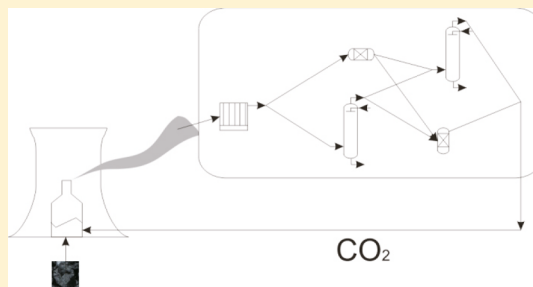


Optimal Flue Gas Treatment for Oxy-Combustion-Based Pulverized Coal Power Plants

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ABSTRACT: Oxy-combustion is recognized as the cleanest technology which uses coal as an energy source. Flue gas clean-up is essential for sustainable operation. In this work, the optimal selection of the flue gas treatment technologies in oxy-combustion power plants is determined. A two-stage procedure combining heuristics and mathematical programming is used to evaluate the technologies involved including the boiler, denitrification, electrostatic precipitation, sulfur dioxide removal, and carbon capture. For plant operation, the coal feed has to be selected. An extended blending problem is solved to evaluate the coal type to be purchased based on its cost and composition. The optimal flue gas processing consists of electrostatic precipitation, followed by dry SO₂ removal, and CO₂ purification using zeolites. No specific denitrification method is required due to the low concentration levels of NO_x generated in oxy-combustion. This flowsheet is used to select one among a mixture of three different types of coal: national, imported, and crude coal tar. However, no mixture is recommended as crude coal tar was the one selected. Even though the processing costs are higher, it is outweighed by the lower cost of the raw material.



1. INTRODUCTION

In spite of the penetration of renewable sources in the energy mix, coal still contributes to 40% of the world's total power production.¹ Although several countries have issued regulations to reduce and even to eliminate coal in the power production sector, in the following years, it will still be an important resource. To reduce CO₂ emissions aiming at meeting the climate change targets of the Paris Agreement, carbon capture technologies have gained interest,^{2,3} but the need to find uses of CO₂^{4,5} and the issues related to its storage present important challenges to the implementation.^{6,7} One carbon capture technology for a more environmentally friendly use of coal as a source of power is oxy-combustion.^{8,9} The advantages behind oxy-combustion lie in the fact that the coal is burned with pure oxygen instead of air. Therefore, instead of being diluted with nitrogen, CO₂ is the accompanying gas allowing a high concentration. This stream can be better treated for the recycle of the CO₂ reducing the NO_x formation. However, impurities such as SO₂ are generated in the gas, even though the removal efficiency is expected to be larger.¹⁰

Work on oxy-combustion has been extensive in the last decade, particularly on evaluating the combustion efficiency,¹¹ including simulations of the boiler,¹² CFD models at different scales,¹³ and its numerical optimization.¹⁴ The general opinion is that oxy-combustion is the most promising alternative to the use of coal combustion for the production of power.¹⁵ A comprehensive review on oxy fuel combustion can be found in the work by Nemitallah et al.⁹ However, most of the work dealing with the flue gas treatment in oxy-combustion has focused on CO₂ capture for its recycle¹⁶ while the entire process of flue gas processing has not received the same attention.¹⁷ The literature on oxy-combustion discusses the

need for particulate and sulfur control,¹⁸ but no systematic analysis is carried out for the flue gas treatment and CO₂ recycle.

In this work, a two-stage optimization approach is used for the design of the flue gas treatment in oxy-combustion power plant facilities. The aim is to purify the stream for recycle and/or reuse of CO₂. A hybrid approach is used¹⁹ where a prescreening of the technologies is carried out in a first stage. Next, a superstructure of alternatives is formulated by developing surrogate models of all the technologies to select the most promising flue gas processing chain for oxy-combustion facilities. The rest of the work is organized as follows: **Section 2** presents the details of the modeling including operating constraints for the different technologies and regulation constraints on emissions. In **Section 3**, a systematic procedure for the selection of the flue gas processing technologies is described together with the model characteristics. In **Section 4**, the results of the operation of the treatment process and the coal blending problem are presented. Finally, **Section 5** draws some conclusions.

2. PROCESS DESIGN

Over the last few years, a large variety of treatments have been developed for CO₂, SO₂, NO_x, and particle removal. A two-stage procedure is considered for the design of the flue gas treatment in oxy-combustion facilities. In this section, the

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flowsheet design for the processing of the oxy-combustion flue gas treatment is presented as well as its use to formulate an extended blending problem as a tool for the selection of the coal blend to be purchased.

2.1. Design Procedure. The optimization of the gas treatment chain in oxy-combustion plants follows several steps as in a previous work.¹⁹ First, the process flowsheet for the gas treatment is designed. This step consists of two stages. The first stage in the design of the flue gas processing consists of a thorough literature review to preselect a number of technologies for the removal of each one of the pollutants. The preselection of methods is based on the analysis of the alternatives that are predominantly employed at the industrial scale. In oxy-combustion boilers, it should be noted that the NO_x generated originates from the impurities within the coal, and thus, they are in small amounts.²⁰ Typically selective catalytic reduction (SCR) and selective noncatalytic reduction are the more common methods for NO_x abatement.^{19,21} Based on a previous work, the selective noncatalytic reduction is not considered although it is employed in some cases at the industrial scale.¹⁹ In the last few years, several methods have been developed for the removal of SO_2 , HF, and HCl. They are classified into wet, dry, and semi-dry. It should be noted that each class includes a number of methods like lime spray drying (LSD), limestone forced oxidation (LFSO), limestone natural oxidation, Mg–O–lime process, Wellman–Lord process, high-calcium lime process, among others.^{21–23} However, the raw material cost and the yield lead to the selection of LFSO and LSD. These processes represent above 85 and 12% of the industrial practice, respectively.²⁴ It should be noted that, on the one hand, LFSO shows larger efficiency than LSD, resulting in a more flexible technology. However, on the other hand, the LSD adopts a more simple technology.²⁵ Regarding CO_2 capture, over the last few years, the number of alternatives has been increasing.²⁶ Nowadays, methods have been developed to remove carbon dioxide are physical and chemical solvents (particularly monoethanolamine, MEA), membranes, adsorption onto solids, pressure/vacuum swing adsorption (PSA), and cryogenic separation.²¹ In the literature, several reviews presenting the alternative technologies are available.²⁶ However, few are the studies that present the cost of carbon capture in the operation of a power plant.²⁷ Lately, also life cycle assessment comparing the technologies has been presented.²⁸ Based on the results and comments of these works, a selection of technologies is considered in this work. Chemical solvent methods are widely used at the industrial scale, in particular, amine-based liquid solvent systems. They are widely studied and tested at the industrial scale, presenting large CO_2 recovery, but the energy consumption in the solvent regeneration stage is high, resulting in large environmental impact.²⁸ Physical solvents are highly efficient for concentrated CO_2 streams.²⁶ However, membranes²⁹ and physical solvents³⁰ require operation at high pressure. The large flow of flue gas prevents from selecting these alternatives. Carbonation is gaining attention due to the high removal yields.^{31,46} Finally, adsorbent beds such as pressure swing adsorption (PSA) systems require low energy and show high performance.³² The main advantage of PSA is the relative low cost and energy efficiency.^{33–35} Therefore, carbonation, absorption in amine solutions, and adsorption in zeolite beds are the preselected methods for carbon capture.^{3,21–23} In this way, the prescreening of the treatment methods results in the selection of the electrostatic precipitator, for particles removal, SCR, for

NO_x removal, lime spray drying (LSD) process and LFSO for sulfur removal process, and finally carbonation/calcination cycle, amine absorption, and PSA systems with zeolites for carbon dioxide removal.

