Paper No.513

MASS BALANCE CALCULATION METHOD IN METHANE-STEAM REFORMING.

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ABSTRACT:

An attempt was made to calculate the reaction product compositions in moles on a wet basis obtained from experimental work were substituted into equilibrium expression for the methane-steam and the watergas-shift reactions and equilibrium constant calculated. A mass balance calculation method has been developed for the reformed gas composition obtained experimentally from methane-steam reforming at the molar ratio 1:x.[7]

INTRODUCTION:

Methane represents the simplest alkane capable of being reformed. The design of methane-steam reforming processes and the product compositions are calculated using a combination of two equations representing the methane-steam and the carbon-monoxide Shift reaction (1,2,3).

Endothermic $CH_4 + H_2O$ ------ $CO + 3H_2$ (1)

Exothermic $CO + H_2O$ ------ $CO + H_2$ (2)

The equilibrium compositions will depend on temperature, operating pressure and steam-methane ratio. For equilibrium at a particular temperature, the equilibrium constants for the reactions (1) and (2) are as follows:

For reaction (1) K1 = $$\frac{PCO\, p(H_2)^3}{PCH_4 p\, H_2o} = \frac{n\,CO\, n\,(H_2)^3}{n\,CH_4\, n\,H_2O}$$

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For reaction (2) K2 = $\frac{PCO_2\, pH_2}{PCo\, pH_2O} = \frac{nCO\ nH_2}{nCO\ nH_2O}$ (4)

The gases are assumed to be ideal, n is the sum of moles of gas at equilibrium and P is the total pressure. If values of K1 and K2 are known at a given temperature then for a specified total pressure and initial methane-steam ratio the number of moles of each component at equilibrium may be determined (4). A mass balance calculation method has been developed for the reformed gas composition obtained experimentally from methane-steam reforming at the molar ratio 1:x.

DEVELOPMENT OF EQUATIONS:

Suppose, initially, S moles of steam are present per mole of methane. If X is the conversion of methane by reaction (1) and Y is the conversion of carbon-monoxide by reaction (2), then the number of moles of each component present at equilibrium can be calculated as follows:

$$CH_4 + H_2O = CO + 3H_2$$

number of moles: 1-x s-x-y x-y 3x+y

$$CO + H_2O = H_2 + CO_2$$

number of moles: x-y s-x-y 3x+y Y

i.e.

$nCH_4 = 1-x$

$nH2 = 3x+y$

$nH_2O = s-x-y$

$nCO_2 = y$

$nCO = x-y$

Total (n) = 1+8+2x

Now equations (3) and (4) may be written

$$K1 = \frac{(x-y)\ (3x+y)^3}{(1-x)\ (s-x-y)} \quad (5)$$

and

$$K2 = \frac{(y)\ (3x+y)}{(x-y)\ (s-x-y)} \quad (6)$$

It is customary to report the produce composition data in steam reforming reactions on a steam free basis (dry basis) since the steam is not a constituent in any of the synthesis gases produced or in the reformed gas when used as a fuel. The above equations are then solved simultaneously for x and y. Solution is best done by an iterative technique (5).

The calculations mentioned above can be used to predict the theoretical reformed product gas composition at equilibrium for methane-steam reforming for any range of steam ratio, temperature and pressure. Then the number of moles of each component is obtained at equilibrium constants (3) & (4) for a specified temperature, since these equilibrium constants are not affected by steam ratio or pressure except the temperature.

THE MASS BALANCE CALCULATION METHOD FOR THE REFORMED GAS COMPOSITIONS:

The calculation of the reformed gas composition for any type of process and for any set of operating variables can be carried out by the three element balances equations for C-atom balance, H-atom balance, O-atom balance and two equilibrium relationships (6).

Mass balance calculation for methane-steam reforming.

Mass balance calculation of the reformed gas composition for methane-steam reforming at the molar ratio 1:x

$$CH_4 + xH_2O = CH_4 + H_2 + CO_2 + H_2O + CO \qquad (7)$$

For Carbon-free operation, let the output be:

Methane	CH_4 : a moles
Hydrogen	H_2 : b moles
Carbon dioxide:	CO_2 : c moles,
Steam	H_2O : d moles,
Carbon monoxide	CO : e moles.

The element balances give the following relations:

C-atom balances : $a + c + e = 1$ (8)

H2-mole balances : $2a + b + d = x+2$ (9)

O-atom balances : $2c + d + e = x$ (10)

Equation (10) can be written as

$d = x - 2c - e$ (10)

Equation (11) is obtained by subtracting equation (8) for equation (9).

$$a + b + d - c - e = x + 1 \quad (11)$$

Put the value of d from (10) in equation (11)

$$a + b + x - 2c - e - c - e = x + 1$$

$$a + b = 3c + 2e + 1 \quad (12)$$

On dry basis (water-free) the reformed gas composition as mole % is as follows:

$$\frac{a}{a + b + c + e} = CH_4 \quad (13$$

$$\frac{b}{a + b + c + e} = H_2 \quad (14)$$

$$\frac{c}{a + b + c + e} = CO2 \quad (15)$$

$$\frac{e}{a + b + c + e} = CO \quad (16)$$

Equations (15) and (16) can be written as

$$\frac{c}{CO2} = a + b + c + e \quad (15)$$

$$\frac{e}{CO} = a + b + c + e \quad (16)$$

$$\frac{c}{CO2} = \frac{e}{CO}$$

$$c = \frac{CO2}{CO} \quad 17)$$

To solve equaltion (15) substitute the value of (a+b) from equation (12) into (15).

$$\ldots c \qquad = 3c + 2e + 1 + c + e$$

$$c$$

$$CO2 = 4c + 3e + 1 \qquad (18)$$

Then, from the experimental infrared analysis the values for CO_2 and CO (on dry basis) can be put into equation (17), to give the value of c in terms of e. This value of c is further substituted in equation (18) to give the value of e, which is then substituted in equation (17), to give the value for c. The values of c and e are then substituted in equation (8), to give a value for a.

$$a + c + e = 1 \qquad (8)$$

The values of c and e are further substituted into equation (10) this gives the value for d.

$$d = x - 2c - e \qquad (10)$$

Now the equation (9) gives the value for b by substitution of a and d. The values obtained for a, b, c,d, and e are divided by the total number of moles and multiplied by 100. This gives the mole percentage on a wet basis for an equilibrium gas composition. To check whether the reaction approaches equilibrium the values for the above five species are substituted into the equilibrium constants for the reactions (1) and (2).

CONCLUSIONS:

The following conclusions can be drawn from the present study:

(i) A mass-balance calculation method has been developed and presented for the reformed gas composition obtained experimentally from methane steam reforming at the molar ratio 1:x.

(ii) By putting the values for CO2 and CO (on dry basis) from the dry product gas composition (experimental results) in the Mass balance equations, the wet product gas composition can be calculated.

(iii) The data for the reaction product composition on a wet basis obtained from the Mass balance equations can be substituted into equilibrium expressions for the methane-steam and the water gas-shift reactions and thus equilibrium constants may be calculated.

(iv) The Mass balance calculation method can be employed to analytical results obtained from the product gas compositions in moles on a dry basis for alkane-steam, reforming for any range of steam ratio, temperature and pressure.

The present work may prove to be of particular use to Process Engineers who are involved with reformer design or estimating the output (the reformed product gas composition) from a steam reformer as feed stock for down-steam processing.

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