

Coal-Scenedesmus Microalgae Co-Firing in a Fixed Bed Combustion Reactor: A Study on CO₂, SO₂ and NO_x Emissions and Ash

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This study investigated the effect of coal?Scenedesmus microalgae (with blending ratios of 100:0 (coal), 95:5 (Coalgae® 5%), 90:10 (Coalgae® 10%), 85:15 (Coalgae® 15%) and 80:20 (Coalgae® 20%)) on combustion temperature, mass loss, the formation of CO₂, SO₂ and NO_x gases, and ash content under constant atmospheric air flow. Coalgae® refers to a material formed after blending coal and microalgae. The results showed that NO_x came mainly from Coalgae® 10% and 15%, and this observation could be attributed to a variable air concentration level (O₂ level) in the environment that could influence NO_x during the combustion process, irrespective of the blending ratios. CO₂ emission reductions (12%, 17%, 21% and 29%) and SO₂ emission reductions (3%, 12%, 16% and 19%) increased with the increasing coal-microalgae blending ratio (Coalgae® 5?20%), respectively. Bubble-like morphology was observed in the ash particles of coal?microalgae blends through SEM, while the TEM confirmed the formation of carbon-based sheets and graphitic-based nanocomposites influenced by the microalgae amounts. Ash residues of the coal?microalgae blends contained high amounts of fluxing compounds (Fe₂O₃, K₂O, CaO and MgO), which resulted in an increased base/acid ratio from 0.189 (coal) to 0.568 (Coalgae® 20%). Based on the above findings, the co-firing of coal?Scenedesmus microalgae led to a reduction in CO₂, SO₂, and NO_x emissions. As such, lower Coalgae® blends can be considered as an alternative fuel in any coal-driven process for energy generation.

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Article

Coal-*Scenedesmus* Microalgae Co-Firing in a Fixed Bed Combustion Reactor: A Study on CO₂, SO₂ and NO_x Emissions and Ash

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Abstract: This study investigated the effect of coal-*Scenedesmus* microalgae (with blending ratios of 100:0 (coal), 95:5 (Coalgae[®] 5%), 90:10 (Coalgae[®] 10%), 85:15 (Coalgae[®] 15%) and 80:20 (Coalgae[®] 20%)) on combustion temperature, mass loss, the formation of CO₂, SO₂ and NO_x gases, and ash content under constant atmospheric air flow. Coalgae[®] refers to a material formed after blending coal and microalgae. The results showed that NO_x came mainly from Coalgae[®] 10% and 15%, and this observation could be attributed to a variable air concentration level (O₂ level) in the environment that could influence NO_x during the combustion process, irrespective of the blending ratios. CO₂ emission reductions (12%, 17%, 21% and 29%) and SO₂ emission reductions (3%, 12%, 16% and 19%) increased with the increasing coal-microalgae blending ratio (Coalgae[®] 5–20%), respectively. Bubble-like morphology was observed in the ash particles of coal-microalgae blends through SEM, while the TEM confirmed the formation of carbon-based sheets and graphitic-based nanocomposites influenced by the microalgae amounts. Ash residues of the coal-microalgae blends contained high amounts of fluxing compounds (Fe₂O₃, K₂O, CaO and MgO), which resulted in an increased base/acid ratio from 0.189 (coal) to 0.568 (Coalgae[®] 20%). Based on the above findings, the co-firing of coal-*Scenedesmus* microalgae led to a reduction in CO₂, SO₂, and NO_x emissions. As such, lower Coalgae[®] blends can be considered as an alternative fuel in any coal-driven process for energy generation.

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1. Introduction

Coal provides approximately 27.2% of the world's primary energy needs [1] and generates approximately 36% of the world's electricity [2]. This is largely due to the accessibility, affordability, and availability of high-quality coal, particularly in South Africa. Coal generates approximately 85% of South Africa's electricity [3]. The reliance on coal is unlikely to change in South Africa for the next decade, due to a lack of suitable alternative energy sources [3]. Coal combustion poses numerous environmental challenges, as it emits greenhouse gases (GHGs), such as CO₂, SO₂ and NO_x, which directly contribute to the atmosphere and consequently cause health risks [4–6]. South Africa (non-Annex 1) has not been obliged to reduce GHG emissions; however, it is amongst the 20 most carbon-intensive countries. Hence, it has volunteered to reduce its CO₂ emissions by 34% by 2020 and 42% by 2025 at the COP meeting held in Copenhagen in 2009 [7].

The co-firing of coal with biomass (as a renewable energy source), such as microalgae, wood, wheat straw, agricultural waste, etc., in coal-fired power plants has been reported to effectively reduce the emissions of CO₂, SO₂ and NO_x gases [8–13]. In addition, the co-firing of coal and biomass increases energy security and improves green energy production. Although high blending ratios of biomass to coal result to high emission reduction, low blending ratios (20% maximum) are recommended to avoid the technical challenges emanating from firing biomass alone [14–16]. Microalgae are a promising energy source, due to

their high growth rate, productivity, simple nutrient requirements, use of non-productive lands, and their lack of direct competition for food [17,18].

Microalgae can be used to treat coal or any carbonaceous material before thermochemical processing, such as combustion, gasification, liquefaction, distillation, pyrolysis, and coking [19]. Microalgal biomass slurry have also been reported to easily adsorb onto coal fines, forming a new material, “Coalgae[®],” with different properties [20,21]. *Scenedesmus* has been identified as a promising microalgae strain, due to its high efficiency for CO₂ capture amongst green microalgae [22–24]. *Scenedesmus* microalgae have lower ash content (5.9 wt.%), lower sulphur (0.3 wt.%), higher volatile matter (82.2 wt.%) and higher calorific value (21.4 wt.%) [21] compared to most strains reported in the literature [25–28]. Several studies on coal and microalgae (various strains) co-firing have been reported; however, there are few studies focusing on *Scenedesmus* microalgae co-firing, hence the need to address this gap. The characteristics of this strain of microalgae (*Scenedesmus*) make it a potential biomass with excellent combustion performance, unique thermochemical properties, and a high possibility of reducing CO₂ and SO₂. Hence, studying the effect of co-firing this strain with coal on emissions is significant.

In this research, the co-firing of coal–*Scenedesmus* microalgae blends (Coalgae[®] 5%, 10%, 15% and 20%) was studied under atmospheric air using a fixed-bed combustion reactor. The main purpose of this study was to investigate the effect of co-firing coal with *Scenedesmus* microalgae on the emissions of CO₂, SO₂ and NO_x. The objective of this study was to broaden knowledge on the combustion of Coalgae[®] blends through the experimental characterization of CO₂, SO₂ and NO_x emissions as well as their resulting ash residues when two different materials, coal and *Scenedesmus* microalgae, were co-fired in a fixed-bed reactor at various atmospheric air flow rates.

2. Materials and Methods

2.1. Materials

The coal used in this study was supplied by Eskom, in South Africa. The coal was pulverised using a Keegor Vertical Spindle Pulveriser and screened to a particle size of <150 µm for proximate and ultimate analyses, as well as calorific value analysis. Lumpy coal was used for combustion experiments in a reactor. A *Scenedesmus*-dominated culture of microalgae with solids of ~2% per litre was obtained from InnoVenton: Institute for Chemical Technology at the Nelson Mandela University, in Port Elizabeth, South Africa.

