

Refinery Hydrogen Network Management with Key Factor Analysis

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The increment of hydrogen demand in modern oil refineries motivates the industries to optimize the hydrogen network management and rationally use hydrogen sources for cost reduction and sustainable development. This paper presents comprehensive mathematical model for the synthesis of refinery hydrogen network. The hydrogen consuming and supply processes and hydrogen purification processes are investigated in detail and described mathematically. A simple refinery hydrogen network is synthesized for the illustration of the applicability of the proposed approach.

1. Introduction

The heavier crude oil, tighter environmental regulations and policies on sulfide content are leading to more strict oil products quality requirements for refineries. In order to improve the oil products quality, refineries has to increase the depth of hydrotreating and hydrocracking processes, which consume large amount of fresh hydrogen. On the other hand, the operation capacity of traditional naphtha reforming, an important hydrogen producing process, is reduced because of the shrinking market demand for reforming products. Therefore, the gap between these consuming and producing processes aggravates the fresh hydrogen shortage in refineries, making fresh hydrogen a more and more expensive resource for modern refineries. Although several hydrogen purification processes (Pressure Swing Adsorption (PSA), Membrane separation) have been introduced to recover hydrogen from refinery off-gases, such small amount of recovered hydrogen is far insufficient to satisfy the sharp increasing demand. To complement fresh hydrogen, hydrogen production such as Steam Methane Reforming (SMR) is a way to produce fresh hydrogen, and hydrogen purchase outside is also another alternative. To minimize hydrogen production or purchase cost and achieve the sustainable development, it is quite necessary for refineries to enhance the hydrogen network management, indicating hydrogen network synthesis and retrofit.

Generally, the methodologies in previous work on the synthesis and retrofit of refinery hydrogen network can be classified into three aspects: pinch technique, such as, hydrogen surplus diagram (Alves and Towler, 2002), gas cascade analysis (Foo and Manan, 2006), improved limiting composite curve (Agrawal and Shenoy, 2006) and mathematical programming approach, such as first superstructure model with consideration pressure constraint (Hallale and Liu, 2001), systematic methodology for the selection of appropriate purifiers (Liu and Zhang, 2004), state-space superstructure (Liao et al., 2010), multi-component and integrated flash calculation (Jia and Zhang, 2011), hydrogen sulfide removal process embedded optimization model (Zhou et al., 2012), total exergy consumption of the hydrogen utility and compressor work (Wu et al., 2012), comprehensive hydrogen network model (Tahouni et al., 2012) and strategy for hydrogen integration in petroleum refining (Smith, et al., 2012). The mathematical programming approach which can take into account various constraints (multiple impurities, H₂/Oil ratio, pressure, compressor, hydrogen pipeline etc.) has been paid more and more attention.

In this paper, hydrogen consuming and producing processes, as well as hydrogen purifiers are investigated in detail. A comprehensive mathematical model for the synthesis of refinery hydrogen network is established.

Several key factors (i.e. multiple impurities, H₂/Oil ratio and pressure constraint) are incorporated into the mathematical model. A hydrogen network of a practical refinery is synthesized to illustrate the applicability of the proposed approach.

2. Problem Statement

Given a set of hydrogen sources with the total number of NSR , for each internal hydrogen source ($s \in NSR$) with specified maximum flow rate (FSR_s), concentration of component ($y_{s,comp}^{out}$), and pressure (PSR_s). With the appropriate placement of a number of gas compressors (NC), those hydrogen sources can be allocated with a set of hydrogen sinks. A number of hydrogen sinks (NSK), each sink ($k \in NSK$) has its own flow rate requirement (FK_k^{in}), minimum hydrogen purity (y_{k,H_2}^{in}), maximum allowable inlet concentration of impurity ($y_{k,comp}^{in}$) and pressure specification (PK_k^{in}). In addition, a number of external hydrogen sources (NHU), so-called hydrogen utilities, from hydrogen plants would be utilized to compensate the internal hydrogen source to fulfill the requirements of hydrogen sinks. The superstructure of the problem embedding potential configurations of interest is shown in Figure 1. The objective is to achieve the hydrogen utility target with the consideration of several key factors (i.e. multiple impurities, H₂/Oil ratio and pressure constraint).

