

Pyrolytic topping of coal-algae composite under mild inert conditions

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Abstract

Co-processing of coal and biomass has been a focus of several research studies aimed at addressing the negative environmental attributes associated with thermal processing of coal alone, as well as improving the thermal behaviour of coal. Biomass materials are regarded as a clean, renewable source, so thermal co-processing of biomass with coal is considered an effective way to utilise coal in a sustainable manner. In this study, coal fines were blended with *Scenedesmus* microalgae slurry to form a coal-algae composite. Pyrolytic topping of coal-algae composite was performed at 450 °C on a batch reactor. Parent fuels and resultant chars were analysed for their proximate properties using an Eltra thermostep TGA; a Vario EL cube Elementar was used to determine the elemental composition of the chars and oils. A simulated distillation (SimDis) method was used to determine the boiling point distribution of the produced oils. The objective of the study was to examine the effects of microalgae slurry on the pyrolytic behaviour of waste coal fines with respect to product yields, composition and quality. Results showed that the yields of volatile components from pyrolysis of coal-algae composite were high compared with those from pyrolysis of coal alone. A significant degree of deoxygenation, dehydrogenation and denitrification was observed in coal-algae char than coal char. SimDis results showed that the fossil bio-crude oil has different boiling point characteristics from coal tar. The study has shown that microalgae slurry has potential to influence the pyrolytic behaviour of waste coal under mild inert conditions.

Keywords: fossil bio-crude oil, resultant char, mild pyrolysis, coal-algae composite

Highlights

- Pyrolysis of the fuel composite results in low yields of char.
- Coal-algae composite pyrolysis results in a substantial degree of dehydrogenation.
- Fossil bio-crude oil contains more reactive compounds than coal tar.
- Coal-algae chars contains lower contents of sulphur and nitrogen than coal, which is desirable to reduce emissions of sulphur and nitrogen oxides during the combustion process
- Fossil bio-crude oil have compounds that are predominantly in the distillate fuel oil range

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1. Introduction

Thermal co-processing of coal and biomass has received much research interest with an aim to explore ways to effectively use coal in a cleaner and sustainable manner as well as to improve the efficiency of coal conversion processes (Taba *et al.*, 2012; Veras *et al.*, 2009). Biomass is a clean, renewable energy source, with high thermal reactivity. In addition, biomass has a relatively high hydrogen content and high hydrogen-to-carbon (H/C) ratio compared to coal, which is important in improving the yields of coal pyrolysis products during co-pyrolysis of coal and biomass (Chen *et al.*, 2012; Zhang *et al.*, 2007). The use of biomass can potentially influence the thermal behaviour of coal under pyrolysis conditions through the interaction of the biomass volatiles with coal at low temperature range (200–400 °C) (Baloyi and Dugmore, 2018; Wu *et al.*, 2014; Idris *et al.*, 2010). However, in fixed bed co-pyrolysis the interaction of biomass volatiles and coal particles occurs at temperatures ranging from 500–700 °C (Park *et al.*, 2010).

Research work on the thermal co-processing of coal with biomass has shown that, despite the two fuels having different chemical characteristics, the co-processing of the two fuels is possible (Idris *et al.*, 2010; Kumabe *et al.*, 2007; Vuthaluru *et al.*, 2004). Studies have shown that biomass (agricultural, woody or algal) is thermally reactive, and have observed that, when co-pyrolysed with coal, the addition of a varying fraction of biomass in the blends increases the reactivity of coal, due to an increase in the volatiles (Baloyi and Dugmore, 2018; Ferrara *et al.*, 2014; Kirtania and Bhattacharya, 2013; Chen *et al.*, 2012; Idris *et al.*, 2010). Several other researchers investigated the possible synergistic effects on product distribution during co-pyrolysis of biomass and coal. Li *et al.* (2013) studied the co-pyrolysis behaviour of woody biomass and coal in a drop tube reactor and fixed bed reactor and observed that the interaction between the two fuels happens in the gaseous phase at higher temperatures – above 1000°C. Soncini *et al.* (2013), observed co-pyrolysis synergies on product yields (tar, volatiles and gases), particularly for co-pyrolysis of biomass and low ranked coal at temperatures above 900 °C in a semi-drop tube reactor. Wei *et al.* (2011) observed that the existence of co-pyrolysis synergies results in the production of more liquid products.