2.2. Chemical Analyses

Proximate analysis was performed using an oven to determine the moisture content (ASTM E-871); a muffle furnace to determine volatile matter (ASTM D-3175) and ash content (ASTM E-1755); and fixed carbon was calculated by the difference (ASTM E-870). Ultimate analysis was performed using an Elementar Vario EL cube (ASTM D-3176) to determine the composition of C, H, N, S and O (by difference) of the coal and Coalgae[®] blends. The calorific values (often known as high heating values (HHV)) of the coal, the *Scenedesmus* microalgae and their blends (Coalgae[®]) were determined using a bomb calorimeter Leco AC 600 (ASTM D-5865). The chemical properties of the Coalgae[®] 5–20% with reference to the coal and *Scenedesmus* microalgae are summarised in Table 1.

2.3. Combustion System Description

A vertical down-firing fixed-bed combustion reactor, shown in Figure 1, was used to carry out the combustion experiments. A 33 cm long fixed-bed reactor with an inner diameter of 4.1 cm and outer diameter of 4.9 cm was used to carry out the combustion experiments. The reactor was fitted with an air supply line situated below the grate. The flow of air into the reactor was regulated through a flow meter. Above the grate was the ignition inlet (operated manually to ignite the fuel), suspended onto the grate, inside the reactor. During combustion, the flue gas was directed towards the chimney on top of the

reactor. Also, at the top of the reactor, there was a gas flow outlet from which flue gas was analysed.

Table 1. Chemical properties of coal and Coalgae[®] 5–20% (air-dry basis).

	Coal	Coalgae [®] 5%	Coalgae [®] 10%	Coalgae [®] 15%	Coalgae [®] 20%
Proximate analysis (wt. %)					
Moisture	4.61	4.78	4.99	5.05	5.16
Volatiles	24.5	26.9	29.1	31.7	34.9
Ash	15.0	14.9	14.7	13.9	13.0
Fixed carbon	55.9	53.4	51.3	49.4	47.0
Ultimate analysis (wt. %)					
Carbon	65.4	63.4	61.8	61.4	61.1
Hydrogen	5.04	5.06	5.10	5.25	5.61
Nitrogen	1.97	2.74	2.76	2.78	3.22
Sulphur	0.49	0.47	0.40	0.39	0.37
* Oxygen	12.1	13.4	15.2	16.3	16.7
HHV(MJ/kg)	25.9	25.7	25.4	25.3	25.1

* Oxygen calculated by difference.

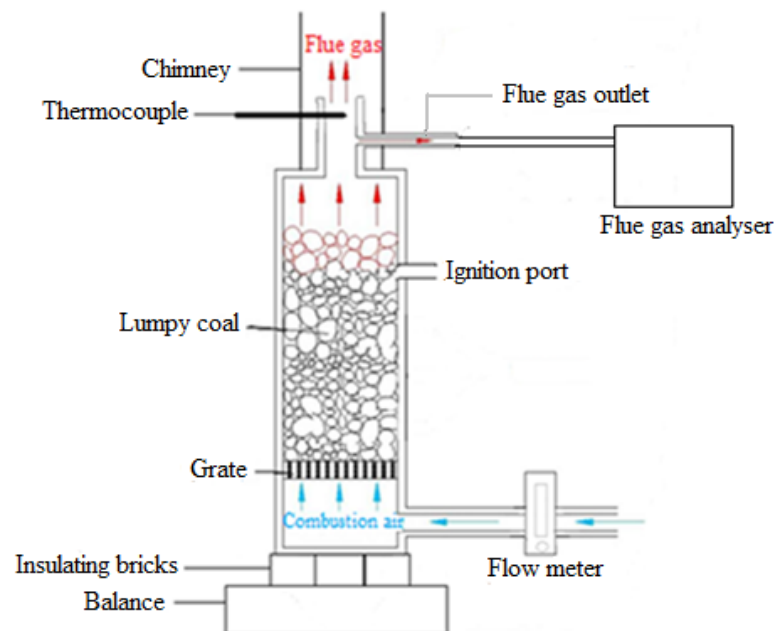


Figure 1. Schematic diagram of a fixed-bed combustion reactor set-up.

2.4. Combustion Method

To carry out the combustion experiments, approximately 200 g of the solid fuel were loaded onto the grate in the reactor chamber as shown in Figure 1. After loading the solid fuel, atmospheric air was pumped into the reactor at a controlled flow rate (16.9–17.5 L/min). This was followed by manual ignition of the fuel, which took approximately 3 to 6 min. During combustion experiments, the temperature at the reactor exit was measured using a thermocouple, and the mass reduction (g) was recorded from the weighing balance. The gas emissions of CO₂ (%), O₂ (%), NO_x (ppm), and SO₂ (ppm) were measured at the flue gas outlet every minute, using a Lancom 4 portable flue gas analyser.

The Lancom 4 gas analyser uses the infrared sensor to directly measure the CO₂ in flue gas. This CO₂ sensor, combined with the measurement capability offered by the flow probe, gave quantitative information on greenhouse gas emissions. The gas analyser drew the sample gas through a sample probe, and a hose connected it to the input connection on the side panel. The sample gas entered the water catchpot where residual water was removed, and then passed through a 0.1-micron particulate filter. Gas concentration readings were

then recorded every minute. The gas analyser automatically performed a zero calibration every time it is switched on, and always purged the sensors with ambient air before switching off. This ensured maximum accuracy and sensor longevity.

2.5. The O₂ Referencing

The statutory guidelines stipulate that the concentration of SO₂ and NO_x should be corrected or normalised for the diluting effect of excess air (Land Instruments International, 2004). The measured O₂, the O₂ reference (6% oxygen content is often used to normalize SO₂ and NO_x for solid fuels such as coal), and the amount of oxygen in the atmospheric air (20.9%) were used in Equation (1) to obtain the normalised concentration of SO₂ and NO_x. An O₂ reference of 6% was used to ensure readings were measured from the same reference.

$$\text{Corrected ppm} = \text{measured ppm} \times \frac{20.9 - \text{O}_2 \text{ reference}}{20.9 - \text{O}_2 \text{ measured}} \quad (1)$$

2.6. Ash Elemental Analysis and Imaging

Ash analysis was carried out to determine the elemental composition using an XRF spectrometer (ARL9800XP SIM-SEQ). XRF analysis is a simple, non-destructive method, which can quantitatively measure minor and trace elements in ash. The elements were determined by fusing the ash sample with lithium tetraborate, which was pressed into a glass disk. For quantification, the intensity of characteristic lines of the element to be analysed was measured. Coal ash typically contains Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S, and Cr, which are reported as oxides by default (Fe₂O₃, Al₂O₃, MgO, MnO, V₂O₃, TiO₂, SiO₂, CaO, Na₂O, K₂O, P₂O₅, SO₃, and Cr₂O₃).

Ash samples were obtained from the combustion of the coal–*Scenedesmus* microalgae blends (Coalgae[®] 5%, 10%, 15% and 20%). The milled coal and Coalgae[®] were gold coated and imaged for morphological evaluation using a JOEL 7001f scanning electron microscope (SEM). TEM imaging of the samples for the determination of nanocomposites was carried out using a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV.

