Development of air and GHG emission calculators integrated in UNISIM-based process simulator: case study of a gas sweetening with effects of process parameters

K S Permana¹, A A Alimin¹, M Ibadurrohman¹ and B H Susanto¹

¹Chemical Engineering Department, Faculty of Engineering, University of Indonesia, Depok, Jawa Barat, 16424, Indonesia.

Abstract. This paper reports the development of air and GHG emission calculators embedded in UNISIM-based process simulators, which are used as a computational tool to generate estimated values of air and GHG emission integrated with process simulation. A gas sweetening unit is taken as an example for the case study, with the effects of process parameters on the resultant emission being emphasized. Air and GHG calculators are developed based on up-to-date standards and national regulations concerning oil and gas processing facilities. The simulation’s base case is designed to produce sweet gas with sales gas specifications using MDEA solvent, which reveals 1,527 tonnes CO₂e/day (representing GHG emission) and 0.348 tonnes SO₂e/day (representing air emission). Pressure decline in the sour gas stream leads to a slight increase in emission up to 1,554 tonnes CO₂e/day and 0.368 tonnes SO₂e/day because of the additional compression systems. Using DEA as a solvent does not significantly affect air and GHG emission for the same sweet gas specification. The simulation also revealed that the gas flow rate (capacity) is not directly proportional to the eventual emission. In this case, the driver for air and GHG emission is the reboiler’s duty, dependent on the amine flow rate. As there is a critical (minimum) lean amine flow rate regarding the sour gas flow rate, the non-proportional relationship between gas flow rate and emission is expected. To produce sweet gas with LNG specification, the emission rises considerably to 2,652 tonnes CO₂e/day and 0.747 tonnes SO₂e/day because CO₂ loading of rich amine is higher in this case, eventually increasing the reboiler duty significantly.

1. Introduction
Natural gas is a fossil fuel that is colourless and odourless. This gas is dominated by methane with one carbon atom and four hydrogen atoms. Natural gas may also contain nonhydrocarbons such as sulfur, nitrogen, hydrogen sulfide, and carbon dioxide. Most of these components must be removed from natural gas. Acid gases also need to be removed because of their toxicity (H₂S) and the low heating value (CO₂) [1]. Several types of sweet gas are based on CO₂ and H₂S content. For sales gas the content of CO₂ < 5 % and H₂S < 4 ppm, while for LNG, the content of CO₂ < 100 ppm and H₂S < 2 ppm [2].

MDEA is a type of amine with several advantages compared to other types of amines in the gas sweetening process. In the gas sweetening process, the advantage of MDEA possesses over the other amines is that it is selective toward H₂S in the presence of CO₂, especially at high ratio CO₂/H₂S, high solution concentration, and low corrosion [3]. In column absorber, acid gas flows upward,
counter-current to lean amine. The sweet gas exits the top of the column. Rich amine (solvent with the absorbed acid gas) is sent to the regenerator to be regenerated.

There is combustion gas flaring in the gas refinery industry, which produces high emissions that reach 560 MMT CO₂ per year [4]. Also, flaring emissions can affect the environment, health implications for humans, and economic effects [5]. Therefore it is crucial to know the total emissions produced to remain below standards and regulations not negatively impact.

2. Emission calculation

Activities in gas sweetening facilities are subject to significant greenhouse gas (GHG) and air emissions, contributing to global warming and air pollution. GHG emissions include the generation of CO₂, CH₄, and N₂O, collectively represented by CO₂ equivalent [6], while the air emissions are calculated based on the generation of particulate matters (PM), NOₓ, SO₂, benzene, and VOC, collectively represented by SO₂ equivalent [7]. Emission sources are thoroughly identified and listed, including acid gas flaring, flash gas venting, combustion units, well specific vents, and fugitive emissions. Emission calculations are based on regulations and standards, namely: Peraturan Menteri Negara Lingkungan Hidup Republik Indonesia Nomor 12 Tahun 2012 (PerMen LH No. 12/2012) [8], API Compendium 2009 [6], US EPA AP-42 [9], OGP report 197 [10], and CAPP 2015 [11]. All the equations are addressed below:

2.1. Emission from flaring

\[ E_{CO_2} = Volume\ flared \times \text{molar volume conversion} \times MW_{CO_2} \times \text{mass conversion} \]

\[ \times \sum \left( \frac{\text{mole hydrocarbon}}{\text{mole gas}} \times \frac{A \text{ mole } C}{\text{mole hydrocarbon}} \times 0.98 \frac{\text{mole } CO_2 \text{ formed}}{\text{mole } C \text{ combusted}} + B \frac{\text{mole } CO_2}{\text{mole gas}} \right) \] (1)

\[ E_{CH_4} = Volume\ flared \times CH_4 \text{ mole fraction} \times \%\text{residual } CH_4 \times \frac{1}{\text{Molar volume conversion}} \times MW_{CH_4} \] (2)

\[ E_i = Volume\ flared \times Emission\ Factor_i \] (3)

2.2. Emission from venting

\[ E_i = Volume\ venting \times F_i \times \frac{MW_i}{\text{Molar Volume Conversion}} \] (4)

2.3. Emission from the combustion unit

\[ E_{CO_2} = Fuel\ Consumption \times \frac{MW_{mixture}}{\text{Molar Volume Conversion}} \times Wt\%C_{mixture} \times \frac{44}{12} \] (5)

Equation (3) can be used to calculate emissions from other components in this source emission.

2.4. Fugitive

\[ E_i = N_j \times EF_j \times \%wt_i \] (6)

2.5. Well specific vent

\[ E_i = N_j \times Emission\ Factor_j \times \left( \frac{\text{mol fraction } %i}{\text{mol fraction } %CH_4 \text{ typical}} \right) \times \left( \frac{MW_i}{MW \ CH_4} \right) \] (7)
3. Simulation

3.1. Base case simulation
The simulation's configuration can be seen in Figure 1, which depicts sour gas entering the absorption column (at 1.231 psig and 48.78 °C, with molar flow sour gas 145.7 MMSCFD). The solvent used for base case simulation is 45%wt MDEA solution. The product's sweet gas from this simulation contains a CO₂ molar fraction of 4.73% and H₂S < 4 ppm. The gas is assumed to be produced from four wells with the same flow rate of 45 MMSCFD. The full composition of sour gas is given in Table 1.

![Figure 1. Base case simulation model.](image)

| Components            | Mole Fraction |
|-----------------------|---------------|
| Methane               | 0.79710       |
| Ethane                | 0.01889       |
| Propane               | 0.00990       |
| i-Butane              | 0.00292       |
| n-Butane              | 0.00289       |
| i-Pentane             | 0.00158       |
| n-Pentane             | 0.00100       |
| n-Hexane              | 0.00153       |
| n-Heptane             | 0.00071       |
| n-Octane              | 0.00044       |
| n-Nonane              | 0.00018       |
| n-Decane              | 0.00018       |
| Nitrogen              | 0.00181       |
| Carbon dioxide        | 0.15736       |
| Hydrogen sulfide      | 0.00100       |
| Benzene               | 0.00055       |
| Water                 | 0.00197       |

3.2. Variation of sour gas pressure
Sour gas pressure is changed to be lower, the compressor and cooler units are needed before the sour gas feed enters the absorber column, the amount of unit is adjusted to the needs. The changed of pressure is from 1,231 psig to 1000, 800, and 600 psig. The adjustment was also made of the sour gas to the absorption column with condition and composition similar to base case simulation.

3.3. Variation of gas flowrate
The change of feed gas flow rate will affect the sweet gas composition. Therefore lean amine flow rate is adjusted to obtain sweet gas with CO₂ content, which is nearly from the base case simulation. The
gas flow rate is varied at 60, 80, 100, 120, and 160 MMSCFD. When the feed gas flow rate is changed, other parameters are kept constant to study the effect of the feed gas flow rate.

3.4. Variation of solvent type
The solvent is changed from MDEA to DEA with the same amount of molar flow with the adjustment of wt% DEA by keeping other parameters constant to obtain sweet gas with CO$_2$ content is nearly from the base case simulation.

3.5. Variation of sweet gas specification
There are two types of simulation. The first (DEA, LNG1) changes the molar flow of lean amine while the second (DEA, LNG2) changes DEA concentration. This simulation is operated to obtain sweet gas with CO$_2$ content < 100 ppm for LNG specification by keeping other parameters constant.

