MODELING AND OPTIMIZATION OF GAS NETWORKS IN REFINERY

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DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

Anoop Jagannath

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SUMMARY

The increased cost of crude oil, stringent environmental regulations and ever increasing demand for energy have made the refineries to adopt a more holistic approach that seeks to integrate energy, economics and the environment in its design and operation. One of the attractive options is to systematically utilize all the existing resources or utilities. Such an option of resource conservation, apart from promoting sustainable development, also plays a greater role in achieving greater cost savings. This thesis focuses on the two main utilities in a refinery namely fuel gas and hydrogen. These (fuel gas and hydrogen) are directly related to the refinery capacity and revenue and any step taken towards their conservation are certainly desirable and are of pivotal significance. To understand this, a network approach is adopted which studies the overall consumption of these utilities/gases in the entire refinery. This thesis mainly addresses the modeling and optimization of such gas networks in a refinery. The refinery gas networks considered here are the fuel gas and hydrogen networks.

First, we study the fuel gas networks. In this work, modeling and optimization of a multimode fuel gas network is carried out, that serves to operate optimally for all the modes of the refinery operation. This was studied for a refinery case study and results showed significant improvement in the capital cost of the network in comparison to the single mode. Apart from this, using the above model several interesting strategies for reducing the flaring and environmental penalties in refinery operation is examined. Next, we deal with the modeling and optimization of hydrogen network in the refinery. The work on the hydrogen network is divided into two parts. In the first part, the hydrogen network models available in the literature are generalized and modified to be solved to global optimality. Some examples were presented to show the optimization of hydrogen networks using the proposed global optimization approach. Results showed that the proposed algorithm showed superior performance when compared with the available commercial global optimization solver BARON. Next, this modified model is extended by considering integration with networks in other plants/refinery. Different integration schemes were proposed, studied and investigated in this regard. The results showed that the overall hydrogen consumption and total annualized cost was decreased when the networks were integrated.

In the second part of the work on hydrogen network, a more realistic model for the hydrogen network was developed. This nonconvex nonlinear programming model for the improved synthesis of hydrogen network, addressed some shortcomings observed in the previous existing models of hydrogen network. The model showed the importance and significance of including non-isothermal conditions on the network design along with non-isobaric conditions. Various challenges and issues relating to the same were also explained.

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CHAPTER 3

Indices

i	Fuel sources
j	Pollutants
k	Fuel sinks
p	Period/mode
s	Specification for fuel gas quality

Parameters

AF	Annualization factor
$CAPEX_{ik}^{B}$	Capital cost of compressor between source i and sink k
$CAPEX_{ik}^{C}$	Capital cost of cooler between source i and sink k
$CAPEX_{ik}^{H}$	Capital cost of heater between source i and sink k
$CAPEX_{ik}^{T}$	Capital cost of transfer line from source i to sink k
$CAPEX_{ik}^{V}$	Capital cost of valve between source i and sink k
c_{ip}	Heat capacity of source i in mode p
E_{kp}^{L}, E_{kp}^{U}	Minimum and maximum energy demand of sink k in mode p
G_{kp}^{L}, G_{kp}^{U}	Minimum and maximum allowable flow to sink k in mode p
HC_{ip}	Hydrocarbon content (mass / MMscf) of source stream i in mode p
e_{jikp}	Amount of pollutant j that sink k would emit in mode p for one 1 MMscf of fuel gas flared
HDP_{kp}	Hydrocarbon dew point temperature for sink k in mode p
hc_{p}^{U}	Limit on hydrocarbons flared without penalty at flare in mode p
e_{jp}^{U}	Regulatory limit on pollutants j flared without penalty at flare in mode p

$LHV_{kp}^{L}, LHV_{kp}^{U}$	Minimum and maximum lower heating value at sink k in mode p
MDP_{kp}	Moisture dew point temperature for sink k in mode p
n_{ip}	Adiabatic compression coefficient of source i in mode p
$OPEX_{ikp}^{B}$	Operating cost of compressor between source i and sink k in mode p
$OPEX_{ikp}^{C}$	Operating cost of cooler between source i and sink k in mode p
$OPEX_{ikp}^{H}$	Operating cost of heater between source i and sink k in mode p
$OPEX_{ikp}^{T}$	Operating cost of transfer line from source i to sink k in mode p
$OPEX_{ikp}^{V}$	Operating cost of valve between source i and sink k in mode p
OST	On-stream time of plant per year
P_{ipo}	Known pressure of source i in mode p
P_{kp}^{L}, P_{kp}^{U}	Minimum and maximum allowable pressure at sink k in mode p
q_{isp}	Value of spec s for source i in mode p
q_{ksp}^{L}, q_{ksp}^{U}	Minimum and maximum value of a spec s at sink k in mode p
R	Gas constant
SG_{kp}^{L}, SG_{kp}^{U}	Minimum and maximum allowable specific gravity at sink k in mode p
T_{ip}^{L}, T_{ip}^{U}	Minimum and maximum allowable temperature of source i in mode p
T_{ipo}	Known temperature of source i in mode p
T_{kp}^{L}, T_{kp}^{U}	Minimum and maximum allowable temperature at sink k in mode p
T_{R}	Reference temperature
x_{isp}	Mole fraction of hydrocarbon component s in stream i in mode p
WI_{kp}^{L}, WI_{kp}^{U}	Minimum and maximum value of Wobbe Index at sink k in mode p
α_{ip}	Cost of source i in mode p
β_{kp}	Revenue from surplus output by flexible sink k in mode p

γ_p	Penalty (\$/mass) for flaring hydrocarbon beyond regulatory limit at flare in mode p
ξ_{jp}	Penalty per unit emission of pollutant j during mode p beyond the regulatory limit
δ_{kp}	Cost of fuel gas for mode p in sink k
η_{ip}	Adiabatic compression efficiency of source i in mode p
π_p	Fractional annual duration of mode p
μ_{ip}	Joule – Thompson expansion coefficient of source i in mode p

Continuous variables

E_{kp}	Energy flow into sink k in mode p
F_{ik}	Capacity of transfer line from source i to sink k
F_{ip}	Flow (MMscf) from source i in mode p
f_{ikp}	Flow from source i to sink k in mode p
G_{kp}	Flow (MMscf) into sink k in mode p
h_{ikp}	Heat content of gas stream from source i to sink k in mode p
hc_p	Hydrocarbon amount flared beyond regulatory limit at flare in mode p
e_{jp}	Pollutant j flared in mode p
LHV_{kp}	Lower heating value at sink k in mode p
P_{kp}	Pressure at sink k in mode p
SG_{kp}	Specific gravity at sink k in mode p
T_{kp}	Temperature at sink k in mode p
ΔH_{ik}^{B}	Maximum duty of compressor in transfer line from source i to sink k
ΔH_{ik}^{C}	Maximum duty of cooler in transfer line from source i to sink k
ΔH_{ik}^{H}	Maximum duty of heater in transfer line from source i to sink k

ΔH_{ik}^{V}	Maximum duty of valve in transfer line from source i to sink k
Δh_{ikp}^{B}	Product of $f_{ikp}c_{ip}$ and temperature change during compression in SS_{ik}
Δh_{ikp}^{C}	Product of $f_{ikp}c_{ip}$ and temperature change during cooling in SS_{ik}
Δh_{ikp}^{H}	Product of $f_{ikp}c_{ip}$ and temperature change during heating in SS_{ik}
Δh_{ikp}^{V}	Product of $f_{ikp}c_{ip}$ and temperature change during expansion in SS_{ik}

CHAPTER 4

Indices

i	Hydrogen sources
j	Fuel gas sinks
k	Existing compressors
m	Purification units
n	New compressors
r	Refinery /plant
p	Origin unit
q	Destination unit
u	Processing unit
nc	Grid points
mc	Grid points

Sets

P_r	Set of origin units p in refinery r
P_{new}	Set of new origin units p to be retrofitted
Q_r	Set of destination unit in refinery r

Q_{new}	Set of new destination units q to be retrofitted
PQ_r	Set of non existing connections from origin p to destination q in refinery r

Parameters

AF	Annualization factor
OD	Operating days of refinery in a year
a_{NC}	Cost coefficient of new compressor
b_{NC}	Cost coefficient of new compressor
a_{PSA}	Cost coefficient of purification unit
b_{PSA}	Cost coefficient of purification unit
a_{pipe}	Cost coefficient of new pipelines retrofitted
b_{pipe}	Cost coefficient of new pipelines retrofitted
OCH_i	Cost of gas from hydrogen source i
OCE	Operating cost of compressors
OCF	Revenue generated by burning surplus hydrogen gas in fuel gas sink
LHV_{H_2}	Lower heating value of hydrogen gas
UF	Upper bound on flow
LF	Lower bound on flow
UP	Upper bound on pressure difference
LP	Lower bound on pressure difference
$UPwr$	Upper bound on compressor power
$LPwr$	Lower bound on compressor power
$Rcvr$	Recovery of purification unit
$Fmax_k$	Maximum capacity of existing compressor k
$Pout_k$	Outlet pressure of existing compressor k
Pin_k	Inlet pressure of existing compressor k

$PONC_n$	Outlet pressure of new compressor n
$PONC_n$	Inlet pressure of new compressor n
$Finu_u$	Feed flow into processing unit u
$Fout_u$	Flow out of processing unit u
$yinu_u$	Purity required at processing unit u
$yout_u$	Outlet purity from processing unit u
$yPPSA_m$	Product stream purity of purification unit m
T	Inlet temperature of the gas stream entering compressor
Cp	Specific heat of the gas stream entering compressor
γ	Adiabatic index
η	Compression efficiency
dx_{mc}	Length of the interval for variable x_{mc}
dy_{nc}	Length of the interval for variable y_{nc}
x^L, x^U	Lower and upper bound on the variable x in bilinear term $z = xy$
y^L, y^U	Lower and upper bound on the variable y in bilinear term $z = xy$

Binary variables

X_{pq}	Existence of pressure difference between origin p and destination q
XF_{pq}	Existence of flow between origin p and destination q
XNC_n	Existence of a new compressor n
$XPSA_m$	Existence of a new purification unit m
θx_{mc}	Binary variable for incremental cost formulation for variable x in $z = xy$
θy_{nc}	Binary variable for incremental cost formulation for variable y in $z = xy$

Continuous variables

F_{pq}	Flow connecting origin p to destination q

FNC_n	Capacity of the new compressor n
FPR_m	Capacity of the purification unit m
Fij_{ij}	Flow from source i to fuel gas sink *j*
Fik_{ik}	Flow from source i to existing compressor k
Fim_{im}	Flow from source i to purification unit m
Fin_{in}	Flow from source i to new compressor n
Fiu_{iu}	Flow from source i to processing unit u
Fkj_{kj}	Flow from existing compressor k to fuel gas sink *j*
Fkm_{km}	Flow from existing compressor k to purification unit m
Fkn_{kn}	Flow from existing compressor k to new compressor n
Fku_{ku}	Flow from existing compressor k to processing unit u
Fmk_{mk}	Flow from purification unit m to existing compressor k
Fmn_{mn}	Flow from purification unit m to new compressor n
Fmu_{mu}	Flow from purification unit m to processing unit u
$Frmj_{mj}$	Flow from purification unit m to fuel gas sink *j*
Fnj_{nj}	Flow from new compressor n to fuel gas sink *j*
Fnk_{nk}	Flow from new compressor n to exist compressor k
Fnm_{nm}	Flow from new compressor n to purification unit m
Fnu_{nu}	Flow from new compressor n to processing unit u
Fuj_{uj}	Flow from processing unit u to fuel gas sink *j*
Fuk_{uk}	Flow from processing unit u to existing compressor k
Fum_{um}	Flow from processing unit u to purification unit m
Fun_{un}	Flow from processing unit u to new compressor n
$Fuu_{uu'}$	Flow from processing unit u to other processing unit u'
$Fuu_{u'u}$	Flow from other processing unit u' to processing unit u
$Fout_i$	Flow of gas from source i

$Finj_j$	Flow into the fuel gas system j
P_p	Pressure at origin unit p
P_q	Pressure at destination unit q
Pwr_k	Power consumption of existing compressor k
$PwrNC_n$	Power consumed by the new compressor n
$ycomp_k$	Purity at the existing compressor k
$yinj_j$	Purity into the fuel gas system j
$yout_i$	Purity out of the source i
yNC_n	Purity at the new compressor n
$yRPSA_m$	Purity of the residue stream from purification unit m
x_{mc}	Continuous variable x in mc^{th} grid point
y_{nc}	Continuous variable y in nc^{th} grid point
Δu_{mc}	Local continuous variable in mc^{th} grid point
Δv_{nc}	Local continuous variable in nc^{th} grid point
Δwx_{mc}	Continuous variable in mc^{th} grid point
Δwy_{nc}	Continuous variable in nc^{th} grid point
$\Delta wxy_{mc,nc}$	Continuous variable at mc^{th} and nc^{th} grid point

CHAPTER 5

Indices

i	Hydrogen sources
j	Fuel gas sinks
m	Processing units
n	Purification units
p	Origin unit
q	Destination unit

Parameters

AF	Annualization factor
a_n	Capital cost coefficient for purification unit n
b_n	Operational cost coefficient for purification unit n
C_{pq}	Specific heat of gas stream in transfer line connecting origin p to destination q
$CAPEX_{pq}^{B}$	Capital cost coefficient of compressor in transfer line connecting origin p to destination q
$CAPEX_{pq}^{C}$	Capital cost coefficient of cooler in transfer line connecting origin p to destination q
$CAPEX_{pq}^{H}$	Capital cost coefficient of heater in transfer line connecting origin p to destination q
$CAPEX_{pq}^{T}$	Capital cost coefficient of pipeline connecting origin p to destination q
$CAPEX_{pq}^{V}$	Capital cost coefficient of valve in transfer line connecting origin p to destination q
c_i	Cost coefficient of hydrogen gas from source i
F_i^L, F_i^U	Minimum and maximum flow of gas from source i
F_m^L, F_m^U	Minimum and maximum flow of gas entering processing unit m
n_{pq}	Adiabatic compression coefficient of gas stream in transfer line connecting origin p to destination q
OP	Operating hours of a refinery in a year
$OPEX_{pq}^{B}$	Operational cost coefficient of compressor in transfer line connecting origin p to destination q
$OPEX_{pq}^{C}$	Operational cost coefficient of cooler in transfer line connecting origin p to destination q

$OPEX_{pq}^{H}$	Operational cost coefficient of heater in transfer line connecting origin p to destination q
$OPEX_{pq}^{T}$	Operational cost coefficient of pipeline connecting origin p to destination q
$OPEX_{pq}^{V}$	Operational cost coefficient of valve in transfer line connecting origin p to destination q
P_p^L, P_p^U	Minimum and maximum pressure limits of origin p
P_q^L, P_q^U	Minimum and maximum pressure limits of destination q
r_n	Recovery of hydrogen in purification unit n
T_p^L, T_p^U	Minimum and maximum temperature limits of origin p
T_q^L, T_q^U	Minimum and maximum temperature limits of destination q
T_{pq}^L, T_{pq}^U	Minimum and maximum temperature limits of in transfer line connecting origin p to destination q
x_m^L	Minimum limit on the purity of feed entering processing unit m
x_j^L, x_j^U	Minimum and maximum limit on purity of gas into fuel sink *j*
y_m	Known purity of hydrogen stream exiting processing unit m
yp_n	Known purity of hydrogen stream from purification unit n
z_i	Weight fraction of hydrogen in the supply from source i
α_m	Fraction of hydrogen that leaves with the hydrogen stream exiting processing unit m
β_j	Economic value or surplus revenue generated by using hydrogen in fuel gas sink *j*
γ_j	Cost coefficient for using /running a fuel gas sink *j*
μ_{pq}	Joule-Thompson coefficient of gas stream in transfer line connecting origin p to destination q

Continuous variables

F_i	Total gas flow from source i
F_{ij}	Gas flow from source i to fuel gas sink j
F_{im}	Gas flow from source i to processing unit m
F_{in}	Gas flow from source i to purification unit n
F_m	Feed flow into processing unit m
F_{mj}	Gas flow from processing unit m to fuel gas sink j
$F_{mm'}$	Gas flow from processing unit m to other processing unit m'
$F_{m'm}$	Gas flow from other processing unit m' to processing unit m
F_{mn}	Gas flow from processing unit m to purification unit n
F_{nj}	Gas flow from purification unit n to fuel gas sink j
$F_{nn'}$	Gas flow from purification unit n to other purification unit n'
$F_{n'n}$	Gas flow from purification unit n to other purification unit n'
F_{nm}	Gas flow from purification unit n to processing unit m
F_{pq}	Flow of gas stream in transfer line connecting source p and destination q
H_{pq}	Variable to represent product of flow, temperature and specific heat of gas stream in transfer line connecting source p and destination q
P_p	Pressure at origin unit p
P_q	Pressure at destination unit q
T_p	Temperature at origin unit p
T_q	Temperature at destination unit q
T_{pq}	Temperature of gas stream in transfer line connecting source p and destination q
yr_n	Purity of residue stream from purification unit n
ΔH_{pq}^{B}	Variable to represent product of flow, specific heat and temperature

	change of gas stream in transfer line connecting source p and destination q due to compression
ΔH_{pq}^{C}	Variable to represent product of flow, specific heat and temperature change of gas stream in transfer line connecting source p and destination q due to cooling
ΔH_{pq}^{H}	Variable to represent product of flow, specific heat and temperature change of gas stream in transfer line connecting source p and destination q due to heating
ΔH_{pq}^{V}	Variable to represent product of flow, specific heat and temperature change of gas stream in transfer line connecting source p and destination q due to expansion

1 INTRODUCTION

1.1 Refinery Process Network

Petroleum refinery is arguably the most complex among all the chemical industries. It encompasses almost all types of unit operations in the area of chemical engineering. It plays a pivotal part in the downstream sector of the petroleum industry. A petroleum refinery is a continuous process plant, whose overall function is to separate the crude oil into various components, process them and also suitably modify them so that they are ready to be sold in the market. Crude oil forms the basic raw material which is obtained by exploring oil wells. This is then stored in tanks, and sent to the crude distillation unit where the crude oil is separated into various fractions like light gases, propane, butane, naphtha, kerosene, light and heavy gas oils, vacuum gas oil and residues. The general configuration of a petroleum refinery includes primary, secondary and tertiary units. The atmospheric distillation unit and the vacuum distillation unit generally form the primary units. These units directly process crude oil which is the raw material of the petroleum refinery. The other units in the refinery such as fluid catalytic cracking, hydrocracker, hydrotreater, coker, visbreaker etc form the secondary units because they process or refine the products from the primary units. The final products from the secondary processing units may themselves not be suitable according to the market specifications to be sold directly. The final products from the secondary units may be mixed or blended with the products from other secondary units or with products from the primary units, so that they reach the required product quality specification which could be sold in the market. The mixing or blending units which ensure that products are brought to desired quality specification form the tertiary units. Apart from these units, a refinery also requires utilities for its operation. The utilities in a refinery are of different types namely fuel oil, fuel gas, natural gas, hydrogen, electrical power, steam at high pressure and low pressure and water. Moreover bound by the stringent environmental regulations, the refineries are also forced to treat/purify their waste streams from dangerous chemicals and hydrocarbons before they are discharged into the environment. Hence purifying or treatment units are also required for the operation of a refinery. Process networks could be defined as interconnection of processing units, such that they process a common stream by consuming it as feed, producing it as a product or both by consuming and producing the stream. This sort of an interconnected system of processing units linked together by a common stream is called a process network. By processing the stream we mean that the processing unit can either consume and/or produce the stream either as a feed or as a fuel. Another important aspect of the process network is that the constituents of the stream have to be the same throughout the entire network, but its composition may be different. Let us explain this by an example. Water network is a classical example of process network in a petroleum refinery. In the water network, the basic common stream is water. This water circulates through the water processing units namely water source (serves to produce water such as lake or freshwater storage in a refinery), water using unit (serves to consume freshwater and produce wastewater -mainly separation units like absorption etc.), water treatment unit (serves to consume wastewater and produce treated water – mainly purification units like reverse osmosis etc) and wastewater sink (serves to consume the treated wastewater for environmental discharge). The common stream is water, however its composition (here impurity level) is different. The water source produces water with almost zero impurities, whereas treatment unit receives water with a lot of impurities and produces treated water with reduction in the impurity level. Since all the conditions of a process network is satisfied by water network, it is called as a process network. When considering specifically for a refinery, there could exist complex interactions among the different units, between the different processing units and utility systems and/or among the processing units, utility systems and the treatment units resulting in the existence of many process networks in a refinery.

Process networks are a fundamental part of the petroleum refinery. A refinery is characterized by many such process networks such as pooling or blending network,[1, 2] wastewater network,[3, 4] integrated water network synthesis,[5-7] hydrogen network,[8-10] fuel gas network[11-13] etc. Some of these may involve important raw materials for the petroleum refining industry like the water for the integrated water networks, hydrogen for the hydrogen networks, natural gas for the fuel gas network etc. Any interest in the conservation of such these materials/resources is a matter of significant interest and is attracting a lot of attention over the recent years due to the increasing cost of these materials and also the environmental regulations. Hence the refiners are trying to adopt approaches in their production planning that can optimally utilize these materials and at the same time minimize the cost of design and operation of such process networks.

Process network design or process design or process flowsheeting forms a quintessential aspect of refinery design. In the chemical process design, a conceptual flowsheet of a specific chemical process is first developed and analyzed. It is then followed by analysis of several suitable alternative flowsheet designs. The description of each flowsheet is based on the type of equipment and how the equipments are interconnected. The different equipments usually dealt in the process design are process related equipments such as reactor, separator, purification unit and basic network related equipments like the mixers and splitters. There may also be equipments which relate to the conditions of stream (temperature, pressure etc) such as heater, cooler, pumps, valves etc. Mass and Energy balance followed by specific process descriptions, if present like rate expressions etc, are used to describe the processes. All these are used to establish the flows, temperature, pressure etc of all the streams in the flowsheet. Using these, the approximate cost evaluations in terms of capital cost and the operating cost of the network are also done. All the above described steps constitute the process network design.[14] An efficient and systematic process network design may involve the following steps namely process synthesis, process analysis and process optimization. Process synthesis is a preliminary stage of process design wherein the different process alternatives are gathered so that they could be studied in the analysis phase. The process analysis as the name indicates involves analysis and complete study of the process such as heat and mass balance, size and cost of the equipments involved followed by the economic feasibility and operability of the entire process. Once all the process alternatives are gathered from the process analysis phase, there is a deep study of the all the process alternatives. Then different process designs are represented as process flow diagrams from which there are a need to identify the best process design from all the available designs. This stage is the process optimization phase. In this, first an objective function is identified which determines the overall result of a particular process design. The objective function is related to the problem variables such as flow, temperature, capacity etc. The entire process operation represented in the form of these variables is described as constraints to the system. These variables are also called as the decision variables. The constraints can also sometimes depict the operational limit of the system such as maximum product purity, maximum equipment capacity etc. The manipulation of such decision variables which could result in the improved process design with regard to a particular objective forms the process optimization. Initially the task of finding the improved process design by the manipulation of decision variables was done by trial and error in an ad-hoc manner. But more recently, optimization was used in the field of process design. The advancement in research in the concepts of mathematical programming and operations research has also aided optimization to obtain the best process design in an efficient manner.

As mentioned previously, the composition of stream flowing throughout the entire network must remain the same in a process network. Also the phase of the stream should also be consistent. Based on the classification of the phase of stream in process networks, different process networks could be present. For example, the wastewater network, integrated water network synthesis and pooling problem involve networks where in liquid flows throughout the network. There could also be networks where there is gas flow. These could include fuel gas network, hydrogen network etc. In this thesis, the study will be focusing on the issues related to the design and optimization of gas process networks or the gas networks. The main motivation for us to choose the gas networks in particular was that though the concept of process network design (having liquid or gas flows) are considered uniformly, differences may exist between them when considering their network design and operation. A typical gas network may be different from process networks involving liquids when considering different standpoints such as distribution and storage. This is because, the gas in gas process network has to be consumed and transported as gas. This may present some challenges. For instance when dealing with gas flows, pressure plays a critical role. The pressure now may direct the network design and operation, and has to be included within the gas network model. Inclusion of this may make the network design more complex and intricate. To deal with the design of gas networks and at the same time consider intricate factors involved in the same forms the major thrust of this thesis. Since a refinery is a place where many gas networks may potentially exist, we chose the system to be a typical petroleum refinery.

1.2 Gas Process Network Design-Challenges and Benefits

Although we stressed on the fact that design of gas process network may not be a trivial task, we in this section highlight some more challenges associated with them. Next we also point out the benefits involved in gas network design. Firstly as pointed out previously, pressure now plays a major role in the design of the network. This is because a substantial cost to maintain the gas flow within a pipeline is related to this pressure. Hence not involving pressure in gas network design may tend to underestimate the cost associated with the network, which may not be desirable. So the major challenge is to incorporate the pressure term in the model formulation and to associate the costs related to pressure changes. Second, the design of gas networks may be simple when the numbers of process units which exist in a network are less. When the number of process units increase, then more interactions can be possible within a network. Third, it may be sometimes required to meet some specific constraints in the process units. For example when considering the case of a hydrogen network, there may be a specific demand in terms of flow and purity of hydrogen required by the hydrocrackers and the hydrotreaters. Though the hydrogen producers in the form of catalytic reformer also exist in the hydrogen network, it may not be able to satisfy the demand requirements for the hydrocracker and hydrotreater units as the flow and purity of hydrogen out of the catalytic reformer units are generally less. Hence, the specific constraints in the process units are also to be satisfied within a process network. In order to deal with the design of such gas networks, all possible design alternative needs to be enumerated to form a superstructure, from which the best design has to be chosen. All the above may require complex decisions that have to be taken to select the best networks among all the alternatives. The enumeration of all possible design network alternatives and to choose the best network among all of them is a hugely cumbersome process and this renders the need for process system tools like optimization for systematically handling such large design problems.

The generalized problem in the gas network synthesis or in general process network synthesis is to select the best network among all the possible designs which conforms to a particular objective. The focal points to be considered during the design of process networks[14] is to enumerate all possible designs and choose the best possible design, and to develop a mathematical model for describing such process networks and optimize it with respect to a particular objective.

The optimization of gas networks yields a lot of benefits. The network optimization has a significant role to play in determining the capital and the operational cost of the entire plant. Cost is not the only element which makes gas network optimization as an attractive option. A proper and efficient network design can save on the energy consumption of the plant. Energy constitutes an integral part of the operating cost in a refinery. Figure 1.1 shows the distribution of operating cost of refineries in USA.[15]

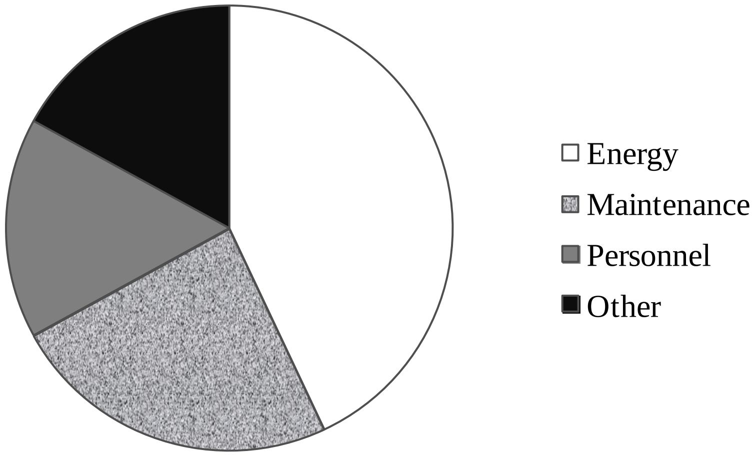


Figure 1.1 U.S. Oil refinery operating cost distribution

The pie chart shows that the majority of operating cost in a refinery is required for energy. In case of gas networks large amount of energy is consumed for the compression process. A well designed process network would seek to reduce the energy consumption by better utilization of gas within the network. Another facet of the benefits of process network optimization could be effect on the environment. For example, when considering the hydrogen networks the hydrotreater and hydrocracker may give out off-gas or purge gas which may contain substantial amount of hydrogen gas. The general trend in the refinery would be to send it to the fuel gas system, so that it can be flared or be used within the refinery as fuel gas. However, a proper network design would seek to utilize these gases in the best possible manner and minimize the feed consumption. This may result in the reduction of the gases going to the flare system. Similar condition may also exist in case of the water networks where some wastewater could still be reutilized in the network if the specific constraints on the process units in the network are satisfied.

By adopting to follow the approaches of network optimization, the petroleum refinery can focus on the trying to integrate the aspects relating to energy, economics and environment into one single framework which could pave way towards achieving a sustainable development. The two important refinery process networks dealt in this study are the refinery hydrogen network and refinery fuel gas network.

1.3 Refinery Fuel Gas Network

Energy is the most important concern in the world today. The global energy demand is expected to rise almost by 57% from 2004 to 2030.[16] The fossil fuels such as coal, petroleum and natural gas, which supply over 85% of world primary energy, will continue to be the major source of energy in the near future. This, however, releases some amount of greenhouse gases into the atmosphere in the form of flares. Gas flaring is one of the most challenging energy and environmental problem known to the mankind today. Approximately 150 billion cubic meters of natural gas are flared in the world each year.[17] This represents an enormous wastage of natural resources and contributing to 400 millionmetric tonnes of CO_2 equivalent of greenhouse gas emissions.[17] This also contributes to a tremendous wastage of energy followed by environmental degradation. Hence, the immediate measure is to reduce energy usage through conservation to reduce the drastic impact on the environment due to Greenhouse Gas (GHG) emissions.

Energy forms the major component of the operating cost of a refinery. Such energy is used in the form of steam, heat or electricity to run the movers in the processing units of the refinery. Most plants buy fuel in the form of fuel gas to generate steam, heat and power required for the plant operation. In addition to this, some of the refineries consume a portion of raw materials, products and byproducts to fulfill their energy demands. For example a refinery in addition to the standard fuel, it uses vaporized LPG and fuel oil to manage its energy demand.

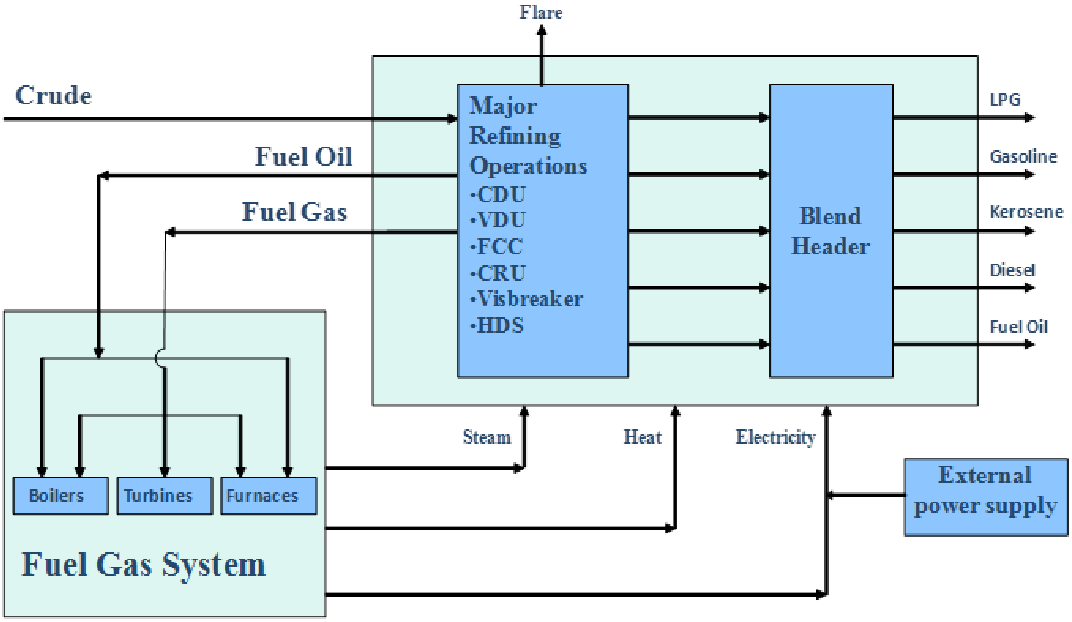


Figure 1.2 Schematic diagram of fuel gas network in a typical refinery

In the interest to conserve energy, many waste/impure/purge streams which are generated within a refinery, have no product value but some heating value associated with them, but can be utilized in the plant to produce fuel required for steam, heat and power generation purposes instead of sending them to the flares. Thus, a fuel gas network plays a key role in this regard. A fuel gas network serves to manage and distribute fuel gas and waste/purge gas streams from different sources in the refinery to the typical fuel gas consumers in the refinery namely turbine, boilers, incinerators and flares in an optimal manner based on the quality and quantity requirement. These fuel gas consumers transform energy within the fuel gas to a practically more useful form such as heat, power and steam. The schematic diagram of a fuel gas network in a typical refinery is shown in Figure 1.2.[12] Such a utilization of waste/purge streams into the fuel gas network operation serves to not only minimize the consumption of the external fuel gas but also reduces the amount of gas going to the flare. This also represents a critical step towards sustainable development.

1.4 Refinery Hydrogen Network

In today’s world, stringent legislative measures and strong environmental regulations have created a great demand for cleaner fuels. To meet such demands, the refineries are forced to produce products which involve cleaner fuel specifications. To meet the new fuel specifications, there is a need to increase the hydrotreating and hydrocracking operations in the refinery facility. To meet new fuel specifications, demand for cleaner fuels and to set up more hydrocracking and hydrotreating facilities, refineries require more pure hydrogen. Hence the refiners are forced with a tremendous challenge of addressing the hydrogen demands and at the same time maintain profitability of their operation. Hydrogen is utilized in most of refinery operations which involve cleaner fuel specifications and breaking down of other heavier hydrocarbons. Apart from this, it also serves as an important utility in other hydrocarbon processing operations. An efficient and responsible utilization of refinery hydrogen will require systematic, adept and proper planning approaches by the refinery.

In order to address this issue, refineries are adopting hydrogen management strategies into their production planning which studies hydrogen gas distribution and utilization over the entire refinery system. Such a methodology focuses on the network perspective, which seeks to develop an in-depth understanding between the various hydrogen producing and hydrogen consuming units to help leverage opportunities for optimal usage and maximize profitability of operation.

The schematic diagram for the refinery hydrogen network is shown in Figure 1.3. The refinery hydrogen balance is set up as a network problem, where minimum hydrogen production and consumption requirements are set for hydrogen producers, consumers

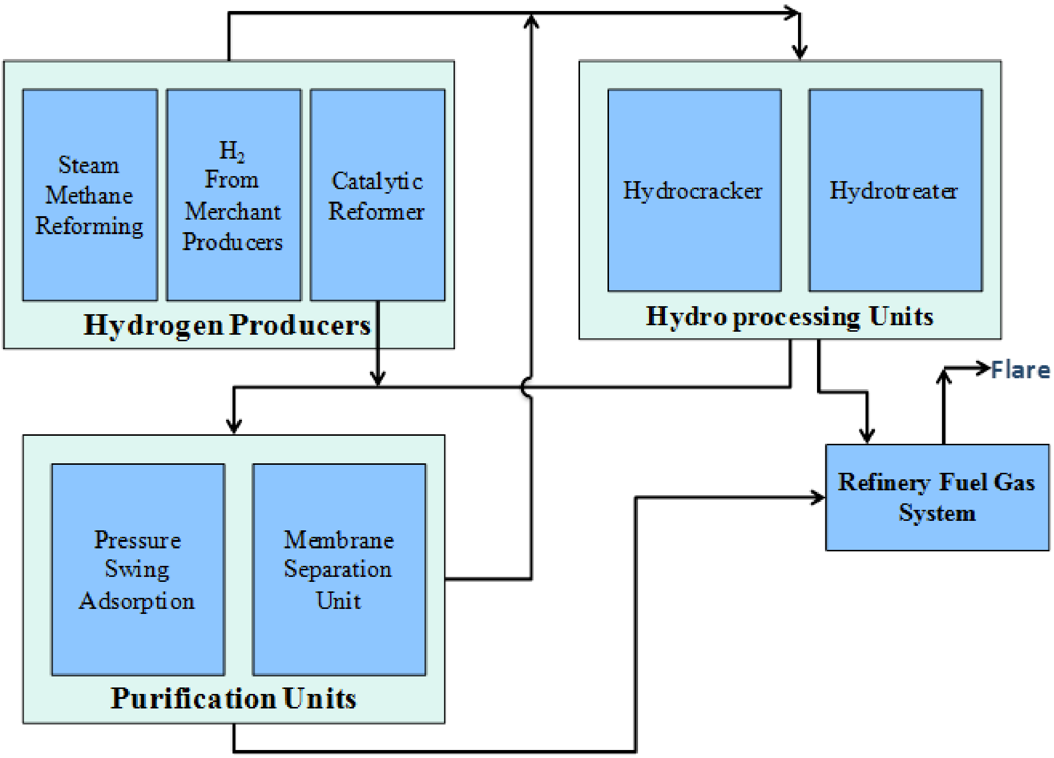


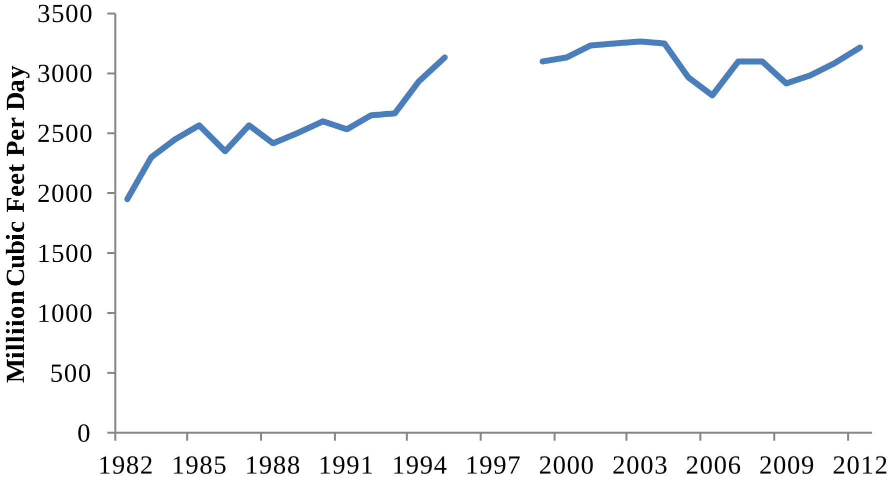
Figure 1.3 Schematic diagram of a hydrogen network in refinery

and the purification units each defined by a separate process model. Such an approach seeks to achieve required hydrogen balance over the entire refinery and this helps to reduce hydrogen consumption and more importantly the hydrogen cost.

The three major sources of hydrogen in a refinery are on-site hydrogen production, catalytic reformer and purchases from other plants called as merchant hydrogen. The main consumers of hydrogen in a refinery are hydroprocessing units namely the hydrocrackers and hydrotreaters. Apart from this there exist purification units which supply purified hydrogen into the network. A fuel gas system exists in a network to collect the excess gas generated in the network.

As explained earlier the refinery demand for hydrogen is increasing in order to satisfy the growing demand for hydrocarbon transportation fuels and the tightening environmental restrictions on vehicle exhaust emissions. Since 1982 there has been a 59-percent expansion of onsite refinery-owned hydrogen plant capacity at an average growth rate of about 1.2 percent per year, until the year 2007.[18] Moreover in USA, petroleum refinery had overtaken Ammonia industry as the leading hydrogen consumer within the hydrogen industry. In 2007, it was predicted that the near-term average annual growth rate of hydrogen consumption, in USA alone, would be about 4 percent per year[19] and that the merchant share of hydrogen to refineries is estimated to grow at an annual rate of about 8 to 17 percent per year.[20] The recent data obtained from the U.S.Energy Information Authority shows that the on-site refinery hydrogen production capacity has increased from 59% in 2007 to 64% in 2012. Figure 1.4 shows the onsite refinery owned hydrogen production capacity from the year 1982 to the year 2012.[21] In another study,[22] it was estimated that refining industry globally will require 14 trillion SCF of on-purpose hydrogen to meet the processing requirements between 2010 and 2030. Asia Pacific and the Middle East will represent

40% of these



Year 1996 and 1998 – No data available

Figure 1.4 U.S. refinery hydrogen production capacity

global requirements. Hence we understand that the hydrogen demand in the refineries have increased and there is a need to optimize the consumption of hydrogen. Optimal utilization of hydrogen within a refinery, as stated earlier, can provide a significant direction towards achieving sustainable development by integrating energy, economics and environment. Optimization of hydrogen network in a refinery will result in lesser hydrogen consumption and subsequently leading to lesser hydrogen cost and lesser operating cost. This also has a greater effect on the environment. It is estimated that production of 1m^3 of hydrogen results in emission of 0.8-2.6 kg of CO_2 depending upon the type of hydrogen production.[8] Thus, an optimal hydrogen production can also reduce the CO_2 emissions. Moreover, optimal hydrogen consumption within a refinery network will also lead to lesser gas going to flare system which could reduce further hydrocarbon emissions.

1.5 Research Objectives

This research focuses on the issues regarding the design and operation of refinery gas networks namely the hydrogen networks and the fuel gas networks. With this focus, the objective of the research work is to use the ideas of process modeling and optimization to minimize the cost of design and operation of the gas networks in the refinery namely the hydrogen networks and the fuel gas networks. Along with cost minimization, we also seek to reduce energy consumption, minimize feed/fuel consumption in the process network and also to reduce waste material generated within the network which ultimately helps in environment conservation. With these aims, the specific objectives of this research are (1) to model the fuel gas network for a multimode operation of the refinery, so that the network developed caters to all the different modes of refinery functioning and also propose strategies which result in minimization of flaring in a refinery (2) to develop efficient mathematical optimization model for the case of refinery hydrogen network and to solve the developed model catering to a particular objective.

1.6 Outline of the thesis

This thesis consists of five chapters. After a brief introduction in Chapter 1, a detailed literature review discussing existing approaches and models for refinery hydrogen networks and fuel gas networks is given in Chapter 2. A number of gaps in the literature are identified and the research focus is explained at the end of this chapter.

In Chapter 3, the focus is on one of the refinery process network namely the fuel gas network. The multimode fuel gas network is formulated to deal with the different operating modes of the refinery. The benefits of using the multimode design for the refinery fuel gas network are compared against that of the single mode design. In order to reduce the flaring in the refinery and to reduce environmental penalties, different strategies are proposed and studied on this multimode fuel gas network model.

In Chapter 4, we move to next gas network under study called the refinery hydrogen network. The nonconvex model for the refinery hydrogen network is solved to global optimality. It is then followed by considering integration of the present network optimization model with the hydrogen network of other refineries to improve the overall recovery of hydrogen. This multi-refinery model for hydrogen network is also solved to global optimality.

In Chapter 5, the focus will be again on modeling and optimization of refinery hydrogen networks. However, this model formulation will now be based on overcoming some of the observed defects in the previous models considered in the literature and incorporating several realistic features such as considering non-isothermal along non-isobaric operating conditions. The model developed is then optimized with minimum total cost as the objective function. This model is then utilized to solve some example problems of refinery hydrogen network.

Finally, conclusions for the aforementioned works are described and recommendations for future research in this direction are summarized in Chapter 6.

2 LITERATURE REVIEW

A comprehensive description of the literature available in this area will be presented in this chapter. Firstly, a brief description about the optimization of gas network synthesis problems is carried out. Then the focus shifts to the two gas networks considered in this study namely the fuel gas network and the refinery hydrogen network. The literature works on the fuel gas network will be reviewed first. This is followed by the review of literature on the refinery hydrogen network. The types of process systems engineering approach for dealing with the hydrogen network is based on the principles of mathematical optimization and the pinch approaches. The approach with the pinch analysis is beyond the scope of this thesis and will not be considered. The literature on the mathematical optimization of refinery hydrogen network will be reviewed. After reviewing all the available literatures, a brief description about the gaps and challenges available in these areas will be studied. Finally the research focus of this thesis will be described.

2.1 Network Optimization

Process network optimization problems are of significant interest in the area of chemical engineering design and operation. Such network optimization problems are developed by using the concept of so called *Superstructure* approach. In this several design alternatives are represented and an optimization problem is formulated which when solved selects the best network among the available network alternatives. The network consists of a series of nodes which are connected with the other nodes or connected among themselves. These mathematical programming models of network optimization serve as an important tool in the oil and gas industries to address their production planning. The different types of network optimization problem usually are water network synthesis, heat exchange network synthesis, pooling problems etc. The gas network optimization typically finds its application in refinery and natural gas industry. Several researchers have worked on the gas network optimization in production planning of gas industries to address their design and operational problems.

Li et al.[23] also modeled the long term planning of natural gas network as a stochastic pooling problem and globally optimized it using the benders decomposition algorithm for nonconvex terms. Wicaksono et al.[24] modeled the different fuel sources and sinks in an liquefied natural gas (LNG) plant as a pooling problem and showed that incorporating Jetty Boil-Off Gas (JBOG) as a potential source results in reduced fuel consumption. Hasan[11] developed an Mixed Integer Nonlinear Program (MINLP) formulation for a fuel gas network within an LNG industry with an objective of minimizing total annualized cost. Many of the works in the literature assumed simplifying assumptions such as isothermal and isobaric conditions to deal with the gas networks in the refinery. However some works have also incorporated such realistic features into their model formulation. Sealot et al.[25] had developed an operational planning model for natural gas supply chain system which included short term contractual rules followed by the technical model for upstream natural gas supply chain. They had used realistic nonlinear pressure flow relationships in their model and solved it to global optimality using the commercial solver for a real world problem. Hasan et al.[12] (2011) developed a suitable Fuel Gas Network (FGN) in an LNG plant and refinery incorporating several realistic features such as non-isothermal and non-isobaric operation to optimally distribute the fuel gases to the fuel gas system and also asserted that by using a FGN, plant energy cost and fuel gas consumption could reduce significantly.

2.2 Fuel Gas Network

The residue gas streams from the Fluid Catalytic Cracking Unit (FCCU), Catalytic Reforming Unit (CRU), Processing Unit (PU) etc contain significant amount of hydrocarbon content. Most of these gases are either flared or vented out directly into the atmosphere. However, these residue/waste/impure/purge streams may not be of any commercial value but may contain some heating value owing to the substantial hydrocarbon content that could be used in the burners, fired heaters, turbines and/or boilers to produce energy for the refinery in the form of heat, steam, power etc. A Fuel Gas Network (FGN) is a systematic arrangement to collect, mix and sends these fuel gases to the fuel gas sinks in the form of turbines, boilers, heaters etc. The sources in the FGN could be the units in the refinery such as FCCU, CRU, PU or any other unit which produces some residue/purge/impure/waste streams and sinks are the units which consumes these gases for producing heat, steam and power such as the boilers, turbines or they could represent equipments which burns these gases into the atmosphere such as the incinerators, flares etc. The role of a FGN is, however, more critical than merely consuming the waste/purge gases in a refinery. It minimizes the fuel requirement in a refinery, in the form of consumption of refinery external fuel gas and fuel oil, which saves a lot of operational cost in a refinery in the form of fuel cost. A properly designed FGN consumes majority of waste/purge gases and this adds value to the efficacy of the refinery operation by reducing the treatment/disposal/incineration/wastage cost associated with it. The most crucial outcome of a FGN is in the fact that it could considerably reduce flaring in the refineries highlighting significant environmental impact.

Flares are indispensable units in the petroleum refineries. They are crucial for disposing of waste and purge gases in a safe manner by burning them at high temperatures, producing carbon dioxide (CO_2) and steam.[26] However, flare emissions can have air quality impacts, even when very high percentages of the flared gases are destroyed.[27-31]

Petroleum refineries face the complex challenge of minimizing air quality impacts, while maintaining essential flare operations. This challenge is made more complex by the wide ranges of waste gas flows and rapid fluctuations in the waste gas flows to flares. Flow rates to flares vary significantly due to changing industrial operation modes (e.g., start-up, shutdown, maintenance activities, emergency releases, etc.). Flare flow variability can be segregated broadly into two different categories: emission events and variable continuous emissions. Emission events are infrequent discrete episodes (such as a plant emergency) in which a very large flow is flared.[27] In contrast, variable continuous emissions can occur frequently and be categorized into multiple modes of operation, depending on the scale of the variability.[29, 31-33]

Currently, refiners usually adopt ad-hoc measures to manage their fuel gas system. Each refinery could have a unique system of fuel gas management based on the experience of the operators and/or some thumb rules. Such approaches may not be generalized and could represent inefficient and ineffective operation. One could possibly burn these waste gases and utilize the heat coming out by burning them by heat integration with the waste heat recovery system. Though this practice could be useful, it may represent a substantial capital cost for the refinery in terms of heat exchangers apart from the other auxiliary equipments required for the movement of the gas like the pipeline, compressor valve etc. The fuel gas network on the other hand only mixes these streams in optimal proportions and sends it to the fuel gas sinks thus requiring only the auxiliary equipments in its network. The auxiliary equipments are also called the conditioning equipments which bring the gases to the required conditions of temperature and pressure. These are coolers, compressors, heaters and valves. Hence apart from the source and the sinks, the auxiliary/conditioning equipments are also an important ingredient of the FGN.

