

CHARACTERISATION OF REFUSE DERIVED FUELS IN VIEW OF THE CORROSION POTENTIAL

Paper 69

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1 DIFFICULT FUELS: APPLICATION OF BIOMASS AND REFUSE DERIVED FUELS (RDF)

The use of biomass in numerous application areas has a very high significance. In the background, there is the contribution to environment protection through the application of biomass in energy generation and thereby a reduction in CO₂ – emissions within the frame of the Kyoto-Protocol and resource conservation. Biomass is quantitatively an important regenerative energy source and that is indicated by its storagability and plannable availability. Decisive for its application in view of CO_{2,(fossil)}-reduction is the selection and optimization of the respective process, which requires a detailed knowledge of the applied Biomass-Fuels and their behavior in the respective processes.

In contrast the fuel RDF exhibits other characteristics, but in view of the fouling and corrosion it likewise belongs to the „difficult fuels“.

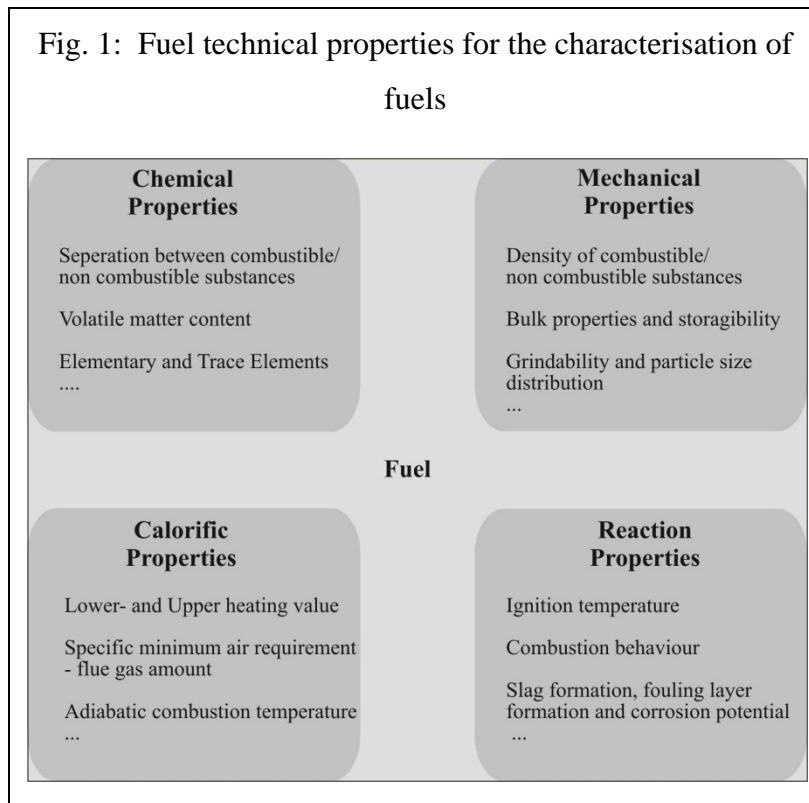
The energy efficiency and the availability of Biomass and RDF-Power plants is limited due to the intensified fouling layer formation on the heat exchanger surfaces and that results mostly in corrosion.

The evaluation of the applied fuel in view of the fouling layer formation and corrosion potential puts an important requirement for the plant designers and operators. Prior to the application of Biomasse and RDF it is essential to know the fouling layer formation and corrosion potential characteristics.

The substitution of fossil fuels through CO₂-neutral fuel is of increasing interest for plant operators. Simultaneously from an ecological and economic view it is necessary to attain high energy efficiency and availability, but as mentioned earlier that is limited due to the corrosion potential of the difficult fuels. Therefore it is essential to limit and assess corrosion risks in advance (prior to application), and hence through the prevention / reduction of corrosion a high energy efficiency and the plant availability can be attained.

2 CORROSION RELEVANT CHARACTERISTICS OF FUELS

The fuel characteristics are shown in Fig.1 with the subdivisions. In the assessment of the characteristics of a fuel, the respective process technical boundaries have to be taken into account i.e. definite criterion are based on relation to the application area, technical process and the respective equipment.



