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Reusability of Hydroxyapatite-Ladle Furnace Slag Composite Catalyst in Co-Pyrolysis of Plastic Waste and Oil Palm Fiber

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ABSTRACT

Background and Objective: Ladle Furnace Slag is a major waste in the steel industry. This study aimed to evaluate the reusability of a Ladle Furnace Slag-Hydroxyapatite (HAP) composite catalyst for the co-pyrolysis of biomass waste and plastic to produce bio-oil. **Materials and Methods:** The HAP-LF catalyst was synthesized and tested for catalytic co-pyrolysis of oil palm fiber and plastic waste using a thermogravimetric analyzer and fixed-bed reactor. The sample was subjected to a temperature ramp from 30-800°C at a rate of 10°C/min, with mass changes monitored to analyze thermal decomposition behavior. To estimate activation energies, the thermograph was divided into three distinct temperature zones: 0-250°C (Zone 1), 250-450°C (Zone 2) and 450-800°C (Zone 3). The study also examined the product yields and composition of organic compounds in the pyrolytic oil across five catalyst reuses. Both TGA and fixed bed experiments were triplicated for reproducibility, with TGA using 0.05 significance in regression and fixed bed reporting average yield and composition. **Results:** Thermogravimetric analysis revealed that catalytic co-pyrolysis (CCP) with the HAP-LF catalyst achieved a maximum mass loss rate of 11.88%/min, exceeding 9.72%/min from thermal co-pyrolysis. The final residue mass was 15.8% with the catalyst, which was significantly higher than the 4.2% obtained from the thermal processes, indicating a synergistic effect on residue formation. Reusability tests in a fixed-bed reactor at 450°C showed that the catalyst promoted alcohol compound formation, with a maximum yield of 19.35 wt (%) after five consecutive uses compared to 11.07 wt (%) without the catalyst. **Conclusion:** Remarkably, the HAP-LF catalyst maintained strong performance for at least four cycles without regeneration, highlighting its potential for sustainable industrial applications.

KEYWORDS

Reusability, hydroxyapatite, ladle furnace slag, co-pyrolysis, bio-oil

INTRODUCTION

The steel industry produces substantial amounts of steel slag, which is a by-product with diverse and complex compositions. When discharged into the environment, this waste poses a significant threat to both ecological systems and human health. However, the valorization of steel slag, which is rich in metal oxides, is a promising solution. By converting this industrial waste into valuable products such as zeolite[1,2]

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or base materials, its environmental impact can be mitigated while harnessing its potential for beneficial use[3]. This approach not only addresses waste management challenges but also contributes to sustainable practices within the steel industry.

The elemental composition of this highly heterogeneous material reveals that its constituent elements are calcium, iron, silicon, magnesium, aluminum, manganese and phosphorus[4,5]. Other constituents usually present in low concentrations are titanium, potassium and sodium[6]. These metals possess catalytic ability because of their capacity to cause C-C and C-H bond scissions of organic materials[6] and to crack high molecular weight hydrocarbons into low molecular weight hydrocarbons. For this reason, some investigations have been conducted on the use of industrial slags in the pyrolysis of biomass and/or plastics.

According to Kholkina *et al.*[7] modification of the structure of industrial steel waste using chemicals and various synthesis routes for use as catalysts in chemical and thermal processes is necessary. In several catalyst developments using steel slag waste, the researchers used mechanical/thermal treatment[6,8], hydrothermal treatment[9-12], impregnation methods[13] and doping with active catalytic agents[7].

Hydroxyapatite [HAP, ($Ca_{10}(PO4)_6(OH)_2$)] has high thermal, chemical and mechanical stability, which qualifies it as a catalytic support material. In addition, it has low water solubility, tunable porosity and acid-basic/weakly alkaline characteristics[10]. Owing to its characteristic acidic and basic properties, it is useful as a catalyst for the synthesis of valuable compounds, such as 1-butanol and 1,3-butadiene from ethanol[14]. In addition, HAP allows a wide range of reactions, such as oxidation and reduction, chemical bonding of carbon with another carbon or with sulfur/oxygen/nitrogen, cycloadditions and multi-component reactions[15]. A deactivated HAP catalyst can be easily regenerated by calcination because of its large external surface area. Despite these interesting characteristics and advantages, the HAP support has not been exploited maximally in the pyrolysis or co-pyrolysis of plastic mixtures and biomass. The synthesis of an efficient and stable slag-HAP composite catalyst may result in the production of high-value-added chemicals and significantly reduce the cost of the CCP process.

