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## ABSTRACT

One of the most attractive and easily utilizable renewable energy sources for co-firing technologies is biomass which can be fired up to 20% with coal in existing pulverized coal (pc) fired boilers. When biomass is used as a supplemental fuel in an existing coal boiler, this renewable energy source can provide several benefits including reduced gaseous emissions. However, there are several operational bottlenecks in terms of ash related issues. Our studies with European collaborator for nearly decade dealt with ash related issues covering ash transformation mechanisms for both pc-fired boiler environments with the objective of developing a Co-firing Advisory Tool (CAT). Some of the research outcomes to date along with status on co-firing activities are addressed in this paper. The studies towards the development of CAT addressed in this collaborative venture are expected to benefit power utilities in making informed decisions while selecting the renewable energy resources for power generation.

## 1. INTRODUCTION

Biomass is considered to be one of the most easily employable resources to reduce the consumption of coal in existing pulverized coal fired boilers. However, when employed in co-firing mode with coal for power generation poses several technical and economic challenges. Both fuels (namely coal and biomass) are complex composite materials containing inorganic species along with organic matter. In the fuel matrix, these inorganics are present as free ions, salts and organically-bonded species as well as in the form of discrete fine crystalline materials such as quartz, carbonates, oxalates, sulfides. During combustion, volatile minerals are released from the fuel matrix in the form of gaseous and condensed ash components with gas phase inorganic species undergoing numerous physical transformations. The

gaseous and fine condensed particles eventually lead to ash related problems such as slagging, fouling, corrosion, erosion and harmful emissions of gases and particulate matter in power utilities.

Extensive research is going on for more than three decades to triumph over the ash related issues with the use of the coal [1]. Biomass is considered as new generation fuel and several issues are still prevailing regarding how biomass material will behave in boilers in terms of combustion and ash related issues. Biomass is considered as a renewable energy source because the carbon in biomass is regarded as part of the natural carbon cycle: trees take in carbon dioxide from the atmosphere and converts it into biomass and when they decay, it is released back into the atmosphere [2]. Whether trees are burned or whether they decompose naturally, they release the same amount of carbon dioxide into the atmosphere. The idea is that if trees harvested as biomass are replanted as fast as the woody fuel is burned, new trees take up the carbon produced by the combustion, the carbon cycle theoretically remains in balance, and no extra carbon is added to the atmospheric balance sheet—so biomass is considered “carbon neutral.” Since nothing offsets the CO<sub>2</sub> that fossil fuel burning produces, replacing fossil fuels with biomass supposedly results in reduced carbon emissions [2]. Biomass makes up half of all U.S. renewable energy and more than 90% of all existing biomass power plants use wood residue. At present, some 230 power and combined heat and power (CHP) plants use co-firing, mostly in northern Europe and the United States, with capacities ranging from 50-700 MWe. Co-firing in combined heat and power CHP plants is currently the most competitive option to exploit the biomass energy potential for both electricity and heat production [3]. Few examples of co-firing practices in UK are given in Table 1 [4]. Among these the UK’s Drax power station has embarked on what is believed to be the largest biomass co-firing project in the world in a bid to reduce its carbon dioxide emissions by 15 per cent. With the second largest number of co-firing installations in the world, the US is projected to have strong growth in electricity generation from co-firing power plants. Compared to the EU and the US, Australia has only limited experience in co-firing biomass in coal-fired power plants. Nevertheless,

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both the government and the power sector are positive in promoting biomass co-firing.

Coals and biomass contain various inorganic matters along with organic structure. The organic matter gets burnt during combustion leaving inorganic residue termed ash. Ash formation during combustion is a complex mineral revolution process due to several physical and chemical transformations occurring just in milliseconds after fuel enters to the furnace. Several methods/models/sub models/ tools are developed to predict or measure the slagging, fouling, corrosion, erosion and environmental and health hazards etc. [5-7]. The predictive tools for the slagging, fouling, corrosion, erosion and aerosol formation often need input in terms of particle size distribution of ash, their respective mass fractions and mineralogical composition at different time steps in the furnace [7]. The particle size distribution of the ash, their respective mass fractions and mineralogical composition are usually obtained using expensive and time consuming lab/pilot/plant scale trials. Several models are also developed in this area to avoid such expensive and time consuming trials.

