Thermodynamic Modeling of the High Temperature Shift Converter Reactor Using Minimization of Gibbs Free Energy

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Abstract—The equilibrium chemical reactions taken place in a converter reactor of the Khorasan Petrochemical Ammonia plant was studied using the minimization of Gibbs free energy method. In the minimization of the Gibbs free energy function the Davidon–Fletcher–Powell (DFP) optimization procedure using the penalty terms in the well-defined objective function was used. It should be noted that in the DFP procedure along with the corresponding penalty terms the Hessian matrices for the composition of constituents in the Converter reactor can be excluded. This, in fact, can be considered as the main advantage of the DFP optimization procedure. Also the effect of temperature and pressure on the equilibrium composition of the constituents was investigated. The results obtained in this work were compared with the data collected from the converter reactor of the Khorasan Petrochemical Ammonia plant. It was concluded that the results obtained from the method used in this work are in good agreement with the industrial data. Notably, the algorithm developed in this work, in spite of its simplicity, takes the advantage of short computation and convergence time.

Keywords—Gibbs free energy; converter reactors; Chemical equilibrium.

I. INTRODUCTION

STUDY of chemical and physical phase equilibrium plays an important role in the chemical process design such as synthetic gas production from steam reforming of methane. Smith [1] classified the algorithm for chemical reaction equilibrium calculation into two main categories, the stoichiometric and non-stoichiometric methods.

In the stoichiometric methods the independent reactions and their stoichiometric coefficients are known and the equilibrium constants are used for the necessary calculations. In the non-stoichiometric methods the Gibbs free energy function in terms of composition, temperature and pressure will be minimized. The advantage and drawbacks of the methods are as follows:

1) While in the stoichiometric method the independent reactions should be totally defined, in the non-stoichiometric method the necessary information is the number of components and their formation Gibbs free energy.
2) The first method is highly sensitive to the values considered as initial guesses in the phase equilibrium calculations. This, in fact, makes the phase chemical equilibrium calculations untraceable and time consumable. But in the second method developing the new optimization procedure the previous pitfalls were removed.
3) In the first method it is necessary to have the related data on the equilibrium constants for the chemical reaction occurred in the system and it doesn't lend itself to standardization so as to allow a general program to be written for computer solutions.

White et al. [2-3] calculated the equilibrium concentration in ideal gas phase using the minimization of Gibbs free energy method. They converted the logarithmic form for Gibbs free energy of system into a quadratic function using the Taylor expansion method.

Dluzniewski and Adler [4] developed the algorithm proposed by White et al. for a heterogeneous mixture containing three solid, liquid and vapor phases.

Heidemann, [5] minimized the Gibbs free energy function for the mixture of water and hydrocarbons in a three phase system (liquid-liquid-vapor) using the Steepest Descant method. Gautam, and Seider [6] used the phase stability analysis method in order to improve the minimization procedure. Jarungthammachote and Dutta [7] minimized the Gibbs free energy and it was application to spouted bed and spout-fluid bed gasifiers. Li et al. [8] used a non-stoichiometric equilibrium model (minimization of Gibbs free energy) to predict the producer gas composition from a circulating fluidized bed coal gasifier. An equilibrium model for studying the biomass gasification with steam in a fluidized bed gasifier was presented by Schuster et al. [9]. They concluded that the accuracy of an equilibrium model is sufficient for thermodynamic considerations. However, they mentioned that thermodynamic equilibrium may not be achieved, mainly because of the relatively low operation temperature. However, lower temperatures than that may not completely meet the equilibrium condition. Li et al. [10]

employed the equilibrium model to predict the producer gas compositions, product heating value and cold gas efficiency for circulating fluidized bed gasification. The prediction results showed good agreement with experimental data.

In this work the equilibrium chemical reactions occurred in a Converter reactor of the Khorasan Petrochemical Ammonia plant was studied using the minimization of Gibbs free energy method. In the minimization of the Gibbs free energy function the Davidon–Fletcher–Powell (DFP) optimization procedure [11] using the penalty terms in the well-defined objective function was used. It should be noted that in the DFP procedure along with the corresponding penalty terms the Hessian matrices for the composition of constituents in the reformer reactor can be excluded. This, in fact, can be considered as the main advantage of the DFP optimization procedure. Also the effect of temperature and pressure on the equilibrium composition of the constituents was investigated.

