

Potential for Producing Liquid Fuels from Co-Processing of Coal Fines and Municipal Solid Waste Plastics Using Red Mud as Catalyst

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Abstract

This study relates to an assessment for the potential to produce liquid oils by co-processing coal fines with municipal solid plastics waste using red mud from aluminium processing as a catalyst. This research seeks to promote environmental sustainability by utilising waste coal fines and municipal solid waste without creating health and environmental hazards. Using municipal solid plastic waste in the process enabled large scale production which reduced costs and prevented downtimes and improved plant economics. Co-processing of coal fines with municipal waste plastics is a brilliant solution for an affordable, fuel from locally available raw materials which securing energy supply, promoting economic sustainability and protected the climatic changes associated with waste management. From experimental work, it was observed that higher temperatures and lower space velocities increase the formation of coke and gas which decreases the yield of oil. All experimental runs were conducted at 350-375 °C and a liquid hourly space velocity of 0.70-1.70/h at hydrogen pressure of 6 MPa yielding oils of 24-34 wt.% for naphtha, 34-45 wt.% for middle distillates and heavy distillates 18-25 wt.%. Co-processing of coal fines and municipal waste is a good waste valorization strategy to produce liquid fuels.

Keywords:

Coal fines, co-processing, heavy distillates, naphtha, middle distillates, liquefaction, red mud, municipal waste plastics, waste valorization

1. Introduction

A lot of studies on the liquefaction of coal to liquid fuels have been at the lead regarding ways of finding profitable energy approaches in the whole world (Akah and Al-Ghrami 2015; Khan et al. 2016). Coal has been regarded as the potential raw material during production of liquid fuels because of its abundance in all nations including Zimbabwe (Ayres et al. 2001). Coal as a natural resource contain more carbon content and provide very little amounts of hydrogen content, therefore there is need to produce large quantities of hydrogen which is quite expensive as it counts a

significant portion of the overall total cost of producing fuels from coal (Ayres et al. 2001). Technological studies have been done regarding coal to liquid methods but unfortunately this approach alone has not been economically feasible especially to developing countries since its energy intensive (Bezergianni et al. 2017). Efforts to mitigate the environmental problems related to municipal solid plastic wastes such as plastics and waste oils have been done through waste valorization (Lin and Yang. 2008).

Solid plastic wastes and oils are petroleum derived products that are technically known to have higher hydrogen content as compared to coal and no one has ever thought of combining it with coal (Bezergianni et al. 2017). From the report given by the Zimbabwe Statistics Agency (Zimstats) it reflected that bulk waste collected in dumpsites results in the non-achievement on Sustainable Development Goals (SDGs) particularly SDG goal 12 which underscores the need to ensure total elimination of dumping waste at the same time increasing recycling and safe re-use of municipal waste by 2030. Pyrolysis of municipal solid wastes has been the most promising technology for municipal waste management however it is having a challenge of low heat efficiency and poor selectivity to fuels (Mileva et al. 2016). Hence co-processing coal with municipal solid waste materials such as waste plastics and oils provides an attractive alternative raw material that increases plant economics by reducing hydrogen production costs and increasing plant capacity (Elizabeth et al. 2022). Waste plastics mainly low density poly ethylene plastics are an attractive source of olefins that are used in liquid fuels production (Bezergianni et al. 2017).

On the other hand, red mud is continually being produced through the Bayer process and has potential to be used as a catalyst for the co-processing of waste plastics and coal waste fines to liquid fuels (Evan, 2016). Red mud also termed bauxite residue is industrial waste generated during the processing of bauxite to alumina via the Bayer process (Evan 2016). Red mud contains several compounds including iron oxide giving it its red colour and the annual production of red mud is approximately 175 million tons per annum (Evan 2016). Red oxides contain various metal oxides such as silica, alumina compounds and titanium oxide with iron oxides taking 60% of the composition (Table 1) Alves et al. 2011). The composition of red mud is shown in Table 1.