3. Results and Discussion

3.1. Effect of Co-Firing Coal and *Scenedesmus* Microalgae on Mass Loss

The co-firing of coal and *Scenedesmus* microalgae biomass were investigated and compared to the combustion of pure coal. The Coalgae[®] blends showed high mass loss rate compared to the coal, as can be seen in the mass reduction curves in Figure 2. The mass loss rate of the Coalgae[®] increased with increasing *Scenedesmus* microalgae proportion. The rapid combustion of the Coalgae[®] blends was attributed to relatively high volatiles. Coalgae[®] 5%, Coalgae[®] 10%, Coalgae[®] 15% and Coalgae[®] 20% combusted in 140 min, 129 min, 106 min, and 103 min, and had mass residues of 32 g, 30.8 g, 29 g, and 27.2 g, respectively. Additionally, the fast combustion of the Coalgae[®] blends was shown by increased fuel consumption rate, which was calculated by averaging the mass difference per time interval. The co-firing tests showed a fuel consumption rate of 2.17 g/min, 2.21 g/min, 2.37 g/min, and 2.62 g/min for Coalgae[®] 5%, Coalgae[®] 10%, Coalgae[®] 15%, and Coalgae[®] 20%, respectively. The coal combustion took approximately 194 min, and gave a residual mass of 33.4 g. When dividing the mass residues by the mass of the sample (200 g) burned and multiplying by 100, the ash yields of the coal and Coalgae[®] 5–20% become 16.7 wt.%, 16 wt.%, 15.4 wt.%, 14.5 wt.%, and 13.6 wt.%, respectively. These ash yields were comparable to the ash yields obtained from proximate analysis and TGA, with a difference of up to 1.8 wt.% [21]. The slower combustion of the coal compared to the biomass has been reported in the literature on co-firing coal with different biomasses, including algae [29–31].

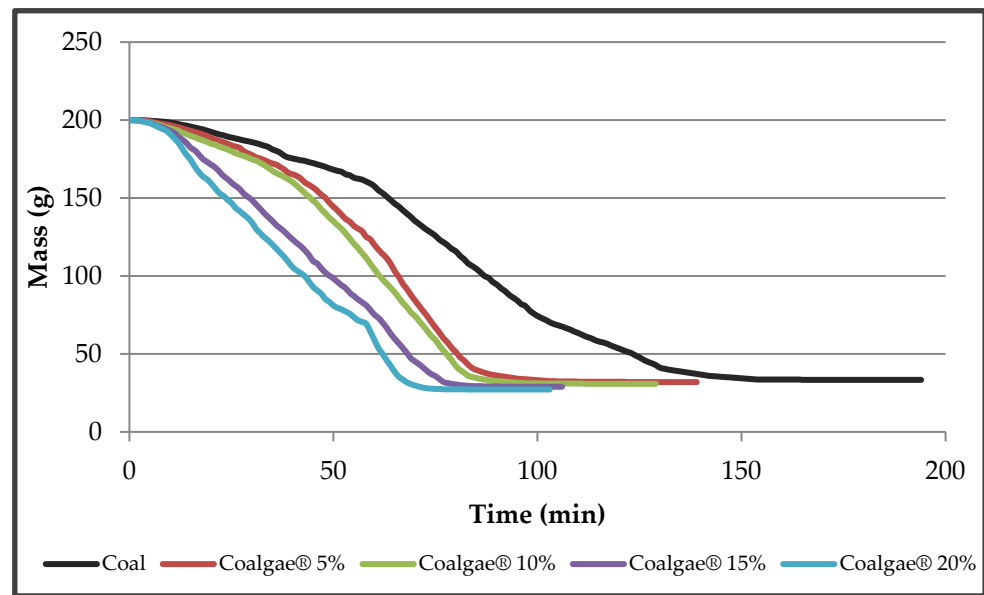


Figure 2. Mass reduction curves.

3.2. Effect of Coal–Scenedesmus Microalgae Co-Firing on Combustion Temperature with Time

The combustion temperatures of the coal and Coalgae® blends were measured at the reactor exit, and the results are shown in Figure 3. Three different stages of combustion were typically established in the reactor. The first stage was associated with ignition and the release of volatiles, shown by a rapid increase in temperature. The second stage was associated with the drastic reduction in mass because of the conversion of the solid fuel to gaseous products, which was due to the (stable) combustion of volatiles and char. The third stage was associated with char burnout (ashing), shown by a large decrease in temperature. These three stages of combustion using different combustion systems have been reported in the literature [25,32,33]. The temperature curve of the coal presented one broad peak, which was attributed to the simultaneous combustion of volatiles and char. However, the Coalgae® blends presented two peaks; the minor peak was attributed to the combustion of volatiles, while the major peak was attributed to the combustion of char. The maximum temperatures reached with the Coalgae® 5%, Coalgae® 10%, Coalgae® 15%, and Coalgae® 20% were 876 °C, 904 °C, 996 °C, and 1020 °C, respectively. The coal, on the other hand, reached a maximum temperature of 838 °C. The higher combustion temperatures of the Coalgae® blends may cause fouling and clinkering on the boilers; however, ash fusion temperatures need to be studied.

3.3. Effect of Coal–Scenedesmus Microalgae Co-Firing and Air Flow Rate on Peak Temperature

Figure 4 shows the effect of the peak temperatures (°C) of the coal and Coalgae® blends observed after 60 min (from Figure 3) with air flow rates. The peak temperature refers to the maximum temperature measured at the reactor exit. It was found that an increased air flow rate resulted in increased oxygen concentration, thus promoting combustion [34]. In addition, increased oxygen concentration has been reported to be stronger at lower temperatures compared to higher temperatures [35]. Generally, it was observed that the coal combusted at lower temperature compared to the Coalgae® blends, as shown in Figure 4 under varying flow rates (8.6–17.2 L/min). The increased temperature of the Coalgae® blends confirmed the presence of a synergetic effect after the microalgae mixing with coal. The increased temperature promoted the reduction of GHG concentrations through various processes reported in the literature [36,37].

