

## OPTICAL ASSESSMENT OF ASH MELTING BEHAVIOR OF SOLID FUELS

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*Ash fusion characteristics of solid fuels are key practical information for co-firing options and further thermochemical conversion processes. The study investigated the optical assessment techniques currently available for ash fusibility analysis, initially developed for characterization of coal ashes, later modified suitable for solid biofuels. Though the standardized procedures are quite similar, but the difference between the common used guidelines were significantly identified with ash conditioning temperatures of  $815 \pm 10^\circ\text{C}$  and  $550 \pm 10^\circ\text{C}$ , respectively. The setting up for ash determination regarding to the shapes of specimens, ash preparation, test sample binding, particle size, and constant heating rates were reviewed. Several variations of definition on characteristic temperatures according to available standard methods for solid fuels were discussed. The initial deformation temperature (DT) was highlighted as an indicative parameter in ash melting determination for main fuel and supplemental biofuels in co-firing options. Further examinations concerning ash contents, transformations of elemental compositions, morphological structural changes are essential for better understanding practical phenomena occurs.*

Keywords: solid fuel, ash fusion, ash melting, deformation temperature

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### 1. Introduction

In every modern economy, being independent on conventional energy sources, diversifying toward renewable energy options, and thus enhancing energy security play very important roles. Moreover, the limited supply of fossil fuels steadily increases the demand of biomass considered as a sufficient alternative. Solid biomass has been highlighted as a key control factor for the global transition to bioenergy due to its commodity and widely availability [1]. Currently, solid biofuel is the fourth most used energy resource, after the conventional oil, coal and natural gas [2]. It is estimated that this type of biofuel contributes between 10% and 14% to the world's energy supply [3]. Beside wood, waste wood and forest residues, the agricultural residues are also important carbonaceous source for energy production [4].

From this perspective, simple and direct energetic utilization of solid biofuels is processing in thermochemical conversion systems, gradually replacing the conventional fossil fuels. Particularly, co-combustion in coal-fired power plant is considered as a feasible and economical option for heat processing and power generations since coal is still the significant main fuel of future energy [5, 6]. A number of studies summarized that the direct, indirect or parallel co-combustions are the most common thermochemical conversion for carbonaceous solid biofuel, with low efficiency and inadequately controlled of gaseous emissions [7-9]. On this point, appropriate thermochemical system designed for solid biofuels provides an opportunity for electricity production and hence secure power supply [10].

However, the growing consumption and utilization of solid biofuels with coal raised considerable ash-related

technical issues. Ash melting and slag formation has occasionally been observed with wood pellets, and incidents are more frequently occurred during combustion of lower quality solid fuels, especially during non-woody biofuels. Ash depositions in apparatuses increased the cleaning and maintenance difficulties. Ash agglomeration on the heat transfer surface of boiler reduced thermal efficiency, increased failure of heaters and economizers. In further even mechanical failure of heat exchangers was discussed [11]. Ash melting phenomena in fluidized bed processes is frequently doubted and become important.

Indeed, those ash thermal behaviors are mainly related to the nature and physico-chemical properties of biomass material [12]. Thus, solid biofuels characterization must always be analyzed and their ash fusion must be evaluated as a first step to define the behavior of the supplemental fuel, and hence support the proper design and operation setting. In ash fusion characterizations, the quantitative and qualitative determinations of inorganic fractions in ash content provide reference information of thermal behavior in biomass ash. The X-ray fluorescence spectrometer (XRF) to determine major elemental compositions, X-ray diffraction (XRD) to identify the crystalline compounds presented in the ashes, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to determine the morphological transformation of ash structure are available standardized methods frequently used for the descriptions of the ash melting properties [13].

Determination of ash fusibility temperatures are commonly performed by empirical assessment on available optical systems. Although the standardized ash conditioning procedures are quite similar, but there are variable definitions between the most common used guidelines DIN 51730 and CEN/TS 15370. Meanwhile,

a representative parameter in ash melting behavior of solid biofuels is essential for main fuel and supplemental biofuels combination in co-firing applications. And thus, the practical aim of this paper is to obtain key empirical figures and analytic interpretation of ash fusibility temperatures in the lab-scale tests.

## 2. Experimental assessment

In lab-scale conditions, a large number of empirical methods have been developed either to assess the slagging characteristics of solid biofuels or to predict the melting behavior of the respective ashes at high temperatures. However, the significance and applicability of those methods for the wide variable properties of solid biofuels frequently show limited variations.

