

THE TRANSFORMATION OF AUTOMOTIVE INDUSTRIAL WASTE TO USEFUL IRON COMPOUNDS

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Abstract

Automobiles are an important factor for the performance of everyday activities, facilitating human transportation. As a result, Thailand's automotive industry is growing rapidly to meet the demand for automobiles, resulting in a high production rate. The disadvantage of large-scale production is an increase in automotive industrial waste in large amounts of 50-60 tons per year. Landfill is used as a traditional form of industrial waste management with an exchange rate of 1,800 baht per ton. In this work, the automotive industrial waste (Thailand source) was studied and used as a precursor to prepare a new chemical compound. The X-ray diffraction (XRD) analysis of the automotive industrial waste used in the study as first priority pointed to a rich source of Fe-iron and Fe₂O₃. The contaminated matter in waste is washed with water and removed by using a magnet. Hydrochloric acid (HCl) and nitric acid (HNO₃) react with the automotive industrial waste to form a new chemical compound of iron. For HCl acid, the phases of Fe-iron and Fe₂O₃ change their composition to form a new composition of FeCl₂·4(H₂O). FeCl₂·4(H₂O) shows high solubility in water with the value of 0.1 g/L at room temperature. For HNO₃ acid, the phase of Fe-iron changes the composition to form a new phase of Fe₂O₃ which is insoluble in water. From the results, the new products (FeCl₂·4(H₂O) and Fe₂O₃) of automotive industrial waste can be utilized as a flocculant in wastewater treatment, a starting material for magnetic ceramics, coatings for drug delivery for anti-cancer drugs, and so on. The results suggested that the reworked automotive waste served to reduce waste and the environmental impact, and to add value to automotive waste from the automotive parts industry.

Keywords: Sustainable waste management, iron, automotive industry, solubility, alternative chemical compound

Introduction

Metal materials are the basic raw materials for other industries (Miller *et al.*, 2000) such as the construction industry, electrical appliance industry, electronics industry, household appliance industry and automotive industry, among others. The automotive industry is one of the world's most important industries and is increasingly important as the world's demand for energy is increasing in terms

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of the economy, employment, and automotive technology development (Orsato and Wells, 2007; Liu and Chen, 2014; Manojit *et al.*, 2019). The main component materials in automobiles are iron and steel, accounting for more than 70% of the total automobile weight (Pomykala *et al.*, 2007). In Thailand, the automobile industry is one of the world's larger automobile parts manufacturing industries and assembly bases. The automobile is an important factor for everyday activities in facilitating human transportation (Preeti *et al.*, 2016), and consumer demand for automobiles has increased. As a result, Thailand's automotive industry is growing rapidly with a high production rate. The high production rate leads to an increase in the level of automotive industrial waste (PRNewswire, 2015) caused as automotive parts are manufactured by metal casting for use as engine components such as bolts and screws, etc. These parts are cut, ground, and polished to meet the specified production standards. This production causes automotive industry waste in large amounts of 50-60 tons per year per small company. Landfill is used as an alternative to automotive industrial waste management with waste disposal costs of 1,800 baht per ton. The consequences of automotive industrial waste in landfills is that chemical reactions in corrosion can occur, leading to toxins contaminating the air, rivers, and soil and posing a danger to human health, animals, and the environment (Geoffrey, 2003).

Nowadays, the automotive industry solves the problem of waste disposal from production lines by incineration, landfill, and the recovery and recycling of iron and aluminum waste. Waste recasting of the automotive industry comprises automotive parts, construction materials, and starting material for the synthesis of new products. Various studies have investigated the recycling of waste from the automobile industry such as Jirang and Hans. That work reported on the recycling of aluminum from the automotive industry by separating the aluminum alloy using laser-induced breakdown spectroscopy and solid-state recycling in aluminum scrap (Jirang and Hans, 2010). This is better than conventional remelting and can result in energy savings and a higher yield of metal. Saeed *et al.* studied the recycling of niobium from the automotive industry to reduce the mining costs for niobium and to reduce the CO₂ gas which is generated as greenhouse gas (GHG) emissions (Saeed *et al.*, 2019). Helmut and Gerhard studied the recycling and refining of magnesium scrap by melting processes, occurring under inhibitive gas or flux to control the factors of annealing temperature leading to the purification of magnesium (Helmut and Gerhard, 2002). However, there are few research studies that examined the

recycling of automotive industrial waste. So, the most important aspect of the recycling of automotive industrial waste is the reduction of traditional waste management problems from the landfill technique and the incineration which causes pollution of the environment.