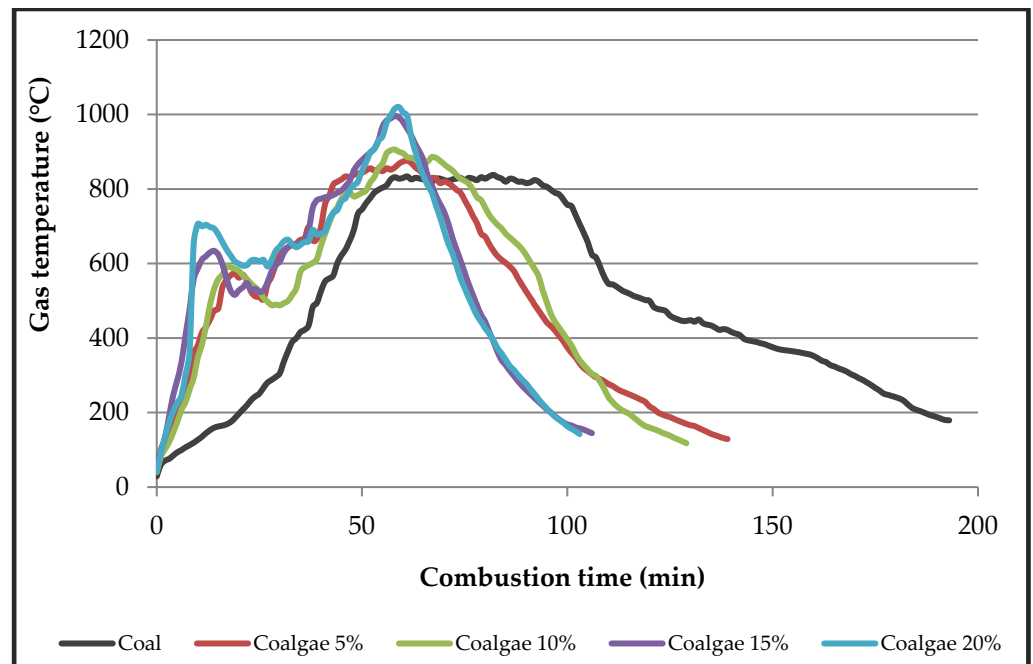


Figure 3. Flue gas temperature at the reactor exit.

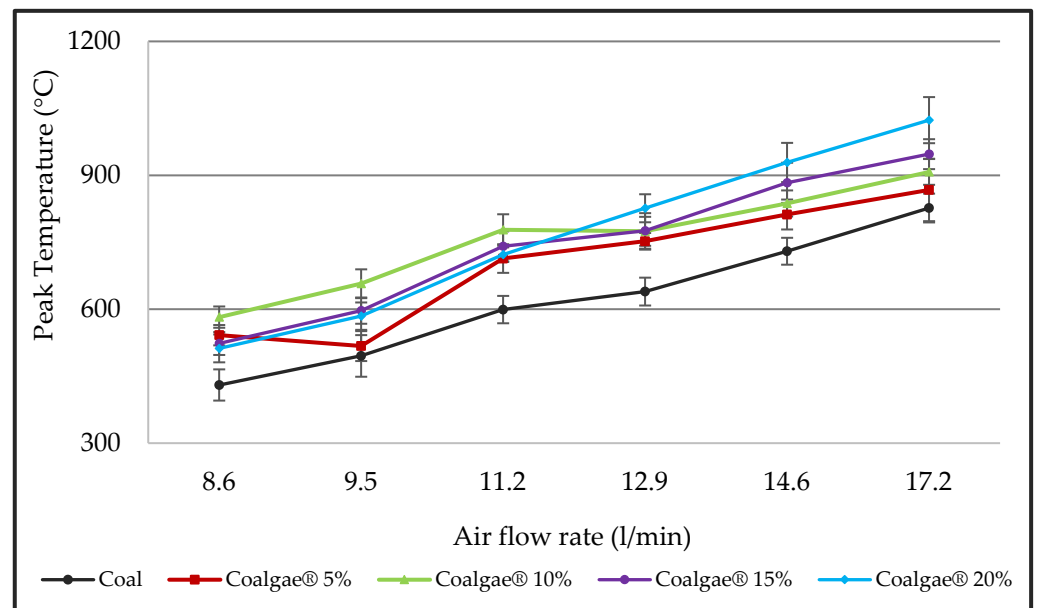


Figure 4. Effect of air flow rate on coal and Coalgae® blends peak temperature.

3.4. Effect of Coal–*Scenedesmus* Microalgae Co-Firing and Air Flow Rate on CO₂ Emissions

Blending coal with *Scenedesmus* microalgae showed positive results, as CO₂ emissions decreased with the increasing microalgae co-firing ratio, regardless of the varying air flow rate, as can be seen in Figure 5. The amount of CO₂ from the combustion of coal increased with increasing air flow rate from approximately 318 g/h at 8.6 L/min to 412 g/h at 12.9 L/min. Similarly, the mass of CO₂ released from the Coalgae® 5%, 10% 15% and 20% co-firing increased with increasing air flow rate up to 12.9 L/min, then decreased thereafter. However, an unexpected decrease in the air flow rate of 11.2 L/min was observed. At higher air flow rate and temperature, the release rate of the volatile matters in the coal–microalgae mixture (solid fuel) becomes fast enough, leading to shorter residence and combustion time of the gas (as shown in Figure 3). This would weaken the oxidization process of the

carbon-containing intermediate products to form CO₂ [38]. The longer residence time of the volatiles may have contributed to the oxidation of more CO₂ in the coal combustion. The air flow rate of 12.9 L/min showed higher CO₂ formation and significant CO₂ reductions for the Coalgae[®] blends.

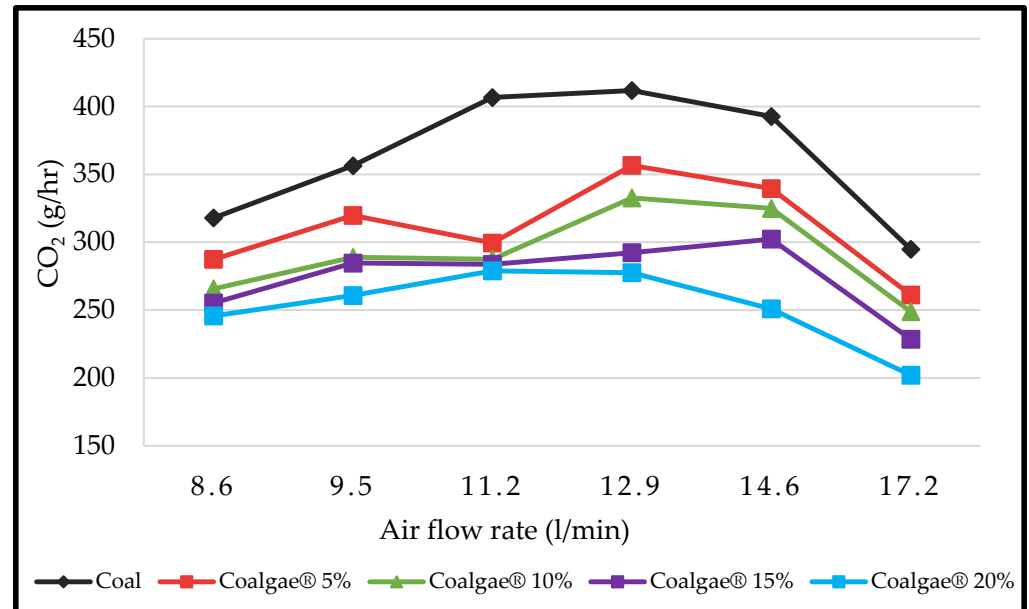


Figure 5. Effect of air flow rate on CO₂ emissions.