**Table 1 Biomass co-firing in UK**

Station	Total Capacity (MWe)	Generator	Status	Biomass Fuels
Aberthaw	1,455	RWE npower	Commercial	Various
Cockenzie	1,200	ScottishPower	Commercial	Wood
Cottam	2,000	EdF	Commercial	Various
Didcot Drax	2,100	RWE npower	Commercial	Wood
Eggborough	4,000	Drax Power	Commercial	Various
Ferrybridge	1,960	British Energy	Commercial	Various
	2,035	Scottish & Southern	Commercial	Various
Fiddler's Ferry	1,995	Scottish & Southern	Commercial	Various
Ironbridge	970	E.ON UK	Commercial	Various
Kingsnorth	2,034	E.ON UK	Commercial	Various
Longannet	2,400	ScottishPower	Commercial	Waste Derived Fuel
Ratcliffe	2,010	E.ON UK	Commercial	
Rugeley	1,000	International	Commercial	Various
Tilbury	1,085	Power RWE	Commercial	Various
West Burton	1,980	npower	Trial	Wood

The present research is focused at predicting the extent of ash formation mechanisms occur during PF combustion or co-firing of coals with biomass. The developed understanding on the ash formation

mechanisms from the present research work will be quite useful for the prediction of several ash related problems. The work carried out in two stages wherein the first four years of effort was towards modeling the aerosol formation by simple calculations on gas-to-particle conversion for alkali chlorides and alkali sulfate [8] whereas the second one centered around modeling several ash transformation mechanisms responsible for coarse ash formation during combustion and/or co-firing of several coals and biomass [9]. Both these efforts led to substantial information which will provide a pathway to fuel planning personnel in gaining first-hand information on fuels and fuel blends for possible implementation in existing power utility boilers.

## 2. Work Approach

The approach presented is based on an extensive experimental work, in which several blends of coal and biomass fuels have been combusted under relevant combustion conditions. The tested renewable resources are of different groups such as woody biomass and forestry residues, energy crop, agricultural/food waste and high rank coals. The study has been carried out in the Lab-scale Combustion Simulator (LCS) at ECN, Netherlands (see Figure 1a) and the experimental methodology is outlined in Figure 1b. The typical pulverized fuel combustion operating conditions employed for the study are atmospheric pressure, 1450–1500°C flame/furnace temperatures and heating rates of 105 K/s. Ash release, conversion, size reduction and size distribution alongside with changes in inorganic chemical compositions are derived at different char burn out levels in the LCS at 20, 90, 210 and 1300 milliseconds of residence times. The following strategic step-by-step approach has been carried out to gain insights into the ash transformations.

- Characterization and quantification of ash formed in terms of particle size and mineralogy.
- Quantification of the release of minerals under given operating conditions
- Model the various ash formation processes for the development of CAT at Energy Research Centre of the Netherlands (ECN)
- Define methods/sub models to arrive at:

- The composition of the gaseous phase as well as the concentration of inorganic elements released;
- The composition and particle size distribution of fly-ash
- Use ash deposition post processor at ECN to model the ash deposition.

