**Michał Głębowski,
Włodzimierz Szewczyk**

**Lodz University of Technology,
Institute of Papermaking and Printing**
ul. Wólczańska 223, 90-924 Łódź, Polska.
E-mail: michal.glebowski@p.lodz.pl,
wlodeksz@p.lodz.pl

Waste Treatment with Supercritical Water

Abstract
Waste with a high water content is particularly difficult to reprocess. Drying, required before the final burning process, consumes large amounts of energy and it is quite expensive. The paper provides an overview of the processing methods of waste generated in both the paper and related industries using supercritical water. The process is technologically advanced and requires a special design approach. The fundamentals, assumptions and conditions of the recycling process are presented. The requirements for waste feedstock and potential environmental benefits are described. This work also presents the results of tests performed on a laboratory scale using various samples from industry, and discusses the design and operation of a prototype waste utilisation line of 200 kg/h capacity. Based on the results obtained, areas of potential application for this method of waste processing in the industry are also described. Plans for the development and implementation of the process on an industrial scale are outlined.

Key words: *supercritical water, waste treatment.*

■ Introduction

The dynamic development of global industry associated with the production of goods and services contributes to the higher consumption of natural resources and causes the emission of harmful substances. The deficiency of raw materials is the cause of the increase in the cost of extraction and impact on the final price of products and competitiveness of micro-enterprises and the economy at the macroeconomic level.

Natural action is to try reducing costs by seeking ways of recovering waste products as well as raising awareness of the problem of solid waste. Effective and efficient processes for resource recovery from waste have two important advantages:
■ reduction of production costs through the use of previously unusable waste,
■ improvement of the environment by reducing landfill waste.

In many developed countries of the world, also in Poland, intensive research on the efficient use of the constantly increasing mass of solid waste has been undertaken. The aim is to find new, cost-effective methods of solid waste utilisation, the use of which does not pose a threat to the environment, and even contributes to the renewal of its resources.

Recovery of recyclable materials

Among the activities undertaken for the purpose of solid waste management, re-cycling plays an important role. The term includes all technical and technology activities related to the separation of raw materials form solid waste. [1]

Generally there are three basic ways of recyclable material recovery from solid waste:
■ recycling (recycling to manufacture) materials - including collecting and processing the waste material feedstock for the production of the same or similar product,
■ energy recovery - includes energy recovery from solid waste during both combustion and indirectly in the production of fuels from solid waste,
■ disposal of materials - includes the separation of raw materials from waste materials and/or their processing for the manufacture of other products.

Fibrous waste

Fibrous waste is an organic waste which includes:
■ shredded paper and cardboard,
■ discards from refining, cleaning and sorting installations,
■ sludge of de-inking plants, sewage sludge,
■ scraps of fabric, ribbon and roving ends, the ends of yarn, etc.,
■ waste paper, paperboard, used paper machine clothing.

The article analyses wastes with a high content of moisture from the paper production process.

Methods of fibrous waste treatment

There are four basic ways of fibrous waste utilisation.
1. Re-use (recycling) – limited to the least processed / degraded part in terms of usability.
2. Thermal processes – such as waste combustion, pyrolysis, gasification.
3. Storage in landfills – for waste, when the disposal cost is too high or disposal is impossible – this method has the lowest cost but is environmentally the most expensive.
4. Biological methods (for organic waste) - such as composting, bio-drying.

This work presents one of the thermal methods, which are characterised by the following advantages:
■ low volumetric residue with respect to the input product (about 10 - 15%),
■ the final solid product is usually ash, which, due to its inorganic nature, has less impact on the environment, can be used e.g. in buildings.

The main and most common method of heat treatment is incineration. The article presents an alternative method of thermal waste treatment based on supercritical water.

