

A Graphical Method for Optimisation of Hydrogen Networks Considering Impurity Removal through Chemical Absorption

Wei Li, Qiao Zhang, Mingbo Yang, Guilian Liu*

School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, 710049, China
 guilianliu@mail.xjtu.edu.cn

In refineries, amine-based chemical absorption is an effective technique to treat acid impurities (i.e. H₂S and CO₂) in hydrogen flows. Therefore, introducing chemical absorption units for acid impurity removal in refinery hydrogen networks could enhance the recovery and reuse of hydrogen, reducing the fresh hydrogen consumption. In this work, a novel pinch-based graphical method is proposed for integration of hydrogen network with chemical absorption units for impurity removal. The proposed method is able to target the maximum fresh hydrogen saved by introducing impurity removal while minimizing the total flow rate of hydrogen sources fed to the impurity removal unit. Any hydrogen sources in a hydrogen network can be treated as the feedstock of the impurity removal unit. A case study is performed to illustrate the applicability of this graphical method.

1. Introduction

Hydrogen is an essential resource in refineries consumed in many processes, such as hydrotreating, hydrocracking, and catalytic reforming, to produce high-quality oil products. In recent years, heavier crude oil, tighter environmental regulations, and rising heavy-end upgrading in the petroleum industry are leading to the increasing hydrogen consumption (Manan et al., 2017). These issues have impelled refineries to develop innovative technologies and processes to improve the utilization of hydrogen.

Pinch technology is an outstanding methodology in the optimization of energy/mass exchange networks for energy saving (Jia, 2015) and fresh source conservation (Liu et al., 2013a). To reduce the fresh hydrogen consumption, Alves and Towler (2002) firstly applied the pinch conception for hydrogen network integration to determine the minimum fresh hydrogen consumption and pinch location. However, the proposed method requires iteration to calculate the hydrogen surplus. El-Halwagi et al. (2003) developed a noniterative graphical technique to target the minimum fresh hydrogen consumption via hydrogen recycle/reuse networks. This method is performed in an impurity load versus flow rate diagram, which could show insights for hydrogen network integration. Focusing on the hydrogen concentration, another graphical method was proposed by constructing hydrogen source and sink composite curves in a hydrogen load versus flow rate diagram for hydrogen network integration (Zhao et al., 2006). Based on these graphical methods, researchers also investigated introduction of hydrogen purification into hydrogen networks, targeting the maximum purification feed flow rate (Liu et al., 2013b), the maximum fresh hydrogen saving (Yang et al., 2014a), and the optimal purification process (Yang et al., 2014b). These contributions focus on upgrading hydrogen concentration of some hydrogen sources in hydrogen networks to facilitate hydrogen reuse.

In terms of a chemical absorption process, only acid components in a hydrogen flow can be removed. Since hydrogen is almost insoluble in water, the recovery ratio of hydrogen can be considered as 100% (Wu et al., 2014). In this light, the aforementioned methods cannot directly coupling hydrogen network and chemical absorption processes. The main reason is that those methods are developed based on specified hydrogen recovery and hydrogen concentration, which cannot be directly determined from the operating line and the equilibrium line of an absorption column.

This work develops a novel graphical method for hydrogen network integration considering chemical absorption for impurity removal. The maximum fresh hydrogen saved by considering impurity removal can be identified by shifting the hydrogen source composite curve along the pinch point. In the case study, a hydrogen network with impurity removal is designed based on results obtained by the proposed graphical method.

2. Model of chemical absorption for impurity removal

For a chemical absorption process, a hydrogen stream enters the absorption column from the bottom and countercurrent contacts with the amine solution from the top. In this work, hydrogen is assumed as an inert component in any hydrogen flows. The operating line and equilibrium line are illustrated in Figure 1(a). For any point on the operating line, the mass balance can be described by Eq(1) - Eq(3).

$$(F^{in} \cdot y^{hydrogen,in}) \cdot (Y^{impurity,in} - Y^{impurity}) = L_s \cdot (X^{impurity} - X^{in}) \quad (1)$$

$$Y^{impurity} = \frac{y^{impurity}}{y^{hydrogen}} \quad (2)$$

$$X^{impurity} = \frac{x^{impurity}}{x^{solvent}} \quad (3)$$

The impurity removal ratio R can be determined as Eq. (4).

$$R = \frac{(F^{in} \cdot y^{hydrogen,in}) \cdot (Y^{impurity,in} - Y^{impurity,pro})}{F^{in} \cdot y^{hydrogen,in} \cdot Y^{impurity,in}} = \frac{Y^{impurity,in} - Y^{impurity,pro}}{Y^{impurity,in}} \quad (4)$$

where F is the flow rate of a hydrogen stream, y is the molar concentration, Y is the ratio of impurity concentration to hydrogen concentration in the gas flow, L_s is the flow rate of solvent, X is the ratio of impurity concentration to solvent concentration in the liquid flow, and superscripts *in* and *pro* are the gas feed and the gas product of the absorption column, respectively.

