Universidade Federal do Rio Grande do Sul
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Síntese e Reprojeto de Redes de Hidrogênio Flexíveis e Economicamente Eficientes Integradas ao Planejamento de Produção

TESE DE DOUTORADO

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Porto Alegre

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UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
ESCOLA DE ENGENHARIA
DEPARTAMENTO DE ENGENHARIA QUÍMICA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

SÍNTESE E REPROJETO DE REDES DE HIDROGÊNIO FLEXÍVEIS E ECONOMICAMENTE EFICIENTES INTEGRADAS AO PLANEJAMENTO DE PRODUÇÃO

Patrícia Rodrigues da Silva

Tese de Doutorado (D.Sc.) apresentada como requisito parcial para obtenção do título de Doutor em Engenharia

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A Comissão Examinadora, abaixo assinada, aprova a Proposta de Pesquisa *Síntese e Reprojeto de Redes de Hidrogênio Flexíveis e Economicamente Eficientes Integradas ao Planejamento de Produção*, elaborada por Patrícia Rodrigues da Silva, como requisito parcial para obtenção do Grau de Doutor em Engenharia.

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Resumo

O hidrogênio é utilizado nas refinarias de petróleo como insumo no hidrotratamento dos combustíveis. Através da reforma catalítica, o hidrogênio é produzido nas refinarias nas chamadas unidades de geração de hidrogênio (UGH), e juntamente com unidades de purificação e unidade de hidrotratamento (consideradas unidades consumidoras), se formam as redes de hidrogênio. Com o aumento das restrições no teor de enxofre nas frações de petróleo, como o diesel, o gerenciamento das redes de hidrogênio começou a ganhar destaque devido a sua importância econômica e ambiental. Ou seja, há interesse no uso de forma mais eficiente do hidrogênio. Através de programação matemática é possível realizar a modelagem e otimização da rede de hidrogênio, visando a sua produção ótima e uma melhor distribuição entre as unidades. Formulações MILP (Mixed Integer Linear Programming) e MINLP (Mixed Integer Nonlinear Programming) foram desenvolvidas em GAMS para representar a rede de hidrogênio. O modelo pode ser utilizado para o caso de *retrofit* ou de novos projetos, prevendo a instalação de novos compressores, unidades de purificação e linhas. Devido às limitações do modelo MILP, foi proposta uma técnica para diminuir a instalação de novos compressores, permitindo a mistura entre correntes, mas mantendo a linearidade do processo. Com o objetivo de facilitar a resolução do modelo não linear, foi proposta uma técnica de inicialização baseada no ótimo obtido através da formulação linear. Como uma extensão das formulações MILP e MINLP nominais e com o objetivo de incluir as incertezas do processo de refino de petróleo, que surgem principalmente devido aos diferentes petróleos e seus teores de enxofre, a otimização multicenário também é abordado neste trabalho. É importante que a rede de hidrogênio seja flexível, ou seja, seja capaz de atender as variações no consumo de hidrogênio nas unidades de hidrotratamento. O planejamento de produção é responsável por conectar os diferentes petróleos disponíveis com a demanda de produtos e assim, consegue-se estimar a quantidade de hidrogênio necessária num horizonte de tempo, normalmente mensal. Nesse sentido, este trabalho une o desenvolvimento de um planejamento de produção para uma refinaria, com o conceito de avaliação de flexibilidade da rede e otimização multicenário, a fim de obter o maior lucro possível, com uma rede mais flexível possível e capaz de atender os cenários estabelecidos, com o menor custo operacional, podendo incluir o redesign da rede. As otimizações foram validadas através de estudos de caso da literatura e de dados reais de uma refinaria brasileira. Como resultados, concluiu-se que a formulação não linear combinada com a inicialização proveniente da formulação MILP e a técnica de rearranjo de compressores é a mais adequada para redesign de redes de hidrogênio, fornecendo economias significativas de custo operacional. Além disso, através do planejamento de produção, foi possível avaliar economicamente a rede de hidrogênio, unindo o maior lucro possível, com o menor custo operacional da rede capaz de atender a demanda.

Palavras-chave: integração mássica, programação matemática, MILP, MINLP, otimização multicenário, planejamento de produção.

Abstract

Hydrogen is used in oil refineries as a raw material in fuel hydrotreatment. Through catalytic reform, hydrogen is produced in refineries in so-called hydrogen generation units (UGH), and together with purification units and hydrotreatment units (considered consuming units), hydrogen networks are formed. With the increase in restrictions on sulfur content in oil fractions, such as diesel, the management of hydrogen networks has begun to gain prominence due to its economic and environmental importance. That is, there is interest in the more efficient use of hydrogen. Through mathematical programming, it is possible to perform the modeling and optimization of the hydrogen network, aiming its optimal production and a better distribution between the units. MILP (Mixed Integer Linear Programming) and MINLP (Mixed Integer Nonlinear Programming) formulations were developed in GAMS to represent the hydrogen network. The model can be used for retrofit or new projects to install new compressors, purification units, and lines. Due to the limitations of the MILP model, a technique was proposed to reduce the installation of new compressors, allowing the mixing between flowrates but maintaining the linearity of the process. In order to facilitate the resolution of the nonlinear model, an initialization technique based on the optimal obtained through the linear formulation was proposed. Multiscenario optimization is also addressed as an extension of nominal MILP and MINLP formulations. It includes the uncertainties of the oil refining process, which arise mainly due to the different oils and their sulfur contents. The hydrogen network must be flexible; that is, it should comply with the variations in hydrogen consumption in hydrotreatment units. Production planning is responsible for connecting the different available oils with the demand for products and thus can estimate the amount of hydrogen needed in a time horizon, usually monthly. In this sense, this work unites the development of production planning for a refinery, evaluating network flexibility and multi-scenario optimization. It is done to obtain the highest possible profit, with a flexible network to secure the established scenarios, with the lowest operational cost. It may also include the redesign of the network. The optimizations were validated through case studies of the literature and actual data of a Brazilian refinery. As a result, it was concluded that the nonlinear formulation combined with the initialization from the MILP formulation and the compressor rearrangement technique is the most appropriate for the redesign of hydrogen networks, providing significant savings in operating costs. In addition, through production planning, it was possible to economically evaluate the hydrogen network, uniting the highest possible profit, with the lowest operational cost of the network capable of achieving the demand.

Keywords: mass integration, mathematical programming, MILP, MINLP, multi-scenario optimization, production planning.

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SUMÁRIO

LISTA DE FIGURAS

LISTA DE TABELAS

Capítulo 1 – **Introdução**

A indústria do petróleo é composta por segmentos que se complementam, desde a exploração, o refino até o transporte e a distribuição. O refino do petróleo compreende operações físicas e químicas capazes de garantir o aproveitamento do seu potencial energético através dos produtos derivados e fracionados. Este processo tem importância tanto técnica quando ambiental e econômica (Smith et al., 2010).

O hidrogênio tem papel de destaque na indústria do refino, tanto a sua produção quanto a sua recuperação são etapas importantes. Seu avanço como insumo é sustentado por três fatores: (I) o aumento do processamento de petróleos mais pesados com altos teores de enxofre e nitrogênio, (II) o aumento das restrições ambientais e (III) a produção de derivados de maior valor agregado (Figueiredo, 2013). A Figura 1.1 apresenta a evolução do uso do hidrogênio nas refinarias nas últimas décadas, indicando um acréscimo de 78% nos últimos 18 anos.

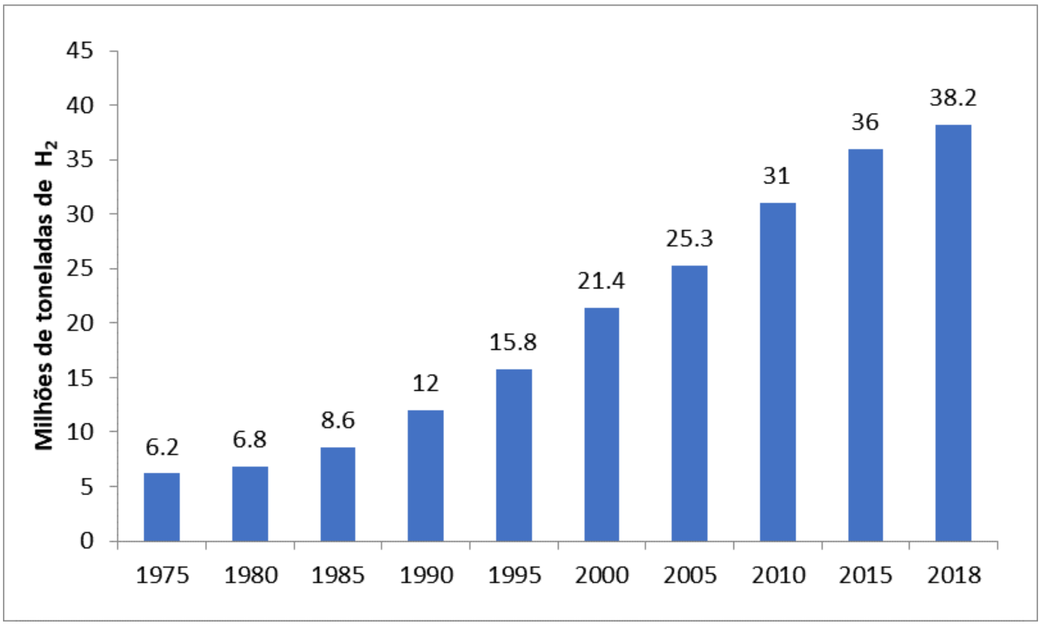

Figura 1.1: Consumo de hidrogênio nas refinarias ao longo dos últimos 43 anos. Adaptado da *International Energy Agency* (IEA , 2019).

O teor de enxofre nos combustíveis é um parâmetro utilizado como indicador de qualidade, porque a presença de enxofre diminui a vida útil dos motores e também aumenta as emissões de óxidos de enxofre, além de contribuir na emissão de material particulado. A Agência Nacional do Petróleo (ANP) é o órgão regulador das atividades que integram as indústrias de petróleo, gás natural e biocombustíveis, por isso tem a atribuição de estabelecer regras e fiscalizar as diversas áreas de atuação como a exploração, o refino e o processamento do petróleo e derivados, incluindo parâmetros como o teor de enxofre. As regulamentações da ANP vêm diminuindo gradativamente o teor de enxofre permitido no óleo diesel e na gasolina, conforme se observa na Figura 1.2. Atualmente, para uso rodoviário, estão vigentes o diesel S10 e o diesel S500.

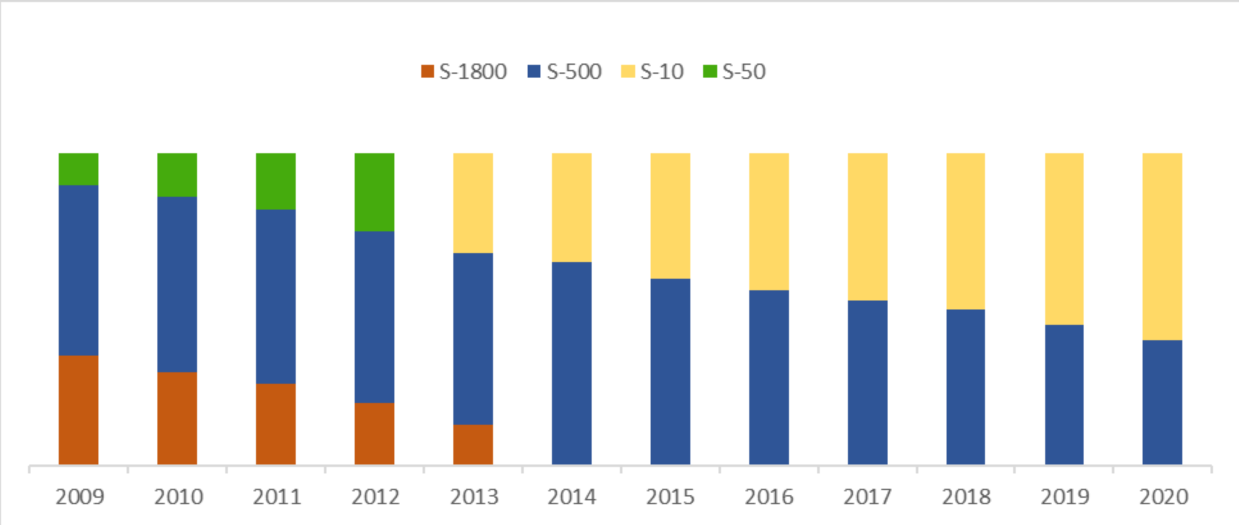

Figura 1.2: Evolução da qualidade do diesel no Brasil (proporções fictícias). Adaptado de Petrobras (2019).

Para atender as legislações que estão cada vez mais rigorosas, as refinarias têm investido muito em processos cuja produção seja mais limpa e com menor emissão de poluentes. Em geral, essa tendência encontra no suprimento de hidrogênio um fator limitante. Devido a demanda constante por diesel e gasolina, os tratamentos que envolvem o hidrogênio são imprescindíveis ao refino moderno de petróleo e a sua utilização de forma mais eficiente se faz necessária (Borges, 2009; Cruz, 2010). Em uma refinaria há uma série de processos consumidores de hidrogênio, como por exemplo, unidades de hidrotratamento, e produtores de hidrogênio (as chamadas unidade geradoras de hidrogênio – UGH). É importante salientar que, dentro da UGH existe um processo de purificação, para fornecer hidrogênio na pureza adequada. Além da UGH, existem outros processos que produzem hidrogênio como fonte secundária e serão mais explorados no Capítulo 2. Essas unidades conectadas formam a rede de hidrogênio. As principais questões a serem respondidas são: qual a melhor maneira de fazer o gerenciamento desta rede de hidrogênio? Quanto produzir, quais unidades preferencialmente utilizar, qual é a demanda estimada de hidrogênio, o que fazer com o hidrogênio excedente em uma unidade? O mais importante e que garante o funcionamento das outras etapas da refinaria, evitando paradas, é que não pode faltar hidrogênio, mas quando produzido em excesso, o mesmo será queimado na tocha (*flare*), uma vez que unidades de armazenamento não estão normalmente disponíveis.

Unindo todos estes conceitos, a programação matemática pode ser utilizada na síntese de um processo novo ou no reprojeto de uma rede existente através da sua otimização. Com isso, viu-se a oportunidade de aplicação no gerenciamento de redes de hidrogênio em uma refinaria, pois o gerenciamento implica no balanço material deste componente em todas as etapas do processo e no seu uso eficiente. A sua finalidade é otimizar a produção de hidrogênio, atendendo o consumo do processo de refino através do reuso de correntes de hidrogênio podendo estas passar ou não por uma purificação. Normalmente, a quantidade de hidrogênio produzida é superior à quantidade consumida e o excedente é queimado. Portanto, como não é economicamente viável produzir e queimar o produto com alto valor agregado, abre-se espaço para estudos de uma produção otimizada de hidrogênio dentro das refinarias (Borges, 2009).

E neste aspecto se insere a importância do planejamento e programação da produção em uma refinaria. A programação da produção é comumente realizada através de um modelo matemático capaz de reproduzir os principais processos na refinaria. Com um planejamento bem estruturado, considerando os petróleos disponíveis, as demandas de mercado dos principais produtos e os preços associados, é possível determinar a operação ótima da refinaria em um horizonte de tempo. O planejamento de produção pode fornecer o consumo de hidrogênio, que é uma informação muito importante para o gerenciamento da rede de hidrogênio, e além disso, fornece como resultado a quantidade de cada petróleo utilizada e os derivados produzidos a cada dia, necessário no mesmo período. Isso permite que uma rede de hidrogênio existente tenha sua estrutura explorada da melhor maneira possível e possivelmente modificada com algum investimento, ou mesmo sintetizada (projetada) de forma a garantir um maior retorno econômico com uso eficiente do hidrogênio produzido. Ainda, caso não seja desejável a realização de novos investimentos, a estrutura da rede existente pode ser levada em consideração como uma restrição imposta ao planejamento de produção. Em qualquer dos casos é fundamental considerar a interação e a troca de informações nos dois sentidos entre o planejamento de produção e a operação da rede de hidrogênio.

1.1 **Objetivos**

O objetivo principal deste trabalho é promover um maior retorno econômico e ambiental de uma refinaria através da integração do planejamento de produção com o gerenciamento eficiente da rede de hidrogênio. Esse objetivo é alcançado através da exploração da estrutura da rede de hidrogênio existente ou pelo projeto novo - ou reprojeto da rede existente - visando atender o planejamento e usando de forma eficiente e econômica o recurso hidrogênio.

Dentre os objetivos específicos, destacam-se:

OB1- Desenvolver modelos nominais de programação matemática baseados em superestrutura capaz de representar redes de hidrogênio;

OB2- Desenvolver técnicas de inicialização e resolução de forma eficiente destes modelos;

OB3- Utilizando os modelos nominais como base, estender esses modelos para uma otimização multicenário, já que a demanda de hidrogênio nas unidades de hidrotratamento varia significativamente devido ao tipo de petróleo e o teor de enxofre associado;

OB4- Avaliar a flexibilidade de redes de hidrogênio e identificar cenários críticos de operação;

OB5- Propor uma metodologia capaz de (re)projetar redes de hidrogênio flexíveis associando a otimização multicenário com a métrica de flexibilidade;

OB6- Desenvolver um modelo de planejamento de produção capaz de representar uma refinaria genérica;

OB7- Desenvolver uma metodologia de integração entre o planejamento de produção da refinaria e sua relação com o consumo de enxofre e de hidrogênio nas unidades de hidrotratamento, fornecendo assim dados para a otimização do processo e para justificar possíveis (re)projetos.

1.2 Contribuições

Os estudos deste trabalho foram direcionados ao desenvolvimento de modelos matemáticos capazes de otimizar a rede de hidrogênio existente. Com a necessidade de considerar a incerteza na quantidade de hidrogênio necessária, o estudo foi estendido para a representação em multicenários, unido ao conceito de flexibilidade da rede de hidrogênio. Essa incerteza no consumo precisa ser estimada ao longo de um tempo de operação para que de fato o hidrogênio seja produzido de forma eficiente, e neste quesito que entra o estudo e desenvolvimento do planejamento de produção.

Desta forma, as principais contribuições do trabalho foram:

C1- Formulação nominal de modelos de programação matemática (MILP e MINLP) para reprojeto de rede de hidrogênio e a comparação diante das diferenças existentes.

C2-Formulação nominal com diversas funções objetivo(restrições) sendo testadas.

C3- Desenvolvimento de técnica de inicialização para facilitar a resolução dos modelos de programação matemática propostos (redução e rearranjo de compressores virtuais).

C4- Formulação multicenários de modelos de programação matemática (MILP e MINLP), para a rede de hidrogênio, para inclusão de incertezas nos processos.

C5- Avaliação da flexibilidade das redes de hidrogênio, aplicadas tanto para o caso de rede atual como reprojeto.

C6- Formulação do planejamento de produção de uma refinaria, através de um modelo NLP.

C7- Integração sistemática incorporando as retroalimentações inerentes do planejamento de produção de uma refinaria associado à programação de produção e sua demanda por hidrogênio.

C8- Proposição de um KPI *(key performance indicator)* relativo ao máximo aproveitamento de hidrogênio na refinaria, via rede existente e máximo aproveitamento através do reprojeto da rede proposto.

1.3 Estrutura

O presente trabalho está estruturado em 7 capítulos. Neste primeiro capítulo é apresentada a motivação do trabalho, os objetivos, contribuições previamente realizadas, estrutura e produção científica durante o projeto.

No Capítulo 2 foi realizada uma revisão bibliográfica descrevendo as redes de hidrogênio e o processo de refino básico, bem como os modelos e trabalhos existentes sobre o assunto.

O Capítulo 3 apresenta o desenvolvimento da formulação linear e não linear, além da validação através de dois estudos de caso. Neste primeiro capítulo a ideia é comparar os resultados fornecidos através dos modelos linear e não linear, além de testar restrições adicionais aplicadas na função objetivo. O Capítulo 4 é uma continuação, pois além de utilizar as formulações linear e não linear em outro estudo de caso, apresenta a evolução do resultado através da técnica de redução de compressores e propõe uma estratégia de inicialização que facilita a resolução dos modelos não lineares.

No Capítulo 5 é feita a extensão do modelo proposto no capítulo 3 e 4, porém agora para um sistema multicenários. Neste caso, o consumo de hidrogênio nas unidades de consumidoras é avaliado em diferentes cenários e no cenário nominal original para a comparação dos resultados, o que significa que a incerteza de processo foi adicionada ao consumo de hidrogênio. Além disso, foi proposta uma metodologia para avaliação de flexibilidade e a síntese de redes de hidrogênio econômicas e flexíveis.

No Capítulo 6 é apresentado o desenvolvimento de um modelo de programação não linear para planejamento de produção de uma refinaria. Como resultado deste modelo é determinado o consumo de hidrogênio e com isso se avalia a flexibilidade da rede existente ou reprojeto caso não seja possível atender aos diferentes cenários.

No Capítulo 7 são apresentadas as considerações finais, as principais conclusões obtidas neste trabalho e sugestões de trabalhos futuros.

A Figura 1.3 faz a relação entre as contribuições e objetivos elencados ao longo dos diferentes capítulos que compreendem esta Tese.

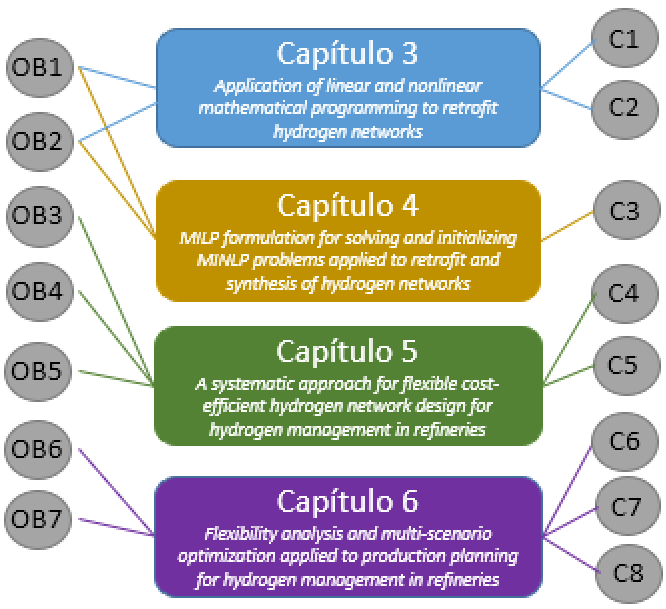

Figura 1.3: Resumo gráfico relacionando objetivos e contribuições do trabalho.

1.4 Produção científica

O desenvolvimento deste trabalho originou a produção científica listada a seguir:

Capítulo 3 deste trabalho: *Application of linear and nonlinear mathematical programming to retrofit hydrogen network.* Submetido e aceito pela Brazilian Journal of Chemical Engineering (ainda não publicado).
Capítulo 4 deste trabalho: *MILP formulation for solving and initializing MINLP problems applied to retrofit and synthesis of hydrogen networks. Processes* 2020, *8*, 1102. https://doi.org/10.3390/pr8091102
Capítulo 5 deste trabalho: *A systematic approach for flexible cost-efficient hydrogen network design for hydrogen management in refineries.* Chemical Engineering Research and Design, 2021, ISSN 0263-8762, https://doi.org/10.1016/j.cherd.2021.05.030.
Capítulo 6 deste trabalho: *Flexibility analysis and multi-scenario optimization applied to production planning for hydrogen management in refineries.* Submetido na Computers and Chemical Engineering.

Além disso, derivações deste trabalho foram publicadas em outros congressos:

Application of an optimization model for hydrogen networks. I Brazilian Congress on Process Systems Engineering – PSE-BR 2019.

A MILP optimization model for hydrogen demand management based on planning and production demand. II NIIC- NECSOS INTERNATIONAL AND INTERINSTITUTIONAL COLOQUIUM. Esta apresentação originou o artigo entitulado *An overview of different approaches in hydrogen network optimization via* mathematical programming. Brazilian Journal of Operations & Production Management, 17(3), 1-20. https://doi.org/https://doi.org/10.14488/BJOPM.2020.031

Capítulo 2 – **Revisão Bibliográfica**

2.1 **Hidrogênio**

O hidrogênio passou a ser considerado de interesse industrial após o advento da síntese da amônia em 1913 e da I Guerra Mundial, mas só começou a ser produzido em maior quantidade depois da II Guerra Mundial já que o desenvolvimento tecnológico foi capaz de reduzir os custos de produção aliado ao baixo preço do gás natural. As principais formas de obtenção do hidrogênio são: a partir de fontes primárias de energia, como combustíveis fósseis (petróleo, gás natural), a partir de intermediários químicos, como produtos de refinaria e etanol, e a partir de fontes alternativas, tais como biomassas e biogás (Silva and Marvulle, 2006)

Apesar da sua gama de aplicações, aproximadamente 99 % do hidrogênio produzido é utilizado nas indústrias química e petroquímicas, fazendo com que a maioria das unidades produtoras de hidrogênio sejam instaladas dentro das refinarias e polos petroquímicos, as chamadas unidades de geração de hidrogênio (UGH) (Cruz, 2010).

As redes de hidrogênio são compostas por fontes de hidrogênio, tanto primárias quanto secundárias, unidades consumidoras, principalmente as unidades de hidrotratamento e unidades de purificação. A unidade de geração de hidrogênio é uma fonte primária, além da reforma catalítica. Já como fonte secundária pode ser citado o gás de purga, que contém hidrogênio e pode ser reaproveitado no processo.

2.1.1 Fontes de hidrogênio

As unidades de Geração de Hidrogênio (UGH) têm se tornado cada vez mais presentes nas refinarias devido à importância das unidades de hidrotratamento, pois sua função é suprir a demanda de hidrogênio complementando o gerado na reforma catalítica. Os principais processos de obtenção de hidrogênio são: reforma a vapor, reforma catalítica, oxidação parcial de hidrocarbonetos pesados e gaseificação de resíduos (Brasil et al., 2012). A reforma a vapor é a principal forma, utilizada em escala industrial, de obtenção de hidrogênio de forma direta e contínua. Além disso, é também o processo mais competitivo economicamente (Silva and Marvulle, 2006). A reforma a vapor de gás natural ocorre a elevadas temperaturas e com presença de catalisadores à base de níquel. O processo consiste basicamente na reação da carga, que pode ser gás natural, metano, nafta, entre outros, com o vapor de água, gerando gás de síntese, de onde o hidrogênio é obtido posteriormente na etapa de deslocamento (Borges, 2009).

A reforma catalítica de nafta tem como objetivo principal a obtenção de nafta rica em hidrocarbonetos aromáticos e ainda gera hidrogênio como subproduto. Os hidrocarbonetos reagem a 470-530°C e em pressões variando de 10 a 40 kgf/cm² com o uso de catalisadores de platina suportados em alumina. Um conjunto de reações complexas ocorre, bem como uma reação de hidrocraqueamento que é indesejada, pois diminui o rendimento da nafta reformada e ainda consome o hidrogênio gerado (Figueiredo, 2013). Na verdade, a reforma catalítica tanto consome quanto gera hidrogênio.

Outra fonte importante a ser considerada é o gás de purga das unidades de hidrorrefino, pois essa corrente possui alto teor de hidrogênio. Se estiver dentro dos padrões de pureza exigidos no processo pode ser usada diretamente ou regenerada. Essa seria uma fonte secundária de hidrogênio dentro do processo de refino, já que as fontes primárias são a própria UGH e a reforma catalítica (Figueiredo, 2013).

2.1.2 Consumidores de hidrogênio

As principais etapas do refino de petróleo que consomem hidrogênio são os hidrorrefinos, que o utilizam para tratar frações leves, médias ou pesadas de petróleo. Atualmente se utiliza deste processo para melhorar a qualidade de naftas, querosenes, solventes em geral, óleo diesel, gasóleos pesados, parafinas e óleos lubrificantes. Os processos de hidrorrefino são classificados de acordo com as reações desejadas, por exemplo, hidrodessulfurização e hidrodesaromatização (Borges, 2009). Ou ainda, de forma genérica, podem ser classificados em dois tipos: unidades de hidrotratamento (que contemplam todos os hidrorrefinos exceto a hidroconversão) e hidroconversão (HC) (Figueiredo, 2013).

No hidrotratamento (HDT) a remoção de contaminantes como enxofre e seus compostos de hidrocarbonetos leves é feita com a utilização de hidrogênio de alta pureza, com a finalidade de atender aos parâmetros exigidos pela legislação vigente. O HDT foi desenvolvido inicialmente na Refinaria de Leuna (Alemanha, 1927) para o tratamento de frações combustíveis obtidos do carvão mineral. No entanto, se tornou aplicável para tratamento de derivados de petróleo a partir de 1950, com a disponibilidade do hidrogênio oriundo da reforma catalítica.

Uma unidade básica de HDT contém duas seções, a reação de alta pressão e a separação dos gases com o fracionamento dos produtos em baixa pressão, conforme se observa na Figura 2.1 (Figueiredo, 2013).

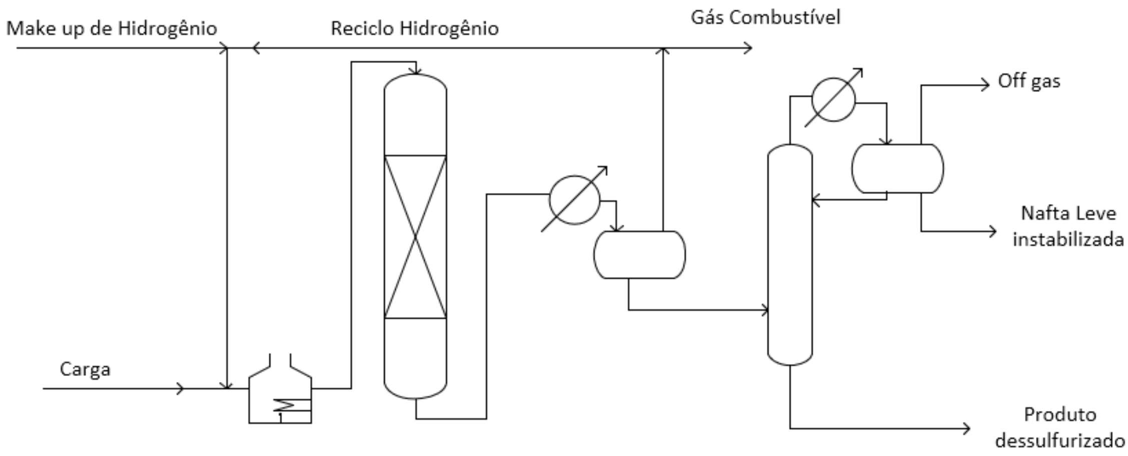

Figura 2.1: Fluxograma simplificado de uma unidade de hidrotratamento de derivados. Adaptado de Figueiredo (2013).

O hidrocraqueamento, que também é considerado um hidrotratamento, porém de maior severidade, consiste na quebra de moléculas existentes na carga e consome hidrogênio diretamente no processo, com ação conjugada do catalisador em altas temperaturas e pressões. Este processo é mais antigo que o craqueamento térmico e catalítico, tendo seu apogeu na década de 60, porém o elevado custo do hidrogênio inviabilizava a sua utilização no refino do petróleo. O hidrocraqueamento é um processo versátil e pode operar com várias cargas, desde nafta até gasóleos pesados e como ocorre em condições severas se consegue especificar os produtos com baixos teores de contaminantes e compostos aromáticos (Brasil et al., 2012; Cruz, 2010). Simultaneamente à quebra, ocorrem reações de hidrogenação, o que acarreta redução da formação de materiais residuais pesados e aumento da produção de gasolina ao reagir com os produtos craqueados. Assim, o emprego do hidrogênio reduz a deposição de coque e, ao hidrogenar compostos aromáticos polinucleados, além de mono e di-olefinas, aumenta a estabilidade química dos produtos finais, produzindo destilados médios de alta qualidade. A diferença principal entre os processos de hidrotratamento e de hidrocraqueamento está na seletividade do catalisador (Borges, 2009; Cruz, 2010).

Há também o processo de isomerização, que é um processo de conversão de cadeias parafínicas normais em cadeias ramificadas, neste caso, nafta leve proveniente da destilação direta é convertida em nafta isomerizada. Este processo é utilizado para melhorar a qualidade antidetonante da nafta, isentando-a de contaminantes e hidrocarbonetos aromáticos e olefínicos. É preciso uma atmosfera de hidrogênio a fim de minimizar a formação e deposição de coque, entretanto o consumo desse gás é bastante reduzido, as condições de temperatura e pressão são brandas e o catalisador é de elevada atividade.

Além disso, o hidrogênio é utilizado no craqueamento catalítico. Este processo é o mais utilizado no refino de petróleo para converter frações pesadas em frações mais nobres como a gasolina e o GLP. O consumo de hidrogênio está ligado à necessidade de dessulfurização das cargas oriundas do processamento de petróleo, evitando a formação de materiais residuais pesados e aumentando o rendimento dos processos (Borges, 2009; Cruz, 2010)

A Figura 2.2 mostra um esquema completo de uma refinaria, com as cargas, os processos e os produtos finais. Esse diagrama é extremamente útil para que seja mapeado o hidrogênio dentro da refinaria.

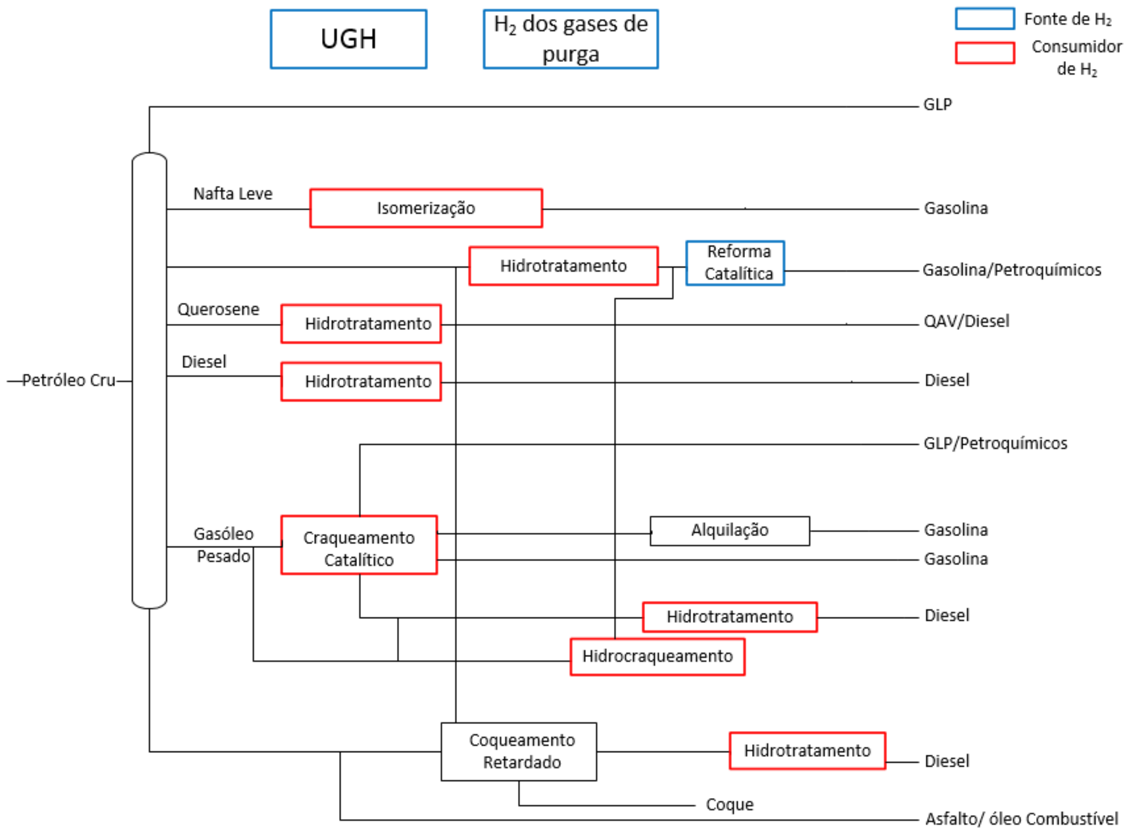

Figura 2.2: Fluxograma simplificado de uma refinaria de petróleo. Adaptado de FIGUEIREDO (2013).

2.2 Integração de processos

A integração de processo é uma abordagem holística para o projeto, adaptação e operação do processo. Baseado na interação entre unidades de processo, recursos, fluxos e objetivos, a integração de processos oferece uma estrutura única para compreender de forma global o processo, determinando suas metas de desempenho atingíveis. A integração de processos envolve a identificação do objetivo que se pretende alcançar, a segmentação que permite comparar o desempenho atual e fornece percepções úteis sobre o potencial e as oportunidades daquele processo, a síntese propriamente dita que seria o mapeamento das alternativas existentes, a seleção e análise da alternativa proposta.

A integração de processos se resume em integração energética e mássica. A integração de energia aborda a utilização de energia dentro do processo, identificando metas de energia e otimização de recuperação de calor e utilidades. A integração mássica é uma metodologia sistemática que estuda o fluxo global de massa dentro do processo, incluindo metas de desempenho e otimização da geração utilização do insumo dentro do processo.

A otimização é uma das ferramentas mais poderosas na integração de processos, baseada na seleção da 'melhor' solução através da escolha de uma função objetivo (por exemplo, custo) que deve ser minimizada ou maximizada. A função objetivo pode estar sujeita a várias restrições que incluem balanços de materiais e energia, equações constitutivas e restrições lógicas operacionais.

Existem diferentes técnicas de integração mássica que combinam ferramentas gráficas e/ou ferramentas de otimização. A principal etapa é fazer uma representação de todo o processo para facilitar o entendimento e mapear as correntes do processo e possíveis gargalos para aplicação da metodologia escolhida para realizar o gerenciamento de redes de hidrogênio (El-Halwagi, 2006; Kemp, 2007).

2.2.1 Metodologias para gerenciamento de redes de hidrogênio

A necessidade de otimização da rede de hidrogênio em refinarias foi reconhecida nos anos 90 e desde então muitas metodologias surgiram. Sendo elas, principalmente, métodos de segmentação (*pinch*) e abordagens de programação matemática baseadas no design das redes.

A tecnologia *pinch* sempre foi muito utilizada em integração energética, mas acabou sendo aplicada na integração mássica com o objetivo de reutilizar águas industriais. Os principais objetivos desta técnica, neste caso, são: maximizar a reutilização de água, reduzir os efluentes gerados e consequentemente diminuir os custos de tratamento de efluentes. No caso do hidrogênio, a análise *pinch* é uma aproximação rigorosa e estruturada capaz de determinar o consumo mínimo de hidrogênio e ainda permite definir a melhor maneira de integrar as unidades e identificar os gargalos do sistema (Borges, 2009).

O método de *pinch* é talvez o mais utilizado devido à sua simplicidade (Figueiredo, 2013). Este método utiliza uma ferramenta gráfica, o diagrama de *pinch*. No método de *pinch*, os processos da refinaria devem ser classificados em fontes e consumidores. Para isso, um mapeamento destas correntes é realizado, avaliando a vazão e a composição. Com estes valores de vazão e composição, um gráfico de perfil de pureza de hidrogênio em função da vazão é criado, chamado curvas compostas de hidrogênio. Com estes valores, é possível calcular o excesso de hidrogênio e construir um novo gráfico, concentração versus excesso. Este último permite identificar o ponto de estrangulamento (*pinch*), que ocorre quando, ao menos, um ponto do diagrama é nulo e qualquer redução no suprimento do hidrogênio neste caso causa um fluxo negativo (Figueiredo, 2013).

A primeira abordagem sistemática para a avaliação de rede de hidrogênio foi desenvolvido por TOWLER et al. (1996). Foram geradas as curvas compostas de custo da recuperação de hidrogênio e valor agregado para processos de refinaria que produzem hidrogênio ou consomem hidrogênio. As curvas compostas de custo e valor podem ser usadas para a análise econômica de uma rede de hidrogênio da refinaria. No entanto, essa abordagem não fornece um método sistemático para a modernização ou o design de redes de hidrogênio. A análise baseia-se na disponibilidade de dados econômicos, como o valor agregado aos produtos de refinaria por unidade de consumo de hidrogênio, que nem sempre está disponível. Depois disso, Alves e Towler (2002) propuseram uma abordagem sistemática que define um sistema de distribuição de hidrogênio baseado no suprimento mínimo de hidrogênio. Os gráficos de pureza da fonte e dos consumidores são construídos com base no valor consumido de hidrogênio fresco. Trabalhos mais recentes sobre gerenciamento e análise da distribuição de hidrogênio baseado na análise gráfica do método *pinch*, foram encontrados na literatura (Fonseca et al., 2008; Liu et al., 2013; Lou et al., 2013a; Oduola and Oguntola, 2015).

Outra maneira de resolver problemas de integração mássica é através da formulação de problemas de otimização ou de programação matemática, mediante a escolha de uma função objetivo e a definição de um conjunto de restrições para o qual as possíveis soluções devem satisfazer, o que não se consegue no *pinch* (Shahraki and Kashi, 2005).

A programação matemática oferece vantagens quando comparada ao *pinch*, pois é mais flexível, aplicável a diferentes casos com restrições e a síntese da rede se dá de maneira automática, como resultado do problema. Já no *pinch* seria necessário o auxílio de outra técnica para avaliação da síntese do processo. Além disso, na programação matemática é possível considerar inúmeras limitações e variáveis ao buscar soluções no problema de otimização. Limitações como de pressão, capacidade, custos operacionais e de investimentos com novos equipamentos, são algumas das restrições que podem ser incluídas no problema matemático. A metodologia basicamente para desenvolver a programação matemática seria: definição da superestrutura (quais unidades estão envolvidas e classificação como fontes e consumidores, além dos compressores e purificadores existentes), a formulação do modelo matemático capaz de representá-la (escolha da função objetivo a ser minimizada ou maximizada mediante as restrições) e a resolução do problema de otimização (Jia, 2010).

