Conceptual design on the integrated CO₂ mineralization process with a sugar plant

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Abstract. Sustainable development goals have set challenges to be achieved in the next ten years. All the stakeholders, including industries, have been forced to take serious action in preserving the environment. Therefore, recycle of waste into energy and valuable chemicals has become attention in industries throughout the world. This paper focused on the integrated-waste utilization in a sugar industry by capturing the CO₂ from the boiler and absorbing it into the mineral solution extracted from filter cake (mud) for producing mineral carbonates with the capacity of 3000 tonnes sugarcane per day. The mud first undergoes the extraction using Ammonium Chloride (NH₄Cl) to extract the minerals. The alkali extracted from the mud then will be converted into Calcium Carbonate and Magnesium Carbonate via mineralization. Simulation using Aspen® plus was carried out using stoichiometric (R_Stoic) and yield (R_Yield) reactor block to find out the heat duty, the thermodynamic feasibility, and the yield distribution. CaCO₃ was produced from both methods with the yield of R_Stoic and R_Yield 0.718 and 0.676 mol CaCO₃/mol CaO, respectively. Based on the capacity of 3000 tonnes sugarcane per day, the process could produce the desired CaCO₃, approximately 210 kg/hr. The CO₂ to mineralize 1 tonne of filter cake was 74.2 kg CO₂, while the heat duty is 76.3 kWh for 2.8 tonnes filter cake/hr. The conceptual design is thermodynamically favorable and would be potential to be applied in sugar mills.

1. Introduction

The demand of sugar is increasing along with the growth of population. In 1943, Indonesia was used to be world rank number 2 for world sugar production. However, the production of sugar from sugarcane nowadays ranks number 12 worldwide due to most of sugar companies suffering from low productivity. The demand for sugar for food and beverages is increasing by 6% in demand for 2018, with the consumption of sugar in 2017 is counted as 6.32 million tonnes. With the annual population growth of 1.3%, sugar consumption has escalated by 4.3% per year[1]. Indonesia currently has 63 sugar mills owned by 18 companies with total production capacity reach 245,900 tonnes cane per day (TCD) with each factory produce 3900 TCD on average [2]. With the demand for sugar keeps increasing, the production of sugar will have to increase eventually.

Sugar is produced along with solid, gas, and liquid waste. The solid waste is produced in the form of sugar bagasse, filter cake, litter, boiler ash, and sludge. The gas waste is produced from the boiler as smoke, and the liquid by-product is the molasses that can be utilized as the raw material for ethanol
production. Sugar bagasse and litter are used as boiler fuel, while the waste with higher moisture content needs to be treated in other ways. The filter cake is commonly used as organic fertilizer through composting.

Filter cake contains various valuable chemicals that can be extracted such as calcium, wax, and protein [3]. The lipids that can be converted into wax come from the sugarcane plant dispersed in the juice and bagasse while the calcium comes from the use of lime milk in the liming process. The common composition of filter cake could be found as stated in Table 1 below. In Indonesia, the filter cake is called blotong and has a similar composition as of common filter cake.

The hazard of untreated filter cake from the sugarcane purification is the depleting oxygen content in the water, resulted in bad odor and darkened water [4]. Waste utilization allows emission reduction by up to 25% [5]. The smoke from the boiler typically contained 10-14% of CO₂. In 2013, Ramadhan [6] studied Karangsuwung Sugar Mills, with the CO₂ emission of boiler using bagasse as the boiler fuel was 0.485 tonnes/MWH and equivalent with 9872 tonnes CO₂/month.

Therefore, this study proposed the complete utilization by integrating the waste as raw material to produce higher value-added material, mineral carbonates. The conceptual designs are to use the filter cake containing calcium and magnesium together with boiler flue gas containing the CO₂ to be converted into the mineral carbonates. Process of removing the wax and protein has already been established by using toluene [7], the liquid that has been separated will contain the needed material to be converted into Calcium Carbonate (CaCO₃) and Magnesium Carbonate (MgCO₃) using mineralization method. Simulation using the Aspen Plus® and calculation using the black-box method of mass balance will be compared and evaluated using this study. The feasibility of the thermodynamically favored process is expected, and the yield of the CaCO₃ will be presented in this paper.