II. THEORY

Assuming the total number of moles of entering component i ($F_{in,i}$), temperature and pressure the total number of moles of component i at equilibrium condition, n(i) should be determined using the following equations:

$$(dG^t)_{T,p} = 0 \qquad (1)$$

$$(G^t)_{T,p} = G(n_1, n_2, ..., n_N) \qquad (2)$$

$$G(n) = \sum_{j=1}^{Nc} \sum_{i=1}^{Np} n(i,j)\mu_{ij} \qquad (3)$$

The chemical potential of component i expressed as:

$$\mu_{ij} = \mu^0_{ij} + RT \ln(f_{ij}/f^0_{ij}) \qquad (4)$$

Where

$$\mu^0_{ij} = \Delta G^f_{ij} \qquad (5)$$

$$\mu^0_{ij} = \Delta G^f_j \qquad (6)$$

The following objective function is used to calculate the unknown variables:

$$G(n) = \sum_{j=1}^{Nc} \sum_{i=1}^{Np} n(i,j)\left[\Delta G_j^f + RT \ln(f_{ij}/f^0_{ij})\right] \qquad (7)$$

As aforementioned the DFP optimization procedure was used to minimize the objective function. Using the penalty function principle the objective function is converted to the following equation as:

$$R(x^{(k)}, r^{(k)}) = R(x^{(k)}) + I(r^{(k)})\sum_{j=1}^{p} H_j^2(x) + \sum_{j=1}^{m} r^{(k)}G_j\left[g_j(x)\right] \qquad (8)$$

The interaction parameters obtained by DFP. The iterative procedure of this method can be stated as follows:

1- Start with an initial point X_1 and a $n \times n$ positive definite symmetric matrix H_1. Usually H_1 is taken as the identity matrix I. Set iteration number as $i = 1$.

2- Compute the gradient of the function, ∇f_i, at the point X_i, and set:

$$S_i = -H_i\nabla f_i \qquad (9)$$

3- Find the optimal step length λ_i^* in the direction S_i and set:

$$X_{i+1} = X_i + \lambda_i^* S_i \qquad (10)$$

Test the new point X_{i+1} for optimality. If X_{i+1} is optimal, terminate the iterative process. Otherwise, go to step (5).

5- Update the H matrix as:

$$H_{i+1} = H_i + M_i + N_i \qquad (11)$$

Where

$$M_i = \lambda_i^* \frac{S_i S_i^T}{S_i^T Q_i} \qquad (12)$$

$$N_i = -\frac{(H_i Q_i)(H_i Q_i)^T}{Q_i^T H_i Q_i} \qquad (13)$$

$$Q_i = \nabla f(X_{i+1}) - \nabla f(X_i) = \nabla f_{i+1} - \nabla f_i \qquad (14)$$

6- Set the new iteration number $l = i+1$, and go to step (2).

III. RESULTS AND DISCUSSION

Table I to IV represents the experimental data 32 bar for the converter reactor of the KHORASN petrochemical Ammonia plant. The data collected at different days of working hours of the converter reactor. Figs. 1 to 4 presents the results obtained for the equilibrium composition of the products of the converter reactor using the method proposed in this work.

As seen good agreement between the calculated and industrial results were achieved using the method proposed in this research. Fig. 5 shows the path of the optimization studied in this work by method of the DFP optimization procedure. As seen the convergence obtained rapidly and with only five iterations. As mentioned before the procedure used in this work is independent of the initial guess.

TABLE I
FIRST DAY

	Tin= 350 , Tout= 413 (^{o}C)	
	Feed (Mol Percent)	Product (Mol Percent)
CO_2	7.3	15.12
CO	13.02	3.49
H_2	56.19	59.88
Ar	0.27	0.25
CH_4	0.43	0.39
N_2	22.79	20.88

TABLE II
SECOND DAY

	Tin= 349 , Tout= 412 (^{o}C)	
	Feed (Mol Percent)	Product (Mol Percent)
CO2	9.6	15.76
CO	11.57	2.49
H2	55.67	60.34
Ar	-	-
CH4	0.46	0.43
N2	23.6	20.98

TABLE III
THIRD DAY

	Tin= 349 , Tout= 411 (^{o}C)	
	Feed (Mol Percent)	Product (Mol Percent)
CO2	8.29	15.69
CO	11.95	2.53
H2	57.1	60.71
Ar	-	-
CH4	0.47	0.44
N2	22.19	20.63

