RESEARCH ARTICLE

Application of stage condensation of tar during pyrolysis of high ash semi-bituminous-Morupule mine coal

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ABSTRACT

Botswana high-ash semi-bituminous coal produced by Morupule mine is under-utilized due to a lack of knowledge in possible applications of derivative products such as tar, syngas, and charcoal. This study is aimed to determine the possibility of producing tar as the main product via stage condensation in a semi-batch pyrolysis plant. A conventional process that incorporates fractional distillation to refine tar makes the low-quality coal uneconomical for coal to tar application because of high energy requirement. Raw and washed peas density medium separated at 50 % yield (DMS 50 %) Morupule coal was used for pyrolysis at 500 ˚C and connected to 3 condensers set to 150 ˚C, 80 ˚C, and 25 ˚C, respectively. The average tar yield from raw coal was about 1% and about 2.4-2.6 % in washed peas coal. Washed coal had the highest oil yield of about 2.5% as compared to the average of about 1% in raw coal. Both yields are extremely low to be considered for commercial pyrolysis (targeting tar as the main product), however, no pyrolysis product goes to waste. If all products (syngas, charcoal, and tar/oils) were marketed, the process would have the potential to become profitable.

1. Introduction

Bitumen for road pavement is predominately produced as a by-product from the refinery of crude oil or coal liquefaction process. Production of bitumen from natural crude oil source has no alternative but to incorporate an energy-intensive distillation process. Nonetheless, the process is still highly profitable from sales of light fuels (petrol, diesel, kerosene, paraffin, etc.). Incorporating the distillation stage in coal tar production could potentially render the whole process uneconomical, because of high energy requirement and expensive catalytic treatment. Light fuels must undergo rigorous catalytic upgrading to

acceptable fuel standards (elimination of carcinogens and cracking of long chains) and the final fuel is bound to sell at a loss/low-profit margins at the current fuel market price.

Furthermore, fuels produced from the fractional distillation of coal tar are known to be rich in carcinogens, therefore, they are currently banned in some parts of the world including the USA and Europe. However, if the pyrolysis process is adapted for direct production of bitumen by applying staged condensation, the technology may become economically feasible. Staged condensation has been developed and successfully applied in the production of bio-oils from pyrolysis of biomass. Similar principles apply during pyrolysis of coal to produce tar, hence, there is a potential financial gain by the introduction of staged condensation in coal pyrolysis to directly produce tar/bitumen.

This study was conducted using Botswana coal from the Morupule mine, located on the outskirts of Palapye, along the Serowe-Palapye road. Botswana coal reserves have been estimated at over 200 billion metric tonnes, but they are under-utilized because of the knowledge gap in the use of this type of coal (Paya, 2011; Phumaphi, 2018). Botswana relies on imported petroleum products, such as petrol, diesel, paraffin, aviation fuel, and bitumen (for road construction), though the country has massive coal reserves that can be converted to these imported products. Generating knowledge on the application of Botswana coal to derivative products will facilitate future development of the coal industry that will alleviate the petroleum import situation.

2.   Coal pyrolysis

Coal pyrolysis is the process of anaerobically applying heat to coal molecules to produce oil, syngas, and charcoal. Pyrolysis temperatures reported in the literature range from 400 to 1100 ºC depending on the products of interest (Odeh, 2017). Low-temperature pyrolysis is associated with favoring high yields of oils (long-chain/heavy oils) and charcoal, while high-temperature pyrolysis favors the high yields of syngas and less charcoal and condensable oil (short-chain/light oils).

