Substrates for slow pyrolysis

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Abstract. Slow pyrolysis of solid materials can produce new materials usable for energy or chemical industry. The advantage of pyrolysis devices is the simple construction and process control and the ability to utilize materials with different properties (composition, ash content). Produced gaseous, liquid and solid materials could be used as a sources of energy, raw materials in chemical industry or substances for improving of soil properties. At article are described products of slow pyrolysis of biomass (wood chips), agrifuels (hay, wheat straw) and sewage sludge.

1 Introduction

Slow pyrolysis is perspective method for transformation of solid fuel into three products – pyrolysis gas, pyrolysis oil (containing main part of pyrolysis water) and solid residue. Pyrolysis is physical-chemical process occurs at temperatures above the heat resistance of the substances (400 – 900 °C). Pyrolysis is carried out without an oxidizer (oxygen from air, water vapour, carbon dioxide etc.).

Processes that occur during pyrolysis can be divided by temperatures up to two temperature intervals. Temperatures up to about 200 °C result in material drying. From 200 to 500 °C, a process of so-called dry distillation takes place, where the macromolecular structures are split into shorter chains due to thermal stability.

Important parameters influencing the pyrolysis process are: pyrolysis temperature, retention time in the reactor, heating rate of the fuel.

Subsequent use of the products depends on their properties. They can be used directly in the process to reduce energy inputs (reactor heating by pyrolysis gas), other equipment (cogeneration unit), or possibly converted to better fuel (liquid refinement).

When compared to other methods of thermal use of materials, it offers the possibility of producing raw materials for transportation liquid fuels, sorption materials or chemical specialties.

Gasification or combustion can produce heat or electricity [1, 2], but there may be problems with melting of ash or incrustation on heat exchangers.

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2 Experimental part

2.1 Substrates

2.1.1 White wood chips

This fuel was made by a knife cutter with dimensions of approx. 30 x 30 x 5 mm and comes mostly with spruce wood. The white wood chips are obtained from debarked wood, usually cuttings for sawmill production. It is mainly used for the production of chipboard or as a high quality fuel.

For our experiments it was chosen as a standard sample of biomass fuel.

2.1.2 Hay and wheat straw

If these materials can’t be used at agriculture (e.g. contamination, mildew), it is possible to use it as a fuel. Dry material has to be dried, shredded and pelletized or briquetted [3]. We used 8 mm agripellets from hay and wheat straw.

![Fig. 1. Samples of white wood chips and hay pellets.](image)

2.1.3 Sewage sludge

The sewage sludge is generated as solid waste from Waste water treatment plants. The dry sludge consists mainly of 60 – 70 % organic matter and the rest is inorganic. 80 % of suspended particles have a size above 0.1 mm and have a large surface area. Our sample was drained, solidified and dried to the actual humidity.

This material was chosen because it would be appropriate to use it as a source of energy [4].
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Fig. 2. Samples of wheat straw pellets and sewage sludge.

Table 1. Fuel properties.

|                  | Proximate analysis (wt.%) | Ultimate analysis (wt.%) | HHV (MJ/kg) |
|------------------|---------------------------|--------------------------|-------------|
|                  | VM | Water | Ash | C  | H  | S  | N  | O  |     |
| White wood chips | 73.4 | 10.6 | 0.3 | 44.3 | 5.28 | 0.00 | 0.45 | 39.1 | 19.497 |
| Hay              | 65.7 | 9.5 | 7.6 | 40.0 | 5.52 | 0.01 | 1.33 | 36.1 | 16.999 |
| Wheat straw      | 67.8 | 8.0 | 6.9 | 41.9 | 5.65 | 0.61 | 0.61 | 36.9 | 17.190 |
| Sewage sludge    | 52.6 | 9.6 | 42.7 | 29.8 | 3.97 | 3.2 | 2.57 | 8.1  | 13.753 |

2.2 Laboratory pyrolysis unit

Laboratory pyrolysis unit is equipped with batch reactor (maximal process temperature up to 900 °C). It consists of four parts: reactor, cooling system, cleaning of pyrolysis gas and gas analysis.