The second stage consists of the development of a superstructure of promising alternative technologies. The units that constitute the superstructure are modeled one by one using experimental data from the literature, first principles, and industrial data. The optimization of the superstructure selects the flue gas treatment technologies. Starting the description at the boiler, its configuration as well as the nozzles^{9,11–13} determine the performance of the oxy-combustion. This performance can be represented by the temperature profile within the boiler is responsible for the flue gas composition. Noncatalyzed reduction was not selected in a previous work,¹⁹ and therefore, only catalytic reduction is preselected to process the flue gas. Next, an electrostatic precipitator is used to remove particulates. Subsequently, the first of the CO_2 capture technologies is allocated. A system consisting of a carbonator and a calcinator is used to capture CO_2 using CaO and producing CaCO_3 . It is a process that must take place at a high temperature, and therefore, it is allocated first downstream. A bypass is allowed in case this technology is not selected. The clean CO_2 recovered after the decomposition of the CaCO_3 is sent to Mx_07 for its reuse. The gases, including O_2 and other traces, are sent to Mx_05 for further treatment. After the carbonator–calciner looping system, the SO_2 removal technologies are used including the wet and dry SO_2 removal methods. A bypass is also allowed in case there is no need for these techniques. Finally, the amine absorption and the zeolite adsorption processes are placed in parallel with a bypass in case CO_2 was already captured in the carbonator–calciner system. The CO_2 captured is recycled. A purge is allowed and an additional feed of CO_2 is also possible. The purge is intended to be further used as a source of CO_2 within the carbon capture and utilization initiative including the production of chemicals such as methane, methanol, and so forth. Each flue gas treatment unit is modeled in detail to formulate a superstructure of alternatives. In this section, the models developed for each of the treatment units are described.

The following section “Superstructure Modeling” presents the modeling issues of the gas treatment units. The superstructure is used to define the optimal selection of flue gas treatments before recycling it to the boiler. The problem formulation becomes a large nonlinear programming (NLP) problem. The flue gas may not be treated in all technologies depending on its purity and processing costs. Thus, bypasses are allowed and the problem is defined using continuous variables instead of integer ones. The main aim is the recycle of the carbon dioxide to the boiler to guarantee the cleaning of the flue gas at a minimum cost.

2.2. Extended Blending Problem. Once the optimal flue gas treatments are installed in the facility, the coal selection problem is evaluated. This is a typical problem in power plants because they have to select the coal to buy based on market price for minimum flue gas treatment costs. The formulation of the problem includes the flowsheet of the treatment technologies while freeing the flows of the different coal types available to be selected.

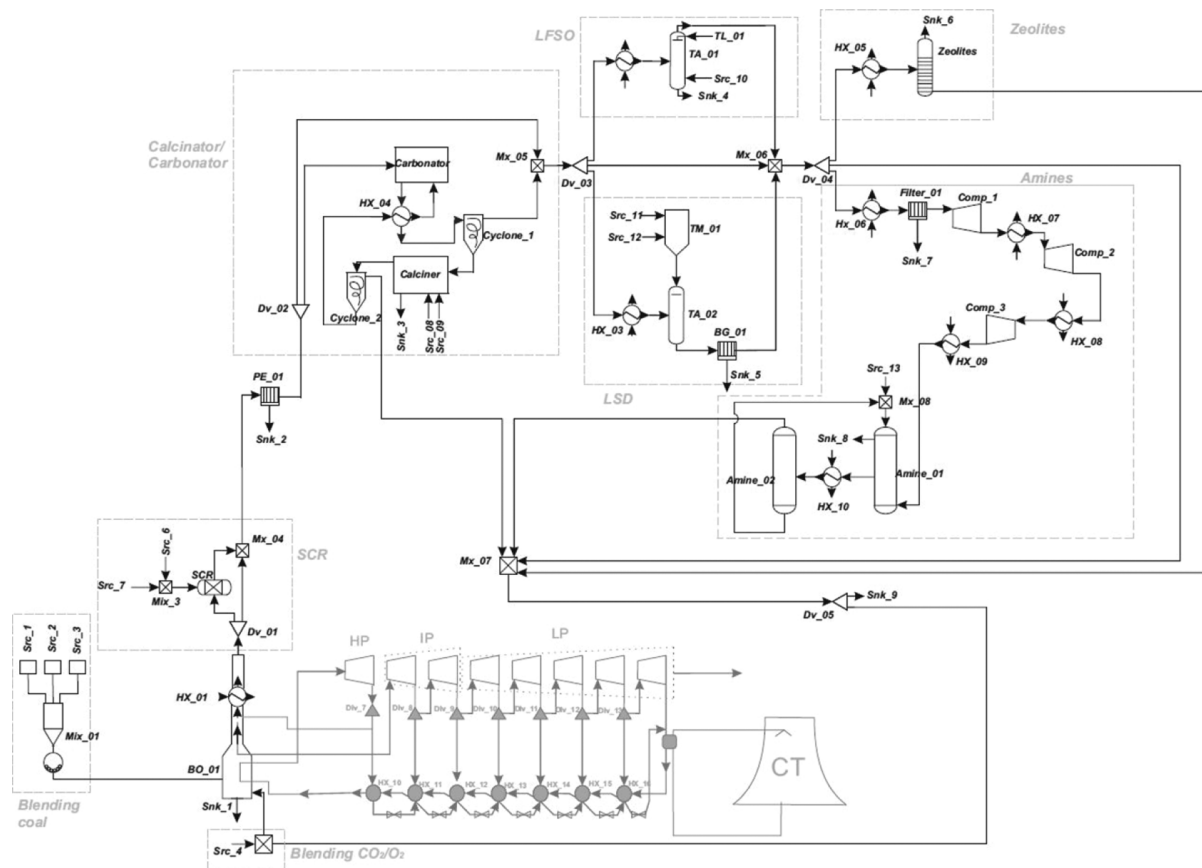


Figure 1. Superstructure for oxy-combustion flue gas processing.

3. SUPERSTRUCTURE MODELING

The process model including all the technologies constitutes a superstructure of alternatives, see Figure 1. In this section, the modeling approach for the different units is presented including the assumptions and the source of the information. The superstructure is based on the selection or nonselection of the different processes described before. For that, splitters are used to allow the use of different processes. In this way, to allow the selection of two or more processes, splitters are used, where the stream can be sent to one or several units.

3.1. Boiler Model. Pulverized coal is burned in the boiler. The composition of the flue gas is computed by determining the equilibrium of the gases assuming two main zones: flame zone and upper region. Each of the zones is modeled similarly considering the average temperature and the equilibria among the chemical species for the production of CO and CO₂, as well as for NO and NO₂. For S, Cl₂, and F₂, a complete conversion is assumed. In the following lines, the equations that model this unit are described. The main difference between coal-fired boilers and oxy-combustion boilers is the inert gas used. In the case of oxy-combustion boiler instead of using nitrogen, carbon is used. The principal advantages are the low generation of NO_x and the reuse of carbon dioxide.

