

A Novel Method of Modeling Simple Thermodynamic System: A Case Study of a Tank Model

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Abstract—In chemical process engineering, engineers are dealing with all kinds of models with arbitrary complexities. Nevertheless these models can be decomposed into a number of atomic, simple thermodynamic systems according to different modeling requirements. Simple thermodynamic system is, by definition, a system that is devoid of any internal adiabatic, rigid, and impermeable boundaries and is not acted upon by external force fields or inertial forces. The state of a simple thermodynamic system can be determined by some state variables. In this work, we present a new formulation of modeling the simple, open thermodynamic system. In this formulation, balance equations of mass and energy are formulated at first. Apart from the conventional approach, which solves energy balance by transforming the energy representation in terms of extensive quantities to temperature explicit representation which is in terms of intensive quantity, we keep the energy balance equation in the form of extensive quantity. The internal energy is calculated from Helmholtz free energy which contains a group of energy of ideal gas mixture and a group of residual energy that deviates from the ideal state. By providing the information of equation of state (EOS) and heat capacity, this procedure can be performed routinely and one of the great advantages is the calculations of all the relevant intensive quantities can be performed by evaluating the partial derivatives of Helmholtz free energy. A tank example which can be modeled as a simple open thermodynamic system according to this method has been built and presented.

Index Terms—modeling, thermodynamic system, energy balance, tank, Helmholtz.

I. INTRODUCTION

Modeling an thermodynamic system is required by many models used in chemical engineering as the units, chemical processes, even a plant can be built based on this generic thermodynamic system. The purpose of this paper is to introduce a novel formulation of model equations on this open system.

As the balance equations of an open system are obtained, transformation of the energy balance may be dealt with in two ways: 1) transform the extensive representation to temperature explicit representation, and 2) keep the form of the energy balance equation untouched. The conventional approach that has been widely used in the past is to transform the extensive representation of the internal energy to enthalpy by using thermodynamic correlation at first. Then take an approximate form of heat capacity correlation, normally is a function of temperature solely to establish the relation between temperature and enthalpy. Finally the time derivative of enthalpy can be converted to the time derivative of temperature. This transformation is straightforward and as a consequence, the system equations end up with T -explicit, ordinary differential

equation set. This approach is primary used when the system is single phase and the affection of pressure to enthalpy is not significantly large. The disadvantage of this approach is that the model generated is not so generic because in order to get the temperature derivative, the model has to undergo a series of assumptions and become a less generic system. This disadvantage led to the exploration of alternative mean for obtaining model representation.

The novel formulation intends to keep the extensive quantities in the balance equation. To find the relationship between internal energy and other desired intensive quantities, Helmholtz free energy is chosen as state variable describing the system energy. Each desired intensive quantities appears as the derivatives of the Helmholtz energy. This formulation is built based upon the rigorous concept of thermodynamic relations of state variables and the understanding of nonideal fluid behavior as well as the practical mathematical method, Legendre Transformation, which is used to convert the relations between U , H and A . The new formulation proposed in this paper decouples the contribution of ideal gaseous mixture and residual contribution to the Helmholtz energy and appears to be more flexible and generic since a wide variety of open thermodynamic systems with different equation of state specifications can be solved by modifying the residual part only. Additionally, the derivatives of Helmholtz energy can be determined by the use of symbolic or automatic differentiation which can improve the efficiency of model building.

Finally a stirred tank model that applies the derivation of such generic balance equation and the transformation has been demonstrated.

II. SIMPLE, OPEN THERMODYNAMIC SYSTEM

There is a special class of systems that plays a central role in the developments of chemical process models. These systems, which is referred as simple thermodynamic system. Simple thermodynamic system is, by definition, a system that is devoid of any internal adiabatic, rigid, and impermeable boundaries and is not acted upon by external force fields or inertial forces. The state of a simple thermodynamic system can be determined by some state variables.[2] An open system includes the mass, energy interactions between itself and environment which is existed as flows of extensive variables, and the production taking place within different chemical species. The open system corresponds to the “Lumped system” in many aspects which is the system considered as homogeneous that all the intensive variables do not show any spartial variation in the scalar field. All the state variables which describes the state

of instest, are uniform[4]. Another concept is the composite system which is a system composed of two or more simple subsystems. The behavior of each simple system results in the behavior of the composite system.