Batch pyrolysis reactor has volume of 2.3 l for 100 – 500 g of fuel (due to it’s density and particle size). It is heated by 3 kW electrical heating elements which can be independently controlled. Hot pyrolysis gas is conducted by heated piping into the tube water cooler. From the bottom part of the cooler is collected pyrolysis liquid (oil and water). Gaseous phase is cleaned in three washers with water, oil and mineral wool. Amount of pyrolysis gas is measured by flowmeter and it is conducted into gas analysis section. Excess gas is combusted in the burner.
Gas analysis is provided by extractive analyser ULTRAMAT 6 (for determination of carbon monooxide, carbon dioxide, methane). Hydrogen amount is measured by CALOMAT 6 (based on thermal conductivity of gas). Total organic carbon TOC is measured by analyser FIDAMAT 6 with flame-ionisation detector. Concentration of higher hydrocarbons are detected by gas chromatograph MASTER GC with flame-ionisation detector.

3 Results and discussion

3.1 Parameters of pyrolysis

For correct pyrolysis, the conditions obtained from the TGA analysis were set. For wood was determined lowest temperature and shortest retention time. Both agrimaterials have similar conditions and highest pyrolysis temperature. This is caused by amount and structure of volatile matter and amount of ash in input fuels.
Table 2. Parameters of pyrolysis.

|                  | Pyrolysis temperature (°C) | Retention time (min) |
|------------------|----------------------------|-----------------------|
| White wood chips | 360                        | 100                   |
| Hay              | 430                        | 130                   |
| Wheat straw      | 430                        | 150                   |
| Sewage sludge    | 480                        | 130                   |

3.2 Pyrolysis products ratios

After pyrolysis were obtained three products – pyrolysis gas, pyrolysis oil and solid residue. Product ratios are mainly influenced by type and structure of input substrates. Pyrolysis of woody biomass produced highest portion of solid residue and lowest amount of gas, sewage sludge produces higher amount of gas and high amount of solid residue (due to high ash content in substrate). Agrifuels produced higher amount of liquid phase and similar amount of gaseous and solid phase.

Table 3. Pyrolysis products ratios.

|                  | Pyrolysis gas (wt.%) | Pyrolysis liquid (wt.%) | Solid residue (wt.%) |
|------------------|----------------------|-------------------------|----------------------|
| White wood chips | 1                    | 26                      | 73                   |
| Hay              | 24                   | 45                      | 31                   |
| Wheat straw      | 31                   | 38                      | 31                   |
| Sewage sludge    | 10                   | 27                      | 63                   |

3.3 Pyrolysis gas composition

Compositions of pyrolysis gases were measured during pyrolysis experiments with different solid fuels. Gas from wood have good heating value, but it has very low volume. Highest portion of hydrocarbons contains gases from agrisubstrates – hay and wheat straw.
Table 4. Pyrolysis gas composition.

|                      | CO (vol.%) | CO₂ (vol.%) | H₂ (vol.%) | CH₄ (vol.%) | Hydrocarbons C₂ – C₄ (vol.%) | Other (vol.%) |
|----------------------|------------|-------------|------------|------------|-------------------------------|---------------|
| White wood chips     | 34         | 36          | 1          | 9          | 7                             | 13            |
| Hay                  | 13         | 36          | 1          | 8          | 35                            | 7             |
| Wheat straw          | 14         | 36          | 2          | 8          | 35                            | 5             |
| Sewage sludge        | 30         | 40          | 1          | 10         | 6                             | 13            |

4 Conclusions

Slow pyrolysis of four substrates was done in laboratory pyrolysis unit. Pyrolysis temperature and retention time was established by TGA. Lowest temperature and retention time was for woody biomass, highest was for sewage sludge. This was caused by amount and structure of volatile matter and amount of ash in substrates.

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For highest amount of solid residue is the best substrate wood chips. For highest amount of liquid and gaseous phases are the best agrimaterials – hay and wheat straw.

This work was supported by project LO1404: Sustainable development of Centre ENET, within the framework of the project CZ.1.05/2.1.00/19.0389: Research Infrastructure Development of the CENET, by project of VŠB-Technical university of Ostrava, ENET Centre, Specific research SP2018/54- Measuring stand for testing of water-ring pumps, was supported by the Ministry of Education, Youth and Sports of the Czech Republic under OP RDE grant number CZ.02.1.01/0.0/0.0/16_019/0000753 "Research centre for low-carbon energy technologies", project Torrefaction CZ.01.1.02/0.0/0.0/15_019/0004771 and project Pyrolysis unit with induction heating CZ.01.1.02/0.0/0.0/15_019/0004681.

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