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EXAMINATION OF THERMIC TREATMENT AND BIOGAS PROCESSES BY LCA

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Abstract: In the waste management system, it will always be an amount of end-of-material where after its method of LCA, it will emerge that it cannot be or impractical to utilize. One of the possible ways for end-ofmethod of LCA, it will emerge that it cannot be or impractical to utilize. One of the possible ways for end-of-life materials is the thermic utilization. According to the possible thermic/energetic utilization alternatives, the utilization can be carried out by incineration, cracking (pyrolysis or gasification) or plasma-based technology. The Life Cycle Assessment method can play an important role in this research. The research can set up prognoses with LCA analyses and the conscious application of scientific methods, which can offer a prognosis for untested situations. This paper summarises new information for the thermic treatment processes with a comparison between the different technologies and for a biogas-technology. The investigations show environmental impact categories, energy efficiency and mass-based parameters for organic industrial waste by thermic treatment processes and for organic waste by biogas technology. While examining the above viewpoints, it worked out a complex model which may mark a new direction for solutions and decision making in the environmental protection. **Keywords**: Thermic treatment processes, Biogas technology, Life Cycle Assessment

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1. INTRODUCTION

The persistent organic pollutants (POPs) wastes used oils, waste with content of PCB/PCT and pesticide wastes; take the main place in the group of organic industrial waste and the residues of the POPs waste generated in the processes of the chemical industry. The chlorination of biphenyl by PCBs can lead to the replacement of 1-10 hydrogen atoms by chlorine. The chemical formula can be presented as $C_{12}H_{10}$ -nCln, where n is the number of chlorine atoms in the molecule. The PCBs are chlorinated hydrocarbons that are manufactured commercially by the progressive chlorination of biphenyl in the presence of a suitable catalyst. Depending on the reaction conditions, the degree of chlorination can vary between 21 and 68% (w/w). The theoretically possible number of different PCTs is several orders of magnitude greater than the number of PCBs, but in practice, as with PCBs, PCTs are sold on the basis of their physical properties, which depend on the degree of chlorination, and not their chemical composition.

Despite the fact that chemical industry and environmental protection are closely interlocked, there is fairly poor national and international professional literature available about the two connected professions. There are green chemistry methods and some other treatment approaches for decreasing the quantity of the organic industrial waste, but currently thermic processes are the most popular alternatives. There has been a growing call for the quantity of organic industrial waste and transition of waste management systems to Waste-to-Energy (WtE) or Energy-from-Waste (EfW) processes. This paper summarises the thermic treatment/energetic utilization processes with a comparison between the different technologies. stressing factors affecting their applicability and operational suitability. The research study can set prognoses with help of new LCA GaBi 5.0 software.

With the application of LCA-software for the technologies, their energetic and environmental efficiency can be determined. Their advantages and disadvantages are examined in such a multicomponent matrix. The LCA results are analyzed with regard to life-cycle segments and as a functional unit of energy consumption and/or the recoverable energy that can be used [10]. With the use of Life Cycle Assessment it can be possible to determine a priority order for the thermic utilization processes. This article would provide some new informations related to the biogas technology for organic waste (poultry manure).

2. METHODOLOGY, GOAL AND SCOPE OF THE RESEARCH

The first step of this research is to compare the available thermic treatment technologies. The conventional incineration is the most used process today, so it is important in comparison to the new thermic technologies. They can be mainly distinguished from conventional incineration by the fact that in their case the treatment of waste occurs with little or no oxygen present. Comparing the prevalence of new thermic technologies to incineration shows that the utilisation of these alternatives is low, and only few reliable data on emissions are available for the time being. There is no reason to suppose that toxic emissions will differ from those of a conventional incinerator. Due to certain technical features of new thermic technologies, their emissions can be considered to be better than incineration emissions. Their advantages and disadvantages are examined in such a multi-component matrix. The main advantages are useful end-products, which can be utilised as materials and also energetically.

The second step of this research is to set up life cycle assessment results and priority order of the thermic treatment technologies. The third step is to work out a modern biogas technology for organic waste with help of life cycle assessment plan. The LCA results show the Global Warming Potential (GWP), the Ozone Layer Depletion Potential (ODP), the Acidification Potential (AP) and the Eutrophication Potential (EP) for hazardous waste (with PCBs) by thermic treatments and for organic waste (poultry manure) by biogas technology.

