



# Optimal gas treatment and coal blending for reduced emissions in power plants: A case study in Northwest Spain

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## ABSTRACT

In this work a decision making framework for the design of the flue gas treatment section of a power plant has been developed, including particle, NO<sub>x</sub> and SO<sub>2</sub> removal operations. It has been applied to a coal based thermal power plant in Spain to select the optimal technologies and its sequence. Surrogate models for the treatments have been developed. The problem corresponds to a mixed integer non-linear programming one including catalytic and non-catalytic NO<sub>x</sub> removal, allowing various allocations for the catalytic technology, electrostatic precipitation and wet or dry SO<sub>2</sub> removal. It is reformulated as a non-linear problem to evaluate bypass opportunities. The optimization suggests the use of electrostatic precipitation, followed by catalytic NO<sub>x</sub> removal and dry SO<sub>2</sub> removal. Next, a coal blending problem has also been solved for two objective functions. When only treatment costs are considered, the use of imported coal is recommended, but an increase of 4% in its price can change the decision into the use of national coal. If the energy within the coal is added to the objective function, crude tar coal is included in the blend and imported coal is used to maintain the emissions within limits. Limestone Forced Oxidation is the selected technology.

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## 1. Introduction

Coal based power plants have been responsible for a fair share of the power production worldwide. However, current trends towards clean and sustainable energy have led to an effort towards reducing SO<sub>2</sub> and NO<sub>x</sub> emissions and water consumption. Modelling has been widely used to evaluate the performance of the facilities and the units. The different works have focused on one the he four main sections of the power plants: the boiler, the power cycle, the cooling units and the flue gas treatment section. Regarding the power island, most of the work in the literature evaluates the steady state operation of the thermal cycle [1], using specialized software such as “Power plant simulator” [2], Cycle Tempo 5.0 [3], or using commercial process simulators such as CHEMCAD [4] or ASPEN [5]. However, the actual operation of power plants is not in steady state. Their production is regulated to meet demand depending on the availability of renewable resources. Thus, the analysis of the dynamics has been presented in a number of studies [6], using specialized software (i.e. or ClaRaCSC [7]) or commercial

software such as SIMULINK, ThermoSysPro [8] or Apros 6 [9]. Apart from the power produced, water scarcity and the water – energy nexus have attracted attention towards evaluating the water consumption involved in the cooling units. Power plants typically consume at least 1.8 L/kWh as a result of condensing the exhaust stream from the turbine, but the actual value depends on the plant allocation [4]. The third section corresponds to emission control and includes the evaluation of the boiler operation. Two approaches have been used to reduce emissions: i) the implementation of measures to reduce the formation of those species by controlling the combustion at the boiler [10], ii) the installation of end of trail gas treatment. Most of the studies on boiler design are carried out to mitigate the production of pollutants by evaluating the temperature [11] and velocity profiles, the burner design [12] and the excess of air [13] and the composition of the oxidizer [14]. Furthermore, flue gas treatment has been widely addressed from an industrial perspective [15] and the technologies are well established [16]. However, the flue gas section has received less attention in the literature focusing on carbon capture. Several simulations of

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the carbon capture section of power plants using ASPEN plus can be found in the literature for coal-based plants using MEA solutions [17], for IGCC technologies using amine solutions [18] or evaluating the CO<sub>2</sub> emissions of the co-firing of biomass with coal [19]. The difficulties in carbon capture from dilute streams have led to study oxycombustion systems. Two approaches to model oxycombustion power plants have been used, the use of process simulators [20] and the development of equation-based models of the various units from the boiler to the air separation system to build a systematic framework for optimization [21]. Together with CO<sub>2</sub>, the emission of NO<sub>x</sub> and SO<sub>2</sub> must be limited. There are several alternative denitrification (DeNO<sub>x</sub>) technologies such as catalytic or non-catalytic processes, as well as wet and dry systems for desulfurization (DeSO<sub>x</sub>). The removal yield and cost of each technology depends on the operating conditions and the addition of chemicals such as ammonia, CaO or CaCO<sub>3</sub> [22]. The actual selection of technologies and their relative position in the treatment chain depends on the coal composition and emission limits. Apart from the industrial experience and guidelines, no systematic study has addressed the optimal allocation of the DeNO<sub>x</sub> and DeSO<sub>x</sub>, the selection of the proper technologies or the operating conditions. The few studies that evaluate the production of NO<sub>x</sub> and SO<sub>2</sub> associated with power plants use empirical correlations to characterize the boiler and the fuel used. The abatement technologies are modeled using fixed removal ratios [23]. The same group extended the work to perform a multiobjective optimization to account for environmental impact of the generation of power from fossil resources [24].

In this work, a framework is developed to select among different denitrification and desulfurization technologies and their relative position along the flue gas treatment chain of a power plant. It consists of a two-stage procedure. The first stage corresponds to the pre-screening of the technologies available based on industrial know-how. The second one consists of formulating a superstructure model [25,26] of alternative technologies from the boiler to the discharge of the flue gas involving denitrifier, desulphurizer and particle removal. Surrogate models for each of the units are developed based on experimental and industrial data providing a flexible framework to evaluate and design the flue gas treatment process.

Once the plant is installed, it may have to process different coals. Price fluctuations in coal, supply agreements, social reasons and the ever-changing policies can result in the interest or need to process different types of coal. Coal blending is a well-known topic aiming at selecting the proper mixture of coal types to meet sulfur content and optimize the combustion properties [27]. However, the blending studies in the literature for different feedstocks either for coal [27], gasoline [28], refrigerants [29], detergents [30], paints [31] are limited to the addition of process constraints on the composition of the feed to the mathematical formulation of the problem. Only lately, raw material blending and/or formulation have been coupled with process analysis and design [32]. Martín and Grossmann [33] considered process and product formulation design in the context of algae growing for biodiesel FAEE production. Furthermore, biodiesel (FAME) has been produced from waste considering the NPK composition of digestate for optimal algae growing and the biogas composition for the optimal production of the methanol required for oil transesterification [34]. Hernández et al. [35] presented a methodology to evaluate the mixture of waste for the production of syngas with the appropriate composition for methanol, ethanol and FT-liquids production including the entire process model in the formulation. In this work we have extended this approach to formulate a coal blending problem that includes a detailed model of the technologies responsible for flue

gas processing as a decision making tool to help select the coal blend.

The rest of the paper is organized as follows. Section 2 presents the details of the modelling including operating constraints for the different technologies and regulation constraints on the emissions. In section 3 the formulation is described and the model characteristics. In section 4 we present the results of the operation of the treatment process and the coal blending problem. Finally, section 5 draws some conclusions.