Synthesis of an FGN, however, poses numerous challenges. The source streams going to the sink in an FGN may vary significantly in their quality, composition, temperature, pressure, density and other properties based on the changing plant operational modes. The waste gases going to the flare from various fuel gas sources also vary in their flows. Moreover based on the different plant operational modes, sources and sinks in an FGN may or may not be present. For example in an chemical LNG plant, the JBOG as a fuel gas source may be present only during the loading and unloading operations and is not present during other modes of plant functioning. Also sinks like turbines, boilers may sometimes be not available during its shutdown. Hence, it may be necessary to synthesize a generalized FGN in face of such changing plant operational modes.

Every sink in an FGN will be characterized by energy demands along with along with specific quality specifications (specs). Low quality gas going to a gas turbine may cause disruption of turbine operation and could eventually cause shutdown of the entire plant. Some of the important qualities governing the sinks are Wobbe Index (WI)[11, 34-36], Lower Heating Value (LHV), Specific Gravity (SG), Methane Number (MN)[12], Dew point temperature (DPT) etc. Wobbe Index (WI) is a measure of interchangeability of fuel and is an important specification for determining the energy content present in the fuel gases. Wobbe Index however is calculated from two other important quality specs namely the Lower Heating Value (LHV) and Specific Gravity

(SG) of the gases in the FGN. Hence a sink in a FGN, apart from satisfying the Wobbe Index (WI) spec must also adhere individually respect the Lower Heating Value requirements along with specific gravity limit. Methane Number (MN) is a performance measure of fuel gases with respect to the gas knock resistance and is measured for gas turbines. Presence of vapor in fuel gas streams in an FGN could lead to more serious consequences when they enter the sinks like boiler or turbine. Hence in order to prevent such conditions, the temperatures of streams after mixing must remain above the Dew point temperature (DPT). In addition to this, presence of moisture or saturated hydrocarbons in the gas stream could also formation of hydrates or acidic components like sulphides which could corrode the equipment inside the fuel gas sinks like turbines and boilers. Hence specific temperature requirements need to when gas streams are mixed in the header before the sinks. Apart from this based on the source, the gas streams entering the FGN may contain impurities in the form tar, coke or other hazardous impurities like the sulphur, VOC etc. The FGN must ensure that such impurity contamination levels should remain well within the limits for the fuel gases. Hasan et al [12] gives a more detailed description regarding the fuel gas specifications required at the fuel gas sinks.

Despite its importance, very few works have been carried out in the area of fuel gas networks. Wicaksono et al.[13] proposed a mixed-integer nonlinear programming (MINLP) model for integrating various fuel sources in an LNG plant. Wicaksono et al.[37] extended this to integrate JBOG gas as an additional source. De Carli et al.[38] designed a controller for FGN in a refinery using fuzzy logic and genetic algorithm. Hasan et al.[11] addressed the optimal synthesis of FGN and presented two superstructures, one with 1-stage and the other with 2-stage mixing. Finally, Hasan et al.[12] addressed the optimal synthesis and operation of a steady-state FGN with many practical features such as auxiliary equipment (valves, pipelines, compressors, heaters/coolers, etc.), non-isobaric and non-isothermal operation, non-isothermal mixing, nonlinear fuel quality specifications, fuel/utility costs, disposal/treatment costs, and emission standards. They proposed an FGN superstructure that embeds plausible alternatives for heating/cooling, moving, mixing, and splitting, and developed a Nonlinear Programming (NLP) model.

2.3 Refinery Hydrogen Network

Hydrogen management in any refinery can be defined as a methodology which analyses the overall hydrogen balance within a refinery as a network problem, and seeks to determine solutions that result in optimized hydrogen consumption in a refinery catering to the demand and availability of hydrogen within the same. The hydrogen in the hydrogen network in a refinery is fed by the hydrogen producers or the sources of hydrogen. This is circulated throughout the network and primarily consumed by the processing units namely hydrotreating, hydrocracking and other units such as isomerization, olefin saturation etc. The hydrocracking involves cracking reactions which convert heavier hydrocarbons to mainly diesel and naphtha. The hydrotreating is a chemical operation which contains a series of organic reactions that coverts sulphur and nitrogen in hydrocarbons to hydrogen sulphide and ammonia. Complex organic chemical reactions takes place in these units and part of the final gas product(containning hydrogen) coming out of this reactor separator system of the processing units is recycled and part is returned to the network as purge/off gas. These purge/off gases may be purified or could be sent to the fuel gas system. The purifiers constitute an integral part of the refinery hydrogen network. They help recover hydrogen within the network by purifying the off/purge gases generated from the hydrogen consumers. The circulation of the hydrogen gas from one processing unit to another leads to wide fluctuations in its partial pressure, temperature and purity due to the differences in the operating conditions of these processing units. The interaction among all the above mentioned units and developing a network capturing these interactions in an optimal manner constitutes the refinery hydrogen network synthesis problem.

The refinery hydrogen network synthesis could be defined as a network system that facilitates optimal distribution of hydrogen throughout the network satisfying process demands. Due to stringent environmental regulations and stricter fuel quality specifications, refiners are forced to consider the option of treating the products with hydrogen. On the other hand, due to restriction on the aromatic content on the gasoline the CRU unit produces lesser hydrogen as a by-product. This imbalance in the demand and availability of hydrogen gas in a refinery, provides the necessary motivation for an effective and optimal strategy of hydrogen management in a refinery since hydrogen has a greater role to play in the refinery profit margins given its effect on the product quality, yield, conversion etc.

The refinery hydrogen network consists of the following entities namely hydrogen sources, hydrogen consumers, purification units and fuel gas sinks. Firstly, the description of all the different elements of hydrogen network in a refinery is carried out. Second, the literatures in this area are reviewed.

2.3.1 Hydrogen Sources

For most of the processes within the refinery, typically high purity (90%-99%) of hydrogen is required. Hence, there is always a need in the refinery for hydrogen producers which produce pure hydrogen. The typical hydrogen sources in a refinery are the hydrogen plants, hydrogen purchased from other vendors in the form of merchant hydrogen and also auxiliary producers of hydrogen namely Catalytic

Reformer Unit (CRU). Among these hydrogen plants and merchant producers of hydrogen usually provide pure hydrogen for the other processes in the refinery. As the name suggest, the CRU produces hydrogen only as a byproduct in its process and hence the hydrogen from this may not be very pure as compared to the hydrogen plants and merchant producers. Brief descriptions of the different sources of hydrogen in the refinery are given as follows.

2.3.1.1 Steam Methane Reforming

The Steam Reforming or the Steam Methane Reforming (SMR)[39, 40] is the most common method to generate hydrogen rich synthesis gas from hydrocarbons. The reaction governing the SMR process is

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The generalized reaction for any hydrocarbon for SMR process is as follows:

$$C_nH_m + n\,H_2O \rightarrow nCO + (0.5m + n)H_2$$

Desulfurized feed is first washed with caustic and water washes and is mixed with steam and passed over a nickel based catalyst in a reforming furnance. The conditions required for reaction are between temperature range of 1350^0F and 1550^0F. The product produced is the Synthetic Gas or Syn Gas which has hydrogen, carbonmonoxide and carbondioxide. The second step is called the Water Gas Shift (WGS) or Shift reaction where the CO produced in the first reaction is mixed with steam over a catalyst to form H_2 and CO_2. In the shift converter CO reacts with steam in the presence of iron oxide catalyst to form CO_2 and H_2. This process takes place in two stages called High Temperature Shift (350^0C) which is endothermic and Low Temperature Shift (200^0C) which is exothermic. Converter effluent gas is cooled and CO_2 is removed by amine washing or any other suitable absorbing agent. Remaining CO_2 is removed by use of additional converters and amine systems or by methanation of residual CO_2. Other impurities present in the effluent such as nitrogen, sulfur, chlorine etc are removed first prior to absorption by amine washing. To obtain higher purity (97%-99%), the outputs from the SMR plants are also purified by separation techniques such as Pressure Swing Adsorption, membrane separation etc.

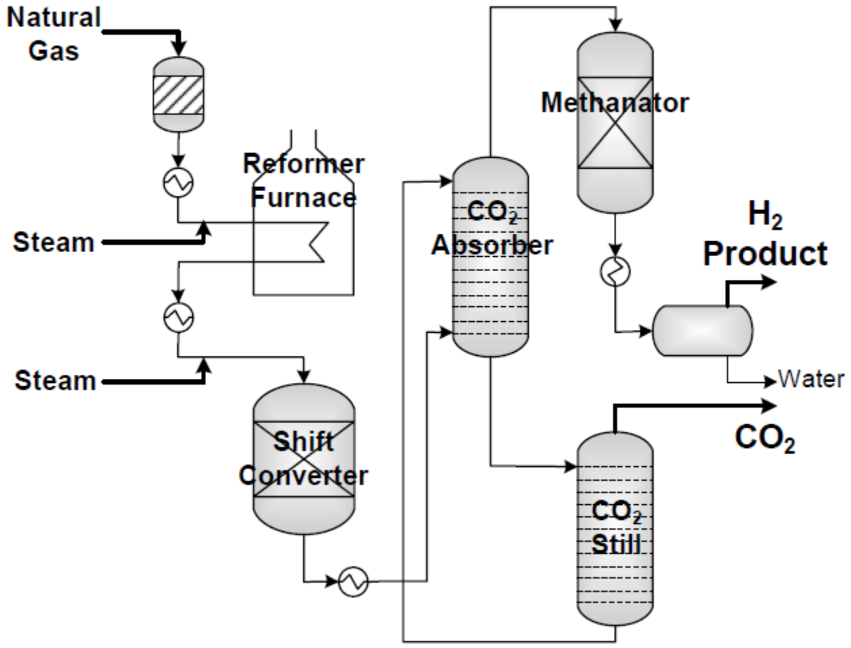


Figure 2.1 Process flow diagram for Steam Methane Reforming Unit

The Steam Reforming of natural gas is the most widely used technique for the production of hydrogen gas in the chemical, refining and petrochemical industries. The efficiency of a commercial SMR is about 65-75% and is highest among all the commercially available production techniques. The cost of producing hydrogen by SMR process is usually dependent on the prices of the natural gas and is less compared to the other hydrogen production techniques. During the production of hydrogen, CO_2 is also produced. Hence a refinery or a petrochemical plant using this technology must also focus on strategies for CO_2 concentration, capture and sequestration to reduce the Greenhouse Gas (GHG) emissions into the atmosphere. Figure 2.1 shows the flow diagram for the Steam Methane Reforming.[41]

2.3.1.2 Steam Naphtha Reforming

The Steam Naphtha Reforming[39, 40] is also similar to the Steam Methane Reforming for the production of hydrogen in the refinery. As explained in the previous section instead of methane, a liquid feed of hydrocarbon such as naphtha is employed as the feedstock. This could be a variety of napthas in the boiling range of gasoline. After the feed pretreatment to remove sulfur, chlorine and nitrogen the feedstock is mixed with steam to produce hydrogen gas. The other procedures are similar to the one used in the SMR process.

2.3.1.3 Other methods of hydrogen production

Partial Oxidation (POX)[42] of natural gas is another process by which hydrogen is produced by partial combustion of methane with oxygen to yield the syn gas. This is an exothermic process and CO produced is further converted to CO_2 and H_2 similar to that of SMR process. The reaction governing this process is

$$CH_4 + 0.5\,O_2 \rightarrow CO + 2H_2 + Heat$$

Authothermal Reforming (ATR)[42] uses oxygen and carbondioxide or steam in reaction with methane to form Syngas. Similar to the partial oxidation, the reaction is exothermic. The CO produced is further converted to CO_2 and H_2 similar to that of SMR process. The reaction for ATR is given as follows.

$$2CH_4 + O_2 + CO_2 \rightarrow 3CO + 3H_2 + H_2O$$

$$4CH_4 + O_2 + 2H_2O \rightarrow 4CO + 10H_2$$

The advantages of ATR and POX is that the units required for the process is small and simple and hence the cost for setting up of these units is less in comparison to the SMR process. However, the main drawback of both these processes (POX and ATR) when comparing against the SMR, is that of the requirement of pure oxygen.

Secondly the efficiency of both these processes (POX and ATR) is less compared to that of SMR.

2.3.1.4 Catalytic Reforming

Catalytic Reforming Unit (CRU)[39, 40] is an important process in refinery operations which converts naphthas with low octane ratings into high octane liquids called as reformates. Depending upon the properties of naphtha feedstock and the catalyst employed, reformates with very high toluene, benzene, xylene and other aromatics can be produced. During this process, restructuring of the hydrocarbon takes place separating hydrogen atoms which produces significant amount of by-product hydrogen gas. This hydrogen gas is utilized by the refinery for carrying out their operations. The primary reactions taking place in a catalytic reformer are dehydrogenation of naphthenes, dehydrocyclization of paraffins, desulfurization, olefin saturation etc. The hydrocarbon composition of the feed, selectivity of the catalyst as well as the reformer operation severity which is a function of pressure, temperature and hydrogen recycle rate determine the primary hydrocarbon reactions for a given reformer. The operating conditions for catalytic reforming ranges from 800-1000^{0}F and pressures between 50-750 psig. Many different commercial catalytic reforming processes used in the refinery are Platforming, Powerforming, Ultraforming, Thermofor Catalytic Reforming etc.

2.3.2 Hydrogen Consumers

Hydrogen consumers are units which primarily consume hydrogen to carry out its processes. Different types of hydrogen consumers exist within a refinery. Hydrocrackers and hydrotreaters are main consumers of hydrogen in a typical refinery. Depending upon the scale of operation of a refinery and the type of products produced, there could be other consumers in the refinery such as isomerization unit, olefin saturation unit etc. In case of hydrogen consumers, specific requirements in the form of flow, purity, pressure, temperature etc of the hydrogen gas are needed. Brief descriptions of the two main consumers of the hydrogen gas in the refinery are given as follows.

2.3.2.1 Hydrotreating

The lack of cheap hydrogen and high pressure requirement had impeded the reformers until 1930 to ‘purify’ the petroleum fractions with hydrogen.[39] However, the development of catalytic reforming process produced significant amount of hydrogen off gas which enecouraged the development of ‘treating with hydrogen’ of the petroleum fractions. Hydrotreating is a hydrogenation process usually aided by a catalyst which is used to remove major contaminant like nitrogen, sulfur, oxygen and other metals from the petroleum fractions. The critical operating variables which affect the efficiency of the process are hydrogen partial pressure, temperature and space velocity. Improvement in the yield of products, reduction in the disposal problems caused by mercaptans and thiphenols, decrease in the corrosion problems caused due to sulfur are some of the advantages of treating the petroleum fractions with hydrogen. They are placed normally prior to the units using catalyst in their operation such as catalytic reforming, fluid catalytic cracking etc. to prevent the contamination of the catalyst due to the untreated feedstock.

Apart from removing major impurities in petroleum fractions like sulfur, nitrogen their function also changes upon the type of feedstock available and the type of catalyst used.[40] Kerosene hydrotreating can be used to improve the burning characteristics (convert aromatics to naphthas) of kerosene which causes cleaner buring. Lube oil hydrotreating improves the product quality of lube oils (improves the acid nature of lube oils).

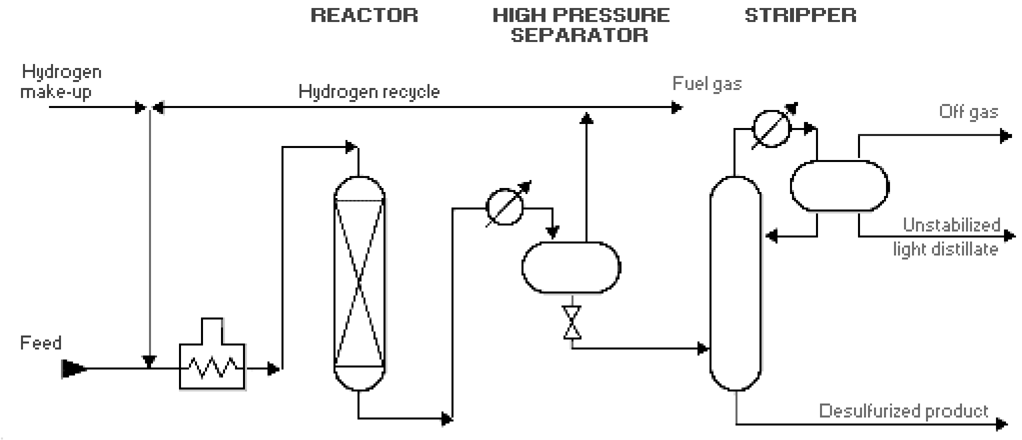


Figure 2.2 Process flow diagram of a Hydrodesulfurization unit

Pyrolysis Gasoline hydrotreating produces a more rich quality of Py gas for motor blending (converts diolefins to monolefins). Figure 2.2 shows the flow diagram for the hydrodesulfurization unit.[40]

2.3.2.2 Hydrocracking

The hydrocracking[39, 40] processes can be regarded as a combination of hydrogenation, cracking and isomerization process. Since it involves hydrogen, it is also a treating process as it removes large quantities of sulfur, nitrogen and other impurities. The feedstock is generally gas oil from the vacuum distillation tower and coker or it could also be kerosene with high smoke point and the products are distillates, gasoline, kerosene, jet fuels which are sent to the blending units in the refinery. Heavy aromatic feedstocks are converted into lighter products under the conditions of high pressure (1000-2000 psia) and temperature (700 – 800^0 F). The catalyst is silica-alumina with the presence of a hydrogenating agent such as platinum, nickel or tungsten oxide. Hydrocracking is used for feedstocks that are difficult to process either by catalytic cracking or reforming because of their (feedstocks) tendency to cause catalyst poisoning or because of their high catalytic or aromatic contents. In the current trend, hydrocracking supplements rather than replaces the conventional catalytic cracking in the refinery.

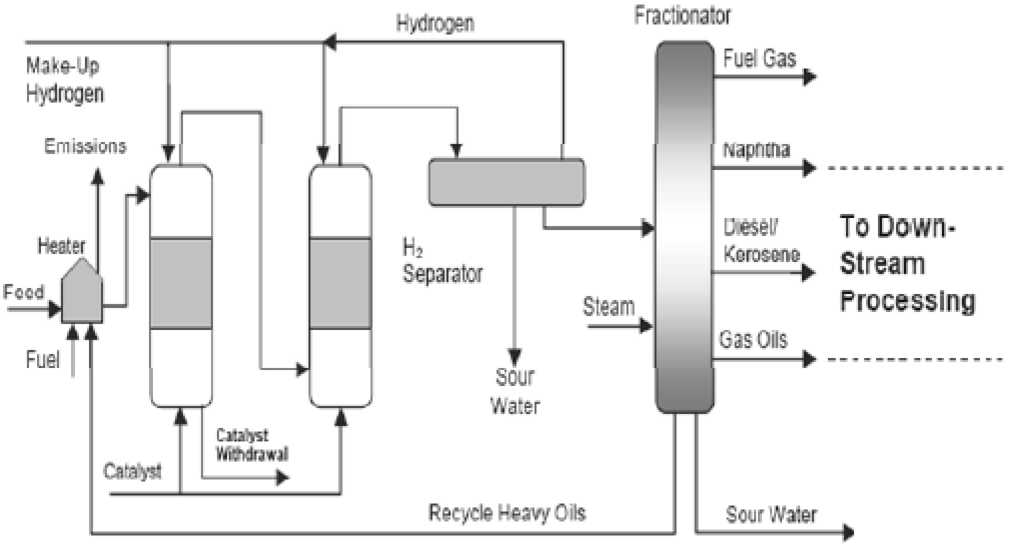


Figure 2.3 Process flow diagram of a Hydrocracking unit

The advantages of hydrocracking could be 1. Better gasoline yield. 2. Improved gasoline pool octane quality 3. Better distillate production by supplementing the basic catalytic cracking units to upgrade heavy cracked stocks, aromatic heavy cracked naphthas, cycle oils, coker oils. 4. Usage of hydrogen for cracking operation reduces the tar formation and prevents the buildup of coke on the catalyst. Figure 2.3 shows the flow diagram for hydrocracking process.[41]

2.3.3 Purification Units

Purification processes help the hydrogen network by purifying the off gas generated by the processing unit in the hydrogen network. Different purification processes rely on different separation methodologies. The different purification technologies used so far in the hydrogen network are the Pressure Swing Adsorption (PSA), Cryogenic Separations and the Polymer Membranes.

The refiners are generally interested in finding out the most cost efficient purification process which is also suitable to their operational and process needs. The usage of a purifier unit reduces the requirement for pure hydrogen and reduces the off gases generated with the network. The different factors considered for the selection of purifier are the feed purity, product purity, maximum hydrogen recovery, hydrogen capacity, feed pressure, product pressure etc. Apart from these, other performance parameters which are significant for purifier selection are reliability, flexibility, ease of expansion, cost etc.[43]

In this work, Pressure Swing Adsorption (PSA) is used as a purification unit because of its relative advantages such as no feed pretreatment, lower pressure drop etc. In principle, any of the purification technologies can be employed based on the process and operational needs as explained earlier. The commercial use of PSA process for hydrogen recovery exist from 1960, but were relatively simple and modest in their operation and performance with only 3-4 bed units. The first large scale commercial multiple bed was developed in late 1970 at the Wintershall AG Linen refinery in Germany which had upto 12 beds, producing a purity of 99% and recovery in range of 85-90% for a feed stream containing 75% hydrogen. For a more detailed understanding and explanation on the mechanism of operation of pressure swing adsorption, the reader can refer to the books[44, 45] on Pressure Swing Adsorption.

Unlike the fuel gas network, much work has been done with respect to the hydrogen network. The two major approaches for optimal design of hydrogen network are pinch analysis and the mathematical programming. Process integration principles have been used in designing the networks based on conceptual approaches. Pinch technology relies on the graphical representation and is based on extension of pinch analysis technique for heat and water integration. Pinch analysis is a method for estimating the minimum energy (Hydrogen) consumption based on the principles of thermodynamics. It uses the concepts of process integration which results in a network with better cost savings and reduced energy utilization. It can provide conceptual insights to hydrogen distribution and is relatively simple and easy to develop. However, the pinch analysis may suffer from major drawbacks which could restrict its usage. The pinch analysis is devised only minimum utility (Hydrogen) consumption. Secondly, the pressure constraints, which are very important when considering the gas flows within the network, are not considered. These drawbacks could be overcome when using mathematical superstructure optimization approach. Inclusion of different type of objective functions such as minimization of cost etc forms an important advantage over the conceptual pinch based methods. The other practical and realistic features which could be incorporated are pressure match constraints among the various units in the network, operational constraints such as capacity of the equipment, restriction on the number of maximum pipeline connections and also allowing only selective connections among the different units of the network. Nevertheless, the conceptual pinch approaches still serve as an important tool for optimal design and debottlenecking of different aspects of the network.

Towler et al.[46] studied the economic importance of hydrogen networks by analyzing the cost associated with it. Alves and Towler[47] developed a methodology for setting minimum hydrogen flowrate target for a refinery based on the concept of hydrogen surplus diagram. Some of the other useful works[48-53] done in this field also provided conceptual insights into the functioning of the hydrogen networks.

The mathematical programming approach involved the optimization of the superstructure. Hallale and Liu[8] introduced the efficient mathematical method for refinery hydrogen network and pointed out the drawbacks of pinch technology. Their model also involved retrofitting purifiers and new compressors into the existing model to improve the hydrogen recovery. They minimized both utilities and the cost with this approach. Zhang et al.[54] developed a simultaneous optimization strategy for overall refinery by integrating the hydrogen network and utilities with the refinery processing and also investigated the strong interactions among them. They showed its superiority over the sequential approach and used linearization and Successive Linear Programming (SLP) for their NLP model. Liu et al.[10] developed a systematic methodology to select appropriate purifiers for increasing the purity of hydrogen fed to the hydrogen network and minimized total annualized cost. They used linear relaxation of bilinear terms to obtain the relaxed solution and to initialize their original MINLP model. The methodology they adopted involved the placement of purifiers between a source sink combinations and select the appropriate one among them. Fonseca et al.[9] addressed the problem of actual hydrogen distribution at the Porto Refinery of the GALP ENERGIA network by using an adapted Linear Programming (LP) method which used traditional conceptual approach along with the mathematical optimization. They claimed their model was more flexible compared to the superstructure methods and minimized utility consumption. Khajehpour[55] solved the MINLP model for refinery hydrogen network using a reduced superstructure approach. They used reduced approach to address the problem of nonconvexity, large size and longer computational times of original superstructure models and their idea were based primarily on engineering insights. They applied Genetic Algorithm (GA) to solve their model and used the data from a refinery in Iran to show significant savings. Liao et al.[56] integrated purifiers in their retrofit study of a refinery in China and minimized total annualized cost. They considered different retrofit scenarios in their state space superstructure model and analyzed the results. The purifier units considered by them were Pressure Swing Adsorption (PSA) and the Membrane Separation.

Kumar et al.[57] worked on the optimal distribution of hydrogen in a refinery network by using LP, NLP, MILP and MINLP models and evaluated the best among them for minimum utility and total annualized cost. They had also used compressor recycle rate in their model to illustrate practical practices in an actual refinery. Liao et al.[58] developed a rigorous methodology for hydrogen network highlighting the need for combining pinch based conceptual approaches with the superstructure approach to reduce the utility consumption in a refinery. In its sequel, Liao et al.[59] used an optimal targeting algorithm for location of one purifier in a hydrogen network and reported superior results compared to the other automated algorithmic targeting papers from their model. Elkamel et al.[60] developed a refinery hydrogen network model allowing retrofit with new compressor and purification unit (PSA) and integrated that with overall refinery planning model and found the total annualized cost for different scenarios of refinery planning. Ahmad et al.[61] developed a multiperiod MINLP model to account for the changing operating conditions and to consider the effect of such changes on the hydrogen network. They were able to show that the total annualized cost of such a multiperiod network was lesser than that of single period network. The solution strategy used by them to solve their model was similar to that of Liu et al.[10] Salary et al.[62] designed a hydrogen network in a refinery by application of process integration principles and proposed a systematic design hierarchy and heursitic rules. By applying the proposed procedure they were able to show reduced hydrogen consumption and total network cost. Jeong et al.[63] determined the hydrogen consumption and hydrogen recovery through pinch analysis and network optimization by using by-product hydrogen recycling between a source and a sink within a petrochemical complex. Jia and Zhang[64] developed an optimization framework for NLP hydrogen model and considered multi-components present in hydrogen network apart from hydrogen and methane. Light hydrocarbons, integrated flash calculation and improved hydroprocessing unit modeling were some features of their approach. An improved optimization approach for refinery hydrogen network optimization was carried out by Liao et al.[58] where they employed a two step methodology to retrofit existing hydrogen system. In another approach, a multiobjective optimization approach was used by Liao et al.[59] to solve the refinery hydrogen network problem with the two objectives being minimizing operational and capital cost. A real case study of refinery in China was used to demonstrate the relationship between the two objective functions. Jiao et al.[65] developed a MINLP multiperiod hydrogen scheduling model for a refinery. They showed that such a systematic model for hydrogen scheduling can ensure stable operation, reduce operating cost and could provide important strategies required for efficient hydrogen management in a refinery. They used an MILP and NLP iterative solution methodology to avoid the composition discrepancy arising by solving the full scale MINLP hydrogen scheduling model similar to that of Li et al.[66]

Besides the academia, the industry sector also focussed on the hydrogen distribution within a refinery. Foster Wheeler[67] highlighted the importance of increasing hydrogen requirement in a refinery and also pointed out the issue of CO_2 emissions from the hydrogen producers. They developed the process of hydrogen optimization through a systemic approach of hydrogen management involving the concepts of both pinch analysis and linear programming. They also studied a project example of hydrogen management where hydrogen production capacity was decreased by 60 metric tonnes per day resulting in a reduction in capital, operating and decrease in CO_2 emissions.

Air Products and Chemicals Inc.[68] in their report on refinery hydrogen management stressed the need for the hydrogen management within a refinery for maximizing refinery profits. They emphasized that the hydrogen management program in any refinery should aim at maximum hydrogen utilization, reduce the dependence on the on-purpose hydrogen producers, make use of hydrogen rich streams from the hydrogen consumers etc. UOP[69] in their report asserted that hydrogen cost is an integral part of the operating cost of a refinery. They highlighted the use of pinch analysis, refinery wide balance, and inclusion of purification unit models for hydrogen management in a refinery.

2.4 Global Optimization

As described earlier, the process network optimization problems are usually modeled as nonconvex NLP or MINLP. These network optimization problems are usually complex and obtaining realistic global solutions could be a challenging task because of the nonlinearity and nonconvexity involved in them. The structural decisions which determine the network topology also adds to the intricacy of such problems in solving them to global optimality in tractable computational times. Moreover due to the presence of the inevitable nonconvexity, most of the commercial solvers either converge to local optimal or even fail to produce a feasible solution. Hence apart from modeling these network optimization process models; there is also the need for solving such optimization problems to global optimality and providing an efficient solution strategy so that the model could be solved in tractable computational time.

The most prominent aspect of the process network synthesis problems is that their model formulations are characterized by the presence bilinear terms. The equations representing these bilinear terms may be of the form of mass and the energy balance constraints. The bilinear term is basically the product of two continuous variables.

Many problems of design and operation in chemical engineering have bilinear terms in their formulation such as pooling problem, heat exchange network synthesis, distillation column sequencing problem, water network synthesis, crude oil blending problem etc. The bilinear term, especially in network problems, could be a product of continuous decision variables such as flowrate and concentration, flowrate and temperature, flowrate and quality etc. In our work, the refinery hydrogen network problem is characterized by the presence of bilinear terms in the component balance equations and the fuel gas network has bilinear terms of product of flow and temperature.

Recognizing the importance of solving such problems to global optimality, many researchers[70, 71] have carried out several works in this area. Many deterministic global optimization algorithms for solving bilinear problems are based on some form of the spatial branch and bound algorithms. In such algorithms, the convergence usually depends upon the lower and upper bounds generated at each node of a branch and bound tree. Hence, the main interest lies in obtaining good quality lower (upper) bounds for minimization (maximization) problems. Such tight lower bounds result in faster convergence of the algorithm which in turn could increase the efficiency of the algorithm and result in producing solutions in tractable computational times. Apart from obtaining bounds in a branch and bound algorithm, other critical issues which govern the solution quality, effectiveness and computational time are selection of branching variable and branching point.

The concept of obtaining tight lower bounds is mostly done using the relaxation technique. Most of the researchers have focused on finding the convex relaxation for the nonconvex problems as the local optimum and global optimum coincide for a convex problem. Linear Programming (LP) relaxation is the widely accepted technique to convexify the nonconvexity arising due to the bilinear terms. McCormick[72] first developed the underestimator and overestimator equations for the bilinear terms. Later Al-Khayyal and Falk[73] identified them as the convex and concave envelopes of the bilinear terms. Foulds[74] used such relaxation into the branch and bound algorithm for optimization of pooling problems. Subsequently, many other researchers[75, 76] have also utilized the LP relaxation for bilinear terms and incorporated them into their formulation to obtain tighter relaxations.

Some of other prominent techniques developed for obtaining stronger relaxations for bilinear terms apart from the LP relaxation are Reformulation Linearization Technique (RLT) and the Lagrangian relaxation. Reformulation Linearization Technique[77] is a valid method for obtaining tighter relaxation by reformulating the original problem. This is done by adding redundant constraints into the relaxed model, and then followed by the linearization step where the product variables are replaced by single continuous variable. Such reformulations apart from increasing the relaxation tightness also serves to provide solutions, based on heuristic procedures, to complex discrete and continuous nonconvex problems. The problem with such reformulation techniques are that, there are no standardized procedures for developing such reformulations and reformulations may have to be customized separately based on the problem. The lagrangian relaxation technique is a powerful construct for obtaining strong lower bounds on the original problems. The methodology for this is that the complicating constraints in the original model are added to the objective function associated with some penalty in the form of lagrangian multipliers. They are called the lagrangian sub problems. The lagrangian multipliers are updated by some suitable iterative procedure until they are stopped by some stopping criterion. For every iteration, from the solutions of the lagrangian sub problems any suitable heuristic is used to obtain solutions to the original problems. The main drawback with this method is that the lagrangian sub problems usually fail to produce any feasible solutions to the original problems. Despite its limitations, several researchers have used such relaxation technique in the context of bilinear terms to obtain tighter relaxations. Adhya et al.[1] used lagrangian relaxation within a branch and bound framework to obtain global solutions to the pooling problems. Almutairi and Elhedli[2] also developed lagrangian relaxation with a feasible heuristic procedure to obtain tight relaxations to pooling problems. These relaxations even produced better solutions than the LP relaxation for standard pooling problems. Karuppiah and Grossmann[6] developed a multiscenario MINLP water network problem for solving the water networks problem under uncertainty. They had used the blend of both Lagrangian relaxation along with LP relaxations or McCormick envelopes to obtain stronger lower bounds for their problem.

Generalized Disjunctive Programming (GDP) has been considered as an effective framework in modeling and optimization of discrete-continuous optimization problems by using disjunctive logic for modeling algebraic equations. Such formulations have been used to model process network synthesis problems.[78, 79] Recently, Ruiz and Grossmann[80] developed a hierarchy of relaxations for solving bilinear and concave GDP to global optimality and showed that it produced stronger lower bounds. The nonconvexity is converted to convex formulation by using the McCormick envelopes for bilinear terms.

Recently, the idea *ab initio* partitioning of the search domain of the variables involved in the bilinear terms has attracted a lot of attention because of its promising approach in accelerating the convergence inside a global optimization algorithm. In this approach one or both the variables of the bilinear term is selected for partitioning of its domain. The partitioning scheme may or may not be uniform. The convex and concave envelopes of the bilinear term rely on the bounds of the variables in the bilinear term. Hence, the envelopes relaxation tightness can be improved by reducing the search domain of the variables. The relaxation efficiency and tightness also increases when considering more subdomains. Some initial works in this field applied to the process network synthesis problems include generalized pooling problem[81], water network synthesis[5], heat exchanger networks synthesis[82], reverse osmosis network[83] and process networks.[84] Wicaksono and Karimi[85] developed and analyzed 15 different formulations for piecewise underestimation of bilinear terms. Their work categorized different formulations mainly under 3 categories namely Big M, Convex Hull or Convex Combination (CC) and Incremental Cost (IC). They applied these formulations on two standard process network optimization problems and compared the performance of each formulation. Gounaris et al.[86] explored more into the formulations developed by Wicaksono and Karimi[85] and in this process also developed certain novel formulations involving the use of Special Ordered Sets (SOS 1) variables. They compared and contrasted the performance of all these formulations by considering the standard pooling problem. From their exhaustive comparison they could identify certain formulation whose performances were considerably better than the other existing formulations. They also showed that the formulation based on uniform partitioning scheme results in tighter relaxation. Pham et al.[87] discretized exhaustively one of the variables in the bilinear term and devised an algorithm to solve certain benchmark standard pooling problems to global optimality. Wicaksono and Karimi[88] extended the piecewise underestimation from univariate partitioning scheme to bivariate partitioning scheme to show better relaxation. Hasan and Karimi[89] also employed the bivariate partitioning scheme to derive even tigher relaxations for the bilinear term and applied it four process network synthesis problems. The relaxations they derived were based on Incremental cost, Convex Combination and Special Ordered Sets (SOS) formulations. They asserted that the relaxation quality and the piecewise gain is considerably improved for bivariate partitioning in comparison to the univariate partitioning scheme. They also showed that a uniform partitioning formulation produced tighter relaxation over non-uniform partitioning scheme. Misener et al.[90] used the piecewise underestimation of bilinear terms to solve the extended pooling problem. Misener and Floudas[91] also applied the same concept of piecewise relaxation of the bilinear terms for addressing the small, medium and large sized generalized pooling problems to global optimality. Apart from the piecewise underestimation, they also highlighted key issues in their branch and bound algorithm like giving variable bounds, and selecting appropriate branching point for branching. Misener et al.[92] developed a tool named - Algorithms for Pooling-problem Optimization in GEneralized and Extended classes (APOGEE) for solving different classes of pooling problems such as standard, generalized and extended pooling problem to global optimality. Though they used piecewise underestimation of bilinear terms in their algorithms, they also discussed that logarithmic partitioning pattern could also be employed for underestimation of bilinear terms. Scheduling of crude oil operations to global optimality by utilizing the piecewise underestimation of bilinear terms was done by Li et al.[93] The same authors[94] also worked on the solving scheduling of crude oil operations problem under demand uncertainty to global optimality. Very recently Misener and Floudas[95] also developed a numerical solver package GloMIQO (Global Mixed Integer Quadratic Optimizer) based on their work[96] on global optimization of Mixed Integer Quadratically-Constrained Quadratic Programs (MIQCQP).

2.5 Summary of Gaps and Challenges

Based on the review of literature, several research gaps and challenges in the area of modeling and optimization of refinery process networks are summarized as follows.

1. As explained earlier the work on the FGN presents many challenges. In this thesis, we identify one of the important concerns governing the design and operation of FGN which is for that of a multimode refinery operation. So far the FGN models described in the literature are designed for only single set of operating conditions, whereas the operating conditions may change in refinery based on the mode of plant functioning. This design may lead to a sub-optimal or even infeasible network when considering operating FGN under different set of operating conditions. There is a clear need to come up with a network design which can cater to the changing modes of plant operation and handle the practical features associated with it such as changes in the flow, quality specification, composition, contaminant concentration etc of the fuel gas streams.
2. Most of the works in the literature for hydrogen network problem are formulated as nonconvex NLP or MINLP. These models are nonconvex due to the presence of bilinear terms in the hydrogen component balance equations. This nonconvexity can give rise to multiple optimum solutions. Hence there is a clear need to develop strategies which help to solve such nonconvex problems to global optimality. Secondly, all the previous literature works on hydrogen network have focused on installation of a purifier unit as a solution to increasing hydrogen recovery within a network. Thus, it is also important to consider and investigate different approaches which could lead to increasing hydrogen recovery within a network.

3. The models for the hydrogen network developed so far in the literature have tried to represent realistic operations by considering non-isobaric conditions. Despite this there are some shortcomings present in the model which needs immediate attention. For example the effect of temperature is not considered in the model. Hence, there is a need to develop a fully comprehensive model that considers simultaneously both temperature and pressure changes and which takes into effect all the gas stream conditioning equipments like heater, cooler and valve along with the compressor.

2.6 Research Focus

1. Understanding that the characteristics of the fuel gas streams vary significantly with changing operation modes in a plant, which could make their routing into FGN a challenge, a multi-period 2-stage stochastic programming model is used to design and operate an FGN that caters to all operating modes. A refinery case study is also shown to demonstrate the importance of an optimized FGN. In addition, several strategies to minimize flaring and environmental penalties in a refinery operation are examined.
2. In this work, we address the problem of optimal synthesis of the refinery hydrogen network. We generalize the model of Elkamel et al.[60] and introduce strategies which help to solve the problem to global optimality. The problem is modeled as a nonconvex MINLP which seeks to minimize total annualized cost. A Specialized Outer Approximation (SOA) algorithm is utilized for optimizing this system in which the bivariate piecewise partitioning scheme is used to underestimate the bilinear terms to obtain a convex relaxation which gives a tight lower bound on the global optimum. A non redundant bound strengthening cut is added to the model. From the solution of lower bounding problem, upper

bound is obtained by incorporating the bound strengthening cut. These two bounds are made to converge to the solution within a Specialized Outer Approximation (SOA) framework. Several examples are proposed to demonstrate the effectiveness of the algorithm in solving problems to global optimality. Moreover to increase the recovery of hydrogen in a hydrogen network, we extend this model to consider integration with other refineries. Such ideas of enhanced integration and coordination among multiple refineries can lead to maximum utilization of the available resource (hydrogen). Different schemes of integration are proposed, studied and investigated in this regard.

3. We focus on some of the drawbacks of the hydrogen networks studied in the literature. In a bid to overcome these drawbacks and also to represent the design of hydrogen networks to a next level of complexity, we develop a new model for the improved synthesis of these hydrogen networks. A nonconvex nonlinear programming model for the hydrogen networks is developed with an objective of minimizing the total annualized cost of the entire network. Two examples are developed in this regard to demonstrate the developed model.

3 MODELING AND OPTIMIZATION OF MULTIMODE FUEL GAS NETWORKS

3.1 Introduction

While most petrochemical plants have multiple sources of waste gases, they also have several potential sinks that can consume these gases as fuel. For example, venting storage tanks, PU, FCCU, CRU and CDU are sources of waste gases; while boilers, turbines, furnace, incinerators etc are potential sinks in petroleum refineries. An attractive option is to utilize such impure, waste, surplus, byproduct, purge, or side streams with varying heating values as fuel, instead of sending them to flare. A systematic network of pipelines, valves, compressors, turbines, heaters, coolers, and controllers can be designed to collect various fuels, fuel gases, and waste gases from all sources (internal or external), mix them in optimal proportions, and supply them to the various sinks (flares, boilers, turbines, fired heaters, furnaces, etc.). Hasan et al.[12] called such a network a Fuel Gas Network (FGN).

In most plants, waste gases are normally insufficient in quality and quantity to meet the fuel and energy needs of the entire plant. Thus, a plant may use them to supplement its needs and thereby reduce its consumption of other costly fuels. For instance, a refinery uses products such as vaporized Liquefied Petroleum Gas (LPG) and fuel oil for its base fuel and energy needs. These are known as FFP or Fuel From Product.[12] Similarly, an LNG plant uses its natural gas feed as a fuel source. This is called FFF or Fuel From Feed.[12] By using the various fuel and waste gases in an optimal manner, an FGN can reduce the usage of costly fuels such as FFF, FFP, or external fuels. In addition, by recycling the waste gases, it can minimize flaring and consequent environmental impacts substantially.

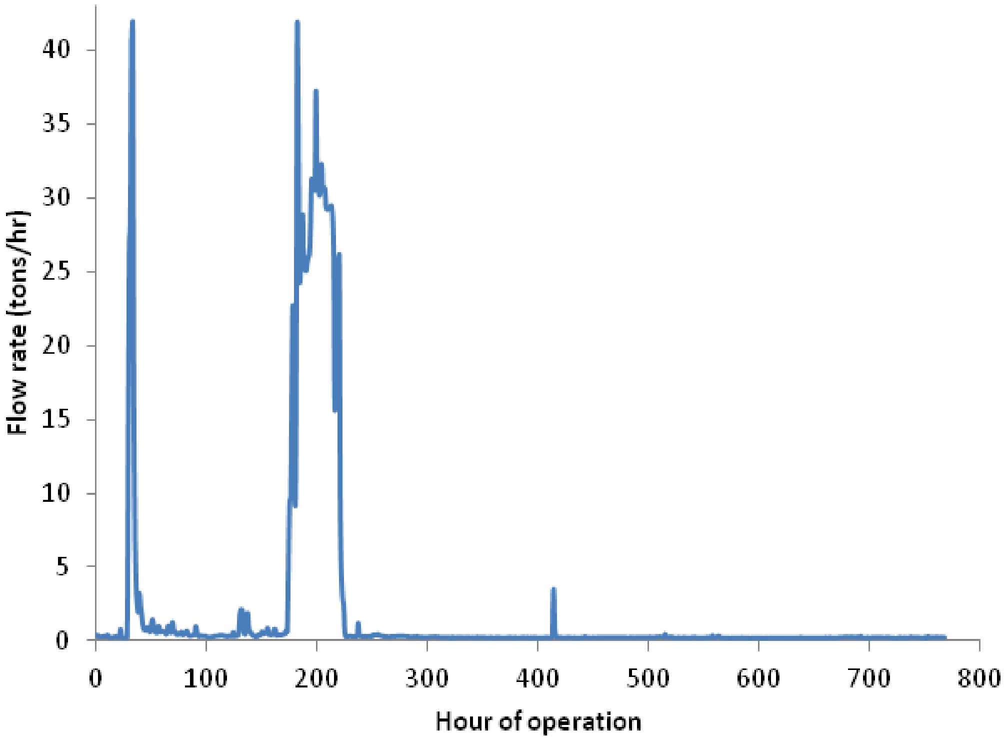


Figure 3.1 Flow to a typical industrial flare in the HG area

However, one major challenge that still remains and demands attention is that most plant operations are highly dynamic and source/flare flows are highly variable in time. Figure 3.1 shows a typical industrial flare showing variability in flow with time.[97] Flow can vary over multiple orders of magnitude. It can also vary substantially over time scales of an hour or less. Since a real plant may transition through several such steady operation modes over a given time horizon, its FGN must be designed to operate in the face of changes in fuel gas sources, sinks, and their characteristics such as flows, compositions, and contaminants, over time. Often, a source or sink may not even exist at certain times. For instance, the Jetty Boil-Off Gas (JBOG) would be available only when an LNG ship loads at the supply terminal. Clearly, the design and operation of FGN will change with variations in sources, sinks, temperatures, pressures, flows, compositions, sink demands, and quality specifications. While

Hasan et al.[12] incorporated many realistic features such as nonisobaric operation, nonisothermal mixing, and nonlinear quality specifications, their FGN model is valid for one steady operating mode or single set of operating conditions. Such an FGN may be suboptimal or even infeasible for a plant with multiple operating modes. Therefore, the FGN model of Hasan et al.[12] must be adapted to handle such variability. Instead of synthesizing an FGN for a single static mode, one must consider the various industrial operating modes and resulting dynamic profiles of waste gases. This requires the design and operation of FGN to be robust and flexible in face of such variability. The objective of this paper is to generalize and substantially revise the model of Hasan et al.[12] to address plant operation comprising several steady operating modes and then demonstrate the reduction in flaring using a refinery case study.

We begin by defining FGN synthesis for a plant with multiple steady operating modes. Then, we develop a new Non Linear Program (NLP) model for this multimodal case using the basic ideas from Hasan et al.[12] Next, we consider an example of refinery complex. We demonstrate the impact of considering dynamic versus steady state operation, and study various operational cases to show the significant impact on flaring.

3.2 Problem Statement

The detailed description of FGN Synthesis (FGNS) problem by Hasan et al.[12] applies to single-mode plant operation. In this work, we not only generalize it for multimodal operation, but also revise and simplify some of its aspects.

Given:

1. I gaseous source streams $(i = 1, 2, \ldots, I)$ containing S species $(s = 1, 2, \ldots, S)$ with known dynamic profiles of pressures, temperatures, flows, and compositions over

time. The species may involve hydrocarbon gases such as methane, ethane, propane, etc.; volatile organic compounds (VOCs) such as aromatics, methanol, acetone, etc.; non-combustibles such as water, nitrogen, CO_2, etc.; and contaminants such as sulphur, NOx, SOx, H_2S, V, Pb, etc.

2. K sinks $(k = 1, 2, \ldots, K)$ with known demand profiles of energy demands (LHV = Lower Heating Value) over time, which require gaseous fuels.
3. Time profiles of the allowable ranges for the flows, temperatures, pressures, compositions, and other specifications (e.g. LHV, Wobbe Index(WI), etc.) of fuel feed to each sink.
4. Operating parameters, capital expenditures (CAPEX), and operating expenditures (OPEX) for valves, compressors, and utility heaters/coolers.
5. Economic (cost, price, value, etc.) data for utilizing, heating, cooling, treating, flaring, and disposing gaseous fuel streams.

Determine:

1. A network (FGN) of transfer lines, mixers, headers, splitters, valves, compressors, heaters, coolers, flares, and other components to obtain acceptable feeds for the K sinks by integrating the I source streams over time.
2. Sizes and dynamic duty profiles of all major equipment (valves, heaters, coolers, and compressors).
3. Flows, temperatures, pressures, compositions, and fuel specs of all streams over time.