Reaction properties of fuels are more specifically the kinetic data e.g. to releasal of volatile components, equilibrium and reaction rate constants etc. In a broader sense, the ignition and burn-out behavior, slagging behavior and fouling layer formation are also classified as reaction properties. The ignition and burn-out behavior is dependent on a series of parameters in addition to the kinetic data e.g. volatile matter, particle size distribution, thermal conductivity. Likewise the corrosion potential cannot be described by a single parameter e.g. Chlorine content. Rather the corrosion potential of a fuel can be considered as a summative parameter, which is influenced by fuel technical characteristics and

furthermore by process technical conditions (process control, operational and constructive parameter).

The chlorine bonding plays an important role by the release and fouling layer formation for thermal applications. For complex reactions and phase transitions the chlorine alongside material group of heavy metals and the alkali have to be considered. This results the formation of inorganic bound chlorine. Problematic for fouling layer formation is the potassium chloride KCl (melting point: 772 °C). With steam pressure (0,1 mbar / 700 °C) it can be noticed that at normal combustion chamber temperatures a large amount of KCl is released in the gas phase. The gaseous potassium compounds are separated at the cold surfaces (e.g. heat exchanger surfaces), whose temperature lies below the respective melting point and solidifies.

The major source for organic bound chlorine is PVC, which thermally decomposes into HCl at temperatures > 180 °C. What is important for the corrosion formation is whether HCl is carried over with the flue gas stream or whether it reacts with heavy metals and alkalis to results in salt deposition. Moreover the sulfur compounds – especially the sulfur trioxide play a decisive role due to the interactions between sulfur and chlorine compounds – sulfation reaction.

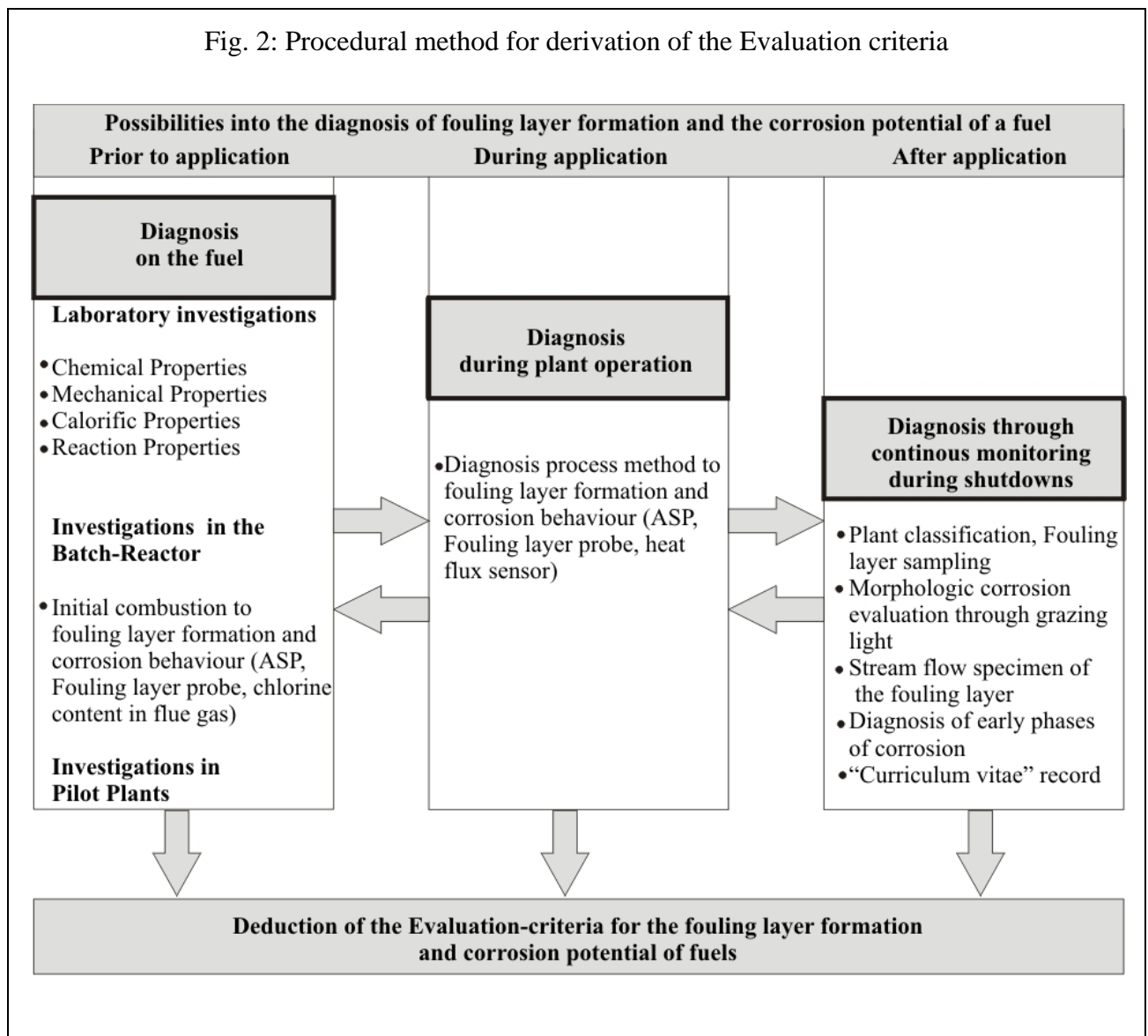
From a material point of view it results overall in a broad field of corrosion relevant elements, exemplary what can be identified from the different corrosion effect of the chlorine and sulfur compounds. It is therefore clear that for e.g. the total chlorine is not insufficient as a quality criterion for refuse derived fuels and biomass. The decisive influence of the chlorine bonding form respectively also the sulfur bonding form on thermal behavior should be considered from an evaluation of the inorganic and the organic chlorine/sulfur amount in the fuel.