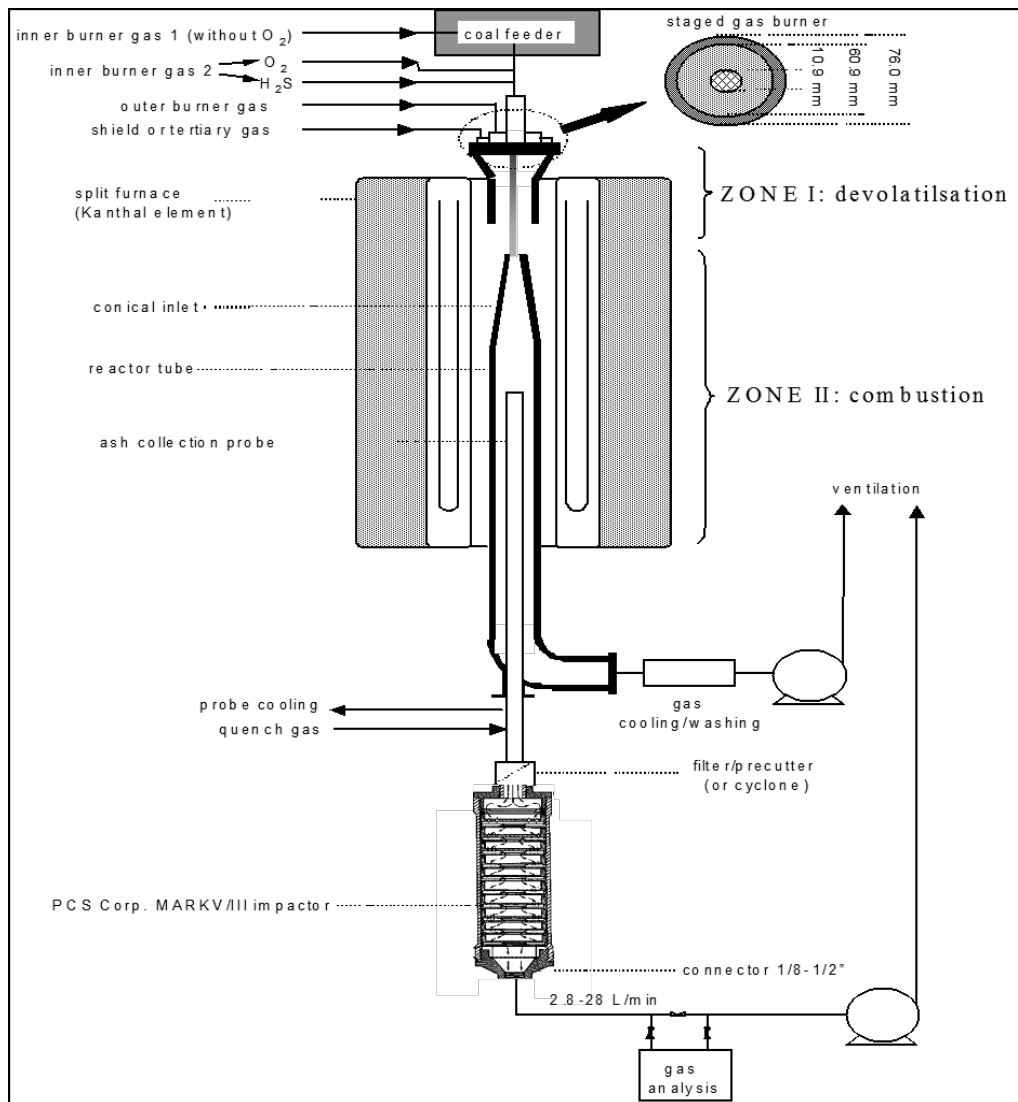


Figure 1a : Schematic of Lab-scale Combustion Simulator (LCS) used to study the formation of ash (incl. aerosols) from biomass and coal

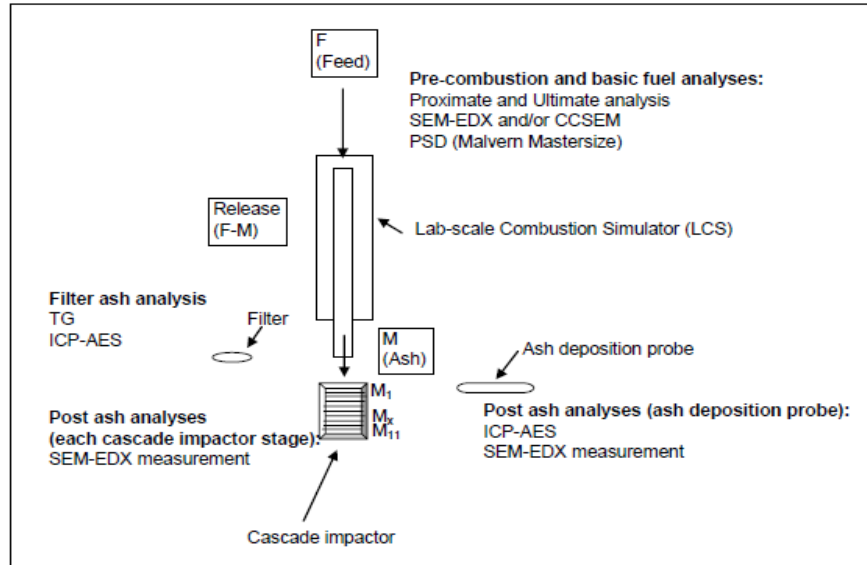


Figure 1b Experimental methodology

### 3. RESULTS AND DISCUSSION

The detailed ash formation map (particle size distribution along with their respective mass fractions and mineralogical compositions etc.) after combustion is really helpful for predicting various ash related problems in the solid fuel firing. Therefore, rather than directly working on the several ash related problems (slagging, fouling, corrosion, erosion, environmental and health hazards etc.), our efforts focused on deriving the ash formation mechanisms during the combustion process in terms of particle size distribution, mass fractions and mineralogy as detailed below.