Using an enhanced pilot fixed bed plant, Zhang *et al*. in 2014 conducted an extensive study on the effects of coal particle sizes and temperature on the yield of syngas and tar. The feed coal was sieved into 0 to 10 mm and 10 to 50 mm particles sizes, and further analyzed the effect of temperature (from 900 to 1100 ˚C) on the yield of syngas composition and the yield of tar. Lower temperatures resulted in slower reaction kinetics and favored high tar yields, regardless of particle size, while higher temperatures resulted in faster reaction kinetics and favored high gas yields at the expense of lower tar

(Krishnamoorthy and Pisupati, 2019). Many other researchers concurred that low-mild temperature pyrolysis (from 400 to 600 ˚C) maximized tar production, while temperatures beyond 600 ˚C led to increased volatile matter, however, with a decrease in tar yield. The increase in syngas yield is associated with the thermal decomposition of tar to syngas (Krishnamoorthy and Pisupati, 2019; Jin *et al.*, 2019).

3.   Pyrolytic cross-linking

Pyrolysis cross-linking is the process by which short-chain hydrocarbon molecules collide and chemically bind to form complex long-chain molecules. This process is usually reversible if the reverse conditions are applied. The first stage of coal pyrolysis is the thermal decomposition of the coal's organic macromolecular network to its simple components such as CO, CO_2, CH_4, C_2H_4, etc. Next, this process is followed by crosslinking of simple molecules to form complex long-chain coal tar components. Crosslinking mechanisms differ across the coal ranks and the temperature at which the molecules associated with crosslinking undergo thermal decomposition.

Low ranking coals, such as lignite coal have been determined to undergo cross-linking at low temperature relative to high coal ranking (anthracite coal). This phenomenon is associated with the release of carbon dioxide from the carboxylic functional group in low coal ranks and the associated crosslinking does not result in any improvement in tar yield. Medium to higher ranking coals (semi-bituminous to anthracite coals) experience crosslinking at a much higher temperature than the low-ranking coal. Its crosslinking is associated with the release of CH_4 molecules during pyrolysis. Low temperature CO_2 crosslinking is independent of the tar yield, while CH4 is directly linked to coal tar yield or the yields of other liquid components (Deshpande *et al.*, 1988; Ibarra et al., 1991).

In a cross-linking experiment performed by Ibarra et al. (1990) using the volumetric swelling technique (VST), for most coals, the first notable cross-linking activity occurred at 250 ˚C. Their experiment was performed in a temperature range from 20 to 600 ˚C, with a slow heating rate of about 6 ˚C per minute. The cross-linking process was significant in the temperature range from 400 to 500 ˚C, where it formed most of the tar and produced less tar above 500 ˚C. Temperatures above 600 ˚C resulted in thermal cracking of tar molecules and therefore promoted the formation of non-condensable short-chain gases.

This experiment also supported the previous theory that crosslinking is associated with CO_2, CH_4, and H_2O molecules, which are linked to the formation of CO_2 in low ranking coals, by the decomposition of carbonyl functional groups (Chaiwat *et al.*, 2009).

4. Pyrolysis Catalysis

Liu *et al*. (2003) researched the effect of inorganic matter on the pyrolysis of coal. They determined that the addition of inorganic matter to demineralized coal has a varying degree of catalytic effect on pyrolysis, depending on the added inorganic compound. Additions of Al_2O_3, CaO, or K_2CO_3 to demineralized coal enhanced pyrolysis, the kinetics of the process increased, and there were more volatiles released, as compared to samples without inorganic components (Liu *et al.*, 2003). Many catalysts have been tested by researchers for improving the oil yield. Zhu *et al*. in 2017 formulated a Ni/MgO catalyst, which they optimally added at 7.3 wt.% to bituminous coal and pyrolyzed at the temperature of 550 ºC. At optimum conditions, the catalyst led to an increase in tar yield from about 5 to 7%. Other catalysts were MoS_2 used on low-rank coal (Amin *et al.*, 2017), Ni/Al_2O_3 and $Ni/MgO-Al_2O_3$ catalyst utilized by Haibin Zhao to enhance tar yield by about 1% (Zhao *et al.*, 2019).

5. Botswana Coal characterization

Botswana coals have been widely characterized by researchers to determine their possible applications. Makoba *et al*. (2018) analyzed 2 raw coals obtained from recently operational mines (Mabesekwa and Mmabula), however, the coal was mostly low quality with high ash content up to 63% in some coal seams and volatile matter ranging from 15 to 27%. This makes both these raw coals highly unsuitable for pyrolysis, as they would result in low oil/volatile matter yield (Makoba et al., 2020).

