Optimization of Carbon Dioxide Reduction in Biohythane Using an Innovative Water Scrubber

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Abstract. The major problem of biohythane production from palm oil mill effluent is the high carbon dioxide (CO₂) content. In this study, an innovative water scrubber system for upgrading biohythane has been experimentally investigated. Biohythane composing of ~53.34% of CH₄, ~39.12% of CO₂, and ~7.54% of H₂ was simulated regarding the composition of biohythane in the lab scale. Response surface methodology (RSM); a 5-level, 3-factor, central composite design (CCD), was employed to optimize three important parameters (biohythane flow-rate, water flow-rate, and operating time) in order to minimize the CO₂ content in the biohythane production. As a result, CO₂ concentration decreased with the increase of both the operating time and water flow-rate but inversely proportion to the biohythane flow-rate, which led to higher CO₂ absorption by water. The optimal condition regarding the maximum value of CO₂ reduction was found at: 3 Nl/min of biohythane flow-rate, 16 Nl/min of water flow-rate, and 9 min of operating time, thereby yielding 77.6% of CO₂ reduction.

1. Introduction
Currently, an interest in the eco-friendly energy from renewable sources seems to be one of the most important issues for any country because fossil fuels are being depleted. Biogas is one of the renewable energy sources used as a fuel to generate heat such as for cooking, for space heating, and for generating electricity. The biogas can be produced from renewable sources, e.g. cow dung, other animal waste, and palm oil mill effluent.

In palm oil milling industries, solid biomasses are used as materials to supply heat (steam) and electricity for milling processes. A study in 2017 revealed that Thailand had a total of 66 palm oil mills, of which 30 mills installed biogas plants. The total gas production was estimated at 315,000 m³/day. Recent development in palm oil mill effluent (POME) biogas production was produced via a 2-stage digestion process in which hydrogen and methane gases are separately generated in the first and second stages, respectively. Thus, this is a good opportunity for using biohythane as power energy production. However, the raw composition of biohythane consists of approximately 35-38% of carbon, and the rests are 53-55% of methane (CH₄), and 5-10% of hydrogen (H₂) [1]. Thus, it is very necessary to remove CO₂ contained in the biohythane in order to upgrade its quality. Jeong et al [3] reported that the biogas
power plant is characterized as relatively low efficiency, especially for internal combustion engine because the low flame speed of \( \text{CH}_4 \) was blamed for adverse effects [4]. Fortunately, hydrogen was used as compliment additive to improve the combustion of biogas and the mixture was named hythane [5]. For these reasons, the upgrading of biohythane is ultimately realized.

In order to enhance both \( \text{CH}_4 \) and \( \text{H}_2 \) of the biohythane, a water scrubbing absorption method was employed for \( \text{CO}_2 \) removal. According to this conventional concept, raw gases were fed into a packed-bed column from the bottom into the water scrubber tank. Then, pressurized water was sprayed from the top. The absorption is thus counter-current flow. The advantage of water scrubbing is that it is a simple technology [6,7]. However, the disadvantage is that the water contaminated by \( \text{CO}_2 \) is needed to be regenerated. In this study, an innovative water scrubbing concept was proposed. Both the pressurized raw gases and water were mixed before entering through the venturi device, which was installed at the top of the water scrubber tank, and they subsequently flowed into the tumbler area in side the tank in the downward direction, thereby absorbing \( \text{CO}_2 \) contained in the biohythane.

The objective of this present work is to study the optimization of three parameters; biohythane flow-rate, water flow-rate and operating time in order to reduce the \( \text{CO}_2 \) concentration that contained in the biohythane. Response surface methodology (RSM) with a 5-level and 3 factor central composite design (CCD) was employed to optimize these three parameters [8]. The goal is to prognosticate the proper response surface models of the relationship according to the reduction of \( \text{CO}_2 \) and these parameters.

