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# Prospective Application of Flue Gas Washing Liquid from the Wet Scrubber Unit at Masaro Plastic Refinery for Pesticides

**Elsye Veradika Y. & Akhmad Zainal Abidin***

Department of Chemical Engineering, Institut Teknologi Bandung, Jalan Ganesa 10, Bandung, 40132, Indonesia
*Email: zainal@che.itb.ac.id

**Abstract.** The plastic refinery represents an advanced technology designed to effectively manage residual waste. This innovative approach integrates the principles of incineration and pyrolysis to yield valuable products, including fuel and flue gas washing liquid obtained from a wet scrubber unit as wastewater. The flue gas washing liquid contains various compounds, such as ammonia, which did not meet the quality standards stipulated by the Ministry of Environment. Furthermore, it also encompasses phenolic compounds, nitrates, and nitrites. These chemical constituents impede the direct discharge into the environment due to their inherent toxicity towards aquatic organisms. However, within the agricultural domain, ammonia, phenol, nitrate, and nitrite are extensively employed as pivotal ingredients, serving as valuable sources of nitrogen in the production of fertilizers and pesticide raw materials. This research endeavors to conduct a comprehensive analysis of the composition of the flue gas washing liquid. The primary objective is to evaluate the potential utilization of its components as principal ingredients in pesticide formulations. To augment the effectiveness of the pesticides, supplementary active ingredients are incorporated, derived from various plant species recognized for their efficacy in combatting plant pests and insects. The extraction process involves combining the flue gas washing liquid with selected plants, such as bintaro fruit, garlic, citronella, neem leaves, and tobacco. This approach not only addresses the issue of environmentally friendly disposal of liquid waste but also provides a sustainable solution to meet the agricultural sector's demand for efficient pesticides.

**Keywords:** *plastic refinery; flue gas washing liquid; pesticides; extraction; active ingredients; agriculture.*

## 1 Introduction

The Masaro Plastic Refinery, an integrated unit of the Masaro waste treatment system, represents a technological that addresses the management of non-decomposable and non-recyclable waste. This plastic refinery facility comprises an integrated unit combining an incinerator for waste combustion and a pyrolysator designed specifically for the pyrolysis process of plastic waste. Furthermore, the plastic refinery unit incorporates a flue gas processing system, encompassing a wet scrubber, which effectively eliminates solid residues and other impurities from the combustion flue gas before its release into the environment through a chimney[1].

The incinerator unit at the Masaro plastic refinery serves as a crucial mechanism for combustion of non-decomposed and non-recyclable waste, characterized as residue waste. Operating at elevated temperatures ranging between 600 to 7000°C, this process generates hot exhaust gases infused with a diverse array of pollutants resulting from combustion, notably including particulate matter[2]. The flue gas generated through the combustion of waste materials can be categorized into four distinct classes: trace hazardous organics, trace heavy metals, acid gases, and particulate matter[3]. To ensure compliance with environmental regulations and facilitate the release of clean air into the atmosphere, wet scrubber used in Masaro Plastic Refinery Unit for flue gas purification, employing water as the designated scrubbing fluid. During this process, Consequently, the water droplets dissolve both minute particles present in the flue gas and soluble gases The effluent derived from the wet scrubber, serving as the flue gas washing liquid[4], necessitates treatment before direct disposal into the environment, as it contains dissolved compounds or particles that doesn’t comply with the liquid waste disposal standards outlined by the Indonesian Ministry of Environment and Forestry regulations.

In modern agriculture, pesticides have become very important to maintain both the quality of production and the quality of agricultural soil. Pesticides are used to kill pests, including insects, rodents, fungi, and unwanted plants (weeds). As an agricultural country, Indonesia where agriculture and food are the main and leading sectors that need to be improved considering that food security must be achieved, one of which is the effective application of fertilizers and pesticides for agriculture[5].

