



Process Systems Engineering and Process Safety

A unified graphical method for integration of hydrogen networks with purification reuse[☆]

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ABSTRACT

Introducing purifiers into hydrogen network can enhance the recovery and reuse of hydrogen in refineries, further reducing the consumption of fresh hydrogen. Based on previous graphical methods, this work proposes a simple and unified graphical method for integration of hydrogen networks with purification processes. Scenarios with different hydrogen concentrations of purified product can be analyzed by the unified procedure. As a result, the maximum hydrogen saved by purification reuse can be identified and the corresponding purification process can be optimized. The proposed method is easy and non-iterative, and it is valid to purification processes with any feed concentration. A conventional hydrogen network is analyzed to test the effectiveness of the proposed method.

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1. Introduction

Hydrogen is an essential raw material in refineries to produce high quality petrochemicals. In recent years, because of the increasing strict environmental regulations and the change of crude oil to heavier and poor in quality, refineries are forced to increase their hydrotreating processes. Consequently, the consumption of fresh hydrogen increases rapidly, posing great challenges for most refineries [1–3].

Process integration is an effective way to achieve reasonable hydrogen networks, avoiding unnecessary waste and minimizing the demand of fresh hydrogen. At present, methods of process integration for hydrogen networks mainly include graphical methods [4–6], algebraic methods [7–9] and mathematical programming methods [10,11]. Among these methods, graphical ones have the characteristics of clear conceptions and easy procedures.

Hydrogen purifiers provide a low-cost way to recover and reuse the hydrogen in streams with low hydrogen concentrations [12–15] and have been widely used in refineries, obviously reducing the consumptions of fresh hydrogen, as well as the total cost for refineries [16]. In order to minimize fresh hydrogen consumptions, a hydrogen network and purification processes should be analyzed as a whole [8,17–21]. Zhang *et al.* [20] proposed a graphical representation of purification processes and combined it with an early graphical method [4], giving a systematic graphical method for integration of hydrogen networks

with purification reuse. This graphical method was improved and extended for further study on the purification reuse of hydrogen networks, including the performance of purifiers [22–24], change rules of pinch [25], and the optimal purification process [26]. In these graphical methods, purification processes with purified product of different purities are divided into three scenarios and identified by different procedures, making these methods complex and inconvenient. Moreover, graphical iterations are needed to determine the final purification processes.

The objective of this work is to propose a unified graphical method for integration of hydrogen networks with purification reuse. Purification processes with purified product of different purities as well as the corresponding fresh hydrogen savings can be identified without divisions. More importantly, the proposed procedure is straightforward and non-iterative, making it easy to apply and understand.

2. Model of Purification Process

Common purification processes include pressure swing adsorption (PSA), membrane separation and cryogenic separation [12]. Although these processes rely on different principles and operations, they can be modeled to separate a hydrogen stream (the feed with F_{in} and C_{in}) into two streams (purified product with F_{pur} and C_{pur} and tail gas with F_{tail} and C_{tail}), as shown in Fig. 1. The mass balance of a purification process can be described as [21].

$$F_{in} = F_{pur} + F_{tail} \quad (1)$$

$$F_{in}C_{in} = F_{pur}C_{pur} + F_{tail}C_{tail} \quad (2)$$

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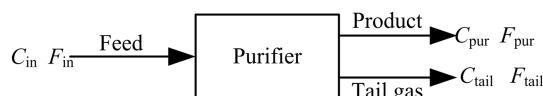


Fig. 1. Purification process model.

$$R = \frac{F_{\text{pur}} C_{\text{pur}}}{F_{\text{in}} C_{\text{in}}} \quad (3)$$

where F and C represent the flow rate and hydrogen concentration, respectively; subscripts in, pur and tail represent the feed, purified product and tail gas, respectively; R is the recovery ratio of hydrogen.

With specified C_{pur} and C_{tail} , Eqs. (1) and (2) can be represented in the hydrogen load versus flow rate diagram for any feed, as the graphical rule shown in Fig. 2. A feed consisting of several streams can be regarded as a mixed stream, as shown by dash lines [20].