The process model can be recursively decomposed into sub-models and devices such as process units, parts of process units or phases, eventually into a number of elementary, simple, open thermodynamic systems being linked by connections. This model decomposition ideal has been applied into many practical modeling tools, such as Modeller[10], Modkit [7] and gPROMS [6], etc. Therefore the key part of formulations of various process model is essentially the formulation of a simple, open thermodynamic system.

III. CONVENTIONAL FORMULATION

Most of the algorithms handle a dynamic open thermodynamic system in the following steps: (1) formulate mass and energy balance equations (here we exclud the momentum balance for the reason of simplicity though eliminating fluid dynamics is not always the case) in the form of extensive quantities; and (2) transform the energy balance in terms of one of the extensive quantities, normally internal energy, to a temperature-explicit equation by manually analytical derivations together with a series of reasonable assumptions. An example from[4] illustrate this common approach:

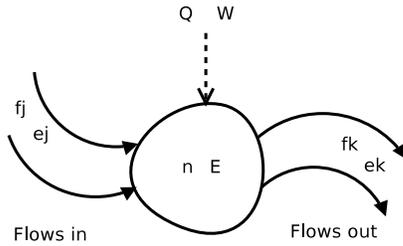


Fig. 1. General open system

A. Balance Equations

Expressions of mass and energy balance equations follow the conservative law of extensive quantities:

$$\frac{dn_i}{dt} = \sum_{j=1}^p f_{i,j} - \sum_{k=1}^q f_{i,k} + \nu_i rV \quad (1)$$

$$\begin{aligned} \frac{dE}{dt} &= \sum_{j=1}^p F_j (h + k_E + p_E)_j \\ &+ \sum_{k=1}^q F_k (h + k_E + p_E)_k + Q + W \end{aligned} \quad (2)$$

B. Transformation of Energy Balance Equation

1) *Assumption 1*: The kinetic (k_E) and potential energy (p_E) can be neglected lead to the right-hand side terms are written in terms of specific enthalpies. The left-hand side represents the total internal energy of the system.

$$\frac{dU}{dt} = \sum_{j=1}^p F_j h_j - \sum_{k=1}^q F_k h_k + Q + W \quad (3)$$

2) *Assumption 2*: In many cases, enthalpy is the preferable variable over internal energy. Applying the thermodynamic relation ($U = H - pV$) and assume p and V are constant so that the time derivatives of both two are neglected, then:

$$\frac{dH}{dt} = \sum_{j=1}^p F_j h_j - \sum_{k=1}^q F_k h_k + Q + W \quad (4)$$

3) *Assumption 3*: If the variation of specific enthalpy of the system due to pressure are not significant, such as the liquid system, the specific enthalpies of system and outlet are assumed to be equal. ($h = h_k \quad k = 1, \dots, q$), yields:

$$\frac{dH}{dt} = \sum_{j=1}^p F_j h_j - \sum_{k=1}^q F_k h + Q + W \quad (5)$$

4) *Assumption 4*: From Eq.(5) we see that the enthalpies are evaluated at temperature conditions of feeds (T_j) and also at the system temperature (T). By making certain assumptions about the enthalpy representation, further simplifications can be made. The enthalpy of the feed (h_j) can be written in terms of the system temperature T :

$$h_j(T_j) = h_j(T) + \int_T^{T_j} c_{pj} T dT \quad (6)$$

If we assume that c_p is a constant, then

$$h_j(T_j) = h_j(T) + c_{pj}(T - T_j) \quad (7)$$

Hence, the modified energy balance become:

$$\begin{aligned} \frac{dH}{dt} &= \sum_{j=1}^p F_j [h_j + c_{pj}(T_j - T)] \\ &- \sum_{k=1}^q F_k h + Q + W \end{aligned} \quad (8)$$

5) *Assumption 5*: Note that enthalpy is a function of temperature, pressure and the moles of species, giving $H = f(T, p, \mathbf{n})$ and hence the time derivative of this relationship is given by

$$\frac{dH}{dt} = \left(\frac{\partial H}{\partial T} \right)_{p, \mathbf{n}} \frac{dT}{dt} + \left(\frac{\partial H}{\partial p} \right)_{T, \mathbf{n}} \frac{dp}{dt} + \sum_i \left(\frac{\partial H}{\partial n_i} \right)_{T, p} \frac{dn_i}{dt} \quad (9)$$

