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## Review Article

# State-of-the-art review of targeting and design methodologies for hydrogen network synthesis

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## ARTICLE INFO

## Article history:

Received 29 April 2016  
Received in revised form  
23 September 2016  
Accepted 26 September 2016  
Available online xxx

## Keywords:

Pinch analysis  
Network design  
Hydrogen management  
Optimisation

## ABSTRACT

The synthesis of hydrogen distribution networks has been an active area of research over the last two decades. The concept of hydrogen management based on an economic cost-driven analysis appeared late in the 1990s and was followed up by numerous insight-based and mathematical optimisation approaches in the 2000s. More recently, several superstructure-based optimisation methods have been proposed to accommodate pressure restrictions, additional equipment and other practical constraints when finding the optimal flowsheet configuration. This paper provides a state-of-the-art review of different process integration technologies adopted for the assessment of hydrogen resources in refineries and petrochemical plants, published from late in the 1990s to the present time. Both targeting and design methods are reviewed. An effective hydrogen management strategy can only be achieved by combining different insight-based approaches with detailed mathematical programming.

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<http://dx.doi.org/10.1016/j.ijhydene.2016.09.179>

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## Introduction

The recent environmental regulations to cut down pollutant gas emissions (e.g., SO<sub>2</sub>, NO<sub>2</sub>, etc.) have lowered the sulphur and nitrogen contents allowed in gasoline and diesel fuels. This fact, along with the increasing drive to process heavy and sour crude oils, and the refining market trends toward gasoline and middle distillate fuels, have led to increased hydrogen demands associated with hydrotreating and hydrocracking processes. To obtain the best value of these less attractive crude oils, refiners must be able to convert heavy ends compounds into lighter fractions, which can be blended in gasoline and diesel pools [1]. Moreover, some petroleum products (e.g., aromatics, olefins, etc.) can be further processed in petrochemical plants to yield high valuable petrochemical compounds such as polyethylene or propylene. An overview of various technical aspects regarding refinery hydrogen management (e.g., hydrogen production, purification and supply), including the impact on several key performance indicators can be found in the literature [1–13].

In recent past, catalytic reforming had been the common source of hydrogen in refineries. However, the current trends toward low-aromatic gasolines are constraining the use of hydrogen from catalytic reforming processes [5]. As a result, many refiners are often faced with temporary hydrogen shortfalls to meet both product quality and environmental specifications, as well as to boost hydrogen partial pressures, essential to enhance hydroprocessing reactors conversion, throughputs, yields and catalyst life [8]. The imbalance between hydrogen supply and demand has compelled refining industries to look for alternative hydrogen production processes such as natural gas steam reforming or partial oxidation of light hydrocarbons. Consequently, numerous projects to revamp the existing or install new “on-purpose” hydrogen plants are being implemented worldwide. As the price of primary energy is increasing, so it is the hydrogen production cost. The typical hydrogen production processes usually require a significant amount of energy and generate a considerable amount of greenhouse gases, particularly CO<sub>2</sub>. Therefore, hydrogen management has become a priority issue

in crude oil processing, not only to boost refinery margins but also to diminish the environmental impact associated with on-site hydrogen production.

The purchase of hydrogen over-the-fence from outside suppliers has also been considered another suitable option to comply with the current hydrogen shortages. Other solutions to mitigate the impact of growing hydrogen demand have been investigated and implemented at industrial scale, namely direct reuse of hydrogen-rich streams from hydroprocessing units in other hydrogen-consuming processes (hydrotreaters and/or hydrocrackers), or purification of refinery off-gases via pressure-swing adsorption, membrane permeation or cryogenic separation. The appropriate selection of a hydrogen purification technology must consider several criteria, e.g., minimum hydrogen product purity required, purifier feed capacity, pressure drop between feed gas and hydrogen product, etc. Without effective recovery, reusing and recycling strategies, the outcome of an increasing hydrogen demand might lead to multiple shortcomings, including restraints on the existing crude oil processing capacity or other environmental issues related to sulphur and nitrogen contents in transport fuels [5].

The recovery, recycle/reuse or disposal of a hydrogen-rich stream from a hydrogen consumer is settled in accordance with its hydrogen content. When the hydrogen content is high, the off-gas is usually routed to another hydrogen consumer. On the other hand, if the hydrogen content is low the off-gas is flared or vented into the refinery fuel system. For intermediate hydrogen contents, the off-gas is typically redirected to a purification unit for hydrogen recovery [14].

Redesigning hydrogen distribution systems to enclose all hydrogen needs generally require significant capital investment, particularly in hydrogen plants, piping systems and compressors. However, both capital and operating costs can be reduced if some of the unreacted hydrogen is collected and reused on-site via re-routing or purification. The optimal flowsheet configuration is that in which the system is operating at the minimum hydrogen utility supply without violating any network constraint. Owing to the importance of hydrogen in the majority of refining processes, before any revamping it is essential to evaluate the current hydrogen

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