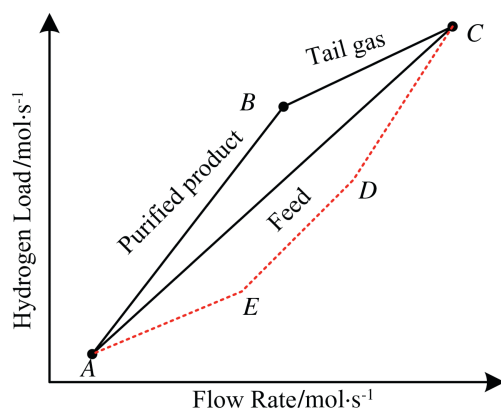


Fig. 2. Graphical rule of purification process.

3. Targeting Procedure

The targeting procedure for a purification process (feed, purified product, and tail gas) and the fresh hydrogen saved by purification reuse can be separated to three parts: (1) identify the minimum fresh hydrogen consumption without purification reuse; (2) identify the fresh hydrogen saved by purification reuse; and (3) optimize the purification process.

3.1. Targeting of the minimum fresh hydrogen consumption without purification reuse [4]

Based on the hydrogen load versus flow rate diagram, Zhao *et al.* [4] proposed a graphical method for integration of a hydrogen network. Fig. 3 illustrates the targeting procedure for the minimum fresh hydrogen consumption. First, each hydrogen source and sink is plotted as a segment in the diagram with its flow rate and hydrogen load. Note that segment of fresh hydrogen is plotted with its maximum flow rate. Second, construct the source composite curve by connecting all segments of sources in the decreasing order of hydrogen concentration, and construct the sink composite curve by the same way. Third, move the source composite curve to intersect the sink composite curve at their top points. Finally, move the part of source composite curve below fresh hydrogen upwards in the decreasing direction of fresh hydrogen until the source composite curve intersects and lies below

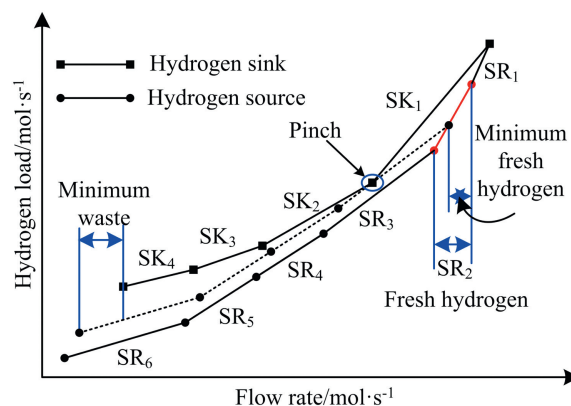


Fig. 3. Graphical method for targeting the minimum fresh hydrogen consumption [4].

the sink composite curve. The intersection is the pinch of this hydrogen network. With the identified pinch, the minimum fresh hydrogen consumption and waste discharge can be determined.

3.2. Targeting of the fresh hydrogen saved by purification reuse

In most refineries, purifiers are used in hydrogen networks to save fresh hydrogen. Based on the graphical representation in Fig. 2, the maximum fresh hydrogen saved by purification reuse can be determined by a unified targeting procedure for any specified C_{pur} and C_{tail} as follows:

- (1) Choose hydrogen source(s) as the feed of purifier and then determine the purified product and tail gas with specified C_{pur} and C_{tail} by the graphical rule in Fig. 2. For example, in Fig. 4, SR₅ and SR₆ are taken as the feed of purifier.
- (2) Re-rank all hydrogen sources including the purified product and tail gas in the decreasing order of hydrogen concentration. Then construct the new hydrogen source composite curve.

