Novel Method for Targeting the Optimal Purification Feed Flow Rate of Hydrogen Network with Purification Reuse/Recycle

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The purification reuse/recycle is one effective resource conservation strategy. In this article, a novel conceptual method is proposed to identify the optimal purification feed flow rate (PFFR) and the corresponding maximum hydrogen utility savings (HUS) of the hydrogen network with purification reuse/recycle. In this method, the sources and sink-tie-lines are divided into three regions according to the purified product and purification feed. The quantitative relationship between the HUS and the PFFR is analyzed for the sink-tie-lines and sources of each region. With the quantitative relationship line between the HUS and the PFFR of each source plotted, the quantitative relationship diagram can be obtained and can be used to identify the pinch point and the HUS for a given PFFR. Furthermore, the optimal PFFR and the maximum HUS can be identified easily. Three cases are studied to illustrate the applicability of the proposed method. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 1964–1980, 2013

Keywords: hydrogen network, purification reuse/recycle, pinch, optimization, purification feed flow rate

Introduction

Nowadays, the combination of low-sulfur fuel specifications, markets shifting toward lighter fuels, and the desire to process heavier, sourer crudes cause the hydrogen demand of refineries increase significantly. Reducing the hydrogen consumption has become the critical problem of many refineries.

With the interaction of different processes considered, the hydrogen network integration can significantly increase the reuse of the process sources and hence minimize the hydrogen utility consumption. Based on the concept of hydrogen surplus, Alves and Towler[1] introduced a graphical method for the analysis of hydrogen distribution systems. The pinch appears at the minimum hydrogen utility consumption and can be identified through the iterative calculation of the purity profiles and hydrogen surplus diagrams. To avoid the cumbersome iteration, El-Halwagi et al.[2] developed a graphical method for mass exchange network with the source and sink composite curves plotted on the impurity load vs. flow rate diagram. However, this method can only be used to systems with pure fresh resources. Kazantzi and El-Halwagi[3] extended this method to the general property integration method, which can be applied to systems with any fresh resources. Based on the pure hydrogen load vs. flow rate diagram, Zhao et al.[4] proposed a graphical method for the hydrogen network with any fresh hydrogen purities. On the basis of the surplus diagram, Saw et al.[5] developed the material surplus composite curve (MSCC) method. With the interval fresh material flow rate introduced, the MSCC diagram can be easily plotted and applied to target the fresh resource consumption of a concentration-/property-based resource conservation networks. By shifting the composite curve, the methods mentioned above can identify the pinch point, the minimum hydrogen utility consumption and waste discharge without repetitive computations. Agrawal and Shenoy[6] proposed a unified conceptual approach for water and hydrogen networks. In this approach, the composite curve is constructed in the contaminant concentration vs. contaminant mass load diagram. Bandyopadhyay[7] proposed the source composite curve method to reduce waste generation through maximizing on-site reuse/recycling. Alwi et al.[8] developed the network allocation diagram to assist designers to select networks that yield either the minimum gas targets or the minimum number of streams.

Manan and Foo[9] proposed a numerical alternative to the graphical targeting technique, the water cascade analysis (WCA). With the tedious iterative steps of the water surplus

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diagram omitted, the WCA can quickly yield accurate minimum water targets and pinch point. Later, Foo et al.[10] generalized this technique to property cascade analysis (PCA) technique. Through the property surplus diagram and the PCA technique, the minimum utility consumption of property-based material reuse network can be targeted.

In a hydrogen network, only the hydrogen surplus with higher purity can be used to supplement the hydrogen deficient with lower purity, whereas that with lower purity cannot be used to supplement the hydrogen deficient with higher purity.[1] To increase the hydrogen utilization, it is necessary to increase the purity of the hydrogen source by purification. Purification reuse/recycle is a good choice to further reduce hydrogen utility consumption and is widely used in practice. As the purification can change the hydrogen purity and the flow rate of source streams, it will affect the hydrogen source composite curve and hence affect the pinch point location and the minimum hydrogen utility consumption. For a purifier with given purification feed purity, purification product purity, and hydrogen recovery, different purification feed flow rates (PFFRs) have different effects. There exists the optimal PFFR, with which the hydrogen utility target can reach the minimum. To identify this optimal PFFR, it is necessary to make an all-around discussion on the quantitative relationship between the minimum hydrogen utility consumption and the PFFR.

Alves[11] and Liu and Zhang[12] analyzed three possible placement of the purifier (above the pinch, across the pinch, and below the pinch), and concluded that the purifier across the pinch is the best choice. Based on the limiting hydrogen profile, Agrawal and Shenoy[6] analyzed the purification problem and calculated the hydrogen utility consumption for fixed PFFR problems. Foo and Manan[13] further generalized PCA to gas cascade analysis (GCA) for targeting the utility gas network. The selection of gas purification techniques was systematically studied via the GCA. However, the purification is taken as a fixed process and is not optimized in this method. Ng et al.[14–17] proposed the automated targeting technique to identify the targets of the property- and concentration-based conservation networks with regeneration/purification reuse/recycle. This method can be applied to optimize the PFFR of the hydrogen network with purification reuse/recycle. Nelson and Liu[18] developed an Excel spreadsheet to solve the problems of multiple-pinch systems with purification. Bandyopadhyay[7] presented the similar methods to identify the minimum utility target for the hydrogen network with purification reuse/recycle. Based on the triangle representation of the hydrogen purification process, Zhang et al.[19] developed a graphical method to identify the pinch point location and the minimum hydrogen utility consumption of the hydrogen system with purification reuse/recycle. However, this method cannot optimize the PFFR.

In addition to graphical methods, the mathematical optimization method can also be used to synthesize the hydrogen systems with purification reuse/recycle. Based on the superstructure, Hallale and Liu[20] set up a mathematical optimization method for maximizing the hydrogen recovery in clean fuels production process. Zhang et al.[21] and Fonseca et al.[22] proposed the linear programming method for the integration of hydrogen network and utility system with material processing system. Later, an automated procedure to target the minimum resource consumption was presented by Ng et al.[14,17] Van den Heever and Grossmann[23] and Khajehpour et al.[24] made further efforts to develop the MINLP optimization model for material network integration. The superstructure model proposed by Tan et al.[25] can also be applied to solve the integration problems of the hydrogen network with purification reuse/recycle, although it is developed for the single-contaminant water networks with partitioning regenerators. Kumar et al.[26] developed the mathematical model for hydrogen networks considering the constraints on pressure, hydrogen purity, flow rate, operating cost, capital cost, and so forth. Liu et al.[27] developed an evolutionary design methodology for resource allocation networks with multiple impurities. Jia and Zhang[28] developed an improved modeling and optimization approach for hydrogen networks with the light hydrocarbon production and flash calculation incorporated. However, purification is not considered in the methods introduced earlier.

Liu and Zhang[12] proposed a systematic methodology to select the appropriate purifier in hydrogen systems. In this method, the shortcut models for different purification units and a superstructure are built with all possible purification scenarios included. The optimal solution can be obtained through the trade-offs among the hydrogen savings, the compression costs, and the capital investment. Liao et al.[29] presented a systematic approach for the integration of hydrogen networks with purifiers. Later, they developed a rigorous targeting approach with the pinch insight combined.[30] This method is extended to hydrogen networks with purification reuse/recycle.[31] Compared with graphical methods, mathematical programming methods can deal with much more complicated problems. However, this kind of methods cannot give clear insights into process operations, unless they are combined with the pinch concept (such as the hybrid methods presented in Refs. 14–17, 29, and 30).

Although some of the graphical and mathematical programming methods mentioned earlier can optimize the PFFR, the quantitative relationship between the PFFR and the hydrogen utility consumption is not considered. Based on the characteristics of the pinch point, Liu et al. (submitted for publication) studied the effect of the PFFR to the minimum hydrogen utility consumption and developed the graphical method for identifying the upper bound of the PFFR. Although this method can identify the upper bound of the PFFR, this method cannot show the quantitative relationship between the PFFR and the hydrogen utility consumption. This article focuses on developing a conceptual method for identifying quantitative relationship between the PFFR and the hydrogen utility consumption and the optimal PFFR of the hydrogen network with purification reuse/recycle. Based on the hydrogen profiles and hydrogen surplus diagram, the quantitative relationship between the hydrogen utility consumption and PFFR is analyzed, and the corresponding diagram is constructed. Hence, the optimal PFFR can be easily identified. Three case studies are presented to illustrate the targeting procedure of the optimal PFFR.

The Conceptual Method for Targeting the Minimum Hydrogen Utility Consumption and the Limiting PFFR

The identification of the minimum hydrogen utility consumption

Based on the hydrogen purity profiles,[4] Liu et al. analyzed the characteristics of the pinch point and concluded that the pinch point only appears at the sink-tie-lines that can

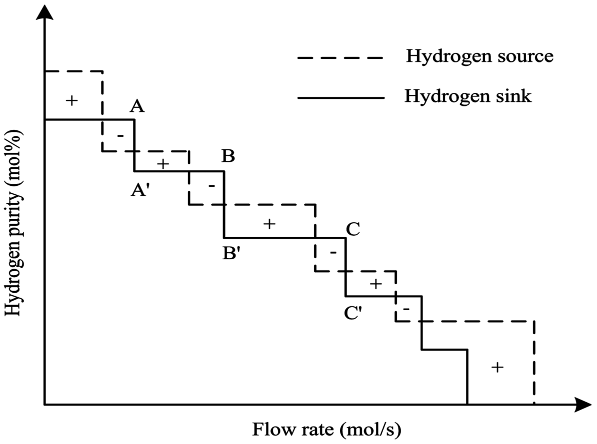


Figure 1. Purity profiles of hydrogen sources and hydrogen sinks

(Liu et al., submitted for publication).[1,4]

intersect with the source composite curve (Liu et al., submitted for publication). A sink-tie-line is the vertical section of the sink purity profile and is used to connect the two adjacent sinks, such as AA′, BB′, and CC′ in Figure 1.

When the pinch point appears, the hydrogen surplus at the sink-tie-line where the pinch appears becomes zero, and that at any other sink-tie-line is larger than zero. For a randomly selected initial hydrogen utility flow rate, the hydrogen purity profiles can be constructed, and the hydrogen surplus at each sink-tie-line (H_i) can be obtained. The hydrogen utility adjustment ($\Delta F_{u,i}$), which denotes the necessary adjustment from the initial utility flow rate, can guarantee the formation of zero hydrogen surplus at the studied sink-tie-line i. the source intersecting sink-tie-line i does not change as the utility flow rate is adjusted, $\Delta F_{u,i}$ can be calculated by Eq. 1.

$$\Delta F_{u,i} = -\frac{H_i}{c_u - c_i^*} \tag{1}$$

where c_u denotes the hydrogen utility purity, c_i^* denotes the purity of the source intersecting sink-tie-line i, and $\Delta F_{u,i}$ denotes the hydrogen utility adjustment of sink-tie-line i.

