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Simulation Study of an Oxy-Biomass-Based Boiler for Nearly Zero Emission Using Aspen Plus

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Abstract: Bioenergy integrated CO_2 capture is considered to be one of the viable options to reduce the carbon footprint in the atmosphere, as well as to lower dependability on the usage of fossil fuels. The present simulation-based study comprises the oxy bio-CCS technique with the objective of bringing about cleaner thermal energy production with nearly zero emissions, CO_2 capture and purification, and with the ability to remove NO_x and SO_2 from the flue gas and to generate valuable byproducts, i.e., HNO_3 and H_2SO_4. In the present work, a simulation on utilization of biomass resources by applying the oxy combustion technique was carried out, and CO_2 sequestration through pressurized reactive distillation column (PRDC) was integrated into the boiler. Based on our proposed laboratory scale bio-CCS plant with oxy combustion technique, the designed thermal load was kept at 20 kW$_{th}$ using maize stalk as primary fuel. With the objective of achieving cleaner production with near zero emissions, CO_2 rich flue gas and moisture generated during oxy combustion were hauled in PRDC for NO_x and SO_2 absorption and CO_2 purification. The oxy combustion technique is unique due to its characteristic low output of NO sourced by fuel inherent nitrogen. The respective mechanisms of fuel inherent nitrogen conversion to NO_x, and later, the conversion of NO_x and SO_2 to HNO_3 and H_2SO_4 respectively, involve complex chemistry with the involvement of N–S intermediate species. Based on the flue gas composition generated by oxy biomass combustion, the focus was given to the fuel NO_x, whereby different rates of NO formation from fuel inherent nitrogen were studied to investigate the optimum rates of conversion of NO_x during conversion reactions. The rate of conversion of NO_x and SO_2 were studied under fixed temperature and pressure. The factors affecting the rate of conversion were optimized through sensitivity analysiês to get the best possible operational parameters. These variable factors include ratios of liquid to gas feed flow, vapor-liquid holdups and bottom recycling. The results obtained through optimizing the various factors of the proposed system have shown great potential in terms of maximizing productivity. Around 88.91% of the 20 kW$_{th}$ boiler's efficiency was obtained. The rate of conversion of NO_x and SO_2 were recorded at 98.05% and 87.42% respectively under parameters of 30 °C temperature, 3 MPa pressure, 10% feed stream holdup, liquid/gaseous feed stream ratio of 0.04 and a recycling rate of the bottom product of 20%. During the simulation process, production of around four kilograms per hour of CO_2 with 94.13% purity was achieved.

Keywords: Oxy biomass combustion; thermal boiler; fuel NO_x; pressurized reactive distillation column (PRDC); NO_x absorption; SO_2 absorption; CO_2 purification; Aspen plus

1. Introduction

Based on a proposed laboratory scale biomass boiler with 20 kW$_{th}$ capacity, a simulation study with an objective of optimizing the oxy biomass with CO_2-enriched flue gas processing system (oxy

bio–CCS) was carried out. The optimization was accomplished by conducting the design specification and sensitivity analysis of the proposed oxy bio-CCS system in order to determine the optimum operational parameters involved during the plant processes. Biomass power, due to its availability and sustainability, is a potential source of heat and power generation on various scales, such as domestic, commercial, semi industrial and industrial. According to International Renewable Energy Agency, 2018 [1], the annual industrial level thermal energy obtained from biomass will exceed 20.2 EJ/year in 2050, compared to an energy output of 8 EJ in 2015. Biomass will account for two thirds of direct utilization of renewable energy according to the estimation for 2050 [2]. The energy and environmental potential of biomass as primary source of fuel has been investigated by several researchers [3–5]. Greenhouse gas emissions associated with biomass boilers comprise 42 and 85 g CO_2-e/kWh, which were recorded to be less than those emitted from solar and wind power of equal installed capacity [6]. Studies on different perspectives of biomass fueled boilers have been conducted, e.g., varying the fuel type [7,8], and rating capacities [9] etc. Maize, being one of the world's top agricultural crops, can play an important role as a biomass feedstock. The world's annual maize production is the largest among all crops; 32% maize is produced than wheat. Around 22.83% of the world's maize is produced in China, while the US accounts for 32.69%. According to FAO statistics from 2016 [10], annually, about 1.88×10^8 tons of maize stalk (dry matter) is burned worldwide, which accounts for 49.29% of total agricultural biomass burned (including residues of maize, wheat, sugar cane and rice). This makes maize stalk biomass a more suitable fuel for extracting thermal energy.

Considering the Chinese perspective of biomass potential, Cheng et al., 2014 [11], have elaborated an evaluation of agricultural biomass potential in China with a methodological development. Accordingly, as per the medium- and long-term development program for renewable energy in China, a biomass power generation capacity of 24 GW was proposed by 2020. Furthermore, the emissions coming from boilers have caused concerns as a source of atmospheric pollution. Due to skyrocketing developments in the global industrialization, the problem of effluents is significant, particularly from power plants fueled with fossil fuels. With broadening awareness regarding the greenhouse effect and air pollution, environmental concerns and clean energy development have attracted much attention [12]. CO_2, being the major constituent of greenhouse gases, accounts for about 65% of radiative forcing by long-lived greenhouse gases, and it has attained its highest levels, i.e., 408.02 ppm, of global annual average concentrations [13], with an annual increase of 0.83% and an accumulative 144% increase from the pre-industrial level of about 278 ppm.

Besides CO_2, air contaminants including NO_x and SO_x have incited global thinkers to search for the possible limiting technologies. Researchers have focused on investigating abatement techniques of SO_x and NO_x in terms of desulfurization and denitrification technologies. The wet process for the removal of NO_x and SO_2 from flue gas mix [14], microwave irradiation over activated carbon [15], air staging along addition of lime (CaO) into the system [16] contribute to efficient denitrification and desulfurization of the flue gas. A study was conducted by Liu et al. [17], whereby the experimental and modeling results of desulfurization under oxy condition were revealed to show increased efficiency of an average of five times compared to values for conventional combustion. Accordingly, the residence time of SO_2 due to flue gas recirculation was extended. Several patented investigations have been carried out in the field of desulfurization, such as the SNOX process, developed by Haldor Topsoe [18], where the inventors claimed to achieve desulfurization through the integration of catalytic CO_2 oxidation and oxy fuel sour compression. Using industrial flue gas as a source of SO_2, an improved lead chamber process of producing sulfuric acid from the industrial flue gas was developed by Keilin et al. [19]. The inventors devised a system to produce HNO_3 and H_2SO_4 through the conversion of NO_x and SO_x in the flue gas mixture. NO_x abatement technique through flue gas treatment can generally be categorized as either dry and wet systems, where selective catalytic reduction (SCR) [20,21], selective non-catalytic reduction (SNCR) [22], air/fuel staging [23], low NO_x burner [24] and flue gas recirculation [25] fall under the category of dry flue gas treatment for NO_x control, and absorption [26] under higher pressure to a wet process of denitrification. These industrial processes can be optimized through the relevant computer

operated simulation programs in order to obtain the best possible operational parameters through design specifications and sensitivity analyses. The Aspen PLUS application is used to simulate and optimize actual plant processes.

Many researchers have conducted simulation studies to get the optimum operational parameters of various plant processes, such as Aspen PLUS simulation of integrated gasification combined cycle thermodynamic with in situ desulfurization and CO_2 capture [27], circulating fluidized bed reactor [28], power cycle [29], CO_2 liquefaction [30], sour compression unit for CO_2 purification [31,32] and oxy fuel combustion [33], etc. White et al. [34–36], devised a mechanism to recover pure CO_2 from the oxy fuel combustion process by deploying computer simulation techniques by Aspen plus.