(1). The average temperature of each zone is computed from temperature profiles, see Figure 2, as in previous work.¹⁹ Given that different O₂ to CO₂ ratios can be used, the temperature profiles vary. In Figure 2, these profiles are shown where O₂/CO₂ volume ratios of OF25, OF27, and OF29 correspond to 25/75, 27/73, and 29/71, respectively. The average temperature is computed out of the spatial distribution

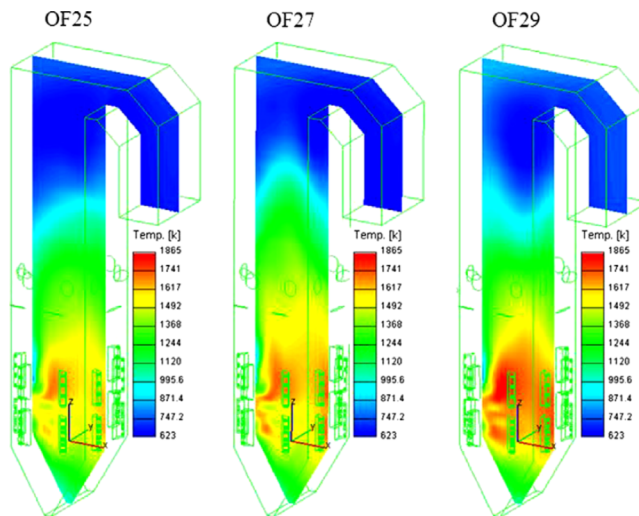


Figure 2. Temperature profiles for oxy-combustion industrial boilers. Reprinted from ref 36, Fuel, 102, Hussein, Naser, Dodds, CFD modeling of air-fired and oxy-fuel combustion in a large-scale furnace at Loy Yang A brown coal power station, 646–665, Copyright 2012, with permission from Elsevier.

of temperatures using eq 1. The relative areas and their correspondent temperatures are taken from³⁶

$$T = \sum_{\text{area}} a_i T_i \tag{1}$$

Table 1 shows the area sectors and their temperatures for the three cases in Figure 2, with regards to zone 2, the flame

Table 1. Temperature Distribution in Zone 1: Upper Zone and Zone 2: Flame Zone

	OF25		OF27		OF29	
	area fraction	T (K)	area fraction	T (K)	area fraction	T (K)
zone 1	1	747.2	1	747.2	1	747.2
	0.0524	871.4	0.0784	912.8	0.1270	912.8
	0.0429	995.6	0.0421	912.8	0.0259	995.6
	0.0310	933.5	0.0619	1120	0.0198	995.6
	0.0310	1000	0.1858	1368	0.2590	1430
	0.1830	1244	0.0867	1492	0.0288	1368
	0.1088	1369	0.1288	1554.5	0.0288	1492
zone 2	0.0429	1461	0.0322	1409.3	0.0576	1492
	0.0381	1430.5	0.0322	1057.8	0.0288	1617
	0.0143	1430.5	0.0607	1741	0.0302	1120
	0.0306	1057.8	0.1586	1617	0.1914	1741
	0.2959	1554.5	0.0334	1679	0.0345	1617
	0.0272	1670	0.0991	1492	0.0604	1679
	0.1020	1399			0.1079	1500

zone. In the upper zone, due to the more homogeneous temperature distribution, a unique division is assumed. *a* corresponds to the fraction of area and *T* indicates the temperature in Kelvin.

Using the average temperature in each zone, the equilibrium that generates the various species is computed. The following species and equilibria are considered in the analysis.

(a). Carbon equilibria: Reactions 2 and 3 show the combustion of carbon and the Boudouard equilibrium. Using this to model the CO₂ to CO ratio does not result in the industrial data. Therefore, experimental data are used. A value of 11 412 from the literature is assumed.³⁷

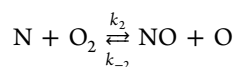
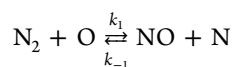


A correlation is developed based on the data in the literature³⁷ to predict the unburned coal for oxy-combustion as a function of the percentage of oxygen, see eq 4.

$$C_{\text{unburned}} = -1.0625 \cdot y_{\text{O}_2} + 0.3611 \quad (4)$$

(1). 20% of the unburned carbon corresponds to slag while the rest, 80%, is dragged by the flue gas³⁸

(b) NO production: it is modeled based on the equations provided in eq 5. The equilibrium constant is computed based on the kinetic constants as given in eq 6¹⁹



$$K_{\text{eq,NO}} = K_1 \cdot K_2 = 22.44 \cdot \exp\left(-\frac{21\,805}{T}\right) \quad (6)$$

(c) NO₂ production: it is modeled using eq 7,³⁹ where the equilibrium constant is given in eq 8



$$K_{\text{eq,NO}_2} = 2.75369 \times 10^{20} \cdot T^{-6.95528} \quad (8)$$

It is assumed that no other nitrogen oxides are present because typically their concentrations are negligible.⁴⁰ To verify that the model reports reasonable results, an industrial reported ratio of 95% of NO and 5% NO₂⁴¹ is expected.

(d) Sulfur combustion:⁴² 100% conversion of the sulfur into SO₂ is assumed³⁸



(e) HCl production:⁴³ 100% conversion is assumed³⁸



(f) HF production:⁴⁴ 100% conversion is assumed³⁸



Apart from the equilibria, the atom balances must also hold, without accounting for the inert CO₂.

Carbon balance

$$(n_{\text{C}})_{\text{inlet}} = (n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{C}})_{\text{outlet}}$$

Hydrogen balance

$$[2(n_{\text{H}_2}) + 2(n_{\text{H}_2\text{O}})]_{\text{inlet}} = [2(n_{\text{H}_2}) + 2(n_{\text{H}_2\text{O}}) + (n_{\text{HCl}}) + (n_{\text{HF}})]_{\text{outlet}}$$

Oxygen balance

$$[2n_{\text{O}_2} + n_{\text{H}_2\text{O}}]_{\text{inlet}} = [2n_{\text{O}_2} + n_{\text{H}_2\text{O}} + 2n_{\text{CO}_2} + n_{\text{CO}} + 2n_{\text{NO}_2} + n_{\text{NO}} + 2n_{\text{SO}_2}]_{\text{outlet}}$$

Nitrogen balance

$$[2n_{\text{N}_2}]_{\text{inlet}} = [2n_{\text{N}_2} + n_{\text{NO}_2} + n_{\text{NO}}]_{\text{outlet}}$$

Sulfur balance

$$[n_{\text{S}}]_{\text{inlet}} = [n_{\text{SO}_2}]_{\text{outlet}}$$

Chlorine balance

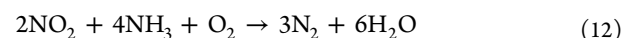
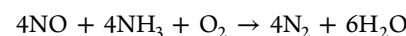
$$[2n_{\text{Cl}_2}]_{\text{inlet}} = [n_{\text{HCl}}]_{\text{outlet}}$$

Fluorine balance

$$[2n_{\text{F}_2}]_{\text{inlet}} = [n_{\text{HF}}]_{\text{outlet}}$$

(g) An excess of oxygen is recommended to improve the combustion yield. The reference is the O₂ required to burn C to CO₂. According to Hu and Yan,³⁷ values of 1.01 and 1.05 are considered as lower and upper bound.