3. APPLICATION OF THE LIFE CYCLE ASSESSMENT METHOD

Before new technologies enter the market, however, their environmental superiority over competing options must be asserted based on a life-cycle approach. Life cycle assessment investigates the environmental impacts of systems, processes or products. LCA models the complex interaction between a product and the environment from cradle-to-grave throughout the full life cycle, from the exploration and supply of materials and fuels, to the production and operation of the investigated objects, to their disposal/recycling [10]. The life cycle assessment method is one of the best methods for innovation in the area of enviro-management. The LCA method is usually applied to comparative analysis, when it is possible to choose among the products, processes, services and systems having the same function, but each of them having significantly different environmental effects. The first results of this method came to the surface during energetic analysis and modelling [1]. There are several databases betting continuously refined and expanded but adequate coverage of the processes concerned has not been completed yet. 'LCA addresses the environmental aspects and potential environmental impacts (e.g. use of resources and the environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal (i.e. cradle-to-grave)'. In the evaluation, it is required to take the environmental effects of human health into account, as well as the ecosystem or abiotic depletion. The impact categories include emission of green-house gases, global warming, eutrophication and acidification. The most frequently used impact categories are: the Global Warming Potential (the most important category with weighting factor 10), the Acidification Potential (AP) and the Ozone Layer Depletion Potential (ODP).

The GaBi 5.0 Software that largely encourages the research work came a year ago into the market and has several advantages for its former versions. The GaBi 5.0 Software with databases 2012 establishes Life Cycle Assessment as an essential tool to develop more sustainable products and processes while increasing resource efficiency, reducing material, energy and cost. The Life Cycle Cost Analysis (LCCA) is a method for assessing the total cost of the facility. It takes into account all costs of acquiring, owning, and disposing of a building or building system [2], [6].

Impact Categories	Reference
Global Warming Potential (GWP)	kg CO2- Equiv.
Acidification Potential (AP)	kg SO2- Equiv.
Eutrophication Potential (EP)	kg phosphate- Equiv.
Human Toxicity Potential (HTP)	kg DCB- Equiv.
Photochemical Ozone Creation Potential (POCP)	kg ethylene- Equiv.
Ozone Layer Depletion Potential (ODP)	kg R11- Equiv.
Terrestric Ecotoxicity Potential (TETP)	kg DCB- Equiv.
Marine Ecotoxicity Potential (MAETP)	kg DCB- Equiv.
Freshwater Aquatic Ecotoxicity Potential (FAETP)	kg DCB- Equiv.
Abiotic Depletion (ADP elements)	kg Pb-Equiv.
Abiotic Depletion (ADP fossils)	kg MĴ

Table 1. Impact categories of the CML 2001 method

4. DETERMINATION OF THE THERMIC TREATMENT PROCESSES

The possible energetic utilisation can be carried out by incineration, cracking (pyrolysis or gasification) and plasma technology, or parallel flow incineration (in equipments). The following sections discuss the most frequently used thermo chemical technologies for WtE. These are:

- 1) Incineration: full oxidative combustion;
- 2) Gasification: partial oxidation;
- 3) Pyrolysis: thermal degradation of organic material in the absence of oxygen;
- 4) Plasma-based technology: combination of (plasma-assisted) pyrolysis/gasification of the organic fraction and plasma vitrification of the inorganic fraction of waste feed [3], [11].

	Purolusis	Gasification	Incineration	Plasma-based technology
Temperature	250-900°C	500-1800°C	800-1450°C	> 3000°C
Atmosphere	Inert/nitrogen	Gasification agent: O2, H2O	Air	Gasification agent: O2, H2O Plasma gas: O2, N2, Ar
End products	H2, CO, H2O, N2, hydrocarbons Ash, coke	H2, CO, CO2, CH4, H2O, N2	CO ₂ , H ₂ O, O ₂ , N ₂	H2, CO, CO2, CH4, H2O, N2
	Pyrolysis oil water	Slag, ash	Slag, ash	Slag, ash

