## Pyrolysis of pig and cattle slurry solids at laboratory scale – is there a potential for gas and char utilization?

Marzena Kwapinska<sup>1</sup>, J.J. Leahy<sup>2</sup>

<sup>1</sup> Department of Chemical Sciences, University of Limerick, Ireland, <u>marzena.kwapinska@ul.ie</u>

<sup>2</sup> Department of Chemical Sciences, Bernal Institute, University of Limerick, Ireland

## Abstract

Livestock slurries are one of the most widely available and underutilised resources in Ireland. Current farming practices are based on land spreading of raw slurries, this results in not optimal nutrients recycling giving rise to nutrients loses through emissions to atmosphere and runoff to surface and groundwater. Farming sector fragmentation is a barrier to deployment of energyrelated infrastructure, which can be overcome via a low-cost system to aggregate slurry solids for transport to centralized energy/nutrient recovery facility.

This study is a part of a project which investigates the potential of pyrolysis as conversion technology for de-watered/filtrated manure slurry solids for energy and nutrients recovery.

Three samples of pig slurry solids were tested in the study: 1) a sample of de-watered pig slurry solids (PSS), 2) a sample of de-watered pig slurry solids with liming agent (calcium hydroxide Ca(OH)<sub>2</sub>) (LPSS1) and 3) a blend of limed pig slurry solids with limed cattle slurry solids (LPSS2-LCSS). All samples were let to dry outside before further analysis.

Pyrolysis tests were carried out in a fixed bed, batch reactor at a temperature of 700 and 800°C and a residence time of 10 minutes. The product gas generated was cooled to room temperature and sampled; its composition was determined by means of gas chromatography and was used to calculate the heating value. The char and condensed liquid fraction were collected and weighed. The average value of distribution of the pyrolysis products was obtained. Gas yield was calculated by difference. Proximate and ultimate properties as well as the calorific value of the pyrolysis chars were examined.

In Table 1 the properties of tested samples are presented. The moisture content of samples varied, the PSS had moisture content of 15 wt. %, the LPSS1 of 30 wt. %, while the blend of LPSS2 with LCSS of 20 wt. %. As a result of liming, the nitrogen content in limed slurry solids was from 0.5 and 1.3 wt. % compared to 2.8 wt. % for dried PSS. The HHV of dried PSS was higher compared to limed slurry solids, LPSS1 and LPSS2+LCSS.

The distribution of pyrolysis products on a dry basis is shown in Fig. 1. The results represent an average of seven separate pyrolysis runs, with 15 g of feedstock per run. Pyrolysis of limed feedstock produced higher quantity of char comprising from 65 to 85 % of the initial residue mass; the remaining mass was split between gas and liquid products. On a dry basis, a ratio of gas to liquid yield was about 2.5 for LPSS1 and LPSS2-LCSS compared to 1 for dried PSS. This means, that in the presence of lime most of the volatile matter released from pig slurry solids during pyrolysis is rather transformed into permanent gases instead of the condensable compounds (oil, tar). Similar observations, with higher yield of gas but lower yield of liquid product, when lime was used as an additive for pyrolysis of another feedstock was reported previously [1, 2]. Liming of pig slurry solids has positive effect on the formation of desirable pyrolysis products (gas).

Properties	Dried Pig Slurry Solids	Limed Pig Slurry Solids 1	Limed Pig Slurry Solids 2 + Limed Cattle Slurry Solids (60/40 %)
HHV, MJ/kg	9.6	1.9	5.3
Moisture, wt.%	15.3	29.9	20.4
C, wt. %, d. b.	32.0	14.3	22.6
H, wt. %, d. b.	3.4	1.3	0.8
N, wt. %, d. b.	2.8	0.5	1.2
S, wt. %, d. b.	0.3	0.6	0.2
O, wt. %, d. b.	17.5	27.8	29.7

Table 1 Properties of slurry solids and limed slurry solids.



Fig. 1 Mass balance for pyrolysis products.

The information obtained from the pyrolysis tests has been used for the energy flow analysis – an indicative energy balance for the pyrolysis products. The energy flow entering with the feedstock was calculated for 1kg of dried slurry solids, while the energy flows of exit streams (char and gas) were evaluated based on the heating value of the products and mass balance for pyrolysis. The fate of nitrogen in pyrolysis products as well as the content of heavy metals in the char was investigated. The acid-neutralizing value (calcium carbonate equivalence) for chars was examined and together with other char properties compared against criteria for component category materials (CMC 14) and liming materials (PFC 2) as specified in the new EU Fertilizing Products Regulation [3].

- 1. Zhang, L., et al., *Pyrolysis behavior of biomass with different Ca-based additives*. RSC Advances, 2014. **4**(74): p. 39145-39155.
- 2. Bedyk, T., et al., *Effect of CaO and Dolomte Additive on the Thermal Decomposition of Sewage Sludge in an Inert Atmosphere.* Journal of Residuals Science & Technology, 2009. **6**.
- 3. Regulation of the European Parliament and of the Council Laying Down rules on the Making available on the Market of EU Fertilizing Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and Repealing Regulation (EC) No 2003/2003., in 2019/1009. European Commission.