Pyrolysis is a thermochemical conversion process that precedes combustion and gasification processes. However, as an independent process, it can be used to transform solid fuels to yield liquid tar and gaseous products as well as devolatilised resultant char in an oxygen-free environment. Coal pyrolysis involves the formation of reactive radicals (i.e. $\bullet\text{CH}_2$ and $\bullet\text{O}$) that undergoes numerous secondary

chemical reactions such as cracking, re-polymerisation, and carbonisation. These formed radicals are stabilised by the addition of hydrogen to form condensable and non-condensable volatile products (Seo *et al.*, 2011; Demirbas, 2003). Under co-pyrolysis conditions, the radical structures generated by coal pyrolysis are stabilised by the hydrogen donated by the biomass to promote the generation of liquid products as well as to improve gas yields and produce other chemicals (Soncini *et al.*, 2013; Li *et al.*, 2011).

This study focuses on the mild pyrolysis of a coal-algae composite formed by blending photosynthetically active *Scenedesmus* microalgae slurry with a low-ranked fine, discard coal. Coal-algae composite pyrolysis aims at improving the product yields, composition and quality of derived products as compared to the pyrolysis of untreated discard coal. It further aims at yielding a fuel oil that possesses a combination of biofuel and fossil fuel characteristics, as well as a semi-devolatilised coal in a single production step. *Scenedesmus* microalgae biomass is a high hydrogen-containing fuel with attractive chemical properties and can be considered environmentally friendly, having a low ash yield (< 8.0 wt. %) and low sulphur content (< 0.5 wt. %) as shown in Table 1.

Table 1: Chemical properties of *Scenedesmus* microalgae biomass.

Proximate (wt. %, dry basis)			Ultimate (wt. %, dry ash free basis)				
VM	ASH	FC	C	H	N	S	O
77.5	7.3	15.2	56.4	8.2	9.9	0.4	25.1

Formation of coal-algae composite can be viewed as a method to improve the thermal processing of discard coal. Low-ranked coals are believed to have the ability to easily interact with a biomass source during pyrolysis process, thereby bringing in synergies, and can capture the donatable hydrogen from a biomass source (Quan and Gao, 2016). In this study, photosynthetically active *Scenedesmus* microalgae slurry is brought into contact with fine discard coal (< 150 μm) by mixing and continuous stirring overnight. This allows the microalgae slurry (at 10 % loading) to blend or mix with the coal fines and form the fuel composite (coal-algae composite), which is attained after decantation of the water phase following centrifugation of the wet coal-microalgae mixture. The wet solid mixture (coal-algae composite) is subjected to overnight drying at 40 °C.

This paper reports on the yields, composition and properties of the derived products from pyro-

