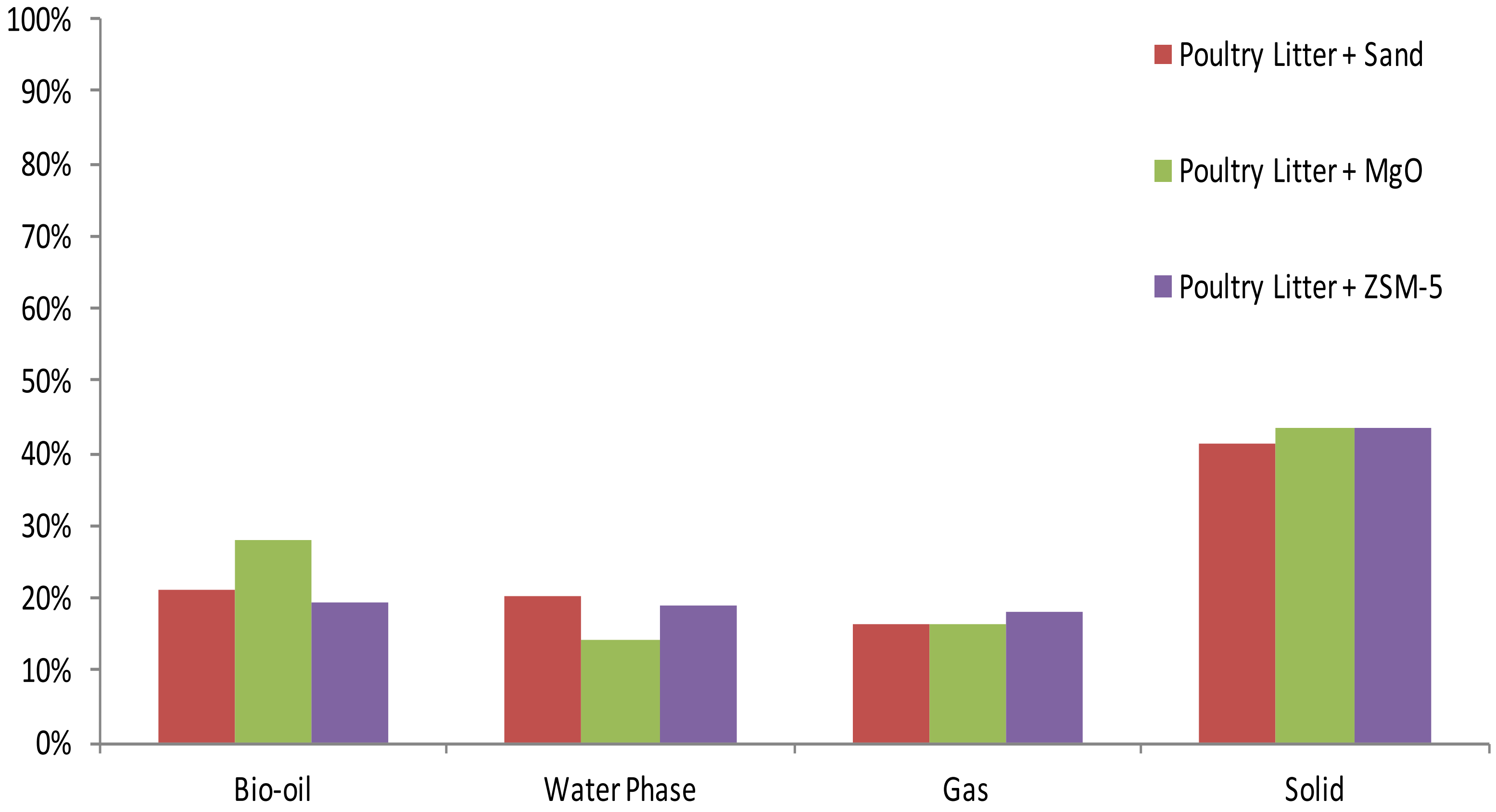
- The catalyst bed temperature (500 °C) was considered as the experiment temperature
- A specially designed piston system was used to introduce the biomass feedstock into the reactor.
- Initially, the reactor was filled with 0.7 g catalyst (ZSM-5 or MgO) or silica sand
- The piston was filled with either 1.5 g of PM or 3 g of PL as feedstock.