Table 1. Red mud composition (Alves et al. 2011)

Oxide present	Composition (wt. %)
Iron oxide (Fe ₂ O ₃)	5-60
Alumina oxide (Al ₂ O ₃)	5-30
Titanium oxide (TiO ₂)	0-15
Calcium oxide (CaO)	2-14
Silica oxide (SiO ₂)	3-50
Sodium oxide (Na ₂ O)	1-10

The direct co-processing of coal and municipal solid waste plastics involves direct liquefaction of the materials into gas, liquids and solid components (Elizabeth et al., 2022). It has been reported that the use of metal catalyst in co-processing of coal and waste plastics enhances fuel production rate by up to 90 % with lower residence times of one hour and temperatures of 220 °C (Gulab et al., 2010). This study therefore investigated the potential to produce liquid fuels from co-processing of waste coal fines and plastic wastes using red mud as a catalyst.

2. Problem statement

Municipal solid plastic wastes challenges have been escalated due to environmental threats to mankind up to the extent that all waste to energy approaches have been intensified including production of liquid fuels (Ayres et al., 2001). Zimbabwe is one of the countries importing oil therefore it is lacking secure, affordable and adequate energy source. Therefore, co-processing coal fines with municipal solid plastic wastes with catalytic enhancement using red mud will make the coal to liquids process more cost-effective because of reduced hydrogen production costs, increased production capacity as well as waste valorisation.

3. Research questions

3.1 Can coal fines and municipal waste plastics be co-processed to produced liquid fuels?

3.2 Is the co-processing of coal fines and municipal waste plastics a waste valorization strategy?

3.3 Are the oils produced from co-processing of coal fines and municipal waste plastics comparable to standard oils?

4. Materials and methods

4.1 Characterization of the coal fines and the municipal waste plastics

Coal fines were obtained from Hwange in Matabeleland North, Zimbabwe, the waste plastics were obtained from the M block local municipal waste dumpsite and were composed of polyethylene, polypropylene and polystyrene plastics. Red oxide was obtained from Nyanga, Mutare and Mwenezi in Zimbabwe. The coal fines and municipal waste plastics were characterized for fixed carbon content, ash content, moisture content, sulphur content and volatiles composition in weight percent (wt.%) using standard methods (ASTM D3173 2011). The fixed carbon is calculated by subtracting from 100% the moisture content value, the ash content value and the volatile matter value (ASTM D3173, 2011). All chemicals and reagents were obtained from Sun firm distributors.

4.2 Sulphur contaminants and ash removal from coal fines

The coal fines had a high sulphur content which had to be removed of 0.7-0.9 wt.% (Watson, 1960). The sulphur contaminants and the ash were removed by sequential leaching with KOH which was then followed by using H₂O₂. A 200g sample of grinded super coal fines (200 mm wire mesh) were placed in a beaker. The first leaching solution was filled with KOH aqueous solution at 95 °C a period of 1 hour. The second leaching solution was filled with aqueous 3.5 wt.% H₂O₂ at 90 °C for a period of 1 hour. The third leaching solution was performed using 10% wt. or 20% wt. of H₂O₂ solution stabilized by 0.2M H₂SO₄ aqueous solution. As the reaction completed, the mixture was recovered and coal fines were separated from the leaching solution using filter paper. The soluble residues remaining in the product were dissolved by washing them with distilled water. The final solid product was then dried and analyzed.

4.3 Thermal activation of red mud as catalyst

Red muds from Nyanga, Mutare and Mwenezi in Zimbabwe were dried over a period of 12 hours at 105 °C before being crushed to a fine powder using an agate ball mill. Using a Retsch sieving stack consisting of 10 sieves, ranging from 4mm to 64 µm, red mud was processed to give a size fraction of < 250µm. A sample containing 1000g of red mud was then placed in a Furna scanning electron microscope (SEM) furnace that had been previously heated to the desired temperatures of 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000 °C (Geng et al., 2016). The sample of red mud was heated for 2 hours. After heating, it was allowed to cool to room temperature before being re-weighted so that the mass loss could be calculated. The red mud was then placed in a desiccator until it was used for catalysis.

4.4 Co-processing of coal fines and municipal solid waste plastics

4.4.1 Catalyst preparation

The coal fines and municipal waste plastics were co-processed using the direct liquefaction approach. The procedure used was as follows: Dry the catalyst carrier in the oven at 100 °C for a period of 8 hours (Fakhroeslam and Sadrammeli, 2019). Cool to room temperature in a desiccator and record the weight of the catalyst carrier. Air dry at room temperature in an air.