The effect of co-firing *Scenedesmus* microalgae and coal on CO₂ emission is presented in Figure 6. It was evident from this figure that an increase in the microalgae ratio led to a decrease in the average CO₂ concentrations (%) emitted. The average CO₂ concentrations measured for the Coalgae[®] blends were 12.79%, 12.05%, 11.44% and 10.25% for Coalgae[®] 5%, Coalgae[®] 10% and Coalgae[®] 15% and Coalgae[®] 20%, respectively, with the reference coal emitting 14.49% CO₂. The decrease in CO₂ concentration was associated with the decrease in relative carbon content. Additionally, the decrease in CO₂ concentrations observed with the Coalgae[®] blends might also be due to the formation of CO during the volatile combustion stage, which is shown by the appearance of peaks at a temperature range of 10–20 °C in Figure 3. Although CO was not measured in this study, the literature has shown that biomasses (including microalgae) produce higher CO concentrations than coal, due to poor combustion at low temperatures, where combustion of the volatiles takes place [39,40]. Comparable results with decreasing CO₂ have been reported in the literature for microalgae co-firing and biomass co-firing [15,40,41]. As Pokothoane [15] stated, CO₂ can either increase or decrease, but what is important is the source of CO₂ (whether it is from fossils or can be recycled). Therefore, microalgae can be considered a carbon neutral fuel, as its CO₂ is recycled back to its cultivation.

The CO₂ reductions, depicted in Figure 7, were calculated from the average CO₂ concentrations in Figure 6. Reductions in the CO₂ emissions achieved with Coalgae[®] 5%, 10%, 15%, and 20% were 11.7%, 16.8%, 21%, and 29.3%, respectively. CO₂ reductions increased proportionally with the increasing *Scenedesmus* microalgae co-firing ratio.

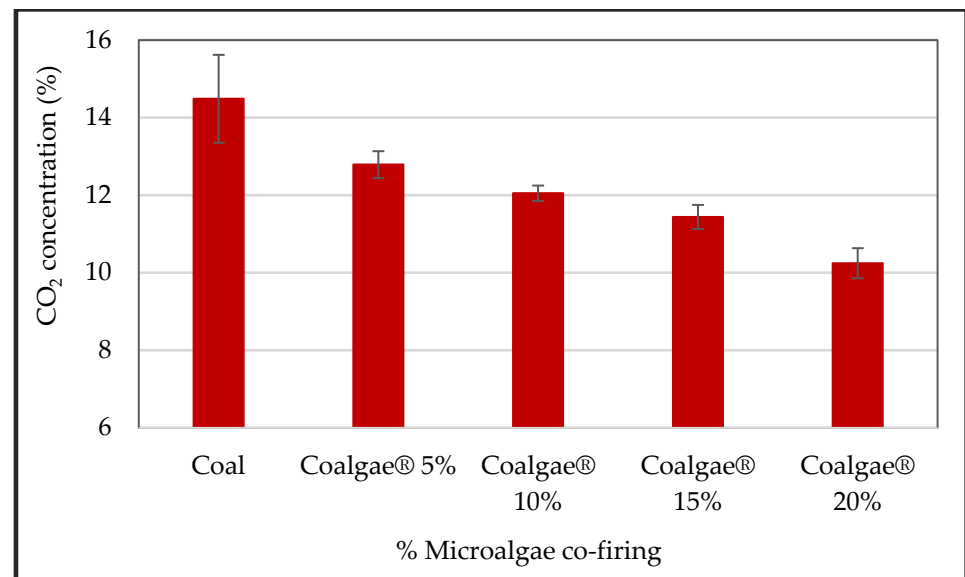


Figure 6. Average concentration of CO₂ in flue gas.

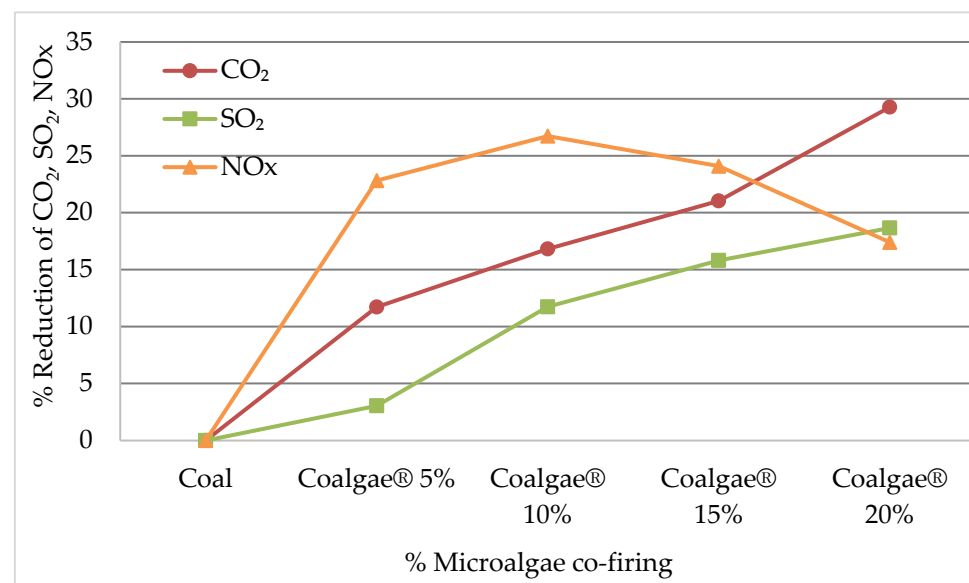


Figure 7. Effect of microalgae co-firing on CO₂, SO₂ and NO_x reduction.

3.5. Effect of Coal–*Scenedesmus* Microalgae Co-Firing and Air Flow Rate on SO₂ Emissions

The emissions of SO₂ (Figure 8) decreased with increasing microalgae loading, corresponding to relative decreases in the fuel sulphur. The SO₂ concentrations measured from the co-firing of the Coalgae® 5–20% were 141.3 ppm, 128.6 ppm, 122.7 ppm, and 118.5 ppm, respectively. The coal as a reference formed a higher SO₂ concentration (145.7 ppm) compared to the Coalgae® blends. The SO₂ reductions achieved with the Coalgae® 5–20% were 3%, 11.7%, 15.8%, and 18.7%, respectively (Figure 7), thus, confirming that SO₂ reductions increased with the increasing microalgae co-firing ratio. The reductions in SO₂ emissions could also be attributed to decreasing combustion time, and sulphur being retained in the alkaline ash of the Coalgae® blends. The effect of the self-desulphurisation of coal co-fired with different biomasses, including microalgae, has been reported in several reports in the literature [18,40]. Gao et al. [9] reported increased SO₂ emissions during the co-combustion of coal and *Chlorella vulgaris*. Therefore, *Scenedesmus* microalgae is a potential strain for the reduction of greenhouse gas emissions.