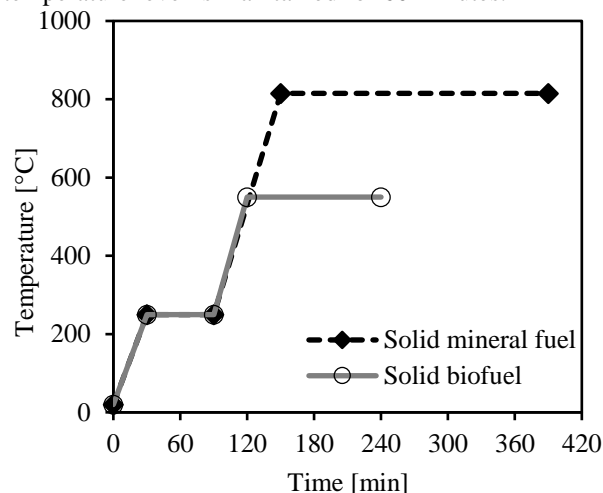
The ash fusion test is the standardized method currently available as described in CEN/TS 15370 for the determination of ash melting behavior of solid biofuels. The significance of this test, initially developed for the fusibility characterization of coal ashes DIN 51730, had been discussed by numerous authors [14-17], and thus consequently efforts were made to modify a more suitable technique in order to better describe the properties of for solid biofuel ashes.

### 2.1. Ashing and conditioning

There are common conditions in preparation a sufficient amount of ash according to the methods specified in DIN 51719 and CEN/TS 14775: 2004 (replaced by EN 14775: 2009 and the later ISO 18122: 2015) concerning plate type dishes or crucibles conditioning, oven dried required at 105°C, minimum ash quantity allowance, additives prohibition, sample refilling restriction. However, there is a remarkable variation in ashing procedure of test portion in accordance to the programed temperatures.

Figure 1 illustrates the heating and conditioning procedure of solid fuel test portion following temperature program. CEN/TS 14775:2004 and the later versions (EN 14775: 2009 and ISO 18122: 2015) require portion of solid biofuel ashes to be placed in a cold furnace at room temperature, then heated by raising the furnace temperature evenly to 250°C over a period of 30 minutes to 50

minutes (heating rate of 4.5 °C/min to 7.5 °C/min). This temperature level is maintained for 60 minutes.



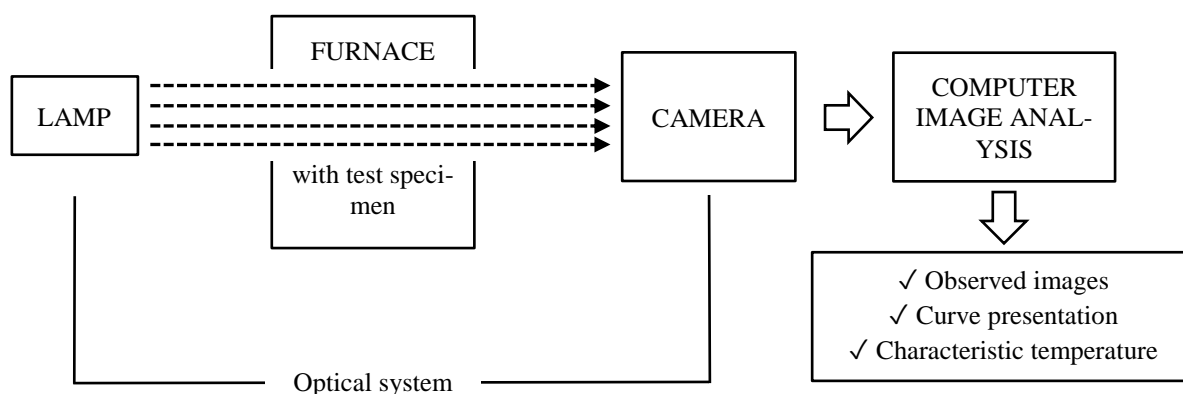
**Figure 1.** Ashing and conditioning of solid fuel test portions in different empirical conditions

The furnace temperature then continue to raise evenly to 550±10°C over a period of 30 minutes (heating rate of 10 °C/min) and maintained constantly for 120 minutes, as represented in the red solid profile.

Meanwhile, ashing procedure of solid mineral fuels specified in DIN 51719 require a remarkable higher temperature of 815°C with similar heating rate of 10 °C/min, and the portion conditioning practically maintained at 815 ±10°C for 240 minutes, as represented by the black dashed profile.

