Engineering Analysis and Economic Evaluation of the Synthesis of Composite CuO/ZnO/ZrO$_2$ Nanocatalyst

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Abstract. The purpose of this study was to evaluate the synthesis process of composite CuO/ZnO/ZrO$_2$ (CZZ) nanocatalyst. The CZZ nanocatalyst is used as a catalyst in the hydrogenation reaction, which is used to convert harmful CO$_2$ gas into liquid fuels such as methanol. In this study, CZZ produced using the sol-gel auto-combustion method was selected as a model of the production procedure. The evaluation was conducted into two factors: engineering and economic analysis. Engineering analysis was analyzed based on the available apparatuses and raw materials in online web. Then, these data were used and compared with the mass balance approximation. The economic analysis was done using several economic parameters, including such as gross margin, internal rate return, payback period, cumulative net value, break even point (BEP), profitability index on sales to investment. Engineering analysis showed the present method can be applied using available apparatuses and raw materials in market. Economic analysis result confirmed that the present project is profitable. The analysis concluded that the present project for the production of CZZ nanocatalyst is prospective in small scale industry and profitable (by positive values in all economic parameters).

1. Introduction

Nanocatalysts is a catalyst with nanometer-size, with the aim of producing it is to make the catalyst active center have a larger area between substrate and catalyst [1]. Heterogeneous catalyst is one type of catalyst, in the form of a single metal catalyst, a metal oxide, or a supported catalyst. The component of a supported catalyst is a catalyst with supporting the active metal and having a large surface area. Examples of supported in catalyst are alumina, silica, zirconia, magnesia, zeolite, and titanium. The addition of this support will cause the catalyst active components to be uniformly distributed, increasing the surface area for contact with the reactants, increasing the mechanical strength, leveling the reaction heat and increasing the catalyst stability [2].

Catalyst is indispensable in industry due to the possibility loses during the reaction [2]. The use of catalysts exists in various applications such as conversion of crude oil, coal, and natural gas to fuel and
chemical raw materials, the production of various petrochemical and chemical product, and control of CO, hydrocarbon and NO emission [3]. The catalyst is one of the components that play an important role in hydrogenation [4].

The advantages of incorporating catalyst technology and nanotechnology will have an impact on the properties it produces. If in materials such as crystal solids, the process of making nanomaterials will make the size of the structure components decreased, there is a much larger interface area in material, and this can greatly affect the mechanical and electrical properties [3].

The catalyst generally has three components; active, support, and promoter; and CZZ catalyst to be analyzed is Cu-based catalyst because it has the active component of Cu. This active component is the most responsible element for the reaction. The support component serves as a component that expands the surface area of active components. The promoter that serves to reduce the process of sintering on active components [5].

This type of CZZ nanocatalyst is more promising in delivering high methanol yields than conventional methanol catalysts. This is due to the unique benefits of zirconium that has reducing, oxidizing, and high thermos table properties [6]. Besides CZZ nanocatalyst, the highly investigated nanocatalyst is CZA or Cu-ZnO-Al₂O₃, which has high efficiency for methanol catalysis reaction. But, CZZ nanocatalyst claimed to have a more active catalytic system due to better zirconia tolerance than alumina [7]. Nikel nanocatalyst supported on silica and alumina is an alloy with the most commonly used aluminium on commercial reactions. But, the residual nickel after the reaction can cause toxicity to the oil. Another study that examines the use of alternative catalysts is Cu-Cr/diatomea, which has the function of Cu-Cr as an active cock, while diatomaceous is used as a supported. This diatomaceous contains Al₂O₃ and SiO₂ with large surface area [4].