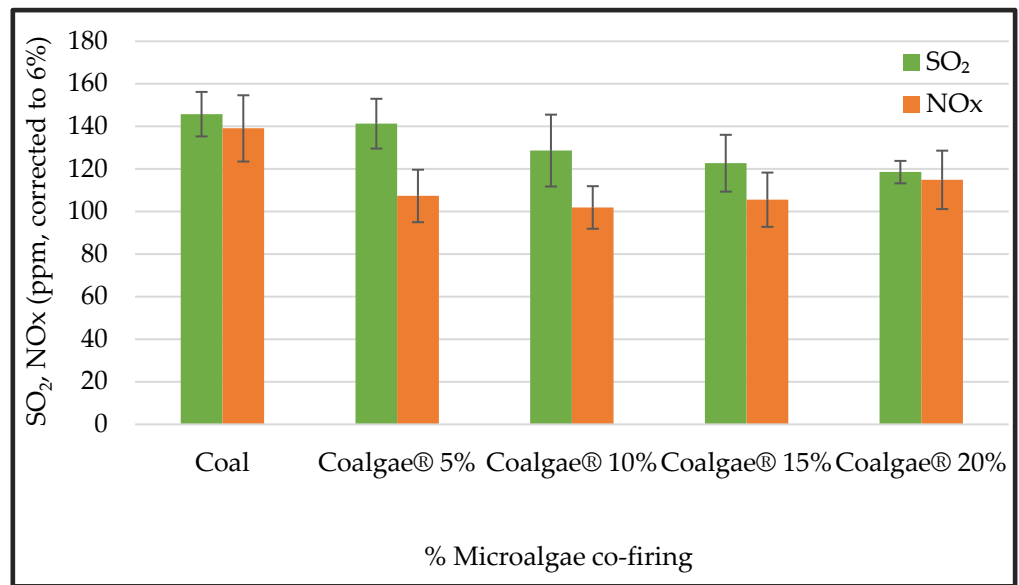


Figure 8. Average concentration of NOx and SO₂ in flue gas.

Figure 9 shows the effect of the air flow rate on SO₂ emissions from the coal and microalgae co-firing. The mass of SO₂ decreased with the increasing microalgae co-firing ratio at almost all air flow rates, except for Coalgae® 20%. The co-firing of Coalgae® 20% released higher SO₂ compared to the other Coalgae® blends at an air flow rate of 8.6–11.2 L/min, and this result was not expected. Since the sulphur content decreased with increasing microalgae loading, the SO₂ was expected to follow the same trend as stated by Van Loo and Koppejan [42]. The mass of SO₂ for the coal increased with the increasing air flow rate up to 12.9 L/min, and then decreased thereafter. The increased air flow rate resulted in improved oxygen concentration, however, the observed variation in SO₂ (g/h) emissions with air flow rates in the coal was believed to be due to deviation in oxygen concentration at maximum combustion temperature [43]. Changing air flow rate during combustion tests of the Coalgae® 5–20% did not have a significant effect on the amount of SO₂ (Figure 9).

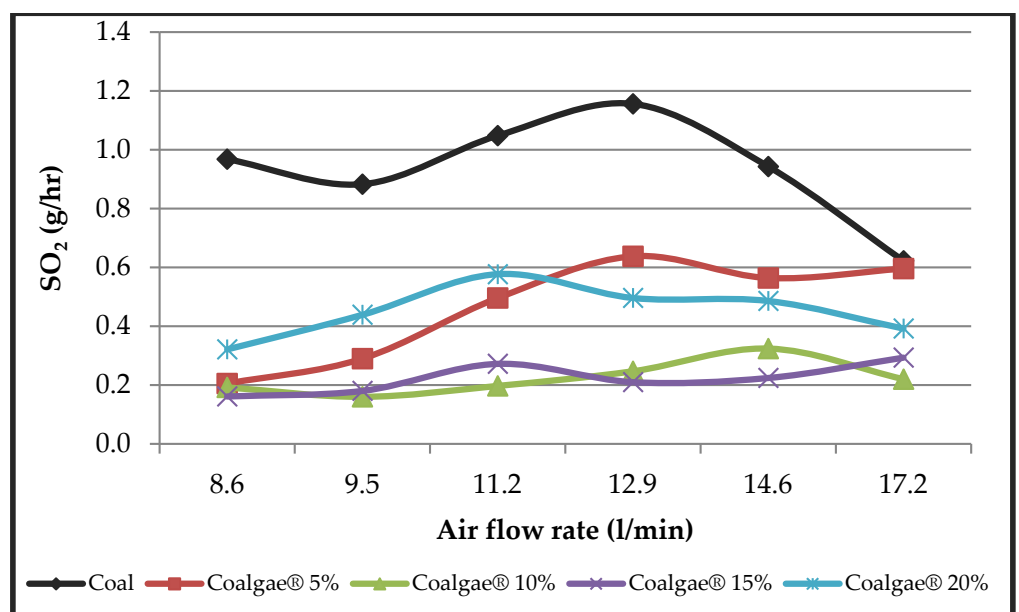


Figure 9. Effect of air flow rate on SO₂ emissions.

3.6. Effect of Coal–Scenedesmus Microalgae Co-Firing and Air Flow Rate on NO_x Emissions

Most biomasses contain lower contents of nitrogen compared to coal, and therefore result in lower NO_x formation [44–46]. However, biomasses with higher nitrogen content have also been reported to decrease the levels of NO_x [47]. The formation of NO_x is complicated and difficult to predict. NO_x may increase, decrease, or remain the same, depending on the biomass type, blending ratio, co-firing conditions, and operating conditions. Fuel NO_x in biomass co-firing evolves as volatile compounds and results in reduced levels of NO_x, while thermal NO_x depends on combustion temperature [44]. The effect of co-firing coal and *Scenedesmus* microalgae on NO_x emissions was investigated, and the results are depicted in Figure 8. The emissions of NO_x were normalised to 6% oxygen for the dilution effect of excess oxygen. Average NO_x concentrations of 107.3 ppm, 101.9 ppm, 105.6 ppm, and 114.9 ppm were measured for Coalgae® 5%, 10%, 15%, and 20%, respectively. An average NO_x concentration of 139.1 ppm was obtained from the combustion of coal. The average concentration of NO_x decreased as the microalgae co-firing ratio increased, and then slightly increased after a co-firing ratio of 10% was reached. However, the NO_x emitted by each Coalgae® blend was still lower compared to the NO_x emitted by coal. The reduction of NO_x was also associated to the formation of NH_x during nitrogen oxidation, which was further decomposed to N₂ [48,49].

The effect of air flow rate on NO_x emissions from the co-firing of coal and microalgae is shown in Figure 10. Generally, increased air flow rate (oxygen concentration) resulted in increased NO_x emissions, with the coal increasing from 0.318 g/h to 0.800 g/h and the Coalgae® 20% increasing slightly from 0.170 g/h to 0.478 g/h from an 8.6 to 14.6 L/min air flow rate. The Coalgae® blends showed lower NO_x emissions compared to the coal at 11.2–17.2 L/min, and this may be attributed to oxygen deviation as gas temperature increased, thus leading to volatile pyrolysis intermediates, such as hydrogen cyanide (HCN) and NH₃ [50,51]. There was generally no clear trend for all the five materials as the air flow rate varied.