Historically, the use of fertilizers and pesticides in Indonesia has been carried out massively since the 1960s with most of them being inorganic fertilizers and pesticides. Since the launch of the "Green Revolution" program in the late 60's, the use of chemical fertilizers has increased dramatically due to the government's push to increase agricultural productivity which has resulted in decades of farmers using excessive chemical and inorganic fertilizers and pesticides on agricultural land resulting in decreased degradation. or the quality of agricultural soil, which becomes more acidic[6]. The magnitude of the negative impact of the use of chemical feedstock has led to an incessant call for the use of organic materials, including for pesticides. The development of organic pesticides derived from plants has great potential for natural pest control, where currently, more than 2400 plant species exhibit properties as pesticides, especially with the main target of insects[7]. Plant secondary metabolites have a broad spectrum of activity against pests and insects, causing the active ingredients in plants to be effective as pesticides, as well as increasing the potential for using plants as a source of active ingredients.

Consequently, this study aims to conduct a comprehensive analysis of the composition of the flue gas washing liquid derived from the wet scrubber unit at the Masaro plastic refinery. The primary objective is to assess the potential utilization of its constituents as key ingredients in pesticide formulations, along with the inclusion of additional active ingredients sourced from diverse plant species known for their efficacy in combating plant pests and insects. By capitalizing on the findings of this investigation, the flue gas washing liquid can be repurposed as a valuable raw material for the development of pesticides, thereby obviating the need for its disposal into the environment and simultaneously fostering its application in the agricultural.

## 2 Method

The study of the Prospective Application of Flue Gas Washing Liquid from the Wet Scrubber Unit at the Masaro Plastic Refinery for the Production of Pesticides is done by analyzing some aspects.

### 2.1 Analysis of Flue Gas Washing Liquid Composition

#### 2.1.1 Analysis of Solids Content

The analysis of solid content in the flue gas washing liquid involved the determination of Total Dissolved Solids (TDS) and Total Suspended Solids (TSS). The measurement procedure commenced with the homogenization of the liquid sample, followed by filtration using filter paper. The filtrate obtained from the filtration process was utilized for the quantification of TDS levels. The filtered filtrate was subsequently evaporated to dryness using a water bath. The resulting residue in the container was then subjected to drying in an oven at 105°C for a duration of 1 hour, followed by cooling in a desiccator prior to weighing. The process of heating and weighing was repeated until a constant weight was attained. Meanwhile, the solids retained on the filter paper were employed to determine the TSS levels, whereby the solids were dried in an oven at a temperature range of 103°C to 105°C for at least 1 hour, until a constant weight was achieved.

#### 2.1.2 Analysis of Metal Content

The metal content analyzed in the flue gas washing fluid includes a range of elements, namely iron (Fe), manganese (Mn), barium (Ba), copper (Cu), zinc

(Zn), chromium (Cr), cadmium (Cd ), mercury (Hg), lead (Pb), tin (Sn), arsenic (As), selenium (Se), nickel (Ni), and cobalt (Co). The quantification of each metal concentrations is achieved through the utilization of mass spectrometry to provide precise and accurate measurements, The selection of an appropriate mass range is crucial to encompass the anticipated mass range of the analytes under investigation. Calibration of the Q-TOF-MS system should be performed daily to ensure accurate mass determination. The fragmentor voltage should be set at 100 V, and the mass range in the mass spectrometer should be configured within the range of 100-1700.

### 2.1.3 Analysis of ammonia content

Analysis of the content of ammonia was carried out using a spectrophotometer, The procedure commences with the collection of a water sample, which is subsequently subjected to preparatory steps involving filtration, extraction, and concentration. These steps are employed to eliminate any potential interfering substances and to enhance the sensitivity of the subsequent analysis. The reagent for analysis is prepared based on the indophenol method, utilizing Nessler's reagent. The preparation of the reagent entails dissolving 50 g of potassium iodide and 10 g of mercuric iodide in 100 mL of water, followed by the addition of 10 mL of 10 N sodium hydroxide solution. The resulting solution is then diluted to a final volume of 1 L with water. Subsequently, the Nessler's reagent is introduced to the water sample and thoroughly mixed. The mixture is allowed to stand for a duration of 10 minutes to facilitate color development. Subsequently, the absorbance of the sample is measured at 420 nm using a spectrophotometer.

### 2.1.4 Analysis of Nitrate, Nitrite, and Fenol Content

Measurement of the concentration of nitrate ($NO_3^-$), nitrite ($NO_2^-$), and Fenol in water samples was carried out with a spectrophotometer, where the analysis process involved a reaction between nitrate, nitrite, or fenol in the sample with reagents that produced colored compounds that could be measured spectrophotometrically. After the reaction occurs, the absorbance of the solution is measured at a certain wavelength and is used to calculate the concentration of nitrate in the sample based on a calibration curve that has been prepared using a standard.