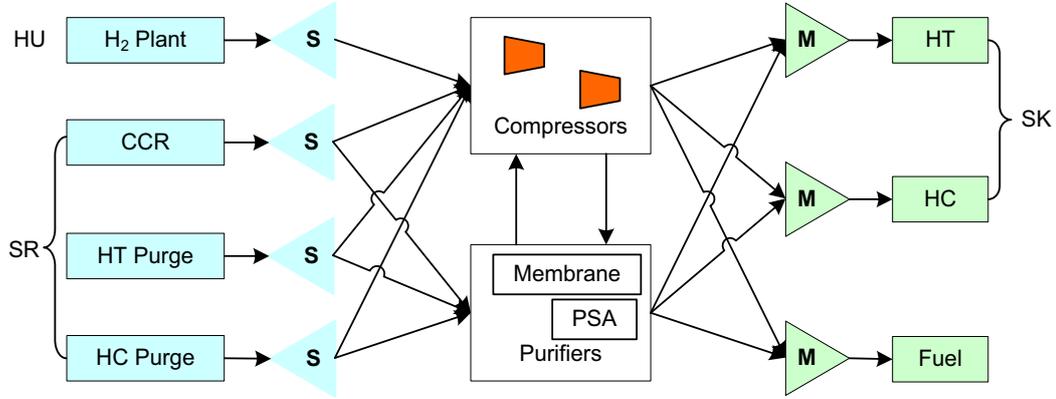


Figure 1. The superstructure of hydrogen distribution network

3. Mathematical Model

The mathematical formulations for the superstructure shown in Figure 1 are presented as follows.

(1) Formulations related to the u^{th} hydrogen utility

Flowrate balance on the splitting node after the u^{th} hydrogen utility,

$$FHU_u = \sum_{k \in NSK} FUK_{u,k} + \sum_{c \in NC} FUC_{u,c} \quad \forall u \in NHU \quad (1)$$

(2) Formulations related to the j^{th} hydrogen source

Flow rate balance for the splitting node after the s^{th} hydrogen source,

$$FSR_s = \sum_{k \in NSK} FSK_{s,k} + \sum_{c \in NC} FSC_{s,c} + \sum_{m \in NM} FSM_{s,m} + \sum_{p \in NP} FSP_{s,p} + FSF_s \quad \forall s \in NSR \quad (2)$$

(3) Formulations related to the c^{th} compressor

Flow rate and component balance for the mixing node before the c^{th} compressor,

$$FC_c^{in} = \sum_{u \in NFU} FUC_{u,c} + \sum_{s \in NSR} FSC_{s,c} + \sum_{\substack{c' \neq c \\ c' \in NC}} FCC_{c',c} \quad \forall c \in NC \quad (3)$$

$$FC_c^{in} \cdot y_{c,comp}^{in} = \sum_{u \in NFU} FUC_{u,c} \cdot y_{u,comp} + \sum_{s \in NSR} FSC_{s,c} \cdot y_{s,comp} + \sum_{\substack{c' \neq c \\ c' \in NC}} FCC_{c',c} \cdot y_{c',comp} \quad (4)$$

$$\forall c \in NC \quad \forall comp \in NCOMP$$

Flow rate and component balance around the outlet and inlet of the c^{th} compressor,

$$FC_c^{out} = FC_c^{in} \quad \forall c \in NC \quad (5)$$

$$y_{c,comp}^{out} = y_{c,comp}^{in} \quad \forall c \in NC \quad (6)$$

Flow rate balance for the splitting node after the c^{th} compressor,

$$FC_c^{out} = \sum_{k \in NSK} FCK_{c,k} + \sum_{m \in NM} FCM_{c,m} + \sum_{p \in NP} FCP_{c,p} + \sum_{\substack{c' \neq c \\ c' \in NC}} FCC_{c,c'} \quad \forall c \in NC \quad (7)$$

