The catalytic activity of Fe₃O₄ transition oxides from wire plating sludge waste for application on efficiency of coal combustion

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Abstract. The catalyst in the combustion process is a material additive. Catalyst is added to the fuel such as a subbitumin-type of coal which is having a caloric value of 4596.45 cal/g at a concentration of ± 0.1% w/w will increase energy of coal. The combustion catalyst are an alkali metal, an alkaline earth, and a transition metal as well as its oxide forms. In addition to having catalytic properties, metal oxide is also shown to have magnetite properties that will increase the catalytic activity such as Fe₃O₄. In this study, the Fe₃O₄ combustion catalyst was prepared from wire plating sludge (sludge) wastes having a high metal content and FeSO₄ dispersed into a vegetable oil, water, and surfactant mixture to form a catalyst suspension. The catalytic activity of the transition oxide is compared with the sludge catalytic activity and mixing the ratio of 1: 1. The result of catalytic activity test using differential thermal analyzer obtained coal combustion efficiency up to 91.00% due to the addition of sludge catalyst suspension at combustion process or an increase of 34.30% combustion efficiency compared without catalyst. In contrast, the addition of Fe₃O₄ catalyst only resulted in a combustion efficiency of 55.63%. The value of this combustion efficiency is lower 6.96% compared without catalyst. This is concluded that the catalytic activity of the Fe₃O₄ transition oxide tends to decrease the combustion efficiency of coal.

1. Introduction
Coal is one of the energy sources besides oil and gas. In Indonesia, the use of coal is increasing rapidly every year, especially as a power plant. In 2003, the use of coal accounted 14.1% of total energy use, and it is expected to continue increasing by 34.6% by 2025. Coal as fuel requires three basic elements, namely hydrogen, carbon, and oxygen. In coal combustion process, while producing energy it’s also produced three main forms of contamination, such as nitrogen oxide (NOx), sulfur oxide (SOx), and particulates. NOx and SOx emissions during combustion can cause acid rain and photochemical mists [1]. According to Zhou et al. environmental pollution of coal combustion can be reduced by adding alkali metals, alkaline earth, and transitions [2]. The addition of metal as a combustion catalyst will decrease the amount of contaminants such as NOx less than 10 ppm, but without addition of combustion catalyst, the amount of NOx produced can reach 25-30 ppm [3]. Transition metal oxide catalysts such as Co₃O₄, CuO, Fe₂O₃, NiO, LaCo₃, LaFeO₃, and LaNiO₃ can also increase catalytic activity by oxidizing CO to CO₂.

Wire plating sludge waste contains Fe, Ca, Cu, Al, and Mn with Fe content of 55.98%, which in acidic condition will form Fe³⁺ ions. When the waste is added to coal, the combustion efficiency of coal can reach 97-98%. Meanwhile, mixing Fe³⁺ and Fe²⁺ (2:1) ions in Fe₃O₄ formation reaction will
produce paramagnetic and catalytic properties[4]. Fe3O4 which is magnetite can be converted from iron sand [5]. In this study, Fe2O3 was synthesized from a mixture of wire plating sludge waste as a source of Fe3+ and FeSO4 and tested its catalytic activity on combustion energy efficiency of coal.

2. Materials and Methods

Materials used in the study are wire plating sludge waste PT Sumiden, Cibinong, Bogor, coal from Lahat (South Sumatra), vegetable oil, surfactant Berol 226, HNO3, HCl (technical), H2O2 50%, NaOH (technical), FeSO4, 95% ethanol, H2SO4 (technical), K2S2O8 (saturated), KSCN 3 N, and aquades.

2.1 Preparation of Fe3O4

The FeSO4 solid is 18.6352 g according to the 2: 1 mole ratio between Fe3+ (Fe2O3) in 1 L of waste wire plating sludge and Fe3+ in FeSO4. Then, that are mixed coprecipitation using 400 mL NaOH 5 M in a 70 °C Ultrasonic bath for 30 min. The Fe3O4 compound was separated from the filtrate using centrifuge at 3500 rpm for 5 min, then it was washed with 95% aquades and 95% ethanol up to pH 7. Particles were dried in oven at 45°C for 2 h.