Geralmente, o problema de otimização pode ser formulado como um problema de Programação Linear (LP), Programação Linear Inteira Mista (MILP), Programação Não Linear (NLP) ou Programação não Linear Inteira Mista (MINLP). Se a função objetivo e as restrições puderem ser expressas por combinações lineares de variáveis, o problema é considerado um problema de otimização linear. Caso contrário, o problema de otimização é não linear. Ainda, se além das variáveis reais tais como vazão, composição, temperatura, pressão dentre outras, variáveis inteiras (ou binárias) são utilizadas na do desenvolvimento do problema matemático, este é considerado programação inteira mista podendo ser linear ou não linear. Na síntese de processos, as variáveis binárias são utilizadas no auxílio da tomada de decisão ou na modelagem de restrições lógicas. Existem muitos softwares de otimização usados para resolver problemas de otimização que já incluem os algoritmos chamados de *solvers* (Petric, 2014).

Os problemas do tipo MINLP são mais difíceis de resolver porque combinam os modelos NLP e MILP e suas características. Baseado nos artigos encontrados para elaboração da revisão bibliográfica (conforme mencionados abaixo), o uso de MILP não é muito recorrente, embora, quando utilizado, apresente resultados significativos. A maioria dos artigos encontrados na literatura utiliza modelos não lineares para otimização da rede de hidrogênio. As vantagens do uso do MILP são a linearidade, que facilita a resolução do problema de otimização e também a modelagem das restrições lógicas feitas neste trabalho, que não foram encontradas claramente na literatura.

Towler et al. (1996) propuseram um método de programação linear para melhorar a abordagem sobre os custos de recuperação de hidrogênio de correntes gasosas em refinarias usando PSA's. Aqui o método foi similar a recuperação de calor em processos. Alves (1999) desenvolveu um modelo linear para otimizar uma rede de hidrogênio, com o objetivo de minimizar a importação total de hidrogênio como uma utilidade externa. Dois procedimentos para o relaxamento de problemas são propostos. As desvantagens deste método são que as restrições de pressão são consideradas desprezíveis e a mistura de correntes deve ser realizada manualmente.

Fonseca et al. (2008) empregaram o modelo de programação linear para otimizar a rede de hidrogênio de uma refinaria, incluindo considerações de pressão e alcançando uma redução de 30% no uso do hidrogênio, com a função objetivo de minimizar a vazão total de hidrogênio fresco. O trabalho também aborda as limitações do uso de técnicas gráficas em projetos reais de redes de hidrogênio.

Considerando a programação não-linear, Hallale e Liu (2001), além de mencionarem o método gráfico de *pinch*, desenvolveram um modelo matemático (NLP) para reduzir o consumo de hidrogênio da rede. O modelo levou em consideração restrições de pressão, compressores existentes e estratégia para instalar um purificador. A função objetivo era o custo total, incluindo custos operacionais e de capital.

Shahraki and Kashi (2005) propuseram uma abordagem de não linear na qual também foram consideradas restrições de pressão. No entanto, o projeto baseia-se na otimização de uma superestrutura de hidrogênio dentro da refinaria e limita-se a mudanças viáveis na tubulação, onde não há consideração pela instalação de novos equipamentos.

Liao, Wang, Yang e Rong (2010) desenvolveram um modelo MINLP, usando uma rede de hidrogênio existente com um purificador. A função objetivo foi o custo total anual e o modelo foi resolvido no GAMS usando o DICOPT. O custo total anual diminuiu 22,6%, e o novo compressor e a PSA (*pressure swing adsorption*) foram incorporados.

Em Kumar et al. (2010), modelos matemáticos foram desenvolvidos com base em restrições de pressão, fontes, consumidores, pureza e custo operacional total e custo de capital. Para isso, foram realizados dois estudos de caso que compararam os tipos de programação (LP, NLP, MILP e MINLP) para obter o melhor problema de otimização para cada caso. Utilizando o modelo LP, a redução no consumo de hidrogênio foi de 15,76%. O modelo de NLP incorporou um compressor e PSA e também levou em conta o conceito de retorno e custo de exportação, porque a função objetivo era o custo total. A rede ideal reduziu em 33,2% o consumo de hidrogênio. O MILP incluía variáveis binárias para denotar a existência de conexão entre uma fonte e um consumidor e este modelo previa uma rede mais simples que o modelo LP, com uma redução de 15,76% no consumo de hidrogênio fresco. Porém, o modelo MILP não incluía a utilização de compressores. O modelo MINLP foi utilizado para minimizar o custo operacional, e as variáveis discretas foram utilizadas para prever a existência de unidades. Esse modelo alcançou uma redução de 22% nos custos operacionais e 21% no consumo total de hidrogênio.

Jiao et al. (2012) propuseram duas técnicas matemáticas que incluem a otimização em duas etapas para redes de hidrogênio e um processo de otimização simultânea para modernizar o sistema de hidrogênio. Devido à complexidade foi utilizado um modelo de programação não linear inteira mista (MINLP). Além disso, um processo de otimização simultâneo é configurado para linearizar os termos bilineares que representam o balanço de hidrogênio nos modelos MINLP, que poderiam ser evitados usando técnicas de linearização MILP.

Saleh et al. (2012) formularam um modelo MINLP com o objetivo de minimizar o hidrogênio fresco e o custo anual total. O modelo foi resolvido no GAMS e a nova rede incluiu um novo PSA gerando uma redução de 20% e 31% no consumo do hidrogênio nas duas refinarias consideradas.

Sardashti Birjandi et al. (2014) desenvolveram uma metodologia para a otimização de uma rede de hidrogênio com base em um problema resolvido simultaneamente do MINLP e da NLP. Técnicas de linearização para modelos não lineares foram usadas para facilitar a resolução, transformando restrições de igualdade não lineares em restrições de desigualdade. A otimização global reduziu os custos operacionais.

Matijasevic (2016) apresentou uma metodologia de integração de rede de hidrogênio em um estudo de caso de uma refinaria local. Para tanto, a superestrutura foi modelada usando um modelo matemático não linear cuja função objetivo era minimizar os custos operacionais totais. O problema foi resolvido com o software GAMS.

Zhang et al. (2016) faz uma abordagem de concentração relativa de hidrogênio considerando impurezas nesta fonte (sulfeto, nitrogênio e carbono) e através de um modelo MILP é feita a síntese da rede deste hidrogênio. O consumo de hidrogênio é relacionado com diferentes processamentos de petróleo e o modelo avalia a tendência na variação do hidrogênio utilizado, por isso a função objetivo aqui minimiza o hidrogênio disponível na fonte. O modelo é desenvolvido no GAMS e o solver utilizado é o Baron. Os resultados mostram que a abordagem de concentração relativa é melhor do que métodos tradicionais baseados em concentração absoluta de hidrogênio disponível nas fontes.

Acevedo e Pistikopoulos (1996) e Deng et al. (2017) utilizam como estudo de caso duas plantas ricas em hidrogênio que podem suprir a necessidade de uma refinaria com déficit em hidrogênio. São testados 3 modelos diferentes para otimização da rede de hidrogênio proposta. O primeiro modelo é considerado MILP e aborda a reutilização direto do hidrogênio proveniente das duas plantas com o objetivo de minimizar a quantidade de hidrogênio disponível como utilizada na refinaria. Os outros dois modelos são MINLP e consideram o uso de unidade de purificação com diferentes funções objetivo: minimizar a quantidade de hidrogênio da refinaria e diminuir o custo total anual.

JAGANNATH et al. (2018) abordaram um projeto de modernização de redes de hidrogênio através de um modelo MINLP com o objetivo de reduzir o custo total anual. A não linearidade é devida aos termos bilineares e também as pressões que variam nos compressores. Um método heurístico para atribuir essas pressões é utilizado e com isso a não linearidade permanece somente devido aos termos bilineares.

2.2.2 Otimização multicenário e flexibilidade da rede

A rede de hidrogênio pode ser projetada de acordo com a demanda das unidades consumidoras. Esta demanda varia conforme alguns fatores, sendo os principais, o tipo de petróleo bruto que está sendo processado, os tipos de produtos finais desejados em determinada campanha e a situação operacional de cada unidade, por exemplo, se estão em início ou final de campanha, já que isto afeta os parâmetros reacionais como temperatura e desativação do catalisador no hidrotratamento. A maioria dos estudos anteriores sobre gerenciamento de redes de hidrogênio assumem parâmetros de processos fixos e definidos, mas sabe-se que as operações reais das redes podem operar de maneira incerta ou numa faixa de operação. Devido a essas condições variadas, é necessário que se faça uma abordagem sistemática capaz de representar a rede de hidrogênio e a flexibilidade com que necessita operar (Jiao et al., 2013).

Em geral, o termo flexibilidade é considerado a capacidade de um processo funcionar adequadamente em um determinado intervalo de condições incertas (Reza et al., 2016). No caso de redes de hidrogênio flexíveis, o objetivo é que a rede tenha capacidade de operar sujeita a incertezas nas condições operacionais, ou seja, no consumo de hidrogênio por parte da refinaria.

As incertezas e a variação dos parâmetros de um processo podem ser classificadas em: (i) incertezas inerentes ao modelo - inclui, por exemplo, constantes cinéticas e propriedades físicas, informações geralmente obtidas de dados da planta piloto; (ii) incertezas inerentes ao processo - variações de vazão e temperatura, flutuações na qualidade do fluxo, entro outras - e podem ser obtidas a partir de medições (on-line); (iii) incertezas externas - incluem a disponibilidade de vazão de alimentação, demandas de produtos, preços e condições ambientais e são técnicas de previsão baseadas em dados históricos, pedidos de clientes e indicadores de mercado; e, (iv) incertezas discretas - utilizadas para disponibilidade de equipamentos e outros eventos discretos aleatórios (Pistikopoulos, 1995).

Como citado acima, é importante que essas incertezas sejam consideradas na etapa de projeto da rede de hidrogênio, para garantir que conseguirá operar em todos os cenários possíveis, ou seja, que a rede seja flexível. Para explicar as incertezas nos valores desses parâmetros, o procedimento normalmente utilizado na prática é assumir valores nominais e depois utilizar fatores empíricos variando os cenários de operação. Como esse procedimento carece de uma base racional firme, vários métodos diferentes e vários estudos nesta área foram desenvolvidos e aplicados a processos com incertezas de uma maneira mais sistemática e uma descrição detalhada (Grossmann e Halemane, 1983).

Imran et al. (2010) falam sobre a otimização multiperíodo, que precisa ser levada em consideração nos projetos de redes de hidrogênio, porque os processos de refinaria que consomem hidrogênio são operados em vários períodos de operação. A metodologia desenvolvida neste trabalho para o projeto multiperíodo de redes de hidrogênio é uma extensão da abordagem de design automatizado de Hallale e Liu (2001) e Liu e Zhang (2004) por múltiplos períodos de operação. A metodologia desenvolvida para o gerenciamento de hidrogênio por períodos múltiplos é aplicável ao retrofit e ao novo design de redes flexíveis de hidrogênio. Neste caso, o modelo MINLP também é linearizado com o objetivo de trabalhar com o modelo MILP. Um modelo MILP é resolvido e a solução é usada para inicializar o MINLP. Desta forma, a convergência para uma solução viável é facilitada e a probabilidade de obter uma boa solução ótima local é aprimorada.

Jiao et al. (2013) apresentam uma abordagem de otimização flexível multiperíodo para solucionar o problema de otimização. O número de cenários é modificado para se ajustarem às flutuações operacionais e o objetivo é minimizar os custos anuais totais. A demanda variável dos consumidores de hidrogênio, as tubulações e os possíveis desligamentos de unidades de hidrogênio são considerados na formulação do problema para garantir a segurança do sistema de hidrogênio em condições operacionais normais e anormais. Variáveis binárias são introduzidas para representar a existência ou inexistência de unidades e fluxos de hidrogênio. O modelo MINLP gerado é então transformado em um modelo MILP de acordo com uma técnica de linearização proposta por McCormick (McCormick, 1976). Pode-se demonstrar que o modelo MILP leva a uma qualidade aceitável e a uma eficiência computacional muito maior que o problema do MINLP.

Lou et al. (2013) descreveram sobre a otimização robusta que é utilizada normalmente em problemas de logística, mas pode ser aplicada para redes de hidrogênio nas refinarias devido aos fatores incertos presentes também nestes casos. O trabalho envolve uma série de cenários que representam possíveis casos futuros. O estudo de caso é testado tanto para um modelo determinístico de otimização para um cenário inicial, quanto para programação estocástica e otimização robusta multi-cenários.

Deng et al. (2014) desenvolveram um modelo matemático para sínteses de redes de hidrogênio operando em diferentes cenários. Foi desenvolvida uma superestrutura da rede com o objetivo de determinar a quantidade mínima de hidrogênio investigando diferentes cenários: número de conexões permitidas (modelo MILP), uso de compressores (modelo MILP e MINLP devido à bilinearidade) e uso de purificadores com avaliação econômica (modelo MINLP).

Wang et al. (2014) dissertaram sobre os métodos para aplicação das incertezas nas condições operacionais, sendo que os principais objetivos que se deseja alcançar nestes tipos de problema são garantir a otimização e a viabilidade da operação para um determinado intervalo de valores de parâmetros. O trabalho partiu de uma estratégia proposta por Grossmann e Sargent (1978) com o objetivo básico de projetar uma planta flexível de hidrogênio. Primeiro, um projeto deve ser selecionado para o qual é possível garantir que as especificações do projeto sejam atendidas para uma região delimitada dos parâmetros. Em segundo lugar, o design deve ser selecionado para otimizar o valor esperado do investimento e do custo operacional assumido no intervalo especificado de valores de parâmetros. A ideia básica dessa estratégia é que seja tirada vantagem do fato de que as variáveis de controle podem ser ajustadas para atender às especificações do projeto durante a operação da planta, pois é apenas o projeto da própria planta que permanecerá fixo. Baseado nisso, o objetivo do trabalho de WANG et al. (2014) é apresentar para a estratégia citada acima uma nova formulação matemática na qual a viabilidade da operação possa ser rigorosamente assegurada. Essa formulação corresponde à modelo MINLP de dois estágios.

Reza et al., (2016) tem como objetivo apresentar o método de avaliação da flexibilidade da rede de hidrogênio que fornecerá mais possibilidades de rede e fontes totais de hidrogênio que atendam às variadas demandas de hidrogênio, considerando a pureza total permitida dos fluxos de entrada enviados aos purificadores e usando a estrutura de rede. Nesse caso, o objetivo principal é minimizar o hidrogênio fresco fornecido à rede de hidrogênio. A rede de hidrogênio é otimizada usando o modelo de NLP. Além disso, num segundo método, a rede de hidrogênio inclui constantes e parâmetros incertos. Por exemplo, as vazões de fontes de hidrogênio, os limites de entrada de purificadores, a recuperação de hidrogênio são parâmetros constantes. As purezas de fontes de hidrogênio, as demandas de hidrogênio podem ser parâmetros incertos. O segundo método considera um conjunto de procedimentos sistemáticos para analisar e depois aprimorar a resiliência operacional de qualquer projeto de rede de hidrogênio, ou seja, é feito uma formulação de programação não linear (NLP). O último caso testado pelos autores considera o custo anual total mínimo para o qual é utilizado um modelo MINLP. Este caso se refere a métodos de otimização anteriores para a rede de hidrogênio sem considerar parâmetros de incerteza.

CHEN et al. (2020) propuseram programação matemática em duas etapas com diferentes tipos de incertezas, como eletricidade, demanda de hidrogênio e mercado de gás combustível. O modelo de programação estocástica de duas etapas avaliado em diferentes cenários de preços precisa satisfazer o teste de flexibilidade para incertezas operacionais através da modelagem com restrições adicionais impostas. Como o modelo proposto é MINLP, os autores utilizaram uma estratégia de solução baseada na desagregação multiparamétrica, um algoritmo MILP-NLP de duas etapas. A estratégia de operação multicenário aumenta a flexibilidade operacional e reduz o custo anualizado total.

2.2.3 Planejamento de produção

A indústria de refino de petróleo representa uma parcela importante do mercado industrial. Em uma refinaria, o planejamento de produção e a programação de produção são ferramentas muito úteis devido à complexidade operacional. Estas ferramentas são desenvolvidas baseadas em modelos matemáticos representativos nas unidades que compõem o processo. O planejamento e a programação de produção podem ser definidos como estratégias de melhor alocação de recursos, mão de obra ou de insumos, possuem diferenças conceituais, mas estão relacionados (Al-Qahtani e Elkamel, 2010).

O planejamento de produção possui um grau mais alto de decisão pois são elaboradas em um horizonte de tempo mais longo. Já a programação de produção possui um detalhamento maior, como por exemplo a ordem e o tempo de execução de etapas de processo. O enfoque deste trabalho é no planejamento operacional, onde é importante definir o que produzir, a quantidade e qual a matéria prima mais adequada. Isso pode ser feito através de modelos matemáticos, capazes de representar de forma genérica as principais etapas de uma refinaria. A otimização é uma técnica utilizada para resolução destes modelos, comumente utilizando o lucro como função objetivo.

Na literatura, a maioria dos modelos descritos é baseado em programação linear, para reduzir a complexidade na resolução. Porém, como a qualidade dos produtos finais é de suma importância, este trabalho resolver considerar como variáveis a vazão final dos produtos em questão e também a pureza. Nem sempre os trabalhos encontrados referem-se somente ao planejamento de produção dentro da refinaria, alguns consideram a logística do petróleo e até mesmo a cadeia final de distribuição.

Shah (1996) descreve o problema de fornecimento de petróleo bruto para as refinarias. O modelo é linear e considera a alocação de petróleo na refinaria, nos portos e bombeamento para destilação. Todas essas decisões são tomadas ao longo de um horizonte de 1 mês.

Moro et al. (1998) apresentam um modelo não linear para planejamento genérico em refinarias. O modelo foi aplicado ao planejamento de produção de uma refinaria de petróleo do mundo real com o objetivo principal da produção de diesel com diferentes especificações e demandas. Em 2000, Pinto et al. desenvolveram um estudo baseado no planejamento e programação da produção. No modelo de planejamento, são consideradas as relações não lineares dos processos envolvidos no refino. O modelo de programação é baseado no modelo MNILP. Este modelo considera o descarregamento de petróleo bruto de dutos, transferência para tanques de armazenamento e unidade de destilação.

Zhang et al. (2001) desenvolveram uma otimização integrada da refinaria, juntamente com a rede de hidrogênio e o sistema de utilidades. Para isso, a otimização da refinaria utiliza técnicas de programação linear (LP) para maximizar o lucro global. Em seguida, a rede de hidrogênio e o sistema de utilidades são otimizados para reduzir os custos operacionais para as condições de processo fixo determinadas a partir da otimização de LP. Embora o modelo original seja MINLP, técnicas de linearização são aplicadas para transformar o problema MINLP a um problema MILP. A partir de um estudo de caso de refinaria, uma melhora de 1,0% no lucro pode ser alcançada utilizando-se a abordagem simultânea em comparação com a abordagem sequencial. Como resultado, esse método fornece novos *insights* sobre o problema de otimização das refinarias e pode proporcionar benefícios significativos para a indústria de refino.

Joly et al. (2002) desenvolveram um modelo não linear de planejamento e programação em refinarias de petróleo. Três aplicações foram apresentadas para problemas de programação, gestão de estoque de petróleo bruto com diversos tipos de petróleo entregue exclusivamente por um único gasoduto de petróleo, modelos de otimização destinados a definir a política de produção ideal, controle e distribuição de estoques. O problema de programação foi modelado como um MINLP, devido aos termos bilineares da viscosidade. Um modelo MILP rigoroso derivado do anterior não linear mostrou-se eficiente para problemas de planejamento e programação.

Alhajri et al. (2008) abordam de forma mais realista o planejamento da produção de refinarias. O modelo proposto é capaz de prever as variáveis operacionais, temperaturas de ponto de corte na destilação bruta e conversão em unidade de craqueamento catalítico. As propriedades dos produtos finais e as especificações do mercado também estão incluídas. Os resultados mostram que o modelo forneceu uma estratégia operacional ideal para a refinaria e, ao mesmo tempo, atende às propriedades e taxas de produção do produto.

Li et al. (2010) apresentam um modelo de planejamento de refinarias que utiliza modelos não lineares empíricos simplificados, incluindo propriedades de petróleo bruto e qualidade do produto. Os modelos são para unidade de destilação, unidade de craqueamento catalítico e mistura de produtos em refinaria. Primeiro, o modelo da destilação é resolvido para determinar as relações de transferência, em seguida, o modelo para craqueamento catalítico é resolvido para obter os rendimentos.

Leiras et al. (2010) propuseram uma metodologia robusta de otimização considerando as incertezas nos processos de refinaria. Foram consideradas as incertezas na venda dos produtos, custos operacionais, demanda do produto e rendimento do produto. Os benefícios da incorporação da incerteza nos diferentes parâmetros do modelo foram avaliados em termos do custo de ignorar a incerteza no problema. O modelo robusto oferece vantagens e também limites de probabilidade de violação dos valores nominais foram calculados a fim de ajudar o tomador de decisão a fazer melhores escolhas no que diz respeito aos parâmetros para controlar a robustez.

Alattas et al. (2011) enfatizaram a questão do planejamento de produção de uma refinaria sendo normalmente desenvolvida como modelo linear (LP). No entanto, as não linearidades do problema original acabam não sendo consideradas. Portanto, este artigo propôs um modelo de índice de fracionamento para adicionar não linearidade aos modelos de planejamento linear das refinarias. O modelo de fracionamento é desenvolvido para a destilação de petróleo bruto e resultando em um modelo simples que otimiza os cortes e temperatura. Essa abordagem previu maior lucro com base em diferentes decisões de compra de petróleo bruto.

Castillo et al. (2017) propuseram um algoritmo de otimização global para resolver o planejamento de refinarias de petróleo. A formulação foi um modelo MINLP e com relaxamentos em termos bilineares usando McCormick, o problema resulta em um modelo MILP. Relaxamentos ajudam a encontrar uma solução viável do problema original através de um solucionador não linear local. Os resultados compararam o desempenho de dois solucionadores comerciais, BARON e ANTIGONE.

Diante de todos os conceitos expostos e diferente do que se encontra na literatura, este trabalho deseja analisar a flexibilidade e a otimização multi-cenários para uma gestão eficiente do uso de hidrogênio, aplicado ao planejamento de produção em refinarias. Embora o foco seja operacional, o problema abordado aqui é mais amplo e tem um interesse industrial significativo. O principal objetivo do gerenciamento de redes de hidrogênio e da interligação desta abordagem com o planejamento de produção é a produção de hidrogênio com folga mínima. O excesso de produção de hidrogênio deve ser minimizado, primeiro porque o hidrogênio não é fácil de manusear ou armazenar e depois porque não é economicamente viável, pois o excesso deve ser queimado como combustível em fornos e/ou outros processos.

Capítulo 3 – **Application of linear and nonlinear mathematical programming to retrofit hydrogen networks**

O presente capítulo é uma reprodução do artigo aceito pela *Braziliand Journal of Chemical Engineering.* Este artigo foi o primeiro trabalho elaborado durante o doutorado e por isso, detalha o desenvolvimento da programação matemática como ferramenta de otimização para redes de hidrogênio. Com isso, o objetivo 1 desta Tese de Doutorado e as contribuições 1 e 2 estão relacionadas a este trabalho. Através da programação matemática, foi desenvolvido um modelo linear (Mixed Integer Linear Programming - MILP) e um modelo não linear (Mixed Integer Nonlinear Programming - MINLP) capazes de representar a rede de hidrogênio, composta por fontes, consumidores e unidade de purificação. A otimização é baseada na minimização do custo operacional, que inclui os custos de produção de hidrogênio, custo de purificação, custo de eletricidade para o caso da necessidade de utilização de compressores e o custo da queima da purga como gás combustível. Através da otimização, é possível propor um *redesign* da rede de hidrogênio, e neste caso pode-se incluir a instalação de novas linhas, compressores ou unidades de purificação. A ideia deste artigo, além da completa descrição dos modelos utilizados, é comparar os resultados obtidos via modelagem linear e não linear com diferentes restrições impostas aplicados em dois estudos de caso, um estudo da literatura e um estudo com dados reais de uma refinaria brasileira. O modelo MILP, além de ter fácil resolução (convergência para ótimo global), se mostrou uma alternativa eficiente em termos de redução de custo operacional. O modelo MINLP, apesar de não garantir uma solução ótima global, gerou menores custos de operação e de capital. Em termos de redução do custo operacional, quando comparado com a rede original, o modelo MILP resultou em 10% e 16,9% para o caso 1 e 2, respectivamente e o modelo MINLP gerou redução de 9,7% para o exemplo 1 e 31,5% para o exemplo 2.

Abstract: Hydrogen network management has economic appeal due to its importance in oil refineries. It has become genuinely relevant due to the restrictions of sulfur content in fuels, which need hydrogen to be removed. Mathematical programming can be used as a tool for optimizing hydrogen networks, and the efficient management of hydrogen within the refineries can be achieved through a material balance of the units that make up the hydrogen network. In this work, an optimization model Mixed-Integer Linear Programming (MILP) and Mixed-Integer Nonlinear Programming (MINLP) for hydrogen networks was applied to minimize the operating costs. The optimization model was developed in GAMS, and it was validated using a literature case study and a real case study from a Brazilian Refinery. The operation cost was reduced by 10% and 19.6% with MILP and 9.7% and 31.5% with MINLP, for example 1 and 2, respectively. Comparing the results, both achieve significant savings in operating costs. The MILP model, which is easier to solve, has proved to be an efficient tool for optimizing hydrogen networks. However, optimization via MINLP, although not guaranteeing the optimal solution, resulted in lower operating and capital costs. The design of the optimized hydrogen networks was also detailed, and other extra restrictions were imposed on the problem.

Keywords: hydrogen network, mathematical programming, optimization, hydrogen management

3.1 Introduction

The growth in the use of hydrogen in oil refineries can be justified by increasing environmental restrictions on sulfur content. The Brazilian National Petroleum Agency (ANP) regulates activities that integrate oil, natural gas, and biofuels industries, so it must establish rules and supervise the different areas of activity such as exploration, refining, and processing, including parameters such as sulfur content. The regulations issued by ANP have been gradually decreasing the sulfur content in diesel and gasoline. There are several processes capable of treating oil fractions to reduce the amount of sulfur. It usually occurs in hydrotreatment units (HDT), which use hydrogen to remove sulfur and other impurities. Hydrogen in refineries can be obtained mainly in hydrogen generation units (UGH), which use catalytic reform reactions for their production. Besides, catalytic cracking also provides hydrogen as a sub product.

Therefore, hydrogen has been an essential raw material in refineries, so it must be used efficiently. Usually, the amount produced is higher than that used in hydrotreating, which leads to the burning of this excess. On the other hand, limiting hydrogen production can make HDT's inefficient and inoperative. Therefore, the efficient management of hydrogen within a refinery is fundamental both in economic and safety terms (Borges, 2009; Cruz, 2010; Figueiredo, 2013). Thus, the management of hydrogen networks has a vital appeal and, when done efficiently, generates a production with minimal hydrogen clearance and with satisfactory financial returns.

Process integration, in the context of mass integration, can be used to manage hydrogen networks. Through material balance in the involved steps (sources, consumers, and purifiers of hydrogen), it is possible to manage hydrogen through network optimization efficiently. Optimization is one of the most potent tools in process integration, based on selecting the 'best' solution by choosing an objective function (for example, operating cost) that must be minimized or maximized. The objective function can be subject to several restrictions that include material and energy balances, process modeling equations, and thermodynamic requirements (El-Halwagi, 2006).

In general, this methodology can be divided into two categories: (i) segmentation methods (pinch) and (ii) mathematical programming approaches based on network design. The focus of this work is the mathematical programming approach. The mathematical programming based on the superstructure presents advantages concerning the pinch, such as, for example, considering many limitations/restrictions and variables when searching for solutions in the optimization problem. The methodology of mathematical programming is: (i) the development of the superstructure (which units are involved and classification as sources and consumers, in addition to the existing compressors and purifiers), (ii) the formulation of the mathematical model capable of representing it (choice of the objective function to be minimized or maximized through restrictions) and (iii) the resolution of the optimization problem (Jia, 2010; Pinheiro, 2012).

Thus, this paper approach is based on evaluating different optimization strategies for hydrogen network management through mathematical programming. For this, two formulations were developed, MILP (Mixed Integer Linear Programming) and MINLP (Mixed Integer Nonlinear Programming), capable of representing hydrogen networks. The modeling has been fully described, and the objective is to compare the results obtained in terms of savings in operating costs and the network designs obtained. Two case studies were used to validate the formulations developed, an example from the literature, and a real case study with project data from a Brazilian oil refinery.

3.2 Literature review

The optimization need in the hydrogen network in refineries was recognized in the 1990s, and since then, many methodologies have emerged. They are mainly segmentation methods (pinch) and mathematical programming approaches based on the design of networks. Mathematical programming offers advantages when compared to pinch, as already mentioned, as it is more flexible, and the network synthesis takes place automatically as a result of the problem. In the pinch approach, it would be necessary to use another technique to evaluate the process synthesis. Besides, it is possible to consider numerous restrictions in mathematical programming, such as pressure limits, equipment capacity, and investments with new equipment. For this reason, the vast majority of works about hydrogen network management was done using mathematical programming (Jia, 2010).

Mathematical programming problems can be elaborated, considering several factors, i.e., different objective functions, pressure restrictions, and equipment capacity limitations. This information characterizes the developed problem. Therefore, they can generally be formulated as a linear programming (LP) problem, mixed-integer linear programming (MILP), nonlinear programming (NLP), or mixed-integer nonlinear programming (MINLP). MINLP problems are more challenging to solve because they combine the NLP and MILP models and their characteristics, including nonlinearity. However, they result in more realistic networks and include several additional restrictions. The use of MILP, due to the fact of linearity, facilitates the resolution of the optimization problem, as they are easier to converge to a global solution, since all subproblems, for fixed binaries, are solved linearly for global optimization. Most of the work on hydrogen network management via mathematical programming uses MINLP models, as can be seen below. For the resolution of this formulation, there are different algorithms found in GAMS solvers or even use linearization techniques to facilitate the resolution of MINLP, as McCormick (Birewar and Grossmann, 1990; Gams, 2020; Petric, 2014).

Hallale and Liu (2001) developed a mathematical model (NLP) to reduce hydrogen consumption. The model considered pressure restrictions, existing compressors, and strategy for installing a purifier. The objective function was to minimize the total cost, including capital and operating costs. Liao et al. (2010) developed a model using an existing hydrogen network with a purifier. The objective function was the total annual cost, and the model was solved in GAMS using DICOPT. The total annual cost decreased by 22.6%, and the new compressor and PSA were incorporated.

In Kumar et al. (2010), mathematical models were developed based on pressure restrictions, sources, consumers, purity, and total operating cost. For this, two case studies were carried out that compared the types of programming. For case study A, NLP, and MINLP model were used, and for case study B, LP, NLP, and MILP were used, and the objective function was minimizing total annual cost. The MINLP model reduced operating costs by 21.9 % in comparison to the NLP model for case A. In case B, the network obtained by the NLP model was more realistic than MILP. So mixed-integer linear and nonlinear programming models are considerably better than linear (LP) because it provides the less complicated and more realistic refinery system, and MINLP can include complexities as compressors, purity constraints, and pressure constraints.

Sardashti Birjandi et al. (2014) developed a methodology for the global optimization of a hydrogen network based on a problem solved simultaneously by MINLP and NLP. A combination of the bound contraction procedure and linearization technique by McCormick for nonlinear models were used for global optimization. Global optimization strategy has reduced operating costs, save the investment cost, and increases the profit.

Matijašević and Petric (2016) presented a methodology for integrating the hydrogen network in a local refinery case study. The superstructure was modeled using a nonlinear mathematical model whose objective function was to minimize total operating costs. The problem was solved with the GAMS software. Network design flows of hydrogen with two units to purify hydrogen proved to be an optimal solution for this case study.

Jagannath et al. (2018) used an MINLP model to reduce the total annual cost focus in nonconvex problems to global optimality. The nonlinearity is due to the bilinear terms and the pressures that vary in the compressors, so the nonlinearity is bilinear, linear fractional, and posynomial terms. The linear fractional and posynomial terms were eliminated by heuristically assigning suction and discharge pressures for the newly retrofitted compressors. Bilinear terms in MINLP was solved to global optimality using a specific tailor-made global optimization algorithm to be solved to ϵ-global optimality. For that, a bivariate partitioning scheme using incremental cost formulation was utilized for the convexification of the bilinear term.

As mentioned, most of the bibliography is about MINLP formulations, and there is no direct comparison between MILP and MINLP models, their characteristics and advantages. This work aims to apply optimization for the retrofit existing hydrogen networks, comparing models developed via linear (MILP) and nonlinear mathematical programming (MINLP). The objective is to minimize the operating cost, with the possibility of installing new pipelines and equipment, such as compressors and purification units. Additional restrictions may also be imposed on the objective function, such as limiting the installation of new equipment or investment costs. The results obtained in case studies are evaluated with other critical economic parameters such as investment cost and payback time.

3.3 Mathematical Model Formulation

The hydrogen network presents a set of sources i ϵ hydrogen sources (HS), a set of consumers j ϵ hydrogen consumers (HC), a set of purifiers k ϵ hydrogen purifiers ($HP = OHP \cup NHP$), considering the existing purifiers, OHU, and the new purifiers, NHP and a set of compressors c ϵ hydrogen compressors $HCP = OHCP \cup NHCP$), considering the existing compressors $OHCP$ and new compressors $NHCP$ For each source is given the maximum and minimum flow rate, the hydrogen composition, and the outlet pressure. For each consumer is given the inlet flowrate demand, pressure, and composition, the outlet purge flow, pressure, and composition. For each purifier is given the maximum flow capacity, the composition of purified flow and purge flow, the pressure of purification, and the hydrogen recovery. It is also considered a fuel system in which waste streams can be burned and used as fuel to the process. For the existing networks, they are also given the existing lines (unit connections), the distance between the units if informed, and the existing compressors and purifiers. Also, it is necessary to know the capacity of the compressors.

The optimization problem is to minimize the operating costs due to hydrogen production and purification, electricity, and economy provided by the streams used as fuel to the process. The optimization problem is subject to the material balances and process operating constraints. For the retrofit case, process modifications are allowed to reduce the total operating costs (the objective function), despite the investment costs due to the installation of new pipelines, compressors, and possibly new purifiers.

Some considerations were made to simplify the model. The flow is considered only a binary mixture of hydrogen and methane, and compressors are associated with each possible connection individually in the MILP problem. Therefore, it is not allowed to merging flows before the compressor units, which would result in an unknown inlet hydrogen composition. Hence, a nonlinear material balance would be necessary. The partial pressure of the hydrogen and the flow are constant at the entrance and exit of the consuming units. In the MINLP problem, compressors are like units, so pressure and purity are variable in the process.

3.3.1 MILP model

The hydrogen network can be represented using the diagram presented in Figure 3.1. Hydrogen sources with specific purity supply hydrogen to the consumer units ($FIJ_{i,j}$), for purification ($FIK_{i,k}$), or for burning if they are in excess (FIW_i). Consuming units can send hydrogen between them $\left(FJJ_{j,j'}\right)$, or purify to achieve the desired purity ($FJK_{j,k}$) or even send for burning (FJW_j). The hydrogen purification unit provides consumers with pure hydrogen ($FKJ_{k,j}$) and the excess can be burned (FKW_k). The amount not purified in PSA according to its capacity is also sent for burning ($FKWrec_k$).

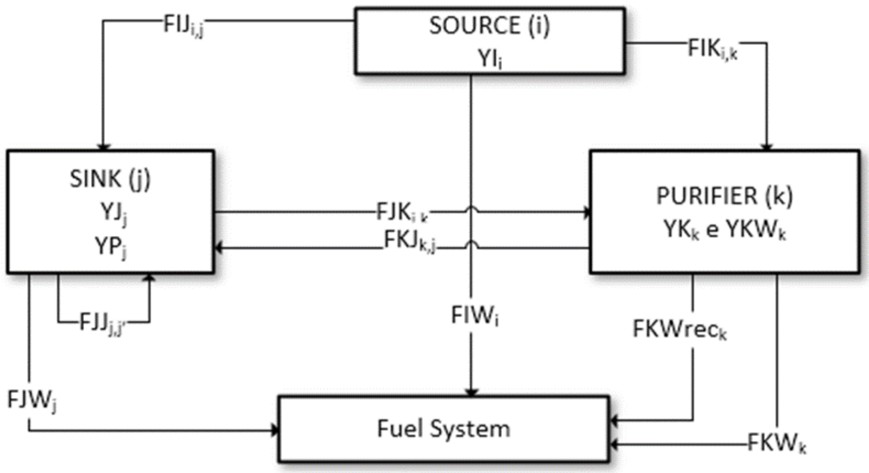

Figure 3.1: Scheme developed for the mathematical modeling of the MILP problem.

The mathematical problem proposed in this article is detailed below, which includes material balances in sources, consumers, and purifiers, besides calculations of operating and capital costs. All variables are shown in the List of Symbols. To consider the capital cost, it is necessary to use binary variables, representing the installation or not of a new pipeline, compressor, or purifier. For this, it was necessary to use constraint modeling, through propositions and logical disjunctions.

Material balance in sources:

$$FH2I_i = \left(\sum_{j \in HC} FIJ_{i,j} + \sum_{k \in HP} FIK_{i,k} + FIW_i\right) \quad \forall\, i \in HS \tag{3.1}$$

$$FH2I_{i,min} \leq FH2I_i \leq FH2I_{i,max} \quad \forall\, i \in HS \tag{3.2}$$

Material balance in consumers:

$$FJ_j = \sum_{i \in HS} FIJ_{i,j} + \sum_{k \in HP} FKJ_{k,j} + \sum_{j \in HC} FJJ_{j,j'} \quad \forall\, j \in HC \tag{3.3}$$

$$FJ_j * YJ_j = \sum_{i \in HS} FIJ_{i,j} * YI_i + \sum_{k \in HP} FKJ_{k,j} * YK_k + \sum_{j \in HC} FJJ_{j,j'} * YP_j \quad \forall\, j \in HC \tag{3.4}$$

$$FP_j = FJW_j + \sum_{k \in HP} FJK_{j,k} + \sum_{j \in HC} FJJ_{j,j\prime} \quad \forall\, j \in HC \tag{3.5}$$

Material balance in purifiers:

$$\sum_{j \in HC} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} = \sum_{j \in HC} FKJ_{k,j} + FKW_k + FKW_{rec,k} \quad \forall\, k \in HP \tag{3.6}$$

$$\sum_{j \in HP} FJK_{j,k} * YP_j + \sum_{i \in HS} FIK_{i,k} * YI_i = \sum_{j \in HP} FKJ_{k,j} * YK_k + FKW_k * YK_k + FKW_{rec,k} * YKW_k \quad \forall\, k \in HP \tag{3.7}$$

$$\sum_{j \in HP} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} \leq \sum_k FPur_{max,k} \quad \forall\, k \in HP \tag{3.8}$$

$$\left(\sum_{i \in HS} FIK_{i,k} * YI_i + \sum_{j \in HP} FJK_{j,k} * YP_j\right) * (1 - rec_k) = FKW_{rec} * YKW_k \qquad \forall\, k \in HP \tag{3.9}$$

$$\sum_{j \in HP} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} = FK_k \qquad \forall\, k \in HP \tag{3.10}$$

For the operating cost, it is necessary to calculate cost of hydrogen, cost of fuel, cost of electricity and cost of purifying.

$$C_{operating} = (CH2I + CH2K + CH2C - CH2F) * t \tag{3.11}$$

Cost of hydrogen from sources:

$$CH2I = \sum_{i \in HS} FH2I_i * C_i \tag{3.12}$$

Cost of fuel:

$$CH2F = C_{fuel} * FW * (y * \Delta H°_{H2} + (1 - y) * \Delta H°_{CH4}) \tag{3.13}$$

Cost of electricity:

$$CH2C = FC * \mathrm{w} * C_{eletric} \tag{3.14}$$

where:

$$w = \overline{(C_P} * T/\eta) * \left(\left(\frac{P_{out}}{P_{in}}\right)^{\frac{\gamma-1}{\gamma}} - 1\right) * (\rho_o/\rho) \tag{3.15}$$

Cost of purifying:

$$CH2K = \sum_{k \in HP} FK_k * C_k \tag{3.16}$$

For the capital cost, it is necessary to calculate the cost of new compressor, new pipelines, and new purifier unit.

$$C_{capital} = \left(C_{new\,PSA} + C_{new\,piping} + C_{new\,compressor}\right) * A_f \tag{3.17}$$

For new PSA unit:

$$C_{new\,PSA} = a * \sum_{k \in NHP} z_{kn} + \mathrm{b} * \left(\sum_{k \in NHP} FK_{new\,k}\right) \tag{3.18}$$

For new pipeline:

$$C_{new\,piping} = (c * z_h + d * D^2) * L \tag{3.19}$$

where:

$$D^2 = (4 * F_{newpipe}/\pi * \vartheta) * \left(\frac{T}{T_0}\right) * \left(\frac{P_0}{P}\right) \tag{3.20}$$

For new compressors:

$$C_{new\,compressor} = e * z_c + f * FC_{new} * w \tag{3.21}$$

The parameters related to the cost of capital are show in Table 3.1. The units of the variables related to the parameters are also in the table.

Table 3.1: Capital costs parameters (Hallale and Liu, 2001).

Cost of new compressors [k$]	$e = 115$
	$f = 1{,}91$
	W in [kW]
Cost of piping [$]	$c = 3{,}2$
	$d = 11{,}42$
	D^2 [in^2] and L [m]
Cost of new PSA[k$]	$a = 503{,}8$
	$b = 347{,}4$
	F in [MMscfd]

It was necessary to create a binary variable representing the flow rate (z); that is, if there is a flow in a given connection shown in the scheme, the variable z assumes the value of 1. Also, other binaries were created, representing the need for a new compressor (z_c) (Equation 3.22), the need for a new pipeline (z_h) (Equation 3.23) and the need for a purification unit (z_{kn}) (Equation 3.24).

$$\begin{cases} z \geq z_c \\ 1 - u_c \geq z_c \\ u_{deltaP} \geq z_c \end{cases} \tag{3.22}$$

$$\begin{cases} z_h \leq z \\ z_h \leq 1 - u_h \end{cases} \tag{3.23}$$

$$\begin{cases} FK_k \geq \varepsilon * z_{kn} \\ FK_k \leq (FPur_{max,k}) * z_{kn} \end{cases} \quad \forall\, k \in NHP \tag{3.24}$$

For a compressor to be installed, there must be flow, no compressor previously installed, and a pressure difference that justifies the installation. For a new pipeline to be installed, it is enough that there are flow and no previous pipeline in that connection. For a new PSA to be installed, it is enough that there is flow from some connection that has PSA as its origin or destination.