### 2.1.5 Analysis of another chemical content

BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) measurement methods are used to measure the dissolved oxygen content in liquid samples. BOD measurement was carried out by adding microorganisms to the BOD sample bottles and incubating at 20°C for five days. At the end of the incubation period, the dissolved oxygen content in the sample was measured using the titration method. Whereas COD is measured by adding a sample with a strong oxidizing reagent, potassium dichromate, to the sample to oxidize organic compounds into oxidation products. Furthermore, the amount of oxygen consumed in the process is measured using the titration method.

### 2.1.6 Analysis of Another Chemical Content

Flue gas washing liquid was also analyzed for the content of sulfide, fluoride and chlorine contained in the solution. The sulfide content was measured by oxidation of the sulfide into sulfur dioxide ($SO_2$) using an oxidizing agent and then reacted with an acid solution and the sulfide concentration was measured using the titration method. Fluoride analysis is carried out with an ion-selective electrode method to detect fluoride and provide an accurate fluoride concentration reading. Meanwhile, the chlorine measurement was carried out using the spectrophotometric method by adding a reagent that would react with the chlorine in the sample and produce a color change to determine the chlorine concentration.

### 2.2 Conversion of flue gas washing liquid into pesticides

The production of pesticides commences by selecting specific plant species as primary sources of active ingredients for pesticide formulations. In this particular study, the active ingredients were sourced from five distinct plant types, namely bintaro fruit, garlic, lemongrass, neem, and tobacco. The initial step involves extracting the secondary metabolites or active compounds from each plant through a heat-induced extraction process. This extraction procedure entails combining all the ingredients, including the flue gas washing liquid, within a single container with a uniform volume of 2 liters. The extraction is conducted in an open container, allowing the mixture to reach its boiling point, which is maintained for approximately 30 minutes. Subsequently, the resulting mixture is cooled to room temperature, followed by the filtration of solid residues. The resultant liquid obtained from this extraction process represents an organic pesticide sample for further analysis and utilization.

## 3 Result and Discussion

### 3.1 Flue Gas Washing Liquid Composition Analysis

The analysis of the constituents present in the flue gas washing liquid shown in the table 1. The obtained analysis results are compared against the established liquid waste quality standards set forth by the Ministry of Environment and Forestry, as stipulated in the official decree of the state minister for the Environment numbered KEP-51/MENLH/10/1995.

**Table 1** Flue Gas Washing Liquid Content

| **Content** | **Unit** | **Result** | **Standard**[8] |
|---|---|---|---|
| Total Dissolved Solids (TDS) | mg/L | 3546 | 2000 |
| Total Suspended Solids (TSS | mg/L | 107 | 200 |
| Iron (Fe) | mg/L | 52.45 | 5 |
| Manganese (Mn) | mg/L | 1.09 | 2 |
| Barium (Ba) | mg/L | <0.12 | 2 |
| Copper (Cu) | mg/L | <0.04 | 2 |
| Zinc (Zn) | mg/L | 0.17 | 5 |
| Chromium (Cr) | mg/L | <0.04 | 0.5 |
| Cadmium (Cd ) | mg/L | <0.003 | 0.05 |
| Mercury (Hg) | mg/L | <0.0008 | 0.002 |
| Lead (Pb) | mg/L | <0.04 | 0.1 |
| Tin (Sn) | mg/L | <0.30 | 2 |
| Arsenic (As) | mg/L | <0.002 | 0.1 |
| Selenium (Se) | mg/L | <0.001 | 0.05 |
| Nickel (Ni) | mg/L | <0.04 | 0.2 |
| Cobalt (Co) | mg/L | <0.04 | 0.4 |
| Ammonia ($NH_3^-$) | mg/L | 4.53 | 0.05 |
| Nitrate ($NO_3^-$) | mg/L | 0.1 | 20 |
| nitrite ($NO_2^-$) | mg/L | 0.02 | 1 |
| Fenol | mg/L | 0.36 | 0.5 |
| BOD (Biochemical Oxygen Demand) | mg/L | 321 | 50 |
| COD (Chemical Oxygen Demand) | mg/L | 1071 | 100 |
| Sulfide ($H_2S$) | mg/L | 0.01 | 0.05 |
| Fluoride ($F^-$) | mg/L | 1.34 | 2 |
| Chlorine ($Cl_2$) | mg/L | <0.01 | 1 |