The stability and reusability of a catalyst are of paramount importance in heterogeneous and industrial processes[16] because they indicate the economic sustainability of the process. Few catalyst reusability studies have been conducted in the fields of catalytic pyrolysis and co-pyrolysis[16-19]. Most studies on the reusability of catalysts have focused mainly on the pyrolysis of single feedstocks and binary feedstocks with catalysts synthesized from biomass or purchased from commercial chemical stores. Reusability studies involving the co-pyrolysis of multicomponent mixtures in the presence of HAP composite catalysts synthesized from industrial slag or mesoporous catalysts such as SBA-15 are missing from the literature. Thus, this work aimed to evaluate the reusability of the ladle furnace slag-HAP (HAP-LP) composite as a catalyst for the co-pyrolysis of a plastic mixture and oil palm fiber for the production of bio-oil.

MATERIALS AND METHODS

Study area: The study was conducted in the vicinity of Universiti Sains Malaysia, Engineering Campus, located in Nibong Tebal, Pinang, Malaysia. The oil palm fibre and ladle furnace slag used in this study were sourced from the United Oil Palm Mill near the university and from Ann Joo Steel Sdn. Bhd, located in the Prai Industrial Estate, Pinang, Malaysia. Before their use, the samples were sent to the Thermodynamic Laboratory at the School of Chemical Engineering for laboratory investigation. The study was carried out from April, 2021 to December, 2021.

Feedstock preparation: The feedstock for the catalytic co-pyrolysis reaction was prepared by mixing 0.3 g of oil palm frond (OPF) with 0.9 g of an equal-mass mixture of high-density polyethylene (HDPE) and Polypropylene (PP). A total of 1.2 g of the sample mixture was combined with 0.32 g of catalyst and used for pyrolysis experiments.

Catalyst synthesis: The Hydroxyapatite-Ladle Furnace Slag Composite Catalyst (HAP-LF) was synthesized[19]. A fixed mass (0.32 g) of this catalyst was used for both thermogravimetric analysis (TGA) and co-pyrolysis.

Thermogravimetric analysis: The sample mixture (1.2 g) and catalyst (0.32 g) were placed in the furnace of a thermogravimetric analyzer. The temperature was increased from 30-800°C at a heating rate of 10°C/min. Changes in sample mass over time were recorded and analyzed to study the thermal decomposition behavior.

Catalyst reusability study: The reusability of the HAP-LF catalyst was assessed in a fixed-bed reactor. Catalytic co-pyrolysis was conducted over five consecutive cycles without recovering or regenerating the catalyst between runs. For each cycle, 0.32 g of catalyst was placed in the reactor bed, separated from the feedstock by a layer of quartz wool to ensure no direct contact. The sample was heated to a maximum temperature of 450°C and pyrolytic oil and char were collected and weighed at the end of each run.

Product analysis: The composition of the pyrolytic oil was analyzed using Gas Chromatography-Mass-Mass Spectrometry (GC-MS) with a Perkin Elmer Clarus 600/600T system. An Elite-5MS capillary column (30 m×0.25 mm×0.25 μm) was used with helium as the carrier gas (1.0 mL/min). The injector and interface were set to 250 and 300°C, respectively. The oven temperature was programmed from 50°C (held for 2 min) to 280°C at 5°C/min, held for 20 min. A 1 μL sample was injected at a 2:1 split ratio. Mass spectrometry was performed at 70 eV over a 50-400 m/z range and compounds were identified using the NIST mass spectral library.