## 2. Process design

A section of coal-based power plants from the boiler to the disposal of flue gas is analyzed to compute the composition of the gas produced and the alternative technologies to remove ash, NO<sub>x</sub>, SO<sub>2</sub> and acids such as HF and HCl. The optimization of the flue gas treatment consists of two stages combining heuristics and superstructure optimization for the selection of the technologies and their allocation.

### 2.1. Heuristic based selection of technologies

There are a number of technologies that have been proposed for particle, NO<sub>x</sub> and SO<sub>2</sub> removal. Particle removal can be carried out using gravity settling chambers, impingement separators, cyclone (centrifugal) separators, electrostatic precipitators (ESPs), fabric filters and wet collectors/scrubbers. Among them, ESPs are typically used when very high efficiencies are required for removing fine particulate matter and very large volumes of gas are to be handled. Therefore, we disregard the rest [36]. Three types of sources are identified for the production of NO<sub>x</sub>, namely, thermal, prompt (fixing N<sub>2</sub> from the atmosphere) and fuel nitrogen. Mostly, there are two types of technologies used in industry, those aimed at reducing their generation by modifying combustion characteristics, including low NO<sub>x</sub> burners, and those that treat the flue gas. We assume that the first measurements have already been included in the current design of the thermal plant and we focus on post combustion modifications that include catalytic (SCR) and non-catalytic (SNCR) abatement [36]. There is also a large number of alternatives to remove SO<sub>2</sub> from a flue gas. They are commonly classified between wet and dry scrubbers. There is a large number of alternatives such as the use of limestone combined with natural or forced oxidation, the use of a mixture of MgO and CaO, the use of high – calcium lime, dual –alkali, dry scrubbing, dry injection, Wellmann-Lord and regenerable MgO [36]. However, in industry, approximately 85% of the flue gas desulfurization units installed in the US are wet scrubbers, 12% are spray dry systems, and 3% are dry injection systems. The removal efficiencies of wet systems are higher than 90% while last dry designs can also reach 90% removal [37]. Thus, for this work we have selected two alternatives: A wet removal system known as the Limestone Forced Oxidation (LFSO) and the dry removal using a Spray drier, Spray dry scrubbers (LSD). Therefore, for the superstructure we only focus on these two.

### 2.2. Process superstructure

In a second stage a superstructure optimization model is formulated for the selection of flue gas treatment technologies by modelling each of the units. The flue gas generated in the boiler can be treated using a non-catalytic NO<sub>x</sub> removal unit within the boiler structure, selective non-catalytic reduction (SNCR). We allow the presence or absence of this technology by defining a split of the flue gas stream. The hot flue gas is later used to reheat up steam before it is sent to the medium pressure section of the turbine. Next, the

possibility of treating the flue gas using a selective catalytic reduction (SCR\_1) as deNOx technology is considered. This technology operates within a range of temperatures. A heat exchanger is allocated before the catalytic reactor to adjust the temperature. However, it is possible that the SCR is not selected at that point of the flue gas treatment chain, thus a bypass is allowed. The subsequent treating step is the removal of particles. We allow the presence or absence of this technology by creating a divider that sends the flue gas to the electrostatic precipitator or through a bypass. The next treatment stage is the removal of SO<sub>2</sub>. Three alternatives are allowed, a bypass, if the SO<sub>2</sub> concentration is already below limits, a wet and a dry removal technology. In the last two cases the flue gas must be cooled down before being fed to the absorption column and heat exchangers are placed before the treatment units. In the case of the dry removal technology, the solids are recovered, and the flue gas is sent to further treatment. Only a fraction of the liquid is reused, the rest is discarded. Finally, it may be interesting to locate the catalytic removal of NOx by the end of the trail (SRC\_2). A bypass is also allowed in case the concentration of particles NOx and SO<sub>2</sub> is already within the limits. Otherwise, at this point the flue gas must be heated up before feeding the catalytic reactor using a heat exchanger. The concentrations of SO<sub>2</sub> and NOx must meet the legal limits at the end of the processing train. Fig. 1 shows the superstructure of alternatives that is solved towards the optimal flue gas deNOx and deSO<sub>2</sub>.

**3. Superstructure model formulation**

All the units involved in the process are modeled using experimental data, mainly for removal ratios as a function of process conditions, rules of thumb, thermodynamic and chemical

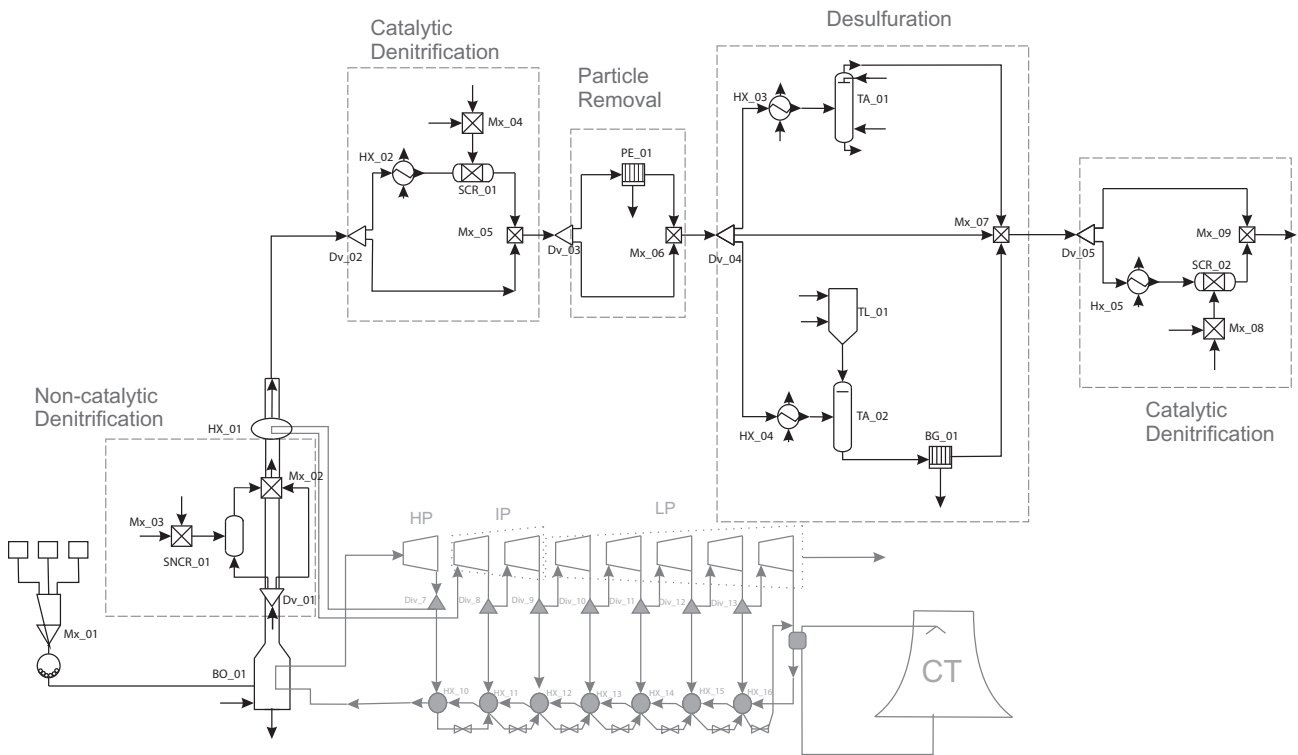
equilibrium and mass and energy balances applied to the following list of species:

{C, CO, CO<sub>2</sub>, O<sub>2</sub>, S, SO<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, F<sub>2</sub>, NO, NO<sub>2</sub>, ash, NH<sub>3</sub>, H<sub>2</sub>O, CaO, CaCO<sub>3</sub>, CaSO<sub>3</sub>, CaSO<sub>4</sub>, HCl, HF, CaCl<sub>2</sub>, CaF<sub>2</sub>, H<sub>2</sub>}.

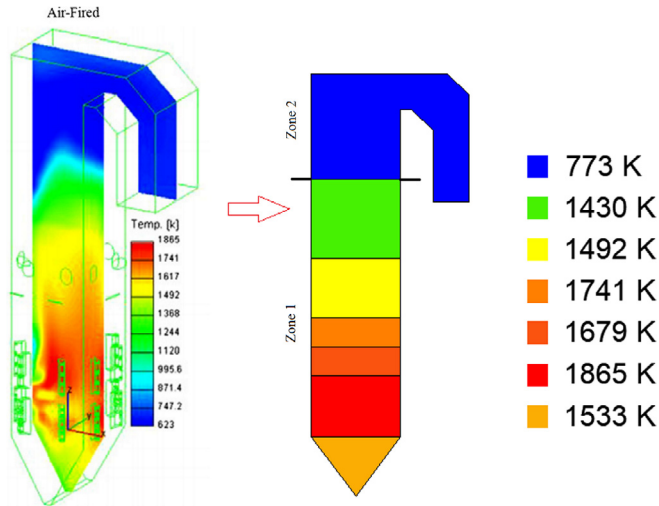
In this section we present the modelling issues of each of the main units. Splitters, triangles in Fig. 1, and mixers, crossed squares in Fig. 1, are modeled based on simple mass and energy balances. Stream mixing is assumed to be adiabatic and stream splitting is isothermal. Heat exchangers are modeled using a mass balance assuming no species change and an energy balance assuming no losses, using heat capacities as a function of the temperature in the form of polynomials [38]. The rest of the units are modeled based also on mass and energy balances. However, along the following subsections we present the particularities of the models for the main units such as boiler, selective non-catalytic reduction of NOx, (SNCR), selective catalytic reduction of NOx (SCR), electrostatic precipitator, wet and dry systems for SO<sub>2</sub> removal.

*3.1. Boiler model*

The operation of the boiler depends on the actual design of the boiler and the burners, the composition of the coal used, resulting in the energy generated and the composition of the gas. In this work we assume that the geometries of the boiler and of the burners are given and the implementation of measures to reduce NOx and SO<sub>2</sub> formation is already considered. Typically, within the boiler a temperature distribution is generated. The particular profile depends on the fuel and the fuel to air ratio. Thus, the gas composition is computed as a function of the temperature profile



**Fig. 1.** Superstructure for flue gas denitrification and desulfurization.



**Fig. 2.** Temperature profile of an air fired coal burner. Zone 1: Flame section. Zone 2: Upper region, Experimental data from [11].

where atom balances and chemical equilibria must also hold. Experimental data or a detailed CFD model of the boiler can be used to compute the temperature profile. For proprietary issues, public data from the literature of an industrial air fired burner are used instead [11]. To compute the species equilibrium, we divide the boiler into two parts, zone 1, the flame section, and zone 2, the upper one, see Fig. 2. The temperature of each region is computed as an area average. To determine this temperature from the profile, each of the regions is discretized using a grid. For zone 1, 6 subregions are considered, while for zone 2, that presents a more homogeneous temperature distribution, only 1 region has been used. We compute the equilibria in the lower section and later we recomputed the NO to NO<sub>2</sub> equilibrium in the cooler region.

### 3.1.1. Flame section (zone 1)

The average temperature is computed out of the spatial distribution of temperatures using eq. (1). The relative areas and their correspondent temperatures are computed from [11].

$$T = \sum_{area} a_i T_i \quad (1)$$

The 6 subregions of zone 1 represent, from bottom to top in Fig. 2, areas of 13.3, 23.6, 31.8, 11.3, 12.2 and 7.6%. Using this temperature, we compute the equilibrium that generates the various species. The following species and equilibria are considered in the analysis.

1. Carbon burning. It is the source of energy in the process.



Experimental data at industrial scale shows that around 99% of the coal is burned into CO and CO<sub>2</sub>. Thus, 1% unburned coal based on this rule of thumb is assumed. Out of it, 20% is slang while the rest, 80%, is dragged by the flue gas [39]. The actual ratio between CO and CO<sub>2</sub> depends on a number of other reactions such as Boudard reaction [38]. The equilibrium is given by the following equation:

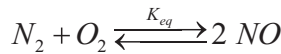


$$K = \frac{P_{CO}^2}{P_{CO_2}} \Rightarrow \log(K) = 9.1106 - \frac{8841}{T} \quad (4)$$

However, we use experimental data from the literature to impose a CO<sub>2</sub> to CO ratio of 1.198 [40].