If the flow rate of the source intersecting sink-tie-line i is insufficient, the source intersecting this sink-tie-line might change as the utility flow rate is adjusted. Take the case shown in Figure 2, for example, sink-tie-line AA′ intersects source BD (with purity c_1) at point C, and its hydrogen surplus is H_0 at the initial hydrogen utility flow rate, as shown in Figure 2a. When the hydrogen surplus of AA′ is zero, the source with higher purity (c_2) intersects AA′ at point E, as shown in Figure 2b. For this case, $\Delta F_{u,i}$ can be obtained by Eq. 2.

$$\Delta F_u = -\frac{H_0 + F_{BC}(c_2 - c_1)}{c_u - c_2} \tag{2}$$

For sink-tie-line i, its hydrogen surplus will be zero, if the hydrogen utility is adjusted by $\Delta F_{u,i}$. Each sink-tie-line, which can intersect with the source composite curve, has the corresponding hydrogen utility adjustment. To ensure the formation of the pinch point, that is, the hydrogen surplus at a sink-tie-line is zero, whereas that at any others is not less than zero, the maximum one of all these adjustments can be taken as the hydrogen utility flow rate adjustment of the system, ΔF_u^*, that is

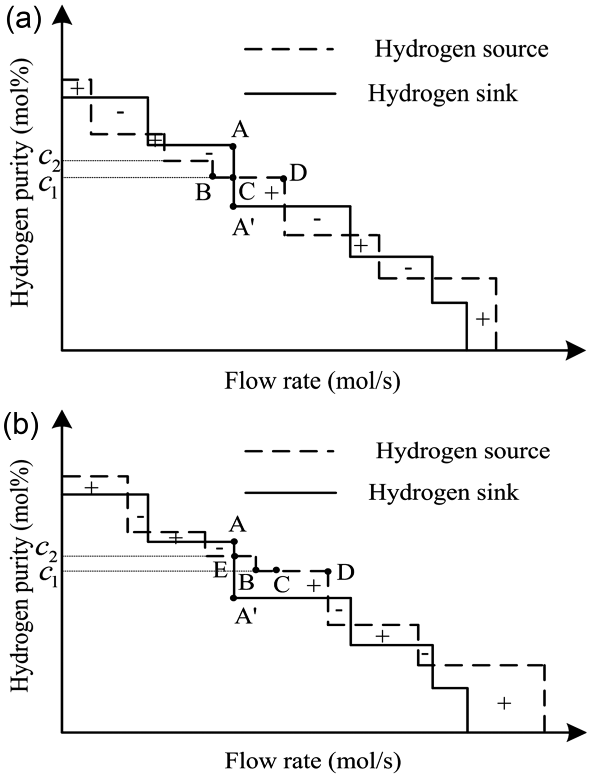


Figure 2. Hydrogen purity profiles at different utility flow rates.

(a) The purity profiles at the initial hydrogen utility flow rate and (b) the purity profiles when the hydrogen surplus of AA′ is zero.

$$\Delta F_u^* = \max\{\Delta F_{u,i}\}_i \quad \forall i = 1, 2, 3\ldots \tag{3}$$

ΔF_u^* can be either positive or negative. The minimum hydrogen utility flow rate can be obtained by adding ΔF_u^* to the initial hydrogen utility flow rate. The pinch appears at the sink-tie-line, whose hydrogen utility adjustment ($\Delta F_{u,i}$) equals to ΔF_u^*. The purity of the source intersecting this sink-tie-line is the pinch purity. The steps to identify minimum hydrogen consumption are similar to the MSCC method of Saw et al.[5]

Targeting the limiting PFFR

When the purification reuse/recycle technique is applied, the hydrogen utility consumption can be reduced further. The purifier can separate the feed stream (with purity c_{pur}) into two streams, the product stream (with purity c_g) and the tail gas (with purity c_w), as shown in Figure 3.

As the tail gas contains hydrogen and is generally sent to the fuel system, there is the hydrogen loss, H_w. The hydrogen recovery (R), the ratio of hydrogen in the product stream to that in the feed stream, can be used to denote the recovered hydrogen in the purified product. According to the material balance, the following equations can be deduced.

$$R = \frac{F_g c_g}{F_{pur} c_{pur}} \tag{4}$$

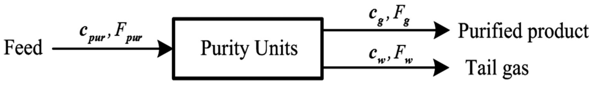


Figure 3. The general hydrogen purification process.

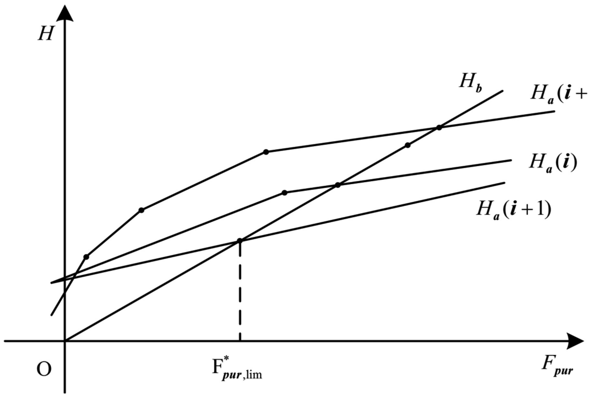


Figure 4. The variation of the hydrogen surplus.

$$H_w = F_{\text{pur}} c_{\text{pur}} (1-R) \tag{5}$$

$$F_{\text{g}} = F_{\text{pur}} c_{\text{pur}} \frac{R}{c_{\text{g}}} \tag{6}$$

$$F_{\text{w}} = F_{\text{pur}} \left(1 - c_{\text{pur}} \frac{R}{c_{\text{g}}}\right) \tag{7}$$

$$c_{\text{w}} = \frac{1-R}{\frac{1}{c_{\text{pur}}} - \frac{R}{c_{\text{g}}}} \tag{8}$$

The quantitative relationship between the hydrogen surplus and the PFFR is shown by Eq. 9.

$$\begin{aligned} H_i = {} & H_{\text{p},i} - H_{\text{w}} + F_i c_i + F_{i+1} c_{i+1} + \cdots \\ & + \left(F_{\text{pur}} \frac{c_{\text{g}} - c_{\text{pur}} R}{c_{\text{g}}} - F_i - F_{i+1} - \cdots - F_{l-1}\right) c_l \end{aligned} \tag{9}$$

where H_i denotes the hydrogen surplus of sink-tie-line i when the purification is applied, $H_{\text{p},i}$ denotes the initial hydrogen surplus at sink-tie-line i when the purification is not applied, c_i denotes the purity of the source intersecting the studied sink-tie-line when the purification is not applied, and F_i denotes its flow rate on the right of sink-tie-line i. Source l is the one intersecting or vertically below sink-tie-line i when the purification is applied. c_{i+1}, c_{i+2},... and F_{i+1}, F_{i+2},... denote the purities and flow rates of the sources between the sink-tie-line i and the source l.

For simplification, Eq. 9 can be written as Eq. 10. H_{a} denotes the hydrogen surplus without considering the hydrogen loss, and H_{b} denotes the hydrogen loss in the tail gas (H_{w}).

$$H = H_{\text{a}} - H_{\text{b}} \tag{10}$$

$$\begin{aligned} H_{\text{a}} = {} & H_{\text{p},i} + F_i c_i + F_{i+1} c_{i+1} + \cdots \\ & + (F_{\text{pur}} \frac{c_{\text{g}} - c_{\text{pur}} R}{c_{\text{g}}} - F_i - F_{i+1} - \cdots - F_{l-1}) c_l \end{aligned} \tag{11}$$

$$H_{\text{b}} = H_{\text{w}} = F_{\text{pur}} c_{\text{pur}} (1-R) \tag{12}$$

Each of the sink-tie-lines, which can intersect the source composite curve, has its own H_{a}. From Eq. 12, it can be seen that, H_{b} is only related to the purification parameters and hence is same for all sink-tie-lines. All H_{a} and H_{b} curves can be plotted in the same hydrogen surplus vs. PFFR diagram, as shown in Figure 4. The vertical distance between H_{a} curve and H_{b} curve stands for the new hydrogen surplus at the corresponding sink-tie-line. At each intersection point of the H_{a} curve and H_{b} curve, the hydrogen surplus at the corresponding sink-tie-line is zero. To ensure that the hydrogen surplus at each sink-tie-line is not less than zero, the PFFR should not exceed the horizontal ordinate of the far left intersection point. Therefore, the horizontal ordinate of the far left intersection point is the upper bound of the PFFR, $F^*_{\text{pur,lim}}$, as shown in Figure 4.

Problem Statement

In this work, the problem definition of a hydrogen network with single impurity and purification reuse/recycle can be stated as follows.

A set of hydrogen sources, SR_i (i = 1, 2,..., N_{sources}), consisting of process streams that can be allocated to every hydrogen sink or discharged to the fuel gas system. Each hydrogen source, SR_i, has a flow rate, F_i, and a constant hydrogen concentration, c_i.

A set of hydrogen sinks, SK_j (j = 1, 2,..., N_{sinks}), that accept sources via reuse/recycle. Each sink, SK_j requires a flow rate, F_j, and can accept an average inlet hydrogen concentration from source that is higher than its minimum allowable hydrogen concentration, $c_j^{\min}$.

For a hydrogen purifier with specified purification feed purity (c_{pur}), purified product purity (c_{g}), and the hydrogen recovery (R) or tail gas purity (c_{w}), different PFFRs (F_{pur}) have different effects on the minimum hydrogen utility flow rate. There exists the optimal PFFR, $F_{\text{pur,opt}}$, with which the hydrogen utility target can reach the minimum. The objective of this work is to make an all-around discussion on the quantitative relationship between the minimum hydrogen utility consumption and the PFFR and identify the optimal PFFR.

The Quantitative Relationship Between HUS and PFFR

For a hydrogen network without purification reuse/recycle, the hydrogen surplus at the pinch point is zero, and the minimum hydrogen utility consumption is $F_{\text{u},0}$. When the purification reuse/recycle is applied, the hydrogen utility flow rate can be reduced further. The decrement of the hydrogen utility flow rate is termed as the hydrogen utility savings (HUS) in this work. However, for the given purification feed, purified product and tail gas purities, increasing the PFFR might decrease the HUS. For example, when the PFFR is less than $F^*_{\text{pur,lim}}$, the hydrogen surplus is positive at each sink-tie-line and hence the HUS is positive. When the PFFR is increased to $F^*_{\text{pur,lim}}$, the hydrogen surplus at a sink-tie-line will decrease to zero, and hence the HUS will decrease to zero. To reduce the hydrogen utility consumption, it is necessary to study the quantitative relationship between the HUS and the PFFR and identify the maximum HUS and the corresponding PFFR in the region, [0, $F^*_{\text{pur,lim}}$].

For simplification, the hydrogen network at the minimum hydrogen utility flow rate ($F_{\text{u},0}$) and without considering purification reuse/recycle is taken as the initial state of the analysis. The corresponding hydrogen utility flow rate, hydrogen surplus at each sink-tie-line, and the pinch point are termed as the initial value.

For a given PFFR lying in the region, [0, $F^*_{\text{pur,lim}}$], the hydrogen surplus will be positive at each sink-tie-line when the hydrogen utility flow rate ($F_{\text{u},0}$) is unchanged. When the hydrogen utility flow rate is reduced to F'_{u}, the hydrogen surplus at a sink-tie-line becomes zero while that at any other sink-tie-lines are positive. The new pinch point appears at the sink-tie-line with zero hydrogen surplus. The decrement of the hydrogen utility flow rate, $(F_{u,0} - F'_u)$, is the HUS at this PFFR.

The purification reuse/recycle has different effects on the sink-tie-lines lying in different places. In this work, the sink-tie-lines are classified as three types according to their location, the sink-tie-lines above the purified product, the sink-tie-lines between the purified product and the purification feed, and the sink-tie-lines below the purification feed. The quantitative relationship between the HUS and PFFR will be discussed for these three types of sink-tie-lines.

The quantitative relationship for sink-tie-lines above purified product

The purities of the sinks connected by the sink-tie-lines above the purified product are greater than that of the purified product. In the hydrogen purity profiles, their distribution is not affected by the purification. Similarly, the distribution of the source composite curve above the purified product changes when the hydrogen utility flow rate has a variation, but it is not affected by the PFFR. So whatever the PFFR is, the hydrogen surpluses of sink-tie-lines above the purified product are constant at the utility flow rate, $F_{u,0}$. When the hydrogen surplus of sink-tie-line i above the product becomes zero, the relationship between the corresponding HUS ($\Delta_s F_{u,i}$) and the purity of the source intersecting sink-tie-line i (c_i^*) can be obtained according to Eq. 1, as shown by Eq. 13.

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i \tag{13}$$

where H_i is the hydrogen surplus of sink-tie-line i when the hydrogen utility flow rate is $F_{u,0}$ and the purification reuse/recycle is not applied.

