

Process optimisation and valorisation of combustion by-products in transition to circular economy (UPS-Plus)



Politechnika Śląska





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Process optimisation and valorisation of combustion by-products in transition to circular economy (UPS-Plus)

The research presented in this presentation was performed within project on "Process optimisation and valorisation of combustion by-products in transition to circular economy" (UPS-Plus) funded by The Foundation for Polish Science within the Team Teach Core Facility Programme (www.ccf.polsl.pl).



The UPS-Plus project includes research on:

ullet

- Influence of fuel additives on the combustion process, including slagging, fouling, high-temperature corrosion, emission of hazardous substances, e.g. Hg, HCl, HF,
- Preparation of composite materials using UPSs as fillers, and then carrying out strength tests, checking their chemical and mechanical properties, as well as the potential threat to the environment or users,
- Modern tools analysis (e.g. neural networks) of the potential use of UPSs based on a model calibrated on the basis of the obtained data,
- Designing and analyzing subsequent processing cycles of materials containing UPSs in accordance with the principles of the Circular Economy,
- Proof of concept resulting with the technology that allows the production of several qualified granulates from post-consumer materials with the addition of fillers based on UPS and post-consumer materials based on UPS modified with nanostructured materials such as halloysite.



Identification of a full range of UPSs and fuels properties,





Core Combustion Facility

The main objective of the project is to realize the **circular economy ideas by optimizing the** combustion process in order to obtain combustion by-products likely to valorization and usable in industry.

This objectives are carried by an innovative, multifunctional Core Combustion Facility (CCF), semi-technical boiler stand allowing to develop research service concerning modification of combustion process in order to receive the most useful by-products.

CCF is a unique combustion unit with a vibrating grate that allows following research:

- Combustion characteristic of biomass and alternative fuels on a grate (e.g. for thermal utilization of waste, refuse-derived fuel),
- Determination of combustion characteristic for a grate unit,
- Optimization of low quality solid fuels combustion process,
- Upgrading fuel properties with additives, especially connected with slagging, fouling and high temperature corrosion,
- Reduction of harmful compounds emission (e.g. NOx, Hg, HCl, HF, NH₃),
- Formation of combustion by-products subsequently subjected to thermal and chemical functionalization resulting in useful materials, e.g. geomats, insulations or sorption medium.









CCF scheme

1.	Vibriting grate
2.	Furnace pass
3.	Radiant test block
4.	Heated radiant test block
5.	Horizontal pass
6.	Convective test block
7.	Convective test block
8.	Test HX
9.	Ash hoppers
10.	Safety valves
11.	Vertical pass
12.	Air fan
13.	Valves for air cooling
14.	Flow meter
15.	Air heater
16.	Fuel distributor
17.	Flue gas cooler
18.	Fle gas cleaning









Possible application of CCF

Experimental research on:

- Rate of combustion and devolatilization of fuel particles on a grate,
- Fuel and fireside additives and their influence on the combustion process and by-products properties,
- Fuel agglomeration, fouling and slagging control,
- Corrosion control (high and low temperature corrosion),
- Gas and solid emission control,
- SCR and SNCR technology, removal of Hg and Cl

Fuel consumption	120 kg/h (15 MJ/kg)
Air for combustion	800 m3/h
Flue gas cooling unit	93 kW (400 °C> 130 °C)
Flue gas solid particles filter	< 5 mg/Nm3 (250 °C)
Flue gas	1000 m3/h (< 130 °C)
SNCR Module	800 – 1100 °C
SCR Module	<450 °C

CCF operation parameters









CCF under construction













Fuel additives

Fuel additives have a positive impact on the combustion process and can change the parameters of UPSs.

Lime additives (CaO, CaCO₃,Ca(OH)₂)

They reduce sulfur emissions (desulphurization) and increase ash fusion temperatures (AFT)

Sulfur-based additives((NH₄)₂SO₄)

They increase the ash fusion temperatures (AFT) and reduce the risk of chloride corrosion Phosphorus-based additives (CaHPO₄*2H₂O)

They reduce the risk of ash sintering and the formation of agglomerates (especially in fluidized bed boilers)



Copper-based additives (3CuO*CuCl₂·4H₂O)

They facilitate ash deposits removal by making them looser and less sintered Aluminosilicate additives

They increase ash fusion temperatures (AFT)







The properties of fuel additives



Halloysite –SEM picture



The aim of the research is to determine the doses of aluminosilicate additives on the combustion process and their impact on the fly ash characteristic.