Research on hydrothermal, sol-gel, and reversed microemulsion methods have been reported for the preparation of Cu-based catalyst and have been described differently. Many reports have shown the feasibility for the production of Cu-related material [1-14]. But, most of the studies have several limitations, especially relating to complexity and time-fixing procedures, as well as expensive materials requirements [4]. There is also research by solid state method [8]. Another technique used to synthesize this CZZ nanocatalyst is a reverse co-precipitation technique under ultrasonic irradiation with a catalytic precipitation sequence CZZ. The result showed CZZ with total surface area and high dispersion [9]. Other studies with co-precipitation oxide techniques to enhance the catalyst activity is a citrate method [10], which produces solids with high surface area and at relatively low calcination temperatures [11]. But, from various methods, the combustion method is the best. This method has a simple route and a short time process, and can produce the optimal product [12].

In this paper, the purpose of this study is to evaluate the process of synthesis of CZZ nanocatalyst. The CZZ nanocatalyst is synthesized from precursor of Cu, Zn, ZrO₂ nitric metals, and by the addition of a complexing agent with glycine, with preliminary methods and nitric precipitation. The CZZ nanocatalyst production was analyzed using engineering and economic evaluation. The economic evaluation was done using several economic evaluation parameters, such as gross margin (GPM), internal rate return (IRR), payback period (PBP), cumulative net value (CNPV), break even point (BEP), profitability index (PI) on sales to investment. Optimizing the process to get a good profit for solving environmental problems and outcomes was also done. Research begins with analyzing and the needs of the factory. Then, the study was analyzed financially from the industrial economy evaluation with the source of research.

2. Methods

The method analyzed in this study is a combination of sol-gel with auto-combustion. This method is a very popular for nanomaterial synthesis. This method is started from local ignition techniques, gradual reactions, to the production of desired product oxide. In general, the precursor gel is prepared in a metal nitrate solution with the addition of an organic complexing agent such as citric acid, urea or glycine. Especially for glycine, glycine has a dual role in addition to complexing agents as well as fuel for combustion reactions to be more optimal. The nitrate ion itself acts as a burning oxidizing agent. This procedure has several advantages: use of economical precursor material, short preparation time,
easy use of equipment, and good powder quality [1]. The factory model design uses a medium scale, in which the designed process is illustrated by Figure 1.

To support its evaluation and economic analysis, the evaluation data collection process is based on the average price on the online shopping web. All data is calculated by simple mathematical analysis. The nanocatalyst CZZ synthesis is analyzed by several economic evaluation parameters, including GPM, IRR, PBP, CNPV, BEP, and PI sales to investment.

3. Results and Discussion

Figure 1. Illustration model for the production of CZZ Nanocatalyst

3.1. Engineering perspective

Figure 1 illustrates the steps of the composite CuO/ZnO/ZrO₂ nanocatalyst synthetic process. The synthetic process begins with the dissolution of nitrate metal solids (Cu²⁺, Zn²⁺, Zr⁴⁺) as precursors with aquadest with constant stirring until completely dissolving. Also, the process is also done dissolution method of glycine (H₂NCH₂COOH) with aquadest. This glycine acts as an adjuvant that serves as an organic complexing agent. Glycine is also compatible with citric acid, carboxylate azides, and urea. After all materials dissolve perfectly in the aquadest, the process is mixed in one container. Then, the solution is added ammonium hydroxide (NH₄OH) dropwise until the pH of the mixture solution reaches 9.5. This addition is accompanied by vigorously stirring to the expected pH value. Then, the solution is evaporated by heating the mixture at temperature of 80-90°C and accompanied by stirring. The addition of oxygen is carried out during oven combustion because the evaporator uses heating with pressure techniques; so it is expected to contact with oxygen.

