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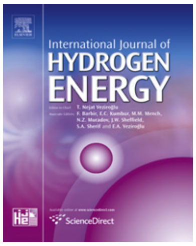

Hydrogen sulfide removal process embedded optimization of hydrogen network

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ABSTRACT

Due to the trend in tighter environmental regulations on heavier crude oil processing, hydrogen has become an important strategic resource in modern refineries. Refiners have to improve the efficiency of hydrogen distribution networks to satisfy the increasing demand of hydrogen. Consequently, plenty of work has been focusing on optimizing hydrogen reuse and purification schemes, which is known as hydrogen network integration (HNI). In refineries, hydrogen purification techniques include hydrocarbon removal units and hydrogen sulfide (H_2S) removal units. Hydrocarbon removal units such as membrane separation and pressure swing adsorption (PSA) are frequently employed in the HNI study. However, the possibility of integrating H_2S removal units into HNI study has been overlooked until recently. H_2S removal units are usually modeled as mass exchangers and independently studied as mass exchange networks (MEN). In the present work, an improved modeling and optimization approach has been developed to integrate H_2S removal units into HNI. By introducing a desulfurization ratio, $R_{ds_{pl,i'}}$, simplified MEN is incorporated into hydrogen distribution network. Total annual cost (TAC) is employed as the optimizing object to investigate the tradeoffs between hydrogen distribution network cost and MEN cost. Pressure constraints and impurity concentrations are considered, and cost equations are established to determine the installation of new equipments in order to synthesis an economical network. A practical case study is used to illustrate the application and effectiveness of the proposed method.

1. Introduction

Green house gas (GHG) emission has become a hot issue in modern society. A great number of GHG emissions are related to fuels. The largest fuel suppliers, oil refineries, are now facing challenges of producing cleaner fuels. The challenge comes from the unbalance between hydrogen demand and supply. On the one hand, crude oil resources are getting heavier and the content of sulfur and nitrogen is increasing, while the product fuels with lower aromatic, sulfur and nitrogen content are required in order to meet environmental regulations. As a result, more and more hydro-treating

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Abbreviations: DHT, Diesel hydro-treater; GCA, Gas cascade analysis; G/DHT, Gasoline and diesel hydro-treater; GHG, Green house gas; GHT, Gasoline hydro-treater; HNI, Hydrogen network integration; HP, High Pressure; HPlant, hydrogen plant; LP, Low Pressure; MEN, Mass exchange network; MINLP, Mixed integer non-linear problem; MSAs, Mass separating agents; PP, polypropylene unit; PSA, Pressure swing adsorption; RF, catalytic reformer; PE, polyethylene unit; TAC, Total annual cost.

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processes are under construction to remove the undesired contents. Hydrogen demand will keep growing. On the other hand, reduction in the aromatics content of gasoline specification has cut down hydrogen production in the catalyst reforming unit, which used to be the traditional source of hydrogen in refineries. Consequently, hydrogen is becoming a critical issue for refineries. As it was considered as the best potential energy of the future [1], hydrogen resource is of great importance to our society. In a word, efficient usage of hydrogen is both critical to the refineries and our society.

Though investments have been made in building up new hydrogen plants and work has been done on investigation of the efficient producing of hydrogen through steam methane reforming [2], the HNI technique is still of great importance for refinery hydrogen management. This is because hydrogen production is a GHG emission intensive industry. Implementing HNI requires full consideration of the performance of the whole hydrogen network. There are several practical considerations which must be tackled when optimizing hydrogen network as a whole: 1). Hydrogen concentration, which is the first essential stream property concerned when considering hydrogen reuse; 2). Impurity concentration, for example hydrogen sulfide, which can not only corrode the equipments but also cause damage to certain catalyst must be controlled at a certain level; 3). Pressure constraints, which is one of the essential considerations for a practical model.

During the past decade, HNI has been extensively explored and the studies carried out can simply be classified into two major categories:

- Pinch analysis approaches
- Mathematical programming approaches based on superstructures.