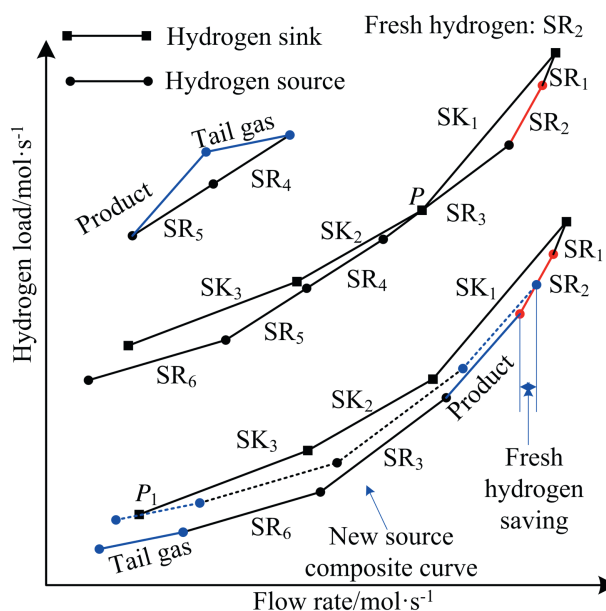


Fig. 4. Targeting of the maximum fresh hydrogen saving.

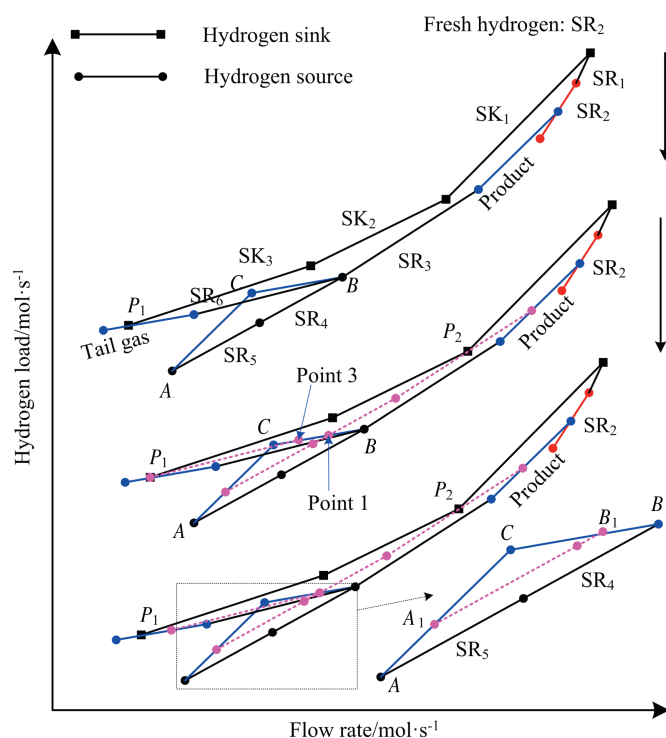


Fig. 5. Optimization of purification process.

Table 1

Hydrogen data for case study [21]

Streams	Hydrogen mole concentration/%	Flow rate/MMscfd ^①
Sources		
Fresh	99	200
SR ₁	91	500
SR ₂	85	350
Sinks		
SK ₁	92.8	400
SK ₂	87.5667	600

^① MMscfd: million standard cubic feet per day.

- (3) Identify the new pinch by the targeting procedure in Section 3.1. As shown in Fig. 4, P_1 is identified as the new pinch of this hydrogen network.

With the new pinch identified, the maximum fresh hydrogen saved by purification reuse is determined, as shown in Fig. 4. All of the purified product is reused by hydrogen sinks. As a result, the consumption of fresh hydrogen is reduced.

3.3. Optimization of purification process

Generally, the cost of purification increases proportionally with the flow rate of feed entering the purification process [27]. Based on the initial purification process in Section 3.2, the flow rate of feed is optimized to give a better process with the maximum fresh hydrogen saving unchanged.

Fig. 5 shows a hydrogen network with a purification process. For convenience, taking the feed as reference, the hydrogen source composite curve can be divided into three parts: Curve 1 locates between purified product and feed, such as SR₃; Curve 2 is the feed, such as SR₄ and SR₅; Curve 3 locates below Curve 1, such as SR₆. On this base, the purification process can be identified by the following procedures:

- (1) Move Curves 1 and 2 in the decreasing direction of purified product until Curve 1 intersects the sink composite curve at one point while lying below the sink composite curve. During such moving procedure, Curve 1 increases and Curve 2 (feed) decreases, while the fresh hydrogen saving is constant, as shown in Fig. 5. These moved curves are represented by dash curves.
- (2) Similarly, move Curve 3 in the decreasing direction of tail gas until Curve 3 intersects the sink composite curve at one point while lying below the sink composite curve, as shown in Fig. 5.
- (3) Name the lower end of Curve 1 as Point 1 and the top of Curve 3 as Point 3, both being on segment BC. To make the final hydrogen network feasible, if Point 3 locates at the left side of Point 1, move Curve 3 in the increasing direction of tail gas (along BC) to intersect Curve 1 at Point 1, as shown in Fig. 5; if Point 1 locates at the left side of Point 3, move Curve 1 in the increasing direction of purified product (along AC) to intersect Curve 3 at Point 3.