The first term of right-hand side appears to have $c_p = \left(\frac{\partial H}{\partial T} \right)_{p, \mathbf{n}}$. In case of liquid systems, the term $\left(\frac{\partial H}{\partial p} \right)_{T, \mathbf{n}}$ is close to zero and is identically zero for ideal gases. The term $\left(\frac{\partial H}{\partial n_i} \right)_{T, p}$ is the partial molar enthalpy of species i . By substituting the mass balance, the last term can be transformed to a term containing the change in molar enthalpy for reactions and is denoted as ΔH_R , or the heat of the reaction. Hence, the final expression for the energy balance can be written as:

$$\begin{aligned} V \rho c_p \frac{dT}{dt} &= \sum_{j=1}^p F_j c_{pj} (T_j - T) \\ &+ rV (-\Delta H_R) + Q + W \end{aligned} \quad (10)$$

Now the energy balance equations has been transformed from temperature implicit expression to the temperature explicit expression. This is the most common form of energy balance for reacting systems. The first term on the right-hand side

represents the energy needed to adjust all feeds to the system conditions. The second represents the energy generation or consumption at the system temperature. The last two terms are the relevant heat and work terms.

IV. FORMULATION USING HELMHOLTZ FREE ENERGY

A. Legendre Transformation

It is known from thermodynamics that the relationship of internal energy $U = f(S, V, \mathbf{n})$ completely describes all of the stable equilibrium states of a simple system. This relationship is called the *Fundamental Equation* and the above expression is termed internal energy representation.

In the energy representation of the Fundamental Equation, the properties S, V, \mathbf{n} are treated as independent variables. This is not always convenient set of independent parameters. For example, since temperature can be measured much more conveniently than entropy, we might like to use T, V, \mathbf{n} as the independent variables.

The strategy behind the use of Legendre transforms is to shift the dependence of a function from one independent variable to another (the derivative of the original function with regard to this independent variable) by taking the difference between the original function and their product. They are used to transform among the various thermodynamic potentials.

For example, the Legendre transformation of U with respect to TS

$$A = U - TS \quad (11)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \mathbf{n}} \quad (12)$$

becomes a function of the intensive quantity, temperature, volume as natural variables[2].

B. Choice of Helmholtz Free Energy

In thermodynamics, the Helmholtz free energy is a thermodynamic potential which measures the “useful” work obtainable from constant temperature, constant volume thermodynamic systems. For a simple system, with a fixed number of particles, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature is held constant.

In principle it makes no difference whether a thermodynamic system choose U, H, A or G to construct the Fundamental equations. In addition, one can freely use the one from each of the following pairs: $S, T; V, P; \mathbf{n}, \boldsymbol{\mu}$ (These pairs of variables are usually referred to as *conjugate coordinates*) as independent variables[2]. For a system of constant composition U, H and S are the most dominant functions, however, in a mixture the chemical potential is becoming increasingly more important. In order to let T instead of S as a independent variable, either Gibbs free energy (G) or Helmholtz free energy (H) can be chosen since $\mu_i = (\partial G / \partial n_i)_{T, p, n_j \neq i} = (\partial A / \partial n_i)_{T, V, n_j \neq i}$

The residual function of Helmholtz free energy is defined as the difference in Helmholtz energy between a real fluid and

ideal gas at a given temperature, volume (not pressure) and composition. In this case the form of integration is simpler since T, V, \mathbf{n} are the canonical variable set of Helmholtz free energy. Moreover, applying the residual function of Helmholtz energy at same volume has another advantage of making the pressure explicit in the integration. This is especially beneficial as most of the existing equation of state are given as the function explicit in pressure rather than volume[3]:

$$\begin{aligned} A^{r,V}(T, V, \mathbf{n}) &= A(T, V, \mathbf{n}) - A^{ig}(T, V, \mathbf{n}) \\ &= \int_{\infty}^V \left(\frac{NRT}{V} - p \right) dV \end{aligned} \quad (13)$$

C. System Equations

The new derivation of system equations diverges from Eq.(3). Instead of transforming the extensive energy balance equation to temperature explicit, we keep the equation unchanged as the extensive quantities remaining in the expression.

$$\frac{dU}{dt} = \sum_{j=1}^p F_j h_j - \sum_{k=1}^q F_k h_k + Q + W \quad (14)$$