TABLE IV
FOURTH DAY

	Tin= 349 , Tout= 412 (^{o}C)	
	Feed (Mol. Percent)	Product (Mol Percent)
CO2	8.7	15.86
CO	11.63	2.52
H2	56.75	60.31
Ar	-	-
CH4	0.52	0.47
N2	22.4	20.84
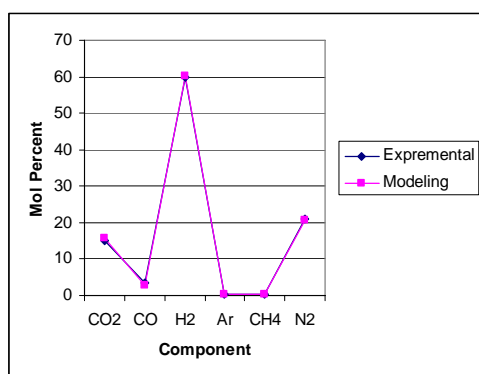
Fig. 1 Comparing the result model with output data from Table I
(Tout of model= 418.95 ^{o}C)
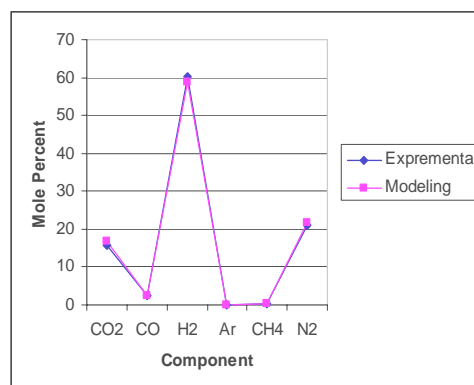
Fig. 2 Comparing the result of model with output data from Table II
(Tout of model= 408.354 ^{o}C)
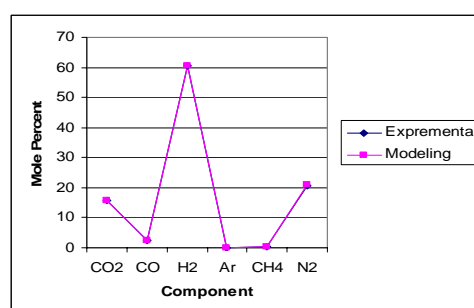
Fig. 3 Comparing the result of model with output data from table III
(Tout of model= 409.515 ^{o}C)
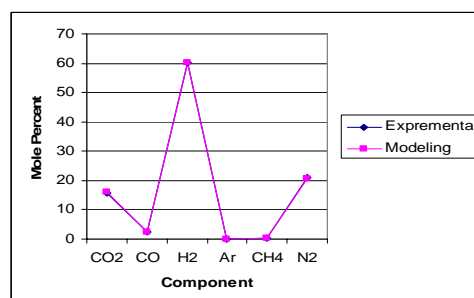
Fig. 4 Comparing result of model with output data from Table IV
(Tout of model= 409.482 ^{o}C)

Thermodynamics system:

The water-gas shift reaction (WGRS):

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (15)$$

ΔH^o= -41.09 KJ.mol^{-1}, ΔG°= -28.6 KJ.mol^{-1}

Is a reversible slightly exothermic chemical reaction [12] with an equilibrium constant that decreases with increasing temperature (Fig. 6). Since the reaction is

exothermic and reversible, WGRS is, for thermodynamic and kinetic reasons, normally performed in two steps. Industrially, WGSR is carried out at tow temperature regimes, high temperature (583-803 K) and low temperature (between 473- 523 K) shift reactions.

The effects of feed temperature into reactor on conversion of CO to CO_2

As it is seen on fig.6, the reaction of conversion of CO to CO_2 in HTS reactor reaches to equilibrium at 500 °C. The equilibrium of the reaction will lead to an increase in the amount of CO exiting from the reactor if the temp of the whole reactor rises.

On the software provided by the thermodynamic modeling, if the feed temperature into reactor HTS is assumed 460 °C, the exit temperature of the products will reach up to 502 °C. The Model shows the amount of mole percent of CO 4.7 which is equal to exiting CO on fig. 6. Thus it is concluded that the thermodynamic model bears acceptable results.

Now, the effects of temperature on converting CO to CO_2 within the temperature range of 310– 530 °C under constant pressure will be reviewed. The Conversion of CO to CO_2 is shown in temperatures between 310-530 °C which produce with model in Fig. 7.

