



# Economic Evaluation of Different Solvents in the Production of LaCoO<sub>3</sub> Nanoparticles Prepared by the Co-precipitation Method

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## Abstract

**Background/Objectives:** This study aims to investigate the feasibility of undertaking an economic evaluation of different solvents in the production of LaCoO<sub>3</sub> NPs prepared by the co-precipitation method. **Methods/Statistical analysis:** Several economic evaluation parameters were calculated in an ideal condition. **Findings:** The result showed that the production of LaCoO<sub>3</sub> NPs is prospective to be carried out for more than 20 years. The GPM, PBP, CNPV/TIC, and PI showed positive while BEP, BEC, ROI, and IRR were negative. The NPs with aquadest solvent were better than ethanol and ethylene glycol. To confirm its feasibility, these calculations were varied by changing raw materials-sales and income tax costs. Changing raw materials-sales confirmed that the NPs with aquadest can maintain the GPM for increasing raw material up to 300% and decreasing sales up to -100%. The NPs with aquadest and ethanol solvents can survive up to 75% of increasing income tax while ethylene glycol is only less than 50%. **Improvements/Applications:** This study is very useful for predicting the feasibility in carrying out a project that produces LaCoO<sub>3</sub> NPs.

## Index Terms

Economic evaluation, feasibility study, different solvents, lanthanum cobaltite nanoparticles, perovskite.

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## I. INTRODUCTION

Lanthanum cobaltite ( $\text{LaCoO}_3$ ) is an oxide compound which has a perovskite-type structure  $\text{ABO}_3$  (A = rare-earth cation, B = transition metal cation). This compound has excellent structural, morphological, and particle size characteristics.  $\text{LaCoO}_3$  exhibits interesting electrical and electrocatalytic properties, very high electronic conductivity, good ionic conductivity [1], and unique magnetic transitions from nonmagnetic to paramagnetic behaviour at about 100 K and a broad transition at 500 K accompanied by insulator-metal transition [2]. These properties make  $\text{LaCoO}_3$  widely used as a material in various technological applications such as an intermediate temperature solid oxide fuel cell [3], cathode catalysts for a borohydride fuel cell [4], CO gas sensors [5], enzyme mimetics [6], a catalyst for syngas production [7], and certainly a perovskite solar cell.

Several studies have been carried out to synthesize  $\text{LaCoO}_3$  in different methods such as heteronuclear complex decomposition [8], co-precipitation [8], aqueous gel-casting [3], polymerizable complex [9], solid state [10], pechini [11], low temperature combustion [12], microwave-assisted colloidal [13], and hydrothermal [14]. From these methods, co-precipitation is the best method for producing  $\text{LaCoO}_3$  on a large scale. It produces higher purity and better stoichiometrically while it only requires one more material than its precursors, precipitation agent, which is economically very affordable.

Synthesis of  $\text{LaCoO}_3$  using the co-precipitation method has been studied by Chandradass [15]. They produced pure nano-sized  $\text{LaCoO}_3$  in high quantities with different solvents (aquadest, ethanol, and ethylene glycol). Their study showed that ethanol is the best solvent that can produce the smallest particle diameter of  $27 \pm 4.49$  nm. It would be very interesting to study which solvent is most appropriate for using in the production of  $\text{LaCoO}_3$  from an economic point of view. Economic evaluation is the first and most important step in carrying out a project. It can determine whether a project is prospective and feasible to run or not. In this study, we will investigate the production of  $\text{LaCoO}_3$  with different solvent through engineering and economic perspectives. To analyze its feasibility, various conditions will be carried out such as changing raw materials-sales and income tax costs.

## II. METHODS

### A. Theoretical Synthesis of $\text{LaCoO}_3$ Nanoparticles

Lanthanum cobaltite nanoparticles ( $\text{LaCoO}_3$  NPs) can be synthesized using the co-precipitation method. Chandradass [15] successfully synthesized  $\text{LaCoO}_3$

NPs by dissolving 0.04 M of lanthanum (III) nitrate hexahydrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and 0.04 M of cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) into different solvents such as aquadest, ethanol, and ethylene glycol. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was then added to that precursor solution until it reaches pH 9 with continuous stirring for 2 h at room temperature. The formed precipitate is then separated from the solution using centrifugation method and washed several times with ethanol. The precipitate is dried at  $80^\circ\text{C}$  for 48 h and calcined at  $600^\circ\text{C}$  for 2 h. To get the NPs, grinding process is carried out for 2 h. The NPs synthesis scheme using co-precipitation method is shown in this following Fig. 1.