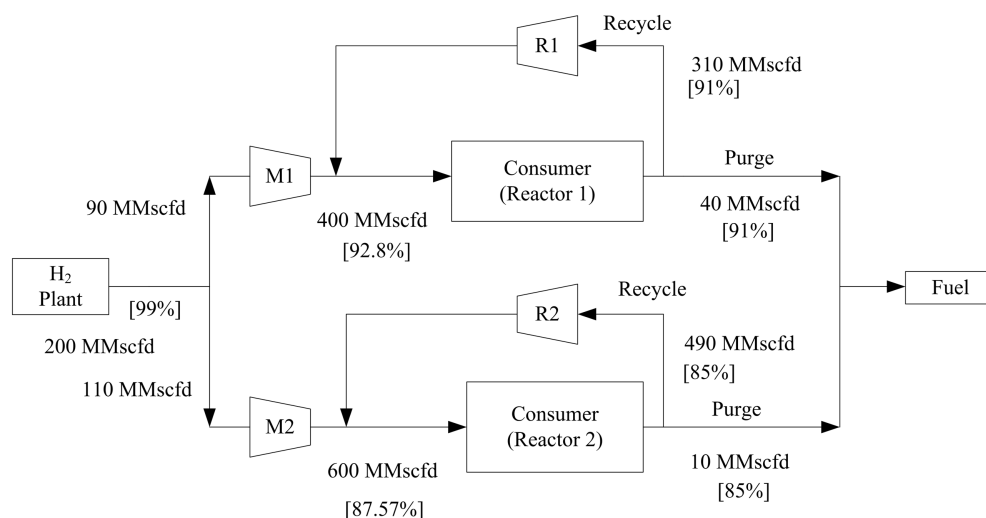


Fig. 6. Flow sheet of a hydrogen network [21].

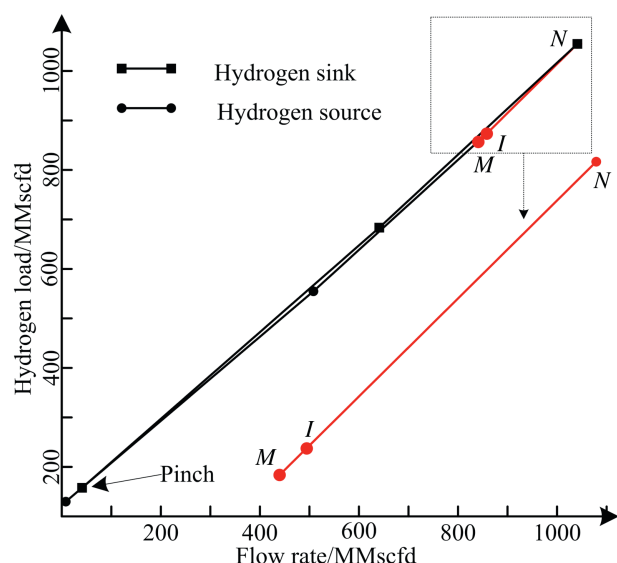


Fig. 7. Targeting of the minimum fresh hydrogen (case study).

Finally, the new source composite curve, as well as the optimized purification process is determined as shown in Fig. 5. Besides, another pinch P_2 occurs. As a result, the feed of purification process is reduced from AB to A_1B_1 , and corresponding purified product and tail gas decrease as well, from AC to A_1C and BC to B_1C . On this base, if the flow rate of feed is reduced further, the consumption of fresh hydrogen will increase.