The oxy fuel combustion technique results in a flue gas comprising mainly CO_2, with impurities of NO_x and SO_2; thus, this technique is appropriate for effective CCS processes. The total amount of impurities in CO_2 stream depend on the boiler's operating conditions, fuel type and its composition. According to Leung et al., 2014 [37], the resultant CO_2 rich flue gas stream must be purified in order to make it feasible for transportation and geological storage in saline aquifers. Researchers have sought more feasible CO_2 purification processes with simultaneous removal of NO_x and SO_2 from the flue gas stream. Siddiqi et al. [38], for example, have studied the effects of NO_x on SO_2 in wet flue gas cleaning process. A multi-stage process for CO_2 purification and acid formation was invented by Degenstein et al. [39]; the inventors claimed to have developed a means of treating the carbon dioxide stream at elevated pressure of at least 2 bar pressure. The inventors focused on the interchangeability of NO_x and H_2SO_4 through the desorption of NO_x and the conversion of NO to NO_2 by stripping and converting units. In the invention of Petrocelli et al. [40], a SO_2-rich CO_2 gas stream was used in their research, in which catalytic oxidation of SO_2 and sour compression through SO_3 conversion to H_2SO_4 were the focus. In his patent, Allam et al. [40,41] demonstrated the removal of SO_x and/ or NO_x from a gaseous CO_2 steam at elevated pressure in the presence of molecular oxygen and water. Where NO acted as oxidant for SO_2 conversion to SO_3 and then to H_2SO_4, before spontaneously converting to HNO_3. This invention was noteworthy for its demonstration of the oxy fuel combustion process. Laura Torrente-Murciano et al. [42] studied the oxidation of SO_2 in the presence of NO_2 under conditions which were similar to those of the sour compression process, and determined the importance of the presence of liquid water in the completion of these reactions. The research carried out by Normann et al. [43] was focused on the chemistry involved in the binary interactions of SO_2 and NO_x compounds in pressurized flue gas systems. Pursuing the same technique, Sima et al. [44] further extended this research and investigated the effects on pH on the components involved during the acidification of SO_2 and NO_x in pressurized flue gas stream enriched with CO_2.

In our Aspen plus-based simulation study, the flue gas generated during oxy biomass combustion was subjected to a pressurized reactive distillation column (PRDC) process. This process involved the occurrence of a number of chemical reactions which resulted in the removal of SO_2 and NO_x from the CO_2-enriched flue gas in the form of valuable byproducts, i.e., H_2SO_4 and HNO_3. The conversion rates of NO_x and SO_2 into their respective acidic distillates correspond to the purification of CO_2.

The ratio of liquid to gaseous feed stream, rate of bottom product recycling, and ratio of holdup of the feed streams at the distillation column are important factors for PRDC which can play key roles in meeting the objectives of achieving oxy biomass–CCS. These factors are relevant to the specific operation of the distillation column, and have been analyzed in the relevant section through a sensitivity analysis using Aspen plus a simulation program. Keeping in view the negative carbon feature of oxy biomass combustion and CO_2 purification for CCS, the present work provides insights into the use of renewable energy with nearly zero emissions.

2. Materials and Methods

2.1. Methodology

A proposed 20 kW$_{th}$ biomass boiler with oxy combustion and CCS techniques was analyzed using the Aspen plus simulation program. The objectives of this simulation were to determine the best possible operational parameters for the integrated sensitivity analysis, where the maximum efficiencies for oxy biomass thermal process and the CO_2 purification process could be attained by the least effort and with nearly zero emissions. The process industry-designed Aspen plus simulation software includes a wide range of tools such as components, physical property databases and process models. The whole simulation process was divided into two parts in the present work: oxy biomass combustion with CO_2-enriched flue gas recirculation, and purification of the produced CO_2-enriched flue gas through conversion of NO_x and SO_2.

For the first step of the simulation, the Peng Robinson equation of state physical property [45] was used to simulate the operations of the thermal boiler. The advantage of using Peng Robinson property method is that its equations of state give better agreement between the experimental and simulation results, and it can be used in both the gaseous and liquid phases. In this equation, the pressure term of the Van der Waals equation was modified. The empirical form of this equation is mentioned in Equation (1):

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + (b(V_m - b))} \tag{1}$$

where $b = 0.0778 \frac{RT_c}{P_c}$; $a = a(T_c\alpha)$; $a(T_c) = 0.45724 \frac{R^2 T_{re}^2}{P_c}$; $a^{0.5} = 1 + ak(1 - T_{re}^{0.5})$; $k = 0.37464 + 1.54226\omega - 0.26992\omega^2$; and $T_{re} = \frac{T}{T_c}$.

Equation (1) can be re-written as:

$$Z^3 - (1 - B)Z^2 + \left(A - 3B^2 - 2B\right)Z - \left(AB - B^2 - B^3\right) = 0 \tag{2}$$

where $A = \frac{ap}{R^2 T^2}$; $B = \frac{bp}{RT}$; and $Z = \frac{pv}{RT}$.

The ELECNRTL as one of the electrolyte property method was used to calculate and predict the best possible process results for simulating the PRDC process in order to purify the CO_2 rich stream of flue gas. Furthermore, the Steam-TA property method was used to better predict the water/steam properties. During the simulation study of the oxy biomass with CCS techniques, the most suitable process models available in Aspen plus were assigned to specify the operational functions of process units, which were interconnected through material, and energy flow to build the process flowsheet. The properties of maize stalk biomass were used in the present simulation study, whose proximate and ultimate analyses data, as described in Table 1, were obtained using laboratory instruments i.e., TRGF-8000 (Hebi Tianrun Electronic Technology Company, HeBi, China) and EA-3000 Euro Vector EA-IRMS (EUROVECTOR Srl, Italy) respectively.

Table 1. Ultimate & proximate analyses of biomass fuel used in Aspen simulation.

C [%ad]	H [%ad]	N [%ad]	S [%ad]	O [%ad]	M [%ad]	A [%ad]	VM [%ad]	FC [%ad]	HHV [MJ/kg·db]
42.2	5.56	1.74	0.22	31.85	11.51	6.92	71.67	9.9	19.99

A pressurized reactive distillation column (PRDC) was used to model the conversion of SO_2 and NO_x into H_2SO_4 and HNO_3 along with purification of CO_2 during the present simulation study. In this model, the following three main factors were investigated for their effects on the process operations:

- Ratio of liquid feed to gaseous feed of PRDC;
- Ratio of holdup of the feed streams in PRDC; and
- Rate of recycling of bottom product (by-products in the present case).

These variable factors have shown great influence on the overall process of PRDC in terms of achieving nearly zero emission along with the purification of CO_2 for CCS.

2.2. Simulation Model

The simulation model is based on two interconnected processes: oxy biomass combustion with flue gas recirculation, and CO_2 purification unit processing, including the conversion of SO_2 and NO_x, and the generation of by-products in the form of H_2SO_4, HNO_3 and CO_2 purification. A synchronized process flow according to the proposed laboratory scale plant process is illustrated in Figure 1. In the oxy biomass combustion part of the understudied simulation system, three reactor models, namely RYield, RGibbs and RStoic, were used respectively to simulate the conversion of non-conventional maize stalk biomass fuel into conventional form, the combustion by minimizing the Gibbs free energy, and the conversion of fuel inherent nitrogen into NO_x at the pre-specified temperature under an oxy atmosphere. RYield model generates the elemental building blocks of non-conventional components. The RGibbs model produces the combustion products and the RStoic model converts the fuel inherent nitrogen into NO_x.