Mass based fuel conversion as a function of residence time is plotted in Figure 2.

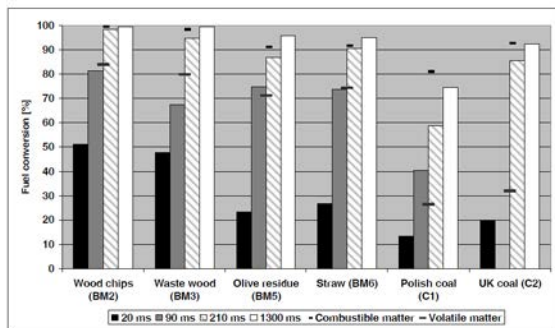


Figure 2: Mass based fuel conversion as a function of residence time

The volatile matter (from the proximate analysis) and the combustible matter content (taken as 100 % of the dry ash base) are included for reference. All studied biomass are found to be much more chemically reactive than coals due to the comparatively lower ash and the high volatile matter contents. Both the Polish and the UK coals are much richer in ash and significantly less volatile, hence their conversion is lower and delayed considerably as compared to the biomasses. For example, the wood chips and the waste wood are reaching higher overall degrees of conversion already in the flame (20 ms).

Figure 3 gives an overview of the amount of the different elements released after 1300 ms of residence time in the combustion chamber.

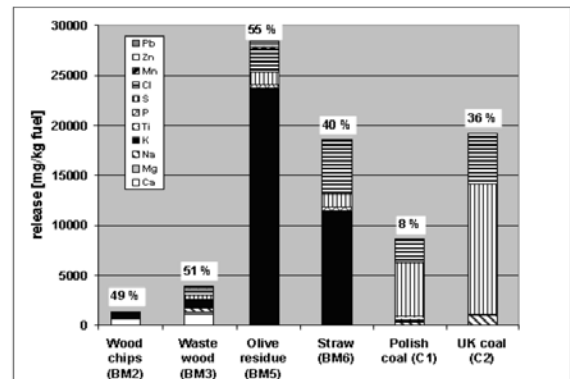


Figure 3: Distribution of inorganic elemental release

The data are expressed as the amount of element X released in milligrams per kilogram of dry fuel, so they can be easily applied in combustion process calculations. The percentage plotted over each stacked bar represents the mass ratio of the sum of inorganic elements released to the sum of inorganic elements in the fuel. Large differences are observed between fuels. The release in mg/kg is influenced by the fuel's ash content and the reactivity of the ash constituents. The relatively small ash release from the wood type fuels reflects their low ash content, while the high ash release from olive residue and straw is caused by the higher ash content but especially by the high ash volatility. The release from both coals is dominated by the elements sulfur and chlorine. If the sulfur content of the coal is high, then the release will be high too.

The results and further detailed analysis of the experimental data is described elsewhere [8]. Some of the experimental observations on char chemical conversion, devolatilization and fragmentation enabled to develop a qualitative tool for several fuels and fuel blends (see Table 2). It has been established that char chemical conversion is found to be dependent on the ash and the volatile matter contents at typical pc fired firing conditions. Fuels having high ash content form fewer active carbon sites for smooth char oxidation and are therefore converted more slowly. Among the tested fuel sets, examples of such fuels include the Polish coal, the UK coal, and to a lesser extent the olive residue and the straw. The Polish and the UK coals are further characterized by high ash and low volatile matter contents. Therefore,

