Acid Tar Waste Beneficiation Through Blending With Coal

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ABSTRACT: Acid tar waste has been regarded as a low value waste which was routinely disposed of in landfills without exploring its alternative uses. The possibility of blending acid tar waste with coal as a beneficiation method was explored in this work. The material properties of the acid tar and coal samples together with the fixed blending of the blends were established in terms of proximate analyses. Acid tar waste to coal blending ratios of 3:1, 1:1 and 1:3 were used. In its pure form acid tar waste showed higher volatile and moisture content, and lower ash and carbon content when compared with coal. Comparison of the 3:1 blends with coal showed a decrease of 56.9% and 7.6% for ash and fixed carbon content respectively, and 38.1% increased volatile matter. An inverse trend was observed with 1:3 blends. The 1:1 blend tended to decrease the volatile and ash content by 8.3% and 52.7% respectively whilst fixed carbon boosted by 4.2%. The choice for application of the blended fuel is therefore a trade-off between fixed carbon and volatile matter. If volatile matter is of any significance then 3:1 blends would be ideal and 1:3 blends where higher fixed carbon fraction is desired.

Keywords: Acid tar waste; blending; binary mixture; proximate analysis

1. Introduction

The daily activities that support human existence have resulted in the generation of huge quantities of waste. Traditionally waste handlers were not concerned much about the physical, chemical and biological properties of solid waste, since all waste, particularly solid waste, was dumped on landfills (Musademba, 2016). But, today, it is no longer business as usual; attention is now being channelled towards environmental protection. This has led increasingly to the development of proper waste management systems involving recycling, re-use, transformation and disposal (Musademba, 2016). Recently much discussion has been directed at generating useful energy from waste material (Musademba, 2016). It is now imperative to know the specification of the waste in terms of physical, chemical, energy and biological properties so as to develop processes for its efficient handling with the least negative impacts (Musademba, 2016). The issue of different waste management practices has become topical debate as increased human activities have overloaded the assimilative capacity of the biosphere (Marchettiini et al., 2007). The sustainable management of waste now considers energy and materials recovery as important steps for an environmentally sound waste management system (Musademba, 2016).

The present work focuses on beneficiation of acid tar wastes derived from the carbonization by-products. Acid tar wastes are basically generated from three processes namely; the refining of spent lubrication oils, refining of petroleum fractions and production of benzene, toluene and xylene fractions from crude benzol processing (Danha et al., 2015). One industry in Kwekwe, Zimbabwe generates huge quantities of acid tar waste following the extraction of benzene, toluene and xylene (BTX) fractions from crude benzol by washing with sulphuric acid to remove sulphur contaminations mainly thiophene, styrane, and indene (Musademba, 2016). The acid tar which has no further use is being disposed of to designated lagoons that are located close to the banks of Kwekwe River (Musademba, 2016). In the lagoon, the acid tar is pre-treated with calcium carbonate to neutralize the excess sulphuric acid and left exposed (Musademba, 2016). The lagoon is not immediately buried; but may remain for over 10 years to allow the lagoon to fill up before final burial (Musademba, 2016).

Acid tar waste has been regarded as a low value waste and has been routinely disposed of in landfills and lagoons. Alternative uses of acid tar have not been fully explored as millions of tons of acid tar waste are being disposed of by land filling. On the contrary, huge amounts of thermal energy from oil, natural gas, and/or coal are consumed to generate power (Musademba, 2016). The energy content available in acid tar waste residues represents a significant “alternative” energy which can be harnessed so as to extend the use and dependency on fossil fuels in a safe and sustainable way. With the escalating energy costs,
there is an increasing need to focus attention towards the reduction in use of conventional fuels through fuel substitution (Musademba, 2016). Harnessing the energy from acid tar waste that would have been discarded to landfill; may therefore translate to an efficient use of locally available or would be wasted resources (Musademba, 2016). Using it efficiently is also pivotal in balancing the energy matrix for processing industries. In this respect landfill can no longer be regarded as the first choice for acid tar waste disposal but rather as the last step after all possible material and energy recovery; the resulting ash can then be discarded into the landfill (Musademba, 2016).

