EFFECTS OF OPERATIONAL PARAMETERS ON SO$_2$ EMISSION IN A CIRCULATING FLUIDIZED BED COMBUSTOR

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ABSTRACT

Reducing SO$_2$ emission from power plants is one of the main issues for the environmental protection. One of the advantages of the CFB combustion technology of coal is in situ SO$_2$ capture by added sorbents, usually uncalcined limestone (CaCO$_3$). In this theoretical study effects of operational parameters such as sorbent particle diameter, Ca/S molar ratio and superficial velocity on SO$_2$ emission have been estimated using a previously developed dynamic 2D model for CFBCs. In the model, the unreacted shrinking core model has been adopted for desulphurization. As a result of this study; it is observed that operational bed velocity has positive effect on SO$_2$ emission. Air-staging strongly influences the concentration and distribution of sulphur compounds in the combustion chamber of fluidized beds. Feeding limestone with high proportion of fines into the combustor causes high sulphur retentions.

Keywords: Circulating fluidized bed, coal combustion, modeling, SO$_2$ emission

SİRKÜLASYONLU BİR AKIŞKAN YATAKLI YAKICIDA İŞLETME PARAMETRELERİNİN SO$_2$ EMİSYONU ÜZERİNDEKİ ETKİLERİ

ÖZET

Çevresel korunma göz önüne alındığında, güç santrallerinde SO$_2$ emisyonunun indirgenmesi ana konulardan biridir. Kömürün sirkülasyonlu akışkan yatak (SAY) yakma teknoloji ile yakılmasının en önemli avantajlarından birisi de genellikle kalsine olmamış kireçtaşı (CaCO$_3$) gibi sorbentlerin eklenmesiyle doğal SO$_2$ tutma kabiliyetidir. Bu teorik çalışmada, sorbent tane çapı, Ca/S mol oranı ve yatak işletme hızı gibi işletme parametrelerinin SO$_2$ emisyonu üzerindeki etkileri; daha önce SAY yakıcılar için geliştirilmiş olan dinamik model kullanılarak tahmin edilmiştir. Modelde reaksiyona girmemiş büzülen tanecik modeli kükürt indirgenmesine adapte edilmiştir. Bu çalışma sonucunda; yatak işletme hızının SO$_2$ emisyonu üzerinde pozitif bir etkiye sahip olduğu, ikincil hava kullanmanın yatak içerisindeki sülfür dağılımı ve konsantresi üzerinde güçlü bir etkiye sahip olduğu ve beslenen kireçtaşının içeriğinin yüksek oranda toz içermesi durumunda yatak içerisinde kükürt indirgemesini arttırdığı görülmüştür.

Anahtar Kelimeler: Sirkülasyonlu akışkan yatak, kömür yanması, modelleme, SO$_2$ emisyonu

1. INTRODUCTION

Circulating fluidized bed (CFB) combustion is receiving wide research attention in view its potential as an economic and environmentally acceptable technology for burning low grade coals. In addition to highly efficient operation, a

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combustion system should comply with the requirement of minimizing environmental impact. The emission rate of various pollutants from the combustion of coal depends on fuel analysis, combustor design and operating conditions. Fluidized bed combustion allows clean and efficient combustion of coal. Designing of the CFB combustor (CFBC) is very important because of burning coal with high efficiency and within acceptable levels of gaseous emissions [1, 2].

A detailed review of studies concerning CFB combustion and their modeling has been presented by Reh [2] who argues that there must be a balance between the computational modeling and verification by experimental and operational results. It is claimed that there has to be a cooperation between the plant designers-operators and the academia to provide a reliable basis of experimental data. The most important demands to be considered for future efforts in research, design and operation of CFBC are to improve multi-scale two-phase modeling in direction of the improvement of validation using CFB data bases. The improved mastery of CFBC design basics as a gas-solid reactor is still essential.