2. NO production.

It is produced following two reactions given by eq. (5):



The kinetic constants for the direct and indirect reactions for the two original ones are given as eq. (6) [41] and allow us to compute the equilibrium constants for each reaction and the overall production of NO.

$$\begin{aligned} k_1 &= 1.8 \cdot 10^8 \cdot \exp\left(-\frac{38,370}{T}\right) \\ k_{-1} &= 3.8 \cdot 10^7 \cdot \exp\left(-\frac{425}{T}\right) \\ K_1 &= \frac{k_1}{k_{-1}} \\ k_2 &= 1.8 \cdot 10^8 \cdot \exp\left(-\frac{4,680}{T}\right) \\ k_{-2} &= 3.8 \cdot 10^7 \cdot \exp\left(-\frac{20,820}{T}\right) \\ K_2 &= \frac{k_2}{k_{-2}} \end{aligned} \quad (6)$$

Due to numerical issues when using the individual equations, the individual kinetic constants in eq. (6) have been rearranged into a global equilibrium constant as follows, eq. (7):

$$K_{eqNO} = K_1 \cdot K_2 = 22.44 \cdot \exp\left(-\frac{21,805}{T}\right) \quad (7)$$

3. NO<sub>2</sub> production: It follows the reaction below [42], eq. (8):



$$K_{eqNO_2} = 2.75369 \cdot 10^{20} \cdot T^{-6.95528} \quad (9)$$

Other nitrogen oxides can also be produced in the boiler, such as N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>, but the concentrations are negligible in the flue gas [43]. Typically, NO<sub>x</sub> consists of 95% NO and 5% NO<sub>2</sub> [44]. We use this proportion to validate the model results.

4. Sulfur combustion [45]. We assume 100% conversion of the sulfur into SO<sub>2</sub> [39]



5. HCl production [46]. We assume 100% conversion [39].



6. HF production [47]. We assume 100% conversion [39].



Apart from the equilibria, the atom balances must also hold, eq. (13):

$$\begin{aligned} \sum_{in=\{C\}} n_C &= \sum_{out=\{CO, CO_2, C, ash\}} n_C \\ \sum_{in=\{N, N_2\}} n_N &= \sum_{out=\{NO, NO_2, N_2\}} n_N \\ \sum_{in=\{O_2, H_2O\}} n_O &= \sum_{out=\{O_2, NO, NO_2, SO_2, H_2O, CO, CO_2\}} n_O \\ \sum_{in=\{F\}} n_F &= \sum_{out=\{HF\}} n_F \\ \sum_{in=\{Cl\}} n_{Cl} &= \sum_{out=\{HCl\}} n_{Cl} \\ \sum_{in=\{H_2, H_2O\}} n_H &= \sum_{out=\{H_2, HCl, HF, H_2O\}} n_H \end{aligned} \quad (13)$$

### 3.1.2. Upper section (zone 2)

In this section an average temperature computed from the temperature profile is assumed to recompute the equilibrium using eqs. (8) and (9) again to determine the ratio between NO and NO<sub>2</sub> in the flue gas exiting the boiler.

The composition of the gases provided by the model is validated by personal communication with the company.

Finally, the excess of air, up to 30%, determines the efficiency of the combustion [48]:

$$\eta_{Boiler} = 0.2473 \cdot \%_{excess,air} + 0.6016 \quad (14)$$

### 3.2. Electrostatic precipitator

The electrostatic precipitator is in charge of removing the particles in suspension. It provides them with an electric charge so that they are attracted by the walls. The removal efficiency depends on the particle size and the strength of the electric field [49,50]. The unburned coal is also removed at this point [39]. With the appropriate field generated, the efficiency is already close to 100% and thus the particle size is the yield defining parameter [51]. The target is to reduce the particle concentration below 50 mg/Nm<sup>3</sup> [52].

The precipitator is modeled using a mass balance where only the solids are removed from the gas stream, a removal ratio and an energy balance, see eq. (15). The typical exit temperature is around 423 K [53].

$$\begin{aligned} \eta(d) &= f(\text{size}) \\ \text{Particle}_{\text{Removal}} &= \sum \eta(d) n_{\text{Particle}}(d) \\ \eta_{PE} &= \frac{\text{Particle}_{\text{Removal}}}{\text{Particle}_{\text{in}}} \end{aligned} \quad (15)$$

To compute the removal yield,  $\eta$ , the information on the performance of an electrostatic precipitator as a function of the particle size as presented by Nichols and McCain [54] is used. We consider a particle size distribution discretized into 7 sizes, eq. (16). Most of the particles are of 10  $\mu\text{m}$ , based on industrial experimental data

[39]. Using the removal efficiency from the literature discretized per particle size [54], the matrixes in eq. (16) are developed:

$$\begin{aligned} \text{PSD}(\phi_{\text{particle}}) &= \begin{pmatrix} 0.075 & 0 \\ 0.2 & 0 \\ 0.5 & 0 \\ 1.5 & 0 \\ 2 & 0 \\ 5 & 0.01 \\ 10 & 0.99 \end{pmatrix} \eta(\phi_{\text{particle}}) \\ &= \begin{pmatrix} 0.075 & 0.99 \\ 0.2 & 0.95 \\ 0.5 & 0.90 \\ 1.5 & 0.96 \\ 2 & 0.97 \\ 5 & 1 \\ 10 & 1 \end{pmatrix} \end{aligned} \quad (16)$$

The estimation of the cost for the electrostatic precipitator is given by Miller [36], where  $Q_y$  is the volume of gas (Nm<sup>3</sup>) processed in a year. The advantage of this type of cost functions is that if the technology is not selected, no flowrate is processed and, as a result, there is no cost associated.

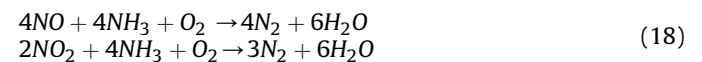
$$\text{Cost}_{PE} = 2.85 \cdot (Q_y) + 8.50 \cdot (Q_y) \quad (17)$$

### 3.3. Denitrifier

The limit for NO<sub>x</sub> concentration in the flue gas in the Spanish law is 600 mg/Nm<sup>3</sup> [52]. Therefore, the concentration of NO<sub>x</sub> in the flue gas after processing must be below this limit.

#### 3.3.1. Selective catalytic reduction (SRC)

The allocation for the denitrifier technology in the flue gas treatment chain depends on the source of the flue gas. Coal thermal plants generate flue gases that contain high concentration of dust. To process these kind of flue gases, the selective catalytic denitrifier (SCR), is typically located just after the boiler and before the electrostatic precipitator (SRC\_1) [55]. Alternatively, tail end denitrifier technology can also be used (SRC\_2). This option requires flue gas reheating. To provide generality to the superstructure we consider both alternatives for the allocation of the SCR technology. In both cases the reduction of NO<sub>x</sub> takes place using NH<sub>3</sub> following the reactions given by eq. (18). Before the SRC, the temperature must be adjusted using a heat exchanger so that the operating temperature ranges within 545–650 K [44]. The ammonia is fed at 423 K with a composition of 99.5% ammonia and the rest dry air [56]. An excess of ammonia with respect to the stoichiometric is used, typically 5% [57].