Definition and properties of supercritical water

Water in a supercritical state (supercritical water, SCW) at a temperature above T_{cr} = 374.2 °C and pressure higher than p_{cr} = 22.05 MPa. Supercritical water is neither a liquid nor gas (see ***Figure 1***).
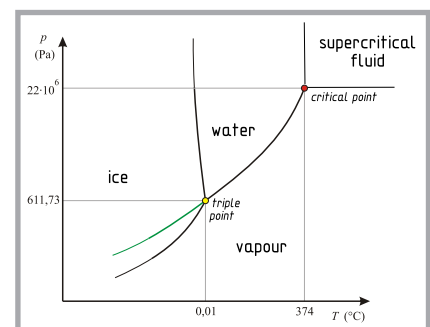
Figure 1. *Phase diagram for water in p(T) coordinates.*

As with other substances in a supercritical state, the physical properties of water are between a gaseous and liquid state. The density of water in a supercritical state is comparable to that of liquid water, and the viscosity and diffusivity values are closer to a gaseous state. In addition, supercritical water achieves a high solvation capacity due to a low dielectric constant. Under these conditions, most of the hydrogen bonds are disrupted and the water becomes a non-polar solvent (see **Table 1**).

Most organic chemicals and gases have unlimited miscibility with supercritical water. Supercritical water can serve as a solvent, catalyst as well as a reactant in the chemical synthesis and decomposition of organic compounds. Changes in temperature and pressure allow to obtain properties suitable for a particular application. The high temperature and very good solubility of organic substances and oxygen speed up oxidation in a SCW.

Application of supercritical water
General purpose
Supercritical water is successfully used as a reaction medium for carrying out chemical synthesis such as hydrogenation, dehydrogenation, C-C bond formation, hydrolysis, hydration, dehydration, elimination, rearrangement, partial oxidation, free radical reactions or stereoselective synthesis [2].

Apart from applications in waste treatment, to be discussed later in the article, supercritical water is used in:

■ synthesis of terephthalic acid,
■ synthesis of metal nanoparticles [3],
■ cooling of nuclear reactors [4], [5],
■ biomass gasification [6], [7],
■ distribution of toxic materials [8],
■ degradation of phenols [9],
■ disposal of chemical weapons
■ neutralisation of black liquor (papermaking) [10].

SCWO and SCWG processes
There are two basic types of processes using SCW:
■ supercritical water oxidation (SCWO),
■ supercritical water gasification (SCWG).

The main difference is the presence of oxygen in both processes. In SCWO oxygen is fed to the reaction mixture, while in SCWG we avoid the presence of

Table 1. Comparison of selected properties of supercritical water

Water parameter	Normal conditions	Supercritical state
Temperature, °C	25	> 374.2
Pressure, MPa	0.1	25 – 50
Density, kg/m³	997	170 – 580
Permittivity, -	78.5	5.9 – 10.5
Ionic product pK	14.0	11.9 – 19.4
Dynamic vicosity, mPa*s	0.89	0.03 – 0.07
Enthalpy of vaporization, kJ/kg	2257	0
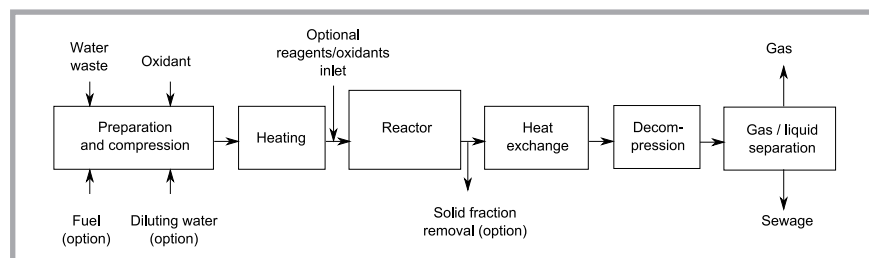
Figure 2. Diagram of typical supercritical water oxidation.

oxygen, which would lead to undesirable chemical reactions.

SCWO causes the oxidation of organic matter into CO_2, water and nitrogen, and inorganic compounds to oxides or inorganic acids, while obtaining energy.