2. Material and Methods

2.1. Materials

Biohythane was formed by the mixing of \( \text{CH}_4 \), \( \text{H}_2 \), and \( \text{CO}_2 \) via gas mixture. Impurities contained in the real biohythane, such as \( \text{H}_2\text{S} \) and ammonia (\( \text{NH}_3 \)), were ignored due to its negligible amount. \( \text{CH}_4 \) was obtained from natural gas (CNG) for vehicles from the gas stations. Therefore, it was anticipated that the presence of some constituents such as propane and butane in the mixture would have slightly increased the heating value than the intended biohythane. Both the commercial \( \text{H}_2 \) (95% purity) and \( \text{CO}_2 \) (99.99% purity) were purchased form Linde, while the CNG used in this experiment was obtained from the gas station in Tasae District, Chumphon province, Thailand. Certificate of CNG compositions, listed in Table 1, was provided by the gas separation plant, and its composition mainly composed of 73.8 % of \( \text{CH}_4 \) and 17.1% \( \text{CO}_2 \). This data was also utilized in the calculations of simulated biohythane compositions.

**Table 1** Compositions of natural gas (Tasae District, Chumphon province, Thailand) [9]

| Gas composition (%) by volume                  |
|-----------------------------------------------|
| Methane \( \text{CH}_4 \)                     | 73.836 |
| Ethane \( \text{C}_2\text{H}_6 \)             | 4.146  |
| Propane \( \text{C}_3\text{H}_8 \)           | 1.938  |
| Isobutane \( \text{i-C}_4\text{H}_{10} \)    | 0.548  |
| n-Butane \( \text{n-C}_4\text{H}_{10} \)     | 0.384  |
| Isopentane \( \text{i-C}_5\text{H}_{12} \)   | 0.174  |
| n-Pentane \( \text{n-C}_5\text{H}_{12} \)    | 0.104  |
| Hexanes \( \text{C}_6\text{H}_{14} \)        | 0.229  |
| Carbon dioxide \( \text{CO}_2 \)             | 17.149 |
| Nitrogen \( \text{N}_2 \)                    | 1.492  |
| Specific gravity, (SG.)                      | 0.791  |
| Water \( \text{H}_2\text{O} \) (Lb/MMscf)    | 0.17   |

2.2. Methods

2.2.1. Procedure. Schematic diagram of experimental set up is illustrated in Figure 1. It mainly consists of the fuel supply system (\( \text{H}_2 \), \( \text{CO}_2 \), and \( \text{CH}_4\text{(CNG)} \)), water scrubber tank and water system.
The key part of biohythane upgrading is the water scrubber tank. It composed of a vertical cylindrical tank (22 cm diameter) with two layers inside (total height: 29 cm and total volume: 11 L) according to Figure 2.

The water scrubber tank is made of a metallic alloy (~2 mm wall thickness). It is pierced at the bottom to allow the passage of an outlet tube from which the water with CO\textsubscript{2} is drained after experiments. One pressure gage is positioned at the top of the tank for measuring the pressure inside the water scrubber tank, while the gas outlet port is placed at the top of the cylindrical part.

H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} (CNG) were mixed via gas mixture under pressure (1.8 bar) to be simulated as biohythane. The simulated biohythane was then fed into the scrubber tank along with water. To control gas flow-rate, H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} mass flow controllers (Kofloc model 3660 ±1% full scale) were installed between the gases supply and water scrubber tank to control the composition of simulated biohythane. To complete mixing, a receiver tank was installed after a gas mixing unit. For safety concern, an anti-backfire valve was mounted at the H\textsubscript{2} fuel pipe line. An ultrasonic flow meter was used to measure the water flow-rate, which the reading was confirmed by the Rotameter. The operating temperature was controlled at ~20-25 °C (ambient temperature) throughout experiment. The mixing of biohythane and water was sprayed to the tumbler inside the scrubber tank (Figure 2b), thus producing bubbles and thereby absorbing CO\textsubscript{2} by water. The CO\textsubscript{2}-rich water was drained through the outlet port after experiments. The experiments were carried out according to the experimental design matrix (Table 1).
3. After experiments, the sampling biohythane was collected by gas sampling bags and then analysed by gas chromatography (model: GC-2014, Shimadzu).