Oxygen is added using an air to ammonia ratio of 20:1, to work below flammability limits [55]. The air is assumed to be atmospheric air with moisture. The removal yield, or the conversion of the reactions, is a function of the temperature as given by a figure in Rosenbert and Oxley [57]. We developed a correlation to predict the removal efficiency as a function of temperature as follows, eq. (19). Good fitting between the data and the equation is achieved:

$$\begin{aligned} \eta &= 6.6537 \cdot 10^{-6} \cdot T(K)^3 - 1.523 \cdot 10^{-2} \cdot T(K)^2 + 11.43 \cdot T(K) \\ &\quad - 2,731.8 \end{aligned} \quad (19)$$



The SRC is modeled based on the stoichiometry of the reactions taking place, eq. (18), the conversion as a function of the operating temperature, eq. (19), a mass balance accounting for the feed of  $\text{NH}_3$  and additional air, and an adiabatic energy balance [38].

The investment cost of this unit is estimated using the correlation from Miller [36], eq. (20), where  $m_{\text{NOx}}$  is tons processed in a year of NOx:

$$\text{Cost}_{\text{SCR}} = 5,000 \cdot \frac{1}{0.8} (m_{\text{NOx}} \cdot (1 - \eta_{\text{SCR}})) \quad (20)$$

### 3.3.2. Selective non catalytic reduction (SNCR)

The SNCR is actually installed within the boiler since it requires high operating temperatures. In our model the SNCR is located between zone 1 and zone 2. This region corresponds to the section of the boiler that produces overheated steam for the turbine. The operating temperature is the same as that computed for the boiler. We can use ammonia or urea. However, the use of urea increases the production of  $\text{N}_2\text{O}$  and ammonia is used instead. The chemical reactions for the reduction of the NOx are the same as those presented for the SCR technology, eq. (18). However, in this case the removal efficiency depends on the excess of ammonia [55]. Ammonia is fed to the boiler with an air to ammonia ratio of 20:1, to avoid safety issues [55]. The air is atmospheric humid air and ammonia is provided with the same composition as before, 99.5 ammonia and the rest dry air [55].

The SNCR is modeled based on the stoichiometry of the reactions taking place, eq. (18), accounting for the feed of  $\text{NH}_3$  and additional air, the yield as a function of the excess of ammonia, eq. (21), and an adiabatic energy balance for stream mixing because we neglect the reaction heat due to the small amount of NOx in the stream. An empirical model is developed to predict the removal yield, eq. (21), using experimental data in a figure by Dobrei [58]. The removal efficiency is correlated versus the stoichiometric excess of ammonia,  $\eta$ . Good fitting between eq. (21) and the data is achieved.

$$\text{NH}_{3,\text{excess}} = 0.0267 \cdot \eta - 0.0202 \quad (21)$$

The investment cost is estimated using the information in Miller [36], where  $m_{\text{NOx}}$  is tons of NOx processed in a year.

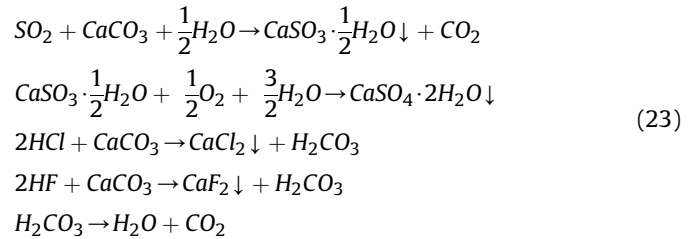
$$\text{Cost}_{\text{SCR}} = 2,500 \cdot \frac{1}{0.8} (m_{\text{NOx}} \cdot (1 - \eta_{\text{SCR}})) \quad (22)$$

## 3.4. Desulfuration

The target for  $\text{SO}_2$  in the flue gas exiting the treatment is 200  $\text{mg}/\text{Nm}^3$  according to the Spanish regulations [52]. LFSO and LSD operate at a reduced temperature. Thus, heat exchangers are used to adjust the temperature before treatment.

### 3.4.1. Wet removal (LFSO)

The optimal operating temperature is 323 K [59]. Thus, a heat exchanger is needed to cool down the flue gas before feeding it to the absorber column. The mechanism for the removal of  $\text{SO}_2$  using a wet process follows the reactions below, eq. (23), where  $\text{SO}_2$  is treated with limestone and the product is oxidized to gypsum [60].



To obtain gypsum, a 3 to 1 ratio of moles of  $\text{O}_2$  to  $\text{SO}_2$  is needed [60]. The removal efficiency depends on the ratio between the flue gas flow and the slurry containing the  $\text{CaCO}_3$ . Typically, a slurry 20% w/w of  $\text{CaCO}_3$  is used [61]. Using the experimental data in Zhong et al. [61], we developed a surrogate model to estimate the removal ratio as a function of the liquid to gas ratio given in liters per  $\text{Nm}^3$  of gas, eq. (24). Good fitting with the experimental data is obtained.

$$\begin{aligned} \eta = & -5.06993 \cdot 10^{-4} \cdot \left(\frac{L}{G}\right)^2 + 2.591958 \cdot 10^{-2} \cdot \left(\frac{L}{G}\right) \\ & + 0.653958042 \end{aligned} \quad (24)$$

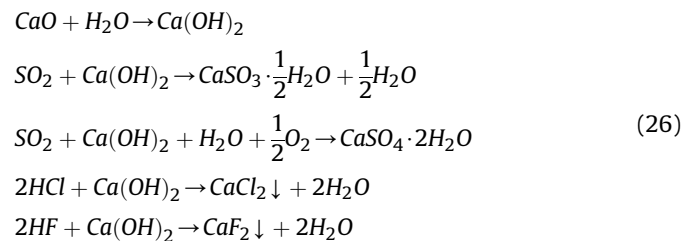
The LFSO process is modeled using a mass balance based on the stoichiometry of the reactions shown above, eq. (23), the removal efficiency as a function of the (L/G) ratio, eq. (24), and an adiabatic energy balance to compute the exit temperature. The gas exits the unit saturated at the operating temperature. Antoine correlation is used to compute the moisture in the flue gas.