The advantage of both methods is non-toxic by-products - the process proceeds at temperatures which reduce the formation of substances such as dioxins and nitrogen oxides.

SCWO process
SCW oxidation takes place in reactors suitable to high temperatures and pressures. The pressure is usually between 24 and 28 MPa and temperatures as high as 400 to 600 °C. A simplified diagram of the process is shown in **Figure 2**.

The SCWO process begins by introducing an oxidant (such as hydrogen peroxide, pure oxygen or air) to the organic material treated. This mixture may be diluted, if necessary. A high pressure pump causes compression of the batch to the pressure required. An external heater can be used in the case of insufficient operating temperature in the reaction chamber or when starting the system.

After the batch reaches the predetermined temperature, oxidation reactions occur. The organic compounds break down to CO_2 and H_2O. If nitrogen is present N_2 and N_2O are formed, and compounds such as chlorine, sulfur or phosphorus are converted into corresponding acids. The reaction time is usually from dozens

of seconds to several minutes, with the conversion degree exceeding 99.99%.

Assuming proper thermal insulation of the system under normal operating conditions, the process is energy self-sufficient. The content of the reactor passes the excessive heat through the heat exchanger and heats the feedstock and oxidant. After cooling down to a safe temperature the mixture is expanded in a pressure controller and directed to a separator where gas liquid phase separation occurs. The result is a pure gas, metal oxides and water, and the remaining inorganic sludge is insoluble in water, easy to separate and harmless to the environment [10 - 12].

SCWG Process
Supercritical water gasification is typically run at a pressure of 25 - 30 MPa and temperature ranging from 500 to 650 °C.

The biomass used in the process is refined (a particle size of less than 1 mm) and diluted to a degree that allows efficient pumping. The batch treated in this way is fed to the reactor containing SCW by means of a high pressure pump.

Gaseous components of the mixture are soluble in supercritical water. Salts separating from the mixture in a solid form fall to the bottom and are removed at the bottom of the reactor. The rest of the mixture is collected at the bottom of the reactor and fed to the heat exchanger, where it heats the feed streams and water. During cooling, gases are separated from the liquid phase and can fill high pressure containers or be used for energy purposes.

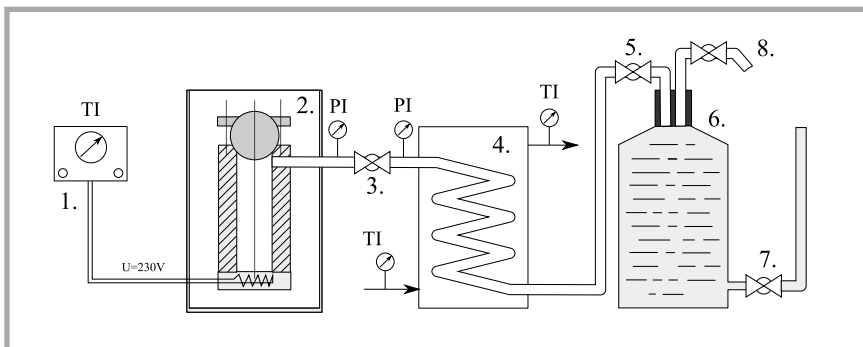***Figure 3.*** *Photo of apparatus on laboratory scale.*

Figure 4. *Scheme of system on a laboratory scale; 1. Temperature controller, 2. Reactor, 3. Discharge valve, 4. Cooler, 5. Valve, 6. Volume measuring vessel (with gauge), 7. Discharge and supply valve for make-up water, 8. Output valve for further sampling (for analysis of composition).*

Table 2. *Sample compositions of gas mixture after the process; * - within the limits of measurement error.*

