PYROLYSIS PROCESSING OF WASTE PEANUTS CRISPS

Barbora Grycová, Ivan Koutník, Adrian Pryszcz, Kateřina Chamrádová
VSB – Technical university of Ostrava, Institute of Environmental Technologies,
17. listopadu 15/2172, Ostrava-Poruba, 708 33, Czech Republic.
e-mail: barbora.grycova@vsb.cz, ivan.koutnik@vsb.cz, adrian.pryszcz@vsb.cz,
katerina.chamradova@vsb.cz

Abstract

Wastes are the most frequent "by-product" of human society. The Czech Republic still has a considerable room for energy reduction and material intensiveness of production in connection with the application of scientific and technical expertise in the context of innovation cycles. Pyrolysis waste treatment is a promising alternative to the production of renewable hydrogen as a clean fuel. It can also reduce the environmental burden and the amount of waste in the environment at the same time.

This paper presents the laboratory pyrolysis experiments of peanuts crisps waste to the final temperature of 800 °C. After the pyrolysis process of the selected waste a mass balance of the resulting products, off-line analysis of the pyrolysis gas and evaluation of solid residue in terms of adsorption properties and energy production and liquid products were carried out. The highest concentration of measured hydrogen (66 vol. %) was analysed during the 4th gas sampling at the temperature varying from 750 to 800 °C.

Keywords: pyrolysis, food waste, adsorption, energy production

1 INTRODUCTION

Every year billions tons of waste are generated and these amounts have been rising steadily. In spite of the reasonably successful 3R strategy (Reduce-Recover-Recycle) to reduce landfill volumes, there are still significant quantities of waste to be disposed. Consequently, waste disposal can cause negative impacts on health and the environment, including air and water pollution.

Waste also represents a loss of natural resources (such as the metals or other recyclable materials it contains, or its potential as an energy source). Therefore, proper waste treatment can protect public health and quality of an environment whilst supporting conservation of natural resources. A wide range of waste is produced in the food industry. These biodegradable wastes are an important group of wastes that threaten the environment in the case of landfilling. Directive No. 1999/31/EC on the landfilling of waste [1] requires the Member States of the European Union to reduce the amount of biodegradable waste deposited in landfills until 2020 to 35 wt. % of the weight of this type of waste generated in the year 1995. Wastes from the food production are still mostly disposed of by landfilling, only a small part is used for feed purposes or for the production of biogas [2], technical ethanol [3] and compost [4].

Disposal or rational use of food wastes represents today a major challenge from an economic perspective. Thermo-chemical methods are promising technologies that allow transforming certain types of wastes to quality fuel or valuable chemical raw materials [5]. For these reasons, suitability of waste peanuts crisps for the pyrolysis process was verified by laboratory experiments with subsequent assessment of the individual products. The above mentioned type of waste is generated in the amount of 80 to 100 tons per month. Most of this waste is disposed by landfilling.

In general, pyrolysis represents a process of thermal degradation of the waste in the total absence of air that produces recyclable products such as char, oil and combustible gases. Pyrolysis has been used to produce charcoal from biomass for thousands of years. Currently, the pyrolysis condensate (a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water) has attracted considerable interest due to its several applications in industry. Although it has been proven to be a promising alternative to petroleum fuels, it also has a potencial for use in producing value-added chemicals. The possibility of using food wastes through thermal reduction methods is presented in the paper [6], the authors focused mainly on the process gas. Pyrolysis of food waste with respect to the production of bio-oil is the subject of the paper [7]. Microwave pyrolysis with catalysts is a feasible method to handle food waste [8]. In work [9] catalytic cracking of biomass waste oil fractions separated from food waste leachate using microporous catalysts is presented. Nowadays a new trend is growing up for production of sorbents from biomass and various kinds of food waste materials [10]. Adsorbents are highly porous materials with a developed inner surface, which are capable to capture some substances from gaseous or liquid mixtures. Their application is primarily in the so-called purification technologies.

2   MATERIALS AND METHODS

For the experimental part waste peanuts crisps (PC) was chosen (Figure 1):

PC

waste peanuts crisps

(Cervus Inc.)