The next step is to construct the expression of Helmholtz energy and to link it with internal energy. The chemical potential of gas (either ideal or real) at certain temperature (T) and pressure (p) can be related to a reference chemical potential at same temperature (but at a reference pressure) together with a pressure integration. For ideal gas:

$$\mu_i^{ig}(T, p, \mathbf{n}) = \mu_i^{\circ}(T, p_{\circ}) + RT \ln \left(\frac{n_i p}{N p_{\circ}} \right) \quad (15)$$

$$\begin{aligned} \mu_i^{\circ}(T, p_{\circ}) &= h_{f,i}^{\circ}(T_{\circ}) + \int_{T_{\circ}}^T c_{p,i}^{\circ}(T) dT \\ &\quad - T s_i^{\circ}(T_{\circ}, p_{\circ}) - T \int_{T_{\circ}}^T \frac{c_{p,i}^{\circ}(T)}{T} dT \end{aligned} \quad (16)$$

Applying the thermodynamic relation $A = G - pV$, the Helmholtz energy of ideal gas mixture can be represented as:

$$\begin{aligned} A^{ig}(T, V, \mathbf{n}) &= G^{ig}(T, V, \mathbf{n}) - pV \\ &= \sum_i n_i \mu_i^{ig} - NRT \\ &= \sum_i n_i \mu_i^{\circ}(T, p_{\circ}) \\ &\quad + RT \sum_i n_i \ln \left(\frac{n_i RT}{V p_{\circ}} \right) - NRT \end{aligned} \quad (17)$$

Transforming Eq.(13), one get the representation of Helmholtz energy of real fluid as the sum of two contributions from ideal gas and residual.

$$A(T, V, \mathbf{n}) = A^{ig}(T, V, \mathbf{n}) + A^{r,V}(T, V, \mathbf{n}) \quad (18)$$

Subquently, the internal energy can be easily obtained by using integrated form of Legendre Transformation:

$$U = A + TS = A - T \left(\frac{\partial A}{\partial T} \right)_{V, \mathbf{n}} \quad (19)$$

Likewise, the enthalpy, which also appears in Eq.(3) can be presented as:

$$\begin{aligned} H &= A + TS + pV \\ &= A - T \left(\frac{\partial A}{\partial T} \right)_{V,\mathbf{n}} - \left(\frac{\partial A}{\partial V} \right)_{T,\mathbf{n}} V \end{aligned} \quad (20)$$

Note that the 1st-order derivatives of Helmholtz free energy with respect to its canonical variables generated as the *conjugate coordinates* of the canonical variables of Helmholtz free energy, and all of them are the functions of T, V, \mathbf{n} :

$$\begin{aligned} S(T, V, \mathbf{n}) &= - \left(\frac{\partial A}{\partial T} \right)_{V,\mathbf{n}} \\ &= - \left(\frac{\partial A^{ig}}{\partial T} \right)_{V,\mathbf{n}} - \left(\frac{\partial A^{r,V}}{\partial T} \right)_{V,\mathbf{n}} \end{aligned} \quad (21)$$

$$\begin{aligned} p(T, V, \mathbf{n}) &= - \left(\frac{\partial A}{\partial V} \right)_{T,\mathbf{n}} \\ &= - \left(\frac{\partial A^{ig}}{\partial V} \right)_{T,\mathbf{n}} - \left(\frac{\partial A^{r,V}}{\partial V} \right)_{T,\mathbf{n}} \end{aligned} \quad (22)$$

$$\begin{aligned} \mu_i(T, V, \mathbf{n}) &= \left(\frac{\partial A}{\partial n_i} \right)_{T,V} \\ &= \left(\frac{\partial A^{ig}}{\partial n_i} \right)_{T,V} + \left(\frac{\partial A^{r,V}}{\partial n_i} \right)_{T,V} \end{aligned} \quad (23)$$

Thus, combining the equations Eq.(14), Eq.(17), Eq.(18), Eq.(19),Eq.(20), Eq.(21), Eq.(22), Eq.(23) yields the complete set of system equations for an simple, open thermodynamic system.

V. DISCUSSION

A. Assumptions Reduction

A common job in dealing with the models in chemical process engineering is to narrow down the huge scale of potential models. To that end, a number of choices (assumptions) need to be made in the course of developing a model. Good modeling assumptions make works easier and don't adversely affect the results, while bad ones will produce results that diverge wildly from reality. For example, in the conventional approach, neglecting kinetic and potential energy would probably be a good assumption if momentum balance is not being taken into account. However, assumption 4, assuming the specific enthalpy of the feed can be written in terms of system temperature, Eq.(6), is not a very realistic one because specific enthalpy is a function of temperature, pressure and composition. Specific enthalpy in the inlet is normally different from the tank since the two compositions can hardly be the same, especially chemical reactions are taking place.