### 2.2. Optical technique

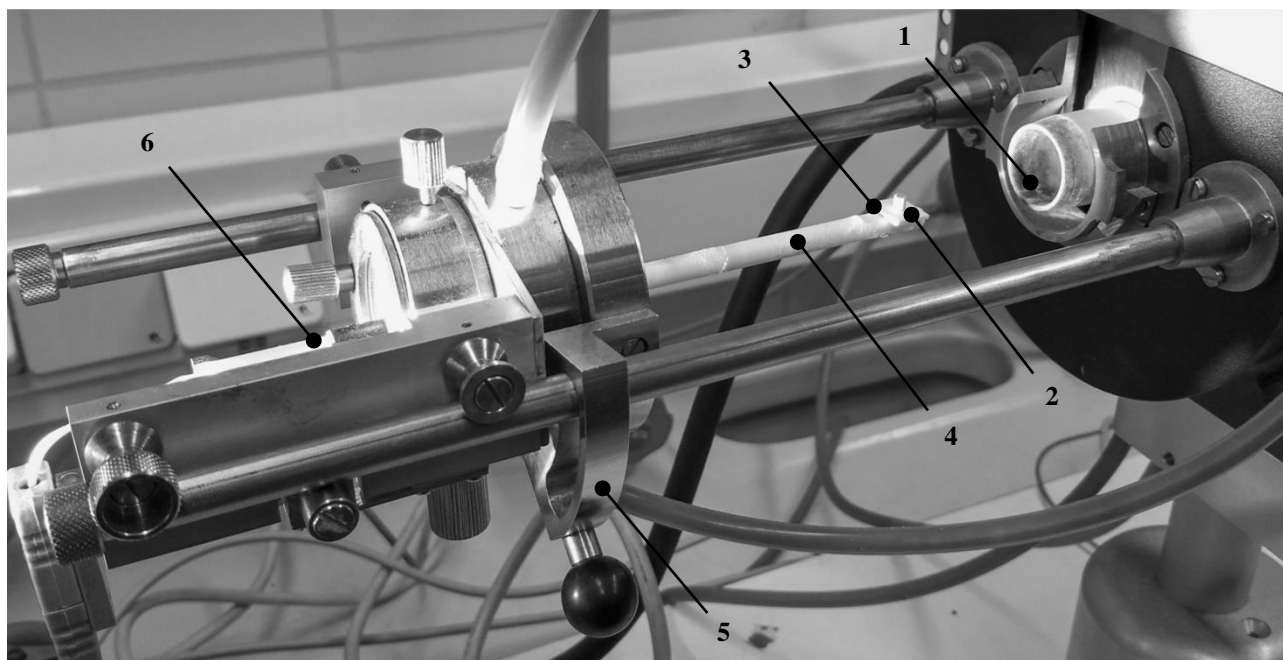
Determination of the characteristic temperatures for ash melting behavior of solid fuels using an optical system is illustrated in Figure 2. The standardized method for solid biofuels was specified in CEN/TS 15370-1, based on the method described in DIN 51730 initially developed for solid mineral fuels. The main components were electrically heated furnace, optical instruments consisting a lamp and camera or video equipment.



**Figure 2.** Optical standard lab-scale testing technique

Figure 3 shows an actual scale of holding mechanism with test specimen pulled out of the tube furnace. Test pieces were pressed to the small geometric bodies, put on the platinum sheet on the slide, and then placed on the specific position on the holder. The thermocouple was located in the sample holder, just below the specimen. Heat was generated continuously at the constant rates in the range of 3 °C/min to 10 °C/min, then the

changes in geometric shape were simultaneously recorded by the optical system (camera or video equipment) at least every 10°C. Specific temperatures where characteristic changes with regard to the shape of the specimens were used for the description of the ash melting behavior. The recorded melting profile of the test specimen consists of image, curve presentation and characteristic temperatures.



**Figure 3.** Test device (1-tube furnace; 2-specimen; 3-slide; 4-sample holder; 5-pivot lever; 6-thermocouple)

### 3. Results and discussion

In recent thermochemical conversion experiments, standard method DIN 51730 and the more popular European standard CEN/TS 15370 are considerably used in solid fuels characterization, as a principle baseline for further empirical investigations. The characteristic temperatures for the description of the ash melting behavior according to both standards are summarized in Table 1. Similarity in definition terms was identified with brief description according to the respective assessment criteria.