Table 1. Typical composition of filter cake from sugar industry

| Components       | Content (%) | Common filter cake [8,9] | Blotong [10] |
|------------------|-------------|--------------------------|--------------|
| C                | 33.73       | 26.51                    |              |
| N                | 2.36        | 1.04                     |              |
| CaO              | 1-4         | 5.785                    |              |
| P₂O₅             | 1-3         | 6.142                    |              |
| MgO              | 0.5-1.5     | 0.419                    |              |
| Wax, lipids, resin | 4-14     | -                        |              |
| Fiber            | 15-30       | -                        |              |
| Protein          | 5-15        | -                        |              |
| Total ash        | 9-20        | -                        |              |

2. Materials and Methods

While the integration of the whole waste utilization is complicated using only one simulation tool, the aspen simulation will include the main process of alkali extraction and mineralization. Figure 1 shows the simplified block flow diagram for this study. Alkali extraction is basically separating the mineral content in the filter cake by diluting it using the ammonium chloride (equation 1). There is no built-in model for the mineralization process; therefore, the calculation will be carried out using the available mode of reactor in comparison to stoichiometric reaction and to yield reactor. Mineralization of the extracted solution is conducted by flowing CO₂ into solution which contains mineral salts in order to be converted into the solid mineral carbonates (equation 2). For the complete process of waste utilization, calculation using black-box mass balance was provided in the Aspen file. The Aspen® Plus V9 is then used to calculate the mass balance for the process as schemed in Figure 1.
The two main reactions are involved in the alkali extraction and mineralization as follows

$$\text{Alkali Extraction: } 2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O \quad (1)$$

$$\text{Mineralization: } CaCl_2 + 2NH_3 + H_2O + CO_2 \rightarrow CaCO_3 + 2NH_4Cl \quad (2)$$

The schematic model and process parameters used in the simulation are presented in figure 2 and Table 2, respectively. Note that the operating parameter for process and yield were collected from the available literature. Some assumptions have to be made in order to allow the simulation running. Note that the fluid package in both types of reactors is NRTL which is the best result for predicting the thermodynamic properties in this study. In stoichiometric reactor calculation, the base yield is 0.76 mol CaCl_2/mol CaO for alkali extraction and 0.95 mol CaCO_3/mol CaCl_2. In the yield reactor calculation, the same yield was applied for alkali extraction, while in the mineralization, the yields for CaO and CaCl_2 has to be determined to obtain convergence result. Therefore in this case, the conversion for mineralization from CaO 50%, while from CaCl_2 in the extract 85%\[11\]. The resulted calcium oxide (CaO) and calcium carbonate (CaCO_3) are considered as slurry in the model. Particle size distribution and pure component data were all provided by NIST (National Institute of Standards and Technology) through the Aspen Plus analysis.

In order to complete the simulation, a set of properties of pure components and binary interactions are determined using the NRTL method. All the material type is conventional and available in Aspen® Plus. NIST data is provided to make assumptions in the NRTL method calculation as provided in Table 3. The heat duty is calculated using the standard free energy of formation (DHFORM) and the standard Gibbs energy of reaction (DGFORM). Heat duty for each block is the result of outlet heat streams subtracted from outlet heat stream. Binary interaction included in the calculation is Ammonia (NH_3) and water with the property unit on-hand by APV90 VLE-IG. Heat capacity of each component in each phase, density, surface tension, boiling temperature, and vapor pressure also has to be defined and assumed using NRTL method calculation in each pure component state before executing the $R_{Yield}$ calculation.
Figure 2. Typical flow chart for filter cake mineralization; (a) Stoichiometric reactor (b) yield reactor