Increased loads of HCl are negatively evaluated. However the distribution of chlorine in the fuel in both partial streams of HCl and chloride salt are very much dependent on the plant operational conditions and can fluctuate widely. HCl is the inert and ineffective partial stream. Corrosion relevant foremost is the chlorine bound in the fouling layers.

In the first step what is important for this process method, is the timely indication of the effects of plant operations on a combustion/firing unit, characteristics of the applied fuel, related fouling layer formation and the corrosion tendencies. Hence in the second step using the above information an evaluation criterion for difficult fuels can be developed.

3 PROCEDURAL METHOD FOR THE EVALUATION OF FOULING LAYERS FORMATION AND CORROSION POTENTIAL FOR FUELS

Fundamentally there exists the possibility to carry out an analysis of technical characteristics of fuels (Fig.1) and a diagnosis of the fouling layer formation and corrosion prior, during and after the application of the fuel in the respective plants (Fig. 2). One can broadly differentiate the procedure:



- Diagnosis of the fuel
- Diagnosis in plant operation
- Diagnosis through continual monitoring at shutdowns (for maintenance)

The easiest but also the most accurate possibility to evaluate the fouling layer formation and corrosion potential is after application of the fuel in the plant during a shutdown. An early detection of the negative influences of the plant or the suitability of the fuel for the respective plants is with the aid of this method not possible. The effects can only be attained through gathered positive or negative experiences of the applied fuel.

For the evaluation of the fouling layer formation and corrosion potential, there is the possibility of a diagnosis of the fuel. This can be done through the application of a proven method ASP and a fouling layer monitor i.e. Fouling Layer-Probe developed by CheMin GmbH, Augsburg for industrial plants [8]. Currently this process is applied for diagnosis during plant operations and is in a position to indicate the fouling layer formation. The information about the chemical-mineral milieu parameters of the formed fouling layers on the monitor are evaluated by a point-resolved analysis process.

Through initial combustion experiments in combination with isokinetic sampling prior to application of the fuel in plant – initial statements could be made about the fouling layer formation and corrosion behavior of the fuel. In view of the timely availability of the data, accuracy of the prognosis, the possibility of process illustration, the effort work and the related prevention of damage potential (Fig. 3); it appears reasonable to carry out the first experiments and compare with the evaluated data of the isokinetic sampling - prior to application- and -during the application - in the Batch-Reactor.

Fig. 3: Evaluation of the diagnosis possibilities into Fouling layer formation and Corrosion potential.

