State Equation Determination of Cow Dung Biogas

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Abstract. A state function is a thermodynamic function which relates various macroscopically measurable properties of a system (state variable) describing the state of matter under a given set of physical conditions. A good understanding of a biogas state function plays a very important role in an effort to maximize biogas processes and to help predicting combustion performance. This paper presents a step by step process of an experimental study aimed at determining the equation of state of cow dung biogas. The equation was derived from the data obtained from the experimental results of compressibility (κ) and expansivity (β) following the general form of gas state equation \(dV = βdT + κdP\). In this equation, \(dV\) is gas volume variation, \(dT\) is temperature variation, and \(dP\) is pressure variation. From these results, we formulated a unique state equation from which the biogas critical temperature \((T_c)\) and critical pressure were then determined \((T_c = 266.7\,K, P_c = 5096647.5\,Pa)\).

1. Introduction
The equation of state of a gas is a mathematical expression describing a state of a gas under a given set of physical conditions. Having this equation, one can formulate a unique relationship between gas state variables such as temperature, volume, pressure, gas concentration, or internal energy \([1, 2, 3]\). Since this relation can be microscopically associated with a complex interaction of all the particles composing the gas, different gas or different gas mixture will result in different equation of state \([4]\). In fact, until now no single equation can describe behavior of all gasses. Even, one gas or one gas mixture under different physical condition is described with different equation of state.

Knowing equation of state of a gas or a mixture of gasses plays a very important role in many industrial processes especially on calculating phase equilibrium. By exploiting a gas equation of state, a minimum condition for achieving a phase equilibrium can be obtained \([5, 6, 7]\). Any thermodynamic processes carried out in such condition can thus save energy. In addition, by exploiting a gas equation of state, one can determine whether any processes can proceed under certain condition.

Biogas processing is one of interesting example that has drawn much attention \([8, 9]\). Upon combustion, biogas which mainly contains methane produces energy. Unfortunately, biogas cannot be treated in the same way as liquid petroleum gas. So far, biogas is used as a fuel both for cooking and powering motor vehicles in the form of compressed gas. Nowadays, improving biogas processing method as well as on studying biogas mixtures are intesively researched. This paper presents a simple method to derive the equation of state of cow dung biogas from simple experiment to determine gas compressibility and expansivity. From this equation, the important gas thermodynamic property, critical point, can be obtained.
2. Experiment

Figure 1 is experiment setup used to measure cow dung biogas isobaric expansivity and isothermal compressibility. It mainly contains gas container (1), water bath (2), thermometer (3), syrinx (4), load (5) and Mercury filled U Pipe (6). Gas container is filled with cow dung gas such that for a given mass load, piston was raised to a particular scale.

![Figure 1](image.png)

Figure 1. Experimental setup used to measure (a) isobaric expansivity and (b) isothermal compressibility of cow dung biogas. Set up consists of gas container (1), water bath (2), thermometer (3), syrinx (4), load (5) and Mercury containing U Pipe (6).

Figure 1 (a) is experimental set up used to measure isothermal compressibility carried out by following equation (2). Experiment was performed at several constant temperatures. Each carried out as function of mass load. The volume change resulted from a given mass load was read directly from syrinx scale after bringing the mercury level at the left side of the U pipe to point A. At this condition, the magnitude of the gas pressure was calculated from the different height of mercury surface levels (between A point and B point) using equation:

\[ \Delta P = \rho g h \]  

(1)

Where \( \rho \), \( g \), and \( h \) are mercury density, gravitational acceleration, and different height between points A and B, respectively.

Figure 1 (b) is isobaric expansivity experiment carried out by following equation (3). Constant gas pressure was created by keeping the mass load constant. As gas container was heated up to a constant temperature, the gas volume was change to some degree that can be read directly from syrinx scale.

3. Results and Discussion

3.1. Isothermal Expansivity

Isothermal expansivity experiment was carried out by observing the relation between cow dung temperature \( (T) \) and its volume change \( (\Delta V) \) (Figure 2). The way the volume change as function change is best fitted \( (R^2 = 0.9981) \) with the exponential function as

\[ \Delta V = a + b \frac{\exp(kT) - 1}{k} \]  

(2)
Where \(a\), \(b\), and \(k\) are -0.02375, \(4.63047 \times 10^{-9}\), and 0.9981, respectively. Remembering that the isobaric expansivity (\(\beta\)) is defined as

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P
\]

Figure 2. Volume change of cow dung gas as function of temperature measured at a constant pressure.

Figure 3. Volume change of cow dung gas as function of pressure measured at a constant temperature.