Table 2. The more advanced WtE technologies

The more advanced thermochemical approaches such as pyrolysis, gasification and plasma-based technologies have been applied to selected smaller scale waste streams, and attempt to control temperatures and pressures of the process (Table 2). While the application of pyrolysis at low, mid- and high temperature is mainly possible for wastes, gasification is suitable for all burnable materials. In connection with plasma technology, the elimination of dangerous wastes is done by oxidation, and in this method of reduction the goal is to extract raw material. Plasma-based technology is the least-known process. This process is very suitable for the treatment of organic industrial waste [7]. The emission levels will be sensitive to the accidental inclusion of waste (emission limits are given in the Waste Incineration Directive). The main issue is syngas cleaning. The main constituents in syngas are hydrogen, carbon monoxide, carbon dioxide and methane. If syngas cleaning is omitted, the level of post-combustion emissions requiring capture will be greater. Dioxins will be reduced but not eliminated by syngas cleaning. They are destroyed by higher temperature, but can re-form once the temperature drops. Gasification plants produce large quantities of carbon dioxide and, if the syngas output is used for electricity generation only, and many times greater, on a power for power comparison basis, than a conventional power plant. Gas engines and turbines typically have low tolerances to impurities in the syngas [4]. With pyrolysis the emission of heavy metals is lower (due to lack of oxygen), but one of the disadvantages is that the use of pyrooil is accompanied by significant emissions. Besides this, pyrolysis produces a large quantity of pyrocoke with a high concentration of heavy metals in the cinders. Plasma-based technology has a low gas flow, fast warming and cooling. At the end of the process, with minimal environmental effects, materials of glass and ceramics can be obtained, which can be utilised in the building industry [5].

The new technologies differ from the traditional incineration processes in that chemical energy is recovered from the waste. The derived chemical products may be used as feedstock for other processes or as secondary fuel in some cases. The waste is converted into a secondary energy source (a combustible liquid, gas or solid fuel), while it is utilised e.g. in a steam turbine, gas turbine or gas engine in order to produce heat and/or electricity. Smaller fuel gas volumes allow reduced gas cleaning equipment sizes. Furthermore, the new technologies enable a greater market penetration, since these secondary energy sources are compatible with gas turbines and gas motors [3]. As for gasification, a disadvantage is that the calorific value of the synthesis gas is below that of natural gas. Therefore, the energy necessary for the operation is more than the energy content of the gas produced. In simple terms, this means that for every 5 units of energy in the waste feedstock, only 1 will emerge as electric power. Gasification can be used in conjunction with higher efficiency energy recovery technologies; however, because the higher efficiency modes of energy recovery are less proven, the financial and environmental benefits are offset by the increased risk. Where pyrolysis and gasification (P&G) processes are integrated with more efficient energy recovery, significant greenhouse gas savings per kW of electricity generated are possible relative to incineration [4].

5. COMPLEX MODEL FOR THERMIC TREATMENTS

Application with different viewpoints was carried out a complex model for the thermic treatment processes, which beside of the parameters examined by LCA method, considers time and probability at the same time. Incineration, pyrolysis, plasma-based technology and gasification can be considered on the basis of three viewpoints: load of environment, energy efficiency and economic efficiency. This theoretical model was worked out by me. The main key-questions, the test parameters and the possible methods by the different viewpoints can be seen in the Table 3. By the viewpoint of load of environment the key-questions are in connection with emissions, environmental reliability and treatment of residual materials. From the viewpoint of energy efficiency we can determine a mix from the previous viewpoints. The key-questions are frequently the cost efficiency and the pay-out period.

	Load of environment	Energy efficiency	Economic efficiency
Main key- questions	 Emissions Environmental reliability Treatment of residual materials 	- Energetic usefulness	 Extraction and utilization of raw materials Recirculation in the technology Costs and cost efficiency Pay-out period
Test parameters	 Input-output balance of material Emissions in CO₂- Equiv. Other and toxic emissions 	 Input-output balance of energy Quantity of the energy efficiency Improving and retarding coefficients for the energy efficiency 	 Input-output balance of energy and material Amount of recovery/utilization Initial, maintenance and other costs
Possible methods	 Material balance equations and technological layout Sankey diagram Life Cycle Assessment EIO-LCA (Economic Input-Output Life Cycle Assessment) 	 Energy balance equations and technological layout Sankey diagram Life Cycle Assessment (LCA) EIO-LCA (Economic Input- Output Life Cycle Assessment) 	 Material and energy balance equations and technological layouts Cost analysis Cost efficiency analysis Life Cycle Cost (LCC) Life- Cycle Cost Analysis (LCCA)