4.4.2 Continuous trickle bed reactor for gas-liquid separation

The feed slurry was pumped into the top of the reactor by using a Milton Roy piston pump through a 3 mm stainless steel feed line (Gulab et al., 2010). The pump speed could be manually controlled by a micrometer adjustment. The feed line was wrapped with flexible heating cords. The liquid feed temperature was adjusted by a power stat, connected to the heating cord. Technical grade hydrogen was fed to the top of the reactor through a pressure regulator, and a Brooks Thermal Mass Flow meter. Fine adjustments to the flow rate were made by a micrometer screw. Gases and liquids from the reactor passed through a gas-liquid separator. The exit gases were then scrubbed with a 20% NaOH-H₂O solution before venting. The liquids passed from the gas-liquid separator into a catch pot. The catch pot was modified to collect liquid samples continuously by adding a double U-bend copper tube. The U-bend formed a liquid seal/ allowing the sampling to take place continuously.

4.4.3 Characterization of the liquid fuels

The liquid fuels were characterized for the calorific value, kinematic viscosity, density, water content, flash point and the boiling point. The calorific value was measured using a TBCF bomb calorimeter in mega joules per kg (MJ/kg), the kinematic viscosity was measured in mm²/s at 40 °C using the ASTM D445 methodology (Jan et al., 2010). The density of the liquid fuels was determined using a Kruss oscillation type density meter. The water content in the liquid fuels was measured using a Mitchel Instruments hygrometer. The liquid fuels flash point was measured using

the ASTM D93 and the boiling point was measured in accordance to the ASTM D2887 methodology (Elizabeth et al., 2022).

5. Results and Discussion

5.1 Raw material composition

After treatment with KOH solutions a slight darkening of the solution appeared, due to low temperature and low concentrations of potassium humates, while sulphates and pyritic sulphur were able to react with KOH and moved into filtrate. The removal of pyrite from coal fines was best achieved in oxidize a substance an oxidizing reagent hydrogen peroxide (Lucia et al., 2022). The composition for the coal fines is shown in Table 2. The coal fines had a fuel ratio of 2.8.

Table 2. Hwange coal fines composition (Watson, 1960)

Property	Composition (wt. %)
Fixed carbon	63.7-65.8
Ash	7.3-9.8
Moisture	1.4-1.8
Sulphur	0.7-0.9
Volatiles	19.1-21.7

A summary of the characteristics of the municipal waste plastics are shown in Table 3.

Table 3. Municipal waste plastics composition

Property	Composition (wt. %)
Fixed carbon	4.9-5.1
Ash	1.8-2.2
Moisture	3.5-3.8
Sulphur	0.007-0.1
Volatiles	85.5-88.8

5.2 Red mud catalyst characterization

The red mud was catalytically cracked through heating it at higher temperatures of 200–1000 °C with the presence of oxygen, in order to remove water, carbon dioxide or to oxidize a substance. The possible changes that occurred during catalytic cracking include increase in surface area, pore volume and average pore diameter. Iron oxides in red mud could be used as an active catalyst for hydrocarbon decomposition (Elizabeth et al., 2022).

5.3 Yield and composition of liquid fuels

An overall process flow for co-processing of municipal waste a thermal coal fines to produce liquid fuels is shown in Figure 1.