	Diagnosis on the fuel			Diagnosis during plant operation	Diagnosis through continuous monitoring during shutdowns
	Lab	Batch	Pilot		
Availability of data (time)	++	++	+	O	-
Accuracy of prognosis	-	+	+	+	++
Process-mapping	--	O	+	++	++
Evaluation time of the results	--	--	O	+	+
Prevention of damage potential	++			+	+

Evaluation:
++ high → -- low

4 DIAGNOSIS OF THE FUEL WITH AID OF BATCH-REACTOR

4.1 Description of the Batch-Reactor and the possible Fuel Technical Investigations

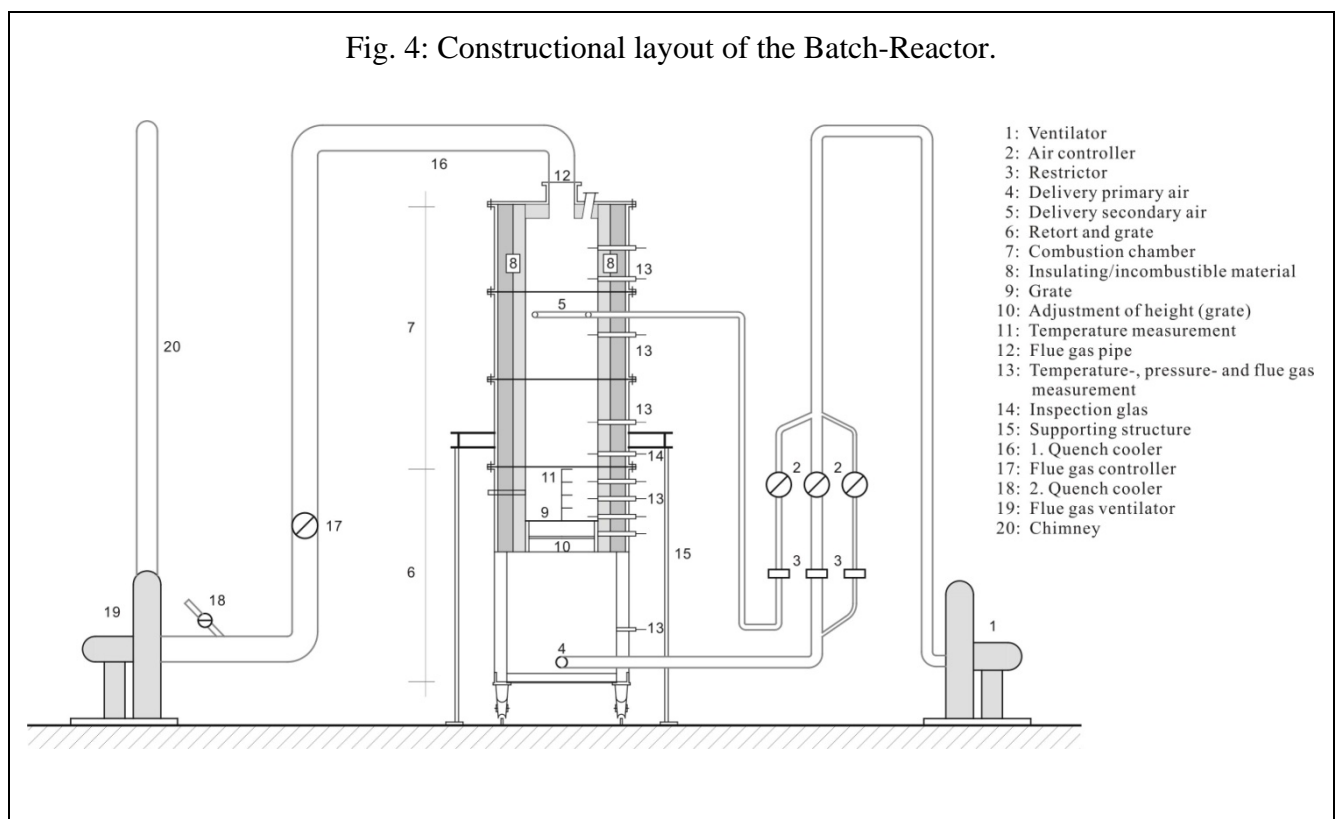
In a continual operated grate systems (with a movable grate) the process steps i.e. drying, devolatilisation, gasification and burn-out of the fuel – occur almost concurrently along the reaction paths (grate length). In the Batch-Reactor the fuel is discontinuously fed. The single processes steps occur timely in succession for instationary operation.