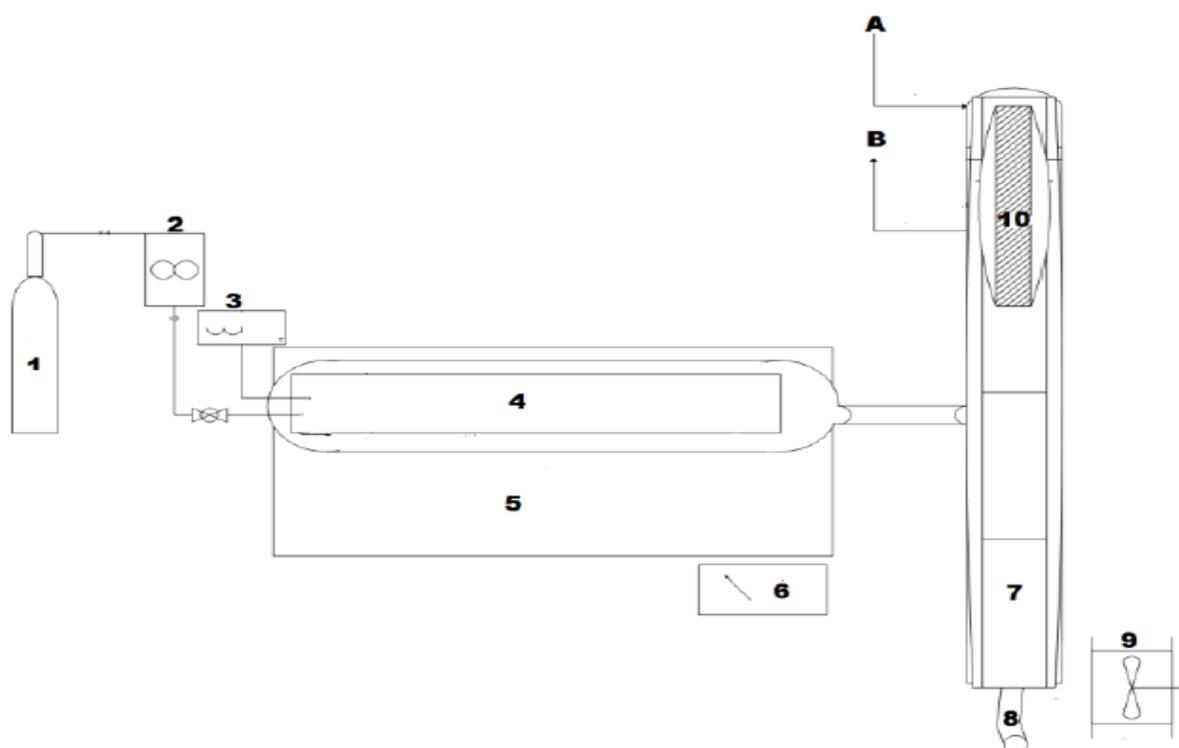
lytic topping of coal and coal-algae composite conducted on an in-house-designed batch reactor, at atmospheric pressure under mild inert conditions. Parent fuels and resultant chars were analysed for their proximate and ultimate properties. Simulated distillation (SimDis) by gas chromatography analysis was performed to determine the boiling point characteristics and estimation of petroleum fractions of the produced oils. The heating properties and elemental composition of the produced oils was done by estimation of the higher heating values (HHV) and elemental (CHNS) analysis respectively.

2. Experimental

2.1 Pyrolysis experiments

Pyrolytic topping experiments were carried out on a batch reactor as shown in Figure 1. A desired amount of sample was loaded into a horizontal tube reactor (700 mm x 65 mm) that had a carrying capacity of 600 g of sample. To start the experiment, the packed tube reactor was slid through the furnace, the chiller unit (set at 2 °C) was switched on to allow the inflow and outflow of circulation of chilled

water in the condenser unit. The sample was purged with nitrogen at 4 L/min to displace any residual air. After purging, the thermo-control unit was switched on and the four heating elements were set at 450 °C. During the experiment, the nitrogen flow was kept at 0.4 L/min. The temperature within the reactor tube was monitored using an inserted K-type thermocouple. At the end of the experiment, the two-phased liquid product (pyrolytic water and oil phase) were drained out into a pre-weighed sample bottle. The devolatilised coal was collected from the reactor tube. The two-phase liquid was separated by storing it in a laboratory refrigerator at 4 °C; the wax-like tar product settled at the bottom and the pyrolytic water phase could be decanted to a clean pre-weighed bottle. The tarry phase derived from coal-algae composite pyrolysis was described as fossil-bio-crude oil. The product (reaction water, oils, chars) yields were determined as the ratio mass of product measured to the initial mass of the sample fed, expressed as weight percentage. The mass of sample fed was corrected to an ash-free basis, based on Equation 1.



(1- nitrogen gas; 2 - flow meter; 3 - digital thermometer-coupled to thermocouple; 4 - reactor tube; 5 - furnace; 6 - thermo-control unit (with four heating elements); 7 - receiver; 8 - drain valve; 9 - heater; 10 - condenser a - outflow water-chiller, b - inflow water-chiller).