Table 3. Key-questions, test parameters and possible methods

In case of the traditional incineration it would also be worth carrying out an examination with a wider spectrum, and besides recoverable energy (and, of course, relief of dumps), attention should be paid to the emission and other alternatives of utilisation [8], [9]. In order to do so, data from manufacturers and system operators are compiled with the help of the GaBi 5.0 database and complemented with data from different LCA literature. Within the special program system of MATLAB (Matrix Laboratory) based on the background of the pure mathematical statistics

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(relative frequency- probability), each and every environmental effect would mean the aleatory variable of a thermal treatment process – within an operational process. The main key-questions, test parameters and possible methods of the developed complex model can be the following (see Table 3). In order to do so, data from manufacturers and system operators are compiled with the help of the GaBi database and complemented with data from different LCA literature. The general process scheme of the material- and energy scale related to the thermic treatment methods is shown on Figures 1-2.



Figure 1: Input-output balance of material for WtE technologies [12]



6. LCA RESULTS FOR THERMIC TREATMENTS

The LCA data represents the the pyrolysis at 500°C, the conventional incineration at 1100°C (with fume purification), the gasification at 1200°C and the plasma-based technology at 3000°C for hazardous waste (with PCBs) in the EU 27 with application of GaBi 5 LCA-software. The inventory data for the system must be mathematically normalized to a functional unit, which has to be set a priori and is not a decision variable.

The functional unit was 1 kg hazardous waste (with PCBs) with energy recovery by electricity transfer and thermal convection. The calorific values are calculated from the elementary composition of hazardous wastes (database GaBi 5 Software). The remaining heat is assumed to be used completely. The emissions to air, the waste transport (truck on road with diesel mix) and the land filling of residues are included in the system.

The wastes are transported from production to the thermic treatment technology and the waste disposal in this model (system limit: from production process generated hazardous waste to waste disposal). The applied interpretation method was CML 2011 (November 2010) (Table 4).

Table 4. LCA parameters for thermic processes			
Functional Unit	Method	Impact Categories	
organic industrial waste (hazardous waste with PCBs) of 1 kg	CML 2001, (november 2010) (database of 2012)	GWP ODP AP HTP	

For the calculation of the mass balance of the process, all input components are split into their composition. The investigations show the values of the Global Warming Potential (GWP), the Acidification Potential (AP) and the Ozone Layer Depletion Potential (ODP) by thermic processes. There are: conventional incineration without fume purification, conventional incineration with fume purification, pyrolysis, gasification and plasma-based technology at 3000 °C (Figures 3-5).

By conventional incineration (T = 1100 $^{\circ}$ C) the main constituents of syngas are: NO₂ (71,37%), CO₂ (13,38%), SO₂ (11,15%), HCl (3,56%), CH₄ (0,44%), heavy metals and dioxins (0,10%). Dioxins will be not eliminated by syngas cleaning. Due to the contamination with heavy metals, the ash and slag go to landfill for hazardous waste.

1000 kg hazardous waste burnt can be expected, based on its carbon content, to produce 230 kg slag, 45 kg soot and 725 kg syngas. The heat output is used for electricity generation and thermal convection. The complex process will be used 78 kWh of electrical power and 23,5 kWh of thermal energy from natural gas.



Figure 5. The Acidification Potential (AP) for thermic technologies



Figure 4. The Ozone Layer Depletion Potential (ODP)

The input streams to the system are hazardous waste input, thermal energy from natural gas, electricity and water for flue gas cleaning. Output streams leaving the system as solid materials are ash and slag.

The emissions to the atmosphere contained in the clean gas come from the flue gas purification. The auxiliary materials used for the flue gas precipitation in the waste incineration plant are lignite, ammonia and lime.