Equation 13 can be written as the following equation

$$\Delta_s F_{u,i} \cdot c_u - \Delta_s F_{u,i} \cdot c_i^* = H_i \tag{14}$$

In Eq. 14, $\Delta_s F_{u,i} \cdot c_u$ represents the hydrogen decrement due to the decrease of the hydrogen utility flow rate, such as area A shown in Figure 5a; $\Delta_s F_{u,i} \cdot c_i^*$ represents the hydrogen supplement to the left of sink-tie-line i (CC′ in Figure 5), such as area B shown in Figure 5a. Their difference represents the net hydrogen decrement of sink-tie-line i when the hydrogen utility flow rate is decreased by $\Delta_s F_{u,i}$. When this decrement is exactly equal to H_i, the hydrogen surplus of this sink-tie-line becomes zero. This is the physical significance of Eqs. 13 and 14. For the case shown in Figure 5a, the hydrogen purity profiles when the hydrogen surplus of sink-tie-line CC′ becomes zero are shown in Figure 5b.

The quantitative relationship for sink-tie-lines between purified product and purification feed

For a hydrogen system without purification reuse/recycle, the source with purity c_i^* ($c_i^* \neq c_g$) intersects sink-tie-line i, and its flow rate locating in the negative region is $F_{e,i}$. The sources locating on the left of this sink-tie-line have purity $c_u, c_{1,i}, c_{2,i}, c_{3,i}, \cdots, c_{n,i}$ ($c_{n,i} > c_i^*$) in decreasing order, and their flow rates are $F_u, F_{1,i}, F_{2,i}, \cdots, F_{n,i}$, respectively. c_u and F_u are the purity and flow rate of the hydrogen utility, respectively. The total hydrogen demand of all hydrogen sinks on the left of this sink-tie-line (K_i) and the hydrogen surplus of this sink-tie-line (H_i) satisfy the following equation

$$F_u c_u + F_{1,i}c_{1,i} + F_{2,i}c_{2,i} + \cdots + F_{n,i}c_{n,i} + F_{e,i}c_i^* = K_i + H_i \tag{15}$$

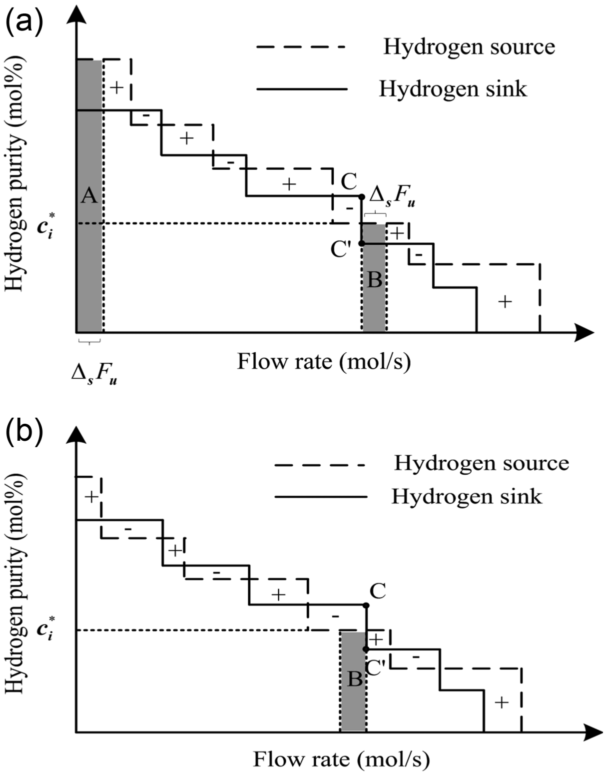


Figure 5. The hydrogen purity profiles.

(a) The initial hydrogen purity profiles and (b) the hydrogen purity profiles when the hydrogen surplus of sink-tie-line CC′ is zero.

For sink-tie-line i, its hydrogen surplus will increase when the purification reuse/recycle is applied, as the purified product is added above it. When its hydrogen surplus becomes zero, the hydrogen utility flow rate ($F'_{u,i}$), and the flow rate of the source (with purity c_i^*) intersecting it in the negative region ($F'_{e,i}$), should satisfy the following equation

$$F'_{u,i}c_u + F_{1,i}c_{1,i} + F_{2,i}c_{2,i} + \cdots + F_{g,i}c_{g,i} + \cdots + F_{n,i}c_{n,i} + F'_{e,i}c_i^* = K_i \tag{16}$$

From the difference of Eqs. 15 and 16, Eq. 17 can be derived.

$$(F_u - F'_{u,i})c_u - F_g c_g + (F_{e,i} - F'_{e,i})c_i^* = H_i \tag{17}$$

Based on the mass balance between sources and sinks, Eq. 18 can be deduced and can be simplified as Eq. 19.

$$F_u + F_{1,i} + F_{2,i} + \cdots + F_{n,i} + F_{e,i} = F'_{u,i} + F_{1,i} + F_{2,i} + \cdots + F_g + \cdots + F_{n,i} + F'_{e,i} \tag{18}$$

$$F_u - F'_{u,i} = F_g + F'_{e,i} - F_{e,i} \tag{19}$$

As the difference between F_u and $F'_{u,i}$ is the HUS of sink-tie-line i ($\Delta_s F_{u,i}$), Eq. 19 can be transformed to Eq. 20.

$$F_{e,i} - F'_{e,i} = F_g - \Delta_s F_{u,i} \tag{20}$$

By substituting Eq. 6 in Eq. 20, Eq. 21 can be deduced.

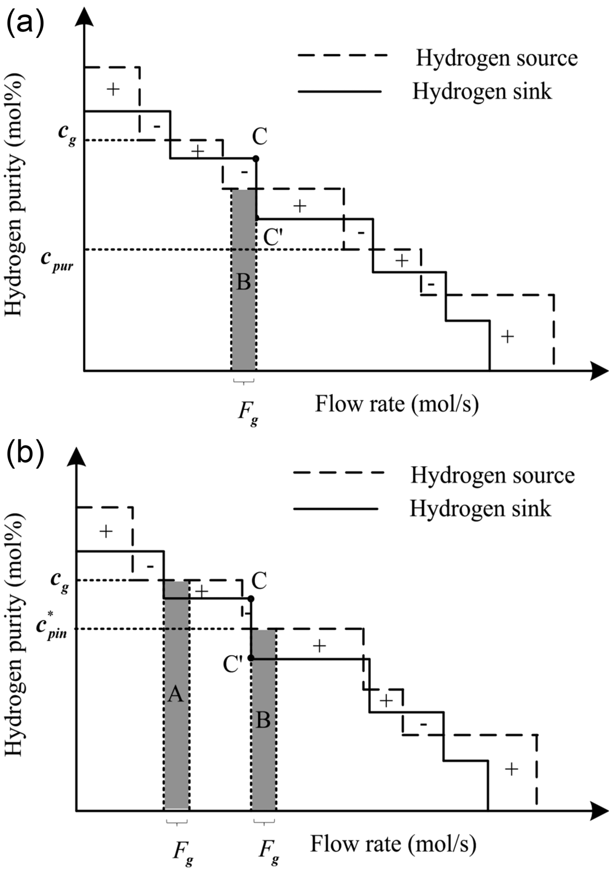


Figure 6. The hydrogen purity profiles when the purification is applied.

(a) The initial hydrogen purity profiles and (b)tThe hydrogen purity profiles with the purified product flow rate equals to F_g.

$$F_{e,i} - F'_{e,i} = F_{pur}\frac{c_{pur}R}{c_g} - \Delta_s F_{u,i} \tag{21}$$

According to Eq. 17, Eq. 21 can be written as

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i + F_{pur}c_{pur}R\left(1 - \frac{c_i^*}{c_g}\right) \tag{22}$$

Referring to Eq. 6, Eq. 22 can be transformed into Eq. 23.

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i + F_g(c_g - c_i^*) \tag{23}$$

According to Eq. 23, the physical significance of Eq. 22 can be explained. $F_g c_g$ represents the hydrogen increment for the sinks above sink-tie-line i (CC′ in Figure 6) that is brought by the purification, such as area A in Figure 6b, and $F_g c_i^*$ gives the hydrogen loss of the sinks above sink-tie-line i that is due to the right shift of the source composite curve, such as area B in Figure 6. $F_g(c_g - c_i^*)$ represents the net hydrogen increment above sink-tie-line i. The sum of $F_g(c_g - c_i^*)$ and H_i gives the new hydrogen surplus of sink-tie-line i. As discussed in the above section, $\Delta_s F_{u,i}(c_u - c_i^*)$ gives the net hydrogen loss of the sources above sink-tie-line i because of reducing the hydrogen utility flow rate. When this net hydrogen loss equals to the new hydrogen surplus of sink-tie-line i, the hydrogen surplus of this sink-tie-line becomes zero. To ensure that the hydrogen surplus of each sink-tie-line between the purified product and the purification feed is not less than zero, the following inequality should be satisfied.

$$\Delta_s F_{u,i}(c_u - c_i^*) \le H_i + F_{pur}c_{pur}R\left(1 - \frac{c_i^*}{c_g}\right) \tag{24}$$

The quantitative relationship for sink-tie-lines below the purification feed

The quantitative relationship between the HUS and the PFFR for the sink-tie-lines below the purification feed can also be deduced according to the condition that the hydrogen loss caused by the reduction of the hydrogen utility flow rate should equal to the hydrogen surplus at sink-tie-line i. The hydrogen surplus at sink-tie-line i can be calculated according to Eq. 25 (Liu et al., submitted for publication).

$$\mathrm{H} = H_i - H_w + F_w c_i^* \tag{25}$$

As discussed earlier, the net hydrogen loss due to the reduction of the hydrogen utility flow rate is $\Delta_s F_{u,i}(c_u - c_i^*)$. So when the hydrogen surplus of sink-tie-line i becomes zero, Eq. 26 should be satisfied.

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i - H_w + F_w c_i^* \tag{26}$$

United with Eqs. 5 and 7, Eq. 26 can be written as

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i + F_{pur}\left(1 - \frac{c_{pur}R}{c_g}\right)c_i^* - F_{pur}c_{pur}(1 - R) \tag{27}$$

Similarly, for each sink-tie-line below the purification feed, to ensure that its hydrogen surplus is not less than zero, the following inequality should be satisfied

$$\Delta_s F_{u,i}(c_u - c_i^*) \le H_i + F_{pur}\left(1 - \frac{c_{pur}R}{c_g}\right)c_i^* - F_{pur}c_{pur}(1 - R) \tag{28}$$

From the hydrogen purity profiles, it can be seen that, one or more sources can intersect a sink-tie-line when the source composite curve distribution is changed. Thus, the quantitative relationships for a sink-tie-line have different forms when the PFFR is modified. On the other hand, a source can only intersect a sink-tie-line, as there is no overlap between the sink-tie-lines. For simplification, the quantitative relationship of a sink-tie-line can be calculated according to each source it can intersect. That is to say, each source has its own quantitative relationship between the HUS and the PFFR.

According to the location of the sink-tie-line, a source can intersect, the relationship between the HUS and the PFFR of a source can be calculated by Eqs. 13, 22, or 27. However, the HUS directly calculated by these equations may not be accurate. The reason is that, H_i is the hydrogen surplus at the initial state, and it may not be the hydrogen surplus when the studied source intersecting sink-tie-line i. The right relationship can be obtained with H_i corrected by adding the pure hydrogen corresponding to the area surrounded by the studied source line, sink-tie-line i and the initial source intersecting sink-tie-line i. Take the sink-tie-line AA′ shown in Figure 7 as an example, it intersects the source EF at the initial hydrogen utility flow rate, and the corresponding hydrogen surplus is H_1. As the hydrogen utility flow rate is increased and/or the purification is applied, it might intersect source BC. To calculate the corresponding $F_{pur} \sim \Delta_s F_u$ line, H_1 should be corrected by adding the area of the shaded region (CFED).

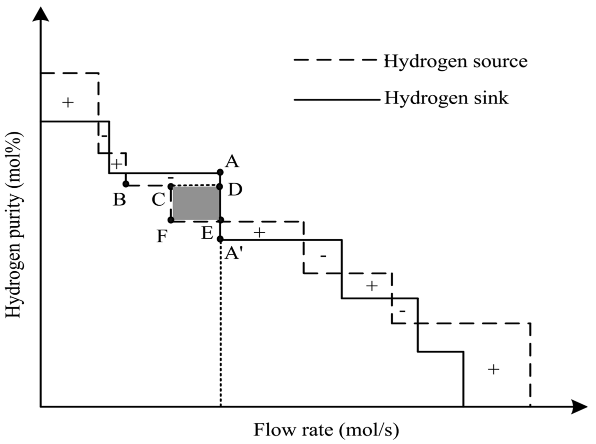


Figure 7. The correction of the hydrogen surplus.