Aiming to minimize the Total Annualized Cost (TAC) of FGN:

We include three components in TAC. The first is the annualized CAPEX of the entire network and its equipment. The second is the OPEX related to the various fuels, products, byproducts, utilities, treatments, disposals, heating, cooling, compressing, and flaring. The third is the environmental cost of flaring in terms of emission fees for the total amount of hydrocarbons flared.

Assuming:

1. Plant operation comprises P steady-state scenarios or operation modes ($p = 1, 2, \dots, P$) with π_p denoting the fraction of time for which mode p occurs annually. π_p can also be interpreted as the probability of occurrence of mode p.
2. Sources (sinks) with identical properties or attributes in a mode are lumped into a single source (sink).
3. LHVs of fuel components do not change with temperature.
4. All expansions are Joule-Thompson expansions. In other words, FGN uses only valves, but no turbines.
5. All streams are below their inversion temperatures for Joule-Thompson expansions. No stream is sufficiently pure hydrogen to have a negative J-T coefficient.
6. All compressions are single-stage and adiabatic.
7. Unlimited utilities at any desired temperature.
8. Zero pressure drops in heaters, coolers, headers, and transfer lines.
9. All gas flows are in MMscf/h defined at 14.7 psia and 68 °F.

Hasan et al.[12] classified and described various types of sources and sinks. A source is essentially any gas stream (internal or external) with some heating value, which is available for mass integration via recycle. The waste/purge gases from CDU, FCCU, or PU in a refinery, feed/product/byproduct gases such as feed natural gas in an LNG plant and LPG in a refinery, and purchased fuel gases such as natural gas are some examples of source streams. The source gases may require some treatment or processing (e.g. heating, cooling, expansion, compression, and purification), before they can be reused in sinks. Thus, FGN may need auxiliary equipment such as heaters, coolers, compressors, valves, separators, and pipelines to achieve acceptable feeds to sinks. While Hasan et al.[12] treated waste/purge gases, FFF, FFP, and external fuels as different types of source streams, we make no such distinction and treat all of them in a uniform manner. We achieve this by controlling the flow of source streams that enter the FGN. For instance, we force all of the available flows of waste/purge gases to enter the FGN, but keep the flows of other source streams to be variables and below some upper bounds.

A sink is any plant unit that needs or consumes fuel gas. Some examples of sinks are turbines, boilers, incinerators, furnaces, fired heaters, and flares. Some sinks such as boilers, turbines, and furnaces produce some heat and power, while others such as incinerators and flares do not. All sinks produce emissions, and these emissions may be regulated. In contrast to Hasan et al.[12] who classified sinks into fixed and flexible, we treat all of them uniformly as flexible sinks. As per Hasan et al.[12], a sink is fixed (flexible), if it has a fixed (variable) energy need and cannot (can) generate heat/power that can be sold for additional revenue. Furthermore, while Hasan et al.[12] considered the flare as a separate entity, we consider it as just another sink with appropriate specifications and zero energy demand.

3.3 Model Formulation

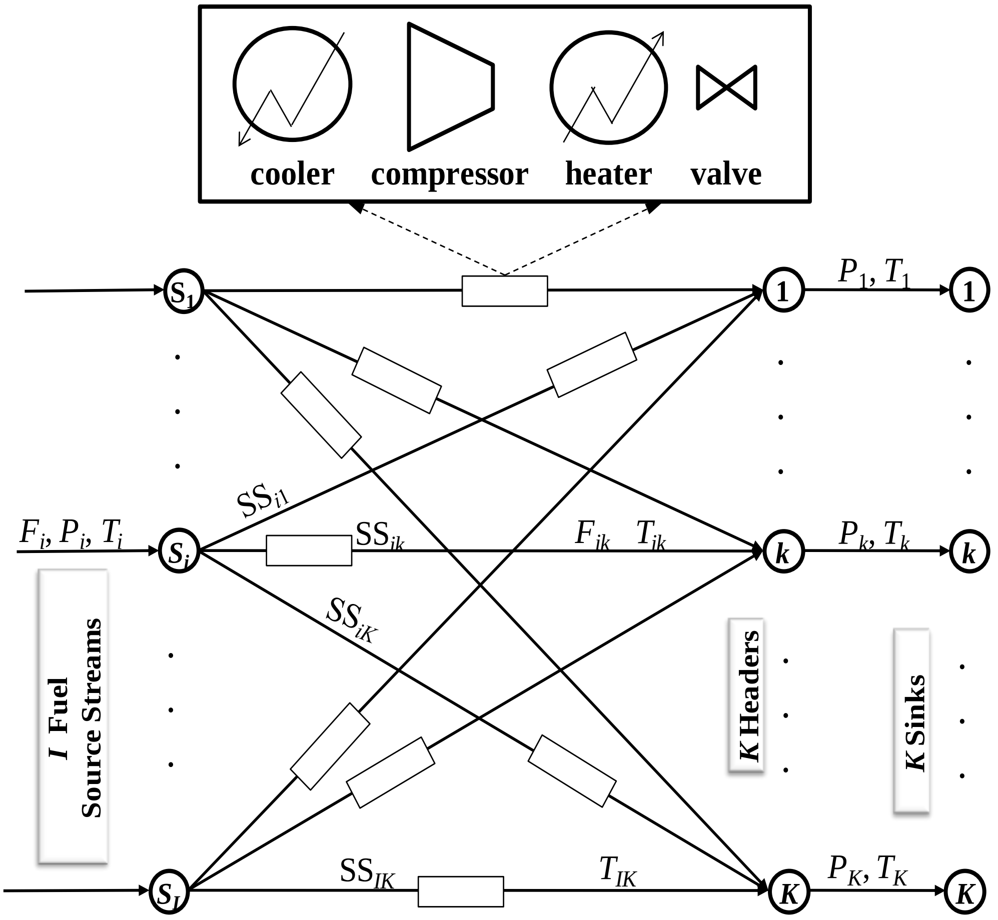


Figure 3.2 Schematic superstructure for an FGN

In this section, we explain the model formulation governing the multimode FGN. Figure 3.2 shows the superstructure proposed by Hasan et al.[12] for a single steady operating mode. For addressing P operating modes ($p = 1, 2, \dots, P$), we need a hyperstructure of P superstructures. However, designing and using a different FGN for each operating mode is clearly unacceptable, so the physical details of the FGN must be the same across all operating modes, but its operational details will change from one operating mode to another. Since we consider operating modes with varying probabilities, we need a 2-stage stochastic programming formulation[98], in which physical design decisions related to the existence and sizes of various equipment (transfer lines, heaters, valves, compressors, etc.) are first stage (or mode-independent) and operating decisions related to flows, temperatures, and duties are second stage (or mode-dependent) variables.

We begin with the source streams ($i = 1, 2, \dots, I$) and define the following parameters and variables to describe their operation during mode p ($p = 1, 2, \dots, P$).

P_{ip0}: Pressure of i (known)

T_{ip0}: Temperature of i (known)

F_{ip} ($F_{ip}^L \leq F_{ip} \leq F_{ip}^U$): Usage (MMscf/h) of source stream i

HC_{ip}: Hydrocarbon content of i (known)

For a waste/purge stream that must be used or disposed in the plant, we set $F_{ip}^L = F_{ip} = F_{ip}^U$ as the known usable flow of source i. For FFF, FFP, and external fuel gas, we treat F_{ip} is an optimization variable with appropriate bounds.

Now, consider the distribution of sources to various sinks. Call SS_{ik} as the transfer line feeding the header of sink k from source stream i. To describe the operation of SS_{ik} during mode p, we define the following.

f_{ikp}: Gas flow (MMscf/h) in SS_{ik}

T_{ikp} ($T_{ip}^L \leq T_{ikp} \leq T_{ip}^U$): Gas temperature at the outlet with allowable bounds

h_{ikp}: $f_{ikp}c_{ip}T_{ikp}$

Δh_{ikp}^B: Product of $f_{ikp}c_{ip}$ and temperature change during compression in SS_{ik}

Δh_{ikp}^H: Product of $f_{ikp}c_{ip}$ and temperature change during heating in SS_{ik}

Δh_{ikp}^C: Product of $f_{ikp}c_{ip}$ and temperature change during cooling in SS_{ik}

Δh_{ikp}^V: Product of $f_{ikp}c_{ip}$ and temperature change during valve expansion SS_{ik}

P_{kp} ($P_{kp}^L \leq P_{kp} \leq P_{kp}^U$): Pressure of sink k

Mass balance around source i demands,

$$F_{ip} = \sum_{k=1}^{K} f_{ikp} \tag{3.1}$$

The gas in SS_{ik} may undergo valve expansion, compression, heating, and/or cooling. For compression and valve expansion, we use,

$$\eta_{ip}\Delta h_{ikp}^{B} \geq (c_{ip}T_{ip0}f_{ikp} - \Delta h_{ikp}^{C})\left[\left(\frac{P_{kp}}{P_{ip0}}\right)^{n_{ip}} - 1\right] \tag{3.2}$$

$$\Delta h_{ikp}^{V} \geq \mu_{ip}c_{ip}f_{ikp}(P_{ip0} - P_{kp}) \tag{3.3}$$

where, $c_{ip}$is the known constant-pressure heat capacity (C_p) of source stream i, $\mu_{ip}$is its Joule-Thompson expansion coefficient, $n_{ip} = R/c_{ip}$ is its adiabatic compression coefficient, and η_{ip} is the adiabatic compression efficiency of the compressor on SS_{ik}. Since the use of a valve or compressor will incur cost, Eqs. (3.2) and (3.3) ensure that FGN uses a valve (compressor), only when $P_{ip0} > P_{kp}$ ($P_{ip0} < P_{kp}$). While the four possible operations will change the temperature of gas in SS_{ik}, the temperature at the outlet of SS_{ik} can be computed using,

$$h_{ikp} = c_{ip}T_{ip0}f_{ikp} + \Delta h_{ikp}^{B} + \Delta h_{ikp}^{H} - \Delta h_{ikp}^{C} - \Delta h_{ikp}^{V} \tag{3.4}$$

However, we must maintain gas temperature to be within $[T_{ip}^{L}, T_{ip}^{U}]$ throughout SS_{ik}. The lowest temperature in SS_{ik} will occur, when a cooler is used with a valve. This is because valve and cooler decrease temperature and this must exceed T_{ip}^{L}.

$$\Delta h_{ikp}^{V} + \Delta h_{ikp}^{C} \leq c_{ip}(T_{ip0} - T_{ip}^{L})f_{ikp} \tag{3.5}$$

As discussed earlier, the compressor inlet must be at the lowest temperature to minimize the compression work. Therefore, the highest temperature will be at the outlet of SS_{ik}, which must not exceed T_{ip}^{U}.

$$h_{ikp} \leq c_{ip}T_{ip}^{U}f_{ikp} \tag{3.6}$$

Note that $f_{ikp} = 0$ forces $\Delta h_{ikp}^{V} = \Delta h_{ikp}^{C} = 0$ via Eq. (3.5), and then Eq. (3.6) forces $\Delta h_{ikp}^{B} = \Delta h_{ikp}^{H} = 0$.

After the operation of SS_{ik}, we now use the following to describe the operation of sink k and its header.

T_{kp} ($T^L_{kp} \leq T_{kp} \leq T^U_{kp}$): Temperature of sink k

G_{kp} ($G^L_{kp} \leq G_{kp} \leq G^U_{kp}$): Gas flow into sink k

E_{kp}($E^L_{kp} \leq E_{kp} \leq E^U_{kp}$): Energy flow in terms of LHV into sink k

SG_{kp} ($SG^L_{kp} \leq SG_{kp} \leq SG^U_{kp}$): Specific Gravity of feed to sink k

LHV_{kp} ($LHV^L_{kp} \leq LHV_{kp} \leq LHV^U_{kp}$): LHV of feed to sink k

C_{kp}: $\sum_{i=1}^{I} c_{ip} f_{ikp}$

If a sink (e.g. fired heater with a given heating duty) is dedicated to a specific use and cannot consume more energy than its demand, then we set $E^L_{kp} = E_{kp} = E^U_{kp}$ to be its known energy demand. If a sink (e.g. boiler or gas turbine) can consume beyond its demand to produce extra utility such as steam or power, then we treat E_{kp} as an optimization variable with appropriate bounds. If a sink is a flare, incinerator, or disposal, then we set $E^L_{kp} = 0$, and $E^L_{kp} = \infty$. Then, using the above, we write the following for each mode p.

$$G_{kp} = \sum_{i=1}^{I} f_{ikp} \tag{3.7}$$

$$E_{kp} = \sum_{i=1}^{I} f_{ikp} LHV_{ip} \tag{3.8}$$

$$T_{kp} C_{kp} = \sum_{i=1}^{I} h_{ikp} \tag{3.9}$$

$$C_{kp} = \sum_{i=1}^{I} c_{ip} f_{ikp} \tag{3.10}$$

where, LHV_{ip} is the known LHV (heat per MMscf) of source stream i.

Hasan et al.[12] identified several specifications such as LHV, Wobbe Index (WI), and Methane Number (MN) for fuel gas quality, which may be essential for a sink to operate satisfactorily. For instance, gases entering even a flare or incinerator must have sufficient LHV. Plants may even add some natural gas to boost the LHV of a flare gas, so that the flare would operate adequately. We now consider some specifications individually.

Specific gravity (SG) of a gas is the ratio of its density and that of the air at the same temperature and pressure. For an ideal gas, this is nothing but the ratio of molecular weights of the gas and the air. If SG_{ip} denotes the known specific gravity of source stream i during mode p, then we can have the following bilinear constraint,

$$SG_{kp}G_{kp} = \sum_{i=1}^{I} f_{ikp}\, SG_{ip} \tag{3.11}$$

As mentioned earlier, a minimum LHV is usually required for satisfactory flaring and fuel combustion in a sink. We can compute the LHV of feed to sink k during mode p by,

$$LHV_{kp}G_{kp} \leq \sum_{i=1}^{I} f_{ikp}\, LHV_{ip} \tag{3.12}$$

WI is another critical spec for fuel gas quality with the same units as LHV.

$$WI = \frac{LHV}{\sqrt{SG}}$$

Note that the above definition of WI does not have a correction factor for temperature as suggested by Elliot et al.[34] and used by Hasan et al.[12] We decided to go with the above, because it seems to be the more widely used definition in the literature.[35, 36] Most sinks other than flares and incinerators require adequate WI. WI is a key factor in analysing the heating value of a gas. The higher the WI, the greater the heating value of the gas flowing through a hole of given size in a given amount of time. For any given orifice, all gas mixtures with an identical WI will deliver the same amount of heat.[99] If $[WI_{kp}^{L}, WI_{kp}^{U}]$ denotes the acceptable limits on WI of the feed to sink k during mode p, then we can write the following bilinear constraint:

$$(WI_{kp}^{L})^2 SG_{kp} \leq \left(LHV_{kp}\right)^2 \leq (WI_{kp}^{U})^2 SG_{kp} \tag{3.13a, b}$$

A plant may have a regulatory limit on the amount of hydrocarbons that it may burn in its flares or incinerators. It may incur a penalty, if the limit is exceeded. To accommodate this environmental aspect into our model, let HC_{ip} denote the mass of hydrocarbon in source stream i. Then, let hc_p^U denote the total mass of hydrocarbons that the plant can burn without incurring a hydrocarbon penalty during mode p, and hc_p denote the amount of hydrocarbons burnt by the plant in excess of the allowable limit (hc_p^U). Thus, the following should hold in each period for the hydrocarbon emissions from a flare or incinerator.

$$hc_p \geq \left(\sum_{i=1}^{I} \sum_{k=1}^{K} HC_{ip}\, f_{ikp}\right) - hc_p^U \tag{3.14a}$$

Later, we will impose an emission fee on hc_p in the FGN cost. Note that the sum in Eq. (3.14a) includes all sinks that are flares or incinerators.

Similarly, a plant may have regulatory limits on emissions such as NOx and SOx from all sinks. These limits and the corresponding emission fees can be handled in the same manner as the hydrocarbon penalty discussed above. To this end, define e_{jikp} as the amount of pollutant j that sink k would emit, when it uses 1 MMscf of gas from source i during mode p. Furthermore, let e_{jp}^U be the regulatory limit on this emission during mode p. Then, the following constraint will compute the amount of emissions of pollutant j for any environmental penalty.

$$e_{jp} \geq \sum_{i=1}^{I} \sum_{k=1}^{K} e_{jikp} f_{ikp} - e_{jp}^U \tag{3.14b}$$

Methane Number (MN)[12] measures the knock resistance of a gaseous fuel entering a gas turbine. If x_{isp} is the mole fraction of a hydrocarbon component s in source stream i during mode p, then Hasan et al.[12] proposed the following for ensuring an adequate MN for a sink k that is a gas turbine.

$$0.242 \sum_i f_{ikp} x_{i,CH_4,p} \geq$$
$$\sum_i [1.516 f_{ikp} x_{i,C_2H_6,p} + 3.274 f_{ikp} x_{i,C_3H_8,p} + 5.032 f_{ikp} x_{i,C_4H_{10},p}] +$$
$$\sum_i [6.79 f_{ikp} x_{i,C_5H_{12},p} + 8.548 \sum_i f_{ikp} x_{i,C_{5+},p}] \tag{3.15}$$

Hasan et al.[12] had used a treatment factor or removal ratio for each component s in the above equation, which we have assumed to be unity in this work.

Hasan et al.[12] also proposed the following constraints for preventing condensation in FGN and ensuring sufficient superheating.

$$\left\{MDP_{kp} + \frac{5}{9}\left[5.15\left(\frac{P_{kp}}{100}\right) - 312\right]\right\} \leq T_{kp} \tag{3.16}$$

$$\left\{HDP_{kp} + \frac{5}{9}\left[2.33\left(\frac{P_{kp}}{100}\right)^2 - 2.8\left(\frac{P_{kp}}{100}\right) - 305\right]\right\} \leq T_{kp} \tag{3.17}$$

where, MDP_{kp} is the moisture dew point temperature and HDP_{kp} is the hydrocarbon dew point temperature for the sink k in period p .

Apart from the above fuel specifications, most sinks may impose limits on the levels of some gas components in its feed. Let q_{isp} denote the amount of component s in source stream i during mode p, and $[q_{ksp}^L, q_{ksp}^U]$ represent the acceptable limits on this amount, then we need,

$$q_{ksp}^L G_{kp} \leq \sum_{i=1}^{I} q_{isp} f_{ikp} \leq q_{ksp}^U G_{kp} \tag{3.18}$$

One can suitably modify the above to accommodate groups of components rather than individual ones. Similarly, one could use appropriate weights for various constituents.

Having modelled the operational aspects of FGN for a given mode, we now define the following mode-independent or design variables and relate them to the various mode-dependent variables.

F_{ik}: Flow capacity (MMscf/h) of SS_{ik}

ΔH_{ik}^B: Maximum duty of the compressor on SS_{ik}

ΔH_{ik}^{H}: Maximum duty of the heater on SS_{ik}

ΔH_{ik}^{C}: Maximum duty of the cooler on SS_{ik}

ΔH_{ik}^{V}: Maximum Δh_{ikp}^{V} for SS_{ik}

Physically, the above represent the sizes or capacities of the auxiliary equipment in FGN. For instance, F_{ik} measures the capacity or the maximum flow that SS_{ik} must allow. We will compute the OPEX and CAPEX of various units as linear functions of these sizes or capacities. The following link the design variables with the operational ones.

$$F_{ik} \geq f_{ikp} \tag{3.19}$$

$$\Delta H_{ik}^{B} \geq \Delta h_{ikp}^{B} \tag{3.20}$$

$$\Delta H_{ik}^{H} \geq \Delta h_{ikp}^{H} \tag{3.21}$$

$$\Delta H_{ik}^{C} \geq \Delta h_{ikp}^{C} \tag{3.22}$$

$$\Delta H_{ik}^{V} \geq \Delta h_{ikp}^{V} \tag{3.23}$$

Lastly, the expected total annualized cost (TAC) of an FGN with P modes is given by the sum of its CAPEX costs and the weighted sum of its OPEX costs under various modes. If OST denotes the on-stream time of the plant per year, and AF denotes the annualization factor, then the expected TAC is:

$$
\begin{aligned}
TAC = AF \Bigg[& \sum_{i=1}^{I}\sum_{k=1}^{K} CAPEX_{ik}^{T}\, F_{ik} + \sum_{i=1}^{I}\sum_{k=1}^{K} CAPEX_{ik}^{B}\, \Delta H_{ik}^{B} + \sum_{i=1}^{I}\sum_{k=1}^{K} CAPEX_{ik}^{H}\, \Delta H_{ik}^{H} \\
& + \sum_{i=1}^{I}\sum_{k=1}^{K} CAPEX_{ik}^{C}\, \Delta H_{ik}^{C} + \sum_{i=1}^{I}\sum_{k=1}^{K} CAPEX_{ik}^{V}\, \Delta H_{ik}^{V} \Bigg] \\
& + OST \sum_{p=1}^{P} \pi_p \Bigg[\sum_{i=1}^{I} \alpha_{ip}\, F_{ip} - \sum_{k=1}^{K} \beta_{kp} (E_{kp} - E_{kp}^{L}) + \sum_{k=1}^{K} \delta_{kp}\, G_{kp} \\
& + \gamma_p hc_p + \sum_{j=1}^{J} \xi_{jp}\, e_{jp} + \sum_{i=1}^{I}\sum_{k=1}^{K} OPEX_{ikp}^{T} f_{ikp} + \sum_{i=1}^{I}\sum_{k=1}^{K} OPEX_{ikp}^{B} \Delta h_{ikp}^{B} \\
& + \sum_{i=1}^{I}\sum_{k=1}^{K} OPEX_{ikp}^{H} \Delta h_{ikp}^{H} \\
& + \sum_{i=1}^{I}\sum_{k=1}^{K} OPEX_{ikp}^{C} \Delta h_{ikp}^{C} \sum_{i=1}^{I}\sum_{k=1}^{K} OPEX_{ikp}^{V} \Delta h_{ikp}^{V} \Bigg]
\end{aligned}
\tag{3.24}
$$

where, the first five terms represent the annualized CAPEX costs for various equipment in SS_{ik}: $CAPEX_{ik}^{T}$ for transfer line, $CAPEX_{ik}^{B}$ for compressor, $CAPEX_{ik}^{H}$ for heater, $CAPEX_{ik}^{C}$ for cooler, and $CAPEX_{ik}^{V}$ for valve. The remaining terms represent the operating costs of the network. The OPEX for each period is weighed according to its probability of occurrence. The various cost coefficients are as follows:

α_{ip} = Cost of source stream i (\$/MMscf): This is normally positive for FFF, FFP, and fuel gas purchased externally. It is zero for waste/purge gases.

β_{kp} = Revenue (\$ per unit energy) from the surplus energy generated by a flexible sink that can produce beyond its demand: This is usually zero for the fixed and flare sinks, but nonzero for boilers that may produce extra steam and gas turbines that may produce electricity.

δ_{kp} = Cost (\$/MMscf) of using fuel gas in a sink: It can be zero for a normal sink with a genuine fuel need, and positive for a sink for dilution, disposal, incineration, etc.

γ_p = Penalty (\$/kg) for flaring or incinerating hydrocarbons beyond the regulatory limit

ξ_{jp} = Penalty per unit emission or pollutant j beyond the regulatory limit

The last five terms in the OPEX term represent the operating costs for various equipment in SS_{ik}: $OPEX_{ik}^{T}$ for transfer line, $OPEX_{ik}^{B}$ for compressor, $OPEX_{ik}^{H}$ for heater, $OPEX_{ik}^{C}$ for cooler, and $OPEX_{ik}^{V}$ for valve.

This completes our NLP formulation (Eqs. (3.1)-(3.24)) for FGN synthesis for P operating modes. We now illustrate its application using a refinery case study. This demonstrates the impact of considering dynamic plant operating modes versus a single average static mode. Further, we also consider several cases to demonstrate the reduction in flaring arising due to the integration with plant FGN.

3.4 Refinery Case Study

A refinery network, as shown in Figure 3.3, has seven possible sources (S1-S7, $i = 1, 2, \ldots, I$ = 7) of fuel gases and six sinks (C1-C6, $k = 1, 2, \ldots, K$ = 6). S1, S2, and S3 are gas streams from CDU, PU and CRU respectively. S4 is a product stream from one of these units, thus is an FFP stream. This is usually the gas stream whose constituents are similar to that of an LPG stream. S6 is a lean purge stream that the refinery usually flares due to low LHV. S5 is a standard external fuel gas (lean natural gas), and S7 is another external fuel gas (rich natural gas). C1-C4 are gas turbines with fixed energy demands, C5 is a boiler with some capacity to produce extra steam, and C6 is the flare. Using the terminology of Hasan et al.[12], C1-C4 are fixed sinks and C5 is a flexible sink. Table 4.1 gives the data and parameters for S1-S7 and C1-C6. Table 3.2 lists the cost parameters for various FGN units. We do not consider pollutant emissions in this study. The refinery operation involves five steady-state modes ($p = 1, 2, \ldots, P = 5$) with occurrence probabilities of 0.60, 0.10, 0.20, 0.05, and 0.05. For this case study, we assume that all data and parameters except the flows of source streams remain unchanged across the five modes. Figure 3.4 shows how the source flows vary across the five modes of operation. We assume an on-stream time of 8000 h per year, and an annualization factor of 10%

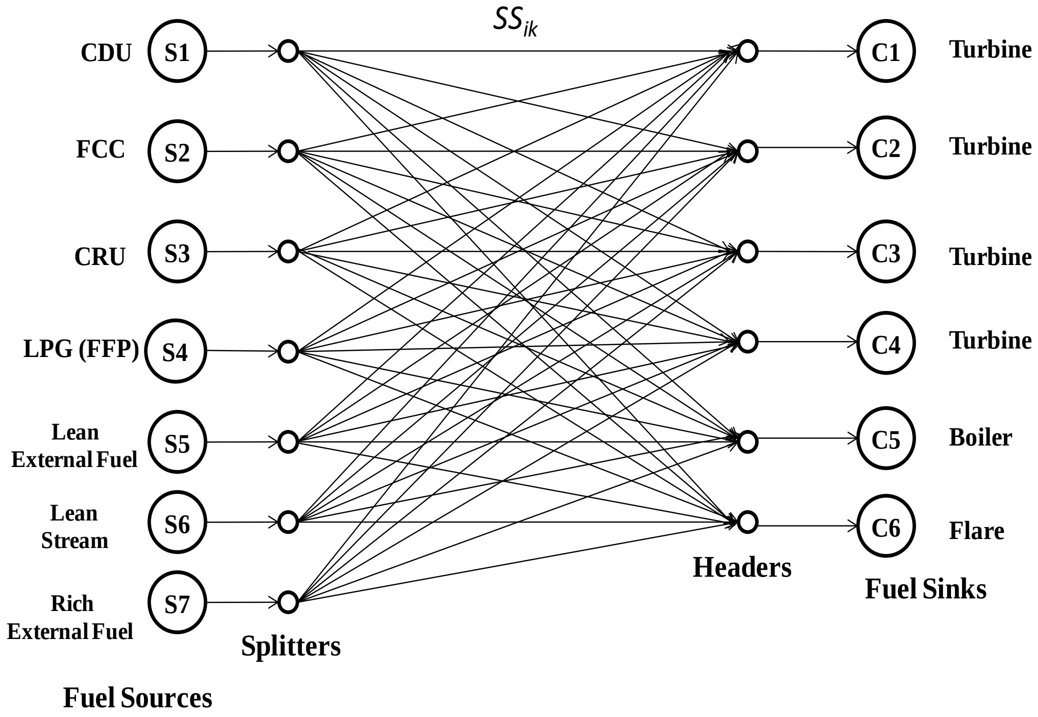


Figure 3.3 Fuel sources and sinks for the refinery case study

3.4.1 Impact of Multi-mode Model

To study the effect of multiple modes on the design and operation of FGN, we compare the FGN from our multi-mode stochastic model with that derived using a single-mode model such as that of Hasan et al.[12] For simplification, we assume that the refinery does not use S7 at all, and C5 is a fixed sink with an energy demand of 225 MMBtu/hr. Then, we construct a base FGN using the single-mode model as follows. We solve our model in a deterministic manner for each mode separately to get five distinct FGNs. If an equipment item (e.g. valve) or transfer line does not exist

Table 3.1 Data and Parameters for the sources and sinks in the refinery case study

Spec/Parameter	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Flow (MMscf/h) – Mode 1	0.04	0.40	0.18	≤5.00	≤5.00	0.09	≤5.00
Flow (MMscf/h) – Mode 2	0.08	0.50	0.12	≤5.00	≤5.00	0.10	≤5.00
Flow (MMscf/h) – Mode 3	0.02	0.45	0.15	≤5.00	≤5.00	0.08	≤5.00
Flow (MMscf/h) – Mode 4	0.04	0.27	0.10	≤5.00	≤5.00	0.03	≤5.00
Flow (MMscf/h) – Mode 5	0.06	0.25	0.24	≤5.00	≤5.00	0.03	≤5.00
Temperature (K)	373	400	350	320	320	380	320
Pressure (psia)	50	35	25	25	50	50	50
Cp (kJ/MMscf K)	42791	43210	42270	100626	44000	44403	45757
μ (K/psia)	0.030	0.028	0.030	0.028	0.028	0.028	0.028
η	0.75	0.75	0.75	0.75	0.75	0.75	0.75
n	0.2	0.2	0.17	0.18	0.2	0.17	0.2
LHV (MMBtu/MMscf)	880	915	850	2659	1000	807	1130
SG	0.769	0.740	0.769	1.425	0.909	0.772	0.912
Methane (mol%)	88	90	88	0	94	62	90
Ethane (mol%)	2	3	2	2	3	5	5
Propane (mol%)	0.5	2	0	56	1	4	3
C3+ (mol%)	1	0	0	42	1	2	2
Hydrogen (mol%)	0.5	0	4	0	0	1	0
Carbon Monoxide (mol%)	1	0	3	0	1	1	0
Nitrogen (%)	7	5	3	0	0	25	0
Sulfur (ppm)	55	70	55	65	65	65	65
H2S (ppm)	0.05	201	0.05	198	198	198	198
VOC (ppm)	4	6	5	5	5	6	6
Price ($/MMscf)	0	0	0	500	800	0	975
Benzene, Aromatics, Lead, Vanadium, NOX, and Oxygen levels are zero for all source streams.							
Spec/Parameter	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**-**
Flow Range (MMscf/h)	0.08-0.11	0.09-0.145	0.10-0.13	0.09-0.12	0.20-0.25	≥0	
Temperature (K)	273-800	273-800	273-800	273-800	273-800	273-800	
Pressure (psia)	25-360	25-360	25-360	25-360	25-360	14-17	
Demand (MMBtu/h)	120	140	110	110	≥150	≥0	
WI	750-1590	750-1590	750-1590	750-1590	750-1590	-	
MN	>80	>80	>80	>80	>80	-	
MDP(K)	277	277	277	277	277	-	
HDP(K)	277	277	277	277	277	-	
LHV (MMBtu/MMscf)	500-2000	500-2000	500-2000	500-2000	500-2000	300-2000	
SG	0.5-1	0.5-1	0.5-1	0.5-1	0.5-1	0.5-1	
Methane (mol%)	>85	>85	>85	>85	>85	-	
Ethane (mol%)	<15	<15	<15	<15	<15	-	
Propane (mol%)	<15	<15	<15	<15	<15	-	
C3+ (mol%)	<5	<5	<5	<5	<5	-	
Hydrogen (mol%)	<5	<5	<5	<5	<5	-	
Carbon Monoxide(mol%)	<10	<10	<10	<10	<10	-	
Oxygen(mol%)	<4	<4	<4	<4	<4	-	
Nitrogen (mol%)	<15	<15	<15	<15	<15	-	
Aromatics (mol%)	<50	<50	<50	<50	<50	-	
Benzene (mol%)	<2	<2	<2	<2	<2	-	
Sulfur (ppm)	<500	<500	<500	<500	<500	-	
H2S (ppm)	<200	<200	<200	<200	<200	-	
Lead (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	-	
Vanadium (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01	-	
NOX (ppm)	<50	<50	<50	<50	<50	-	
VOC (ppm)	<50	<50	<50	<50	<50	-	
Handling Cost ($/MMscf)	0	0	0	0	0	5	
Revenue ($/Mmbtu)	0	0	0	0	0.2	0	
Hydrocarbon Penalty ($/kg)	0	0	0	0	0	0.1	

Table 3.2 CAPEX and OPEX coefficients for various equipment units

Unit	CAPEX ($/kW)	OPEX ($/kWh)
Compressor	100000	0.100
Heater	50000	0.010
Cooler	50000	0.020
Valve	5000	0.001
Pipeline	-	0.500 ($-h/MMscf)

Table 3.3 CAPEX ($/MMscf) values for various source-sink pipelines

Source	**Sink**					
	C1	C2	C3	C4	C5	C6
S1	62500	64000	65000	63000	62500	62500
S2	62500	66000	65500	62500	63500	63000
S3	61000	64000	60000	62000	63500	63000
S4	62500	63500	64500	65500	67000	68500
S5	62500	64000	65000	66000	66500	68000
S6	61500	61000	60500	64000	64500	66000

in any mode, then we eliminate that item or line from our base FGN. For each item or line that exists in at least one mode, we identify its maximum capacity from among all five modes and take that as its capacity in the base FGN. This fixes the design of the base FGN. Then, we optimize the operation of this base FGN for each mode individually. To this end, we fix the capacity variables in our model and minimize OPEX for each mode one at a time.

For the multi-mode FGN, we solve our model to get TAC = $684,510.21 with CAPEX = $108,075.84, OPEX = $673,704/yr, and fuel cost = $531,912 /yr. The multi-mode FGN needs no heater, cooler, or compressor. It uses FFP and the standard external fuel in all five modes. All sinks except the flare need the external fuel and FFP to meet their fuel needs. The header pressure at the flare is 17 psia for all modes with flaring. The header pressures at all the sinks are 25 psia. Table 3.3a and Table 3.3b give the percent distribution of flows from the source to the sinks for various modes in the multimode and base FGN respectively. Table 3.4a and Table 3.4b give

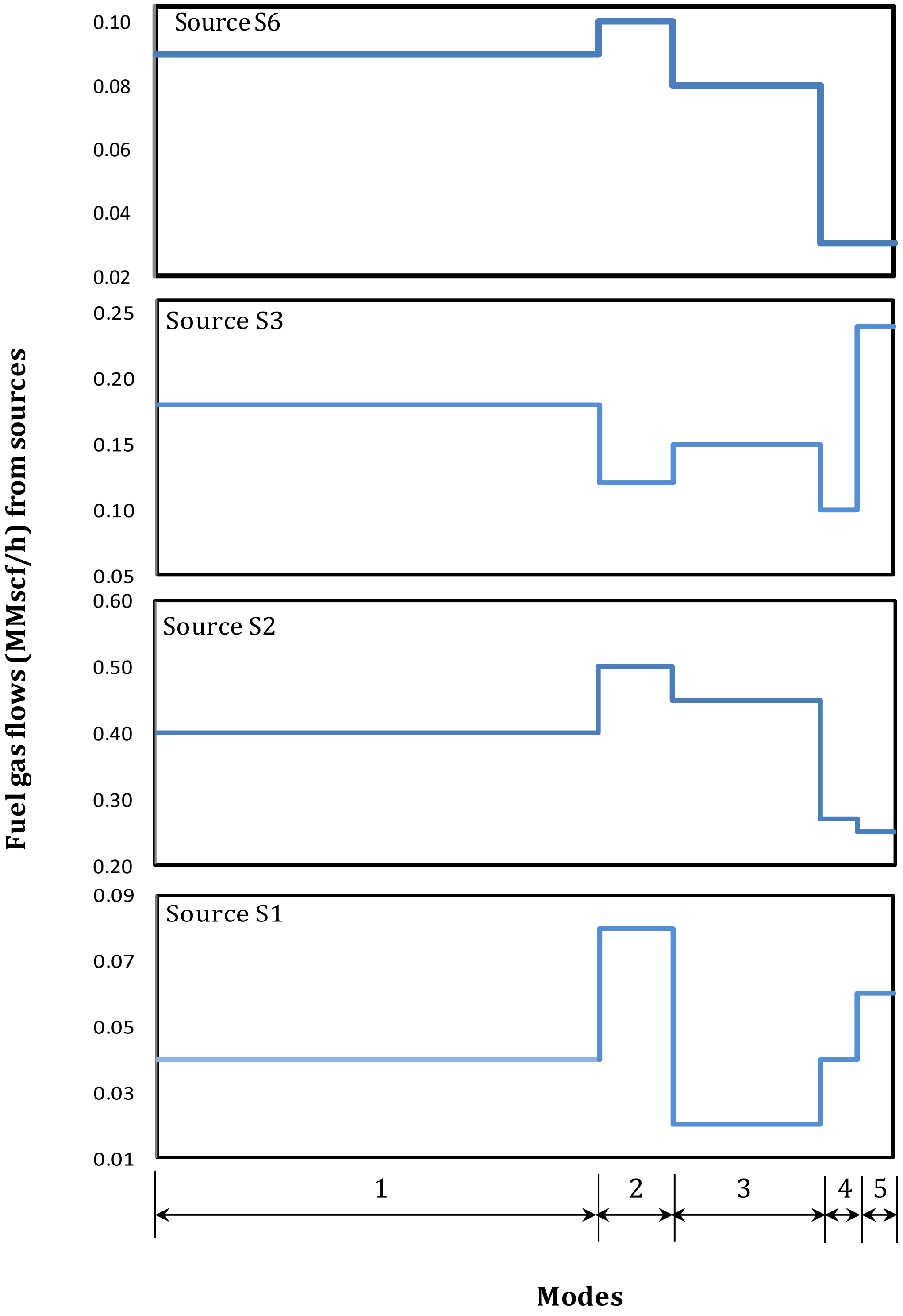


Figure 3.4 Modes of operation for the refinery case study with relative duration

Table 3.4 Distribution (%) of flows into sinks from sources for various modes in the Multimode FGN

	Sinks					
Source	C1	C2	C3	C4	C5	C6
Multi-mode FGN Mode 1						
S1	79.25	1.23	14.28	0.79	4.45	0.00
S2	0.98	30.17	0.00	26.36	42.49	0.00
S3	0.00	7.31	60.76	0.99	30.94	0.00
S4	53.90	32.04	0.00	5.80	8.26	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	6.35	16.58	12.84	23.67	40.56
Multi-mode FGN Mode 2						
S1	39.62	0.62	32.14	0.40	0.46	26.76
S2	0.79	25.84	0.00	20.19	38.24	14.95
S3	0.00	0.00	73.89	0.00	0.00	26.11
S4	52.98	30.33	0.00	7.64	9.05	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	10.51	14.92	17.54	57.03	0.00
Multi-mode FGN Mode 3						
S1	100	0.00	0.00	0.00	0.00	0.00
S2	0.759	28.72	0.59	26.51	43.43	0.00
S3	7.103	4.37	74.96	0.40	13.17	0.00
S4	60.55	33.31	0.00	0.96	5.17	0.00
S5	100	0.00	0.00	0.00	0.00	0.00
S6	0	5.73	18.65	0.00	42.60	33.03
Multi-mode FGN Mode 4						
S1	52.33	1.23	45.64	0.79	0.00	0.00
S2	0.00	27.17	0.98	37.15	34.70	0.00
S3	10.65	15.95	9.96	2.12	61.31	0.00
S4	15.65	15.96	14.26	11.04	43.09	0.00
S5	41.61	21.23	37.16	0.00	0.00	0.00
S6	0.00	0.00	0.00	0.00	100.00	0.00
Multi-mode FGN Mode 5						
S1	52.83	0.82	42.85	0.53	2.97	0.00
S2	1.57	46.37	0.00	40.12	11.94	0.00
S3	0.00	6.65	38.98	0.89	53.49	0.00
S4	17.39	15.43	6.08	12.48	48.63	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	0.00	0.00	0.00	100.00	0.00

Table 3.5 Distribution (%) of flows into sinks from sources for various modes in the Base FGN

	Sinks					
Source	C1	C2	C3	C4	C5	C6
Base FGN Mode 1						
S1	79.22	0.00	0.00	4.41	16.37	0.00
S2	0.98	32.31	0.00	28.92	35.84	1.95
S3	0.01	0.28	64.62	1.28	12.22	21.58
S4	42.17	24.17	15.06	1.19	17.41	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	11.65	4.28	0.00	82.94	1.13
Base FGN Mode 2						
S1	39.62	0.62	58.90	0.74	0.12	0.00
S2	0.79	25.84	0.00	23.86	34.55	14.97
S3	0.00	0.00	55.49	0.00	0.00	44.51
S4	52.97	30.32	0.00	0.79	15.93	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	10.51	14.83	0.00	74.66	0.00
Base FGN Mode 3						
S1	100.00	0.00	0.00	0.00	0.00	0.00
S2	0.76	25.84	0.13	26.12	47.15	0.00
S3	7.10	12.79	76.68	1.50	1.92	0.00
S4	60.55	36.56	0.42	1.40	1.08	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	5.53	17.93	0.00	43.51	33.03
Base FGN Mode 4						
S1	1.65	95.59	1.62	1.15	0.00	0.00
S2	0.90	0.00	27.25	37.14	34.70	0.00
S3	28.30	0.00	8.39	2.00	61.31	0.00
S4	15.81	18.08	11.98	11.03	43.09	0.00
S5	41.83	47.74	10.43	0.00	0.00	0.00
S6	0.00	0.00	0.00	0.00	100.00	0.00
Base FGN Mode 5						
S1	52.83	6.52	2.85	2.36	35.44	0.00
S2	1.57	28.44	0.52	39.67	29.80	0.00
S3	0.00	26.40	47.15	0.95	25.50	0.00
S4	17.39	13.61	8.54	12.42	48.05	0.00
S5	100.00	0.00	0.00	0.00	0.00	0.00
S6	0.00	0.29	0.37	0.00	99.34	0.00

Table 3.6 Flows and specs into the sinks for various operating modes in the Multimode FGN

Sink	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Sink	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5
LHV (MMBtu/MMscf)						Specific Gravity (SG)					
C1	916.2	916.2	916.6	918.7	916.2	C1	0.902	0.902	0.904	0.909	0.902
C2	829.2	828.7	828.7	881.2	850.2	C2	0.767	0.765	0.764	0.833	0.780
C3	763.2	765.8	763.1	916.9	796.4	C3	0.769	0.769	0.768	0.905	0.785
C4	799.6	800.1	798.4	855.1	855.1	C4	0.748	0.751	0.741	0.778	0.778
C5	791.1	790.7	790.4	897.9	886.9	C5	0.753	0.751	0.748	0.830	0.837
C6	531.0	566.2	531.0	-	-	C6	0.769	0.752	0.769	-	-
Flow (MMscf/h)						Energy (MMBtu/h)					
C1	0.110	0.110	0.110	0.110	0.110	C1	120.0	120.0	120.0	120.0	120.0
C2	0.145	0.145	0.145	0.134	0.140	C2	140.0	140.0	140.0	140.0	140.0
C3	0.130	0.129	0.130	0.101	0.122	C3	110.0	110.0	110.0	110.0	110.0
C4	0.120	0.120	0.120	0.109	0.109	C4	110.0	110.0	110.0	110.0	110.0
C5	0.250	0.250	0.250	0.208	0.213	C5	225.0	225.0	225.0	225.0	225.0
C6	0.037	0.127	0.026	-	-	C6	29.4	113.8	21.3	-	-
Wobbe Index (MMBtu/MMscf)						Methane Content (mol fraction)					
C1	894	894	897	899	894	C1	0.850	0.850	0.850	0.850	0.850
C2	815	812	813	860	833	C2	0.856	0.850	0.861	0.850	0.850
C3	785	783	785	897	812	C3	0.850	0.850	0.851	0.850	0.859
C4	789	789	788	834	834	C4	0.866	0.850	0.899	0.850	0.850
C5	788	781	783	874	875	C5	0.867	0.831	0.858	0.753	0.750
Pressure (psia)						Temperature (K)					
C1	25	25	25	25	25	C1	335.6	335.6	332.8	331.1	335.6
C2	25	25	25	25	25	C2	388.5	392.3	391.2	363.3	385.2
C3	25	25	25	25	25	C3	354.5	357.9	354.5	332.5	352.9
C4	25	25	25	25	25	C4	395.5	394.8	399.2	389.2	389.2
C5	25	25	25	25	25	C5	386.0	393.9	392.5	366.4	353.3
C6	17	17	17	-	-	C6	379.1	382.8	379.1	-	-

Table 3.7 Flows and specs into the sinks for various operating modes in the Base FGN

Sink	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Sink	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5
LHV (MMBtu/MMscf)						Specific Gravity (SG)					
C1	916.2	916.2	916.4	917.4	916.2	C1	0.902	0.902	0.904	0.909	0.902
C2	829.8	828.7	829.6	918.6	832.3	C2	0.765	0.765	0.769	0.907	0.784
C3	793.2	768.7	764.2	871.3	805.3	C3	0.785	0.769	0.769	0.812	0.791
C4	798.6	798.4	799.4	855.1	854.6	C4	0.742	0.741	0.742	0.778	0.778
C5	792.5	791.5	790.1	897.9	894.3	C5	0.761	0.756	0.745	0.83	0.831
C6	553.1	564.2	540.5	-	-	C6	0.764	0.752	0.769	-	-
Flow (MMscf/h)						Energy (MMBtu/h)					
C1	0.11	0.11	0.11	0.11	0.11	C1	120	120	120	120	120
C2	0.145	0.145	0.145	0.128	0.145	C2	140	140	140	140	140
C3	0.123	0.129	0.13	0.107	0.123	C3	110	110	110	110	110
C4	0.12	0.12	0.12	0.109	0.109	C4	110	110	110	110	110
C5	0.25	0.25	0.25	0.208	0.21	C5	225	225	225	225	225
C6	0.048	0.128	0.026	-	-	C6	40.9	113.8	21.3	-	-
Wobbe Index (MMBtu/MMscf)						Methane Content (mol fraction)					
C1	894	894	896	896	893	C1	0.85	0.85	0.85	0.85	0.85
C2	814	812	812	858	832	C2	0.865	0.874	0.869	0.85	0.85
C3	785	784	785	902	813	C3	0.85	0.851	0.85	0.85	0.858
C4	790	787	787	833	832	C4	0.894	0.899	0.899	0.85	0.85
C5	786	780	783	873	875	C5	0.848	0.867	0.854	0.753	0.75
Pressure (psia)						Temperature (K)					
C1	25	25	25	25	25	C1	335.6	335.6	332.8	328.8	335.6
C2	25	25	25	25	25	C2	392.2	392.3	386.7	333.5	370.9
C3	25	25	25	25	25	C3	349.3	361.7	353.5	373.1	348.7
C4	25	25	25	25	25	C4	398.1	399.4	398.5	389.2	388.9
C5	25	35	25	25	25	C5	386.2	391.7	396.1	366.4	364.2
C6	14	17	17	-	-	C6	358.6	379.1	379.1	-	-

Table 3.8 Comparison of CAPEX and OPEX for the Base and Multimode FGN

Multimode FGN		Base FGN	
	Capital Cost ($)		
Pipelines	80311.81	Pipelines	91724.58
Valves	27764.81	Valves	31984.43
CAPEX	108075.84	CAPEX	123709.01
	Operating Cost ($/yr) for Mode 1		
Cost of fuel	290682.20	Cost of fuel	301022.40
Sink operations	878.05	Sink operations	1142.40
Valve cost	15.09	Valve cost	14.40
Piping cost	1899.60	Piping cost	1910.40
Hydrocarbon penalty	0.00	Hydrocarbon penalty	0.00
OPEX	293472.81	OPEX	304089.60
	Operating Cost ($/yr) for Mode 2		
Cost of fuel	48553.76	Cost of fuel	48556.00
Sink operations	599.89	Sink operations	512.80
Valve cost	3.34	Valve cost	3.20
Piping cost	352.71	Piping cost	352.80
Hydrocarbon penalty	137021.84	Hydrocarbon penalty	136959.20
OPEX	186441.54	OPEX	186384.00
	Operating Cost ($/yr) for Mode 3		
Cost of fuel	97535.83	Cost of fuel	97536.00
Sink operations	211.36	Sink operations	211.20
Valve cost	4.85	Valve cost	4.80
Piping cost	625.14	Piping cost	625.60
Hydrocarbon penalty	0.00	Hydrocarbon penalty	0.00
OPEX	98377.19	OPEX	98377.60
	Operating Cost ($/yr) for Mode 4		
Cost of fuel	64415.99	Cost of fuel	64416.00
Sink operations	0.00	Sink operations	0.00
Valve cost	1.18	Valve cost	1.20
Piping cost	132.33	Piping cost	132.40
Hydrocarbon penalty	0.00	Hydrocarbon penalty	0.00
OPEX	64549.50	OPEX	64549.60
	Operating Cost ($/yr) for Mode 5		
Cost of fuel	30721.90	Cost of fuel	30722.00
Sink operations	0.00	Sink operations	0.00
Valve cost	0.88	Valve cost	0.80
Piping cost	138.80	Piping cost	138.80
Hydrocarbon penalty	0.00	Hydrocarbon penalty	0.00
OPEX	30861.58	OPEX	30861.60
	Total Annualized Cost ($/yr)		
TAC	684510.21	TAC	686015.70

the various operating variables for all modes for both multimode and base FGN respectively.