The investment cost of the technology is estimated by the  $\text{SO}_2$  eliminated in tons per year [36] using eq. (25):

$$\text{Cost}_{\text{LFSO}} = 3,700 \cdot ((m_{\text{SO}_2}) \cdot (1 - \eta_{\text{LFSO}})) \quad (25)$$

### 3.4.2. Dry removal (LSD)

Dry removal uses a CaO slurry with 35% of water to the spray tower. The feed temperature must be between 393 K and 448 K. The reaction mechanism is as follows, eq. (26) [62]:



The typical molar ratio  $\text{CaSO}_3$  to  $\text{CaSO}_4$  is 9:1, because the absence of forced oxidation leads to a low yield of gypsum [63]. The removal efficiency depends on the fraction of S in the coal and the stoichiometric molar ratio between Ca and S. A two-stage fitting procedure [64] is used to produce a general model considering both variables. A range of sulfur concentrations, %S, from 2.5 to 6% and Ca/S ratios of 0.7–1.5 are common and will be imposed as lower and upper bounds for these variables. Eq. (27) shows good fitting with the experimental data.

$$\begin{aligned} \eta = & (-0.4554 \cdot (\%S) + 1.2451) + (0.3469 \cdot (\%S) + 0.6286) \cdot \left(\frac{\text{Ca}}{\text{S}}\right) \\ & + (-0.0243 \cdot (\%S) - 0.56325) \cdot \left(\frac{\text{Ca}}{\text{S}}\right)^2 \end{aligned} \quad (27)$$

The LSD process is modeled using a mass balance based on the stoichiometry of the reactions shown above, eq. (26), the removal efficiency, eq. (27), and an adiabatic energy balance. The gas exits the unit saturated at the temperature, typically from 338 K to 448 K. Antoine correlation is used to compute the moisture in the flue gas. The investment cost of the technology is estimated as a function of the SO<sub>2</sub> eliminated in tons per year [36].

$$Cost_{LDS} = 4,400 \cdot ((m_{SO_2}) \cdot (1 - \eta_{LFSO})) \quad (28)$$

### 3.5. Solution procedure

The optimization of the gas treatment chain presents several steps. After the pre-screening of technologies based on industrial experience, a model for a superstructure with the most used/promising ones is formulated. Surrogate models for all units are developed as presented along section 3.

We consider two steps in the solution of the mathematical problem, namely, technology selection and operation.

The first step corresponds to a design problem. We formulate the problem as a large non-linear programming (NLP) for the optimal selection of technologies for a fixed carbon feed to the boiler. Due to the complexity of the non-linear models we avoid the use of integer variables by allowing bypasses. The optimization uses an economic objective function since the aim is to be able to meet the current limits imposed by the legislation. We consider a typical mix of coals based on actual data of a particular day. The model is 4500 var and 4100 eqs, written in GAMS and solved using a multistart procedure with CONOPT. 3.0 as the preferred solver with eq. (29) as the objective function.

$$Cost_{Annual} = \frac{1}{3} \left( \sum_{deNOx \in \{SCR, SNCR\}} Cost_{NOx} + Cost_{PE} + Cost_{LSD} + Cost_{LFSO} \right) + Cost_{NH3} + Cost_{CaCO3} \quad (29)$$

Once the technologies are installed in a facility, the market and/or political decisions are behind the selection of the coal or coal blend to be processed. Thus, the second step is the everyday problem that the managers of the plants must solve on the decision on the coal blend to burn. An extending blending problem is formulated for the optimal set of technologies to select on the optimal coal blend used including the detail models for the flue gas treatment technologies.

Two different objective functions are used. First, we consider the treatment costs. The model is slightly smaller than the entire superstructure, 3100 var and 2800 eqs. written in GAMS and solved using a multistart procedure with CONOPT. 3.0 as the preferred solver using eq. (30) as objective function.

$$Cost_{Annual} = \frac{1}{3} (Cost_{SCR-1} + Cost_{PE} + Cost_{SOx}) + Cost_{NH3} + Cost_{CaCO3} + Cost_{NatCoal} + Cost_{ImpCoal} + Cost_{FuelCoal} \quad (30)$$

Finally, the different heating values of the various coals provide another interesting tradeoff. Even though in this work the power island of the plant is not considered, in eq. (30) we add the benefit of the power produced by each coal type. Assuming 50% efficiency from thermal energy to power, based on the ratio of the actual

power capacity of the plant (350–400 MW) and the thermal energy involved in the coal blends used (700–780 MW), and an electricity price of 0.07 €/kWh we reevaluate the blending problem. The size of the blending model remains the same, 3100 var and 2800 eqs. written in GAMS and solved with eq. (31) as objective function using a multistart procedure with CONOPT. 3.0 as the preferred solver.

$$Cost_{Annual} = \frac{1}{3} (Cost_{SCR-1} + Cost_{PE} + Cost_{SOx}) + Cost_{NH3} + Cost_{CaCO3} + \sum_{i \in coal} Cost_{coal} - P_{Electricity} \cdot \eta_{ToE} \cdot \sum_{i \in coal} HHV_i \cdot Coal_i \quad (31)$$

Note that no global optimal solution is claimed. The complexity of the mathematical model involving non-linear a non-convex terms may yield local solutions. Furthermore, the solution is also subjected to the decision criteria, the objective function. For that purpose, two different ones are evaluated to evaluate the robustness of the solution.

## 4. Results

We consider the use of three types of coal, national, imported and crude tar coal. The compositions and the prices are presented in Table 1. A feed of 23 kg/s of coal or coal mixture is used as reference for a typical production capacity of around 350–400 MWe [39]. To compute the flue gas exiting the boiler, the temperature profile provided in the literature was used [11]. Other examples from the literature have also been studied with average temperatures within 5% error [65]. The resulting flue gas composition was corroborated with industry to validate the model [39,52]. This section is divided in two. The first one presents the process design problem. The second one presents an extended coal blending problem evaluating the selection of technologies as a function of the coal mixture.

### 4.1. Process design

The superstructure in Fig. 1 is applied to a particular case based on data provided from a power plant in the Northwestern of Spain, La Robla, using a coal blend of 26% national, 26% imported and the rest crude coal tar. This blend shows an availability of 717 MW. The optimization of the superstructure in Fig. 1 for this case, selects the use of selective catalytic reduction and dry removal of SO<sub>2</sub> using LSD. However, in some of the units there is a fraction of the total flow of flue gas that is not processed through the units, but a bypass is suggested, see Table 2. The results are reported per thermal energy available in the coal or coal blend used in each case.