Kaolinite – SEM picture [kyoritsu-kcm.co.jp]





The influence of fuel additives on AFT



Ash Shrinkage Starting Temperature (SST) for selected fuels with a different dose of halloysite



AFT – Ash Fusion Temperatures



Ash Initial Deformation Temperature (IDT) for selected fuels with a different dose of halloysite





The influence of fuel additives on ash composition

Compound/Fuel	WS	BZ0	BZ2	SPK0	SPK4	DS0	DS4	DM0	DM4
SiO ₂ ,%	54.94	46.17	46.06	62.46	53.55	56.46	54.93	62.54	53.61
Fe ₂ O ₃ , %	9.93	2.07	7.86	0.85	8.58	1.87	3.91	0.77	8.82
Al ₂ O ₃ , %	24.99	4.92	13.48	1.26	13.18	4.21	13.40	1.05	14.64
Mn ₃ O ₄ , %	0.02	0.31	0.36	0.22	0.34	0.07	0.12	0.09	0.26
TiO ₂ , %	0.87	2.51	3.15	0.10	1.22	0.22	0.58	0.08	1.19
CaO, %	1.95	15.69	10.46	7.66	5.35	9.76	7.60	9.54	6.66
MgO, %	1.37	4.33	2.98	2.21	1.64	2.90	2.26	1.52	1.08
SO ₃ , %	0.80	4.11	2.71	2.48	1.64	2.22	1.50	2.56	1.36
P ₂ O ₅ , %	0.18	4.46	3.20	3.35	2.62	2.84	2.38	4.52	3.38
Na ₂ O, %	2.47	1.03	0.82	0.32	0.25	0.97	0.84	0.33	0.32
K ₂ O, %	2.39	14.22	8.72	18.97	11.53	18.40	12.36	16.94	8.61
BaO, %	0.07	0.13	0.15	0.08	0.09	0.05	0.07	0.03	0.05
SrO, %	0.03	0.05	0.04	0.02	0.02	0.04	0.04	0.02	0.02

Chemical composition of fly ash with and without the additive of the halloysite



It has been shown that:

- Halloysite has a **positive effect on the ash fusion** temperatures and the content of K and Na in the ash.
- There is no one-size-fits-all method for calculating the dose of an additive. Each fuel requires a different dose of additive.
- For most biomass, a dose of 1% 2% of the ulletadditive (by weight) is appropriate.
- The additive contamination needs to be taken into account in the dose calculations.





The influence of fuel additives on sorption properties

CO₂ sorption properties of the ashes in the function of the absolute press





ure	
	SUPS
	-Hal Kal 4%
	Hal 2% Kal
	-Hal 4% Susz
	Hal susz 2%
	-Hal Raw 2%
	-Hal Raw 4%
	Kao 2%
	Kao 4%
1	1200000

It has been shown that:

- SUPS is a reference sample with no additive pure \bullet straw.
- Different types of additives and the mass share are \bullet described: Kal – calcinated, Susz – dried, Raw
- Fuel additives positively influenced the sorption \bullet properties of the ash
- The sorption capacity of the ash increases with ulletincreased share of the additive
- Increased pressure of the process increases the \bullet sorption capacity
- Further analysis are under investigation to determine \bullet the impact and the properties of different kinds of ash









The impact of fuel additive on KCl - Thermoanalytical experiments T, ℃

Additive/KCl - SR_{0.5}, SR_{1.0}, SR_{2.0}; ٠

 $SR_i = i \cdot \frac{M_{Additive}}{M_{2KCl}}$

where:

i – multiple of stoichiometric ratio (0.5; 1.0; 2.0),-; M_{Additive} – molar mass of additive, g/mol; M_{2KCI} – molar mass of 2KCl, g/mol.