The important main influential parameters are described in [7]. For the grate system especially the oxygen, temperature and the residence time can be controlled independently from each other.

Basic investigations in a continuous grate system are extensive due to longer experimental duration. In order to reduce the experimental testing effort the application of a batch operated experimental grate is necessary [2], [3] and [4]:

The processes in the Batch-Reactor (Fig. 4) can be characterized by the following steps:

- The fuel is fed in a reaction chamber whose walls are initially heated (800 °C till 900 °C).
- The reaction gas (e.g. air) flows through the fuel bed upwards.
- The required high temperature for the carbon matter conversion is attained through the radiation from the walls and is transferred to the solid material and the gas.
- With rising temperature the reaction rate and the carbon matter conversion increase.
- At adequate high conversion rates the walls become repeatedly heated. In this case heat is transferred from the fuel bed to the combustion chamber walls.
- With increasing carbon matter conversion the reactive surface of the fuel reduces and hence the renewed releasal of the chemical energy occurs.



Thereafter the further progression of the reaction is dependent on the stored energy in the bed. For a fuel with low storage capacity (low inert material amount) the temperature of the bed reduces fast as a result of the cooling effect from the reaction gas, such that the reaction is interrupted at high residual carbon content (cold air flow).

If the fuel has a large heat storage capacity (high inert amount) the cooling-down is slower. The required reaction temperature is maintained for a longer period such that the carbon bound in the inert bed can be further converted. At the end the residual carbon content further decreases.

Experiments into the characterization of the combustion process for anthracite coal and the temperature characteristics in the fuel bed were initially carried out in early 1930s on the Batch-Reactor [9], [10]. During that period the Batch-Reactor was used for optimization of the construction and operation of grate-fired systems. Particularly in [10] the following question was asked: Do we know our fuels very well - such that during combustion the best possible conditions can be established and how do the fuels behave during combustion under forced operational conditions?

From this question then various methods were developed [11] for convectional fuels that allow them to be classified depending on their application.

Currently the same question is being repeatedly asked, for e.g. biogenic fuels as earlier mentioned have a very important role in numerous application areas and in environment protection. This is through the application of biomass for energy generation and thereby a reduction in CO₂ – emissions within the frame of the Kyoto-Protocol and a contribution to resource conservation.

The developed method for the characterization of convectional fuels cannot be simply used on biogenic fuels or refuse derived fuels i.e. there is a need to develop a method into the evaluation of fuel technical characteristics for the biogenic and refuse derived fuels. As a result of the lacking information about the fuel behavior of these fuels in different combustion/firing units, it is therefore difficult to evaluate in single cases the criteria to fix definite parameters. For convectional fuels the criterion is known especially in power plants and that is strictly monitored, in order to prevent the problems with respect to ignition, burn-out, slagging and corrosion.

The possibility of fuel characterization of biogenic fuels and refuse derived fuels amongst other things (ignition, drop tube- and slagging test reactor [5]) was investigated with the aid of a Batch-Reactor in a research study project [1]. In the project different parameters like e.g. reaction-front velocity [3], [5] were compared with each other, from the investigations of different fuels at nearly the same experimental conditions, in three Batch-Reactors of different constructional design. The evaluated results of the investigations indicated small variations. Therefore the suitability of the Batch-Reactor as a method into the characterization of fuels could be verified.

In the second step it should only be investigated the corrosion relevant characteristics (isokinetic sampling, flue gas analysis) and to develop a process method that makes it possible – the evaluation of fouling layer formation and corrosion potential for fuels - prior to application - in the industry. The information used is based on the chemical fuel analysis and the reaction properties of the respective fuels.

With the aid of a Batch-Reactor (at technical testing/ technical scale) it is possible e.g. through variable air staging [4] to control the steps of solid matter conversion (pyrolysis, gasification and combustion) and to change the process technical conditions for thermal treatment. The fuel technical behavior can be investigated depending on the fuel and the related process control.