Figure 1. Waste peanuts crisps (PC)

Selected type of waste had to be modified before the experiment. The knife mill was used to adjust the required size of 8x8 mm. For the sample proximate and ultimate analysis were carried out (see Table 1). For the determination of moisture W, ash A and total combustible Ċ thermogravimetric analyzer TGA - 601 was used according to the standards ČSN 44 1377, ČSN ISO 562 and ČSN ISO 1171. Thermogravimetric curves are shown in Figure 2. Elemental analysis was performed with the use of the unit LECO CHSN628. The higher heating value (HHV) was determined according to ISO 1928 with the use of the unit LECO AC – 350 and lower heating value (LHV) was calculated according to the formula (1). Proportion of volatiles matter was measured 79 wt. %.

$$Q_{i,net,m} = \{Q_{s,gr,d} - 212\,W_{H,d} - 0{,}8\left(W_{O,d} + W_{N,d}\right)\} \cdot (1 - 0{,}01\,M_T) - 24{,}4\,M_T \qquad (1)$$

$Q_{i,net,m}$ calorific value of the original waste sample at constant pressure (J·g⁻¹),

$Q_{s,gr,d}$ calorific value of the sample in dry condition (J·g⁻¹),

$W_{H,d}$ weight percentage of hydrogen in the anhydrous sample (wt. %),

$W_{O,d}$ weight percentage of oxygen in the anhydrous sample (wt. %),

$W_{N,d}$ weight percentage of nitrogen in the anhydrous sample (wt. %),

M_T weight percent of water in the original sample (wt.%).

Table 1. Proximate and ultimate analysis

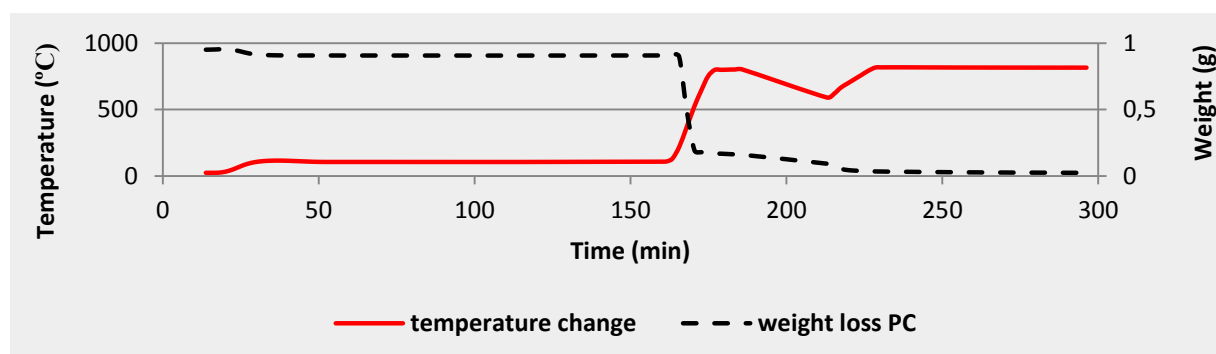| Sample	W^r (wt.%)	A^r (wt.%)	$\dot{C}^r$ (wt.%)	C^r (wt.%)	H^r (wt.%)	N^r (wt.%)	S^r (wt.%)	O^r (wt.%)	HHV^d (MJ·kg⁻¹)	LHV^d (MJ·kg⁻¹)
PC	4.60	2.20	93.20	49.80	6.66	1.93	0.10	34.70	24.75	22.13

Figure 2. Thermogravimetric curves of PC

Experimental device

Laboratory apparatus assembled for the purpose of experiments is shown in Figure 3. The apparatus consisted of the stainless steel retort (length 30 cm, inner diameter 5.5 cm) placed in an electric furnace. The exhaust gases from the retort were conducted through cooler, where the liquid phase were condensed and captured in steel container. For purging the retort nitrogen was used as an inert medium. The heating of the retort was set up to 15 K per minute to the final temperature of 800 °C based on the references. The pyrolysis gas was cleaned in two gas washing bottles. The first was filled with water, the second with acetone. Prior to the collection of pyrolysis gas the gasometer was included. The pyrolysis gas samples were taken discontinuously

into the gas sampling bags. The selected gaseous components were analyzed by gas chromatography (methane, ethene, ethane, propane, propene, hydrogen, carbon monoxide and carbon dioxide).
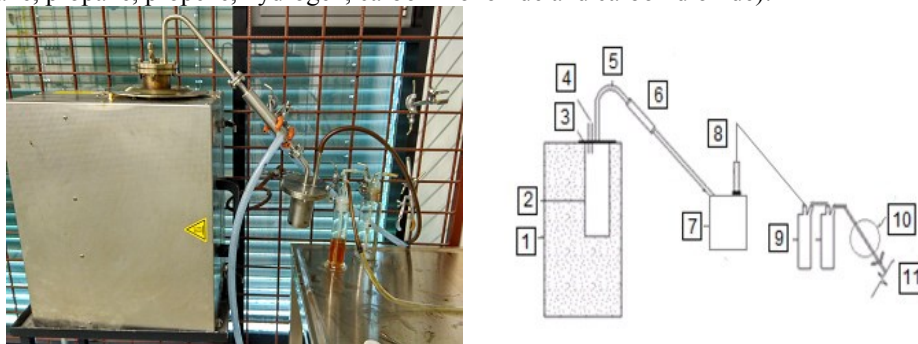