Quantitative Relationship Line

Quantitative relationship line of sources above purified product

For each source above the purified product (including the purified product), it can only intersect the sink-tie-line above the purified product. Equation 13 can be used to target the relationship between the HUS and the PFFR. From this equation, it can be seen that the HUS is not affected by the PFFR. To satisfy the pinch principle, the HUS should not be larger than the minimum one of all $\Delta_s F_{u,i}$ of the sources above the purified product. The upper bound of $\Delta_s F_u$, $\Delta_s F_u^{upper}$, can be identified by Eq. 29. It can be represented by a vertical line in the $F_{pur} \sim \Delta_s F_u$ diagram, as shown in Figure 8. Feasible points of $\Delta_s F_u$ and F_{pur} should lie on the left of this line.

$$\Delta_s F_u^{upper} = \min(\Delta_s F_{u,i}), i = 1, 2, 3, \ldots \tag{29}$$

Quantitative relationship line of sources between the purified product and purification feed

For each source between the purified product and the purification feed (including the purification feed, but excluding the purified product), it can only intersect the sink-tie-line lying in the same region. Equation 22 can be used to target the relationship between the HUS and the PFFR, and it can be transformed to Eq. 30.

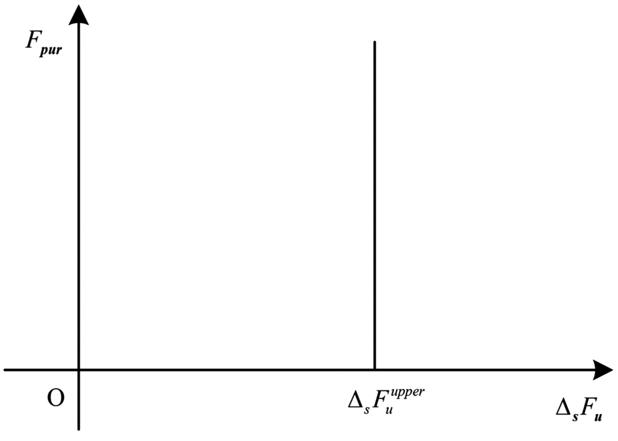


Figure 8. The upper bound of the $\Delta_s F_u$.

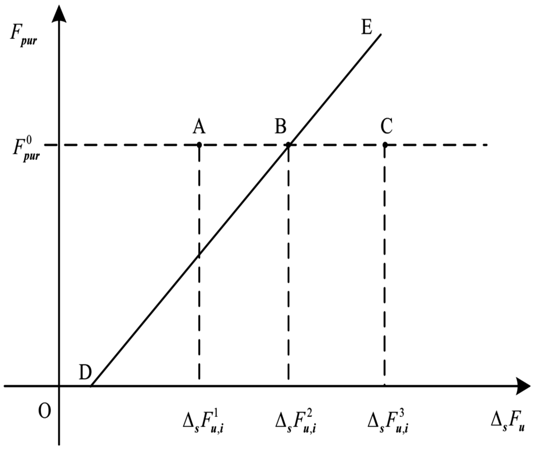


Figure 9. The quantitative relationship line of a source between the purified product and purification feed.

$$F_{pur} = \frac{c_g}{c_{pur}R} \cdot \frac{c_u - c_i^*}{c_g - c_i^*} \Delta_s F_{u,i} - H_i \frac{c_g}{c_{pur}R(c_g - c_i^*)} \tag{30}$$

According to Eq. 30, the relationship between the HUS and the PFFR can be shown by a straight line plotted in the $F_{pur} \sim \Delta_s F_u$ diagram, such as DE shown in Figure 9. From this figure, it can be seen that the HUS increases with the PFFR. The reason is that the hydrogen surplus at each sink-tie-line between the purified product and the purification feed increases when the PFFR is increased.

Furthermore, the points locating on the left of DE are all feasible, whereas that locating on the right are all infeasible. For a specified PFFR, the $\Delta_s F_u$ of the point lying on the quantitative relationship line is the maximum decrement of the hydrogen utility flow rate. For example, when the PFFR is F_{pur}^0, the maximum HUS is $\Delta_s F_{u,i}^2$, as shown by point B. If the HUS is $\Delta_s F_{u,i}^1$ and $\Delta_s F_{u,i}^1 < \Delta_s F_{u,i}^2$, as shown by point A in Figure 9, the net hydrogen loss brought by the reduction of the hydrogen utility flow rate is less than the new hydrogen surplus of sink-tie-line i, and the relationship between $\Delta_s F_{u,i}^1$ and F_{pur}^0 can be written as Eq. 31. If the HUS is $\Delta_s F_{u,i}^3$ and $\Delta_s F_{u,i}^3 > \Delta_s F_{u,i}^2$, as shown by point C in Figure 9, the net hydrogen loss brought by the reduction of the hydrogen utility flow rate is greater than the new hydrogen surplus of sink-tie-line i, as shown by Eq. 32. The hydrogen surplus at the studied sink-tie-line will be negative, and this does not satisfy the pinch principal. In the following discussion, unless specific stress, the HUS represents the maximum hydrogen utility decrement of a sink-tie-line at the given PFFR.

$$\Delta_s F_{u,i}^1 (c_u - c_i^*) < H_i + F_{pur}^0 c_{pur} R \left(1 - \frac{c_i^*}{c_g}\right) \tag{31}$$

$$\Delta_s F_{u,i}^3 (c_u - c_i^*) > H_i + F_{pur}^0 c_{pur} R \left(1 - \frac{c_i^*}{c_g}\right) \tag{32}$$

The quantitative relationship line of each source between the purified product and the purification feed can be plotted in the same diagram. In this case, the feasible points should lie on the left of all lines, as shown by the shaded region in Figure 10.

Quantitative relationship curve of sources below purification feed

For each source below the purification feed, it can only intersect the sink-tie-line lying in the same region. Equation

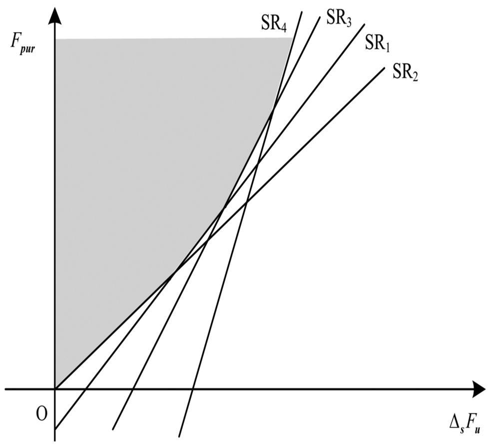


Figure 10. The $F_{pur} \sim \Delta_s F_u$ lines of the sources a sink-tie-line can intersect.

27 can be used to target the relationship between the HUS and the PFFR when it intersects the corresponding sink-tie-line and can be transformed to Eq. 33. When the hydrogen surplus of sink-tie-line i below the purification feed becomes zero and the purity of the source (c_i^*) intersecting this sink-tie-line is larger than that of the tail gas (c_w), Eq. 33 can be represented by a straight line with positive slope in the $F_{pur} \sim \Delta_s F_u$ diagram, as shown in Figure 9.

$$F_{pur} = \frac{c_g(c_u - c_i^*)}{(c_g - c_{pur}R)c_i^* - c_{pur}c_g(1-R)}\Delta_s F_{u,i} - \frac{c_g}{(c_g - c_{pur}R)c_i^* - c_{pur}c_g(1-R)}H_i \qquad (33)$$

$$\Delta_s F_{u,i}(c_u - c_i^*) = H_i \qquad (34)$$

When the purity of the source intersecting sink-tie-line i is exactly equal to the tail gas purity, that is, $c_i^* = c_w$, Eq. 33 can be simplified to Eq. 34 according to Eqs. 5 and 7. From Eq. 34, it can be seen that the HUS is constant, independent of the PFFR. In the $F_{pur} \sim \Delta_s F_u$ diagram, Eq. 34 can be represented by a vertical line.

If the purity of the source intersecting sink-tie-line i, c_i^*, is less than the tail gas purity (c_w), Eq. 33 is a straight line with negative slope, as shown in Figure 11. Similar to that in Figure 9, only the points on the left of the line are feasible. The difference between the line shown in Figure 11 and that shown in Figure 9 is that the $\Delta_s F_u$ decreases with the increase of PFFR. The reason is that when $c_i^* < c_w$, the H_a curve and H_b curve move close to each other as the PFFR increases.

Similar to the case introduced in the previous section, the quantitative relationship lines of all sources below the purification feed should be plotted in the same diagram, and the feasible points lie on the left of all lines.

Quantitative Relationship Diagram

For a hydrogen network, once the purity of the purification feed (c_{pur}), the purified product (c_g), and the hydrogen recovery (R), are specified, the purity of the tail gas (c_w) can be identified. With these data, the quantitative relationship of each source can be obtained and can be plotted in the quantitative relationship diagram.

If the purities of all sources are larger than c_w, the slopes of all $F_{pur} \sim \Delta_s F_u$ lines are positive, as shown in Figure 12.

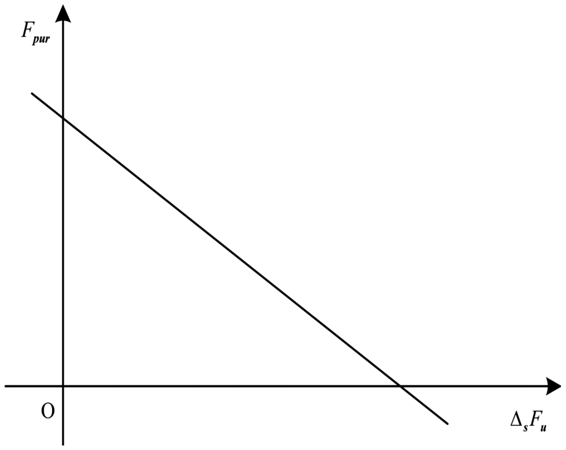


Figure 11. The $F_{pur} \sim \Delta_s F_u$ lines of the source whose purity is less than c_w and intersects the sink-tie-line below the purified feed.

For the sources above the purified product, all the $F_{pur} \sim \Delta_s F_u$ lines of the sources that can intersect the sink-tie-line are vertical. As the feasible points should lie on the left of all $F_{pur} \sim \Delta_s F_u$ lines, only the vertical line corresponding to the minimum $\Delta_s F_u$, $\Delta_s F_u^{upper}$, is plotted in Figure 12.

For a randomly selected PFFR, $F_{pur,1}$, a horizontal line can be plotted, as shown by PQ in Figure 12. PQ can intersect all the $F_{pur} \sim \Delta_s F_u$ lines. Point Q is the intersection point between PQ and the far left $F_{pur} \sim \Delta_s F_u$ line, which corresponds to source SR_2 and has the minimum HUS, $\Delta_s F_{u,1}$. At this point, the hydrogen surplus of the sink-tie-line intersecting SR_2 is zero while that of any other sink-tie-lines is larger than zero. According to the pinch principal, the pinch point forms at the sink-tie-line intersecting SR_2. If the HUS is larger than $\Delta_s F_{u,1}$, the hydrogen network will be infeasible as the hydrogen surplus of the sink-tie-line intersecting SR_2 will be negative. Therefore, for a given PFFR, the far left curve in the quantitative relationship diagram determines the feasible HUS, $\Delta_s F_u$, and the location of the pinch point. For example, according to the broken line OABCDE shown in Figure 12, the pinch point and the feasible HUS can be identified for different PFFR. The initial hydrogen utility flow rate minus the HUS gives the minimum hydrogen utility target after the purification reuse/recycle is applied.