Pressure ratio constraint for the c^{th} compressor,

$$\varepsilon_c^{LB} P_c^{in} \leq P_c^{out} \leq \varepsilon_c^{UB} P_c^{in} \quad \forall c \in NC \quad (8)$$

(4) Formulations related to the purification system

Flow rate and hydrogen balance on the mixing node before the m^{th} membrane process,

$$FM_m^{in} = \sum_{s \in NSR} FSM_{s,m} + \sum_{c \in NC} FCM_{c,m} \quad \forall m \in NM \quad (9)$$

$$FM_m^{in} \cdot y_{m,comp}^{in} = \sum_{s \in NSR} FSM_{s,m} \cdot y_{s,comp}^{out} + \sum_{c \in NC} FCM_{c,m} \cdot y_{c,comp}^{out} \quad \forall m \in NM, comp = H_2 \quad (10)$$

Flow rate and hydrogen balance around the m^{th} membrane process,

$$FM_m^{in} = FM_m^{prod} + FM_m^{resd} \quad \forall m \in NM \quad (11)$$

$$FM_m^{in} \leq FM_m^{in,UB} \quad \forall m \in NM_{\text{exsit}} \quad (12)$$

$$FM_m^{in} \cdot y_{m,comp}^{in} = FM_m^{prod} \cdot y_{m,H_2}^{prod} + FM_m^{resd} \cdot y_{m,comp}^{resd} \quad \forall m \in NM, comp = H_2 \quad (13)$$

$$FM_m^{prod} \cdot y_{m,comp}^{prod} = RR_m \cdot FM_m^{in} \cdot y_{m,comp}^{in} \quad \forall m \in NM, comp = H_2 \quad (14)$$

Flow rate balance on the splitting node after the m^{th} membrane process,

$$FM_m^{prod} = \sum_{k \in NSK} FMK_{m,k}^{prod} \quad \forall m \in NM \quad (15)$$

$$FM_m^{resd} = \sum_{k \in NSK} FMK_{m,k}^{resd} + FFM_m^{resd} \quad \forall m \in NM \quad (16)$$

$$PM_m^{in,LB} \leq PM_m^{in} \leq PM_m^{in,UB} \quad \forall m \in NM \quad (17)$$

Pressure relationships around the m^{th} membrane process,

$$PM_m^{resd} = PM_m^{in} \quad \forall m \in NM \quad (18)$$

$$PM_m^{resd} = PR_m \cdot PM_m^{prod} \quad \forall m \in NM \quad (19)$$

$$M_m^{resd} \cdot y_{m,comp}^{resd} \geq PM_m^{prod} \cdot y_{m,comp}^{prod} \quad \forall m \in NM, comp = H_2 \quad (20)$$

Flow rate and hydrogen balance on the mixing node before the p^{th} PSA,

$$FP_p^{in} = \sum_{s \in NSR} FSP_{s,p} + \sum_{c \in NC} FCP_{c,p} \quad \forall p \in NP \quad (21)$$

$$FP_p^{in} \cdot y_{p,comp}^{in} = \sum_{s \in NSR} FSP_{s,p} \cdot y_{s,comp}^{out} + \sum_{c \in NC} FCP_{c,p} \cdot y_{c,comp}^{out} \quad \forall p \in NP, comp = H_2 \quad (22)$$

$$y_{p,H_2}^{prod} = \text{Const.} \quad (23)$$

Flow rate and hydrogen balance around the p^{th} PSA,

$$FP_p^{in} = FP_p^{prod} + FP_p^{resd} \quad \forall p \in NP \quad (24)$$

$$FP_p^{in} \cdot y_{p,comp}^{in} = FP_p^{prod} \cdot y_{p,comp}^{prod} + FP_p^{resd} \cdot y_{p,comp}^{resd} \quad \forall p \in NP, comp = H_2 \quad (25)$$

$$FP_p^{prod} \cdot y_{p,comp}^{prod} = RR_p \cdot FP_p^{in} \cdot y_{p,comp}^{in} \quad \forall p \in NP, comp = H_2 \quad (26)$$