Upon comparing the properties of the flue gas washing liquid obtained from the wet scrubber unit at the Masaro plastic refinery with the industry's liquid waste quality standards, as outlined in the official decree of the Minister of State for the Environment, Kep-51/MenLH/10/1995, it was observed that the ammonia, BOD, and COD levels in the smoke washing water failed to comply with the prescribed environmental quality benchmarks. Consequently, direct discharge of this particular liquid into the environment poses a substantial risk of environmental pollution.

The measurement of Biological Oxygen Demand (BOD) provides an indication of the oxygen requirement by microorganisms for the biological decomposition or oxidation of organic matter, while the Chemical Oxygen Demand (COD) reflects the extent of chemical decomposition[9]. Discharging flue gas washing water with elevated BOD and COD values into water bodies can lead to oxygen depletion due to the uptake of oxygen by organic matter, resulting in adverse consequences such as aquatic life mortality.

The preservation of the environment is crucial to prevent any detrimental effects resulting from the release of substances such as high levels of BOD and COD into aquatic ecosystems. Ammonia, in particular, poses a significant threat to the ecological balance of aquatic environments due to its toxic nature towards aquatic organisms. The toxicity of ammonia arises from its ability to accumulate in internal tissues and bloodstream, leading to adverse effects on microorganisms inhabiting aquatic systems. The removal of this toxicant becomes challenging for aquatic organisms once absorbed, as their physiological mechanisms are inadequate in efficiently eliminating ammonia from their systems. Consequently, ammonia tends to accumulate in their tissues and blood, ultimately reaching toxic levels[10]. Moreover, ammonia can contribute to the process of eutrophication in aquatic ecosystems, characterized by the excessive enrichment of nutrients within water bodies. This enrichment can lead to the proliferation of harmful algae and subsequent oxygen depletion. Being a highly soluble form of nitrogen in water, ammonia plays a role in promoting eutrophication processes[11]. The environmental impact of elevated biochemical oxygen demand (BOD), chemical oxygen demand (COD), and ammoniavalues is mitigated when proper measures are taken to prevent their discharge into aquatic environments.

Furthermore, despite complying with the established quality standards, the flue gas washing water exhibits a considerably elevated concentration of phenol. Phenol, known as a toxic and persistent organic compound, possesses the potential to exert significant impacts on aquatic ecosystems when present in water bodies. Phenolics have been found to influence the rate of oxygen consumption and can disrupt the process of oxidative phosphorylation, leading to a subsequent reduction in ATP generation. The effects of phenolics extend to various aspects of behavior, and a lethal phase characterized by poisoning has been documented in fish and invertebrates. Moreover, phenol can inhibit the activity of enzymes within aquatic ecosystems, further interfering with cellular processes in aquatic organisms and resulting in impaired metabolic function and diminished overall fitness[12].

All of these constituents that fail to meet the established quality standards render the flue gas washing liquid unsuitable for direct disposal into the environment, necessitating further treatment prior to discharge. However, conversely, these components can serve alternative purposes. The presence of elevated phenol content, for instance, can be utilized as a compound in the formulation of pesticides possessing insect-repellent and antifeedant properties, owing to the aversive aroma exhibited by phenol towards insects [13]. Moreover, the ammonia ($NH_3$) content can serve as a crucial source of nitrogen for plants. Ammonia serves as the foundational element for the nitrogen fertilizer industry and can be directly applied to the soil as a vital plant nutrient or transformed into various forms of nitrogen fertilizers. Nitrogen constitutes an essential nutrient for plant growth and development, particularly in the synthesis of proteins, chlorophyll, and other vital molecules. Ammonia can undergo conversion into diverse nitrogen forms, such as ammonium ($NH_4+$), which can be readily absorbed by plant roots[14].