2.2 Fabrication of catalyst

In to 80 mL of Vegetable oil was added surfactant Berol 226 of 8 mL, aquades of 12 mL, and a amount of Fe2O3-Fe3O4 (100: 0, 50:50, 0: 100)% of each total 3 g on different cup glass. The sample was stirred until dispersed, yielding successive catalysts (Fe2O3, Fe2O4, Fe3O4, and Fe3O4).

2.3 Determination of Catalytic Activity

The catalyst (Fe2O3, Fe2O4, Fe3O4, and Fe3O4) have been mixed with coal. The ratio of catalyst to coal is 1: 10000. This sample was homogenised respectively by using mortar for ± 1.5 h then weighed ± 25 mg into platinum crucible and tested using DTA with nitrogen gas. The temperature is increased gradually to 1000 °C in 50 minutes. Coal without catalyst is also measured using DTA.

3. Result and Discussion

Fe3O4 with mole ratios Fe3+ and Fe2+ 2: 1 respectively from the mixture of wire plating sludge and FeSO4 have been successfully synthesized. The mole ratio is required to form iron oxide into Fe3O4 phase (Ajay et al., 2002). The reaction is as follows:

FeSO4 + 2FeCl3 + 8NaOH → Fe3O4 + Na2SO4 + 6NaCl + 4H2O

In this study, the formation of Fe3O4 occurred at pH 12 because Fe3O4 was formed between pH 8 and 14 without any oxidation effect from the environment. In the case of oxidation, maghemite (γ-Fe2O3), which has the same magnetic properties with Fe3O4 has a Fe2+ void in its structure [6]. The reaction of Fe3O4 formation is accelerated by ultrasonic stirring, and heating at 70 °C, there is a process of water release or dehydration in iron hydroxide[7]. According to Roonasi et al, iron oxide in the solution system act as Lewis acid to water or hydroxyl groups [8]. This hydroxyl group revealed hydrogen bonding with one or more Fe atoms. The sludge that has formed Fe3O4 exhibits magnetic properties due to antiparallel-lined spin arrangement, but the magnetic moment magnitude in different directions is not the same resulting in the resultant magnetic moment. The moment of the magnetite Fe ions occupying the octahedral (sub lattice A) and tetrahedral (sub lattice B) in each lattice will be paired together (Figure 1). Each sub lattice B has one Fe2+ and Fe3+ ions paired with A sub condition occupied by an Fe5+ ion [9].
X-ray diffraction of Fe$_3$O$_4$ showed a degree of crystallinity of 62.25%. The result was compared with JCPDS for Fe$_3$O$_4$ No. 19-0629, to have a cubic crystal structure based on the highest peak of 2θ = 35.47°, and other peaks at 2θ angles corresponding to the Miller Fe$_3$O$_4$ index (Figure 2).

In addition, FTIR spectrum data shows the absorption of Fe-O bond at wave number 572.86 nm. According to Lakay, the wave number 474-636 cm$^{-1}$ shows vibration of Fe-O in the tetrahedral part of Fe$_3$O$_4$ [9], whereas the wave number <400 cm$^{-1}$ is derived from the vibration of Fe-O in the octahedral part (Figure 3).
Based on the DTA curve in Figure 4, coal combustion activity with Fe₃O₄ revealed removal of H₂O at 4-6 min at 116.20 °C. The devolatilization process for tar formation and the release of CH₄ and CO₂ gases starts at 20-22 minutes at about 170°C and ends at 467.45°C.

![Figure 4 DTA Curve Coal combustion with catalyst of Fe3O4.](image)

Coal particles interact with iron oxide through a reduction process. This process is very slow due to lack of direct contact between the particles. Therefore, the actual reduction process occurs between carbon monoxide (CO) and iron oxide solids (Baliarsingh and Mishra 2008). The results of Tristao et al. indicates that methane (CH₄) at 600 °C will occurred carbon gasification to CO which acts as iron oxide redactor [10]. The energy value of this gasification reaction activation is high because of its endothermic run.