Figure 1. Oxy Biomass Combustion and CCS.

The combustion product achieved using the RGibbs model is a mixture of flue gases containing CO_2, CO, H_2O, SO_2, N_2, NO, NO_2, and excess O_2, with ash as solid residue. In modeling the oxy biomass combustion, NO produced by the model does not actually represent the exact NO_x formation. To accurately determine the fuel nitrogen conversion into NO_x, the RStoic model was introduced into the flue gas flow channel based on our previous experimental work [46]. The detailed reaction mechanism occurring in the RStoic reaction model involves the conversion of fuel nitrogen into fuel NO_x or elemental nitrogen, as illustrated in Section 2.3.1. The enthalpy of combustion taken by the flue gas is transferred to water for heating in the boiler through a heat exchanger. Ash removal was modelled by integrating the solid separator process model. The flue gas exiting the RStoic reactor model was set at 1000 °C, which was reduced to 180 °C after passing through the boiler. The thermal energy of the flue gas at 180 °C was used in the economizer for heat recovery by the introduced water. The relative low temperature flue gas stream was allowed to heat up the oxidizers by air preheater, where the temperature of the oxidizers was raised to 80 °C. The flue gas produced during the combustion process contains moisture, which should be minimized to a certain level in order to not impede the process efficiency. The exhaust flue gas stream was connected to the condenser followed by flash for the removal of moisture in the flue gas. The condensate stream containing 0.99 mole fraction of water after flushing from the flue gas stream was used as a liquid feed for the CO_2 purification unit for the absorption of NO_x and SO_2 to yield the acidic condensates. The cooled dry flue gas stream was

then split into two segments; one was allowed to return to the combustion reactor RGibbs after mixing with the pure O_2 stream (considering an excess O_2 factor of not more than 4% in the flue gas exiting the boiler), while the second (Stream 9) was set as the feed source for the CO_2 purification unit.

The CO_2-enriched flue gas was compressed by the compressor process model. The resultant flue gas was cooled through the cooler model prior to entering the PRDC model. A RadFrac column was used to perform the functions of the pressurized reactive distillation column (PRDC), where the gaseous feed stream (11) entered through the bottom end, and the liquid feed stream (L5) was injected through the top stage of the column. In the RadFrac model, kinetic and equilibrium reaction models must be synchronized in the Reaction module of the Aspen plus. The detailed NO_x and SO_2 absorption mechanisms involving the formation of complex species is described in Section 2.3.2. The pre-defined kinetic parameters of NO_x and SO_2 absorption reactions were integrated into the Reaction module to study their respective conversion into acids. Similar to the CO_2-enriched flue gas stream, the condensate stream was used as the liquid feed for the reactive distillation column. Its pressure and temperature values were synchronized according to flue gas stream, and absorption studies were carried out by varying the liquid to gas ratio in order to determine the best possible values for CO_2 purification. During the PRDC process, NO_x and SO_2 underwent the pre-specified reaction scheme and was converted to HNO_3 and H_2SO_4 respectively. The acidic forms were obtained as liquid condensate from the bottom stage of the reactive column, whose fractional compositions were adjusted by varying the recycle ratio to get the best possible values of NO_x and SO_2. The resulting CO_2-rich and effluent-lean vapor stream leaving the reactive column was compressed through the compressor model to obtain CO_2 liquefaction, whereby liquefied CO_2 is available for transportation and storage under saline aquifers or for further use. The operational parameters and their ranges in the present simulation process are summarized in Table 2.

Table 2. Parameters and operating conditions used in the steady state simulation.

Parameters	Unit	Value	Operating Range
Biomass flow rate	kg/hr	3.6	-
Excess O_2 (*v/v*)	%	3.46	-
Water flow rate	kg/hr	210	-
Fuel N conversion to NO	-	0.5	0.5–0.7
L/G feed ratio	-	0.04	0.02–0.2
Absorber Holdup	%	10	2–40
Bottom Recycling	-	0.2	0.2–0.8

2.3. Reaction Mechanism

The reaction mechanism involved in the RStoic reactor model used for the conversion of fuel nitrogen to NO_x or elemental nitrogen and absorption of NO_x and SO_2 in RadFrac reactive distillation column model of the Aspen plus simulation are described in the following sections:

2.3.1. Fuel N Conversion

Fuel–NO_x is formed from oxidation of fuel nitrogen within the fuel matrix [47]. It may evolve as volatile nitrogen or may remain in the char [48]. NO formed from fuel inherent nitrogen can be greatly influenced by its distribution in the volatiles and char of fuel matrix [49]. Fuel NO_x formation through char nitrogen undergoes heterogeneous reactions due to the interaction of formed NO_x with the active carbon sites at the surface of char leading to its reduction to elemental nitrogen. Volatile nitrogen after the formation of intermediate species in the form of HCN and NH_3 follows various possible routes, due to reactions with H, O, OH radicals to become oxidized, yielding NO_x, or it may be reduced to elemental nitrogen. The volatile nitrogen in biomass converts directly to NH_3 which may react with

char to form HCN (Equation (3)). It worth noting that more NH_3 is produced than HCN in biomass combustion [50].

$$NH_3 + CH \rightarrow HCN \tag{3}$$

The liberated NH_3 and formed HCN from the fuel nitrogen undergo various reaction processes which may result in the formation of NO through oxidation, or may reduce to N_2. NO_x formation from fuel nitrogen depends on various factors such as residence time, temperature and char particle size. The fate of fuel nitrogen contributing to the formation of NO or N_2 is illustrated in Figure 2 (as part of our previous work) [46]; the conversion rate to NO for a maize stalk biomass fuel was considered in the present simulation study.

Figure 2. Reaction mechanism – Fuel inherent nitrogen conversion to NO and N_2 Adapted from [46].

2.3.2. NO and SO_2 Absorption

The overall reaction mechanism involving the conversion of NO_x and SO_2 into several by-products is comprised of a series of binary phase reactions, where the gaseous phase chemistry involves the conversion of NO to NO_2 and SO_2 to SO_3. Major reactions take place in the liquid phase which involve the formation of intermediate N–S complex species during the formation of by-products in forms of N_2O, H_2SO_4, HNO_3, and N_2. The characteristics of the involved N–S complex species can be derived from the interactions between SO_2 and NO_x. It involves the formation of Oxo Sulfamic Acid $[ONSO_3^-]$, Hydroxy (Sulfo) Sulfamic Acid $[HON(SO_3)_2^{-2}]$, Hydroxy Sulfamic Acid $[HONHSO_3^-]$, Disulfo Sulfamic Acid $[N(SO_3)_3^{-3}]$, Sulfo Sulfamic Acid $[HN(SO_3)_2^{-2}]$, Sulfamic Acid $(NH_2SO_3^-)$, and Hydroxylamine (NH_2OH). The reaction scheme is shown in Figure 3.

During the present simulation, the main reactions were integrated with the aim of optimizing the maximum absorption of NO_x and SO_2 in binary phases. The gas phase chemistry involves the oxidation and hydrolysis of oxides of nitrogen and sulfur. Oxidation of NO into NO_2 i.e. Reaction (4) is the governing reaction in the gas phase; it is strongly influenced by pressure.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \tag{4}$$

NO oxidation is favored by low temperatures and high pressures [51]. The reaction is more prominent at elevated pressure, even for shorter reaction times. Maximum conversion to NO_2 can be achieved within a shorter residence time due to its greater solubility in water [52]. The rate of the reaction is first order with respect to O_2 and second order with respect to NO [51,53].