Table 2. Operating parameter for model simulation using Aspen Plus

| Operating Parameter                          | Value (unit)                     |
|---------------------------------------------|----------------------------------|
| NH₄Cl Concentration                         | 2 M [11]                         |
| Extraction Temperature and Pressure         | 25°C, 1.013 bar [11]             |
| Extraction Efficiency                       | 76% [11]                         |
| Mineralization Mass Yield                   | 0.858 tCaCO₃/tCaCl₂ [12,13]      |
| Mineralization Mol Yield                    | 0.95 mol CaCO₃/mol CaCl₂ [12,13] |
| Mineralization Temperature and Pressure     | 40°C, 1.013 bar [12,13]          |
| CO₂ mol fraction inlet                      | 15% CO₂, 85% N₂                  |
| Filter cake feed                            | 2.8 tonnes/hr                    |
| Mol ratio Ca²⁺:NH₄Cl                         | 1:2                              |
Table 3. NIST data for heat duty calculation

| Parameters | Units   | Data set | Component | Component | Component | Component |
|------------|---------|----------|-----------|-----------|-----------|-----------|
| VB         | cc/mol  | 1        | NH₄Cl     | 542.318   | CACO₃     | 140.903   |
| RKTZRA     |         | 1        | 0.291852  | 0.291766  | 0.291767  |
| VLSTD      | cc/mol  | 1        | 434.571   | 866.928   | 46.1659   |
| TB         | C       | 1        |           | 186.82    |           |
| DHFORM     | cal/mol | 1        |           |          -135299 |
| DGFORM     | cal/mol | 1        |           |          -124962 |

3. Results and Discussion

3.1 Aspen simulation of alkali extraction and mineralization

The molar balance (in fractions) of the process using stoichiometric reactor, so-called $R_{Stoic}$ model, is presented in Table 4. The total yield obtained from the mass balance calculation was 0.718 mol CaCO₃/mol CaO. Note that CaO was presented in 5.785% of Calcium in the filter cake. Hence, 74.2 kg CaCO₃ was produced per tonne of filter cake using the assumption of stoichiometric reaction occur in the system.

The needs of CO₂ to mineralize 1 tonne of filter cake was 74.2 kg CO₂ per tonne of filter cake with the yield of CaCO₃ 2.27 tCaCO₃/tCO₂. The kinetics of the process is not yet known; thus, using the stoichiometric reactor the error was found in molar balance 12%. The error in the stoichiometric calculation may be caused by the valid phase of the reactants and products, which was only available in vapor-liquid phase, without considering solid phase as the reaction naturally occurred in the presence of solid. However, the simulation tool was limited to calculate the liquid and vapor phase under condition of unknown solid data such as particle size distribution and phase equilibrium.

The heat duty needed to process the reaction was calculated based on the reaction stoichiometry as much as 274.5 MJ/h or 76.3 kWh with an outlet temperature of 40°C as needed for the mineralization reaction.

Table 4. Molar fraction of stream in the Aspen using Stoichiometric Reactor ($R_{Stoic}$ Model)

| Component | Stream names | CaO | NH₄Cl | CaCl | CO₂ | CaCO₃ |
|-----------|--------------|-----|-------|------|-----|-------|
| NH₄Cl     |              | 0.734797 | 0.280918 | 0.327351 |
| CaCl₂     |              | 0.104073 | 0.003956 |
| H₂O       |              | 0.405531 | 0.265203 | 0.188997 |
| CaO       |              | 0.594469 | 0.032865 | 0.02253 |
| NH₃       |              | 0.208145 | 0.007912 |
| CO₂       |              | 0.15 | 0.381865 |
| N₂        |              | 0.85 | 0.067388 |
| CaCO₃     |              | 0 | 0 | 0.067388 |

$R_{Yield}$ Model is the block in the Aspen Plus tool used for calculation based on the yield of reaction. The block does not require exact information of the reaction stoichiometry and kinetics. The inert component could be defined using the condition if the unreacted component is known. Also, there is no need to separate the feed stream as in using the $R_{Stoic}$ block. The model is closer to the actual process using the $R_{Yield}$ block. However, the heat duty could not be calculated based solely on the yield data. Therefore, the use of both calculations represents the model complementary to each other and both could be compared and analyzed. Table 5 shows the molar fraction balance using the $R_{Yield}$ model.