Despite their relatively low concentrations, the presence of nitrate and nitrite in the flue gas washing liquid raises concerns regarding their potential impact on aquatic ecosystems. If these compounds are introduced into a water body, they have the potential to stimulate plankton growth, leading to a reduction in dissolved oxygen levels. Consequently, this can adversely affect fish populations while promoting the proliferation of algae[15]. However, same with ammonia, nitrate and nitrite are also utilized in industrial applications as nitrogen compounds, particularly as fertilizers and pesticides for plants. Nitrates, in particular, have been recognized for their capacity to enhance water use efficiency and provide protective benefits to plants against temperature-related stresses, such as heat and cold[16].

### 3.2 Active Ingredients in Plants as an Additive to Organic Pesticides

Plants possess inherent defense mechanisms against insect infestation, characterized by constitutive and inducible responses. These defense mechanisms primarily rely on the synthesis of diverse secondary metabolites[17]. Secondary metabolites play a pivotal role in influencing insect populations, exhibiting acute toxicity as well as sublethal effects that disrupt crucial physiological and behavioral processes such as fecundity reduction, morphological abnormalities, and growth retardation[18]. Secondary metabolites can be broadly categorized into terpenes, phenolics, sulfur-containing compounds, and nitrogen-containing compounds, each exhibiting distinct properties in insect control. Terpenes function as potent insecticidal agents and deterrents for both insects and mammals, while phenolics can directly act as toxins for herbivores or undergo oxidation processes, yielding toxic metabolites that impede insect growth and developmen. Sulfur-containing secondary metabolites have demonstrated remarkable efficacy as insecticides, displaying high toxicity towards herbivorous insects and acting as repellents Furthermore, nitrogen-containing secondary metabolites exhibit toxicity towards herbivores by disrupting nerve signal transduction, DNA replication, protein synthesis, and enzyme activity[19].

The selection of plants as a viable source for obtaining active ingredients is predicated upon multiple factors, encompassing their native availability within Indonesia, the composition of the active ingredients, and their efficacy in acting as pesticides, as delineated in Table 2.

**Table 2** Flue Gas Washing Liquid Content

| | Plant | Parts | Active Ingredients |
|---|---|---|---|
| Bintaro | *Cerbera Odollam Gaertn.* | Fruit | Cerberin[20] |
| Garlic | *Allium sativum L.* | Tuber | Quercetin, Kaempferol, Myricetin[21] |
| Lemongrass | *Cymbopogon citratus* | Stem, Leaves | Citral, Geraniol[22] |
| Neem | *Azadirachta indica A. Juss* | Leaves | Nimbin, Azadirachtin, Triterpenoids[23] |
| Tobacco | *Nicotiana tabacum L.* | Leaves | Nikotin[24] |

### 3.3 Pesticides from Flue Gas Washing Liquid and Plant Extracts

The incorporation of plant-derived active ingredients into pesticides results in the formulation containing varying amounts of these compounds. However, the extraction and mixing processes do not guarantee the extraction of all active ingredients as the same concentration in the real plants. The qualification of active ingredients in the pesticides after the extraction and mixing procedures is shown that the pesticide contains smone moyor ingredients of each plants include Cerberin, Quercetin, Citral, Triterpenoids, and Nikotin. The findings demonstrate that the conversion process successfully transforms the flue gas washing liquid into pesticide formulations by integrating specific active ingredients to target particular pests. Nonetheless, the efficacy of these formulations necessitates further investigation and direct testing on plant pests to evaluate their effectiveness.

## 4 Conclusion and Future Outlook

In contemporary agriculture, the utilization of fertilizers and pesticides plays a vital role in ensuring both the productivity of crops and the health of agricultural soil. The flue gas washing liquid obtained from the Masaro plastic factory exhibits noteworthy concentrations of ammonia, nitrate, nitrite, and phenol, which can be utilized as essential components in the development of organic pesticides. To enhance their efficacy, additional active ingredients sourced from extracts of Bintaro fruit, garlic, lemongrass, neem, and tobacco plants can be incorporated. This approach not only addresses the issue of disposing of liquid waste into the environment but also provides a sustainable solution to the agricultural sector's need for effective pesticides. Consequently, further research into the overall effectiveness and composition of these organic pesticides is warranted. This approach offers the dual advantage of waste reduction and the production of valuable agricultural products.

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