The formed NO_2 is in equilibrium with its dimer N_2O_4 (Reaction 5). The dimer formation favors by low temperatures [54].

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)} \tag{5}$$

Figure 3. Reaction mechanism involving N-S complex species.

The hydrolysis of N_2O_4 is the main reaction. N_2O_4 may be absorbed directly in the liquid phase, yielding nitric acid directly (Reaction 6) or through the intermediate formation of nitrous acid (Reaction 7).

$$N_2O_{4(aq)} + H_2O_{(l)} \leftrightarrow HNO_{3(aq)} + HNO_{2(aq)} \tag{6}$$

$$3HNO_{2(aq)} \leftrightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(l)} \tag{7}$$

Miller et al. [55] combined these reactions (6) and (7) into a single reaction (8);

$$\frac{3}{2}N_2O_{4(aq)} + H_2O_{(l)} \leftrightarrow 2HNO_{3(aq)} + NO_{(g)} \tag{8}$$

The interaction between SO_2 and NO_2 has been studied extensively by Jaffe et al. [56] and Armitage et al. [57]. Both publications studied experimentally the catalytic oxidation of SO_2 in the presence of NO_2. The oxidation of SO_2 is significant at temperatures higher than 900 °C; thus, at lower temperatures in the PRDC, direct oxidation was not included in the reaction scheme. Rather, NO_2, instead of the available O_2, reacts as an oxidizer in the conversion of SO_2 into SO_3 (Reaction 9), and subsequently produces H_2SO_4 on hydrolysis according to reaction (10).

$$SO_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + SO_{3(g)} \tag{9}$$

$$SO_{3(g)} + H_2O_{(l)} \leftrightarrow H_2SO_{4(aq)} \tag{10}$$
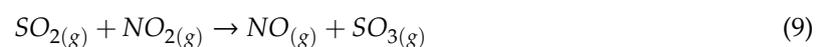
A detailed kinetic scheme of the involved reactions is illustrated in Table 3.

Table 3. Reaction kinetics of NO_x and SO_x absorption.

Reaction No.	Reactions	Kinetic Rate/Equilibrium Expression	Reference
4	$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$	$1.197 \times 10^3 \exp^{\frac{(530.4}{T)}} C_{NO}^2 C_{O_2}$	[58]
5	$2NO_{2(g)} \leftrightarrow N_2O_{4(g)}$	$\frac{5.625 \times 10^5}{RT}\left(P_{NO_2}^2 - \frac{P_{N_2O_4}}{K_{eq(5)}}\right)$	[53]
6	$N_2O_{4(aq)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + HNO_{2(aq)}$	$10^{16.34-\frac{4139}{T}} C_{N_2O_4}$	[53]
7	$3HNO_{2(aq)} \rightarrow HNO_{3(aq)} + 2NO_{(aq)} + H_2O_{(l)}$	$9.2 \times 10^{-7} C_{HNO_2}^3$	[59]
8	$\frac{3}{2}N_2O_{4(aq)} + H_2O_{(l)} \leftrightarrow 2HNO_{3(aq)} + NO_{(aq)}$	$K_{6,7} = \frac{p_{NO}}{p_{N_2O_4}^3} \cdot \frac{a_{HNO_3}^2}{a_{H_2O}}, \frac{kmol}{m^3} \cdot kPa^2$	[55]
9	$SO_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + SO_{3(g)}$	$6.31 \times 10^9 \exp\left(\frac{-1359}{RT}\right) C_{NO_2} C_{SO_2}$	[57]
10	$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$	$r_{10} = 10^8\left(C_{H_2SO_4} - \frac{C_{SO_3}C_{H_2O}}{K_{eq,10}}\right),$	-

2.4. System Performance Calculations

2.4.1. Thermal Performance

Thermal efficiency is a direct indication of fuel resource conservation and emission reduction. In the present work, an indirect method to determine the boiler efficiency when ASME (American Society of Mechanical Engineers) standards are used was included in the first part of simulation. All the system and process losses were first taken into consideration, and the difference between the cumulative losses and the energy input was taken as the boiler efficiency. The losses include dry flue gas exiting the boiler (L_{DFG}), moisture produced due to oxidation of H_2 plus evaporation of moisture content of the fuel (L_{H_2O}), unburnt combustibles in the form of CO (L_{CO}), unburnt losses and fly and bottom ashes (L_{ASH}), and radiation and convection losses (L_R). These losses were calculated using a set of empirical equations, as shown in Equations (11)–(14);

$$L_{DFG} = \frac{m_{DFG} \times C_p \times (T_{FG} - T_a)}{GCV_{BM}} \times 100 \tag{11}$$

where

$$m_{DFG} = \frac{\left[10^{-2}\{44CO_2 + 32O_2 + 28N_2\} + 10^{-6}\{30NO + 46NO_2 + 64SO_2\}\right] \times \dot{m}_{oxidizer}}{22.4 \times \dot{m}_{biomass}} \tag{11a}$$

$$C_p = \frac{\left[\left(m_{CO_2}C_{p_{CO_2}}\right) + \left(m_{N_2}C_{p_{N_2}}\right) + \left(m_{O_2}C_{p_{O_2}}\right)\right]}{\left(m_{CO_2} + m_{N_2} + m_{O_2}\right)} \tag{11b}$$

$$L_{CO} = \frac{m_{CO} \times C_{pCO} \times (T_{FG} - T_a)}{GCV_{BM}} \times 100 \tag{12}$$

where

$$m_{CO} = \frac{28 \times CO \times \dot{m}_{oxidizer}}{22.4 \times 10^{-2} \times \dot{m}_{biomass}} \tag{12a}$$

$$L_{H_2O} = \frac{\left(M + 9 \times H_2 + \left(\dot{m}_{oxidizer} \times HF\right)\right) \times \left(h_g - h_f\right)}{GCV_{BM}} \times 100 \tag{13}$$

$$L_{ASH} = \frac{\dot{m}_{ASH} \times C_{pASH} \times (T_{FG} - T_a)}{GCV_{BM}} \times 100 \tag{14}$$

The efficiency of the boiler was determined using Equation (15).

$$\eta = 100 - \left(L_{DFG} + L_{CO} + L_{H_2O} + L_{ASH} + L_R \right) \tag{15}$$

2.4.2. Conversion Performance

The abatement efficiency of the effluents, i.e., NO and SO_2, is a direct indication of the CO_2 purification, since these effluents settle in the distillation unit in acidic forms and are separated as the acidic condensate product of the reactive column, whereas the purified CO_2 stream leaves as vapor product of the reactive column. During simulation, the NO_x and SO_2 removal efficiencies were calculated using Equations (16) and (17) respectively;

$$\text{NO Conversion} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \tag{16}$$

$$SO_2 \text{ Conversion} = \frac{[SO2]_{in} - [SO2]_{out}}{[SO2]_{in}} \tag{17}$$

where $[NOs]_{in}$, $[NO]_{out}$, $[SO_2]_{in}$, $[SO_2]_{out}$ are the NO and SO_2 concentrations (in mole fraction) at inlet and outlet of PRDC (RadFrac).