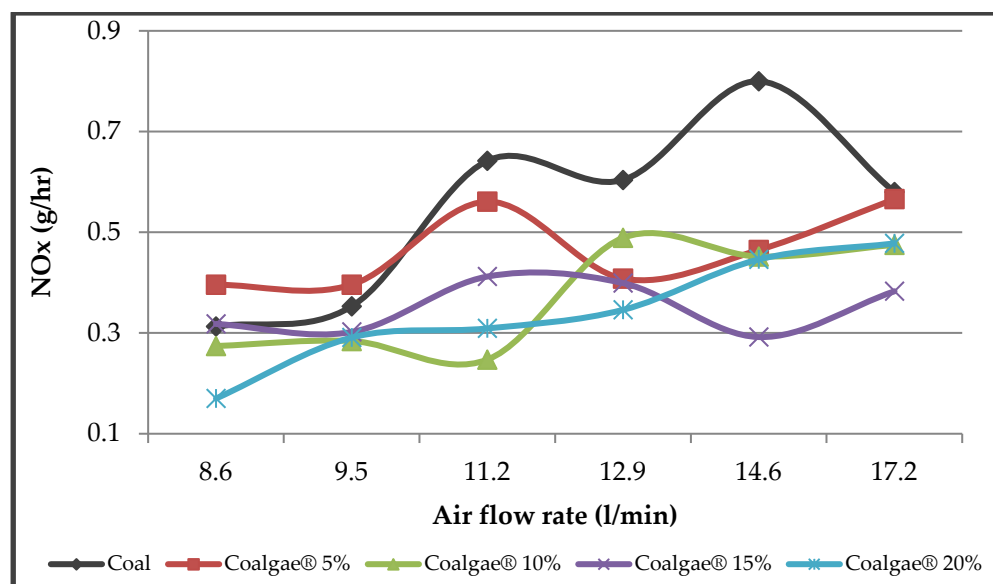


Figure 10. Effect of air flow rate on NO_x emissions.

Generally, the considerable reduction in GHG emissions was achieved with Coalgae® 5%, Coalgae® 10%, Coalgae® 15%, and Coalgae® 20% (Figure 7). NO_x reductions achieved with the Coalgae® 5–20% were 22.8%, 26.7%, 24.1%, and 17.4%, respectively. However, Kucukvar and Tatari [18] reported increased NO_x emissions when co-firing coal and algae (strain not mentioned). Also, Gao et al. [9] reported an increase in NO emissions when co-firing coal and *Chlorella vulgaris*. NO_x reduction variation with microalgae-coal ratio has

been reported in the literature [29]. Oxygen concentration, volatile decomposition, flue gas temperature and volatile pyrolysis contributed to NO_x emissions.

3.7. Combustion Efficiency

The co-firing of microalgae biomass and coal is a potential way of reducing net CO₂ emissions in coal power plants. Biomass co-firing may result in increased or decreased combustion efficiency compared to pure coal, depending on the characteristics of different blends and combustion environments [52,53]. Combustion efficiency, also referred to as burnout of carbon, was calculated using the Equation (2) [54]. The combustion efficiency calculated in this study refers to the measure of how well the coal and Coalgae[®] blends burned during the combustion tests, and results are depicted in Table 2.

$$n_c(\%) = 1 - \frac{C_{unburned}}{C_{initial}} \times 100 \quad (2)$$

where n_c = the combustion efficiency in %, $C_{unburned}$ = the content of unburned carbon in ash fraction, and $C_{initial}$ = the content of carbon in the coal and Coalgae[®] blends.

Table 2. Content of carbon in ash and combustion efficiency.

Fuels	Carbon in Fuel (% db)	Carbon in Ash (% db)	Combustion Efficiency (%)
Coal	68.54	9.32	86.40
Coalgae [®] 5%	66.57	1.96	97.06
Coalgae [®] 10%	65.07	0.99	98.48
Coalgae [®] 15%	64.65	0.67	98.96
Coalgae [®] 20%	64.40	0.71	98.90

The combustion efficiency increased insignificantly from Coalgae[®] 10% to Coalgae[®] 15% (increased by 0.6%), and slightly decreased at Coalgae[®] 20%. This shows that microalgae co-firing ratios beyond 10% are not necessary, as these result in decreased combustion efficiency, due to increases in moisture content. High moisture content in biomass blends is one of the factors that can affect the efficiency of combustion [52,53]. Another factor which negatively impacts the burnout of carbon is the increased composition of fluxing compounds (CaO, Fe₂O₃ and K₂O) [45] in the Coalgae[®] blends, as is shown in Table 3.

Table 3. Ash analysis.

Compounds (%)	Coal	Coalgae [®] 5%	Coalgae [®] 10%	Coalgae [®] 15%	Coalgae [®] 20%
Al ₂ O ₃	27.726	25.719	24.13	19.475	18.191
SiO	45.989	38.601	33.748	31.063	27.828
P ₂ O ₄	1.992	4.113	4.744	5.813	7.912
SO ₃	–	0.172	0.179	0.207	0.216
K ₂ O	1.051	1.219	2.151	3.029	3.134
CaO	5.624	7.987	9.818	11.451	12.714
TiO	5.861	5.741	5.575	5.526	5.151
Fe ₂ O ₃	8.358	9.282	10.192	11.306	12.631
MgO	–	0.395	0.440	0.459	0.569
* B/A ratio	0.189	0.270	0.356	0.468	0.568

* B/A – base/acid ratio = (MgO + K₂O + CaO + Fe₂O₃)/(Al₂O₃ + SiO + TiO).

The addition of biomass to coal reduces the ash fusion temperature of coal, due to increased fluxing elements [15]. The decrease in combustion efficiency of the Coalgae[®] 20% suggests that the high combustion temperature affected the rate of char reaction. The presence of an inorganic-rich layer on the char surface acted as a barrier of oxygen diffusion to the reacting surface [45]. This ash layer may form when the char is oxidized on or near the external surface of the particle, leaving mineral constituents on the char surface [44,55]. The fluxing elements melt at high temperatures during the late stage of combustion, as

these minerals get exposed when most of the char conversion has occurred, whereas, during early combustion stage, these minerals are protected by carbon, as carbon does not melt at typical temperatures. This melting of minerals blocks the oxygen access to the active site of carbon and reduces the availability of carbon in the char matrix [44,55].

3.8. Ash Analysis with XRF

The elemental composition (reported as oxides) of the coal ash and Coalgae[®] blends ashes is presented in Table 3. The ash residue of the coal was mainly composed of SiO and Al₂O₃, followed by some fluxing compounds (TiO, Fe₂O₃, CaO and K₂O); therefore, this ash was relatively refractory and was unlikely to cause slagging and fouling [56]. Similarly, the ash residue of the Coalgae[®] blends composed mainly of SiO and Al₂O₃ but these minerals decreased with the increasing microalgae co-firing ratio. On the other side, the fluxing compounds (Fe₂O₃, K₂O, CaO and MgO) increased with the increasing microalgae co-firing ratio, resulting in an increased base/acid ratio from 0.189 with the baseline coal up to 0.568 with the Coalgae[®] 20%. P₂O₄ also increased significantly from the baseline coal (1.99%) to the Coalgae[®] 20% (7.91%), while TiO decreased insignificantly.

3.9. Scanning Electron Microscopy (SEM)

The SEM images of the coal and coal–*Scenedesmus* microalgae blends (0% to 20%), and the ash contents of the combusted coal and blends are presented in Figure 11A–J. Milled samples of the coal and coal–*Scenedesmus* microalgae blends (0% to 20%) presented showed highly aggregated particles that were irregularly shaped, while the ash content of the coal and Coalgae[®] blends presented fluffy and bubble-like surface particles, due to combustion of the volatiles (Figure 11F–J). The coal ash had fluffy and dispersed morphology, while the lower coal–*Scenedesmus* microalgae ratio (Coalgae[®] 5%) presented a bubble-like morphology which was not very visible compared to the higher blend ratios (Coalgae[®] 10%, 15% and 20%). SEM images showing the ash of coal and Coalgae[®] 5–20% are presented in Figure 11F–J. The dense and bubble-like morphology observed in the ash particles of the coal–microalgae blend was due to the combustion of volatiles (originating mainly from the *Scenedesmus* microalgae) and fluxing compounds at high temperatures, through the process of decomposition, nucleation, coagulation and condensation [29,56]. The pore morphology of the char burnout changed as the raw solid fuel composition changed and this was due to the different degree of volatile content [57]. The increase in fluxing compounds seen with the Coalgae[®] blends is likely to cause slagging and fouling in the boilers.