Flow rate balance on the splitting node after the p^{th} PSA,

$$FP_p^{prod} = \sum_{k \in NSK} FPK_{p,k}^{prod} \quad \forall p \in NP \quad (27)$$

$$FP_p^{resd} = \sum_{k \in NSK} FPK_{p,k}^{resd} + FPF_p^{resd} \quad \forall p \in NP \quad (28)$$

Pressure relationship around the p^{th} PSA,

$$PP_p^{in, LB} \leq PP_p^{in} \leq PP_p^{in, UB} \quad \forall p \in NP \quad (29)$$

$$PP_p^{in} = PP_p^{prod} \quad \forall p \in NP \quad (30)$$

(5) Formulations related to the k^{th} hydrogen sink

Flow rate and component balance on the mixing node before the k^{th} hydrogen sink,

$$FK_k^{in} = \sum_{u \in NHU} FUK_{u,k} + \sum_{s \in NSR} FSK_{s,k} + \sum_{c \in NC} FCK_{c,k} \quad (31)$$

$$+ \sum_{k \in NSK} FMK_{m,k}^{prod} + \sum_{k \in NSK} FMK_{m,k}^{resd} + \sum_{k \in NSK} FPK_{p,k}^{prod} + \sum_{k \in NSK} FPK_{p,k}^{resd} \quad \forall k \in NSK$$

$$FK_k^{in} \cdot y_{k,comp}^{in} = \sum_{u \in NHU} FUK_{u,k} \cdot y_{u,comp}^{out} + \sum_{s \in NSR} FSK_{s,k} \cdot y_{s,comp}^{out} + \sum_{c \in NC} FCK_{c,k} \cdot y_{c,comp}^{out} \quad (32)$$

$$+ \sum_{k \in NSK} FMK_{m,k}^{prod} \cdot y_{m,comp}^{prod} + \sum_{k \in NSK} FMK_{m,k}^{resd} \cdot y_{m,comp}^{resd}$$

$$+ \sum_{k \in NSK} FPK_{p,k}^{prod} \cdot y_{p,comp}^{prod} + \sum_{k \in NSK} FPK_{p,k}^{resd} \cdot y_{p,comp}^{resd} \quad \forall k \in NSK, comp \in NCOMP$$

Flowrate and hydrogen balance for the inlet of the reactor for the k^{th} hydrogen sink,

$$FK_k^{feed} = FK_k^{in} + FK_k^{recycle} \quad \forall k \in NSK \quad (33)$$

$$FK_k^{feed} \cdot y_{k,comp}^{feed} = FK_k^{in} \cdot y_{k,comp}^{in} + FK_k^{recycle} \cdot y_{k,comp}^{recycle} \quad \forall k \in NSK, comp = H_2 \quad (34)$$

Constraint for the minimum ratio H_2/Oil for the reactor for the k^{th} hydrogen sink

$$FK_k^{feed} \cdot y_{k,comp}^{feed} \geq LFK_k^{feed} \cdot \text{Ratio}^{\min}(H_2/OIL) \quad (35)$$

(6) Formulations related to the fuel system

Flow rate and component balance on the mixing node before the fuel system,

$$FF^{in} = \sum_{s \in NSR} FSF_s + \sum_{m \in NM} FMF_m^{resd} + \sum_{p \in NP} FPF_p^{resd} \quad (36)$$

$$FF^{in} \cdot y_{fuel,comp}^{in} = \sum_{s \in NSR} FSF_s \cdot y_{s,comp}^{out} + \sum_{m \in NM} FMF_m^{resd} \cdot y_{m,comp}^{resd} + \sum_{p \in NP} FPF_p^{resd} \cdot y_{p,comp}^{resd} \quad (37)$$

$$\forall comp \in NCOMP$$

Objective functions:

The objective function can be simply formulated to minimize the hydrogen consumption.

$$\min FHU = \sum_{u \in NHU} FHU_u \quad (38)$$

Subjected to Eqs.(1)-(37).