Deriving the base FGN as outlined earlier gives TAC = \$686,015.70, CAPEX = \$123,709.01 and OPEX = \$673,644.80 /yr. Table 3.5 compares the various costs for the multimode and base FGN. The multimode FGN has 12.6% lower CAPEX than the base FGN, but nearly the same OPEX for all modes. Thus, the multimode FGN gives operational flexibility at reduced capital cost.

3.4.2 Impact of Integration

For this study also, we assume that the refinery does not use S7 at all, and C5 is a fixed sink. Now, the goal of FGN is to mix the available source streams in the best possible manner to meet the demands of the sinks with the least TAC. In the absence of FGN, the refinery may use some source streams in an ad hoc manner to minimize flaring. Since the actual usage patterns may vary considerably, we assume arbitrary policies for the sake of establishing some bases for comparison.

In the worst case, the refinery may flare all waste streams (S1, S2, S3, and S6). This amounts to flaring 5576 MMscf/yr with a flare operating cost of \$27,880/yr and hydrocarbon penalty of \$9,029,540.2 /yr. In contrast, the multi-mode FGN flares only \$320.8 MMscf/yr with a flaring cost of \$1600/yr and hydrocarbon penalty of \$137,024/yr. Thus, the proposed FGN reduces flaring by 94.2% and hydrocarbon penalty by 98.48%.

On a standalone basis, the refinery may flare S6 completely due to its lean nature. In that case, the refinery flares 664 MMscf/yr of gas with a flaring cost of \$3320 /yr and hydrocarbon penalty of \$88,3771.2 /yr. Our multi-mode FGN, in contrast, flares 219.2 MMscf/yr and no hydrocarbon penalty is incurred by flaring this

Table 3.9 Impacts of various factors on the performance of refinery FGN

Factor	TAC ($/yr)	CAPEX ($)	OPEX ($/yr)	Hydrocarbon Penalty ($/yr)	Flare Amount (MMscf/yr)
No FGN	-	-	-	9029540	5576.0
Integration with FGN	684510	108076	673704	137024	320.8
Fuel Quality	736772	109475	725824	125240	273.6
Flexible sink	652631	103350	642296	131592	303.0
Fuel Quality + Flexible sink	704625	105287	694096	119816	255.2

stream, thus reducing both flaring and hydrocarbon penalty by 67% and 100% respectively.

The above cases illustrate the impact on flaring of integration with FGN. The reductions are significant from the environmental perspective. However, the economics associated with flaring do not seem significant incentive in the absence of heavy regulatory penalties. To further highlight the opportunities to minimize flaring in a refinery, we now investigate some more cases.

3.4.3 Impact of Fuel Quality

The FGN needs an external fuel (lean natural gas, S5) in addition to S4, which is an FFP. This is because of the presence of quality specs for sinks such as methane content and methane number. We now introduce a richer external fuel into the FGN and assess its impact. This rich external fuel (S7) has lower methane content in comparison to the lean external fuel, but has a higher heating value and heat capacity due to the presence of other higher hydrocarbons such as ethane and propane. Hence, we replace the standard refinery fuel (S5) by a richer fuel (rich natural gas, S7). We limit its usage to 5 MMscf/h at 320 K and 50 psia. For the sake of comparison, we consider all sinks to be fixed. The TAC increases to $736,771.47 (7.1% increase) compared to the FGN using the S5. The flared amount reduces by 14.7% to 273.6 MMscf /yr compared to 320.8 MMscf /yr for the multimode FGN. The hydrocarbon penalty reduces from $137,024 /yr to $125,240 /yr (8.6%). Thus, the use of a richer fuel may offer some environmental advantages depending on the operating constraints of the FGN.

3.4.4 Impact of Flexible Sinks

The use of waste/purge gases is limited by the fuel needs of the refinery. Flexible sinks with some boost from an external fuel can enable the refinery to utilize more of such gases. To demonstrate this, we now make C5 (boiler) flexible. The additional fuel into C5 can now generate electricity. Solving for the new FGN, we get TAC = \$652,631.04, which is about 4.7% lower than the multimode FGN. The flared amount reduces by 5.5% and the hydrocarbon penalty by 4.0%. This indicates that the FGN is able to use more of the waste/purge gases.

3.4.5 Impact of Fuel Quality and Flexible Sinks

Now, in the above case with flexible sink, we allow the use of the richer standard fuel (S7). The TAC of the FGN increases marginally (by 2.8%) from the base case to \$704,624.68. However, the flaring and hydrocarbon penalty decrease substantially. The former reduced by 20.5%, while the latter by 12.6%. This further affirms that the use of richer fuel enables better utilization of waste/purge gases and reduces flaring. Table 4.6 summarizes the impact of all these various factors on the performance of refinery fuel gas system comparing the TAC, CAPEX, OPEX, hydrocarbon penalty and flared amount.

3.5 Conclusion

A two-stage stochastic programming model was developed for the design and operation of an FGN with minimum total annualized cost to address multiple modes or periods of plant operation. In contrast to the single-mode model of Hasan et al.[12], this model treats sources and sinks in a more unified manner, includes penalty for hydrocarbon flaring, and simplifies the model equations. The proposed model is expected to yield designs that are robust for dynamic plant operation. A refinery case study was also shown to show that a multi-mode FGN may not impact operating costs much, but can reduce capital costs. Integrating plant flares and FGN, flexible fuel gas sinks, and richer fuel gases can improve waste gas utilization substantially, thus reducing flaring and hydrocarbon penalty.

4 GLOBAL OPTIMIZATION OF HYDROGEN NETWORKS

4.1 Introduction

Hydrogen management/distribution is one of the critical issues in the refinery owing to the stringent legislative measures, environmental regulations and high price of hydrogen gas. The driving force for the hydrogen distribution within the refinery is the demand in the hydrogen processing unit in the form of flow and purity. Thus, there is movement of hydrogen gas across the different entities in the hydrogen network namely the hydrogen source, processing unit, purification unit and the fuel gas sinks. Since the hydrogen network is gas network, apart from the flow and purity, the hydrogen consumers must receive the same in appropriate pressure conditions as well. Hence apart from the usual entities of hydrogen network namely hydrogen source, processing unit, purification unit and fuel gas sink, there is also a need to include compressors into the hydrogen network to ensure pressure requirements are satisfied. This requires optimization of hydrogen network because complex interactions could occur among different nodes (hydrogen source, processing unit, purification unit, fuel gas sinks and compressor) within the network. This forms the need for refinery hydrogen network optimization problem.

This chapter addresses the design and operation of hydrogen networks present in a refinery. The approach in this paper is a mathematical superstructure optimization which seeks to minimize the total annualized cost of the entire system. This problem is formulated as a nonconvex Mixed Integer Nonlinear Program (MINLP). This nonconvex network optimization MINLP problem formulation results in the existence of multiple locally optimal solutions. Consequently there is a need to solve such problems to global optimality using some global optimization approaches. The nonconvexity, in this formulation, is attributed to the bilinear terms present in the component balance equations of some of the units/entities involved in the hydrogen network. We use the piecewise linear relaxation approach for relaxing the bilinear terms occurring in the model and utilize this concept within the framework of specialized Outer Approximation (SOA) algorithm to globally solve the problem to a specified optimality tolerance.

This chapter is organized as follows. Firstly, the problem statement of the refinery hydrogen network problem is discussed clearly in section 4.2. In section 4.3, we revisit the hydrogen network model of Elkamel et al.[60] and generalize the same and present a mathematical model for the refinery hydrogen networks. We then compare our model with the work of Elkamel et al.[60] In section 4.4, the convex relaxation of the bilinear term arising in the model is explained. In section 4.5, there is the description of the global optimization algorithm to solve the problem to specified optimality tolerance. Examples for demonstrating the model effectiveness and proposed algorithm are given in section 4.6, followed by computational results in section 4.7. Then we move to section 4.8, which describes the modeling and optimization of multi-refinery hydrogen networks. Finally the conclusions are presented in section 4.9.

4.2 Problem Statement

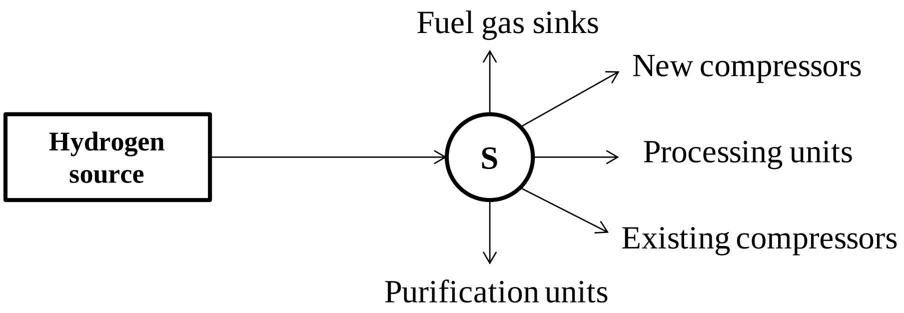
A typical refinery hydrogen network consists of hydrogen sources $i \in I$, processing units $u \in U$, existing compressors $k \in K$, new compressors $n \in N$, purification units $m \in M$ and fuel gas sinks $j \in J$. The model formulation is suitable to the type of network which requires retrofit either to improve an existing network or to retrofit any new equipment into the already existing network. A hydrogen source $i \in I$ is the supplier of the hydrogen gas into the entire network. The refinery may have different ways of producing hydrogen gas. It can produce hydrogen by having an in-house hydrogen plant which uses reforming methods like steam methane reforming or steam naphtha reforming or it can produce hydrogen gas by other methods such as partial oxidation of methane or it can procure hydrogen gas in the form of an external import as merchant hydrogen. Alternatively, a refinery may also have units such as Catalytic Reformer Unit (CRU) which produces hydrogen gas as its byproduct. Each of these sources has known flow, purity and pressure. The source is modeled as having the hydrogen generation unit followed by a splitter.

A processing unit $u \in U$, in a hydrogen network, is one which uses hydrogen to carry out its operation. It is modeled as a rector-separator combination preceeded by a mixer and succeeded by a splitter. The mixer mixes the different feeds into one single stream which is sent to the reactor. The reactor utilizes the hydrogen stream to carry out complex chemical reactions giving out various products and byproducts. This gas stream is then sent to a separator (assuming 100% recovery) which separates the useful product from the off-gases. This off gas, which may be rich in hydrogen, is directed to a product splitter which splits the stream into different streams. The mixer receives feed from the hydrogen sources, existing compressors, new compressors, purification units, other processing units and as a recycle stream from the same processing unit. The product splitter sends its streams to the other processing unit, as a recycle stream, to the existing compressor, to the new compressor, the purification unit and the fuel gas sinks. The most common processing units in a refinery are hydrotreater, hydrocracker, isomerization unit and olefin saturation unit. The processing units have known inlet and outlet flows and pressures followed by known lower (upper) bound on their inlet (outlet) purity.

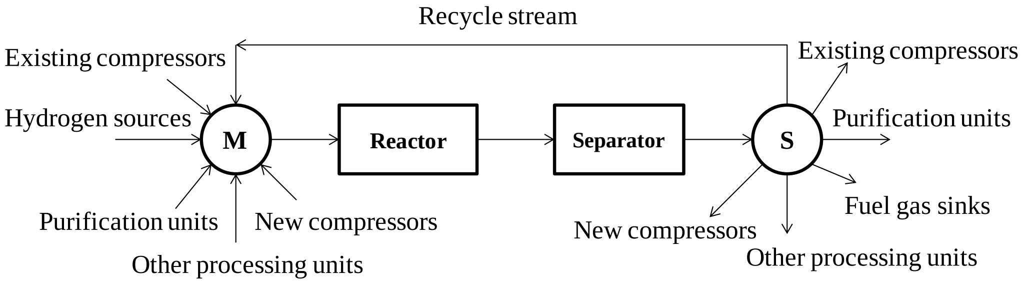
An existing compressor $k \in K$ represents the compressors which are already present in a existing refinery hydrogen network. The design pressures (both inlet and outlet pressures) and the capacity of these compressors is known already. Each compressor consists of a feed mixer which mixes the different inlet streams to the compressor. This is then sent as a single feed to the compressor unit, which compresses the gas stream to a higher pressure. The stream coming out of the compression unit is sent to a splitter which splits the outlet stream. The inlet to the existing compressor could be from the hydrogen sources, the processing units, new compressors and purification units. The outlet stream from the existing compressors goes to the processing units, new compressors, purification units and the fuel gas sinks.

The new compressor $n \in N$ is usually retrofitted into the existing refinery hydrogen network. The design pressures are known for these compressors may be known or not known, but only an upper bound on their maximum capacity is known. Similar to the existing compressors, the new compressor also has a feed mixer, compression unit and product splitter. The inlet to the new compressor could be from the hydrogen sources, the processing units, existing compressor and the purification units. The outlet stream from the new compressors goes to the processing units, existing compressors, purification units and the fuel gas sinks.

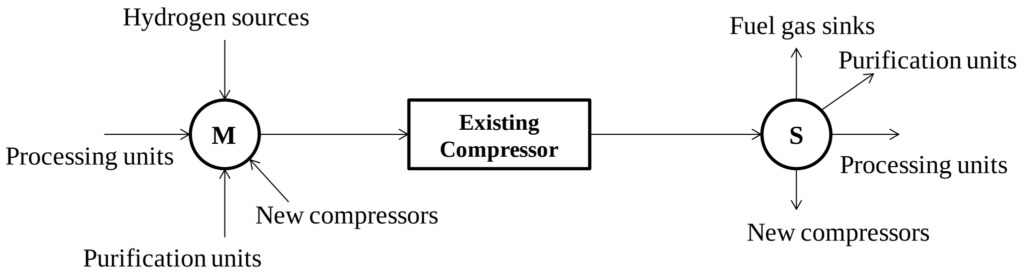
A purification unit $m \in M$ in the refinery hydrogen network purifies or upgrades a stream with low hydrogen content to a higher purity. In this model formulation, they are usually retrofitted into the existing refinery network. As we did for the processing units, we model each purification unit to comprise four units, namely feed mixer, purifier, product splitter, and residue splitter. The feed mixer combines the low-purity


Fuel gas sinks
New compressors
Hydrogen source
S
Processing units
Existing compressors
Purification units

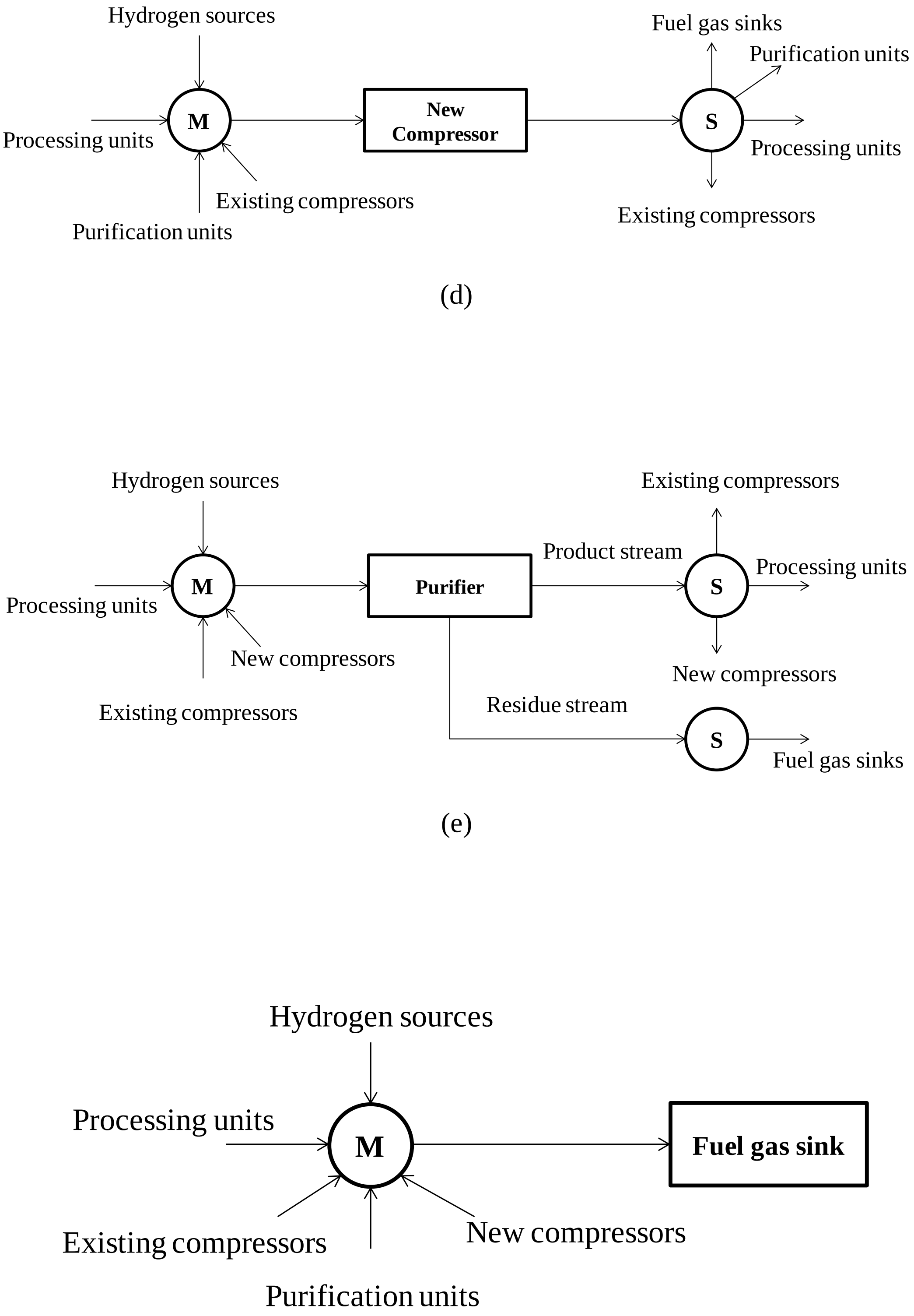
(a)


Recycle stream
Existing compressors
Hydrogen sources
M
Reactor
Separator
S
Existing compressors
Purification units
Purification units
New compressors
Other processing units
New compressors
Fuel gas sinks
Other processing units

(b)


Hydrogen sources
Processing units
M
Existing Compressor
S
New compressors
Purification units
Fuel gas sinks
Purification units
Processing units
New compressors

(c)



(d)

(e)

(f)

Figure 4.1 Schematic diagram of various units in hydrogen networks (a) Hydrogen sources (b) Processing units (c) Existing compressors (d) New compressors (e) Purification units (f) Fuel gas sinks

streams from various entities of the hydrogen network. These inputs can be from various hydrogen sources, processing units, existing compressor and new compressors. This is sent as a single stream feed to the purifier unit. The purifier separates this single feed into two outlet streams called the product stream and the residue stream. The product stream which is rich in pure hydrogen goes to the product splitter, which then splits the stream to the different units of network such as processing unit, exist compressors, and new compressors. The residue stream which has a low hydrogen purity goes to the residue splitter which then goes to the fuel gas sinks. The pressures of the inlet and the two outlet streams are known to vary over a known range. A constant recovery and product purity are assumed.

The fuel gas sink $j \in J$ in any refinery serves to receive waste/impure/purge gases generated within the refinery so that it can be used to supplement the refinery fuel system. In the hydrogen network, it serves to receive the unutilized gas streams generated in the network. We model each sink to have a mixer followed by a consumer. The mixer receives inputs from various hydrogen sources, processing units, purification units (residue stream only), existing compressors and new compressors. This combined feed stream is then sent to the fuel gas consumer. The fuel gas sinks have known pressure and have large bound on the flow. There is no purity requirement at the fuel gas sinks. The examples of fuel gas sinks are turbines, boilers, furnaces, incinerators and flares. However, in this work we consider fuel gas sinks to be only a single entity which serve to receive unutilized gas within the network. After understanding the various units of hydrogen network from our perspective, we now proceed to the problem statement. Figure 4.1 shows the schematic of various units in a hydrogen network with their possible connections where units M and S stand for mixer and splitter respectively.

The hydrogen network synthesis problem in a typical refinery can be stated as follows.

Given:

1. Hydrogen sources $i \in I$ with known flows, pressures, and purities.
2. Processing units $u \in U$ with known inlet flows, pressures and known range of inlet purity. The outlet stream has known flow, pressure and purity.
3. Existing compressors $k \in K$ which have known inlet and outlet pressures and has a known capacity.
4. New compressors $n \in N$ which can possibly be retrofitted into the network. Unlike the existing compressor, these have known bound on capacity and assume that the inlet and outlet pressures are known.
5. Purifiers $m \in M$ which can be retrofitted into the existing network. The feed stream to the purification unit has a known range of pressure, flow and capacity. The product stream from the purification unit has a constant recovery and constant product purity, whereas the residue streams have a large upper bound on purity. Similar to the feed, the product and residue streams may have an upper bound on their flow.
6. Fuel gas sinks $j \in J$ with known pressures and large upper bound on flow and purity.
7. CAPEX data for all units to be retrofitted such as purification unit, new compressor and pipeline.
8. OPEX for hydrogen consumption and compression operation.

Determine:

1. Amount of hydrogen required by the overall refinery.

2. Optimal network topology of hydrogen network with flows, purities and pressures of the units in network.
3. Existence of equipments such as purification units and new compressors along with the duties and capacities.

Aiming to minimize the total annualized cost (TAC) of the hydrogen network

We include two components in TAC. The first is the annualized capital expenditure (CAPEX) of the entire network, which includes the capital costs of all the retrofitted equipments such as new compressor, purification unit and new pipelines. The second is the operating expenditure (OPEX), which consists of the cost of hydrogen consumed, operating/electricity costs of the compression process involved in the network (both new and existing compressors) and the costs/savings due to the use of hydrogen in the fuel gas sinks.

Assuming:

1. The network optimization here is based on material balance; hence the gas flowrate considered here is standard volumetric flowrate. The standard conditions assumed are 60^0 F and 14.7 psia.
2. No phase change or chemical reaction occurs within the network flow.
3. Uncertainties may arise in terms of gas flowrate and purity in the real cases, but such uncertainties are neglected and constant availability, supply and demand is assumed.
4. The recycle compressor handles only the recycle stream from the processing units and this cannot be moved to other units. Thus, the compression cost for the recycle compressor is not considered in the model formulation.
5. Adiabatic compression is employed in the compressor.
6. The pressure drops are assumed to be zero in the pipelines.

7. All network streams are gaseous binary mixtures of hydrogen and inerts. The inert represents the generalized term for other hydrocarbons which are present along with hydrogen such as methane, ethane etc.

4.3 Model Formulation

We adopt the superstructure of hydrogen network from Elkamel et al.[60] The model here is formulated based on total gas flow. Alternatively, it can also be modeled based on component flowrate. The nonlinearity in the model is caused by the bilinear terms in the component balance equations. These bilinear terms, which is the product of total gas flow and purity, arises due to the mass balance equations for the units in which mixing take place. The complication in the form of bilinearity induces nonconvexity in the model resulting in multiple optimum solutions. The discrete nature of the model is represented by existence of new equipment, existence of pressure difference between the sources and sinks enabling prospective flow between them and existence of piping flow connections. Hence, the refinery hydrogen model is formulated as a nonconvex mixed integer nonlinear program (MINLP).

4.3.1 Balance Equations

We start the balance equations for the hydrogen source streams $i \in I$ and define the following variables and parameters.

Fij_{ij} : Flow from source i to fuel gas sink j

Fik_{ik} : Flow from source i to existing compressor k

Fin_{in} : Flow from source i to existing compressor n

Fiu_{iu} : Flow from source i to processing unit u

Fim_{im} : Flow from source i to purification unit m

$yout_i$: Purity out of the source i

Let $Fout_i$ denote the flow out of the source i, then the mass balance equations for this is given by Eq. (4.1).

$$Fout_i = \sum_j Fij_{ij} + \sum_k Fik_{ik} + \sum_u Fiu_{iu} + \sum_m Fim_{im} + \sum_n Fin_{in} \tag{4.1}$$

Next, we consider the modeling equations for the existing and new compressors. The variables and parameters describing the existing and new compressors are as follows.

Fkj_{kj} : Flow from existing compressor k to fuel gas sink j

Fku_{ku} : Flow from existing compressor k to hydroprocessing unit u

Fkm_{km} : Flow from existing compressor k to purification unit m

Fkn_{kn} : Flow from existing compressor k to new compressor n

$ycomp_k$: Purity of hydrogen gas at compressor k

Fnj_{nnj} : Flow from new compressor n to fuel gas sink j

Fnu_{nu} : Flow from new compressor n to hydroprocessing unit u

Fnm_{nm} : Flow from new compressor n to purification unit m

Fnk_{nk} : Flow from new compressor n to exist compressor k

yNC_n : Purity of hydrogen gas at new compressor n

Fuk_{uk} : Flow from processing unit u to exist compressor k

Fmk_{mk} : Flow of product stream from purification unit m to compressor k

Fun_{un} : Flow from processing unit u to new compressor n

Fmn_{mn} : Flow from product stream of purification unit m to new compressor n

$yPPSA_m$: Purity of the hydrogen rich product stream out of purification unit m

$yout_u$: Purity out of processing unit u

The amount of gas entering the compressor must be equal to the amount of gas leaving. The purity of hydrogen gas entering must also be equal to the purity of gas leaving. The material and component balance equation for the existing compressor k is given by Eq. (4.2) and Eq. (4.3). The flow into each of these compressors should not exceed the compressor capacity. This is ensured by Eq. (4.4). The power of the compressor k is given by Eq. (4.5) where $Pout_k$ and Pin_k stands for inlet and outlet pressures respectively. In case of retrofit design problems, these compressors are already operational and present in the network and hence their design pressures and their capacities are known. The other parameters in Eq. (4.5) are explained as follows. Cp stands for heat capacity at constant pressure, T stands for temperature, γ is the ratio of heat capacity at constant pressure to heat capacity at constant volume, η is the compressor efficiency and $Fmax_k$ is the compressor capacity.

$$\sum_i Fik_{ik} + \sum_u Fuk_{uk} + \sum_m Fmk_{mk} + \sum_n Fnk_{nk} = \sum_j Fkj_{kj} + \sum_u Fku_{ku} + \sum_n Fkn_{kn} + \sum_m Fkm_{km} \tag{4.2}$$

$$\sum_i Fik_{ik}\, yout_i + \sum_u Fuk_{uk} yout_u + \sum_m Fmk_{mk} yPPSA_m + \sum_n Fnk_{nk}\, yNC_n = ycomp_k(\sum_j Fkj_{kj} + \sum_u Fku_{ku} + \sum_m Fkm_{km} \sum_n Fkn_{kn}) \tag{4.3}$$

$$(\sum_i Fik_{ik} + \sum_u Fuk_{uk} + \sum_m Fmk_{mk} + \sum_n Fnk_{nk}) \leq Fmax_k \tag{4.4}$$

$$Pwr_k = \frac{CpT}{\eta}\left(\left(\frac{Pout_k}{Pin_k}\right)^{\frac{\gamma-1}{\gamma}} - 1\right)(\sum_i Fik_{ik} + \sum_u Fuk_{uk} + \sum_m Fmk_{mk} \sum_n Fnk_{nk}) \tag{4.5}$$

The new compressors, which can be retrofitted into the existing network system, also has material and component balance equations similar to that of the existing compressors given by Eq. (4.6) and Eq. (4.7). The power of the new compressor is given by the Eq. (4.9) where $PONC_n$ and $PINC_n$ is the inlet and outlet pressures from the new compressor. It is assumed in this model formulation that the design pressures of the new compressors are known a priori. Introducing these design pressures as variables (unknown design pressures) could make the network optimization problem highly nonlinear and nonconvex because of the posynomial terms present in the new compressor power equation. The combination of bilinear and posynomial terms could result in a high degree of nonconvexity. Hence in the interest of solving this problem to global optimality, we restrict the nonlinearity to be only from bilinear terms and make an assumption that the design pressures are known before hand thereby eliminating the nonconvexity due to posynomial terms. The capacity constraint on the new compressor is given by Eq. (4.8). The variable FNC_n will have a known upper bound on the compressor capacity indicating that the maximum possible compressor capacity which can be retrofitted into the network. Thus the capacity of the new compressor is now an optimization (decision) variable unlike the case of existing compressor for which capacity of the compressor was known before hand. This is the first difference between the modeling equations of the existing and new compressors. Eq. (4.10) and Eq. (4.11) give the constraints which depicts the existence of the new compressor by the binary decision variable. Second difference between the existing and new compressors is that for the latter both the capital and operating cost are involved whereas for the former only operational cost is involved.

$$\begin{aligned}\sum_i Fin_{in} + \sum_u Fun_{un} + \sum_m Fmn_{mn} + \sum_k Fkn_{kn} &= \sum_j Fnj_{nj} + \sum_u Fnu_{nu} \\ &\quad + \sum_n Fnm_{nm} + \sum_m Fnk_{nk} \qquad (4.6)\end{aligned}$$

$$\begin{aligned}&\sum_i Fin_{in}\, yout_i + \sum_u Fun_{un} yout_u + \sum_m Fmn_{mn} yPPSA_m + \sum_k Fkn_{kn}\, ycomp_k \\ &\qquad = yNC_n\left(\sum_j Fnj_{nj} + \sum_u Fnu_{nu} + \sum_m Fnm_{nm} \sum_k Fnk_{nk}\right) \qquad (4.7)\end{aligned}$$

$$\left(\sum_i Fin_{in} + \sum_u Fun_{un} + \sum_m Fmn_{mn} + \sum_k Fkn_{kn}\right) \le FNC_n \qquad (4.8)$$

$$PwrNC_n = \frac{CpT}{\eta}\left(\left(\frac{PONC_n}{PINC_n}\right)^{\frac{\gamma-1}{\gamma}} - 1\right)\left(\sum_i Fin_{in} + \sum_u Fun_{un} + \sum_m Fmn_{mn} + \sum_k Fkn_{kn}\right)$$

$$(4.9)$$

$$PwrNC_n - XNC_n UPwr \le 0 \qquad (4.10)$$

$$PwrNC_n - XNC_n LPwr \ge 0 \qquad (4.11)$$

The processing units are the key entities of the refinery hydrogen network. The variables and parameters describing the same are given as follows.

$Finu_u$: Inlet flow into the processing unit u

$Fout_u$: Outlet flow into the processing unit u

$yinu_u$: Inlet purity into the processing unit u

Fuj_{uj} : Flow from processing unit u to fuel gas sink j

Fum_{um} : Flow from processing unit u to purification unit m

Eq. (4.12) and Eq. (4.13) give the required material and component balance equations for the inlet to the processing units. The processing units also give off gas whose material balance is given in Eq. (4.14). The problem under study is a retrofit of an existing refinery network, so the processing unit flow demands are usually known and hence the variables $Finu_u$ and $Fout_u$ are fixed to these values. The inlet purity demand of a processing unit $yinu_u$ is generally within a known range. Since it may not represent a cost efficient operation to have more pure hydrogen into the processing unit than what is required, these variables are fixed to their lower bounds. Even in the case of outlet purity from the processing unit $youtu_u$, for optimization of the process networks the trend is to normally have highest purity available from the processing unit so that it could be reused within the network. Hence the purity of the stream from the outlet of the processing units is fixed at their upper bounds. The assumptions made above represent no loss of generality and hence can be used in model.

$$Finu_u = \sum_i Fiu_{iu} + \sum_k Fku_{ku} + \sum_m Fmu_{mu} + \sum_n Fnu_{nu} + \sum_{u'} Fuu_{uu'} \qquad (4.12)$$

$$Finu_u yinu_u = \sum_i Fiu_{iu} yout_i + \sum_k Fku_{ku}\, ycomp_k + \sum_n Fnu_{nu}\, yNC_n$$
$$+ \sum_m Fmu_{mu} yPPSA_m + \sum_{u'} Fuu_{uu'}\, yout_u \qquad (4.13)$$

$$Fout_u = \sum_j Fuj_{uj} + \sum_k Fuk_{uk} + \sum_m Fum_{um} + \sum_n Fun_{un} + \sum_{u'} Fuu_{uu'} \qquad (4.14)$$

The variables and parameters describing the purification units are as follows.

Fmu_{mu} : Flow from purification unit m to processing unit u

Fmk_{mk} : Flow from purification unit m to existing compressor k

Fmn_{mn} : Flow from purification unit m to new compressor n

$Frmj_{mj}$: Flow of residue stream from purification unit m to fuel gas sink j

$yRPSA_m$: Purity of the residue stream out of purification unit m

$Rcvr$: Recovery of the purification unit m

The material and component balance constraints for the purification units are given by Eq. (4.15) and Eq. (4.16). Similar to the new compressor, the capacity of the purification unit to be retrofitted is unknown. The constraint for this condition is given in Eq. (4.17) where the variable FPR_m gives the capacity of the purification unit. The binary variable for the existence of the purification unit is activated by flow connections shown in Eq. (4.18) and Eq. (4.19). Since the recovery $Rcvr$ of the purification unit is known beforehand, the component balance equations given in terms of the purification unit recovery are shown in Eq. (4.20) and Eq. (4.21).

$$\sum_i Fim_{im} + \sum_k Fkm_{km} + \sum_u Fum_{um} + \sum_n Fnm_{nm} = \sum_k Fmk_{mk} + \sum_u Fmu_{mu} + \sum_n Fmn_{mn} + \sum_j Frmj_{mj} \qquad (4.15)$$

$$\sum_i Fim_{im} yout_i + \sum_k Fkm_{km} ycomp_k + \sum_u Fum_{um} yout_u + \sum_n Fnm_{nm}\, yNC_n = yPPSA_m\left(\sum_k Fmk_{mk} + \sum_u Fmu_{mu} + \sum_n Fmn_{mn}\right) + yRPSA_m \sum_j Frmj_{mj} \qquad (4.16)$$

$$\left(\sum_i Fim_{im} + \sum_k Fkm_{km} + \sum_u Fum_{um} + \sum_n Fnm_{nm}\right) \leq FPR_m \qquad (4.17)$$

$$\left(\sum_i Fim_{im} + \sum_k Fkm_{km} + \sum_u Fum_{um} + \sum_n Fnm_{nm}\right) - XPSA_m UF \leq 0 \qquad (4.18)$$

$$\left(\sum_i Fim_{im} + \sum_k Fkm_{km} + \sum_u Fum_{um} + \sum_n Fnm_{nm}\right) - XPSA_m LF \geq 0 \qquad (4.19)$$

$$Rcvr\left(\sum_i Fim_{im} yout_i + \sum_k Fkm_{km} ycomp_k + \sum_u Fum_{um} yout_u + \sum_n Fnm_{nm}\, yNC_n\right) = yPPSA_m\left(\sum_k Fmk_{mk} + \sum_u Fmu_{mu} + \sum_n Fmn_{nm}\right) \qquad (4.20)$$

$$(1 - Rcvr)\left(\sum_i Fim_{im} yout_i + \sum_k Fkm_{km} ycomp_k + \sum_u Fum_{um} yout_u\right.$$

$$+\sum_n Fnm_{nm}\, yNC_n) = yRPSA_m \sum_j Frmj_{mj} \qquad (4.21)$$

Fuel gas sinks are the units in a refinery which receive the waste/purge/impure and unutilized gases generated. These are used to supplement the refinery fuel gas in managing the energy demands of the refinery. $Finj_j$ be the flow of gas going to the refinery fuel gas unit and $yinj_j$ be the purity of gas to the fuel gas, then the material and component balance is given by Eq. (4.22) and Eq. (4.23) respectively. We do not place any restrictions on the flow and purity of the gas entering the fuel gas system and hence the variable $Finj_j$ and $yinj_j$ are associated with ususally a large upper bound.

$$Finj_j = \sum_i Fij_{ij} + \sum_k Fkj_{kj} + \sum_u Fuj_{uj} + \sum_n Fnj_{nj} + \sum_m Frmj_{mj} \qquad (4.22)$$

$$Finj_j yinj_j = \sum_i Fij_{ij}\, yout_i + \sum_k Fkj_{kj}\, ycomp_k + \sum_u Fuj_{uj}\, youtu_u$$

$$+\sum_n Fnm_{nm}\, yNC_n + \sum_m Frmj_{mj} yRPSA_m \qquad (4.23)$$

4.3.2 Flow Connections to/from the Units

To understand the flow connection to/from the units it is first necessary to know a about generalized origin and destination units. By general origin unit, we mean any unit which produces hydrogen stream as its product. Similarly a general destination unit is one which consumes hydrogen as its feed. Going by this generalized consideration, hydrogen sources (fuel gas sink) form a general origin (destination) unit. The processing unit can act as both origin and destination units, whereas purification unit acts as single destination and two origin units (product and residue streams). The existing and new compressors, also similar to the processing unit, act as both origin and destination units. Consider a general origin unit $p \in P$ and a general destination unit $q \in Q$. Also let $P_{new} (p \in P_{new} \subset P)$ represent a set of generalized origin which is the new equipment to be retrofitted into the system and Q_{new} $(q \in$

$Q_{new} \subset Q$) is a set which consists of generalized destination unit which could be the new equipment retrofitted into the system.The following equations are used to establish connections to and from all units in the network. These equations are generic in that they can be used for all the source sink combinations. The variables and parameters describing this section are given as follows.

P_p: Pressure of origin p

P_q: Pressure of destination q

UP: Parameter for upper bound on pressure difference between origin and destination

LP: Parameter for lower bound on pressure difference between origin and destination

UF: Parameter for upper bound on the flow between origin and destination

LF: Parameter for lower bound on the flow difference between origin and destination

The two levels of binary decision variables involved are first to determine whether there exist a pressure difference between a source and sink and second is to see a flow exist between the general origin and destination combination. The definitions of these variables are given as follows.

$$X_{pq} = \begin{cases} 1 & if\ pressure\ difference\ exists\ between\ origin\ p\ and\ destination\ q \\ 0 & otherwise \end{cases}$$

$$XF_{pq} = \begin{cases} 1 & if\ flow\ exists\ between\ origin\ p\ and\ destination\ q \\ 0 & otherwise \end{cases}$$

The model equations corresponding to the flow connections to/from units are given as follows.

$$\left(P_p - P_q\right) - X_{pq}UP \le 0 \qquad \forall p, \forall q \qquad (4.24)$$

$$\left(P_p - P_q\right) - (1 - X_{pq})LP \ge 0 \qquad \forall p, \forall q \qquad (4.25)$$

$$F_{pq} - XF_{pq}UF \le 0 \qquad \forall p, \forall q \qquad (4.26)$$

$$F_{pq} - XF_{pq}LF \ge 0 \qquad \forall p, \forall q \qquad (4.27)$$

$$XF_{pq} \le X_{pq} \qquad \forall p, \forall q \qquad (4.28)$$

$$XF_{p,q} \leq X_q \qquad \forall p, \forall q \in Q_{new} \qquad (4.29)$$

$$XF_{p,q} \leq X_p \qquad \forall p \in P_{new}, \forall q \qquad (4.30)$$

The equations Eq. (4.24) –(4.25) represent that if pressure between a source and sink is greater than or equal to zero, then the binary variable X_{pq} takes the value of one. Eq. (4.25) is valid only if the parameter LP be a negative number. The equations Eq. (4.26) and (4.27) indicate the existence of flow where the binary variable XF_{pq} takes the value of one if the flow exists or else it is zero. The equation Eq. (4.28) links the pressure and flow constraints portraying that flow between a source and sink is possible only when the pressure match between them is satisfied. In addition to the above constraints, the new equipments (usually the one to be retrofitted like the new compressor and purification unit) are modeled by Eq. (4.29) and (4.30). These constraints characterize the existence of new equipments by their incoming and outgoing flows. For a general hydrogen network, to represent equations for flow connections to/from the units, requires writing all the equations for all the units depicting the connection among all the units. This may be a tedious and a cumbersome task. Thus writing the equations representing generalized origin and destination units can present the same idea in a more simple and precise way. Hence, this is the rationale for writing the generalized equations for origin and destination unit connections.

4.3.3 Bound Strengthening Cut

We also add the following redundant constraint given by Eq. (4.31). This constraint represents the overall component balance of the entire hydrogen network. The addition of this constraint tightens the relaxation by providing better lower (upper) bounds on the global optimum for a minimization problem. The usefulness of adding such redundant constraints into the process network model was mentioned in some of the literature works.[5, 100]

$$Fout_i yout_i + Foutu_u yout_u - Finu_u yinu_u - Finj_j yinj_j = 0 \tag{4.31}$$

Objective Function

The objective function of this network synthesis problem would be to minimize the total annualized cost of the network. The total annualized cost is obtained as a sum of the operating cost of the network and the capital/investment cost of the equipments. The operating cost is multiplied by the number of annual working days in a year and the investment cost is multiplied by the annualization factor AF. The total annualized cost (TAC) of the network is given by Eq. (4.32). The first two terms in Eq. (4.32) give the annualized capital cost of the equipments involved in the hydrogen network., a_{NC}, b_{NC} are cost coefficients of the new compressor to be retrofitted, a_{PSA}, b_{PSA} are capital cost coefficients for the purification unit and a_{pipe}, b_{pipe} are capital cost coefficients or the laying of pipelines. The cost of pipeline here refers to the cost of laying the new pipeline which was not present in the existing network. To represent this, we now define a set PQ which is a set of origin destination combination for piping which is not present in the existing network. The remaining terms give the operational cost of the network. The various coefficients are as follows.

OCH_i (k\$/MMscf): This is the cost of the hydrogen gas. This is positive for conventional hydrogen producers and is zero for auxiliary producers like catalytic reformer etc.

OCE (k\$/kWhr): This gives the operating cost of compressors (both new and existing compressors)

OCF (k\$/MMBtu): This is basically the cost associated with the fuel value of the gas going to the refinery fuel gas system which can potentially produce surplus energy.

LHV_{H_2} (MMscf/MMBtu): Lower heating value of hydrogen

OD : Operating days in a year

$$TAC = AF\left[\sum_{n}\{a_{NC}XNC_n + b_{NC}(\sum_{i} Fin_{in} + \sum_{k} Fkn_{kn} + \sum_{u} Fun_{un} + \sum_{n} Fmn_{mn})\} + \sum_{m}\{a_{PSA}XPSA_m + b_{PSA}(\sum_{i} Fim_{im} + \sum_{k} Fkm_{km} + \sum_{u} Fum_{um} + \sum_{n} Fnm_{nm})\} + \sum_{p\in PQ}\sum_{q}(a_{pipe}\, XF_{pq} + b_{pipe}F_{pq})\right] + OD\left[\sum_{i} OCH_i\, Fout_i + OCE(\sum_{k} Pwr_k + \sum_{n} PwrNC_n) + \sum_{j} OCF(Finj_j\, yinj_j LHV_{H_2})\right] \quad (4.32)$$

4.3.4 Comparison to previous work

In this section we compare our work with that of Elkamel et al.[60] and present some improvements to the model on hydrogen network.

1. Elkamel et al.[60] had modeled the flow connections from/to among the units using the constraints given by Eq. (4.33) – (4.35). This says that the flow between any origin to destination can exist if the pressure difference between them exist which is given by the binary variable XF_{pq}. This is different from what we had stated in our model equations given by Eq. (4.24) – (4.30) which had used two levels of binary decisions, one to represent the pressure difference between an origin and destination and other to represent the flow between them. We believe that by

formulating the model as shown in Eq. (4.24)-(4.30) may allow more flexibility to the model and at the same time modeling the flows by using two levels of binary decision may not represent any loss of generality. However, this may increase the number of binary variables substantially in the model.

$$(P_p - P_q) \geq UF\left(XF_{pq} - 1\right) \tag{4.33}$$

$$(P_p - P_q) \leq UF\ XF_{pq} \tag{4.34}$$

$$F_{pq} - XF_{pq}\ UF \leq 0 \tag{4.35}$$

2. We also added redundant bound strengthening cut to our model. Such cuts tremendously strengthen the otherwise weak lower bound and accelerate convergence when used with a global optimization algorithm. These cuts can also be included directly into the original MINLP model, where they substantially reduce the number of nodes and also improve the computational time when solved using a commercial global optimization solver such as BARON.
3. We reformulated the model of Elkamel et al.[60] and thereby reduced the number of bilinear terms occurring in the model by $[|K|+|U|+|M|+|N|]$ where $|K|$, $|U|$, $|M|$ and $|N|$ are the number of existing compressors, processing units, purification units new compressors to be retrofitted respectively.

   For instance, we consider the case for number of bilinear terms for existing compressor. By carefully investigating the model of Elkamel et al.[60] the number of bilinear terms involving existing compressor was given by $|K|\ |J|+|K|\ |U|+|K|\ |M|+|K|\ |N|+|K|$ terms, where $|J|$ represented number of fuel gas sinks. On the other hand, the model developed by us for existing compressors, given by Eq. (4.3), had $|K|\ |J|+|K|\ |U|+|K|\ |M|+|K|\ |N|$ bilinear terms. This represents a reduction of $|K|$ bilinear terms in the modeling equations for existing compressors. Similarly on examining the model equations for all units of hydrogen network of Elkamel et al.[60] and comparing with ours, a total reduction of $[|K|+|U|+|M|+|N|]$ bilinear terms were observed. Reduction of bilinear terms in the model formulation may not affect the global optimum, but can definitely lead to tighter relaxations and reduce the solution time when model is solved to global optimality.

4.4 Convex Relaxation of Bilinear terms

The nonconvex MINLP model represented by Eq. (4.1) – (4.32) usually requires specialized deterministic global optimization algorithms for them to be solved to global optimality. The lower bound (upper bound) for the minimization (maximization) problem on the global optimum can be obtained by solving a relaxation of the original MINLP model. Such a relaxation of the original MINLP can be obtained by replacing the nonconvex terms in the model by their convex under and over estimators.

For the bilinear terms ($z = xy$), the relaxation of this term is given by their convex and concave envelopes. The first underestimators were derived by McCormick[72] and later they were characterized as concave and convex envelope by Alkhayyal and Falk.[73] The term wise underestimation of each bilinear term is given replacing each term with an auxiliary variable z and incorporating the under and over estimator equations. The convex and concave envelopes of the bilinear term is given by Eq. (4.36) where x and y are the continuous variables and z is an auxiliary variable, x^L, $x^U$and y^L, $y^U$are the bounds on x and y respectively.

$$z \geq xy^L + x^L y - x^L y^L \tag{4.36a}$$

$$z \geq xy^U + x^U y - x^U y^U \tag{4.36b}$$

$$z \leq xy^L + x^U y - x^U y^L \tag{4.36c}$$

$$z \leq xy^U + x^L y - x^L y^U \tag{4.36d}$$

$$x^L \leq x \leq x^U \tag{4.36e}$$

$$y^L \leq y \leq y^U \tag{4.36f}$$

The concept of Reformulation Linearization Technique (RLT)[77] could also be used to develop such relaxations. This relaxation serves to add redundant constraints into the model which tightens the relaxation. The convex and concave envelopes[72] could also be derived using the Reformulation Linearization Technique (RLT). Usually the relaxation obtained by using the convex and concave envelope for the bilinear term is referred to as LP relaxation, because of the relaxation equations being linear in nature. The addition of these LP relaxation equations usually yield a weaker bound which slows down the convergence when solved in a global optimization framework such as branch and bound. The recent developments in the literature found that for a bilinear term tighter relaxations can be obtained by piecewisely relaxing each bilinear term. Such piecewise relaxations when combined in a seamless manner usually are transformed from LP relaxation to MILP relaxations needing the usage of binary variables.[85] Such a partitioning is done on the variable domains of one or both the variables involved in the bilinear term. Studies have shown that such piecewise linear relaxations for bilinear term results in a tighter bound, in comparison to the one obtained by the conventional LP relaxation. Such tight bounds tend to accelerate convergence and this reduces the solution time of the algorithm when solved using a branch and bound framework. Several piecewise relaxation schemes have been developed and investigated in literature. These relaxation schemes were based on Big M, convex hull, incremental cost, SOS1 and SOS2 formulation. Among all the studies done so far, the incremental cost formulation[85, 89] offered a reasonably tight relaxation for the bilinear terms. Recently, Hasan and Karimi[89] also showed that relaxation quality was better when the partitioning is done on the domains of both the variables. Hence in this study, we adopt a piecewise relaxation scheme based on the incremental cost formulation which involved partitioning of both the variable domains.