3. Results and Discussion

Various parameters of the present simulation study have been evaluated regarding the subsequent combustion of maize stalk biomass under an oxy atmosphere with flue gas recirculation and the treatment of flue gas channel drawn out for pressurized reactive distillation column (PRDC). The results of the oxy biomass thermal system are comprised of thermal performance and evaluation of losses incurred during the combustion process. In addition, the heating and cooling curves of the boiler are evaluated and presented. As an important part of the present study is to optimize the extent of CO_2 purification through the subsequent conversion of NO_x and SO_2 into their respective by-products through PRDC, the variable factors relevant to the specific operation of distillation column were analyzed and the respective results are described in detail. The ratio of liquid to gaseous feed stream, rate of bottom product recycling, ratio of holdup of the feed streams at the distillation column are important factors affecting the operation of the PRDC. These factors can play key roles in meeting the objectives of achieving oxy biomass–CCS. The results are described below:

3.1. Oxy Biomass based Thermal System

3.1.1. Thermal Efficiency

The losses occurring in the boiler vary widely due to boiler design and operational modes. Biomass fuels have their distinguished primary characteristics in terms of elemental or proximate analysis. In the present scenario, maize stalk comprises a higher ratio of H_2O and H_2 in its fuel matrix. The inherent moisture evaporates during the combustion process and accompanies the flue gas. Hydrogen contained in the biomass fuel matrix is excessively oxidized, forming H_2O, which is added into the already evaporated moisture content in the flue gas. Considering Equation (13) regarding losses due to H_2O formation, it gives a clear overview of an inverse relationship between the concerned losses and the calorific value of the biomass. Alternatively, the thermal performance of the boiler is adversely influenced by the higher moisture contents of the flue gas. The major losses in the present study are those due to moisture formation in the flue gas, accounting for 74.12% (1.64 kW$_{th}$) of the total thermal losses. The detailed losses are plotted in Figure 4.

On the other hand, the radiation and convection losses rely mainly upon the design and structure of thermal boiler. In the present study, it was kept at constant value. Other incorporated losses include dry flue gas leaving the boiler through a vent fan, which accounts for 7.17% (0.16 kW$_{th}$). The unburnt

organic material left behind in the ash portion of the fuel, and the subsequent formation of CH_4 and CO, contribute to the increase in losses which lowers the thermal efficiency of the boiler. During actual boiler operation, the flue gas heat losses calculated are based on the flowrate, temperature and composition of flue gas; Dias et al., 2004, among others, studied conventional combustion in a biomass boiler and obtained thermal efficiencies of up to 77% [7]. Under an oxy atmosphere in the present study, the thermal efficiency was shown to be 88.91%, which is comparatively under oxy conditions compared to the referenced conventional condition.
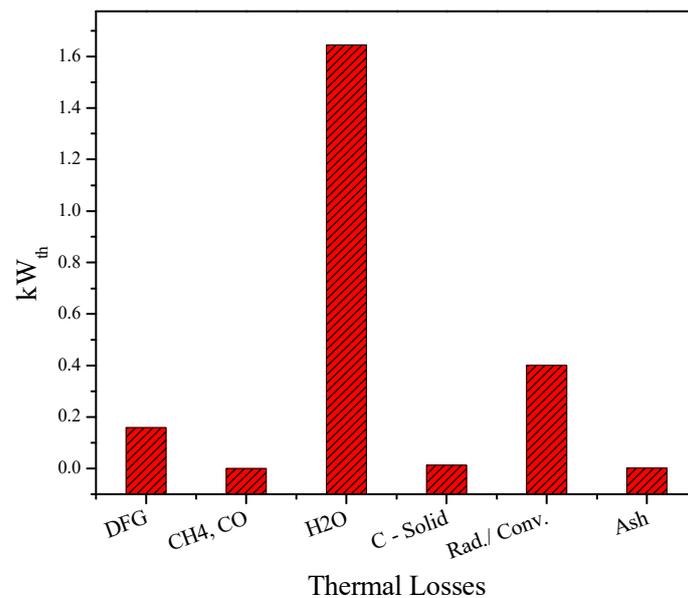
Figure 4. Thermal losses (in kW_{th}) of the 20 kW_{th} oxy combustion based thermal boiler.

In order to address the extent of GHGs and pollutant reduction in the boiler, it is important to have a comparative overview of oxy and conventional combustion techniques. The main difference lies in the oxidizer atmosphere, where the nitrogen of the air acts as a diluent during the conventional combustion process. In the case of oxy the combustion technique, nitrogen is replaced by recycled flue gas, whereas pure oxygen is required as the main oxidizer. The pure oxygen (up to 95%) is usually obtained through a cryogenic air separation process which splits air into its components. To make CO_2 capture viable, it will be necessary to enhance its formation, which is carried out by recycling the produced flue gas as a result of combustion under an oxy atmosphere. The average flue gas composition of both the combustion systems is illustrated in Table 4:

Table 4. Average flue gas composition of conventional and oxy combustion (3.5% Excess O_2).

Parameters	Unit	Conventional	Oxy
CO_2	%	15.94	89.01
N_2	%	74.39	1.25
NO	Mol-frac.	0.0172	0.0084
NO_2	Mol-frac.	7.75×10^{-7}	9.54×10^{-8}
SO_2	Mol-frac.	0.00292	0.0016

It can be inferred through Table 4 that the resultant flue gas during conventional combustion is enriched mainly with N_2, whereas CO_2 is prevalent in cases of oxy combustion. The corresponding SO_2 and NO_x results can be justified with similar results to those observed by Shao et al., 2013 [60], where adequate NO_x and SO_2 emission reductions were observed by changing the conventional air to oxy combustion atmospheres. Li et al., 2013 [61], considering the internal flue gas recirculation in

a co-firing boiler, observed the same phenomenon of lower NO_x and SO_2 emissions in oxy atmosphere compared to the corresponding conventional one. Through flue gas recycling, NO_x can be highly reduced due to char nitrogen reacting with the produced NO_x [62].

Usually, CO_2 formation in conventional air combustion accounts for around 16% of the total flue gas; the rest of the flue gas is composed of N_2. This order is different in case of oxy air combustion, where the exhaust stream is mainly composed of 80–95% CO_2. CO_2, having different thermal and chemical characteristics and being denser than nitrogen in the air, impacts on the overall process. Consequently, heat accumulation and reclamation due to recycling is advantageous for the efficiency of the process.

3.1.2. Heating/Cooling Curves of Heat Exchangers

The heating rates of the heat exchanger are a function of the varying temperature with the passage of time. The heating curve obtained through the operation of the heat exchanger is considered a measure of heat exchanger's effectiveness. Due to the steady state simulation, the time factor was not included in the present study. However, heat duties (kW) of the boiler heat exchanger model were calculated, corresponding to the change in temperatures of both the cold and hot streams. The curves obtained by heat transfer in the heat exchanger with gradual variations in the hot and cold side temperatures is illustrated in Figure 5.
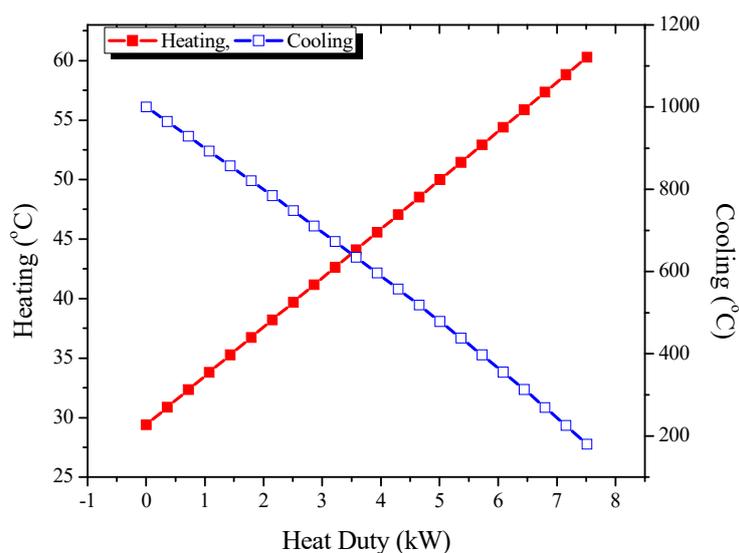
Figure 5. Heating and Cooling Curves of Boiler.

