Pyrolysis Processing of Organic Residues and Operating Parameters Influence on Products Distribution

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The paper presents the results of experimental research aiming at using a new organic residue as potential renewable energy source for derived fuel production through non-oxidant thermal-chemical processing. Low and medium temperature pyrolysis process at atmospheric pressure was conducted using meat processing residues sampled directly from an industrial line. A laboratory scale batch reactor was used for the experimental study using representative waste samples. The influence of process temperature on sample mass variation rate was investigated along with pyrolysis products distribution. The devolatilization process was continuously monitored through the analysis of process gas with respect to volatile organic compounds, correlated with sample mass decrease and reaction products formation. The research revealed the residue potential to be applied as renewable energy source for derived fuel production through thermal-chemical conversion.

Keywords: organic residue, pyrolysis, renewable energy

The continuous evolution and changes of the society involve significant economic and cultural transformations with direct impact on resources consumption. The life standard modifies as well as life style leading to cultural exchange. As direct consequence the food consumption is also affected in terms of quantities and type along with the demographic expansion. Consequently, the high rate increase of industrial waste to be disposed challenges the waste management strategies, requiring fast, efficient and environmentally friendly disposal processes.

In food processing industry the waste properties are influenced by the final product characteristics. Such an example is the meat processing industry waste that requires special attention due to its high rate of development and specific related problems. This type of waste mainly consists of organic residues from slaughterhouses and meat processing industry lines. Their disposal is difficult due to biological instability, potential pathologic risk, high water content, high auto-oxidizing potential and increased enzymatic activity [1]. These organic residues represent an important fraction from processed livestock i.e. between 46-50 % from cow weight and about 38-40% from pig weight [2].

Some problems related to this waste type disposal are summarized here bellow and address also economic and environmental issues:

- high technological cost for the conversion into technical grease or protein rich substances; this solution is also conditioned by the existence of a specific market demand, the country or region economic development level along with the interest in developing a sustainable economy;
- ban of meat and bone meal use as feeding product for livestock, according to enforce regulation CE 999/2001 and CE 1234/2003, due to disease transmission potential to animals and people; consequently there is no interest in transforming the organic residues into a protein compound just to be disposed to the landfill;
- the lack of adequate controlled disposal landfills as well as the health risk potential of these residues;
- the neutralization costs when using incineration as the main treatment process; the low combustible properties of waste given by the high water content (up to 42% in mass) and high ash content (up to 27% in mass) limits waste calorific value and additional support fuel is required for its incineration; consequently, the neutralization process is characterized by high energy consumption and pollutant emissions as fossil fuels are used;
- the high cost of transport to waste neutralization facilities due to specific requirements (sealed containers).

The current neutralization thermal technologies use the well known combustion processes that proved to be the safe solution for this waste type disposal along with undeniable advantages including: high mass reduction down to waste inert fraction, complete neutralization, high treatment capacities and increased specific load [3]. Nevertheless there are some drawbacks of these technologies related to high energy consumption and pollutant emissions. To overcome these disadvantages of thermal chemical processes with respect to high energy consumption the waste energy potential recovery represents a priority for the researchers in the field. Previous works of the research team from Power Engineering Faculty - University Politehnica of Bucharest revealed an important energy potential of various organic residues from food industry. Previous experiments conducted on representative samples showed that residues like feathers, offal and bones have calorific values in the range of 20000 kJ/kg to 26000 kJ/kg (dry basis) while pork meat residues have a specific energy content about 19000 kJ/kg [4]. The product sampled directly from the industrial processing line is characterized by a high water content reducing these values to about 7000 kJ/kg [4]. Even under these conditions the residue low heating value is similar to that of the inferior coal (lignite). Nevertheless, the waste physical structure raises mechanical operation problems due to high agglutinant properties and elastic consistency that make

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fuel preparation (grinding) and manipulation (automatic feed-in systems) difficult and costly (high maintenance costs and power consuming). All these characteristics influence the waste combustible properties making it difficult to be utilized as fuel in energy conversion units despite the high energy potential. Consequently, advanced pre-treatment processes are required to qualify its physical-chemical characteristics to superior combustible properties. The aim of the paper was to transform this waste type into derived alternative fuel being biodegradable stable, biological neutral and having higher specific energy content. In our research pyrolysis process treatment was used. The second objective was to set and use experimental conditions that could be easily replicated at industrial level: high heating rates, atmospheric pressure and low oxygen content. Moreover the paper presents the influence of process parameters on devolatilization kinetics as well as on pyrolysis products formation and distribution.