In Figure 12, the hydrogen surplus of each sink-tie-line increases, as the PFFR increases. In the corresponding

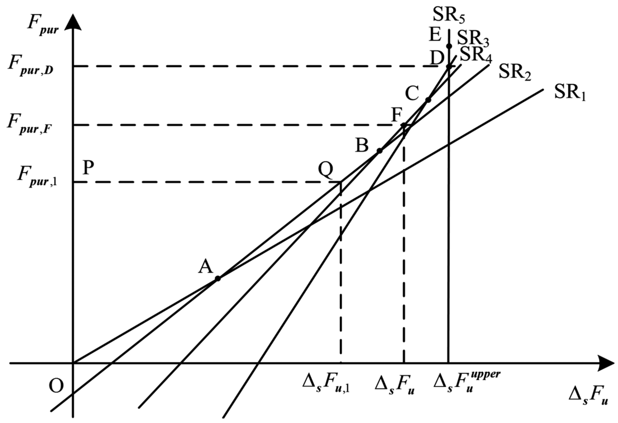


Figure 12. The quantitative relationship diagram when the purities of all sources are larger than c_w.

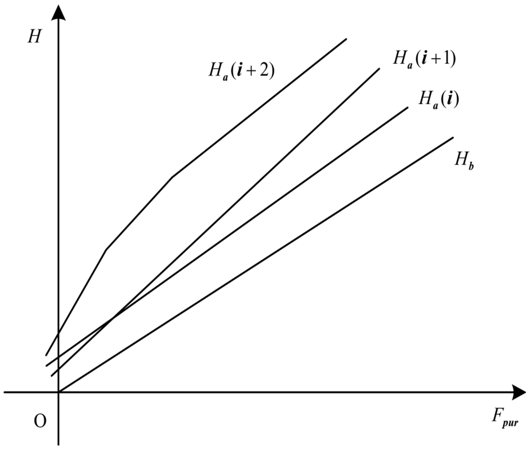


Figure 13. The variation of the hydrogen surplus for the case that the purities of all sources are larger than c_w.

hydrogen surplus variation diagram shown in Figure 13, there is no intersection point between the H_a curves and H_b curve, and hence there is no upper bound of the PFFR ($F^*_{\mathrm{pur,lim}}$). However, the PFFR should be less than the flow rate of the source being purified, $F^{\mathrm{SR}}_{\mathrm{pur}}$, therefore, $F^{\mathrm{SR}}_{\mathrm{pur}}$ can be taken as $F^*_{\mathrm{pur,lim}}$, that is

$$F^*_{\mathrm{pur,lim}} = F^{\mathrm{SR}}_{\mathrm{pur}} \tag{35}$$

If the $F^{\mathrm{SR}}_{\mathrm{pur}}$ is large enough, the $\Delta_s F_u$ reaches the maximum value ($\Delta_s F_u^{\mathrm{upper}}$) when the PFFR reaches point D of Figure 12. The $\Delta_s F_u$ will no longer increase, as the ($\Delta_s F_u$, F_{pur}) points can only move upward along the vertical line, DE. At point D, the maximum $\Delta_s F_u$ can be achieved, and hence the corresponding PFFR ($F_{\mathrm{pur},D}$) is termed as the optimal PFFR ($F_{\mathrm{pur,opt}}$). The corresponding maximum $\Delta_s F_u$, $\Delta_s F_u^{\max}$, equals to $\Delta_s F_u^{\mathrm{upper}}$ in this case. If the total flow rate of the source being purified ($F^{\mathrm{SR}}_{\mathrm{pur}}$) is not enough, the $F^{\mathrm{SR}}_{\mathrm{pur}}$ can be taken as the optimal PFFR. For example, if $F^{\mathrm{SR}}_{\mathrm{pur}}$ equals to the horizontal ordinate of point F, $F^{\mathrm{SR}}_{\mathrm{pur}}$ can be taken as the optimal PFFR ($F_{\mathrm{pur,opt}}$), that is

$$F_{\mathrm{pur,opt}} = \min(F^{\mathrm{SR}}_{\mathrm{pur}}, F_{\mathrm{pur,D}}) \tag{36}$$

The $\Delta_s F_u$ corresponding to point F is the maximum HUS ($\Delta_s F_u^{\max}$).

If there are sources with purity lower than c_w in the hydrogen network, the $F_{\mathrm{pur}} \sim \Delta_s F_u$ lines of these sources have negative slope, and the HUS will decrease with the increasing PFFR. For the sources with purity higher than c_w, the slopes of their $F_{\mathrm{pur}} \sim \Delta_s F_u$ lines are positive, and the $\Delta_s F_u$ increases as the PFFR increases. Figure 14 shows the general form of the quantitative relationship diagram for this case.

According to the same analysis method, it can be obtained that the far left curve in the quantitative relationship diagram determines the feasible $\Delta_s F_u$ and the location of the pinch point. This is similar to that of the case with the purity of all sources larger than c_w. For example, in Figure 14, broken line OABCDE gives the quantitative relationship of the HUS and the PFFR.

Before the PFFR reaches that corresponding to point C, the HUS increases with the PFFR. When the PFFR reaches that of point C, the HUS decreases as the PFFR increases further. When the PFFR reaches that corresponding to point E, the HUS becomes zero. Further increasing PFFR will result in negative HUS. Therefore, the PFFR corresponding to point C is the optimal PFFR ($F_{\mathrm{pur,opt}}$) for this case, while that corresponding to point E is the upper bound of the PFFR ($F^*_{\mathrm{pur,lim}}$). If the total flow rate of the source being purified ($F^{\mathrm{SR}}_{\mathrm{pur}}$) is less than the PFFR corresponding to point C, the $F^{\mathrm{SR}}_{\mathrm{pur}}$ can be taken as the optimal PFFR, $F_{\mathrm{pur,opt}}$.

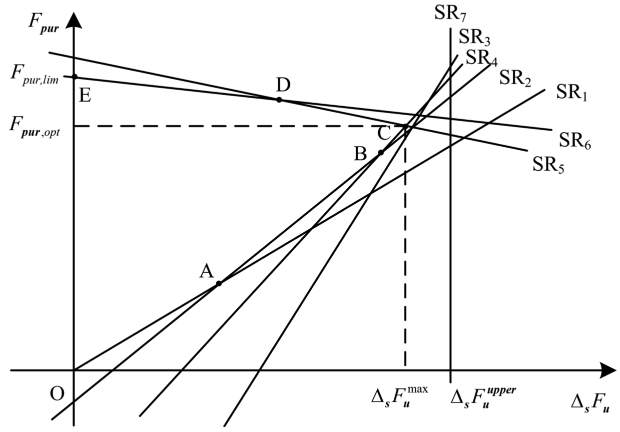


Figure 14. The quantitative relationship diagram for system with the purity of some sources lower than c_w.

It should be noted, when the PFFR equals to that corresponding to the intersection point of two lines, there are two pinch points, which appears at the intersection point of the corresponding sink-tie-line and source. For example, in Figure 14, when the PFFR equals to that corresponding to point A, there are two pinch points: one is the intersection point of SR_1 and the corresponding sink-tie-line that can intersect it, and the other is the intersection point of SR_2 and the corresponding sink-tie-line that can intersect it.

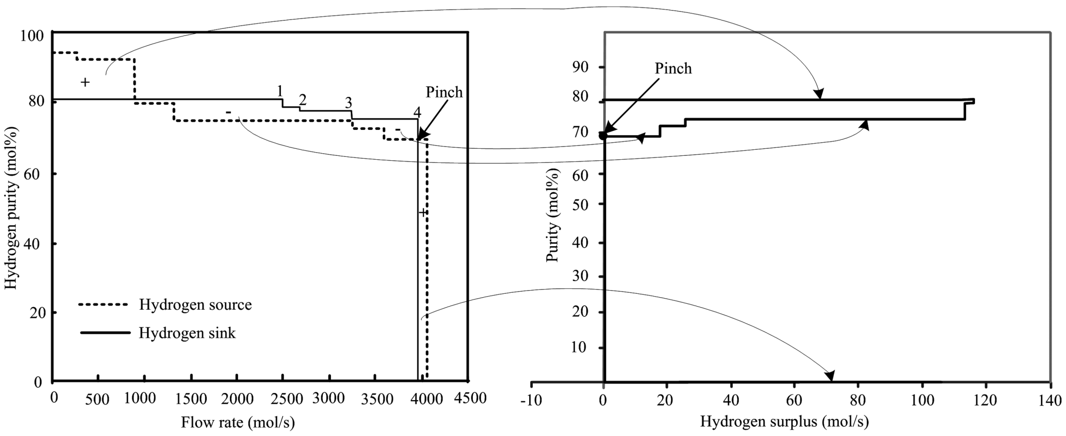
Case Study

Case 1

This refinery hydrogen network is taken from Refs. 1, 14, and 17. The fresh hydrogen stream with hydrogen purity 95% is the utility. Except that, there are four sinks and six sources, and their limiting data are listed in Table 1. Ng et al.[17] analyzed this hydrogen network by the automated targeting technique and identified that the minimum hydrogen utility consumption is 268.82 mol/s, the hydrogen purity of the pinch point is 70%, and the tail gas flow rate is 102.52 mol/s. According to this value, the hydrogen purity

Table 1. Data of Hydrogen Source and Hydrogen Sink Streams (Case 1)

Streams		Hydrogen Purity (mol %)	Flow Rate (mol/s)	Hydrogen Load (mol/s)
Hydrogen sink				
SK_1	HCU	80.61	2495.0	2011.22
SK_2	NHT	78.85	180.2	142.09
SK_3	CNHT	75.14	720.7	541.53
SK_4	DHT	77.57	554.4	430.05
Hydrogen source				
SR_1	HCU	75.0	1801.9	1351.43
SR_2	NHT	75.0	138.6	103.95
SR_3	CNHT	70.0	457.4	320.18
SR_4	DHT	73.0	346.5	252.95
SR_5	SRU	93.0	623.8	580.13
SR_6	CRU	80.0	415.8	332.64
Utility	Fresh supply	95.0	∞	



(a) Hydrogen purity profiles

(b) Hydrogen surplus diagram

Figure 15. The hydrogen purity profiles and hydrogen surplus diagram of Case 1 (the utility flow rate is 268.82 mol/s).

profiles and the hydrogen surplus diagram can be plotted, as shown in Figure 15. The utility flow rate and the pinch point are taken as the initial value for analyzing the effect of the purification reuse/recycle. When the initial pinch point exists, the corresponding data of each sink-tie-lines are shown in Table 2.

To reduce the hydrogen utility consumption further, a membrane system with a hydrogen recovery (R) of 95% is applied. With SR_3 taken as the purification feed and the purity of the purified product (c_g) taken as 98%,[14] it can be calculated according to Eq. 8 that the corresponding tail gas purity (c_w) is 10.89% (mole fraction). From Table 1, it can be seen that the purities of all sources are larger than that of the tail gas. The quantitative relationship diagram of this system can be constructed through the following steps.

1. Identify the upper bound of $\Delta_s F_u$, $\Delta_s F_u^{\text{upper}}$. As no source's purity is larger than the purified product, there is no $\Delta_s F_u^{\text{upper}}$.
2. Identify the quantitative relationships of the sources between the purified product and the purification feed. All sources lie between the purified product and the purification feed. From Table 2, it can be seen that no sink-tie-lines can intersect the source SR_5. Hence, the pinch point of the studied hydrogen network with purification reuse/recycle cannot appear at SR_5, and its $F_{\text{pur}} \sim \Delta_s F_u$ relationship does not need to be identified. According to Eq. 30, the quantitative relationships of SR_1, SR_2, SR_3, SR_4, and SR_6 can be obtained and are shown by Eqs. 38–41, respectively. As SR_1 and SR_2 have the same hydrogen purity, their $F_{\text{pur}} \sim \Delta_s F_u$ relationships are the same, as shown by Eq. 38.

$$F_{\text{pur}} = 1.28\Delta_s F_u - 158.09 \tag{38}$$

$$F_{\text{pur}} = 1.32\Delta_s F_u \tag{39}$$

Table 2. Data of Each Sink-Tie-Line When the Initial Pinch Point Exists (Case 1)

Sink-Tie-Line	The Sinks Connected by It	The Source Intersecting It	Other Sources Can Intersect It	Hydrogen Surplus (mol/s)
1	SK_1, SK_2	–	SR_6	46.9
2	SK_2, SK_4	–	–	–
3	SK_4, SK_3	–	–	–
4	SK_3	SR_3	SR_1, SR_2, SR_4	0

$$F_{\text{pur}} = 1.30\Delta_s F_u - 62.76 \tag{40}$$

$$F_{\text{pur}} = 1.23\Delta_s F_u - 869.46 \tag{41}$$

3. Identify the quantitative relationships of the sources below the purification feed. There is no source lies below the purification feed.
4. With the lines corresponding to Eqs. 38–41 plotted in the same $F_{\text{pur}} \sim \Delta_s F_u$ diagram, the quantitative relationship diagram can be obtained, as shown in Figure 16.