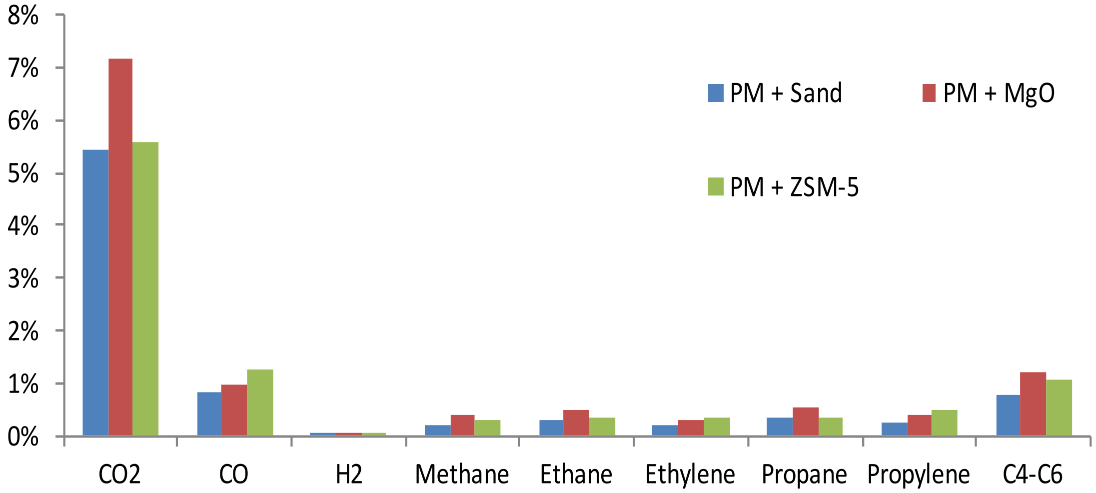
Product yield distribution-poultry meal

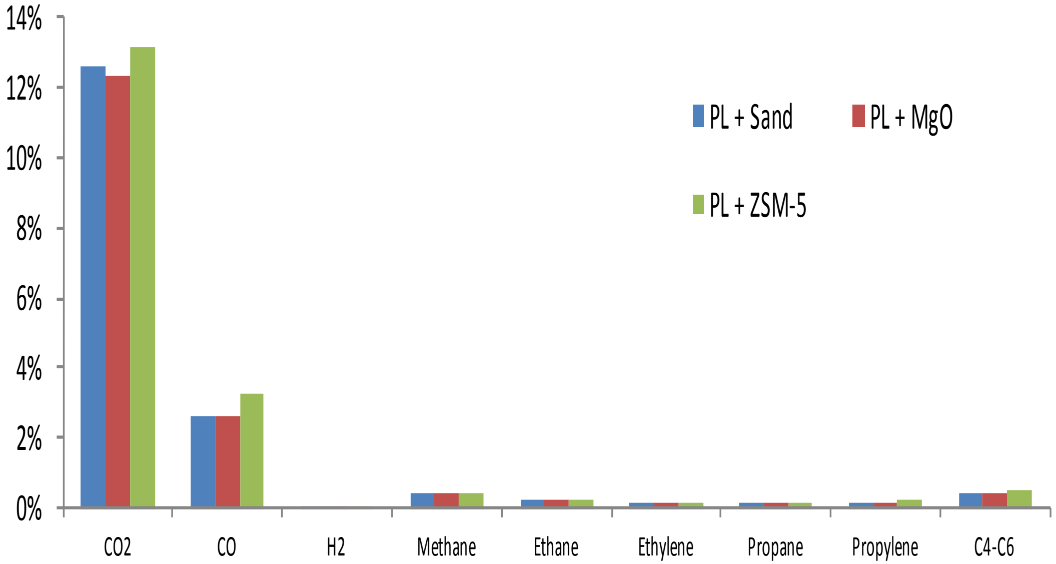


Product yield distribution-poultry litter



Gas product yields





✓ZSM-5 increased the gas yield from PL, which was noticeable as an increase in CO yield.

✓Acidic catalysts were reported to have the tendency to favor CO production in the study of Stefanidis et al.(2011)

✓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.