Experimental part

Materials and methods

The waste product

The product used in the experimental study was sampled directly from an industrial meat processing line and consisted in a mixture of pork bones and meat residues. The experimental procedures (sampling, preparation) were conducted in order to preserve the sample representative characteristics. The product was shredded, ground and dried according to laboratory procedure at 105°C for 24 h in a drying stove SLW53ECO.

Previous researches developed in the same laboratory revealed interesting characteristics of the waste product namely the average water content of about 41.7%, the volatile fraction of about 38.65 %, the fixed carbon of 3.73 %, the inert fraction obtained after the complete oxidation of about 15.9% [4]. In dry basis the volatile fraction of about 66.3 % is similar to that of fast biodegradable biomass products while the inert fraction is about 27.3%. In dry basis the fixed carbon fraction does not exceed 7% [4]. The elemental composition of the waste i.e. C – 41.5%, H – 6 %, N – 4.3%, O_2 – 20.9% confirms the important specific energy content of the product given by the increased carbon and hydrogen ratio [4]. The low heating value of the dried product is about 19205 kJ/kg while for the raw waste does not exceed 10523 kJ/kg [4]. These values reveal the high energy potential of this residue which is superior to low quality coals.

The experimental set-up

Two batch reactors were used in our study that can process samples of up to 300 g. The sample mass assures representative characteristics of the waste product compared to other laboratory analyzers (TG-DTA for example). The experimental conditions were non-oxidant thermal treatment corresponding to atmospheric pyrolysis. The influence of process temperature on sample mass variation rate and reaction products distribution was studied.

To investigate the pyrolysis process parameters influence on sample devolatization process kinetics and sample mass variation rate, a calcination oven (Nabertherm L9/11/SW, Germany) connected to a precision balance was used. The oven controller allowed programming the heating rate and the peak temperature. The sample mass was continuously measured.

To investigate the pyrolysis reaction products formation, an electrically heated tubular batch reactor designed using a Nabertherm tubular reactor platform was used (fig. 2). The reactor consisted in an external heated refractory steel tube with a capacity from 30 to 100 g (that depends on product specific mass). The maximum process temperature that can be reached is 1100°C. The experimental set-up was specially designed for the study of thermal-chemical processes transitory state. The sample was introduced while nitrogen was fed in at volumetric flow rate of 100 cm^3/min through the nozzles 1 and 2. The reactor controller enabled the setting of the heating rate and peak temperature. The process gases were evacuated through the nozzle 6. The heavy hydrocarbons were collected separately as pyrolysis tar using a condensing unit. The char was colleted from the crucible at the end of the experiment. The non-condensable gas fraction was determined by difference.

To quantify the carbon evolution from the solid matrix of the product into the gas phase during the thermal treatment, the pyrolysis gas was continuously analyzed using a volatile organic compound analyzer (Sick Mainhak 3006) equipped with Flame Ionization Detector (FID). The results were provided as total organic carbon (TOC).

Results and discussions

The important data used in devolatilization processes and technologies design related to potential fuel products pre-treatment are the minimum residence time for the volatile fraction release and that for char stabilization at a specific process temperature. Consequently, the samples were submitted to atmospheric pressure pyrolysis in the calcination oven. The main parameters that influence the process energy balance are the process peak temperature

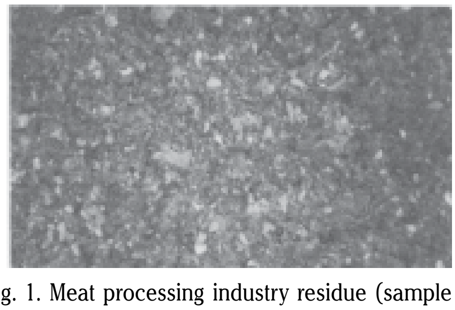

Fig. 1. Meat processing industry residue (sample prepared for experiments)