3.2. Denitrifier. Two main methods that are commonly considered for the removal of NO_x from flue gas are: catalytic (SCR) and noncatalytic reduction. In this case, only SCR is evaluated based on previous results.¹⁹ The removal of nitrogen oxides is based on the chemical equations below, in the presence of ammonia and oxygen



This unit is modeled using mass and energy balances as well as empirical correlations for the yield and rules of thumb for

the feed ratios. The mass balance follows the stoichiometry of the reactions in eq 12. The oxygen to ammonia ratio used is 20:1, to avoid flammability issues, and the oxygen is fed as atmospheric humid air. In a previous work,¹⁹ the conversion of the reactions was fit from the experimental data in Rosenbert and Oxley⁴⁵ to eq 13

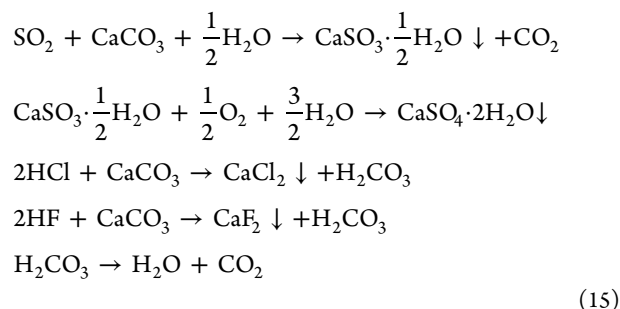
$$\eta_{\text{SCR}} = 6.6537 \times 10^{-6} \cdot T(K)^3 - 1.523 \times 10^{-2} \cdot T(K)^2 + 11.43 \cdot T(K) - 2731.8 \quad (13)$$

The temperature of the gas exiting the reactor is computed using an adiabatic energy balance.⁵ The investment cost of this unit is estimated using the correlation from Miller,²¹ eq 14, where m_{NO_x} corresponds to the tons of NO_x processed in a year

$$\text{Cost}_{\text{SCR}} = 5000 \times \frac{1}{0.8} (m_{\text{NO}_x} (1 - \eta_{\text{SCR}})) \quad (14)$$

3.3. Desulfuration. The removal of the SO_2 is a major issue in oxy-combustion flue gas treatment because NO_x concentration is expected to be well below that of air-fired boilers. Two methods are evaluated: wet removal (LFSO) and dry removal (lime spray drying, LSD).

3.3.1. LFSO. The wet removal of SO_2 is based on the reactions that can be seen in eq 15 where a slurry of CaCO_3 is fed to a gas liquid contactor operating at 323 K⁴⁶ and the product is oxidized with air to gypsum.⁴⁷ The model for this unit is based on the mass balance given by the stoichiometry of these set of reactions. The feed ratio of O_2 to SO_2 used is 3:1,⁴⁷ and the slurry contains 20% w/w of CaCO_3 . In a previous work,¹⁹ an empirical model was developed using experimental data reported by Zhong et al.⁴⁸ to predict the removal of SO_2 as a function of the liquid to gas ratio (in liters per N m^3) as presented in eq 16. The exit gas temperature is computed using an adiabatic energy balance, and the gas exits the contact equipment saturated.



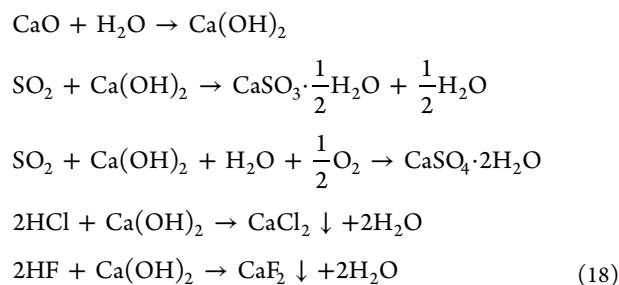
$$\eta_{\text{LFSO}} = -5.06993 \times 10^{-4} \left(\frac{L}{G}\right)^2 + 2.591958 \times 10^{-2} \left(\frac{L}{G}\right) + 0.653958042 \quad (16)$$

The investment cost of the method is estimated by the SO_2 eliminated in tons per year²¹ using eq 17

$$\text{Cost}_{\text{LFSO}} = 3700((m_{\text{SO}_2}) \cdot (1 - \eta_{\text{LFSO}})) \quad (17)$$

3.3.2. LSD. The dry removal method treats the flue gas with a slurry 35% in CaO operating within 393 and 448 K. The mechanisms of the removal process⁴⁹ can be seen in eq 18. The stoichiometry of the reactions allows computing the performance of this unit. Because of the absence of forced oxidation, the molar ratio CaSO_3 to CaSO_4 is 9:1. The removal yield of SO_2 is estimated using a model developed from experimental data⁵⁰ reported in a previous work¹⁹ as a function

of the fraction of S in the coal and the molar ratio between Ca and S, see eq 19. The common range of sulfur concentrations, %S, and Ca/S ratios for the use of this correlation are from 2.5 to 6% and 0.7 to 1.5, respectively. The exit temperature of the gases is computed assuming an adiabatic energy balance. The gas exits saturated.



$$\begin{aligned} \eta_{\text{LSD}} &= (-0.4554 \cdot (\%S) + 1.2451) \\ &+ (0.3469 \cdot (\%S) + 0.6286) \left(\frac{\text{Ca}}{\text{S}}\right) \\ &+ (-0.0243 \cdot (\%S) - 0.56325) \left(\frac{\text{Ca}}{\text{S}}\right)^2 \end{aligned} \quad (19)$$

The investment cost of the method is estimated based on SO_2 eliminated in tons per year.²¹

$$\text{Cost}_{\text{LDS}} = 4400((m_{\text{SO}_2}) \cdot (1 - \eta_{\text{LFSO}})) \quad (20)$$

3.4. Particle Removal. The electrostatic precipitator is modeled using a mass balance to the particles. The removal ratio is computed based on the particle size, see eq 21, using the experimental results reported by Nichols and McCain.⁵¹ Seven diameter sizes are considered 0.075, 0.2, 0.5, 1.5, 2, 5, and 10 μm with removal ratios of 0.99, 0.95, 0.9, 0.96, 0.97, 1, and 1, respectively. Together with the mass balance, an energy balance is also performed. The exit temperature is typically 423 K⁵²

$$\begin{aligned} \eta(d) &= f(\text{size}) \\ \text{Particle}_{\text{removal}} &= \sum \eta(d) n_{\text{particle}}(d) \\ \eta_{\text{PE}} &= \frac{\text{particle}_{\text{removal}}}{\text{particle}_{\text{in}}} \end{aligned} \quad (21)$$

The estimation cost for the electrostatic precipitator is reported by Miller,²¹ where H_v is the volume of gas (N m^3) processed in a year. The advantage of this type of cost functions is that if the method is not selected, no flowrate is processed and, as a result, there is no cost associated.

$$\text{Cost}_{\text{PE}} = 2.85(H_v) + 8.50(H_v) \quad (22)$$

3.5. Carbon Capture. After a prescreening of technologies, three alternatives are considered based on their application to power plants such as carbonation,³¹ amine absorption,³⁰ and PSA systems.⁵³ The gas purified is recycled to the boiler.