The proposed model belongs to nonlinear programming (NLP) problem. It is coded in General Algebraic Modeling System -GAMS (Rosenthal, 2010) and the global solver BARON (Sahinidis, 1996) is utilized to solve it with appropriate lower and upper bounds for the variables.

4. Case study

The limiting data for hydrogen sources and sinks as shown in Tables 1 and 2 are extracted from certain refinery plant. Note that, the purification process (PSA and membrane) is not considered. The contaminant H_2S and other light hydrocarbons C_nH_m are selected as key component and are taken into consideration in the

optimization model. The pressure constraint is fulfilled according to the installation of compressor. The minimum flow rate that allocated from H₂ plant is 1,3567.68 Nm³/h Mscfd and four compressors are installed as shown in the optimal hydrogen network (Figure 1).

Table 1. Given data for hydrogen sources

Hydrogen Sources		Nm ³ /h	V H ₂ /%	V H ₂ S/%	V C _n H _m /%	P (MPa)
HU	H ₂ plant	-	93	0	7	2.758
SR1	CCR	26,320	79	0.5	20.5	2.413
SR2	DHT	11,390.4	76	1	23	2.413
SR3	CNHT	6,160	79	1.27	19.73	1.379
SR4	JHT	8,870.4	70	1.4	28.6	2.413
SR5	NHT	11,356.8	69	2	29	2.069
SR6	HCU	39,916.8	89	1	10	2.069

Table 2. Given data for hydrogen sinks

Hydrogen Sinks		Nm ³ /h	V H ₂ /%		V H ₂ S/%		V C _n H _m /%		P (MPa)
			max	min	max	min	max	min	
SK1	DHT	12,667.2	100	79.8	0.85	0	19.35	0	4.137
SK2	CNHT	9,195.2	100	85	1.5	0	13.5	0	3.4475
SK3	IS4	5,600	100	76	1	0	23	0	2.0685
SK4	NHT	13,529.6	100	75.5	0.85	0	23.7	0	2.0685
SK5	JHT	22,400	100	82.5	1	0	16.5	0	3.4475
SK6	HCU	43,433.6	100	85	0.5	0	14.5	0	13.79