From Figs. 4 and 5, it can be seen that the fresh hydrogen saving can be determined and corresponding purification process can be optimized by the unified procedure. The procedures for different scenarios ($C_{\text{pur}} > C_{\text{fresh}}$, $C_{\text{pur}} = C_{\text{fresh}}$ and $C_{\text{pur}} < C_{\text{fresh}}$, where C_{fresh} is the hydrogen concentration of fresh source) in previous work [20, 23,24] can be replaced by the unified procedure in this work. Without iteration, this method is simpler and easier than the previous ones [20,23,24].

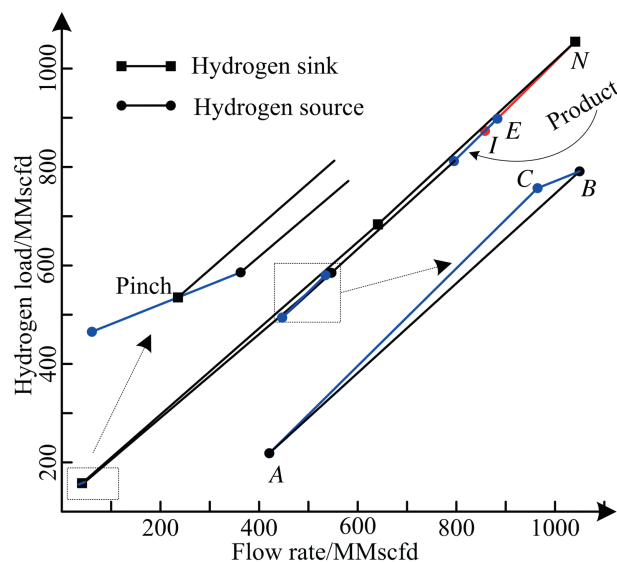


Fig. 8. Targeting of the fresh hydrogen saving (case 1).

4. Case Study

Table 1 shows the data extracted from the hydrogen network in Fig. 6 [21]. By the method of Zhao *et al.* [4], the minimum fresh hydrogen consumption is identified as segment NI of 182.86 MMscfd, as shown in Fig. 7. The waste discharge is identified as 32.86 MMscfd. Such results are the same as that obtained by Agrawal and Shenoy [21].

4.1. Case 1

Hydrogen purification is achieved by a PSA process with specified $C_{\text{pur}} = 0.98$ (lower than C_{fresh} of 0.99) and $C_{\text{tail}} = 0.4$. Assuming that 100 MMscfd of SR_2 is taken as the feed of PSA, the corresponding fresh hydrogen saving can be determined as segment IE of 25.06 MMscfd by the proposed procedure in Section 3.2. As a result, the fresh hydrogen consumption decreases from 182.86 MMscfd to 157.80 MMscfd, as shown in Fig. 8.

Next, the purification process is optimized to minimize its flow rate of feed with the fresh hydrogen saving unchanged. Following the procedure in Section 3.3, the flow rate of feed can be targeted as segment A_1B_1 of 64.60 MMscfd, as shown in Fig. 9. The flow rates of purified product and tail gas are 56.80 MMscfd and 7.80 MMscfd, respectively. The hydrogen network with the PSA process is designed in Fig. 10.

4.2. Case 2

Hydrogen purification is achieved by another PSA process with specified $C_{\text{pur}} = 0.995$ (higher than C_{fresh} of 0.99) and $C_{\text{tail}} = 0.4$. Similarly, SR_2 is taken as the feed with a flow rate of 100 MMscfd. By the method proposed in Section 3.2, the fresh hydrogen saving can be identified as segment IE of 25.06 MMscfd, as shown in Fig. 11. As a result, the fresh hydrogen is reduced from 182.86 MMscfd to 157.80 MMscfd. Next, the purification process is optimized to reduce the flow rate of feed by the procedure in Section 3.3. The minimum flow rate of feed is identified as A_1B_1 of 54.58 MMscfd, as shown in Fig. 12. The flow rates of purified product and tail gas are identified as 46.78 MMscfd and 7.80 MMscfd, respectively. The hydrogen network with the PSA process is designed in Fig. 13.