3.5.1. Amines. Among the different amines, MEA has been traditionally used for power plants.⁵⁴ To compute the flow of amine fed to the gas liquid contactor, a mass balance is performed, eq 23, where the molar ratio of CO_2 recovered per mol of amine (MR) and the MEA concentration (MEA_{conc}) are given in Table 2. 95% removal of CO_2 , $\text{CO}_{2\text{eff}}$ is assumed.⁵⁵

$$\frac{MW_{\text{MEA}}}{\text{MEA}_{\text{conc}}} \left(\frac{\text{CO}_2_{\text{eff}} \cdot f_{\text{CO}_2}}{MW_{\text{CO}_2}} \right) \left(\frac{1}{\text{MR}} \right) = f_{\text{CO}_2}^{\text{MEA}} \quad (23)$$

Table 2. CO₂ Capture Using Alkali Solutions³⁰

	MEA
gas pickup mol/mol amine	0.33
solution concentration (wt %)	15–25 (0.2)
heat of reaction (BTU/lb CO ₂)	620–700
MR	0.35
density	1.018
cost (€/kg)	1.3
molecular weight	61.08
reboiler (BTU/h)	72 000 GPM
condenser (BTU/h)	30 000 GPM
amine feed to distillation (BTU/h)	45 000 GPM
amine cooler (BTU/h)	15 000-GPM

The gas may need to be compressed. The compressors are modeled assuming polytropic behavior. The efficiency of the compression stages is assumed to be 0.85, and the polytropic coefficient is assumed to be 1.4.⁵⁶ The absorption process is exothermic, and the column must be continuously cooled. The cooling needs are computed using eq 24 based on the amount of CO₂ absorbed by the amine and the heat reaction

$$Q_{(\text{col1})} = \Delta H_{\text{react,amine}} \cdot \text{CO}_2_{\text{eff}} \cdot f_{\text{CO}_2} \quad (24)$$

The loaded amine flow is sent to regeneration in a distillation column. Rules of thumb from the literature,³⁰ see Table 2, are used to compute the energy involved in heating the amine flow (q_{amine}) before being fed to the column, eq 25, as well as the energy required by the reboiler and the cooling needs for the condenser eq 26.

$$Q_{(\text{feed})} = F_{\text{feed}} \cdot q_{\text{amine}} \quad (25)$$

$$Q_{(\text{cond})} = F_{\text{cond}} \cdot q_{\text{amine}}$$

$$Q_{(\text{reb})} = F_{\text{reb}} \cdot q_{\text{amine}} \quad (26)$$

According to the literature, the inlet temperature to column 2, T_{col2} , is equal to 93 °C, with the bottom temperature, T_{bottoms} , of 125 °C while at the condenser, T_{top} , is assumed to be 54 °C. The factors F_i in eqs 25–27 are given in Table 2.

The MEA solution recovered from the bottom is recycled back to the gas–liquid contactor. From the reboiler, the regenerated amine is cooled down heating up the feed to the column. Next, a heat exchanger is used to adjust the temperature to 29 °C. Equation 27 computes the cooling needs. The make-up and the recycled solution are mixed adiabatically and fed to the gas–liquid contactor.

$$Q_{(\text{feed-col1})} = F_{\text{cooler}} \cdot q_{\text{amine}} \quad (27)$$

The cost correlations, for the investment, eq 28, and for the operating costs, eq 29, are given by empirical correlations developed using data from the literature.⁵⁷ The experimental data reported by David and Herzog⁵⁷ show the operation of a facility with and without the carbon capture technology. Based on these data, the contribution of the amine absorption to the capital and operating costs is computed based on the thermal energy generated at the boiler by burning the coal and the actual flow of CO₂ fed to the process, see eqs 28 and 29.

$$\text{Capital}_{\text{cost}} = \left(623 \frac{\$}{\text{kW}} \right) \cdot (\text{Pot}_{\text{CO}_2}) \cdot (F_{\text{CO}_2})_{\text{In}} \quad (28)$$

$$\text{Operation}_{\text{cost}} = \left(\frac{5.5}{1000} \frac{\$}{\text{kWh}} \right) \cdot (\text{Pot}_{\text{CO}_2}) \cdot (F_{\text{CO}_2})_{\text{In}} \quad (29)$$

The parameter Pot_{CO_2} is related to the power generated per kilogram of coal used where F_{CO_2} is the carbon dioxide fed into the process.

3.5.2. Zeolites. The PSA system is modeled to compute the absorbent bed required and the vessel that contains it. The bed of zeolites is designed based on the amount of CO₂ to be captured, considering the adsorption equilibrium between the CO₂ and the material. The adsorption yield of the CO₂ on the zeolite bed is computed based on experimental adsorption equilibrium data. The large model of the superstructure suggested the development of a surrogate model of the adsorption capacity, q , in mol per kg of the zeolite 13X, based on the operating temperature and the CO₂ partial pressure, P_{CO_2} . The range of operation is from 0.2 to 1 atm and 25 to 60 °C.³²

$$q = (2 \times 10^{-5} T^2 - 0.0025 T - 1.1968) P_{\text{CO}_2}^2 + (0.0027 T + 2.1451) \cdot P_{\text{CO}_2} + (-0.035 T + 3.9061) \quad (30)$$

The breakthrough curve for the zeolite determines the operating time and the size of the bed. It shows that the operating time must be below 20 min so that the exit gas contains only traces of CO₂. An operating time around 15 min is selected ($\tau = 15$ min) because in the flue gas, there exist more components although in small proportions. In this way, the purity of the CO₂ is guaranteed. The yield, η , is assumed to be 95%. Thus, the mass of the zeolite bed required is given by eq 31

$$m_{\text{zeolite}} = \frac{1 \cdot f_{\text{CO}_2} \cdot 1000}{q \cdot MW_{\text{CO}_2}} \cdot \eta \cdot \tau \quad (31)$$

In order to recycle high purity CO₂, the tails of the desorption curve must be cut. The order of desorption is N₂, NO_x, CO₂, SO₂, O₂, and H₂O. Therefore, the traces of N₂ and NO_x will be removed before recycling as well as the traces of SO₂, O₂, and H₂O.⁵⁸

The estimation of the cost of the PSA system consists of the vessel and the adsorbent bed, eqs 37 and 38. The vessel is sized as follows.⁵⁹ The volume of the bed is computed using the apparent density of the zeolite.

$$V_{\text{zeolites}} = 1.1 \cdot \frac{m_{\text{zeolites}}}{\rho_{\text{bed}} \cdot 0.454} \quad (32)$$

The bed is to be installed in a vessel. Assuming L/D equal to 3, the diameter becomes

$$D_{\text{vessel}} = \left(\frac{V_{\text{zeolites}}}{3 \cdot \pi} \right)^{1/3} \quad (33)$$

$$L_{\text{vessel}} = 3 \cdot D_{\text{vessel}} \quad (34)$$

The thickness of the vessel is computed using a correlation developed in the work by Martín and Grossmann.⁵⁹

$$\text{Thickness} = 0.023 + 0.003 \cdot D_{\text{vessel}} \quad (35)$$

The cost of the vessel is computed by the weight of metal. Thus, the material of the vessel is computed as

$$\text{Weight}_{\text{vessel}} = \rho_{\text{steel}} \left(\pi \left(\left(\frac{D_{\text{vessel}}}{2} + \text{thickness} \right)^2 - \left(\frac{D_{\text{vessel}}}{2} \right)^2 \right) \cdot L_{\text{vessel}} \right) + \frac{4}{3} \cdot \pi \left(\left(\frac{D_{\text{vessel}}}{2} + \text{thickness} \right)^3 - \left(\frac{D_{\text{vessel}}}{2} \right)^3 \right) \quad (36)$$

Finally, the investment cost of the vessel.⁶⁰

$$\text{Cost}_{\text{vessel}} = 56.181 \cdot (\text{weight}_{\text{vessel}})^{0.878} \quad (37)$$

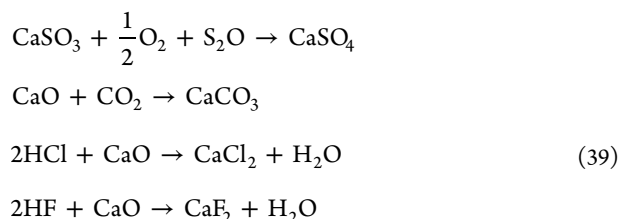
The zeolites can be regenerated only a number of times. It is a complex issue because their adsorption capacity decays over time.³² The cost of the operation is assumed to that of the bed that is to be bought over the plant lifetime.

$$\text{Cost}_{\text{zeolite_bed}} = C_Z \cdot m_{\text{zeolite}} \cdot N_{\text{beds}}^0 \quad (38)$$

3.5.3. Carbonation. Carbonation/calcination is a looping system to regenerate the adsorbent. Even though it is a closed cycle, losses and efficiency decay results in the need to feed a make-up of solids.⁶¹ Besides, secondary reactions such as sulfonation occur. This reaction also represents SO₂ removal.⁶² It is possible to use either CaCO₃ or CaO as adsorbents. However, CaCO₃ is the one of choice as it is the cheapest.