- Two fuel additives: halloysite oraz kaolinite; ٠
- **Thermogravimetric analysis** performer for additive/KCl **mixtures** and **additives**: ٠
 - 10 mg of sample;
 - from ambient temperature (25 °C) to 1100 °C at a heating rate of 10 K/min;
 - an air atmosphere.





TG/DSC SETARAM LABSYS[™]







The impact of fuel additive on KCl - Thermoanalytical experiments





- Melting point of KCl **773.1°C**;
- At **1100 °C** complete evaporation of KCl was not • observed.

- metakaolinite;
- amorphous silica;



Up to 400°C, the mass of the sample is lost during the heating process (elimination of absorbed water molecules on the external surfaces of particles);

At temperature of 517.1°C for halloysite and at 535.2°C for kaolinite they changed in

Slight endothermic peaks immediately followed by exothermic peaks, around 950 – 1000°C metakaolinite transformation to a spinel structure or Si-containing gamma-alumina (γ -Al₂O₃) and

No further endothermic and exothermic reactions were noted up to the temperature of **1100** °C.





The impact of fuel additive on KCl - Thermoanalytical experiments



Temperatures of transformation into meta-kaolinite

An increase in this temperature with an increase \bullet in the amount of additive in the additive/KCl mixtures (SR_{0.5}<SR_{1.0}<SR_{2.0}<100% for halloysite and $SR_{0.5} < SR_{1.0} < SR_{2.0} < 100\%$ for kaolinite);

Melting points of samples

- (SR_{0.5}>SR_{1.0}>SR_{2.0});



Temperatures of complete evaporation

Initial and final evaporation process temperatures decrease with the amount of additive

In the case of SR_{0.5}, no end of the evaporation process was noted for both additives (>1100 °C);

As the amount of additive increases, the evaporation process takes place in a smaller temperature range (halloysite: $SR_{1,0} \Delta t = 262,6^{\circ}C i SR_{2,0} \Delta t = 231,8^{\circ}C$; kaolinite: $SR_{1,0} \Delta t = 278,4^{\circ}C i SR_{2,0} \Delta t = 151,6^{\circ}C$).







The impact of fuel additive on KCl Semi-technical scale tests

Additive/KCl – $SR_{0.5}$, $SR_{1.0}$, $SR_{2.0}$, $SR_{6.0}$; ٠

 $SR_i = i \cdot \frac{M_{Additive}}{M_{2KCl}}$

where:

i – multiple of stoichiometric ratio (0.5; 1.0; 2.0; 6.0),-; M_{Additive} – molar mass of additive, g/mol; M_{2KCI} – molar mass of 2KCl, g/mol.

- Semi-technical scale tests were carried out by the Pulverized Fuel Combustion Chamber (PFCC); ٠
- The feeding rate was maintained at **0.25 kg/h**; ٠
- The test was performer without combustion at reactor wall temperature of **900°C**; ٠
- The temperature of **480°C** was maintained on the wall of the deposit probe in order to imitate ٠ conditions of the working bank of superheater tubes;
- The time of deposition was **60 minutes** for each sample. ٠





Pulverized Fuel Combustion Chamber (PFCC)







Ammonium compounds in fly ash methods of ammonia removal

Usually, it is concluded that **fly ash should contain no more than 50-100 mg NH₃/kg** to be attractive for use in civil engineering. The mechanophysical properties of the concrete are not degraded by ammonia contaminated fly ash, however the odor is unacceptable to any concrete manufacturer or user. Ammonia odor was found not to be objectionable when using fly ashes containing 100-200 mg NH₃/kg.

Ammonia slip in fly ash is an important issue for both ash producer and customer.



Samples of fly ash before and after ammonia desorption tests



- **0-** Various **methods of ammonia removal** from fly ash are developed and generally, they can be subdivided into thermal and chemical:
 - •Thermal methods are usually characterized by lower investment costs and typically are based on the desorption of ammonia at 300-450°C .
 - •The basis of most **chemical methods** is the phenomenon of ammonia release into the gas phase in ammonium salts solutions with pH above 7.