The objective function chosen for the optimization of hydrogen networks is the minimization of the operating cost, which includes the cost of hydrogen from the sources, the cost of purification, the cost of electricity from the use of compressors, and the cost of burning the excess (Equation 3.11). The new equipment, pipelines, compressors, and PSA are accounted for in the capital cost (Equation 3.17). The total annual cost is the sum of the operating cost and capital cost penalized with the annualization factor.

The MILP model formulated in this work is described by the equations 3.1-3.24. The proposed model has the advantage of being a linear model, for which very robust solvers can be used. However, the main disadvantage is that a compressor is associated with each possible connection individually to avoid nonlinear material balances to identify the composition of the current being compacted. In this case, the streams cannot be mixed to use the same compressor, and the resulting network may end up with more compressor units than an alternative NLP model, in which the streams can mix.

3.3.2 MINLP model

In the nonlinear model, the process variables listed above are used. However, also the variables of the compressors are now considered, which in the MINLP structure are part of the hydrogen network as a unit, as shown in the diagram below (Figure 3.2).

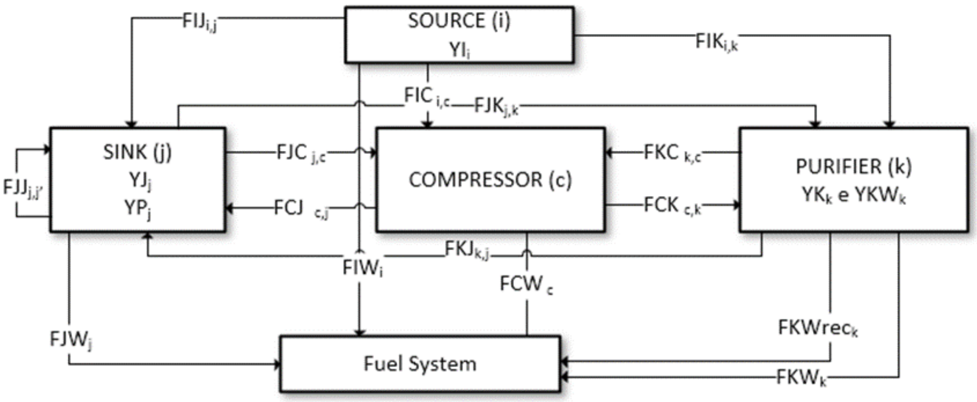

Figure 3.2: Scheme developed for the mathematical modeling of the MINLP problem.

The equations 3.25-3.35 that describe the MINLP model are below; also, the equations 3.11-3.21 are used (equations about operating cost and capital cost). The operating and capital costs are calculated in the same way as in the linear problem, as well as the logical flow restrictions. It is worth mentioning that the binaries involving the compressors in the connections are included here, and the same occurs with the binary variables associated with new pipelines. The binary variables associated with the new compressors are not part of this model, as here they are considered as units of the network.

Material balance in sources:

$$FH2I_i = \left(\textstyle\sum_{j \in HC} FIJ_{i,j} + \sum_{k \in HP} FIK_{i,k} + FIW_i + \sum_{c \in HCP} FIC_{i,c}\right) \quad \forall\, i \in HS \tag{3.25}$$

$$FH2I_{i,min} \le FH2I_i \le FH2I_{i,max} \quad \forall\, i \in HS \tag{3.2}$$

Material Balance in consumers:

$$FJ_j = \textstyle\sum_{i \in HS} FIJ_{i,j} + \sum_{k \in HP} FKJ_{k,j} + \sum_{j \in HC} FJJ_{j,j'} + \sum_{c \in HCP} FCJ_{c,j} \quad \forall\, j \in HC \tag{3.26}$$

$$FJ_j * YJ_j = \textstyle\sum_{i \in HS} FIJ_{i,j} * YI_i + \sum_{k \in HP} FKJ_{k,j} * YK_k + \sum_{j \in HC} FJJ_{j,j'} * YP_j + \sum_{c \in HCP} FCJ_{c,j} * YC_c \quad \forall\, j \in HC \tag{3.27}$$

$$FP_j = FJW_j + \textstyle\sum_{k \in HP} FJK_{j,k} + \sum_{j \in HC} FJJ_{j,j'} + \sum_{c \in HCP} FJC_{j,c} \quad \forall\, j \in HC \tag{3.28}$$

Material balance in purifiers:

$$\sum_{j \in HC} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} + \sum_{c \in HCP} FCK_{c.k} = \sum_{j \in HC} FKJ_{k,j} + FKW_k + FKW_{rec,k} + \sum_{c \in HCP} FKC_{k,c} \quad \forall\, k \in HP \tag{3.29}$$

$$\sum_{j \in HP} FJK_{j,k} * YP_j + \sum_{c \in HCP} FCK_{c.k} * YC_c + \sum_{i \in HS} FIK_{i,k} * YI_i = \sum_{j \in HP} FKJ_{k,j} * YK_k + \sum_{c \in HCP} FKC_{k,c} * YK_k + FKW_k * YK_k + FKW_{rec,k} * YKW_k \quad \forall\, k \in HP \tag{3.30}$$

$$\sum_{j \in HP} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} + \sum_{c \in HCP} FCK_{c,k} \le FPur_{max,k} \qquad \forall\, k \in HP \tag{3.31}$$

$$\left(\sum_{i \in HS} FIK_{i,k} * YI_i + \sum_{j \in HP} FJK_{j,k} * YP_j + \sum_{c \in HCP} FCK_{c.k} * YC_c\right) * (1 - rec_k) = FKW_{rec} * YKW_k\Big) \qquad \forall\, k \in HP \tag{3.32}$$

Material balance in compressors:

$$FC_c = \sum_{c \in HCP} FIC_{i,c} + \sum_{c \in HCP} FJC_{j,c} + \sum_{c \in HCP} FKC_{k,c} \quad \forall\, c \in HCP \tag{3.33}$$

$$\sum_{c \in HCP} FIC_{i,c} + \sum_{c \in HCP} FJC_{j,c} + \sum_{c \in HCP} FKC_{k,c} = \sum_{c \in HCP} FCJ_{c,j} + \sum_{c \in HCP} FCK_{c.k} + FCW_c \quad \forall\, c \in HCP \tag{3.34}$$

$$FC_c * YC_c = \sum_{c \in HCP} FIC_{i,c} * YI_i + \sum_{c \in HCP} FJC_{j,c} * YP_j \sum_{c \in HCP} + FKC_{k,c} * YK_k \quad \forall\, c \in HCP \tag{3.35}$$

The methodology developed in this article is summarized in Figure 3.3. To compare the optimization through the linear and nonlinear models, the cost of the original network was first calculated. The procedure performed was: (i) the flows are fixed according to the current network (base case), including the binary. So, the problem is solved, and the actual cost is accounted. The variables were then released, including lower and upper bounds, and the problem was optimized using the MILP and MINLP model. In the MILP formulation, additional restrictions on the objective function have also been tested, such as limiting the installation of a new PSA or not yet allowing any investment. The same procedure was performed in both examples and the results are discussed in the next session.

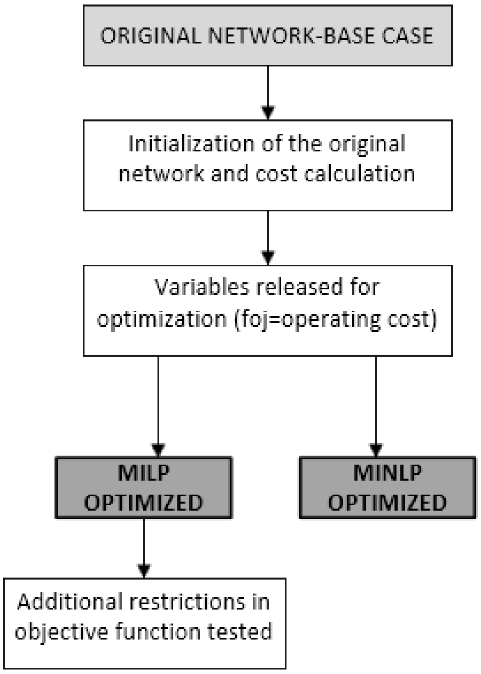

Figure 3.3: Methodology used to optimize hydrogen networks.

In this work, no other different initializations were addressed, but an alternative that proved satisfactory results is the initialization of the linear problem result for the nonlinear model. This subject was addressed in another article, using the MILP and MINLP models with different case studies (Silva et al., 2020).

3.4 Results and discussion

The MILP and MINLP optimization problems were validated using an adapted example of a hydrogen network found in the literature, from Liao et al. (2010) and another using a real example of a Brazilian refinery. The entire formulation was implemented in the modeling system GAMS on a 3.6 GHz Intel® Core ™ I7 CPU. The solvers used in MILP and MINLP are CPLEX and DICOPT, respectively. Other solvers have been tested and will be discussed in the examples below.

The CPLEX solver is a high-performance solver for Linear Programming, Mixed Integer Programming and Quadratic Programming problems. For problems with integer variables, CPLEX uses a branch and cut algorithm which solves a series of LP, subproblems. Because a single mixed integer problem generates many subproblems, even small mixed integer problems can be very compute intensive and require significant amounts of physical memory. DICOPT is based on the extensions of the outer-approximation algorithm for the equality relaxation strategy. The MINLP algorithm inside DICOPT solves a series of NLP and MIP sub-problems. More information on the operation of solvers can be found in the GAMS Manual (Gams, 2020).

3.4.1 Example 1

The hydrogen network is composed of five sources, two hydrogen plants (H_2 plant1 and H_2 plant2), a catalytic reforming unit (CCR), a semi regenerated catalytic reformer (SCR), and a fertilizer plant (FER). In addition, there are six consumer units (HC- hydrogen cracker, WHT- wax oil hydrotreater, KHT- kerosene hydrotreater, DHT- diesel hydrotreater, SDHTstraight run diesel hydrotreater, and CDHT- catalytic diesel hydrotreater), and one purification unit(PSA). Also, there are four compressors. The MILP model included 1180 single equations, 505 single variables, and 362 discrete variables. The MINLP present 1297 single equations, 731 single variables, and 444 discrete variables. The network is shown in Figure 3.4 and the parameters used are shown in Tables 3.2 and 3.3.

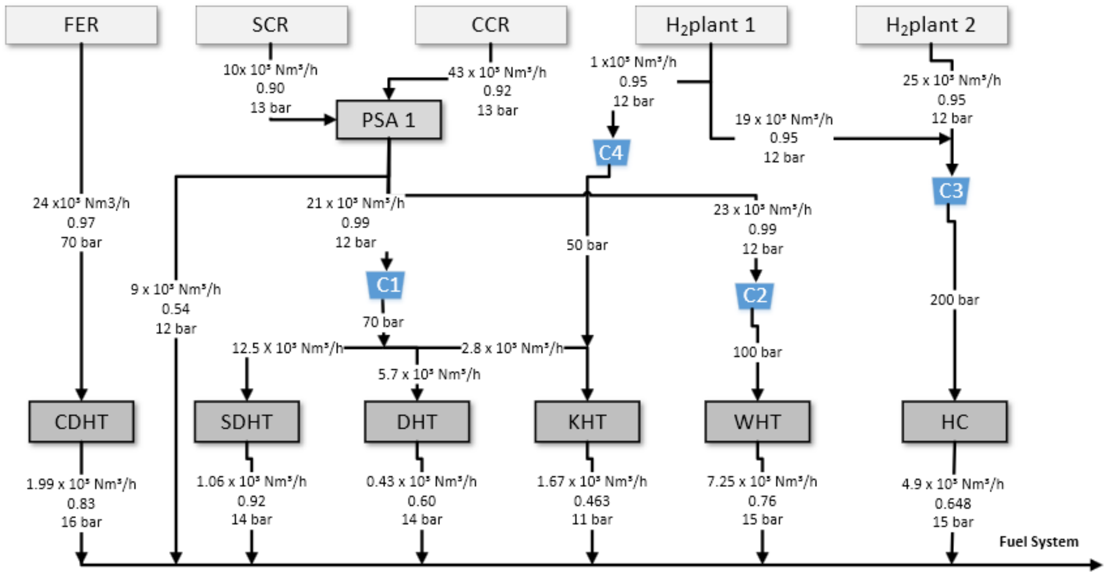

Figure 3.4: Existing hydrogen network - Adapted from Liao et al. (2010).

Table 3.2: Operating Costs Parameters (Hallale and Liu, 2001; Liao et al., 2010)

Hydrogen cost	C_i	0,08 \$/Nm³
Hydrogen cost –FER	C_i	0,066 \$/Nm³
Electricity cost	$C_{eletric}$	0,03 \$/kWh
Purification cost	C_k	0,0011 \$/Nm³
Fuel cost	C_{fuel}	2,5 \$/ MMBtu

Table 3.3: Parameters used to optimize the available network.

Parameters	
Waste pressure	6 bar
Temperature	300 K
Pressure	12 bar
$\overline{Cp}$	30 J/mol.K
ΔH°_{H2}	286 kJ/mol
ΔH°_{CH4}	891 kJ/mol
Standard conditions	T_0=288.7 K P_0=1 bar
Annual Operation time (t)	8760 h
Annualization Factor (A_f)	0,5

For the case study, the retrofit of the existing network was considered to minimize the operational cost. First, the original network (base case) operating cost was calculated using the same model developed following the parameters listed. This was done by setting the flow values according to the original network. Using the equations described in section 3.2.1 and the parameters listed in Table 3.2 and 3.3, the original network (base case) cost is 71.428 million $ / year. The Hydrogen Network BASE CASE (HN- BASE CASE) corresponds to the existing basic topology, that is, the values obtained from operating costs are the current costs in which the refinery is operating, used as a base case for later comparison with the networks obtained through optimization.

After that, using the optimization initialization strategies, the MILP problem was solved. As it is a case of a retrofit, it was possible to increase the efficiency of the hydrogen network through the installation of new equipment, computed in the capital cost. The economy saving is obtained by the operating cost reduction compared to the original solution. However, there is also an investment cost associated with non-existing equipment and pipelines. Another economic indicator, the turnaround time, was also used to evaluate the optimized network. The payback time is defined as the annualized cost of capital divided by the savings obtained.

Then, the hydrogen network was optimized based on the minimum operating cost. It resulted in a savings of almost 7.4 million. The proposed new network design includes one new PSA, nine new compressors, and eighteen new lines, which generates a total investment of 20.6 million. The payback is 33 months. It is the result obtained through the MILP optimization problem and will be called HN1 -MILP OPTIMIZED.

A new optimization was made, not allowing the installation of a new PSA. This proposed new network presented savings of 7.1 million. However, the total investment is 1.4 million, which includes nine new pipelines and five new compressors. The payback time is 2.3 months. This optimized network is HN2 -MILP OPTIMIZED and its design is shown in Figure 3.5. It is worth noting that hydrogen plants were not necessary. As the existing compressors 3 and 4 in the original network were not used in the proposed design and 5 new compressors are needed, they will be reused. With that, it would be necessary to install only 3 new compressors, which reduces the total investment cost to 1.13 million.

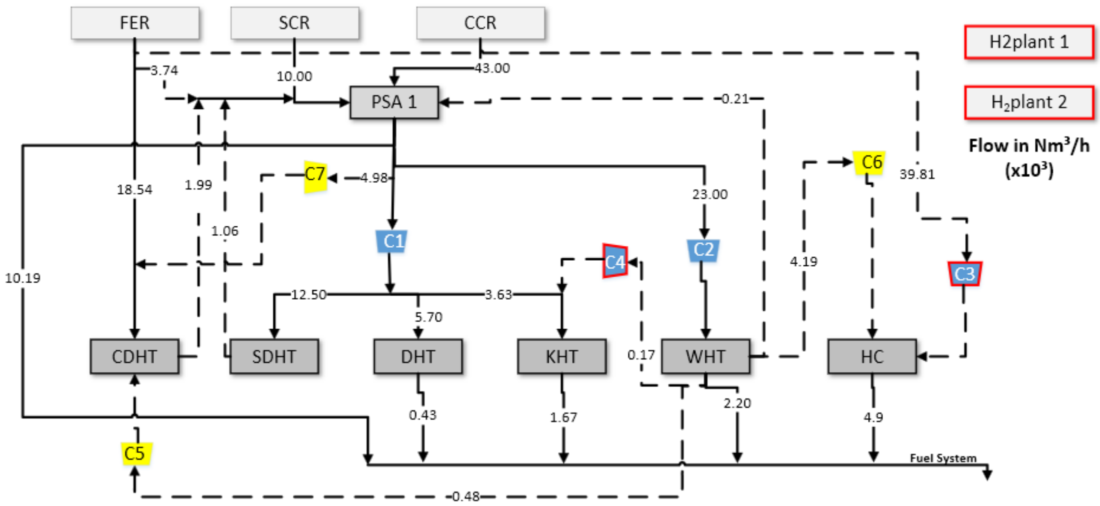

Figure 3.5: Optimized network HN2 -MILP OPTIMIZED.

To compare the results obtained through different models, the original network was also optimized through a nonlinear mathematical programming model (MINLP). About solvers, the best solution was found with DICOPT, comparing with SBB, and solver BARON was unable to find a solution. As a result, savings of 6.9 million were obtained compared to the HN-BASE CASE network. As in the nonlinear model, it is possible to mix flows in the compressors, and this makes the investment cost less. The optimized network only required the installation of 10 new lines. There is no installation of PSA, and the four existing compressors were used. Thus, the total investment is 0.51 million, with a payback of less than one month. This optimization result from the MINLP is called HN3-MINLP OPTIMIZED. This optimized network is represented in Figure 3.6. Table 3.4 summarized the obtained results.

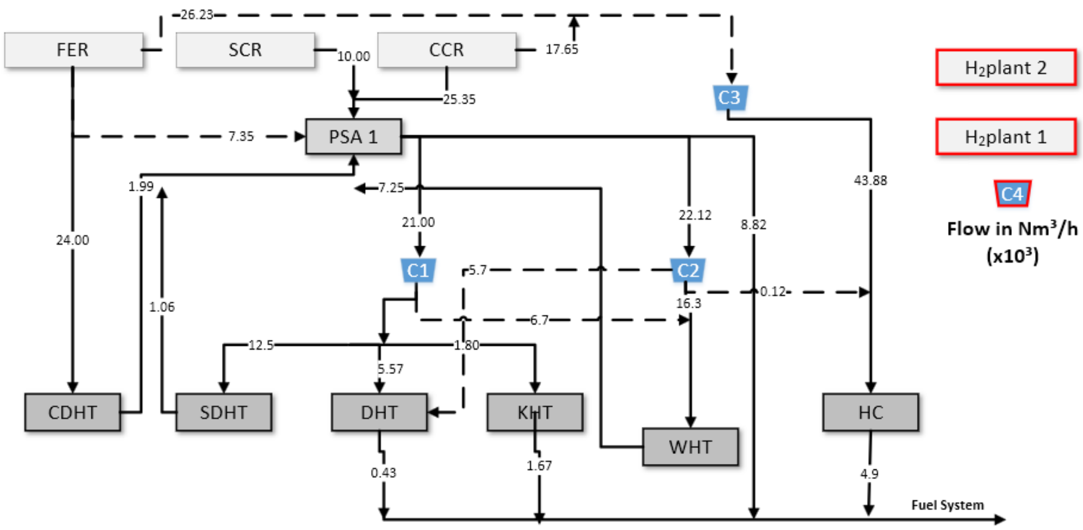

Figure 3.6: Optimized network HN3-MINLP OPTIMIZED.

Table 3.4: Results of minimizing operating cost for example 1.

	HN-BASE CASE	HN1-MILP OPTIMIZED	HN2-MILP OPTIMIZED	HN3-MINLP OPTIMIZED
	[x10^6 \$/year]			
CH2I (Hydrogen)	82.554	71.779	73.038	71.589
CH2F (Fuel)	11.992	8.925	9.538	7.956
CH2C (Compressor)	0.354	0.297	0.223	0.392
CH2P (Purification)	0.511	0.857	0.578	0.500
Operating cost	**71.428**	**64.009**	**64.301**	**64.526**
CH2CN (New compressor)	-	1.050	0.497	-
CH2PN (New purification)	-	8.690	-	-
CH2PIPE (New pipeline)	-	0.388	0.069	0.253
Annualized capital cost	-	10.131	0.567	0.253

Compared to the original network (HN-BASE CASE), the MILP result was reduced by 10.4% (HN1), 10% (HN2), and MINLP by 9.7% the operating cost (HN3). Comparing the models, the MILP model reduced the operating cost by 0.8% from the result of the nonlinear model. However, the investment cost is much higher. The payback of the HN3 network is approximately 1 month, and the HN2 network is 2 months. In this example, the cost of operation was very close between linear and nonlinear formulation. The lowest cost of capital was obtained in the HN3 network. However, the result obtained through MINLP is not a global optimum, which allows for improving the solution. It shows that the MILP model is good enough and capable of providing significant results to manage hydrogen networks. As the MINLP model is relatively more challenging to implement; it contains many nonlinearities such as pressure and purity varying in the compressors, making convergence difficult. Also, proper and adequate initialization is necessary to converge and facilitate the achievement of the optimal global.

The original article of this case study, from Liao et al. (2010), was based on hydrogen network optimization minimizing the total annual cost (TAC). For this, two conditions were tested, allowing or prohibiting recycle off-gases in the hydrogen system via recovery. In this case, the retrofit achieved a 22.8 % reduction in TAC. The direct comparison between the results of this article and the original cannot be made because the objective function is different, and some parameters were not informed. But through the MILP and MINLP formulation of this article, it was possible to achieve around 10 % reduction in operating cost with meager investment cost.

3.4.2 *Example 2*

The MILP and MINLP optimization problems were also validated using a real example of a Brazilian refinery. As the data is confidential, flowrates, pressures, and purities will not be reported in Figure 3.7 and the results. The network consists of two hydrogen generation units (UGH I and UGH II), two purification units (PSA I and PSA II), and 3 consumption units, two hydrotreatment units (HDT I and HDT II), and one hydrodesulfurization (HDS), as shown in Figure 3.10. The MILP model included 524 single equations, 226 single variables, and 158 discrete variables. The MINLP presents 764 single equations, 383 single variables, and 249 discrete variables. Because this example uses actual plant data, the flow and purity values were not reported in the figures.

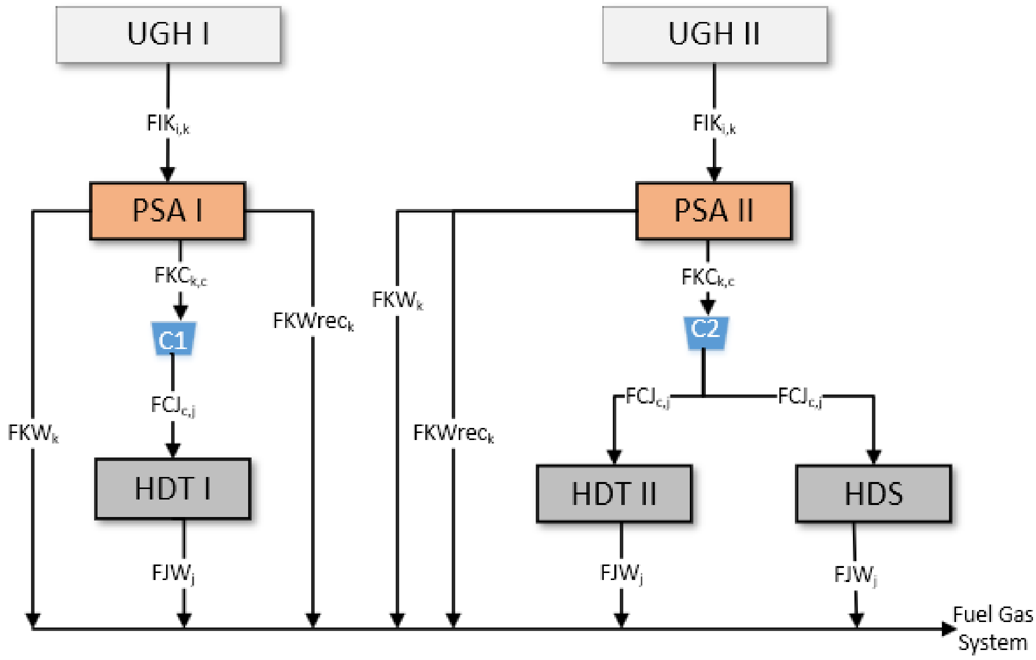

Figure 3.7: Existing hydrogen network in a Brazilian Refinery.

The retrofit of this real existing network was considered to minimize the operational cost. For that, first, the operation cost of the original network was calculated, fixing the values of flowrates and the existing topology (binary variables- indicating compressors, lines, and purifiers). The operating cost is 40.624 million $ / year. The Hydrogen Network BASE CASE (HN- BASE CASE) corresponds to the existing basic topology, that is, the values obtained from operating costs are the current costs in which the refinery is operating (project data), used as a base case for later comparison with the networks obtained through optimization.

To optimize the network via the MILP linear formulation, the variables were released (considered only lower and upper limits), including the binary ones that indicate characteristics of the network topology. It results in an optimal solution of $32.444 million per year. It presents an associated annualized capital cost of approximately $6 million/year, including 12 new lines, 4 new compressors, and a new PSA. This optimal solution will be called HN4 -MILP OPTIMIZED.

As the original network already has two purification units and the cost associated with a new PSA installation is high (around 80% of the capital cost), a new restriction was added to the objective function, forbidding its installation. Thus, in the new optimal solution, the operating cost is $ 32,444 million per year, with an annualized capital cost of $ 0.393 million per year. This solution requires the installation of 3 new compressors and 7 new lines. As one of the existing compressors was not used in the optimal solution by optimization, it can be used in place of one of the new, so only 2 new compressors are installed, and the capital cost reduces by 15% ($ 0.36 million /year). This result, obtained through the MILP optimization problem, will be called HN5 -MILP OPTIMIZED (Figure 3.8).

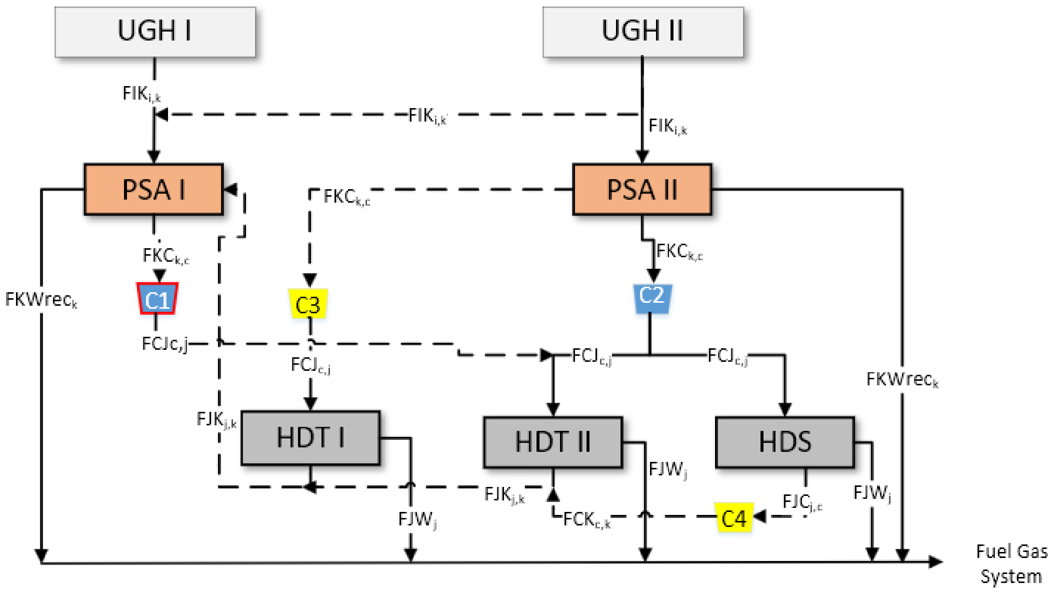

Figure 3.8: Optimized network HN5-MINLP OPTIMIZED.

Another test that can be performed, limiting the cost of investment, that is, not allowing the installation of any new equipment. The optimal solution found has an operating cost of 33,903 million $ / year. As there is no change in the original network, the cost reduction implies fewer hydrogen imports. This optimal solution results in around 20% less hydrogen coming from each source, which means that less excess hydrogen is burned.

To compare the results obtained through different models, the original network was also optimized through a nonlinear mathematical programming model (MINLP). About solvers, the best solution was found with DICOPT, comparing with SBB and BARON. As a result, the operating cost is around 15% less, and 12.8 million savings were obtained compared to the HN-BASE CASE network. In the nonlinear model, it is possible to mix flows in the compressors, and this makes the investment cost less. The optimized network only required the installation of 1 new compressor and 6 new pipelines. Thus, the annualized capital cost is 0.211 million per year. This optimization result from the MINLP is called HN6-MINLP OPTIMIZED, and it is represented in Figure 3.9.

Table 5 summarized the obtained results. It is essential to highlight that other solvers were tested for the MINLP model, such as The Baron and SBB, but the best value achieved was using DICOPT. The solution obtained is an integer solution.

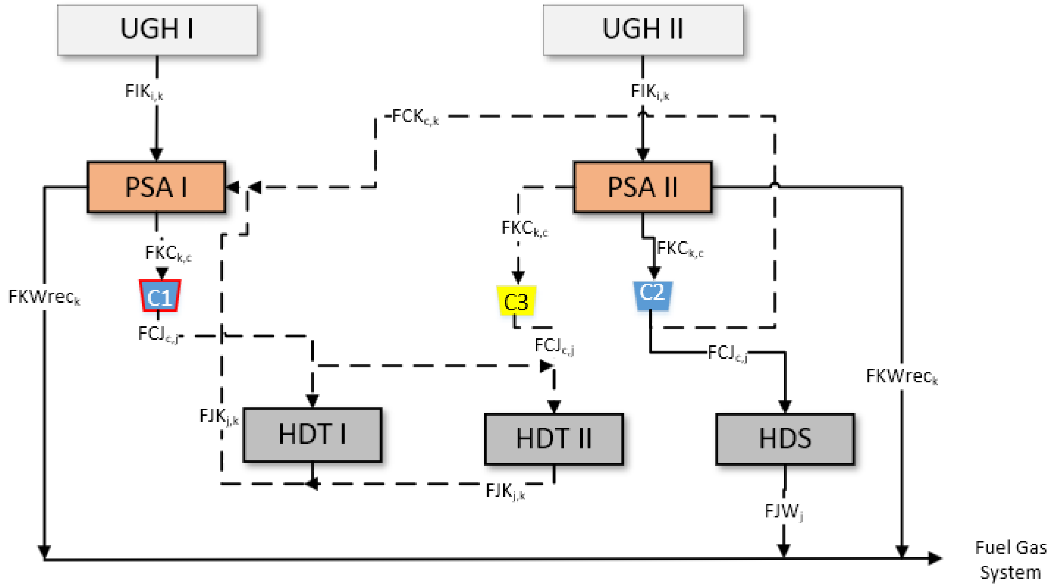

Figure 3.9: Optimized network HN6-MINLP OPTIMIZED.

Table 3.5: Results of minimizing operating cost for example 2.

	HN-BASE CASE	HN4-MILP OPTIMIZED	HN5-MILP OPTIMIZED	HN6-MINLP OPTIMIZED
	[x10^6 $/year]			
CH2I (Hydrogen)	72.896	54.639	54.919	57.911
CH2F (Fuel)	33.494	23.186	23.243	31.387
CH2C (Compressor)	0.076	0.068	0.069	0.074
CH2P (Purification)	1.145	0.922	0.920	1.228
Operating cost	**40.624**	**32.444**	**32.666**	**27.825**
CH2CN (New compressor)	-	0.388	0.277	0.179
CH2PN (New purification)	-	4.668	-	-
CH2PIPE (New pipeline)	-	0.892	0.059	0.032
Annualized capital cost	-	5.948	0.336	0.211

Compared to the original network (HN-BASE CASE), MILP result was reduced by 20.1% (HN4) and 19.6% (HN5). Trough MINLP formulation, the operating cost decrease by 31.5%

(HN6), the highest value achieved. Comparing the models, the MINLP model reduced the operating cost by 14.8 % from the result of the linear model. Besides, the investment cost is also lower (37% comparing HN5 and HN6). Optimization via MILP (HN5) guarantees significant savings of 7,958 million per year. However, in this case, the MINLP formulation proved to be the best option in terms of savings for the retrofit of the hydrogen network, even if it did not guarantee that the solution is the global minimum.

3.5 Conclusions

In this work, a MILP model was proposed to optimize hydrogen networks. In addition, a nonlinear model was also proposed to compare its results. Both models are based on superstructures that include sources, consumers, purification units, and compressors. The proposed models were validated using an existing adapted hydrogen network found in the literature and a real case from a Brazilian Refinery. The goal of minimizing operational cost has been achieved. Different restrictions were explored, as done in this article, for example, limiting investments and different designs were obtained.

The result obtained through the MILP model was satisfactory, with a 10 % reduction in operating costs in example 1 and 19.6% in example 2. It is an optimization problem that is easier to solve and has proved to be an efficient way of solving along with initialization strategies.

The MINLP model also satisfies the needs of the retrofit case and has shown best results, but the nonlinearity problems are more difficult to converge and requires initialization strategies to facilitate resolution. Although it did not guarantee the overall optimal, in example 2 it provided a lower operating cost than the optimal solution via MILP, and in example 1 the results were similar between MILP and MINLP. It is worth mentioning that the MINLP model uses a superstructure different from MILP, as the compressors are seen as a unit. The resolution time for nonlinear problems is also longer, which can be challenging when this type of mathematical programming is extended to the multi-scenario formulation, necessary to capture uncertainties in a real industrial application.

Therefore, the linear formulation presented satisfactory results and has its advantages of use, but the MINLP formulation guaranteed lower operational cost combined with the lower cost of capital, besides providing more realistic designs. It is important to evaluate the use of formulations to ensure that one is working with a robust model capable of meeting the needs of each process.

List of symbols

$FH2I_i$	*Flow rate of hydrogen sources*
$FH2I_i, max$ $FH2I_i, min$	*Maximum and minimum flow rate of hydrogen sources*
$FIJ_{i,j}$	*Flow from source to consumer*
$FIK_{i,k}$	*Flow from source to purifier*
FIW_i	*Flow from source to waste (fuel system)*
FJ_j	*Total consumer flow*
$FKJ_{k,j}$	*Flow from purifier to consumer*
$FJJ_{j,j'}$	*Flow from consumer j to consumer j'*
YJ_j	*Consumer purity*
YI_i	*Source purity*
YK_k	*Purifier purity*
YP_j	*Purge purity of consumer*

FP_j	*Total purge consumer flow*
FJW_j	*Flow from consumer to waste (fuel system)*
$FJK_{j,k}$	*Flow from consumer to purifier*
$FPur_{max,k}$	*Maximum capacity of purifier*
FKW_k	*Flow from purifier to waste (fuel system)*
$FKW_{rec,k}$	*Purge flow from purifier to waste (fuel system)*
YKW_k	*Purity of purge flow from purifier*
rec_k	*Purifier recovery*
$C_{operating}$	*Operating cost*
$CH2I, C_i$	*Total and hydrogen production cost*
$CH2K, C_k$	*Total and purification cost*
$CH2C, C_{eletric}$	*Total and electricity cost*
$CH2F, C_{fuel}$	*Cost of burning purge as fuel*
t	*Annual operating time*
FK	*Total purifier flow*
FW	*Total waste flow (fuel system)*
y	*Hydrogen fraction in the purge flow*
$\Delta H°_{H2}, \Delta H°_{CH4}$	*Combustion heat of hydrogen and methane*
FC	*Total flow that compressor needs*
$\overline{Cp}$	*Heat capacity*
T	*Temperature*
η	*Compressor efficiency*
P_{out}	*Outlet pressure*
P_{in}	*Inlet pressure*
γ	*Cp / Cv Ratio*
ρ_o	*Density in initial condition*
ρ	*Density*
$C_{capital}$	*Capital cost*
$C_{new\ PSA}$	*Cost of new purifier*
C_{piping}	*Cost of new pipelines*
$C_{new\ compressor}$	*Cost of new compressor*
Af	*Annualized factor*
c, d	*Parameters of piping cost*
z_h	*Binary variable from new pipeline*
$F_{newpipe}$	*Total flow in new lines*
ϑ	*Superficial gas velocity*
L	*Distance*
a, b	*Parameters of new purifier cost*

z_{kn}	*Binary variable from new purifier*
$FK_{new\ k}$	*Purification flow in the new purifier*
e, f	*Parameters of new compressor cost*
z_c	*Binary of new compressor*
FC_{new}	*Total flow in new compressor*
z	*Binary associated with flow*
$FIC_{i,c}$	*Flow from source to compressor*
$FCJ_{c,j}$	*Flow from compressor to consumer*
YC_c	*Purity in compressor*
$FJC_{j,c}$	*Flow from consumer to compressor*
$FCK_{c.k}$	*Flow from compressor to purifier*
$FKC_{k,c}$	*Flow from purifier to compressor*
FC_c	*Total compressor flow*
FCW_c	*Purge flow from compressor to waste (fuel system)*

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Capítulo 4 – MILP Formulation for Solving and Initializing MINLP Problems Applied to Retrofit and Synthesis of Hydrogen Networks

O presente capítulo é uma reprodução do artigo publicado na *Processes* e apresenta o objetivo 2 e as contribuições 3 e 4 desta Tese de Doutorado. Este artigo segue a mesma formulação desenvolvida no artigo apresentado no Capítulo 3, incluindo a otimização através das duas formulações MILP e MINLP. A programação linear restringe a mistura de correntes na alimentação ou saída das unidades. Em termos de custo de capital, este fator impacta significativamente na instalação de novas linhas e compressores, já que cada um destes itens deve estar associado a apenas uma corrente de hidrogênio. Para contornar esta limitação, foi proposto um procedimento denominado "Virtual Compressor Approach", ou Abordagem de compressores virtuais. Assim, depois de obtida a solução ótima através da formulação MILP, as correntes que necessitam de compressores podem ser direcionadas para um mesmo compressor, desde que estejam indo para a mesma unidade ou estejam saindo da mesma unidade. Além disso, é preciso respeitar a capacidade nominal do compressor. Assim, o número de compressores e linhas necessários é reduzido e consequentemente o custo de capital também. Neste artigo, também foi abordada a questão da inicialização do modelo não linear (MINLP). A inicialização é importante neste caso de formulações não lineares, pois estas são otimizações mais difíceis de resolver, despendem mais tempo e não se garante a obtenção do ótimo global. A técnica de inicialização aqui proposta foi a utilização da solução ótima obtida através da otimização linear (MILP), seguida do rearranjo dos compressores através da proposta do "Virtual Compressors Approach". Com essa metodologia proposta, os custos operacionais reduziram em torno de 30% para os estudos de caso abordados.

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Abstract: The demand for hydrogen in refineries is growing due to its importance as a sulfur capture element. Therefore, hydrogen management is critical for fulfilling demands as efficiently as possible. Through mathematical modeling, hydrogen network management can be better performed. Cost-efficient Mixed-Integer Linear Programming (MILP) and Mixed-Integer Nonlinear Programming (MINLP) optimization models for (re)designing were proposed and implemented in GAMS with two case studies. Linear programming has the limitation of no stream mixing allowed; therefore, to overcome this limitation, an algorithm-based procedure called the Virtual Compressor Approach was proposed. Based on the MILP optimal solution obtained, the streams and compressors were merged. As a result, the number of compressors was reduced, along with the inherent investment costs. An operational cost reduction of more than 28% (example 1) and 26% (example 2) was obtained with a linear model. The optimal MILP solution after rearranging compressors was then provided as a good starting point to the MINLP. The operating costs were decreased by more than 31% (example 1) and 32% (example 2). Most of the cost reduction was obtained only with the usage of the MILP model. Besides, a higher level of cost reduction was only obtained when the linear model was used as the starting point.

Keywords: hydrogen network; mathematical programming; initialization strategy; MILP optimization; MINLP optimization; virtual compressor approach

4.1 Introduction

Hydrogen has a prominent role in the refining industry, as both its production and its recovery are essential steps. Hydrogen consumption in oil refining increased from approximately 7 million tons in 1980 to 38 million tons in 2018 (IEA, 2019). Its importance is sustained by three factors: (i) the increase in the processing of heavier oils with high levels of sulfur and nitrogen; (ii) the increase in environmental constraints; and (iii) the production of derivatives of higher added value (Ceric, 2012; Figueiredo, 2013). Due to this trend, it is necessary to use more efficient hydrogen within the petroleum refining process.

A hydrogen network consists of hydrogen-producing units, hydrogen-consuming units, and purification units, capable of purifying hydrogen to achieve the required purity. The hydrogen generation units (HGU) have become increasingly present in refineries due to the importance of hydrotreatment units (HDT) because its function is to supply the hydrogen demand complementing those generated in the catalytic reform. The steam reform is the primary process used at the industrial scale to obtain hydrogen as a primary product. Catalytic reform and purge gas can be used as a secondary source of hydrogen. The main hydrogen-consuming units are hydrotreating, which uses hydrogen to improve the quality of naphtha, kerosene, solvents in general, diesel oil, heavy gas oils, paraffin, and lubricating oils (Silva and Marvulle, 2006). The management of the hydrogen network in a refinery implies in the material balance at all these units.

The need for optimization of the hydrogen network in refineries was recognized in the 1990s, because, usually, the amount of hydrogen produced is higher than the amount consumed. This excess is usually incorporated into the fuel gas system or burned directly into the flare. Therefore, it is necessary to have greater control in the sources and consumers of hydrogen through network management as a whole, because it is not economically feasible to produce and burn the product with an excellent added value (Borges, 2009). It is known that the cost of hydrogen is the second-highest cost in a refinery, behind only the cost of crude oil (Jiao et al., 2012). Therefore, savings in terms of the amount of hydrogen consumed and the operating cost of the network have great economic appeal.