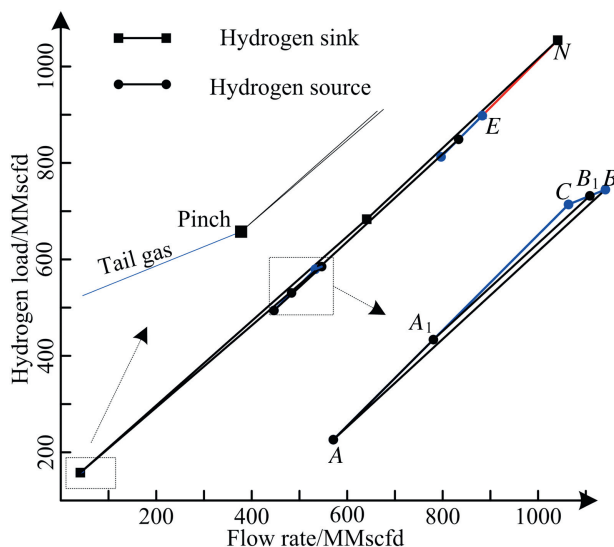


Fig. 9. Optimization of purification process (case 1).

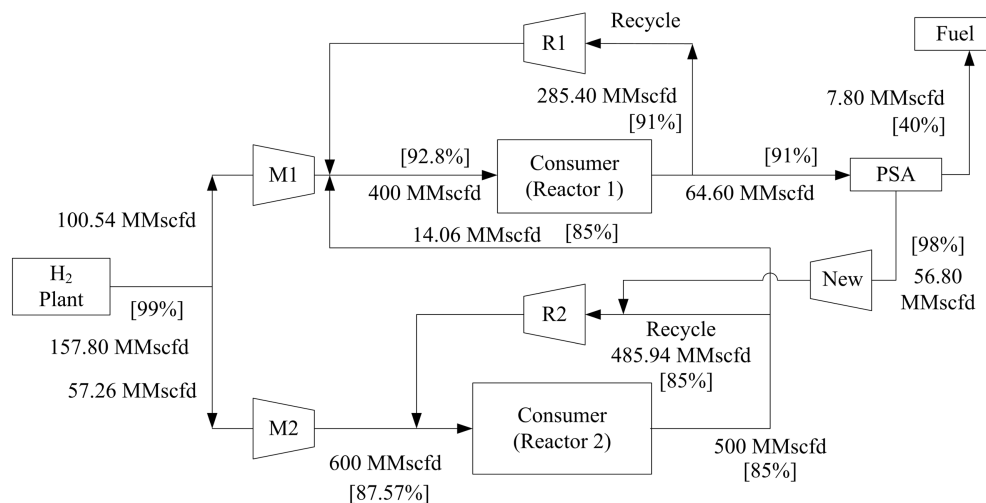


Fig. 10. Hydrogen network with PSA process (case 1).

From all above, scenarios with different purities of purified product ($C_{\text{pur}} = 0.98$ and $C_{\text{pur}} = 0.995$) can be analyzed and targeted by the unified method proposed. Furthermore, the targeting procedure is non-iterative. Thus, this method is easier and more efficient than previous ones [20,23,24]. For $C_{\text{tail}} = 0.4$, 25.06 MMscfd of fresh hydrogen is saved by purification reuse. This result agrees with that calculated by the method of Yang *et al.* [24].

5. Conclusions

A unified graphical method is proposed for integration of hydrogen networks with purification reuse, targeting the maximum fresh hydrogen saved by purification process and optimizing the corresponding purification process. The procedure has clear conceptions and no iteration. Scenarios with different purities of purified product can be analyzed by the unified procedure, so this method is simpler and easier for applications and understanding

than the existing ones [20,23,24]. A case study illustrates the ease and effectiveness of the proposed method. However, the proposed method can only analyze the purification process with given feed and specified C_{pur} and C_{tail} , with the capital cost and operating cost ignored. These factors also affect the hydrogen network integration with purification reuse and will be studied in the future work.