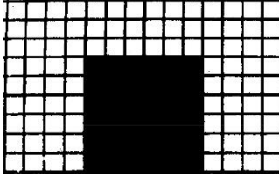
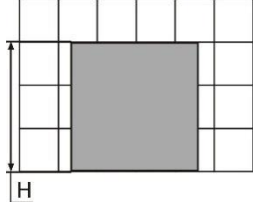
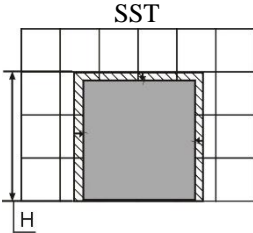
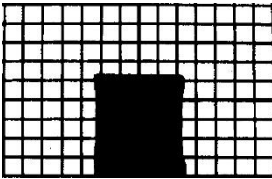
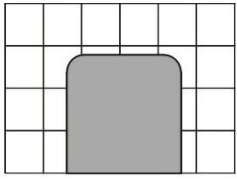
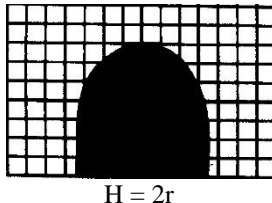
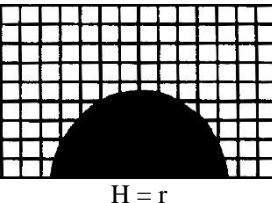
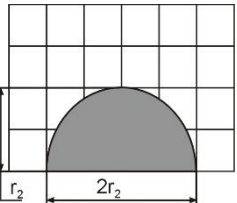
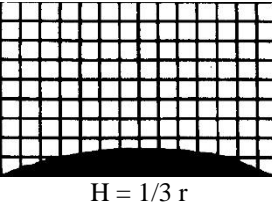
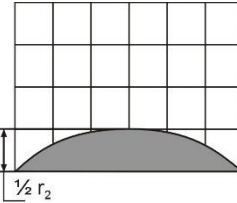
The definition criteria of original test piece shape and area specified a considerable difference in ashing temperatures of  $815 \pm 10^\circ\text{C}$  and  $550 \pm 10^\circ\text{C}$  described in the procedures of standard methods DIN 51719 and CEN/TS 14775: 2004 (replaced by EN 14775: 2009 and the later ISO 18122: 2015), required as indispensable referenced parts of DIN 51730 and CEN/TS 15370, respectively. At a significant higher temperature, remarkable difference in the ash content can be explained by the decomposition of carbonates, by losses of volatile inorganic compounds and further oxidation of inorganic compounds to higher oxidation states mainly through segregation, evaporation, reaction, nucleation, coalescence and coagulation mechanisms.

Maximum particle size (less than 0.075 mm as required in CEN/TS 15370 or 0.063 mm as described in DIN 51730) during preparation of the test specimens might also be considered as result of a significant difference in initial quality of the test ash portion. In addition, co-combustion with conventional mineral fuel such as coal, similarly to supplementation with inorganic additives, was able to change the size distribution of ultrafine particles, affects thermal behavior of some biofuels, and thus influencing their ash melting temperature profile.

The shrinkage starting temperature specified as SST in CEN/TS 15370, on the basis of test piece area fallen below 95% of its original value, was not defined in DIN 51730. This typical behavior was frequently observed in test pieces of solid biofuels as initial shrinking phenomena before the deformation state due to a high mass fraction of basic oxides included  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{MnO}_2$ , because of low fusion temperature [18].

Meanwhile, a similarity in definition terms and common description in criteria were found in softening temperature (specified as SOT in DIN 51730) and deformation temperature (defined as DT in CEN/TS 15370) based on the observed first sign of rounding the edges of the test specimens. SOT was an evaluation index applied to analyze the ash fusion of coal.

**Table 1.** Definitions of characteristic temperatures on the basis of volume or shape

Term	Definition criteria	Typical shape	
		DIN 51730	CEN/TS 15370
Original shape	Shape and size at ashing temperatures		
Shrinkage starting temperature	Area of the test piece falls below 95% of the original test piece		
Softening or deformation temperature	First sign of rounding of the edges of the test piece Shape factor changed		
Spherical temperature	Spherical shape Height = Base		
Hemisphere temperature	Hemispherical shape Height = half of base		
Flow temperature	Spread out in a layer Height = ratio of radius		

The shape factor change of 15% in computerized evaluation was reliable supporting information in biofuels ashes. During deformation and melting, this characteristic temperature can be considered as an indicative parameter in ash melting determination of main fuel and supplemental biofuels in co-firing options.

Nevertheless, the spherical temperature specified as SPT in DIN 51730, on the geometric basis of the specimen height became equal to the base diameter,  $H = 2r$ , at which the test piece forms approximately a spherical shape, was not defined in CEN/TS 15370. This reform phenomenon was observed regularly in the specimens of solid mineral fuels after the softening state due to a large quantity of acid oxides included  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{TiO}_2$ , in relation to high fusion temperature [18].