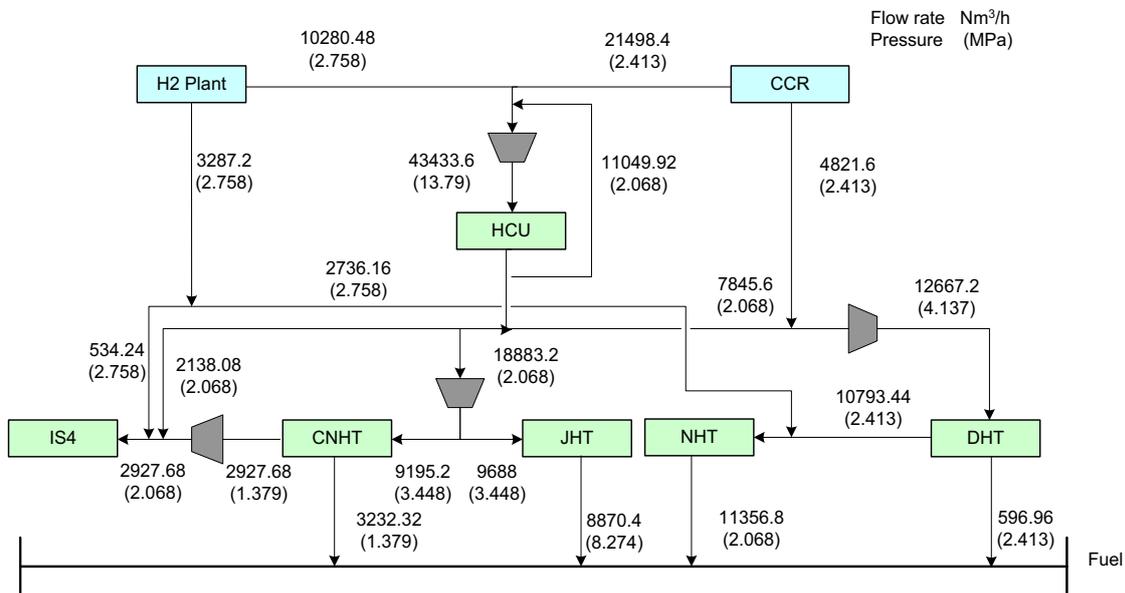


Figure 2: An optimal hydrogen distribution network

5. Conclusions

This paper aims to establish a comprehensive mathematical model for the synthesis of refinery hydrogen network with the consideration of several key factors (i.e. multiple impurities, H₂/Oil ratio and pressure constraint). The hydrogen consuming and producing processes, as well as hydrogen purifiers are investigated in detail and are described mathematically. The synthesis of a simple refinery hydrogen network illustrates the

applicability of the proposed approach. However, the influence of those key factors (i.e. multiple impurities, H₂/Oil ratio and pressure constraint) on the synthesis of hydrogen network is still ongoing.

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References

- Agrawal, V., Shenoy, U. V., 2006, Unified conceptual approach to targeting and design of water and hydrogen networks, *AIChE Journal*, 52, 1071-1082.
- Alves, J. J., Towler, G. P., 2002, Analysis of refinery hydrogen distribution systems, *Industrial & Engineering Chemistry Research*, 41, 5759-5769.
- Foo, D. C. Y., Manan, Z. A., 2006, Setting the minimum utility gas flowrate targets using cascade analysis technique, *Industrial & Engineering Chemistry Research*, 45, 5986-5995.
- Hallale, N., Liu, F., 2001, Refinery hydrogen management for clean fuels production, *Advances in Environmental Research*, 6, 81-98.
- Jia, N., Zhang, N., 2011, Multi-component optimisation for refinery hydrogen networks, *Energy*, 36, 4663-4670.
- Liao, Z. W., Wang, J. D., Yang, Y. R., Rong, G., 2010, Integrating purifiers in refinery hydrogen networks: a retrofit case study, *Journal of Cleaner Production*, 18, 233-241.
- Liu, F., Zhang, N., 2004, Strategy of purifier selection and integration in hydrogen networks, *Chemical Engineering Research and Design*, 82, 1315-1330.
- Rosenthal, R. E., 2010, *GAMS - A User's Guide*. Washington, DC, USA: GAMS Development Corporation.
- Sahinidis, N. V., 1996, BARON: A general purpose global optimization software package, *Journal of Global Optimization*, 8, 201-205.
- Smith R., Zhang N. Zhao J., 2012, Hydrogen integration in petroleum refining, *Chemical Engineering Transactions*, 29, 1099-1104
- Tahouni N., Shariati M. Panjeshahi M. H., 2012, Comprehensive modeling of hydrogen network in petrochemical complexes, *Chemical Engineering Transactions*, 29, 1093-1098
- Wu, S., Liu, G., Yu, Z., Feng, X., Liu, Y., Deng, C. 2012, Optimization of hydrogen networks with constraints on hydrogen concentration and pure hydrogen load considered, *Chemical Engineering Research and Design*, 90, 1208-1220.
- Zhou, L., Liao, Z., Wang, J., Jiang, B., Yang, Y. 2012, Hydrogen sulfide removal process embedded optimization of hydrogen network, *International Journal of Hydrogen Energy*, 37, 18163-18174.