the overall chemical conversion is lower for both these fuels. On the contrary, the olive residue and the straw have relatively high proportions of volatile matter. Therefore, the initially slow conversion is quickly accelerated when fuels reach a certain critical temperature. The high volatiles result in a high overall conversion. Also, lower size particles convert more quickly than higher size particles. Devolatilization of the fuel mineral also depends on the mineral matter and its association with the carbon matrix. Fuels rich in volatile mineral matter are found to be devolatilizing quickly and to a high degree. Chlorine and sulfur start devolatilizing early on during the combustion process. Alkalis release will be limited under the presence of silicon and aluminum (particularly when in the form of aluminosilicates) in the fuel. Other more conservative oxides such as those of calcium and magnesium are also found to be devolatilizing in some of the fuels, where their content is high. Fragmentation is found to be dependent on the overall fuel chemical conversion and devolatilization. The quicker and the higher the fuel chemical conversion and the devolatilization, the more pronounced will be the fragmentation. Woody biomass is a good example of this mechanism. Three kinds of fragmentations are observed: attrition, breakage, and percolative fragmentation. During the initial heat up and devolatilization, biomass and coal were found to be fragmenting attritively. Percolative fragmentation was observed only after a critical conversion of the char (approximately 60-70%). Higher-sized particles fragment more compared to the lower-sized ones.

**Table 2 Qualitative prediction of the devolatilization, char conversion and fragmentation [9, 10]**

FUEL	Ash Content	Volatile matter content	Si & Al content	Sulfur content	Devolatilization	Conversion	Fragmentation
Wood chips	Low	High	Low	Low	Less (but quicker)	High	High
Waste wood	Low	High	Low	Low	Less (but quicker)	High	High
Olive Residue	High	High	Low	Low	High (but slower)	High	High
Straw	High	High	High	Low	Medium	Medium	High
Polish coal	High	Low	High	Low	Less	Less	Less
UK Coal	High	Low	Medium	High	Medium	Medium	High

Ash release of individual mineral matter has been investigated as a function of elemental mineral matter composition and their association in the fuel matrix under the PF operating conditions. Ash release calculations involved the assessment overall material balance, release and recovery. Younger/pure biomasses and low rank coals will contain more water soluble (free ions, salts and organically bound) minerals than elder/waste/by-product coal or biomass fuels which will have more insoluble. This difference in mode of occurrence of the minerals in the fuel matrix has direct effect on their release. The presence of silica and aluminum in the fuel limits the release of alkaline metals. This underscores the effect of mineralogical composition on elemental release. The release of sulfur and chlorine will be nearly complete at high temperature and high heating rate PF combustion conditions for all the fuels. Calcium and magnesium will only release in the younger fuel when their content in the fuel ash is high and not counterbalanced by aluminum and silicon.

It is observed from the ash release calculations that the minerals of the same group/ rank of biomass and coal have similar association in the fuel matrix and behave almost same during combustion. Significantly better correlations for the elemental release can be derived for each class/rank separately. The correlations derived from this work shown below and the proposed methodology based on the limited number of fuels possibly provides a platform for arriving at a robust predictive tool, if a greater number of fuels and their groups could be included in follow-up studies.

$$\text{For Potassium: } K(R) = 0.5437 (K + Cl / Si + Al + 2S)(F) + 0.0359$$

$$\text{For Sodium: } Na(R) = 0.8993 (Na / K + Si + Al)(F) - 0.005$$

$$\text{For Sulfur: } S(R) = 1.0181 S(F) - 0.0138$$

$$\text{For Chlorine: } Cl(R) = 2.1716 (Cl / Na + K + 2S + Si + Al)(F) - 0.0244$$

$$\text{For Calcium: } Ca(R) = 0.4096 Ca(F) - 0.0749$$

$$\text{For Magnesium: } Mg(R) = 0.3965 Mg(F) - 0.025$$

Comparison of empirical indices developed under this work showed good agreement with the experimental data with R2 value 0.999. Figure 4 shows the validation of empirical indices for potassium. BM1 to BM4 in Figure 4 refer to bark wood chips, waste wood and saw dust respectively.

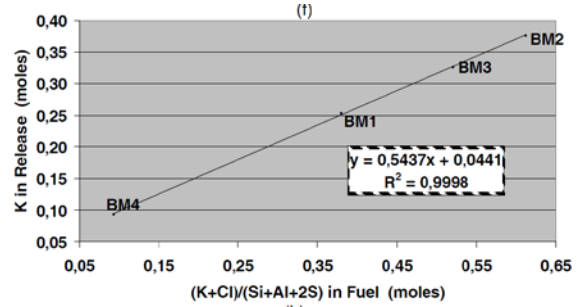


Figure 4 Standard deviation between the model and experiments [ 9, 10]

For particle size evolution after combustion, particle population balance model was selected. The present simplified model predicts the cumulative mass fraction using a PSD derived from the particle number calculations at different distinct time steps.