Morupule mine is the largest coal supplier in Botswana and is also located in the same town as our research facility. The datasheet provided by the mine states that the average raw coal ash is around 25% and about 14% in washed coal peas (DMS 50%) (Morupule Coal Mine, 2017). This figure is by far the best in all encountered coal sources (Mabesekwa and Shumba), which were mostly raw coals since both mines have not started commercial operations. Preliminary pyrolysis experiments have been performed using the equipment setup that will be discussed in the later chapter using Morupule raw and washed coals.

6. Bitumen standards

Desirable asphalt aggregate properties include resistance to water damage, good wheel traction to avoid wheel skidding, good elasticity, and cohesion (resistance to permanent deformation or cracks consistent traffic load), resistance to temperature change within the normal operating conditions to avoid cracks or melting in cold and hot conditions, respectively Also, asphalt should produce minimal noise when vehicles are driving through. Due to the diverse chemical nature of bitumens, there is no specific chemical composition defining its standards. Nevertheless, physical characterization tests are widely accepted for determining the quality of bitumen, such as the needle penetration test, ductility test, density and softening point measurements, viscosity test, flash point test, water content determination and evaluation of chemical safety (Singh and Jain, 1997; Haque, 2001).

Ultimate analysis of bitumen in the literature reports carbon content in range of 80-87%, hydrogen 9.8-10.9%, sulphur 0.99-6.6%, oxygen 0.2-1.0%, nitrogen from 0.26 to 1.2%, and different inorganic trace mineral contribution (RAHA, 2020; Mortazavi and Moulthrop, 1993; Petersen, 1984). Functional groups reported in bitumen vary greatly from one source to another. Common bitumen functional groups are poly-nuclear aromatic, phenolic, 2-quinolone type, pyrrolic, pyridinic, sulphide, sulfoxide, anhydride, carboxylic acid, and ketones. Bitumen comprises different functional groups according to their source (coal, crude oil, natural bitumen, or bio-bitumen, etc.) (Jiang *et al.*, 2007). Consequently, conflicting structures of bitumen have been proposed. Coal tar composition is similarly unique from one source to another, and even across different seams within the same source. There are different bitumen grades, which are classified using the physical tests mentioned above, and each grade has a specific suitable application during road construction, including specific road layer (asphalt aggregate, topcoat, base, etc.), and climatic conditions.

7. Coal tar PAHS concerns

Refinery bitumen comprises some polycyclic aromatic hydrocarbons (PAHs) and coal tar sources. Starting in the 1950s, there has been extensive research on the environmental and human safety of coal tar because of the carcinogenic effects associated with its PAHs components. Some coal tars, such as the Limburg coal tar was determined, however, to contain only insignificant amounts or no PAHs. This is not surprising considering the extensive variation in coal sources across different prehistoric vegetation and climates. PHAs are formed during pyrolysis or incomplete combustion of fossil fuels or other hydrocarbons fuels (Chadwick *et al.*, 1987). PAHs produced by incomplete combustion either during fuel combustion or coal pyrolysis and are ultimately released into the atmosphere, as gases. Tiny particulate tar molecules will be easily inhaled from polluted air to cause respiratory health diseases, while the heavy or condensed PAHs will stick to the surface, causing both short-term irritations and chronic health complications.

The mutagenic effect of coal PAHs was first reported in 1776, by English surgeon P. Pott. He observed that

chimney sweepers developed mutagenic skin growth, which was later associated with contact with coal soot (Chadwick *et al.*, 1987). In a controlled investigation performed by Cook et al. in 1932, the laboratory rats skin were painted with 0.3% PAHs mixture, and within 6 months of the experiment, about half of the rats developed some cancerous papilloma on their skin. This study established the carcinogenic effect of PAHs predominantly found in coal tar.