4.2 Initial Exemplary Results

As explained in section 3, there exists fundamentally the possibility to determine the fuel technical characteristics of fuels. The diagnosis into the fouling layer formation and corrosion potential (Fig 2) can be carried out as follows:

- prior to application (diagnosis of the fuel)
- during application (diagnosis during plant operation)
- after the application in the respective plant (diagnosis through continual monitoring during plant shutdowns)

Fig. 5: Pictures of the fuels (Left – Anthracite coal, Right – Wood pellets)



The indicated results (not fully extensive) are from investigations in a Circular Fluidized Bed (CFB), whereby the effect of the substitution of convectional fuel (anthracite coal) through biomass fuel (wood pellets) was determined. Pictures of the investigated fuels are shown in Fig. 5.

Initially investigations were carried out in laboratory for the evaluation of chemical, calorific and mechanical properties, whereby an initial comparison of the fuel characteristics is possible. The elementary analysis and the heating value are shown in Tab. 1

Laboratory analysis is the necessary initial step into fuel characterization, e.g. such that the biomass fuel requirements for substitution can be determined. Since the thermal input should remain constant despite the substitution of fossil fuel anthracite coal (reduction of the mass flow rate) with biomass-fuel wood pellets, one can theoretically calculate the laboratory-determined heating value of both fuels.

The further laboratory analysis are important for the further experimental tests in the Batch-Reactor e.g. in view of the expected temperature in the reactor and the supplied air amount respectively for the balancing of the experiments.

Based on laboratory results isokinetic sampling conditions will be analyzed in the Batch-Reactor and the Circular fluidized bed. Fouling Layer-Probe measurements were carried in the both plants. The sampling was carried out at identical and similar temperature conditions (approx. 300 °C), such

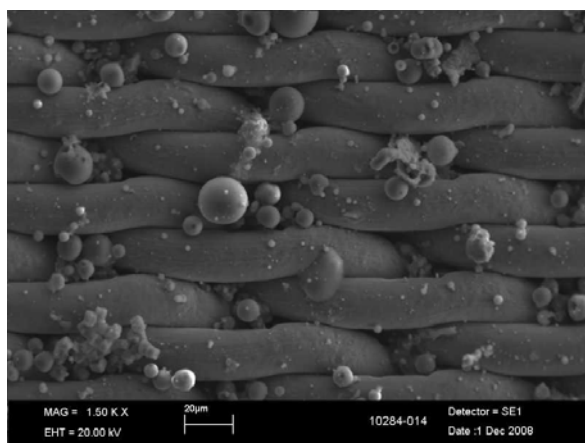
that the initial results of the Batch-Reactor could be compared with those from Circular fluidized bed.

Tab. 1: Laboratory analysis of the fuel

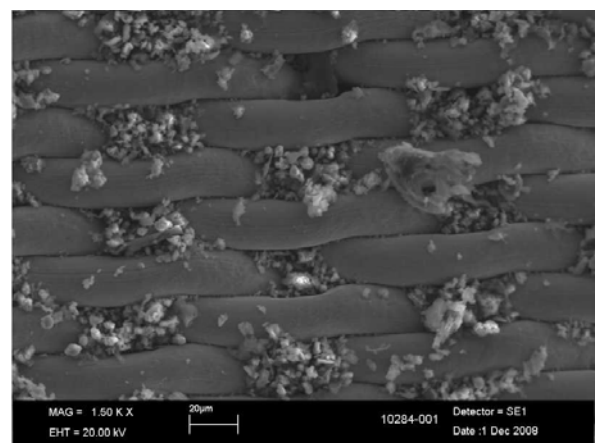
	Units	Anthracite coal	Wood pellets
Chemical Properties			
Water, H ₂ O	Ma.-[%] - an	9,81	4,82
Ash	Ma.-[%] - wf	12,1	0,32
Carbon, C	Ma.-[%] - wf	76,9	50,2
Hydrogen, H	Ma.-[%] - wf	4,04	6,06
Nitrogen, N	Ma.-[%] - wf	1,8	0,52
Sulphur S, total	Ma.-[%] - wf	0,76	0,005
Chlorine Cl, total	Ma.-[%] - wf	0,13	0,02
Ash-fusibility characteristics (Melting point)	°C	> 1300	> 1400
Calorific Properties			
Lower Heating Value (h _u)	[MJ/kg] - wf	29,8	18,8
Mechanical Properties			
Bulk density	kg/ m ³	800	650