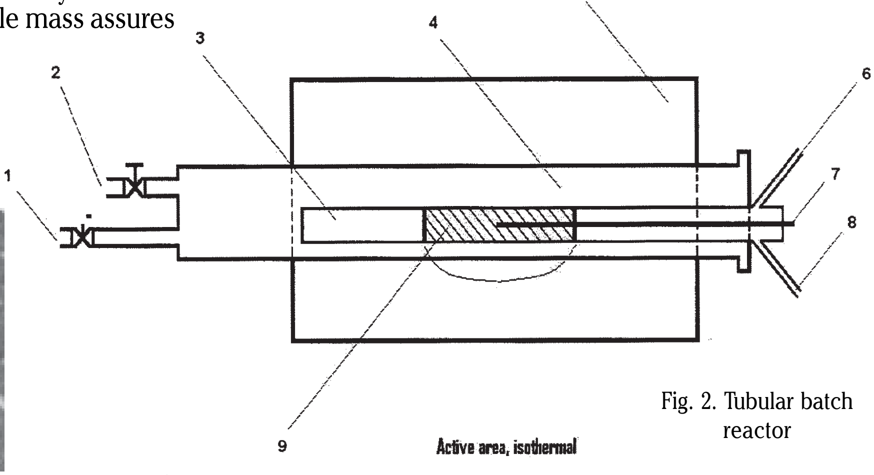

Fig. 2. Tubular batch reactor

1. Nitrogen injection; 2. Air injection; 3. Refractory steel crucible; 4. Refractory steel tube; 5. Electrically heated chamber; 6. Exhaust gases; 7. Thermocouple; 8. Liquid reaction products (tar); 9. Sample