#	Compound	% of volume				
		sample 1	sample 2	sample 3	sample 4	sample 5
1	H_2	wlme*	wlme*	wlme*	wlme*	wlme*
2	O_2	0.55	8.05	11.50	0.86	1.41
3	N_2	5.62	32.40	39.90	3.26	9.17
4	CH_4	13.98	7.42	23.46	16.37	8.11
5	CO	wlme*	0.00	0.00	10.50	2.93
6	CO_2	21.25	34.90	2.07	49.60	62.70
7	unidentified	58.60	17.23	23.07	19.41	15.68
	sum	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Characteristics of recyclable waste

SCW properties make it possible to be used as a reaction medium for the utilisation of the majority of organic substances. Using typical biomasses, which with high efficiency are used in ordinary combustion, is economically unreasonable. The most cost-effective is the treatment of waste which requires the removal of large amounts of water (traditional combustion is then inefficient). These are, for example:
■ sludge from papermaking processes,
■ municipal wastewater or wet biomass (fermentation, agricultural, from forestry and food industry, etc.),
■ fibrous materials with a high content of organic substances.

There are many types of biomass which due to the lack of economic processing technology have not been applied despite widespread occurrence.

The other types where utilisation of supercritical water is justified are hazardous wastes, especially those whose combustion results in the emission of harmful volatile compounds. Printed circuits, chemical weapons, explosives, and many other materials can be successfully disposed in a safe way.

Some polymers in various forms can be decomposed in supercritical water into single polymers and then re-used to produce polymers.

An important group of materials that can be processed with SCW is waste containing valuable mineral substances that cannot be efficiently extracted in other treatment methods. An example is the sludge waste left after de-inking, where valuable mineral fillers can be successfully recovered, ready for re-use in the production process [11].

An important limitation of the choice of material for recycling using SCW is the content and type of inorganic salts in these materials. Large amounts of dissolved salts cause agglomeration and closing of the pipe cross-section, which may lead to destabilisation of the reactor and stop the process.

■ Goal of the work

The goal of the work was to examine possibilities of utilising paper industry wastes with supercritical water. The well-known capacities of supercritical water systems to utilise various waste and toxic materials led us to perform similar trials for fibrous materials of the paper industry.

To achieve this goal, cooperation between the Institute of Papermaking and Printing at the Technical University of Lodz and the EkoAqua company was initiated.

Implementation of the process in industrial conditions

In 2011, in Lodz, EkoAqua started a project co-financed by EU funds aimed at the construction of an industry-scale installation to recycle energy waste using supercritical water in the SCWG process. The project consists of four main stages.

1. Process modelling and design of equipment.
2. Building of equipment and carrying out experiments on a laboratory scale.
3. Building of process apparatus for continuous operation on a semi-industrial scale (the prototype), (200 kg/h).
4. Construction and start-up of a production scale plant (3 t/h).

Currently the project is at stage three, with the experiments of step 2 still taking place as well as preparation for investment for stage 4.

Due to the high cost of construction and process for supercritical water, return on the investment and its advantages over other solutions may be obtained in the following two cases:
- neutralisation of toxic waste,
- waste of high water content.

In the first case, other processes (eg. combustion) may not adequately neutralise the toxic waste, and during the process may emit toxic gases into the atmosphere. In the latter case, other methods of processing typically require large amounts of energy to provide pre-drying.

SCW process steps

Regardless of the scale of the apparatus the biggest challenge is the selection of suitable materials capable of withstanding the pressure (25 - 30 MPa) and temperature (500 - 650 °C) required. In general, the process can be divided into stages.
1. Preparation of batch material: fragmentation and optional hydration.
2. Compressing the feed to the pressure required for the process.
3. Transport of the batch to the reaction chamber.
4. Heating the feed to the supercritical water process temperature.
5. Discharge of gas products and inorganic solid residue of the process, together with pressure reduction and temperature decrease.

Requirements to be met by the feed supplied to the reaction in SCW:
- availability of large amounts of material (for continuous process),
- high costs of alternative methods of disposal / neutralisation
- a small amount of post-reaction solid sludge,
- the greatest heat of combustion / post-reaction gas calorific value,
- low viscosity of post-reaction sludge (in the case of a continuous process).