According to measurements for Global Warming Potential (GWP) we can determine 5,03 kg CO₂-

Equiv. for incineration without fume purification. The value of the Ozone Layer Depletion Potential (ODP) is 0,001 kg R11- Equiv. and the Acidification Potential (AP) is 0,259 kg SO₂-Equiv. Dioxins will be not eliminated by syngas cleaning.

The value of the Global Warming Potential (GWP) is 0,707 kg CO₂-Equiv. for incineration with fume purification. The value of the Ozone Layer Depletion Potential (ODP) is 0,0001 kg R11-Equiv. and the Acidification Potential (AP) is 0,209 kg SO₂-Equiv. [12].

By gasification (T = 1200 °C) will be used 50 kWh of electrical power for the complex process. The input streams to the system are hazardous waste input, natural gas (only by start) and electricity. Output streams leaving the system as solid materials are ash and slag. The GWP is 0,989 kg CO₂-Equiv. for the gasification. The value of ODP is 4,09·10⁻¹¹ kg R11- Equiv. and the value of AP is 0,18 kg SO₂-Equiv. By pyrolysis (T = 500°C) the input streams to the system are hazardous waste input and electricity (70 kWh).

Output streams leaving the system are pyrolysis coke, pyrolysis oil and pyrolysis gas. The Global Warming Potential is 15,4 kg CO₂-Equiv. for the pyrolysis. The value of the Ozone Layer Depletion Potential is 0,0032 kg R11- Equiv. and the Acidification Potential is 0,376 kg SO₂-Equiv. The investigations show that the values of Potentials are higher by pyrolysis. By plasma-based technology (T = 3000 $^{\circ}$ C) the Global Warming Potential is 0,836 kg CO₂-Equiv., the value of the ODP is 4,03·10⁻⁸ kg R11- Equiv. and the Acidification Potential is 4,48·10⁻³ kg SO₂-Equiv. [12].

Global Warming Potential (GWP), the Ozone Layer Depletion Potential (ODP), the Acidification Potential (AP) and the Human Toxic Potential (HTP) for hazardous waste (with PCBs) by thermic treatments are shown on Table 5.

The Figure 6 represents the different potentials for the thermic technologies. The investigations show that the values of GWP, the AP the ODP, and the HTP are very good by the plasma-based

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technology at 3000-5000 °C [13]. In the research work have been introduced environmental impact categories and additional parameters e.g. energy efficiency parameters and mass-based parameters. The values of these parameters related to the thermic treatment methods are shown on Table 6. With application of the values of the environmental impact categories, the energy efficiency parameters and the mass-based parameters this research study can set up prognoses with LCA analyses between thermic treatment processes and their priority.

	0	-			
Thermic treatment processes		Environmental impact categories [kg -impact Equiv]			
	HTP	GWP	ODP	AP	
Conventional incineration without fume purification (at 1100°C)	96,7	5,03	1E-3	0,259	
Conventional incineration with fume purification (at 1100°C)	28,5	0,707	1E-4	0,209	
Pyrolysis (at 500°C)	0,645	15,4	3,2E-3	0,376	
Gasification (at 1200°C)	0,433	0,989	4,09E-11	0,18	
Plasma-based technology (at 3000°C)	3,66E-2	0,836	4,03E-08	4,48E-3	
Plasma-based technology (at 5000°C)		0,128	4,48E-10	1,37E-4	
Notation: HTP- Human Toxic Potential [kg DCB- Equiv.], GWP - Global Warming Potential [kg CO ₂ -					
Equiv.], ODP - Ozone Layer Depletion Potential [kg R11-Equiv.]					
AP - Acidification Potential [kg SO ₂ -Equiv.]					

Table 5. Value of environmental impact categories



Figure 6. The values of different Potentials for thermic technologies Table 6. Energy efficiency and mass-based parameters

	Énergy efficiency parameters [%]		Mass-based parameter [kg/1kg waste]	
	$\eta_{\rm NV}$	$\eta_{ m NH}$	Δm_{hull}	K _{fg}
(with and without fume purification) 14,93 10,82		10,82	0,725	0,875
Pyrolysis	15,54	66,33	0,884	0,958
Gasification	17,29	65,34	0,725	0,833
Plasma-based technology (3000°C)	32,96	64,04	0,80	1,231
Plasma-based technology (5000°C)	35,98	61,02	0,83	1,142
<u>Notation:</u> η _{NV} net electric efficiency [%], η _{NH} net thermal efficiency [%] Δ m _{hull} weight loss of waste [kg/1kg waste], K _{fg} size of flue gas emissions [kg/1kg waste]				

7. LCA RESULTS FOR BIOGAS-TECHNOLOGY

The biogas-technology was planned by our research team. The used materials were poultry manure and grass silage. The LCA data represents the biogas-technology with fermentation for 1000 kg waste (functional unit) in the EU 27 with application of GaBi 5 LCA software (table 7).