Reducing SO_2 emission from power plants is one of the main issues for the environmental protection. One of the advantages of the circulating fluidized bed combustion technology of coal is in situ SO_2 capture by added sorbents, usually uncalcined limestone ($CaCO_3$). During the combustion of coal, the sulphur in it is oxidized to the pollutant, SO_2. Limestone ($CaCO_3$) of the bed materials calcine to CaO which reacts with SO_2 producing $CaSO_4$. Thus instead of leaving the combustor as a gaseous pollutant, sulphur is discharged as a solid residue. Numerous experimental and theoretical studies about the sulfur retention in CFBCs are present in the literature [3-10]. Some models have already been proposed for predicting the sulfur retention in CFBC, but there are important differences between their submodels, especially as far as the CFB hydrodynamics is considered [3, 5].

In this theoretical study effects of operational parameters such as sorbent particle diameter, Ca/S molar ratio and superficial velocity on SO_2 emission have been estimated using a previously developed dynamic 2D model for CFBCs. In the model, different SO_2 generation rates, depending on the height in the bed, are considered. These differences are due to differences in the char combustion rate because of the existence of radial and axial oxygen concentration profiles. In CFBC the SO_2 generation and retention processes take place simultaneously in the bed. The sulphur retention depends on many factors as gas velocity, Ca/S molar ratio, sorbent particle properties, bed height, solid inventory, etc. In the model, the unreacted shrinking core model has been adopted for desulphurization.

2. MODEL DESCRIPTION

Modeling of CFB combustor is rather difficult. The fluid dynamics of this gas-solid two-phase flow is very complex and strongly dominated by particle to particle interactions. Furthermore, the numerous homogeneous and heterogeneous catalytic gas-phase reactions and their kinetics for the description of the combustion phenomena and the emission formation and destruction are not completely known. A well-designed CFB combustor can burn coal with high efficiency and within acceptable levels of gaseous emission. A good understanding of the combustion and pollutant generating processes in the combustor can greatly avoid costly upsets. The present CFB combustor model can be divided into three major parts: a sub-model of the gas-solid flow structure; a reaction kinetic model for local combustion and a convection/dispersion model with reaction. The latter formulates the mass balances for the gaseous species and the char at each control volume in the flow domain. Kinetic information for the reactions is supplied by the reaction kinetic sub-model, which contains description of devolatilization and char combustion, and emission formation and destruction respectively. In the present study, a previously developed 2-D coal combustion model for CFBs is used for the simulation [8]. Fig.1 shows a schematic view of the system considered.

2.1. Hydrodynamic Structure

The fluidized beds exhibit very complex hydrodynamics due to the non-linear interactions between the two independent media with their own individual movement tendencies - the particles and the fluid. Combustor hydrodynamic is modeled taking into account previous work [11]. The model addressed in this paper uses particle based approach which considers two-dimensional motion of single particles through fluids. According to the axial solid volume concentration profile, the riser is axially divided into the bottom zone and the upper zone.

In the present model, bottom zone in turbulent fluidization regime is modeled as two-phase flow which is subdivided into a solid-free bubble phase and a solid-laden emulsion phase. A single-phase back-flow cell model is used to represent the solid mixing in the bottom zone. A two phase model is used for gas phase material balance. The bubble rise velocity, the bubble size, the bubble volume fraction and the suspension porosity is calculated by Horio [12]. A single-phase back-flow cell model is used to represent the solid mixing in the bottom zone. Solids exchange, between the bubble and the emulsion phases is a function of the bubble diameter and varies along the axis of the riser [13]. In the upper zone core-annulus solids flow structure is established. Particles move upward in the core and downward in the annulus. Thickness of the annulus varies according to the bed height [14].
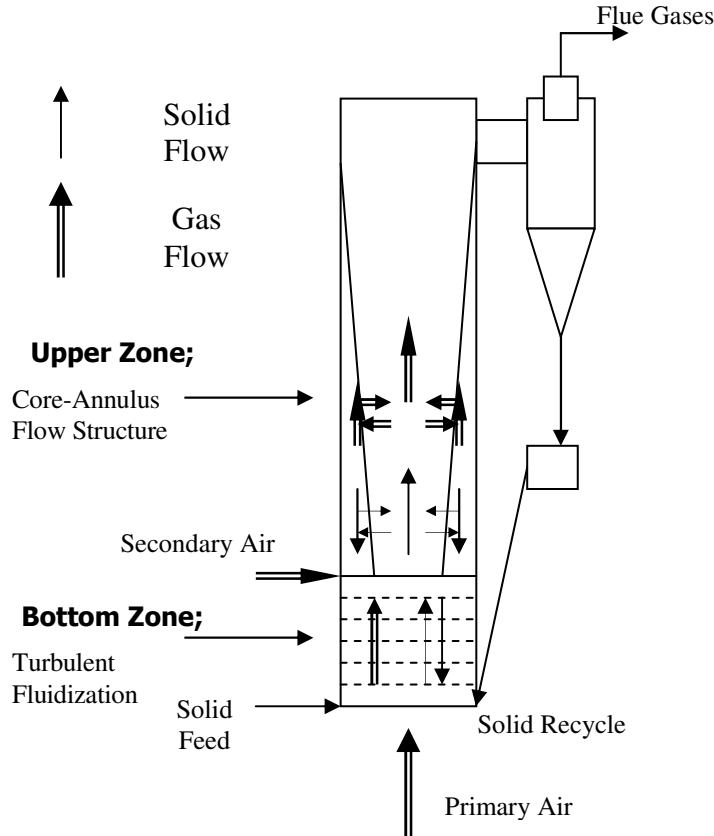