Table 1. Coal tar components and their molar mass. (Chaiwat *et al.*, 2009; Jiang *et al.*, 2007; Harris et al., 1953; Kershaw, 1993)

Molecular Mass	Components
154	Acenaphthene
168	5-, 3-, and 4-Methylacenaphthene (Isomers)
184	Dibenzothiophene
178	Phenanthrene/ Anthracene
192	Methyl phenanthrenes/ methyl anthracenes
190	4H-Cyclopenta/ phenanthrene
206	Dimethyl phenanthrene/ dimethyl anthracene
204	2-Phenyl naphthalene
202	Fluoranthene/ Pyrene
218	Benzo(k1) xanthene
216	Benzofluorene/ methyl fluoranthene/methyl pyrene
230	Dimethyl pyrene/ dimethyl fluoranthene
234	Benzonaphthothiophene
228	Benzo(c) phenanthrene/ Benz(a) anthracene/ Chrysene/ triphenylene/ Naphthalene
242	Methyl chrysenes
240	4H-Cyclopenta(def) / chrysene/ 4H-cyclo penta (def) triphenylene
252	Benzopyrene/ benzo fluoranthene/ perylene
266	Dibenzo fluorene
264	Cyclopenta (ghi) perylene
276	Anthanthrene/ benzo(ghi)perylene

More than 25 PAHs have been detected in coal tar samples and most of them existed as isomers. Table 1

lists some of the identified coal tar components, determined using either UV fluorescence, GC/MS, or liquid/gas chromatography. It was documented that coal tar produced at temperatures ranging from 400 to 600 ˚C started to exhibit carcinogenic properties, and the carcinogenic PAHs components compositions increased when distillation was performed from 800 to 850 ˚C (Van Metre and Mahler, 2014). As more and more research scientists confirmed the carcinogenic nature of coal tar, it eventually led to the banning of coal tar home products, such as roof/construction sealant in some parts of America (in 2006) and Europe. Eventually, several other nations banned it, as well (Van Metre and Mahler, 2014).

Past research on coal safety, dating back to the 1900s, revealed that most coal tars contained carcinogenic PAHs. Nevertheless, coal tars free of PAHs have also been reported. Henceforth, it is important to determine the presence of any known PAHs in Botswana coal tar and/or their quantities. Should they be detected, a remedial plan must be devised to reduce their concentrations to acceptable set limits, either by modifying the production process to eliminate them by catalytic cracking, or lowering the PAHs content by blending of coals with refinery bitumen.

8. Materials and Methods

Coal from the Morupule mine was used for this study. The sample preparation process entailed crushing the coal sample in a jaw crusher and screening it to the desired particle sizes, using selected sieves and a shaker. An electrically heated semi-batch reactor (see Figure 1) was utilized for pyrolyzing coal samples. The reactor temperature capability ranges from ambient to slightly over 750 ºC, however, 500 ºC was selected for all experiments because it promoted the best yield of tar compared to other temperatures. The apparatus comprises a batch reactor in which the coal sample was pyrolyzed and it is connected to 3 condensers in series that were all equipped with temperature control capability.

The first condenser temperature was set to 150 ºC, followed by 80 ºC in the second condenser, and 25 ºC in the final condenser. The first condenser temperature was chosen to selectively condense heavy hydrocarbons from the volatile matter, while the light hydrocarbons and water condensed in condensers Nos. 2 and 3. Finally, the non-condensable gasses were bubbled through a water bottle to trap any residual matter before the syngas being stored in a tank.