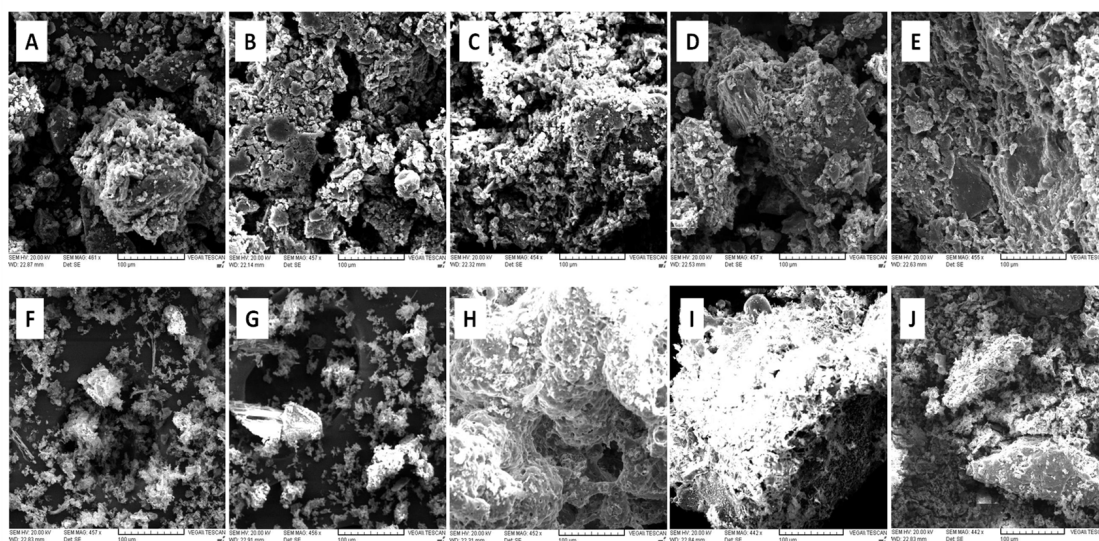


Figure 11. SEM images of coal (A), Coalgae[®] 5% (B), Coalgae[®] 10% (C), Coalgae[®] 15% (D), and Coalgae[®] 20% (E) and ash residues of coal (F), Coalgae[®] 5% (G), Coalgae[®] 10% (H), Coalgae[®] 15% (I), and Coalgae[®] 20% (J).

3.10. Transmission Electron Microscope (TEM)

TEM images of the coal and coal–*Scenedesmus* microalgae blends (0% to 20%) and the ash contents of the combusted coal and blends are presented in Figure 12A–J. Carbon-based sheets and graphitic-based nanocomposites were mainly observed on the combusted coal–*Scenedesmus* microalgae (Figure 12F–J).

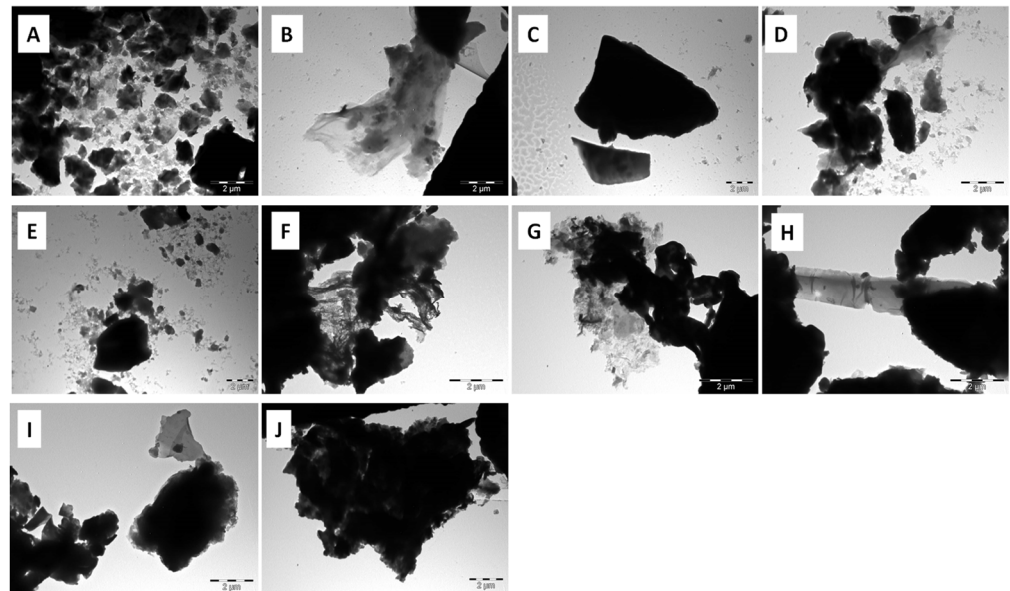


Figure 12. TEM images of coal (A), Coalgae[®] 5% (B), Coalgae[®] 10% (C), Coalgae[®] 15% (D), and Coalgae[®] 20% (E) and ash residues of coal (F), Coalgae[®] 5% (G), Coalgae[®] 10% (H), Coalgae[®] 15% (I), and Coalgae[®] 20% (J).

4. Conclusions

Coal, *Scenedesmus* microalgae, and their blends (Coalgae[®] 5–20%) were combusted using a vertical down-firing fixed-bed combustion reactor. The CO₂ emission concentrations decreased with the increasing microalgae blending ratio, reaching a reduction of up to 29% with the Coalgae[®] 20%. The SO₂ emission concentrations were reduced from the baseline coal by up to 19% with the Coalgae[®] 20%. On the other hand, the NO_x emission concentrations decreased with the increasing microalgae blending ratio, reaching a reduction of 27% with the Coalgae[®] 10% and then decreased thereafter. The ash of the Coalgae[®] blends showed high amounts of Fe₂O₃, K₂O, CaO and MgO, as well as a dense and bubble-like surface morphology, compared to the coal. The bubble-like morphology observed in the ash particles of the coal–microalgae blends was confirmed with SEM, and the TEM confirmed the formation of carbon-based sheets and graphitic-based nanocomposites. Therefore, co-firing coal with *Scenedesmus* microalgae has a potential to mitigate the emissions of CO₂, SO₂ and NO_x compared to other microalgae strains reported in the literature. Additionally, lower Coalgae[®] blends can be used as an alternative energy source to coal for energy generation in grate stoker boilers. Higher proportions of microalgae to coal are not recommended, due to potential damage to boilers caused by clinkering and fouling by higher fluxing compounds and higher combustion temperatures compared to coal. However, studies on the ash deposition of coal and *Scenedesmus* microalgae blends are required.

5. Patents

Zeelie, B. Processing carbonaceous materials. US 2016/0289567 A1.

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