Since then, many methodologies have emerged to accomplish it. In general, these methodologies can be divided into two categories: pinch methods and optimization methods (deterministic in this case) as mathematical programming approaches based on network design (Jia, 2010). Graphical methods provide an essential insight into the integration of the refinery process and provide theoretical goals for minimum hydrogen use. As oil refining and the hydrogen network involve many restrictions, they must be considered during network modeling and optimization, such as pressure, impurities, and equipment capacity. However, in graphic methods, this is not possible, as only flow and purity restrictions are considered. Therefore, mathematical programming is the best alternative and the most used, providing more realistic results and networks (Marques et al., 2017).

In this work, a mathematical programming approach was used to develop a model to solve the problem of hydrogen network optimization based on operating costs and constraints, as illustrated in Figure 4.1. The idea is to apply the proposed model to existing networks. The optimization allows the possibility of including new equipment and finding better ways of connection between units. For linear optimization, a compressor rearrangement technique was proposed in this work to decrease the capital cost. It is called Virtual Compressor Approach (VCA). The methodology was proposed to make the linear model competitive and satisfactory for the retrofit of hydrogen networks, due to its advantages and characteristics. Besides, a nonlinear model was also developed for comparison, with an initialization strategy using the MILP solution. This proposal was developed to facilitate the resolution of nonlinear and obtaining more competitive hydrogen networks.

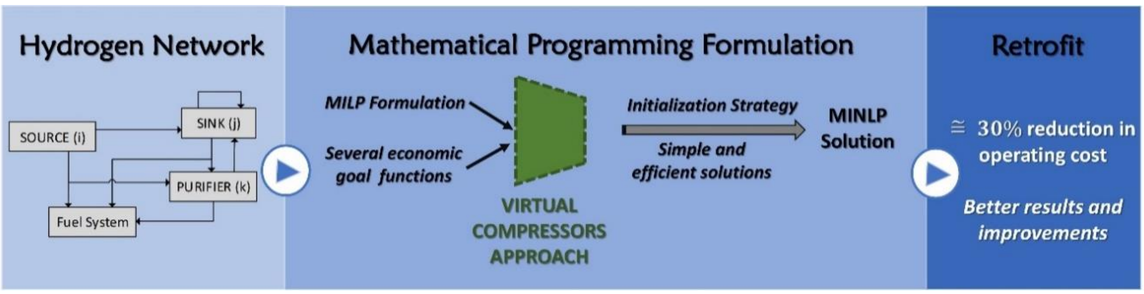


Figure 4.1: Graphic summary of the article**.**

4.2 Literature Review

Previous works on hydrogen distribution management and analysis using a linear programming model, based on the graphical analysis of the pinch method, were found in the literature. Towler et al (1996) proposed a linear model to optimize a hydrogen network, aiming to minimize the total hydrogen import as an external utility. Two procedures for problem relaxation were proposed. The disadvantages of this method are that pressure constraints are negligible, and the flow merging must be performed manually (Towler et al., 1996). Fonseca et al. (2008) employed the linear programming model to optimize the hydrogen network of a refinery taking account pressure considerations and achieved a 30% reduction in utility use with the objective function minimizing the total flow rate of fresh hydrogen from a hydrogen plant (Fonseca et al., 2008).

Considering nonlinear programming (NLP), Hallale and Liu (2001), in addition to mentioning the graphical pinch method, developed a nonlinear mathematical model to reduce the hydrogen consumption of the network. The model took into account pressure constraints, existing compressors, and a strategy to install a purifier. The objective function was to minimize the total cost, including operating and capital costs (Hallale and Liu, 2001). Liu and Zhang (2004) developed a systematic procedure for integrating purification in hydrogen network design. For this, an MINLP (Mixed-Integer Nonlinear Programming) model for purifier selection and integration was used, and with linear relaxation of bilinear forms MINLP model was solved first as MILP because of the advantages of using linear models for problem solution(Liu and Zhang, 2004). Kumar et al. (2010) developed mathematical models (LP (linear programming), NLP, MILP (Mixed-Integer Linear Programming), and MINLP) to obtain the best optimization problem in two case studies. Comparing MINLP and NLP for case 1, MINLP showed a more significant reduction in operating costs and equal capital costs. For case 2, the formulations LP, NLP, and MILP were compared. The NLP model imports less hydrogen and features a more realistic network than the others. The conclusions were that mixed-integer linear and nonlinear programming models are considerably better than linear because it provides the less complicated and more realistic refinery system, and MINLP can include complexities as compressors, purity constraints, and pressure constraints (Kumar et al., 2010).

Liao et al. (2010) developed an MINLP model using an existing hydrogen network with a purifier. The objective function was the total annual cost, and the model was solved in GAMS (General Algebraic Modeling System) using DICOPT. The MINLP problem is decomposed into a series of NLP and MILP solvers. The total annual cost decrease by 22.6% and both the new compressor and PSA were incorporated (Liao et al., 2010). Birjandi et al. (2014) developed a methodology for the optimization of a hydrogen network based on a simultaneously resolved MINLP and NLP problem. Linearization techniques for nonlinear models were used to facilitate resolution by transforming nonlinear equality constraints into inequality constraints. Global optimization has reduced operating costs (Sardashti Birjandi et al., 2014). Matijasevic (2016) presented a hydrogen network integration methodology for a case study of a local refinery. The minimum consumption of hydrogen was determined by pinch analysis. Then, the superstructure was modeled using a nonlinear mathematical model whose objective function was to minimize total operating costs. The problem was solved with the GAMS software (Matijašević and Petric, 2016).

Unlike what was found in the literature, this paper developed a cost-efficient MILP and MINLP optimization models for (re)designing of hydrogen networks or a new project. The main difference from the MILP model to the MINLP is that it is not possible to mix streams in the compressors as it generates nonlinearity. To reduce the cost of capital from the MILP, in this work, a compressor-retrofitting tool was proposed respecting the nominal capacities. Also, to facilitate the resolution of the nonlinear formulation, an initialization strategy was used using the linear solution as a feasible starting point.

4.3 Mathematical Programming Approaches

Mathematical programming based on superstructure has advantages over pinch, in that it considers numerous limitations and variables when looking for solutions to the optimization problem. Limitations such as pressure, capacity, purity, operating costs, and investments in new equipment are some of the restrictions that may be included in the mathematical model formulation. The methodology to develop mathematical programming would be the development of the superstructure, including the sources, consumers, existing compressors, and purifiers. The formulation of the mathematical model also includes the objective function to be minimized or maximized subject to the set of constraints, the initialization strategy, and the resolution of the optimization problem. Typically, the objective function is the total annual cost of the hydrogen network [8].

Generally, the optimization problem can be formulated as a linear programming, mixed linear programming, nonlinear programming, or mixed-integer nonlinear programming problem. If linear combinations of variables can express the objective function and constraints, it is a linear optimization problem. Otherwise, the optimization problem is nonlinear. There are many optimization software used to solve optimization problems and already include algorithms called solvers (Petric, 2014).

Network management through mathematical modeling can be applied to an existing fixed topology, or to develop a new hydrogen network design. Thus, the approach of this article is based on the evaluation of the model developed for initial hydrogen network projects, through the validation with networks presented in articles already published. New equipment is considered, and the problem then becomes MILP or MINLP. Although the focus is operational, the problem addressed here is broader and has a significant industrial interest. The primary purpose of managing hydrogen networks is their production with minimum slack. Excess hydrogen production must be minimized, first because hydrogen is not easy to handle or store, and second, because it is not economically viable since the excess must be burned as fuel and furnaces and other processes.

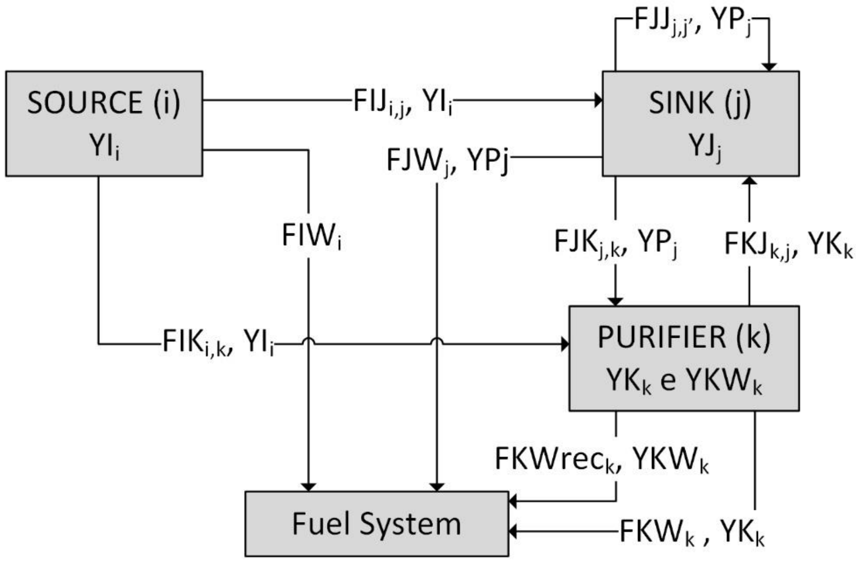
The MINLP problems are more challenging to solve because they combine the NLP and MILP models and their characteristics. However, they result in more realistic networks and include several additional restrictions. According to the literature review, the use of MILP is not very recurrent, although when used, it presents significant results. Most articles found in the literature use nonlinear models for hydrogen network optimization. The advantages of using MILP is the linearity that facilitates the resolution of the optimization problem and the modeling of the logical constraints made in this article, which were not found in the literature. MILP problems are easier to converge to a global solution, since all the subproblems, for fixed binaries, are linear solved to global optimality (Georgiadis et al., 1999; Grossmann and Guillén-gosálbez, 2010)

4.3.1 Problem Statement

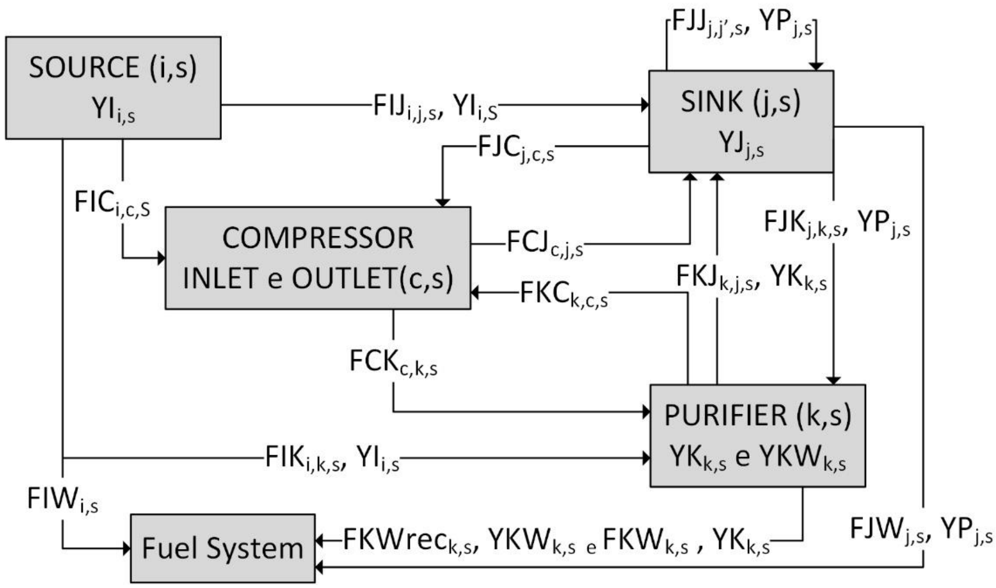
The problem to be addressed in this paper can be stated as follows: (i) a set of sources i ϵ hydrogen sources (HS), (ii) a set of consumers j ϵ hydrogen consumers (HC), and (iii) a set of purifiers k ϵ hydrogen purifiers ($HP = OHP \cup NHP$), considering the existing purifiers, OHP, and the new purifiers, NHP. In the case of nonlinear formulation, there is still a set of compressors c ϵ hydrogen compressors ($HCP = OHCP \cup NHCP$), considering the existing compressors $OHCP$ and new compressors $NHCP$. Figure 2 shows the two superstructures considered in this problem for the linear formulation (Figure 4.2a) and the nonlinear formulation (Figure 4.2b).

For each source, the maximum and minimum flowrate, as well as the hydrogen composition, and the outlet pressure are given. For each consumer, the inlet flowrate demand, pressure, and composition, the outlet purge flow, pressure, and composition are given. For each purifier, the maximum flow capacity, the composition of purified flowrate and purge flowrate, the pressure of purification, and the hydrogen recovery are given. It is also considered a fuel system in which waste streams can be burned and used as fuel to the process. For the existing networks, also given are the existing lines (unit connections), the distance between the units if informed, and the existing compressors (capacity and pressures) and purifiers.

The optimization problem is subject to the material balances and process operating constraints. For the retrofit case, process modifications are allowed to reduce the total operating costs (the objective function), despite the investment costs due to the installation of new pipelines, compressors, and possibly new purifiers.



(**a**)



(**b**)

Figure 4.2: (a) Scheme of the Superstructure developed for the Mixed-Integer Linear Programming (MILP) problem. (**b**) Scheme of the Superstructure developed for the Mixed-Integer Nonlinear Programming (MINLP) problem.

4.3.2 Mathematical Model: MILP Formulation

Figure 2a shows the superstructure and all the possible connections among these four units between sources and consumers, sources and purifiers (existing and new ones), as well as flows between consumers and the purifying units for sources *i* and consumers *j*. The first step for the modeling development is to define which units are involved in the hydrogen network, for instance, which units provide hydrogen, which units consume hydrogen and the existing purifiers, and the potential purifiers that should be considered in the model.

The optimization problem of hydrogen network design in this work can be summarized as follows: the superstructure is formed by a set of sources of hydrogen *i*, a set of hydrogen consumers *j* and set of units of hydrogen purification *k*, account for the existing and new purifiers. The hydrogen sources have their minimum and maximum flow according to their capacity ($FH2I_{i,min}$ e $FH2I_{i,max}$) as well as their hydrogen purity (YI_i). The hydrogen-rich stream can be sent to the consumers *j* ($FIJ_{i,j}$), to purification units *k* ($FIK_{i,k}$), or can be sent to the fuel system (FIW_i). The consumer's units also have their known, and constant input required flows for the process (FJ_j), as well as its hydrogen purity (YJ_j), in addition to the outflows (FP_j) and hydrogen purity (YP_j), according to the hydrogen consumption of each specific process. The outlet flows from the consumers can be sent to purification ($FJK_{j,k}$), can be used as a source for other consumers ($FJJ_{j,j'}$) or can be sent to the fuel system (FJW_j) to be used as the burning fuel. The purifying units have a known hydrogen recovery ratio (rec_k), as well as the maximum inlet flow capacity ($FPur_{max,k}$) and the constant purities of the hydrogen product pure streams (YK_k) and the composition for the stream of hydrogen not recovered stream (YKW_k). The purified hydrogen stream from the purification can be used as a source for the consumers ($FKJ_{k,j}$) who need higher purity or can be referred to the fuel system (FKW_k), if there is excess. The stream with the unrecovered hydrogen, $FKWrec_k$, has a small hydrogen composition, and it is sent directly to the fuel system. In this work, some considerations were made to simplify the model. The flowrates are considered only a binary mixture of hydrogen and methane. The partial pressure of the hydrogen and the flowrate are constant at the entrance and exit of the consuming units.

<u>4.3.3.1 Sources</u>

The overall material balance for each source is represented by Equation (4.1):

$$FH2I_i = \left(\sum_{j \in HC} FIJ_{i,j} + \sum_{k \in HP} FIK_{i,k} + FIW_i \right) \quad \forall\ i\ \in HS \tag{4.1}$$

where $FH2I_i$ is the total flow from each source *i*, $FIJ_{i,j}$ is the hydrogen flow from the source *i* to the consumer *j*, $FIK_{i,k}$ is the flow from the source *i* for the purification unit *k*, and FIW is the flow from source *i* sent to the fuel system. The available flow rate is limited by the capacity of the hydrogen generating units according to the following inequality constraints:

$$FH2I_{i,min} \leq FH2I_i \leq FH2I_{i,max} \quad \forall\ i\ \in HS \tag{4.2}$$

4.3.3.2 Consumers

Equation (4.3) represents the overall material balance in the inlet of consumer units.

$$FJ_j = \sum_{i \in HS} FIJ_{i,j} + \sum_{k \in HP} FKJ_{k,j} + \sum_{j \in HC} FJJ_{j,j'} \;\; \forall j \in HC \qquad (4.3)$$

where FJ_j is the total flow directed to consumers, $FJJ_{j,j\prime}$ is the flow from one consumer *j* to another consumer *j'* and $FKJ_{k,j}$ is a flow rate from the purification unit *k* for the consumer units *j.* The index *j'* which is used for cases where there is a connection between consumers. In this case, as it is not allowed between the same unit, *j'* must be different from *j*. The hydrogen balance is then defined by Equation (4.4):

$$FJ_j * YJ_j = \sum_{i \in HS} FIJ_{i,j} \times YI_i + \sum_{k \in HP} FKJ_{k,j} \times YK_k + \sum_{j \in HC} FJJ_{j,j'} \times YP_j \;\; \forall j \in HC \qquad (4.4)$$

where YJ_j, YI_i, YK_k and YP_j are the volumetric fractions of hydrogen in the respective streams, consumer *j*, sources *i*, purifiers *k,* and purge of the consumer unit *j*. Besides, it is possible to calculate how much each consumer unit used hydrogen depending on the chemical process involved.

Equation (4.5) represents the overall material balance in the outlet of consumer units:

$$FP_j = FJW_j + \sum_{k \in HP} FJK_{j,k} + \sum_{j \in HC} FJJ_{j,j\prime} \;\; \forall j \in HC \qquad (4.5)$$

where FP_j is the total flow out of consumers, $FJK_{j,k}$ is the flow rate from the consumer unit *j* for the purification unit *k,* and FJW_j is the surplus flow of consumers directed to the fuel system.

4.3.2.3. Purification Units

The purification unit is used, so that process streams are purified, providing hydrogen in a given purity, such as 99.99% in the case of PSA units. The overall material balance in these units is expressed as:

$$\sum_{j \in HC} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} = \sum_{j \in HC} FKJ_{k,j} + FKW_k + FKW_{rec,k} \;\; \forall k \in HP \qquad (4.6)$$

where FKW_k the flow rate of the purifying unit *k* stream rich in hydrogen routed to burning and $FKW_{rec,k}$ is the hydrogen flowrate not recovered by the purifying unit *k* sent to the burner. The hydrogen balance for each purifier is described as follows:

$$\sum_{j \in HP} FJK_{j,k} \times YP_j + \sum_{i \in HS} FIK_{i,k} \times YI_i = \sum_{j \in HP} FKJ_{k,j} \times YK_k + FKW_k \times YK_k + FKW_{rec,k} \times YKW_k \;\; \forall k \in HP \qquad (4.7)$$

where YKW is the fraction of hydrogen in the purge stream of purified k. The total flow entering the purifier is limited by the capacity of the purifying unit.

$$\sum_{j \in HP} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} \leq \sum_{k} FPur_{max,k} \quad \forall\, k \in HP \tag{4.8}$$

Given the hydrogen recovery of the purification unit, it is possible to calculate how much hydrogen is sent to the purge stream, i.e., the hydrogen not recovered.

$$\left(\sum_{i \in HS} FIK_{i,k} \times YI_i + \sum_{j \in HP} FJK_{j,k} \times YP_j\right) \times (1 - rec_k) = FKW_{rec} \times YKW_k \,\forall\, k \in HP \tag{4.9}$$

The total flow through the PSA (FK_k) can then be defined as:

$$\sum_{j \in HP} FJK_{j,k} + \sum_{i \in HS} FIK_{i,k} = FK_k \quad \forall\, k \in HP \tag{4.10}$$

4.3.3.4. Logical Constraints

To consider the capital cost associated with new equipment, it is necessary to use constraint modeling, through logical propositions and disjunctions, so binary variables and logical inequality equations were included in the model with binary parameters. First, through the modeling of disjunctions, a binary variable z is associated with the existence of a particular flow F (e.g., $FIJ_{i,j}$, $FKJ_{k,j}$, $FJK_{j,k}$, etc.). If the positive flowrate is greater than or equal to a small value ε, e.g., $\varepsilon = 10^{-5}$, the corresponding binary variable z assumes the value of 1. On the other hand, if the flowrate is lower than ε, the binary variable assumes the value of 0. F_{max} are the flowrates between the units involved. These conditions are ensured by the following constraints:

$$\begin{cases} F \geq \varepsilon \times z \\ F \leq (\min(F_{max})) \times z \end{cases} \tag{4.11}$$

A binary variable z_c is associated with the installation of a compressor for the corresponding flow. For this case three events must hold simultaneously: (i) there is a non-zero flow, i.e., z = 1; (ii) there is no compressor previously installed identified by a binary parameter u_c (1 if there is an existing compressor, 0 otherwise); and (iii) there is a pressure difference between the current unit and destination unit that requires a compressor identified by a binary parameter u_{deltaP} (1 if the current pressure unit is lower than the destination pressure unit, 0 otherwise).

$$z_c \geq z + u_{deltaP} + (1 - u_c) - 2 \tag{4.12}$$

If any of these three events is false, then there is no need to install a compressor (z_c = 0), which is ensured by the set of constraints described in the set of Equation (4.13).

$$\begin{cases} z \geq z_c \\ 1 - u_c \geq z_c \\ u_{deltaP} \geq z_c \end{cases} \tag{4.13}$$

A similar procedure was used to consider the investment cost of piping. A binary variable z_h is associated to the need of installing a new pipeline if two events hold: (i) there exists a non-zero flow in that connection, i.e., z = 1; (ii) there is no pipeline previously installed identified by a binary parameter u_h (1 if there is a line, 0 otherwise).

$$z_h \geq z + (1 - u_h) - 1 \tag{4.14}$$

If any of these two events do not hold, it must be ensured that no pipeline must be installed.

$$\begin{cases} z_h \leq z \\ z_h \leq 1 - u_h \end{cases} \tag{4.15}$$

There is also the possibility of installing new purification units. In this case, it is enough that there is any flow entering or leaving this unit. In this case, a binary variable z_{kn} is associated with the installation of a new purifying unit and the logical constraints can be expressed by:

$$\begin{cases} FK_k \geq \varepsilon \times z_{kn} \\ FK_k \leq (FPur_{max,k}) \times z_{kn} \end{cases} \quad \forall\, k \in NHP \tag{4.16}$$

The same procedure for installing new compressors was also done (constraints in Equations (4.12) and (4.13)) if it is necessary to install new compressors on streams involving a new PSA.

4.3.3.5. Operating Costs

Operating costs include the production of hydrogen, the cost of electricity used in compressors, the operating cost of the purifying units, and the economic value corresponding to the burning gas in the fuel system. The cost of hydrogen production is assumed directly proportional to the flowrate, and it is defined as follows:

$$CH2I = \sum_{i \in HS} FH2I_i \times C_i \tag{4.17}$$

where C_i is the cost of producing hydrogen. The electricity cost of the compressor is directly proportional to the power (W):

$$W = F \times w \tag{4.18}$$

where W is the power of the compressor with the flowrate being compressed F, w is the intensive power estimated from the stream properties (C_P, C_V, z), the inlet and outlet pressure, and the compressor efficiency (Hallale and Liu, 2001).

$$w = \overline{(C_P} \times T/\eta) \times \left(\left(\frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \times (\rho_o/\rho) \tag{4.19}$$

where C_P is the heat capacity, T is the stream temperature, η the efficiency of the compressor, P_{out} and P_{in} are the outlet and inlet pressure, respectively, ρ_o and ρ are the densities at design conditions and standard conditions, respectively, γ is the ratio of the heat capacity at constant pressure to that at constant volume. For a given connection, e.g., $FIJ_{i,j}$, the corresponding intensive power $w_{i,j}$ is previously calculated as a model parameter. For the complete model, the total electricity cost is calculated by the following Equation (4.20). The indices α and *β* represents the possible connections involved (*i,j; j,k; k,j; j,j'; i,k; i-waste; j-waste; k-waste*):

$$CH2C = \left(\sum_{\alpha} \sum_{\beta} F_{\alpha,\beta} \times u_{deltaP_{\alpha,\beta}} \times w_{\alpha,\beta} \right) \times C_{eletric} \tag{4.20}$$

where $C_{eletric}$ is the electricity cost. It is worth to note that each term is multiplied by the binary parameter u_{DeltaP} (1 if the pressure ratio is higher than one), for the cases in which the flowrate is not zero, but there is no need for compression. It does not matter if a new compressor is installed or an existing compressor is used, both consumes energy. Equation (4.20) will compute the energy cost correctly, and it takes into account the electricity used in existing and new compressors.

The cost of purifying unit is proportional to the feed flowrate:

$$CH2K = \sum_{k \in HP} FK_k \times C_k \tag{4.21}$$

where C_k is the cost of using the PSA purification units, new and existing ones.

The economy value corresponding to the burning of excess purge flows is corresponding to the cost of hydrogen and methane used as fuel and calculated as:

$$CH2F = C_{fuel} \times F \times (y \times \Delta H°_{H2} + (1 - y) \times \Delta H°_{CH4}) \tag{4.22}$$

where C_{fuel} the cost per unit of energy, F is the gas flowrate, and y is the hydrogen composition. Assuming a binary mixture, $1 - y$ represents the methane composition. The parameters $\Delta H°_{H2}$ and $\Delta H°_{CH4}$ are the standard heat of combustion of hydrogen and methane, respectively. For the complete model, taking into account the total contributions, the economic value corresponding to the total cost of fuel is calculated as follows:

$$CH2F^T = C_{fuel} \times \sum_{\alpha} F_\alpha W_\alpha \times [y_\alpha \times \Delta H°_{H2} + (1 - y_\alpha) \times \Delta H°_{CH4}] \tag{4.23}$$

The subscript α denotes all units sending streams to the fuel system (*i, j, k*). Since it corresponds to a saving cost, this value must be subtracted from the total operating cost. The operating cost parameters assumed in this work are presented in Table 4.1. The assumed values were the same used in example 1 (Hallale and Liu, 2001), a case study of this work, also chosen based on the reviewed articles.

Table 4.1: Parameters used to calculate the operating cost .

Hydrogen cost—H_2 plant	C_i	0.07 \$/Nm³
Hydrogen cost—CCR	C_i	0.08 \$/Nm³
Electricity cost	$C_{eletric}$	0.03 \$/kWh
Purification cost	C_k	0.0011 \$/Nm³
Fuel cost	C_{fuel}	2.5 \$/MMBtu

4.3.3.6. Investment Costs

The capital cost includes the cost of new compressors ($C_{new\ compressor}$), new purification units ($C_{new\ PSA}$) and new pipelines (C_{piping}). Hallale and Liu (2001) describe the cost for the inclusion of new compressors for a particular flowrate, with a fixed cost with a binary variable and a variable cost associated with the flow:

$$C_{new\ compressor} = a \times z_c + b \times W \tag{4.24}$$

W is calculated by Equation (4.18) and z_c is the binary variable associated with the installation of a compressor for the corresponding flow and multiplied the fixed part of the new compressor cost, so it is considered only when the compressor is installed. The complete equation for accounting the new compressor cost is given by Equation (4.25). The indices α and β represents the possible connections involved (*i,j; j,k; k,j; j,j'; i,k; i-waste; j-waste; k-waste*).

$$C^T_{new\ compressor} = a \times \left(\sum_{\alpha} \sum_{\beta} z_{c_{\alpha,\beta}} \right) + b \times \left(\sum_{\alpha} \sum_{\beta} F_{\alpha,\beta} \times u_{deltaP_{\alpha,\beta}} \times w_{\alpha,\beta} \times \left(1 - u_{c_{\alpha,\beta}}\right) \right) \times C_{eletric} \tag{4.25}$$

The cost associated with the installation of new piping is described below, including a fixed part with a binary variable and a variable part dependent on flowrate. For these calculations, it is necessary to inform the distances between the already installed units of design.

$$C_{new\ piping} = (c \times z_h + d \times D^2) \times L \tag{4.26}$$

With

$$D^2 = (4 \times F/\pi \times \vartheta) \times (\rho_o/\rho) = (4 \times F/\pi \times \vartheta) \times \left(\frac{T}{T_0}\right) \times \left(\frac{P_0}{P}\right) \tag{4.27}$$

where L is the pipe length [m], c and d are constants, ϑ is the gas surface velocity (usually 15–30 m/s; assumed an average value of 22.5 m/s in this work), and D^2 is the equivalent square diameter (Hallale and Liu, 2001). The binary variable z_h indicates the need to install the new pipeline. Equation (4.27) is replaced in Equation (4.26) in order to express the cost of piping as a function of the flowrate. The equation for the model (total cost of new piping) is represented by Equation (4.28). The indices α and β represents the possible connections involved (*i,j; j,k; k,j; j,j'; i,k; i-waste; j-waste; k-waste*). Each term is multiplied by $\left(1 - u_{h_{\alpha,\beta}}\right)$ in order to consider only the cost of new piping.

$${C_{new\ piping}}^T = c \times \left(\sum_{\alpha} \sum_{\beta} z_{h_{\alpha,\beta}} \times L_{\alpha,\beta} \right) + d \times \left(\sum_{\alpha} \sum_{\beta} F_{\alpha,\beta} \times L_{\alpha,\beta} \times w \times \left(1 - u_{h_{\alpha,\beta}}\right) \times \left(\frac{T}{T_0}\right) \times \left(\frac{P_0}{P}\right) \right) \tag{4.28}$$

There is also the possibility of installing new purification units. For this case, the cost of a PSA unit (purifier considered in this work) is a linear function of the unit flowrate (variable part) and include binary variable corresponding to the fixed installation cost:

$$C_{new\ PSA} = a_{PSA} z_{kn} + b_{PSA} \times F_{in,PSA} \tag{4.29}$$

where a_{PSA} and b_{PSA} are constants and $F_{in,PSA}$ is the inlet flowrate of the PSA unit (MMscfd). The binary variable z_{kn} is associated with the installation of a new purifying unit. The model equation is described as:

$$C_{new\ PSA}{}^{T} = a_{PSA} \sum_{k \in NHP} z_{kn} + b_{PSA} \times \left(\sum_{k \in NHP} FK_k \right) \tag{4.30}$$

This cost is only considered for new purifying units. The capital cost parameters used in this work are presented in Table 4.2. Different coefficients exist for calculating capital costs, including variations in temperature and materials involved. The most frequently used data in the reviewed papers were used, following Hallale and Liu (2001). The objective is to facilitate the comparison of the results obtained.

Table 4.2: Parameters used to calculate the capital cost (Hallale and Liu, 2001).

Cost of new compressors (k$)	$115 + 1.91 \times W$ *W* in (kW)
Cost of new piping ($)	$(3.2 + 11.42 \times D^2) * L$ D^2 (in^2) and *L* (m)
Cost of new PSA (k$)	$503.8 + 347.4 \times F$ *F* in (MMscfd)

4.3.3 Formulation of the Optimization Problem

Based on all the costs involved in managing the hydrogen network described in the previous section, annual operating and annual capital costs are defined as:

$$C_{operating} = (CH2I + CH2K + CH2C - CH2F) \times t \tag{4.31}$$

$$C_{capital} = \left(C_{new\ PSA} + C_{new\ piping} + C_{new\ compressor}\right) \times A_f \tag{4.32}$$

where Af is the annualizing factor, and t is the considered operating time of the plant in one year. The annualizing factor is defined by:

$$A_f = f_i \times (1 + f_i)^n / (1 + f_i)^n - 1 \tag{4.33}$$

where *n* is the number of years of interest for the return on investment and f_i is the interest rate. The Total Annual Cost (TAC) consists of the summation of the operating and investment cost:

$$TAC = C_{operating} + C_{capital} \tag{4.34}$$

For the retrofit case of existing networks, the economy saving used as economic criteria is calculated as:

$$E = C_{OP}^{actual} - C_{OP}^{new} \tag{4.35}$$

where $C_{OP}^{actual}\ and\ C_{OP}^{new}$ are the operating cost of the actual and new networks, respectively. The payback time is defined by the ratio of the total investment cost and the economy saving, and the following equation can estimate it.

$$pt = \frac{C_{capital}/Af}{E} = \frac{\left(C_{new\ PSA} + C_{piping} + C_{new\ compressor}\right)}{C_{OP}^{actual} - C_{OP}^{new}} \tag{4.36}$$

The MILP model formulated in this work is described by the set of constraints (4.1, 4.2, 4.3–4.17, 4.20, 4.21, 4.23, 4.25, 4.28, and 4.30—HNS LM (Hydrogen Network Synthesis—Linear Model)). For process optimization, different objective functions can be chosen to be minimized. In this case, operating cost (4.31) for the retrofit case was chosen. The proposed model has the advantage of being a linear model, for which quite robust solvers can be used. However, the main drawback is that a compressor is associated with each possible connection individually in order to avoid nonlinear material balances to identify the composition of the stream being compressed. For this case, streams cannot be mixed to use the same compressor, and the resulting network may end up with more compressor units than an alternative nonlinear model, in which streams are allowed to mix.

4.3.4 Mathematical Model: MINLP Formulation

A nonlinear model was also developed. In this model, the compressors are considered as independent units that may be used to connect units that need compression (see Figure 4.2b). Different from the other units, the inlet and outlet pressure of each compressor are free variables. The maximum number of compressors to be considered is set in the superstructure modeling, and it is obtained in the model solution previously. In this model, streams are mixed to enter the compressor. Therefore, the hydrogen composition is unknown and must be treated as a variable. Besides, since no compressors are associated with each stream individually, the flowrates are only possible if the current origin pressure is higher than the destination pressure. For a particular flow F with upper bound F^{max}, the constraints (4.37) ensure that flow is only possible for this case (higher pressure to lower pressure):

$$F \leq F^{max} \times (1 - u_{deltaP}) \tag{4.37}$$

Despite the possibility of generating networks with fewer compressors, the nonlinearity comes up with a more difficult problem to be solved that is very dependent on the initial guess, as will be discussed later.

In the MINLP model, the superstructure is a bit different from the one presented, as illustrated in Figure 4.2b. In this case, the compressor is considered a unit of the network and, therefore, can have the same source (the compressor outlet) and consumer (the compressor inlet) functionality and must be present in the balance equations. The only nonlinearity in this model arises in the hydrogen balance in the inlet of the compressors because there is the merging of flows and, consequently, the product flow/purity. It is necessary to know the inlet composition because the outlet flow with this composition is sent to other units, and the hydrogen balances depend on this value.

The equations that describe the nonlinear model are described below. Equations (4.1), (4.3)–(4.9) of the linear model are replaced by the equations below, as compressors need to be considered in material balances. In sources, in addition to Equation (4.2), there is Equation (4.38), which describes the sum of flow rates from sources for consumers, purifiers, compressors ($FIC_{i,c}$) and for burning. Hydrogen from the source can be sent to all these units.

$$FH2I_i = \left(\sum_{\substack{j \in HC \\ \in HS}} FIJ_{i,j} + \sum_{k \in HP} FIK_{i,k} + FIW_i + \sum_{c \in HCP} FIC_{i,c} \right) \quad \forall\, i \tag{4.38}$$

For consumers, global and component material balances are made, where $FCJ_{c,j}$ is the flowrate from the compressor to the consumers and $FJC_{j,c}$ is the flow rate from consumers to compressors. The sum of the flowrate at the entrance of each consumer corresponds to the sum of the flowrate from the source, the purifier, another different consumer, and the compressor.

$$\begin{aligned} FJ_j = {} & \sum\nolimits_{i \in HS} FIJ_{i,j} + \sum\nolimits_{k \in HP} FKJ_{k,j} \\ & + \sum\nolimits_{j \in HC} FJJ_{j,j'} + \sum\nolimits_{c \in HCP} FCJ_{c,j} \quad \forall\, j \in HC \end{aligned} \tag{4.39}$$

The same is true for the hydrogen balance, where in addition to flowrates, purities are considered. Here there is the purity of the compressor (YC_c).

$$\begin{aligned} FJ_j \times YJ_j = {} & \sum\nolimits_{i \in HS} FIJ_{i,j} \times YI_i \\ & + \sum\nolimits_{k \in HP} FKJ_{k,j} \times YK_k + \sum\nolimits_{j \in HC} FJJ_{j,j'} \times YP_j \\ & + \sum\nolimits_{c \in HCP} FCJ_{c,j} \times YC_c \quad \forall\, j \in HC \end{aligned} \tag{4.40}$$

The sum of the outlet flowrate of each consumer corresponds to the sum of the flowrate that the consumer forwards to the burn (waste), to the purification unit, to another different consumer, and the compressor if necessary.

$$\begin{aligned} FP_j = FJW_j + {} & \sum\nolimits_{k \in HP} FJK_{j,k} \\ & + \sum\nolimits_{j \in HC} FJJ_{j,j'} + \sum\nolimits_{c \in HCP} FJC_{j,c} \qquad \forall\, j \in HC \end{aligned} \tag{4.41}$$

The global material balance and for hydrogen is also applied for purifiers. The material balance corresponds to the sum of all flowrates at the entrance of the PSA, which include the flowrates from consumers, sources, and compressors. The purification unit, in turn, can send flow to consumers, compressors and can burn the excess (waste), which can be seen in Equation (4.42). Equation (4.43) corresponds to the hydrogen balance, considering the flows directed to the purifier and forwarded from the purifier. In addition to these equations, the purified flow rate must not exceed the PSA capacity (Equation (4.44)), and, through the recovery of the PSA, the flowrates that are sent for burning are obtained (Equation (4.45)).

$$\begin{aligned} \sum\nolimits_{j \in HC} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} + \sum\nolimits_{c \in HCP} FCK_{c.k} = {} & \sum\nolimits_{j \in HC} FKJ_{k,j} \\ & + FKW_k + FKW_{rec,k} + \sum\nolimits_{c \in HCP} FKC_{k,c} \quad \forall\, k \in HP \end{aligned} \tag{4.42}$$

$$\begin{aligned} \sum\nolimits_{j \in HP} & FJK_{j,k} \times YP_j + \sum\nolimits_{c \in HCP} FCK_{c.k} \times YC_c + \sum\nolimits_{i \in HS} FIK_{i,k} \times YI_i \\ & = \sum\nolimits_{j \in HP} FKJ_{k,j} \times YK_k + \sum\nolimits_{c \in HCP} FKC_{k,c} \times YK_k \\ & + FKW_k \times YK_k + FKW_{rec,k} \times YKW_k \quad \forall\, k \in HP \end{aligned} \tag{4.43}$$

$$\sum\nolimits_{j \in HP} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} + \sum\nolimits_{c \in HCP} FCK_{c,k} \leq FPur_{max,k} \qquad \forall\, k \in HP \tag{4.44}$$

$$\left(\sum\nolimits_{i \in HS} FIK_{i,k} \times YI_i + \sum\nolimits_{j \in HP} FJK_{j,k} \times YP_j + \sum\nolimits_{c \in HCP} FCK_{c.k} \times YC_c\right) \times (1 - rec_k) = FKW_{rec} \times YKW_k \Big) \forall\, k \in HP \tag{4.45}$$

where $FCK_{c.k}$ is the flow rate from compressors to purifier, $FKC_{k,c}$ is the flow rate from the purifiers to the compressors. Also, as the compressors are like units in the hydrogen network, material balances are made. The sum of the flow that enters the compressors is called FC_c, which consists of the sum of the flows from sources, consumers, and purifiers.

$$FC_c = \sum_{c \in HCP} FIC_{i,c} + \sum\nolimits_{c \in HCP} FJC_{j,c} + \sum\nolimits_{c \in HCP} FKC_{k,c} \quad \forall\, c \in HCP \tag{4.46}$$

Therefore, any flow that enters the compressor must be directed to the consumers and purifications units. If necessary, some part of the compressor flow that is not used can be sent directly for burning.

$$.\textstyle\sum_{c \in HCP} FIC_{i,c} + \sum_{c \in HCP} FJC_{j,c} + \sum_{c \in HCP} FKC_{k,c} = \sum_{c \in HCP} FCJ_{c,j} + \sum_{c \in HCP} FCK_{c.k} + FCW_c \quad \forall\, c \in HCP \tag{4.47}$$

It is also necessary to carry out the hydrogen balance in the flows that make up FC_c.

$$FC_c \times YC_c = \sum_{c \in HCP} FIC_{i,c} \times YI_i + \sum\nolimits_{c \in HCP} FJC_{j,c} \times YP_j \sum\nolimits_{c \in HCP} + FKC_{k,c} \times YK_k \quad \forall\, c \in HCP \tag{4.48}$$

In the same manner as in the MILP model, a binary variable z is associated with each possible flowrate, including the flowrates involving the compressor units, e.g., $FIC_{i,c}$, $FJC_{j,c}$, $FKC_{k,c}$, $FCJ_{c,j}$, $FKC_{k,c}$, and FCW_c. The corresponding constraints are as described by Equation (4.10). Also, binary variables are associated with new pipelines (Equations (4.13) and (4.14)) and for new PSA (Equation (4.15)). The binary variable $z_{c_{\alpha,\beta}}$ are used to define if the compressor unit is installed assuming the value of 1, 0 otherwise. Differently from the MILP model, zc is not defined over a pair of streams; it depends only on the compressor unit. FC_c is associated with the flow of each compressor. Constraints (Equation (4.49)) is used to establish which compressors are used and their flow rates.

$$\begin{cases} FC_c \geq \varepsilon \times zc \\ FC_c \leq F^{max} \times zc \end{cases} \tag{4.49}$$

As the pressures vary in the nonlinear model, pressure restrictions must be included, which guarantees the compressor inlet and outlet pressures. They are formulated in the same format as the logical flow restrictions. For a given compressor unit, the inlet pressure is set as lower than the minimum pressure among the pressure of the mixed streams entering the compressor (Equation (4.50)). The outlet pressure is set as higher than the maximum pressure among the pressure of the streams, leaving the compressor according to the pressure of the stream destination (Equation (4.51)). It is important to mention that, due to the minimization of the energy cost associated with the compressor in the objective function, which is proportional to the pressure ratio ($PC_{out,c}/PC_{in,c}$), the inlet pressure is set as the minimum stream pressure entering the compressor *c*, and the outlet pressure as the maximum stream pressure leaving the compressor *c*.

$$\begin{cases} PC_{in,c} \le PP_j + (P^{max} - PP_j) \times (1 - z_{j,c}) \\ PC_{in,c} \le PI_i + (P^{max} - PI_i) \times (1 - z_{i,c}) \\ PC_{in,c} \le PK_k + (P^{max} - PK_k) \times (1 - z_{k,c}) \end{cases} \tag{4.50}$$

$$\begin{cases} PC_{out,c} \ge PJ_j - P^{max} \times (1 - z_{c,j}) \\ PC_{out,c} \ge PK_k - P^{max} \times (1 - z_{k,j}) \\ PC_{out,c} \ge PW - P^{max} \times (1 - z_{c,w}) \end{cases} \tag{4.51}$$

where $PC_{in,c}$, and $PC_{out,c}$ are the compressor *c* inlet and outlet pressures, respectively, the binary variable z is associated with flowrates (i.e., $z_{i,c}, z_{j,c}, z_{k,c} \ldots$) and P^{max} is the maximum pressure of the network used to make the constraints (4.50) and (4.51) redundant for the corresponding non-existent connection (the corresponding binary is set to zero due to the zero flowrate).