Figure 1: Schematic representation of the pyrolysis experimental set-up.

$$M_{S_{ashfree}} = M_{S_{fed}} - \left[\left(\frac{Ash\ yield}{100} \right) \times M_{S_{fed}} \right] \quad (1)$$

The total product (reaction water, oil, char) yields (wt %) were calculated on ash free basis based on Equation 2.

$$Product\ yield = \frac{M_p}{M_{S_{ashfree}}} \times 100 \quad (2)$$

where $M_{S_{fed}}$ = mass of sample fed (g); M_p = mass of pyrolysis product (g); $M_{S_{ashfree}}$ = sample fed (g) on ash free basis.

The ash yield (wt %) was obtained from the proximate analysis of the sample. Gas yields were calculated by difference.

2.2 Compositional analysis

2.2.1 Proximate, ultimate and calorific value analysis

Standard methods (ASTM D-7582) were used to determine the proximate properties (moisture, volatile matter, ash yield and fixed carbon (by difference) of the solid fuels. Proximate analyses were performed on an Eltra Thermostep Thermogravimetric analyser (TGA). A Vario EL cube Elementar (ASTM D-3176) was used for determining the elemental C, H, N, S and O (by difference) of the solid fuels and derived oils. Higher heating values (HHV) of the derived oils were estimated as a function of carbon (C), hydrogen (H), sulphur (S) and oxygen (O), according to the Dulong's formula as shown in Equation 3 (Channiwala and Parikh, 2002).

$$HHV\ (MJ/kg) = (0.3383 \times C) + 1.443 [H(O/8)] + (0.0942 \times S) \quad (3)$$

2.2.2 Simulated distillation by gas chromatography

The SimDis analyses of the derived oils were performed on an Agilent Technologies 7890A GC in accordance with standard method D2887 for the determination of the boiling range distribution and the estimation of petroleum fractions in the fossil bio-crude oil. A calibration blend was prepared from 2 ml of Polywax (C5-C44) (AC no: 25950.150) and 15 g of carbon disulphide (CS_2) in a 20 ml volumetric flask to establish the correlation between retention time and distillation temperature. A reference oil sample (AC no: 25650.150) was used for validation of the system. CS_2 was run as blank prior to calibration and analysis of samples to verify the system for cleanliness and column performance. About 2 g of the oil was dissolved in 10 ml of dichloromethane (DCM) to form a DCM solution. 1.5 ml of the DCM solution was transferred into a clean vial, and 0.1 μ L of the solution was injected into the column for analysis. Gas chromatography (GC) operating conditions for the SimDis analysis of the produced oils are summarised in Table 2.

Table 2: Gas chromatography operating conditions for the SimDis analyses.

<i>Flame ionisation detector</i>	
Temperature: 200 °C; H ₂ 40 ml/min; Air 295 ml/min	
<i>Oven programme</i>	
Temperature: 100 °C; Time: 0.5-1.2 min; Rate: 15 °C/min	
<i>Injector programme</i>	
Temperature: 350 °C; Time: 0-2.5 min; Rate: 35 °C/min	
<i>Column</i>	
Injector volume: 0.1 μ l; Column flow: 19 ml/min; gas flow (Helium): 26 ml/min; column dimension: 10 m X 0.53 mm	

3. Results and discussion

Yields of pyrolysis products derived at 450 °C are presented in Figure 2, which makes it evident that pyrolysis of the fuel composite results in low yields of char and high yields of volatile components than pyrolysis of coal alone. The results show that the presence of microalgae biomass in the fuel composite has an influence on the devolatilisation of coal under mild pyrolysis conditions. As shown in Table 3, the coal-algae composite contains high volatile matter content and low fixed carbon than raw coal.