The possibility of blending acid tar waste with coal as a beneficiation method is explored in this work. No published literature on the blending of acid tar waste and coal has been found. In order to provide essential indicators for the blending of acid tar with coal, it is necessary to determine the material properties in terms of its proximate analyses. This paper investigated the effect of blending acid tar waste with sub-bituminous coal and analysed the proximate of the blends.

2. Materials and Methods

2.1 Material Preparation

The acid tar waste samples (landfill acid tars) were collected from landfill lagoons in Kwekwe, Zimbabwe and the coal samples used for blending with the acid tar waste originated from Hwange Colliery mine, Zimbabwe and Table 1 shows the coal specifications.

| Tabel 1. Technical specification of the collected coal samples |
|-------------------------------------------------------------|
| Coal Parameter | Specification |
| Sample type | Sub-bituminous coal |
| Size | Pea (≤ 14 mm) |

2.2 The Proximate Analysis (PA) of acid tar and coal samples

The proximate analysis of the coal and acid tar waste samples as defined by a group of (American Society for Testing Methods) ASTM test methods is an assay to determine the moisture, volatile matter, ash, and fixed carbon contents (Musademba, 2016). Other constituents such as sulphur and phosphorus are not included. The ASTM Protocols: D3173-11, D3175-11 and D3174-12 were adopted for determining the moisture content, volatile matter and ash content, for the landfill acid tar and coal samples respectively.

Moisture content (MC) was determined by establishing the loss in weight resulting from heating the fuel sample under rigidly controlled conditions. Several researchers have reported the use of this protocol in the determination of a fuel’s volatile matter (Basu, 2013; Miller, 2013; Ilham, 2022; Tillman et al., 2012). This protocol as adapted by Chihobo et al. (2016) and Kolmakov et al. (2006) for volatile matter determination for acid tar waste was also used in this work. The weight loss, corrected for moisture as determined in TEST Method D3175-13 establishes the volatile matter content (ASTM D3175, 2011). A test sample of approximately 1g was put in a crucible with a close fitting lid and was placed in a furnace which was preheated and maintained at a temperature of 950 ± 20°C for 7 minutes. The tight fitting lid helps to exclude air from the crucible during the heating process so as to prevent oxidation (ASTM D3175, 2011).

The ASTM D3174-12 Standard test method for determining the ash content for both the coal and acid tar waste was applied. 1g of the sample was heated in open crucibles at furnace temperature of 750°C. The weight of the inorganic residue (ash) on complete combustion of the fuel samples was then determined (ASTM D3174, 2012). An average of 30 trial runs was repeated for each test parameter.

The fixed carbon (FC) content is a calculated value from the material balance equation:

\[
\text{Fixed carbon(\%)} = 100 - (\text{moisture(\%)} + \text{ash(\%)} + \text{volatile matter(\%)})
\]

The proximate analysis for the mixtures of landfill acid tars with coal samples were also determined following the procedure described for the landfill acid tar and coal. The coals were mixed with land-fill acid tar in the following mass ratios (Musademba, 2016):

i)  25 % land-fill acid tar - 75% coal;  
ii)  50 % land-fill acid tar - 50% coal,  
iii) 75% land-fill acid tar - 25% coal.

The volatile matter (VM) was determined by establishing the loss in weight resulting from heating the fuel sample under rigidly controlled conditions. Several researchers have reported the use of this protocol in the determination of a fuel’s volatile matter (Basu, 2013; Miller, 2013; Ilham, 2022; Tillman et al., 2012). This protocol as adapted by Chihobo et al. (2016) and Kolmakov et al. (2006) for volatile matter determination for acid tar waste was also used in this work. The weight loss, corrected for moisture as determined in TEST Method D3175-13 establishes the volatile matter content (ASTM D3175, 2011). A test sample of approximately 1g was put in a crucible with a close fitting lid and was placed in a furnace which was preheated and maintained at a temperature of 950 ± 20°C for 7 minutes. The tight fitting lid helps to exclude air from the crucible during the heating process so as to prevent oxidation (ASTM D3175, 2011).