The operating and capital costs are calculated in the same way as in the linear problem, as well as the logical flow restrictions. The cost of hydrogen production is obtained by Equation (4.17), Equation (4.52) represents the electricity cost, Equation (4.53) represents the purification cost, and cost of fuel is represented in Equation (4.54).

$$CH2C = C_{eletric} \times \sum_{c \in HCP} FC_c \times (C_P * T/\eta) \times \left(\left(\frac{PC_{out,c}}{PC_{in,c}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \times (\rho_o/\rho) \tag{4.52}$$

$$CH2K = \sum\nolimits_{k \in HP} \left(\sum\nolimits_{j \in HC} FKJ_{k,j} + FKW_{rec} + FKW_k + \sum\nolimits_{c \in HCP} FKC_{k,c} \right) \times C_k \tag{4.53}$$

$$CH2F^T = C_{fuel} \times \sum_{\alpha} F\alpha W_\alpha \times [y_\alpha \times \Delta H^\circ{}_{H2} + (1 - y_\alpha) \times \Delta H^\circ{}_{CH4}] \tag{4.54}$$

The subscript α denotes all units sending streams to the fuel system (*i, j, k, c*). Equation (4.55) represents the cost of new compressors and Equation (4.56) the cost of new piping.

$$C_{new\ compressor} = a \times z_{c_{newc}} + b \times FC_{c_{newc}} \times (C_P * T/\eta) \times \left(\left(\frac{P_c^{out}}{P_c^{in}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \times (\rho_o/\rho) \tag{4.55}$$

$$C_{new\ piping} = c \times \left(\sum_{\alpha} \sum_{\beta} z_{h_{\alpha,\beta}} \times L_{\alpha,\beta} \right) + d \times \left(\sum_{\alpha} \sum_{\beta} F_{\alpha,\beta} \times L_{\alpha,\beta} \times w \times \left(1 - u_{h_{\alpha,\beta}}\right) \times \left(\frac{T}{T_0}\right) \times \left(\frac{P_0}{P}\right) \right) \tag{4.56}$$

The indices α and β represents the possible connections involved (*i,j; j,k; k,j; j,j'; i,k; i-waste; j-waste; k-waste; i,c; j,c; k,c; c,j; c,k; c-waste*). The MINLP model formulated in this work is described by the set of constraints (4.1, 4.2, 4.11, 4.14, 4.15, 4.16, 4.17, 4.37–4.56). The objective function is described in Equation (4.31). This MINLP model will be named to facilitate the description of the results by HNS NLM (Hydrogen Network Synthesis—Nonlinear Model).

4.3.5 Virtual Compressors

The main difference between the MILP model and the MINLP model is how the compressors are treated. In MILP, the compressors are associated with each particular flowrate. In this case, the streams are not mixed. However, in the MINLP, the compressors are treated as independent units, not associated with a flowrate. Then the stream can be mixed to enter the compressor and split leaving the unit. Besides the class of the resulting model (either linear or nonlinear), the linear model may result in a network with more compressors and pipelines than the nonlinear model. Both the linear and the nonlinear formulation are capable of representing the hydrogen network, so what differentiates them is the issue of allowed linearity (which can be improved through this proposed technique), the linear model is simpler to solve, and the global optimum solution is guaranteed.

To overcome a large number of compressor units and further investment cost reduction, a strategy to reduce the use of this equipment was carried out through an algorithm based on non-real streams or virtual compressors, i.e., it is possible to rearrange the streams and compressors if the compressor capacities were not reached. This developed technique is one of the contributions of this work. Through it, the linear model becomes competitive, compared to the nonlinear model, due to its advantages.

There are two cases where it is possible to perform this unit reduction: (Option 1) when there are streams with different composition being compressed and forwarded to the same unit or (Option 2) when streams coming from the same unit are compressed and forwarded to different units, as can be seen in Figure 4.3. In other words, it is possible to group streams and use the same compressor, thus decreasing the fixed part of the new compressor capital cost, since the variable part is flow dependent and does not change. It is worth nothing that the fixed cost of piping is also minimized due to the rearrangement of the streams.

For each option, the inlet pressure (in Option 1) and the outlet pressure (in Option 2) must be corrected according to the minimum and maximum pressure of the involved streams, respectively. In that case, the energy cost and the variable part of the investment cost must also be recalculated. It should be noted that using this procedure, the solution is not unique, and the best solution is that with the maximum total cost reduction. Despite eventually unfavorable pressure changes, the number of compressor units can be reduced. Therefore, when this procedure is performed, the investment cost is almost always reduced, because parameter a and greater than parameter b (equation 4.55). In this work, since the number of possible rearrangements is small, this procedure was performed by enumeration.

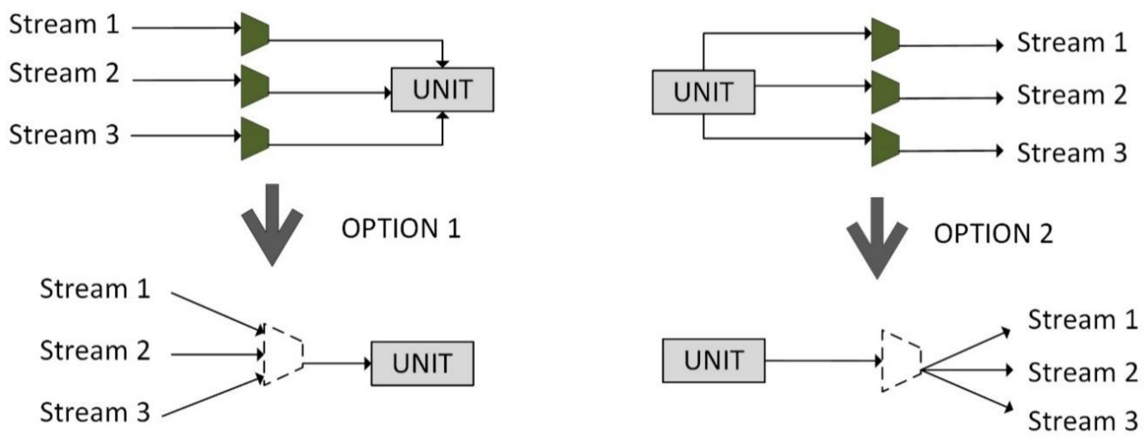


Figure 4.3: Virtual Compressor Approach–Possibilities of mixing streams in the compressors.

4.3.6 Solution Strategy

In this work, the MILP and the MINLP model were used to the network (re)design. Compared to the linear models, nonlinear models are wholly dependent on the initialization, which has a more challenging convergence. Also, for MILP models, the global solution can be obtained without a high computational effort. The MILP solution can be rearranged to reduce the compressor units, with the virtual compressors approach. Besides, the solution obtained by the MILP model can be used as a good and feasible initial point for the MINLP model. It is crucial to the grassroots designs since, in the retrofit case, the existing network can be used as an initial point. All these possibilities were evaluated in this work, and further discussion is presented in the results section.

The initialization strategy used can be described as follows:

1. The flowrates are fixed according to the existing network for the retrofit cases, and an LP subproblem with F_{obj} = 0 subject to the material balances is solved to obtain a feasible solution.
2. The binary variables (z) are initialized according to the existing network, i.e., z = 1, where there is a non-zero flowrate, z = 0 otherwise. Also, the other binary variables (z_c, z_h, z_{kn}) are fixed to zero, since they represent the installation of new compressors, piping, and purifying units.
3. The complete MILP model is solved. This result is defined as the existing network of each case study for later optimization (BASE CASE).
4. With all the variables values in the feasible solution defined by the existing network, the variables are set as free according to their lower and upper bounds. The complete MILP (HNS LM) is solved (objective function = minimize operating cost). The MINLP (HNS NLM) proposed model is also solved to compare with the item (6).
5. The optimized network obtained through the linear model is evaluated with the rearrangement of compressors. Here the values of operating cost and capital differ

between them due to the decrease in the number of compressors and the possible increase in electricity.

6. This network design is used to initialize the MINLP nonlinear model (HNS NLM).

For all cases, it was possible to ensure that the starting point was a feasible point. Figure 4.4 summarizes the initialization techniques performed.

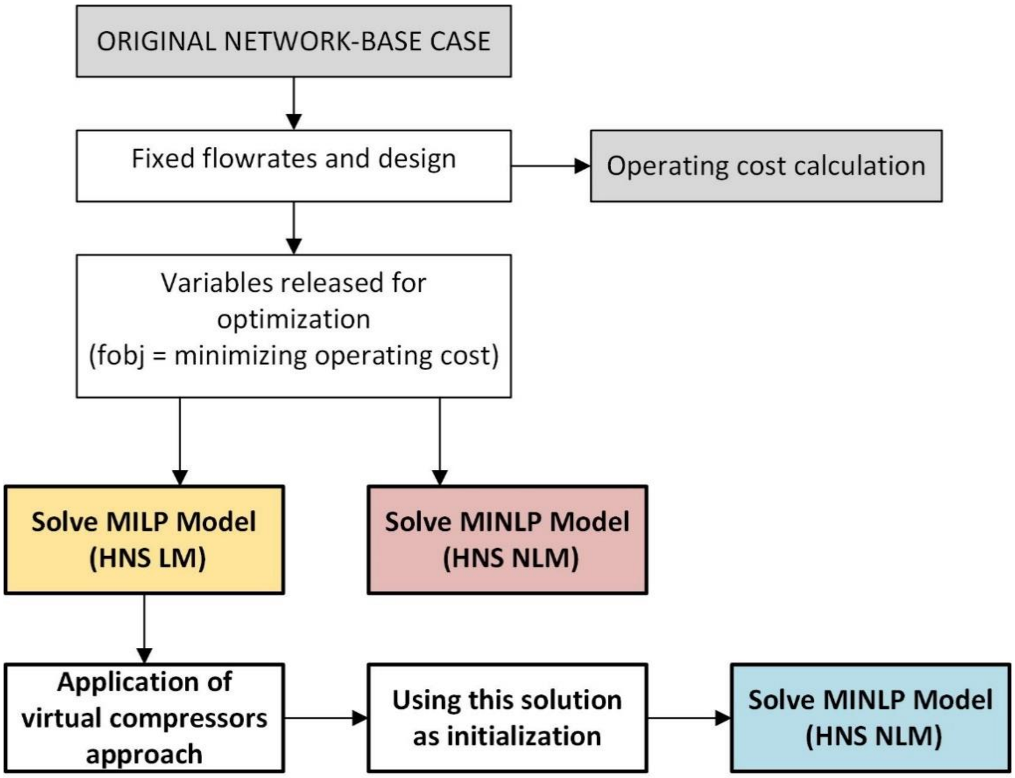


Figure 4.4: Summary of the methodology proposed in this article, through optimization via linear and nonlinear model.

4.4 Results

The model described in the previous section was validated using two examples of hydrogen networks proposed in the literature. The mathematical programming model was implemented in the modeling system GAMS 22.2 on a 3.6 GHz Intel® Core™ I7 CPU (GAMS Development Corporation, Washington DC, USA).The solver used to solve HNS LM was CPLEX (CPLEX 10, GAMS Development Corporation, Washington DC, USA, 2006), and for HNS NLM it was DICOPT (/DICOPT 2x-C, GAMS Development Corporation, Washington DC, USA, 2006).

For the case studies, it was considered the retrofit design for existing hydrogen networks. Therefore, the existing structure was explored considering the installation of new pipelines, new compressors, and purifying units. The economy saving is obtained by the operating cost reduction compared to the original solution. However, there is also an investment cost associated with non-existing equipment and pipelines. The payback time, i.e., the investment cost divided by annual operating cost savings was also used as an economic indicator for comparing the model solution.

The original network was ensured as a feasible starting point for all optimization problems. It was accomplished by fixing all the values of stream flowrates according to the existing network, and the total operating costs were calculated according to the parameters listed in this work for each case study. For all cases, the original network was a feasible point. However, some authors have not presented the value of the parameters used to estimate the costs. Therefore, for a fair comparison, the costs were recalculated with the listed parameters in this work, and hence, despite the network configurations and flowrates are the same presented here, the costs are similar but not the same. Further discussion and considerations are given for each example.

4.4.1 Example 1

The first example is from Hallale and Liu (2001). The hydrogen network depicted in Figure 4.5 consists of a primary hydrogen production unit (H_2plant) and a secondary source, which is catalytic cracking (CCR). In this process, there are six consumer units: HC (hydrocracker), JHT (kerosene hydrotreater), CNHT (cracked naphtha hydrotreater), DHT (diesel hydrotreater), NHT (naphtha hydrotreater), and IS4 (hydrodealkylation). Two previously installed compressors are used, and there are no purification units. Flowrates are expressed in MMscfd (million ft^3/day, under standard conditions), stream purity, flowrates, and pressures are shown in Table 4.3.

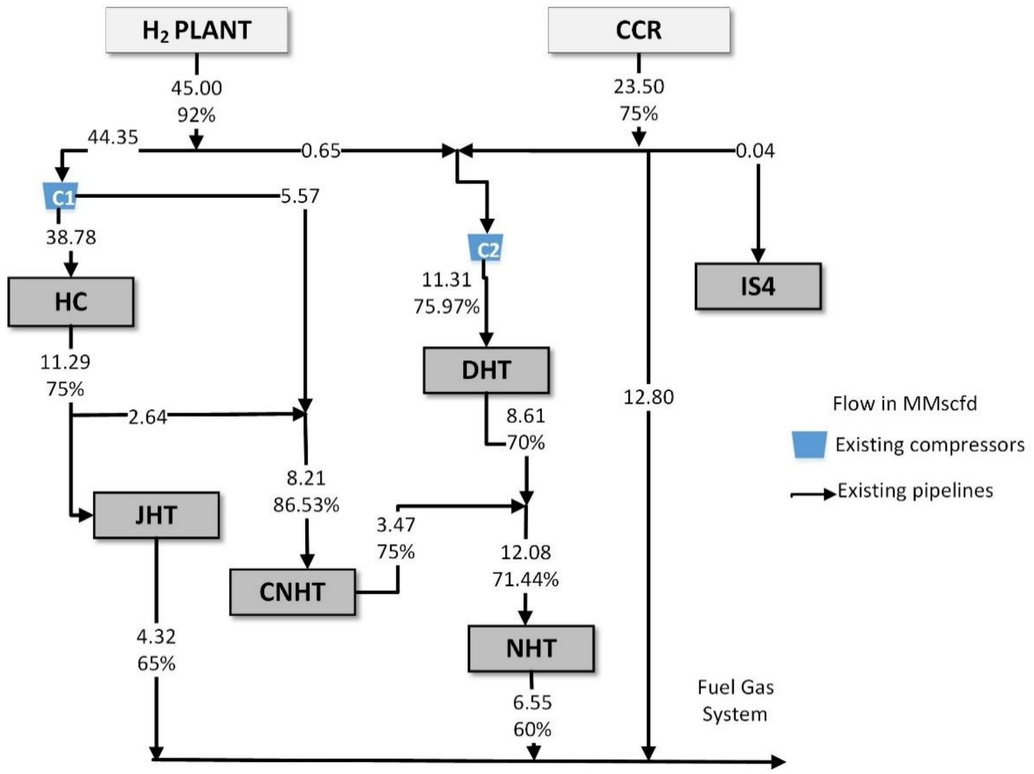


Figure 4.5: Existing hydrogen network for Example 1.

Table 4.3: Flowrate, purity, and pressure information used in Example 1.

Sources	$FH2I_i$ (MMscfd)	$FH2I_{i,max}$ (MMscfd)	$YI_i\%$	PI_i (psia)		
H_2 plant	45.00	50.00	92.50	300		
CCR	23.50	23.50	75.00	300		
Consumers	FJ_j **(MMscfd)**	$YJ_j\%$	PJ_j **(psia)**	FP_j **(MMscfd)**	$YP_j\%$	PP_j **(psia)**
HC	38.78	92.00	2000	11.29	75.00	1200
JHT	8.65	75.00	500	4.32	65.00	350
CNHT	8.21	86.53	500	3.47	75.00	350
DHT	11.31	75.97	600	8.61	70.00	400
NHT	12.08	71.44	300	6.55	60.00	200
IS4	0.04	75.00	300			

The objective function chosen for the problem analysis was to minimize the operating cost of the hydrogen network, Equation (4.31), using the parameters listed in Table 4.3 and the network configuration depicted in Figure 4.5. A variation of $\pm$10% (v_p) in the nominal flow of consumers was allowed, FJ_j and FP_j were allowed in the original article. For the installation of a new PSA, the purity of 99.99% with a maximum operating capacity of 50 MMscfd, a recovery rate of 90%, and purge purity of 40.2% was considered.

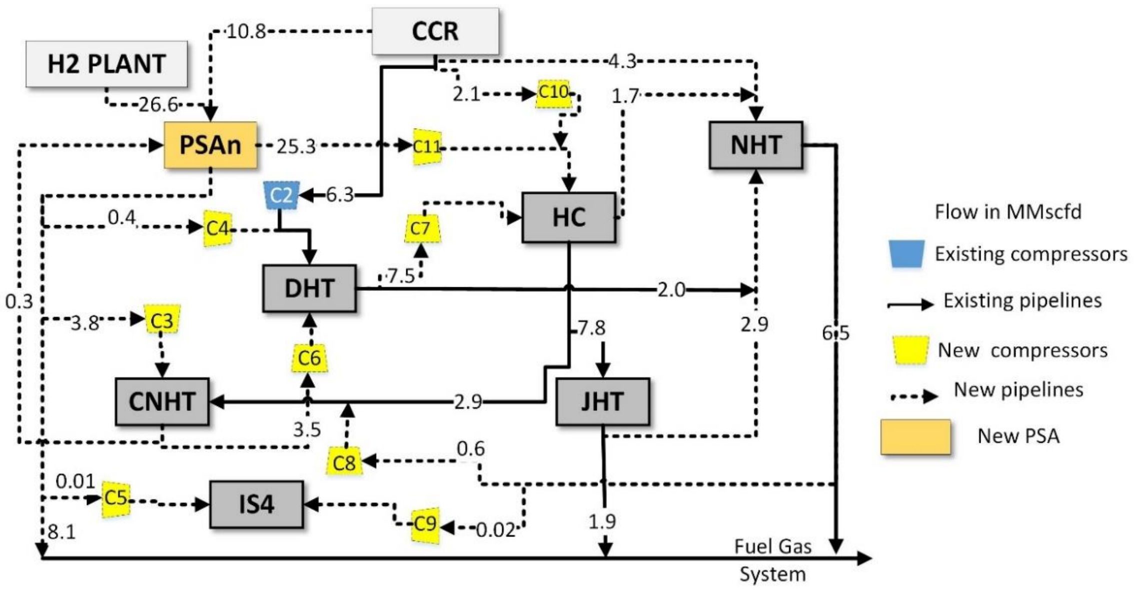
The annual operating costs for the original network were estimated at 39.819 \$/year. This solution is referred here as Hydrogen Network -BASE CASE (HN0). The Hydrogen Network -BASE CASE corresponds to the existing basic topology.

The HNS LM model has about 763 single equations, 323 single variables, and 227 discrete variables. Through linear optimization, savings of \$11 million per year were achieved with a total investment of \$16 million. In this case, 9 new compressors and 16 new pipelines were installed, as well as a new PSA (HN1). Nearly a 28% reduction in operating cost was achieved. This network is shown in Figure 4.6a. The HN1 optimized network MILP model only imports 26.5 MMscfd, and the original network uses 44.9 MMscfd of hydrogen from H_2 Plant, which represents a reduction of almost 41% in the amount of imported pure hydrogen.

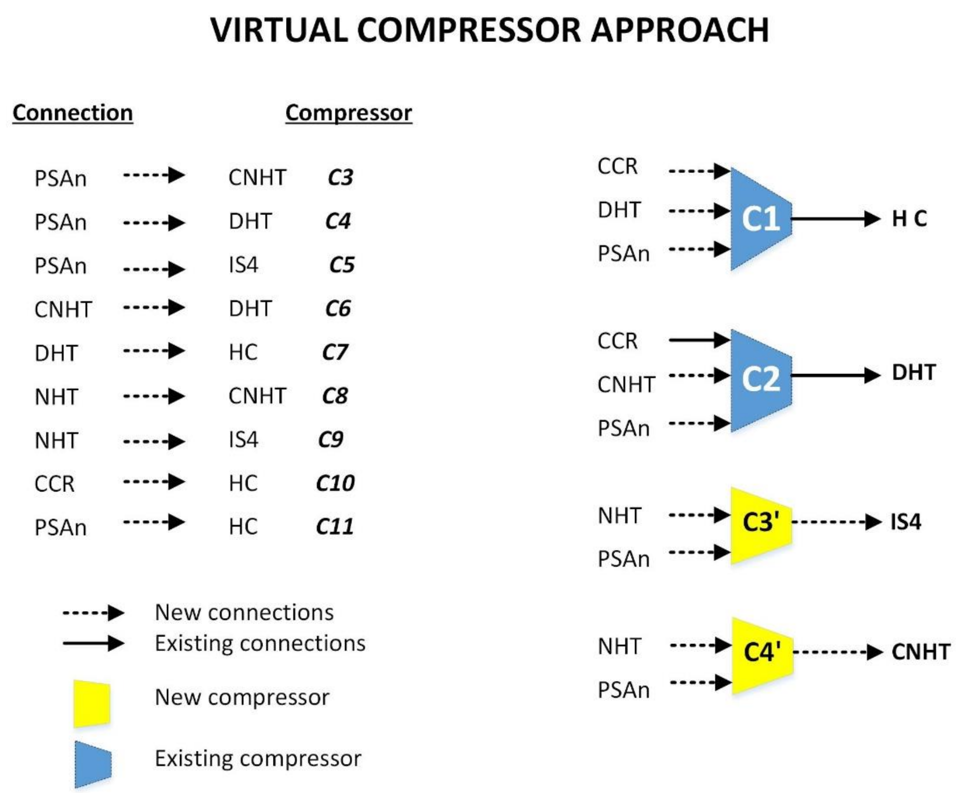
In the HNS LM optimization, the merging of flows before the compressor units is not allowed. Therefore, the solution may result in a large number of installed compressors. However, the number of compressors can be reduced after the optimization, evaluating the obtained network, and, possibly, an even more significant cost reduction can be achieved. For the cases in which more than one stream leaving one unit is compressed and/or more than one stream is compressed to one unit, the streams can be rearranged to be compressed in a unique compressor unit saving the fixed cost associated to the compressor investment. According to the distance of the units, the cost of the pipeline must also be recalculated. As more than one alternative for the evolutionary network is possible, but they are only a few, this procedure can be executed manually by the designer. Therefore, we analyzed which compressors were already previously installed based on the units and purity involved and if their nominal capacity allowed them to receive more streams. If positive, the stream was directed to it, and the new associated compressor could be eliminated. The rearrangement technique using virtual compressors applied to the compressors of example 1 can be seen in Figure 4.6b.

According to the optimization result (HN1), 9 new compressors were installed, which can be rearranged, as explained in Figure 4.6. According to option 1, where different flow rates that go to the same unit are grouped, rearranging in only 2 new compressors and using the two existing ones. The total cost of these new compressors is $0.271 million ($0.230 million of the fixed cost and $0.041 million of the variable cost), and this represents an 86.4% reduction in the total investment in new compressors. The total cost of piping also reduces by 40% due to the rearrangement of the compressors. This impact on total investment is 12.4% less.

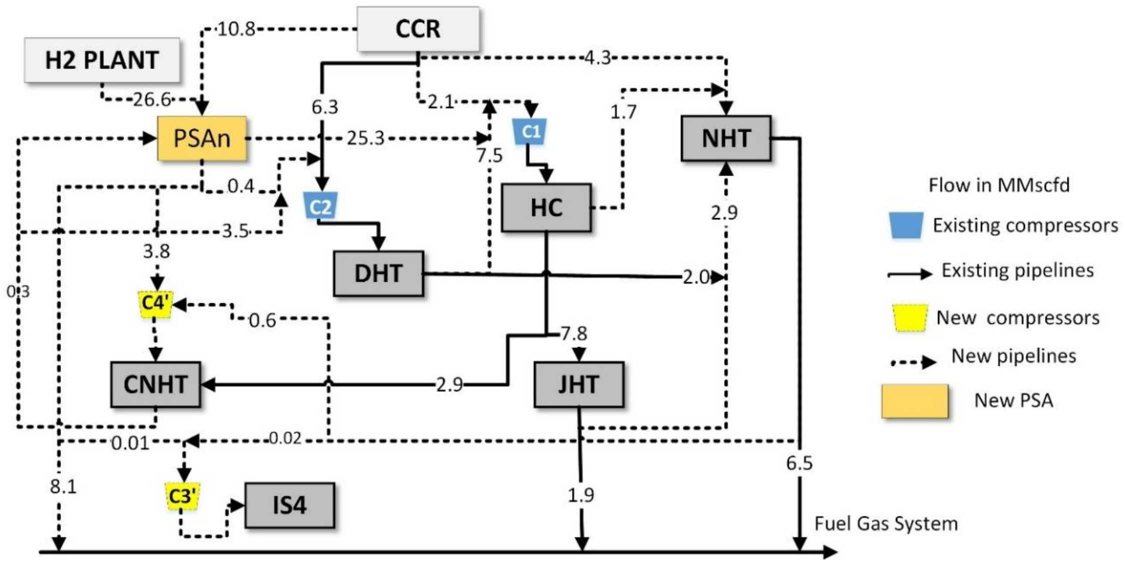
It should be noted that as the compressors are rearranged, the inlet pressure is the lowest pressure between the flows. Therefore, the cost of electricity is slightly changed due to this, so the cost of electricity increased by 14.5% (from $0.136 million to $0.156 million) and an increase of 0.06% in operating costs. The proposed new topology can be analyzed in Figure 4.6c, and HN1 will represent that network.



(a)



(b)



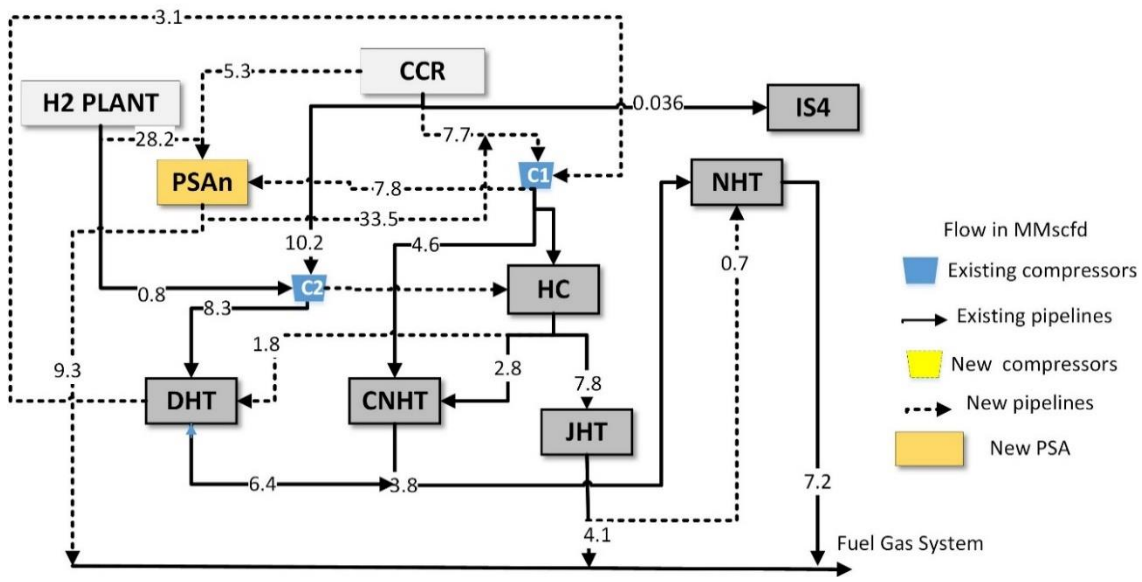
(c)

Figure 4.6: (**a**) Optimized network HN1 via HNS LM, for Example 1. (**b**) Virtual compressor approach applied to HN1 network. (**c**) Optimized network HN1’ with rearranged compressors.

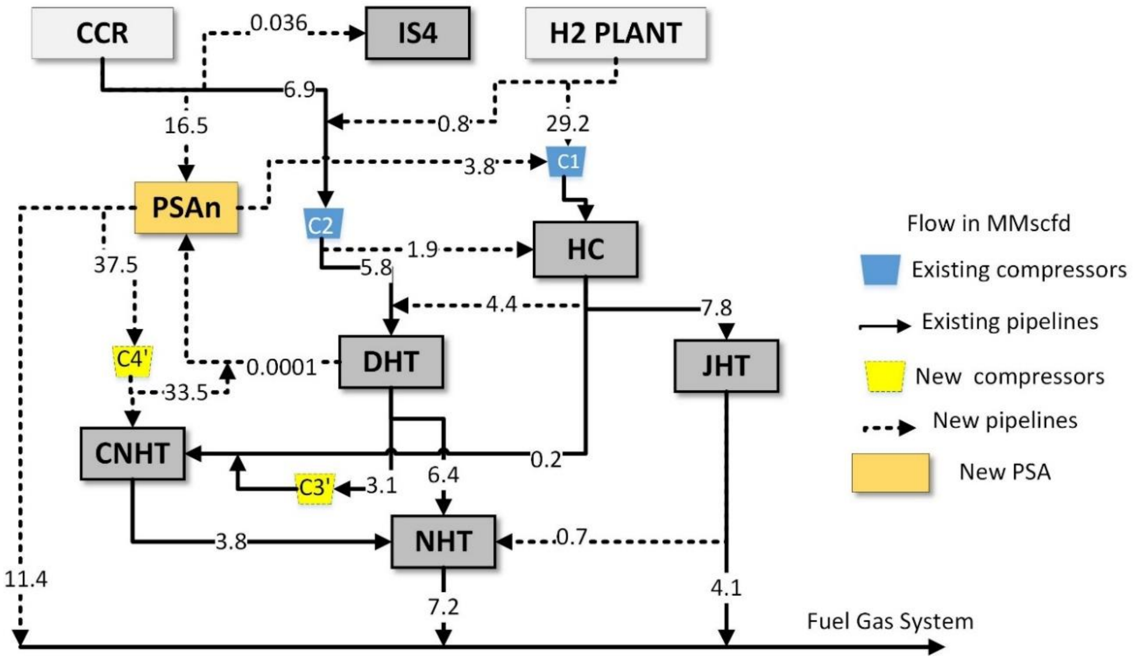
To compare the linear and nonlinear formulations, the original network was optimized through the nonlinear model HNS NLM, described in Section 4.3.4. The first initialization used here was the original network, in example 1 (Figure 4.5). The HNS NLM model has 944 single equations, 473 single variables, and 308 discrete variables. The operating cost obtained was \$28.183 million per year and \$7.846 million per year of capital cost (one PSA and 10 pipelines), called network HN2. The result obtained in the two proposed optimized networks is very similar; however, the nonlinear has fewer connections (Figure 4.7a). The most significant portion of the cost of capital corresponds to the quantity to be purified. The optimization of HN2 network is an integer solution (not an optimal as in HNS LM), which usually happens in nonlinear problems as it is not possible to guarantee optimum global optimization.

The second initialization made, which is the biggest contribution of this work, uses the result obtained from the HNS LM (HN1'- with compressors rearrangement) as the initialization of the nonlinear model HNS NLM, to facilitate the resolution of the nonlinear model. As already mentioned above, the HN1' network with the rearrangement of the compressors has a significant reduction in the cost of new compressors. For this reason, it is an excellent point option for the nonlinear model. Besides, as can be seen in the results, since nonlinear optimization has great locations, this initialization helped to improve the result. The HN3 network (obtained using MILP as a feasible point in MINLP) resulted in the lowest operating cost, a reduction of 31.2% (Figure 4.7b). However, comparing the payback, which refers to both the economy and the necessary investment, the network with the lowest payback is HN1'. This shows that with the HNS LM model, good and significant results are achieved, but through nonlinear optimization, less complicated networks with lower operational costs are achieved. For this, it is important to evaluate the design of the proposed network through different initializations.

All the results obtained in the different optimizations are summarized in Table 4.4. It is observed that the most significant reduction in the operation cost was obtained in the HN3 network. However, taking into account the investment and the payback time, the HN1' network proves to be an excellent alternative. Through the results obtained, it can be concluded that the two described models (linear and nonlinear) are efficient for the proposed optimization. The linear model is good enough and capable of providing considerably improved solutions. Besides, as an initial guess for the nonlinear model, it proved to be an even more competitive alternative. The compressor rearrangement technique provides a reduction in investments. When used to initiate the optimization of the nonlinear model, it provides designs with fewer lines and compressors.



(a)



(**b**)

Figure 4.7: (**a**) Optimized network HN2 via HNS NLM for example 1. (**b**) Optimized network HN3 via HNS NLM with HNS LM as initialization, for example 1.

Table 4.4: Results obtained in the different optimizations models for example 1.

	COST (x 10^6)			
	HNS LM	**HNS LM**	**HNS NLM**	**HNS LM INITIALIZATION-HNS NLM**
	HN1	**HN1'**	**HN2**	**HN3**
H_2 production (\$/year)	38.659	38.659	40.439	41.117
Electricity (\$/year)	0.136	0.156	0.204	0.198
Fuel (\$/year)	10.576	10.576	12.931	14.448
Purification (\$/year)	0.429	0.429	0.470	0.568
Operating cost (\$/year)	28.648	28.667	28.183	27.435
New compressor (\$/year)	0.992	0.135	-	0.290
New piping (\$/year)	0.415	0.405	0.419	0.341
New PSA (\$/year)	6.801	6.801	7.426	8.937
Capital cost (\$/year)	8.209	7.342	7.846	9.568
Total capital cost (\$)	16.418	14.684	15.692	19.136
TAC (\$/year)	36.857	36.009	36.029	37.003
Economy (\$/year)	**11.214**	**11.195**	**11.679**	**12.427**
Payback (year)	1.464	1.312	1.344	1.540
Resource time (s)	0.040	0.040	1.337	5.427

As the original article of this case study does not present clear information about parameters and conditions used in the optimization (Hallale and Liu, 2001), this work differs in values from the presented network. However, it is noteworthy that although the cost of the original network is different due to the explained, in this work, we considered the same calculation methodology for the original network (base case- HN0) and optimized network (HN1, HN2, HN3 …), with specific parameters and conditions chosen.

The result obtained from the optimization in Hallale and Liu (2001) is a 26.6% reduction in operating cost and payback time of 1.6 years, whose objective function was to reduce operating costs, limiting the payback time to 2 years. The achieved results obtained here with the proposed methodology are satisfactory as HN1 (HNS LM) optimized network reduced by 28.1% the cost of operating with a payback of 18 months. The optimized HN2 (HNS NLM) network achieved a 29.3% reduction in the operating cost with a payback time of 16 months, while Hallale and Liu (2001), reduced operating cost by 15%, with a 17 months payback. For this reason, the result obtained was better than that presented in the original article, as in percentage, a more significant reduction in operating cost and payback was achieved. With the proposal to use the linear solution as a feasible point, HN3 network, the reduction was even higher (31% in operating cost), which shows the efficiency of the proposed technique.

4.4.2 Example 2

The second example used is from Sardashti Birjandi et al. (2014) .The network is made up of two hydrogen producing units, a catalytic cracking plant (CCR) and a hydrogen generating unit (H_2plant), two purifying units (PSA), and 3 hydrogen consuming hydrotreating units (HDT I, HDT II, and HC), as illustrated in Figure 4.8. In addition to the information, some parameters described in Table 4.5 are required. This HNS LM model has 524 single equations, 224 single variables, and 158 discrete variables.

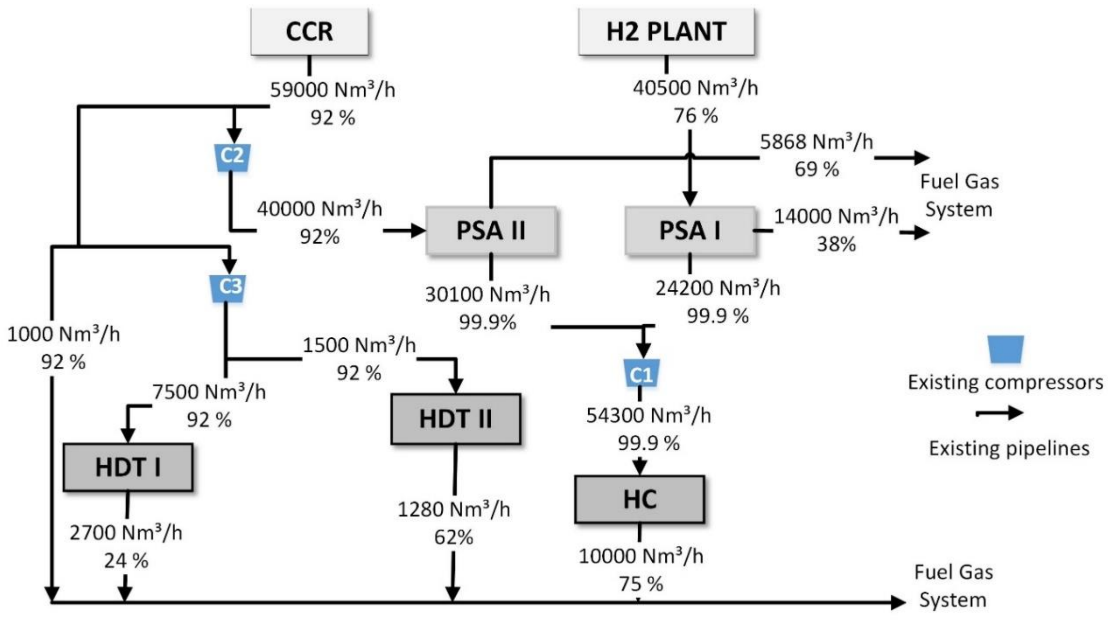


Figure 4.8: Existing hydrogen network for Example 2.

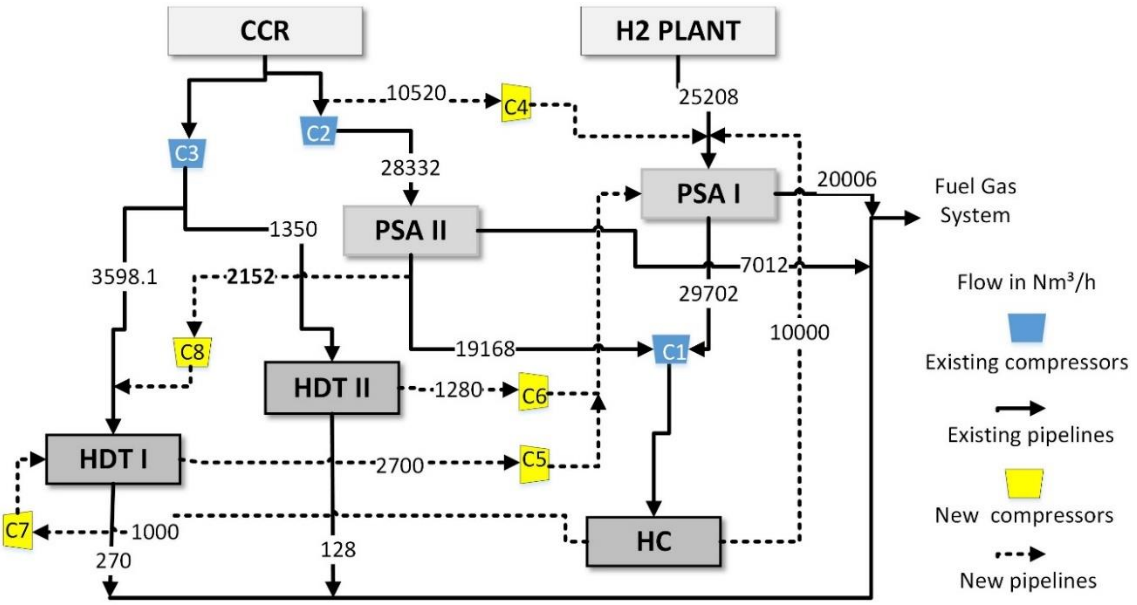
Table 4.5: Flowrate, purity and pressure information used in Example 2.

