Unified Model of Purification Units in Hydrogen Networks[*]

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Abstract   Purification processes are widely used in hydrogen networks of refineries to increase hydrogen reuse. In refineries, hydrogen purification techniques include hydrocarbon, hydrogen sulfide and CO removal units. In addition, light hydrocarbon recovery from the hydrogen source streams can also result in hydrogen purification. In order to simplify the superstructure and mathematical model of hydrogen network integration, the models of different purification processes are unified in this paper, including mass balance and the expressions for hydrogen recovery and impurity removal ratios, which are given for all the purification units in refineries. Based on the proposed unified model, a superstructure of hydrogen networks with purification processes is constructed.

Keywords   purification process, hydrogen network integration, impurity removal ratio, refinery

1   INTRODUCTION

In recent years, increasingly strict environmental and product-quality regulations, and the change of crude oil to high-sulfur and heavier oil are forcing refineries to increase their hydrotreating and hydrocracking. The result is that the hydrogen demand is increasing sharply, which made hydrogen become an expensive utility [1].

To cope with this problem, the effective use of hydrogen is of significant importance. By now, hydrogen network integration (HNI) is recognized as the most effective method for refinery hydrogen management [2]. For hydrogen network integration, process hydrogen streams should be reused as fully as possible to reduce the hydrogen utility consumption. Purification, by upgrading hydrogen concentration of some streams, is an effective way to increase the hydrogen reuse at relative low cost [1, 3].

In a hydrogen network, in addition to hydrogen concentration, each hydrogen sink (for example, hydrotreating or hydrocracking units) requires also limits on certain impurities such as H_2S and CO [2]. Therefore, in refineries, hydrogen purification techniques include hydrocarbon, hydrogen sulfide (H_2S) and CO removal units.

Hydrocarbon removal units include pressure swing adsorption (PSA), membrane and cryogenic process [4]. There are several methods to remove H_2S: dry desulfurization, wet desulfurization, bio-desulfurization and desulfurization by membrane. Wet desulfurization process is widely used. This process utilizes an aqueous absorbent in a column to absorb H_2S and yields a substantial H_2S-free gas [5]. In industrial applications, the CO removal process is usually coupled with a PSA process. Thus, a PSA process can be either with or without CO removal. Currently, light hydrocarbon recovery from hydrogen source streams is a trend to increase economic benefit of a refinery.

In the work on hydrogen network integration, at first the purification is treated as a fixed process and both the concentration and flowrate of purification streams are termed as fixed values [6–14]. Then, it is realized that a hydrogen network should be optimized with purification processes as a whole to achieve the minimum hydrogen utility consumption [1]. Hydrocarbon removal units were considered first [1, 4, 12]. After that, hydrogen sulfide removal processes were also considered [5]. Up to now, CO removal processes and light hydrocarbon recovery processes are not concerned.

Because different purification processes have different separation principles (adsorption, membrane, *etc.*), up to now, each purification process has its own model. Even in the superstructure of a hydrogen network, different purification processes have different blocks [2, 4, 5]. This makes the superstructure complicated and the solving process more difficult.

Although different purification processes have different separation principles, from the point of view of hydrogen network integration, the main description for each purification process only concerns mass balance and concentration constraints. Therefore, the models of purification processes can be unified, which is just the aim of this paper.

2   EXISTING MODELS

2.1   PSA process without CO removal

The PSA process separates the mixture stream by utilizing an adsorbent with different adsorb abilities for different components. The total mass balance is [2]

$$F_R^{(PSA)} = F_{in}^{(PSA)} - F_P^{(PSA)} \qquad (1)$$

where F is flowrate, the superscript (PSA) means PSA

process, and the subscript R, in and P denote residual, inlet and product, respectively.

The mass balance for component i is [2]

$$F_R^{(PSA)} y_{R,i}^{(PSA)} = F_{in}^{(PSA)} y_{in,i}^{(PSA)} - F_P^{(PSA)} y_{P,i}^{(PSA)} \qquad (2)$$

where y is concentration and subscript i means component i.