The mass of the containers together with the coal sample was measured pre- and post pyrolysis to determine the mass change during the pyrolysis process. The oil containers were also calibrated to measure the condensable liquid volume.
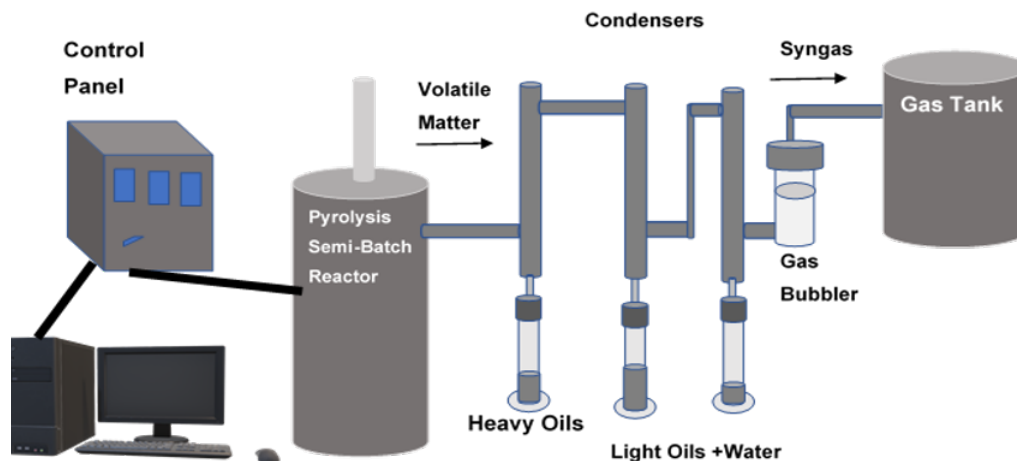
Figure 1. Pyrolysis apparatus designed and built by Pyro Carbon Energy. The setup is equipped with a control panel where all the set-points are inputted, and a computer control interface. The sample is enclosed in the reactor and the volatile matter will leave through the outlet pipe to the condensers where it will be cooled down and converted to liquid hydrocarbons and water. The syngas is bubbled through water and stored in the gas tank. The apparatus was operated at a pressure of 1 atmosphere.

The pyrolysis process was run until the gas stopped bubbling (when volatile matter production stopped), and then we determined the final container masses together with the charcoal. The tar/water mixture was separated by using a simple distillation unit to evaporate most of the water, and further dried on anhydrous sodium sulfate.

9. Results and discussion

Coal composition varies greatly within the same source or same coal seam. To ensure the credibility of experimental results, an average of at least three experiments was used for the results listed in Table 2. The table shows the yield of syngas, tar, and charcoal for Morupule raw coal at different particle sizes. The reactor temperature was set to 500 ºC which was based on the literature optimum conditions for similar coals and was also confirmed by preliminary trial runs (Zhu *et al.*, 2008).

The average oil yield for different particle size (10 mm to -2 mm) was calculated to be 1.01%, 1.07%, and 0.79% for samples RCS003 to RCS005, respectively.

The finer coal contained significantly less tar compared to other considered particle sizes. This was expected since fine coal was observed to contain light coloured particles, which are suspected to be inorganic matter (mostly particles of iron oxide ores and silicates). Most of the condensable liquid was captured in condenser 2, which was determined to contain at least 95% water and 5% light oils in raw coal samples.

Washed and density separated at CV 50% Morupule coal was also used in pyrolysis to compare with raw coal. Coal samples were supplied as washed coal peas with particle size ranging from 6 to 25 mm and three pyrolysis experiment were performed, as shown in Table 3. Experimental conditions similar to raw coal were applied in washed coal for easy comparison. In contrast, washed coal had a better overall oil yield of 2.6% (for 6-25 mm) compared to figures around 1% for raw coal This proved that washing coal enhanced the quality for application in coal to tar. The heating rate of the reactor was maintained the same for both raw and washed coal, and data acquisition was started, when the element temperature reached 100 ºC. Graph in Figure 2 shows the internal reactor temperature against time from the

Table 2. Average percentage yields for Pyrolysis of raw Morupule coal

ID	Sample Mass (g)	Particle Size (mm)	Pyrolysis Temp (ºC)	% Yield-Condenser 1	% Yield-Condenser 2	% Yield-Condenser 3	% Yield-Syngas	% Yield-Charcoal
RCS	1096.2	10…4	500	0.6	7.8	0.4	5.8	85.5
RCS	1022.7	+2…4	500	0.6	8.8	0.1	6.6	83.9
RCS	1103.1	-2	500	0.4	8.5	0.8	6.5	83.8