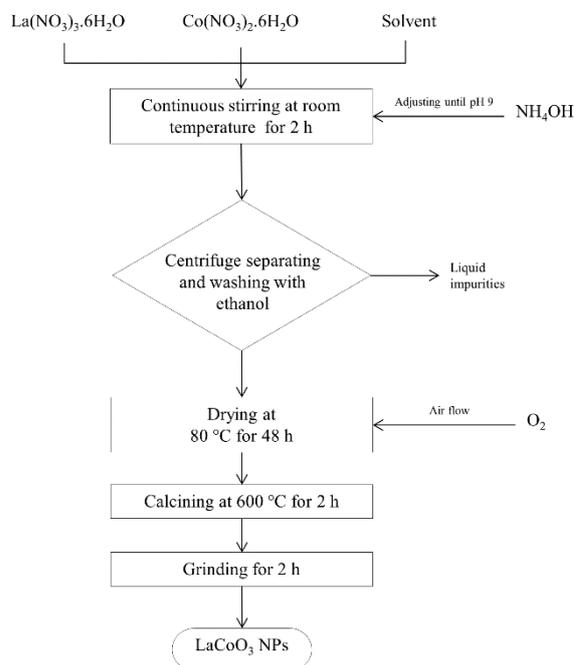


Fig. 1. Schematic synthesis of  $\text{LaCoO}_3$  NPs prepared by the co-precipitation method.

### B. Energy and Mass Balance

Fig. 2 shows a process flow diagram for producing  $\text{LaCoO}_3$  NPs on an industrial scale. To calculate energy and mass balance, the following assumptions are used stoichiometrically:

- The process is carried out based on co-precipitation method;
- All reactants exactly react. No byproducts are formed;
- A precipitant,  $\text{NH}_4\text{OH}$  25%, is added until solution reaches pH 9 with continuous stirring for 2 h;
- The reactor works at room temperature while drying and calcining processes are  $80^\circ\text{C}$  and  $600^\circ\text{C}$  respectively;
- Reduced mass of the NPs in the reactor, separating, drying, calcining, and grinding are 5% each of the

- process;
- The conversion of  $\text{LaCoO}_3$  NPs production with a solvent is as much as 80%;
- All products produced are  $\text{LaCoO}_3$  NPs.