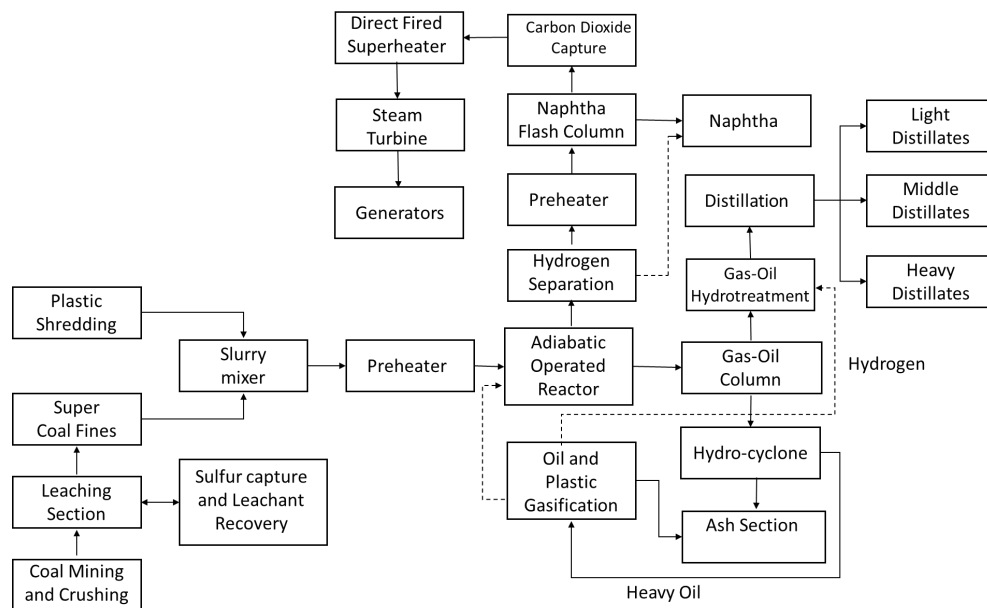


Figure 1. Process flow diagram for co-processing of coal and municipal plastics to get liquid fuels

The analysis for liquid fuels yield was based on the naphtha, middle distillates and heavy distillates yield.

5.3.1 Yield of naphtha

Naphtha is a flammable liquid hydrocarbon mixture formed from the co-processing of coal fines and municipal waste plastics. The yield of naphtha (C_6-C_{14}) ranged from 21.6-30.8 wt. % with a maximum being reached at 490 °C (see Figure 2).

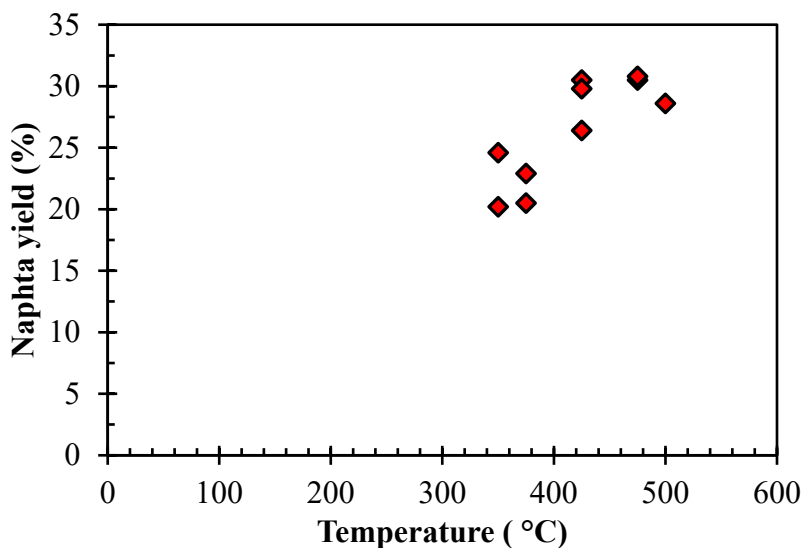


Figure 2. Yield of naphtha during co-processing of coal fines and municipal waste plastics

5.3.2 Yield of middle distillates

Middle distillates liquid fuels were obtained from the middle range boiling point of 180-360°C during the co-processing of coal fines and municipal waste plastics. Middle distillates are mainly comprised of diesel fuel, jet fuel and other light grade liquid fuels. Middle distillates have a carbon range of $C_{12}-C_{16}$. The yield

of middle distillates ranged from 33.8-44.6 wt.% (see Figure 3). The highest middle distillate yield of 44.6 wt.% was obtained at 350°C.

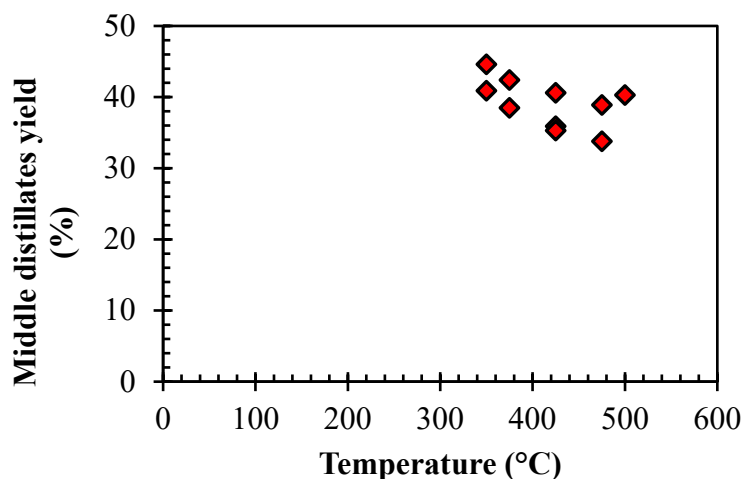


Figure 3. Yield of middle distillates during co-processing of coal fines and municipal waste plastics

5.3.3 Yield of heavy distillates

Heavy oil fuels are made up of tar like substances. The highest heavy oil fuel composition of 25.4 wt.% was obtained at 375 °C (see Figure 4) with a range ranging from 19.7-9 wt.% to 25.4 wt. %.