Both the variables x and y in a bilinear term ($z = xy$) are selected for partitioning of the variable domains $Dx = [x^L, x^U]$ and $Dy = [y^L, y^U]$ into a total of MC and NC partitions respectively. The partitioning is defined by grid points x_{mc} , $mc = 0,1,2 \ldots\ldots MC$ such that $x_0 = x^L$ and $x_{MC} = x^U$ and y_{nc} , $nc = 0,1,2 \ldots\ldots NC$ such that $y_0 = y^L$ and $y_{NC} = y^U$. The grid points are then generated in an efficient manner as shown in Eq. (4.37*a*) and (4.37*d*). The length of the interval, given by dx_{mc} and dy_{nc} for x and y respectively, are given in Eq. (4.37*c*) and (4.37*d*).

$$x_{mc} = x^L + \left(\frac{mc}{MC}\right)^{\alpha} (x^U - x^L) \qquad 0 \le mc \le MC \tag{4.37a}$$

$$y_{nc} = y^L + \left(\frac{nc}{NC}\right)^{\beta} (y^U - y^L) \qquad 0 \le nc \le NC \tag{4.37b}$$

$$dx_{mc} = \left[\left(\frac{mc}{MC}\right)^{\alpha} - \left(\frac{mc-1}{MC}\right)^{\alpha}\right] (x^U - x^L) \qquad 1 \le mc \le MC \tag{4.37c}$$

$$dy_{nc} = \left[\left(\frac{nc}{NC}\right)^{\beta} - \left(\frac{nc-1}{NC}\right)^{\beta}\right] (y^U - y^L) \qquad 1 \le nc \le NC \tag{4.37d}$$

For the incremental cost formulation[88, 89], θx_{mc} and θy_{nc} binary variables are used for modeling the partitions of the variable domain. The definition of θx_{mc} and θy_{nc} are given as follows

$$\theta x_{mc} = \begin{cases} 1 & if\ x \ge x_{mc} \\ 0 & otherwise \end{cases} \qquad 1 \le mc \le MC - 1 \tag{4.37e}$$

$$\theta y_{nc} = \begin{cases} 1 & if\ y \ge y_{mc} \\ 0 & otherwise \end{cases} \qquad 1 \le nc \le NC - 1 \tag{4.37f}$$

Using the θx_{mc} and θy_{nc} binary variables and local continuous variables Δu_{mc} and Δv_{nc}, where $0 \le \Delta u_{mc} \le 1$ and $0 \le \Delta v_{nc} \le 1$, the modeling equation governing the partitioning of both the variable domain x and y is given by Eq. (4.37*g*)-(4.37*h*).

$$x = x^L + \sum_{mc=1}^{MC} dx_{mc}\, \Delta u_{mc} \tag{4.37g}$$

$$y = y^L + \sum_{nc=1}^{NC} dy_{nc}\,\Delta v_{nc} \qquad (4.37h)$$

Where the bounds of Δu_{mc} and Δv_{nc} in terms of binary variables θx_{mc} and θy_{nc} respectively are given as follows.

$$\theta x_{mc} \le \Delta u_{mc} \le \theta x_{mc-1} \qquad \forall\, mc > 1\ \&\ mc < MC \qquad (4.37i)$$

$$\theta y_{nc} \le \Delta v_{nc} \le \theta y_{nc-1} \qquad \forall\, nc > 1\ \&\ nc < NC \qquad (4.37j)$$

$$\theta x_1 \le \Delta u_1 \le 1 \qquad \forall\, mc = 1 \qquad (4.37k)$$

$$\theta y_1 \le \Delta v_1 \le 1 \qquad \forall\, nc = 1 \qquad (4.37l)$$

$$0 \le \Delta u_{MC} \le \theta x_{MC-1} \qquad \forall\, mc = MC \qquad (4.37m)$$

$$0 \le \Delta v_{NC} \le \theta y_{NC-1} \qquad \forall\, nc = NC \qquad (4.37n)$$

A new set of continuous variables Δwx_{mc} and $\Delta \mathrm{wy}_{nc}$ are defined as follows.

$$\Delta wx_{mc} = \Delta u_{mc}(y - y^L) \qquad (4.37o)$$

$$\Delta wy_{nc} = \Delta v_{nc}(x - x^L) \qquad (4.37p)$$

$$0 \le \Delta wx_{mc} \le (y^U - y^L) \qquad \forall\, mc = 1,2 \ldots.MC \qquad (4.37q)$$

$$0 \le \Delta wy_{nc} \le (x^U - x^L) \qquad \forall\, nc = 1,2 \ldots.NC \qquad (4.37r)$$

The bilinear term $z = xy$ in case of a bivariate partitioning scheme is given as

$$z = x^L y + y^L x - x^L y^L + \sum_{mc=1}^{MC} \sum_{nc=1}^{NC} dx_{mc} dy_{nc}\,\Delta wxy_{mc,nc} \qquad (4.37s)$$

Where $\Delta wxy_{mc,nc}$ is a continuous variable having the grid points of both the variable x and y variables.

Following the approach of Gounaris et al.[86] in their incremental cost formulation 'nf6', the incremental cost formulation equations for a bivariate partitioning is given as follows.

$$\Delta wxy_{mc,nc} \ge \Delta u_{mc} + \Delta v_{nc} - 1 \qquad (4.37t)$$

$$\Delta wxy_{mc,nc} \le \Delta u_{mc} \qquad (4.37u)$$

$$\Delta wxy_{mc,nc} \le \Delta v_{nc} \qquad (4.37v)$$

In our formulation the bilinear terms occur in the component balance equation for the compressors, fuel gas sinks and in the purification unit for the residue stream. Eq. $(4.37a)$ - $(4.37v)$ is incorporated into the formulation for each bilinear term present in the model. Equal partitioning of both the variables domains were considered for the relaxation. The number of partitions imposed on both the variables are maintained to be same, by setting $c = nc = N_{part}$. Equal partitioning on the domain of both the variables was obtained by setting $\alpha = \beta = 1$ in Eq. $(4.37c)$ and Eq. $(4.37d)$.

Tight bounds can be obtained by increasing the number of partitions in the variable domain. This increasing number of partitions increases the number of binary and continuous variables demanding increased computational effort for it to be solved. But such increased computational effort can be compromised when considering stronger relaxations, tight bounds and reduced solution times to obtain the solution.

4.5 Global Optimization Algorithm

A Specialized Outer Approximation algorithm[101] was used for solving the mixed integer nonlinear program MINLP to global optimality. The steps of the algorithm are as follows.

1. The bounds on all the variables are determined by physical inspection of the network and accordingly assigned to all the variables. The original MINLP is also solved using a local solver to determine any known upper bounds.
2. The lower bound (LB) on the original MINLP is determined by solving the optimization problem obtained by using the technique as outlined in the Section 4. The lower bounding problem is obtained by incorporating Eq. $(4.37a)$ – $(4.37v)$ (outlined in section 4) into the all the bilinear terms in the original model given by Eq. (4.1)-(4.32). The bilinear terms in the original model occur in the component balance equations of the existing compressor, new compressor, residue stream

balance of the purification unit and the fuel gas sinks. This results in a convexified MILP model. Solving this convexified problem provides a bound on the global optimum of the original MINLP. It is necessary to obtain tight bounds, as these bounds reduce solution time by accelerating algorithmic convergence.

3. From the solution of the convexified lower bounding problem in the previous step, the binary variables are fixed and the continuous variables are initialized and then the resulting nonconvex nonlinear program (NLP) is solved to global optimality. The NLP model is obtained by fixing the binary variables in the original MINLP model (Eq. (4.1)-(4.32)) to the values in the previous step. The solution to this problem constitutes the upper bound (UB).
4. The solutions of the lower bounding problem and the upper bounding primal problems are compared. If the gap between the upper bound and the lower bound (relaxation gap) are within a certain specified tolerance criterion, then the algorithm is terminated. The solution to the problem is the upper bound (UB) obtained at this particular step.
5. The algorithm terminates if the desired convergence is achieved in the previous step. In other cases, an integer cut[102] is provided which selects a new combination of design integer variables and renders infeasible any previously obtained integer configuration.
6. It should be noted that when the upper bounding problem is solved, the nonconvex nonlinear problem (NLP) must be optimized using any global solver. This condition is important, because the integer cuts provided in the step 5 may cut off any part of the feasible region when the nonconvex NLP is solved using local solvers.[101]

7. Bound contraction[5, 84] as an optional step could be added into the algorithm before the step 2. This plays a critical role in contracting the bounds of all the variables involved in the problem and accelerates convergence by eliminating a part of the feasible region where the optimum does not lie. But it should be noted that the algorithm can reach convergence even in the absence of this step.
8. The algorithm could also be terminated when the integer cuts are not able to provide any further better feasible solution resulting in infeasibility of the lower bounding problems. Any infeasibility encountered when solving the lower bounding problem in step 2 for the first iteration, essentially means that the relaxation of the problem is infeasible thereby indicating that the original nonconvex MINLP is infeasible.

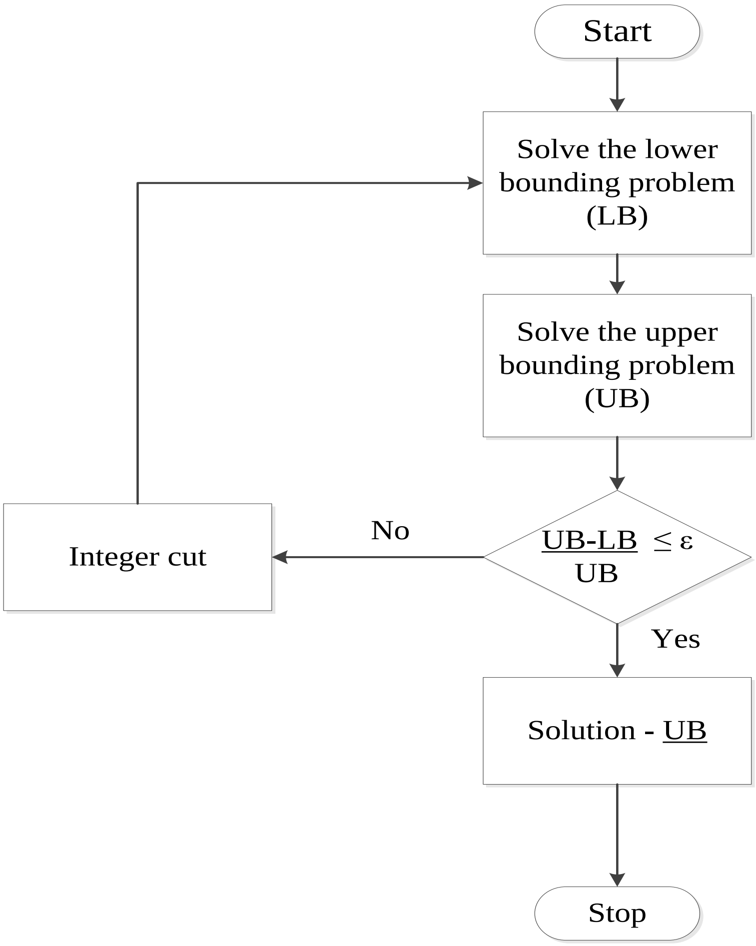


Figure 4.2 Flowchart for Specialized Outer Approximation algorithm

4.6 Examples

The proposed algorithm was used for solving the problems in the refinery hydrogen network. All the examples were modeled using GAMS[103] platform. GAMS 23.7/CPLEX was used for solving the MILP problems, whereas GAMS 23.7/BARON and GAMS 23.7/DICOPT were used for solving the MINLP problems to global optimality and local optimality respectively. GAMS 23.7/BARON was used to solve the NLP problems to global optimality. The computational time of the proposed algorithm includes the time to solve the lower bounding problem and time to solve upper bounding problem in each iteration. The computational time required by GAMS 23.7/DICOPT to solve the problem is not included in the total time taken by the algorithm. Within the algorithm, the lower bounding problem and upper bounding problems were solved by setting the optimality tolerance to zero. The algorithm was terminated when the gap between the lower bound and the upper bound was found to be within sufficient tolerance of each other. All the computations were done using a Dell Optiplex GX620 PC with Intel Pentium 4 processor having 3 GHz speed and 2GB memory running Windows XP Professional 32-bit operating system except for example 6 which, being a large example, was solved using Dell Precision T7400 Workstation with Intel Xeon processor having 3.4 GHz speed and 64 GB memory running Windows 7 Enterprise 64-bit operating system.

The model formulation assumes that the gases can move from origin to the destination only when the pressure of the origin is equal or higher than that of the destination. In case the pressure of the origin is lower than of the destination especially for the existing equipments in the refinery network, then the flow variables for that particular origin destination combination is fixed to zero to disallow such a flow. Hence, Eq. (4.24)-(4.30) is now written only for the new equipments/units which are to be retrofitted into the network. This is done to prevent the substantial increase in the number of binary variables which greatly reduces the combinatorial complexity of problem which in turn aids in reducing the solution time. The existing equipments (exist compressors and pipelines) are assumed to be having a sufficiently higher capacity than the operating value in the existing hydrogen network.

Table 4.1 Cost parameters for all examples

Operating cost	
Hydrogen cost	\$ 2000/ MMscf
Electricity cost	\$ 0.03/ kW hr
Fuel value	\$ 2.5/MMBtu
Capital cost	
Compressor	(k\$) = 115 + 1.91* power (kW)
PSA	(k\$) = 503.8 + 347.4* Feed (MMscfd)
Piping	(k\$) = 3.2 + 5* Flow (MMscfd)

For all the examples, the exist compressors are having 5% more capacity than their operating value in the existing network and each pipeline in the existing network can hold upto a maximum flow of 100 MMscfd except for example 2 for which it is upto 500 MMscfd. The cost data for the capital and operating cost for all the examples are shown in Table 4.1.[8] The purifier product purity is assumed to be 99% and recovery is assumed to be 90% for all the examples. It is assumed that the fuel gas sinks is at the lowest pressure in comparison to all the entities in the network. For all the examples in this study, the fuel gas sinks inlet pressure is 200 psia. The purity shown as parameter for all the examples represents hydrogen gas purity.

4.6.1 Example 1

Consider an existing refinery hydrogen network which consist one hydrogen source, two existing compressors (K1 and K2) along with two processing units and one refinery fuel gas sink. The processing units are hydrocracker (HT) and diesel hydrotreater (DHT). The parameters for the existing compressors are given in Table 4.2. The parameters for processing units are given in Table 4.3 and Table 4.4. The maximum availability of pure hydrogen is 80 MMscfd which is at 300 psia and 95% pure. The existing refinery hydrogen network is shown in Figure 4.3. The objective of this problem is to minimize the overall TAC (total annualized cost) of the system. The total annualized cost of this system was found to be 52,613.45 k$. From the solution we observe that there is a 3.3% reduction in the hydrogen consumption in case of the optimized refinery hydrogen network. The optimized structure is given in Figure 4.4.

4.6.2 Example 2

This example is taken from the work of Hallale and Liu[8] which has one hydrogen source, two existing compressors (K1 and K2) along with two processing units and one refinery fuel gas sink. The parameters for the existing compressors are given in Table 4.5. The parameters for processing units are given in Table 4.6 and Table 4.7. The maximum availability of pure hydrogen is 200 MMscfd which is at 300 psia and 99% pure. This is has to be now retrofitted with one new compressor to see if there is any effect on the hydrogen consumption. The objective of this example is to minimize the operational cost of the entire refinery hydrogen network system. The existing and optimized structure is given in Figure 4.5 and Figure 4.6 respectively. From the result, we find that the hydrogen consumption reduced to 182.9 MMscfd from 200 MMscfd which is similar to the solution obtained by Hallale and Liu.[8] This is because of the installation of the new compressor into the network which enables the effective utilization of hydrogen gas within the network thereby reducing hydrogen consumption.

Table 4.2 Example 1 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	42	300	2000
K2	42	300	600

Table 4.3 Example 1 - Operating conditions of processing units

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
HC	87.2	80	2000	1200
DHT	85.8	75	500	350

Table 4.4 Example 1 - Data for processing units

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
HC	40	95	10.871	43.585	83.585	54.456
DHT	40	95	15.477	34.045	74.045	49.522

Table 4.5 Example 2 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	94.5	300	1600
K2	115.5	300	2200

Table 4.6 Example 2 - Operating conditions of processing units

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
Unit 1	92.8	91	1600	1500
Unit 2	87.6	85	2200	1700

Table 4.7 Example 2 - Data for processing units

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
Unit 1	90	99	40	310	400	350
Unit 2	110	99	10	490	600	500

Table 4.8 Example 3 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	47.25	300	2000
K2	10.50	300	600

Table 4.9 Example 3 - Data for hydrogen sources

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
HP	< 50	96.5	300
CR	8.5	75.0	300

Table 4.10 Example 3 - Operating conditions of processing unit

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
HC	90.5	87.0	2000	1200
DHT	87.6	85.3	500	350
NHT	84.3	80.0	300	200

Table 4.11 Example 3 - Data for processing units

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
HC	35.0	95.0	0.650	60.050	95.050	60.700
DHT	12.2	93.2	3.614	13.070	25.270	16.684
NHT	2.8	90.0	1.425	0.950	3.750	2.375

Table 4.12 Example 4 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	42.0	300	2000
K2	42.0	300	600
K3	52.5	300	2000
K4	42.0	300	600

Table 4.13 Example 4 - Data for hydrogen sources

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
HP1	≤ 80	95	300
HP2	≤ 90	96	300

Table 4.14 Example 4 - Operating conditions of processing units

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
HC	87.2	80	2000	1200
DHT	85.8	78	500	350
NHT	90.9	85	2000	1200
RHT	87.6	78	500	350

Table 4.15 Example 4 - Data for processing units

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
HC	40	95.0	10.871	43.585	83.585	54.456
DHT	40	95.0	15.477	34.045	74.045	49.522
NHT	50	96.0	20.660	42.560	92.560	63.220
RHT	40	96.0	17.140	35.240	75.240	52.380

4.6.3 Example 3

Consider an existing refinery hydrogen network which has two hydrogen sources, two existing compressors (K1 and K2), three processing units a refinery fuel gas system. Among the two hydrogen producers one of them is the on-purpose hydrogen plant (HP) to produce pure hydrogen and other is the catalytic reforming unit (CR) also produces hydrogen as its by-product. The purity of hydrogen from the catalytic reformer source is considerably less than that of the hydrogen plant. The processing units involved in the network are hydrocracker (HC), diesel hydrotreater (DHT) and naphtha hydotreater (NHT). The existing refinery hydrogen network for this example is given in Figure 4.7.This system now has to be retrofitted with a purifier prefarably a pressure swing adsoption (PSA) unit. The parameters for the existing compressors and hydrogen sources are given in Table 4.8 and Table 4.9 respectively. The parameters for processing units are given in Table 4.10 and Table 4.11. The optimized structure resulted in a total annualized cost (TAC) of 28,840.32 k$ and the optimized network is shown in Figure 4.8.

4.6.4 Example 4

Consider an existing refinery hydrogen network which has two hydrogen sources, four existing compressors (K1-K4) along with four processing units and one refinery fuel gas sink. The processing units are hydrocracker (HC) and diesel hydrotreater (DHT), naphtha hydrotreater (NHT) and residue hydrotreater (RHT). The refinery has only one in-house hydrogen producing unit in the form of hydrogen plant (HP1), however, this is not enough to meet the refinery requirements. Hence the refinery imports some hydrogen from the neighbouring merchant hydrogen producer (HP2).

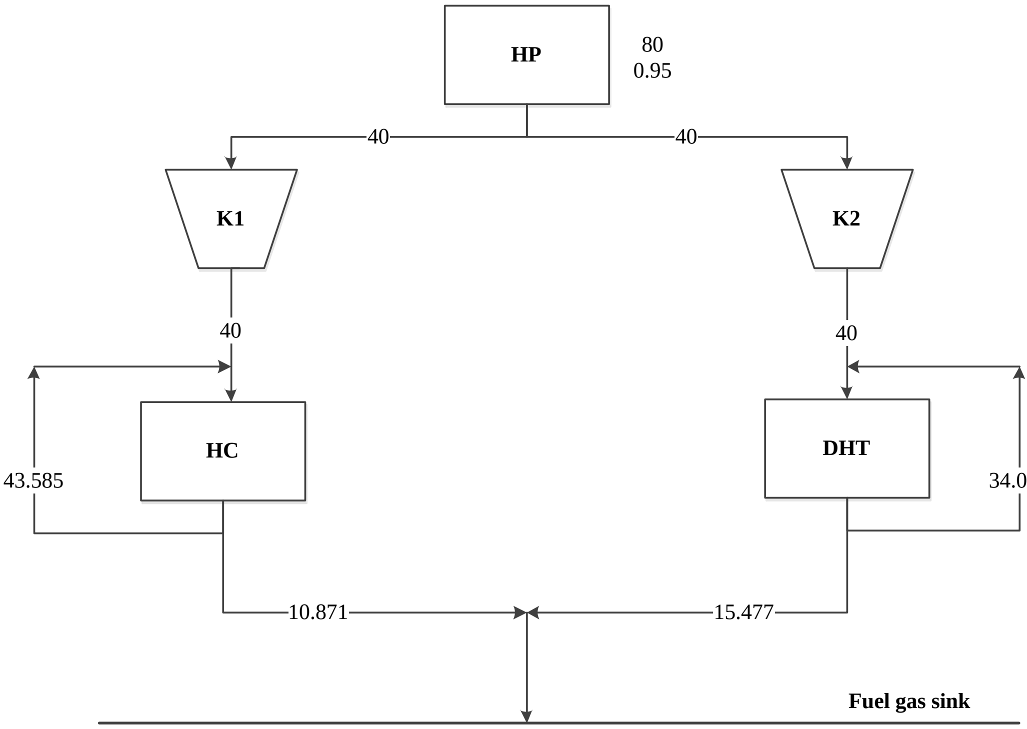


Figure 4.3 Existing network for example 1

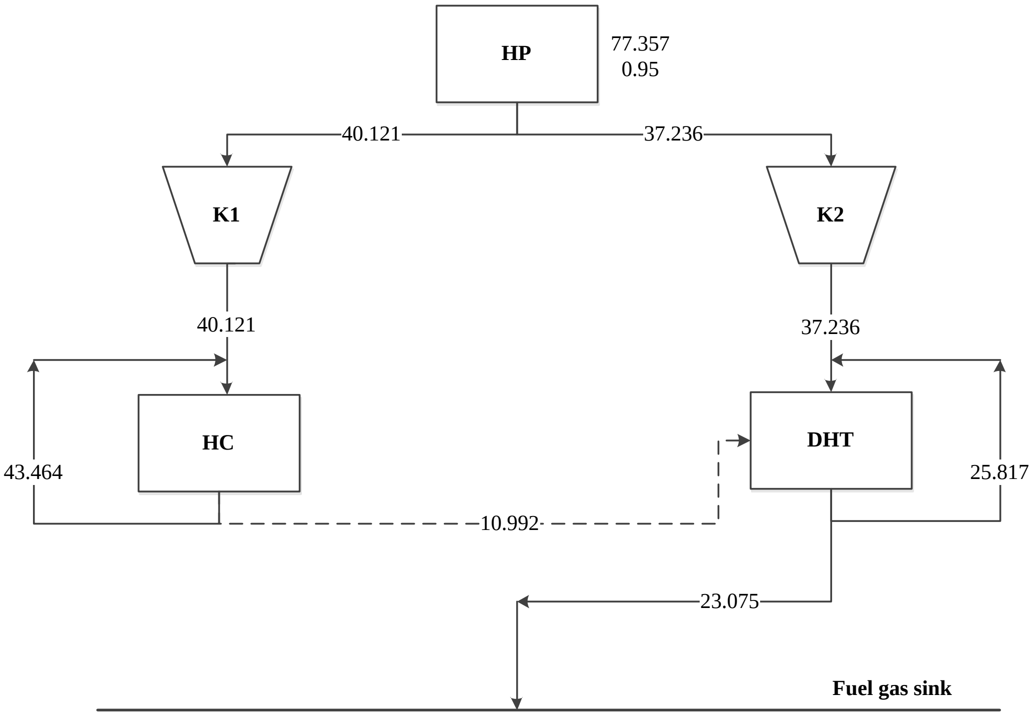


Figure 4.4 Optimal solution for example 1

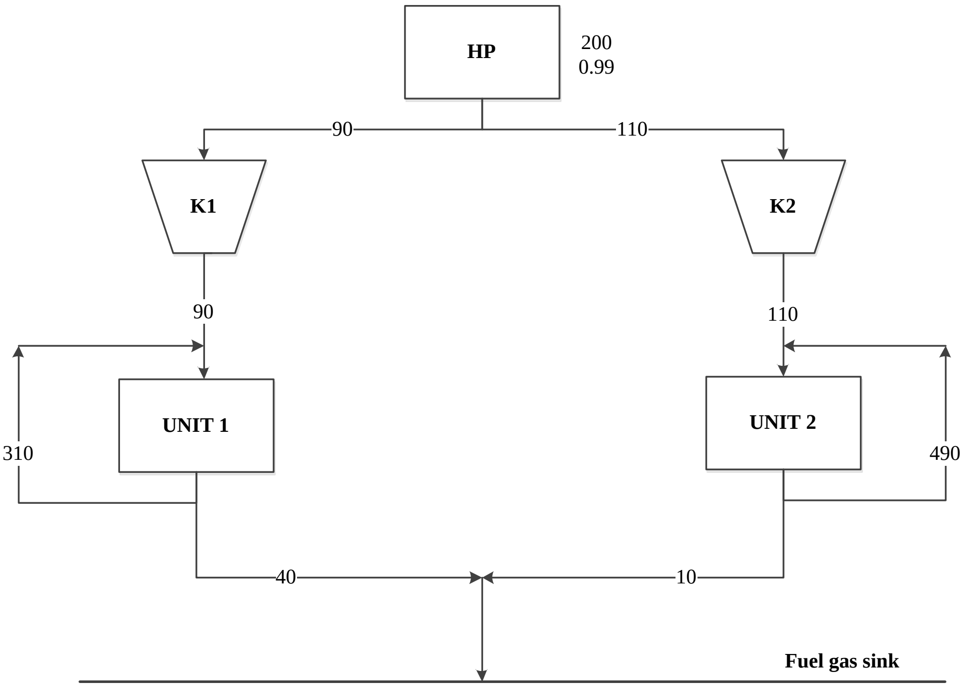


Figure 4.5 Existing network for example 2

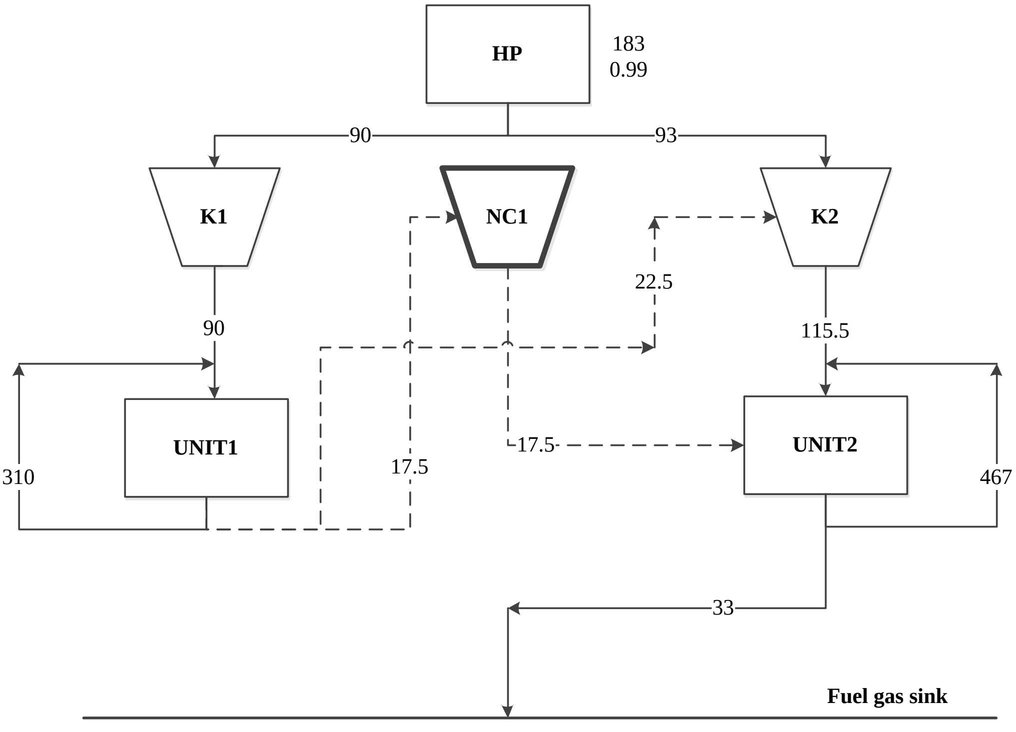


Figure 4.6 Optimal solution for example 2

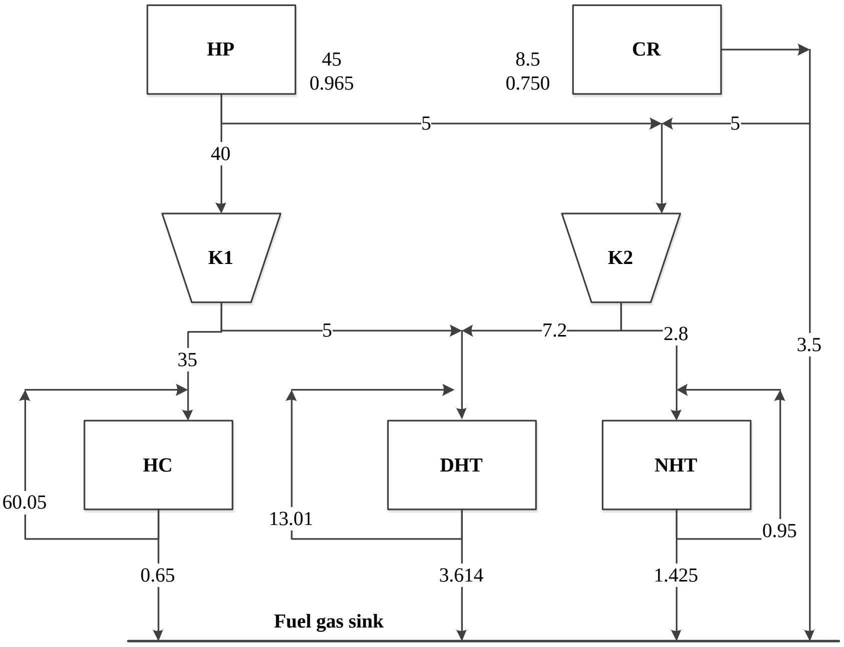


Figure 4.7 Existing network for example 3

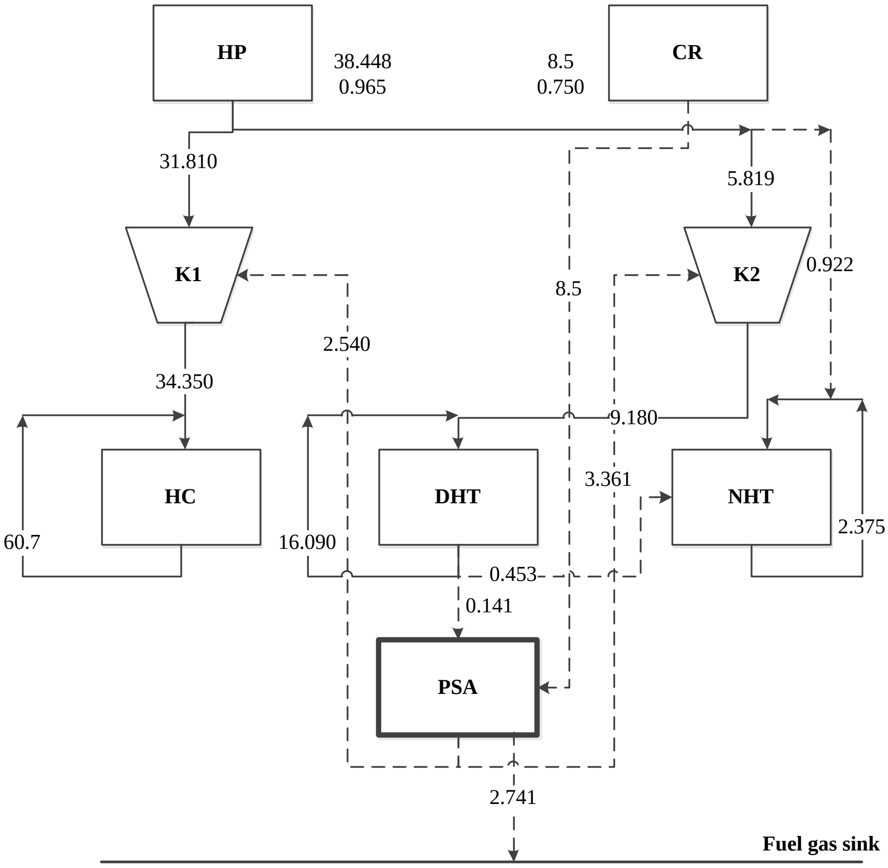


Figure 4.8 Optimal solution for example 3

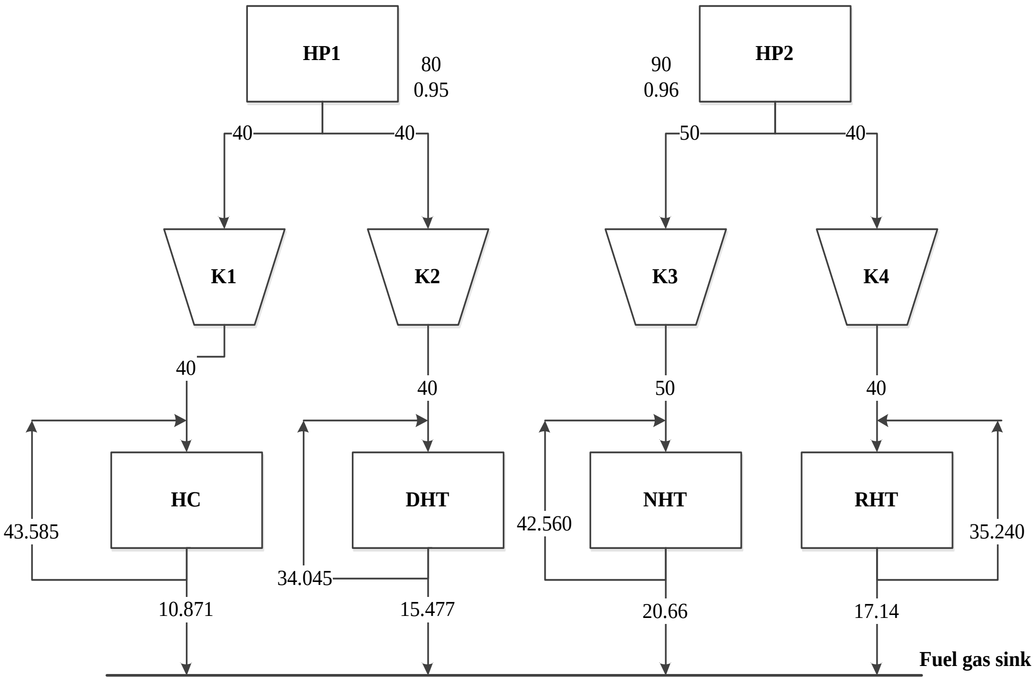


Figure 4.9 Existing network for example 4

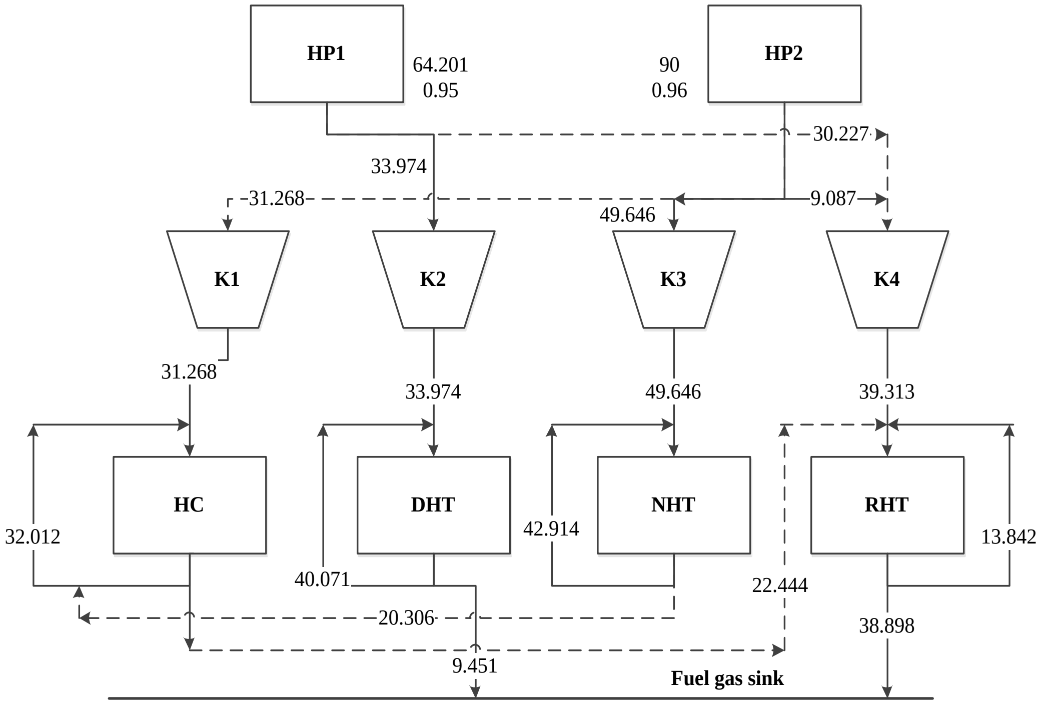


Figure 4.10 Optimal solution for example 4

The parameters for the existing compressors and hydrogen sources are given in Table 4.12 and Table 4.13 respectively. The parameters for processing units are given in Table 4.14 and Table 4.15. The existing network diagram is shown in Figure 4.9. The objective is to minimize the overall TAC (total annualized cost) of the system and was found to be 104240.21 k$. The optimized structure is given in Figure 4.10.

4.6.5 Example 5

This example taken from the work of Elkamel et al.[60] which an existing refinery hydrogen network having two hydrogen sources, three existing compressors (K1-K3), five processing units and one fuel gas system. Similar to the previous example, the hydrogen producers are the hydrogen plant (HP) and the catalytic reformer unit (CR). The five different processing units in this example are hydrocracker (HC), gas oil hydrotreater (GOHT), residue hydrotreater (RHT), diesel hydrotreater (DHT) and naphtha hydrotreater (NHT). The parameters for the existing compressors and hydrogen sources are given in Table 4.16 and Table 4.17 respectively. The parameters for processing units are given in Table 4.18 and Table 4.19. The existing refinery hydrogen network for this example is given in Figure 4.11.This system now has to be retrofitted with a pressure swing adsoption (PSA) unit. The global optimization of this network resulted in a solution of 47808.67 k$ and optimized structure is shown in Figure 4.12. The payback period, which is defined as the return on investment or the time taken by the capital or the investment to repay or “pay by itself,” is also calculated to be 0.7 years. The payback period is calculated as the capital/investment cost divided by the change in operating cost of the new network after investment from the operating cost in the existing network.

Table 4.16 Example 5 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	31.5	300	2000
K2	31.5	300	2000
K3	31.5	300	600

Table 4.17 Example 5 - Data for hydrogen sources

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
HP	≤ 80	95	300
CR	15.5	80	300

Table 4.18 Example 5 - Operating conditions of processing units

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
HC	86.7	80	2000	1200
GOHT	83.6	75	500	350
RHT	82.6	75	600	400
DHT	74.9	70	500	350
NHT	72.7	65	300	200

Table 4.19 Example 5 - Data for processing units

Processing Unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
HC	37.382	95.0	8.153	46.203	83.585	54.456
GOHT	34.915	93.2	10.392	39.130	74.045	49.522
RHT	17.703	90.0	5.794	17.381	35.084	23.175
DHT	5.437	80.0	1.434	5.736	11.173	7.170
NHT	3.925	75.0	2.236	1.204	5.129	3.440

Table 4.20 Example 6 - Data for existing compressors

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	31.5	300	2000
K2	31.5	300	2000
K3	31.5	300	600
K4	52.5	300	2000
K5	42.0	300	600

Table 4.21 Example 6 - Data for hydrogen sources

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
HP1	≤ 80	95	300
CR	15.5	80	300
HP2	≤ 90	96	300

Table 4.22 Example 6 - Operating conditions of processing units

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
HC1	86.7	80	2000	1200
GOHT	83.6	75	500	350
RHT	82.6	75	600	400
DHT	74.9	70	500	350
NHT	72.7	65	300	200
HC2	90.9	85	2000	1200
CNHT	87.6	78	500	350

Table 4.23 Example 6 - Data for processing units

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
HC	37.382	95.0	8.153	46.203	83.585	54.456
GOHT	34.915	93.2	10.392	39.130	74.045	49.522
RHT	17.703	90.0	5.794	17.381	35.084	23.175
DHT	5.437	80.0	1.434	5.736	11.173	7.170
NHT	3.925	75.0	2.236	1.204	5.129	3.440
HC2	50.000	96.0	20.660	42.560	92.560	63.220
CNHT	40.000	96.0	17.140	35.240	75.240	52.380