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![Figure 1. RM 200 mortar grinder](image)

The acid tar waste and the coal samples were mixed and ground to a mean particle size of 212μm by means of a RM
200 mortar grinder. The weighted ratios of the two samples were force fed into the RM 200 mortar grinder through a scraper in the space between the mortar and pestle. The force feeding mechanism of the solid samples subjects the mixture to a continuous grinding and intense mixing of the solid powders. The grinder pulverizes and triturates the solid particles whilst mixing and homogenising the two samples by pressure and friction. Figure 1 shows a schematic of the RM 200 mortar grinder.

3. Results and Discussions

Characterization of the acid tar waste and coal samples was carried out in conformity with the protocol for proximate analyses (PA). Determination of the moisture content, volatile matter, ash content and fixed carbon content is important in characterising the combustible fraction of the fuel samples (Musademba, 2016). The average PA results for the landfill acid tar waste (LAT) and the sub-bituminous coal samples are presented in Table 2 and Figure 2.

Table 2 Proximate analyses for the acid tar waste and coal samples

| Parameter | Land fill acid tar (LAT) % | Sub-bituminous Coal % |
|-----------|---------------------------|-----------------------|
| MC        | 8.24 ± 0.82               | 1.91 ± 0.11           |
| VM        | 35.68 ± 0.34              | 21.05 ± 0.35          |
| Ash       | 8.13 ± 0.14               | 18.69 ± 0.55          |
| FC        | 47.95 ± 0.17              | 58.35 ± 0.17          |

The moisture content for the landfill acid tar waste derived from crude benzol processing to BTX fractions was found to vary within the range of 7 - 9 %, a much higher figure compared with that for coal samples used in this study (Musademba, 2016). In an earlier study Chihobo et al. (2015) similarly reported moisture content in the range of 7 - 11% for acid tar waste derived from crude benzol processing; Nichol (2006) also reported a moisture content of 6% for acid tar waste originating from benzol. The results reported in this work were, found to be in agreement with those obtained by Milne et al. (1986) and Leonard et al. (2010) for acid tar wastes derived from processing of lube oils. Xu and Smith (2005) indicated that acid tar wastes converts into a collection of diverse appearance depending on the extent of how it loses its water content and organic solvents. The high moisture content will, however, impact negatively on the heat content for the waste when it is desired to use it as a fuel. The moisture content does not only reduce the heat content but also influences the combustion characteristic of the fuel (Musademba, 2016).

The results also indicate very high volatile matter for the landfill acid tar, low fixed carbon and ash content when compared to coal samples. The high volatile matter for the acid tars suggests the presence of highly combustible organic components; and its low ash content is indicative of good quality fuel characteristics. On the other hand the coal samples exhibited relatively high carbon and ash content with moderate volatile matter when compared to the acid tar waste.

The proximate analysis for the blended LAT and coal in the ratios of 1:3, 1:1 and 3:1 were determined and compared with the parameters for coal as presented in Table 3. The investigation was aimed at establishing a suitable land-fill acid tar to coal combination that would result in good fuel characteristics.