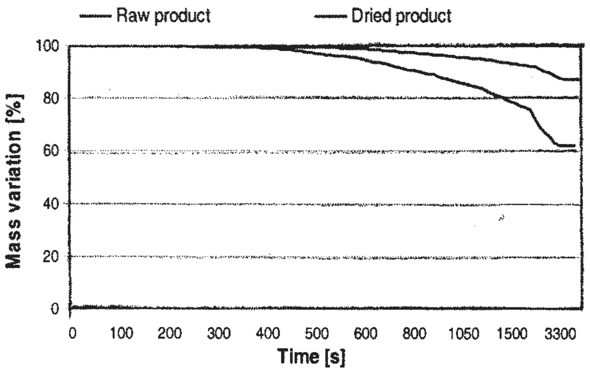

Fig. 3. Sample mass variation–pyrolysis at 300 °C

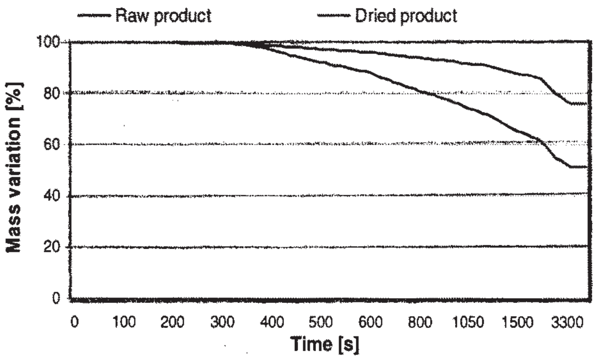

Fig. 4. Sample mass variation–pyrolysis at 350 °C

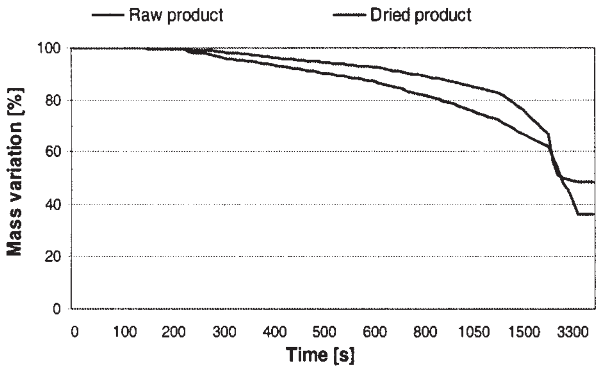

Fig. 5. Sample mass variation – pyrolysis at 400 °C

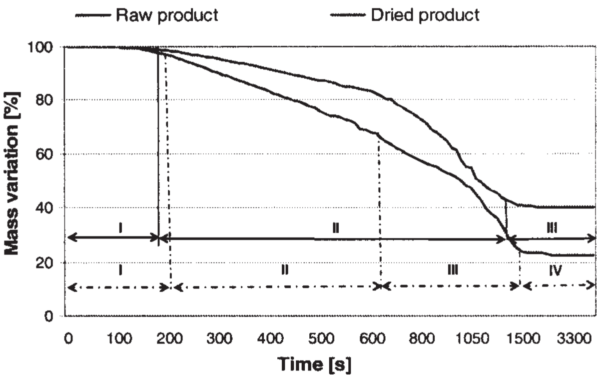

Fig. 6. Sample mass variation – pyrolysis at 500 °C

and the residence time of the product in the active zone of the device. This information is very important for the industrial applications where the interest is in using low processing temperatures to minimize the thermal energy consumption. As the waste humidity has a major impact both on process dynamics and energy balance as well, the influence of water content on sample mass variation rate was determined using both raw residue and completely dried product. The process temperature was varied between 350 and 500 °C. This temperature range is characteristic to low and medium temperature pyrolysis. The heating rate (between 15 and 30 °C/min) was imposed by the process peak temperature, the sample being introduced from the ambient temperature directly into the heated reactor and preserving industrial operation conditions that are different from usual laboratory determinations. The results are presented in figures 3 - 6.

As expected, an increase in volatile fraction release at higher temperatures was noticed. The direct observation of char revealed a porous structure at temperatures above 400°C. The maximum mass loss of about 77.5% from the raw product was obtained at 500°C. The dynamics of devolatilization process can be clearly observed in figure 6. During the sample mass variation 3 distinctive zones can be noticed for the dried product and 4 zones for the raw one, respectively.

When applied to dried product 3 transformations zones can be noticed: zone I characterized by the product heating and some primary volatiles release, zone II where devolatilization occurs and zone III of char stabilization. When applied to raw product the non-oxidant process consists in 4 zones: zone I of sample heating, zone II corresponding to drying stage and some primary volatiles release, zone III of volatiles release; and zone IV of char stabilization.

At higher temperatures the volatile release period is shorter with 100% compared to low processing temperature. At 500 °C the volatile release ends after 20-25 min from product feed-in moment compared to 40-45 min required for complete devolatilization at 300°C. Consequently the shorter periods necessary for product stabilization at higher treatment temperatures may compensate the thermal energy consumption to achieve this processing temperature level. The option for specific process parameters mainly depends on process energy balance and the final conversion stage type.

The pyrolysis products consists of permanent gases, a pyrolytic liquid and a solid residue, or simply of volatiles and char. These fractions result from primary reactions of solid material devolatilization as well as secondary reactions of primary products degradation, including char aromatization and cracking of condensable volatile organic compounds (VOCs) into low molar mass gases (6, 7). Pyrolysis products distribution represents an important issue for the process energy balance computation. Using the tubular batch reactor and the specific experimental configuration, the mass fractions of these products were measured. As the preliminary tests revealed that low treatment temperatures are insufficient for volatile release process (the sample was not entirely carbonized) the processing temperature range was chosen superior to 400 °C. The results are presented in figure 7.

It can be noticed that at higher temperature the char fraction decreases due to carbon bonds breaking whereas the release of volatile substances increases [5]. The char fraction is maximum at 400°C, with about 32.5% of the pyrolysis products mass. The tar production (about 44.2% in mass) is maximum at 450°C, followed by its decrease due to cracking secondary reactions of condensable VOCs at higher temperatures leading to an increase in non-condensable gases along with a decrease in liquid yield [8-10]. The non-condensable gas fraction reaches its maximum of 35.1 % at 500°C while the minimum of 29.4 % is delivered at 450 °C. At higher processing temperatures (500 °C) the pyrolysis gas quantity slightly increases due to cracking secondary reactions that produce non-condensable gas compounds [11-13].