Heat given by hot stream through a step change in temperature is transferred to heat the cool stream. Flue gases exiting RStoic model were adjusted at 1000 °C; they were then allowed to cool to below 200 °C in the boiler model. Heat duty generated during cooling process of the flue gas in the heat exchanger was used to raise the temperature of the cool water stream from ambient temperatures to around 60 °C.

3.2. Pressurized Reactive Distillation Column (PRDC)

In order to achieve the maximum conversion rates of SO_2 and NO_x for the purification of CO_2 and consequent formation of by-products (H_2SO_4 and HNO_3 etc.) during the pressurized reactive distillation column (PRDC) process, the effects of the various parameters such as fuel inherent nitrogen conversion rate and the variable factors affecting PRDC process have been analyzed. The results obtained through sensitivity analysis of the involved factors were in agreement with the relevant results obtained by referenced researchers.

3.2.1. Effect of Conversion Rate of Fuel Inherent Nitrogen on Rate of Conversion

In the case of oxy combustion, where nitrogen in air is replaced by a pure oxygen stream, the NO_x formation is sourced by fuel nitrogen only. The conversion mechanism of fuel nitrogen into NO_x or elemental nitrogen (N_2) depends on many factors, such as the fuel characteristics, devolatilization conditions and combustion mode on the selectivity of oxidation toward NO_x formation or reduction towards elemental nitrogen [63]. One of the factors is the surrounding atmosphere of the burning fuel particles, which dictates the fate of fuel inherent nitrogen [47]. Accordingly, the formation of intermediate species such as NH_3 and HCN does not quantify the ratio of NO_x produced to elemental nitrogen in flue gas. Analyzing the fuel inherent nitrogen conversion into NO_x and extending it further to PRDC gives an good idea of achieving the enhanced conversion efficiency at comparatively higher concentrations of NO_x in the flue gas.

As explained in the simulation model, the mechanism of nitrogen distribution into NO_x and N_2 was integrated into Aspen by varying the conversion rates based on our similar experimental work [47]. During the present simulation study, various ratios of NO to elemental N_2 were assigned to quantify the subsequent conversion of NO into HNO_3 in the reactive distillation column. The results, as illustrated in Figure 6, show that through enhancing the Fuel-N conversion rate to NO accelerated the absorption of NO into PRDC, a similarly higher ratio of HNO_3 as a by-product of the PRDC process is obtained. Although higher NO_x formation is not considered favorable due to its atmospheric deterioration characteristics, in order to achieve the purification of CO_2 simultaneously with HNO_3 production as the bottom product, higher concentrations do not adversely affect the conversion in the PRDC process.
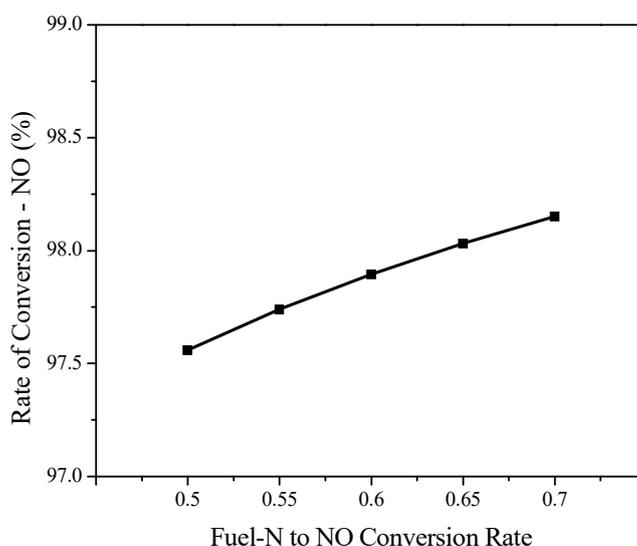
Figure 6. Profile of fuel N to NO conversion versus NO Conversion (%) in pressurized reactive distillation column (PRDC).

3.2.2. Effect of Liquid/Gaseous Feed Ratio on Rate of Conversion

Large scale usage of water in the industries has created shortages of drinking water. Based on this fact, the moisture content leaving the boiler with flue gas after condensing and flashing out from the gas stream was used as a liquid feed for the present simulation study. Keeping in view the optimum level of liquid required to achieve maximum reactive distillation, a series of liquid feed to gaseous feed ratios was established, and its effects on NO and SO_2 reduction were observed, as shown in Figure 7. From Figure 7, the mole fraction of NO and SO_2 are shown to decline with increases in the ratio of liquid to gaseous feed rate. Although the mole fractions of NO and SO_2 are decreasing with the liquid to gaseous feed ratio, the decrease in the mole fraction of SO_2 is more prominent, showing a linear

decrease, whereas NO fraction decreases sharply in the lower liquid to gas feed ratio due to a faster absorption reaction compared to the corresponding higher ratios.
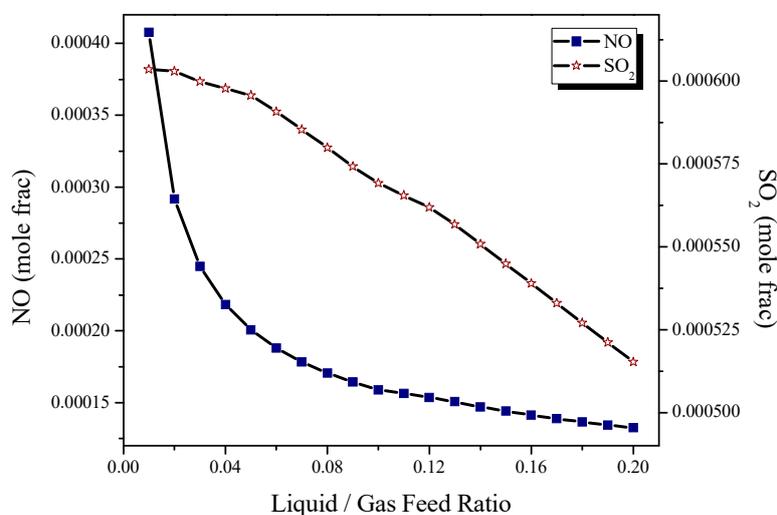
Figure 7. Effect of liquid/gas feed ratio on vapor product composition.

The maximum removal efficiencies of NO and SO_2 have been achieved at higher liquid to gaseous feed ratios due to the availability of more moisture in the liquid phase, as shown in Figure 8. A higher moisture content gives rise to more surface area for absorption of the acidic gases; however, on an industrial scale, limiting the level of moisture required for maximum reactive distillation is more economical and favorable, as keeping the liquid to gaseous feed ratio at its optimum level is necessary to achieve maximum CO_2 purification.
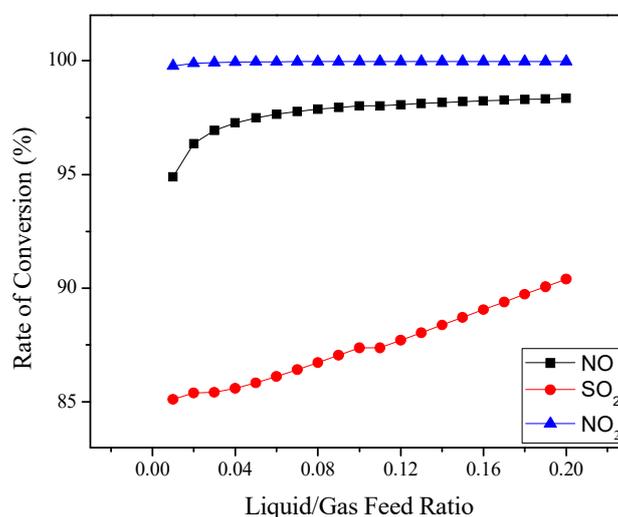
Figure 8. Effect of liquid/gas feed ratio on rate of conversion (%).