$$\frac{dN_{i,k}}{dt} = \underbrace{-S_{i,k}N_{i,k} + \sum_{j=1}^i \sum_{\lambda=1}^K (b_{ij,k\lambda}S_{j,\lambda}N_{j,\lambda})}_{\text{Fragmentation}} - \underbrace{C_{i,k}N_{i,k} + C_{i-1,k}N_{i-1,k}}_{\text{Size}} - \underbrace{D_{i,k}N_{i,k} + D_{i,k-1}N_{i,k-1}}_{\text{Density}}$$

In the present kinetic-empirical model, it is assumed that the particle combustion rate depends on the instantaneous particle diameter. Changes in the particle density, due to the steady diameter char oxidation or to cenospheres formation are neglected. The assumptions of the model are described elsewhere [8]. Three types of fragmentations are considered: attrition, breakage and percolation. The fragmentation rate constant  $S_{i,k}$  and  $C_{i,k}$  were derived from experiments. An algorithm was developed. The code was written in MATLAB. The model validation with experimental data is given in Figure 5 for UK coal.

Finally, overall ash formation model was developed. The above two sub models (i.e. empirical indices and PDS evolution model) have been integrated in overall ash formation model for predicting the overall ash

release and ash formation in terms of PSD, the respective mass fractions and the corresponding elemental mineral compositions. The details of the model can be found elsewhere [9]. Figure 6 shows the validation of the model with experimental data for the ash formation of Olive residue in terms of mineral release and PSD after combustion.

In the model calculations, the release of mineral elements calculated using empirical indices have been subtracted from each size bin. The residual amount of the inorganics has then been normalized for each size bin and compared with the results of the ICP-AES analyses performed for different particle size bins, as obtained from the LCS experiments. The result of the said comparison for polish coal is graphically presented in Figure 7.

No co-firing experimental data were available to predict the ash formation during ash formation under this project. The work on co-firing experiments is still on-going. The ash formation model developed under this work was used as input to the ash deposition post processor code as shown in Figure 6. The research outcomes from the present work will

lead to the development of a Co-firing Advisory Tool (CAT) which fitted well within the expectations of collaborative program (see Figure 8). As a follow-up activity, several activities are planned to make the CAT much more robust by incorporating diversified fuels and fuel blends with additional parametric effects as well as several sub models/indices. (CAT) which fits well within the expectations of collaborative program (see Figure 8).

#### 4. CONCLUDING REMARKS

From an extensive experimental parametric test matrix (performed with two goals and six different biomass fuels) valuable information and understanding on the ash formation mechanisms have been gained in terms of particle size and mineralogy. Based on the analytical data quantitative analysis could be performed for the release of minerals under given operating conditions which enabled to develop ash formation models for the development of CAT (Co-firing Advisory Tool).

It is concluded from the experiments that the ash transformations and char combustion will be in