Considering some of these assumptions as fixed throughout the conventional approach, we can find it does not mean that there is no other valid assumption, but a single approach cannot cover everything in this context. For example, heat capacity can be evaluated by polynomials instead of being assumed as constant. Therefore, the new representation has the advantage of making minimum number of assumptions which brings the possibility of making more accurate model without losing too much informations.

B. Flexibility

The new formulation decouples the expression of Helmholtz free energy of real fluids into two groups. The ideal gas mixture group and a residual group. The contribution of the first group remains unchanged in any models while the second group is up to the modeler's choice. They can change the equation of state model, for example, to adapt the requirements of the model. Correspondingly, the residual group is being modified. There is no need to rearrange the whole set of the equation systems. As a consequence, new formulation instinctively facilitates extensions of adding more modeling flexibility that allows modeler to explore multiple design options to satisfy stated modeling goals and reuse the previous model with ease and accuracy.

C. Phases Equilibrium Calculation

Meanwhile the new formulation can also extend the treatment to multiphase equilibrium calculation with minimum modifications. By introducing temperature, pressure and component chemical potential for each phases and applying the criteria of phase equilibria:

$$\begin{aligned} T^\alpha &= T^\beta = \dots = T^\gamma = \dots = T^\pi \\ p^\alpha &= p^\beta = \dots = p^\gamma = \dots = p^\pi \\ \mu_i^\alpha &= \mu_i^\beta = \dots = \mu_i^\gamma = \dots = \mu_i^\pi \quad (i = 1, \dots, n_C) \end{aligned}$$

then, changing the chemical potential regarding to a whole system to the potentials to each phases, we obtain modified equation systems, and the transformations can then be carried out to compute the component compositions of chemical species in each phase.

Note that the above criteria for coexistence of phases in equilibrium indicates that temperatures, pressures and component chemical potentials are equal in each phases. These criteria are also valid if chemical reactions occur in one or more phases. They may not, however, necessarily be valid if there are any constraints to the flow of mass or energy between phases (To deal with problems in this category, it is preferable to separate the two phases into two systems).

D. Calculation of Derivatives

We noticed that a great deal of the efforts of making assumptions in the conventional approach is to transform the internal energy representation to the temperature explicit representation. In the new formulation, temperature is obtained by applying Legendre Transformation and this makes the analytical calculation of the partial derivatives of the Helmholtz free energy a simple task.

Several methods can be used to perform this calculation. Besides the numerical differentiation, it is of a particular interest to apply *symbolic differentiation*[8] in that it finds the derivative of a given formula with respect to a specified variable, producing a new formula as its output. This symbolic mathematics manipulate formulas to produce new formulas, rather than performing numeric calculations based on formulas. Therefore in order to make the formulation more generic, symbolic treatment is an excellent choice. Alternatively, *automatic differentiation* [1], [9] may become a good solution.

E. Minimum Information

In this representation, the Helmholtz free energy is the key element need to be solved in order to get other thermodynamic quantities. Now we have seen that through the mass and Helmholtz free energy representation, one can develop any thermodynamic quantities of a system. However, we are also keen to answer the question that what is the minimum information we need to establish the representation of Helmholtz free energy?

We can see that three parts of information are necessary. First is the relationship of $p - V - T$, i.e. the equation of state (EOS) of the real mixture that is explicit in pressure, $p = f(T, V, \mathbf{n})$. This is easy to get since most of the EOSs meet this requirement. Secondly a correlation for the heat capacity of pure component in ideal gas state should be available. The heat capacity, in most cases, is a function of temperature, $c_p^{ig}(T)$, and pressure (very occasionally). Many books containing the thermo-data express heat capacity in form of polynomial of temperature, like: $c_p^{ig}/R = A + BT + CT^2 + DT^{-2}$. This form is sufficient enough to calculate the integrations in Eq.(16). The last one should be provided the data of formation enthalpy and entropy at standard state of each pure component in the mixture.