Chemical composition of the bio-oil (peak area %)

	AR	ALI	PH	AC	EST	AL	ETH	ALD	KET	PAH	NIT	SUL	Oxy PH	UN
Poultry Meal + Sand	0.95	7.36	1.18	**17.60**	3.85	2.90	0.07	19.43	1.64	0.00	16.45	0.42	0.00	28.10
Poultry Meal + MgO	2.95	**15.89**	1.70	0.00	2.84	5.37	0.25	1.03	4.02	0.00	14.66	0.00	0.00	51.27
Poultry Meal + ZSM-5	3.62	7.73	1.05	7.34	1.85	3.12	0.00	1.01	1.55	0.23	**32.80**	2.67	0.00	36.85
Poultry Litter + Sand	1.08	4.59	4.36	5.15	2.97	4.56	0.14	0.78	5.99	0.00	7.08	1.40	6.84	**54.00**
Poultry Litter + MgO	2.79	7.69	6.23	2.57	1.41	1.48	0.25	0.83	7.25	0.00	9.48	0.84	4.80	**54.25**
Poultry Litter + ZSM-5	4.54	5.11	4.65	2.94	0.14	0.00	0.00	0.21	3.55	0.36	14.75	0.00	6.53	**57.07**

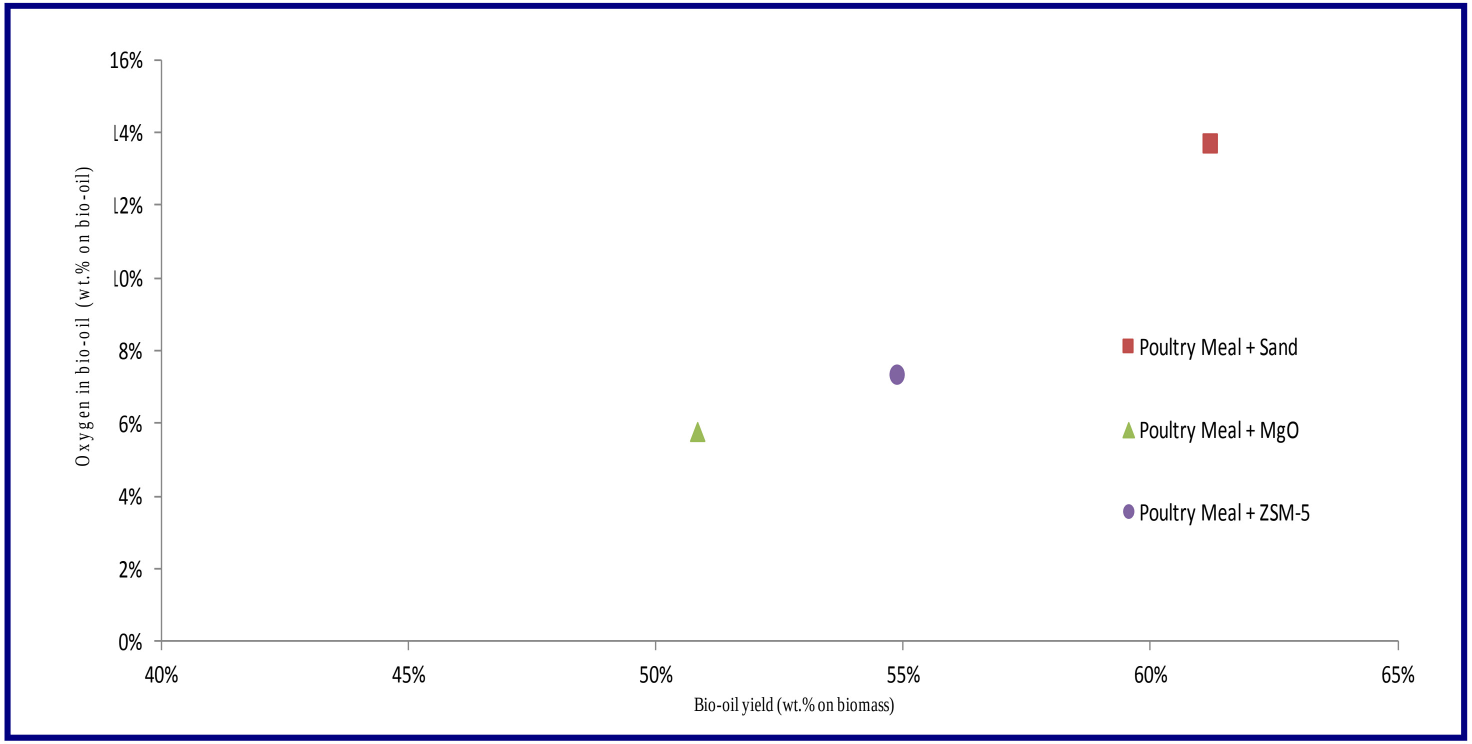
aromatic hydrocarbons **(AR)**, aliphatic hydrocarbons **(ALI)**, phenols **(PH)**, furans **(FUR)**, acids**(AC)**, esters **(EST)**, alcohols **(AL)**, ethers **(ETH)**, aldehydes**(ALD)**, ketones **(KET)**, polycyclic aromatic hydrocarbons **(PAH)**, nitrogen containing compounds **(NIT)**, sulphur containing compounds **(SUL)**, phenolics with oxygenated substitutes **(OXYPH)**.