Figure 1. The scheme of the CFBC.

The pressure drop through the bottom zone is equal to the weight of the solids in this region and considered only in axial direction. In the upper zone, pressure drop due to the hydrodynamic head of solids is considered in axial direction while pressure drop due to solids acceleration is also considered in axial and radial directions. The solids friction and gas friction components of pressure drop are considered as boundary conditions in momentum equations for solid and gas phases, respectively in the model. Solids friction is defined as the frictional force between the solids and the wall, while the gas friction is the frictional force between the gas and the wall.

Hydrodynamic model takes into account the axial and radial distribution of voidage, velocity and pressure drop for gas and solid phase, and solids volume fraction and particle size distribution for solid phase. The model results are compared with and validated against atmospheric cold bed CFB units' experimental data given in the literature for axial and radial distribution of void fraction, solids volume fraction and particle velocity, total pressure drop along the bed height and radial solids flux. Ranges of experimental data used in comparisons are as follows: bed diameter

from 0.05-0.418 m, bed height from 5-18 m, mean particle diameter from 67-520 μm, particle density from 1398 to 2620 kg/m^3, mass fluxes from 21.3 to 300 kg/m^{2}s and gas superficial velocities from 2.52-9.1 m/s. The structure and details of the hydrodynamic model are given in previous study [11].

2.2. Kinetic Model

The char comprises mainly carbon, ash, nitrogen and sulphur. Above 750°C, char oxidizes to gaseous products; CO, CO_2, SO_2 and NO_x. The transition of these products should be taken into consideration in modeling, depending on solid mixing. In the model, volatiles are entering the combustor with the fed coal particles. It is assumed that the volatiles are released in the bottom zone of the CFB combustor at a rate proportional to the solid mixing rate. Volatile yield is estimated by the following empirical correlations in the model given by Gregory and Littlejohn [15],

$$V = VM - A - B \tag{1}$$
$$A = \exp\left(26.41 - 3.961 \cdot \ln T + 1.15 \cdot VM\right)/100 \tag{2}$$
$$B = 0.2 \cdot \left(VM - 0.109\right) \tag{3}$$

The composition of the products of devolatilization in weight fractions is estimated from the following correlations [16]:

$$CH_4 = 0.201 - 0.469 \cdot VM + 0.241 \cdot VM^2 \tag{4}$$
$$H_2 = 0.157 - 0.868 \cdot VM + 1.388 \cdot VM^2 \tag{5}$$
$$CO_2 = 0.135 - 0.900 \cdot VM + 1.906 \cdot VM^2 \tag{6}$$
$$CO = 0.428 - 2.653 \cdot VM + 4.845 \cdot VM^2 \tag{7}$$
$$H_2O = 0.409 - 2.389 \cdot VM + 4.554 \cdot VM^2 \tag{8}$$
$$Tar = -0.325 + 7.279 \cdot VM - 12.880 \cdot VM^2 \tag{9}$$