In this work, to solve this problem, we study the recycling of automotive industrial waste that is generated by the grinding process. The automobile waste was first washed by using water to obtain a high purity of waste, before use as a next step precursor. Before use the structural phase and chemical composition of the automobile waste could be identified by XRD and XRF. Then, the washed waste was mixed and reacted with acids (HCl and HNO₃) and bases (NaOH) to change the chemical composition of the waste, to form a new chemical composition of Fe-waste. Finally, the structural phase, particle size distribution, microstructure, and solubility in water were analysed by XRD, Laser-PSD, SEM and dissolution of powder in water, respectively.

Materials and Methods

Waste Preparation

The Fe-waste from Thailand's automobile industry (Rayong province) is generated by a grinding process. The ground waste was contaminated with some auto parts, dust, cutting fluid, and solid grinding stone. The waste powder was dried in the oven at 100°C for 24 h to remove water and the cutting fluid which is a physical liquid derived from the grinding process. The dried waste powder was sieved through 325 mesh (45 microns) to eliminate some contamination from auto parts. After that, the structural phase and chemical composition of the Fe-waste were analysed by X-ray diffraction (XRD) using Bruker D2 Advance with the analytical 2-theta range of 10°-80° (Step size = 0.02°/step; step time = 0.5 sec/step) and X-ray fluorescence (XRF). After confirming a structural phase of the Fe-waste, The Fe waste powder was washed by using the water to remove oil and the magnetic was used to separate a contaminant from the grinding process. After that, the Fe-waste slurry was dried in the oven at 100°C for 24 h to create a dark brown powder. The Fe-waste powder was crushed and sieved through a 325 mesh again before use as a precursor for synthesis of a new Fe-structure.

Synthesis of the Fe-Structure from Automotive Industrial Waste

After removing the contaminated matter from the automotive industrial waste, the dried waste precursor was used as a starting raw material.

In should be noted that acids and bases are highly reactive chemicals with reactive metals such as Fe-waste powder. Therefore, hydrochloric acid 36% (HCl, Ajax Finechem), nitric acid 70% (HNO₃, Ajax Finechem) and sodium hydroxide 99% (NaOH, QR&C) were candidates as a reactive chemical to combine with Fe-waste precursor in a chemical reaction to form a new Fe-structure. The stoichiometry of the waste powder and reactive chemical was calculated and a weighted balance was achieved before mixing in water. The mix solution was soaked in a glass container for 20 min to form a complete chemical reaction. During the chemical reaction, there was a lot of foam on the surface and inside of the mixture, indicating the decomposition of the gas state. After the chemical reaction was complete, the mixture was dried at 80°C for 24 h to remove the remaining water and gas. Then the dried powder was crushed and sieved through 325 mesh (45 microns) before characterization and property testing. The flowchart explaining the experiment is presented in Figure 1.

Characterization and Property Test

The structural phase of the new Fe-chemical composition from automotive waste was identified by X-ray diffraction (XRD, Bruker D2 PHASER) with the analytical 2-theta range of 10°-80°, using a step time of 0.5 sec/step and step size of 0.02°/step. In addition, a Topas-based software computer was used for quantitative analysis.

Particle size distribution (PSD, Horiba LA-950V2) was used to determine and characterize the new Fe-chemical composition, and then the microstructure of the new Fe-chemical composition was observed via scanning electron microscope (SEM, JEOL Neoscope JCM-5000). Finally, the solubility in water of the new Fe-chemical composition was measured by using the dissolution of the new Fe-chemical composition in water at room temperature.