Elemental composition of bio-oils

	Carbon	Hydrogen	Nitrogen	Oxygen
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 Litter + Sand	71.88	7.42	N.D.	N.D.
Poultry Litter + MgO	71.97	8.26	8.07	11.70
Poultry Litter + ZSM-5	**82.85**	7.64	4.92	4.59

- The addition of catalytic materials resulted in an increase of the carbon content of the bio-oil from PM.
- C content of bio-oil from PL was significantly increased to 82.9 % with the use of ZSM-5 as catalyst

Bio-oil yield versus oxygen content in the bio-oil



✓Removal of oxygen as CO_2, CO and H_2O

✓More oxygen removed, less boi-oil collected.

✓The most deoxygenated bio-oil in expense of bio-oil yield.

➢Conclusion

- 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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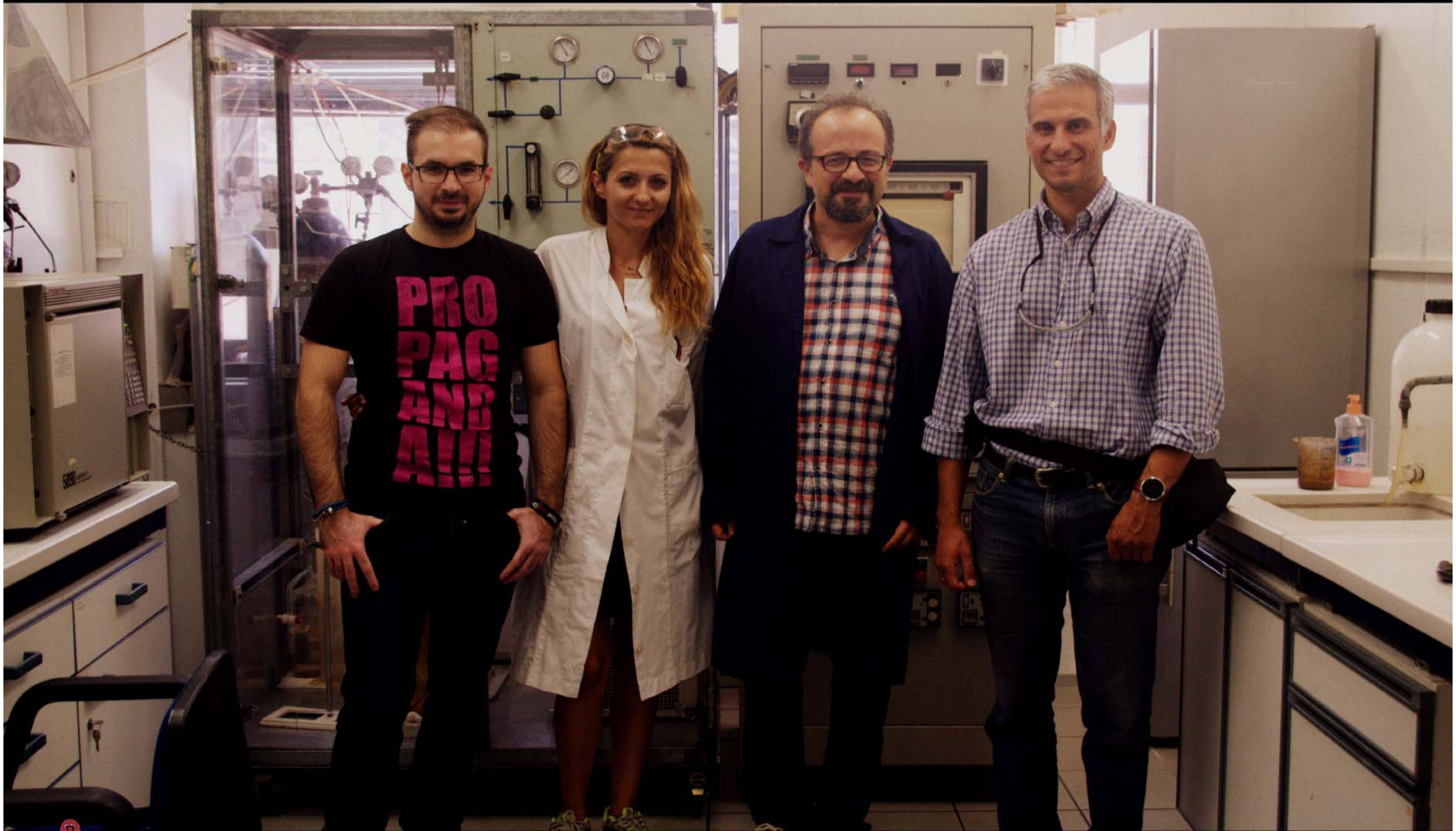
BRISK
Biofuels Research Infrastructure for Sharing Knowledge



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Thank You!