For a given feedstock, the mass balance of the overall absorption column is described as Eq(5), which can also be represent as a triangle in the impurity load versus flow rate diagram, as shown in Figure 1(b).

$$F^{in} = F^{pro} + F^{in} \cdot y^{impurity,in} \cdot R \quad (5)$$

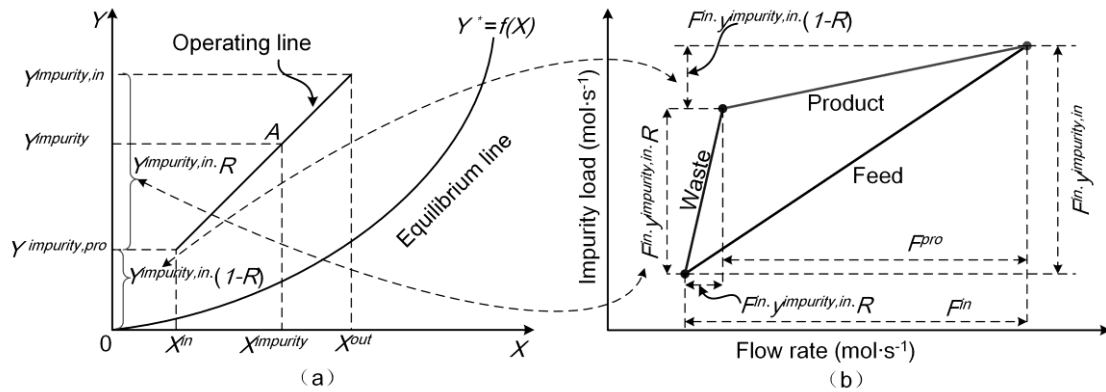


Figure 1: Illustration of the chemical absorption process: (a) operating line and equilibrium line of an absorption column; (b) graphical representation of the mass balance.

3. Graphical method for hydrogen network integration considering impurity removal

In this work, the proposed graphical method is developed by coupling the existing method (El-Halwagi et al., 2003) with the impurity removal model. The targeting procedure for the minimum fresh hydrogen consumption considering impurity removal includes two main parts. The first part is to identify the minimum fresh hydrogen consumption without impurity removal. The second one is to determine the fresh hydrogen saved by impurity removal and hydrogen sources fed into the impurity removal unit.

3.1 Identify the minimum fresh hydrogen consumption without impurity removal

The graphical procedure for targeting the minimum fresh hydrogen consumption without consideration of impurity removal is illustrated in Figure 2. Detailed information of the procedure can be found from the literature (El-Halwagi et al., 2003).

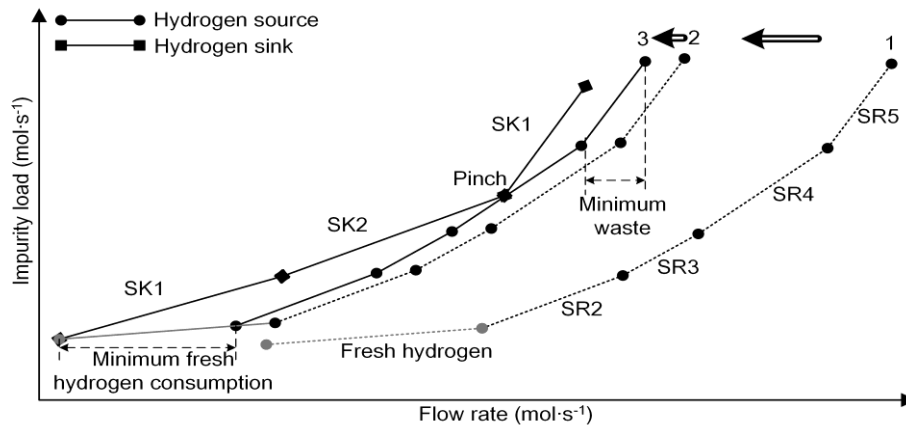


Figure 2: Graphical procedure for the minimum fresh hydrogen consumption without impurity removal

3.2 Identify the fresh hydrogen saved by considering impurity removal

As aforementioned, for a given hydrogen source and a desired impurity removal ratio, the corresponding product can be easily determined. Based on the graphical representation in Figure 1(b), the graphical procedure for determining the fresh hydrogen saved by considering impurity removal is presented as below:

- (1) Select a hydrogen source as the feedstock of the impurity removal unit. For example, the hydrogen source SR4 is selected. For convenience, the part of source composite curve above the feedstock is named as curve 1, and the part of source composite curve between curve 1 and the segment of fresh hydrogen is named as curve 2, as shown in Figure 3(a).
- (2) In order to meet the demand of all hydrogen sinks, all hydrogen sources should satisfy Eq(6). The maximum fresh hydrogen saving reaches when the equality holds. Therefore, construct a vertical line AA_1 as a guiding line, as shown in Figure 3(a). There is no hydrogen source at the right side of AA_1 when the fresh hydrogen saving is maximum. It means that waste gas comes from the impurity removal unit.

$$\sum_{i=1}^m F_i - \sum_{j=1}^n F_j \geq F^{in} \cdot y^{impurity,in} \cdot R + F^{saving} \quad (6)$$

where F_i is the flow rate of hydrogen source i , F_j is the limiting flow rate of hydrogen sink j , F^{saving} is the fresh hydrogen saved by introducing the impurity removal unit.

- (3) Move curve 1 downwards along curve 2 until its top end sits on AA_1 . If curve 1 intersects the sink composite curve at a point during the movement, move curve 1 continuously along this intersection until its top end sits on AA_1 , as shown in Figure 3(a). In this situation, the bottom end of curve 1 does not sit on curve 2.
- (4) Extend the segment that represents fresh hydrogen, as shown in Figure 3b.
- (5) Move curve 2 upwards along BC until one of the following two conditions reaches: (I) the bottom end of the source selected as feedstock sits on curve 1, and (II) the bottom end of curve 1 sits on the selected source as feedstock (see Figure 3(b)).
- (6) The condition (I) means that the selected hydrogen source is fed into the impurity removal unit at its maximum flow rate. Regard the product of the impurity removal unit and the hydrogen sources except SR4 as a new set of hydrogen sources. Afterwards, identify the minimum fresh hydrogen consumption of the new hydrogen network according to the graphical procedure introduced in Section 3.1.
- (7) For condition (II) shown in Figure 3(b), MD is not included into the hydrogen source composite curve. Thus, MD can be treated as the initial feedstock for the impurity removal unit. According to the desired R , plot ME to represent the corresponding product of the impurity removal unit and DE to represent the corresponding waste. Plot another line B_1F with the same slope of ME to represent the product, as depicted in Figure 3(c).
- (8) Move curve 2 together with B_1F upwards along the bottom end of curve 1. During this movement, MD, ME, and DE increase. Besides, B_1F intersects the segment of fresh hydrogen at point G, and B_1G represents the reused product, as shown in Figure 3(d). Therefore, this movement could terminate until B_1G is equal to ME. Finally, the maximum fresh hydrogen saved by considering impurity removal is identified as BG. MD represents the hydrogen source fed into the impurity removal unit, and DE is the waste gas. As can be seen in Figure 3(d), only a part of SR4 is fed into the impurity removal unit. However, if the flow rate of feedstock increases further, the removed impurity will increase as well. It can be deduced that the fresh hydrogen saving will decrease according to Eq(6).