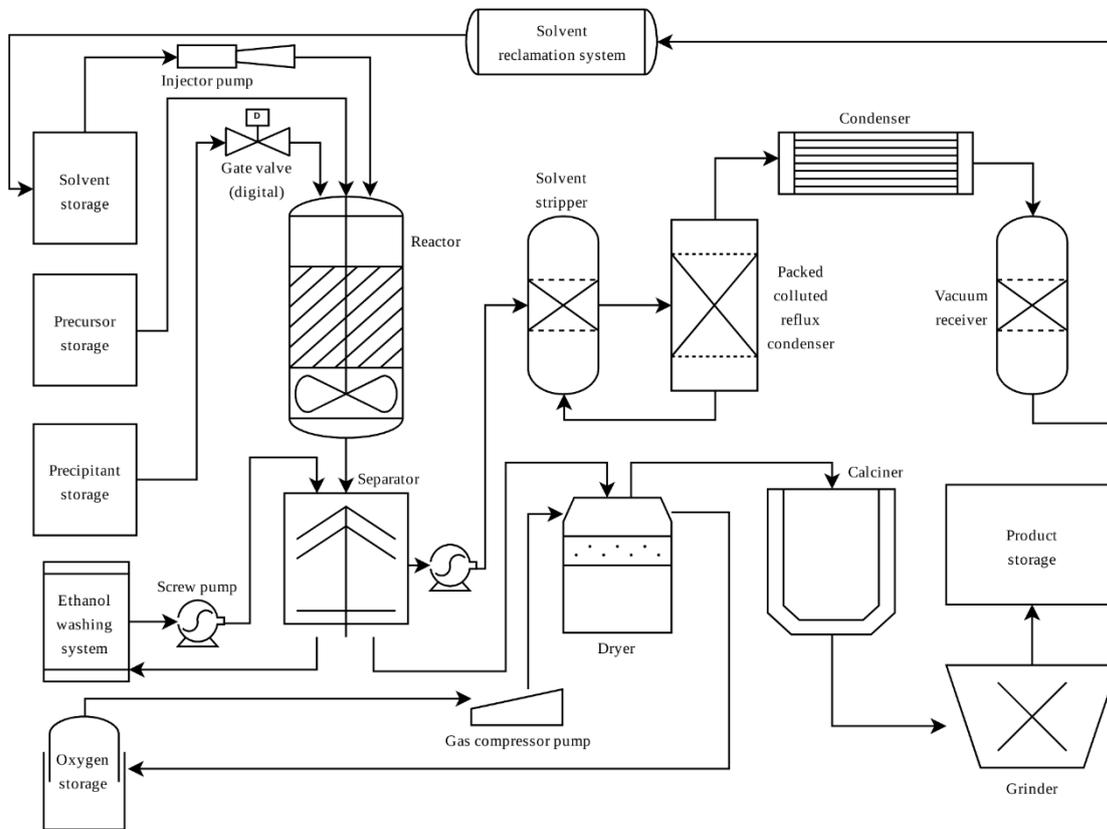


Fig. 2. Process flow diagram of  $\text{LaCoO}_3$  NPs production

### C. Economic Evaluation

To determine economic evaluation parameters such as gross profit margin (GPM), payback period (PBP), break-even point (BEP), break-even capacity (BEC), internal rate of return (IRR), cumulative net present value (CNPV), return on investment (ROI), and profitability index (PI), all need data of equipment, raw materials, and utility costs. In this study, these costs are obtained from online shopping websites such as *Alibaba* and *Tokopedia*. All data are used to calculate economic evaluation parameters through simple mathematical equations based on literature [16–19].

- GPM was calculated by reducing sales and raw material costs.
- PBP was life time point (y axis) when  $\text{CNPV}/\text{TIC}$  (x axis) equals to zero.
- BEP was calculated by dividing fixed costs against sales with variable costs difference.
- BEC was calculated by dividing BEP with production capacity in units over a period of time.
- IRR was calculated through this following equation:

$$\text{IRR} = \sum_{t=1}^t \frac{C_t}{(1+r)^t} - C_0 \quad (1)$$

Where:

- $C_t$  = net cash inflow during the period of  $t$
- $r$  = discount rate
- $t$  = number of time periods
- $C_0$  = total initial investment cost

- CNPV was obtained from NPV at specific time. In short, it was by adding up NPV from the initial establishment of a project. NPV could be obtained by multiplying cash flow with discount factor.
- ROI was calculated by dividing gained total profits with investment costs.
- PI was calculated by dividing sales and manufacturing costs difference with sales (profit-to-sales) or investment (profit-to-TIC).

To determine these values in an ideal condition, assumptions are needed to simplify the calculation. In this study, the assumptions are as follows:

- The calculation used fixed currency on conversion of 1 USD = 14000 IDR;

- Prices of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  per kg are 728,000 IDR and 1,820,000 IDR respectively. Then, prices of aquadest, ethanol 96%, ethylene glycol,  $\text{NH}_4\text{OH}$  25%, and oxygen per L are 5,400 IDR, 14,000 IDR, 21,840 IDR, 7,000 IDR, and 26,250 IDR respectively;
- Labor wages for 7 people are 336,000,000 IDR per year;
- The project works 6 cycles production per week (5 working days);
- The project operates for 20 years;
- Utility costs that must be paid per year are 158,332,111 IDR;
- The discount rate is 15%;
- The income tax is 10%;
- Total investment cost (TIC) is calculated based on the Lang Factor;
- Direct-type depreciation is used to calculate depreciation.

The economic evaluation parameters will be calculated for  $\text{LaCoO}_3$  NPs production with aquadest, ethanol, and ethylene glycol solvents. Furthermore, the results of these calculations are manipulated with some variations such as changing raw material-sales and income tax costs in order to investigate the feasibility.

### III. RESULTS AND DISCUSSION

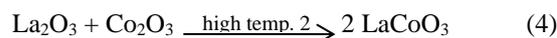
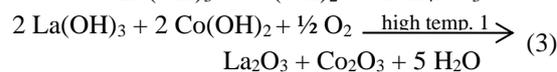
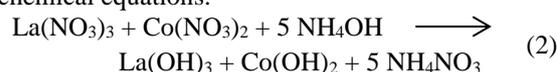
#### A. Engineering Perspective