Due to the high reaction temperature, operating costs are high. In order to balance energy input in SCW systems, energy recovery through the burning of post-reaction gases is planned. Therefore it is worth measuring the heat of combustion and/or calorific power of these gases.

Test methodology on a laboratory scale

A laboratory scale system (*Figure 3*, see page 134) was primarily built to examine small amounts of feed from various sources to get information about the composition of post-reaction gases. Burning analysis (heat of combustion) of post-reaction gases and the amount of post-reaction solid fraction are important factors when selecting a batch source.

A diagram of laboratory equipment is shown in *Figure 4*. The main element is the reactor in which the reaction takes place. The reactor is equipped with heaters capable of providing the necessary temperature of 550 °C. Because of the small volume of the appropriately chosen reaction, heating results in the reaction pressure desired.

The reactor is equipped with cast iron housing to protect against any sudden depressurisation of the reactor chamber. The reactor itself has an adequate construction and wall thickness to provide process safety at high temperature and pressure.

The batch with water is fed into the reaction space (2). After sealing the reactor, heating to a temperature of 550 °C starts (about 20 min). For the isochoric process the pressure is raised as well. After 5 - 10 minutes at the reaction temperature the heating is turned off and partial cooling of the gas takes place. The gas is then passed through the cooler (4), where water vapour condensation occurs. In container 6 the gas volume is measured. Valve 8 is used for post-reaction gas sample downloading. In order to minimise the absorption of CO_2, the water is salted with an adequate amount of NaCl.

Results

The gas samples were tested using gas chromatography. *Table 3* shows sample compositions of gases produced from waste charges sampled after a Bellmer press from a production line for decorative paper for laminates.

Source of samples
- Sample 1 - 3: waste paper pulp
  - Initial m.c.: 5.5 to 6.5 g of water / dry mass g.
  - Solid (inorganic) content after process: 20 to 39%.

Table 3. Real amounts of methane estimated in samples.

% of volume		
sample 1	sample 2	sample 3
14.1	18.7	44.3

- Samples 4 - 5: cellulose pulp
  - Initial m.c.: 6.0 to 7.0 g of water / dry mass g.
  - Solid (inorganic) content after process: 11 to 23%.

The moisture content presented was obtained after saturating each sample with water at a ratio of c.a. 6:1, required to achieve a proper reaction environment (see calculations in further part of text). A wide range of solid content after the process is the result of the non-homogeneity of sample volumes.

Due to 1) sampling difficulty in a laboratory reactor, 2) the absence of oxygen in the theoretical SCWG process in the reaction mixture, 3) the presence of oxygen and nitrogen at a ratio similar to the content iof air in the test samples: it can be assumed that the presence of oxygen and nitrogen derived from the air is the same as that in the sample during the download. On this basis, the methane content was estimated in the subsequent samples (percentages by volume, *Table 3*):

Two additional gases in the samples were detected. The extra gases were not identified with the technique used; they are probably (according to the SCWG processes products) heavier hydrocarbons: ethane and propane. Due to inaccuracies in the sampling method further measurements are planned.

Calculation of the heat of combustion / calorific value can be done in two ways:
- by burning gas in the calorimeter,
- by performing calculations.

The results from the calculations are presented below.

In order to simplify the calculations an assumption was made that only the calorific value was formed from the methane during the process. In fact, due to the existence of unidentified compounds the calorific value may be higher.

Due to difficulty of sampling in the apparatus, the accuracy of the measurements was about 10% of the value measured, which is sufficient at this stage.