It can further be observed that the resultant coal-algae char contains high amount volatile matter than coal char; however, the pyrolysis of the coal-algae composite results in the retention of a lesser amount of volatile matter content (<50%) as compared to coal pyrolysis. Moreover, the substantial devolatilisation during coal-algae pyrolysis results in approximately 80% of the fixed carbon in the resultant coal-algae char, which is relatively lower than the 90% of fixed carbon retained in the coal char. The extent to which the volatiles and fixed carbon content were retained in the resultant chars following mild pyrolysis is indicated by the retention efficiency (RE), which was calculated according to Equation 4.

$$RE = \frac{Mass\ of\ residual\ char}{Mass\ of\ parent\ sample} \times \frac{X_{char}}{X_{sample}} \quad (4)$$

where X denotes proximate property (volatile matter or fixed carbon) of the fuel (parent sample or resultant char) as measured on an Eltra Thermostep TGA.

Table 4 shows that pyrolysis of parent fuels results in a decreasing trend in the hydrogen and oxygen contents of resultant chars, which is attributable to the transitional changes that occur during pyrolysis. Reductions in oxygen and hydrogen contents are a result of an increase in the release of volatile components. A decrease in the hydrogen content in

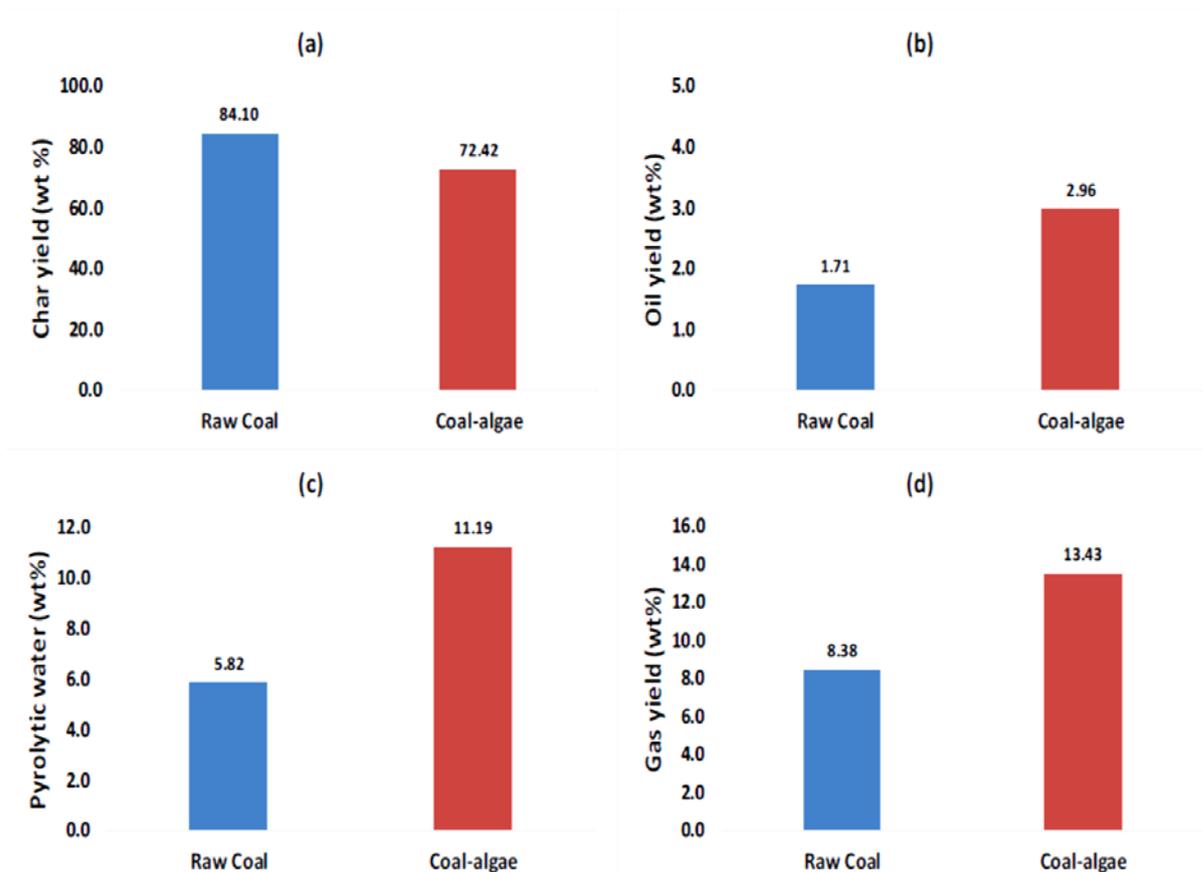


Figure 2: Product yields: (a) resultant chars; (b) coal tar and fossil bio-crude oil; (c) pyrolytic water; (d) product gas.