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in aquadest, ethanol, and ethylene glycol as a precursor solution. The reactants easily dissolved in polar compounds due to their properties as salt. Synthesis of the NPs by the coprecipitation method required a substance that could yield precipitate. Adding  $\text{NH}_4\text{OH}$  25% to a precursor solution acts as a precipitant. In the precipitation process, several phenomena occur, i.e. adsorption on particle surfaces and trapping occlusion of foreign substances during rapid crystal growth. The reaction worked in a 1000 L semibatch-type reactor. The reactor was made of 316L stainless steel featuring an aluminum silicate insulator and top centre-entry agitator system with a propeller working on a frequency speed of 10 ~ 120  $\text{r min}^{-1}$ . In the semibatch reactor, the reactants were first added to form a precursor solution before being added continuously a precipitant during operation. This operating model is used when it is desirable to maintain a low concentration of one reactant (the injected reactant) [20]. Moreover, it also increases the selectivity of the desired product and to supply or remove heat by injecting an inert species. This semibatch reactor is used to prevent byproducts forming [21]. Adding precipitant to a precursor solution accompanied by continuous stirring allows

the reactants to dissolve and react perfectly at room temperature. In the other case, continuous stirred-tank reactor (CSTR) is being used. The CSTR is a mathematical model that describes an important class of continuous reactors: continuous, steady, and well-agitated [20]. On an industrial scale, the study was not suitable due to the CSTR readily achieved in small-scale agitated reactors.

In the separator, the results of the reactor were separated using a fluid-solid separation operation by the centrifugation method. Centrifugation was very effective in increasing sedimentation rates, especially when the particles were very small (<10 mm), the liquid was very viscous, and the differences in density between particles and liquids were very small [22]. The centrifugal separator was made of 316L stainless steel with an ethanol washing system. The materials were fed into the drum through the feeding pipe on the hermetic closure casing and rotated by a centrifuge device. The solid phase was stopped at the filter layer. Meanwhile, the undesired liquid phase was removed under the action of the centrifuge force field; the phase then passed through the filter media and was discharged out of the machine. The solid phase was maintained in the drum and washed with ethanol. After the machine has stopped, the solid can be taken manually or pushed into pipes to be distributed in the next process. Centrifugation has attractive and good features such as a smooth, easy, and comfortable operation as well as being able to conduct, feed, wash, and dehydrate under the state of hermetic closure.

The reaction mechanisms occurring in the synthesis of  $\text{LaCoO}_3$  NPs can be described by these following chemical equations:



The first precipitates formed (Equation 2) were a mixture of  $\text{La}(\text{OH})_3$  and  $\text{Co}(\text{OH})_2$ . At the first heating stage,  $\text{Co}^{2+}$  underwent oxidation to  $\text{Co}^{3+}$  through hot air flow with a high temperature 1 = 80 °C (Equation 3) in the drying oven [23]. The machine took on a cold-rolled steel plate and a surface electrostatic spraying process. Furthermore, a large window with a double layer of toughened glass was convenient to observe the changes of contents in the box. It had a sufficiently thick insulation layer to ensure it was heated and insulated effectively, a good thermostatic effect, and maximized safety. To optimize the oxidation process, the hot air circulation system adopted the double air duct circulation of the low noise fan.

Heating with a high temperature 1 produced a mixture of  $\text{La}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3$  which were then calcined at a high temperature 2 = 600 °C (Equation 4).

Calcination was done to remove volatile substances and form nano-sized crystalline compounds. The powder formed usually consisted of irregular agglomerates which have a broad size distribution. Upon that process, the porous network structure consisting of fine agglomerate particles was retained. These agglomerated particles act as defect centers [24]. This agglomerated defect crystal was removed by grinding process. The wet grinding process was effective in reducing agglomeration [11]. The results of the calcining and grinding processes were  $\text{LaCoO}_3$  NPs. The difference of solvent in the production of  $\text{LaCoO}_3$  NPs affected particle diameters. The average diameter of particles prepared with ethanol and aquadest were  $27 \pm 4.49$  nm and  $64.4 \pm 12.92$  nm, respectively [15]. On the other hand with ethylene glycol as a solvent,  $\text{Co}_3\text{O}_4$  was found as a pure intermediate phase. As discovered by Murugadoss and co-workers [25], ethylene glycol acts as a barrier due to its viscous nature and forms a weakly-bonded paint around each individual particles that can inhibit phase transformation to  $\text{LaCoO}_3$  NPs at low temperature ( $600^\circ\text{C}$ ).