From Figure 16, it can be seen that the $\Delta_s F_u$ increases as F_{pur} increases. However, the sum of $\Delta_s F_u$ and F_w should not excess the tail gas flow rate, 102.52 mol/s, as shown by Eq. 42. Otherwise, the hydrogen network with the minimum hydrogen utility flow rate will be infeasible, as the total flow rate of the hydrogen sources (including the purified product and hydrogen utility flow rate) will be less than that of the hydrogen sinks.

$$\Delta_s F_u + F_w \leq 102.52 \tag{42}$$

$$F_{\text{pur}} \leq -3.11\Delta_s F_u + 318.95 \tag{43}$$

United with Eq. 7, Eq. 42 can be written as Eq. 43. According to this equation, line AB can be plotted, and it intersects the line corresponding to source SR_3 at point C, as shown in Figure 16. Only when the point ($\Delta_s F_u$,F_{pur}) lies in the region OCA, will applying the purification reuse/recycle result in the reduction of the hydrogen utility consumption. Otherwise, it

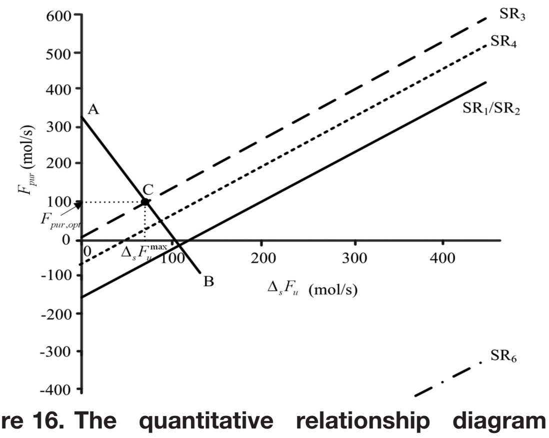


Figure 16. The quantitative relationship diagram of Case 1.

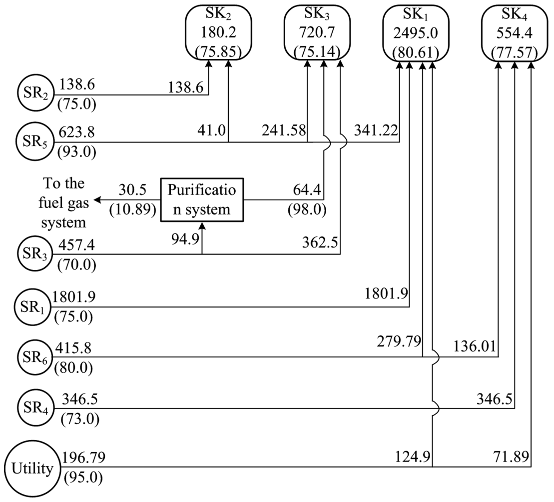


Figure 17. Network design for Case 1 with the minimum utility consumption (flow rate in mol/s, hydrogen purity in mol %, given in parentheses).

Table 3. Data of Hydrogen Source and Hydrogen Sink Streams (Case 2)

Streams	Hydrogen Purity (mol %)	Flow Rate (mol/s)	Hydrogen Load (mol/s)
Hydrogen source			
SR$_1$	87	90	78.3
SR$_2$	85	40	34
SR$_3$	80	135	108
SR$_4$	73	180	131.4
SR$_5$	62	160	99.2
SR$_6$	56	135	75.6
SR$_7$	53	35	18.55
SR$_8$	45	136	61.2
SR$_9$	38	96.5	36.67
SR$_{10}$	35	142	49.7
Hydrogen sink			
SK$_1$	90	130	117
SK$_2$	83	140	116.2
SK$_3$	77	155	119.35
SK$_4$	70	115	80.5
SK$_5$	64	110	70.4
SK$_6$	58	135	78.3
SK$_7$	52	110	57.2
SK$_8$	40	130	52
SK$_9$	30	90	27

might increase the hydrogen utility consumption or make the hydrogen network infeasible. When the PFFR lies between that corresponding to point O and that corresponding to point C, the pinch point will appear at the intersection point of sink-tie-line 4 and SR$_3$, the pinch purity is 70%, and the corresponding $\Delta_s F_u$ can be calculated according to Eq. 39. Similarly, when the PFFR lies between that corresponding to point C and that corresponding to point A, no pinch point appears in this system, as there is no tail gas, and the corresponding $\Delta_s F_u$ can be calculated according to Eq. 43.

From Figure 16, it can also be seen that point C corresponding to the maximum HUS, $\Delta_s F_u^{\max}$, 72 mol/s, the optimal PFFR ($F_{\text{pur,opt}}$) is 94.9 mol/s, and the corresponding minimum hydrogen utility consumption is 196.79 mol/s. The results are in good accordance with that obtained by the automated targeting technique.[17] The network with the minimum utility consumption is shown in Figure 17.

Case 2

In a hydrogen network, there are 10 hydrogen sources (excluding the hydrogen utility) and 9 hydrogen sinks, as shown in Table 3. The purity of hydrogen utility is 98%.

The hydrogen utility consumption is assumed to be 60 mol/s first, then the purity profiles diagram and the hydrogen surplus diagram can be plotted, as shown by the solid line in Figure 18a. From this figure, it can be seen that the initial hydrogen utility consumption is deficient. The hydrogen utility increments to supplement the deficit at the sink-tie-lines intersecting with the SR$_4$, SR$_5$, SR$_7$, SR$_8$, and SR$_9$ are 1.8, 8.47, 11.55, 15.28, and 8.97 mol/s, respectively. To ensure the hydrogen surplus at each sink-tie-line is not less than zero, the maximum one is taken as the hydrogen utility increment, that is, the hydrogen utility consumption should be increased by 15.28 mol/s. Therefore, the minimum hydrogen utility consumption target of this hydrogen network is 75.28 mol/s, and the pinch purity is 45%. When the hydrogen utility consumption is increased to 75.28 mol/s, the hydrogen purity profiles are shown in Figure 18b, and the hydrogen surplus diagram is shown by the dashed line in Figure 18a. The utility flow rate and the pinch point are taken as the initial value for analyzing the effect of the purification reuse/recycle. When the initial pinch point exists, the corresponding data of each sink-tie-lines are shown in Table 4.

If source SR$_6$ is taken as the purification feed, and the purity of purified product (c_g) and the hydrogen recovery (R) are set to be 73% and 0.8, respectively, the purity of the tail gas can be calculated according to Eq. 8, and the result shows that $c_w = 0.29$. According to Table 3, it can be seen that the purities of all sources are larger than that of the tail gas. The quantitative relationship diagram of this system can be constructed through the following steps.

1. Identify the upper bound of $\Delta_s F_u$, $\Delta_s F_u^{\text{upper}}$. The sources above the purified product are SR$_1$, SR$_2$, SR$_3$, and SR$_4$. According to Eq. 13, the $\Delta_s F_u$ of these sources can be calculated. They are 39.82, 39.13, 25.83, and 13.48 mol/s, respectively. Note, when calculate the $\Delta_s F_u$ of SR$_2$, which can intersect sink-tie-line 1, the hydrogen surplus of this sink-tie-line should be corrected by adding the area of the neighboring shaded region A (0.71 mol/s), as shown in Figure 18b. According to Eq. 29, the minimum one can be taken as the upper bound of the $\Delta_s F_u$, $\Delta_s F_u^{\text{upper}}$, that is

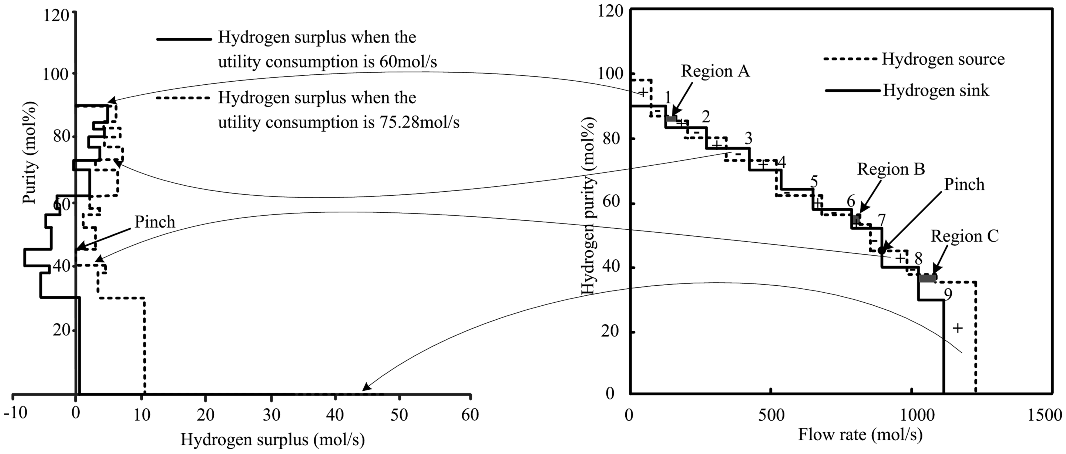
$$\Delta_s F_u^{\text{upper}} = 13.48 \text{ mol/s} \tag{44}$$

2. Identify the quantitative relationships of the sources between the purified product and the purification feed. Source SR$_5$ and SR$_6$ lie between the purified product and the purification feed. According to Eq. 30, their quantitative relationships can be obtained and are shown by Eq. 45 and Eq. 46, respectively.

$$F_{\text{pur}} = 5.33\Delta_s F_u - 36.32 \tag{45}$$

$$F_{\text{pur}} = 4.02\Delta_s F_u - 15.04 \tag{46}$$

3. Identify the quantitative relationships of the sources below the purification feed. Source SR$_7$, SR$_8$, SR$_9$, and SR$_{10}$ lie below the purification feed, and their quantitative relationships can be obtained by Eq. 33 and are shown by Eqs. 47–50, respectively. Note when calculate the $\Delta_s F_u$ of SR$_7$,



(a) Hydrogen surplus diagram

(b) Hydrogen purity profiles (the utility flow rate is 75.28mol/s)

Figure 18. The hydrogen surplus diagram and hydrogen purity profiles of Case 2.

which can intersect sink-tie-line 6, the hydrogen surplus of this sink-tie-line should be corrected by adding the area of the neighboring shaded region B (0.91 mol/s), as shown in Figure 18b. Similarly, when calculate the $\Delta_s F_u$ of SR_{10}, which can intersect sink-tie-line 8, the hydrogen surplus of this sink-tie-line should be corrected by adding the area of the neighboring shaded region C (1.73 mol/s).

$$F_{pur} = 4.85\Delta_s F_u - 26.71 \tag{47}$$

$$F_{pur} = 8.57\Delta_s F_u \tag{48}$$

$$F_{pur} = 17.24\Delta_s F_u - 108.92 \tag{49}$$

$$F_{pur} = 27.15\Delta_s F_u - 238 \tag{50}$$

4. With the lines corresponding to Eqs. 44–50 plotted in the same $F_{pur} \sim \Delta_s F_u$ diagram, the quantitative relationship diagram can be obtained, as shown in Figure 19.