Table 3: Chemical properties of coal, coal-algae and resultant chars.

(Weight %, dry basis)	Raw coal	Coal char	Coal-algae	Coal-algae char
Volatile matter	25.4	15.1	30.1	19.2
Ash yield	20.8	27.3	19.6	23.3
Fixed carbon	53.8	57.7	50.3	57.6
Retention efficiency (volatile)		0.50		0.46
Retention efficiency (fixed carbon)		0.90		0.82

Table 4: Ultimate analysis of coal, coal-algae and resultant chars (dry, ash free basis).

	wt. % C	wt. % H	wt. % N	wt. % S	wt. % O
Raw coal	79.3	4.0	2.2	1.0	13.4
Coal char	81.8	3.5	2.9	0.8	11.0
Coal-algae	73.6	4.5	3.0	0.6	18.4
Coal-algae char	79.5	3.0	2.2	0.5	14.8

wt. = weight; C, H, N, S, O = carbon, hydrogen, nitrogen, sulphur, oxygen respectively

the chars is due to hydrogen transferred from hydro-aromatic groups within the parent fuels to stabilise the forming radical groups, to promote the formation of gaseous hydrocarbon and liquid products (Soncini *et al.*, 2013). Oxygen reduction is generally because of the elimination of oxygen in the parental

fuels in various forms, such as water and oxides of carbon during pyrolysis (Serio *et al.*, 1987; Yu *et al.*, 2007). It can be noted that coal-algae composite pyrolysis results in a greater degree of dehydrogenation, deoxygenation and denitrication than coal pyrolysis, as reflected in the contents of elemental

hydrogen, oxygen and nitrogen of the resultant chars. It can be further noted that coal-algae chars contain lower contents of sulphur and nitrogen than coal, which is desirable to reduce emissions of sulphur and nitrogen oxides during the combustion process should these chars be used as input feedstock for such processes (Pedersen *et al.*, 1996).

The elemental composition and estimated higher heating values of fossil bio-crude oil and of coal tar obtained from the pyrolytic topping of raw coal and coal-algae composite under mild conditions is presented in Table 5. As shown there, the pyrolysis of coal-algae composite produces fossil bio-crude oil with relatively higher amounts of oxygen and hydrogen and lower carbon content than coal tar. The high oxygen content in the fossil bio-crude oil suggests that the fossil bio-crude oil contains more reactive compounds than coal tar (Vreugdenhil and Zwart, 2009). However, the high oxygen content results in the lower HHV, and hence the lowering of the oxygen content of the fossil bio-crude oil would be required to improve the heating value (Patel and Hellgardt, 2015).

Boiling point characteristics of the produced oils are shown in Table 6. The Kessler method (Escallon, 2008) was used to calculate the average boiling

point (on mass percentage recovered) of the fossil bio-crude oil and coal tar from selected temperature cut-point. It can be observed that the pyrolysis of coal-algae composite produced an oil product with a slightly higher average boiling point than coal tar. Boiling points of the fossil bio-crude oil at various cut-points are much higher than those of coal tar, except at 90% recovered mass, where the boiling point is the same as that of the coal tar.

The boiling point fractions of the produced oils are shown in Figure 3, which shows that the produced fossil bio-crude oil has compounds that are predominantly in the distillate fuel oil range (277–343 °C) and are in higher proportions (25.5 wt. % distillate fuel oil) than (17.2 wt. %) coal tar. Moreover, fossil bio-crude oil contains relatively high amounts of compounds compared to coal tar in the higher boiling point cut (455–566 °C). Generally, there are smaller quantities of compounds in fossil bio-crude oil (6.9 wt. %) and coal tar (7.4 wt. %) that are confined in the low boiling point heavy naphtha region (121–191 °C), and a large quantity of compounds are found in the light vacuum gas oil fraction. However, the compounds in the fossil bio-crude oil within this region are relatively lower than those in the coal tar.