2.2.2. Experimental design. Response surface methodology (RSM), with a 5-level and 3-factor central composite design (CCD), was employed in order to optimize the reduction of CO2 in biohythane. Biohythane flow-rate ($\dot{q}_{gas}$), water flow-rate ($\dot{q}_{water}$), and time (t) are three independent variables that were used to find the optimization of the reduction of CO2 in the biohythane after scrubbing process. Regarding the three independent variables, the axial parameter ($\alpha_s$) is 1.68 (for rotatable CCD), which was calculated by equation (1) [10].

$$\alpha_s = \sqrt{2k}$$  

where $\alpha_s$ is the axial parameter for rotatability, and k is the number of variables.

The experiments were considered for 5 levels of the independent variable identified as -1.68, -1, 0, 1, and 1.68 according to Table 2.

| Independent variable | Coded level |
|----------------------|-------------|
| $\dot{q}_{gas}$: biohythane flow-rate (NL/min) | -1.68, -1, 0, 1, 1.68 |
| $\dot{q}_{water}$: water flow-rate (NL/min) |            |
| t: time (min)        |            |

Table 2 Coding of independent variables

3. Results and Discussion

3.1. Experimental results

Table 3 summarizes the experimental design matrix generated by Multiple regression software according to the range of independent variables in Table 2 and experimental results for 17 experimental runs in a water scrubber.

| No. | Independent variable | Simulated biohythane (%v) | product gas (%v) | CO2 reduction (%v) |
|-----|----------------------|---------------------------|------------------|--------------------|
|     | $\dot{q}_{gas}$ (NL/min) | $\dot{q}_{water}$ (NL/min) | T (min) | H2 | CH4 | CO2 | H2 | CH4 | CO2 |     |
| 1   | 10.18               | 14.4                      | 9.46            | 7.3 | 53.7 | 39.0 | 9.8±0.28 | 65.8±0.07 | 24.5±0.35 | 37.2±0.90 |
| 2   | 7.5                 | 16                        | 8               | 7.3 | 53.7 | 39.0 | 11.9±0.41 | 69.9±0.09 | 19.0±0.32 | 51.3±0.83 |
| 3   | 4.82                | 9.6                       | 9.46            | 7.3 | 53.7 | 39.0 | 11.8±0.12 | 62.0±0.05 | 26.6±0.16 | 32.9±0.42 |
| 4   | 10.18               | 14.4                      | 6.13            | 7.3 | 53.7 | 39.0 | 7.5±0.05 | 66.3±0.01 | 26.2±0.05 | 32.7±0.14 |
| 5   | 10.18               | 9.6                       | 9.46            | 7.3 | 53.7 | 39.0 | 7.1±0.06 | 60.0±0.07 | 32.9±0.13 | 15.6±0.34 |
| 6   | 7.5                 | 12                        | 8               | 7.3 | 53.7 | 39.0 | 9.6±0.20 | 64.0±0.02 | 26.3±0.22 | 32.4±0.56 |
| 7   | 7.5                 | 12                        | 5               | 7.3 | 53.7 | 39.0 | 6.7±0.01 | 65.4±0.01 | 27.9±0.02 | 28.4±0.02 |
| 8   | 3                   | 12                        | 8               | 7.3 | 53.7 | 39.0 | 14.1±0.47 | 70.6±0.35 | 15.3±0.12 | 60.7±0.31 |
| 9   | 4.82                | 9.6                       | 6.13            | 7.3 | 53.7 | 39.0 | 11.5±0.10 | 62.3±0.16 | 26.1±0.06 | 33.0±0.15 |
| 10  | 10.18               | 9.6                       | 6.13            | 7.3 | 53.7 | 39.0 | 7.4±0.13 | 59.9±0.05 | 32.8±0.09 | 16.0±0.23 |
| 11  | 7.5                 | 12                        | 8               | 7.3 | 53.7 | 39.0 | 9.6±0.20 | 64.0±0.02 | 26.3±0.22 | 32.4±0.56 |
| 12  | 7.5                 | 8                         | 8               | 7.3 | 53.7 | 39.0 | 9.9±0.01 | 57.4±0.02 | 32.7±0.03 | 16.2±0.07 |
| 13  | 4.82                | 14.4                      | 6.13            | 7.3 | 53.7 | 39.0 | 13.5±0.04 | 65.9±0.29 | 17.0±0.33 | 56.4±0.84 |
| 14  | 7.5                 | 12                        | 11              | 7.3 | 53.7 | 39.0 | 10.9±0.03 | 63.4±0.05 | 25.7±0.08 | 34.0±0.21 |
| 15  | 12                  | 12                        | 8               | 7.3 | 53.7 | 39.0 | 9.0±0.02 | 63.2±0.04 | 27.7±0.02 | 28.9±0.04 |
| 16  | 4.82                | 14.4                      | 9.46            | 7.3 | 53.7 | 39.0 | 10.9±0.05 | 72.0±0.05 | 17.1±0.01 | 56.1±0.01 |
| 17  | 7.5                 | 12                        | 8               | 7.3 | 53.7 | 39.0 | 9.6±0.20 | 64.0±0.02 | 26.3±0.22 | 32.4±0.56 |
Experiments were carried to determine the reduction of CO₂ in the biohythane. The composition of simulated biohythane, by volume, was kept constant at 7.3% of H₂, 53.7% of CH₄, and 39.0% of CO₂. After completing experiments, it was reported that the reduction of CO₂ was in the range of 15.6-60.7% by volume. Noted that no amount of the water contained in the product gases after scrubbing was detected.