Table 4. *Expenditures and incomes of energy in the process.*

	Energy in MJ to process 1 kg of dry mass and 6 dm³ of water	
Expenditure	A: To heat 6 kg (333 moles) of water (to 550 °C)	9.54
Income (post-process gas combustion)	B: Energy acquired from burning 100 g (6.25 mole) of CH_4	5.00
	C: Assuming 20% larger calorific value from unidentified flammable gases	6.00
	D: Assuming 20% of heat recovery in continuous process	7.20
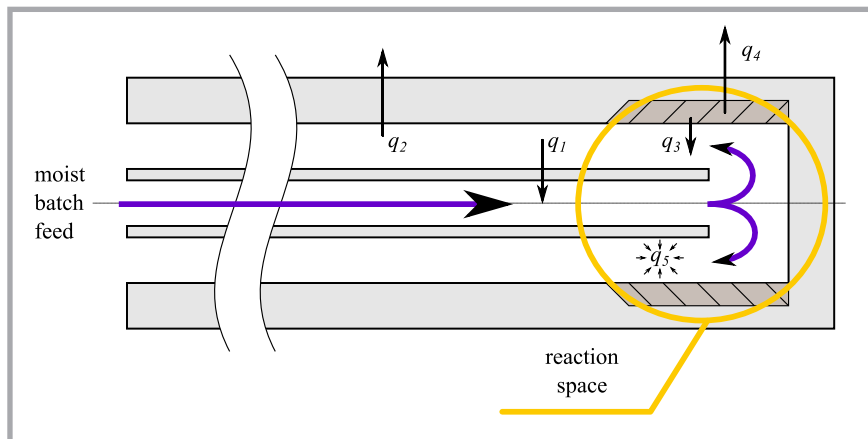
Figure 5. *Apparatus in semi-industrial scale; q1: heat from the reaction mixture to preheating incoming feed. q2: heat loss through the insulation from the reaction mixture. q3: heat form the heater to reaction chamber. q4: heat loss from the heater to the environment. q5: heat required for chemical reactions.*


Figure 6. *Photo of system on an semi-industrial scale.*

The amount of post-reaction gas

In the measurement, 10 g of dry material was mixed with 60 ml of water. After the process and water vapour condensation, the gas volume obtained was 6.3 dm³. 22% of the volume was methane, that is, about 1.4 dm³ of methane. According to the law of Avogadro, the amount of methane obtained was about 1.4 dm³/22.4 dm³/mol = 0.0625 mol, which is a mass of

16.04 g/mol × 0.0625 mole =
= approximately 1 g of pure CH_4.

10 g dry mass + 60 g H_2O →
→ 6.3 dm³ × 22% CH_4 = 0.0625 mol =
= 1 g of pure CH_4.
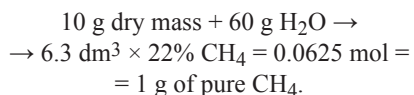
The calorific value of methane is about 50 MJ/kg [13], which for 1 g gives 50 kJ. The heat of combustion, respectively, will be about 55 kJ.

Returning to the initial amount of dry matter, it can be assumed that the delivery of 1 kg of dry matter in the process would provide about 6.25 moles of pure methane (about 100 g) with a calorific value of 5 MJ.

Since, as was mentioned previously, only the balance of methane is taken into account, it is estimated that the result will have a greater calorific value of 10 to 40%.

Energy expenditure

On the basis of the above data the amount of energy required to carry out the process on a laboratory scale was calculated. For the amount of 10 g dry mass, 60 ml of water was applied. Water heating from room temperature to SCW requires much energy, which is calculated below.

The C_p specific heat of water in standard conditions is 4.2 kJ/kg K [14]. Given the specific heat of water is only an approximation, the real value is hard to obtain and is represented by a nonlinear function, fluctuating between $3.2×10^3$ and $17.4×10^3$ in the 350 to 500 °C temperature range [16]. C_p/C_v H: 1.41, oxygen: 1.40. Assuming adiabatic exponent k ≈ 1.4:

$$c_v = \frac{c_p}{k} \approx \frac{4.2}{1.4} \approx 3, \frac{kJ}{kg \cdot K}$$

If, therefore, on the basis of previous calculations for methane, it was calculated that the reaction of 1 kg of dry matter can give a gas with a calorific value about 5 MJ, it will require about 6 liters of water. To preheat 6 kg (333 mol) of water of 1° we need about 18 kJ/K. Obtaining a temperature of 550 °C (20 °C) requires 18 kJ/K × 530 K = 9.54 MJ of energy.

