Emissions from Pyrolysis of Tyres and Municipal Waste

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Abstract

The main aim of the work is to characterize possibilities of energy recovery from waste (first of all from tyres and municipal waste without biomass and inert material). Attention is given to advanced technology which can be used for energy recovery from waste. This includes pyrolysis units. There are emission values that were measured on the pyrolysis equipment of a new construction. The equipment is being prepared for practical use at present. The equipment more or less fulfils both emission limits valid in the Czech Republic and the emission standards of the European Union. The conclusion of this contribution is devoted to the current and future situation in the area of energy recovery from waste in the Czech Republic.

Keywords: pyrolysis, waste, tyres, plastics, energy recovery

Introduction

Both tyres and plastics (in this case from municipal waste) have been used in modern societies in almost everything, which have created increasing amounts of wastes with negative impact on environment. Due to the fact that the main solutions, used so far, to deal with these wastes present several problems and do not seem to be the right ones, to decrease, in an effective way, the increasing amount of wastes produced all over the world. Landfilling of tyres and plastics residues is not a solution, because it has been increasingly difficult to find suitable places for building technically adequate landfills due to the danger of leaching and soil impregnation, with the subsequent contamination of underground waters. Apart from this, landfilling does not allow the recovery of organic content of these wastes that should be part of the organic lifetime cycle [1]. Incineration has the advantage of taking profit of wastes energetic content, but produces pollutants like nitrous and sulphur oxides, dust, hydrocarbons, and dioxins, which have highly negative bearing on the environment. On the other hand, this combustion of wastes destroys completely an important resource, as wastes organic content are converted only into CO_2 and H_2O.

Pyrolysis technology applied to these wastes may have an important role in future, as it may allow the conversion of these residues into economical valuable products, which can be used as fuels or as feedstock in petrochemical industry.

It is often required (especially within the process of environment impact assessment – EIA) to compare "classical equipment (grate boilers including the SCR – the DeNOx and DeDiox catalytic reactor)" with such equipment that has not been sufficiently many times used in the Czech Republic or the other countries of the European Union. This especially includes pyrolysis.

Pyrolysis

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen-containing media (air, carbon dioxide, water vapour) which leads to the formation of gaseous, liquid and solid fractions. This process is an alternative to combustion.

The essence of this method is that organic compounds are less stable at higher temperatures. High molecular substances are decomposed to low molecular ones, which leads to their breakdown into volatile products and coke. Pyrolysis is carried out at the temperatures ranged from 150°C to 1000°C. According to the temperatures [2], we distinguish:

- Low-temperature pyrolysis (reaction temperature up to 500°C),
- Medium-temperature pyrolysis (reaction temperature from 500°C to 800°C),
- High-temperature pyrolysis (reaction temperature above 800°C).

Advantages of pyrolysis processes [3]:

- Easier and less capital-intensive plants,
- There is only a small fraction of gaseous products of incineration compared to the same amount of fuel.

Disadvantages of pyrolysis processes:

- More expensive operation,
- A problem to remove the pyrolysis residue (pyrolysis coke), liquid hydrocarbons, containing a high content of heavy metals.

Pyrolysis can be used in addition to the thermal treatment of municipal waste and sewage sludge also to:

- Decontamination of soils,
- Treatment of plastic waste and used tires,
- Treatment for the substance utilization of cable waste, metal and plastic materials.

For a long time, the pyrolysis technologies are considered to be very promising also in the field of energy recovery from waste. Although research in this area is quite wide and technological development is well advanced, neither of these technologies is still established in the waste area so that the future operator in the Czech Republic could get it complete, as we say "turn-key". This is currently a big problem, because there is nothing in this field in the Czech Republic the entrepreneurs could equipped with the intended operations for treatment of waste (municipal waste, tires) that they would like to operate as a plant for waste energy recovery [4].

Nevertheless, one piece of equipment available for tyre processing (applicable also other types of waste) is a pyrolytic line M3RP supplied by AmbientEnergy LLC (USA) and made by Scogen (India) [5].

Facility of company Shangqiu Jinpeng Industrial Co., Ltd. (China) is also often offered in abroad [6]. This company offers both continuous and discontinuous (batch type – Figure 1) pyrolysis plant. The facilities can recycle and utilize waste plastics, waste rubber, tyres and waste engine oil. According to the actual situation in every country and district, it was developed by company Shangqiu Jinpeng Industrial Co., Ltd. series of machine for disposing scrap tyre and plastics that includes 4 tons, 6 tons, 8 and 10 tons (at most about 30 tons per batch) of different capacity. Unfortunately there are not emission values measured on the pyrolysis equipment by accredited laboratory.