3.2. Response surface models of results and statistical analyses

After considering the results of the effect of three independent variables regarding biohythane flow-rate, water flow-rate, and operating time on the reduction of CO₂, response surface models were applied to analyse the data in Table 3 by utilizing a multiple regression model to fit a second-order polynomial equation according to equation (2).

The equation (2) shows the relationship between the CO₂ reduction values and the other independent variables in the form of squared model.

\[
CR = \beta_0 + \beta_1(q_{gas}) + \beta_2(q_{water}) + \beta_3(T) + \beta_4(q_{gas}^2) + \beta_5(q_{water}^2) + \beta_6(t^2) + \beta_7(q_{gas}) + \beta_8(q_{water}) + \beta_9(t)
\]  

(2)

Where CR is the reduction of CO₂ (%), \(q_{gas}\) is biohythane flow-rate, \(q_{water}\) is water flow-rate, \(t\) is time, and \(\beta\) is the coefficient value.

The model was considered by the probability of error value (p-value) in the detailed Table 4. The p-value was employed to exam the statistical significance of each regression coefficient. When their p-values are higher than 0.1, at 90% confidence level, the independent variables in a model were considered as negligible effects. In contrast, when their p-values are lower than 0.1, the independent variables were considered as significant parameters.

After considering the p-values, the negligible parameters in equation (2) were suppressed, thereby resulting in a new second-order polynomial equation according to equation (3).

\[
CR = \beta_0 + \beta_1(q_{gas}) + \beta_2(q_{water}) + \beta_3(q_{water}^2) + \beta_4(t^2) + \beta_5(q_{water}^2) + \beta_6(t^2)
\]  

(3)

Table 4 shows coefficient values, p-values, R², and R² adjusted of equation (3) after suppressing the negligible parameters. According to this table, the operating time became to be the most significant term in the response models because of its p-value being lowest (0.04682). Therefore, it is very necessary to keep this parameter for calculating the reduction of CO₂ in biohythane by water scrubbing. Note that \(\beta_1\) and \(\beta_3\) were kept in the equation (3), although their P-values were higher than 0.1 because their coefficient values are important to be considered for the calculation in the reduction of CO₂.