The amount of volatile nitrogen and sulphur increases as a function of bed temperature and during devolatilization is expressed as [17],

$$N = 0.001 \cdot T - 0.6 \quad \left(\text{kg/kg coal}\right) \tag{10}$$
$$S = 0.001 \cdot T - 0.06 \quad \left(\text{kg/kg coal}\right) \tag{11}$$

The combustor model takes into account the devolatilization of coal, and subsequent combustion of volatiles followed by residual char. The char particles resulting from the devolatilization process consist of the remaining carbon fraction (1-X_c) and ash only. Kinetics of char combustion is modeled with a shrinking core with attiring shell i.e. the dual shrinking-core model (assuming that the ash separated once formed) with mixed control by chemical reaction and gas film diffusion (the char particles after devolatilization are considered to be porous). The stoichiometric conversion of char-C to CO and CO_2 can be written as;

$$\Phi C + O_2 \rightarrow 2(\Phi - 1)CO + (2 - \Phi)CO_2 \tag{12}$$
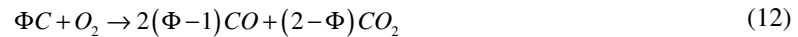
where the mechanism factor Φ determines the ratio of CO to CO_2 produced and is calculated as suggested by [18]. The mechanism factor, Φ is equal to 1.0 for CO_2 transport from the surface, and is equal to 2.0 for CO transport [19].
Since the particle size distribution is known to have a strong influence on the hydrodynamics and combustion behavior, its variations should not be neglected in the simulation of CFBs [20]. The model also considers the particle size distribution due to fuel particle fragmentation, char combustion and particle attrition [8].

Typically, significant amounts of the fuel-nitrogen remain in the char after the devolatilization. The oxidation of this char-nitrogen gives an important contribution to the total nitrogen oxide emissions from the combustor. The mechanism of char-nitrogen oxidation to the products is very complex, and includes not only several homogeneous and heterogeneous reactions but also mass transfer effects inside the pore system of the char and in the boundary layer surrounding the particle [21]. In the present study, fuel-NO_x can be formed through: Combustion of the nitrogenous species released with volatile matter (such as HCN, NH_3), and oxidation of the nitrogen retained in the char. These reactions, resulting in rapid formation of NO_x, are most likely to proceed in the bottom zone. Meanwhile, in zones with volume O_2 concentrations lower than 10–12%, the NH_3 concentration is probably elevated due to the rapid formation of NH_3 from HCN [22] as well as because of the emission of NH_3 released with volatiles from fuel particles present in these zones. In the upper zone (with lower O_2 concentrations) this may lead to NO_x reduction through its reaction with NH_3, followed by formation of nitrogen gas and water vapor, i.e. neutral products. The alternative mechanisms of NO_x reduction in the upper zone involve reactions of NO_x with carbon and CO on the char surface [23] which are highly probable when firing high-ash fuels. In the model, NO_x is produced from the oxidation of both volatile-bound nitrogen and char-bound nitrogen. The production of NO_x from char-bound nitrogen is proportional to the combustion rate of char [19]. The production of NO_x from volatile-bound nitrogen is present in the literature [24]. The chemical reactions with their corresponding reaction rates for NO_x emissions formation and retention in the model are given in the literature [8].

Oxides of sulfur produced in burning the coal may be retained in solid form by reaction with particles of limestone or dolomite which is directly fed to the CFBC together with the solid fuel. At the combustion temperatures, usually in the range of 800–900°C, the $CaCO_3$ calcines to CaO and CO_2. The porous alkaline solid, CaO, produced by the calcination of limestone reacts with SO_2:

$$CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \qquad (12)$$

Based on the stoichiometry of the sulphur capture reaction with calcium oxide, a theoretical limestone feed of one mole calcium per mole of sulphur would be enough for complete sulphur capture. However, the molar volume of the reaction product $CaSO_4$ is about three times greater than the molar volume of CaO, therefore complete conversion of the adsorbent particle is impossible, because sulphation only proceeds at the outer shell of the CaO particle and formation of $CaSO_4$ causes pore mouth closure and reaction stops before all the CaO is consumed by the reaction [25]. This sulfation pattern is commonly referred to as the unreacted-core model [26, 27]. The Ca utilization of limestone is known to be highly dependent on the flue gas temperature and particle size. Several researchers have found that increasing particle size reduces the utilization significantly, and that the sulfur capture capacity passes through a maximum at temperatures between about 800 and 850°C [28]. As a result, Ca/S mole ratio is usually chosen between two and four in a classical fluidized bed combustor [29]. On the other hand, high SO_2 retention efficiencies were obtained for Ca/S mole ratios of less than two in a circulating fluidized bed combustor [30].