Table 5: CHNS-O distribution and higher heating values (HHV) of fossil bio-crude oil and coal tar.

	<i>wt. % C</i>	<i>wt. % H</i>	<i>wt. % N</i>	<i>wt. % S</i>	<i>wt. % O</i>	<i>HHV (MJ/kg)</i>
Coal tar	74.1	10.3	1.9	0.4	13.3	37.6
Fossil bio-crude oil	59.7	12.4	2.8	0.3	24.8	33.7

wt. = weight; C, H, N, S, O = carbon, hydrogen, nitrogen, sulphur, oxygen respectively

Table 6: Average boiling points (°C) of the produced fossil bio-crude oil and coal tar.

<i>Cut-point</i>	<i>Mass recovered</i>	<i>Coal tar</i>	<i>Fossil bio-crude oil</i>
	<i>weight %</i>	<i>Boiling point (°C)</i>	
T10	10	200.2	204.4
T30	30	269.6	277.0
T50	50	328.6	333.4
T70	70	387.4	390.0
T90	90	466.2	466.8
	AveBP	330.4	334.3

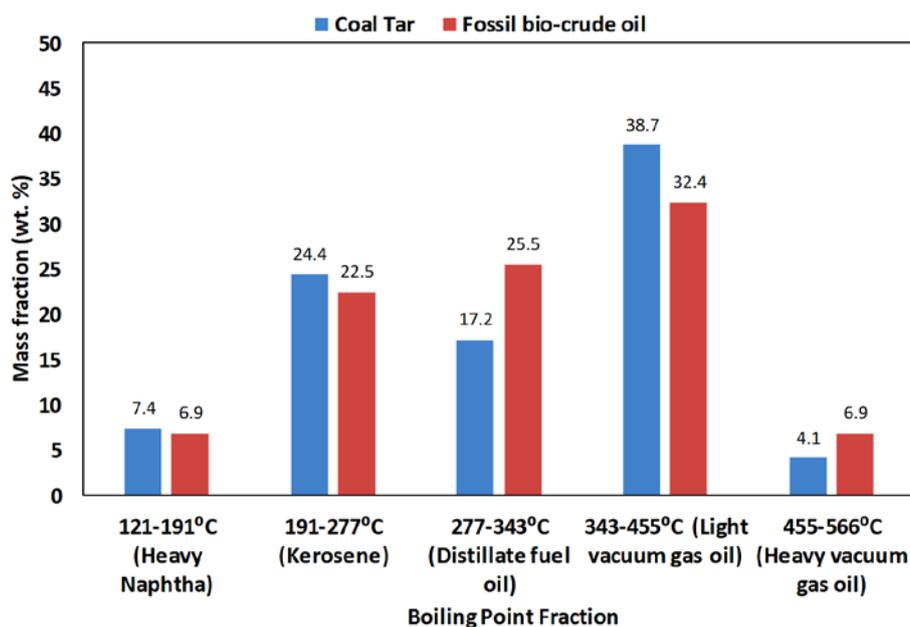


Figure 3: Simulated distillation of coal tar and fossil bio-crude oil.

4. Conclusions

Pyrolytic topping of coal-algae composite has shown that it is possible to pyrolyse coal-algae composite under mild reaction conditions and yield a char with a substantial degree of deoxygenation, dehydrogenation and denitrification compared to the resultant coal char. Furthermore, coal-algae composite results in significant levels of devolatilisation, as reflected in the high amounts of volatile components produced during coal-algae pyrolysis. Fossil bio-crude oil has properties that potentially differ from those of coal-derived tar, with notable differences in the chemical composition as well as the distribution of boiling point fractions. Mild pyrolysis of coal-algae composite may be a suitable process to produce a clean coal residue product that can be used as input fuel for cleaner combustion processes.

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Author roles

Hope Baloyi: Write-up of the article, data collection and all the analytical discussions here.

Gary Dugmore: Project supervision, research formulation and technical advice

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