Statistical analysis: To ensure reproducibility, both the TGA test and the fixed-bed reaction experiment were conducted in triplicate. For the TGA test, regression analysis was used to estimate the activation energy based on the data collected, with a significance level of 0.05 applied to assess the statistical reliability of the results. Similarly, the fixed-bed reaction experiment was repeated three times and the average product yield and composition were calculated to ensure consistent and reliable outcomes.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the feedstock: The DTG curves (Fig. 1) illustrate that catalytic co-pyrolysis (CCP) achieved a maximum mass loss rate of 11.88%/min at approximately 466°C, surpassing the 9.72%/min observed during thermal co-pyrolysis. Both the thermal and catalytic processes exhibited a gradual increase in the mass loss rate as the temperature increased, indicating the effectiveness of the HAP-LF catalyst in enhancing thermal decomposition.

The TG curves in Fig. 2 demonstrate that the addition of the HAP-LF catalyst increased the degradation temperature, which significantly affected the mass of the final residue. The final residue mass for the HAP-LF-catalyzed co-pyrolysis was 15.8%, which was notably higher than the 4.2% obtained from the thermal processes.

This difference suggests a synergistic effect of the catalyst, potentially enhancing the polymerization, cracking and recondensation reactions of the volatile products, thereby increasing the residue mass. These findings align with previous kinetic analyses, such as the HZSM-5 catalyzed co-pyrolysis of cellulose, pine, sawdust and LDPE[20], reinforcing the role of the catalyst in improving the overall yields and residue formation.

The activation energies for the thermal and catalytic co-pyrolysis of the feedstock, analyzed in Fig. 2, are presented in Table 1. To estimate the activation energies, the thermograph (Fig. 2) was divided into three zones depicting three different temperature ranges. the temperature range, 0-250°C, 250-450°C and 450-800°C were assigned zone 1, 2 and 3, respectively.