4. Result and discussion
4.1. Development of emission calculator integrated in unisim
The development of an integrated calculator at UNISIM for calculation emission from process gas sweetening can be divided into eight stages:

4.1.1. General characteristics of gas.
General characteristics of gas (shown in Figure 2) are data from components in the form of hydrocarbon components and other components such as water, carbon dioxide, nitrogen, benzene, and hydrogen sulfide, which are constituent components of sour gas. These components’ general characteristics are the molecular weight obtained from the software used, i.e., UNISIM, the number of C atoms, and the heating value of these components obtained from the 2009 API Compendium [6].

| Component   | Formula | Mw  | Number of C | HtBtu/MMSCF |
|-------------|---------|-----|-------------|--------------|
| Methane     | CH$_4$  | 16.04| 1,000       | 100,2        |
| Ethane      | C$_2$H$_6$ | 30.07| 2,000       | 176,5        |
| Propane     | C$_3$H$_8$ | 44.10| 3,000       | 246,7        |
| Butane      | C$_4$H$_{10}$ | 58.12| 4,000       | 326,8        |
| Isobutane   | C$_8$H$_{10}$ | 58.12| 4,000       | 326,8        |
| n-Butane    | C$_8$H$_{12}$ | 72.15| 5,000       | 406,8        |
| Pentane     | C$_{10}$H$_{22}$ | 72.15| 5,000       | 406,8        |
| n-Heptane   | C$_{11}$H$_{22}$ | 86.19| 6,000       | 476,6        |
| n-Octane    | C$_{11}$H$_{22}$ | 100.2| 7,000       | 505,2        |
| n-Decane    | C$_{12}$H$_{26}$ | 114.2| 8,000       | 534,5        |
| n-Dodecane  | C$_{12}$H$_{22}$ | 128.2| 9,000       | 589,7        |
| n-Tridecane | C$_{13}$H$_{26}$ | 142.2| 10,000      | 644,4        |
| Ar          | H$_2$   | 13.95| 0,0000      | 90,2         |
| Carbon Dioxide | CO$_2$ | 44.01| 1,000       | 100,000      |
| Nitrogen    | N$_2$   | 28.01| 0,0000      | 90,2         |
| Benzene     | C$_6$H$_6$ | 78.11| 6,000       | 376,5        |
| Hydrogen Sulfide | H$_2$S | 34.08| 0,0000      | 90,2         |
| Methane     | C$_8$H$_{10}$ | 78.11| 6,000       | 376,5        |

**Figure 2.** General characteristics of gas.

4.1.2. List of conversion factors.
The list of conversion factors (shown in Figure 3) is the conversion factor used to calculate emissions from the gas sweetening process with emission sources such as acid gas flaring, flash gas venting, combustion units, fugitives, and well specific vent. This conversion factor is obtained from Peraturan Menteri Negara Lingkungan Hidup Republik Indonesia Nomor 12 Tahun 2012 (PerMen LH No. 12/2012) [8], API Compendium 2009 [6], US EPA AP-42 [9], OGP Report 197 [10], CAPP 2015 [11], and TSAP Report 15 [7].
4.1.3. Data and calculation of acid gas flaring.

Data and calculation of these emissions can be seen in Figures 4 and 5. In Figure 4, there are some data from the simulation results (in black) in the form of flow rate and mole fraction of the output component of the top regenerator column (acid gas) and the calculation data needed (in red) is the total mole fraction of CO₂ in acid gas for the calculation of CO₂ emissions and the total heating value used as a correction factor for individual components based on the references used. After the data is obtained, the emissions can be calculated using emission factors with reference sources used, as shown in Figure 5.

Figure 3. List of conversion factors.

| Table Title | Conversion Factor | Value |
|-------------|------------------|-------|
| 3rd International Conference on Smart City Innovation | | |
| IOP Conf. Series: Earth and Environmental Science 673 (2021) 012009 | doi:10.1088/1755-1315/673/1/012009 |

Figure 4. Simulation data and calculation results for acid gas flaring.
4.1.4. Data and calculation of flash gas venting.

The data needed to calculate these emissions is simulation data, which is the flash gas flow rate and mole fraction of the CO$_2$ and CH$_4$ components (shown in Figure 6) because releasing gas into the air only produces emissions from these two components. After the data is obtained, the emissions can be calculated (can be seen in Figure 7) by referring to equation (4).

$$\text{Emission}_{\text{flash gas venting}} = \text{Flow rate} \times \text{Mole fraction} \times \text{Specific gravity}$$

![Figure 5. Emission calculation for acid gas flaring.](image)

4.1.5. Data and calculation of combustion units.

In this simulation, the calculation of emissions from the internal and external combustion units can be calculated simultaneously because the fuel comes from the sweet gas produced. The data needed to calculate these emissions is the mole fraction of the sweet gas flow (can be seen in Figure 8), which will affect the calculation of the molecular weight of the mixture, Wt%Cmix, and the heating value that will be used to calculate CO$_2$ emissions. Data on reboiler duty needed to get the amount of fuel used because this amount of fuel will determine the number of emissions produced. After the data is obtained, the emissions can be calculated (can be seen in Figure 9) by referring to equations (3) and (5).

$$\text{Emission}_{\text{combustion units}} = \text{Fuel flow rate} \times \text{Mole fraction} \times \text{Specific gravity}$$

![Figure 6. Simulation data for flash gas venting.](image)

![Figure 7. Emission calculation for flash gas venting.](image)
Figure 8. Simulation data and calculation results for combustion units.