VI. CONCLUSION

In this paper, the conventional approach of modeling general open thermodynamic systems is reviewed. The new approach of using Helmholtz free energy with its link to internal energy rather than transform the energy balance equation to temperature explicit equation is presented. It is concluded that the new approach uses less assumptions and therefore more accurate and more generic. New approach provides a more flexible formulation because new model can be implemented by only modifying on the residual part of the Helmholtz free energy. This is especially effective in development of a number of models with different EOS specifications, while new equations are easier to add and changes are less expensive to make.

In addition, it is demonstrated that certain modifications can transform a single phase system model to a multiphase system model. By using the new approach, one can determine the first order derivatives of Helmholtz free energy with respect to temperature, volume and molar mass through either numerical or symbolic treatments. The symbolic, interpretive solution can be easily adapted and the equation manipulation capabilities typically available in such formulation can be used to improve the efficiency of the modeling work.

APPENDIX I A TANK EXAMPLE

A stirred tank is being filled with gas mixture which consists of 5 components: nitrogen, methane, ethane, propane and n-butane. The temperature, molar flow rate and volumetric flow rate of inlet stream are given. Outlet stream is manipulated by a valve and its flowrate has a linear relationship with the pressure drop within the tank and the environment. The volume of the tank is $6m^3$. At initial state, the tank has some amount of gas inside, with its initial temperature, 298K. As

the gas mixture continuously feeds in, the state of the tank begin to change. Our work is to get the dynamic behavior of composition, temperature and pressure inside the tank.

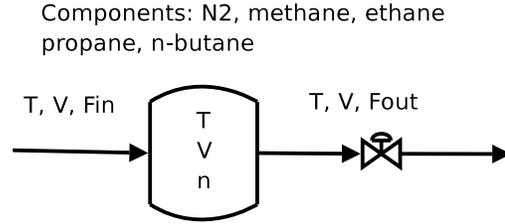


Fig. 2. Sketch of the tank example

A. Balance Equations

The general conservation balance for mass and total energy over the tank is given by:

$$\frac{dn_i}{dt} = f_{in,i} - f_{out,i} \quad (24)$$

$$\frac{dU}{dt} = F_{in}h_{in} - F_{out}h_{out} + Q + W \quad (25)$$

Since the kinetic and potential energy are neglected since they are not so important to this model $E \approx U$. Besides, there is no convective heat transfer to the tank, so $Q = 0$.

$$\frac{dU}{dt} = F_{in}h_{in} - F_{out}h_{out} + Q + W \quad (26)$$

Now we introduce some new variables particularly for transfer of extensive quantities, also known as flows. We apply the symbol $\hat{\cdot}$ to denote the transfer. Thus, \hat{H} means the enthalpy transfer which is a certain amount of enthalpy transferred within a certain period of time. It has the unit of enthalpy divided by unit of time. Similarly, we can define \hat{A} , \hat{S} , and \hat{V} representing the Helmholtz free energy flow, entropy flow and volumetric flow, respectively.

$$\begin{aligned} U_{tank} &= (A + TS)_{tank} = U_{tank}(T_{tank}, V_{tank}, \mathbf{n}) \\ &= n \cdot u_{tank}(T_{tank}, V_{tank}, \mathbf{x}) \end{aligned} \quad (27)$$

$$\begin{aligned} \hat{H}_{in} &= \left(\hat{A} + T\hat{S} + p\hat{V} \right)_{in} \\ &= \hat{H}_{in}(T_{in}, \hat{V}_{in}, \mathbf{f}_{in}) \end{aligned} \quad (28)$$

$$\begin{aligned} \hat{H}_{out} &= \left(\hat{A} + T\hat{S} + p\hat{V} \right)_{out} \\ &= \hat{H}_{out}(T_{out}, \hat{V}_{out}, \mathbf{f}_{out}) \end{aligned} \quad (29)$$

According to the Euler's rule, enthalpy flow is a function which is homogeneous to the first degree of molar mass flow. If the molar mass decreased by a factor of F_{in} , the value of \hat{H} will be decreased by a factor of F_{in} as well, namely, the specific enthalpy is obtained.

$$\begin{aligned} h_{in} &= \hat{H}_{in}(T_{in}, \hat{V}_{in}, \mathbf{f}_{in}) / F_{in} \\ &= h_{in}(T_{in}, \hat{V}_{in}, \mathbf{x}_{in}) \end{aligned} \quad (30)$$

$$\begin{aligned} h_{out} &= \hat{H}_{out}(T_{out}, \hat{V}_{out}, \mathbf{f}_{out}) / F_{out} \\ &= h_{out}(T_{out}, \hat{V}_{out}, \mathbf{x}_{out}) \end{aligned} \quad (31)$$

in which,

$\mathbf{x} = \mathbf{n}/n$, $\mathbf{x}_{in} = \mathbf{f}_{in}/F_{in}$, $\mathbf{x}_{out} = \mathbf{f}_{out}/F_{out}$ and $n = \sum_i n_i$.