Figure 3. Pyrolysis apparatus
(1 chamber; 2 retort; 3 retort lid; 4 inlet of media; 5 gas outlet; 6 cooler; 7 container to catch the liquid residue; 8 gas outlet; 9 washing bottles; 10 gasometer; 11 gas offtake)

3   RESULTS AND DISCUSSION

The mass balance of the pyrolysis tests was determined by weighing the solid and liquid products from the pyrolysis. The amount of resulting gas (15 wt. %) was calculated up to 100 % (see Figure 4).
Distribution of the individual products is primarily based on the reaction temperature and heating rate. The elemental composition of the input material plays also an important role. Based on the mass balance of the experiments can be observed the significant proportion of liquid residue (62 wt. % of tar, oil and water). The appreciable amount of the liquid residue is probably caused by higher content of oxygen in original material. Materials with a higher content of oxygen yield oxygenated products during the pyrolysis more.
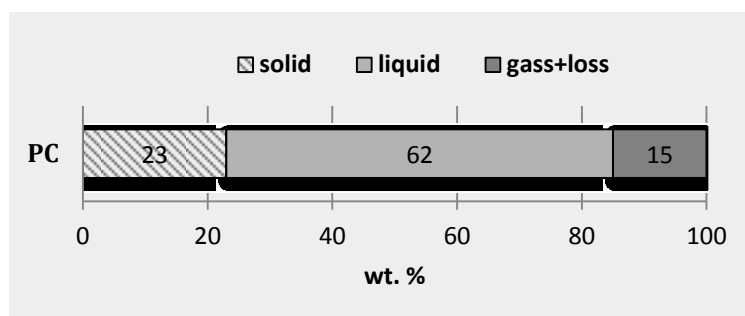
Figure 4. Mass balance of pyrolysis proces

Analysis of gaseous products

Analysis of the pyrolysis gas was performed with the use of the Agilent 7890A gas chromatograph with flame ionization detector and thermal conductivity detector. For separation of gaseous components the Micropacked column (2 m x 0.53 mm) was used. For dosing the gaseous samples a metering loop was used and the output signal was recorded and processed by the HP ChemStation computer software. Conditions for the chromatographic analysis are shown in Table 2.

Table 2. Conditions for the chromatographic analysis

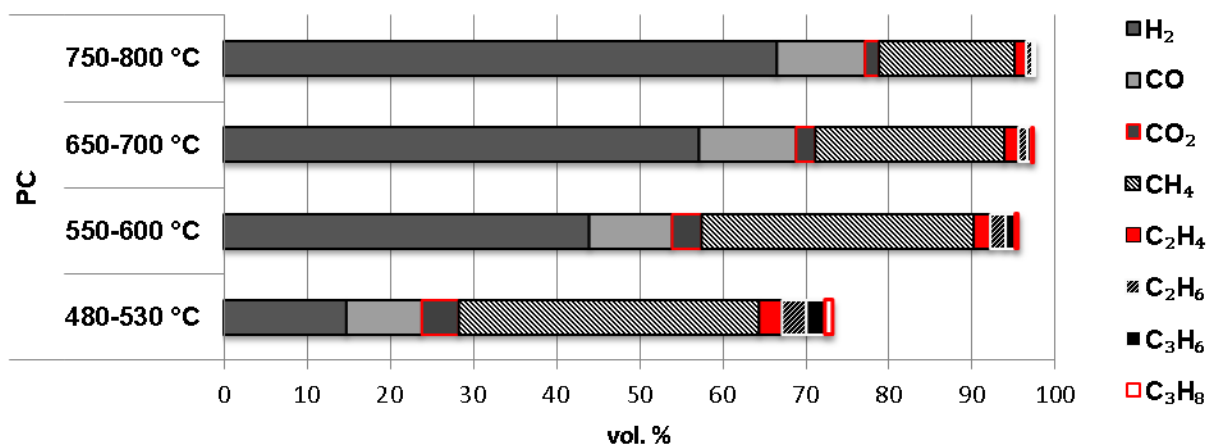| Column setting		FID detector setting		TCD detector setting	
Temperature (^{o}C)	300	Temperature (°C)	250	Temperature (°C)	250
Flow rate (ml·min^{-1})	4.8072	Flow rate of H_2 (ml·min^{-1})	30	Flow rate of H_2 (ml·min^{-1})	10
Split ratio	4:1	Airflow (ml·min^{-1})	400		
		Flow rate of He (ml·min^{-1})	25	Flow rate of He (ml·min^{-1})	5