Assuming a complete combustion, the reaction that takes place between nitrates and glycine. Detailed reaction can be expressed as follows:
\[
\frac{1}{2} \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} + \frac{1}{5} \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + \frac{3}{10} \text{Zr(NO}_3\text{)}_4 \cdot 5\text{H}_2\text{O} + m\text{H}_2\text{NCH}_2\text{COOH} + \left(9m/4 - 13/4\right) \text{O}_2 \\
\rightarrow (\text{CuO})_{0.5} (\text{ZnO})_{0.2} (\text{ZrO}_2)_{0.3} + \left(9m/2 + 13/10\right) \text{N}_2 + 2m\text{CO}_2 + \left(9m/2 + 21/5\right) \text{H}_2\text{O}
\]

After the evaporation process, dark blue viscous liquid is obtained in the form of intermediates of product with water and other wastes. Then, by adding oven combustion process and accompanied by a vacuum process at a temperature of 250-300°C, solution with dark brown dry powder was obtained.

The waste from this synthesis process consists of gas waste in the form of nitrogen gas, carbon dioxide gas, and water vapor. Utilization of CO\(_2\) waste can be used as a gas source for hydrogenation reactions if the catalyst product has been obtained. However, the processing of waste from the process and production of fuel from carbon dioxide gas is not described in this study.

To calculate the mass balance of this process, we use the following assumptions:
- The process using sol-gel auto-combustion method.
- The operating temperature range in temperature 90 and 300°C
- The combustion efficiency is approximately on 100%
- The assumption loss of solvent in this form is aquades as much 80%

Based on the mass balance calculations listed above, with the composition in Table 1. Above generates about 248.16 grams of CZZ nanocatalyst. The price calculation approach is not based by price comparisons because the production of CZZ synthesis is more in the field or research and still sought variables and circumstances that produce optimal results.

**Table 1. Composition comparison of reactants and products**

| Name of molecule | Phase | Molecular Mass (g/mol) | Mass (gram) | Mol |
|------------------|-------|------------------------|-------------|-----|
| Cu(NO\(_3\))_2 \cdot 3H\(_2\)O | Solid | 241.6 | 120.8 | 0.5 |
| Zn(NO\(_3\))_2 \cdot 6H\(_2\)O | Solid | 297.47 | 59.494 | 0.2 |
| Zr(NO\(_3\))_4 \cdot 5H\(_2\)O | Solid | 447.32 | 134.196 | 0.3 |
| CuO/ZnO/ZrO\(_2\) | Solid | 248.16 | 248.16 | 1.0 |

**3.2. Economic perspective**

GPM analysis showed that the excellent value 10 US/kg product. These results are calculated from the production of CZZ nanocatalyst for one manufacturing cycle. A technical point of view indicates the project is profitable. However, to ensure analysis, additional other economic parameters are required. Therefore, to evaluate the economic evaluation, the following assumptions used:
- All the calculation was used USD with currency rate of 1 USD = Rp. 10,000
- The labor wage is Rp. 3,600,000 /month (near to 360 USD/month).
- The basic electricity cost is assumed to be Rp 1,467 / kWh (close to 0.15 USD / kWh).
- The length of business operation is 20 year.
- Discount rate is 15% /year.
- Income tax is 10% annually.
- Imports and shipping costs of purchased materials or equipment are eliminated in the economic evaluation.

From the relationship between investment and the production year of the CZZ nanocatalyst (Figure 2), the PBP is about 2 years to recover the initial investment fund. From the curve, this business still survives up to 20 years of production. Based on GPM even this is more profitable, because of its price and quality.
To support the economic evaluation of CZZ nanocatalyst production in the perspective of PI, IRR, and BEP, insert table in Figure 2 is shown. CNPV last was 1453.41% compared with total investment fund. BEP analysis of this production is profitable after 5 production cycle. In 20 years, the investment profit from this production is USD 2,424,771 per year, meanwhile the total investment cost is USD 9,633,511. From this economic evaluation information, the project is profitable.

4. Conclusions
This study shows the engineering perspective and economic evaluation of the production CZZ nanocatalyst. The engineering perspective suggests this project is potential to be done in small scale industry. Economic analysis shows that the project is profitable. However, for being more profitable, further processing of the plant is required in the form of a hydrogenation reactor, in which this will be used for converting the emission gas into a liquid fuel with CZZ nanocatalyst as the catalyst.

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