Another facility sold as PTR (= eng. STD – slow thermal decomposition) is from Czech firm HEDVIGA GROUP plc and it is capable of energy recovery from waste rubber, tyres and municipal waste as well as a whole number of other waste (sewage sludge, oil waste, plastics, biomass) [7].

The PTR principle (= STD – slow thermal decomposition) is based on the principles of pyrolysis, however it is modified. Unlike the standard pyrolysis process, the qualitative technical and technological shift with the PTR technology is the following [7, 8, 9]:

- it is low-heat decomposition with the temperature below 480°C with a higher efficiency of energy use for heating without chimney waste,
- it is a slow process (slow thermal decomposition); thermal decomposition has therefore sufficient time (in terms of tens of minutes) for a complete separation of fractions and consequently for a higher efficiency of creation of gas and liquid products. The yield on these products from comparable raw materials is about 5 ÷ 8% higher than bibliography mentions (measured for decomposition of tyres at the temperature of up to 480°C),
- the process starts with slow heating in terms of minutes when fine separation of fractions happens without formation of crust on the surface,
- it is a batch process which itself is not continuous, therefore the slowness of the process allows a complete separation of products and control of the

Fig. 1. Discontinuous pyrolysis plant XY-8 (batch process) of company Shangqiu Jinpeng Industrial Co., Ltd. – reactor or rather rotary pyrolysis kiln (photo – author)

Rys. 1. Instalacja pirolizy okresowej XY-8 (process okresowy) firmy Shangqiu Jinpeng Industrial Co., Ltd. – reaktor albo piec obrotowy temperature increase in the raw material according to temperature curve without thermic shock,

- the slowness of the process allows to collect all gas products into tanks and to use them to operate a cogeneration unit without discharging exhaust gases into the air. As a result, no emissions happen (except the outlet from the cogeneration unit).

The PTR unit consists of two modules: the thermal (heating – see Figure 2) and the cooling one. Both modules have a shape and size of a 20-foot transport container for the capacity of 1 ton per hour.

The thermal module (Figure 2) is built on the basis of an electric chamber furnace with side heating by resistance bars and a maximum input of 200 kW. The furnace is bricked with fireclay bricks in the floor and heat insulation on the basis of fibreglass in the walls. In the upper part of the furnace there are three ventilators allowing for stable heat convection and speed of flowing around fuel elements. Raw material is put in the furnace in steel compartments, fuel elements made of stainless steel of the class 17 with the thickness of the wall of 5 ÷ 10 mm with three outlets for gas products and with bayonet valves for raw material in the upper and side part of the element with the diameter of 50 ÷ 80 cm with insulation that prevents air from getting into the compartment. The fuel element is transported to the furnace on rails. As to the manipulation with fuel elements, the PTR unit needs 8 fuel elements for its operation, two being in the furnace, two in the exchanger, two being cooled and two being filled.

Fuel element is filled from the top with ground raw material which is transported from the mill by means of a conveyor belt. The element is manipulated by a radial crane which places it on the rails in front of the furnace. The element enters the furnace (the thermal module) on the rails. After finishing a cycle, the hot element is pulled out on the rails by means of a magnetic lock and is then left in a thermal exchanger with a newly filled element. After cooling (approx. 6 hours), the element is lifted by a crane and the carbon rest is dumped into a container.

The cooler of the PTR process is placed in a 20-foot container and has two circuits with a total length of 84 metres. Each circuit of the cooler is attached individually on one fuel element. The input temperature of gases entering the cooler is on average 450°C and the output temperature is 80°C. The cooling liquid is water with ethyleneglycol (in a closed circuit). Hydrocarbons and oil fractions condense in the cooler and pyrolysis oil occurs. Its composition depends on the composition of the raw material. Oil from the process is accumulated at the outlet of the cooler in its bottom part. The gas is subsequently treated, i.e. dried and purified [7, 8, 9].

The weight balance of the fraction production from the PTR 1000 process differs according to the raw material: approx. 330 kg of gas, 450 kg of pyrolysis oil and 220 kg of the carbon rest is produced from 1,000 kg of tyres (raw material).

The technology is connected with the TEDOM Cento T 180 (Czech Republic) cogeneration unit which produces heat and electric current from the formed pyrolysis gas. The liquid fraction (oil) from the technology may be used as fuel and also for other purposes [10, 11]. Solid outputs will be subject of commercial sale.