IV. CONCLUSION

The equilibrium chemical reactions taken place in a converter reactor of the Ammonia unit for a specified Petrochemical Complex (PC) was studied using the minimization of Gibbs free energy method. In the minimization of the Gibbs free energy function the Davidon–Fletcher–Powell (DFP) Optimization procedure using the penalty terms in the objective function was used. The results obtained in this work were compared with the data collected from the converter reactor of Ammonia unit in a specified petrochemical complex. It was concluded that the results obtained from the method used in this work are in good agreement with the industrial data. Notably, the algorithm developed in this work, in spite of its simplicity, takes the advantage of short computation and convergence time.
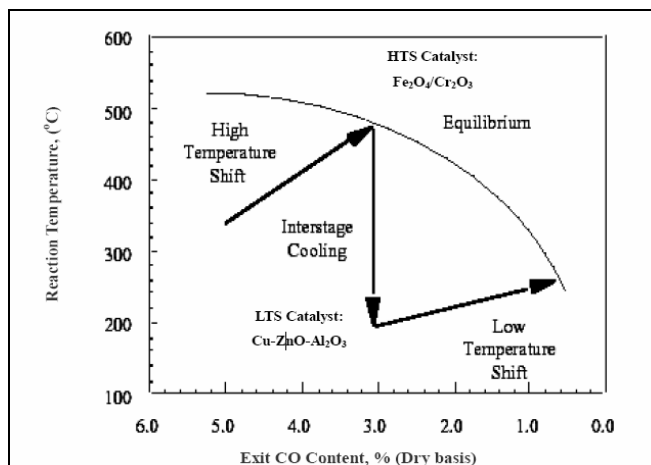

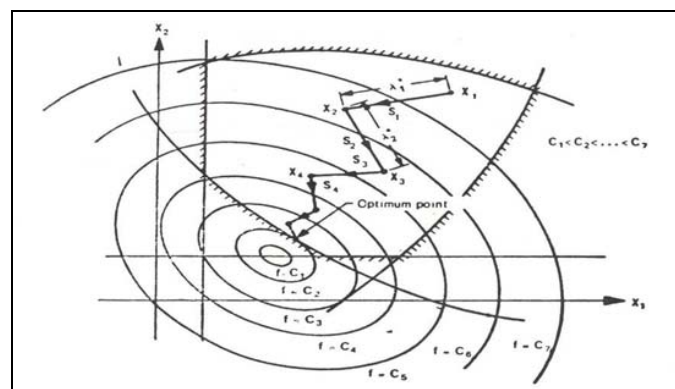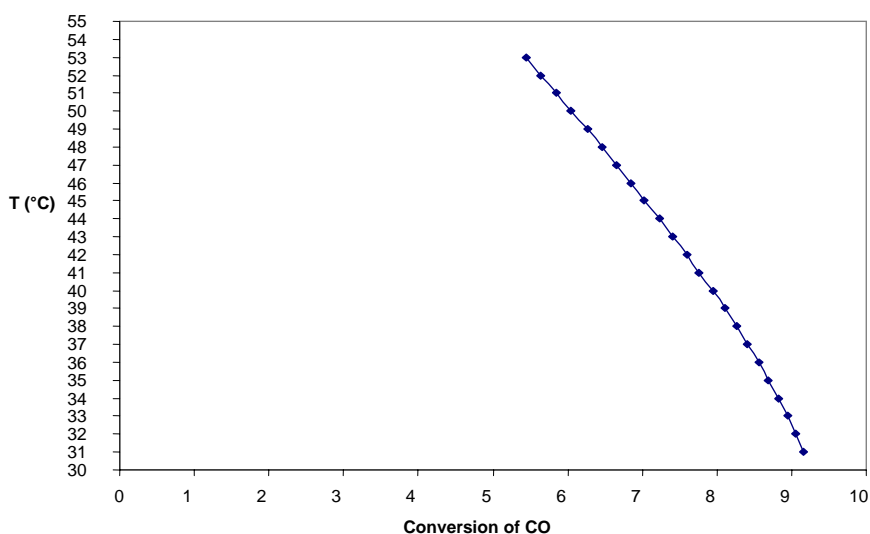Fig. 6 Schematic graph of water gas shift reaction [12]

Fig. 5 The optimization path for reformer reactor using the DFP Optimization Procedure

Fig. 7 The Conversion of CO to CO2 versus feed temperature (Between 310-530 ^{o}C)

Nomenclatures

G^t	*total Gibbs free energy of system*
f_{ij}	*fugacity*
f^o_{ij}	*fugacity in Standard state*
ΔG^f_{ij}	*Standard Gibbs free energy of formation*
R	*Universal gas constant*
H	*Hessian matrix*
S_i	*direction*
T	*Temperature*

Greek letters

μ	*chemical potential*
λ^*_i	*step length*

Superscripts

o	*Standard reference state*
T	*Matrix transposed*

Subscripts

i	*Chemical element*
j	*Chemical element*

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