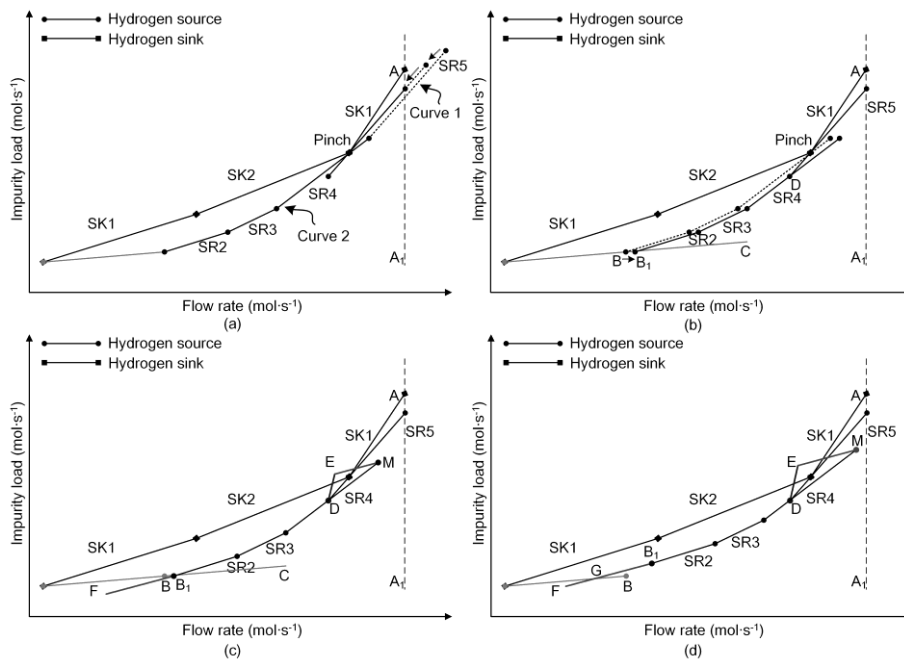


Figure 3: Graphical procedure for the maximum fresh hydrogen saved by considering impurity removal.

4. Case study

The applicability of the developed graphical method is illustrated based on the following case of hydrogen network integration. The data of the studied hydrogen network is given in Table 1. The impurity in hydrogen sources is assumed to be H_2S , which is absorbed by methyldiethanolamine in the case study.

Table 1: Data of hydrogen sinks and sources of the case study (El-Halwagi et al. 2003)

Streams	Flow rate (mol/s)	Impurity concentration (mol%)	Impurity load (mol/s)
SK1	2495	19.39	483.8
SK2	180.2	21.15	38.1
SK3	554.4	22.43	124.4
SK4	720.7	24.86	179.2
SR1 (Fresh hydrogen)	To be determined	5	To be determined
SR2	623.8	7	43.7
SR3	415.8	20	83.2
SR4	1801.9	25	450.5
SR5	138.6	25	34.7
SR6	346.5	27	93.6
SR7	457.4	30	137.2

The minimum fresh hydrogen consumption without impurity removal is identified as 268.8 mol/s according to the graphical method proposed by El-Halwagi et al. (2003). The minimum waste gas is 102.5 mol/s of SR7.