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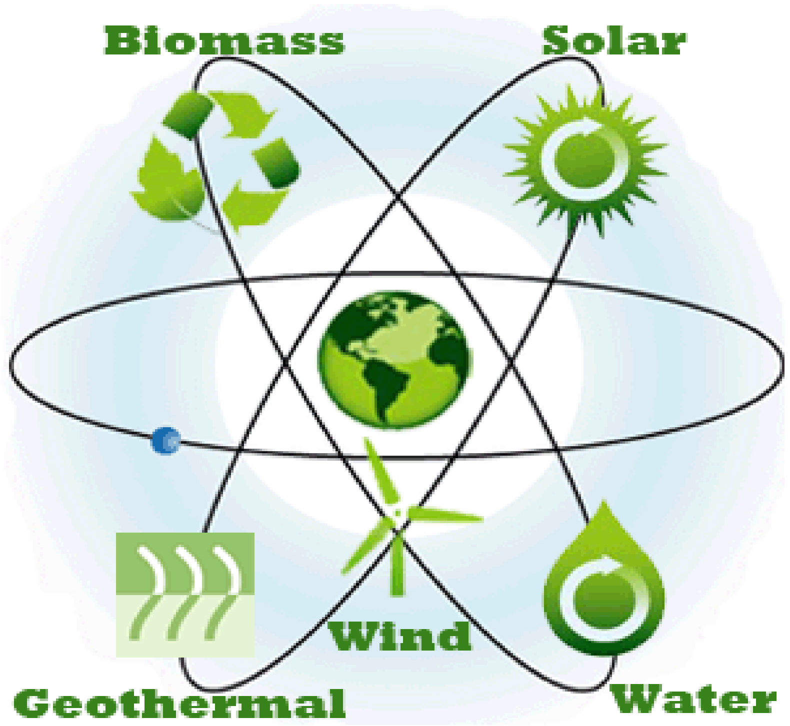
- Depletion of fossil fuel resources that the world currently relies on is an inevitable truth.
- Sustainable, clean-energy sources must be produced and used more extensively than ever before.



http://www.rebltd.ca/markets/

- One of those sources is bio-energy, which is produced when chemical energy stored in biomass is utilized.

✓ First generation biofuels try to meet the bio-energy demand of the world commercially.

1st generation biofuels
(using mostly edible feedstocks)

Bioethanol from
- Sugarcane
- Maize
- Wheat

Biodiesel from
- Vegetable oils
- Animal fats
- Waste oil

http://www.southampton.ac.uk/~lg1e08/cenv6141/

✓ The main issue associated with the **first generation bio-fuels** is the global rise in food prices due to the intensive usage of food crops as feedstock.

2^{nd} generation biofuels

- Limitations of first generation bio-fuels resulted in a growing attention on second generation bio-fuels which do not compete with food and feed resources.

Non-food feedstocks → **Conversion Processes** →

Agricultural Wastes
Forest Wastes
Animal Wastes
Industrial Wastes
Municipal Wastes

- Combustion
- Gasification
- **Pyrolysis**
- Hydrothermal Conversion
- Enzymatic Hydrolysis
- Fermentation
- Anaerobic Digestion

Bio-Fuel

- bio-ethanol
- syngas
- **bio-oil**
- bio-gas
- bio-hydrogen
- bio-char

Electricity

Heat

Bio-oil Characterization

- The organic phase **(bio-oil)** collected as a solution using dichloromethane was then submitted for GC-MS analysis.
- For GC-MS analysis, 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) was used. The NIST 05- mass spectra library was used for the identification of the compounds found in the bio-oil.
- In bench-scale in-situ fast pyrolysis experiments and slow pyrolysis experiments, 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 gaseous products were analyzed in a HP 5890 Series II gas chromatograph, equipped with four columns (precolumn: OV-101; columns: Porapak N, molecular sieve 5 Å and Rt-Qplot 30 m × 0.53 mm ID) and two detectors (TCD and FID) except slow pyrolysis.