The yield of CaCO₃ production using $R_{Yield}$ Model was 0.676 mol CaCO₃/mol CaO. Lower mass yield of CaCO₃ using this model was found around 69.83 kg CaCO₃ per tonne of filter cake. However, using
the $R_{Yield}$ model, the consumption of CO$_2$ was found to be lower, around 44%. Calculation using $R_{Yield}$ Model distributed the yield based on the known yield composition. The error calculated using the $R_{Yield}$ block was significantly lower than $R_{Stoic}$ model which is only 1%. Calculation using $R_{Yield}$ shows equilibrium between the ammonium salts, water, and ammonium ions present in the system. In terms to satisfy the condition of all the components inside the system, $R_{Yield}$ block calculation assume that there must be the same amount of element N, Ca, and CO$_2$. Hence, the error for the mol balance is significantly low. The weakness of the process is that clearly it does not take into account that CaCO$_3$ is produced in solid-state despite its solubility in the aqueous state, and thus the lower yield than $R_{Stoic}$ is obtained.

| Component | Stream Name | FEED | EXTRACT | CO$_2$ | CACO$_3$ |
|-----------|-------------|------|---------|-------|---------|
| NH$_4$Cl   | 0.67        | 0.2359 | 0       | 0.0948 |
| NH$_3$    | 0           | 0.2359 | 0       | 0.0948 |
| CaO       | 0.33        | 0.0566 | 0       | 0.0415 |
| H$_2$O    | 0           | 0.2359 | 0       | 0.0948 |
| CaCl$_2$  | 0           | 0.2359 | 0       | 0.0124 |
| N$_2$     | 0           | 0     | 0.85    | 0.4958 |
| CaCO$_3$  | 0           | 0     | 0       | 0.0828 |
| CO$_2$    | 0           | 0     | 0.15    | 0.0829 |

3.2 Pretreatment and Purification

As stated above, the utilization of sugar waste using the integrated concept is to produce pure CaCO$_3$. Magnesium and Calcium are both found in the filter cake because it is difficult to separate during the extraction and mineralization process as they possess quite similar properties. The method proposed to separate the CaCO$_3$ from the MgCO$_3$ produced from the mineralization is by floatation with addition of Sodium Napthenate (C$_{10}$H$_{17}$NaO$_2$) in the suspension of the solution. After the mixing, CaCO$_3$ will float and be easily separated from MgCO$_3$ [14]. In addition to the high value-added products, the environmentally friendly process supports sustainable development goals. Taken into account the purification method, the mass balance was calculated based on the yield data using a black-box method, CaCO$_3$ was produced using the method 105.90 kg/hr and MgCO$_3$13.07 kg/hr.

4. Conclusion

The conceptual design for accommodating the zero waste principle has been applied in the sugar mills industries for producing valuable minerals. Using mineralization with low pressure and temperature, the capital cost is quite low. Mineralization also allows the recycle of ammonium salts in the process. The simulation showed that design was thermodynamically favorable and would be potential to be applied in sugar mills. Calcium carbonate was produced in the ambient pressure and low temperature with reactor stoichiometric model and also using the reactor yield model. Based on the capacity of 3000 tonnes of sugarcane per day, the process could produce the desired CaCO$_3$, approximately 210 kg/hr. The CO$_2$ to mineralize 1 tonne of filter cake was 74.2 kg/hr with heat duty 76.3 kWh for 2.8 tonnes filter cake/hr.

5. References

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