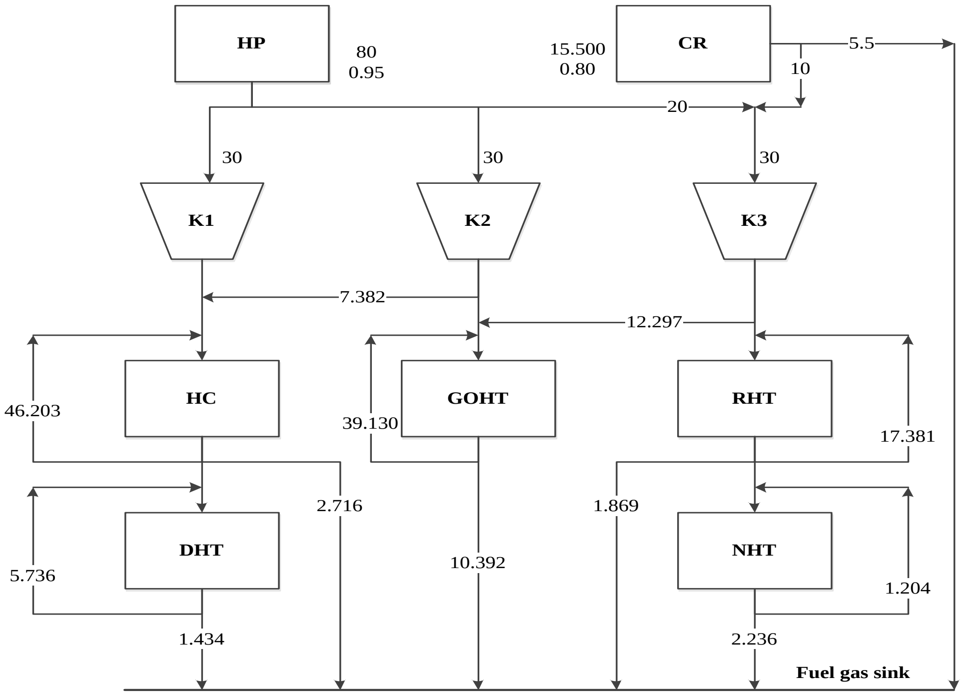


Figure 4.11 Existing network for example 5

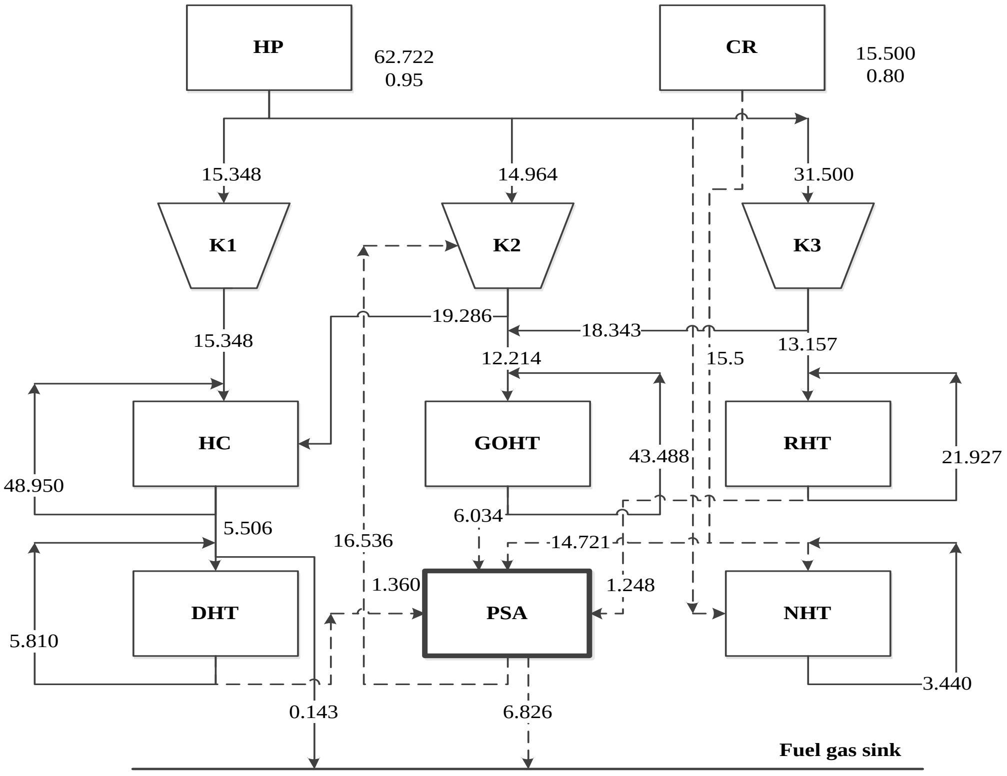


Figure 4.12 Optimal solution for example 5

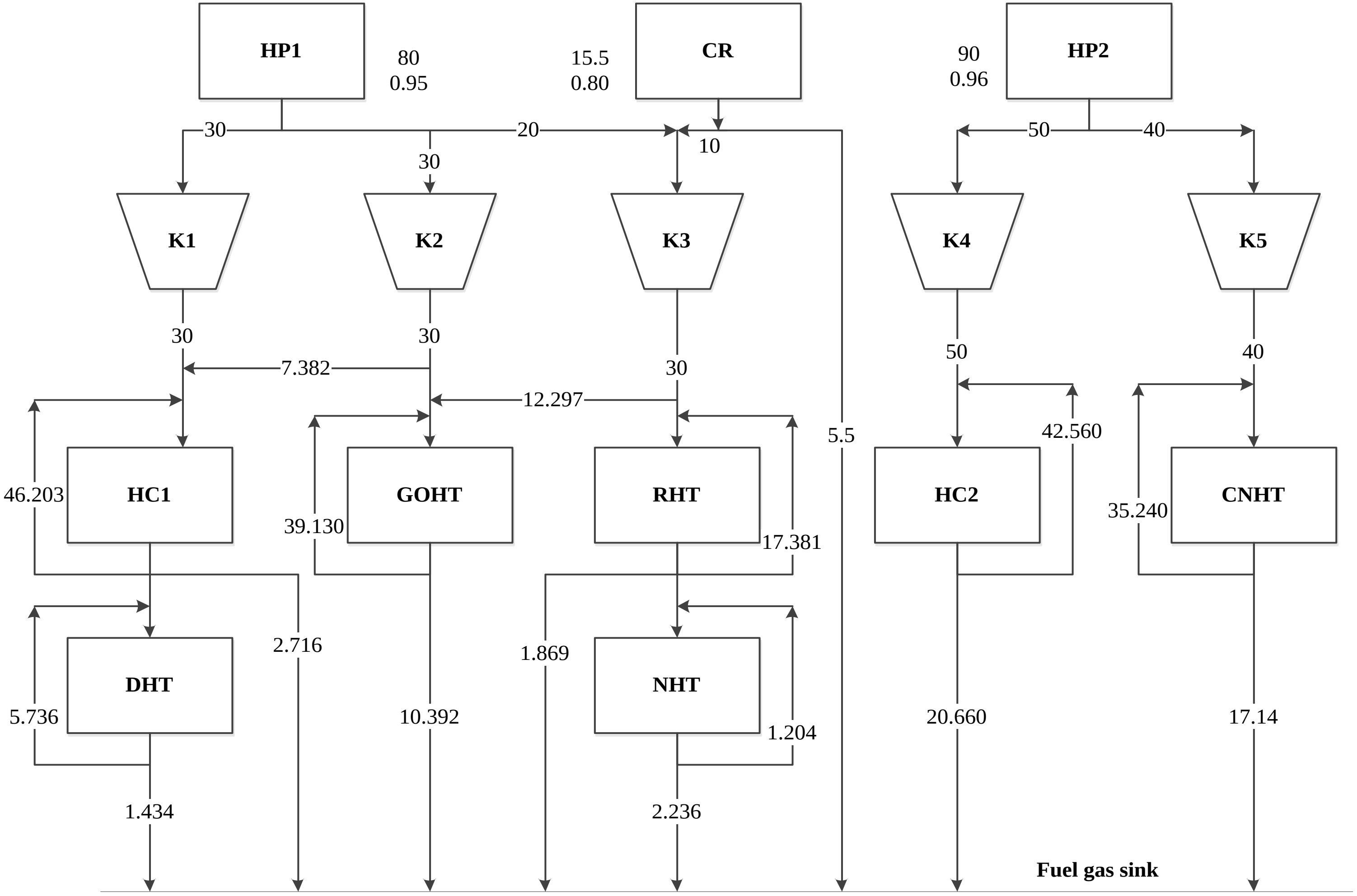


Figure 4.13 Existing network for example 6

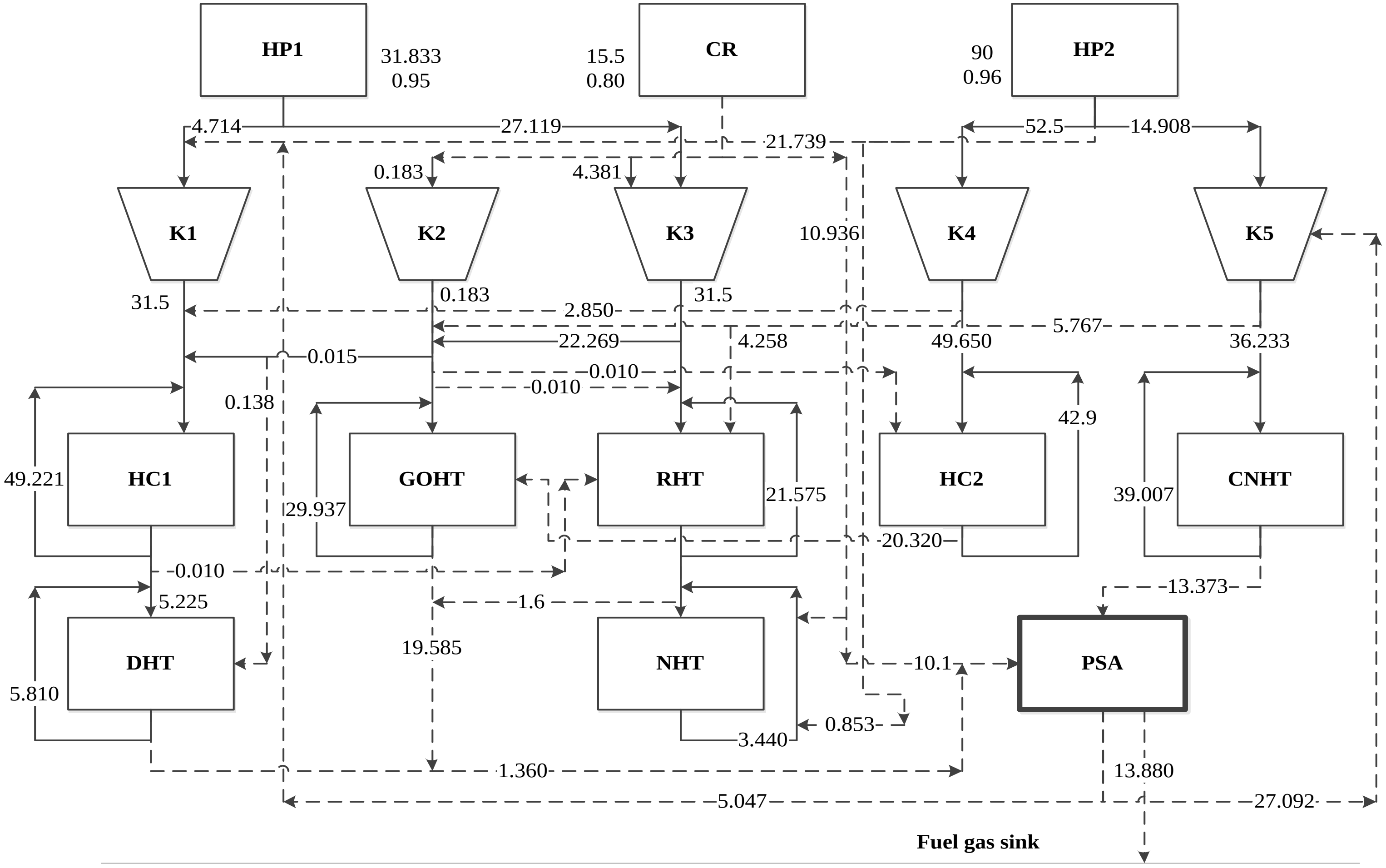


Figure 4.14 Optimal solution for example 6

4.6.6 Example 6

Next we consider a large refinery which has three hydrogen sources, five existing compressors, seven processing units and a fuel gas system. One of the hydrogen producer (HP1) is an on purpose hydrogen plant utilized for the refinery functioning. The refinery also imports some amount hydrogen from the neighbouring merchant hydrogen production system (HP2) to meet its demand. There is also present a catalytic reformer (CR) unit which produces some hydrogen which is relatively less pure in comparison to the other hydrogen producers. Five existing compressors (K1-K5) are present in this network to aid the flow of hydrogen in the network. Seven processing units are two hydrocrackers (HC1 and HC2), gas oil hydrotreater (GOHT), residue hydrotreater (ROHT), diesel hydrotreater (DHT) and naphtha hydrotreater (NHT) and cracked naphtha hydrotreater (CNHT). The existing refinery hydrogen network for this example is given in Figure 4.13. The parameters for the existing compressors and hydrogen sources are given in Table 4.20 and Table 4.21 respectively. The parameters for processing units are given in Table 4.22 and Table 4.23. This system now has to be retrofitted with a pressure swing adsoption (PSA) unit. The globally optimized refinery hydrogen network for this example is shown in Figure 4.14. From the solution we see that majority of the gas stream from the the catalytic reformer (CR) is sent to the purifier, so that it can be supplied to the network. As a result, the hydrogen requirement in the overall requirement is minimized which ultimately results in decreased operating cost. Some processing units also send their off gas to the purifier, resulting in a more decreased hydrogen requirement. The globally optimized design yields a minimum total annualized cost of 93996.73 k$. The payback period is also found to be 0.5 years which shows the benefit of retrofit into the network.

Table 4.24 Model sizes for all examples

Example	Original MINLP model			
	Continuous variables	Discrete variables	Number of constraints	Number of Bilinear terms
1	62	21	68	7
2	86	32	96	14
3	142	64	190	12
4	177	74	189	21
5	252	119	321	23
6	466	226	569	47

4.7 Computational results

Table 4.24 gives the size of the model considered along with the number of bilinear terms for each of the example considered in this work. The computational results for all the examples are provided in Table 4.25. The upper and lower bound mentioned in Table 4.25 refers to the value of the objective function of the lower and upper bounding problem at the iteration when the algorithm is terminated. Results from the Table 4.25 also point that the global optimizer BARON is not able to guarantee global optimality for medium to relatively large examples in tractable computational times. This is because, these network optimization problems are NP-hard and increase in the sizes of the problem may lead to substantial increase in the nonlinear terms resulting in the commercial solvers also not being able to find any solution in tractable computational times when solving to global optimality. However, the proposed algorithm can find the solution in much lesser computational times than in comparison to the commercial global solvers. This further demonstrates the use of the proposed algorithm in finding global solutions based on specified tolerance in tractable computational times. For all the examples, the algorithms were terminated at the end of the first iteration because the gap between the lower bound and upper bound was within acceptable tolerance of the global optimum except for example 5

Table 4.25 Results for examples 1-6

Example	Proposed algorithm					BARON without cuts	
	Global optimum	Solution of Lower bounding problem (LB)	Solution of Upper bounding problem (UB)	Relaxation gap (%)	Time taken by proposed algorithm (s)	Global optimum	Time taken by BARON (s)
1	52613.45	52613.45	52613.45	0	1.1	52613.45	0.3
2	361.95	361.95	361.95	0	8.7	361.95	30.7
3	29463.65	29463.65	29463.65	0	1.05	29463.65	22.3
4	104240.22	104240.22	104240.22	0	177.4	-	> 30,000
5	47808.67	47807.18	47808.67	0.003	85.1	-	> 30,000
6	93996.73	93976.26	93996.73	0.021	2915.9	-	> 30,000

Table 4.26 Comparison study of the effect of cuts on BARON solver

Example	Global Optimum	BARON with cuts			BARON without cuts		
		Lower bound at root node	Number of Nodes	Time (s)	Lower bound at root node	Number of Nodes	Time (s)
1	52613.45	44017.4	27	0.33	52403.6	11	0.42
2	361.95	322.4	43	1.14	315.7	2052	30.66
3	29463.65	28829.5	1559	19.86	27309.7	1867	22.7
4	104240.22	85967.7	438	11.83	79899.1	-	-

for which two iterations were preferred. In our approach for solving these example problems using the proposed algorithm, we preferred to obtain tight relaxations at the very first iteration as these relaxations could provide strong lower bounds which could help the problem to be solved faster. Hence the level of partitioning chosen was different for every example problem and this in turn depended upon the size of the model and number of bilinear terms. For smaller example problems (example 1, 2 and 3), a partitioning scheme of four ($N_{part} = 4$) could provide tight relaxations which is also equal to that of the global optimal solution. For relatively larger examples (example 4, 5 and 6) we, in an attempt to derive effectively tight relaxation, used different partitioning levels. A partitioning scheme of eleven ($N_{part} = 11$), five ($N_{part} = 5$) and nine ($N_{part} = 9$) were chosen for example 4, example 5 and example 6 respectively.

The significance of the bound strengthening cut on the global optimality was studied by experimenting it with the global solver like BARON. Its effects were investigated by solving the original MINLP problem both with and without the cuts. It was found that these cuts provide a tight relaxation at the root node thereby reducing the gap between the upper and lower bound in a branch and bound algorithmic framework resulting in reduced computational times. Table 4.26 gives a detail study for examples 1-4 which compares the root node relaxation, number of nodes required and time taken by the solver BARON to solve these problems to global optimality with and without the presence of these cuts. The effect of this cut however was absent for smaller examples like example 1 for which BARON provided superior bounds. For the other examples, a clear advantage could be observed by the inclusion of these cuts which was shown by tighter root node relaxation, reduced number of nodes required for evaluation and lesser computational time. Examples 5 and 6 could not be compared because these examples were relatively large and incorporating these cuts may also not provide solution in tractable computational times. However, the root node relaxation values were superior when the cuts were added rather than in the absence of them. For example 5, the root node relaxation value was 45977.7 when the cuts were added in comparison to 42219.7 when the cuts were not added. Similarly for example 6 when cuts were included, the bound generated at the root node was 89126.7 compared to 81522.1 when cuts were not included. Hence such redundant cuts could be of importance and should be incorporated into the model formulation to strengthen relaxations eventually helping the problem to be solver in relatively lesser computational times.

4.8 Optimization of multi-plant/refinery hydrogen networks

The escalating prices of crude oil and petroleum products have forced the refiners and petrochemical producers to operate under tight margins. In a bid to reduce costs, these industries continually seek innovative methods to conserve and manage their resources. Hydrogen is an important resource/utility that is acquiring significant importance due to its high cost and stringent environmental regulations. One of the prominent ways of systematic hydrogen utilization is to have a proper design and optimal operation of the individual hydrogen consumption units such as hydrocracker and hydrotreater units which results in better utilization and lesser wastage. Another way to minimize the hydrogen consumption and to increase the recovery of hydrogen in a refinery is to install a purifier so that it purifies the hydrogen circulating in a refinery and reduces the dependence on pure hydrogen. Third, it is also beneficial to make use of other hydrogen streams in the refinery such as the stream from catalytic reformer into the hydrogen network which could possibly minimize hydrogen consumption. Despite all these, refiners are still interested in ways to achieve minimum hydrogen consumption and are continuing to seek more opportunities on innovative methods required for the same. Most of the approaches so far have only considered optimizing the hydrogen flow within a single refinery, or have focused on improving the performance of the network by minimizing the hydrogen consumption within a single refinery. One of the innovative solutions in this regard is to have enhanced integration and coordination among multiple refineries or multiple plants within a petroleum refinery to utilize all of the available resources. This will result in optimal management of the entire operating system at different operating sites by allowing proper integration among all the plants. The effect of these ideas of integration is more pronounced in petrochemical complexes where many plants are situated close to one another and there is a lot of scope for sharing of resources. In refining / petrochemical complexes such as Jubail, Jurong Island, Houston, and Rotterdam, where multiple refineries and petrochemical plants exist in close proximity, it is better to expand the scope of integration and coordination from intra-plant to inter-plant. This may allow one to exploit inter-plant synergies and reduce costs.

The benefits of integration in planning, scheduling and supply chain in general has prompted many researchers to work in this area given its potential advantages. Shah[104] pointed out the issues in the production planning and scheduling in single and multiple facilities and stressed that multiple facilities are complex and are the areas of future research. The production planning of chemical systems especially petroleum refineries have been widely studied given its potential advantages. Many works have also been carried out on petroleum refinery and petrochemical industry integration. Neiro and Pinto[105] conducted modelling and optimization for the entire petroleum supply chain. They asserted that a coordinated strategy could play a greater role in operational planning when managing different aspects of petroleum supply chain. Al-Qahtani and Elkamel[106] tackled the problem of multisite refinery network, where they analysed key aspects such as production capacity expansion, combination of different feedstocks etc. The problem was formulated as a mixed integer linear program (MILP) which sought to minimize investment and operational cost. Al-Qahtani and Elkamel[107] developed an MILP model for long term planning for integration of multiple refineries and petrochemical industry. Their production planning model for an integrated complex was aligned in such a manner that the downstream petroleum refinery products form the raw materials for the petrochemical plant/industry. Other notable works in the area of integrated petroleum refinery and petrochemical unit planning were by Swaty[108] who integrated ethylene plant with a petroleum refinery and Gonzalo et al.[109] who showed the benefits between refinery and steam cracker plant by installing a hydrocracker in Repsol refinery in Spain.

The integration in the production planning of chemical industries has also led to a flurry of research activities for the integration of the utilities in a chemical plant such as energy, water etc. Chew et al.[110] studied inter-plant water network synthesis both by direct and indirect integration. The indirect integration was through a centralized storage unit. Better cost savings and lesser freshwater consumption were reported by them in their results. Chen et al.[111] mentioned the importance of water mains in the water networks and developed an interconnected network with centralized and decentralized water mains. The resulting MINLP was solved to local optimality. Energy (heat) integration has also been studied in the literature.[112-114] This gives the motivation for one to understand the benefits of integration in case of hydrogen which can be considered as an important utility in refinery and petrochemical plants. Chew et al.[115, 116] in their work on inter-plant resource conservation network developed a flow targeting algorithm which used the concepts of pinch and applied it to examples in the field of hydrogen and water networks. To the best of our knowledge of the literature, any work on considering integration of hydrogen networks among multiple plants as a possible means to increase hydrogen recovery is lacking and hence there is a need to develop some integration strategy which is useful not only in conserving resources (hydrogen) but also minimize the overall cost of the operation.

In this section, we present a mathematical model for integration of refinery hydrogen networks using the model developed in the section 4.3. The rest of the section is organized as follows. Problem statement and model are shown in sub sections 4.8.1 and 4.8.2 respectively. A case study for demonstrating the benefits of the proposed approach is shown in section 4.8.3.

4.8.1 Problem Statement

The problem here is to determine the optimal network integration strategy among the multiple refineries/plants in a petrochemical complex which results in a minimal total annualized cost (TAC) of the entire network and at the same time satisfy process demands. The problem in the design of refinery hydrogen network is to synthesize an optimal network configuration for hydrogen distribution essentially linking the different entities within the refinery. In the integrated refinery hydrogen network model, we aim to optimize the overall superstructure obtained by extending the refinery hydrogen network model across refineries/plants to yield an optimum configuration based on a particular objective. The problem can be mathematically defined as follows. Two schemes of integration are presented in this section. Next, we will be describing the specific problem statement for both the types of integration.

For direct integration, the problem is stated as follows. Consider a petrochemical complex which has a set of hydrogen sources $i \in I$, a set of fuel gas sinks $j \in J$, a set of processing units $u \in U$, set of existing compressors $k \in K$, a set of refineries/plants $r \in R$ and there is scope for retrofitting these entities with purification units $m \in M$ into the network. Let $p \in P$ and $q \in Q$ represent the set of generalized sources and sinks. As mentioned earlier, hydrogen sources and fuel gas sinks act as a generalized origin and destination respectively. Existing compressors, processing units can function as both generalized origin and destination units. Purification units behave as a generalized destination and as two generalized origin units (because of product and residue streams). Let $p \in P_r$ represent a set of generalized sources which belong to the refinery/plant r such that $p \in P_r \subset P$. P_r gives the description of the set which contains generalized origin units in the refinery/plant r. Similarly the set Q_r $(q \in Q_r \subset Q)$ contains elements which represent generalized destination units in the refinery/plant r. Also let P_{new} $(p \in P_{new} \subset P)$ represent a set of generalized origin units, which is the new equipment to be retrofitted into the system and Q_{new} $(q \in Q_{new} \subset Q)$ is a set which consists of generalized destination units which could be the new equipment retrofitted into the system. The problem is to develop an optimal network of interconnected flow among the refineries resulting in a minimal annualized cost (TAC) of the entire network.

For the case of indirect integration, there exists a centralized unit through which the networks should be integrated. The purification units (pressure swing adsorption, membrane separation) generally have a very high capital/installation cost, so we propose to use purification units as the centralized equipment to indirectly integrate the networks. The problem statement for the indirect integration can now be stated as follows. Consider a petrochemical complex which has a set of hydrogen sources $i \in I$, a set of fuel gas sinks $j \in J$, a set of processing units $u \in U$, set of existing compressors $k \in K$, a set of refineries/plants $r \in R$, a set of generalized origin units

$p \in P$ and $q \in Q$ be a set of generalized destinations. Let the set P_r $(p \in P_r \subset P)$ and Q_r $(q \in Q_r \subset Q)$ contains elements which represent generalized origin and destinations respectively in the refinery/plant r. $m \in M$ represent a set of purification unit which can be centrally retrofitted in the overall network. Also let P_{new} $(p \in P_{new} \subset P)$ represent a set of generalized origin units, which is the new equipment to be retrofitted into the system and Q_{new} $(q \in Q_{new} \subset Q)$ is a set which consists of generalized destination units which could be the new equipment retrofitted into the system. The problem is to find an optimum network integration strategy which links the centralized unit with other units in the system which minimizes the total annualized cost of the entire operation. All the assumptions as explained in the previous section for the refinery hydrogen network also hold in case of integration of refinery hydrogen networks. In addition to them, some of other assumptions are as follows.

1. There is equal preference/weightage in the usage of resources among all the plants which are a part of network integration operation.
2. The gases from the hydrogen network burnt in fuel gas sinks could produce energy and this energy converted into cost is subtracted from the operating cost of the entire plant. We, however, in this section consider the fuel gas sinks to have only flaring operation. Since flares do not produce any useful energy which could be utilized by the plant, this cost is zero and is eliminated from the operational cost of the plant. So the gases going to the fuel gas sinks essentially mean the gases which are going to be flared. We, however, do not associate any penalty for flaring in this study.
3. The cost of piping required for transfer of material from inter-plant is higher than that of the transfer intra-plant.

In this study, we will be considering two types of integration namely direct and indirect integration. As the name suggests, in case of direct integration the networks from different plants are directly connected to one another. In case of indirect integration, the integration is possible only through the existence of a centralized unit. The centralized unit, considered for this study, is the purification unit. In the indirect integration scheme, we also consider another type of indirect integration wherein the networks in addition to integration through the centralized purification unit also are integrated directly. This form of indirect integration can bring about combined synergistic effects of both direct and indirect integration. Figure 4.15 shows a schematic for the direct integration of networks for three plant case. Figure 4.16 shows the indirect integration for three plant case where the networks are integrated by central purifier unit and Figure 4.17 shows the integration for a three plant case where the networks are integrated through the centralized purification equipment as well as integrated directly.

4.8.2 Model Formulation

This formulation addresses the problem of determining the optimal integration and coordination strategy among the refinery hydrogen networks by integrating their networks. Such integration could increase the practicable synergies among the plants leading to the maximum utilization of all the existing resources. The model for the refinery hydrogen network was explained in detail in section 4.3. This model is suitably modified to account for the integration among the refineries. The model is formulated as follows. All the variables and parameters carry the same nomenclature and definitions mentioned in section 4.3. The model is described as follows.

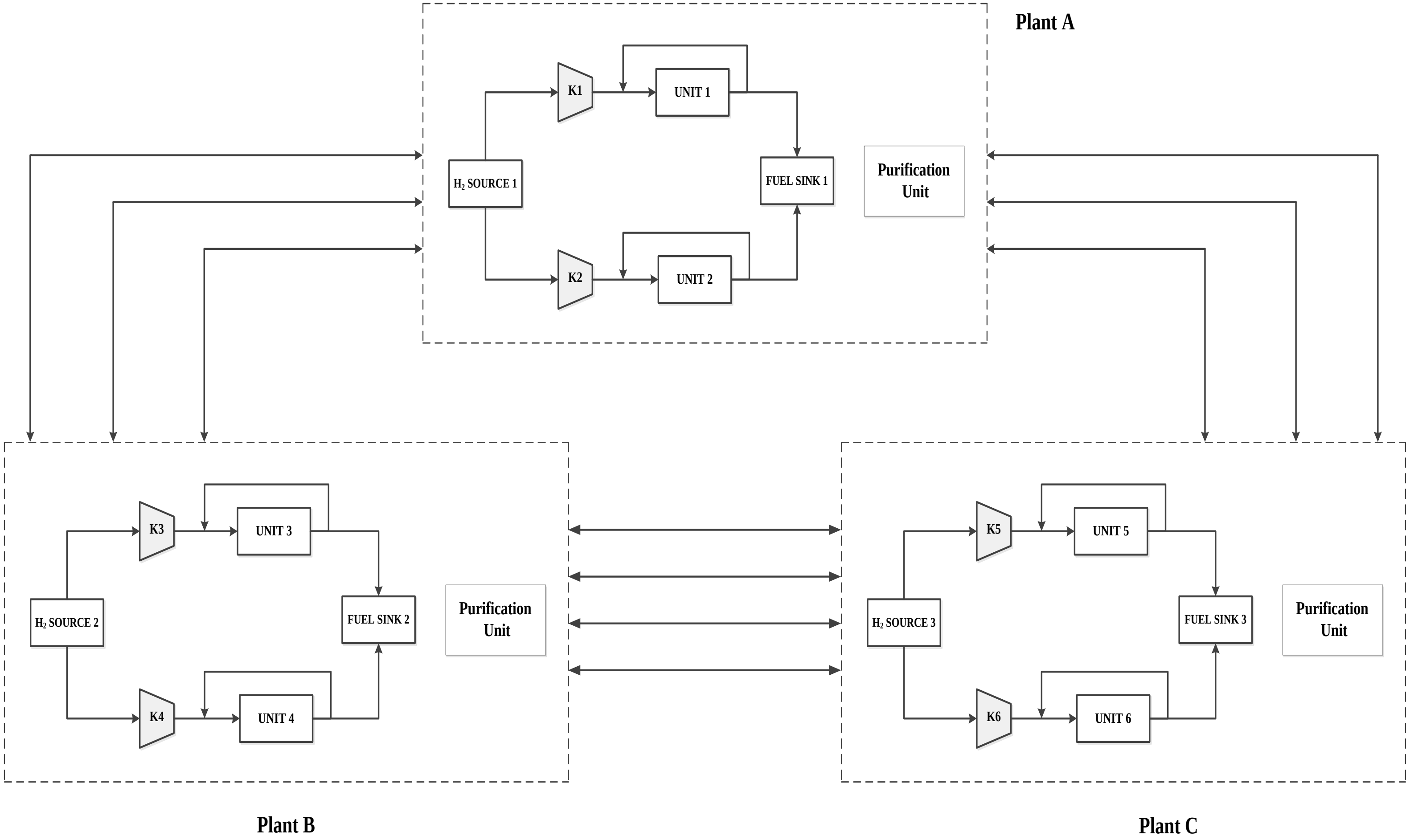


Figure 4.15 Schematic diagram for direct integration for three plant case

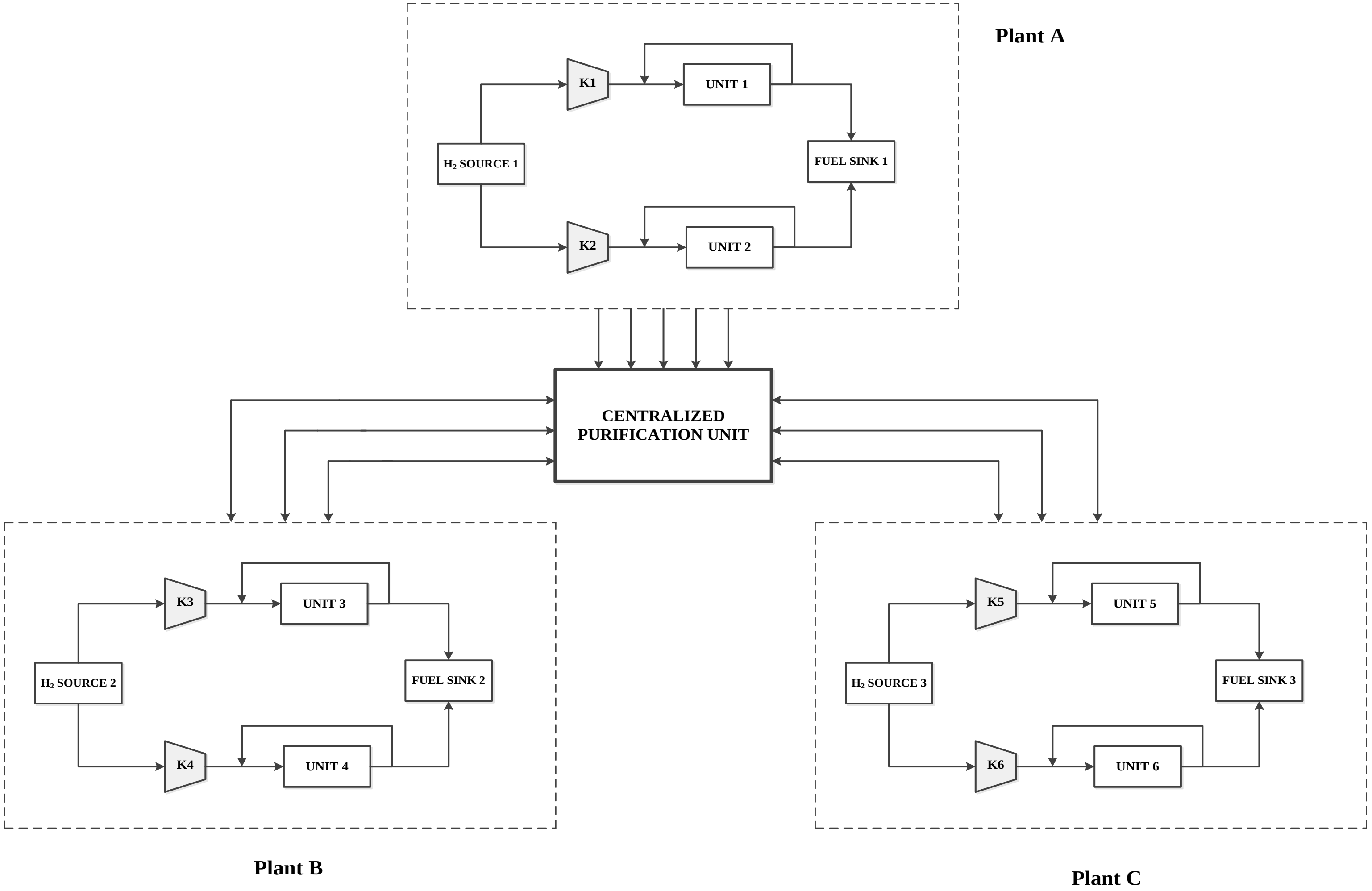


Figure 4.16 Schematic diagram for indirect integration for three plant case integrated by centralized unit

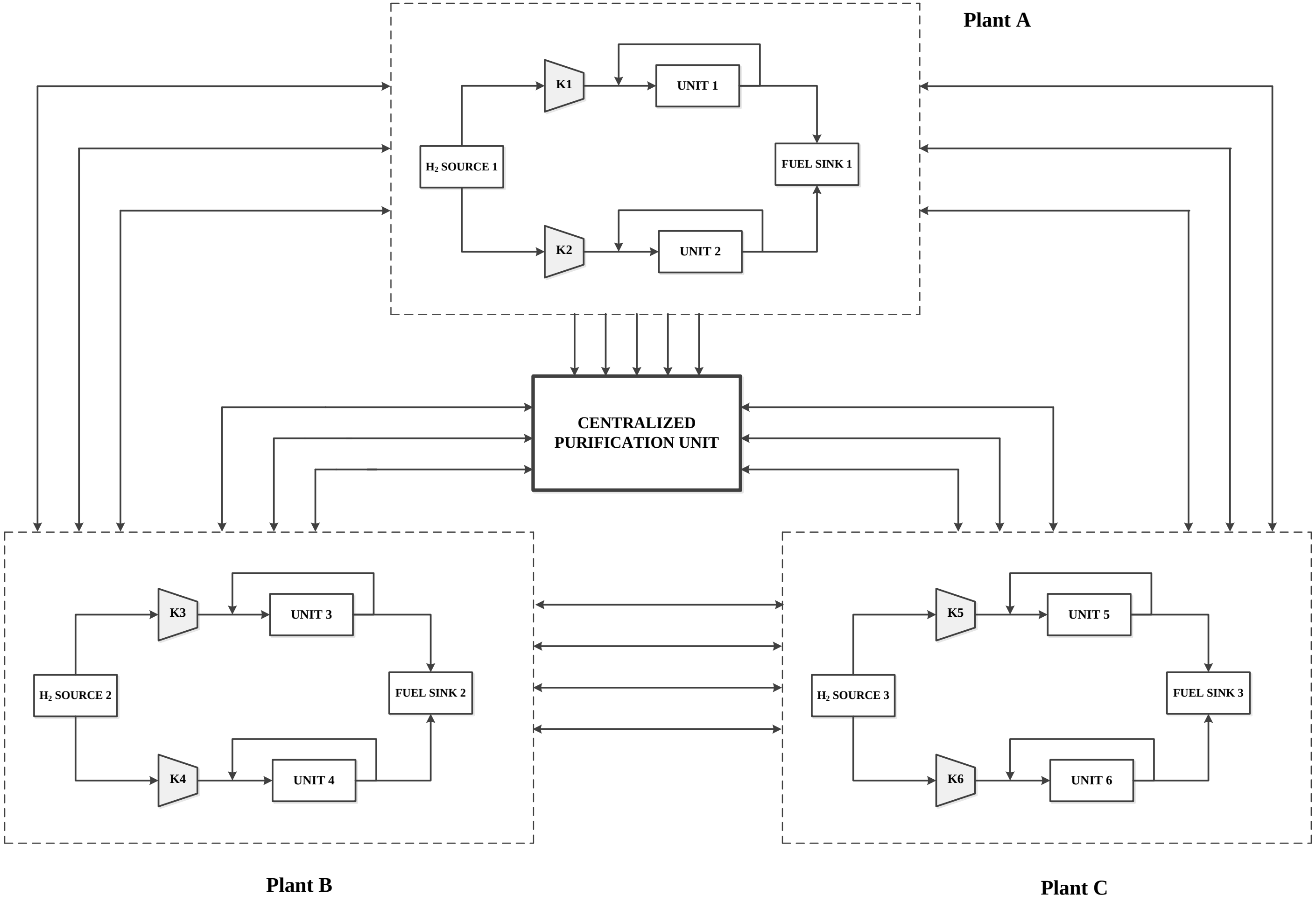


Figure 4.17 Schematic diagram for indirect integration for three plant case integrated directly and also through centralized unit

$$Fout_i = \sum_{j\epsilon J} Fij_{ij} + \sum_{k\epsilon K} Fik_{ik} + \sum_{u\epsilon U} Fiu_{iu} + \sum_{m\epsilon M} Fim_{im} \quad \forall i \;\epsilon\; I \tag{4.38}$$

$$\sum_{i\epsilon I} Fik_{ik} + \sum_{u\epsilon U} Fuk_{uk} + \sum_{m\epsilon M} Fmk_{mk} = \sum_{j\epsilon J} Fkj_{kj} + \sum_{u\epsilon U} Fku_{ku} +$$

$$\sum_{m\epsilon M} Fkm_{km} \quad \forall k \;\epsilon\; K \tag{4.39}$$

$$\sum_{i\epsilon I} Fik_{ik}\, yout_i + \sum_{u\epsilon U} Fuk_{uk} youtu_u + \sum_{m\epsilon M} Fmk_{mk} yPPSA_m$$

$$= ycomp_k\left(\sum_{j\epsilon J} Fkj_{kj} + \sum_{u\epsilon U} Fku_{ku} + \sum_{m\epsilon M} Fkm_{km}\right) \quad \forall k \;\epsilon\; K \tag{4.40}$$

$$\left(\sum_{i\epsilon I} Fik_{ik} + \sum_{u\epsilon U} Fuk_{uk} + \sum_{m\epsilon M} Fmk_{mk}\right) \le Fmax_k \quad \forall k \;\epsilon\; K \tag{4.41}$$

$$Pwr_k = \frac{CpT}{\eta}\left(\left(\frac{Pout_k}{Pin_k}\right)^{\frac{\gamma-1}{\gamma}} - 1\right)\left(\sum_{i\epsilon I} Fik_{ik} + \sum_{u\epsilon U} Fuk_{uk} + \sum_{m\epsilon M} Fmk_{mk}\right)$$

$$\forall k \;\epsilon\; K \tag{4.42}$$

$$Finu_u = \sum_{i\epsilon I} Fiu_{iu} + \sum_{k\epsilon K} Fku_{ku} + \sum_{m\epsilon M} Fmu_{mu} + \sum_{u'\epsilon U} Fuu_{uu'} \quad \forall u \;\epsilon\; U \tag{4.43}$$

$$Finu_u yinu_u = \sum_{i\epsilon I} Fiu_{iu} yout_i + \sum_{k\epsilon K} Fku_{ku}\, ycomp_k$$

$$+ \sum_{m\epsilon M} Fmu_{mu} yPPSA_m + \sum_{u'\epsilon U} Fuu_{uu'}\, youtu_u \quad \forall u \;\epsilon\; U \tag{4.44}$$

$$Fout_u = \sum_{i\epsilon I} Fuj_{uj} + \sum_{k\epsilon K} Fuk_{uk} + \sum_{m\epsilon M} Fum_{um} + + \sum_{u'\epsilon U} Fuu_{uu'}$$

$$\forall u \;\epsilon\; U \tag{4.45}$$

$$\sum_{i\epsilon I} Fim_{im} + \sum_{k\epsilon K} Fkm_{km} + \sum_{u\epsilon U} Fum_{um} = \sum_{k\epsilon K} Fmk_{mk} + \sum_{u\epsilon U} Fmu_{mu}$$

$$+ \sum_{j\epsilon J} Frmj_{mj} \quad \forall m \;\epsilon\; M \tag{4.46}$$

$$\sum_{i\epsilon I} Fim_{im} yout_i + \sum_{k\epsilon K} Fkm_{km} ycomp_k + \sum_{u\epsilon U} Fum_{um} youtu_u$$

$$= yPPSA_m\left(\sum_{k\epsilon K} Fmk_{mk} + \sum_{u\epsilon U} Fmu_{mu}\right) + yRPSA_m \sum_{j\epsilon J} Frmj_{mj} \quad \forall m \;\epsilon\; M \tag{4.47}$$

$$Rcvr\left(\sum_i Fim_{im} yout_i + \sum_k Fkm_{km} ycomp_k + \sum_u Fum_{um} youtu_u\right)$$

$$= yPPSA_m\left(\sum_{k\epsilon K} Fmk_{mk} + \sum_{u\epsilon U} Fmu_{mu}\right) \quad \forall m \;\epsilon\; M \tag{4.48}$$

$$(1 - Rcvr)\left(\sum_{i\epsilon I} Fim_{im} yout_i + \sum_{k\epsilon K} Fkm_{km} ycomp_k + \sum_{u\epsilon U} Fum_{um} youtu_u\right)$$

$$= yRPSA_m \sum_{j\epsilon J} Frmj_{mj} \quad \forall m \;\epsilon\; M \tag{4.49}$$

$$\left(\sum_{i\epsilon I} Fim_{im} + \sum_{k\epsilon K} Fkm_{km} + \sum_{u\epsilon U} Fum_{um}\right) \le FPR_m \quad \forall m \;\epsilon\; M \tag{4.50}$$

$$\left(\sum_{i\epsilon I} Fim_{im} + \sum_{k\epsilon K} Fkm_{km} + \sum_{u\epsilon U} Fum_{um}\right) - XPSA_m UF \le 0 \quad \forall m \;\epsilon\; M \tag{4.51}$$

$$\left(\sum_{i\epsilon I} Fim_{im} + \sum_{k\epsilon K} Fkm_{km} + \sum_{u\epsilon U} Fum_{um}\right) - XPSA_m LF \ge 0 \quad \forall m \;\epsilon\; M \tag{4.52}$$

$$Finj_j = \sum_{i\epsilon I} Fij_{ij} + \sum_{k\epsilon K} Fkj_{kj} + \sum_{u\epsilon U} Fuj_{uj} + \sum_{m\epsilon M} Frmj_{mj} \quad \forall j \,\epsilon\, J \tag{4.53}$$

$$Finj_j yinj_j = \sum_{i\epsilon I} Fij_{ij}\, yout_i + \sum_{k\epsilon K} Fkj_{kj}\, ycomp_k + \sum_{u\epsilon U} Fuj_{uj}\, youtu_u$$
$$+ \sum_{m\epsilon M} Frmj_{mj} yRPSA_m \quad \forall j \,\epsilon\, J \tag{4.54}$$

$$\left(P_p - P_q\right) - X_{pq} UP \le 0 \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q \tag{4.55}$$

$$\left(P_p - P_q\right) - (1 - X_{pq}) LP \ge 0 \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q \tag{4.56}$$

$$F_{pq} - XF_{pq} UF \le 0 \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q \tag{4.57}$$

$$F_{pq} - XF_{pq} LF \ge 0 \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q \tag{4.58}$$

$$XF_{pq} \le X_{pq} \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q \tag{4.59}$$

$$XF_{p,q} \le X_q \qquad \forall p \,\epsilon\, P, \forall q \,\epsilon\, Q_{new} \tag{4.60}$$

$$XF_{p,q} \le X_p \qquad \forall p \,\epsilon\, P_{new}, \forall q \,\epsilon\, Q \tag{4.61}$$

$$Fout_i yout_i + Foutu_u youtu_u - Finu_u yinu_u - Finj_j yinj_j = 0$$
$$\forall i \,\epsilon\, I,\ \forall u \,\epsilon\, U,\ \forall j \,\epsilon\, J \tag{4.62}$$

$$\sum_{p\in P_r} \sum_{q\in Q_{r'}} XF_{pq} = 0 \qquad \forall r \,\epsilon\, R \tag{4.63}$$

$$\sum_{p\in P_r} \sum_{q\in Q_{r'}} XF_{pq} \le N_{max} \qquad \forall r \,\epsilon\, R \tag{4.64}$$

$$TAC = AF \left[\sum_{m\epsilon M} \{ a_{PSA} XPSA_m + b_{PSA} (\sum_{i\epsilon I} Fim_{im} + \sum_{k\epsilon K} Fkm_{km} + \sum_{u\epsilon U} Fum_{um}) \} \right.$$
$$+ \sum_{p\epsilon PQ_r} \sum_{q\epsilon Q_r} (a_{pipe} XF_{pq} + b_{pipe} F_{pq}) + \sum_{p\epsilon P_r} \sum_{q\epsilon Q_{r'}} (a'_{pipe} XF_{pq}$$
$$\left. + b'_{pipe} F_{pq}) \right] + OD \left[\sum_{i\epsilon I} OCH_i\, Fout_i + \sum_{k\epsilon K} Pwr_k\, OCE \right] \tag{4.65}$$

Eq. (4.38) gives the balance equation for the hydrogen producers. Eq. (4.39) - (4.42) gives the equations describing the existing compressors in the system. For these the design pressures and capacity are known. The maximum capacity of each compressor is given in Eq. (4.41) and the compressor power is calculated by Eq. (4.42). The power of the compressor is proportional to the inlet flow into the compressor. The material and component balance equations for the processing units are represented by Eq. (4.43) - (4.45). The modelling equations for the purification unit are given by Eq. (4.46) - (4.52). Similar to the new compressor, if the existence of the pressure swing adsorption unit is modelled by using a binary variable, then Eq. (4.51) and (4.52) are required in the model. The equations for the sinks, namely the fuel gas system are shown in Eq. (4.53) and Eq. (4.54). The existence of pressure difference between generalized origin and destination units, flow between them, equation connecting the pressure difference and flow and the equation connecting the flow between generalized origin and destination units and existence of new equipment are given in Eq. (4.55) - (4.61). The bound strengthening redundant cuts are given in Eq. (4.62). The inter-plant/refinery connections are shown by Eq. (4.63) and Eq. (4.64). Eq. (4.63) forbids any inter-plant/refinery connection and is applicable for the indirect type of integration where there may not be any direct connection among the plants and connection may take place through some centralized unit common to all the plants. Eq. (4.64) is used to control the complexity of connections and is used to limit the number of inter-plant pipelines where N_{max} is the maximum number of cross-plant or inter-plant pipelines. The objective function Eq. (4.65) gives the minimization of the total annualized cost of the overall network. The total annualized cost here is made up of the investment cost and the operational cost. The first term in the objective function is the annualized investment cost on the purification unit. Both intra-plant and inter-plant piping cost are included in the capital/investment cost. The intra-plant piping refers to the new piping connections which may be required during retrofitting of existing networks. The second term is the annualized cost on the retrofitted intra-plant pipelines. As defined previously, the set PQ_r now gives the set of origin destination combination for piping which is not present in the refinery r. The third is annualized cost of the inter-plant pipelines where a'_{pipe} and b'_{pipe} are the capital cost coefficients for the same. The fourth and fifth terms give the operational cost of the network.

Table 4.27 Data for existing compressors in plant A

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K1	42	300	2000
K2	42	300	600

Table 4.28 Data for hydrogen sources in plant A

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
Source 1	≤ 80	95	300

Table 4.29 Operating conditions of processing units in plant A

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
Unit 1	87.2	80	2000	1200
Unit 2	85.8	75	500	350

Table 4.30 Data for processing units in plant A

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
Unit 1	40	95.0	10.871	43.585	83.585	54.456
Unit 2	40	95.0	15.477	34.045	74.045	49.522

Table 4.31 Data for existing compressors in plant B

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K3	52.5	300	2000
K4	42.0	300	600

Table 4.32 Data for hydrogen sources in plant B

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
Source 2	≤ 90	96	300

Table 4.33 Operating conditions of processing units in plant B

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
Unit 3	90.9	85	2000	1200
Unit 4	87.6	78	500	350

Table 4.34 Data for processing units in plant B

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
Unit 3	50	96.0	20.660	42.560	92.560	63.220
Unit 4	40	96.0	17.140	35.240	75.240	52.380

Table 4.35 Data for existing compressors in plant C

Compressor	Capacity (MMscfd)	Inlet pressure (psia)	Outlet pressure (psia)
K5	34	300	2000
K6	12	300	600

Table 4.36 Data for hydrogen sources in plant C

Hydrogen Sources	Flow (MMscfd)	Purity (%)	Pressure (psia)
Source 3	≤ 50	95	300

Table 4.37 Operating conditions of processing units in plant C

Processing unit	Inlet purity (%)	Outlet purity (%)	Inlet pressure (psia)	Outlet pressure (psia)
Unit 5	89.0	84	2000	1200
Unit 6	86.3	80	500	350

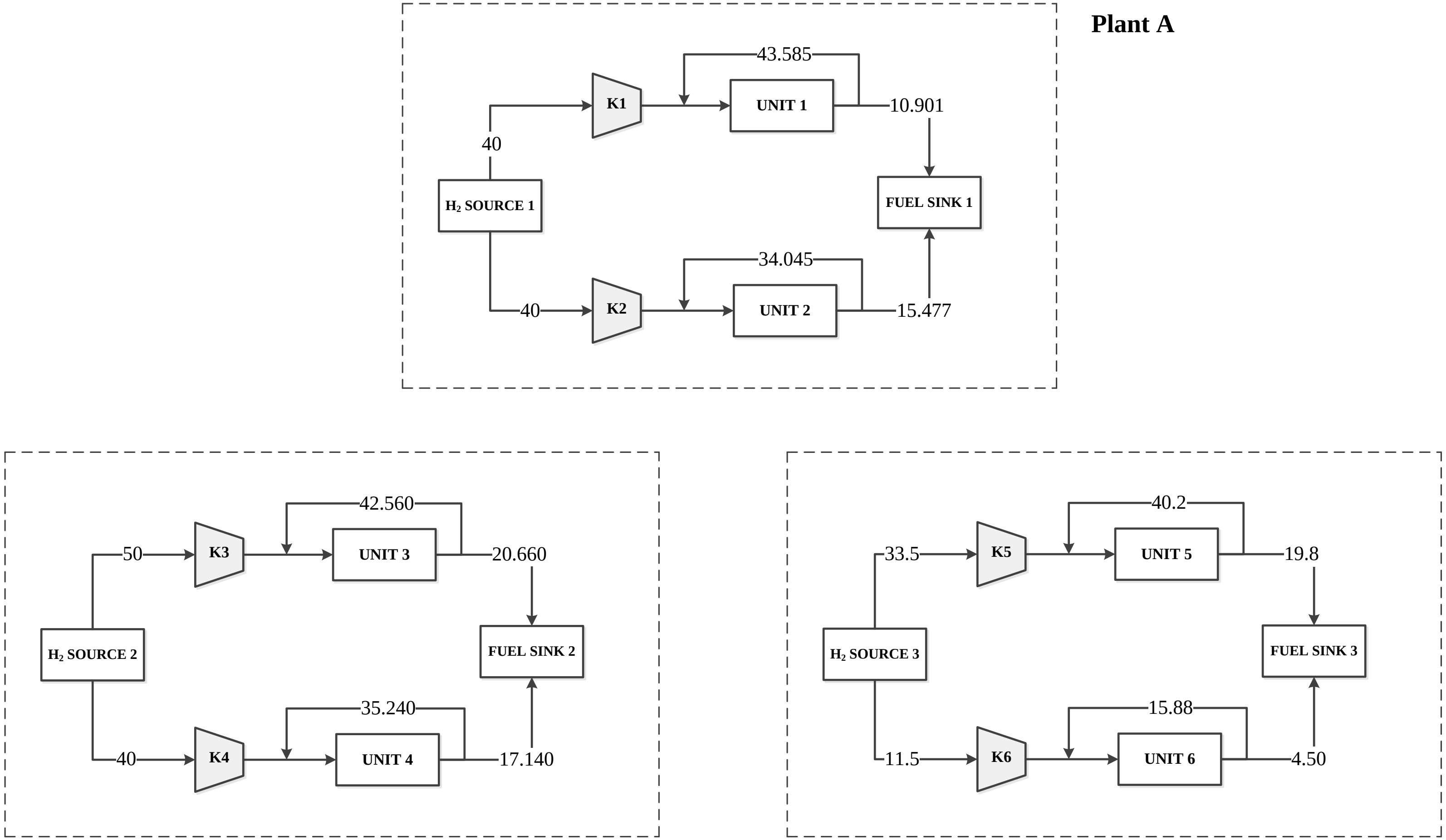
Table 4.38 Data for processing units in plant C

Processing unit	Make-up flow (MMscfd)	Make-up purity (%)	Purge flow (MMscfd)	Recycle (MMscfd)	Inlet flow (MMscfd)	Outlet flow (MMscfd)
Unit 5	33.5	95.0	19.800	40.200	73.700	60.000
Unit 6	11.5	95.0	4.500	15.880	27.380	20.380

The operational cost constitutes the cost of hydrogen consumed (fourth term) and the electricity cost (fifth term) due to the compressor power. There may be other operational expenses involved within the network such as the operational cost of pipe, operational cost of purification unit etc. But these costs are not considered in this model in comparison to the operational costs considered.