	Table 7. LCA parameters for biogas-technology	
Used materials	Method and parameters	Categories
Poultry manure:	Applied method:	GWP
922 kg	CML 2001, november 2010 (database of 2012)	ODP
Grass silage:	Functional unit:	AP
78 kg 🛛	1000 kg organic waste	EP

Beside the main fermenter unit it added a cogeneration unit, a gas motor with electricity power of 150 kW. All the raw materials are stored on the site. This process generates 309 kg-s biogas and 691 kg-s end product. The end product is utilized on soil with help of transportation by truck within 5 km. The biogas gets into a cogeneration unit, where it results flue gas, thermal and electrical energy (Figure 7).

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Figures 8-11: The values of different impact categories for biogas technology Table 8. Results of the biogas technology process [14]

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Parameters	Values	Notations
GWP	3,94	Global Warming Potential [kg CO ₂ -Equiv.]
ODP	1,78E-10	Ozone Layer Depletion Potential [kg R11-Equiv.]
AP	1,30	Acidification Potential [kg SO ₂ -Equiv.]
EP	0,338	Eutrophication Potential [kg phosphate- Equiv.]
ηνν	33,71%	Net electric efficiency [%]
ηνн	44,16%	Net thermal efficiency [%]
t	3-4 years	Pay-out period

The applied interpretation method was CML 2011 with database of 2012. The investigations show the values of the Global Warming Potential (GWP), the Ozone Layer Depletion Potential (ODP), the Acidification Potential (AP) and the Eutrophication Potential (EP) by the biogas process (Fig. 9). The Table 8 shows the results of the biogas process. According to measurements for Global Warming Potential (GWP) we can determine 3,94 kg CO₂-Equiv. for biogas technology. The value of the Ozone Layer Depletion Potential (ODP) is 1,78E-10 kg R11- Equiv. the Acidification Potential (AP) is 1,30 kg SO2-Equiv and the value of Eutrophication Potential (EP) is 0,338 kg phosphate- Equiv.

8. CONCLUSIONS

The data records used are based on measurements made on EU plants and calculated data. Pyrolysis, incineration, gasification and plasma-based technology at different temperatures can be considered on the basis of viewpoints: environmental effects and energy efficiency. While the pyrolysis on low, mid- and high temperature is mainly possible for homogeneous wastes, gasification is suitable for all burnable spent materials.

In connection with plasma-based technology, the elimination of wastes is done by oxidation, and in reduction the goal is to extract raw material. The investigations show the environmental impact categories, the energy efficiency and the mass-based parameters by thermic treatments processes and by biogas technology for organic waste.

The experimental results for thermic processes show that the values of environmental impact categories and the values of energy efficiency are very better by the plasma-based technology at 3000-5000°C.

According to the load of environment and energy efficiency can be determined that the plasmabased technology is the most enviro-friendly technology. Before we bring a final decision for the thermicutilization processes in respect of various wastes and fractions, the LCA-method can be an suitable implement.

While examining the above mentioned viewpoints, it worked out a new mathematical method which, in addition to the LCA, takes time and probability into consideration with the combination of a programming language, and which may mark a new direction for solutions and decision making in waste management.

According to the LCA-s it can be found the hierarchy not only some wastes processing methods but some thermic utilization processes. Combining the different LCA software with mathematical programming languages, a new and effective solution-decision trend can be set for chemical environment protection and for the issues of the management of wastes from chemical processes.

The experimental results for biogas process show that with the transportation of the end product the ODP values are unimportant and without the transportation we have no ODP-values. The value of the energy efficiency parameters is very good (between 33-45%) and the pay-out period is 3-4 years.

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