Table 3. Pyrolysis of washed and density separated (DMS 50%) Morupule coal Morupule coal

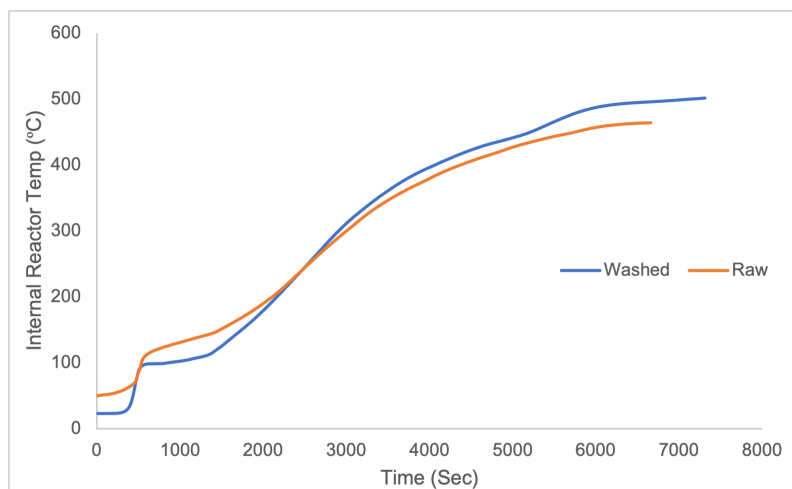| ID	Sample Mass (g)	Particle Size (mm)	Temp Setpoint (ºC)	% Yield-Condenser 1	% Yield-Condenser 2	% Yield-Condenser 3	% Yield-Syngas	% Yield-Charcoal
WCS001	1646.9	6-25	500	1.6	10.2	1.9	5.7	80.5
WCS002	1361.1	6-25	500	1.3	10.3	0.5	7.0	80.8
WCS003	1605.7	6-25	500	2.4	10.2	1.9	4.6	80.9

Figure 2: Reactor core temperature (ºC) against time

beginning to the end of the reaction (i.e., when bubbling stops). Raw coal demonstrated better heat absorption properties up to 200 ºC, where washed coal started absorbing heat better than raw coal. Also, it can be interpreted that washed coal contained significantly more water than raw coal since its graph flattened around 100 ºC for a much longer time when water started evaporating from the sample. There is no apparent oil production zone identified on the graph.

Raw coal pyrolysis reaction ended faster with a lower internal temperature than for washed coal. The light oil and tar started forming, when the internal temperature of the reactor reached about 250 ºC and continued until it reached about 500 ºC, where gas bubbling stopped.

10. Conclusions and recommendations

Washed coal had the highest oil yield of about 2.5% as compared to the average of about 1% for raw coal. Both yields are extremely low to be considered for commercial pyrolysis (targeting tar as the main product), however, no pyrolysis product goes to waste. If all products (syngas, charcoal, and tar/oils) were marketed, the process would have the potential to become profitable. Our further research milestones include:

(1) Tar standard test. Characterizing condensed oils to determine whether they satisfy road construction tar standards, and how they can be modified to meet the set standards through catalytic upgrading and/or blending with refinery tar if needed. Ensuring the concentrations of PAHs does not exceed safety limits by blending with refinery oils or applying catalytic cracking to break down some of the PAHs.

(2) Upgrading the coal quality prior to its pyrolysis by reducing the ash content with techniques like leaching (using an acidic or basic solution) or impregnating with a catalyst to improve the oil yield and quality.

(3) Characterizing charcoal to determine its caloric value and emission level compared to raw coal and potentially reduce coal-powered station emission.

(4) Characterize the syngas to determine their potential market value (or the potential to be processed to derivative products, including cooking gas, colour pigment, and other synthetic chemicals).

(5) Application of direct coal liquefaction or indirect coal liquefaction, which both have proven to be more efficient than coal pyrolysis.

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