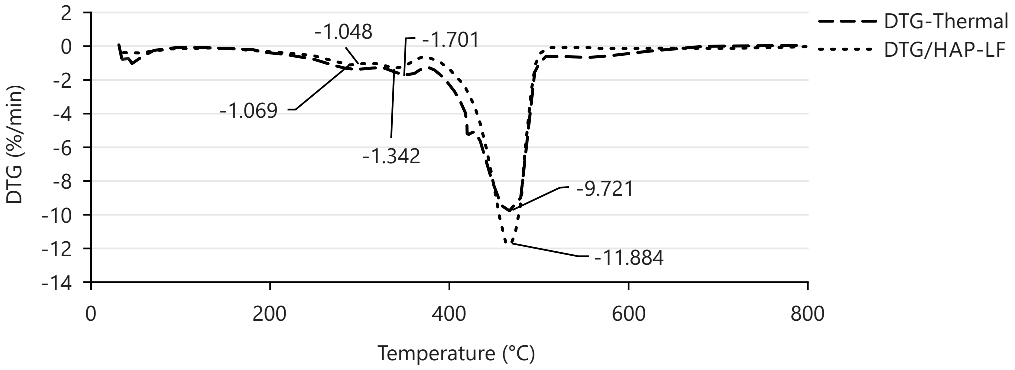

Fig. 1: DTG Thermograph of the HAP-LF co-pyrolysis

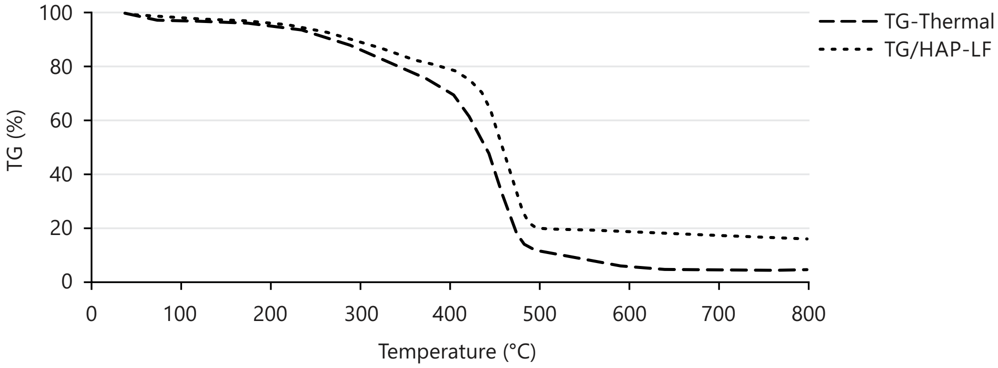

Fig. 2: TG Thermograph of the HAP-LF co-pyrolysis

Table 1: Comparison of activation energy for thermal and catalytic co-pyrolysis

Co-pyrolysis reaction	Zones	E (kJ/mol)	n	R
Thermal	1	13.98	0.9	0.955
	2	18.3	2.0	0.995
	3	92.11	1.2	0.977
Catalytic	1	21.58	2.0	0.998
	2	13.34	0.3	0.962
	3	59.33	0.4	0.933

n: Reaction order and R: Coefficient of determination

As seen in Table 1, the activation energy was reduced for the second and third zones of the catalytic co-pyrolysis, except for the first zone. The energy required to start the second and third reaction zones of the catalytic co-pyrolysis was reduced by 27.1 and 35.6% from 18.3 and 92.11 kJ/mol required for thermal co-pyrolysis. In the first zone, the activation energy of catalytic co-pyrolysis was 54.36% higher than that of thermal co-pyrolysis (13.98 kJ/mol). There are very few studies on the impact of catalysts on the activation energies of the different degradation zones of the catalytic co-pyrolysis reaction of a plastic mixture and biomass. However, it was found that the overall activation energy of HZSM-5 catalyzed co-pyrolysis of LDPE and cellulose was reduced by 33.49%[19], indicating that the catalyst reduces the amount of energy required to initiate a co-pyrolysis reaction.

Catalyst reusability performance: An experiment on the effect of the number of recycling cycles on the product yield was conducted in a fixed-bed reactor. Figure 3 presents the changes in the product yield as a function of catalyst reuse.

As seen in Fig. 3, the extended use of the catalyst did not result in increased yields of gas products but increased the production of oil. This may be because there were fewer acid sites available on the HAP-LF due to progressive coking that could promote the fracture of C-H bond, which in turn promotes H transfer