The system operates as follows: the flue gas is fed to the carbonator where carbon dioxide is removed. The product stream consisting of gases and solids is fed to a heat exchanger, Hx_4, where it is used to heat up the recycled adsorbent. Next, in cyclone 1, the solids are recovered from the stream and the gas is sent to further treatment. The solids must be regenerated in the calciner. This stage consists of the decomposition of the CaCO₃ recovering the CaO and CO₂. The solids, CaO, are separated from the stream in cyclone 2, while the CO₂ can be reused in the boiler. The solids are heated up before being fed to the carbonator.

3.5.4. Carbonator. This unit is responsible for the removal of CO₂, SO₂, HCl, and HF following eq 39 that is used to compute the mass balance to this unit. The flue gas and regenerated solids enter the carbonator.



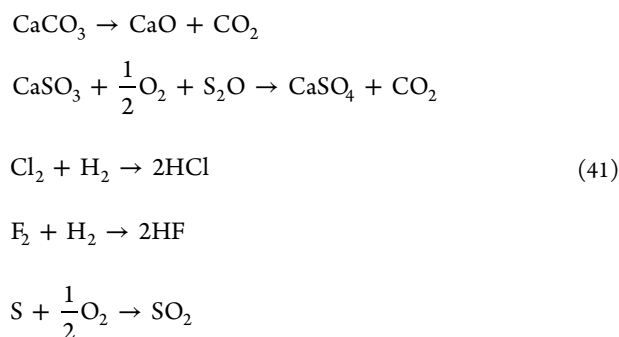
The sulfonation and carbonation reactions are competitive. Because SO₂, HCl, and HF can be considered traces in the gas flow compared to the proportion of CO₂, it is assumed that these reactions will have a 100% conversion. The operating temperature must be higher than 600 °C but lower than 680 °C.⁶¹ The range shows a significant effect on the CO₂ uptake in the diffusion controlled stage. In the pilot plants, the operation temperature is around 650 °C, and hence this temperature is used in the carbonator.⁶³ The efficiency of the carbon capture of this technology is computed using the correlation reported by Abanades,⁶¹ eq 40

$$\eta_{\text{carbonator}} = \frac{1 + \frac{F_0}{F_R}}{\left(\frac{F_0}{F_R}\right) + \left(\frac{F_{\text{CO}_2}}{F_R}\right)} \left[\frac{f\left(\frac{F_0}{F_R}\right)}{\left(\frac{F_0}{F_R}\right) + 1 - f} + b \right] \quad (40)$$

The parameters *b* and *f* are constants with values of 0.782 and 0.174, respectively. The *F_R/F_{CO₂}* ratio is limited by the experimental conditions. This ratio is limited between the values of 2 and 5. Another constraint is that the *F₀/F_R* ratio, which represents the ratio between the fresh and regenerated sorbent, should be within the range of 0 and 0.05.

The stream exiting the carbonator is fed to the cyclone (cyclone_1). In the cyclone, the solids are recovered and fed to the calciner for their regeneration.

3.5.5. Calcination. The calciner is used to regenerate the CaO from CaCO₃. High temperatures are needed for the decomposition of the CaCO₃.^{61,63,64} In this work, a temperature of 950 °C is used. Thereby, the regeneration yield obtained is assumed to be 100%.⁶³ This unit can be considered as a furnace because the operation consists of combustion with carbon and oxygen. The ratio between both is paramount for the operation and typically takes a value of 2.49.⁶³ The set of reactions that take place in this unit are shown in eq 41, which are used to compute the mass balance to the unit.



Taking into account that the sorbent collects impurities and losses activity, a purge Sink_3 is considered, *F₀* in eq 40, to remove a small fraction of the sorbent. Sorbent make-up is fed to the unit, Src_08, equal to the amount deactivated by the impurities, *F₀*.

The cost correlations to compute the investment and operation costs of this technology are given by eqs 42 and 43.⁶⁵

$$\text{Capital}_{\text{cost}} = 675 \cdot (\text{Pot}_{\text{CO}_2}) \cdot (F_{\text{CO}_2})_{\text{In}} \quad (42)$$

$$\text{Operation}_{\text{cost}} = 0.023 \cdot (\text{Pot}_{\text{CO}_2}) \cdot (F_{\text{CO}_2})_{\text{In}} \quad (43)$$

The clean stream is recycled back to the boiler, with a purity above 99.9%, to dilute the mixture instead of using the nitrogen in the air.

3.6. Problem Formulation. Two mathematical problems are formulated: one for the design of the flowsheet, the second stage in the process design problem, and the extended blended problem, that is a tool for industry to select the coal blend to purchase for the sustainable operation of their facility.

The process design problem consists of an NLP describing the flowsheet shown in Figure 1 including the models of the boiler, the denitrifier, the carbon capture, and SO₂ removal techniques described in the previous section. The objective function is given by eq 44

$$\text{Cost}_{\text{total}} = \frac{1}{3} \left(\sum_i \text{cost}_i \right) + \sum_i \text{cost}_{\text{operation}_i} \quad (44)$$

where the term cost_i refers to the investment cost to each unit, that is annualized, and $\text{cost}_{\text{operation}_i}$ corresponds to the operation cost.

Because the oxy-combustion of coal can be carried out with different carbon dioxide and oxygen concentrations and the main effect of varying oxygen concentration is the flue gas composition,⁴¹ the effect of the oxygen concentration on the selection of flue gas treatment is also analyzed. In this case study, data from the literature is used for the temperature profiles inside the boiler for oxygen concentrations of 25, 27, and 29%.³⁶ In all three cases, the superstructure consists of 4815 equations and 5422 variables. It is written in GAMS and is solved using the multistart procedure with CONOPT 3.0 as the preferred solver.

The extended blending problem requires an alternative objective function to add the cost of the coal. The problem also includes the models for the boiler, the denitrifier, the carbon capture, and SO₂ removal techniques. The objective function becomes:

$$\text{Cost}_{\text{total}} = \frac{1}{3} \left(\sum_i \text{cost}_i \right) + \sum_i \text{cost}_{\text{operation}_i} + \sum_k \text{cost}_k \quad (45)$$

where the term cost_k is the cost of imported coal, national coal, and crude coal tar. In this step, the optimal blending of coal is selected to be of minimum cost based on flue gas treatment and coal costs. The blending model consists of 4818 equations and 5425 variables. It is written in GAMS and is solved using the multistart procedure with CONOPT 3.0 as the preferred solver.