In a continuous process, the energy balance should be advantageous if one takes into account that energy is consumed to maintain the temperature and pressure of the process; however, only at startup will it be required to heat the water to the parameters of SCW (construction of the apparatus in the form of a tube in a tube (Field's reactor) enable intensive exchange of heat).

Roughly estimating, if the calorific value (or heat of combustion, depending on how utilisation of the steam trial proceeds) is higher after taking into account other flammable gases, for example 20%, and we assume that in a continuous regime the amount of energy required is lower (heating water of a higher temperature by heat recovery by a further 20% during the heat exchange in the process), the value of the energy balance can thus be represented as in *Table 4*.

Values of B and, consequently, C and D will vary depending on the batch material used. For the sake of simplicity of rough calculation of the required heat, the heat to dry feed was omitted. In the final calculation the energy efficiency of the sys-

Figure 7. *Feeding and compressing system. Industrial scale installation.*

tem (including the heat loss to the environment) should be taken into account.

The balance does not include the heat of reaction taking place during the process (see **Figure 5**, the stream q_5). In the apparatus, on a semi-industrial scale, additional energy will be consumed for the initial mixture compression.

Therefore calculation on a laboratory scale will differ from that valid for the semi-industrial and industrial scale, for the following reasons:

- various batches used (with varying calorific capacity),
- need to supply the auxiliary systems, including transport and grinding, pre-pressurisation,
- additional heat recovery in double tube system,
- formation of other flammable gases.

Apparatus on a semi-industrial scale (prototype)

In order to investigate the possibility of carrying out the process continuously a prototype plant with a capacity of 200 kg/h was built. The system operates in a continuous regime and the process is realised by a double pipe reactor (Field's reactor, **Figure 5**). Heat is delivered over the entire length of the reactor. At the present time, initial integrity tests are being performed.

Figure 5 shows a diagram of the apparatus with heat streams. **Figure 6** shows system on a semi-industrial scale.

Figure 7 shows the feeding and compressing system.

Industrial scale installation

An industrial scale installation is being currently designed. The target performance is 2 tons per hour of wet feed on a regimen of continuous operation. Due to the early stage of the project we are not able to provide more information.

■ **Conclusions**

Processes in a supercritical water environment require the construction of expensive and complex equipment. The presence of high pressure will require using durable materials, and the high-temperature performance significantly limits the choice of these materials. Due to these difficulties the SCW process is not common in industrial practice.

Due to the search for alternative ways of waste disposal i.e. improving the balance between energy utilisation and giving a better effect on the environment, in the last 20 years SCW processes have been the subject of detailed research.

Efficient heat recovery methods along with the development of new materials that are resistant to extreme conditions make it likely that the processes of SCW will become more common in the recycling and neutralisation of materials.
There are fields of application in which the SCW processes are unrivalled - neutralisation of toxic materials.

Wastes from paper production usually contain a high percentage of water, which is a problem for conventional utilisation methods based on combustion. In the SCW reaction, the moisture content is an advantage offering ample opportunities to apply this technology for the treatment of wastes from the paper and textile industries. According to our preliminary studies, methane, which reaches a value of 44% (**Table 3**), should be sufficient to balance the energy input needed for the process.

The project presented in the work is being carried out by the EkoAqua company (with scientific help from the Lodz University of Technology) and is unique in the national scope because of the size. Moreover the throughput planned is rarely seen in the world.

The positive results of the pilot studies for feeds from the paper and textile industry will open new possibilities for the disposal of these wastes on an industrial

scale. The equipment is designed to dispose of any waste organic matter. Therefore other producers of energy waste, including slaughterhouses and hospitals, are sought.

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