The production of  $\text{LaCoO}_3$  NPs has been calculated stoichiometrically for industrial scale. The amount of 10,000 kg of La-nitrate and 6,721 kg of Co-nitrate dissolved in 577 L of solvent (distilled water or ethanol or ethylene glycol) at pH 9; it produced 3,515 kg of  $\text{LaCoO}_3$  NPs in one cycle. The results from the energy and mass analyses, from an engineering point of view, are very prospective. In addition to the scaling-up process that can be carried out using commercial equipment, the use of solvents such as aquadest, ethanol, and ethylene glycol is very likely to be done on an industrial scale. These three solvents are very suitable for making nano-sized  $\text{LaCoO}_3$ . Although the use of ethylene glycol as solvent allowed impurities in the form of oxides, the presence of  $\text{LaCoO}_3$  is still the main product. Under ideal conditions, the project could scale up to 288 cycles as well as produced more than 1,012.17 kg per year.

Furthermore, an analysis of the total equipment costs per batch required a total equipment purchase cost of 2,647,400,000 IDR. When adding the Lang Factor into the calculation, the TIC value was around 11,754,456,000 IDR. This value is relatively economical for producing nanomaterials made from rare earth metals. Moreover, the application of this  $\text{LaCoO}_3$  product is used as an energy material in renewable technologies such as perovskite solar cells, gas sensors, solid oxide fuel cells, membrane fuel cells, etc. Today, a green environment of renewable technologies is being instated by many countries to be used, showing the importance of using technologies based on climate change resource efficiency or

sustainable consumption and production. Therefore, the technology-developing companies' demand for  $\text{LaCoO}_3$  NPs will be very large later.

### B. Ideal Condition

Fig. 3 shows an ideal conditions of CNPV/TIC (%) against the project life time for the production of  $\text{LaCoO}_3$  NPs with different solvents, i.e. aquadest, ethanol, and ethylene glycol. In the graph, there is decreasing income in the first to third year for all solvents. CNPV/TIC started to grow into the third year with a different trend in each of solvents. Moreover, the final CNPV/TIC value in the 20th year looks very different. The project could still run up to more than 20 years. The NPs with aquadest solvent have higher final CNPV/TIC than they do with ethanol and ethylene glycol solvents.

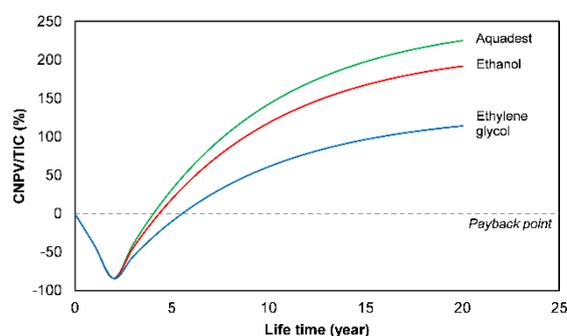


Fig. 3. Ideal condition of different solvents for cumulative net present value/total investment cost (%) to life time (year).

To support the results of the analysis in an ideal condition, Nandiyanto [16] has studied and showed several economic evaluation parameters in the fabrication of activated carbon and silica particles from rice straw waste. In this study, economic evaluation parameters such as GPM, PBP, BEP, BEC, IRR, CNPV, ROI, and PI were shown in Table 1.

The decrease in CNPV/TIC in the early years was caused by the start-up fee at the beginning of the project. This was the same circumstance for CNPV/TIC. It started to increase when the production process entered its third year. These things were impacted by variable costs, fixed costs, sales, depreciation, pre-tax profits, and income taxes that started to be paid and obtained from third year. The difference of increasing trend was due to different variable costs of raw materials to produce with a solvent. The costs of raw materials to produce with ethanol and ethylene glycol solvents were more expensive than with aquadest. That made the red and blue lines (ethanol and ethylene glycol) are longer to reach the CNPV/TIC point equal to zero (payback point).

**Table 1.** THE ECONOMIC EVALUATION PARAMETERS OF DIFFERENT SOLVENTS IN AN IDEAL CONDITION

Economic evaluation parameters	Aquadest	Ethanol	Ethylene Glycol
	Value		
GPM (IDR/pack)	673,703	627,328	518,934
PBP (years)	4.12	4.40	5.59
BEP (packs)	4,995	5,439	6,865
BEC (%)	24.67	26.87	33.91
IRR (%)	51.84	47.06	35.22
Final CNPV/TIC (%)	225.13	191.82	113.97
ROI (% per year)	4.34	3.90	2.86
PI profit-to-sales (%)	45.39	40.76	29.92
PI profit-to-TIC (%)	78.18	70.19	51.52

Based on the analysis that has been done, the values of GPM, PBP, final CNPV/TIC, and PI showed positive while other economic parameters (BEP, BEC, ROI, and IRR) showed negative. These values showed that this project seems to be a less attractive perspective for industrial investors. This perspective is based on the standard capital market in Indonesia. For further discussion, the analysis in the ideal case is carried out as follows.