Results and Discussion

Characterizations of Dried Waste Powder from Automobile Industry

The chemical composition of waste powder from the automobile industry was analyzed by ED-XRF as shown in Table 1. The oxides in Fe-waste powder can be categorized into the rich source of iron (III) oxide (Fe₂O₃, 97.14wt%) and other additive oxides (2.86 wt%) such as chromium (III) oxide (Cr₂O₃), aluminum oxide (Al₂O₃), nickel (II) oxide (NiO) and copper (II) oxide (CuO). From the result, iron oxide is a key raw material for manufacturing a wide range of steel products, but

using only iron in the production of steel often has disadvantages such a high stiffness and high corrosion with humidity and water. To improve the properties of Fe-steel, the other additive oxides were added in the manufacturing process, such as chromium (Cr), aluminum (Al), nickel (Ni), and copper (Cu). There are various advantages to adding dopants into a steel. Cr metal is used for increasing the resistance to oxidation, and the resistance increases with an increasing amount of Cr. Al additive matter is used as a deoxidizer and denitrizer in steel production. Ni metal is added and mired with Cr to form the most important class of corrosion and heat resisting steel. Finally, Cu is added to enhance the corrosion resistance in sea water and sulphuric acid environments. That is the reason why analysis results of Fe- waste powder from the automobile industry have the iron oxide value of less than 100wt%.

The XRD pattern of the dried Fe-waste powder is shown in Figure. 2. The Fe metal structure was observed in the analytical XRD pattern, consisting of 2 crystal structures of body center cubic structure (Lattice parameter, a = 2.86 Å) as JCPDS No. 01-1252 with Im-3m space-group symmetry at 2-theta of 44.142° and body center cubic structure (Lattice parameter, a = 2.85 Å) as JCPDS No. 03-1050 at 2-theta of 44.833°.

Characterizations of the New Fe-chemical Composition from the Automobile Industry

The analytical XRD patterns of the new Fe-chemical compositions are shown in Figure 3. The new Fe product from the reaction of Fe-waste

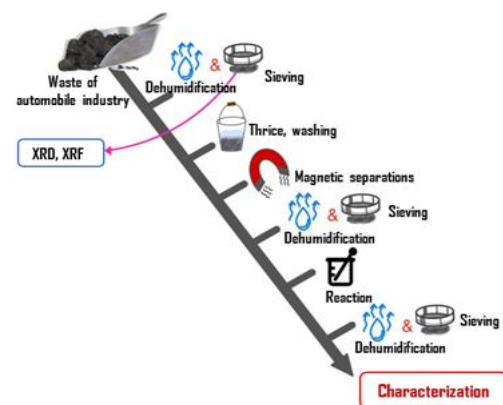


Figure 1. The experimental process in this work

Table 1. The chemical composition of Fe-waste (mass fraction, %)

Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃	NiO	CuO
97.14	1.45	1.01	0.24	0.16

powder and HCl acid is presented in (Figure. 3(a)). Iron chloride hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) with monoclinic structure as JCPDS No. 71-0668 and iron oxide chloride hydroxide (FeOOHCl) with monoclinic structure as JCPDS No. 42-1315 are identified as the major components in the XRD pattern. The Topas-based computer program was used to analyse the amount of structural phase. In that result, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with the value of 59.73% was higher than FeOOHCl (40.27%). The chemical reaction of Fe-waste and HCl was explained in Equations (1) and (2) as follows:

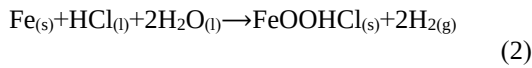
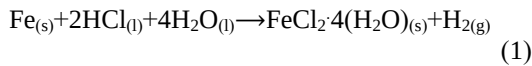
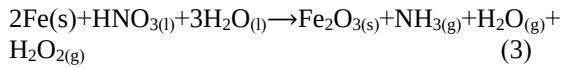
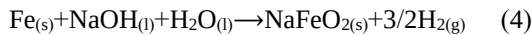


Figure 3(b) is the new Fe_2O_3 structure that resulted from the chemical reaction between Fe-waste powder with HNO_3 . The maghemite with the chemical formula of Fe_2O_3 is presented in the XRD pattern, indicating the complete chemical formula of Fe-waste powder and HNO_3 reactive acid. The occurring Fe_2O_3 phase is a cubic structure as JCPDS No. 39-1346 with lattice parameter, $a = 8.35 \text{ \AA}$. The Topas program also confirms that the Fe_2O_3 phase is 100%. The chemical reaction between Fe-waste powder and HNO_3 was predicted and defined in Equation (3) as follows:



The result of XRD from the chemical reaction between Fe-waste powder and NaOH is shown in (Figure 3(c)). Sodium iron oxide (NaFeO_2) is identified as the major component with an orthorhombic structure as JCPDS No. 82-1495. The Topas-based program was used to confirm the complete chemical reaction between Fe-waste powder and NaOH with 100% of the NaFeO_2 phase. And then finally, the chemical reaction of Fe-waste powder and NaOH was presented in Equation (4) as follows:



The particle size distribution of the new Fe-waste powder is shown in (Figure 4). The cumulative mass percent larger (CMPL) and cumulative mass percent finer (CMPF) curves intersect at D50, indicating that the average particle size of the new Fe-chemical composition is 6.09 microns. In addition, a size variation from 1.43 microns (D10) to 13.51 microns (D90) and

distribution range (D90-D10) is 12.08 microns. The histogram confirmed the agglomeration of Fe-particles. The curve is shifted to the left-hand side, indicating that the most of synthesized Fe-particles tend to be larger than the average sized Fe-particle.

The microstructure of new Fe-chemical compositions was measured using SEM at 15kV

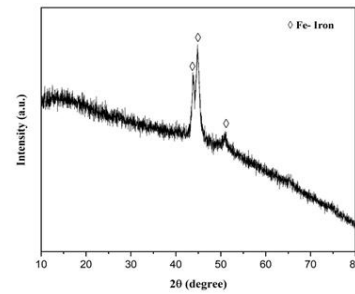


Figure 2. The XRD pattern of dried Fe-waste powder

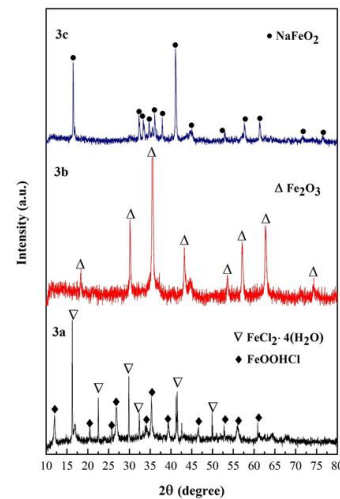


Figure 3. The XRD pattern of new Fe- chemical compositions: (a) Fe-waste reacted with HCl, (b) Fe-waste reacted with HNO_3 and (c) Fe-waste reacted with NaOH

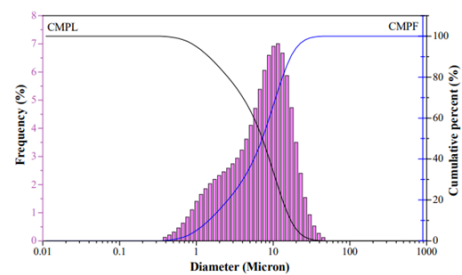
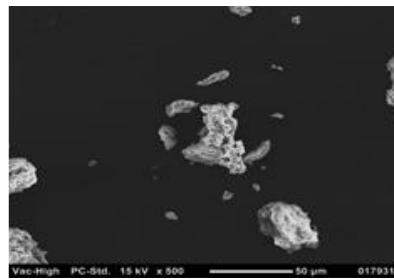


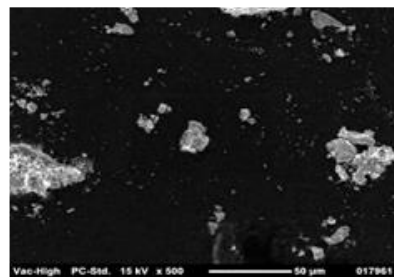
Figure 4. Particle size distribution of the Fe-waste reacted with HNO_3

Table 2. Solubility in water of the new Fe-chemical composition

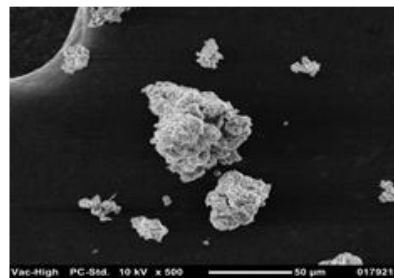
Product	Amount of powder (g)	Amount of water (L)	Solubility in water (g/L)
Fe-iron	0.1	Insoluble	Insoluble
FeOOHCl and FeCl ₂ ·4(H ₂ O) (Fe reacted with HCl)	0.1	1	0.10
Fe ₂ O ₃ (Fe reacted with HNO ₃)	0.1	Insoluble	Insoluble
NaFeO ₂ (Fe reacted with NaOH)	0.1	Insoluble	Insoluble



(a)



(b)



(c)

Figure 5. Scanning electron microscopy images of the new Fe-chemical compositions: (a) Fe-waste reacted with HCl, (b) Fe-waste reacted with HNO₃ and (c) Fe-waste reacted with NaOH

with resolution of 500x as displayed in (Figure 5). The different micrograph images of all powders after reaction with acids and bases are non-significant as found in (Figures 5(a), 5(b), and 5(c)). The distribution of the new Fe-chemical composition was shown in the form of a wide distribution, consisting of small sized to large sized particles. However, the SEM micrographs were

observed to show small particle agglomeration into larger particles.