From equation (2), one can obtain

\[
\beta = \frac{1}{a + \frac{b}{k} (e^{(kT)})} \frac{d}{dT} \left( a - \frac{b}{k} + \frac{b}{k} e^{(kT)} \right)
\]

or

\[
\beta = \frac{e^{(kT)}}{ \left( \frac{a}{b} - \frac{1}{k} + \frac{1}{k} e^{(kT)} \right)}
\]

(4)

3.2. Isothermal compressibility

Isothermal compressibility is obtained in a similar way to that of finding isobaric expansivity. From figure 3, the curve is best fitted \((R^2 = 0.99759)\) with the equation:

\[
\Delta V = c \exp \left( -\frac{P}{d} \right) + f P + e
\]

(5)

Where \(c = 0.52\), \(d = 18088.80\), \(e = -0.36\) and \(f = -1.09 \times 10^{-5}\). Inserting equation (5) to the isothermal compressibility equation defined as

\[
\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

(6)

We found
\( \kappa = \frac{c \cdot e^{\left(\frac{-p}{d}\right)} - fd}{dc \cdot e^{\left(\frac{-p}{d}\right)} + ed + fdP} \)  

### 3.3. State Equation and Critical Point

State equation of any gas can be obtained from thermodynamic relation

\[
dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP
\]

Inserting equation (3) and (6) into equation (7) we found

\[
dV = \beta V dT - K dp
\]

Equation (9) is general state of equation. If isobaric expansivity \((\beta)\) and isothermal compressibility \((\kappa)\) are experinetally known, a state equation relating \(P, V,\) and \(T\) characterizing a gaseous state of a material can be derived. Bearing this in mind, the state equation of cow dung biogas can be derived by inserting equation (4) and (7) into equation (9):

\[
\frac{dV}{V} = \frac{b \cdot \exp(kt)}{(a - \frac{p}{k} + \frac{1}{k}) \cdot \exp(kt))} \cdot \frac{dV}{dT} - \frac{c \cdot \exp\left(\frac{-p}{d}\right) - fd}{dc \cdot \exp\left(\frac{-p}{d}\right) + ed + fdP} \cdot dP
\]

we found

\[
\ln V = \ln \left[ dc \cdot \exp\left(\frac{-p}{d}\right) + ed + fdP \right] + \ln \left[ \left( \frac{a}{b} - \frac{1}{k} + \frac{1}{k} \exp(kt) \right) \right]
\]

or

\[
V = \left[ dc \cdot \exp\left(\frac{-p}{d}\right) + ed + fdP \right] \left[ \left( \frac{a}{b} - \frac{1}{k} + \frac{1}{k} \exp(kt) \right) \right]
\]

Using state equation expressed by equation (12), one can then calculate the very important parameters usually used in a process dealing with phase transformation from gas phase to liquidus phase. They are critical temperature \((T_c)\), critical pressure \((P_c)\), and critical volume \((V_c)\). In pressure volume diagram (P-V diagram), critical point is isothermal line deflection point. At any temperatures above this isothermal line, a gas cannot be liquified no matter how much pressure is applied. Since critical point is a deflection point, this point can be calculated from the mathematical conditions

\[
\frac{\partial P}{\partial V} = 0 \quad \text{and} \quad \frac{\partial^2 P}{\partial V^2} = 0
\]

Inserting equation (12) into equation (13) and utilizing the reciprocal equation

\[
\left( \frac{dV}{dT} \right) = \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T}
\]

We found \(T = T_c = 266.7\) K and \(P = P_c = 5096647.5\) Pa. With this result, we can see that cow dung biogas cannot be liquified for the purpose of gas packaging in the same way as liquid petroleum gas (LPG) at room temperature. A new mixture of biogas with critical point higher than room temperature has to be found. For this purpose, critical point of each mixture can be calculated from gas equation of state derived from simple compressibility and expansivity experiment.
4. Conclusion

Cow dung biogas has been thermodynamically studied in order to derive its state equation. The equation was derived based on experimental results of isobaric expansivity and isothermal compressibility. We found that the equation of state of cow dung biogas is

\[ V = \left[ d c \exp \left( -\frac{P}{d} \right) + ed + f dP \right] \left( \frac{a}{b} - \frac{1}{k} + \frac{1}{k} \exp(kT) \right) \].

From this equation we calculated the critical temperature and pressure: \( T_c = 266.7 \text{ K} \), \( P_c = 5096647.5 \text{ Pa} \). From this experiment, it can be seen that cow dung biogas cannot be liquified for the purpose of gas packaging in the same way as liquid petroleum gas (LPG) at room temperature.

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