On the other hand, through focusing on the bottom (liquid) products, satisfactory results validating the conversion of NO and SO_2 into their respective acidic forms were achieved. The mole fractions of H_2SO_4 and HNO_3 in the bottom products were plotted with an increasing trend of liquid to gaseous feed ratio, as displayed in Figure 9, in which a linear decline in the molar concentrations of HNO_3 and H_2SO_4 occurs, which, by contrast, is a direct indication of abatement of NO_x and SO_2 from the flue gas stream, thus allowing CO_2-enriched stream to be purified.
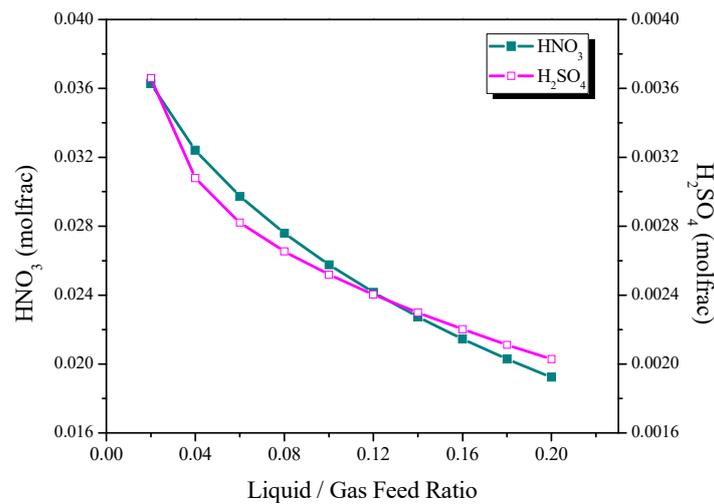
Figure 9. Effect of liquid/gas feed ratio on liquid product composition.

3.2.3. Effect of Column Holdup on Rate of Conversion

Liquid holdup is one of the most important hydrodynamic parameters in characterizing the vapor/liquid flow configuration in the structured distillation columns [64]. The column performance is influenced by holding up a certain percentage of the total feed streams by keeping the recycle ratio, liquid to gaseous feed ratio, column pressure and temperature at constant levels. Holdup is the ratio of feed volume kept in the bed compared to the total volume of column occupied by the packing material. It is influenced by the feed flow rate, viscosity and density of the working medium. The effect of holdup on the column performance could be positive or negative. In the present study, liquid feed holdup showed effects on the column performance in terms of reduction of NO_x and SO_2. The vapor holdup did not show any effect on the column performance. The obtained results of liquid feed holdup show the effects of increasing rate of holdup on NO_x and SO_2 removal efficiency from the flue gas. Figure 10 illustrates the holdup rate profile on variations of the mole fraction values of NO and SO_2, which are declining with an increasing holdup ratio (%). NO reduction is more prominent at a lower rate of holdup, whereas SO_2 saw a linear decline along the holdup ratio. It may be concluded that the conversion of SO_2 to H_2SO_4 could be enhanced with gradual holdup increments. The sudden change in the mole fraction of NO and SO_2 at lower holdup rates was observed by Mujtaba et al., 1998 [65], where a relative easy distillation was observed at the start of the batch process at lower holdup ratios.
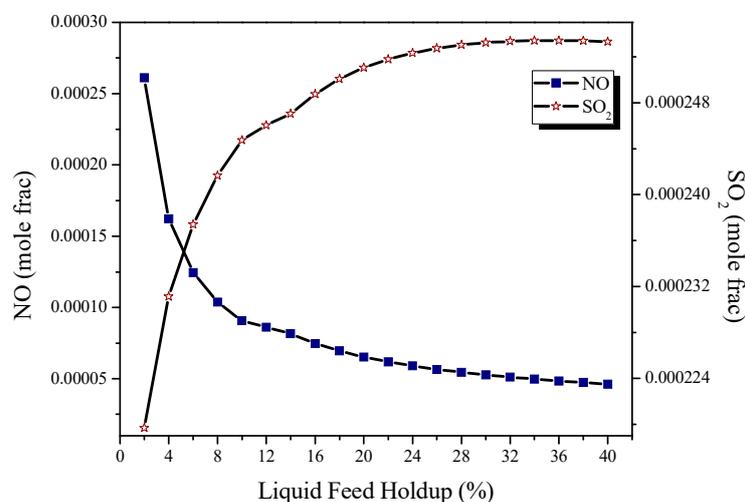
Figure 10. Effect of liquid holdup on vapor product composition.

The column performance in terms of NO_x and SO_2 conversion efficiencies (%) is presented in Figure 11, where NO at a much higher level of removal efficiency is affected a little as compared to SO_2. The rate of liquid feed holdup is seen to be more favorable to the conversion of NO to HNO_3 at lower rates, till a certain holdup rate i.e. 20% occurs, at which time there is no prominent effect on NO conversion. SO_2 conversion to H_2SO_4 is enhanced at an average rate of 0.02% on every 6% increment of holdup, attaining a maximum efficiency of 75% at 40% holdup. SO_2 removal efficiency is enhanced at a faster rate than NO under the similar trend of liquid feed holdup ratio. Meanwhile, there is no visible negative effect on the NO_2 removal performance by holdup ratio. Iloeje et al. 2015 [66] observed there inverse relationship between NO_x concentration in flue gas stream and holdup volume per stage of a single column absorber. The present simulation result shows good agreement with the modeling studies conducted by Iloeje et al., in such a way that lower NO_x concentrations are observed at higher holdup rates. In contrast to NO_x behavior, the SO_x concentration shows the opposite trend. The reason for this behavior depends on the selectivity of the conversion rate of NO_x over SO_2, such as NO after oxidation to NO_2 acting as the oxidizing agent for the oxidation of SO_2 to form SO_3, as shown in reaction (4) and reaction (9). Therefore, the NO_x concentration is reduced first among the holdup rates, which results in an increase of SO_2 concentration (as shown in Figure 10); however, the conversion rate of SO_2 to H_2SO_4 becomes constant at 85% after 20% of liquid holdup is attained (Figure 11).
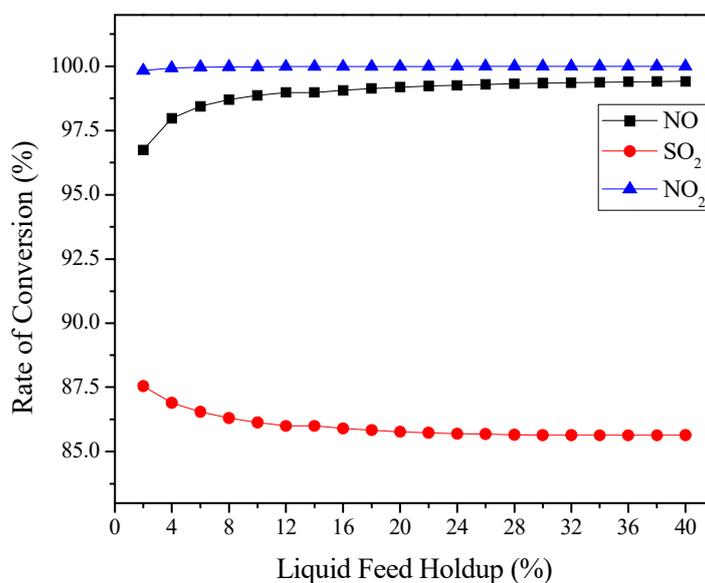
Figure 11. Effect of Feed holdup on Rate of Conversion (%).