The solution to the superstructure in Fig. 1 involves the selection

**Table 1**  
Coal composition and price [66,67].

	National [54]	Imported [55]	Crude coal tar [55]
H <sub>2</sub> O	0.1357	0.0988	0.1038
C	0.688493	0.705099	0.779552
H <sub>2</sub>	0.022585	0.030706	0.03033
O <sub>2</sub>	0.000165	0.000579	0.021109
S	0.018631	0.004351	0.041942
N <sub>2</sub>	0.013844	0.018164	0.017093
Cl	0.000140	0.00012	0.00004
F	0.000072	0.000076	0.000017
Ash	0.12037	0.142105	0.006117
Price (€/t)	69.36	103.3	23.59
HHV(kj/kg)	26.380	28.073	35.426

**Table 2**  
Costs of the units selected by case.

Costs	PE (€/kW)	NOx Removal (€/kW)	SO <sub>2</sub> Removal (€/kW)	Total (M€/yr)
Superstructure	10.691	142.633	200.651	94.5
Bypass not processed		16%	1%	

**Table 3**  
Costs of the units selected by case.

Costs	PE (€/kW)	NOx Removal (€/kW)	SO <sub>2</sub> Removal (€/kW)	Total (M€/yr)
SCR_1 + LFSO	12.114	171.438	165.690	96
LFSO + SCR_2	11.735	228.015	165.690	135
SCR_1 + LSD	10.592	142.640	200.671	89
LSD + SCR_2	10.427	181.328	200.580	123

of PP followed by SCR and LSD. However, 16% of the flue gas is not fed to the SCR and it is suggested that 1% of the flow is not fed to the LSD. The decision on the installation of fractional bypasses to the desulphurizer and denitrifier is difficult to be implemented in industry. It is easier to process the entire flow of flue gas through the units. Therefore, instead of solving the mathematical model for the entire Fig. 1, we consider four flowsheets consisting of the combination among the two deNOx and the two deSOx removal technologies, disregarding the use of the deNOx by the end of the processing train.

In Table 3 we compare the solution to the four main alternative flowsheets without the possibility of bypass. It is possible to see that the values of the objective function, column Total (M€/yr) in the table, are of the same order of magnitude as those in Table 2. Furthermore, the optimal solution involves the same technologies and in the same order as described in the solution of the complete superstructure given by Fig. 1, SCR and LSD. The main operating conditions for the units are presented in Table 4.

The differences in the objective function using LFSO or LSD are within 10% margin for the coal blend used in this case study. However, it is more interesting to use the catalytic removal of NOx before the electrostatic precipitator than any other alternative for the removal of NOx. Actually, the cost for the removal of NOx is the same no matter the allocation of the unit. The main difference is that by the end of the processing train the flue gas is already cold and thermal energy is required to heat up the flue gas, reducing the efficiency of the plant. In terms of the operating conditions, see Table 4, the removal ratio of NOx is always above 70% and the variability in the yield is related to the removal ratio required to meet the emission limits. In the case of the removal of SO<sub>2</sub>, the optimal operation conditions are always the same for the technology no matter the option selected for the removal of NOx. Note that we do not claim global optimum.

**Table 4**  
Main operating conditions.

	Electrostatic Precipitator (PE)	NOx Removal	SO <sub>2</sub> Removal
SCR_1 + LFSO	Yield:100	$\eta = 72.667$ T(K) = 580.457	L/G: 15 $\eta = 0.929$
LFSO + SCR_2	Yield:100	$\eta = 83.263$ T(K) = 608.5	L/G:15 $\eta = 0.929$
SCR_1 + LSD	Yield:100	$\eta = 89.240$ T(K) = 638.446	Ca/S = 0.949 $\eta = 0.946$
LSD + SCR_2	Yield:100	$\eta = 74.241$ T(K) = 583.9	Ca/S = 0.931 $\eta = 0.956$

## 4.2. Coal selection: blending problem

The blending problem is analyzed considering a fixed flowsheet consisting of the SCR, PE and either LFSO or LSD. Four items are considered in this analysis: 1) Optimal blend as a function of the cost of processing the emissions. 2) Cost of the coals so that the national one is selected. 3) Cost of the technology for the selection of the national coal and 4) Optimal blend for maximum power production with emissions limitations. Taking into account that around 85% of the industrial plants already have LFSO technologies installed, including La Robla thermal plant, León (Spain), we will be considering this technology first for our evaluation of the optimal blend considering the three coals presented in Table 1. In a second case, the LSD technology is also evaluated following the same procedure.

Thus, we optimize first the coal selection among the national coal from Spain, the imported coal and crude coal tar, using eq. (30) as objective function. The flue gas treatment train consists of SCR followed by PE and the LFSO desulphurizer technology. The tradeoff corresponds to the coal cost versus its sulfur content. It turns out that the optimization selects the imported coal. No blend is selected. In spite of being the most expensive coal, see Table 5, the operating costs of the facility including the flue gas processing are the lowest. In Table 5 it is possible to see that the cost of the LFSO process for SO<sub>2</sub> removal is 4 times larger when using the national coal compared to the use of imported one mitigating the difference in the cost of the raw materials, which results in a small difference in the total operating cost.

Based on these results, a sensitivity analysis was carried out to determine the critical price of the imported coal so that national coal was preferred. It turns out that for a price of imported coal from 107.4 €/t, national coal is preferred. Thus, for imported coal prices 4% above the current value, national coal can be competitive.

The cost of the treatment technologies also evolves in time. Apart from evaluating the critical cost for imported coal, the effect of the cost of the technology on the coal selection is also evaluated. By performing a sensitivity analysis, the cost for LFSO technology must decrease by 12.5% with respect to the base case provided by eq. (25) for national coal to be preferable. Thus, by technology development and optimization it would be attractive to use national coal. These two issues, coal price and treatment technology costs, have many social implications. Many families in the North-west region of Spain live by the coal and related industries. After generations, the expertise is in coal industry and mining operations. Therefore, either the operators are trained otherwise, or we provide a more efficient and cost-efficient sulfur removal process. Alternatively, subsidies can be provided so that the economic advantage of using imported coal is mitigated. Note that these solutions are local, not global optimization is claimed and therefore further studies can be carried out.

The energy per kg of coal is inversely related to the sulfur content in these three coals. As a result, the crude coal tar, in spite of presenting large costs for desulfurization, is the one that shows the best cost per unit of power produced, as seen in Table 5. The blending problem is solved for a different objective function that includes the power produced as benefit, eq. (31). By solving the updated blending problem with eq. (31) as objective function, it turns out that the optimal blend consists of 25% imported coal and the rest crude coal tar. Table 6 summarizes the breakdown of the treatment cost and the total amount of SO<sub>2</sub> and NOx removed. Note that the power within the coal blend is 773 MW, 7% larger than the base case used in the design study. Using this objective function, for national coal to be used the cost of imported coal must be around twice its current cost. A more integrated approach including the evaluation of the power cycle is to be added.



**Table 5**

Cost for gas processing for the various coal types.