Ammonia compounds balance in a stoker boiler with secondary denitrification installation



The balance of ammonium compounds was determined for the WR-25 stoker boiler operating with SNCR system. The substrate in the process was a **40% urea water** lacksquare

- **solution** fed to the boiler.
- The products were **ammonium compounds slip in the** flue gas and fly ash.
- The calculations also took into account the \bullet stoichiometric amount of urea consumed in the **reduction of nitrogen oxides** from 310 to 125 mg/m³n.

Balance incorrectness was determined. The concentration of NH₃ and NO in the flue gas was measured on-line with a FTIR analyzer. The concentration of ammonia in the fly ash collected from the electrostatic precipitator was determined by the spectrophotometric method according to the PN-ISO 7150-1: 2002 standard.









Ammonia removal from fly ash low-temperature desorption

Ammonia desorption from fly ash was investigated for four different types of fly ash collected from different combustion units: CFB boiler, stoker boiler, biomass combustion unit and RDF combustion unit.

Potential of ammonia desorption was determined by low- and high temperature thermal desorption:

- The total amount of ammonia released in the temperature of 130 and \bullet 150°C after 10, 20, 30, 60 i 120 minutes was measured by NDIR gas analyzer and by analytical method (figure on the top)
- Thermogravimetric analysis of 10 mg ash samples in air atmosphere in temperature range 25-650°C (figure on the bottom)

It has been shown that:

- Fly ash from a stoker boiler has a potential of low-temperature \bullet ammonia desoprtion (130 and 150°C)
- The possibility to remove ammonia from fly ash depends on the fuel \bullet type, the furnace type and the method of denitrification.









TG, %

Ammonia removal from fly ash high-temperature desorption

The principle of the process is that **fly ash is recirculated into the boilers' combustion chamber** (1) and **ammonium compounds are thermally** decomposed onto the grate (2).

Fly ash separated in the de-dusting device (4) and/or chute (3) is transported by a mechanical feeder or by pneumatic transportation (5) to the fuel feeder (6) or directly to the fuel tank (7) instead of being removed by slag hopper (8) or by slag removing system (9). Next fly ash goes onto the grate together with the fuel. At a temperature of >800°C ammonium compounds are reduced together with remaining carbon. In the end, fly Results of high temperature ammonia desorption in laboratory and full-scale conditions ash is removed with slag into the slag hopper (8).

Such installation does not require construction of any external reactor hence the reduction process takes place in the combustion chamber.

It has been shown that high temperature desorption is a very efficient method for ammonia removal. For both laboratory and full-scale ammonia content in fly ash after the process was greatly reduced.



cient	Sample number	Initial NH ₃ content in fly ash mg/kg	NH ₃ content after laboratory desorption mg/kg	NH ₃ content after full-scale desorption mg/kg
tests	1	479	>6.1	7.3
	2	1326	>6.1	32.3
	3	3796	>6.1	>6.1







Optimization of UPS processing paths for use in engineering and building materials

- UPS classification.
- New directions of UPS application:
 - plastics:
 - □ targeted conversion for plastic applications,
 - dedicated functionalisation for applications in plastics,
 - optimization of the properties of composites based on UPS and plastics,
 - ✓ geocomposites:
 - □ targeted conversion for geocomposite applications,
 - dedicated functionalisation for applications in geocomposites,
 - Optimization of the properties of geocomposites based on UPS,
 - ✓ ceramic materials:
 - Targeted conversion for applications in ceramic materials,
 - dedicated functionalisation for applications in ceramic materials,
 - optimization of the properties of composite ceramic materials based on UPS.



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, composites, ased on UPS,

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allowing for their unambiguous identification and classification

- sieve analysis,
- particle size distribution,
- specific surface,
- microscopic observations:
 - SEM,
 - optical microscope,
- chemical composition (EDS),
- phase composition (XRD),
- FTIR analysis.