4.8.3 Case Study

The case study is of a petrochemical complex which contains three plants A, B and C whose existing networks are given in Figure 4.18. The parameters for the existing compressors and hydrogen sources for the plant A are given in Table 4.27 and Table 4.28 respectively. The parameters for processing units for plant A are given in Table 4.29 and Table 4.30. The data and parameters of the existing compressors, hydrogen sources and processing units required for the plant B are given in Tables 4.31, 4.32, 4.33 and 4.34. Similarly the data and parameters for the plant C are given in Tables 4.35, 4.36, 4.37 and 4.38. The purification unit considered in this study is pressure swing adsorption. We do not impose any restrictions on the interconnections among the different plants, and hence Eq. (4.64) is not included for this study. In the base case, each of the plant A, B and C are retrofitted with the pressure swing adsorption unit and are optimized individually. The objective to be optimized is the total annualized cost. The optimized result for the hydrogen networks in plants A, B and C are 46311.40 k\$, 46466.31 k\$ and 19894.54 k\$ respectively. In case of direct integration, the entire combined network is solved in which all possible interconnections exist among all the refineries. When these three networks are integrated directly, the resultant total annualized cost is 110739.99 k\$. From the base case, the operational cost has reduced by 1826.82 k\$/year (1.66% reduction) and the hydrogen consumption has decreased by 900 MMscf/year (1.7% reduction). Although



Plant A

Plant B

Plant C

Figure 4.18 Existing networks for plant A, B and C

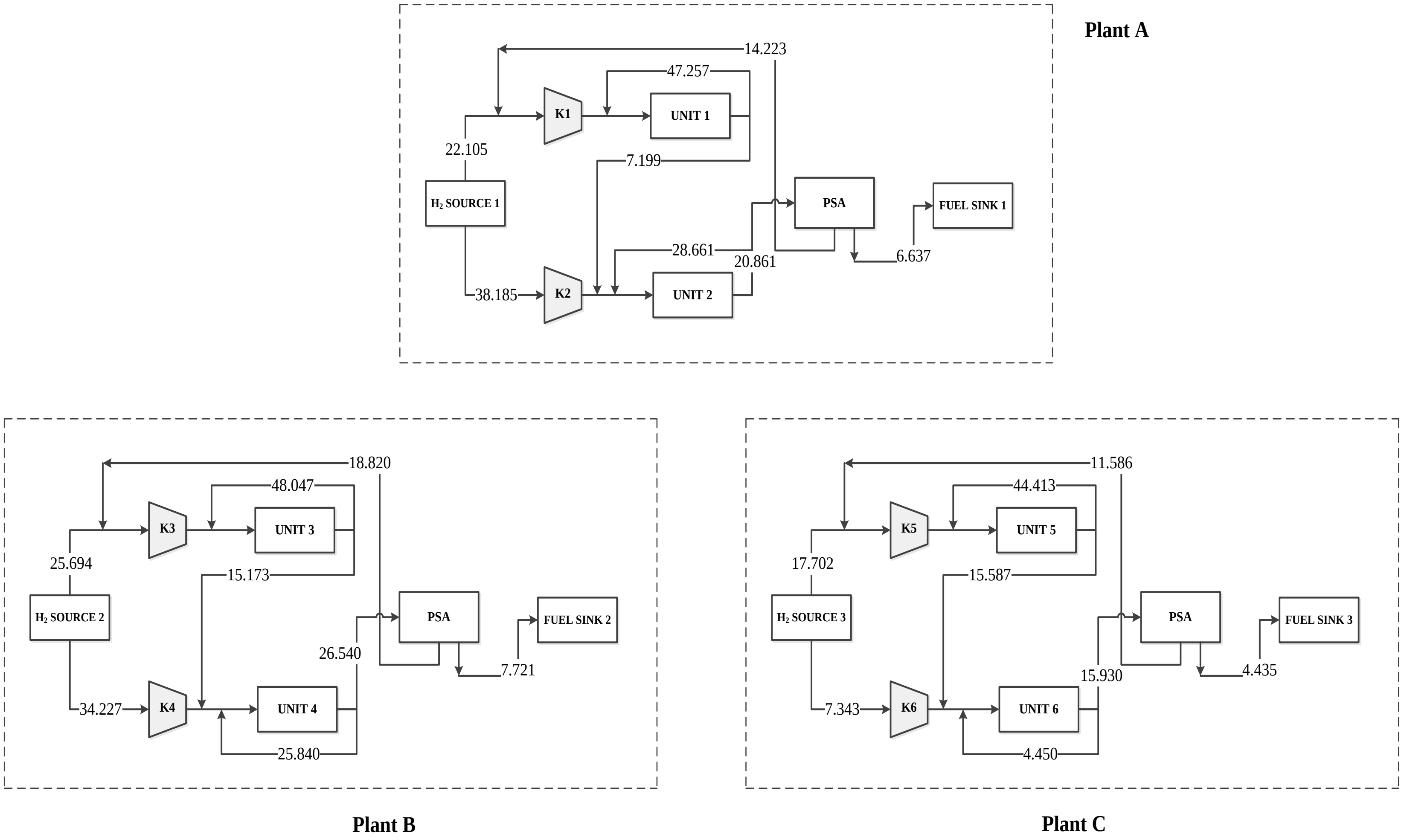


Figure 4.19 Optimized network for plant A, B and C individually

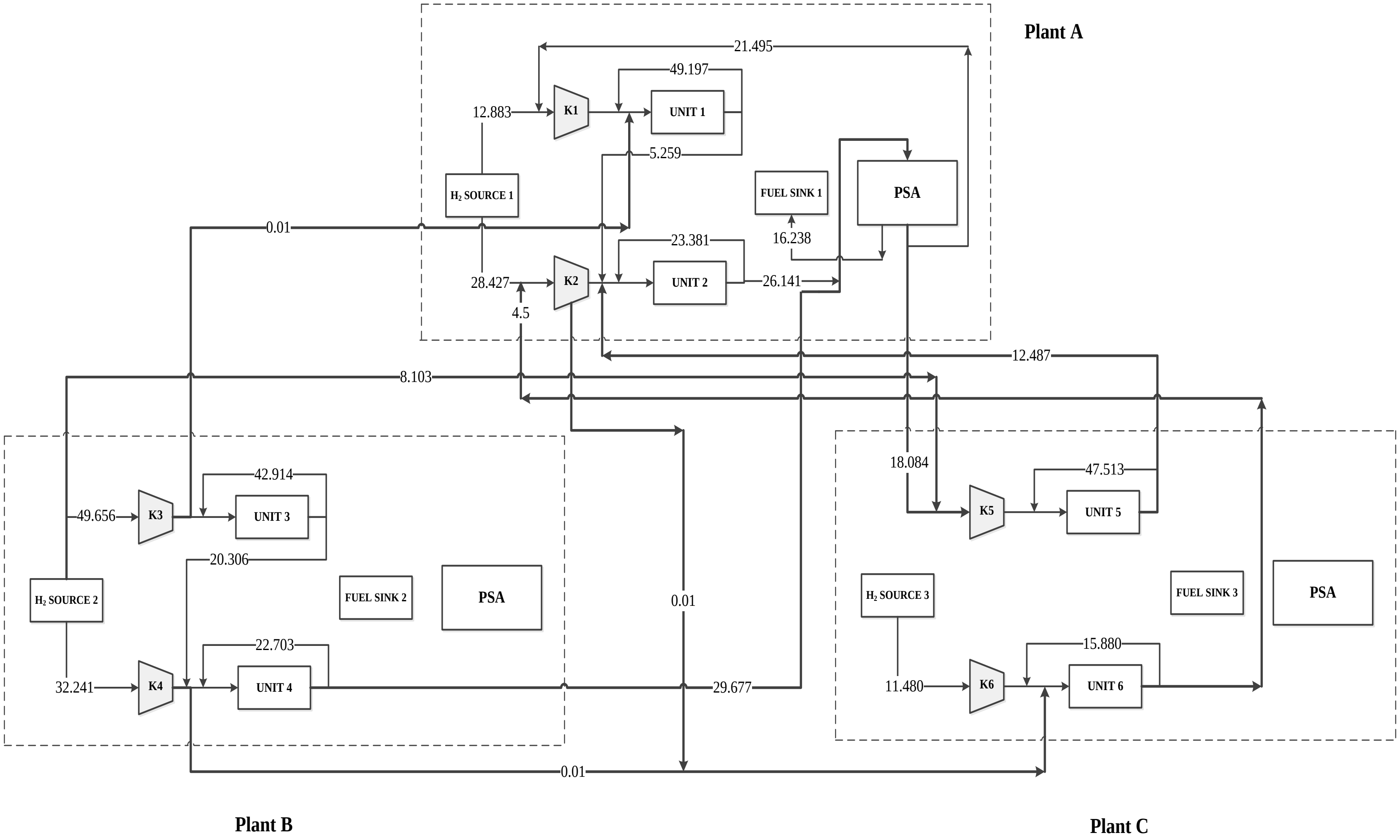


Figure 4.20 Optimized network for direct integration

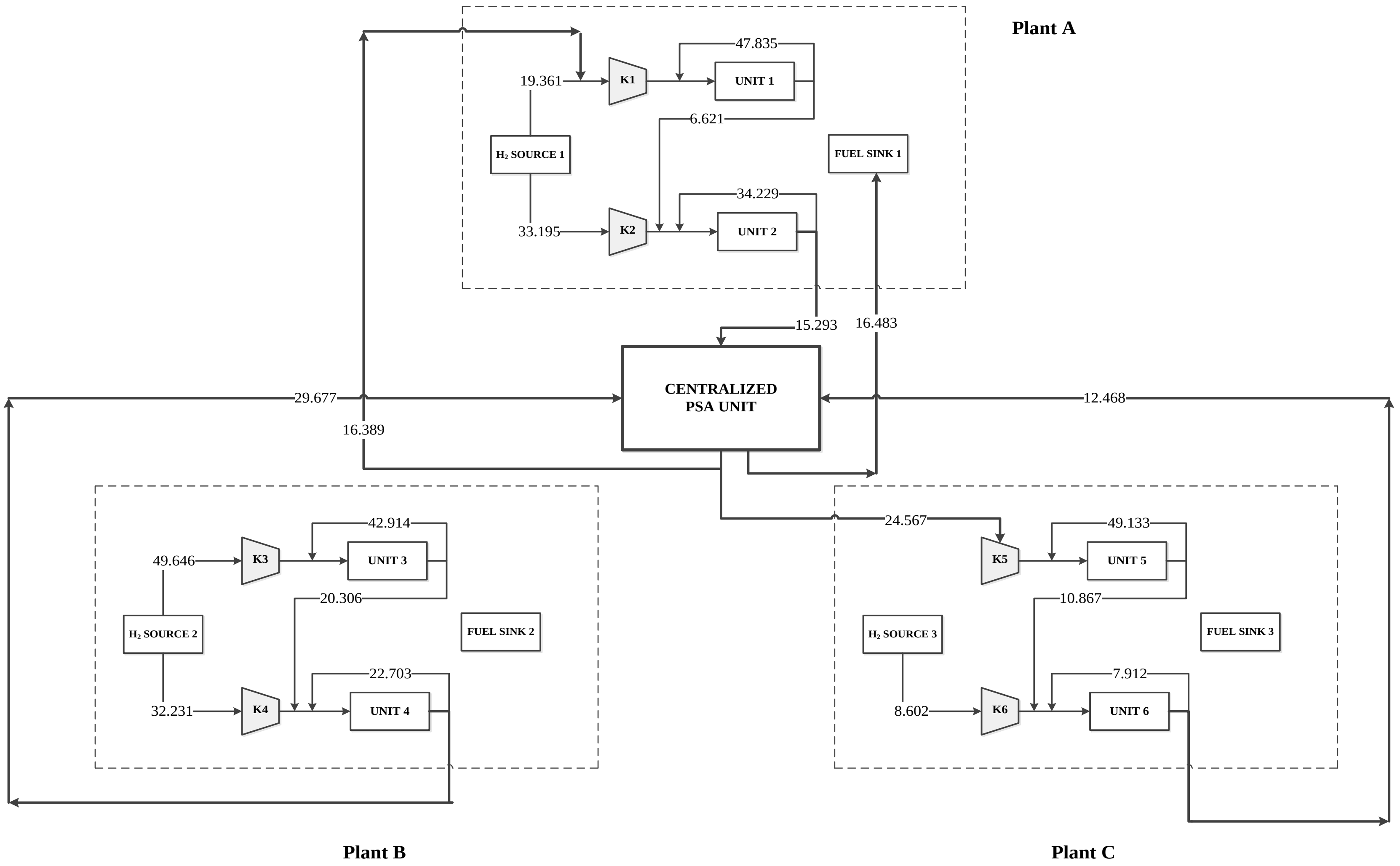


Figure 4.21 Optimized network for indirect integration scheme 1

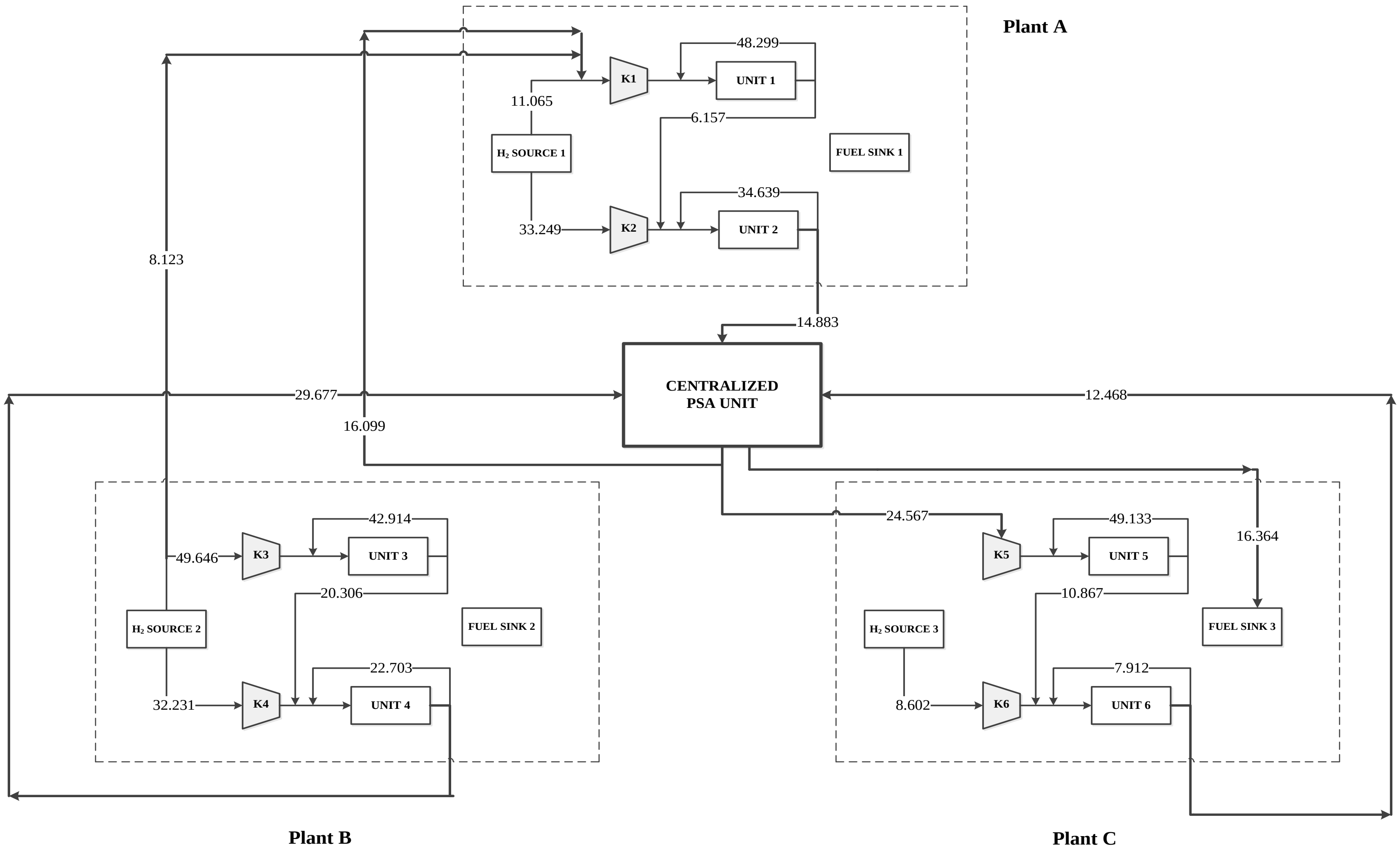


Figure 4.22 Optimized network for indirect integration scheme 2

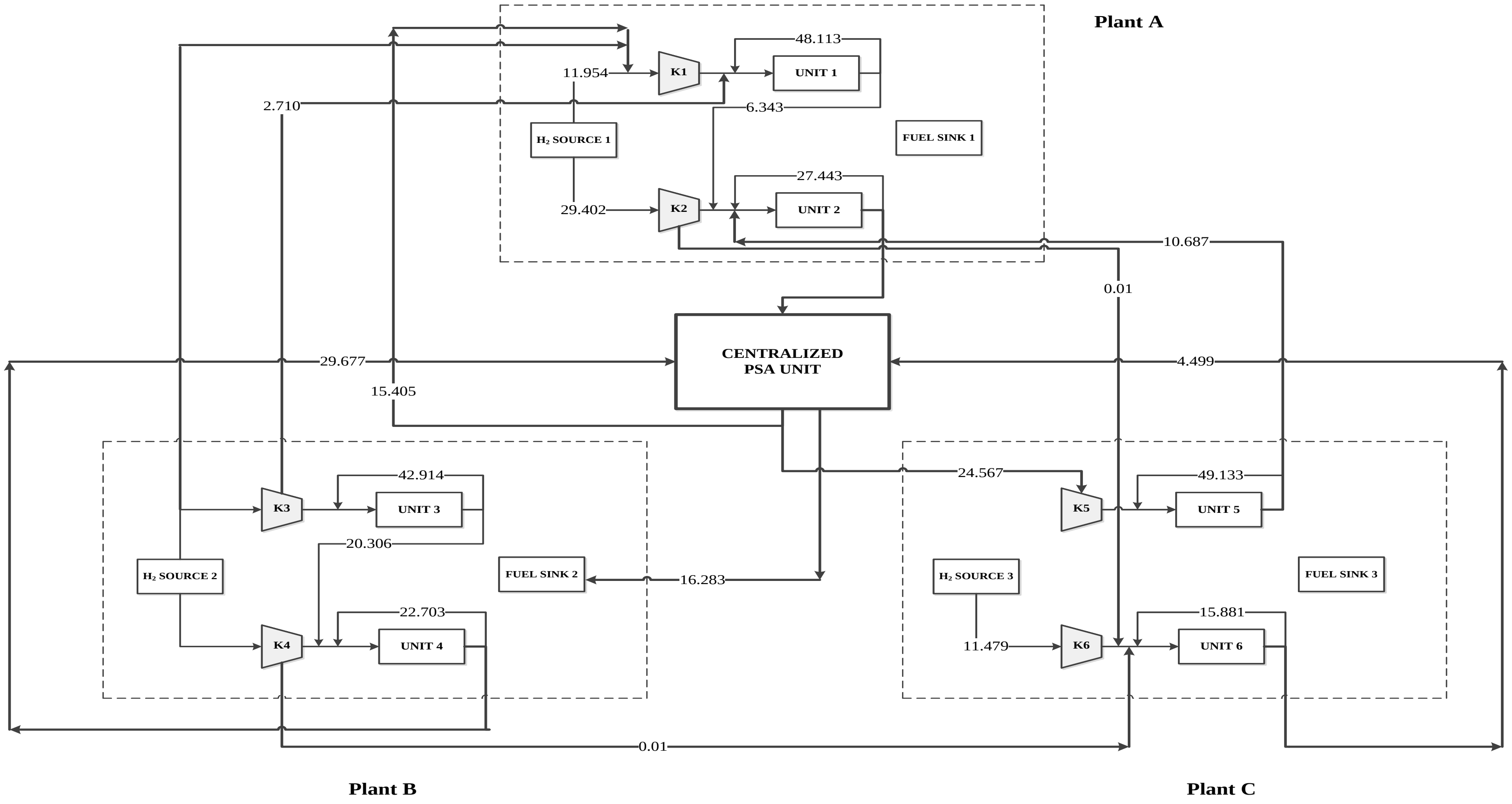


Figure 4.23 Optimized network for indirect integration scheme 3

the direct integration resulted in a large network; the optimized network topology showed that only one purifier unit is enough to manage the entire operation. The optimized network for the case of no integration and direct integration are shown in Figure 4.19 and Figure 4.20 respectively.

Next we consider the indirect integration scheme, where there exists a centralized purification unit through which the refinery interactions take place. We will call this as indirect integration scheme 1. Since the refinery interactions now takes place through a centralized unit, Eq. (4.63) is now included in the model while solving the case for indirect integration. In the first case of indirect integration, all the refineries are connected to only the centralized pressure swing adsorption unit and no connections exist among the refineries. The results show that in comparison to the base case the operational cost and the hydrogen consumption improved by 1681.19 k$/year (1.52% less) and 810 MMscf/year (1.53% less) respectively. The TAC decreased by 1653.59 k$ (1.47% less), whereas the capital cost for the indirect network was 273.94 k$ more than that of the base case. The optimized network for the indirect integration scheme 1 is shown in Figure 4.21.

Next we propose a different indirect integration scheme, called as indirect integration scheme 2, in which the hydrogen producer namely the hydrogen plant is allowed to connect with the other units of the other refineries. Due to the better interactions, the operational cost is further reduced in comparison to the previous indirect integration scheme where no connections exist among the refineries. Compared to the base case, the operational cost reduced by 1782.29 k$/year (1.62% less) and hydrogen consumption by 853.73 MMscf/year (1.60% less). From the solution we observe that the network topology remained the same as that of the previous scheme for the connections going to the centralized purifier unit, but it also showed hydrogen source

Table 4.39 Optimization results for the case study

Cost (k$)	No integration	Direct integration	Indirect scheme 1	Indirect scheme 2	Indirect scheme 3
Hydrogen	106036.150	104236.700	104415.185	104328.315	104269.550
Electricity	4198.960	4171.950	4138.370	4124.500	4121.215
Operational	110235.110	108408.650	108553.920	108452.815	108390.765
Piping	861.508	3421.181	4190.125	4390.770	4634.309
PSA	23512.636	19894.848	20457.954	20315.696	20046.700
Capital	24374.144	23316.029	24648.079	24706.465	24681.010
TAC	112672.261	110739.991	111018.670	110923.608	110858.956
Hydrogen required (MMscf)/year	53018.075	52118.350	52207.775	52164.340	52134.775
Gas sent as fuel (MMscf)/year	6286.595	5926.870	6016.295	5972.860	5943.295

Table 4.40 Computational results for the case study

Case Study	Proposed algorithm					BARON without cuts	
	Global optimum	Solution of Lower bounding problem (LB)	Solution of Upper bounding problem (UB)	Relaxation gap (%)	Time taken by proposed algorithm (s)	Global optimum	Time taken by BARON (s)
Plant A	46311.4	46311.4	46311.4	0	1.6	46311.4	50.5
Plant B	46466.31	46466.31	46466.31	0	1.8	46466.31	75.2
Plant C	19894.54	19894.54	19894.54	0	1.3	19894.54	42.1
Direct integration	110739.99	110725.99	110739.99	0.0126	510.4	-	> 30,000
Indirect integration 1	111018.66	111018.66	111018.66	0	35.1	-	> 30,000
Indirect integration 2	110923.61	110923.61	110923.61	0	44.7	-	> 30,000
Indirect integration 3	110858.95	110844.86	110858.95	0.0127	1403.6		> 30,000

from plant B supplying to the existing compressor in plant A. The optimized network for the indirect integration scheme 2 is shown in Figure 4.22. This shows that an efficient and systematic joint policy making strategies among the participating organizations of the integrated network could play a great role in maximization of resource utilization and also achieve significant cost savings.

We propose another indirect integration scheme, called as indirect integration scheme 3, in which all the generalized sources in all the plants are allowed to interact with all the sinks and at the same time interactions could also take place through centralized pressure swing adsorption unit. Evidently due to increased interactions among the plants, the TAC, operational cost and hydrogen consumption for this case was better than that of the other indirect integration schemes. Table 4.39 gives a detailed comparative study among the direct, indirect and base case. It was observed from the optimization results in Table 4.39 that all schemes of integration (both direct and indirect) offers better cost savings when compared to the case when there is no integration among the plants (base case). From the results we also observe that the direct integration offers better cost savings in comparison to the indirect integration. The optimized network for the indirect integration scheme 3 is shown in Figure 4.23. Moreover due to the integration, there is also a better utilization of the gas circulating within the overall network. This results in reduced energy consumption which is evident from the electricity cost due to compression. Another important and pivotal significance of the network integration is that the quantity of gas going to the fuel gas (flare) as unutilized gas is less when the networks are integrated in comparison to the base case when the networks are not integrated.

Similar to the previous section, all the problems were solved to global optimality using the specialized outer approximation algorithm. The computational results for all the cases considered in the integration of networks are given in Table 4.40. GAMS 23.7/CPLEX was used for solving the MILP problems and GAMS 23.7/BARON for solving NLP problems. When solving the lower and upper bounding problem within the algorithm using GAMS 23.7/CPLEX and GAMS 23.7/BARON respectively, the optimality tolerance was set to zero. All the computations were done using a Dell Optiplex GX620 PC with Intel Pentium 4 processor having 3 GHz speed and 2GB memory running Windows XP Professional 32-bit operating system, except for the case of indirect integration 3 and direct integration which was solved using Dell Precision T7400 Workstation with Intel Xeon processor having 3.4 GHz speed and 64 GB memory running Windows 7 Enterprise 64-bit operating system because of their huge model sizes.

Experiments were also done by solving these problems to local optima by using local solvers. In this regard GAMS 23.7/DICOPT and GAMS 23.7/SBB were used to solve these problems. On locally optimizing the individual networks for plants A, B and C, the solutions (TAC) obtained by GAMS 23.7/SBB were 20451.41 k$/year, 46834.24 k$/year and 46476.25 k$/year. Also in the case of indirect integration scheme 1, the solution obtained by GAMS 23.7/DICOPT was 111186.66 k$/year. All the above costs represent an overestimated value for the total annualized cost. The design of hydrogen networks based on such an overestimation costs not only represent the increased cost, but also may have other effects such as increased production of hydrogen for the entire system, more energy consumption of the overall network and also increased gas going unutilized and more generation of waste material in the network resulting in more drastic environmental effects. This further demonstrates the need to solve such network optimization problems to global optimality.

4.9 Conclusion

A superstructure based mathematical optimization approach is used for solving hydrogen network problems involving retrofit. This model was also solved to global optimality using the specialized outer approximation algorithm with specified tolerance. Piecewise linear relaxation scheme with bivariate partitioning was used to underestimate the nonconvex bilinear terms arising in the model. In the first part of the chapter, this algorithm was used to solve some example problems. In the second part of the chapter, this optimization model was modified to account for inter-plant hydrogen network synthesis. Different integration schemes were studied and results were analysed. These were solved to global optimality using the specialized outer approximation algorithm similar to that in the first part of the chapter. The results show that significant cost savings could be achieved in the case of integrated networks in comparison to the individual networks optimized separately.

5 IMPROVED SYNTHESIS OF HYDROGEN NETWORKS

5.1 Introduction

In this chapter, we will be highlighting some of the drawbacks that we had observed in the works relating to the hydrogen network and will be trying to address some aspects of the same. In most of the previous works in the area of refinery hydrogen network, along with our work in chapter 4, only the effect of pressure is considered while designing a hydrogen network. The effect of temperature on the refinery hydrogen network model seems to be almost neglected. A typical refinery may have many processing units and significant variations could exist in the operating temperature of these units. This could necessitate heating or cooling of gas streams within the network, and the cost associated with such heating and cooling of streams may sometimes become substantial, requiring it to be included in the operating cost of the network. Hence making the model non-isothermal along with non-isobaric may represent a more generalized and realistic representation of the hydrogen network. Many of the previous works though have discussed the usage of valve in the hydrogen network for pressure reduction; it has not been explicitly modeled into the network formulation superstructure. Moreover including the equations representing valves in the model along with considering the effect of temperature in the hydrogen network, in addition to increasing the challenge involved in formulating the model, could also have complexity associated with given the property of the hydrogen gas. Sufficiently pure hydrogen gas may undergo a heating effect when expanded through a valve because of its negative inversion temperature. Such process related intricacy also needs to be considered when trying to depict a more generalized formulation. The fuel gas system, which happens to be one of the entities of the refinery hydrogen network, serves to merely receive the unutilized gas streams circulating within the network according to some previous works in the literature. On investigating some recent works on the fuel gas network, it was shown that the fuel gas sinks in the form of equipments like gas turbines, boilers, flares, fired heaters, incinerator etc. may have specific temperature, pressure and quality specification associated with them. Hence it may necessary to include these requirements when considering the inclusion of fuel gas system into the hydrogen network model formulation. Thus in this chapter, as mentioned earlier, the focus will be to develop a model of refinery hydrogen network which may overcome some of the above mentioned issues and represents a more realistic description of the refinery hydrogen networks. In this chapter, we propose a nonconvex NLP model for the hydrogen network which includes the conditioning units such as heater, cooler, compressor and valve along with the other conventional hydrogen network ingredients such as the hydrogen sources, processing units, purification units and the fuel gas sinks.

The outline of this chapter is as follows. We first define the problem statement, where we introduce the problem of refinery hydrogen network for the model proposed above. This is then followed by the description of the mathematical model formulation. Finally, we solve some case studies to illustrate the usefulness of the proposed model.

5.2 Problem Statement

A typical refinery hydrogen network consists of I sources $(i = 1, 2, \dots, I)$, M processing units $(m = 1, 2, \dots, M)$, N purification units $(n = 1, 2, \dots, N)$ and J fuel gas sinks $(j = 1, 2, \dots, J)$. In addition, it has conditioning units such as valves, heaters

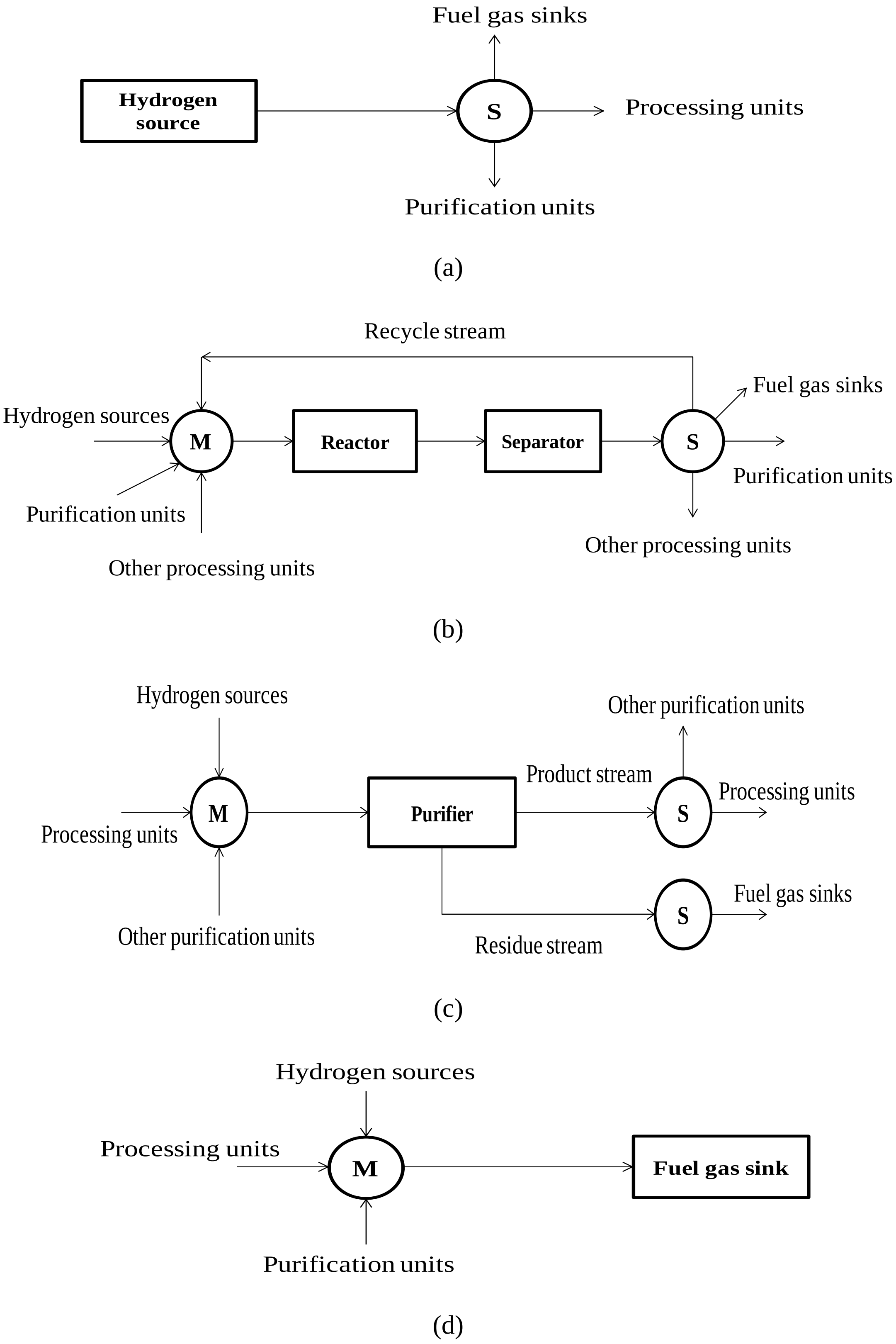


Figure 5.1 Schematic diagram of different processing units in a hydrogen network. (a) Hydrogen source (b) Processing unit (c) Purification unit (d) Fuel gas sink

compressors and coolers that bring the network streams to their desired conditions of pressure and temperature. Figure 5.1 shows the schematic representation of various units in hydrogen network. Entities M and S in Figure 5.1 represent a mixer and a splitter respectively.

A source is any supplier of hydrogen gas to the network. While a refinery may import hydrogen from an external supplier, a typical refinery may have its own plant to produce hydrogen. Steam Methane Reforming (SMR) unit is one such example, but other methods of hydrogen production include steam naphtha reforming and partial oxidation of natural gas. In addition to plants that specifically produce hydrogen, other units in a refinery may also produce hydrogen-containing streams. Catalytic Reforming Unit (CRU) is an excellent example. All these units and suppliers constitute the I sources ($i = 1, 2, \dots, I$), and we assign a unique price to the hydrogen stream from source i. A source can supply hydrogen to any of the processing, purification, or fuel gas sink units.

A processing unit ($m = 1, 2, \dots, M$) is any unit that needs hydrogen as a reactant. Hydrotreaters, hydrocrackers, isomerizers, and olefin saturators are the typical processing units in a refinery. We model each processing unit via a series of four units as shown in Figure 5.1. The first unit is a mixer. It combines the various hydrogen inputs to the processing unit to make a single feed stream. These inputs may include the recycle streams from the processing units including itself, purified hydrogen streams from the purification units described later, and streams from the hydrogen sources described earlier. The mixer feeds this single stream to the second unit called the reactor. The reactor uses the hydrogen from the feed stream to produce various products and byproducts. Since it may receive excess hydrogen, some hydrogen may remain unconverted and hence may exit the reactor. This could be recycled back to the reactor or sent to another processing or purification unit. The output from the reactor goes to a separator. The separator recovers all of the unreacted or unutilized hydrogen from other reactor products. The separator may produce two or more product streams, but we ignore the stream that does not have hydrogen, and consider only the one with hydrogen. We assume that the purity of this hydrogen-containing stream is known. This stream enters a splitter that may distribute this stream to various units as follows. First, it may send a portion to one or more processing units including its own unit. Second, it may purge a portion to one or more fuel gas sinks. Last, it may send a portion for upgrade to one or more purification units. We also demand that the reactor feed (mixer output) must meet some known specifications in terms of flow, hydrogen purity, pressure, temperature, and other properties. Similarly, the separator output (splitter input) also has some known specifications on flow, purity, temperature, and pressure.

A purification unit ($n = 1, 2, \ldots, N$) in the refinery hydrogen network purifies or upgrades a stream with low hydrogen content to a higher purity. The most common purification units in a refinery use pressure swing adsorption or membrane separation. Other techniques such as cryogenic separation are rarely used in practice. We assume that the purification units may not all exist in the refinery. Some may exist, and some may need to be installed as part of the network synthesis. Thus, we allow the refinery to have at most N purification units. As we did for the processing units, we model each purification unit to comprise four units, namely feed mixer, purifier, hydrogen splitter, and residue splitter. The feed mixer combines the low-purity streams from various entities of the hydrogen network. These inputs can be from various hydrogen sources, processing units, and other purification units, and feeds that to the separator. The purifier separates this single feed into two outlet streams called raffinate (hydrogen-rich or hydrogen stream) and extract (hydrogen-lean or residue stream). The hydrogen (residue) stream goes to the hydrogen (residue) splitter. The hydrogen splitter distributes its output to the processing units and other purification units. Since the residue stream is low in hydrogen, the residue splitter distributes it to various fuel gas sinks. Clearly, the purifiers may demand their feeds to have flows, temperatures, and pressures in some desired ranges. For a given purifier, the outlet purities may depend on feed purity, but we assume that each purifier recovers a fixed fraction of hydrogen in the hydrogen stream and produces a hydrogen stream with fixed purity. This fixes the amount and purity of the residue stream automatically. We allow the temperatures and pressures of the two outlet streams to vary within some ranges, but assume that the residue (hydrogen) is the low (high) pressure stream.

We define a fuel gas sink ($j = 1, 2, \ldots, J$) as any unit in the refinery that can consume or dispose a gas with some acceptable calorific value. In the hydrogen network, it serves as the destination for any unutilized stream. Typical examples for fuel gas sinks are turbines, boilers, furnaces, incinerators, and flares. Some of these such as the boilers, turbines, and furnaces may produce heat, steam, and power, whereas the others such as flare and incinerator simply burn the gases into the atmosphere. We model each sink to have a mixer followed by a consumer. The mixer receives inputs from various hydrogen sources, processing units, and purification units (residues only) and combines them to make a feed stream for the consumer with some given specifications[117] of flow, purity, density, contaminants, pressure, temperature, and calorific value. The possible outputs from the consumer are power and steam, whose economic values will reduce the overall cost of the hydrogen network.

Lastly, a conditioning unit is a unit that changes the temperature or pressure of a stream circulating within the hydrogen network. We allow four types of conditioning units. Valves and compressors change pressure, and heaters and coolers change temperature. These units are essential in a hydrogen network, because the various gaseous streams must flow from one unit to another. The temperatures and pressures of these units can vary significantly in a refinery. As described earlier, all units (processing, purification, and sinks) demand certain specifications from their feeds in terms of purity, flow, temperature, pressure, and other variables. Thus, conditioning of streams at various points in the hydrogen network is a must, and cannot be ignored in economic optimization. While the previous work on hydrogen networks has included the compressors due to their high costs, they did not include heaters, coolers, or valves. While valves may not cost much, they do significantly impact the temperature of a gas stream due to the Joule-Thomson expansion effect. Temperatures can vary much in a refinery, and exchanger costs can be significant for gaseous streams. Thus, we believe that it is essential to include all four units (valve, compressor, heater, and cooler) for a more realistic synthesis of hydrogen network. We assume that every possible flow stream in the network may require a separate set of conditioning units, thus one or more of the four units may exist.

With the above understanding, we now state the hydrogen network synthesis problem as follows.

Given:

1. I hydrogen sources $(i = 1, 2, \dots, I)$ with known flows, temperatures, pressures, and purities.
2. M processing units $(m = 1, 2, \dots, M)$ with known bounds on the flows, temperatures, pressures, and purities of the feed and outlet streams, known per pass conversion of hydrogen, and known purity of the hydrogen stream of the outlet hydrogen stream.

3. At most N purification units $(n = 1, 2, \dots, N)$ with known recoveries of hydrogen, known purities of the residue and hydrogen streams, and known ranges of pressures, temperatures, and flows for the feed, residue, and hydrogen streams.
4. J fuel gas sinks $(j = 1, 2, \dots, J)$ with known ranges of the flows pressures, temperatures, purity, and quality of the feeds.
5. CAPEX and OPEX data on the conditioning units.
6. OPEX for each purification unit, and economic returns from using hydrogen in each fuel gas sink.

Determine:

1. Amount of hydrogen required by the overall refinery.
2. Structure of the hydrogen network with flows, purities, temperatures, and pressures at all points and units.
3. Existence and duties of all conditioning units.

Aiming to minimize the total annualized cost (TAC) of the hydrogen network

We include three components in TAC. The first is the annualized capital expenditure (CAPEX) of the entire network, which includes the capital costs of all conditioning units, purification units, and transfer lines. The second is the operating expenditure (OPEX), which consists of the cost of hydrogen sourcing and the operating costs of the purification units, fuel gas sinks, and conditioning units. The third is the costs/savings due to the use of hydrogen in the fuel gas sinks.

Assuming:

1. All network streams are gaseous binary mixtures of hydrogen and inert. As mentioned in the previous chapter, the inert could represent any hydrocarbon gas. In this chapter, we consider the other gas to be methane for the purpose of evaluation of gas stream properties.

2. All parameters and data are deterministic with no uncertainty.
3. All compression processes are single-stage and adiabatic.
4. All expansions are Joule-Thompson expansions; only valves are used for expansions and not expander turbines.
5. Zero pressure drops in heaters, coolers, and transfer lines.

5.3 Model Formulation

Figure 5.2 shows our proposed superstructure for the refinery hydrogen network. Since a source may feed any of the processing, purification, or fuel sink units, it may split its outlet stream into $M + N + J$ streams. Similarly, the splitter of each processing unit also generates $M + N + J$ streams. The hydrogen stream from a purification unit splits into $M + N - 1$ streams, and the residue stream into J streams for J fuel gas sinks. Lastly, each fuel gas sink may receive $M + N + I$ streams from various units.

Each transfer stream between two units in the superstructure may have one or more conditioning units, namely heater, cooler, compressor, or valve. In addition to the existence of these units, their sequence is also important. As argued by Jagannath et al.[117] we assume their sequence to be cooler, valve, compressor, and heater. Since both valve and compressor cannot exist on a stream, the issue of their order is mute. Thus, we keep them together with valve followed by compressor. To ensure that the compressor uses the least energy, we try to minimize its feed temperature by placing cooler before the compressor (valve). Finally, we place the heater at the end to adjust the final stream temperature.

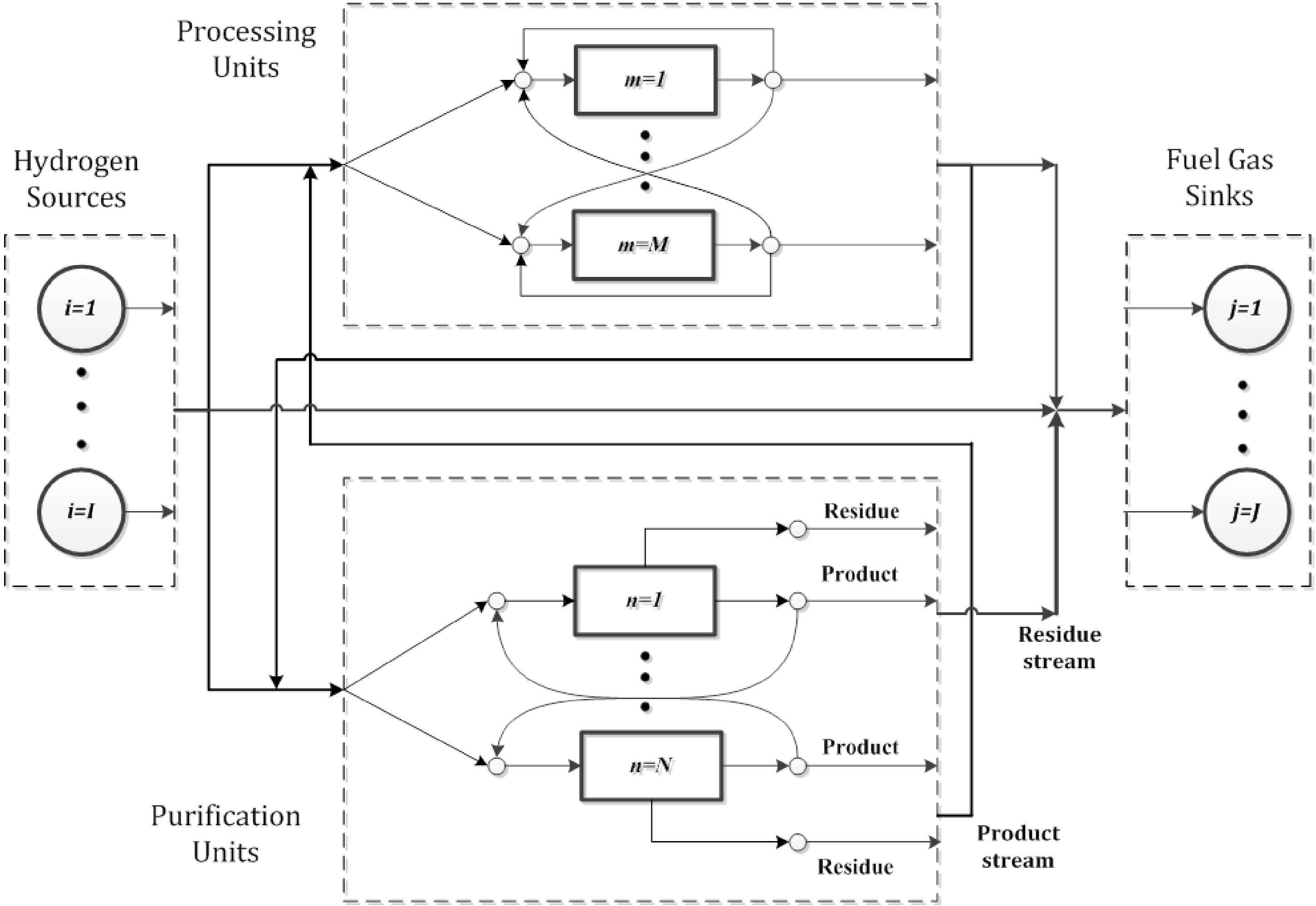


Figure 5.2 Superstructure of a hydrogen network

With the above discussion and superstructure as our basis, we now develop the model that describes the synthesis of a refinery hydrogen network. We begin with flow balances.