To correlate the sample mass evolution with the transformation phase, the carbon presence into the flue

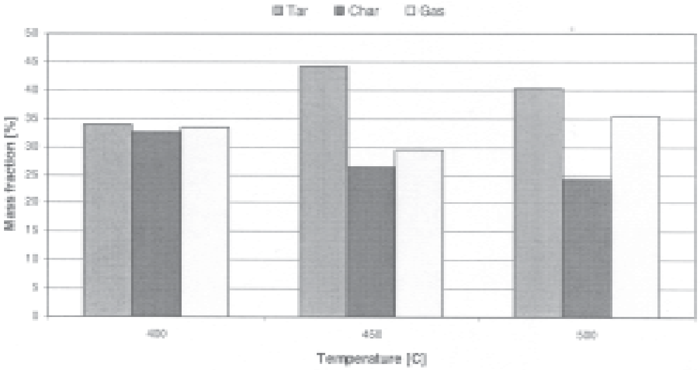

Fig. 7. Pyrolysis products distribution at different processing temperatures (for raw product)

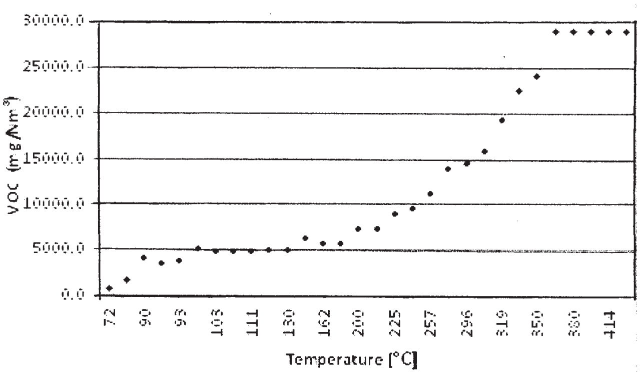

Fig. 8. VOCs concentration in pyrolysis gas in transitory regimes (for raw product)

gas was investigated. The devolatilization phase was continuously monitored through the analysis of process gas with respect to VOCs. Using the flame ionization detection TOC was measured within pyrolysis gas. The compounds presented in the gas led to an increase in ionization current level proportional to the carbon atoms. VOCs expressed as TOC were measured in mg_{TOC}/m^3. The results are presented in figure 8.

It can be noticed the primary volatiles release even at low processing temperatures (about 90°C). This can be explained by the presence of fat in the raw product that start to convert to volatiles in the same time with water vapor formation during the drying stage. The carbon based volatile matter reaches its maximum at 350 – 380°C. That confirms that minimum pyrolysis temperature for this type of waste is 380 – 400°C.

Conclusions

The paper presents experimental results of thermal-chemical processing applied to meat processing industry residues. The research focused on product transformations under low and medium temperature pyrolysis. The influence of process run on pyrolysis products formation and characteristics was investigated. The experimental conditions used in the process were similar to the ones possible to replicate at industrial level with respect to heating rate, pressure and atmosphere type. Representative waste, sampled directly from the industrial meat processing line, was used in the study.

The direct observation of pyrolysis char revealed a porous structure at temperatures above 400°C. The maximum mass loss through the devolatilization of the product was about 77.5 at 500°C. For the same temperature the volatile release ends after 20-25 min from process start, compared to 40-45 min required for complete devolatilization at 300°C. Consequently, the shorter periods necessary for product stabilization at higher treatment temperatures may compensate the thermal energy consumption to achieve this processing temperature level.

The char fraction is maximum at 400°C, with about 32.5 % of the pyrolysis reaction products. The tar production is maximum (44.2%) at 450°C. The non-condensable gas fraction reaches its maximum (33.4 %) at 400 °C while the minimum (29.4 %) is delivered at 450 °C.

The atmospheric low-medium temperature pyrolysis can be used as pre-treatment stage for meat processing line residues conversion into carbon based products prior to their energy recovery valorization and disposal.

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