The outlet flow has the same intensive quantities as those inside the tank and the outlet flow rate is controlled by a valve that is proportional to the pressure difference between the tank and surrounding.

$$T = T_{out} \quad (32)$$

$$p = p_{out} \quad (33)$$

$$\mathbf{x} = \mathbf{x}_{out} \quad (34)$$

$$F_{out} = CV \cdot \left(\frac{p - p_{env}}{p_o} \right) \quad (35)$$

B. Equation of State

Redlich-Kwong equation is used as equation of state for calculation of gas phase properties

$$p = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \quad (36)$$

$$\begin{aligned} A^{r,V} &= \int_{\infty}^V \left(\frac{NRT}{V} - p \right) dV \\ &= NRT \ln \left(\frac{V}{V-Nb} \right) + \frac{Na}{bT^{1/2}} \ln \left(\frac{V}{V+Nb} \right) \end{aligned} \quad (37)$$

The derivatives of $A^{r,V}$ for Redlich-Kwong Model:

$$\left(\frac{\partial A^{r,V}}{\partial T} \right)_{V,n} = NR \ln \frac{V}{V-B_c} + \frac{A_T}{B} \ln \frac{V}{V+B_c} \quad (38)$$

$$\left(\frac{\partial A^{r,V}}{\partial V} \right)_{T,n} = NRT \frac{B_c}{V(V-B_c)} - \frac{A_c}{V(V+B_c)} \quad (39)$$

$$\begin{aligned} \left(\frac{\partial A^{r,V}}{\partial n_i} \right)_{T,V} &= RT \ln \left(\frac{V}{V-B_c} \right) + NRT \frac{b_i}{V-B_c} \\ &+ \frac{1}{B_c} \left(A_i - \frac{A_c b_i}{B_c} \right) \ln \left(\frac{V}{V+B_c} \right) \\ &- \frac{A_c b_i}{B_c (V+B_c)} \end{aligned} \quad (40)$$

The coefficients are defined below:

$$\Omega_a = \frac{1}{9(2^{1/3}-1)}$$

$$a_i = \Omega_a \frac{R^2 T_{c,i}^{5/2}}{p_{c,i}}$$

$$\Omega_b = \frac{2^{1/3}-1}{3}$$

$$b_i = \Omega_b \frac{RT_{c,i}}{p_{c,i}}$$

$$a = \left(\sum_i a_i^{1/2} y_i \right)^2$$

$$b = \sum_i b_i y_i$$

$$A_c = \sum_i \sum_j \left(\frac{a_i a_j}{T} \right)^{1/2} n_i n_j = \left(\sum_i \alpha_i^{1/2} n_i \right)^2$$

$$B_c = \sum_i b_i n_i$$

$$A_T = -\frac{A_c}{2T}$$

$$A_i = 2\alpha_i^{1/2} \sum_j \alpha_j^{1/2} n_j = 2(\alpha_i A_c)^{1/2}$$

$$\alpha_i = \frac{a_i}{T^{1/2}}$$

C. Thermodynamical Data

Constants in equation $c_p^{ig}/R = A + BT + CT^2 + DT^{-2}$, T (kelvins) from 298 to T_{max} , together with some other thermodynamic properties of specified components [5].

	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
T_{max}	2000	1500	1500	1500	1500
c_p^{ig}/R	3.502	4.217	6.369	9.001	11.928
A	3.280	1.702	1.131	1.213	1.935
$10^3 B$	0.593	9.081	19.225	28.785	36.915
$10^6 C$	-2.164	-5.561	-8.824	-11.402
$10^{-5} D$	0.040				
h_f [kJ/mol]	0.000	-74.873	-84.684	-103.847	-126.148
s [J/K mol]	191.609	186.214	229.602	270.019	310.227
T_c [K]	126.2	190.4	305.4	369.8	425.2
p_c [bar]	33.9	46.0	48.8	42.5	38.0

D. Simulation Results

The volume of the tank is $6m^3$. Gaseous inflow is fed at 298K with the volumetric rate $0.06m^3/s$ and molar flow rate 50mol/s. The composition of the inflow is set at $\mathbf{x}_{in} = [0.05, 0.35, 0.20, 0.25, 0.15]$. The chosen reference state is at $T_o = 298.15K$ and $p_o = 101325Pa$. At initial state, the tank contains 5000mol mixture with the composition $\mathbf{x}_{tank,ini} = [0.05, 0.35, 0.20, 0.25, 0.15]$ at the temperature 298K.