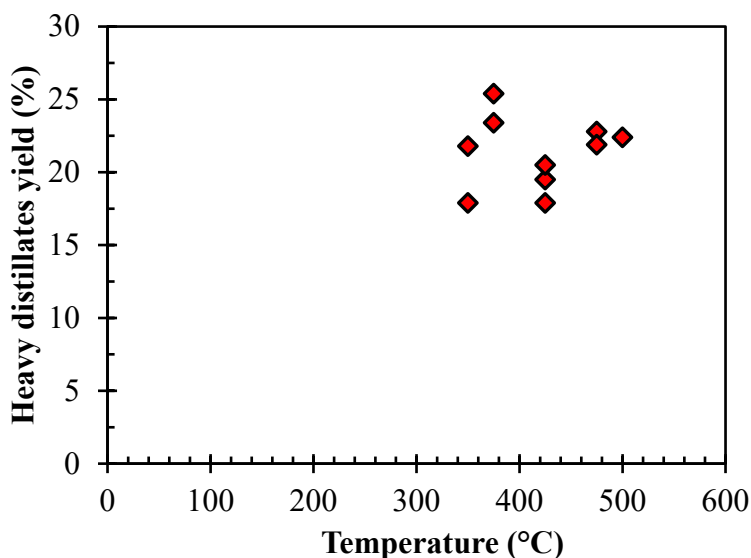


Figure 4. Yield of heavy distillates during co-processing of coal fines and municipal waste plastics

5.3.4 Total yield of oils

The yield increased with increase in temperature until it started to decrease at 400 °C (Figure 5). This applied to all the temperatures investigated with the exception of 350 °C whereby a lower space velocity resulted in a higher wt.% yield of oil. The data indicates that 475 °C gives the maximum amount of distillable liquids when operating at a LHSV of 0.70 h. (Figure 4). This condition also, results in the widest distribution of the product into the naphtha, middle, and heavy distillates.

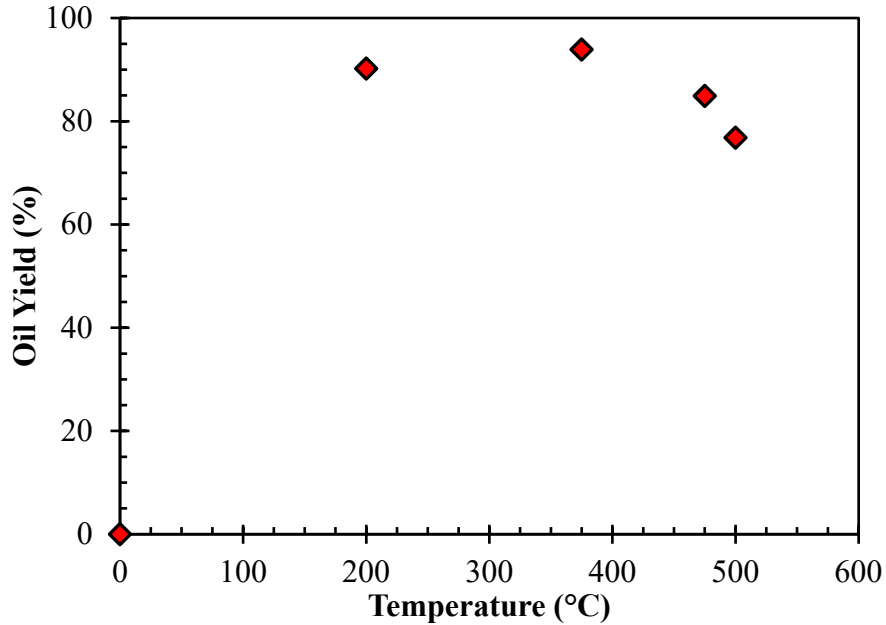


Figure 5. Average oil yield during co-processing of coal fines and waste plastics

The higher temperatures cause formation of greater amounts of coke which deposit in the pores of the catalyst causing a decrease in the pore volume thus deactivating the catalyst (Figure 6) (Jan et al., 2010; Panda et al.2010).