In economic evaluation, the first analysis that needs to be done is GPM. This analysis can determine the profitability. Project efficiency for using materials to produce and selling products could be calculated through the value of GPM. The project in this study has greatly benefit when selling products with water solvent rather than ethanol and ethylene glycol. With price of 1,000,000 IDR per pack (50 g) for any solvents, the GPM showed very satisfying result for project revenue whereas the profitable more than 50%. Although the results indicate a high profitable in a chemical process, GPM cannot be used directly because the project based on other basic economic evaluation parameters and production costs [19].

PBP analysis showed that investment can return the total initial expenditure after more than 4-6 years. The products with aquadest solvents obtained payback faster than other solvents. Ethylene glycol was the worst whereas the PBP is almost 1.5 years longer than aquadest. Investing more than 800,000 USD in 4-6 years is considered not too long so it showed quite competitive result when compared to standard capital market's PBP. The standard capital market in Indonesia for investment of 800,000 USD usually promotes PBP around 30-32 years.

BEP is minimum product that must be sold to cover total production costs [19] while BEC is the percentage of minimum products compared to produced products per year. Corresponding to BEP analysis, LaCoO<sub>3</sub> NPs production must be able to sell at least 5,000-7,000 packs per year. In this ideal condition, the amount of products that are ready to be sold are 20,243 packs per year. It means 24.67%, 26.87%, and 33.91% of available products (20,243 packs) should be sold for products with aquadest,

ethanol, and ethylene glycol respectively. These value are relatively difficult for Indonesian industries who are not yet interested in buying and managing perovskite nanomaterials.

IRR indicated an indicator of efficiency level from an investment. IRR analysis in an ideal conditions showed the value of 51.84%, 47.06%, and 35.22% for products with aquadest, ethanol, and ethylene glycol solvents during 20 years. The calculation of this value gives a very low rate for each year which is only 1-3%. This value indicated that the IRR is not promising and creating conflicts against Indonesian local bank interest, which is 5-6% [26]. However, investment for a project can be accepted when the IRR is greater than IRR investing in other places such as deposit rates.

Positive result was also shown in the final CNPV/TIC analysis. The value seems very high for the project to run for 20 years. The final CNPV/TIC showed that product with aquadest solvent is more prospective than ethanol and ethylene glycol solvents. Product with ethylene glycol solvent just reaches final CNPV/TIC of about 100%. The best is product with aquadest solvent that can reaches more than 200%. It means the project always get more additional benefits than the invested funds.

Another parameter is ROI which showed negative result with a value of around 3-4%. This assumed that investing fund of 100 USD, for example, generated additional benefits of only 3-4 USD. Compared to bank interest and capital markets, the additional benefits are relatively unattractive. The local capital market in Indonesia should be at least 10% of profit per year, in which 2.5% of it was usually used for zakat [16].

Analysis of PI profit-to-sales and PI profit-to-TIC showed positive results. PI value is used as a way to identify the relationship between costs and impacts of a project. Product with water solvent showed the best result for creating a good impact to project. That result indicated that the project is sufficient prospective against sales and investment costs.