UPS - RDF ashes



Qualitative XRD analysis of the phase composition of ash from RDF combustion



PS fication and classification





Quantitative and qualitative EDS analysis of ash from RDF combustion

Ca-Fe-O O-Si Ca-O-S Photo of ash from RDF combustion







Research characterizing UPS allowing for their unambiguous identification and classification

UPS - lignite ash



The FtiR analysis – verification of the success of the performed chemical functionalisation - hydrolytic condensation of silane compounds on the ash surface BET adsorption test - specific surface area of lignite ashes: 5.5834 m²/g



Photo of ash from lignite combustion



UPS - biomass ashes

c:'edax32'genesis'genmaps.spc 10-Feb-20; LSe	Element	Wt%	At%
2.9 — Са	СК	31.73	50.93
1	ОК	18.49	22.28
	NaK	00.54	00.46
2.3 -	MgK	01.82	01.44
	AlK	01.39	00.99
	SiK	06.32	04.33
L7 -	РК	01.98	01.23
KCnt	SK	01.88	01.13
	ClK	00.97	00.53
L2 - 58	KK	04.77	02.35
C K	CaK	28.99	13.94
	FeK	01.11	00.38
a.e - A P Ca	Matrix	Correction	ZAF
ng re ^{Fe}			
2.00 4.00 6.00 8.00	10.00 12.0	00 14,00 16,00	18,00 2

Quantitative and qualitative analysis of EDS of ash from wood biomass combustion



Photo of ash from wood biomass combustion





Particle size distribution of the ash fraction from wood biomass below $25 \,\mu\text{m}$, made by laser diffraction





Structural characteristics of UPSs of various origins using scanning electron microscopy – SEM



UPS - wood biomass ashes (SEM)



UPS - lignite ashes (SEM)





UPS - RDF ashes (SEM)







Targeted conversion of UPS and optimization of the properties of materials based on them

Activities in carrying out e.g. tests that characterize the following properties:

- thermal,
- processing,
- mechanical (e.g. strength properties)
- optical,
- exploitation.

Optimization of the properties of composite materials containing UPS, for commercial applications on an industrial scale, can be supported by artificial intelligence (modeling based on artificial neural networks).







A selected example of strength testing the properties of materials based on UPS



Graph of the strain-stress function for the tested samples: LLDPE and LLDPE with the addition of 5% ash



The course of the test on the testing machine tested LLDPE sample with the addition of 5% ash.





before and after testing on a testing machine





A selected example of the impact of dedicated UPS fictionalization on the properties of materials with their addition



The results of the strength tests presented in the diagram as a function of strain-stress for LDPE and LDPE samples with the addition of 5% UPS (ash)





The results of the strength tests presented in the diagram as a function of strain-stress of LDPE and LDPE samples with the addition of 5% UPS (ash) functionalized through the hydrolytic condensation reaction of silane compounds on their surface





A selected example of the dedicated UPS functionalisation and testing the properties of materials with their addition



The results of the mass flow index (MFR) tests: low density polyethylene (LDPE) and composites on its matrix with the addition of fly ash and silanized fly ash, presented in a graphical form.



Measuring device - Mflow plastometer with which the processing properties of composites based on UPS and plastics are optimized







A selected example of dedicated UPS functionalisation and testing the properties of materials with their addition



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different mass content of the additive in the form of basis of the enthalpy of the tested system, recorded during the DSC test.





A selected example of dedicated UPS optimization characterisation and processing of plastic materials from recycling



FTIR – spectral analysis of waste materials to proper management of them in further processing







Recycling of PE collected from waste

The results of the strength tests presented in the diagram as a function of strain-stress for recycled PE





Targeted conversion of UPS on the example of porous glass-ceramic



SEM image of porous glass-ceramic – cullet glass with addition of 10% of wood derived fly ash (fraction below 25 μ m) and foaming agents



Light microscopy image of porous glass-ceramic – cullet glass with addition of 10% of wood derived fly ash (fraction below 25 μ m) and foaming agents





SEM image of porous glass-ceramic – cullet glass with addition of 50% of wood derived fly ash (fraction between 160-500 μ m) and foaming agents



Light microscopy image of porous glass-ceramic – cullet glass with addition of 50% of wood derived fly ash (fraction between 160-500 μ m) and foaming agents







Targeted conversion of UPS on the example of porous glass-ceramic



SEM image of porous glass-ceramic – cullet glass with addition of 50% of RDF fly ash and foaming agents



Light microscopy image of porous glass-ceramic – cullet glass with addition of 50% of RDF fly ash and foaming agents