In CFBC the SO_2 generation and retention processes take place simultaneously in the bed [8]. In the model, it is also assumed that the particle size of limestone particles change during the sulphation reaction and the attrition of limestone particles are taken into account. Moreover, the estimation of limestone particles is assumed instantaneous. The chemical reaction with their corresponding reaction rate for SO_2 retention regarding the gas temperature and particle size are given in Table 1.

Table 1. The SO_2 retention reaction and reaction rate used in the model [4]

Reaction	Reaction Rate
$CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \qquad k_L = \dfrac{\pi}{6} d_s^3 k_{vL} C_{SO_2} \; \left(\tfrac{1}{s}\right)$	$k_{vL} = 490 \exp\left(\dfrac{-17500}{R_g T}\right) S_g \lambda_s \; \left(\tfrac{kg}{m^2 s}\right)$ $S_g = -384T + 5.6\times10^4 \qquad T \geq 1253 \text{ K}$ $S_g = 35.9T - 3.67\times10^4 \qquad T < 1253 \text{ K}$

3. NUMERICAL SOLUTION

The set of differential equations governing mass, momentum and energy for the gas and solid phases which are solved using an IBM-PC-Pentium4 (CPU speed is 2800 MHz) with a computer code developed by the authors in FORTRAN language where the time step is 10^{-6} seconds. In these equations, the dependent variables are the vertical and the horizontal components of the void fraction, the solid volume fraction, the gas pressure, the gas concentration, the vertical and the horizontal velocity and temperature components of the gas and solids. The Gauss-Seidel iteration which contains successful relaxation method and combined Relaxation Newton-Raphson methods are used for solution procedure. The backward-difference method is used the discretization of the governing equations. Flow chart of the numerical solution of the model is shown in Fig.2. The structure and details of numerical solution have been given in previous study [8, 11].
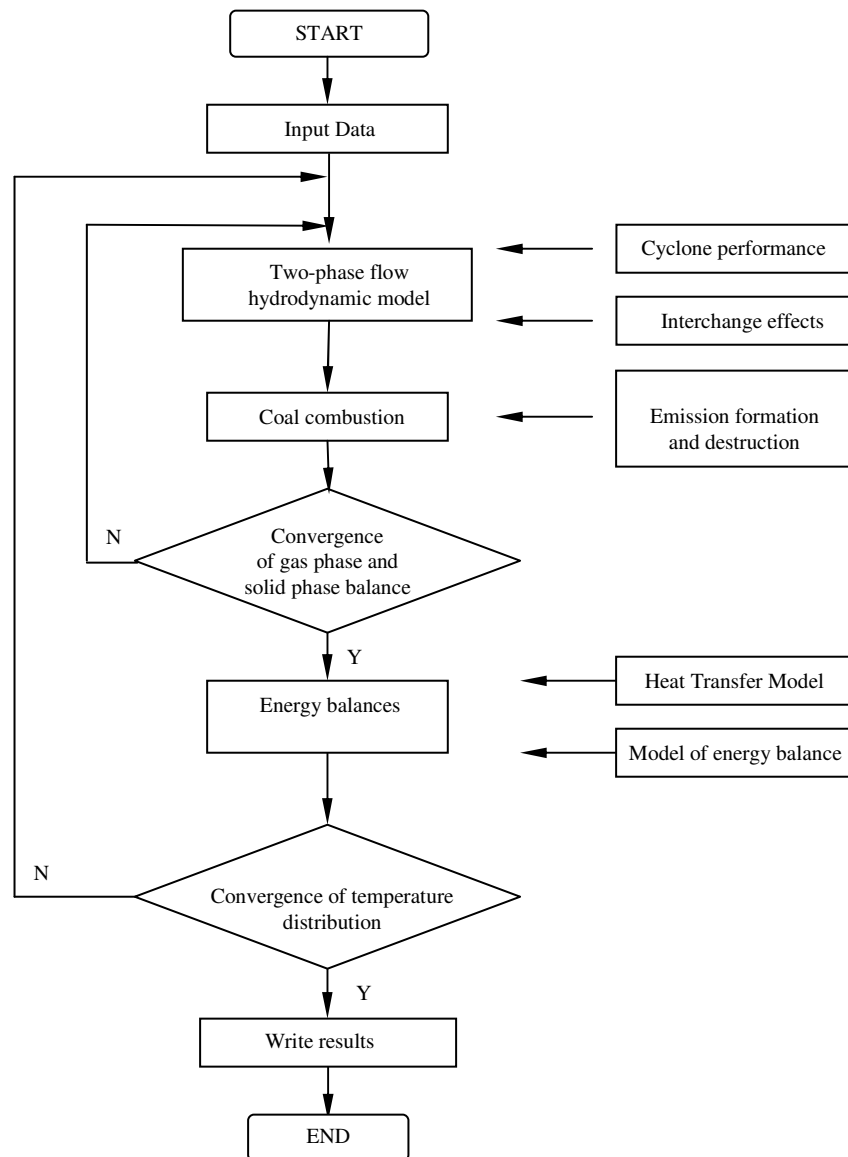