At this criterion, description of terms and criteria were similar in hemisphere temperature, specified as HT in both DIN 51730 and CEN/TS 15370. The definition based on the geometric transformation of specimen when its height became equal to half of the base diameter,  $H = r$ , at which the test piece forms approximately a hemispherical shape.

Moreover, the flow temperature term, specified as FT in both standard methods, consists remarkable differences in definition criteria. The phenomena described as the ash was spread out over the supporting tile in a layer. The height of this layer was defined as equal to one-sixth of the base diameter ( $H = 1/3r$  in DIN 51730), but equal to one-fourth of the base diameter ( $H = 1/2r$  in CEN/TS 15370 considering bubbling effects). On this basis, FT was an uncertain characteristic temperature in ash melting behavior of solid biofuels since internal bubbling effects frequently observed. Indeed, this occurrence had a significant influence on the accuracy of computerized image analysis.

From this viewpoint, Figure 4 shows a broad fusion variety of solid biofuels ashes. Even though biomass material might have similar origin, but difficulties may be encountered to the fact of transformation effects and phenomena such as blistering, distortion, shrinkage, swelling

and bursting of internal gas bubbles. In addition, the determined characteristic temperatures can be applied for comparison of the tendency of the ashes from different origins (amylaceous, woody, herbaceous, agro-industrial), types and qualities of solid biofuels. Besides optical assessment of geometrical shape or calculated area and volume, various physical properties were used for the characterization.

#### 4. Conclusion

The key empirical figures of ash melting temperatures assessment in the lab-scale optical technique were described. The descriptions of fusion phases and definition of characteristic temperature in the ash melting process of mineral fuels and biofuels were comparatively interpreted. The obtained analytical interpretation enables us to predict the ash melting behavior or slag formation tendency of solid fuels including main mineral fuels and supplemental biofuels in common co-firing options. In full-scale practical conditions, the complex thermochemical processes and ash fusion involve non-homogeneous mixtures of particles, variable heating rates and gas compositions. Thus, complex evaluations consisting ash contents, transforming of elemental compositions, crystal compounds identification, morphological structure changes certainly provide more detailed information of occurred phenomena.

In the perspective of the broad range of solid biofuels, the recent database on fuel properties and ash fusibility characteristics is still essential to be amplified to extent current knowledge regarding groups showing similar slag formation behavior, at most allowing for a respective classification of deformation temperature. The similarity in definition terms and common description in criteria highlighted deformation temperature as a valuable informative parameter in ash melting determination of main fuel and supplemental biofuels in co-firing options.

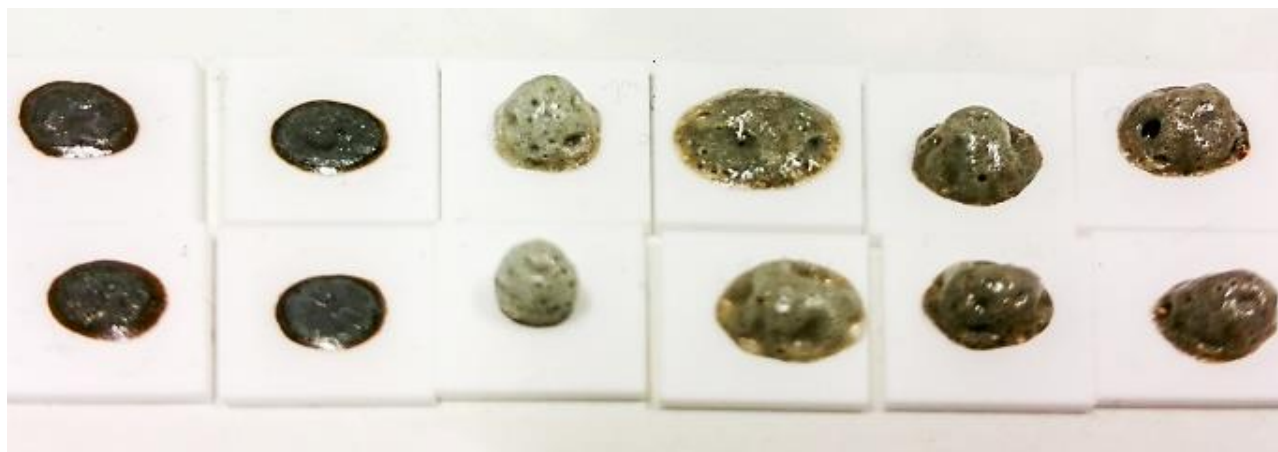


Figure 4. Broad variety in ash melting behavior of solid biofuels

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