Depending on the sampling position (instrumentation openings in the boiler) and the specified flue gas temperature – isokinetically - the loading differs physically (solid, liquid) and materially (silicates, oxides, chlorides, sulfates, hydroxides etc.).

Fig. 6: REM-Pictures of Fouling Layer-Probe measurements



Batch-Reactor
"Diagnosis on
the fuel"

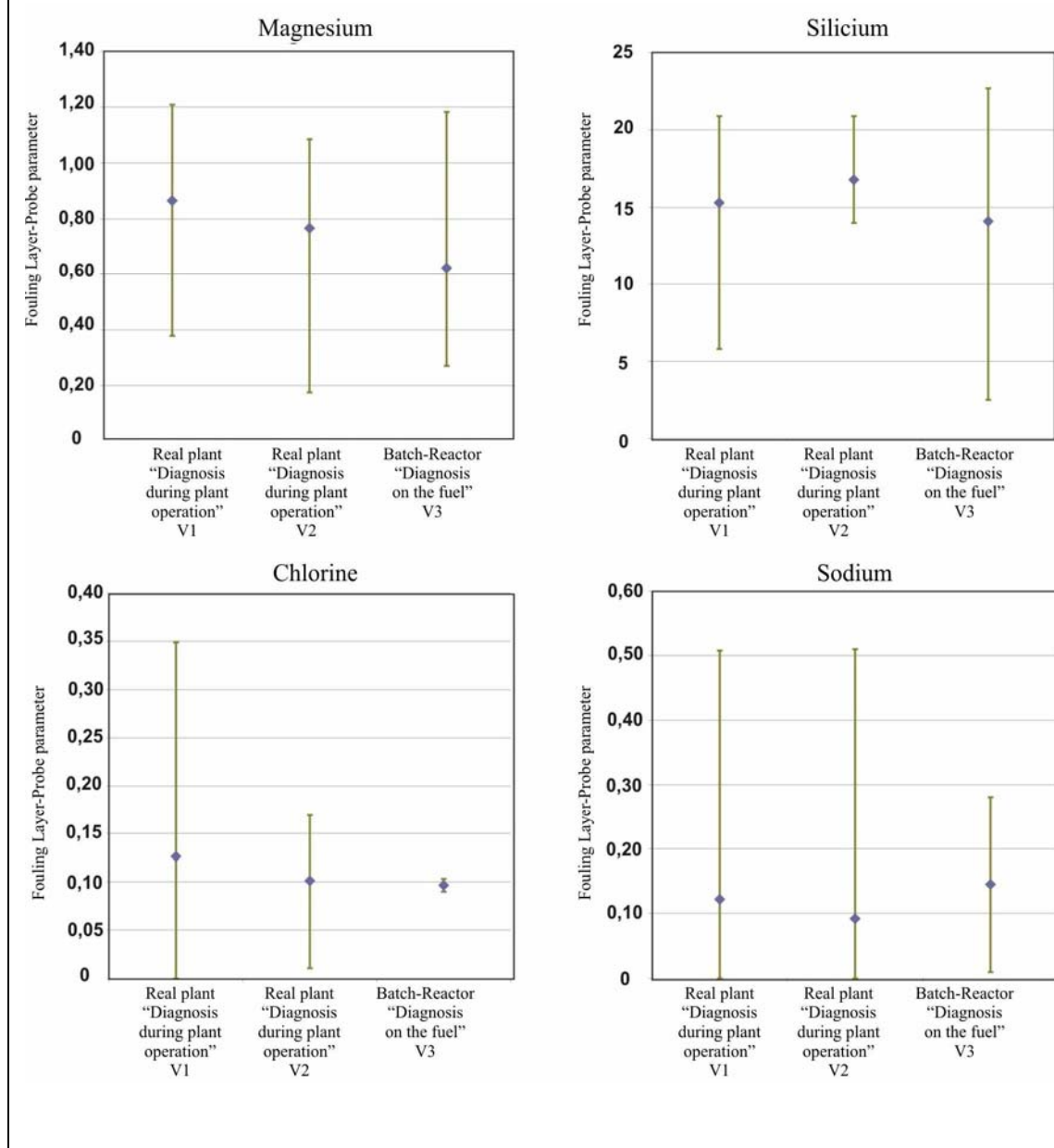


Real plant
"Diagnosis during
plant operation"