Sources	$FH2I_i$ **(Nm³/h)**	$FH2I_{i,max}$ **(Nm³/h)**	YI_i **(%)**	PI_i **(bar)**		
H_2 Plant	40,500	90,000	76.00	22		
CCR	59,000	65,000	92.00	4.50		
PSA	$FPur_{max,k}$ **(Nm³/h)**	YK_k	YKW_k	**Rec**		
PSA I	80,000	99.90	38.00	0.85		
PSA II	50,000	99.99	67.80			
Consumers	FJ_j **(Nm³/h)**	$YJ_j\%$	PJ_j **(bar)**	FP_j **(Nm³/h)**	$YP_j\%$	PP_j **(bar)**
HC	54,300	99.99	198	10,000	75.00	29.50
DHT	7500	92.00	55	2700	24.00	7.50
NHT	1500	92.00	55	1280	62.00	10.00

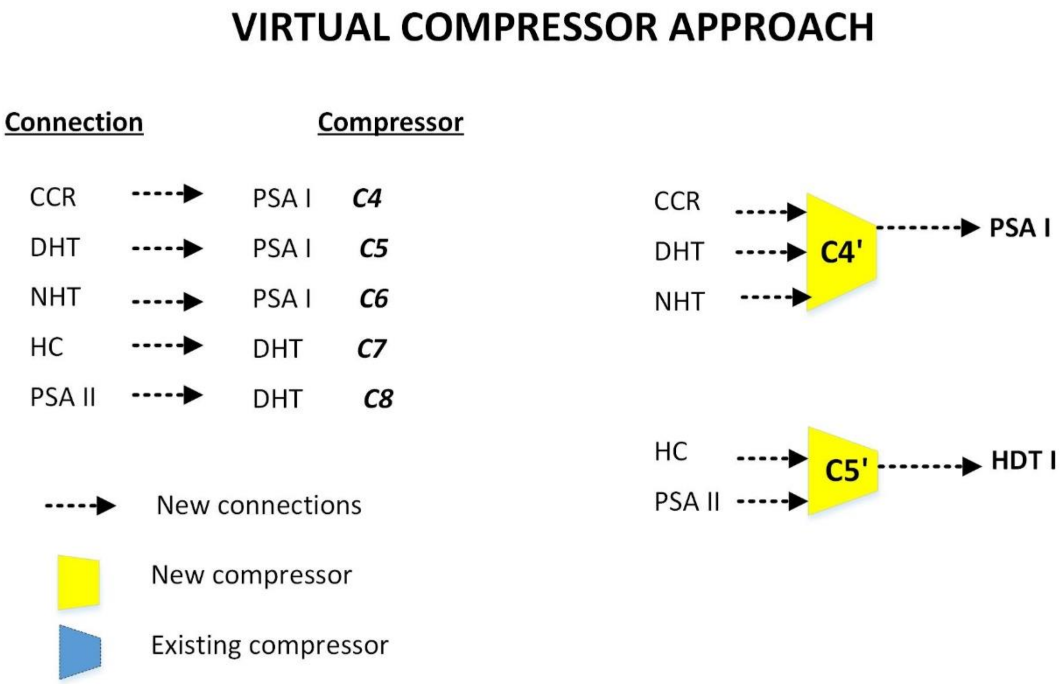
The annual operating costs for the original network were estimated at 44.017 \$/year. This solution is referred here as Hydrogen Network -BASE CASE for example 2. This network corresponds to the existing basic topology (Figure 4.8).

Minimizing only the operating cost of the hydrogen network, savings around \$12.4 million per year are achieved (HN4). For this design, the total investment of \$22 million is paid off in 22 months. Six compressors, 10 new lines, and a new PSA were installed. The operating cost was reduced by 28.3%. To avoid the installation of a new PSA, the network has been further optimized (HN5), resulting in \$11.7 million per year savings and with an even shorter payback time of approximately 2 months. Five new compressors and 6 new pipes were installed (HN5, Figure 4.9a). Almost a 26.5% reduction in operating cost was achieved.

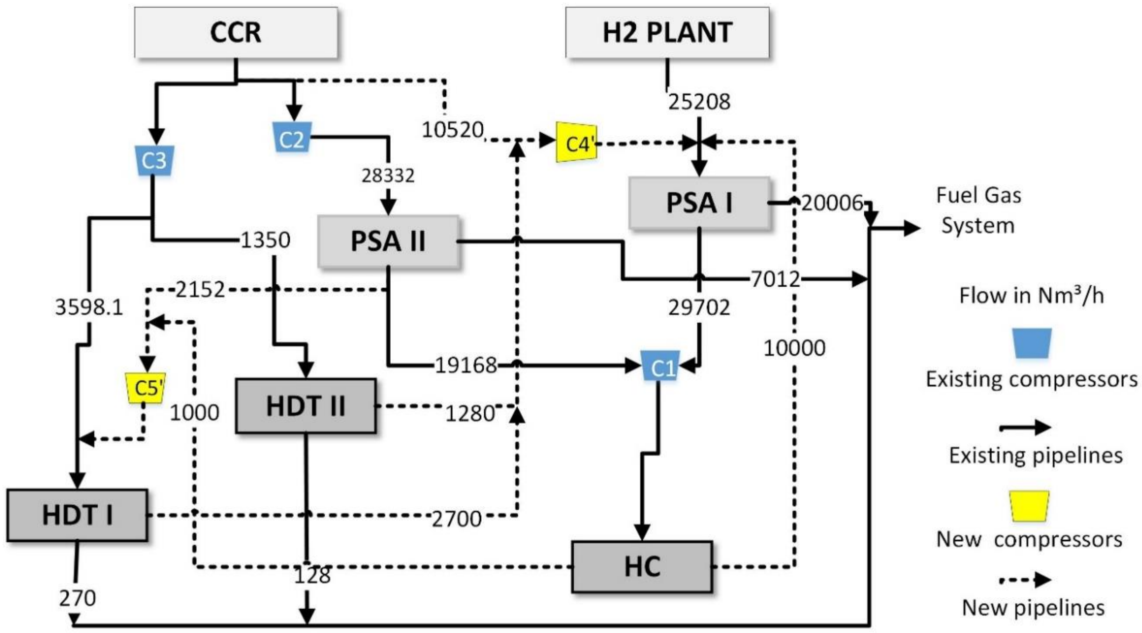
In this case, when rearranging the compressors respecting the nominal capacity, there is a reduction from 5 new compressors to only 2 new ones and using the 3 already installed. The rearrangement technique using virtual compressors applied to the compressors of example 2 can be seen in Figure 4.9b. In terms of total compressor cost reduces from \$1.194 million (\$0.575 million fixed cost and \$0.620 million variable costs) to \$0.934 million (\$0.230 million fixed cost and \$0.704 million variable costs). It represents a 21.8% reduction in the total investment in new compressors. It is worth mentioning that the cost of electricity increased from \$ 0.765 to 0.777 million per year due to the pressure drop in the rearrangement. The total investment cost reduces from \$1.406 to \$1.099 million. The proposed network design through the rearrangement of the compressors is represented by HN5', as shown in the Figure 4.9c.


CCR
H2 PLANT
10520
C4
25208
C2
C3
28332
PSA I
20006
Fuel Gas
System
1350
PSA II
3598.1
2152
7012
29702
Flow in Nm³/h
10000
19168
C8
C1
Existing compressors
HDT II
1280
C6
Existing pipelines
HDT I
2700
C5
New compressors
C7
1000
HC
270
128
New pipelines

(a)


VIRTUAL COMPRESSOR APPROACH
Connection
Compressor
CCR
PSA I
C4
DHT
PSA I
C5
NHT
PSA I
C6
HC
DHT
C7
PSA II
DHT
C8
CCR
DHT
NHT
C4'
PSA I
HC
PSA II
C5'
HDT I
New connections
New compressor
Existing compressor

(b)



(**c**)

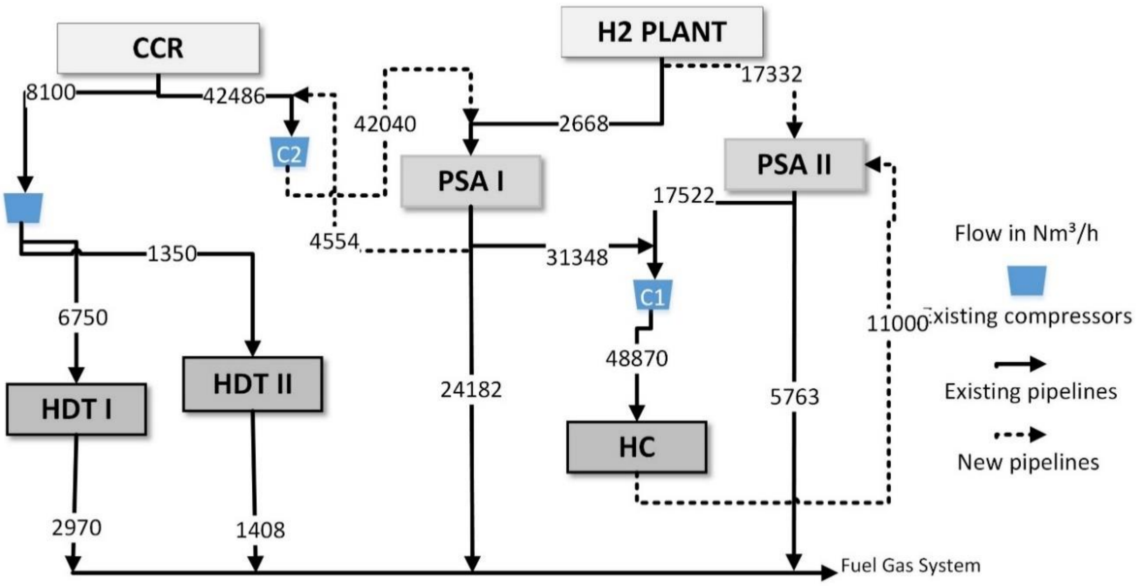
Figure 4.9: (**a**) Optimized network HN5 via HNS LM for Example 2. (**b**) Virtual compressors applied to HN5 network. (**c**) Optimized network HN5' with rearranged compressors.

To make a more direct comparison with the retrofit results obtained in the original paper, the existing network was tested using the HNS NLM model described in Section 4.3.4. The HNS NLM has 787 single equations, 430 single variables, and 249 discrete variables.

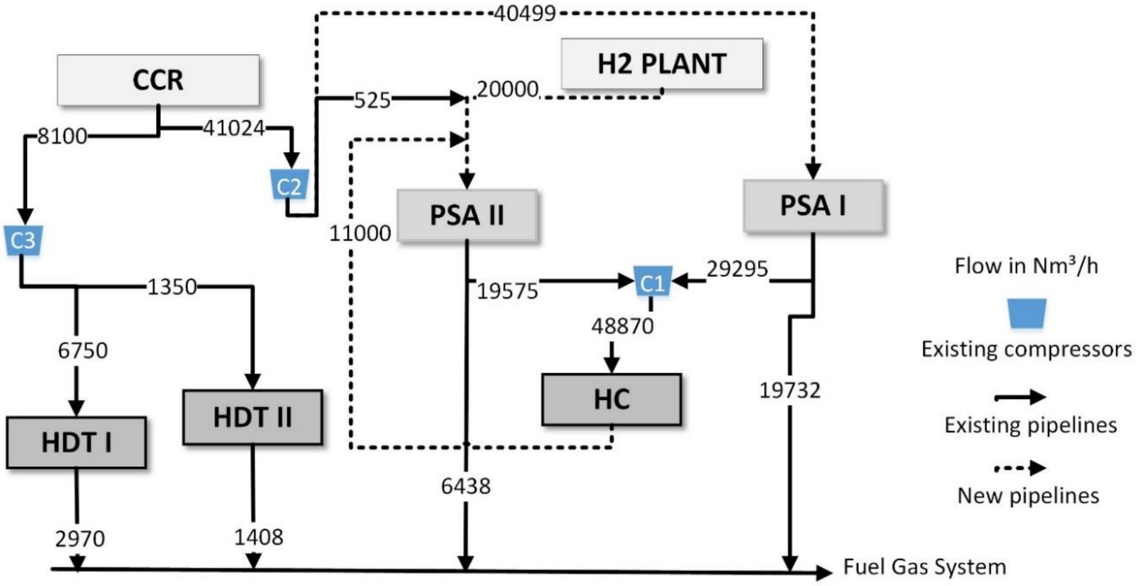
The cost of operation in the nonlinear (HN6) problem is 4.7% lower than in the HNS LM problem (HN5). However, it is observed that the most significant difference is the amount sent to burning as fuel. The optimization of HN6 network is an integer solution, which usually happens in nonlinear problems as it is not possible to guarantee optimum global optimization. The design obtained in HN6 optimized network through an HNS NLM model is shown in Figure 4.10a. It is remarkable to highlight that the HN6 network has 3 new lines. However, the cost of piping in this problem is calculated as a percentage of the cost of capital, which in this case, is zero. Therefore, it is necessary to estimate an average value for the cost of piping, which can be obtained with the number of lines in previous examples. The average cost for 3 new lines is between \$0.08 and \$0.1 million per year, taking into account that the fixed part is the predominant value and does not vary much with the flow.

Using the same methodology as in example 1, the network optimized through the HNS LM (HN5') was used as an initial value to solve the nonlinear problem. The idea of using the result obtained in the linear model to initialize the nonlinear model guarantees an even more significant reduction in operating cost, of 13.9%, with zero capital cost (despite 3 new lines). The initialization of the rearranged network generates better results, in addition to a network with fewer connections. The design network HN7 is shown in Figure 4.10b.

Table 4.6 summarizes the principal results obtained through linear and nonlinear models for example 2. The lowest operating cost is obtained with the initialization of the linear model in the HNS NLM resolution (HN7), in addition to presenting the advantage of easier convergence.



(**a**)



(**b**)

Figure 4.10: (**a**) Optimized network HN6 via HNS NLM for Example 2. (**b**) Optimized network HN7 via HNS NLM with HNS LM as initialization for example 2.

Table 4.6: Results obtained in the different optimizations models for example 2.

	COST (x 10^6)			
	HNS LM	**HNS LM**	**HNS NLM**	**HNS LM INITIALIZATION-HNS NLM**
	HN5	**HN5'**	**HN6**	**HN7**
H_2 production ($/year)	46.153	46.153	46.690	47.714
Electricity ($/year)	0.765	0.777	0.790	0.826
Fuel ($/year)	15.339	15.339	17.397	19.761
Purification ($/year)	0.762	0.752	0.723	0.803
Operating cost ($/year)	32.331	32.343	30.806	29.583
New compressor ($/year)	0.597	0.467	-	-
New piping ($/year)	0.105	0.082	-	-
New PSA ($/year)	-	-	-	-
Capital cost ($/year)	0.703	0.549	-	-
Total capital cost ($)	1.406	1.099	-	-
TAC ($/year)	33.034	32.892	30.806	29.583
Economy ($/year)	**11.685**	**11.674**	**13.211**	**14.434**
Payback (year)	0.120	0.094	-	-
Resource time (s)	0.067	0.067	4.495	1.906

In their original article, Sardashti Birjandi et al. (2014) proposed the hydrogen network optimization through an MINLP model and obtained a 12% reduction in TAC. Considering TAC, this proposed HNS NLM model was able to reduce TAC by 30% (HN7), and the proposed HNS LM model was able to reduce TAC by 25.3%, which is a promising result. It is important to note that this case study was adapted from the example taken from the literature and that as many parameters are not described, the results would not be the same.

This example also shows that optimization through the linear model achieves considerable savings. Besides, as an initial guess for the nonlinear model, it proved to be an even more competitive alternative, further reducing operating costs.

4.5 Conclusions

In this work, an HNS LM (Mixed-Integer Linear Model) and HNS NLM (Mixed-Integer Nonlinear) optimization model is proposed for designing hydrogen networks for efficient use of this resource with cost reduction and environmental benefits.

The mathematical model is based upon superstructures, and it accounts for hydrogen sources, consumer units, purifying units, a fuel system, pressure constraints, and existing equipment and pipelines. The model can be used for grassroots designs and the retrofitting case. In the former, all the structure must be installed with an investment cost. In the later, the existing infrastructure is explored to reduce costs allowing the installation of new compressors, purifying units, and pipelines with an inherent investment cost. For both cases, the operating costs and the investment costs are the standard objective function to be minimized. Economic issues such as economy savings, maximum investment available, the payback time can be considered while delivering the optimal network design.

The model is thoroughly described, with all constraints, including the logical modeling equations used to accomplish design decisions and a proper estimation of costs, and all the model parameters. Initialization strategies for new design and retrofit cases were developed, which showed satisfactory results and efficiency for this work, both for existing and new networks.

The model was implemented in the modeling system GAMS solved with the solver CPLEX, and DICOPT and case studies from the literature were used to validate and explore the model features. For all examples, the proposed model was able to represent the existing networks as a feasible point, as well as to optimize them. Significant economic savings have been achieved when compared to existing networks, which shows that it is possible to work towards minimum hydrogen production and with investments payable in short periods.

The main breakthrough is the assumptions made in the mathematical modeling resulted in a linear model, which always converges to a global optimum, and it is speedy and robust. On the other hand, the drawback is that the solution may end up with a large number of compressor units. This issue can be overcome with the proposed algorithm basis evolution strategy to reduce the number of compressor units and pipelines and, therefore, the investment costs. This strategy has presented an excellent performance for the examples considered in this work. Besides, this technique can be extended to other problems of mass integration, such as pumps in water reuse, where the structure could also be represented through a linear model to facilitate resolution.

For comparison purposes, an HNS NLM model was also developed, in which streams can be mixed to be compressed at the same compressor unit. In this case, the number of compressors units is reduced when compared to the HNS LM model. However, the solution is influenced by the initial value, and it does not always converge, leading to a poor local minimum. The HNS NLM model also satisfies the needs of this work for the retrofit case and presented good results. However, the nonlinearity increases significantly the time need to solve the optimization problem. It is noteworthy that the HNS NLM model uses a superstructure that is different from the HNS LM, as the compressors are seen as a unit. The results obtained through nonlinear optimization compared to the linear ones, it has more flexibility of operation, because of the possibility of merging flowrates and share compressors. Resource time is not one of the main advantages when comparing linear with nonlinear. However, in the future, this work will be applied for multi-scenario optimization combined with production scheduling, so faster and more efficient resolution will be a critical issue.

For each case, different networks were proposed with different constraints. In general, the results were better than the original works of the case studies. Even though it was explored, the model versatility design networks allowing different constraints generating alternative designs according to the process requirements.

Different comparisons were made between the optimized networks in this work. With that, it can be concluded that the HNS LM model is satisfactory to optimize the hydrogen networks, even more with the rearrangement of the compressors, capable of reducing the investment costs. A reduction of 28% (example 1) and 26% (example 2) was obtained in the operating cost. In terms of the nonlinear model, the best results were obtained with the initiation of the network obtained from linear optimization. As a result, the operating cost was reduced by 31.2% (example 1) and 32.8% (example 2). This initialization technique was not found in the literature and proved to be an excellent tool for the optimization of hydrogen networks.

In this work, the importance of optimizing hydrogen networks is evident, aiming to minimize the operational cost. In addition, it is known that networks actually operate not only under nominal conditions as considered here, but also operate under different scenarios and different uncertainties. Since several factors affect this process, it is essential that the network must be able to work in various conditions. Therefore, the importance of working with uncertainties and multi-scenario optimization is evident. The MILP formulation proposed here can be easily extended to a multi-scenario version. In our future works, the uncertainty level will be addressed.

List of Symbols

i, j, k, c	Sets of sources, consumers, purifiers, and compressors
$FH2I_i$	Flowrate of hydrogen sources
$FH2I_{i,max}, FH2I_{i,min}$	Maximum and minimum flow rate of hydrogen sources
$FIJ_{i,j}$	Flowrate from source to consumer
$FIK_{i,k}$	Flowrate from source to purifier
FIW_i	Flowrate from source to waste (fuel system)
FJ_j	Total consumer flowrate
$FKJ_{k,j}$	Flowrate from purifier to consumer
$FJJ_{j,j'}$	Flowrate from consumer *j* to consumer *j'*
YJ_j	Consumer purity
YI_i	Source purity
YK_k	Purifier purity
YP_j	Purge purity of consumer
FP_j	Total purge consumer flowrate
FJW_j	Flowrate from consumer to waste (fuel system)
$FJK_{j,k}$	Flowrate from consumer to purifier
$FPur_{max,k}$	Maximum capacity of the purifier
FK_k	Total flowrate in the purifier
FKW_k	Flowrate from purifier to waste (fuel system)
$FKW_{rec,k}$	Purge flowrate from purifier to waste (fuel system)
YKW_k	Purity of purge flowrate from the purifier
$F, F_{\alpha,\beta}$	Flowrate
F^{max}	Maximum flowrate
E	Parameter associated with the existence of flowrate
z	Binary associated with flowrate
z_c	Binary of a new compressor
u_{deltaP}	Binary of the pressure difference between the units
u_c	Parameter associated with existence compressor
z_h	Binary variable from a new pipeline
u_h	Parameter associated with existence pipeline
z_{kn}	Binary variable from the new purifier
α, β	Represents the possible connections involved
rec_k	Purifier recovery
$C_{operating}$	Operating cost

$CH2I, C_i$	Total and hydrogen production cost
$CH2K, C_k$	Total and purification cost
$CH2C, C_{eletric}$	Total and electricity cost
W	Power compressor
w	Intensive power compressor
$\overline{Cp}$	Heat capacity
T	Temperature
η	Compressor efficiency
γ	Cp/Cv Ratio
ρ_o	Density in standard condition
ρ	Density
P_{out}	Outlet pressure
P_{in}	Inlet pressure
$CH2F^T, CH2F, C_{fuel}$	Cost of burning purge as fuel
y	Hydrogen fraction in the purge flow
$\Delta H°_{H2}, \Delta H°_{CH4}$	Combustion heat of hydrogen and methane
$C_{new\ PSA}, C_{new\ PSA}{}^T$	Cost of new purifier
a_{PSA}, b_{PSA}	Parameters of new purifier cost
$C_{new\ piping}, C_{new\ piping}{}^T$	Cost of new pipelines
ϑ	Superficial gas velocity
L	Distance
c, d	Parameters of piping cost
$C_{new\ compressor}$, $C_{new\ compressor}{}^T$	Cost of a new compressor
a, b	Parameters of new compressor cost
t	Annual operating time
Af	Annualized factor
$C_{capital}$	Capital cost
f_i	Interest rate
TAC	Total annual cost
E	Economy
$C_{OP}^{actual}, C_{OP}^{new}$	Actual and new operating cost
pt	Payback
FC_c	Total compressor flow
$FIC_{i,c}$	Flow from source to compressor
$FCJ_{c,j}$	Flow from the compressor to consumer
YC_c	Purity in compressor
$FJC_{j,c}$	Flow from consumer to compressor
$FCK_{c.k}$	Flow from compressor to purifier
$FKC_{k,c}$	Flow from purifier to compressor
$PC_{out,c}$	Outlet pressure in the compressor
$PC_{in,c}$	Inlet pressure in the compressor
P^{min}	Minimum pressure
P^{max}	Maximum pressure
PI_i	Source pressure
PK_k	Purifier pressure
PW	Waste pressure

PJ_j	Inlet consumers pressure
PP_j	Outlet consumers pressure

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Capítulo 5 – **A systematic approach for flexible cost-efficient hydrogen network design for hydrogen management in refineries**

O presente capítulo é uma reprodução do artigo aceito na *Chemical Engineering Research and Design.* Este capítulo inclui os objetivos 3, 4 e 5 e as contribuições 5 e 6 desta Tese de Doutorado. Dos dois trabalhos apresentados acima, ambos consideravam a rede de hidrogênio em termos de vazões nominais. Porém, sabe-se que vários fatores afetam o processamento de petróleo nas refinarias e isso impacta diretamente no consumo de hidrogênio. Com isso, é essencial que a rede de hidrogênio seja capaz de operar de forma viável em diferentes condições de operação e processamento de petróleos, mais especificamente com incerteza no consumo de hidrogênio nas unidades consumidoras. Por isso, as formulações desenvolvidas e detalhadas nos Capítulos 3 e 4 foram estendidas para a versão multicenário, onde é possível considerar diferentes situações e consumos de hidrogênio (etapa de projeto). Além disso, este trabalho também aborda o conceito e flexibilidade da rede de hidrogênio, importante para avaliar a viabilidade de operação em diferentes cenários e identificar quais os cenários críticos de operação (etapa de operação). As duas etapas foram integradas através de uma metodologia iterativa para a obtenção de redes de hidrogênio que fossem flexíveis e econômicas. Neste artigo, para os dois estudos de caso, também foram incluídos os conceitos do Capítulo 4, rearranjo de compressores e técnica de inicialização. Com isso, através da otimização multicenário e cálculo do índice de flexibilidade, o redesign obtido (com flexibilidade de 10% desejado) reduz em 13,8% e 16% o custo operacional nos exemplos 1 e 2, respectivamente.

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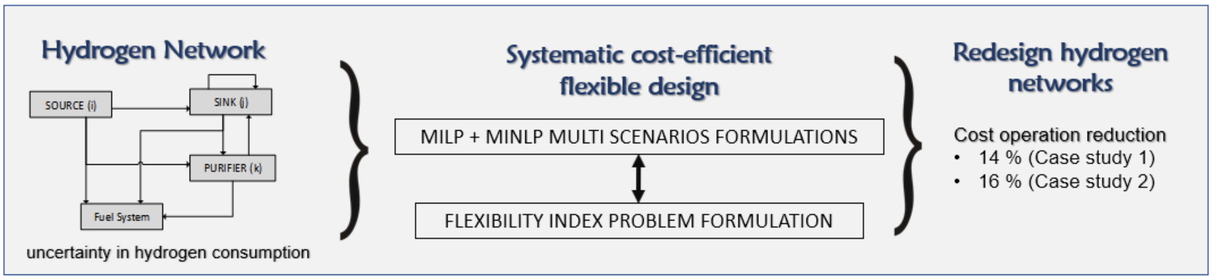
Abstract: The study of a better use of hydrogen in refineries is essential due to its increasing use in hydrotreating fractions obtained from petroleum. Since several factors affect this process, it is essential not only that the hydrogen network must be able to operate feasibly in various conditions but also accomplish it with minimum costs. In this work, a systematic approach is proposed considering a multi-scenario optimization problem formulation for the network design coupled with the flexibility evaluation of the proposed design to verify the flexibility and identify critical scenarios that are used to update the previous set of scenarios for the design problem. As a result, it is obtained a cost-efficient flexible design. The proposed approach can be used for new designs or for the retrofit case. For the design a superstructure-based MILP and MINLP multi-scenario models were developed and completely described, to optimize hydrogen networks through uncertainties in hydrogen consumption in consumer units. The flexibility index problem formulated for hydrogen networks is presented. All the optimization models were implemented in the modeling system GAMS. The initialization strategy consist of using the network obtained from linear optimization as a starting point for nonlinear optimization. In addition, it was also used the proposed technique of virtual compressors, able to reduce the cost of capital even further. Two case studies were used to validate the proposed approach. A case study from the literature was used and also a second case using real data of a Brazilian refinery. Compared to the initially proposed network, the model through optimization achieved flexible design with a reduction of more than 13.8 % (example 1) and 16% (example 2) in the operating cost. For both cases, the procedure could find a cost-efficient flexible design that can be coupled with the refinery production planning for the whole process economy.

Keywords: hydrogen network, mathematical programming, optimization, flexibility analysis

Graphical Abstract:



5.1 Introduction

The main causes of the increased use of hydrogen in oil refineries are the more substantial supply of different crude oil (sulphur content), changing environmental regulations restricting contaminant levels in products, and, consequently, the need for more advanced technologies capable of addressing these peculiarities. Therefore, a detailed study of hydrogen networks is essential for this raw material to be used as efficiently as possible (Jia and Zhang, 2011).

The hydrogen network is composed of hydrogen-producing units, consumer units, and purification units, which depending on the refinery configuration, are already inserted within the hydrogen source, the so-called hydrogen generation units (HGU). The hydrogen network, for example, flowrates and purity, are configured according to the demand of hydrotreating units, which are the main hydrogen consuming units within the network, as they remove impurities such as sulfur. This process is currently used to improve the quality of naphtha, kerosene, general solvents, diesel oil, heavy diesel, paraffin, and lubricating oils. Hydrorefining processes are classified according to desired reactions, for example, hydrodesulfurization and hydrodesulfurization (Ceric, 2012).

The hydrogen network can be designed according to the demand of the consumer units. This demand may vary according to several factors, the main ones being the type of crude oil being processed, the types of products desired in a given period and the operating conditions of each unit. For example, if they are at the beginning or end of the production as this affects reaction parameters such as temperature and catalyst deactivation in hydrotreating. Most previous studies on hydrogen network management assume fixed and defined operating conditions, i.e., nominal conditions. However, it is known that the actual network may operate under process variability, i.e., uncertainty conditions, such as heavier oils or specific campaigns for lighter diesel production.

The uncertainties and the variation of process parameters can be classified into (i) *model inherent uncertainty* that includes, information generally obtained from pilot plant data; (ii) *process inherent uncertainty,* for example, flowrates and temperature variations, and can be obtained from measurements (online); (iii) *external uncertainty* includes feed flow availability, product demands, prices; and, (iv) *environmental conditions*. To consider the uncertainties in parameter values, the usual procedure is to assume nominal values and then use empirical factors to vary operating scenarios. Since this procedure does not use a systematic and rational basis, several different methods and studies in this area have been developed and applied to processes with uncertainties in a more systematic and detailed description (Grossmann and Halemane, 1983; Pistikopoulos, 1995).

Therefore, it is essential to consider the uncertainties during hydrogen network design to ensure that it will be able to operate in all possible scenarios with varying operating conditions, defined as the uncertainty region. If the hydrogen network can operate whitin this uncertainty region, the network design is called flexible. In general, the term *flexibility* is defined as the ability of a process to feasible operate under a specific range of uncertain conditions, and it is one of the most critical components in the operability of chemical plants (Grossmann and Floudas, 1987; Reza et al., 2016). A more flexible design may result in a more expensive design, so it is important to achieve the desired level flexibility taking into account the associated cost.

Therefore, a systematic approach that represents an optimal design in the hydrogen network and the flexibility with which it needs to operate is an important way to cost reduction and for efficient resource usage. Thus, this paper aims to (re)design a cost-efficient flexible hydrogen network defined from a superstructure and modeled according to all constraints involved. The flexibility level is defined by the designer in order to accomplish the refinery production planning.

This work considers the inclusion of different operating scenarios focused on the variation of the hydrogen demand of the consuming units. For the design problem, a linear model (MILP) and a nonlinear model (MINLP) were developed, based on mathematical programming, for optimization of the hydrogen network, to find an optimal and flexible design. The initialization strategy, where the nonlinear model is initialized with the result obtained from the linear is a competitive alternative used to facilitate resolution and obtain even better results (Silva et al., 2020), different from what is found in the literature described in section 5.2.

Besides, it is essential to assess how flexible the optimal design obtained through optimization is. For this, a systematic approach was proposed: (i) solving the multi-scenarios optimization problem, where the scenarios are obtained through the critical points of the existing network, (ii) evaluation of the obtained network flexibility, and (iii) update of the current set of scenarios with critical points.

The remainder of this work is organized as follows. Section 5.2 presents a literature view and section 5.3 describes the mathematical programming applied in this work, including linear and nonlinear models. Section 5.4 describes the systematic for optimal and flexible network design development and summarizes the proposed methodology. In section 5.5, the proposed approach is validated with two case studies: one example from literature and another example that uses real data from a Brazilian oil refinery.

5.2 Literature review

Mathematical programming is the most used technique for analyzing hydrogen networks due to the advantages over pinch (Silva et al., 2020). Therefore, this session reviews the main works that include multi-scenario optimization for hydrogen network management.

Imran et al. (2010) proposed multi-period optimization, which needs to be taken into account in hydrogen network designs because hydrogen-consuming refinery processes are operated at various operating times. The methodology developed in this work for multi-period hydrogen network design is an extension of Hallale and Liu (2001) and Liu and Zhang (2004) automated design approach for multiple operating periods. The methodology developed for multi-period hydrogen management is applicable to retrofit and the new design of flexible hydrogen networks. In this case, the MINLP model is also linearized to work with the MILP model. A MILP model is solved, and the solution is used to initialize MINLP. In this way, convergence to a viable solution is facilitated, and the likelihood of obtaining a good local optimal solution is improved.

Jiao et al. (2013) present a flexible multi-period optimization approach to solve the optimization problem. The number of scenarios is modified to fit operating fluctuations, and the goal is to minimize total annual costs. Hydrogen consumers' varying demand, pipelines, and possible shutdowns of hydrogen units are considered in formulating the problem to ensure the safety of the hydrogen system under normal and abnormal operating conditions. Binary variables are introduced to represent the existence or not of hydrogen units and flows. The generated MINLP model is relaxed as a MILP model with a linearization technique proposed by McCormick. It was shown that the MILP model leads to acceptable quality and high efficiency than the MINLP problem.

Deng et al. (2014) developed a mathematical model for hydrogen network synthesis operating in different scenarios. A network superstructure was developed to determine the minimum amount of hydrogen by investigating different scenarios: number of allowed connections (MILP model), use of compressors (MILP and MINLP model due to bilinearity) and use of economically evaluated purifiers (model MINLP).

Wang et al. (2014) disserted the methods for applying uncertainties in operational conditions. They pointed out that the main objectives to be achieved in these problems are to guarantee the optimization and the viability of the operation for a specific range of parameter values. The work started from a strategy proposed by Grossmann and Sargent (1978) to design a flexible hydrogen plant. First, a design must be selected for which it can be ensured that design specifications are met for a delimited region of the parameters. Second, the design must be selected to optimize the expected value of the investment and assumed operating cost over the specified range of parameter values. The basic idea of this strategy is to take advantage of the fact that control variables can be adjusted to meet project specifications during plant operation, as it is only the design of the plant itself that will remain fixed. Based on this, the objective of the work is to present for the strategy mentioned above a new mathematical formulation in which the viability of the operation can be rigorously assured. This formulation corresponds to the two-stage MINLP model.

Reza et al. (2016) aim to present the hydrogen network flexibility evaluation method that will provide more network possibilities and total hydrogen sources that meet the varied hydrogen demands, considering the total allowable purity of the input streams sent to the purifiers and using the network structure. In this case, the main objective is to minimize the fresh hydrogen supplied to the hydrogen network. The hydrogen network is optimized using the NLP model. Also, in a second method, the hydrogen network includes constants and uncertain parameters. For example, hydrogen source flow rates, purifier input limits, hydrogen recovery are constant parameters. The purity of hydrogen sources, hydrogen demands may be uncertain parameters. The second method considers a set of systematic procedures to analyze and then improve the operational resilience of any hydrogen network design, i.e., a nonlinear programming formulation (NLP) is made. The last case tested by the authors considers the minimum total annual cost for which an MINLP model is used. This case refers to previous optimization methods for the hydrogen network without considering uncertainty parameters.

Chen et al. (2020) proposed two-stage stochastic programming with different types of uncertainties, such as electricity, hydrogen utility, and fuel gas markets. The two-stage stochastic programming model evaluated at discrete price scenarios with adjustable flexibility constraints needs to satisfy the flexibility test for operational uncertainties through the active constraints approach. As the proposed model is MINLP, the authors used a solution strategy based on multiparametric disaggregation, a two-step MILP-NLP algorithm. Multi-scenario operation strategy increases operational flexibility and reduces the total annualized cost in terms of the value of the stochastic solution.

So, unlike what is found in the literature, this paper uses hydrogen network management in refineries through an MINLP model with an initialization strategy based on a linear optimized network to compare the results in case studies, for the nominal case, and different scenarios. Besides, a systematic assessment of the flexibility of hydrogen networks is also proposed, based on the retrofit of existing network design.

5.3 Formulation of mathematical models

One of the objectives of this work is to develop a linear and nonlinear mathematical model to optimize hydrogen networks that operate with uncertainties in hydrogen consumption in hydrotreatment units. The purpose is to minimize the operational cost of the network capable of operating in a given region defined by different scenarios.

Network management through mathematical modeling can be applied to an existing fixed topology or to develop a new hydrogen network design. Thus, the approach of this article is based on retrofit of hydrogen network, through the validation with a network from Hallale and Liu (2001), and another example with real plant data of a Brazilian refinery.

5.3.1 Definition of superstructures

According to the literature review, the use of a linear model (MILP) is not very recurrent, although it presents significant results. The advantage of using MILP is the linearity that facilitates the solution of the optimization problem and guarantees convergence to a global optimum. Also, the linear model can be used in the initialization of the nonlinear model, facilitating the convergence and obtaining significant and better results than its simple resolution. In previous work, Silva et al. (2020) developed and described the linear (MILP) and nonlinear optimization (MINLP) models in the mono scenario version for hydrogen network optimization, and the linear was used as an initialization strategy for nonlinear. In sections 5.3.1 and 5.3.2, the formulation was extended to the multi-scenario version. Figure 5.1a shows the superstructure that represents the MILP model and all the possible connections among these four units between sources and consumers, sources and purifiers (existing and new ones), as well as flows between consumers and the purifying units for sources *i* and consumers *j* in each scenario. The superstructure for the nonlinear model is slightly different from the MILP, as illustrated in Figure 5.1b.

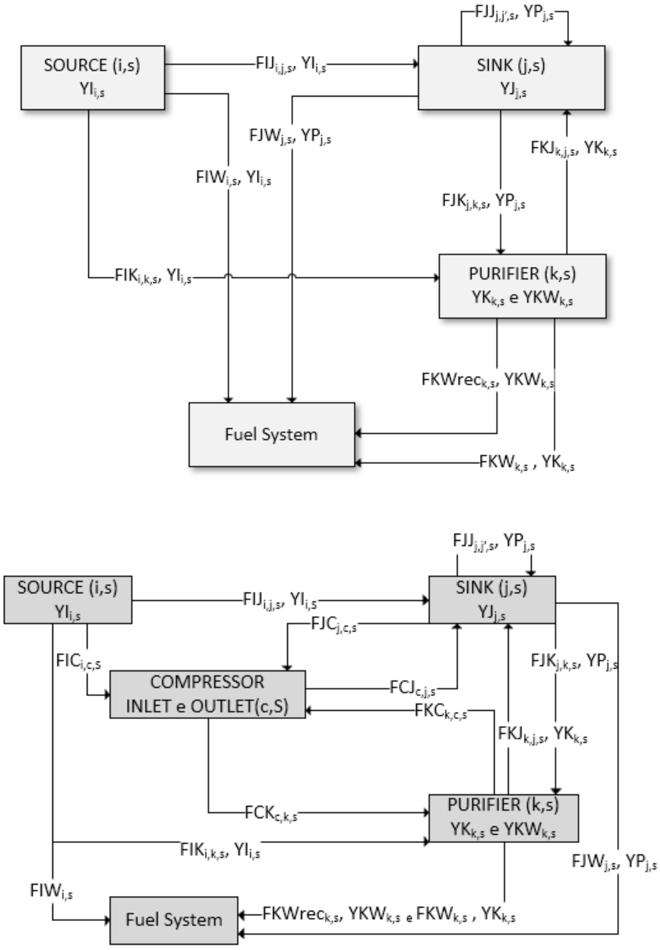


Figure 5.1: a) Scheme developed for the mathematical modeling of the MILP problem. b) Scheme developed for the mathematical modeling of the MINLP problem.

5.3.2 Linear Model

5.3.2.1 Problem Statement

Given a set of sources i ϵ hydrogen sources (HS), a set of consumers j ϵ hydrogen consumers (HC), and a set of purifiers k ϵ hydrogen purifiers ($HP = OHP \cup NHP$), considering the existing purifiers, OHU, and the new purifiers,NHP, in each scenario given by the set of scenarios sϵ scenarios (S).

For each *source* is given: (i) the maximum and minimum flow rate, (ii) the hydrogen composition, and (iii) the outlet pressure. For each *consumer* is given: (i)the inlet flow, pressure, and composition, (ii) the outlet purge flow, pressure, and composition. In this case, the uncertainty is added in the hydrogen consumption in the consuming units, since the parameter is more representative when it is desired to include hydrogen planning and programming forecasts in the future. As such, consumers' inlet flow and outlet flow may vary, as the purity is kept constant to ensure linearity.

For each *purifier* is given: (i) the maximum flow capacity, (ii) the composition of purified flowrate and purge flowrate, (iii) the pressure of purification, and (iv) the hydrogen recovery. It is also considered a fuel system in which waste streams can be burned and used as fuel to the process. For the *existing networks*, it is also necessary to include (i) the existing lines (unit connections), (ii) the distance between the units if informed, and (iii) the existing compressors and purifiers.

Possible connections in the hydrogen network are shown in the superstructure depicted in Figure 5.1a. The optimization problem is to minimize the operating of the hydrogen network (HN), i.e., the (i) operating costs due to hydrogen production and purification, electricity, and economy provided by the streams used as fuel to the process, and (ii) the investment costs in new pipelines, compressors, and purifiers. The optimization problem is subject to material balances and process operating constraints. For the retrofit case, process modifications are allowed to reduce the total operating costs (the objective function), despite the investment costs due to the installation of new pipelines, compressors, and possibly new purifiers. In this case, for different network alternatives, it is useful to consider constraints on maximum capital cost available or maximum payback time.

Some considerations were made to simplify the model. The flow is considered as a binary mixture of hydrogen and methane, and compressors are associated with each possible connection individually. Therefore, it is not allowed to merging flows before the compressor units, which would result in an unknown inlet hydrogen composition. Hence, a nonlinear material balance would be necessary. The partial pressure of the hydrogen is constant at the entrance and exit of the consuming units.

5.3.2.2 Formulation of the linear mathematical model

The first step for the modeling development is to define which units are involved in the hydrogen network, for instance, which units provide hydrogen, which units consume hydrogen and the existing purifiers, and the potential purifiers that should be considered in the model.

The optimization problem of hydrogen network design in this work can be summarized as follows: the hydrogen sources have their minimum and maximum flow according to its capacity ($FH2I_{min\,i,s}\ e\ FH2I_{max\,i,s}$) as well as their hydrogen purity ($YI_{i,s}$). The hydrogen stream can be sent to the consumers j ($FIJ_{i,j,s}$), to purification units k ($FIK_{i,k,s}$), or to the fuel system ($FIW_{i,s}$). The consumer's units have their input required flows for the process ($FJ_{j,s}$), as well as its hydrogen purity ($YJ_{j,s}$), in addition to the outflows ($FP_{j,s}$) and hydrogen purity ($YP_{j,s}$), according to the hydrogen consumption ($H_2\_C_{j,s}$) of each specific process. The required flow rate to consumers ($FJ_{j,s}$) and outflows ($FP_{j,s}$) haven its nominal value established. Also, multi-scenarios optimization will be based on those variables, which will have different established values with an associated probability of occurrence since it is desired to consider the uncertainty in the amount of hydrogen consumed. The outlet flows from the consumers can be sent to purification ($FJK_{j,k,s}$), can be used as a source for other consumers ($FJJ_{j,j,s}$) or can be sent to the fuel system ($FJW_{j,s}$) to be used as the burning fuel. The purifying units have a known hydrogen recovery ratio ($rec_{k,s}$), as well as the maximum inlet flow capacity ($FPur_{max\quad k,s}$) and the constant purities of the hydrogen product pure streams ($YK_{k,s}$) and the composition for the stream of hydrogen not recovered stream ($YKW_{k,s}$). The purified hydrogen stream from the purification can be used as a source for the consumers ($FKJ_{k,j,s}$) who need higher purity or can be referred to the fuel system ($FKW_{k,s}$), if there is excess. The stream with the not recovered hydrogen, $FKWrec_{k,s}$, has a small hydrogen composition, and it is sent directly to the fuel system.