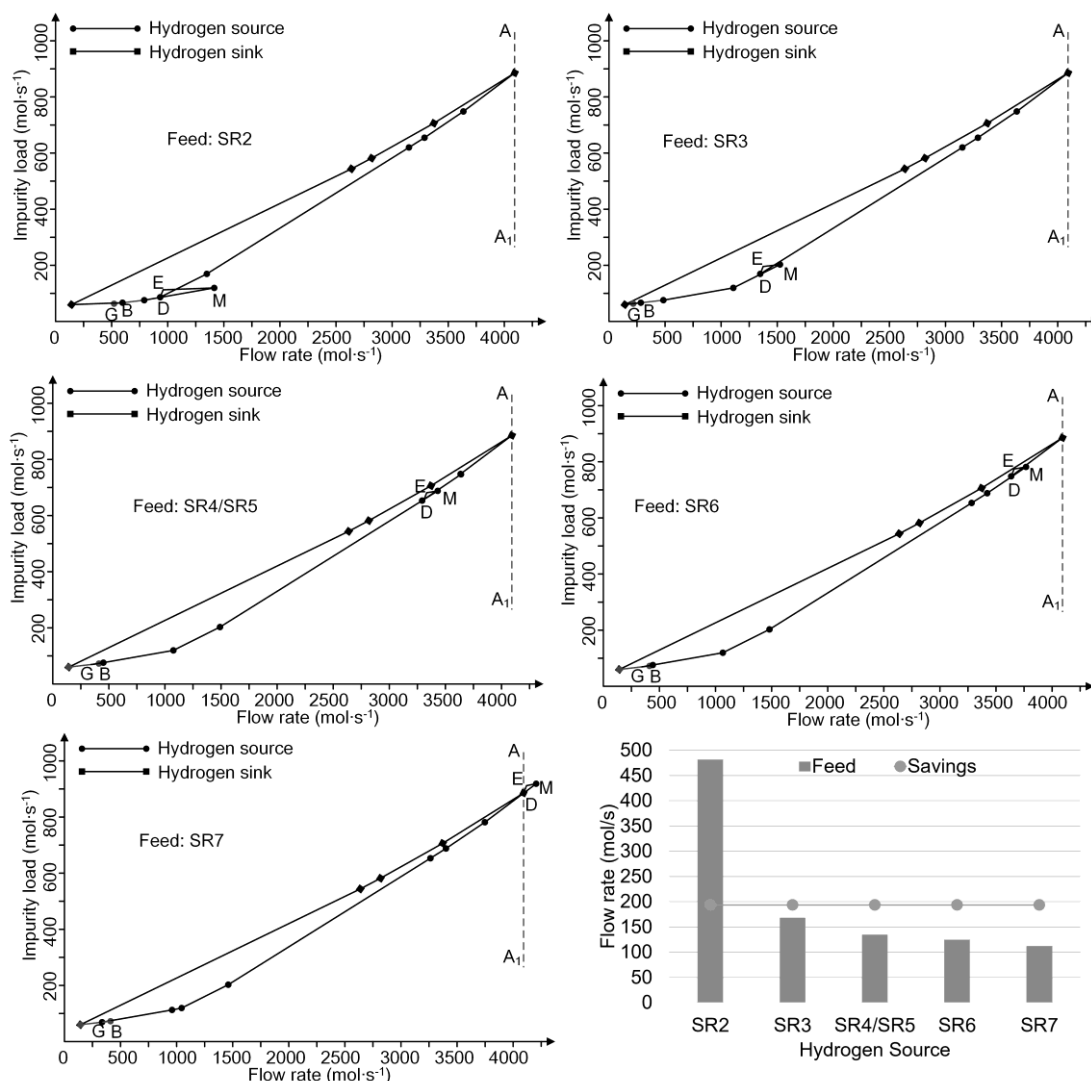


Figure 4: Identify the maximum fresh hydrogen saved by introducing impurity removal.

To reduce the fresh hydrogen consumption, the impurity removal technology is employed in this hydrogen network. In this study, the impurity removal ratio is assumed to be 80% for any selected feedstock. Following the procedure proposed in Section 3.2, the maximum fresh hydrogen saving of each hydrogen source selected as the feedstock is identified as shown in Figure 4. MD represented the hydrogen source fed into the impurity removal unit. It is interesting to find that all hydrogen sources result in the same fresh hydrogen saving of 75.5 mol/s. As a result, the fresh hydrogen consumption reduces from 268.8 mol/s to 193.3 mol/s by considering impurity removal. The obtained results also show that the same amount of impurity is removed for each selected hydrogen source. Therefore, the flow rate of the hydrogen source fed into the impurity removal unit increases as the impurity concentration of the hydrogen source decrease, as can be seen in Figure 4. A possible design of the hydrogen network considering impurity removal based on SR7 is given in Figure 5.

5. Conclusions

This work presented a novel graphical method for hydrogen network integration considering impurity removal by chemical absorption. The method was developed by coupling the impurity removal model with an existing graphical method. The maximum fresh hydrogen saved by considering impurity removal and the corresponding hydrogen sources fed into the impurity unit were identified based on the pinch conception. The results of case study showed that introducing impurity removal unit into the hydrogen network could obviously reduce the fresh hydrogen consumption. Furthermore, the proposed graphical method is also suitable to water network integration. However, this work only focuses on the development of the graphical method for hydrogen network

integration. The performance and optimization of the impurity removal unit will be taken into account to enrich the proposed graphical method in future work.

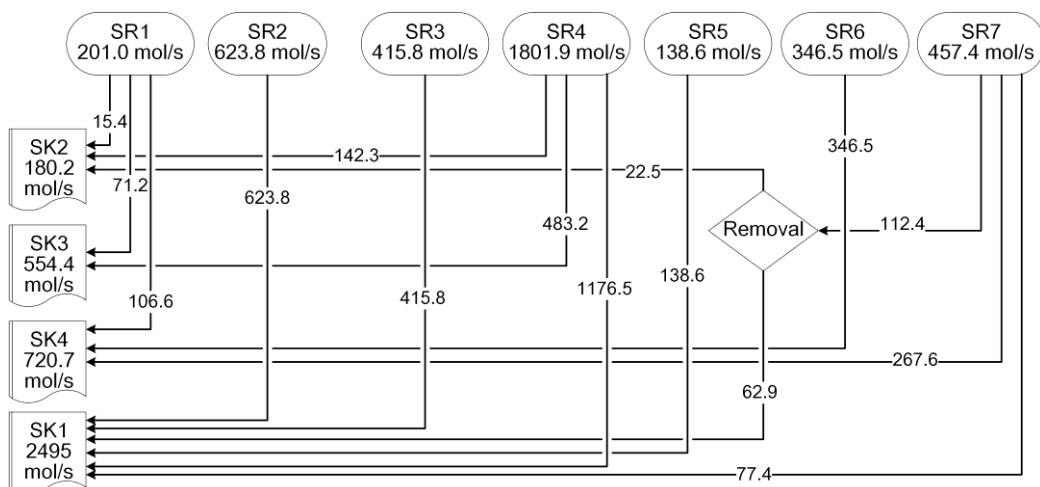


Figure 5: One possible design of the hydrogen network with impurity removal.

Acknowledgments

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