It can be concluded that based on the reaction mechanism involved during the PRDC process, a mild liquid holdup ratio on one side may enhance the conversion rate of NO_x into HNO_3, while on the other hand, it may lower the conversion rate of SO_2 into H_2SO_4. In order to balance the formation of both by-products, a value of 10% for holdup was taken for the present simulation study.

3.2.4. Effect of Recycling Rate of Column's Bottom on Rate of Conversion

The bottom recycling in the pressurized reactive distillation column (PRDC) influences the performance of the PRDC process by altering the composition of liquid stream in the reactive distillation column. In the present scenario, the rate of bottom recycling tends to raise the mole fraction of NO_x and SO_2 in the reactive column's gaseous (top) product, as illustrated in Figure 12. It shows the adverse impact of bottom recycling on CO_2 purification, as it will reduce the conversion of effluents, i.e., NO_x and SO_2 to HNO_3 and H_2SO_4, and consequently, will enhance the mole fraction of these effluents in the gaseous product stream.
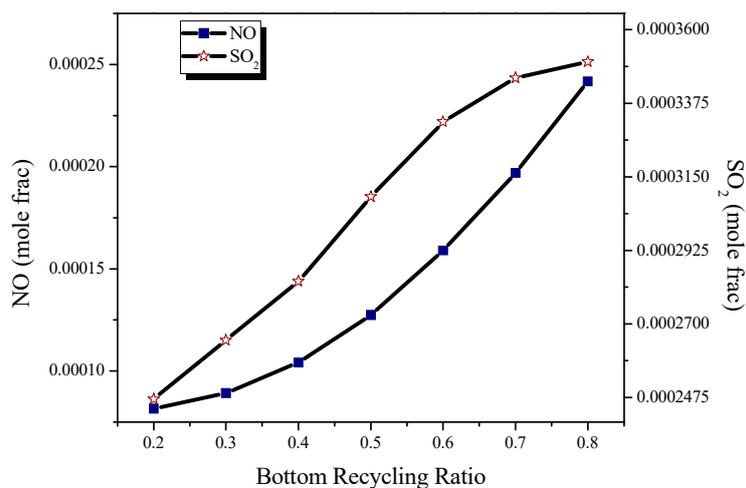
Figure 12. Effect of Bottom Recycling ratio on vapor product composition.

Modeling work done by Iloeje et al. 2015 [66] supports the present trend of increased NO_x concentrations along with enhancing the bottom recycle fraction.

From Figure 13, it is inferred that even though SO_2 conversion is at a lower level than NO, its variation in rate of conversion is more influenced by enhancing the bottom recycle ratio than NO. The SO_2 conversion rate is seen to reduce at an average rate of 1% on enhancing the recycling ratio of 0.1, whereas the NO conversion rate is reduced at a comparatively lower pace that is a 0.333% average decrease on enhancing the recycling ratio of 0.1.
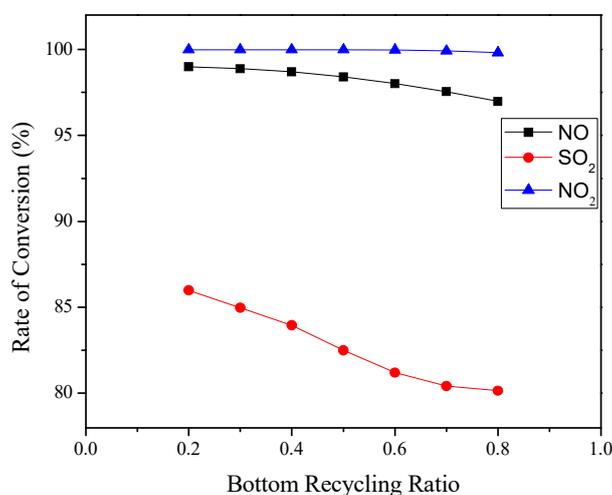
Figure 13. Effect of Bottom Recycling ratio on Rate of Conversion (%).

This further elaborates the reaction scheme implemented in the PRDC process, where the rate of H_2SO_4 yield was shown to be 1/3 times less than the corresponding yield of HNO_3 by keeping bottom recycling rate at 0.2. At this rate of bottom recycling, around 99% of NO is converted to HNO_3 and 86% of SO_2 is converted to H_2SO_4. It is worth noting that NO_2 in the aforementioned sensitivity studies has not shown any visible changes in its concentration; such behavior illustrates that the studied parameters did not have a prominent effect on the NO_2 characteristics.

4. Conclusions

A simulation-based study of oxy biomass combustion using maize stalk as the primary fuel for the boiler with flue gas recirculation was conducted with the main objectives of determining the

thermal performance of the boiler and the optimization of CO_2-enriched flue gas cleaning up process for CCS. The unique characteristics of the proposed system included fuel inherent nitrogen conversion to NO_x and the use of flushed out condensate water as the liquid feed for the CCS system, which can be considered as the novelty of the prescribed system. An indirect method of determining the thermal efficiency was adopted which resulted in 88.91% efficiency of the proposed 20 kW_{th} biomass boiler. On further pursuance, NO concentration in flue gas enriched with CO_2 was treated through pressurized the reactive distillation column (PRDC) process, where up to 98.05% NO and 87.42% SO_2 were converted into valuable by-products including HNO_3 and H_2SO_4, respectively Sensitivity analysis through varying the factors of liquid to gas ratio, holdup ratio and bottom recycle ratio were performed. Around four kilograms per hour of CO_2 with 94.13% purity was achieved by optimizing the simulation system with variable parameters. The total gas stream leaving the reactive distillation column comprised 3.47% O_2, 1.57% N_2 and 0.83% H_2O along with 94.13% CO_2. After separation of moisture through cooling and condensing the mix stream, the pure CO_2 can be available to transport for storage under saline aquifers or for use in enhanced oil recovery operations.

However, certain economic factors, such as retrofitting of the existing boilers to make them suitable for oxy combustion and the cryogenic production of pure oxygen through the air separation technique are being considered as the main issues for industrial applicability. Oxy combustion and flue gas processing techniques are among the possible mechanisms of cleaner production. The investigated simulation model based on the oxy biomass–CCS technique can play a potential role, as negative emission technology and can boost the likelihood of achieving low concentration targets [67]. Based on this simulation system, the arrangements of a proposed laboratory scale boiler, i.e., setting up CO_2-enriched flue gas compressor and packed bed pressurized reactive distillation column, are in progress for future experimentations. The proposed laboratory scale system will not only validate the applicability of the oxy biomass–CCS technique, but will serve as a basis for attracting investment projects for plant scale operation.

Author Contributions: I.A.S. designed and carried out the simulation. I.A.S. and X.G. participated in the analysis of data. I.A.S. wrote the manuscript. X.G. and J.W. revised the manuscript. All authors have read and approved the manuscript.

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