5.3.2.2.1 Sources

The material balance for each source is represented by Equation 5.1:

$$FH2I_{i,s} = \left(\sum_{j \in HC} FIJ_{i,j,s} + \sum_{k \in HP} FIK_{i,k,s} + FIW_{i,s}\right) \quad \begin{matrix} \forall\, i \in HS \\ \forall\, s \in NS \end{matrix} \quad (5.1)$$

where $FH2I_{i,s}$ is the total flow from each source *i*, $FIJ_{i,j,s}$ is the hydrogen flow from the source *i* to the consumer *j*, $FIK_{i,k,s}$ is the flow from the source *i* for the purification unit *k*, and $FIW_{i,s}$ is the flow from source *i* sent to the fuel system. The available flow rate is limited by the capacity of the hydrogen generating units according to the following inequality constraints

$$FH2I_{\min\ i,s} \leq FH2I_{i,s} \leq FH2I_{\max\ i,s} \quad \begin{matrix} \forall\, i \in HS \\ \forall\, s \in NS \end{matrix} \quad (5.2)$$

5.3.2.2.2 Consumers

Equation 5.3 represents the overall material balance in the inlet of consumer units.

$$FJ_{j,s} = \sum_{i \in HS} FIJ_{i,j,s} + \sum_{k \in HP} FKJ_{k,j,s} + \sum_{j \in HC} FJJ_{j,j',s} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.3)$$

where $FJ_{j,s}$ is the total flow directed to consumers, $FJJ_{j,j',s}$ is the flow from one consumer *j* to another consumer *j'* and $FKJ_{k,j,s}$ is a flow rate of from the purification unit *k* for the consumer units *j*. Here appears the index *j'* which is used for cases where there is a connection between consumers. In this case, as it is not allowed between the same unit, *j'* must be different from j. The hydrogen balance is then defined by equation (5.4).

$$FJ_{j,s} * YJ_{j,s} = \sum_{i \in HS} FIJ_{i,j,s} * YI_{i,s} + \sum_{k \in HP} FKJ_{k,j,s} * YK_{k,s} + \sum_{j \in HC} FJJ_{j,j',s} * YP_{j,s} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.4)$$

where $YJ_{j,s}, YI_{i,s}, YK_{k,s}$ and $YP_{j,s}$ are the volumetric fractions of hydrogen in the respective streams, consumer *j*, sources *i*, purifiers *k*, and purge of the consumer unit *j*. In addition, it is possible to calculate how much each consumer unit used hydrogen depending on the chemical process involved.

Equation 5.5 represents the overall material balance in the outlet of consumer units.

$$FP_{j,s} = FJW_{j,s} + \sum_{k \in HP} FJK_{j,k,s} + \sum_{j \in HC} FJJ_{j,j',s} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.5)$$

where $FP_{j,s}$ is the total flow out of consumers, $FJK_{j,k,s}$ is the flow rate from the consumer unit *j* for the purification unit *k* and $FJW_{j,s}$ is the surplus flow of consumers directed to the fuel system.

In order to perform the multi-scenarios optimization, a new equation was introduced in the model, which calculates the consumed hydrogen flow ($H_{2\_}c_{j,s}$). This variable will be an uncertainty parameter in optimization.

$$H_{2}\_c_{j,s} = FJ_{j,s} * YJ_{j,s} - FP_{j,s} * YP_{j,s} \quad \begin{smallmatrix} \forall\, j \in HC \\ \forall\, s \in NS \end{smallmatrix} \tag{5.6}$$

Thus, in order for hydrogen consumption to vary and as the purity is kept constant, the inlet and outlet flow rates of consumers can vary.

5.3.2.2.3 Purification units

The purification unit is used, providing hydrogen in a given purity, such as 99.99% in the case of PSA units. The overall material balance in these units is expressed as:

$$\sum_{j \in HC} FJK_{j,k,s} + \sum_{i \in HS} FIK_{i,k,s} + \sum_{i \in HS} FIKW_{i,k,s} = \sum_{j \in HC} FKJ_{k,j,s} + FKW_{k,s} + FKW_{rec\ k,s} \quad \begin{smallmatrix} \forall\, k \in HP \\ \forall\, s \in NS \end{smallmatrix} \tag{5.7}$$

where $FKW_{k,s}$ the flow rate of the purifying unit *k* stream rich in hydrogen routed to burning and $FKW_{rec\ k,s}$ is the hydrogen flowrate not recovered by the purifying unit *k* sent to the burner. The hydrogen balance for each purifier described as follows:

$$\sum_{j \in HP} FJK_{j,k,s} * YP_{j,s} + \sum_{i \in HS} FIK_{i,k,s} * YI_{i,s} = \sum_{j \in HP} FKJ_{k,j,s} * YK_{k,s} + FKW_{k,s} * YK_{k,s} + FKW_{rec\ k,s} * YKW_{k,s} \quad \begin{smallmatrix} \forall\, k \in HP \\ \forall\, s \in NS \end{smallmatrix} \tag{5.8}$$

where $YKW_{k,s}$ is the fraction of hydrogen in the purge stream of purified *k*. The capacity of the purifying unit limits the total flow entering the purifier.

$$\sum_{j \in HP} FJK_{j,k,s} + \sum_{i \in HS} FIK_{i,k,s} + \sum_{i \in HS} FIKW_{i,k,s} \leq \sum_{k} FPur_{\max k,s} \quad \begin{smallmatrix} \forall\, k \in HP \\ \forall\, s \in NS \end{smallmatrix} \tag{5.9}$$

Given the hydrogen recovery of the purification unit, it is possible to calculate how much hydrogen is sent to the purge stream, i.e., the hydrogen not recovered.

$$\left(\sum_{i \in HS} FIK_{i,k,s} * YI_{i,s} + \sum_{j \in HP} FJK_{j,k,s} * YP_{j,s}\right) * \left(1 - rec_{k,s}\right) = FKW_{rec\ k,s} * YKW_{k,s} \quad \begin{smallmatrix} \forall\, k \in HP \\ \forall\, s \in NS \end{smallmatrix} \tag{5.10}$$

The total flow through the PSA ($FK_{k,s}$) can then be defined as:

$$\sum_{j \in HP} FJK_{j,k,s} + \sum_{i \in HS} FIK_{i,k,s} = FK_{k,s} \quad \begin{smallmatrix} \forall\, k \in HP \\ \forall\, s \in NS \end{smallmatrix} \tag{5.11}$$

5.3.2.2.4 Logical Constraints

To consider the capital cost associated with new equipment, it was necessary to use constraint modeling through logical propositions and disjunctions, so binary variables and logical inequality equations were included in the model with binary parameters. The elaboration of logical restrictions is similar to that performed in (Silva et al., 2020), but it is worth noting that the inclusion of scenarios requires some changes.

First, through the modeling of disjunctions, a binary variable z is associated with the existence of a particular flow F (e.g.$FIJ_{i,j,s}$, $FKJ_{k,j,s}$, $FJK_{j,k,s}$, etc.). If the positive flowrate is greater than or equal to a small value ε, e.g., $\varepsilon = 10^{-5}$, the corresponding binary variable z assumes the value of 1. On the other hand, if the flowrate is lower than ε , the binary variable assumes the value of 0. F_{max} are the flowrates between the units involved. These conditions are ensured by the following constraints:

$$\begin{cases} F \geq \varepsilon * z \\ F \leq (\min(F_{max})) * z \end{cases} \tag{5.12}$$

A binary variable $z_c s$ is associated with the installation of a compressor for the corresponding flow in each scenario. For this case three events must hold simultaneously: (i) there is a non-zero flow, i.e., *z=1*; (ii) there is no compressor previously installed identified by a binary parameter u_c (1 if there is a compressor, 0 otherwise); and (iii) there is a pressure difference between the current unit and destination unit that requires a compressor identified by a binary parameter u_{deltaP} (1 if the current pressure is lower than the destination pressure, 0 otherwise).

$$z_{c,s} \geq z + u_{deltaP} + (1 - u_c) - 2 \tag{5.13}$$

If any of these three events is false, then there is no need for a compressor ($z_{c,s}$=0), which is ensured by the set of constraints described in the set of equations 5.14.

$$\begin{cases} z \geq z_{c,s} \\ 1 - u_c \geq z_{c,s} \\ u_{deltaP} \geq z_{c,s} \end{cases} \tag{5.14}$$

To account for the cost of new equipment in the case of a multi-scenario optimization, for example, the addition of new compressors, it is sufficient that one of the proposed scenarios requires a new compressor to be installed because the proposed general network should achieve and operate under all conditions.

Thus, the variable z_c is used to identify whether or not to install a new compressor in the network, based on the binary variable $z_c s$ that indicates the need for installation in the specific scenario.

$$\begin{cases} z_c \geq z_{c,s} \\ z_c \leq sum(s, z_{c,s}) \end{cases} \tag{5.15}$$

A similar procedure was used to consider the cost of piping. A binary variable$z_{h,s}$ is associated to the need of installing a new pipeline in each scenario if two events hold: (i) exists a non-zero flow in that connection, i.e., z=*1*; (ii) there is no pipeline previously installed identified by a binary parameter u_h (1 if there is a line, 0 otherwise).

$$z_{h,s} \geq z + (1 - u_h) - 1 \tag{5.16}$$

If any of these two events do not hold, it must be ensured that no pipeline must be installed.

$$\begin{cases} z_{h,s} \leq z \\ z_{h,s} \leq 1 - u_h \end{cases} \tag{5.17}$$

Thus, the variable z_h is used to identify whether or not to install a new pipe in the network, based on the binary variable $z_{h,s}$ that indicates the need for installation in the specific scenario.

$$\begin{cases} z_h \geq z_{h,s} \\ z_h \leq sum(s, z_{h,s}) \end{cases} \tag{5.18}$$

There is also the possibility of installing new purification units. In this case, it is enough that there is any flow entering or leaving this unit. In this case, a binary variable $z_{kn,s}$ is associated with the installation of a new purifying unit in each scenario and the logical constraints can be expressed by:

$$\begin{cases} FK_k \geq \varepsilon * z_{kn,s} \\ FK_k \leq (FPur_{max,k}) * z_{kn,s} \end{cases} \quad \forall\, k \in NHP \tag{5.19}$$

Thus, z_{kn} is used to identify whether or not to install a PSA on the network, based on the binary variable $z_{kn,s}$ that indicates the need for installation in the specific scenario.

$$\begin{cases} z_{kn} \geq z_{kn,s} \\ z_{kn} \leq sum(s, z_{kn,s}) \end{cases} \tag{5.20}$$

The same procedure for installing new compressors was also done (constraints 5.13, 5.14 and 5.15) if it is necessary to install new compressors on streams involving a new PSA.

5.3.3 Nonlinear model

5.3.3.1 Problem statement

In the nonlinear model, the compressors are considered as independent units that may be used to connect units that need compression, so the inlet and outlet pressure of each compressor and also the hydrogen composition in the compressor are variables. The only nonlinearity in this model that arises in the hydrogen balance in the inlet of the compressors is the multiplication of the flow and composition. Thus, the model is based, in addition to sources, consumers, and purifiers, on a set of compressors c ϵ hydrogen compressors ($HCP = OHCP \cup NHCP$), considering the existing compressors $OHCP$ and new compressors $NHCP$, in each scenario (s).

The maximum number of compressors to be considered is set in the superstructure modeling, and it is obtained in the linear model solution previously. The superstructure is illustrated in Figure 5.1b. Therefore, the material balance in the compressor must be present in the equations.

5.3.3.2 Nonlinear mathematical model formulation

In this model, the flowrates are only possible if the flow origin pressure is higher than the destination pressure. For a particular flow F with upper bound F^{max}, constraints (5.21) ensure that flow is only possible for this case (higher pressure to lower pressure):

$$F \leq F^{max}(1 - u_{deltaP}) \tag{5.21}$$

Despite the possibility of generating networks with fewer compressors, the nonlinearity comes up with a more difficult problem to be solved that is very dependent on the initial guess. For this reason, an initialization strategy discussed in the next sessions was proposed.

5.3.3.2.1 Sources

In sources, in addition to Equation (5.2), there is Equation (5.22), which describes the flow rates from sources for consumers, purifiers, compressors ($FIC_{i,c,s}$) and for burning in each scenario.

$$FH2I_{i,s} = \left(\sum_{j \in HC} FIJ_{i,j,s} + \sum_{k \in HP} FIK_{i,k,s} + FIW_{i,s} + \sum_{c \in HCP} FIC_{i,c,s}\right) \quad \begin{matrix} \forall\, i \in HS \\ \forall\, s \in NS \end{matrix} \quad (5.22)$$

5.3.3.2.2 Consumers

Equation 5.23 (inlet) and 5.24 (outlet) represents the global material balance for each consumer in each scenario, where $FCJ_{c,j,s}$ is the flowrate from the compressor to the consumers, $FJC_{j,c,s}$ is the flow rate from consumers to compressors and $YC_{c,s}$ is the purity of compressors.

$$FJ_{j,s} = \sum_{i \in HS} FIJ_{i,j,s} + \sum_{k \in HP} FKJ_{k,j,s} + \sum_{j \in HC} FJJ_{j,j',s} + \sum_{c \in HCP} FCJ_{c,j,s} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.23)$$

$$FP_{j,s} = FJW_{j,s} + \sum_{k \in HP} FJK_{j,k,s} + \sum_{j \in HC} FJJ_{j,j',s} + \sum_{c \in HCP} FJC_{j,c,s} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.24)$$

The material balance of hydrogen in consumers is:

$$FJ_{j,s} * YJ_{j,s} = \sum_{i \in HS} FIJ_{i,j,s} * YI_{i,s} + \sum_{k \in HP} FKJ_{k,j,s} * YK_{k,s} + \sum_{j \in HC} FJJ_{j,j,s} * YP_{j,s} + \sum_{c \in HCP} FCJ_{c,j,s} * YC_{c} \quad \begin{matrix} \forall\, j \in HC \\ \forall\, s \in NS \end{matrix} \quad (5.25)$$

5.3.3.2.3 Purification units

The global material balance and for hydrogen for purifiers in each scenario are:

$$\sum_{j \in HC} FJK_{j,k,s} + \sum_{i \in HS} FIK_{i,k,s} + \sum_{c \in HCP} FCK_{c.k,s} = \sum_{j \in HC} FKJ_{k,j,s} + FKW_{k,s} + FKW_{rec,k,s} + \sum_{c \in HCP} FKC_{k,c,s} \quad \begin{matrix} \forall\, k \in HP \\ \forall\, s \in NS \end{matrix} \quad (5.26)$$

$$\sum_{j \in HP} FJK_{j,k,s} * YP_{j,s} + \sum_{c \in HCP} FCK_{c.k,s} * YC_{c,s} + \sum_{i \in HS} FIK_{i,k,s} * YI_{i,s} = \sum_{j \in HP} FKJ_{k,j,s} * YK_{k,s} + \sum_{c \in HCP} FKC_{k,c,s} * YK_{k,s} + FKW_{k,s} * YK_{k,s} + FKW_{rec,k,s} * YKW_{k,s} \quad \begin{matrix} \forall\, k \in HP \\ \forall\, s \in NS \end{matrix} \quad (5.27)$$

The purified flow rate must not exceed the PSA capacity, and, through the recovery of the PSA, the flow rates that are sent for burning are obtained.

$$\sum_{j \in HP} FJK_{j,k,s} + \sum_{i \in HS} FIK_{i,k,s} + \sum_{c \in HCP} FCK_{c,k,s} \leq FPur_{max,k,s} \quad \begin{matrix} \forall\, k \in HP \\ \forall\, s \in NS \end{matrix} \quad (5.28)$$

$$\left(\sum_{i \in HS} FIK_{i,k,s} * YI_{i,s} + \sum_{j \in HP} FJK_{j,k,s} * YP_{j,s} + \sum_{c \in HCP} FCK_{c.k,s} * YC_{c,s}\right) * (1 - rec_{k,s}) = FKW_{rec,s} * YKW_{k,s}\Big) \quad \begin{matrix} \forall\, k \in HP \\ \forall\, s \in NS \end{matrix} \quad (5.29)$$

where $FCK_{c.k,s}$ is the flow rate from compressors to purifier and $FKC_{k,c,s}$ is the flow rate from purifiers to compressors.

5.3.3.2.3 Compressors

The sum of the flow that enters the compressors in each scenario is called $FC_{c,s}$ and, if necessary, some part of the compressor flow that is not used can be sent directly for burning ($FCW_{c,s}$).

$$FC_{c,s} = \sum_{c \in HCP} FIC_{i,c,s} + \sum_{c \in HCP} FJC_{j,c,s} + \sum_{c \in HCP} FKC_{k,c,s} \quad \begin{matrix} \forall\, c \in HCP \\ \forall\, s \in NS \end{matrix} \qquad (5.30)$$

The global material balance and for hydrogen in each compressor are:

$$\sum_{c \in HCP} FIC_{i,c,s} + \sum_{c \in HCP} FJC_{j,c,s} + \sum_{c \in HCP} FKC_{k,c,s} = \sum_{c \in HCP} FCJ_{c,j,s} + \sum_{c \in HCP} FCK_{c.k,s} + FCW_{c,s} \quad \begin{matrix} \forall\, c \in HCP \\ \forall\, s \in NS \end{matrix} \qquad (5.31)$$

$$FC_{c,s} * YC_{c,s} = \sum_{c \in HCP} FIC_{i,c,s} * YI_{i,s} + \sum_{c \in HCP} FJC_{j,c,s} * YP_{j,s} + \sum_{c \in HCP} FKC_{k,c,s} * YK_{k,s} \quad \begin{matrix} \forall\, c \in HCP \\ \forall\, s \in NS \end{matrix} \qquad (5.32)$$

For each flowrate $FIC_{i,c,s}$, $FJC_{j,c,s}$, $FKC_{k,c,s}$, $FCJ_{c,j,s}$, $FCK_{c.k,s}$, and $FCW_{c,s}$, a binary variable is associated. The corresponding constraints are as described by equation (5.13). Also, binary variables are associated with new pipelines (Equation 5.15) and new PSA (Equation 5.20). A binary variable is used to define if the compressor unit is installed assuming the value of 1, 0 otherwise. Differently from the MILP model, $zc_{c,s}$ is not defined over a pair of streams; it depends only of FC_c, associated with the flow of each compressor. Constraints (Equation 5.33) is used to establish which compressors are used and their flow rates.

$$\begin{cases} FC_{c,s} \geq \varepsilon * zc_{c,s} \\ FC_{c,s} \leq F^{max} * zc_{c,s} \\ zc_c \geq zc_{c,s} \\ zc_c \leq sum(s, zc_{c,s}) \end{cases} \qquad (5.33)$$

Pressure restrictions are formulated as logical flow restrictions. For a given compressor unit, the inlet pressure is set as lower than the minimum pressure among the pressure of the mixed streams entering the compressor (equation 5.34). The outlet pressure is set as higher than the maximum pressure among the streams' pressure, leaving the compressor according to the pressure of the stream destination (equation 5.35).

$$\begin{cases} PC_{in,c,s} \leq PP_{j,s} + (P^{max} - PP_j) * \left(1 - z_{j,c,s}\right) \\ PC_{in,c,s} \leq PI_{i,s} + (P^{max} - PI_i) * \left(1 - z_{i,c,s}\right) \\ PC_{in,c,s} \leq PK_{k,s} + (P^{max} - PK_k) * \left(1 - z_{k,c,s}\right) \end{cases} \qquad (5.34)$$

$$\begin{cases} PC_{out,c,s} \geq PJ_{j,s} - P^{max} * (1 - z_{c,j,s}) \\ PC_{out,c,s} \geq PK_{k,s} - P^{max} * \left(1 - z_{c,k,s}\right) \\ PC_{out,c,s} \geq PW - P^{max} * \left(1 - z_{cw,s}\right) \end{cases} \qquad (5.35)$$

where $PC_{in,c,s}$, and $PC_{out,c,s}$ are the compressor c inlet and outlet pressures, respectively, the binary variable z is associated with flowrates (i.e.$z_{i,c,s}$, $z_{j,c,s}$, $z_{k,c,s}$ ...) and P^{max} is the maximum pressure of the connections envolved in the network.

5.3.4 *Operating and capital costs*

Operating costs include the production of hydrogen, the cost of electricity used in compressors, the operating cost of the purifying units, and the economic value corresponding to the burning gas in the fuel system. The cost equations, both for the linear and nonlinear models, are similar, except for the exceptions explained.

The production of hydrogen cost for each scenario is defined as follow

$$CH2I_s = \sum_{i \in HS} FH2I_{i,s} * C_i \tag{5.36}$$

where $FH2I_{i,s}$ is the sum of the flows from hydrogen sources in each scenario (see equation 5.22) andC_i is the cost of producing hydrogen.

The electricity cost of the compressor is directly proportional to the power (W):

$$W = F * w \tag{5.37}$$

where W is the power of the compressor with the flowrate being compressed $F. w$ is the intensive power estimated from the stream properties (C_P, C_V, z), the inlet and outlet pressure, and the compressor efficiency (Hallale and Liu, 2001).

$$w = \overline{(C_P} * T/\eta) * \left(\left(\frac{P_{out}}{P_{in}}\right)^{\frac{\gamma-1}{\gamma}} - 1\right) * (\rho_o/\rho) \tag{5.38}$$

where C_P is the heat capacity, T is the stream temperature, η the efficiency of the compressor, P_{out} and $P_{in}$are the outlet and inlet pressure, respectively, ρ_o and ρ are the densities at design conditions and at standard conditions, respectively, γ is the ratio of the heat capacity at constant pressure to that at constant volume. For a given connection, e.g., $FIJ_{i,j,s}$, the corresponding intensive power $w_{i,j,s}$ is previously calculated as a model parameter.

For the complete linear model, the total electricity cost is calculated by equation 5.39. $F_{\alpha,\beta,s}$ is the flowrate in each scenario and the indices α and β represents the possible connections involved in each scenario (i,j,s; j,k,s; k,j,s; j,j',s; i,k,s; i-waste,s;j-waste,s;k-waste,s). It is worth to note that each term is multiplied by the binary parameter u_{DeltaP} in linear model (1 if the pressure ratio is higher than one), for the cases in which the flowrate is not zero, but there is no need for compression.

$$CH2C_s = \left(\sum_\alpha \sum_\beta F_{\alpha,\beta,s} * {u_{deltaP}}_{\alpha,\beta,s} * w_{\alpha,\beta,s}\right) * C_{eletric} \tag{5.39}$$

Especially for the cost of electricity and new compressors, the flowrate used in the nonlinear model is represented by the variable $FC_{c,s}$.

$$CH2C_s = \left(\sum_c FC_{c,s} * w_{c,s}\right) * C_{eletric} \tag{5.40}$$

where $C_{eletric}$ is the electricity cost.

The cost of purifying unit is proportional to the feed flowrate in each scenario ($FK_{k,s}$):

$$CH2K_s = \sum_{k \in HP} FK_{k,s} * C_k \tag{5.41}$$

where C_k is the cost of using the PSA purification unit. The economy value corresponding to the burning of excess purge flows is corresponding to the cost of hydrogen and methane used as fuel and calculated as:

$$CH2F = C_{fuel} * F * (y\Delta H°_{H2} + (1-y)\Delta H°_{CH4}) \tag{5.42}$$

where C_{fuel} the cost per unit of energy, F is the gas flowrate, and y the hydrogen composition. Assuming a binary mixture,$1-$y represents the methane composition. The parameters $\Delta H°_{H2}$ and $\Delta H°_{CH4}$ are the standard heat of combustion of hydrogen and methane, respectively.

Taking into account the total contributions, the economic value corresponding to the cost of fuel in each scenario is calculated as

$$CH2F_s = C_{fuel} * \sum_\alpha FW_{\alpha,s} * [y_\alpha \Delta H°_{H2} + (1-y_\alpha)\Delta H°_{CH4}]) \tag{5.43}$$

where $FW_{\alpha,s}$ is the total flowrate send to burned in each scenario. The subscript α denotes all units sending streams to the fuel system (i, j, k). Since it corresponds to a saving cost, this value must be subtracted from the total operating cost.

The capital cost includes the cost of new compressors ($C_{new\,compressor}$), new purification units ($C_{new\,PSA}$) and new pipelines (C_{piping}). Hallale & Liu (2001) describe the cost of including new compressors for a particular flowrate, with a fixed cost with a binary variable and a variable cost associated with the flow.

$$C_{new\,compressor} = (a * z_c) * NS + b * W \tag{5.44}$$

W is calculated by the equation (5.37). The constants *a* and *b* vary according to the reference. z_c is the binary variable associated with the installation of a compressor for the corresponding flow and multiplied the fixed part of the new compressor cost, so it is considered only when the compressor is installed. NS is the number of scenarios and should be included here due to the new way of calculating costs in multi-scenario optimization which will be explained in more detail below.

The complete equation for accounting the new compressor cost in each scenario is given by equation 5.45 for linear model. The indices *α* and *β* represents the possible connections involved in each scenario (*i,j,s; j,k,s; k,j,s; j,j',s; i,k,s; i-waste,s; j-waste,s; k-waste,s*).

$$C_{new\,compressor_s} = a * \left(\sum_\alpha \sum_\beta z_{c_{\alpha,\beta}}\right) * NS + b * \left(\sum_\alpha \sum_\beta F_{\alpha,\beta,s} * u_{deltaP_{\alpha,\beta,s}} * w_{\alpha,\beta,s} * \left(1 - u_{c_{\alpha,\beta}}\right)\right) * C_{eletric} \tag{5.45}$$

And equation 5.46 for nonlinear model.

$$C_{new\,compressor_s} = a * \left(\sum_{NHCP} zc_{c,s}\right) * NS + b * \left(\sum_{NHCP} FC_{c,s} * w_{c,s}\right) * C_{eletric} \tag{5.46}$$

The cost associated with the installation of new piping is described below, including a fixed part with a binary variable and a variable part dependent on flow. For these calculations, it is necessary to inform the distances between the already installed units of design.

$$C_{piping} = (c * z_h * NS + d * D^2) * L \tag{5.47}$$

with

$$D^2 = (4 * F/\pi * \vartheta) * (\rho_o/\rho) = (4 * F/\pi * \vartheta) * \left(\frac{T}{T_0}\right) * \left(\frac{P_0}{P}\right) \tag{5.48}$$

where L is the pipe length, c and d are constants, ϑ is the gas surface velocity (usually 15-30 m/s; assumed an average value of 22.5 m/s in this work), and D^2 is the equivalent square diameter (Hallale and Liu, 2001). The binary variable z_h indicates the need to install the new pipeline. The equation (5.48) is replaced in equation (5.47) in order to express the cost of piping as a function of the flowrate.

The equation for cost of new pipingin each scenario is represented by

$$C_{new\ piping_S} = c * \left(\sum_\alpha \sum_\beta z_{h_{\alpha,\beta}} * L_{\alpha,\beta}\right) * NS + d * \left(\sum_\alpha \sum_\beta F_{\alpha,\beta,s} * L_{\alpha,\beta} * \frac{4}{\pi * \vartheta} * \left(1 - u_{h_{\alpha,\beta}}\right) * \left(\frac{T}{T_0}\right) * \left(\frac{P_0}{P}\right)\right) \tag{5.49}$$

The indices α and β represents the possible connections involved in each scenario (i,j,s; j,k,s; k,j,s; j,j',s; i,k,s; i-waste,s; j-waste,s; k-waste,s). Each term is multiplied by $(1 - u_h)$ in order to consider only the cost of new piping.

There is also the possibility of installing new purification units. For this case, the cost of a PSA unit (purifier considered in this work) is a linear function of the unit flowrate (variable part) and include binary variable corresponding to the fixed installation cost:

$$C_{new\ PSA} = a_{PSA} z_{kn} * NS + b_{PSA} \times F_{in,PSA} \tag{5.50}$$

where a_{PSA} and b_{PSA} are constants, and $F_{in,PSA}$ is the inlet flowrate of the PSA unit. The binary variable z_{kn} is associated with the installation of a new purifying unit. The model equation for new purifiers in each scenario is described as:

$$C_{new\ PSA_S} = a_{PSA} \sum_{k \in NHP} z_{kn} + b_{PSA} * \left(\sum_{k \in NHP} FK_{k,s}\right) \tag{5.51}$$

This cost is only considered for new purifying units. The capital cost parameters used in this work are presented, and the operating cost parameters are showed in more detail in (Silva et al., 2020).

Based on all the costs involved in managing the hydrogen network described in above, annual operating and annual capital costs are defined as:

$$C_{operating} = \frac{\sum_s (CH2I_S + CH2K_S + CH2C_S - CH2F_S) * t}{NS} \tag{5.52}$$

$$\mathrm{C_{capital}} = \frac{\sum_s \mathrm{C_{new\ PSA}}_S * \mathrm{A_f} + \mathrm{C_{piping}}_S * \mathrm{A_f} + \mathrm{C_{new\ compressor}}_S * \mathrm{A_f}}{\mathrm{NS}} \tag{5.53}$$

where NS is the number of scenarios, A_f is the annualizing factor, and t is the considered operating time of the plant in one year. It is important to highlight that the operating cost was calculated as an average cost, assuming the same probability of occurrence of all scenarios. In the case of different probabilities, a weighted average should be considered. In addition, the cost of capital, each scenario has an associated cost of new investments, proportional to the flowrate. In this work, it was assumed that the capital cost is an average of the investments required in each scenario, which does not influence the minimization of the objective function because it is a function only of the operational cost.

The annualizing factor is defined by:

$$A_f = f_i * (1 + f_i)^n / (1 + f_i)^n - 1 \tag{5.54}$$

where *n* is the number of years of interest for the return on investment and f_i is the interest rate. The Total Annual Cost (TAC) consist of the summation of the operating and investment cost:

$$TAC = C_{operating} + C_{capital} \tag{5.55}$$

For the retrofit case of existing networks, the economy saving used as economic criteria is calculated as

$$E = C_{OP}^{actual} - C_{OP}^{new} \tag{5.56}$$

where C_{OP}^{actual} and C_{OP}^{new} are the operating cost of the actual and new networks, respectively. The payback time is defined by the ratio of the total investment cost and the economy saving, and it can be estimated by the following equation:

$$pt = \frac{C_{capital}/Af}{E} \tag{5.57}$$

5.3.5 Formulation of the optimization problem

Uncertainty was added to the parameter that calculates the hydrogen consumed, based on the required demand of each consuming unit. Since the purity is constant, allowing flexibility in this parameter means that consumer demand and purge flow may vary. The uncertainty is then added to a percentage of interest on the nominal value. Thus, for each scenario, a probability of occurrence should be attributed that impacts the operating cost and capital calculations.

Considering that the probability of occurrence of each scenario is the same, the calculation of the operating cost can be determined as an average cost of each scenario, since it is dependent on the flow rates of the streams involved. As for the cost of new investment, what changes is the fixed part of each equation because it is based on binary z_c, z_h and z_{kn} and it is enough that a scenario needs this new equipment for its fixed part to be accounted for. The variable part of the equations of new equipment (5.28, 5.30, and 5.33) remains unchanged as it will also be calculated as an average based on the flows and the same probability of occurrence of each scenario.

The MILP model formulated for multi-scenario optimization of the hydrogen network in this work is described by the set of constraints defined by equations (5.1-5.20, 5.36, 5.39, 5.41, 5.43, 5.45, 5.49, and 5.51). The objective function is represented by equation 5.52 for the retrofit case. The proposed model has the advantage of being a linear model, for which quite robust solvers can be used.

For the initialization, first, an LP subproblem was solved (the binary variables were not included). For each variable is defined the lower and upper bound. For each connection between sources and consumers, the flowrate is initiated at the average value, the compressor inlet composition as the average source composition, and for all other connections, the flowrate is initiated in the lower bound. Then, the binary variables are included, and the variables are set as free according to their lower and upper bounds, and the complete MILP is solved.

The limitation found in the use of the linear model instead of the nonlinear model is the possibility of mixing different flowrates in the compressors before the units. As proposed and better described in Silva et al. (2020), this limitation can be mitigated by using the virtual compressor approach (VCA).

To overcome a large number of compressor units and further investment cost reduction, a strategy to reduce the use of this equipment was carried out through an algorithm based on non-real streams or virtual compressors. There would be compressor reuse if the compressor capacities were not reached and reduced capital cost. There are two cases where it is possible to perform VCA: i) when there are streams with the different compositions being compressed and forwarded to the same unit. ii) when streams coming from the same unit are compressed and forwarded to different units. In other words, it is possible to group streams and use the same compressor. For each option, the inlet pressure (i) and the outlet pressure (ii) must be corrected according to the minimum and maximum pressure of the involved streams, respectively. Thus, the fixed part of the new compressor capital cost decrease, since the variable part is flow dependent and does not change. It is worth notice, the fixed cost of piping is also minimized due to the rearrangement of the streams. Through it, the linear model becomes competitive, compared to the nonlinear model, due to its advantages (Silva et al., 2020).

The convergence of a nonlinear model in multi-scenario optimization is complex. Therefore, initializations and limitations in variables are necessary to reduce the variables involved and facilitate resolution. For this reason, the linear model is a competitive alternative where the achievement of the global optimum is guaranteed, and this virtual compressor approach was performed to achieve even better results with the MILP model.

The initialization of the nonlinear model through the result obtained with the linear formulation and the rearrangement of the compressors is a proposal with significant results because it facilitates the resolution of the nonlinear problem (Silva et al., 2020). For this, the nonlinear formulation used is described by the set of restrictions (5.21-5.36, 5.40, 5.41, 5.43, 5.46, 5.49, and 5.51). The objective function is described in Equation (5.52).

Thus, the flowrates, connections, compressors, and other new equipment, if necessary, are initialized before the resolution of the nonlinear model. First, only the balance equations (NLP) are solved, and then the binary equations (MINLP) are added. This improves the processing time of the optimization problem and facilitates convergence.

5.4 Systematic Method for optimal and flexible network design

As already mentioned, the main idea of this work is to find an optimal and flexible hydrogen network design, capable of operating under different scenarios. The intention is to approach operating intervals in variables and not only nominal values, so the choice was made by this approach with uncertainties. Scenarios are related to process uncertainties, in this case, uncertainties in hydrogen consumption in hydrotreatment units. This uncertainty is due to several factors, such as the processing of different oils and production planning to meet the different products and their different specifications in terms of sulfur content. When retrofitting hydrogen networks, it is possible to improve the existing network by merely changing connections or installing new equipment. This can be done for both nominal and multi-scenarios projects. In addition, it is necessary to assess the flexibility of this new design.

(Grossmann and Halemane (1983) and Pistikopoulos (1995) presented this approach (uncertainty and flexibility) as a generic idea, without an applied solution. In fact, the idea of process flexibility and its relationship with uncertainty is not a new concept. However, unlike the studies mentioned, this work has applied these concepts in hydrogen networks. Here, a model for hydrogen network design and retrofit is proposed and extended to a multi-scenario. Despite the idea of solving the design problem under uncertainty through a multi-scenario problem is old, the development of that model and the proposed strategy to solve this problem is a new feature. The flexibility is only an index that verifies if the design is capable of feasible operation given the uncertainty level. The formulation of this problem to the hydrogen networks and the proposition of a method to design hydrogen networks for a given flexibility design is a novelty of this work.

Then, given a hydrogen network, with nominal operating conditions, the optimization of this network can be made, seeking to reduce the operational cost. Based on the assumption that chemical processes vary and are subject to uncertainties in the variables, the network's flexibility is tested. The first point is defining the degree of flexibility on the design process, in this case, in a hydrogen network.

5.4.1 Feasibility test and flexibility index of a network

Swaney and Grossmann (1983) mathematically formulated how to analyze flexibility in chemical process design and proposed a quantitative index that measures the permissible variation of a parameter in a feasible plant operating region. To evaluate the flexibility index, first consider the set of equality and inequality constraints for the design problem, where d are the design variables (binary), z are the independent variables (degrees of freedom), x are the dependent variables, and θ are the uncertain parameters.

$$\begin{cases} h_i(d, z, x, \theta) = 0 & i \in I \\ g_j(d, z, x, \theta) \leq 0 & j \in J \end{cases} \tag{5.58}$$

It is defined the feasibility function $\psi(d, \theta)$ for a given design (fixed d) and a given realization of the uncertain parameters (fixed θ) within the uncertainty region $T(\theta)$. The T region is defined by the maximum ($\Delta\,\theta^+$) and minimum deviation ($\Delta\,\theta^-$) from the nominal conditions (θ^N) for each uncertainty parameter θ. These deviations are defined by the designer, and a flexible design is, for which it is possible to feasibly operate for all the uncertainty region T. The feasibility function $\psi(d, \theta)$ is determined by the solution of the following optimization problem:

$$\begin{aligned} \psi(d, \theta) &= \min u \\ s.t\ \ h_i(d, z, x, \theta) &= 0 \\ g_j(d, z, x, \theta) &\leq u \end{aligned} \tag{5.59}$$

where u is a scalar-free auxiliary variable allowing the relaxation of the inequality constraints. For the fixed pair d, θ, if the value of the feasibility function is lower or equal to zero, all the constraints are satisfied, and the design can operate for this uncertain parameter realization. On the other hand, if the feasibility function is positive, some constraints are violated, and the feasible operation cannot be achieved. The zero values of ψ defines the boundary of the feasible region in the uncertain parameters space. Moreover, the point with the maximum value of ψ, for all θ in T, i.e., the point of a maximum constraint violation, consist of the critical point for the operation. These ideas are illustrated in Figures 5.2a and 5.2b. For a fixed design and two uncertain parameters (θ_1 and θ_2) is shown the uncertainty region (blue area) and the boundary of the feasible region for two different situations. For the case (a) for any θ in T, the uncertainty region is inside the feasible region and the ψ is negative for all θ realization. However, for case (b) the right upper corner of the uncertainty region is outside the feasible region, and one constraint is violated. For this example, the right upper corner vertex of the uncertainty region corresponds to the critical point for the operation, since it is the point of maximum constraint violation.

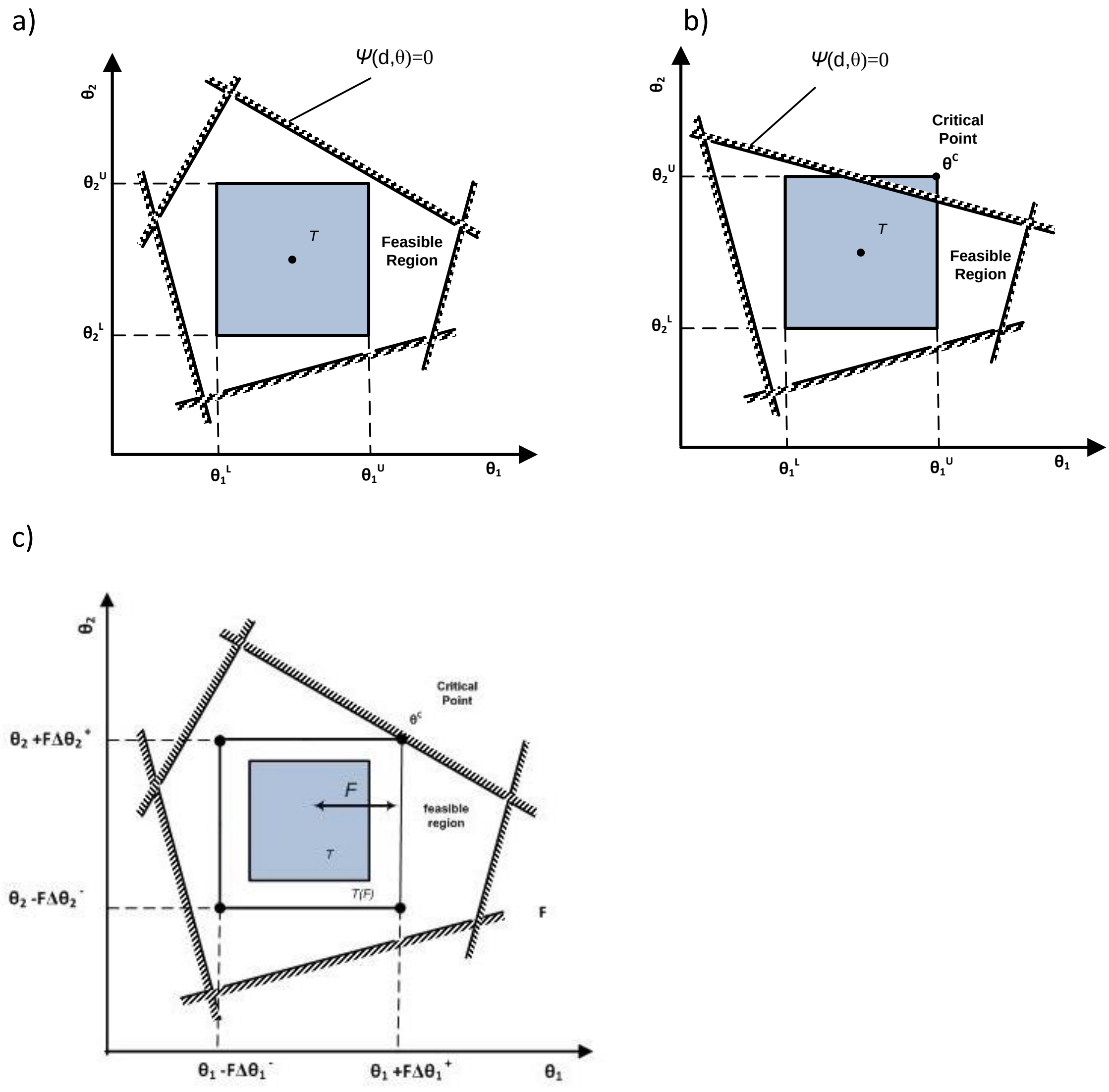


Figure 5.2: Geometric interpretation of feasibility test. a) feasible design b) infeasible design. c) feasibility index.