The rate of carbon gasification is influenced by the mass transfer rate of the oxide gas (CO₂ and O₂) to oxidize carbon. The higher the temperature, the higher the rate of diffusion and convection of the oxide gas so that the rate of carbon gasification also increases. Figure 5 shows the addition of Fe₂O₃ catalyst improves the energy efficiency of combustion because in the presence of CO around the temperature of 700 - 900 °C, Fe₂O₃ will be reduced in 2 phases to form FeO and CO₂. The use of Fe₂O₃ and CeO₂ catalysts in coal combustion can increase combustion activity by accelerating the combustion of bound carbon.
However, the value of combustion efficiency calculated on the basis of weight loss shows a decrease with the addition of Fe$_3$O$_4$ catalyst compared to Fe$_2$O$_3$. This is due to the direct combustion process through stage 2. In addition, according to Zhang et al., the use of Fe$_3$O$_4$ reacted with H$_2$ / N$_2$ gas on 300°C will form Fe$_3$O$_{4\cdot\vartheta}$ which is oxygen deprived and there is an electron excitation between Fe$^{2+}$ and Fe$^{3+}$ in Fe$_3$O$_{4\cdot\vartheta}$ adsorbed CO$_2$ structure by Fe$_3$O$_{4\cdot\vartheta}$ facilitates the electron from Fe$_3$O$_{4\cdot\vartheta}$ transferred to the C atom of CO$_2$ [11]. Oxygen from CO$_2$ will be in the form of O$^2-$ and transferred into an empty Fe$_3$O$_{4\cdot\vartheta}$ lattice and it produces C (stage 3). This process can increase the weight loss on the use of Fe$_3$O$_4$ catalysts when compared to burning coal without catalyst.

**4. Conclusion**

Catalyst of Fe$_3$O$_4$ has been succeed synthesis from wire sludge. The result of catalytic activity test using Differential Thermal Analysis was obtained coal combustion efficiency up to 91.00% due to the addition of sludge catalyst suspension at combustion process or an increase of 34.30% combustion efficiency compared without catalyst. In contrast, the addition of Fe$_3$O$_4$ catalyst only resulted in a combustion efficiency of 55.63%. The value of this combustion efficiency is lower 6.96% compared without catalyst. This is concluded that the catalytic activity of the Fe$_3$O$_4$ transition oxide tends to decrease the combustion efficiency of coal.

**REFERENCES**

[1] Guan R, Li W, Chen H, Li B 2003 Fuel Process Technol. 85 1025-1037
[2] Zhou B, Wu Z, Fransson M 2010 Headwaters Technology Innovation LLC Crystalline nanocatalyst combustion properties of fuel and fuel compositions incorporating such catalysts US Patent 7 758 660 B2
[3] Ovez ON 2007 The removal of carbon monoxide by iron oxide nanoparticle in car exhaust [Thesis] Turki (TK) Dokuz Eylul University
[4] Akasaki I, Sota S, Sakai H, Tanaka T, Koike M and Amano H 1996 Electron Lett 32 1105
[5] Wu S, Sun A, Zhai F, Wang J, Xu W, Zhang Q, Volinsky A 2011 \textit{J Mat Lat} \textbf{65} 1882-1884
[6] Laurent S, Forge D, Port M, Roch A, Robic C, Elst LV, Muller RN 2008 \textit{Chem Rev} \textbf{108} 2064-2110
[7] Grabis J, Heidemane G, Rasmame D 2008 \textit{Mater Sci} \textbf{14}(4) 292-295
[8] Roonasi P 2007 Adsorption and surface reaction properties of synthesized magnetite nanoparticles [Thesis] Sweden (SE) Lulea University of Technology
[9] Lakay EM 2009 Superparamagnetic iron-oxide based nanoparticles for the separation and recovery of precious metals from solution [Thesis] Matieland (ZA) University of Stellenbosch
[10] Tristao JC, Oliveira AS, Ardisson JD, Dias A, Lago RM 2011 \textit{J Mat Res Bull} \textbf{46} 748-754
[11] Zhang CL, Li S, Wang LJ, Wu TH, Peng SY 1999 \textit{J Chem Phys} \textbf{62} 52-61
[12] Ishizaki K, Nagata K, Hayashi T 2007 \textit{ISI J Int} \textbf{47}(6) 817-822