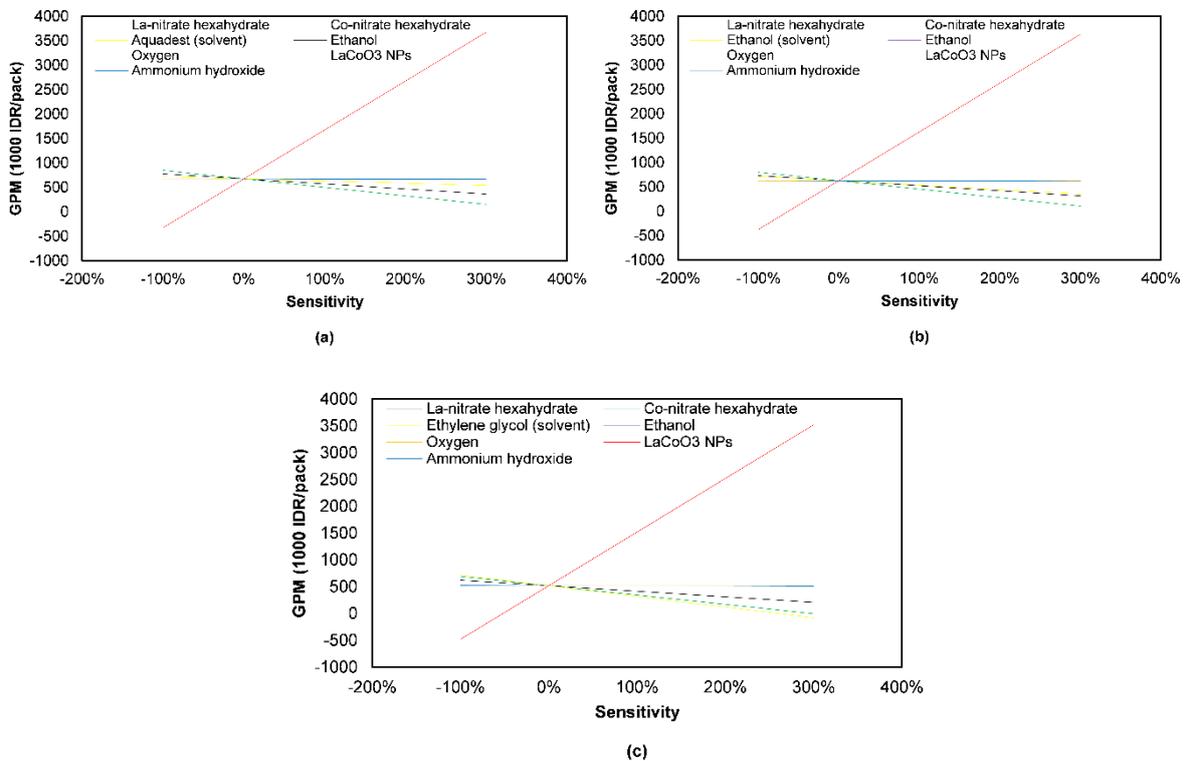
Through the above discussions, it can be seen that the use of aquadest as a solvent in the production of LaCoO<sub>3</sub> NPs is better than ethanol and ethylene glycol both engineering and economic point of views. The new idea in this research is intended to provide information and knowledge about feasibility in producing LaCoO<sub>3</sub> NPs with different solvents. The results of engineering showed sufficient prospective but unattractive from economic analysis for industrial investors in Indonesia. However, other perspectives must be reconsidered and the negative economic evaluation parameters need to be further improved.

**C. Effect of Changing Raw Materials and Sales Costs**

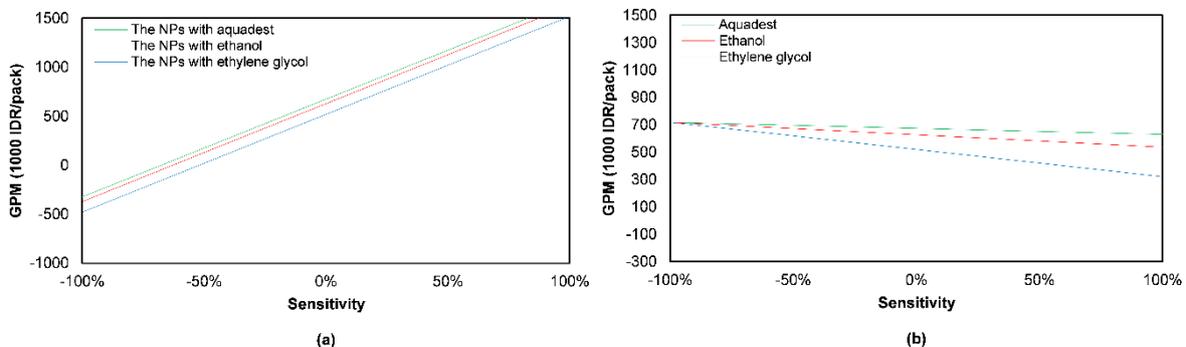
Fig. 4 shows the results to evaluate the effect of changing raw materials and sales costs (from -100% to 300%) against GPM for products with aquadest, ethanol, and ethylene glycol solvents. The figure showed that changing sales ( $\text{LaCoO}_3$  NPs) greatly affect to GPM while changing raw materials do not really show significant impact. The trend of changing raw materials costs is relatively same for each solvent. Increasing raw materials costs has an impact to decrease the GPM. On the contrary, increasing sales made the GPM is more (profitable). It means increasing sales obtained a benefit while increasing

raw materials make the project will suffer losses.