The hydrogen recovery ratio R is defined in Eq. (3), which varies according to the feed purity, adsorption pressure and tail gas pressure [3].

$$R = \frac{F_P^{(PSA)} y_{P,H_2}^{(PSA)}}{F_{in}^{(PSA)} y_{in,H_2}^{(PSA)}} \qquad (3)$$

The concentration of hydrogen sulfide is assumed to be identical during the process, that is [2]

$$y_{P,H_2S}^{(PSA)} = y_{in,H_2S}^{(PSA)} \qquad (4)$$

The hydrocarbon components are assumed to be removed at an equal proportion as follows [2].

$$\frac{y_{P,i}^{(PSA)}}{1 - y_{P,H_2}^{(PSA)} - y_{P,H_2S}^{(PSA)}} = \frac{y_{in,i}^{(PSA)}}{1 - y_{in,H_2}^{(PSA)} - y_{in,H_2S}^{(PSA)}} \qquad (5)$$

It should be noted that CO is not considered in the model.

2.2 Membrane process

The membrane separation is operated by adopting a permselective membrane with permeability varying along with components. The total mass balance is [2]

$$F_R^{(memb)} = F_{in}^{(memb)} - F_P^{(memb)} \qquad (6)$$

where superscript memb means membrane process.

The mass balance for component i is [2]

$$F_R^{(memb)} y_{R,i}^{(memb)} = F_{in}^{(memb)} y_{in,i}^{(memb)} - F_P^{(memb)} y_{P,i}^{(memb)} \quad (7)$$

The hydrogen recovery ratio is [2]

$$R = \frac{F_P^{(memb)} y_{P,H_2}^{(memb)}}{F_{in}^{(memb)} y_{in,H_2}^{(memb)}} \qquad (8)$$

The hydrogen sulfide concentration of the product stream is assumed to be equivalent to the inlet stream [2].

$$y_{P,H_2S}^{(memb)} = y_{in,H_2S}^{(memb)} \qquad (9)$$

It should be noted that not only CO but also the removal proportion of each hydrocarbon component are not considered in the model.

2.3 Desulfurization process

H$_2$S removal units are usually modeled as mass exchangers. The hydrogen sulfide removed by a desulfurization column is a very tiny part of the mass stream, and therefore the inlet and outlet flowrates of a desulfurization column are assumed to be identical, as shown in Eq. (10) [5].

$$F_{in}^{(ds)} = F_P^{(ds)} \qquad (10)$$

where superscript ds means desulfurization process.

From the removal ratio $r_i^{(ds)}$ of component i, the outlet concentrations are [5]

$$y_{out,i}^{(ds)} = \left(1 - r_i^{(ds)}\right) y_{in,i}^{(ds)} \qquad (11)$$

3 THE UNIFIED MODEL OF PURIFICATION PROCESSES

A purification process usually generates two outputs from the feed (F_{in}, $y_{in,i}$), one of which with higher hydrogen concentration is the purified product (F_P, $y_{P,i}$), and the other with lower hydrogen concentration is termed as residual or tail gas (F_R, $y_{R,i}$), as shown in Fig. 1.
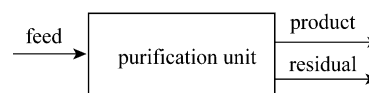

Figure 1   A purification unit

For a process with only one output like the desulfurization process, it can be taken as a specific case of the unified model with $F_R = 0$.

Then we have the total mass balance as shown in Eq. (12).

$$F_R = F_{in} - F_P \qquad (12)$$

The mass balance for component i is

$$F_R y_{R,i} = F_{in} y_{in,i} - F_P y_{P,i} \qquad (13)$$

The hydrogen recovery ratio R is

$$R = \frac{F_P y_{P,H_2}}{F_{in} y_{in,H_2}} \qquad (14)$$

The removal ratio r_i of component i during the purification process is defined as

$$r_i = \frac{F_{in} y_{in,i} - F_P y_{P,i}}{F_{in} y_{in,i}} = 1 - \frac{F_P y_{P,i}}{F_{in} y_{in,i}} \qquad (15)$$

Equations (12) to (15) are the unified model of purification processes. Compared to all the existing models for different kinds of purification processes, it can be seen that the unified model is in full agreement.

From the above equations, the outlet concentrations (the concentration of the product stream) of hydrogen and other components from a purification process can be calculated by Eqs. (16) and (17), respectively.

$$y_{P,H_2} = y_{in,H_2} R \frac{F_{in}}{F_P} \qquad (16)$$

$$y_{P,i} = \left(1 - r_i\right) y_{in,i} \frac{F_{in}}{F_P} \qquad (17)$$