The model has been implemented in Matlab 7. The simulation time was specified from 0 to 2000 seconds. As shown in Fig.(3) and Fig.(4). At the beginning, the inhold of tank tends to increase as the inlet flow rate is larger than outlet. As the result, the temperature and pressure inside the tank increase sharply. Later, with the escalating pressure difference between the tank and the environment, outlet flow rate become larger until it equals the inflow rate. It's shown the model reached the steady state after about 600 seconds and this result completely corresponds to the conventional method.

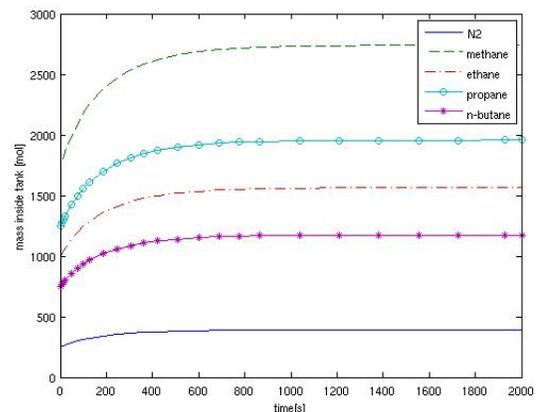


Fig. 3. Molar mass profile inside the tank

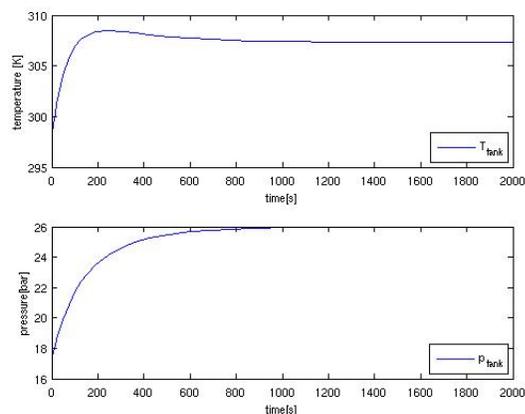


Fig. 4. Temperature and pressure profile inside the tank

NOMENCLATURE

A	Helmholtz free energy, first virial coef.
\hat{A}	Helmholtz free energy flow
B, C, D	virial coefficients
CV	valve coefficient
E	energy
F	molar flow rate
G	Gibbs free energy
H	enthalpy
\hat{H}	enthalpy flow
ΔH_R	heat of reaction
N	total molar mass
Q	heat
R	gas constant
S	entropy
\hat{S}	entropy flow
T	temperature
T_c	critical temperature
T_{max}	maximum suitable temperature
U	internal energy
V	volumn
\hat{V}	volumetric flow
W	work
\mathbf{f}	vector of molar flow rate
\mathbf{n}	vector of component molar mass
\mathbf{x}	vector of composition
c_p	specific heat capacity
e	specific energy
f	component molar flow rate
h	specific enthalpy
h_f	specific enthalpy of formation
k_E	specific kinetic energy
n	component molar mass
n_C	component number
p	pressure
p_o	reference pressure
p_c	critical pressure
p_E	specific potential energy
r	reaction rate
s	specific entropy
t	time
u	specific internal energy
a, b, a_i, b_i	coefficients in Redlich-Kwong EOS
A_c, B_c, A_T, A_i	coefficients in derivatives of RK model

Greek letters

ν	stoichiometric coefficient
μ	chemical potential
ρ	density
Ω_a, Ω_b	coefficients in Redlich-Kwong EOS

Subscripts

i	component index
j	inflow index
p	inflow number
k	outflow index
q	outflow number
\circ	at reference state
in	inflow
out	outflow
$tank$	tank
env	environment
ini	at initial state

Superscripts

r	residual
V	constant volumn
ig	ideal gaseous mixture
\circ	at reference state
α, β, γ	phase index

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