4.1.6. Data and calculation of fugitive.

For fugitive emissions, data in Figure 10. is obtained from the CAPP 2015, which regulates the unit and the number of components in a typical gas sweetening process. These fugitive emissions are emissions generated from the use of units based on the emission factor approach. After the data is obtained, the emission can be calculated, as shown in Figure 11. using equation (6). It should be noted that in Figure 10, there is a column "number of compressor units" and "number of HE units". This column needs to be adjusted according to the number of units used, especially in the variation of sour gas pressure because in the change in sour gas pressure there will be possible differences in the number of units used.

Figure 9. Emission calculations for combustion units.

Figure 10. Data for fugitive emission sources.
4.1.7. Data and calculation of wells specific vent.

These emissions are affected by the number of pneumatic units and the mole fraction of CH$_4$ and CO$_2$ components in gas wells (can be seen in equation (7)). In this simulation, every well is assumed to produce 45 MMSCFD. After the data is obtained, the emission can be calculated. It should be noted that in Figure 12. there is a column "number of wells". This column can be calculated by dividing the amount of gas capacity by each well’s gas capacity, assuming each well produces the same gas capacity, with the final value rounded up to the unit value.

4.1.8. Total emissions generated.

The calculation of emissions from the six sources described previously can be simplified, as shown in Figure 13. Total emissions generated will be converted on a CO$_2$-equivalent basis for greenhouse gas pollution (conversion factor is obtained from API Compendium in 2009 (6)) and on an SO$_2$-equivalent basis for air pollution (a conversion factor is obtained from TSAP Report 15 (7)). After the base case simulation and the emission calculator are completed using the spreadsheet tools, the total emissions generated can be obtained immediately by changes the parameters process. It should be noted, as explained earlier in points 6 and 7, the number of units and wells must be adjusted to the simulation.

4.2. Base case simulation

Base case simulation emissions are 1.527 CO$_2$e tonne/day and air pollutions are 0.3484 SO$_2$e tonnes/day. The biggest emission load is on the acid gas flaring with CO$_2$ component emissions of 919.5 tonne/day because the sour gas in the simulation has a high CO$_2$ content (15.73%). For flash gas venting emissions, the emissions have no significant effect due to the low flow rate.

For external combustion units, the emissions are dominated by CO$_2$ because the calculation of CO$_2$ emissions is affected by the weight percent component carbon, which is the fuel used from sweet gas with 90.15% methane. While the other components’ calculation emissions are used the variable of fuel consumption and the unit’s emission factor, the emissions produced depend on the emission factor.
used. Fugitive and well specific vent emissions have low emission because they affect the amount of unit and emission factors. Comparison of total emission can be seen in Table 2.

### Table 2. Emission total for every simulation.

| Simulation          | Variable            | Value          | Emission (tonne/day) |
|---------------------|---------------------|----------------|----------------------|
|                     |                     |                | CO$_2$e   | SO$_2$e   |
| Base case           | Sour gas pressure   | 1,231 psig     | 1,527    | 0.3484   |
|                     | Feed gas flow rate  | 145.7 MMSCFD   |           |           |
|                     | Solvent             | MDEA           |           |           |
|                     | Spec sweet gas      | Sales Gas      |           |           |
|                     |                     |                |           |           |
|                     | Sour gas pressure   | 1,000 psig     | 1,534    | 0.3542   |
|                     | 800 psig            | 1,543          | 0.3607   |
|                     | 600 psig            | 1,554          | 0.3685   |
|                     | 160 MMSCFD          | 1,709          | 0.4018   |
| Variation of process parameter | Feed gas flow rate | 120 MMSCFD     | 1,25     | 0.2829   |
|                     | 100 MMSCFD          | 1,175          | 0.3058   |
|                     | 80 MMSCFD           | 1,066          | 0.3090   |
|                     | 60 MMSCFD           | 1,097          | 0.3781   |
|                     | Solvent             | DEA            | 1,522    | 0.3383   |
|                     | Spec sweet gas      | DEA, LNG1      | 2,652    | 0.7474   |
|                     |                     | DEA, LNG2      | 1,713    | 0.3106   |

#### 4.3. Effect of sour gas pressure variation

Emissions in the variation decreasing of source gas pressure will increase but not significantly because of the additional emissions generated from compressor units with low duty and fugitive emissions that have no significant effect. A comparison of total emission can be seen in Figure 14.