Figure 2. Flow chart of the numerical solution of the CFBC model.

Inputs for the model are combustor dimensions and construction specifications (insulation thickness and materials, etc.), primary and secondary air flow rates; coal feed rate and particle size distribution, coal properties, Ca/S ratio, limestone particle size distribution, gas inlet pressure and temperature, ambient temperature and the superficial gas velocity. The superficial gas velocity is considered as inlet air velocity in this study. In the model, the excess air is introduced as secondary air where the bottom zone is considered to be operating under the stoichiometric conditions. A continuity condition is used for the gas phase at the top of the cyclone. The cyclone is considered to have 98% collection efficiency.

4. RESULTS AND DISCUSSION

SO$_2$ emission performance has been performed to show how different model input values affect the modeling results. In the present study, model input values of the sorbent particle diameter, Ca/S molar ratio and superficial velocity on have been considered for SO$_2$ emission performance for small-scale 80 kW CFBC. Detailed listing of the model input variables are given in Table 2. The thermodynamic properties of reference environment are the ambient external conditions (T$_0$=25°C, P$_0$=101.3 kPa and relative humidity of the air 60%). These conditions are considered for the superficial gas velocity.

The influence of the bed operational parameters on SO$_2$ emissions is shown in Figures 3-5 which plot the variation of the SO$_2$ emissions along bed height for three different sorbent particle diameter, superficial velocities and Ca/S molar ratios.
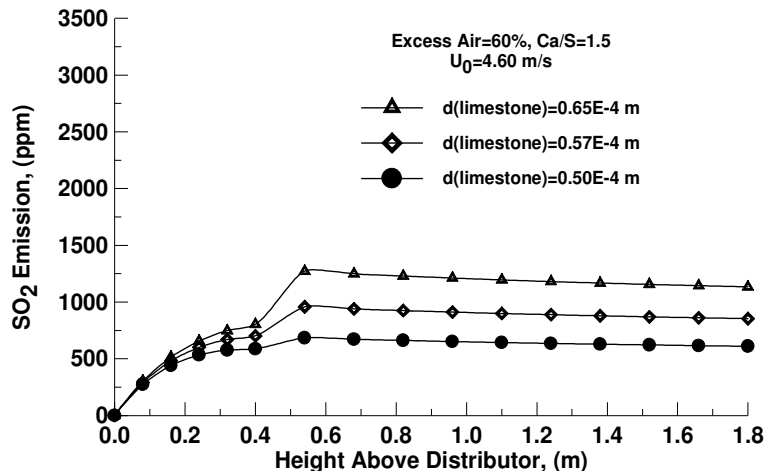