4. RESULTS

Three types of coal, national, imported, and crude coal tar, are considered for the study with a composition as shown in Table 3. In all cases, a feed of 23 kg/s of coal or coal mixture is used to generate around 350–400 MW_e. Similar to previous works,¹⁹ an efficiency of the thermal cycle of 50% is used.

4.1. Process Design. The first study corresponds to the design of the process that treats the flue gas. The flowsheet is extracted from the superstructure in Figure 1 by solving the NLP problem formulated in a previous section. To evaluate the robustness of the solution, three cases of the study with various oxygen concentrations in the boiler are considered. In these

Table 3. Coal Composition and Price

	national	imported	crude coal tar
H ₂ O	0.1357	0.0988	0.1038
C	0.688493	0.705099	0.779552
H ₂	0.022585	0.030706	0.03033
O ₂	0.000165	0.000579	0.021109
S	0.018631	0.004351	0.041942
N ₂	0.013844	0.018164	0.017093
Cl	0.00014	0.00012	0.00004
F	0.000072	0.000076	0.000017
ash	0.12037	0.142105	0.006117
price (\$/t)	77.68	97.91	22.36
HHV (kJ/kg)	26 411.535	28 106.46	35 467.875

studies, a coal blend of 26% national, 26% imported, and the rest crude coal tar is used, generating around 717 MW, based on a typical composition used in a power plant.

Three oxygen concentrations in the boiler, 25, 27, and 29%, are evaluated. The model is optimized for each one of all of them. In all cases, the solution found shows the same flowsheet. The gas treatment chain consists of the electrostatic precipitator, to remove the particles, LSD, to remove sulfur, and the PSA system based on zeolites 13X to clean the carbon dioxide stream. This solution is important due to the fact that the selection of technologies is robust with the oxygen feed to the boiler providing certain general processing chain. Analyzing the solution, the electrostatic precipitator is employed in all cases because the flue gas always contains ash and unburned coal that must be removed before further processing. The presence of these species in the gas flow affect other units in particular the bed of the PSA system, poisoning it. In addition, one on the characteristics of oxy-combustion is the low levels of NO_x production. Due to this feature, it is not necessary to use any denitrification technique because the traces of NO_x will be removed by adsorption in the zeolites. The superstructure allows bypasses. Thus, the LSD process is selected over the LFSO as the main technology to remove sulfur while the zeolites only deal with the traces of SO₂ remaining. In this way, the use of LFSO, a technique with a larger removal efficiency but also more expensive, is not selected. This result is similar to the one shown in previous work for conventional coal-based facilities.¹⁹ However, note that most facilities use LFSO techniques for their flexibility in dealing with a wider range of sulfur contents.²⁴ The recovery and purification of CO₂ is carried out using zeolites over MEA or the calcinator/combustion system. The PSA system is simpler and requires less energy. Moreover, it presents a high carbon capture yield as well as it serves as a trap for traces of NO_x and SO₂. In all three cases, the solution suggests a bypass at the sulfur removal section that takes a value of around 10%, which means that around 90% is fed in the LSD process to remove sulfur. Table 4 summarizes the results of the cost per unit of power

Table 4. Costs Per Power Generated of the Units Selected from the Different Alternatives

	OF25	OF27	OF29
PE cost (\$/kW)	10.86	10.34	9.89
LSD cost (\$/kW)	361.09	291.02	292.36
zeolites adsorption cost (\$/kW)	25.19	23.93	22.86
CaO cost (\$/kW-year)	14.41	11.62	11.68
investment cost (\$/kW)	397.14	325.30	325.11
operation cost (\$/kW-year)	38.86	34.87	33.89
total annual cost (\$/kW)	171.23	143.30	142.26

generated by the coal mix for the three oxygen concentrations. It is possible to see that the cost decreases with the concentration of oxygen because lower CO₂ must be recycled. Note that the air separation unit cost is not included in the analysis. In addition, the LSD cost drops abruptly from 25 to 27% oxygen concentration and remains almost constant for 29%. Note that NLP is solved obtaining a local solution and no global solution is claimed. It can also be seen a decrease in the cost of CO₂ capture as the amount of CO₂ in the stream is lower due to the oxygen concentration.

4.2. Blending Problem: Coal Selection. In the previous section, the optimal technologies for flue gas treatment were

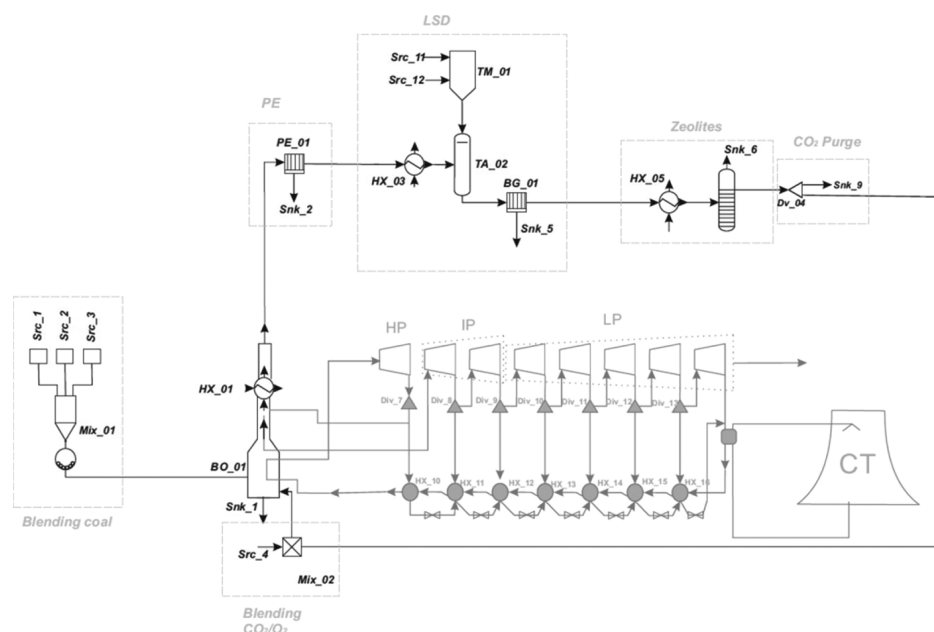


Figure 3. Process flow diagram of the blending problem.

Table 5. Coal for Gas Processing for Various Coal Types

		PE cost (\$/kW)	LSD cost (\$/kW)	zeolites cost (\$/kW)	CaO cost (\$/kW-year)	coal cost (\$/kW-year)	investment cost (\$/kW)	operation cost (\$/kW-year)	TAC (\$/kW-year)
OF25	national	12.10	334.19	27.94	13.39	135.33	374.23	41.78	301.86
	imported	11.70	72.03	26.83	4.46	251.32	110.56	31.70	319.87
	crude coal tar	10.01	210.47	23.38	8.39	45.48	243.86	32.36	159.13
OF27	national	11.52	334.19	27.44	13.39	135.33	372.26	40.31	299.72
	imported	11.14	72.03	25.49	4.46	251.32	108.67	30.29	317.83
	crude coal tar	9.52	210.47	22.22	8.39	45.48	242.20	31.11	157.33
OF29	national	11.03	338.03	25.36	13.54	135.33	374.42	39.20	299.33
	imported	10.67	72.03	24.36	4.46	251.32	107.05	29.08	316.08
	crude coal tar	7.84	181.44	18.29	7.23	39.21	207.57	25.91	134.30

determined. It is important to notice that industry does not use partial bypasses to the flue gas treatment units because it is easier to feed the entire flow to the unit. Thus, the flowsheet is fixed as the one shown in Figure 3 to select the coal blend to be purchased. The bypass is avoided by fixing the flowrate of that stream to 0. Similar to the previous section, the study is carried out for three different initial concentrations of oxygen to determine the optimal coal blend. The same three types of coal, national coal, imported coal, and crude coal tar, are used. However, in this case, the amount of each type of coal is not fixed, only the total feed of coal mixture that is 23 kg/s.