![Sour Gas Pressure vs Total Emission](image1)

(a) GHG Emission on CO$_2$e

![Sour Gas Pressure vs Total Emission](image2)

(b) Air Pollution on SO$_2$e

**Figure 14.** Comparison of total emission base case with the variation of sour gas pressure

(a) GHG emission on CO$_2$e and (b) Air pollution on SO$_2$e.

#### 4.4. Effects of gas flowrate variation

Emissions generated in the gas flow rate variations are not linear because changes in feed gas flow rate will affect emissions from reboiler units. There will be a minimum lean amine flow rate in reboiler emissions, which is in the variation of the gas capacity of 120 MMSCFD. Therefore the lowest emission of air pollution is produced. A comparison of total emission can be seen in Figure 15.
4.5. Effects of solvent type

Emissions generated in the use of DEA as a replacement for MDEA do not have a significant effect. However, besides the generated emission, the value of rich amine loading should be noted, determining the process’s success. Using MDEA solvent, the value of rich amine loading is 0.12 with a maximum value of 0.45-0.5, while using of DEA solvent, a value of rich amine loading is 0.675 with a maximum value of 0.35-0.4, it means that using the DEA solvent will cause potential corrosion compared to using MDEA solvent. The potential corrosion of using DEA solvent in this simulation can be reduced by increasing the flow rate or increasing DEA concentration in lean amine flow rate to the absorber. However, this change can result in higher absorption of sour gas by lean amine, and the consequence is higher emission released.

4.6. Effects of sweet gas spec

Emissions generated for the change of specification sweet gas from sales gas to LNG using DEA solvent will increase the total emissions because of higher CO₂ absorption impacts to higher CO₂ emissions. The lower SO₂e emission in "DEA, LNG2" compared to DEA for gas sales is caused by higher CO₂ and less water component in "DEA, LNG2" effect at a lower heating value compared to "DEA, gas sales", which is the heating value affects the emission of air pollution produced depending on the references of the emission factor.

Besides emissions generated, rich amine loading at "DEA, LNG1" will have a higher rich amine loading (0.345) compared to "DEA, LNG2" (0.254) because increasingly solvent concentrations will reduce rich amine loading where CO₂ and H₂S (as a cause of corrosion) will be bound to the DEA solvent affect the low potential for corrosion. On the other hand, increasing the amine flow rate will reduce the value of rich amine loading. Therefore the value of rich amine loading in "DEA, LNG1" is lower than "DEA, gas sales". A comparison of total emission can be seen in Figure 16.

Figure 15. Comparison of total emission base case with the variation of feed gas flow rate
(a) GHG emission on CO₂e and (b) Air pollution on SO₂e.

(a) GHG Emission on CO₂e

(b) Air Pollution on SO₂e

Feed Gas Flow Rate vs Total Emission

Feed Gas Flow Rate vs Total Emission
Figure 16. Comparison of total emission base case with the variation of sweet gas spec
(a) GHG Emission on CO₂e and (b) Air Pollution on SO₂e.

5. Conclusion
In this paper, we report developing an automated calculator for air and GHG emission in a gas sweetening unit, integrated in a UNISIM-based process simulator. The developed calculator is then used to perform simulation of several process parameters, emphasizing their effects on the estimated GHG and air emission (represented by CO₂e and SO₂e, respectively). Base case simulations using MDEA solvents and sales gas specifications produce 1,527 tonnes CO₂e/day and 0.348 tonnes SO₂e/day. The emission generated increases to 1,554 tonnes CO₂e/day and 0.368 tonnes SO₂e/day due to the compression system units at a decrease in sour gas pressure. Variation in the feed gas flow rate produces non-linear emissions because it affects emissions from reboiler units. DEA as a solvent produces total emissions of 1,522 tonnes CO₂e/day and 0.338 tonnes SO₂e/day. To produce LNG specifications using DEA solvents (with the comparison simulation is the variation using DEA solvent because in the base case simulation the solvent used is MDEA), the resulting emission load rises significantly to 2,652 tonnes CO₂e/day and 0.747 tonnes SO₂e/day because of more absorption by lean amine results in higher emissions released.

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