Nomenclature

C_{fresh}	hydrogen mole concentration of fresh hydrogen, %
C_{in}	hydrogen mole concentration of feed, %
C_{pur}	hydrogen mole concentration of purified product, %
C_{tail}	hydrogen mole concentration of tail gas, %
F_{in}	flow rate of feed, $\text{mol} \cdot \text{s}^{-1}$
F_{pur}	flow rate of purified product, $\text{mol} \cdot \text{s}^{-1}$
F_{tail}	flow rate of tail gas, $\text{mol} \cdot \text{s}^{-1}$
R	recovery ratio of hydrogen

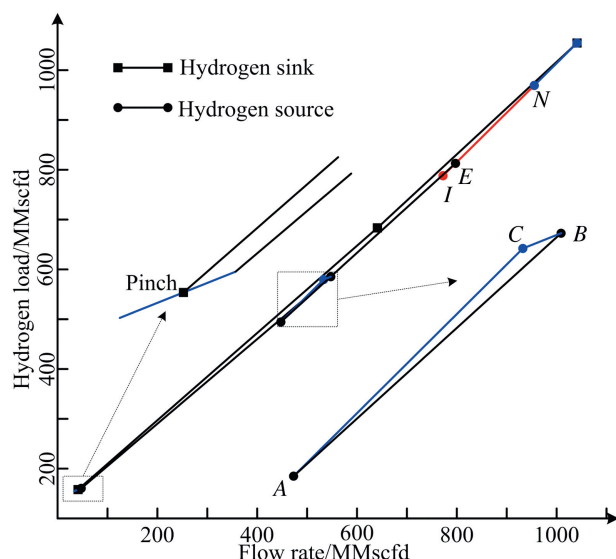


Fig. 11. Targeting of the fresh hydrogen saving (case 2).

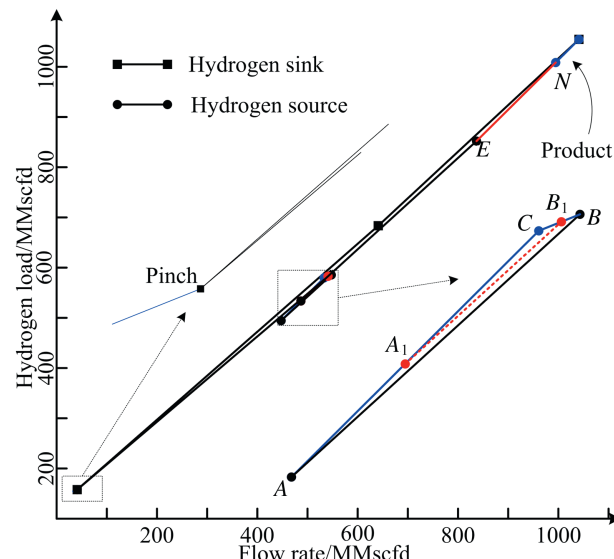


Fig. 12. Optimization of purification process (case 2).

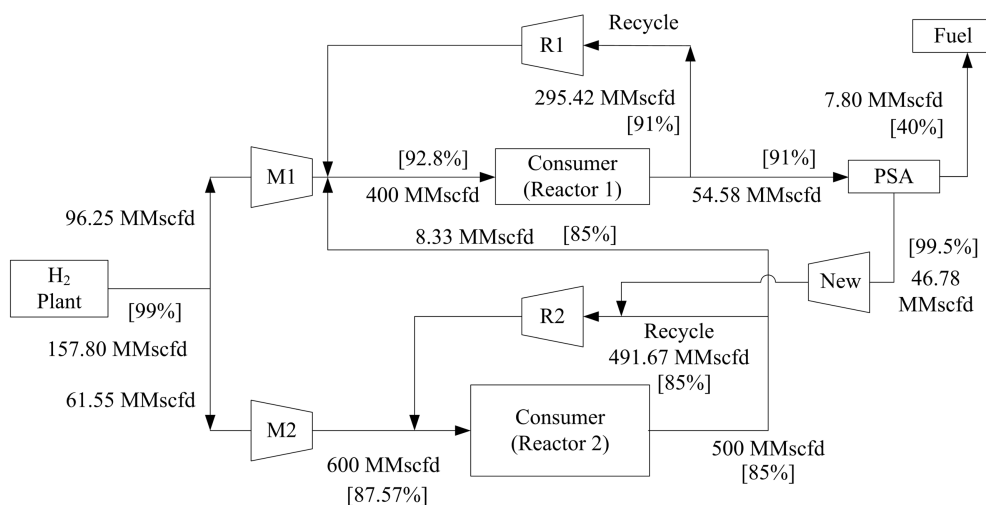


Fig. 13. Hydrogen network with PSA process (case 2).

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