From Figure 19, it can be seen that, as the PFFR increases, the $\Delta_s F_u$ increases along the broken line OABCD. When the PFFR is less than that corresponding to point A, the initial pinch point still locates at the intersection point of sink-tie-line 7 and SR_8. Thus, the corresponding $\Delta_s F_u$ can be calculated by Eq. 48. When the PFFR lies between that corresponding to point A and that corresponding to point B, the pinch point will appear at the intersection point of sink-tie-line 8 and SR_9, the pinch purity is 38%, and the corresponding $\Delta_s F_u$ can be calculated according to Eq. 49. Similarly, when the PFFR lies between that corresponding to point B and that corresponding to point C, the pinch point appears at the intersection point of sink-tie-line 8 and SR_{10}, the pinch purity is 35%, and the corresponding $\Delta_s F_u$ can be calculated according to Eq. 50.

Table 4. Data of Each Sink-Tie-Line When the Initial Pinch Point Exists (Case 2)

Sink-Tie-Line	The Sinks Connected by It	The Source Intersecting It	Other Sources Can Intersect It	Hydrogen Surplus (mol/s)
1	SK_1, SK_2	SR_1	SR_2	4.38
2	SK_2, SK_3	SR_3	–	4.65
3	SK_3, SK_4	SR_4	–	3.37
4	SK_4, SK_5	–	–	–
5	SK_5, SK_6	SR_5	–	2.45
6	SK_6, SK_7	SR_6	SR_7	1.57
7	SK_7, SK_8	SR_8	–	0
8	SK_8, SK_9	SR_9	SR_{10}	3.79
9	SK_9	–	–	–

When the PFFR equals to that corresponding to point C, two pinch points appear. One is the intersection point of sink-tie-line 3 and SR_4, and the corresponding pinch purity is 73%; the other is the intersection point of sink-tie-line 8 and SR_{10}, and the corresponding pinch purity is 35%. Furthermore, the HUS reaches the upper bound of $\Delta_s F_u$ ($\Delta_s F_u^{upper}$) 13.48 mol/s, and the corresponding PFFR is 127.97 mol/s. Therefore, for this hydrogen network, if the purity of the feed and the product are chosen to be 56 and 73%, respectively, when the PFFR gets 127.97 mol/s, the maximum HUS can be obtained and equals to 13.48 mol/s. The minimum hydrogen utility target is 61.8 mol/s, and the corresponding hydrogen distribution network is shown in Figure 20. Similarly, when the PFFR equals to that corresponding to point A, there are also two pinch points, one is the intersection point of sink-tie-line 7 and SR_8, and the other is the intersection point of sink-tie-line 8 and SR_9. When the PFFR equals to that corresponding to point B, the sink-tie-line overlaps the source-tie-line connecting SR_9 and SR_{10}, and the pinch point appears at this sink-tie-line.

Case 3

In another hydrogen network, there are 10 hydrogen sources (excluding the hydrogen utility) and 8 hydrogen sinks, as

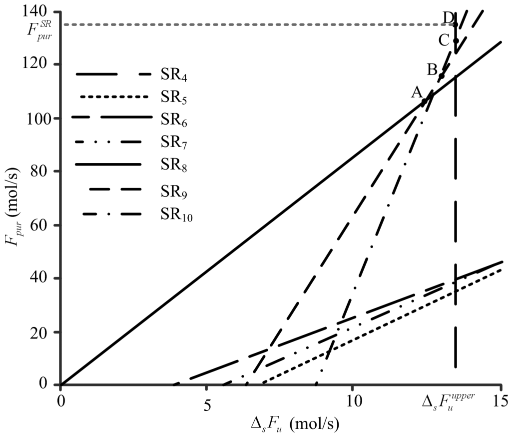


Figure 19. The quantitative relationship diagram of Case 2.

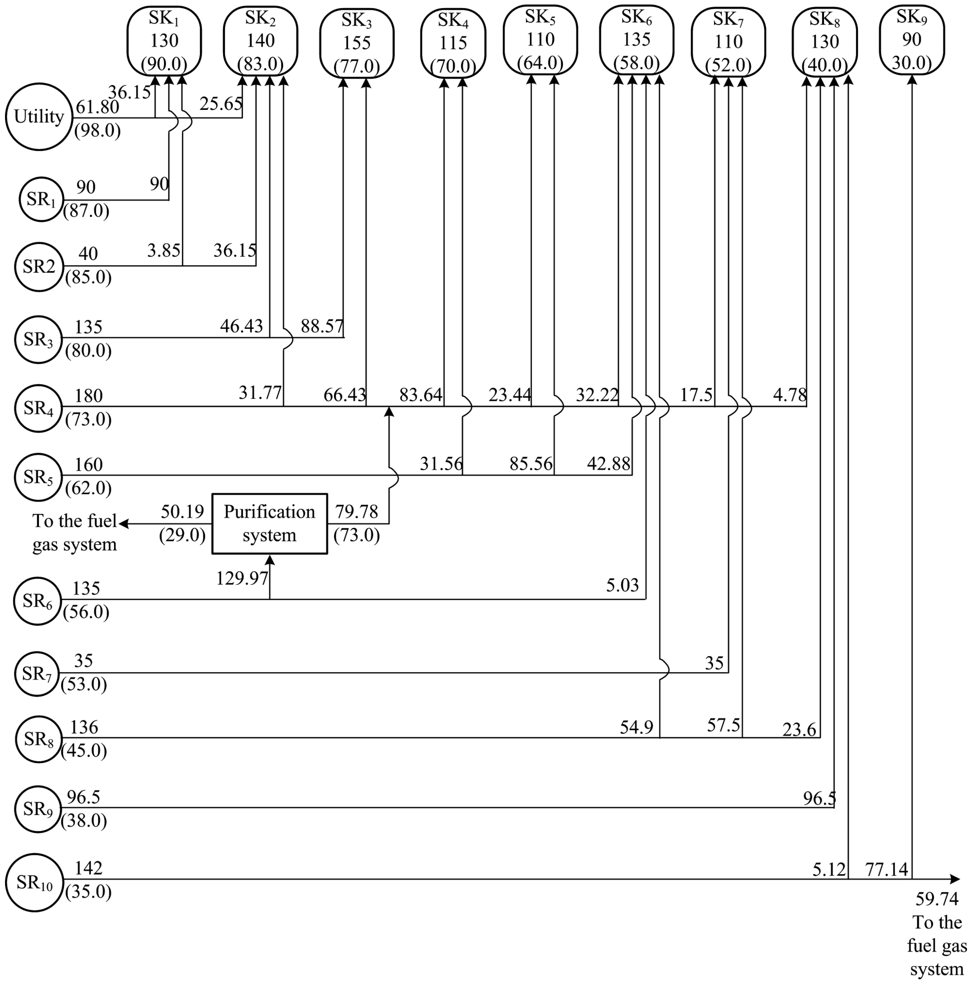


Figure 20. Network design for Case 2 with the minimum utility consumption (flow rate in mol/s, hydrogen purity in mol %, given in parentheses).

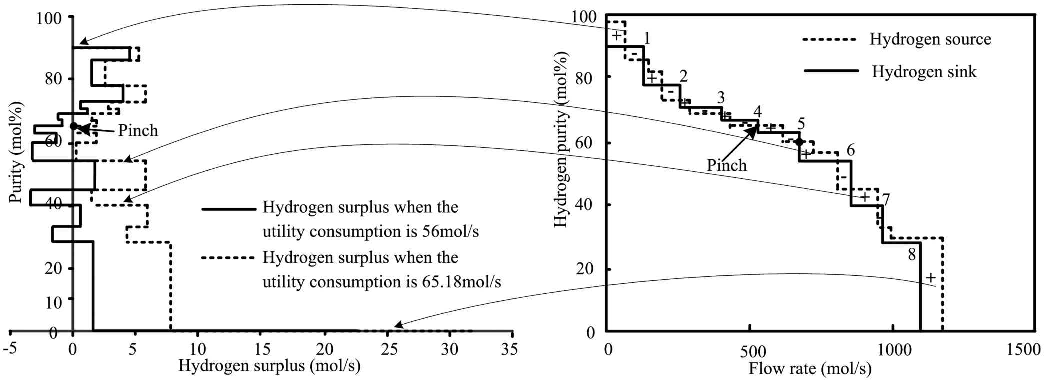
shown in Table 5. The purity of hydrogen utility is 98%, and the consumption is unknown. The location of the pinch point and the minimum hydrogen utility consumption target can be identified by the new conceptual method (Liu et al., submitted for publication).

The hydrogen utility consumption is assumed to be 56 mol/s first, then the hydrogen surplus diagram can be plotted, as shown by the solid line in Figure 21a. Through the calculation, it can be obtained that the hydrogen utility consumption should be increased by 9.18 mol/s. In other words, the minimum hydrogen utility consumption target of this hydrogen network is 65.18 mol/s. The pinch appears at the intersection point of sink-tie-line 4 and SR_5, and the pinch purity is 65%. When the hydrogen utility consumption is increased to 65.18 mol/s, the hydrogen purity profiles are shown in Figure 21b, and the hydrogen surplus is shown by the dashed line in Figure 21a. When the initial pinch point exists, the corresponding data of each sink-tie-lines are shown in Table 6.

To reduce the hydrogen utility consumption further, it is necessary to purify the hydrogen source with low purity. The purity of the feed (c_{pur}) is chosen to be 57%, and that of the product (c_{g}) and the hydrogen recovery (R) are set to be 73% and 0.75, respectively. By Eq. 8, it can be calculated that $c_{\mathrm{w}} = 0.34$. From Table 5, it can be seen that the purities of SR_9 and SR_{10} are less than that of the waste gas. As the steps of constructing the quantitative relationship diagram are similar with that in Cases 1 and 2, only the final consequence is given and the details are omitted. The upper bound

Table 5. Data of Hydrogen Source and Hydrogen Sink Streams (Case 3)

Streams	Hydrogen Purity (mol %)	Flow Rate (mol/s)	Hydrogen Load (mol/s)
Hydrogen source			
SR_1	86	80	68.8
SR_2	82	50	41
SR_3	73	100	73
SR_4	69	135	93.15
SR_5	65	190	123.5
SR_6	60	100	60
SR_7	57	90	51.3
SR_8	45	136	61.2
SR_9	33	51	16.83
SR_{10}	30	180	54
Hydrogen sink			
SK_1	90	130	117
SK_2	78	125	97.5
SK_3	71	150	106.5
SK_4	67	123	82.41
SK_5	63	145	91.35
SK_6	54	185	99.9
SK_7	40	110	44
SK_8	28	130	36.4



(a) Hydrogen surplus diagram (b) Hydrogen purity profiles (the utility flow rate is 65.18mol/s)

Figure 21. The hydrogen surplus diagram and hydrogen purity profiles of Case 3.

of the maximum HUS is shown by Eq. 51; the relationships of the sources between the purified product and the purification feed (SR_4–SR_7) are shown by Eqs. 52–55, respectively; whereas the relationships of the sources below the feed (SR_8–SR_{10}) are shown by Eqs. 56–58, respectively.

$$\Delta_{s,P}F_{u,max} = 11.38 \text{ mol/s} \tag{51}$$

$$F_{pur} = 12.38\Delta_s F_u - 62.08 \tag{52}$$

$$F_{pur} = 7.04\Delta_s F_u \tag{53}$$

$$F_{pur} = 4.99\Delta_s F_u - 3.4 \tag{54}$$

$$F_{pur} = 4.38\Delta_s F_u - 17.87 \tag{55}$$

$$F_{pur} = 12.05\Delta_s F_u - 33.8 \tag{56}$$

$$F_{pur} = -113.1\Delta_s F_u + 760 \tag{57}$$

$$F_{pur} = -37.4\Delta_s F_u + 288.4 \tag{58}$$

With the lines corresponding to Eqs. 51–58 plotted in the same $F_{pur} \sim \Delta_s F_u$ diagram, the final quantitative relationship diagram can be obtained, as shown in Figure 22.

From Figure 22, it can be seen that, to obtain the maximum hydrogen utility decrement at each corresponding PFFR, the HUS should increase with the PFFR along the broken line OABC. Note that the PFFR corresponding to point C equals to the total flow rate of the source being purified.