Figure 5. Analysis of the gaseous products

Samples of pyrolysis gas were taken discontinuously at temperatures above with respect to the thermogravimetric analysis (see Fig. 5). These temperatures have been programmed in the furnace. The production of hydrogen is an important parameter, which is discussed in a number of papers [11]. The highest concentration of hydrogen (66 vol. %) was analyzed during 4th gas sampling at the temperature of approx. 750 - 800 °C. The amount of generated gas 0.2 l·min^{-1} during these temperatures was measured. Total amount of generated gas was 17.5 l. The concentrations of measured hydrocarbons and carbon monoxide decreased with the increasing temperature.

Evaluation of solid residue in terms of adsorption properties and energy production

Basic determinations of solid residue of pyrolysed sample were done to define the sorption capacity (S_{BET}, t-Plot Micropore Area, iodine adsorption number, true density). To determine the iodine adsorption number I, the standard DIN 53 582 [12] was used. The automatic pycnometer PYCNOMATIC ATC was used to analyze the true density ρ of the solid product (helium was used as a medium). Table 3 shows the results of ultimate and proximate analysis, S_{BET}, t-Plot Micropore Area, iodine adsorption number I and true density ρ of sample after pyrolysis. The resulting adsorption properties of carbonized PC sample reached values which indicate no possibility to use this type of waste mentioned above for the production so-called "single-use sorbents" for wastewater treatment. The spatial structure of the original material probably negatively affects the sorption capacity of the resulting solid product. On the other hand the heating values indicate the possibility of its further use for energy recovery. In the next stage technical properties of solid residues will be observed in terms of its subsequent use as additives for refractory materials as well as components into construction and insulating materials.

Table 3. Proximate, ultimate analysis and adsorption properties

Sample	C^r (wt. %)	H^r (wt. %)	N^r (wt. %)	S^r (wt. %)	O^r (wt. %)	HHV^d (MJ·kg^{-1})	LHV^d (MJ·kg^{-1})
PC	80.00	0.35	2.10	0.00	4.20	29.60	28.46
	W^r (wt. %)	A^r (wt. %)	$\dot{C}^r$ (wt. %)	S_{BET} (m²·g^{-1})	t-Plot MicroArea (m²·g^{-1})	I (mg·g^{-1})	ρ (g·cm^{-3})
PC	1.20	12.10	86.70	1.13	2.36	91	1.78

Evaluation of condensate

The water content in condensate was determined by the Karl-Fischer method. The phases were separated by centrifugation. After centrifugation the organic phase was subjected to the determinations as shown in Table 4. The contents of carbon, hydrogen, nitrogen and sulfur were determined with the use of the unit NA 1500 (Fisons Instruments, Milan), operated in the CHNS mode and calibrated according to the commercial phenanthrene standard. The content of oxygen was calculated up to 100 %. The HHV and LHV were calculated according to the Dulong-Petit law.

Table 4. Proximate and ultimate analysis of condensate

Sample	H_2O^r (wt. %)	C^d (wt. %)	H^d (wt. %)	N^d (wt. %)	S^d (% wt.)	HHV^d (MJ·kg^{-1})	LHV^d (MJ·kg^{-1})
PC	73.90	34.00	9.04	0.95	0.04	14.10	12.09

After separation of water energy recovery of the condensate is expected.

4 CONCLUSION

Pyrolysis is considered to be one of the sustainable solution that may be economically profitable and minimise environmental concerns especially in terms of waste minimization and carbon sequestration. The resulting pyrolysis products (solid product, condensate and gas) are dependent on the composition of the treated waste and process conditions. Process conditions can be variously modified with respect to quantity and quality of the products that we want primarily to obtain. The advantage of thermal reduction processes is the emergence of process gas containing combustible components such as methane, hydrogen, and carbon monoxide which can be used for energy production. Some of the advantages of pyrolysis also are that combustion products associated with the burned waste, are not generated, and dioxins formation can be efficiently prevented. The resulting adsorption properties of carbonized PC sample reached values which indicate no possibility to use this type of waste for the production so-called "single-use sorbents". However volume of the solid process residuals to be landfilled is also reduced due to further energy utilization of char. Considering the amount of water energy recovery of the condensate after separation of water is expected.

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