There are dozens of pinch analysis approaches as summarized by Foo [3], and they are graphical or algebraic based methods. These methods have two things in common: 1). They can provide minimum hydrogen utility consumption or off-gas discharge before system structure is obtained; 2). They usually manipulate three basic properties of hydrogen streams: flowrate, purity and impurity load. As early as 1996, Towler et al. [4] employed value composite curves to assess hydrogen resources. The first graphical hydrogen pinch analysis approach was developed by Alves [5], who proposed a hydrogen surplus diagram in the purity versus flowrate coordinate system. Subsequently, El-Halwagi et al. [6] developed an iterative-free graphical methodology in the impurity load versus flowrate coordinate system. This method was extended to systems with both pure and impure hydrogen resources [7,8]. Later, another coordinate system, the purity versus impurity load system, was employed by Agrawal and Shenoy [9] and Bandyopadhyay [10]. Foo [11] introduced an algebraic method, the gas cascade analysis (GCA), for targeting the minimum utility consumption. Liao et al. [12] presented a new algebraic method addressing the relationship between pinch simplification and the mathematical model. Pinch analysis techniques have also been extended to multiple impurity problems by Zhao et al. [13] and pressure constraint problems by Ding et al. [14]. Recently, pinch analysis for placing purifiers has been improved: optimal placements were obtained for both remove ratio specified [15] and tail gas purity specified [16] purifier models.

Pinch analysis methods are useful in giving design targets, while mathematical programming methods are powerful in detailed design. Hallale [17] proposed an MINLP optimization approach based on superstructure that fully accounts for pressure constraints and the existing equipments, which was then modified by Kumar [18] for considering variable inlet and outlet pressures of compressors. Liu and Zhang [19] developed an automated design approach for the selection of appropriate purification processes in hydrogen network, in which shortcut models for purification processes were developed. In order to lower the computation cost and obtain feasible solutions, Khajehpour [20] minimized the hydrogen waste through reduction of the superstructure by heuristic rules. Liao [21] incorporated compressors and purifiers into state-space superstructure, and developed a systematic approach for the integration of hydrogen network with purifiers. Considering the life cycle of hydrogenation catalysts, Ahmad [22] and Xuan et al. [23] extended the problem formula to cope with the multi-period operation problems. Jiao et al. [24] presented a multi-objective optimization approach to explore the tradeoffs between operating cost and investment cost. The aforementioned mathematical programming methods were only valid for single contaminant systems. Recently, Jia [25] considered the multi-component effect of hydrogen streams by integrating flash calculations, which made the obtained result more feasible. However, this approach requires iterative interactions between simulation and optimization procedures which may cause difficulty in convergence when integer variables are introduced. Nevertheless, multi-component consideration will direct the trend of HNI research, because the component constraint like hydrogen sulfide constraint cannot be ignored in real operation. Compared to single component optimization, multi-component HNI concerns not only methane contaminant, but also other impurities such as hydrogen sulfide. Consequently, not only the hydrocarbon removal units but also H_2S removal units should be involved in the HNI study.

However, the incorporation of H_2S removal units into multi-component HNI remains unexplored. In refineries, H_2S is a very important impurity which cannot be ignored because it will not only corrode the equipment but also harm certain catalysts. As a result, the content of H_2S contaminant in the system is strictly controlled at a specific level in real production. There are several methods to remove H_2S: 1) dry desulfurization; 2) wet desulfurization; 3) bio-desulfurization; 4) and desulfurization by membrane. Wet desulfurization process is widely used. This process utilizes an aqueous absorbent in a column to absorb H_2S and yields a substantially H_2S-free gas stream. In some refineries, H_2S absorption unit has already been used to remove the overloaded hydrogen sulfide from the hydrogen flow so as to further excavate the potential of efficient hydrogen utilization.

H_2S removal units are usually modeled as mass exchangers and independently studied as mass exchange networks (MEN). MEN integration was initially introduced by El-Halwagi et al [26], aimed at synthesizing a network of mass exchange units which can preferentially transfer certain species from rich streams to the mass separating agents (MSAs) at