Measurement of Emissions from Pyrolysis of Tyres and Municipal Waste without Biomass

The purpose of the measurement of emissions was to use accredited and authorised emissions measurement methods and procedures to determine output concentrations and mass flows for contaminants

Fig. 2. Pyrolysis plant PTR 1000 (HEDVIGA GROUP plc) – thermal module with so called fuel cell [8, 9]

Rys. 2. Instalacja do pirolizy PTR 1000 (HEDVIGA GROUP plc) – moduł termiczny z tzw komorą paliwa [8, 9]

Tab. 1. Measured emission values – pyrolysis of tyres. Pyrolysis plant PTR 1000 (manufacturer HEDVIGA GROUP plc, Czech Republic), 18.10.2012, O_2 = 5%

Tab. 1. Pomiary emisji- piroliza oon. Instalacja PTR 1000 (producent HEDVIGA GROUP plc, Czech Republic), 18.10.2012, O_2 = 5%

Parameters	**Average values**	**Emission limits**	**Remarks**
NO_x	418 mg/Nm^3	500 mg/Nm^3	Emission limits for cogeneration units (CR)
CO	993 mg/Nm^3	1300 mg/Nm^3	Emission limits for cogeneration units (CR)
TZL (total dust)	0,55 mg/Nm^3	10 mg/Nm^3	Emission limits for incineration of waste (CR)
HF	0,09 mg/Nm^3	1 mg/Nm^3	Emission limits for incineration of waste (CR)
HCl	1,85 mg/Nm^3	10 mg/Nm^3	detto
PCDD/F (Σ TEQ)	0,0307 ng/Nm^3	0,1 ng/Nm^3	detto
Hg metals	0,01600 mg/Nm^3	0,05 mg/Nm^3	detto
Cd metals	0,00088 mg/Nm^3	Σ0,05 mg/Nm^3	detto
Tl metals	0,00070 mg/Nm^3		
PAH	0,813 mg/Nm^3	1 mg/Nm^3	Emission limit (EU)

Tab. 2. Measured emission values – pyrolysis of municipal waste without biomass and inert material. Pyrolysis plant PTR 1000 (manufacturer HEDVIGA GROUP plc, Czech Republic), 23.01.2013, O_2 = 11%

Tab. 2. Pomiary emisji – piroliza odpadów komunalnych bez biomasy i materiału inertnego. Instalacja PTR 1000 (produkcja HEDVIGA GROUP plc, Czech Republic), 23.01.2013, O_2 = 11%

Parameters	**Average values**	**Emission limits**	**Remarks**
NO_x	284 mg/Nm^3	500 mg/Nm^3	Emission limits for cogeneration units (CR)
CO	800 mg/Nm^3	1300 mg/Nm^3	Emission limits for cogeneration units (CR)
TZL (total dust)	1,05 mg/Nm^3	10 mg/Nm^3	Emission limits for incineration of waste (CR)
HF	0,09 mg/Nm^3	1 mg/Nm^3	Emission limits for incineration of waste (CR)
HCl	0,17 mg/Nm^3	10 mg/Nm^3	detto
PCDD/F (Σ TEQ)	0,00167 ng/Nm^3	0,1 ng/Nm^3	detto
Hg metals	0,00027 mg/Nm^3	0,05 mg/Nm^3	detto
Cd metals	0,00061 mg/Nm^3	Σ0,05 mg/Nm^3	detto
Tl metals	0,00046 mg/Nm^3		
PAH	0,000023 mg/Nm^3	1 mg/Nm^3	Emission limit (EU)

Tab. 3. Measured emission values – pyrolysis of tyres. Pyrolysis plant PTR 1000 (manufacturer HEDVIGA GROUP plc, Czech Republic), 03.06.2013, O_2 = 11%.

Tab. 3. Pomiary emisji – piroliza opon. Instalacja PTR 1000 (produkcja HEDVIGA GROUP plc, Czech Republic), 03.06.2013, O_2 = 11%

Parameters	**Average values**	**Emission limits**	**Remarks**
NO_x	244 mg/Nm^3	500 mg/Nm^3	Emission limits for cogeneration units (CR)
CO	52 mg/Nm^3	1300 mg/Nm^3	Emission limits for cogeneration units (CR)
TZL (total dust)	6,94 mg/Nm^3	10 mg/Nm^3	Emission limits for incineration of waste (CR)
HF	0,02 mg/Nm^3	1 mg/Nm^3	Emission limits for incineration of waste (CR)
HCl	0,03 mg/Nm^3	10 mg/Nm^3	detto
PCDD/F (Σ TEQ)	0,00594 ng/Nm^3	0,1 ng/Nm^3	detto
Hg metals	0,00062 mg/Nm^3	0,05 mg/Nm^3	detto
Cd metals	0,00019 mg/Nm^3	Σ0,05 mg/Nm^3	detto
Tl metals	0,00017 mg/Nm^3		
PAH	0,000014 mg/Nm^3	1 mg/Nm^3	Emission limit (EU)

specified below in waste gas at the output of cogeneration unit TEDOM Cento T 180 during combustion of pyrolysis (sync) gas produced at the PTR unit.