The different particle types (coarse and fine particles, especially corrosion relevant salt melting [8]) form significant sedimentation structures on the fouling layer probe. The mineralogical evaluation of the structures and the chemical data from the point- and small area measurements of the deposited particles - leads to a differentiated state evaluation of the fouling layer formation of the participative raw gas particles - at the sampling position. In Fig. 6 exemplars of the pictures of the Fouling Layer-Probe are shown, which were taken through the aid of a Raster Electron Microscopy (REM).

Optically, the differences of deposited particles on the Fouling Layer-Probe are visible, specifically the loading and also the particle sizes. The structure of the particle however is very similar. In the most cases it is about the identification of molten salts at first sight which range from being coarse to fine and mostly they are solid particles.

Fig.7: Comparison of the results of the chemical analysis of Point- and Small area measurements for the deposited particles on the Fouling layer-Probe.



The differences are partly therein founded, since the Fouling Layer-Probe measurements in the Batch-Reactor and the Circular fluidized bed were carried out always based on the thermal input. In

the Batch-Reactor the fuel mixture comprised of 50 % anthracite coal and 50 % wood pellets, whilst for the Circular fluidized bed it was 65 % anthracite coal and 35 % wood pellets – also the 75 % / 25 % ratio was used.

Based on the sedimentation structure the chemical data from points- and small area measurements of the deposited particles was analysed. Below is the comparison of the measurements; Batch-Reactor and Circular fluidized bed plant – for Magnesium (Mg), Silizium (Si), Chlorine (Cl) and Sodium (Na) are shown (Fig. 7).

In the shown diagrams there are exemplars from three Fouling Layer-Probe measurements:

- V1-Circular fluidized bed, Diagnosis during plant operation - 65 % / 35 % - Fuel Mixture
- V2-Circular fluidized bed, Diagnosis during plant operation - 75 % / 25 % - Fuel Mixture
- V3- Batch-Reactor, Diagnosis on the fuel - 50 % / 50 % - Fuel Mixture

The chemical data from the point and small area measurements of the deposited particles from the Fouling Layer-Probe measurements in the Batch-Reactor and in the Circular fluidized bed plant mostly correlate quite well to each other. For scientific validation of the results from the fouling layer formation and corrosion potential further measurements and investigations are necessary. For this reason currently the evaluation of the results of the Fouling Layer-Probe measurements is renounced.

The good correlation especially in view of the average value of the particle loading in the Batch-Reactor - in comparison to values from real plants shows that, realistically the Batch-Reactor can be used to diagnose fuels for their fouling layer formation and the corrosion potential – prior to their application on plants.

5 SUMMARY AND OUTLOOK

The diagnosis of the fuel in the above described method gives information about the potential of the fouling and corrosion. The central aspect of this diagnosis is the combined evaluation of the fuel and the combustion/firing unit features. The exclusive consideration of the fuel is not realistically adequate.

Such diagnoses of fuels under the consideration of the combined effect of the fuel and combustion /firing unit, e.g. using a Batch-Reactor, are based on a lot of parameters from the fuel, combustion/firing unit and steam generator of an industrial plant.

The shown diagnosis on fuels is still lacking consequent steps for the classification of fouling and corrosion risks. For the authors, the intermediate objective is the diagnosis on the fuels through the Batch-Reactor; and the parallel application of ASP and Fouling Layer-Probe in the Batch-Reactor and in an industrial plant - such that it can be applied for a broad spectrum of fuels and plants. Therefore the significance of this evaluation process can be attested and lastly a standardized way for the diagnosis on the fuel can be demonstrated.

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