	Coal (€/t)	SCR 1 (€/kW)	LFSO (€/kW)	TAC (M€)	€/MWh	NOx remov (kg/s)	SO <sub>2</sub> remov (kg/s)
National	69.36	153.123	138.204	116.849	410.4	$6.45 \cdot 10^{-4}$	0.786
Imported	103.3	144.542	30.329	114.457	385.2	$6.48 \cdot 10^{-4}$	0.184
Crude coal	23.59	128.011	231.683	132.132	352.8	$7.24 \cdot 10^{-4}$	1.77

**Table 6**

Cost for gas processing for mixed of coals using LFSO: Economic objective.

	N/I/C	PE (€/kW)	SCR 1 (€/kW)	LFSO (€/kW)	TAC (M€)	€/MWh	NOx remov (kg/s)	SO <sub>2</sub> remov (kg/s)
Mixed	0/25/75	10.280	91.880	193.941	-100.12	-281.6	$4.925 \cdot 10^{-04}$	1.405

**Table 7**

Cost for gas processing for the various coal types.

	Coal (€/t)	SCR 1 (€/kW)	LSD (€/kW)	TAC (M€)	€/MWh	NOx remov (kg/s)	SO <sub>2</sub> remov (kg/s)
National	69.36	158.984	167.593	125.693	450	$6.69 \cdot 10^{-4}$	0.802
Imported	103.3	149.501	36.202	117.19	396	$6.70 \cdot 10^{-4}$	0.184
Crude coal tar	23.59	Does not meet environmental limits					

**Table 8**

Cost for gas processing for mixed of coals using LSD: Economic objective.

	N/I/C	PE (€/kW)	SCR 1 (€/kW)	LSD (€/KkW)	TAC (M€)	€/MWh	NOx remov (kg/s)	SO <sub>2</sub> remov (kg/s)
Mixed	0/58/42	10.721	141.372	153.297	-69.967	-212.110	$7.031 \cdot 10^{-4}$	0.866

A similar study is carried out for considering the LSD technology for the removal of SO<sub>2</sub>. The particular feature of this technology is its lower removal yield. The optimization of the blending problem using eq. (30) as objective function results in selecting imported coal. Table 7 shows the performance and the cost of processing the flue gas using LSD. Comparing Tables 5 and 7 it can be seen that the use of LFSO technologies is cheaper than using LSD technologies when particular coals are used. Furthermore, in spite of the lower cost of the crude coal tar, its larger content in sulfur does not allow meeting the environmental constraints. Again, for national coal to be used the cost of imported coal must be around twice its current cost and it is difficult that a decrease in the cost of the LSD technology makes the use of national coal preferable. Finally, the blending problem is solved again using eq. (31) to evaluate the trade-off between sulfur content and power production of the various coal types. The solution of the model suggests the use of a combination of 58% imported and the rest crude tar coal. This blend contains the same power that the original blend used in the design case study, 717 MW. Note that no global optimum can be claimed. The main operating results are summarized in Table 8. The largest SO<sub>2</sub> removal yield achieved using the LFSO technology results in larger profit using this alternative. As a result, LFSO is the best technology among the two for a wider range of blending ratios.

## 5. Conclusions

In this work we have developed a flexible framework for the optimal selection of flue gas treatment technologies. The extended framework allowed formulating a blending problem that includes process models to evaluate the selection of the coal and the critical prices resulting in a useful tool for decision makers in the power industry. The framework is based on a mathematical optimization approach that models each of the units using surrogate models based on first principles and industrial data developing a superstructure of alternative technologies, catalytic and non-catalytic

NOx abatement, particle removal and SO<sub>2</sub> removal using wet and dry systems, aiming at minimum total annual cost for flue gas processing. Further CFD modelling of the boiler can be performed as a preliminary stage.

This general framework is used to evaluate the optimal gas treatment technologies in a power plant in Spain for particle, NOx and SO<sub>2</sub> removal the operating conditions as well as the limits that would allow selecting the use of local coal in terms of coal price and technology cost. The optimal train of operation consists of the use, in this order, of catalytic NOx removal, an electrostatic precipitator and LSD SO<sub>2</sub> removal. However, this solution is for a particular coal blend. Considering the most typical technology, LFSO, imported coal is the preferred raw material, but if its price increases by 4%, national coal becomes the raw material of choice. Alternatively, a 12.5% decrease in the cost of LFSO also suggests the use of national coal which means that it could be possible to maintain the local industry. If the energy available in the coal is also considered, crude tar coal is included in the blend up to 75% and the rest imported coal so that the SO<sub>2</sub> emissions are maintained within the legal limits. The larger removal yield from the LFSO provides flexibility and shows larger benefits when using this technology. Therefore, this is the technology of choice for general use.

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## Nomenclature

Cost <sub>i</sub>	Cost of item i (€/unit)
k	Kinetic constant (m <sup>3</sup> /mol s)
K	Equilibrium constant (bar <sup>n</sup> )
ESP	Electrostatic precipitator

FAME	Fatty acid methyl ester
FT	Fischer - Tropsch
(L/G)	In L of liquid solution per m <sup>3</sup> of gas
m <sub>i</sub>	tons per year of contaminant (t/yr)
n <sub>i</sub>	Molar flow of species I (mol/s)
n <sub>particle(d)</sub>	Number of particles of sized d
NH <sub>3</sub> excess	Molar excess of ammonia with respect to the stoichiometric one
NLP	Non linear programming
NPK	Nitrogen – Phosphorous-Potassium
P <sub>i</sub>	Partial pressure of species i (bar)
P <sup>Electricity</sup>	Electricity price (€/kWh)
PS	Particle size distribution
Q <sub>y</sub>	: Volume of gas (Nm <sup>3</sup> ) processed in a year (Nm <sup>3</sup> /yr)
T	Temperature (K)

### Symbols

$\alpha_i$	Fraction of area of section i
$\eta_j$	Removal efficiency of technology j
$\eta_{TtoP}$	Thermal to power efficiency
$\phi$	Particle size ( $\mu\text{m}$ )

### Abbreviations

BG	Filter
Div	Splitter
CT	Cooling tower
HP	High pressure turbine
HX	Heat Exchanger
LP	Lower pressure turbine
LSD	Spray dry scrubbers
LSFO	Limestone Forced Oxidation
MP	medium pressure turbine
Mx	Mixer
PE	Electrostatic precipitator
SRC	Selective catalytic reduction of NOx
SRC_1	After boiler
SRC_2	After desulfurization
SNCR	Selective non-catalytic reduction of NOx
TA	Absorption tower
TL:	Tank

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