The PTR 1000 facility has been designed for pyrolysis of rubber pulp from recycled tyres, municipal waste without biomass and inert material, and other materials. Fuel dosage is discontinuous, i.e. batch-based. In addition to other products, pyrolysis (sync) gas is produced from the fuel inside the reactor. The gas is then cooled down, purified and captured in a gas pressure reservoir. The stored gas is brought to a vacuum reservoir through a reducing valve, where from it is taken further and combusted in the cogeneration unit TEDOM Cento T 180. The waste gas (combustion products) is discharged into the surrounding air through a damper and a flue with an output above the roof of the hall. Cogeneration unit is equipped with a catalyst at the waste gas output.

The measurement was performed as authorised measurement for the purposes of Act No. 201/2012 Coll. on air protection, in the scope of Decree No. 415/2012 Coll. of the Ministry of the Environment.

The measurement was performed in the scope below:

- Air-conditioning parameters were determined,
- Concentrations of solid contaminating substances were determined,
- Concentrations of oxygen and carbon dioxide (O_2, CO_2) were determined,
- Concentrations of gaseous contaminating substances were determined,
- Results were evaluated and the report was prepared.

Table 1 shows emission values of pollutants which were recorded in period of the first measurement [12] carried out on the PTR 1000 equipment from the company HEDVIGA GROUP plc (with cogeneration unit TEDOM Cento T 180) during pyrolysis of tyres.

Table 2 shows emission values of pollutants which were recorded in period of the second measurement [13] carried out on the PTR 1000 equipment from the company HEDVIGA GROUP plc during pyrolysis of municipal waste without biomass and inert material.

Table 3 shows emission values of pollutants which were recorded in period of the third measurement [14] carried out on the PTR 1000 equipment from the company HEDVIGA GROUP plc during pyrolysis of tyres.

The emission values (Table 1, 2, 3) suggest that the PTR 1000 facility fulfils (with reserve) the emission limits valid in the Czech Republic (Act No. 201/2012 Coll. on air protection, in the scope of Decree No. 415/2012 Coll. of the Ministry of the Environment) as well as the emission standards of the European Union.

Closing Remarks

As it has been mentioned above, the research in the field of pyrolysis plants is quite extensive and the technological development has made a considerable progress. However, very little from these technologies has been implemented in the area of waste to encourage future operators to use it immediately. Also, it is important to make it work properly. This is currently a big problem, because there is nothing in this field in the Czech Republic the entrepreneurs could equipped with the intended operations for treatment of waste (municipal waste, tyres) that they would like to operate as a plant for waste energy recovery.

Often, citizens and representatives of civic associations talk about the need to prefer new technologies (first of all pyrolysis) for energy recovery from municipal waste, tyres, and other waste (waste rubber, sewage sludge, oil waste, plastics, biomass) and not consider the use of such grate incinerators, although at the output equipped with plants for treatment flue gases at the highest possible technical level. Certainly, it is appropriate to introduce new innovative technologies. However, it should be pointed out that e.g. the plant for gasification of municipal waste shall be equipped with the same equipment for flue gas treatment, as is in grate incinerators equipped with the plant for capturing pollutants at the highest level. Then, of course, it is debatable whether it is necessary at any cost to seek to build often more expensive and technologically complex plant, when securing the air protection is assured in both cases practically by an identical capturing plant.

In case of energetic use of tyres, municipal waste or other waste in pyrolysis facilities, the situation is different. It is not necessary to attach these facilities with additional equipment for flue gas treatment (see the above recorded values in Table 1, 2, 3). The PTR 1000 facility fulfils (with reserve) during pyrolysis of tyres and municipal waste without biomass and inert material the emission limits valid in the Czech Republic as well as the emission standards of the European Union.

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Emisja do powietrza z procesu pirolizy opon samochodowych

Celem pracy było zbadanie możliwości odzysku energii z odpadów (przede wszystkim z pirolizy odpadów komunalnych bez frakcji biomasowej i odpadów inertnych). Uwagę zwrócono na zaawansowaną technologię, którą można wykorzystać do odzysku energii z odpadów. Między innymi użyto urządzenia do pirolizy. Wartości emisji określono w nowej instalacji do pirolizy.Urządzenie w dużym stopniu spełnia zarówno limity emisji obowiązujące w Republice Czeskiej, jak i standardy Unii Europejskiej.

Słowa kluczowe: piroliza, odpady, oony, plastiki, odzysk energii