Solubility of new Fe-chemical compositions was measured by using the dissolution of Fe powder in water at room temperature (30°C) as shown in (Table 2). The Fe-waste powder was shown to be practically insoluble in water, similar to Fe₂O₃ (Fe reacted with HNO₃) and NaFeO₂ (Fe reacted with NaOH). In addition, FeOOHCl and FeCl₂·4(H₂O) (Fe reacted with HCl) is slightly soluble in water at room temperature with the value of 0.10 g/L. However, the solubility in water can also be explained by the intermolecular attraction. If the solute is an ionic compound, it has a very high attraction between ions and dissolves better in a strong solvent than in a less polar solvent. Therefore, ionic compounds are highly soluble in very strong solvents.

Conclusions

The study of the recycling of automotive industry waste to produce a new Fe-chemical composition, can be summarized as:

1. The automotive industry waste is Fe-metal with a high quantitative percentage of 97.14%.
2. The new Fe- products from the chemical reaction between Fe-waste powder with HCl acid, HNO₃, and NaOH are FeCl₂·4(H₂O), FeOOHCl, Fe₂O₃, and NaFeO₂, respectively.

3. The average particle size of the new Fe-chemical composition is 6.09 microns, indicating the high chemical reaction rate to act with surroundings because of the small size of particles.

Thus, the results suggested that the reworked study of automotive waste completely reduces waste and environmental impact, and adds value to automotive waste from the automotive parts industry.

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Reference

- Geoffrey, H. (2003). Solid waste treatment and disposal: effects on public health and environmental safety. *Biotechnology Advances.*, 22(1-2):71-79.
- Helmut, A. and Gerhard, H. (2002). Recycling of different types of magnesium scrap. TMS (The Minerals, Metals & Materials Society). Available from: https://www.researchgate.net/publication/266499198_Recycling_of_different_types_of_magnesium_scrap. Accessed date: Jan, 2015.
- Jirang, C. and Hans, J.R. (2010). Recycling of automotive aluminum. *Trans. Nonferrous Met.*, 20(11):2,057-2,063.
- Liu, Y., Liu, Y., and Chen, J. (2014). The impact of the chinese automotive industry: scenarios based on the national environmental goals. *J. Clean. Product.*, 96:102-109.
- Manojit, G., Arkajit, G., and Avinava, R. (2019). Renewable and sustainable materials in automotive industry. *Encyc. Renew. Sustain. Mat.*, doi: 10.1016/b978-0-12-803581-8.11461-4.
- Miller, W.S., Zhuang, L., Bottema, J., Wittebrood, A.J., Smet, P.D., Haszler, A., and Vieregge, A. (2000). Recent development in aluminium alloys for the automotive industry. *Mat. Sci. Eng.*, A280:37-49.
- Orsato, R.J. and Wells, P. (2007). The automobile industry & sustainability. *J. Clean. Product.*, 15(11-12):989-993.
- Pomykala, J.A., Jr., Jody, B.J., Daniels, E.J., and Spangenberg, J.S. (2007). Automotive recycling in the united states: energy conservation and environmental benefits. *JOM.*, November:41-45.
- Preeti, S., Aksha, S., Ajay, S., and Preeti, S. (2016). Automobile waste and its management. *Chem. Environ. Sci.*, 4(2):01-07.
- PRNewswire. (2015). Waste Management in the Automotive Industry 2015-2019. Available from: <http://www.prnewswire.com/news-releases/waste-management-in-the-automotive-industry-2015-2019-300173788.html>. Accessed date: Nov 15, 2015.
- Saeed, R.G., Nikita, K., Mohammad, E.W., and Andrzej, K. (2019). Environmental sustainability of niobium recycling: the case of the automotive industry. *Recycling*, 4(1):1-23.