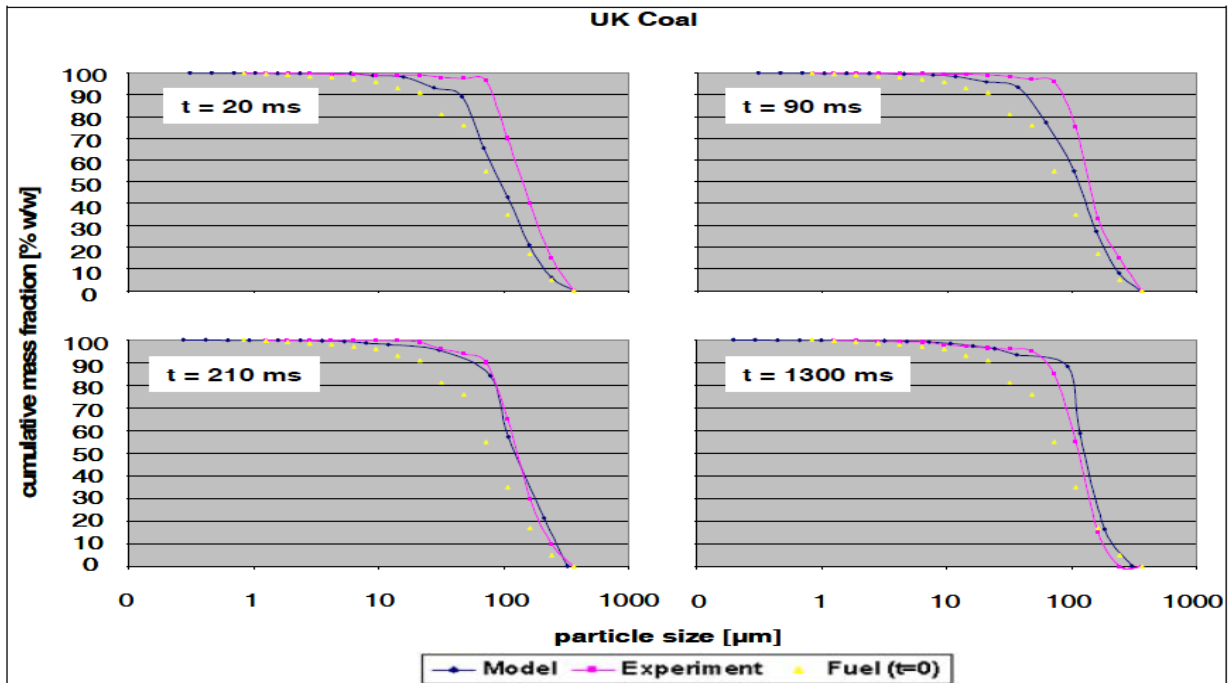


Figure 5: PSD evolution at different residence times: Comparison of model with experimental data

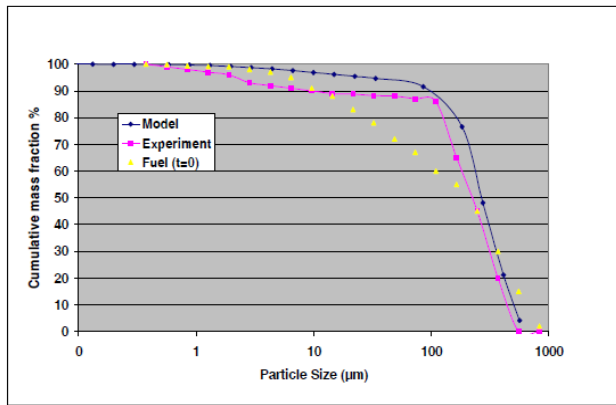
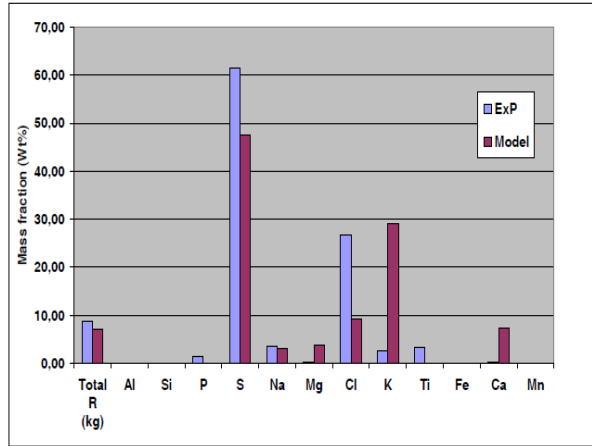