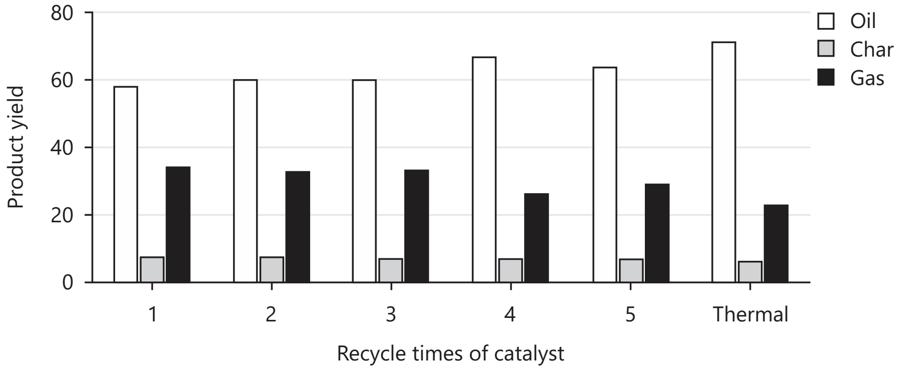

Fig. 3: Effect of recycle times of the catalyst on product yield

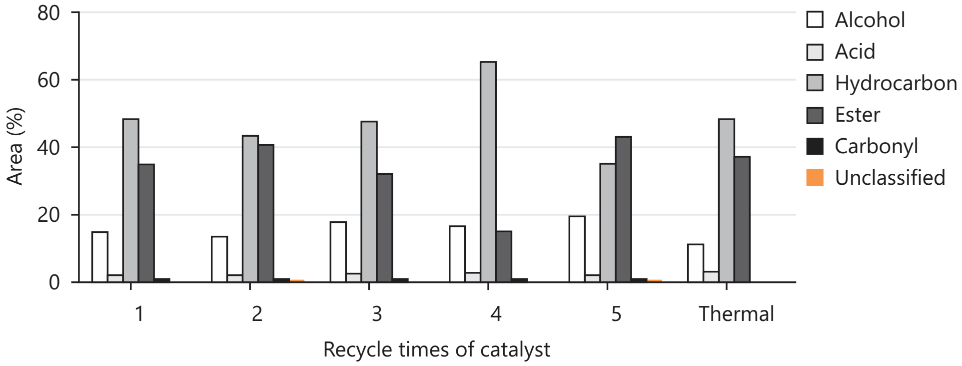

Fig. 4: Effect of recycle times of the catalyst on oil composition

to generate more free radicals. However, contradictory findings were observed in the catalytic pyrolysis of low-density polyethylene using a kaolin catalyst, which favored the production of liquid oil in the early stage of use[17]. The presence of carbon deposition after the use of the catalyst caused slight coking, which may have increased the acidity and particle size of the catalyst.

The Fig. 4 presents the changes in the composition of the organic compounds present in the pyrolytic oil as a function of catalyst reuse. The extended use of the catalyst (Fig. 4) resulted in an increased composition of alcohol.

The highest value of alcohol compound yield (19.35 wt (%)) recorded after the fifth catalyst re-use was higher than the value of 11.07 wt (%) obtained in thermal co-pyrolysis. A similar trend was observed for hydrocarbons after the fourth catalyst reuse. It is also noted that in the thermal co-pyrolysis, the carbonyl compounds were absent, but on the first use and re-use, the catalyst was deactivated, leading to the formation of trace quantities of the oxygenated compound. The number of oxygenated ester compounds increased after the second and fifth reuse. The product composition of the oil rapidly became more complex as the two types of oxygenated products began to form as the catalyst was deactivated. The catalysts did not completely alter the composition of the bio-oil, as most of the primary pyrolysis products were still present and some new compounds were formed. The most significant organic compounds of the primary co-pyrolysis products were cyclohexane, 1,2,3,5-tetraisopropyl- and 1-hentetracontanol, while others, including 1-hexadecanesulfonyl chloride, nonahexacontanoic acid, octadecyl chloride, 9-octadecenoic acid and oleic acid, are products of a less active catalyst. It is possible to observe a decrease in the composition of hydrocarbon compounds after the fifth cycle, which causes an increase in oxygenated ester and alcohol compounds. Figure 4 shows that in the fifth cycle, the catalytic activity of the material is lost. This result is significant because HAP-LF can be used without treatment for at least four consecutive cycles without regeneration. This is beneficial for industrial applications.

CONCLUSION

The HAP-LF catalyst demonstrated significant potential for reusability in the co-pyrolysis of plastic mixtures and oil palm fibers, contributing to sustainable bio-oil production. Synthesis and testing revealed that the catalyst not only enhanced the product yield but also improved the efficiency upon reuse. Notably, the energy requirements for initiating the subsequent reaction zones decreased by 27.1% and 35.6% for the second and third cycles, respectively, compared with traditional thermal co-pyrolysis. This reduction indicated that the HAP-LF catalyst retained its catalytic activity and effectiveness over five (5) uses, making it a promising candidate for industrial applications in biofuel production. These findings support the viability of utilizing waste materials to develop cost-effective and sustainable catalytic systems.

SIGNIFICANCE STATEMENT

Industries, particularly the steel sector, generate large amounts of waste, with ladle furnace slag being a significant byproduct. Rather than discarding this waste, researchers converted ladle furnace slag into a Ladle Furnace Slag-Hydroxyapatite (HAP) composite and used it as a catalyst for the co-pyrolysis of oil palm fiber and plastic waste to produce bio-oil. This study addresses the need for sustainable waste management by transforming industrial byproducts into valuable materials. The results show that the HAP-LF composite effectively catalyzes bio-oil production, maintaining good catalytic activity over four consecutive cycles. However, after the fifth cycle, the activity significantly decreases, indicating the need for regeneration. This is important because the composite can be used for at least four cycles without treatment, making it a cost-effective solution for industrial applications. This research offers an eco-friendly approach to waste management and bio-oil production, contributing to the circular economy and reducing environmental impact. The findings are valuable for industries seeking sustainable alternatives to manage waste and produce renewable energy.

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