When the PFFR is less than that corresponding to point A, the pinch point still appears at the intersection point of sink-tie-line 4 and SR_5. When the PFFR is between that corresponding to point A and that corresponding to point B, the pinch point appears at the intersection point of sink-tie-line 7 and SR_9, the pinch purity is 33%. When the PFFR is between that corresponding to point B and that corresponding to point C, the pinch point appears at the intersection point of sink-tie-line 7 and SR_{10}, and the corresponding pinch purity is 30%.

Table 6. Data of Each Sink-Tie-Line When the Initial Pinch Point Exists (Case 3)

Sink-Tie-Line	The Sinks Connected by It	The Source Intersecting It	Other Sources Can Intersect It	Hydrogen Surplus (mol/s)
1	SK_1, SK_2	SR_1	SR_2	2.62
2	SK_2, SK_3	SR_3	–	2.84
3	SK_3, SK_4	SR_4	–	1.45
4	SK_4, SK_5	SR_5	–	0
5	SK_5, SK_6	SR_6	SR_7	0.26
6	SK_6, SK_7	SR_8	–	1.49
7	SK_7, SK_8	SR_9	SR_{10}	4.37
8	SK_8	–	–	–

Once the PFFR exceeds that corresponding to point A, the HUS will decrease as the PFFR increases. So the HUS corresponding to point A is the maximum HUS ($\Delta_s F_u^{max}$) of this hydrogen network, and the PFFR corresponding to point A is exactly the optimal PFFR ($F_{pur,opt}$). In this case, $F_{pur,opt} = 44.56$ mol/s, $\Delta_s F_u^{max} = 6.32$ mol/s. Therefore, for this hydrogen network, if the purity of the feed and the product are chosen to be 57 and 73%, respectively, the maximum HUS, 6.32 mol/s, can be obtained when the PFFR equals to 44.56 mol/s. The minimum hydrogen utility target is 58.86 mol/s, and the corresponding hydrogen distribution network is shown in Figure 23.

Discussion

In the proposed method, only the effect of the PFFR is considered. In practice, the hydrogen utility consumption

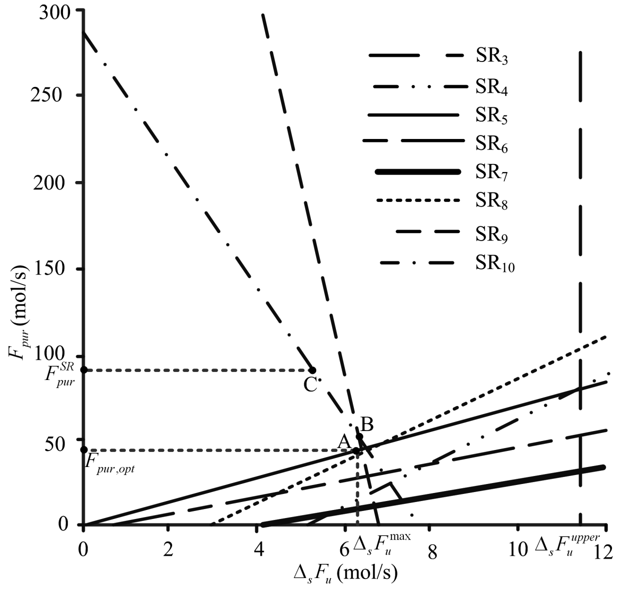


Figure 22. The quantitative relationship diagram of Case 3.

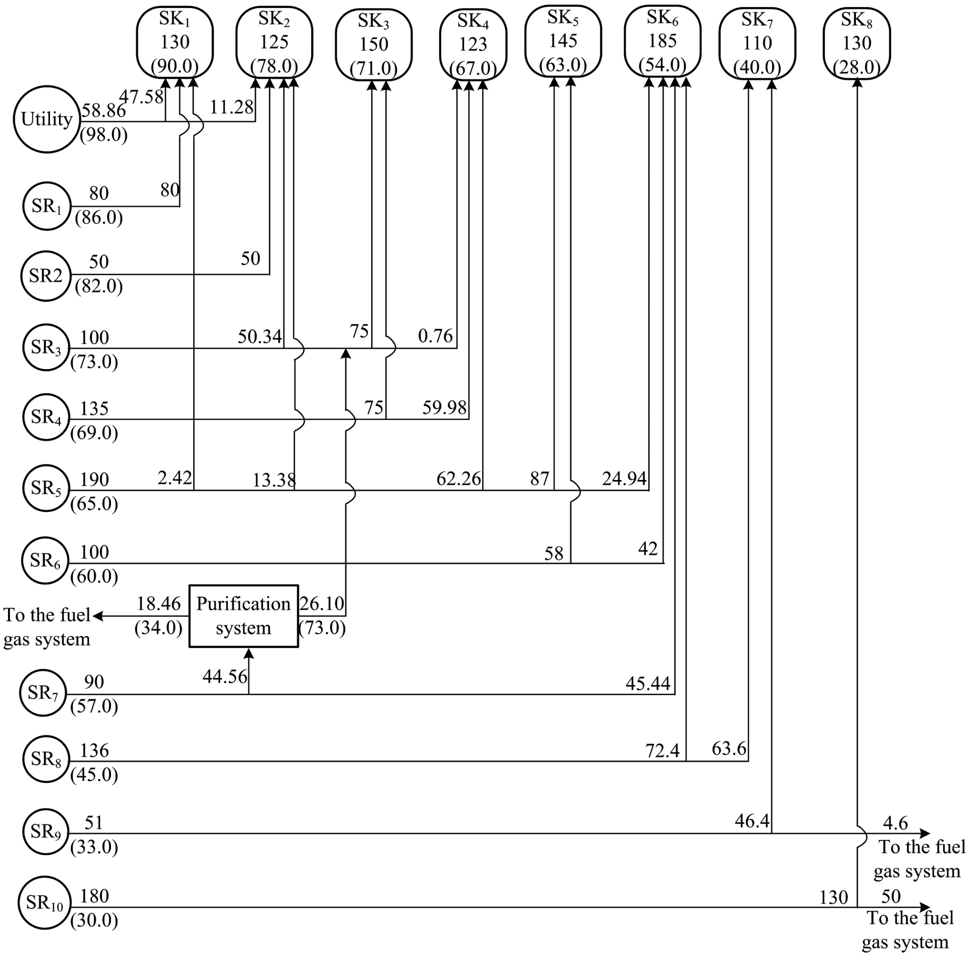


Figure 23. Network design for Case 3 with the minimum utility consumption (flow rate in mol/s, hydrogen purity in mol %, given in parentheses).

and the optimal PFFR are also affected by the purification feed purity, purified product purity, and the hydrogen recovery. A given hydrogen purification equipment has a maximum value and can purify the feed with a certain range of purity. For a given purification feed purity, the maximum recovery increases as the product purity decreases. However, these factors are not considered in this work and should be considered in the future.

Furthermore, there are generally more than one impurity in the practical hydrogen network. For each sink, there are the upper bound limitations on the inlet impurity concentrations. This will significantly affect the integration of the hydrogen network and the optimal PFFR. Besides that, the optimal PFFR is also affected by the operating cost and the capital cost of the hydrogen network, including that of the purification equipment and compressors. If these factors are not considered, the purification with the identified optimal PFFR may demand much more energy or capital cost than the suboptimal PFFR.

To identify the optimal PFFR, all these factors should be considered simultaneously by the mathematical optimization method. The graphical method proposed in this work can only identify the optimal PFFR of the hydrogen network with specified purification feed, purified product, and the hydrogen recovery and with the operating cost and capital cost ignored.

Conclusions

In this article, a novel method is proposed for identifying the pinch point, the minimum hydrogen utility flow rate target, the optimal PFFR and the maximum HUS.

In this method, the quantitative relationships between the HUS and the PFFR are studied. With the quantitative relationship of each source plotted in the same $F_{\mathrm{pur}} \sim \Delta_{\mathrm{s}}F_{\mathrm{u}}$ diagram, the quantitative relationship diagram is obtained. It clearly indicates the pinch point location and the HUS at any PFFR. The pinch point can only appear at the $F_{\mathrm{pur}} \sim \Delta_{\mathrm{s}}F_{\mathrm{u}}$ line that lies on the far left of the quantitative relationship diagram. Based on this, the minimum hydrogen utility consumption target of the hydrogen network with purification reuse/recycle can be identified. More significantly, the quantitative relationship diagram provides an insight on the optimal PFFR and the maximum HUS.

As illustrated by the three case studies, this graphical method is simple, easy understanding. It can be used to deal with the integration problems of the hydrogen network with given purification feed purity and the product purity.

Although the proposed numerical approach can identify the pinch point and the optimum purification feed flow rate, it still requires the conventional hydrogen purity profile diagram and hydrogen surplus diagram in the earlier stage to identify the hydrogen surplus and deficiency at each sink-tie-line. This makes it more complex than the purely "numerical" approach as in cascade analysis. Furthermore, this method can only be applied to the hydrogen network with given purification feed purity, purified product purity, and the hydrogen recovery (or tail gas purity) and with the capital cost and operating cost ignored. However, these factors also affect the integration of the hydrogen network with purification reuse/recycle. Based on the method proposed in this work, these factors will be studied in the future work.

Acknowledgments

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Notation

$c_{1,i}, c_{2,i}, c_{3,i} \ldots c_{n,i}$ = purity of hydrogen sources
c_{g} = purity of purification product
c_i = purity of hydrogen source, SR_i
c_i^* = purity of hydrogen source intersecting with sink-tie-line i
$c_j^{\min}$ = the minimum allowable hydrogen concentration of sink SK_j
c_l = purity of source vertically below sink-tie-line i
c_{pur} = purity of purification feed
c_{u} = purity of hydrogen utility
c_{w} = purity of tail gas
$F_{1,i}, F_{2,i}, \cdots, F_{n,i}$ = flow rate of hydrogen sources
$F_{\mathrm{e},i}$ = flow rate of hydrogen source intersecting with sink-tie-line i in the negative region
$F'_{\mathrm{e},i}$ = flow rate of hydrogen source intersecting with sink-tie-line i in the negative region when hydrogen surplus at sink-tie-line i being zero
F_{g} = flow rate of purification product
F_i = flow rate of source $\mathrm{SR_i}$
F_j = flow rate demanded by sink SK_j
F_{pur} = flow rate of purification feed
$F_{\mathrm{pur}}^{\mathrm{SR}}$ = flow rate of the source being purified
$F^*_{\mathrm{pur,lim}}$ = upper bound of the PFFR
$F_{\mathrm{pur,opt}}$ = optimal PFFR
F_{u} = flow rate of hydrogen utility
F'_{u} = flow rate of hydrogen utility when pinch point forms
$F_{\mathrm{u},0}$ = initial flow rate of hydrogen utility
$F'_{\mathrm{u},i}$ = flow rate of hydrogen utility when hydrogen surplus of sink-tie-line i becomes zero
ΔF_{u}^* = hydrogen utility adjustment that guarantees the formation of the pinch point
$\Delta F_{\mathrm{u},i}$ = hydrogen utility adjustment of sink-tie-line i
$\Delta_{\mathrm{s}} F_{\mathrm{u}}$ = HUS
$\Delta_{\mathrm{s}} F_{\mathrm{u}}^{\max}$ = maximum HUS
$\Delta_{\mathrm{s}} F_{\mathrm{u},i}$ = HUS of sink-tie-line i
$\Delta_{\mathrm{s}} F_{\mathrm{u}}^{\mathrm{upper}}$ = upper bound of HUS
F_{w} = flow rate of tail gas
H_0 = initial hydrogen surplus
H_{a} = hydrogen surplus of one sink-tie-line without considering hydrogen loss in purification reuse/recycle
H_{b} = hydrogen loss in purification reuse/recycle
H_i = hydrogen surplus of sink-tie-line i
$H_{\mathrm{p},i}$ = hydrogen surplus of sink-tie-line i at the initial utility flow rate
H_{w} = hydrogen lost in tail gas
i = sink-tie-line i
K_i = total hydrogen demand of all hydrogen sinks above sink-tie-line i
N_{sources} = the number of hydrogen sources
N_{sinks} = the number of hydrogen sinks
R = hydrogen recovery
SR_i = hydrogen source i
SK_j = hydrogen sink j

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