SEM image of porous glass-ceramic – cullet glass with addition of 50% of RDF fly ash and foaming agents



Light microscopy image of porous glass-ceramic – cullet glass with addition of 50% of RDF fly ash and foaming agents







Neural networks modeling Influence of the chemical composition of the additive (e.g. UPS - ash from biomass combustion; brown coal; RDF, halloysite) on the strength characteristics of a UPS / polymer composite

Application of the neural model to multivariate correlation:

- the chemical composition of the additive representing e.g. UPS (ash from brown coal combustion regular and silanized, ash from biomass combustion, halloysite - calcined, silanized),
- mean particle size, e.g. UPS,
- characteristics of the extruder, temperature, injection pressure, injection time, \bullet
- ratio of additive (e.g. UPS) to polymer (e.g. LDPE), \bullet

with the strength properties of thus obtained polymer composite (UPS / LDPE):

- tensile strength,
- maximum elongation when stretching,
- breaking strength,
- maximum elongation at break.



Optimization of the properties of composite materials containing UPS, for commercial applications on an industrial scale, can be supported by artificial intelligence (modeling based on artificial neural networks).







Neural networks modeling the characteristic ash melting temperatures - IDT, HT, FT

It has been shown that:

- IDT, HT, FT ash (UPS) temperatures can be **effectively** predicted by a neural model based on their chemical composition,
- the neural model enables **more precise prediction** of IDT, HT, FT values based on the chemical composition of the ash (UPS) compared to classical regression models,
- each temperature shows a different type of dependence on the ash composition (UPS) (hierarchy of UPS components),
- model simulations enable the **optimization of technological processes** of biomass energy conversion as early as during the design phase.



Influence of the chemical composition of the ash from biomass combustion (UPS) on





Neural networks modeling Effect of the chemical composition of ash (UPS) from biomass combustion on the characteristic ash melting temperatures (UPS) - IDT, HT, FT











Neural networks modeling Analysis of the operation of a biogas production installation integrated with a wastewater treatment plant - solid post-fermentation residues (preprocessing) as a biomass for energetic purposes - and ash from its combustion (UPS) as a filler for composites

It has been shown, that:

- in an integrated installation it is **possible to obtain increased biogas** production through an appropriate flow modification strategy (retention times, internal redistribution of streams),
- the efficiency of biogas production **depends more on the operating** parameters of the installation than on the characteristics of the feed solution.

The rate of biogas production (efficiency) directly affects the properties of the post-fermentation solids (biogas anaerobic process as a some form of pretreatment for their further energetic applications), their energy value and - indirectly - the ash characteristics - UPS as a starting product for advanced composite applications.









Neural networks modeling Analysis of the operation of a biogas production installation integrated with a wastewater treatment plant - solid post-fermentation residues (preprocessing) as biomass for energetic purposes - and ash from its combustion (UPS) as a filler for composites















Conclusions

- on the heating surfaces of boilers and emission of harmful substances.
- \bullet contribute to the reduction of slagging and fouling of heating surfaces.
- Performing tests characterizing the following UPS properties:
 - thermal, \checkmark
 - processing, \checkmark
 - endurance,
 - optical,
 - exploitation,

is crucial for determining their commercial application and selecting the appropriate UPS processing path for development in engineering and **building materials** such as:

- plastics,
- geocomposites,
- ceramic materials.
- \bullet artificial intelligence (modeling based on artificial neural networks).



The tests carried out with the use of the vibrating grate technology allow for the identification and solution of problems related to the thermal utilization of waste and biomass fuels, including: research on the relationships between the properties (granulation, chemical composition) of fuels and the characteristics of the emerging UPSs, determining the influence of phenomena occurring during combustion to ash deposition

Fuel additives based on aluminosilicates demonstrate positive effect on the characteristic temperatures of ash phase transformations and

Optimization of the properties of composite materials containing UPSs for commercial applications on an industrial scale can be supported by





Acknowledgment

The research presented in this work was performed within "Process optimisation and valorisation of combustion by-products in transition to circular economy' (UPS-Plus) funded by The Foundation for Polish Science within Team Teach Core Facility Programme.

















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