Analysis of different solvents in  $\text{LaCoO}_3$  production showed that aquadest is the best to improve the GPM for increasing sales and to maintain the GPM for increasing raw materials. The worst impvoing and maintaining the GPM is product with ethylene glycol solvent. Thus, changing raw materials must be less than 300% and changing sales must be more than -100%. Changing raw materials is very depends on solvent price (in this case). The sales and raw materials GPM were followed to change according to different each of solvents prices. Fig. 5 shows how important the effect of different solvents in changing raw materials and sales costs against the GPM of the products and solvents.



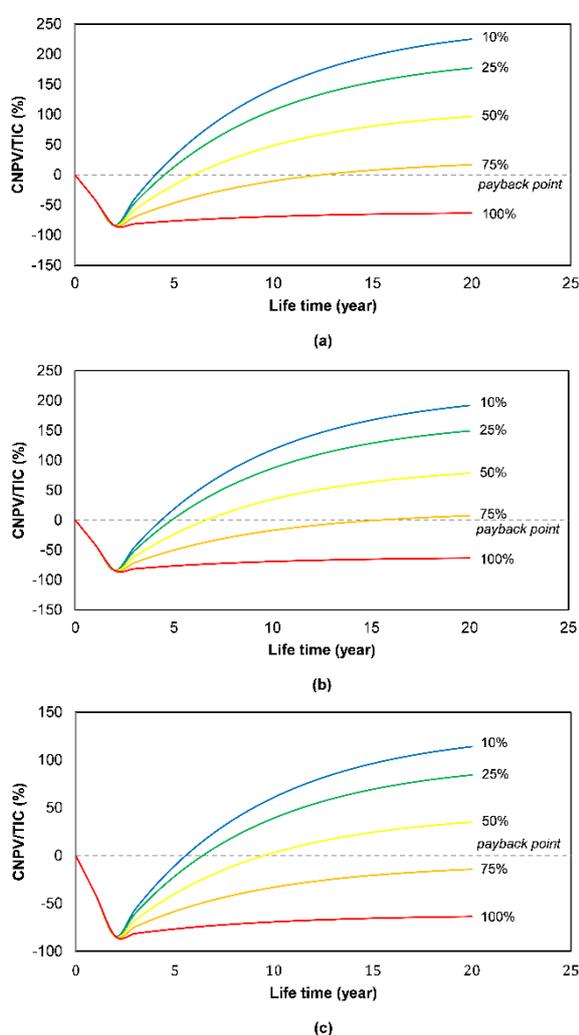
**Fig. 4.** Effect of changing raw materials and sales costs to GPM for product with different solvents: (a) aquadest; (b) ethanol; (c) ethylene glycol.



**Fig. 5.** Effect of changing raw materials and sales costs to GPM for (a) the products; (b) the solvents.

#### D. Effect of Changing Income Tax Costs

Fig. 6 shows the result to evaluate the effect of changing income tax costs from income tax in an ideal conditions (10% of taxable profit) to 100% increasing income tax costs against CNPV/TIC for products with aquadest, ethanol, and ethylene glycol solvents. The figure showed that the changing greatly affects to the value of CNPV/TIC starting from third year. Initial years (from 0 to the end of 2) showed the same results considering that the interval is the initial period of project development. Project profits decreased when the income tax costs are higher. Also, the higher tax costs make a project getting longer to reach the payback period.



**Fig. 6.** Effect of changing income tax costs for CNPV/TIC to life time in the production with different solvents: (a) aquadest; (b) ethanol; (c) ethylene glycol.

Analysis of changing income tax costs is also related to PBP. Products with aquadest and ethanol solvents are able to reach payback up to 75% income tax increase. The difference is products with aquadest

solvent can get payback faster than ethanol. In contrast to aquadest and ethanol solvents, products with ethylene glycol solvent can only get payback up to 50%. Products with aquadest solvents are the best in maintaining profits against increasing income tax up to 75%. Based on the above analysis, the tax costs should be less than 75% of taxable profit for products with aquadest and ethanol as well as less than 50% for products with ethylene glycol solvent.

#### IV. CONCLUSION

We have conducting a study to investigate the feasibility of undertaking an economic evaluation of different solvents in the production of LaCoO<sub>3</sub> NPs prepared by the co-precipitation method. The results show that the production of LaCoO<sub>3</sub> NPs is sufficient prospective to be carried out for more than 20 years from an engineering point of view. However, the economic perspective shows opposite results. The GPM, PBP, CNPV/TIC, and PI show positive while BEP, BEC, ROI, and IRR are negative. In short, the production is unattractive for industrial investor. The NPs with aquadest solvent are better than ethanol and ethylene glycol both engineering and economic point of view.

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