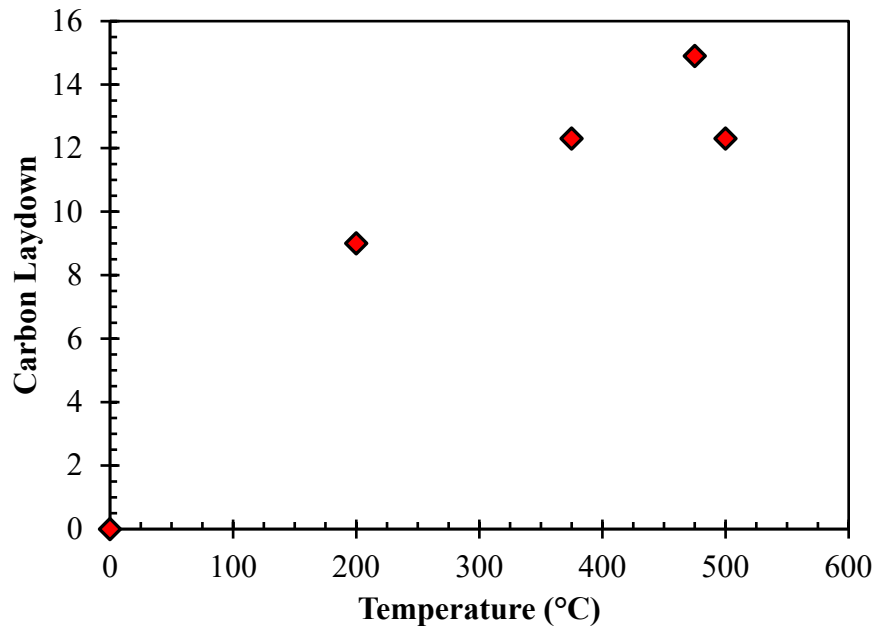


Figure 6. Carbon laydown against temperature at constant LHSV during co-processing of coal fines and municipal waste plastics

From this study, higher temperatures and lower space velocities increase the formation of coke and gases and thus decrease the overall wt.% yield of oil. Therefore, higher temperatures allow the use of higher space velocities such as 1.75 h⁻¹. The liquid hourly space velocity is calculated as represented in Equation 1. The liquid hourly space velocity is a method for relating the reactant liquid flow rate to the reactor volume at a standard temperature. The volumetric flow rate is treated as a liquid at these conditions, even though the actual material may be a gas under normal operating conditions (Jijiang et al. 2022). Lower space velocities cause the formation amounts of coke which deposit in the pores of the catalyst thus causing a decrease in the pore volume.

$$\text{Liquid hourly space velocity (LHSV)} = \frac{\text{Reactant Liquid Flow Rate}}{\text{Reactor Volume}} \dots\dots\dots (1)$$

A summary of the oils from the co-processing of waste coal fines and municipal waste plastics are shown in Table 4.

Table 4. Properties of oils from co-processing of coal fines and municipal waste plastic using red mud

Property	Naphtha	Middle distillates	Heavy distillates
Calorific value (MJ/kg)	34.4-36.5	44.6	45.4
Kinematic viscosity at 40 °C (mm ² /s)	6.0-6.2	3.5	3.2
Density at 40 °C (kg/L)	0.94-0.95	0.96-0.97	1.8-1.9
Water content (ppm)	144-147	146-148	152-155
Flash point (°C)	35-60	38-65	350-95
Boiling point (°C)	140-220	150-300	160-360

6. Conclusion

Coal fines and waste municipal plastics can be successfully co-processed to liquid fuels as a waste management strategy using red mud as a catalyst. From this study, it was evident that using red mud as a catalyst increases most of the properties of the fuel and also promotes environment sustainability in the form of less emission and fuel consumption. Since red mud is a hazardous waste material from the aluminum industry, utilizing it for liquid fuels productions is an economically viable option. The temperature of 475 °C gives higher space velocities of 1.75h⁻¹ which results in higher yields of 84.9%. This applied to all the temperatures investigated with the exception of 375 °C where a lower space velocity resulted in a higher wt.% yield of oil. The production of liquid oils from coal fines, waste municipal plastics and red mud is a good waste management initiative.

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