| Term | Coefficient value | P-value |
|------|-------------------|---------|
| \(\beta_0\) | -747.02 | 0.06725 |
| \(\beta_1\) | -1.613 | 0.138 |
| \(\beta_2\) | 180.13 | 0.08451 |
| \(\beta_3\) | -14.39 | 0.101 |
| \(\beta_4\) | 2.082 | 0.04682 |
| \(\beta_5\) | 0.387 | 0.110 |
| \(\beta_6\) | -0.154 | 0.06508 |
| R² | 0.809 | - |
| R² adjusted | 0.694 | - |
3.3. Response surface plots

Figure 3 shows contour plots of the influence of biohythane flow-rate, water flow-rate, and operating time on the reduction of CO$_2$. It was found that an increase in the operating time with the reduction of biohythane flow-rate has a positive effect on CO$_2$ reduction (Figure 3a). The percentage of CO$_2$ reduction reached ~60% at the operating time range 7-9 min while injecting biohythane in the range of 3-4 NL/min. This implies that increasing operating time with decreasing biohythane flow-rate showed a positive impact on CO$_2$ reduction. As Figure 3b illustrated, the CO$_2$ reduction increased significantly when increasing water flow-rate, e.g. from 20% at ~9 NL/min to 50% at 15 NL/min, while injecting biohythane in the range of 5-11 NL/min. This can be explained by the fact that higher water flow-rate leads to higher CO$_2$ absorption by water. Moreover, increasing water flow-rate while increasing operating time in the range of 4-8 min favours the reduction of CO$_2$ (40-70%), according to Figure 3c. For these variations, it can be summarised that increasing both water flow-rate and operating time while reducing the biohythane flow-rate inherently promoted the reduction of CO$_2$.

**Figure 3.** Percentage of the reduction of CO$_2$ (%v) as (a) a function of operating time and biohythane flow-rate, (b) a function of water flow-rate and biohythane flow-rate, and (c) a function of time and waterflow-rate.
3.4. **Optimum conditions for reducing the CO\textsubscript{2} content in the biohythane**

An optimal condition of the CO\textsubscript{2} reduction in biohythane via water scrubbing was performed by using Excel solver from Microsoft Excel add-in tool to calculate the optimal point from equation (3) (by taking the ranges of independent parameters in Table 2 into the calculation). The optimal condition for CO\textsubscript{2} reduction in biohythane using a water scrubber system in equation (3) is: biohythane flow-rate of 3 Nl/min, water flow-rate of 16 Nl/min, and operating time of 9 min, thus confirming that a reduction of the biohythane flow-rate with the growth of both water flow-rate and operating time is beneficial for removing CO\textsubscript{2} content. The experiments were conducted twice at the optimal condition to confirm and check the results of CO\textsubscript{2} reduction in the treated biohythane. It was found that the composition of biohythane after scrubbing is: 17.4±1.59% of H\textsubscript{2}, 73.8±2.38% of CH\textsubscript{4}, and 8.8±0.8% of CO\textsubscript{2}, thereby yielding 77.6±2% of CO\textsubscript{2} reduction as compared to the raw gas. Moreover, such the value of CO\textsubscript{2} reduction (~77.6%) is slightly lower than that of the result obtained from the prediction of the equation (3), (85% of CO\textsubscript{2} reduction). Thus, this equation is both reliable for the prediction of the CO\textsubscript{2} reduction in biohythane performed in this water scrubber and beneficial for scaling-up the water scrubber tank.

**4. Conclusions**

The reduction of CO\textsubscript{2} in biohythane was performed in an innovative water scrubbing system. The optimization of three key parameters (biohythane flow-rate, water flow-rate, and operating time) with respect to the maximum of the CO\textsubscript{2} reduction was successfully demonstrated. CO\textsubscript{2} concentration decreased significantly with the increase of both water flow-rate and operating time while the flow-rate of biohythane was decreased. The optimal condition for CO\textsubscript{2} reduction in the biohythane using water scrubber was found at: biohythane flow-rate of 3 Nl/min, water flow-rate of 16 Nl/min, and operating time of 9 min, thereby yielding 77.6% of CO\textsubscript{2} reduction.

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