Figure 3. Effects of sorbent particle diameter on SO$_2$ emission

Fig.3 illustrates the effect of sorbent particle diameter on SO$_2$ emissions. As it is seen from the Fig.3, an increase in SO$_2$ emissions is observed in the bottom zone due to the assumption that the great amount of the volatile matters is released at the feed point in the combustor. The SO$_2$ generation rate from the char depends on its combustion rate, which depends on the temperature, excess air, O$_2$ concentration, etc. [8]. A raised temperature suppresses the increase in SO$_2$ emission observed during air staging point. This phenomenon is also observed in the experimental studies of Lyngfelt et al. [31]. By getting better coal combustion with the secondary air feed (at the 0.4 m height above the distributor plate) it increases a certain amount of the fixed sulphur in its structure between the heights of 0.4 m and 0.6 m above the distributor plate. Air-staging strongly influences the concentration and distribution of sulphur compounds in the combustion chamber of fluidized beds. While the concentration of SO$_2$ under no air-staging conditions is low throughout the combustion chamber, a high SO$_2$ concentration is seen for the air-staging below the secondary air inlets. High SO$_2$ concentrations in the primary combustion zone during normal or intensified

air-staging indicates a release of SO_2 from the sulphated sorbent under reducing conditions. This can be explained by reducing conditions in the primary combustion zone and the release of SO_2 because of reductive decomposition of $CaSO_4$ [32]. This reaction may have an important bearing on the SO_2 emission from the furnace [30]. The SO_2 concentration in the bottom zone also shows that high SO_2 concentrations are associated with the absence of oxygen. Above the secondary air inlet a decrease in the SO_2 concentrations indicates a capture in this more oxidizing zone [32]. Above 0.6 m, adequate presence of oxygen due to secondary air feed increases the sulphur retention with limestone. The limestone reactivity together with its particle size distribution determines the amount of limestone needed to obtain a fixed value of sulphur retention in the CFBC. Feeding limestone with high proportion of fines into the combustor causes high sulphur retentions.
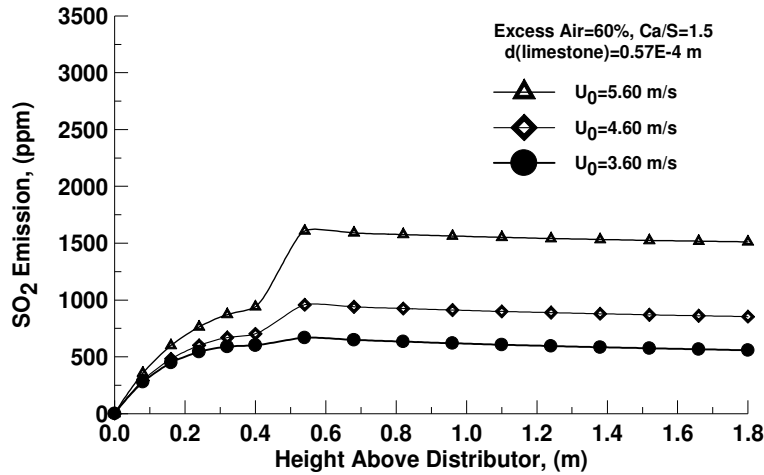

Figure 4. Effects of bed operational velocity on SO_2 emission

Effect of bed operating velocity on SO_2 emission is given in Fig.4. The bed operational velocity in the combustor is one of the basic design variables of the process. The reason is that with the increase of bed operating velocity the hydrodynamic condition of the combustor changes. It is observed that operational bed velocity has positive effect on SO_2 emission. As the operational velocity increases particle residence time in the combustor, char combustion rate and bed temperature decreases which results lower SO_2 emission formation. The superficial velocity also affects net solid mass flux in the riser and also the mean residence time of the limestone particle. Thus increasing limestone particle mass flux decreases SO_2 emission in the CFBC.