The optimization of the extended blending problem solves an NLP problem to define the amount of each coal type to be purchased, see previous section. The trade-offs that the three coals present are related to their price and sulfur content. On the one hand, crude coal tar is cheaper, has the highest energy content, but contains the largest amount of sulfur. On the other hand, the imported coal is the most expensive. However, the sulfur content in the lowest expecting lower processing cost and an intermediate energy content. Finally, the national coal shows an intermediate price and sulfur content while the energy content is the lowest. In principle, the trade-offs have a nontrivial solution as to which coal blend to use. However, by

solving the extended blending problem, no mixture of coal is selected in spite of the trade-offs. The selection of crude coal tar is due to the fact that it is far cheaper than the other coals. Furthermore, if the coal prices per unit of power generated are evaluated, see Table 5, it can be seen that the crude coal tar generates higher power than the others. Thus, if the blending problem is analyzed based on the coal cost and the coal heating values, the same result will be obtained.

However, in Spain, the use of national coal is encouraged for social reasons to support the economy of certain regions. The coal-based power plants are allocated in regions where mining exploitations are also in operation extracting national coal representing a social issue, the self-consumption of national coal. Therefore, because no coal blend is suggested, Table 5 compares the processing costs of the three coal types for the three oxygen concentrations for further insights. The results obtained show that the coal of choice is crude tar, followed by national and imported, regardless of the oxygen composition of the combustion gas. The price of the imported coal is a deterrent to be selected, in spite of the fact that the treatment cost using the LSD is 3 to 5 times lower than the processing of the crude coal tar. The largest investment cost corresponds to the removal of sulfur. Furthermore, the lower ash content in

the crude coal tar reduces its processing costs around 20% compared to the other coals. In addition, in spite of the larger production of CO₂ as a consequence of the higher carbon content, the larger power production out of the crude coal tar results in lower carbon capture cost per unit of power. Note that the investment in the flue gas processing is far lower for the imported coal, one-half of that of the crude coal tar and one-third of the national coal. However, the cost of coal per year outweighs the savings in annualized investment, resulting in selecting the crude coal tar over the other two. Note that the national coal is the second best overall, but it requires the largest investment due to the sulfur content and the low yield to power. While the results point to the crude coal tar, from the company perspective, the risk in funding the flue gas treatment is large for the national and the crude coal tar.

Evaluating the effect of the concentration of oxygen in the processing costs, on average, the higher the oxygen concentration the lower the costs, but the decrease is not as high as selecting one coal type or another. On the one hand, the cost of the PE and the zeolites depends on the oxygen to CO₂ ratio, decreasing the cost with the oxygen fraction in the gas. On the other hand, the LSD costs depend on types of coal, and its sulfur content, but it does not depend on the oxygen concentration in the flue gas. Again, it should be noted that the air separation unit is not included in the total processing cost.

5. CONCLUSIONS

In this work, a flexible framework is developed for the evaluation of the optimal flue gas processing from oxy-combustion power plant facilities. A systematic approach is used to optimally select the methods following a two-stage procedure including heuristic and mathematical optimization steps. After the preselection of promising technologies, a superstructure is developed, where the boiler, the electrostatic precipitator, dry and wet SO₂ removal, NO_x catalytic removal, and CO₂ purification using carbonation/calcination cycle, zeolites, and amines are modeled using first principles, experimental and industrial data, and rules of thumb. Three different ratios of carbon dioxide and oxygen are studied. Once the processing technologies are selected, an extended blending problem is formulated for the selection of the coal blend to be purchased based on the coal composition and price.

At the design stage, for a typical coal mix in a power plant in Spain, dry SO₂ removal, no NO_x removal method, and zeolite beds for CO₂ purification are selected. The treatment cost increases when the oxygen concentration decreases but the selection of technologies holds good. It should be noted that the air separation unit is not included in the cost. Finally, this framework is used to evaluate the best coal blend formulating an extended blending problem that includes detailed yield models for the operation of all the treatment units. The tradeoffs between sulfur content, price, and yield to power result in the fact that no coal blend is selected due to the low cost of the crude coal tar, in spite of larger flue gas processing costs.

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Notes

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NOMENCLATURE

b	constant parameter, 0.782
C_{unburned}	unburned coal (kg/s)
Ca/S	calcium to sulphur molar ratio Q
cost_i	cost of item i (\$/unit)
$CO_{2\text{eff}}$	removal efficiency of CO ₂ in amines
D_{vessel}	diameter of the vessel (m)
F	total flow (kmol/s)
f	constant parameter, 0.174
fc_{CO_2}	mass flow of CO ₂ (kg/s)
F_0	solid flow to fresh sorbent (mol/s)
F_R	solid flow to regenerative sorbent (mol/s)
F_{CO_2}	carbon dioxide feed into the system (mol/s)
fc_i	flow of component i (kg/s)
H_y	volume of gas (N m ³ /year)
K	equilibrium constant (bar ^{n})
L_{vessel}	height of the vessel (m)
L/G	liquid to gas ratio (L/N m ³)
m_i	tons per year of contaminant (t/yr)
m_{zeolites}	amount of zeolites (kg)
MEA_{conc}	MEA concentration
MW_i	molecular weight of component i (kg/kmol)
MR	molar ratio
N_{Neds}^o	number of beds
P_{CO_2}	carbon dioxide partial pressure (atm)
Pot_{CO_2}	power generated by carbon used (kW h/kg)
q	zeolite adsorption capacity (mol/kg)
$q_{\text{unit,amine}}$	experimental value of the thermal energy consumed in amine processing unit. See Table 2
$Q_{\text{(unit)}}$	thermal energy involved in unit (kW)
T	temperature (K)
thickness	thickness of the vessel (m)
V_{zeolites}	volume of zeolite (m ³)
weight _{vessel}	weight of the vessel (kg)
y_{O_2}	percent of oxygen
ΔH_{reac}	heat of reaction (kJ/kg)
τ	residence time (s)
η_{unit}	removal efficiency per unit
ρ_{steel}	density of steel (kg/m ³)
ρ_{bed}	density of zeolite bed (kg/m ³)
%S	sulfur concentrations feed boiler (%)

units

BG	filter
BO	boiler
calciner	calciner
carbonator	carbonator
cyclone (number of unit)	cyclone
comp (number of unit)	compressor
div (number of unit)	split
filter	filter
HX (number of unit)	heat exchanger
mix (number of unit)	mixer
PE	electrostatic precipitator
SCR	SCR of NO _x

Src (number of unit)	source
1	national coal
2	imported coal
3	crude coal tar
4	oxygen
6	air
7	ammonia
8	limestone
9	coal and oxygen
10	air
11	water
12	lime
13	MEA
sink (number of unit)	sink
1	ash
2	ash
3	lime, limestone and impurities
4	gypsum and Ca ₂ SO ₃
5	Ca ₂ SO ₃ and gypsum
6	impurities gas
7	solids
8	impurities gases
9	CO ₂ for utilization
TA (number of unit)	absorption tower
TL	slurry limestone tank
TM	mixer tank to lime and water
zeolites	bed of zeolites
amine (number of unit)	adsorption and desorption amines towers, respectively

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