Figure 6: Mineral release and PSD evolution during Olive residue combustion

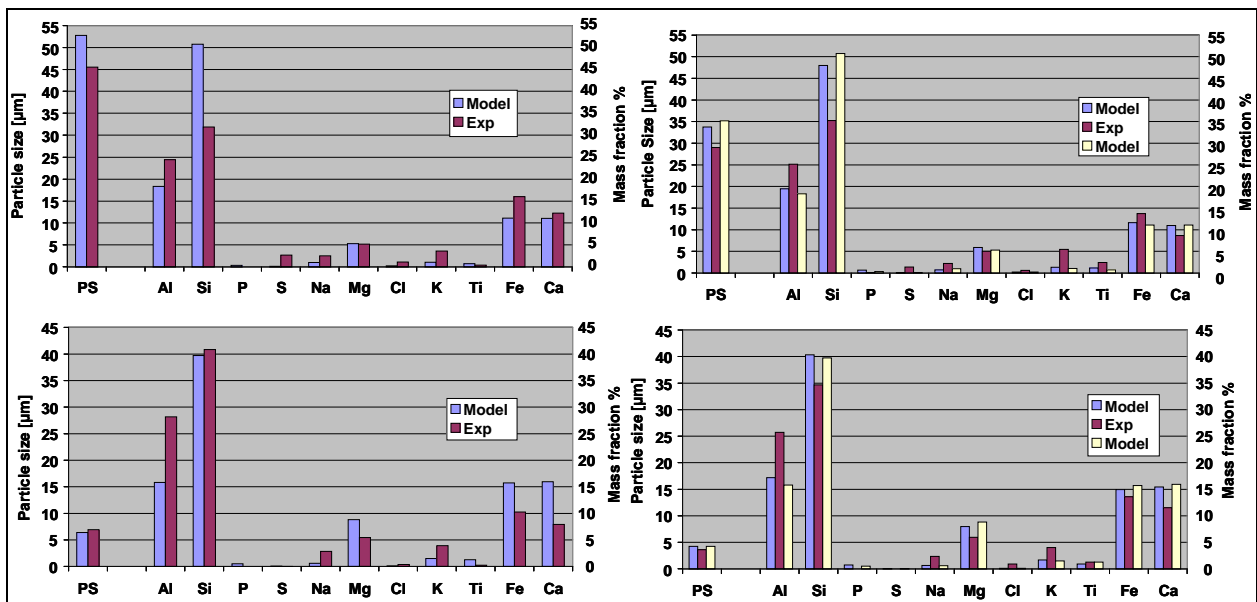


Figure 7: Mineralogical distribution in each size bin for Polish coal



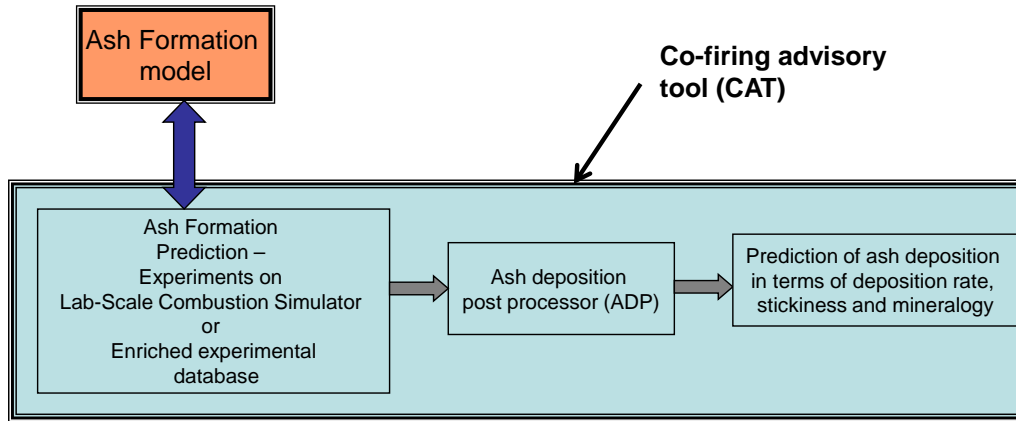


Figure 8 Schematic showing the tasks involved in the development of CAT

in kinetic-diffusion controlled regime, even with extended residence time with typical pulverized fuel firing conditions. Char chemical conversion and devolatilization are found to be dependent on ash content and volatile matter at typical pulverized fuel firing conditions. Devolatilization of the fuels also depends on the mineral matter and its association with carbon matrix. Fragmentation is found to be depending on fuel chemical conversion and devolatilization. Mineral matter and its association in the char matrix can significantly alter the ash release. Ash release of several minerals can be linearly correlated based on the mineral chemistry of the fuel at typical PF firing conditions. The linear correlations can be worked out better for the fuels having similar physical and chemical properties.

From the modeling efforts made in this research work, it is concluded that the empirical indices developed for the different elemental mineral release under PF combustion firing conditions, work well for predicting the overall elemental release. However, it is better to develop such correlations covering more number of different groups of fuels and fuel blends. The PSD evolution model also provided good agreement with experimental data. The overall ash formation model was also able to predict the ash release, particle size and elemental mineral distribution in each size bin for different coal and biomass with maximum +/-10-20% standard deviation. The model will be validated for co-firing

experiments in future. Despite of novel and easy approach, they are very simple and needs to be addressed for further improvements. Further studies are also in progress for the applications of CAT to new processes such as Ultra Super Critical vapor characteristics, colorless combustion (such as oxy firing).

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