5.3.1 Flow Balances

We consider all flows to be in tonne/h, and define purity as the weight fraction of hydrogen in a stream.

For each hydrogen source $(i = 1, 2, \ldots, I)$, we define the following:

F_i : Total gas flow from source i $(F_i^L \leq F_i \leq F_i^U)$

z_i : Weight fraction of hydrogen in the supply from source i

F_{im} : Gas flow from source i to processing unit m

F_{in} : Gas flow from source i to purification unit n

Then, the mass balance for source i is given by,

$$F_i = \sum_{j=1}^{J} F_{ij} + \sum_{m=1}^{M} F_{im} + \sum_{n=1}^{N} F_{in} \tag{5.1}$$

For a source (e.g. SMR or external supplier) with flexible supply, we assign appropriate bounds $(F_i^L \leq F_i \leq F_i^U)$ based on availability. For a source with fixed supply, we set $F_i^L = F_i = F_i^U$.

For each processing unit $(m = 1, 2, \ldots, M)$, we define:

F_m : Feed flow entering processing unit m $(F_m^L \leq F_m \leq F_m^U)$

$F_{m'm}$: Flow from processing unit m' to processing unit m

F_{nm} : Flow from purification unit n to processing unit m

F_{mj} : Flow from processing unit m to fuel gas sink j

F_{mn} : Flow from processing unit m to purification unit n

$F_{mm'}$: Flow from processing unit m to unit m'

x_m : Purity of the feed entering processing unit m $(x_m^L \leq x_m)$

y_m : *Known* purity of the hydrogen stream exiting processing unit m

α_m : Fraction of hydrogen that leaves with the hydrogen stream exiting processing unit m

yp_n : *Known* purity of hydrogen stream from purification unit n

Then, the overall mass and hydrogen balances for each processing unit m are:

$$F_m = \sum_{i=1}^{I} F_{im} + \sum_{n=1}^{N} F_{nm} + \sum_{m'=1}^{M} F_{m'm} \tag{5.2}$$

$$\begin{aligned} &\alpha_m\left(\sum_{i=1}^{I} F_{im} z_i + \sum_{n=1}^{N} F_{nm} yp_n + \sum_{m'=1}^{M} F_{m'm}\, y_m\right) \\ &\qquad = y_m\left(\sum_{j=1}^{J} F_{mj} + \sum_{n=1}^{N} F_{mn} + \sum_{m'=1}^{M} F_{mm'}\right) \end{aligned} \tag{5.3}$$

$$y_m\left(\sum_{j=1}^{J} F_{mj} + \sum_{n=1}^{N} F_{mn} + \sum_{m'=1}^{M} F_{mm'}\right) \geq \alpha_m x_m^L F_m \tag{5.4}$$

For each purification unit ($n = 1, 2, \dots, N$), we define:

F_n : Feed flow into purification unit n ($F_n^L \leq F_n \leq F_n^U$)

$F_{n'n}$: Total flow from purification unit n' to purification unit n

F_{nj} : Flow of residue stream from purification unit n to fuel gas sink j

F_{nm}: Total flow from purification unit n to processing unit m

yr_n : Purity of residue stream from purification unit n

r_n : Recovery of hydrogen in purification unit n

Then, the mass balance equations for each purification unit n are:

$$\sum_{i=1}^{I} F_{in} + \sum_{m=1}^{M} F_{mn} + \sum_{\substack{n'=1 \\ n'\neq n}}^{N} F_{n'n} = \sum_{m=1}^{M} F_{nm} + \sum_{\substack{n'=1 \\ n'\neq n}}^{N} F_{nn'} + \sum_{j=1}^{J} F_{nj} \tag{5.5}$$

$$r_n\left(\sum_{i=1}^{I} F_{in} z_i + \sum_{m=1}^{M} F_{mn} y_m + \sum_{\substack{n'=1 \\ n'\neq n}}^{N} F_{n'n}\, yp_n\right) = yp_n\left(\sum_{m=1}^{M} F_{mn} + \sum_{\substack{n'=1 \\ n'\neq n}}^{N} F_{nn'}\right) \tag{5.6}$$

$$(1 - r_n)\left(\sum_{i=1}^{I} F_{in} z_i + \sum_{m=1}^{M} F_{mn} y_m + \sum_{\substack{n'=1 \\ n'\neq n}}^{N} F_{n'n}\, yp_n\right) = yr_n\left(\sum_{j=1}^{J} F_{nj}\right) \tag{5.7}$$

For each fuel sink ($j = 1, 2, \dots, J$), we define:

F_j : Total gas flow into fuel sink j

x_j : Purity of gas into fuel sink j ($x_j^L \leq x_j \leq x_j^U$)

Then, the mass balance equations for fuel sink j are:

$$F_j = \sum_{i=1}^{I} F_{ij} + \sum_{m=1}^{M} F_{mj} + \sum_{n=1}^{N} F_{nj} \tag{5.8}$$

$$F_j x_j^L \leq \sum_{i=1}^{I} F_{ij} z_i + \sum_{m=1}^{M} F_{mj} y_m + \sum_{n=1}^{N} F_{nj} yr_n \leq F_j x_j^U \tag{5.9}$$

As discussed by Hasan et al.[12] and Jagannath et al.[117] feed to a fuel gas sink may need to satisfy some quality specifications on lower heating value, specific gravity, gas composition, density, etc. For the sake of simplicity in this work, we consider a specification on purity ($x_j^L \leq x_j \leq x_j^U$) only as in Eq. (5.9).

5.3.2 Pressures and Temperatures

Pressures and temperatures of streams in a hydrogen network will vary or change from point to point. For a gas, these two changes are inseparable, and hence must be addressed in tandem. Unlike previous studies that ignored temperature changes, and considered limited pressure changes, we allow both these to vary across the network. These changes will be more critical along the transfer lines supplying to various units that may demand certain feed quality in terms of pressures and temperatures. Clearly, we must write the constraints describing these changes for each transfer line in the network, such as from source to processing unit, from processing unit to purification unit, etc. Because all transfer lines in the present network have the same superstructure of the conditioning units, we write down these constraints for a generic transfer line.

Consider a transfer line (SS_{pq}) that moves gas from an origin unit p ($p = 1, 2, \dots, P$) to a destination unit ($q = 1, 2, \dots, Q$). Here, an origin (destination) unit represents any unit in the hydrogen network, which has a product (feed) stream. While hydrogen sources, processing units, and purification units are the possible origin units, fuel gas sinks, processing units, and processing units are the possible destination units. Let T_p ($T_p^L \leq T_p \leq T_p^U$) and P_p ($P_p^L \leq P_p \leq P_p^U$) be the temperature and pressure of the stream, as it exits origin unit p; and T_q ($T_q^L \leq T_q \leq T_q^U$) and P_q ($P_q^L \leq P_q \leq P_q^U$) be the same, when it reaches its destination unit q. These temperatures/pressures may change along the transfer line due to the conditioning units, if any.

Jagannath et al.[117] have presented the constraints describing the changes in temperature and pressure of a gas stream along a transfer line that is similar to SS_{pq}. Hasan et al.[12] and Jagannath et al.[117] modeled the change in temperature (T_{pq}, $T_{pq}^L \leq T_{pq} \leq T_{pq}^U$) along SS_{pq} in terms of a variable, $H \equiv FCT$, as that reduces model nonlinearity. Here, F is the gas flow, T is the temperature, and C is an average constant specific heat. Using their constraints, we write the following for SS_{pq}.

$$H_{pq} = C_{pq}T_pF_{pq} - \Delta H_{pq}^C - \Delta H_{pq}^V + \Delta H_{pq}^B + \Delta H_{pq}^H \tag{5.10}$$

$$C_{pq}T_pF_{pq} - \Delta H_{pq}^C - \Delta H_{pq}^V \geq C_{pq}T_{pq}^LF_{pq} \tag{5.11}$$

$$H_{pq} \leq C_pT_{pq}^UF_{pq} \tag{5.12}$$

$$\Delta H_{pq}^V \geq \mu_{pq}C_{pq}F_{pq}(P_p - P_q) \tag{5.13}$$

$$\eta\Delta H_{pq}^B \geq (C_{pq}T_pF_{pq} - \Delta H_{pq}^c)\left[\left(\frac{P_q}{P_p}\right)^{n_{pq}} - 1\right] \tag{5.14}$$

where, ΔH_{pq}^B is the change in H during compression along SS_{pq}, ΔH_{pq}^H is the change during heating, ΔH_{pq}^C is the change during cooling, and ΔH_{pq}^V is the change during expansion. Furthermore, n_{pq} and μ_{pq} are the adiabatic index and average Joule-Thompson coefficient of the stream along SS_{pq}, and η is the efficiency of adiabatic compression. Eqs. (5.10) - (5.12) ensure that the stream temperature remains within allowable bounds of $T_{pq}^L \leq T_{pq} \leq T_{pq}^U$. Eq. (5.13) is for the change in H during expansion through the valve, and Eq. (5.14) is for the change during compression.

Eqs. (5.10) - (5.13) are valid only for a positive Joule-Thompson coefficient. In gas streams involving hydrogen, this coefficient can be negative under certain conditions. Therefore, we need the following in place of Eq. (5.10), (5.11), and (5.13), when μ_{pq} is negative.

$$H_{pq} = C_{pq}T_pF_{pq} - \Delta H_{pq}^C + \Delta H_{pq}^V + \Delta H_{pq}^B + \Delta H_{pq}^H \tag{5.10a}$$

$$C_{pq}T_pF_{pq} - \Delta H_{pq}^C \geq C_{pq}T_{pq}^LF_{pq} \tag{5.11a}$$

$$\Delta H_{pq}^V \geq -\mu_{pq}C_{pq}F_{pq}(P_p - P_q) \tag{5.13a}$$

An additional problem that arises in case of negative μ_{pq} is that the optimizer tends to make (Eq. 5.13) lose, and increases ΔH_{pq}^V at the expense of other positive terms in Eq.(5.10). For this, we use the following, which was not needed in Jagannath et al.[117]

$$\Delta H_{pq}^V.\Delta H_{pq}^B \leq 0 \tag{5.15}$$

When streams coming from different origin units are mixed to form a feed for a destination unit q, Eqs. (5.10) - (5.15) ensure that they all mix at the same pressure, which is P_q. However, the temperature (T_q) of the feed to unit q will be determined by the temperatures of all streams that enter the feed mixer at unit q. Each unit q may demand T_q to be within certain acceptable limits, namely T_q ($T_q^U \leq T_q \leq T_q^L$). To ensure these limits, we use the following constraint.

$$T_q^L \sum_{p=1}^{P} C_{pq}\, F_{pq} \leq \sum_{p=1}^{P} H_{pq} \leq T_q^U \sum_{p=1}^{P} C_{pq}\, F_{pq} \tag{5.16 a,b}$$

Eq. (5.16 a,b) must be written for each possible destination unit, i.e. for each processing, purification, and fuel sink unit.

5.3.3 Total Annualized Cost (TAC)

We use minimum TAC as the objective for our network synthesis model. It involves the following costs. (1) Cost of hydrogen supplies (2) CAPEX and OPEX costs of purification units (3) OPEX for fuel gas sinks (4) CAPEX and OPEX of transfer lines and conditioning units. We use the following to compute TAC:

1. The price of hydrogen from source i is c_i, which is normally positive for on-purpose hydrogen producers and external hydrogen suppliers, and zero for in-house hydrogen producers like the catalytic reforming unit. The network may or may not consume all the gas available from a source.
2. Processing units have no costs that are meaningful for the hydrogen network.
3. The OPEX and CAPEX of a purification unit are linear functions of its feed gas flow with coefficients a_n and b_n respectively. If a unit already exists, then $a_n = 0$.
4. Fuel gas sinks have no CAPEX, but only OPEX. The latter consists of two parts. The first part is the cost of running the sink, which is a linear function of the total into the sink. This is zero for sinks that produce energy, such as gas turbine, boiler, heater, etc., but positive for disposal sinks such as flare or incinerator. The second part is the economic value or surplus revenue generated by using hydrogen in a sink. This is negative for sinks such as boiler, turbine, and heater, and a linear function of the flow of hydrogen (versus total) into the sink.
5. The CAPEX and OPEX of each transfer line are linearly proportional to the total gas flow through the line.
6. The CAPEX and OPEX of a valve are linearly proportional to $\frac{\Delta H_{pq}^{V}}{(|\mu_{pq}|C_{pq})}$, which is essentially the product of flow and pressure drop.
7. The CAPEX and OPEX of heaters, coolers, and compressors are linearly proportional to their respective ΔH–variables.

8. The TAC of the hydrogen network is given by $TAC = AF * CAPEX + OP * OPEX$, where OP represents the operating hours of a refinery/plant in a year and AF is the annualization factor.

Thus, we write TAC as,

$$TAC = AF\left[\begin{array}{c} \sum_{n=1}^{N} a_n \left(\sum_{i=1}^{I} F_{in} + \sum_{m=1}^{M} F_{mn} + \sum_{\substack{n'=1 \\ n' \neq n}}^{N} F_{n'n} \right) + \\ \sum_{p=1}^{P} \sum_{q=1}^{Q} \left[\begin{array}{c} CAPEX_{pq}^{T} F_{pq} + CAPEX_{pq}^{V} \frac{\Delta H_{pq}^{V}}{(|\mu_{pq}| C_{pq})} + CAPEX_{pq}^{B} \Delta H_{pq}^{B} \\ + CAPEX_{pq}^{H} \Delta H_{pq}^{H} + CAPEX_{pq}^{C} \Delta H_{pq}^{C} \end{array}\right] \end{array}\right] +$$

$$OP\left[\begin{array}{c} \sum_{i=1}^{I} c_i F_i + \sum_{n=1}^{N} b_n \left(\sum_{i=1}^{I} F_{in} + \sum_{m=1}^{M} F_{mn} + \sum_{\substack{n'=1 \\ n' \neq n}}^{N} F_{n'n} \right) + \\ \sum_{j=1}^{J} \gamma_j F_j - \sum_{j=1}^{J} \beta_j F_j x_j + \\ \sum_{p=1}^{P} \sum_{q=1}^{Q} \left[\begin{array}{c} OPEX_{pq}^{T} F_{pq} + OPEX_{pq}^{V} \frac{\Delta H_{pq}^{V}}{(|\mu_{pq}| C_{pq})} + OPEX_{pq}^{B} \Delta H_{pq}^{B} \\ + OPEX_{pq}^{H} \Delta H_{pq}^{H} + OPEX_{pq}^{C} \Delta H_{pq}^{C} \end{array}\right] \end{array}\right] \tag{5.17}$$

In Eq. (5.17), p represents each possible origin unit, and q represents each possible destination unit. The first CAPEX term is the capital cost of purification units, and the second is that of all transfer lines and their conditioning units (pipeline, valve, compressor, heater, and cooler in that order). The first OPEX term involves the cost of hydrogen from various sources, and the operating cost of purification units. The second gives the operating costs of fuel gas sinks. The third gives the OPEX of all transfer lines and their conditioning units, as in the CAPEX. $a_n, b_n, c_i, \gamma_j, \beta_j, CAPEX_{pq}^{T}, OPEX_{pq}^{T}$, etc. are appropriate cost coefficients.

5.4 Examples

As seen from our model many of the model equations of transfer line SS_{pq} have gas stream property attributes such as specific heat, adiabatic coefficient, Joule-Thompson coefficient present in them. These attributes of gas stream are considered as parameters in our model. These will be dependent on the gas composition, pressure and temperature of the gas within the transfer line. While the gas composition does not change along a transfer line, the temperature and pressure may change due to the conditioning operations such as heating, cooling, expansion and compression. Hence it may not be possible for us to know the temperature and pressure before hand and estimate the gas stream attributes. To circumvent this problem, different approaches could be used. One approach in this regard is to consider the temperature and pressure of the origin of a transfer line. The bounds on the temperature and pressure on the origin is known, from which an average temperature and pressure is chosen. The gas stream attributes could be determined at this temperature and pressure. By doing this we make an assumption that, the gas stream attributes such as specific heat, adiabatic coefficient and Joule-Thompson coefficient does not change along the transfer line with the changes in the temperature and pressure of the gas. The other more realistic approach could be to consider the temperature and pressure of both the origin and destination units of a transfer line. Similar to the previous approach, from the known bounds on the temperature and pressure of both the origin and destination units, an average or mean temperature and pressure could be calculated for the entire transfer line and gas stream attributes can be estimated for this mean temperature and pressure. In this study, Aspen HYSYS was used to obtain the value of different gas stream attributes.

To demonstrate our model, we consider two example problems from a typical refinery which is seeking to set up a hydrogen network for an efficient distribution of hydrogen throughout the whole refinery. All our optimization computations were done using GAMS 23.7 modelling language and the NLP solver used was GAMS 23.7/IPOPT. The model was also solved using other available NLP solvers in GAMS such as GAMS 23.7/BARON, GAMS 23.7/SNOPT and GAMS 23.7/CONOPT. From the solution obtained by solving with the all the above mentioned NLP solvers, the best solution was chosen. All the computations were done using a Dell Optiplex GX620 PC with a processor speed of 3 GHz and 2GB memory.

We assign T_{pq}^{L}=250 K and T_{pq}^{U}=1000 K for all the transfer lines connecting the origin and destination units. The annualization factor chosen for the capital cost is 0.1 and we assume the refinery operating hours to be 8000 hrs. The values of the various cost coefficients used in the objective function are shown in Table 5.1.

5.4.1 Example 1

Consider a refinery which contains one on-purpose Hydrogen Plant (HP) to manage its hydrogen needs. It has a Catalytic Reformer Unit (CRU) which also produces some hydrogen gas as a by-product. These together form the hydrogen sources in a refinery. There are three hydroprocessing units in the refinery which utilize the hydrogen gas. They are the Naphtha Hydrotreater (NHT), Kerosene Hydrotreater (KHT) and Gasoil Hydrotreater (GOHT) with their corresponding fractions (α_m) of hydrogen stream leaving being 0.4338, 0.2 and 0.5015 respectively. The fuel gas sinks in a refinery include the Gas Turbine (GT) and Flare (FL). The maximum flow available from HP is 5 tonne/hr and 0.090 tonne/hr is the flow from the CRU. Table 5.2 gives the purity, temperature and pressure of the origin units in the network namely the hydrogen sources and processing units. No purification unit is considered for this example. Table 5.3 gives the flow, purity, temperature and pressure requirement for the destination units in the network namely processing units and fuel gas sinks. Table 5.4, Table 5.5 and Table 5.6 give the gas stream attributes such as specific heat, Joule-Thompson coefficient and adiabatic coefficient along the transfer line for all origin destination connection respectively. For the calculation of these stream attributes, the temperatures and pressures of both origin and destination units are considered.

The model for this example has 191 continuous variables, 187 constraints and 1102 non-zero elements. A good initial guess was always critical for obtaining the solution to a nonlinear problem, hence we adopted the approach of solving the problems

Table 5.1 CAPEX and OPEX for hydrogen network

Type of Cost	Value
Operational cost (OPEX)	
Hydrogen ($/tonne)	900
Pipeline ($/tonne)	0.04
Compressor ($/kW hr)	0.01
Heater ($/kW hr)	0.002
Cooler ($/kW hr)	0.002
Valve ($/tonne bar)	0.5
Flare/incineration ($/tonne)	0.1
Surplus revenue ($/tonne)	0.075
Purification unit ($/tonne)	5
Capital cost (CAPEX)	
Pipeline ($ hr/tonne)	5000
Compressor ($/kW)	10000
Heater ($/kW)	5000
Cooler ($/kW)	5000
Valve ($ hr/tonne bar)	2500000
Purification unit ($ hr/tonne)	250000

Table 5.2 Parameters for the origin units- Example 1

Origin units	Purity (%)	Pressure (bar)	Temperature (K)
Hydrogen sources			
HP	99	20.7	300
CRU	75	20.7	300
Processing units			
NHT	73	10.0-13.0	300-320
KHT	69	15.0-18.0	300-320
GOHT	62	20.0-25.0	300-320

Table 5.3 Parameters for the destination units- Example 1

Destination units	Flow (tonnes/hr)	Purity (%)	Pressure (bar)	Temperature (K)
Processing units				
HC	0.575	≥ 95.0	15.0-20.0	533-573
DHT	0.750	≥ 86.5	20.0-30.0	573-613
NHT	0.605	≥ 84.2	30.0-40.0	593-623
Fuel gas sinks				
Turbine	≥ 0	≥ 40.0	5.0-10.0	298-400
Flare	≥ 0	0-100	2.0-4.0	298-400

Table 5.4 Specific heat (kJ/tonne K) values for various origin destination transfer line combinations - Example 1

Origin units	Destination units				
	Fuel gas sinks		Processing units		
	Turbine	Flare	NHT	KHT	GOHT
Hydrogen sources					
HP	13960	13950	14060	14100	14110
CRU	11240	11240	11390	11430	11450
Processing units					
NHT	11230	11230	11390	11430	11210
KHT	10530	10530	10690	10740	10750
GOHT	9716	9713	9882	9982	9940

Table 5.5 Joule-Thompson coefficient (K/bar) values for various origin destination transfer line combinations - Example 1

Origin units	Destination units				
	Fuel gas sinks		Processing units		
	Turbine	Flare	NHT	KHT	GOHT
Hydrogen sources					
HP	-0.0001	0.0002	-0.0127	-0.0150	-0.0160
CRU	0.0079	0.0082	-0.0066	-0.0098	-0.0108
Processing units					
NHT	0.0095	0.0098	-0.0057	-0.0087	-0.0097
KHT	0.0111	0.0114	-0.0045	-0.0076	-0.0087
GOHT	0.0146	0.0149	-0.0019	-0.0052	-0.0063

Table 5.6 Adiabatic compression coefficients values for various origin destination transfer line combinations- Example 1

Origin units	Destination units				
	Fuel gas sinks		Processing units		
	Turbine	Flare	NHT	KHT	GOHT
Hydrogen sources					
HP	0.2923	0.2923	0.2898	0.2893	0.2893
CRU	0.2888	0.2888	0.2837	0.2837	0.2837
Processing units					
NHT	0.2883	0.2883	0.2847	0.2837	0.2832
KHT	0.2872	0.2872	0.2832	0.2821	0.2821
GOHT	0.2862	0.2862	0.2806	0.2795	0.2795

successively in GAMS using different solvers. The rationale of doing this is that, the solution provided by any solver would automatically serve as an initial point to the next solver. This would help in finding any better solutions, if any, for the problem. The model then was solved successively in GAMS using the different solvers such as BARON, IPOPT, SNOPT and CONOPT. BARON, IPOPT and SNOPT could not find any feasible solution, but CONOPT gave an objective value of $10,347,802.76 /yr which was the total annualized cost (TAC). This solution was then used to initialize both BARON and IPOPT again to see if any further better solution could be obtained, however, now both BARON and IPOPT converged at the same solution. Thus this was the best solution which we could be obtained by us. The operational cost (OPEX) of the network is $9,389,373.68 /yr and the hydrogen consumption cost is $ 9,354,020.69 /yr. The capital cost (CAPEX) of the network is $9,584,290.75. In order to illustrate the benefits of network optimization of refinery hydrogen network, we consider a base case in which there exists no hydrogen network. In such a case the refinery follows some ad-hoc procedures to manage its hydrogen distribution and to satisfy the demands of its hydrogen consumers. Here we consider a base scenario in which the refinery only uses the pure hydrogen gas feed from the Hydrogen Plant (HP) directly to satisfy the needs in the processing units. Then the refinery would then consume 15,440 tonnes of hydrogen annually which translates into a cost

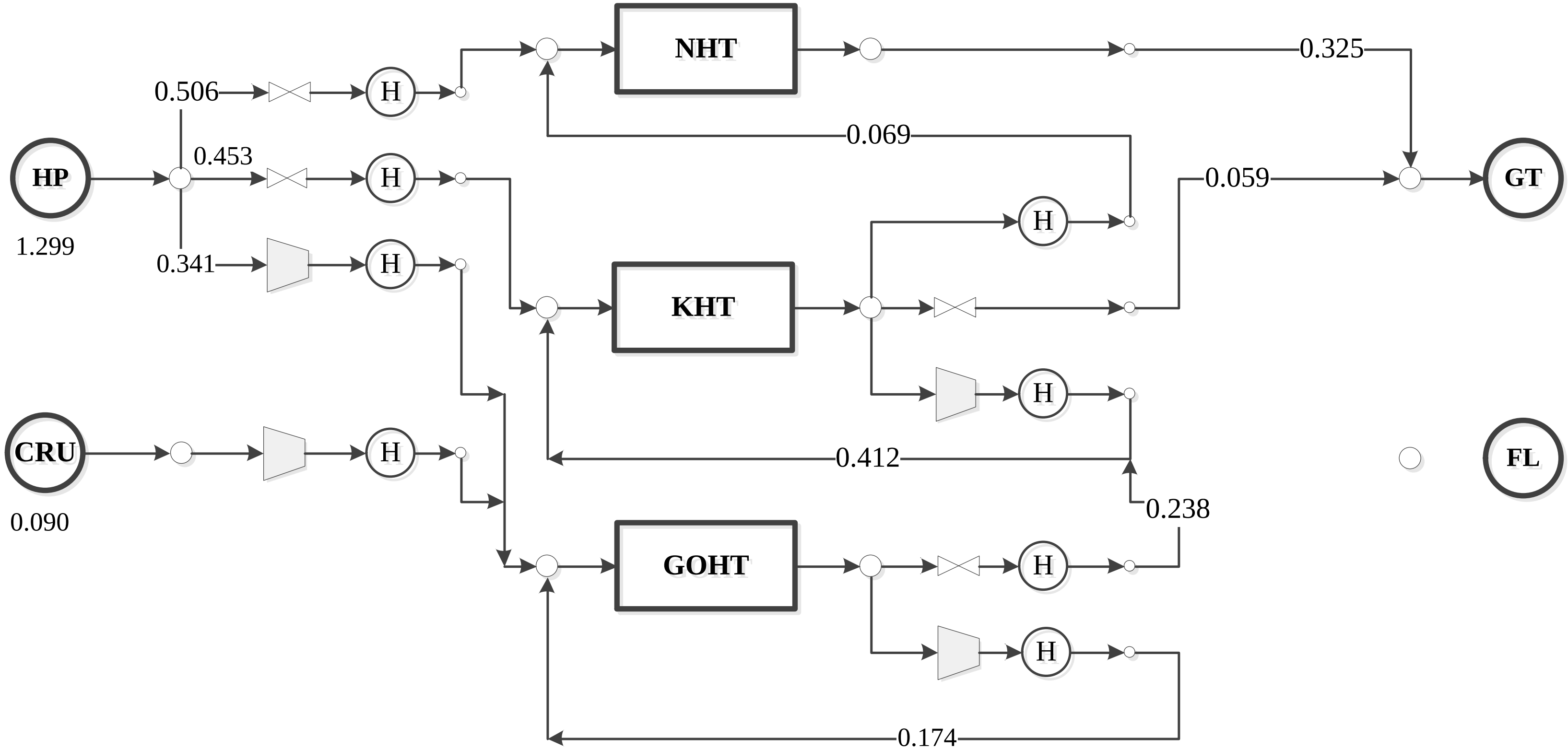


Figure 5.3 Optimal network for Example 1

of \$13,896,000/yr. Meanwhile, the refinery hydrogen network would only consume 10,392 tonnes of hydrogen which is 5048 tonnes (32.7%) lesser than the base case. Since the amount of feed consumption is less, less energy may also be required across the transfer line to distribute comparatively smaller feeds. Other benefit associated with the reduced overall hydrogen feed consumption is that, the emission of carbon dioxide is reduced (as Steam Methane Reforming (SMR) process releases carbon dioxide with the generation of the hydrogen gas). Thus, from this we understand that a well designed refinery hydrogen network could play a tremendous role in promoting sustainable development by integrating energy, economics and environment.

The network optimization of the refinery hydrogen network mixes gas streams in an optimal manner satisfying the demands in terms of flow, purity, temperature and pressure requirements at the hydrogen consumers namely processing units and fuel gas sinks and also minimizing the total cost of the entire operation. From the Figure 5.3, we can see that the stream from a Catalytic Reformer Unit (CRU) is fully utilized within the network and is sent directly to the Gasoil Hydrotreater (GOHT). The Naphtha Hydrotreater (NHT), which has a relatively higher hydrogen purity requirement uses majority of the feed stream from the Hydrogen Plant (HP). Moreover it is also observed from the network that no processing unit completely uses hydrogen gas from the Hydrogen Plant (HP) as the network optimization seeks to utilize the other gases present within the network to minimize hydrogen cost. From the solution we see the presence of a heater in all the transfer line connecting an origin and a destination unit. The capital and the operational cost associated with the heater are \$8,705,774.38 and \$27,858.47 /yr respectively. These substantial cost associated with heating of gas stream may not be known if the effect of the temperature were not considered in the model. This shows one of the usefulness of the present model. The importance of considering the specification of the gas reaching the fuel gas system is also highlighted here. Since the gases reaching the fuel gas sinks were of sufficient quality, these were sent to the gas turbine (GT). Burning the gas in a gas turbine generated surplus revenue of $166.7/yr.

5.4.2 Example 2

In this we consider a relatively larger high conversion refinery which contains five processing units namely Naphtha Hydrotreater (NHT), Kerosene Hydrotreater (KHT), Gasoil Hydrotreater (GOHT), Residue Hydrotreater (RHT) and Hydrocracking unit (HC) with their corresponding fractions (α_m) of hydrogen stream leaving the unit are 0.4338, 0.2, 0.5015, 0.4385 and 0.3080 respectively. The two hydrogen sources of this refinery include an on-purpose Hydrogen Plant (HP) to and a Catalytic Reformer Unit (CRU). Similar to the previous example the maximum flow available from HP is 5 tonne/hr and 0.090 tonne/hr is the flow from the CRU. Unlike the previous example, the refinery may allow for one purification unit in the form of a Pressure Swing Adsorption (PSA). Two gas turbines GT1 and GT2 along with flare (FL) are present in the fuel gas system. Table 5.7 gives the purity, temperature and pressure of the origin units in the network namely the hydrogen sources, processing units and purification units. Table 5.8 gives the flow, purity, temperature and pressure requirement for the destination units in the network namely processing units, fuel gas sinks and purification units. Also for this study, it is assumed that the gas stream attributes in the transfer line will be that of the origin unit itself. Table 5.9 gives the gas stream attributes such as specific heat, adiabatic coefficient and Joule-Thompson coefficient along the transfer line for all origin destination connection.

The model now has 489 continuous variables, 426 constraints and 3045 non-zero elements. IPOPT and SNOPT again failed to produce a feasible solution whereas

Table 5.7 Parameters for origin units- Example 2

Origin units	Purity (%)	Pressure (bar)	Temperature (K)
Hydrogen sources			
HP	99	20.7	300
CRU	75	20.7	300
Processing units			
NHT	73	10.0-13.0	300-320
KHT	69	15.0-18.0	300-320
GOHT	62	20.0-25.0	300-320
RHT	65	25.0-30.0	320-350
HC	60	25.0-30.0	320-350
Purification units			
PSA (Product)	99	20.0-25.0	300-320
PSA (Residue)	-	7.0-10.0	300-320

Table 5.8 Parameters for destination units- Example 2

Destination units	Flow (tonnes/hr)	Purity (%)	Pressure (bar)	Temperature (K)
Processing units				
HC	0.575	≥ 95.0	15.0-20.0	533-573
DHT	0.750	≥ 86.5	20.0-30.0	573-613
NHT	0.605	≥ 84.2	30.0-40.0	593-623
RHT	0.500	≥ 85.0	40.0-50.0	633-653
HC	0.475	≥ 84.0	55.0-65.0	633-653
Fuel gas sinks				
Turbine	≥ 0	≥ 50.0	5.0-10.0	298-400
Flare	≥ 0	0-100	2.0-4.0	298-400
Purification unit				
PSA	≤ 5	-	20.0-25.0	300-330

Table 5.9 Stream attributes along the transfer line - Example 2

Origin units	Specific heat (kJ/tonne K)	Joule-Thompson coefficient (K/bar)	Adiabatic index
Hydrogen sources			
HP	14060	0.0078	0.2948
CRU	9423	0.0280	0.2903
Processing units			
NHT	10950	0.0186	0.2903
KHT	10490	0.0190	0.2903
GOHT	9678	0.0230	0.2898
RHT	10080	0.0137	0.2893
HC	9485	0.0171	0.2883
Purification units	9485		
PSA (Product)	14070	0.0050	0.2948
PSA (Residue)	8216	0.0388	0.2852

BARON gave a local solution of $20,411,842.70. The model then was solved successively in GAMS using the three solvers BARON, IPOPT and CONOPT to see if better solutions could be obtained. CONOPT yielded an optimal solution of $13,210,762.13. Again this was best solution which could be obtained by us. The total annualized cost of the entire refinery was $13,099,318.42, with the operational cost being $11,350,984 /yr and CAPEX being $17,483,370. The hydrogen consumed was $11,260,064 /yr. From the solution, we also observed that a purification unit was required with an operational cost of $12,382.63 /yr and a capital cost of $77391.46. The purification unit consumed purged gas streams from the NHT and KHT and produced a purified stream to the NHT. The residue stream from the purification unit was sent to the fuel gas system. Unlike the previous example, the required fuel gas stream purity at the gas turbine could not be satisfied and hence the gas stream was sent to the flare for disposal. This incurred an additional operational cost of $132 to the refinery. This again demonstrates another feature of our model, which shows the need for the meeting the specification required at the fuel gas sink. The optimized

Table 5.10 Operating conditions for various units in hydrogen network - Example 1

Units	Temperature (K)		Pressure (bar)	
	Inlet	Outlet	Inlet	Outlet
Processing units				
NHT	533	320	18.00	10.00
KHT	573	320	20.00	18.00
GOHT	593	320	30.00	25.00
Fuel gas sinks				
GT	319.9	-	10	-
FL	-	-	-	-

Table 5.11 Operating conditions for various units in hydrogen network - Example 2

Units	Temperature (K)		Pressure (bar)	
	Inlet	Outlet	Inlet	Outlet
Processing units				
NHT	533	300	18.00	13.00
KHT	573	300	20.68	18.00
GOHT	593	320	30.00	25.00
RHT	633	350	40.00	30.00
HC	633	350	55.00	30.00
Fuel gas sinks				
GT1	-	-	-	-
GT2	-	-	-	-
FL	298	-	4.00	-
Purification unit				
PSA	330	300	20.00	20.00
PSA (residue)	-	300	-	7.00

Table 5.12 CAPEX and OPEX for all examples

Type of Cost	Example 1	Example 2
Operating cost ($/yr)		
Hydrogen	9354020.69	11260064.00
Compressor	6917.09	36046.53
Valve	3.70	3.66
Heater	27858.47	41008.92
Cooler	0.00	207.92
Surplus revenue	166.71	0.00
Flare/incineration	0.00	132.10
Pipeline	740.43	1134.34
Purification unit		12382.63
OPEX	9389373.68	11350984.00
Capital cost ($)		
Pipeline	11569.33	17724.10
Compressor	864637.26	4505816.68
Valve	2309.70	2286.34
Heater	8705774.38	12815180.00
Cooler	0.00	64976.47
Purification unit		77391.46
CAPEX	9584290.75	17483370.00
TAC ($/yr)	10347802.76	13210762.13

network for this example is given in Figure 5.3. From the figure, we see that most of the transfer lines have either a heater or cooler associated with them along with a pressure conditioning equipment like a compressor or valve. This again shows the importance of satisfying temperature requirements along with that of the pressure. The stream from the CRU, despite being of low purity, was completely utilized in the HC unit. Conventionally this gas stream would be sent to the fuel gas sinks to be burned in the turbine or would be flared or incinerated. Hence network optimization of hydrogen networks helps in the useful utilization of all the gas stream available within the network. Secondly, all the gas flow out of processing unit was completely

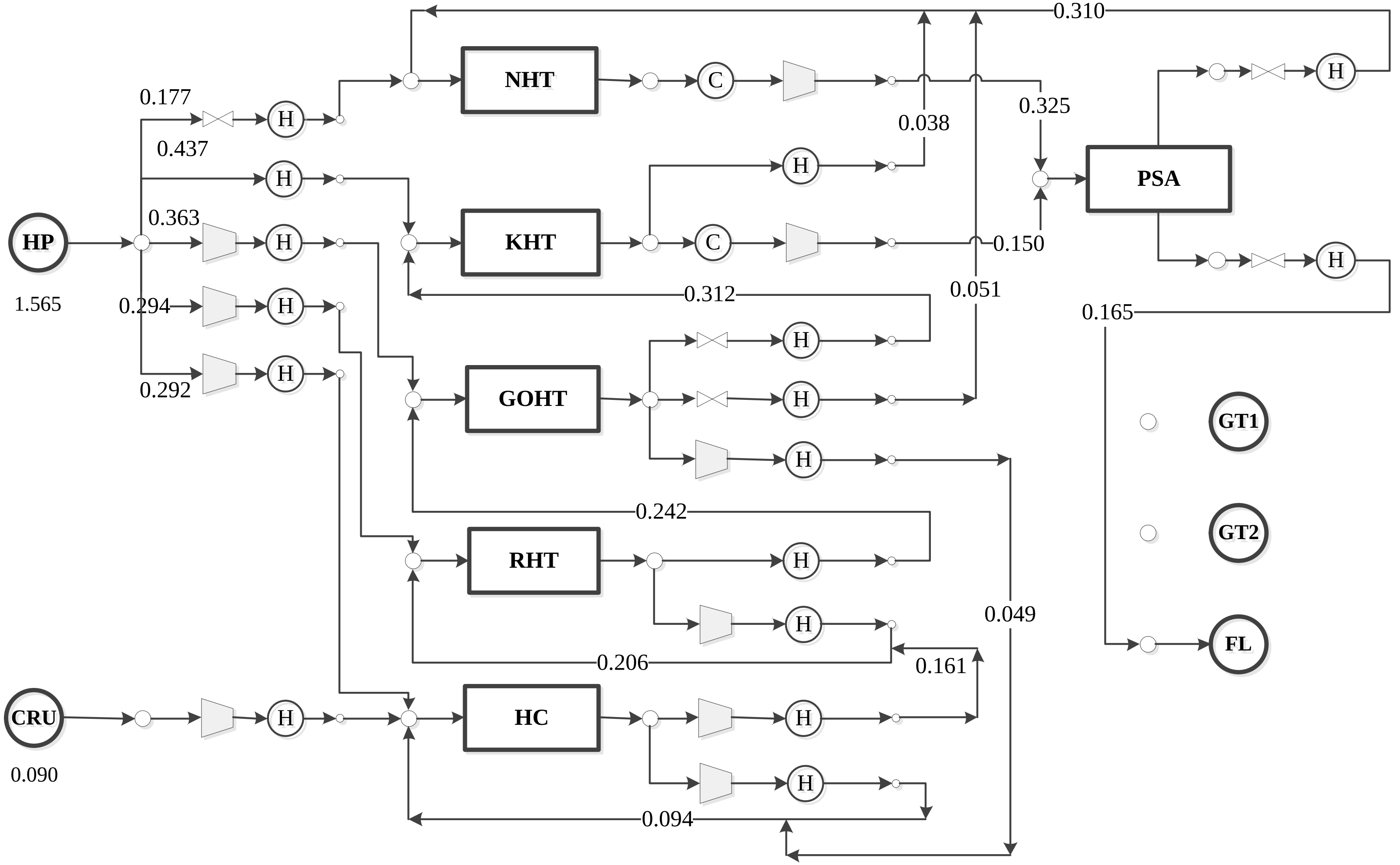


Figure 5.4 Optimal network for Example 2

utilized within the network and none was sent to the fuel gas sinks. Table 5.10 and Table 5.11 show the optimal conditions, in terms of temperature and pressure, for the operation of various units in the hydrogen network for example 1 and example 2 respectively. The capital and operating cost for both the examples are given in Table 5.12.

5.5 Conclusion

In this work, a nonconvex nonlinear programming model for the improved synthesis of hydrogen network was developed. Unlike the other models in the literature which considered the process constraints along with pressure effects, this work also focussed on the effect of temperature as well. Also this work also highlighted the importance of quality requirement at the fuel gas sinks when the unutilized gases from the hydrogen network were sent to the fuel gas system. The issue of location, duty, effect of temperature and pressure and other property related intricacy associated with the gas stream conditioning equipments like the compressor, valve, heater and cooler were also addressed by this model. Two examples were also shown to demonstrate the effectiveness of the model. One limitation of this work is that only locally optimal solutions were obtained, as the underlying model was nonconvex and highly nonlinear. It would be useful in the future to apply some global optimization approaches to this problem, which can guarantee global solutions.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This thesis addresses the issues relating to the modeling and optimization of two important gas networks which are present in a typical refinery namely the fuel gas network and hydrogen network.

The fuel gas network (FGN) in a refinery can save energy and reduce the flaring of impure/waste gas streams by systematically utilizing them. To cater to the changing characteristics of these waste/impure gases as a result of changing modes of refinery operation, a multimode 2-stage stochastic programming model was developed to design and operate a refinery fuel gas network. This multimode model developed utilizes some basic ideas from the literature. Apart from this, some unique features associated with the model include treating fuel gas sources and sinks in a more unified manner, incorporating hydrocarbon penalty and penalty for pollutant emissions, simplified model equations and also coming up with quality specification for the disposal fuel gas sinks like the flare and incinerator. This model developed was applied on a refinery case study. It was shown that the multimode model resulted in reduced capital expenditure of the plant/refinery in comparison to that of single mode model. Moreover flaring was reduced considerably and significant cost savings in hydrocarbon penalty were achieved when this multimode model of fuel gas network was integrated to the refinery compared to the case when no fuel gas network was present in the plant. Apart from this some strategies to reduce flaring in refineries were also studied and analysed such as usage of richer natural gas fuel and usage of flexible sinks for the fuel gas operation.

The next section of the thesis focussed on the modeling and optimization of hydrogen networks in a refinery. The work on the hydrogen network is further divided into two portions (chapter 4 and chapter 5).

In the first portion (chapter 4), a refinery hydrogen network model from the literature was generalized and the resulting nonconvex mixed integer nonlinear program (MINLP) was solved to global optimality, where the reason for nonconvexity was the presence of bilinear terms in the model. Some strategies to solve the model to global optimality such as developing the model in a manner which reduces the number of bilinear terms and developing redundant cuts which greatly strengthens lower bound of the model and accelerates convergence when solved using commercial global solver like BARON was introduced in this study. A specialized outer approximation algorithm was utilized for solving this model to global optimality, where the piecewise linear relaxation technique was used to underestimate the bilinear terms occurring within the model. Several examples were proposed to show the efficacy of the global optimization algorithm in obtaining global or near global solutions in comparison to the conventional global solver BARON. Next in this study, the developed model was extended by considering preliminary integration with the hydrogen network of other refineries. Results showed that the overall hydrogen consumption, operating cost, energy costs due to compression and unutilized gases generated for the overall network was less in comparison to the case when each refinery was optimized individually. Similar to the previous study, all the optimization problems for the integrated networks were solved to global optimality. Different schemes of integration were studied and the results were compared and analysed.

In the second portion of the work (chapter 5), a nonlinear programming model for the refinery hydrogen network was developed. Unlike the other models in the literature which considered the process constraints along with pressure effects, this work also focussed on the effect of temperature as well. Also this work also highlighted the importance of quality requirement at the fuel gas sinks when the unutilized gases from the hydrogen network were sent to the fuel gas system. The issue of location, duty, effect of temperature and pressure and other property related intricacy associated with the gas stream conditioning equipments like the compressor, valve, heater and cooler were also addressed by this model. One limitation of this work is that only locally optimal solutions were obtained, as the underlying model was nonconvex and highly nonlinear. It would be useful in the future to apply some global optimization approaches to this problem, which can guarantee global solutions.

Although the system under study in this thesis is a refinery, the modeling and optimization approach discussed in this thesis could be applied to any chemical or petrochemical plant which involves gas flow.

6.2 Recommendations

During the phase of model development, some key points were observed. Based on these observations, some directions towards future work are given as follows

6.2.1 Fuel Gas Network

1. In chapter 3, a multimode model for the fuel gas network was developed. This model had utilized some ideas from the literature regarding the fuel gas sink quality specifications. Further work is required to find some more quality specifications which would be necessary for the modeling of fuel gas networks. Secondly only a limited number of hydrocarbons were considered in the waste/purge/impure gas source streams in our work, whereas in a typical refinery

the impure/waste/purge gases may have many different hydrocarbons. This could considerably increase the size of model as well as the complexities associated with it. For instance, the Methane Number constraint had correlations only for some of the basic alkanes. Since there could exist many different hydrocarbon, the constraint now has to be modified for different type of hydrocarbons (such as higher alkanes, alkenes or alkynes etc) as well.

2. The multimode model developed in chapter 3 was a nonconvex nonlinear programming model where the nonconvexities in the model were from bilinear and posynomial terms. This model was solved only to local optimality. The drawback of such local solutions is that the quality of such solutions may not be known until the ‘best’ feasible solution (global solution) to the problem is known. Hence further research is necessary to be able to solve such complex models to global optimality.

6.2.2 Hydrogen Network

1. In chapter 4 and 5 while modeling the hydrogen networks only deterministic conditions such as constant availability and supply of gas were assumed. This model may lack in clarity and suffer from lack of resilience in network design and operation. This is because many of the parameters such as hydrogen demand at processing unit, purity out of hydrogen out of the processing unit, recovery of the purification unit, purity of the gas stream from catalytic reformer unit are considered are assumed to be constant and static, whereas these parameters may actually change during the course of network operation. Hence one aspect of the future work in this direction could be to carry out the optimization of hydrogen network under uncertainty. The benefit of optimizing the network under

uncertainty is that the network design is expected to be optimal over the entire range of uncertain parameters.

2. In chapter 4 and 5 while modeling the hydrogen networks, the model expressions describing the flow and purity at the inlet and outlet of the hydroprocessing units were either a fixed parameter (in chapter 4) or given by a simple empirical expression (in chapter 5). The use of a more accurate model equation for depicting the flow and purity at the inlet and the outlet of the processing unit can provide a more realistic approach towards modeling of a processing unit. Such accurate models may also help in a better understanding of the overall hydrogen balance within a refinery.
3. The hydrogen network model can also be integrated with the planning model of the refinery. Such an integration can provide a more clear understanding of the interactions between the two frameworks (one being refinery planning model and other being refinery hydrogen network model) in a simultaneous manner, which otherwise was done in a sequential manner. This sort of simultaneous integration can also equip the refinery planner to understand the deeper impacts of the hydrogen distribution on the refinery economics, and also see if there could be any potential synergies by simultaneously integrating them. These studies can be useful for the issue of hydrogen management within the refinery. Furthermore, the fuel gas network could also be integrated with the refinery planning model for a better understanding of the fuel gas dynamics in a refinery.
4. The hydrogen sources or the producers in this study such as the steam methane reforming (SMR) unit are only considered as an external source of hydrogen which is available when required. However, in reality these units may also have other units associated with them such as a purification unit. Future works should

also focus on developing model equations for these hydrogen sources as well, so that it can be a part of hydrogen network for the overall refinery rather than merely being an external utility.

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List of Publications

Journal Publications

1. **Jagannath, A**.; Hasan, M. M. F.; Al-Fadhli, F. M.; Karimi, I.A.; Allen, D. T., Minimize flaring through integration with fuel gas networks. *Industrial & Engineering Chemistry Research*, published online March 21, 2012, http://pubs.acs.org/doi/abs/10.1021/ie300308g .

2. **Jagannath, A**.; Elkamel, A.; Karimi, I. A., Optimization of multi-refinery hydrogen networks. *Computer Aided Chemical Engineering* 2012**,** 31, 1331-1336.

3. **Jagannath, A**.; Elkamel, A.; Karimi, I. A., Improved synthesis of hydrogen networks. ***(to be submitted)***

Conference proceedings

1. **Jagannath, A**.; Elkamel, A.; Karimi, I. A., Optimization of multi-refinery hydrogen networks. PSE 11, Singapore, 2012