Table 3. Proximate analysis results for LAT-Coal mixtures

| Parameter | LAT: Coal Ratio (%) | Sub-bituminous coal (%) |
|-----------|---------------------|-------------------------|
|           | 1:3                 | 1:1                     | 3:1                     |
| MC        | 2.42±               | 3.54±                   | 1.91±                   | 1.91± 0.11 |
| VM        | 0.29                | 0.47                    | 0.33                   | 0.35       |
| Ash       | 15.10±              | 19.3±                   | 21.05±                 | 21.05± 0.35 |
| FC        | 60.80±              | 58.35±                  | 58.35± 0.11            |

Figure 3 shows the comparison of the PA for the LAT-Coal blends for the ratios 3:1, 1:1 and 1:3 with 100% coal. The moisture content and volatile matter was found to vary directly with increase in landfill acid tar waste in the mixture while inverse is true with respect to ash content and fixed carbon. The binary mixture of land-fill acid tar waste and coal in the ratio of 1:1 when compared with coal was found to boost the fixed carbon by almost 4.2 % whilst decreasing the ash content and volatile matter by 52.7 %
and 8.3 %, respectively. For a 1:3 binary mixture the ash content and volatile matter was found to reduce by 54.6 % and 28.3 % respectively whereas the fixed carbon increased by 19 %. A higher fraction of the acid tar in the binary mixture (3:1) reduces the ash and fixed carbon by 56.9 % and 7.6 % respectively whilst the volatile matter is considerably increased by 38.1 %.

![Figure 3. Proximate Analysis for the LAT-Coal blends](image)

The increase in the moisture content level for the mixtures invariably impacts negatively on combustion since a higher temperature would be required to initiate the combustion. On the contrary, the high volatile matter improves the combustible organic constituents of the fuel. The volatile matter as noted by (Ilham, 2022 and Kumar & Anand, 2019) comprises a mixture of combustible gases; aromatic hydrocarbons, short and long-chain hydrocarbons, carbon monoxide, oxygen and non-combustible gases. The composition of the volatile matter however, was found to affect the character of the remaining residual fixed carbon or char (Miller, 2017) in the fuel sample. The lowering of ash content is imperative as this reduces the tendency for material sintering or ash fusion at the high operating combustion temperatures. The increase in fixed carbon indicates an improvement in the calorific value for the fuel. The choice for a binary ratio to apply is therefore a trade-off between fixed carbon and volatile matter. If volatile matter is of any significance then a 3:1 mixture would be ideal and a 1:3 binary mixture if fixed carbon is the deciding factor. The beneficiation of acid tar waste which is otherwise regarded as waste can thus be found through blending with coal. This is not only economic but also enhances the sustainable utilization of coal.

The composition of acid tar waste however, has not been well studied (Kolmakov et al., 2006). Comprehensive compositional information about the acid tar waste is very important if we are to ascertain the potential risk and toxicity that it might pose to humans, flora and fauna. However, notwithstanding, the potential risks; the acid tar beneficiation has mostly been realized through the incineration route. Miline, et al., (1986) noted that the most competent technique for utilization of acid tar waste was by incineration. A fluidized bed incinerator with limestone as the bed material to arrest the emissions of sulphur dioxide from acid tar waste incineration was investigated with success by Kerr and Probert (1990). Tumanovskii et al., (2004) also investigated the incineration of acid tar waste in circulating fluidized bed technology; and reported that it was possible to generate power in Russia using acid tar waste as the energy carrier. Similarly in Germany, acid tar waste was converted to a stable form and used in power plants that utilize brown coal (Gruss, 2005). Hence the idea of blending acid tar waste with coal can be mooted against the backdrop of sustainable utilization of coal.

### 4. Conclusion

The proximate analysis for the acid tar waste generated from crude benzol processing and that of coal fuel samples were determined using ASTM testing methods. The volatile content of the LAT was irrefutably high and more than twice that of coal. The high volatile content of LAT indicates high burning potential signifying that the material is a suitable candidate for use as a fuel. A LAT to coal blending ratio of 1:3 was found to improve the carbon content for the mixture; which implies an increased calorific value for the fuel blend. Whereas a mixture of LAT with coal in the ratio of 3:1 was found to diminish the ash content with an increase in volatile matter when compared to coal samples. It can therefore be concluded that there is great potential in blending coal with acid tar waste which otherwise is being lost to the landfills.

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