Table 5. Model input variables for small-scale CFBC

| D (m)	H (m)	H_{bot} (m)	Gas inlet pressure (atm)	Excess air (%)	Superficial gas velocity (m/s)	Coal feed rate (kg/h)	Mean coal particle size (mm)	Ca/S (-)	Mean sorbent particle size (mm)
0.125	1.8	0.4	1	60	4.60	6.8	0.2	1.5	0.65
0.125	1.8	0.4	1	60	4.60	6.8	0.2	1.5	0.57
0.125	1.8	0.4	1	60	4.60	6.8	0.2	1.5	0.50
0.125	1.8	0.4	1	60	5.60	6.8	0.2	1.5	0.57
0.125	1.8	0.4	1	60	4.60	6.8	0.2	1.5	0.57
0.125	1.8	0.4	1	60	3.60	6.8	0.2	1.5	0.57
0.125	1.8	0.4	1	60	3.60	6.8	0.2	0.5	0.57
0.125	1.8	0.4	1	60	3.60	6.8	0.2	1.0	0.57
0.125	1.8	0.4	1	60	3.60	6.8	0.2	1.5	0.57
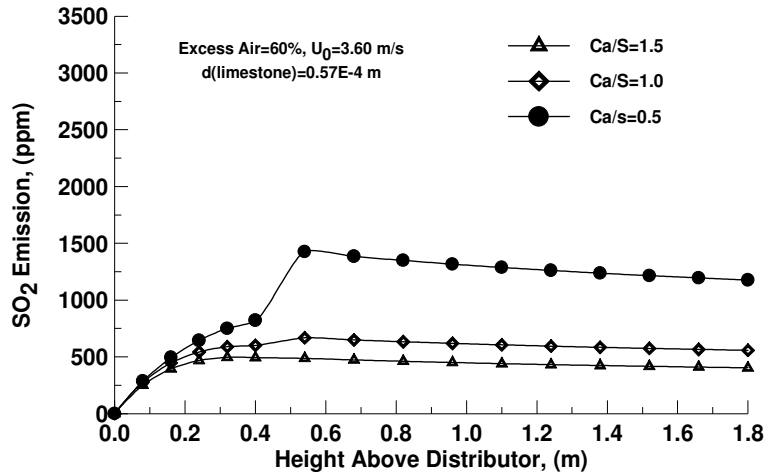
Figure 5. Effects of Ca/S molar ratio on SO$_2$ emission

The limestone reactivity together with its particle size distribution determines the amount of limestone needed to obtain a fixed value of sulphur retention in the CFBC. Feeding limestone with high proportion of fines into the combustor causes high sulphur retentions. This is clearly seen from Fig.5. As the figure displays an increase in the Ca/S ratio gives a significant increase in the sulphur retention reached in the combustor. This phenomenon is also observed in the experimental studies of Adanez et al. [4].

It also proves that the combustor height is a design variable that strongly affects the solid circulation flow rates leaving the combustor and so on has an important effect on the mean residence times of solids. An increase in the combustor height gives a decrease in the solid circulation flux, producing an increase in the mean residence time and thus in the SO$_2$ emission. This effect can be estimated from all simulation results as given in Figs.3-5.

5. CONCLUSION

Considering the natural resources especially fossil fuels, usage of CFBCs will have a crucial importance in the future. Fluidized bed combustion allows clean and efficient combustion of coal. A well-designed CFB combustor can burn coal with high efficiency and within acceptable levels of gaseous emissions. In this theoretical study effects of operational parameters such as sorbent particle diameter, Ca/S molar ratio and superficial velocity on SO$_2$ emission have been estimated using a previously developed dynamic 2D model for CFBCs. As a results of this study;

- Air-staging strongly influences the concentration and distribution of sulphur compounds in the combustion chamber of fluidized beds.
- Feeding limestone with high proportion of fines into the combustor causes high sulphur retentions.
- It is observed that operational bed velocity has positive effect on SO$_2$ emission.
- An increase in the Ca/S ratio gives a significant increase in the sulphur retention reached in the combustor.

NOMENCLATURE

C	gas concentration, kmol m^{-3}
Ca/S	calcium to sulphur ratio
D	bed diameter, m
H	combustor height, m
H$_{bot}$	height of the bottom zone, m

k_L	reaction rate, s^{-1}
k_{vL}	volumetric reaction rate, $kg\ m^{-2}s^{-1}$
S_g	Specific surface area of limestone particles, $m^2\ kg^{-1}$
T	temperature, K
U_0	superficial velocity, $m\ s^{-1}$
VM	volatile matter fraction, kg volatile $(kg\ char)^{-1}$

Greek letters

Φ	mechanism factor
λ_s	limestone reactivity

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