In order to provide a metric, Swaney and Grossman (1985) proposed the solution of the following bi-level optimization problem for the definition of the flexibility index :

$$
\begin{cases}
F = \max \delta \\
s.t.\ \psi(d,\theta) = 0 \\
\psi(d,\theta) = \min u \\
s.t\ \ h_i(d,z,x,\theta) = 0 \\
g_j(d,z,x,\theta) \leq u
\end{cases}
$$

$$T(\delta) = \{\, \theta \mid \theta^N - \delta\Delta\, \theta^- \leq \theta \ \leq \ \theta^N + \delta\Delta\, \theta^+\} \tag{5.60}$$

where F is the flexibility index (a positive scalar variable), δ is a positive auxiliary variable, and $T(\delta)$ is a scaled hyperrectangle according to the uncertainty region.

Considering that ψ is enforced to be zero, the solution to this problem is at the boundary of the feasible region. For $F < 1$, $T(\delta = F)$ is contained in T, and the design is not flexible, since some region of T cannot find feasible operation; this is illustrated for the case (b) of Figure 5.2. For $F \geq 1$, $T(\delta = F)$ contains T (they are strictly the same hyperrectangle for $F = 1$), and the design reaches feasible operation for all T, so it is flexible and illustrated by the case (a) in Figure 5.2.

The geometric interpretation of the flexibility index is presented in Figure 5.2c. The value of F corresponded to the maximum hyperrectangle centered in the nominal condition and scaled according to the uncertainty region that can be inscribed within the feasible region. For this particular illustration, the hyperrectangle, $T(\delta = F)$contains the region T, and hence, the region T is inside the feasible region. The flexibility index would return a value greater than one.

Despite the difficulty of solving this flexibility index problem, its solution provides not only information on whether the design is flexible or not and indirectly where the critical point is. For the illustrated case, the critical point corresponds to the vertex of the uncertainty region at the same vertex position of the $T(\delta = F)$ that defines the solution of the flexibility index problem. It can also be defined as the vector's critical direction starting at the nominal conditions along the critical vertex. For all scenarios in this direction, between the boundary of the feasible region touched by $T(\delta = F)$ and the critical vertex, the design cannot attain feasible operation. This information can be used to define new scenarios for the multi-period design problem to re-design a more flexible network, as will be discussed later.

5.4.1.1 Vertex enumeration method

Whereas h_i and g_j restrictions define a viable and convex region, to solve this convex optimization problem, one can use the vertex enumeration method. Swaney and Grossmann (1983) also highlight the vertex enumeration strategy that, where the constraints are jointly 1-D quasi-convex in θ and in z, the solution of equation (59) is one of the vertices in set $T(\delta)$. In this case, the critical points of the uncertain parameter correspond to the vertices and the function $\psi(d,\theta)$ can be replace for $\psi(d,\theta^k)$, evaluated in the vertex parameter θ^k.The vertices (V) are defined as a set with 2^{Np} vertices, where Np is the number of uncertainties parameters θ. Therefore, the flexibility problem can be reformulated as:

$$F = \min_{k \in V} \delta^k \qquad \forall\ k\ \in\ V \tag{5.61}$$

where δ^k is the maximum deviation along each vertex direction and defined as:

$$\begin{cases} \delta^k = \max_{\delta,z} \delta \\ s.t. h_i(d,z,x,\theta) = 0 \\ g_j(d,z,x,\theta) \leq 0 \\ \theta = \theta^N + \delta\theta^k \\ \delta \geq 0 \end{cases} \tag{5.62}$$

The flexibility problem is solved for a fixed design and its solution provides the maximum level of uncertainty in which the design can operate. In the Vertex Enumeration strategy, this level is searched for all vertices direction and it is defined as the smallest one (the lowest index corresponds to the highest degree of flexibility that all scenarios meet). This is the critical direction with a corresponding critical vertex. Since it is desired the operation within the uncertainty region, critical directions may be used to update the scenarios to the multi-period optimization problem to ensure the operation in these scenarios. This procedure will increase the cost of the design, but also the level of flexibility.

For the illustrative cases presented in Figure 5.2a and 5.2b, the boundaries of feasible region is defined by linear constraints, and the feasible region is then convex. So the vertex enumeration method can be used to solve the problem, despite its computational efforts for a large number of vertices. For the nonlinear case, the critical point may not be a vertex of the uncertainty region, and a more rigorous approach may be used to solve the problem as an active set strategy. However, the nonlinear formulation presents the nonlinearity only at the hydrogen material balance for each compressor for the design problem treated in this work. Moreover, in general, the number of compressors considered in the superstructure is relatively small (3, 4 for the examples), so linear constraints primarily define the feasible region.

Furthermore, the stream mixing can be virtually treated as streams compressed individually with additional investment cost. In order to avoid this complexity, the vertex search was used for both models, the linear and the nonlinear version. Therefore, the flexibility index may be slightly underestimated, but in general, it is not a problem since the final design is delivered with an over flexibility to overcome this limitation

5.4.2 Proposed framework

The goal of network design that operates with uncertainties is to meet the design specifications and the desired level of uncertainty defined by the designer (region T) at the lowest possible cost. In this work, the uncertainty is assumed in the hydrogen consumption of each consumer unit. Despite the uncertainty, the level may be individually defined for each consumer unit, in the examples considered in this work, it is assumed the same uncertainty for all consumers, e.g., a variation of plus or minus 10% from nominal conditions, and this is the desired flexibility level for the design.

This proposed framework for optimal design under uncertainty can be seen in Figure 5.3. For an existing network design (d), the first step is to verify the uncertainty level that the current network can operate by running the flexibility index problem, taking into account the desired uncertainty level, F_d , as plus or minus a percentual of the nominal conditions. The whole procedure is based on a two-stage strategy coupling the (i) multi-scenario optimization problem (design stage) and (ii) the flexibility index problem to evaluate the design (operating stage).

Suppose the actual network (or the nominal value for a new design) has the flexibility index equal or greater than one, $F\geq 1$. In that case, the procedure is over, and the current design is flexible enough according to the desired flexibility level.

If the flexibility obtained in the current network is lower than one (F <1), the procedure to be followed is to create new scenarios for solving the multi-scenario optimization problem, generating a new retrofit design. The new scenarios area created as follows: given the current solution of the flexibility index problem, we can obtain the direction of critical vertices, which defines the flexibility level. It is essential to mention that it may exist more than one critical direction; that is, the flexibility level may be defined by more than one direction. Critical directions are used to update the current scenarios (only nominal scenario at the first iteration). For the case of multiple critical directions, it is possible to include only a subset of these directions because a new set will change the design to include the corresponding operating scenario.

For example, for two uncertain parameters (θ_1, θ_2) the vertex directions set is $V = \{(+,+),(+,-),(-,+),(-,-)\}$ and the critical directions CD is contained at V. The uncertainty of a given critical scenario is then defined:

$$\theta = \theta^N + a * (CD * F_d * \theta^N) \tag{5.63}$$

a is an auxiliary parameter (a percentual of the desired level of uncertainty) used to create the scenario along the critical direction (CD). With the updated set of scenarios, the multi-scenario problem is solved for a new design. Then, the flexibility index problem is solved to evaluate this new design. In this problem, an equation similar to Equation (5.63) is used, replacing a by delta as in the optimization problem (set of equations 5.62). For the case that $F \geq 1$, there are no critical scenarios. The procedure must stop since the desired flexibility level was attached. Otherwise, for the case which F <1, again, new scenarios are generated.

For a practical reason, the parameter a is defined within the actual flexibility (F) and the designed flexibility level, for which F=1, i.e.,, $F(d)< a \leq 1$. It is important to add a critical scenario along the critical direction. It means a scenario that is not capable of achieving feasible operation.

Thus, scenarios are created according to equation 5.63 and inserted as a new scenario into the multi-scenario optimization problem. The retrofit of the existing network can be performed using the multi-scenario optimization problem, which provides a network redesign (a new design d). The flexibility of this network redesign is tested by solving the flexibility index problem. If the design is not flexible enough, the critical direction is identified. The set of scenarios is updated with new critical scenarios, and the value of a should increase. The two-stage strategy is applied, always adding critical scenarios until the flexibility level is achieved ($F \geq 1$).

For economic reasons, if the flexibility is much larger than the desired level (F >>1), a more economical solution with lower flexibility is achieved. For this, critical scenarios can be replaced by others with a smaller a to update the scenarios repeating the two-stage strategy. The idea is to obtain the desired flexibility because an over flexible network design will be more expensive. For the nonlinear models, it is always important to slightly over define the desired level of flexibility to overcome the limitation imposed by the vertex search method.

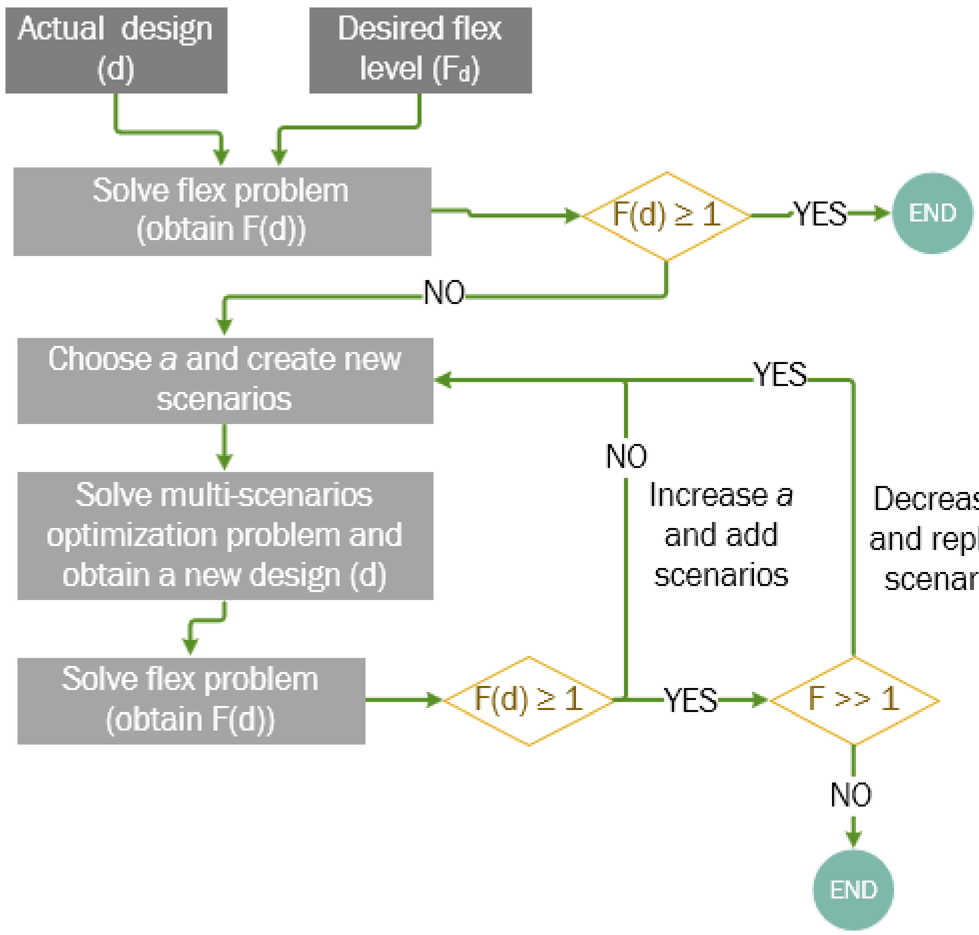


Figure 5.3: Strategy for optimal design under uncertainty.

5.5 Results and discussion

The proposed systematic approach for flexibility analysis and hydrogen network optimization by mathematical programming was validated using two examples. The first case study is from Hallale and Liu (2001), and the second example is with real data from a refinery in south Brazil. The mathematical programming model was implemented in the modeling system GAMS on a 3.6 GHz Intel® Core ™ I7 CPU. The solver used to solve MILP model was CPLEX and for MINLP, SBB (GAMS, 2019).

For the case studies, it was considered the retrofit design for existing hydrogen networks. The objective function considered is the operating cost. Therefore, the existing structure was explored considering installing new pipelines, new compressors, and purifying units. The economy saving is obtained by the operating cost reduction compared to the original network. However, there is also an investment cost economy associated with non-existing equipment and pipelines. The payback time, i.e., the investment cost divided by annual operating cost savings was also used as an economic indicator for comparing the model solution.

In the examples, the procedure was: i) evaluation of the flexibility of the nominal redesign; ii) selection of the critical vertices and addition of uncertainty to hydrogen consumption in the respective critical vertices; iii) multi-scenario optimization MILP and rearrangement of compressors (VCA); iv) multi-scenario optimization MINLP: initialization of the original network and proposed initialization strategy – the result of MILP with the rearrangement of compressors.

5.5.1 Example 1

The hydrogen network from Hallale and Liu (2001), depicted in Figure 5.4a, consist of a primary hydrogen production unit (H_2PLANT) and a secondary source, which is catalytic cracking (CCR). In this process, there are six consumer units: HC (hydrocracker), JHT (kerosene hydrotreater), CNHT (cracked naphtha hydrotreater), DHT (diesel hydrotreater), NHT (naphtha hydrotreater) and IS4 (hydrodealkylation). Two previously installed compressors are used, and there are no purification units. The desired flexibility level is 10% of the variation in the hydrogen-consuming units.

Table 5.1 has information about the nominal values (flow, pressure, and purity) for sources and consumers. The parameters used in this optimization problem can be se with more detail in Silva et al., (2020).The MILP optimization problem has about 4564 single constraints, 1749 continuous variables, and 1246 binary variables. The resource time usage was 0.762 seconds.

Table 5.1: Information available for hydrogen network from example 1.

Sources	$FH2I_{i,s}$ (MMscfd)	$FH2I_{max\,i,s}$ (MMscfd)	$YI_{i,s}$ %	$PI_{i,s}$ (psia)
H2 plant	45.00	50.00	92.50	300
CCR	23.50	23.50	75.00	300

Consumers	$FJ_{j,1}$ (MMscfd)	$YJ_{j,s}$%	$PJ_{j,s}$ (psia)	$FP_{j,1}$ (MMscfd)	$YP_{j,s}$ %	$PP_{j,s}$ (psia)	$H2\_c_{i,1}$ (MMscfd)
HC	38.78	92.00	2000	11.29	75.00	1200	27.210
JHT	8.65	75.00	500	4.32	65.00	350	3.679
CNHT	8.21	86.53	500	3.47	75.00	350	4.502
DHT	11.31	75.97	600	8.61	70.00	400	2.565
NHT	12.08	71.44	300	6.55	60.00	200	4.700
IS4	0.04	75.00	300	0	0	0	0.030

First, the flexibility index of the nominal retrofitted network was evaluated through the flexibility problem developed, and for this, it is necessary to determine the viable region $T(\delta)$. As this network has 6 consumers (6 uncertain parameters), there are 2^6 vertices that make the viable region of study, as shown in Table 5.2. The proposed network is then fixed (binary variables and flows in a range of 10% beyond the nominal capacity), and the flexibility index problem is solved.

Table 5.2: Vertex identifiers (VI) for different consumers in example 1.

Vertex (V)	Consumers (j)					
	HC	JHT	CNHT	DHT	NHT	IS4
(1)	+1	+1	+1	+1	+1	+1
(2)	-1	-1	-1	-1	-1	-1
(3)	-1	+1	+1	+1	+1	+1
⋮	⋮	⋮	⋮	⋮	⋮	⋮
(64)	+1	+1	-1	+1	-1	-1

The hydrogen consumption for each vertex direction ($\mathrm{H_2\_c_V}$) is then defined according to the equation:

$$H_2\_c_V = H_2\_cn_j * \left(1 + VI_{V,j} * \delta * F_d\right) \tag{5.64}$$

$H_2\_cn_\mathrm{j}$ is the nominal hydrogen consumption (given in Table 5.1), $V_{V,j}$ is the vertex identifier given in Table 5.2, and δ is an auxiliary positive variable used in the flexibility problem. For each vertex, a given identifier, a flexibility problem is solved (a total of 64 subproblems for this example) and the Flexibility level (F) is set as the smallest value obtained among all the subproblems, i.e., $F = \min_k F_k$.

For this example, the nominal design presented a flexibility level of F=0 for some directions, considered as critical directions here. In other words, the design cannot feasibly operate for any variations along these directions. For this example, more than one critical direction was identified (F=0), so some of them were randomly chosen to create new scenarios. The vertices chosen were 1, 25, 41, and 55. The problem was solved for different values of a varying from $F< \ a \ \leq 1$. According to the proposed procedure, the solving steps were: select a value for a and create the scenarios, run the problem of multi-scenario optimization, fix the retrofit of the network obtained through optimization, and run the flexibility problem to assess whether the obtained value is within the desirable factor. The uncertainty values, the operational and capital costs of the networks obtained through retrofit, and the flexibility indices are summarized in Table 5.3.

Various percentages of uncertainty were tested (a) on the value of hydrogen consumption. The desirable value stipulated in this work, for the flexibility of the hydrogen network, is around 10% associated with a low operating cost, but the methodology can be applied for any value. Then, the first percentage of uncertainty added was 10%, resulting in a network with flexibility index F=4.7. As this value is much higher than expected, according to the proposed system, a new value of d was chosen, the optimization problem was repeated, and the flexibility of the network obtained was tested, and so on.

The objective function chosen for the problem analysis was to minimize the operating cost of the hydrogen network, using the parameters listed in Table 1 and the network configuration depicted in Figure 5.4a. The annual operating costs were estimated in

39,819 $/year for the original network operating at nominal conditions. This solution is used as a basis for comparison.

The different networks obtained through multi-scenario optimization are summarized in Table 5.3. For each of the uncertainties tested, a letter was assigned to the obtained network.

Table 5.3: Results from different uncertainty and flexibility obtained.

Network	Uncertainty level	Operational cost$/ year (x 10^6)	Capital cost $/ year (x 10^6)	Flexibility index (F)
A	± 10% (a = 100%)	35.676	16.177	4.7
B	± 7.5% (a = 75%)	35.442	16.431	1.7
C	± 5% (a = 50%)	35.227	15.570	0.975
D	± 2% (a = 20%)	34.887	15.579	0.975
E	± 1% (a = 10%)	34.883	15.580	0.975

It is observed that the more flexible the hydrogen network design, the higher the cost because there are greater chances of the project meet the uncertainties. The region of uncertainty served in both the C,D, and E networks are equivalent (same design), 9.75% of uncertainty met, as the interest is a network that is around 10% flexible. The goal is to obtain a network with lower operational cost, so the compressor rearrangement technique was applied in network E.

The network E obtained from retrofit the original network includes installing 15 new compressors, a new PSA, and 23 new lines, so it has a high capital cost of $15.580 million. Using the compressor rearrangement technique, several compressors can be reused, so that only 4 new compressors would be needed and the use of two existing ones. The compressor C1 (as shown in Figure 5.4a) was reused for other units that also refer hydrogen to the HC unit (JHT-HC, CNHT-HC, NHT-HC and PSA-HC), and the same happened for C2 that send hydrogen to the DHT unit (CCR-DHT, CNHT-DHT, and PSAn-DHT). The other 4 new compressors were used upstream of the CNHT (CCR-CNHT, JHT-CNHT), IS4 (NHT-IS4, PSAn-IS4), JHT (CCR-JHT, DHT-JHT, PSAn-JHT), and NHT (PSAn-IS4) units. Thus, all units that had as the same destination a single unit (e.g., C1 for HC), were grouped and the 15 connections requiring compressors were reduced to 6 (4 new and 2 existing). This has a 3.8% reduction in capital cost ($ 15.580 to $12.108 million).

This proposed network is used to initialize nonlinear optimization. The nonlinear model has 7127 single equations, 3427 single variables, and 1856 discrete variables. The resource usage was 55.539 seconds. Once the optimization is done, a new network project with an operating cost of $34.302 Million is obtained, represented in Figure 5.4b. This network has a flexibility index equal to 2.11 (that is, as F is greater than 1, considering 10% uncertainty, the feasible region comprises a variation of 21.1% concerning the nominal value). This network is called network G.

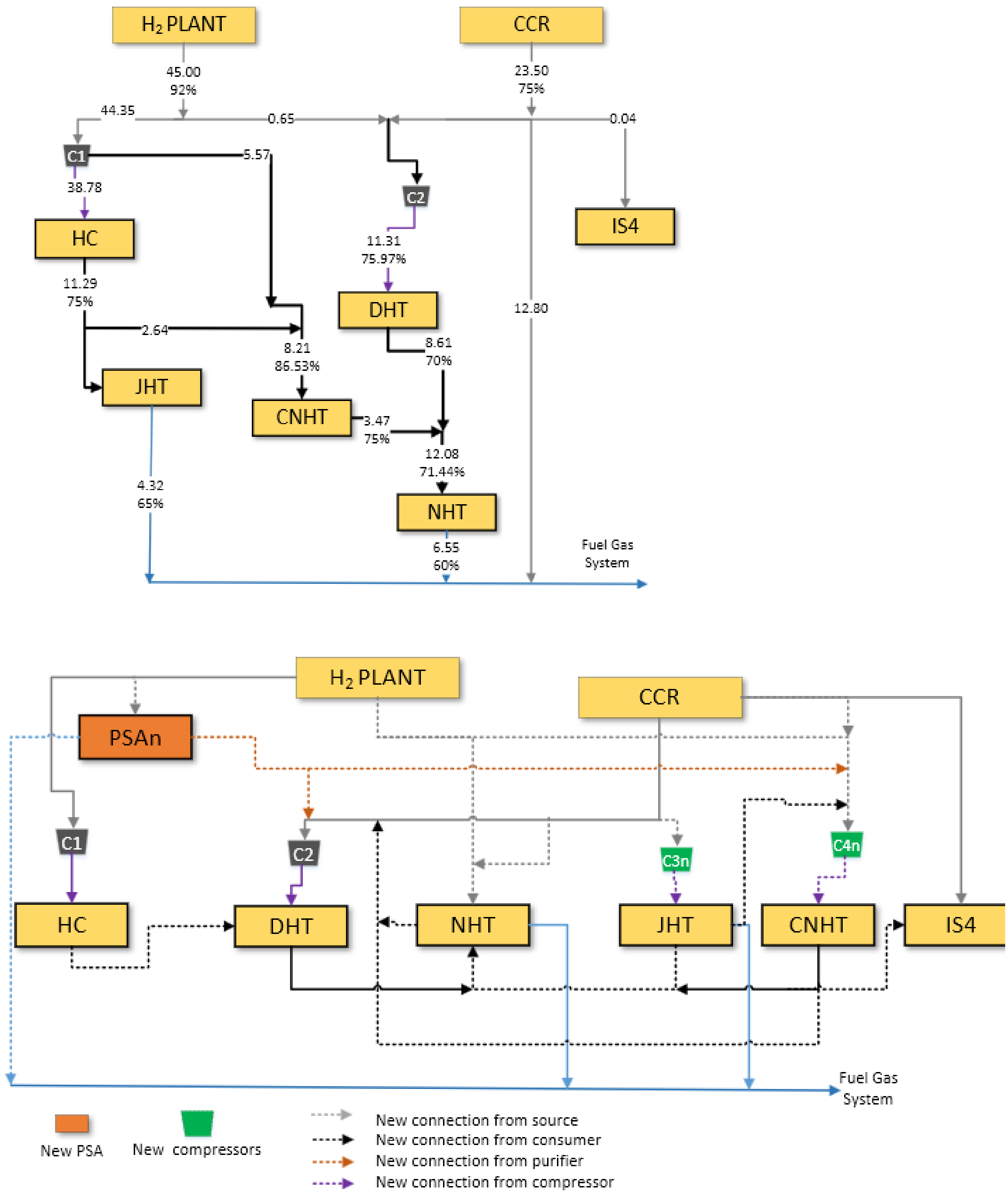


Figure 5.4: a) Existing hydrogen network for example 1 – Adapted from Hallale& Liu (2001). **b)** Optimized network G from example 1.

For comparison, the nonlinear optimization of the original network was evaluated without using as initial guess the project obtained via linear optimization. The resulted network (called network H) has $ 37.011 million as operating cost. The resource usage was

109.637 seconds. All results are all shown in the Table 5.4. The flexibility obtained with this network is below the desired.

Table 5.4: Results from different optimization models and flexibility obtained for example 1.

	MILP (network E)	MINLP initialized by MILP (network G)	MINLP (network H)
Operational cost	34.914	34.302	37.011
Capital cost	12.108	11.787	7.654
Flexibility index	0.9725	2.11	0.33

The original network in example 1 has an operating cost of \$ 39.819 million, being mostly the cost of hydrogen production. Through multi-scenario optimization, in the proposed redesigned Network G, this value has reduced to \$ 34.302 million (reduction of 13.8%). There is a 7% reduction in the value of hydrogen production because it can be better reused within the network due to the new connections. The payback of this new network is 4.7 years since the cost of capital is high. It is also important to note that, although the lowest operational cost was obtained in nonlinear optimization, network E has flexibility closer to 10% (because F is closer than 1) and with an operating cost very close to the G network.

5.5.2 Example 2

In this example, project data from a hydrogen network of a Brazilian refinery were used. The network consist of two hydrogen generation units (UGH I and UGH II), two purification units (PSA I and PSA II) and 3 consumption units, two hydrotreatment units (HDT I and HDT II), and one hydrodesulfurization (HDS), as shown in Figure 5.5a. Due to data secrecy, only normalized hydrogen consumption values will be provided for the units, the other parameters cannot be reported. The consumption in HDS was considered as 1 Nm^3/h, HDT I as 3.35 Nm^3/h, and HDT II as 6.70 Nm^3/h. For the scenarios, the same probability of occurrence was given.

The flexibility index of the nominal network retrofitted was evaluated, through the flexibility problem developed, and for this, it is necessary to determine the viable region $T(\delta)$. As this network has 3 consumers, there are 2^3 vertices that make up the viable region of study, as shown in Table 5.5. The original network is then fixed (binary variables and flows in a range of 10% beyond the nominal capacity), and the flexibility index problem is solved.

Table 5.5: Vertex identifiers (VI) for different consumers in example 2.

Vertex (V)	Consumers (j)		
	HDT I	HDT II	HDS
(1)	+1	+1	+1
(2)	-1	-1	-1
(3)	+1	+1	-1
(4)	+1	-1	-1
(5)	+1	-1	+1
(6)	-1	+1	+1
(7)	-1	-1	+1
(8)	-1	+1	-1

The same procedure performed in example 1 was done. The flexibility of the original network was evaluated in the 8 vertices that make up the viable region. In this case, the original network has a flexibility index of 5.5 (lower value found at vertex 1, 3, 4, and 5). So, these vertices were considered as critical points of the viable region. All these four vertices were used to obtain the scenarios for the optimization problem. Hydrogen consumption was evaluated according to its factor, i.e., the percentage of uncertainty was added for more ($\theta^N + CD * a * \theta^N$) or for less ($\theta^N - CD * a * \theta^N$).

The procedure performed was the same as in example 1. The percentages of uncertainty (a) tested were 10%, 5%, and 1% on the value of hydrogen consumption. The desirable value stipulated in this work, for the flexibility of the hydrogen network is around 10% $(F_d = 10\%)$ associated with a low operating cost. The different uncertainty values, the operational and capital costs of the networks obtained through Retrofit, and the flexibility indices are summarized in Table 6. For each of the uncertainties tested, a letter was assigned to the obtained network.

The objective function chosen for the problem analysis was to minimize the operating cost of the hydrogen network. Using the parameters and the network configuration depicted in Figure 5.5a, the annual operating costs were estimated in 40.666 $/year for the original network operating at nominal conditions. This solution is used as a basis for comparison. The MILP optimization problem has about 3190 single constraints, 1245 continuous variables, and 884 binary variables. The resource time usage was 0.046 seconds.

Table 5.6: Results from different uncertainty and flexibility obtained.

Network	Uncertainty level	Operational cost$/ year (x 10^6)	Capital cost $/ year (x 10^6)	Flexibility index(F)
I	10% $(a = 100\%)$	38.082	1.536	1.99
J	5% $(a = 50\%)$	37.522	1.538	1.99
K	1% $(a = 10\%)$	37.099	1.579 (0.338 after VCA)	1.99

For all the uncertainties tested, the network project obtained was the same. Therefore, the flexibility met of the network was also 1.99 considering the desired 10% uncertainty. Because F is greater than 1, it is possible to meet a demand greater than the 10% desired. The feasible operating region (see Figure 2c) can meet closely 20% uncertainty concerning the nominal. In this case, the network has few consumer units, which limits the possibilities of connections. Network K, which uses 1% uncertainty in hydrogen consumption, has the lowest operating cost. The network retrofit included the installation of 4 new compressors and 8 lines.

The network Khas a capital cost of $ 1.579 million, and by rearranging the compressors, this value reduces to $ 0.338 million (reduction of 78.6%). Network K is used as the initialization of the multi-scenario nonlinear optimization. The MINLP optimization problem has about 5894 single constraints, 2829 continuous variables, and 1719 binary variables. The resource time usage was 12.270 seconds. With this, we obtain a network (Network L) with 20% flexibility, shown in Figure 5.5b.

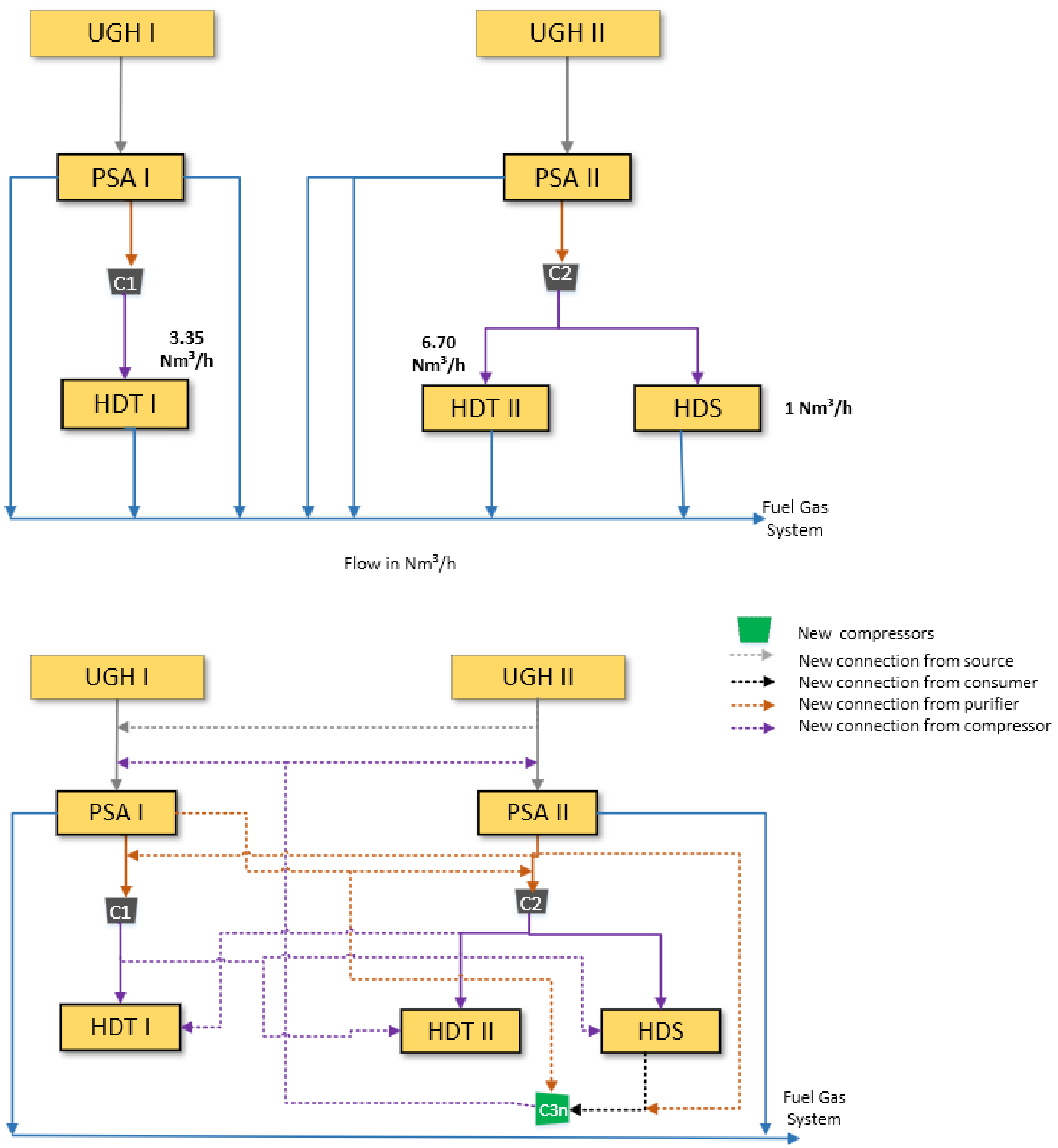


Figure 5.5: a) Existing hydrogen network from example 2. **b)** Optimized network L from example 2.

For comparison, optimization via a nonlinear model was done without using the initialization strategy proposed above (network M). The resource time usage was 49.574 seconds. The results are summarized in Table 5.7.

Table 5.7: Results from different optimization models and flexibility obtained for example 2.

	MILP (network K)	MINLP initialized by MILP (network L)	MINLP (network M)
Operational cost	37.099	34.126	36.947
Capital cost	0.338	0.341	0
Flexibility index	1.99	2.0	1.68

It is observed that the lowest operational cost is found in the network L, which proves that the initialization strategy used is a great tool to improve the results obtained through nonlinear optimization. The reduction in operating costs is 16% compared to the original network. In the original network, the most relevant costs are hydrogen production and fuel system cost. In network L, less hydrogen is needed from the source, and less hydrogen is also directed to the burning system. The new lines proposed in the design allow better integration and use of hydrogen currents. This network flexibility is 20%, above the desired 10%, but satisfies its allied cost. The payback of this network K is approximately 1 month.

5.6 **Conclusion**

This work develops a systematic to evaluate the flexibility of hydrogen network projects, combined with multi-scenario optimization via mathematical programming. It is worth mentioning the importance of multi-scenario optimization, since it achieves a more robust network capable of operating under uncertainties in hydrogen demand.

The mathematical models are developed based on a defined superstructure. The model allows installing new equipment such as lines, purifiers, and compressors and evaluates the payback time based on the investment required according to the optimized network. The model is thoroughly described, with all constraints, including the logical modeling equations used to accomplish design decisions and a proper estimation of costs and all the model parameters.

The methodology developed is tested in two examples, one in the literature and one that uses real plant data, which implies a greater scientific appeal. Finally, the MILP-MINLP model's solutions were able to accomplish reductions in operating costs for the existing hydrogen network, and it proves to be an excellent alternative.

The use of virtual compressors to make the result through linear optimization is more competitive and is an excellent tool, as observed in the networks' costs. In this work, generic modeling was formulated, and for simplicity, multi-staged compressors were not considered explicitly. However, a further optimization step can be performed to optimize (reducing more costs of compression). It could be an improvement for the model, so in the scheme presented in Figure 1b the compressor units can send flowrates to other compressors. Therefore, each compressor unit can be seen as a stage, and the operating cost of compression can be further reduced. In our research work, the hydrogen network is to be integrated with the refinery production planning.

Besides, using the retrofit obtained from the MILP model as the MINLP model's initialization proved to be very advantageous, reducing the operational cost evenly when compared with the simple resolution. With this, it was possible to obtain flexible networks with competitive operational costs. Also, for problems involving more units and scenarios, the nonlinear problem may be slow to solve. Initialization reduces processing time, which is observed by resource time usage in examples.

Although using local solvers for the multi-scenario model and the solution achieved can be underestimated, the results are excellent and can be even better. Anyway, global solvers can be applied, but they will present a much higher computational effort.

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Capítulo 6 – **Flexibility Analysis and Multi-scenario optimization applied to Production Planning for Hydrogen Management in Refineries**

O presente capítulo é uma reprodução do artigo submetido para a *Computers and Chemical Engineering* e inclui os objetivos 6 e 7 e as contribuições 7,8 e 9 desta Tese de Doutorado. No Capítulo anterior, foi abordado a otimização multicenário, com relação à incerteza no consumo de hidrogênio e a questão da flexibilidade da rede de hidrogênio. A incerteza no consumo de hidrogênio nas unidades de hidrotratamento (unidade consumidora) está associada principalmente ao processamento de diferentes petróleos, com diferentes teores de enxofre. O planejamento de produção é a ferramenta utilizada na refinaria para definir quais petróleos serão utilizados, baseado no preço, na disponibilidade e principalmente na demanda dos produtos finais. Através da programação matemática em um modelo não linear (NLP), foi possível representar o planejamento de produção de uma refinaria, sendo otimizado visando o maior lucro. Logo, com base no planejamento de produção se consegue inferir quanto de hidrogênio será necessário para cumprir determinada produção e com isso, se obtém os diferentes cenários num horizonte de tempo estipulado pelo planejamento. O objetivo principal deste trabalho é conectar o planejamento de produção com o consumo de hidrogênio na refinaria, por isso, através dos cenários obtidos é possível fazer a otimização multicenário da rede existente e avaliar a flexibilidade da rede original e do *redesign* proposto. Assim, também é possível avaliar economicamente o uso do hidrogênio na refinaria. Este trabalho foi realizado com base em dados de projeto de uma refinaria e o planejamento de produção com dados históricos de demanda e petróleos.

Abstract : Crude oil, product demands and prices vary over time. Therefore, production programming and planning are challenging in oil refining industry. These variations can be associated to process uncertainties, such as hydrogen consumption in hydrotreatment units. Aiming for a higher profit, an optimized production planning that encompasses uncertainties is fundamental. In this work, a methodology was developed in GAMS that connects production planning with hydrogen consumption in refineries: i) nonlinear mathematical programming of production planning; ii) multi-scenario optimization through mix-integer nonlinear formulation for hydrogen network; iii) flexibility analysis of existing network and redesign. The models were applied to a oil refinery case study. The intention was to compare indicators: profit, flexibility, and operational cost, both the original hydrogen network and redesign. As result, a redesign was proposed, which presents an operational cost about 10% less than the original network and a profit greater than 2.9%, in addition to the flexibility obtained.

6.1 Introduction

The refining industry transforms oil into value-added derivatives through chemical processes. The main commercial interest products are diesel oil, gasoline, kerosene, liquefied petroleum gas, aviation kerosene, and fuel oil. Currently, oil refineries, in addition to acting to meet market demand, also take into account environmental, safety, and product quality issues, such as in the production of diesel, where it is necessary to obey the current legislation (ANP, 2020).

Oil is a mixture of components, mainly formed by hydrocarbons and some contaminants, such as sulfur and metal ions. Therefore, several oils are characterized by hydrocarbons type present, density, sulfur content, etc. It directly influences the refining process, which must be adjusted to achieve market demand and maintain product quality constraints (Pompeo et al., 2018).

It is also known that the economic scenario changes on a daily basis, whether in the price of oil and derivatives and also in the supply and demand of oil and products. Therefore, the management of the processes that encompass refining is crucial, and new technologies and tools can lead to more efficient processes. Optimizing the production planning of a refinery is one of the most used alternatives with this goal.

Production planning and programming (scheduling) can be described as defined strategies for better use of equipment, utilities, or resources. In general, production planning considers high-level decisions in a longer time horizon. Whereas the scheduling is more related to the feasibility of operations, determination of the task sequence, and the viable time for it to occur, meeting the goals established in the planning. More specifically, the tactical production planning that will be addressed in this work, where studies are made on production capacity, product demand, and available resources.

Moreover, a refinery production planning also needs to consider the constraints imposed by current legislation on fuel quality and composition. The most important is the sulfur content in diesel, which is reduced using the hydrotreatment process, applying hydrogen as a capture element. Different oils provide different products with sulfur contents and consequently require different amounts of hydrogen. Therefore, the hydrogen network must be flexible enough to achieve variations in hydrogen demand.

Therefore, the refinery production planning interconected with lean hydrogen production has important economic appeal (Al-Qahtani and Elkamel, 2010).

The main objective of this work is to integrate the production planning of a refinery with the production schedule and its demand for hydrogen. Incorporating the feedback of the process, is possible to optimize the hydrogen network, and getting a redesign or work with the constraints imposed by the original network. In addition, with the proposed methodology, it is possible to economically evaluate the use of hydrogen in the refinery in terms of retrofit in production planning, comparing the redesign and the existing network. Thus, hydrogen production takes place efficiently, aiming at the refinery's highest profit based on market restrictions. In order to accomplish the target, it was necessary to develop models for the production planning, hydrogen network modeling, and network flexibility analysis.

In section 6.2, a literature review was made about the works already published. In section 6.3, the formulation of the nonlinear planning model was described. Section 6.4 covers mathematical modeling for hydrogen network design, network flexibility assessment and framework proposed in this work. Chapter 6.5 is the results obtained, followed by the conclusion in chapter 6.6.

6.2 Literature review

There are several works on refineries production planning and production scheduling in the literature, both in refining, blending, and logistic distribution. Shah (1996)(Shah, 1996) describes the problem of scheduling the crude oil supply to refineries. The model is linear and considers the refinery's oil allocation, ports, and pumping for distillation. All these decisions are made over a 1-month horizon.

Moro et al. (1998) present a nonlinear model based on refinery process units' general representation. The framework was applied to the production planning of a real-world oil refinery. The primary objective was the production of diesel fuel with different specifications and demands. In 2000, Pinto et al. developed a production planning model and the nonlinear relationships of the processes involved in refining are considered. The scheduling model is based on the MILP model. This model considers the unloading of crude oil from pipelines, transfer to storage tanks, and distillation unit.

Zhang et al. (2001) developed an integrated optimization of the refinery, along with the hydrogen network and utilities system. For this, refinery optimization uses linear programming (LP) techniques to maximize overall profit. The hydrogen network and utility system are then optimized to reduce operating costs for the fixed process conditions determined from LP optimization. Although the original model is MINLP, linearization techniques are applied to covert the MINLP problem to a MILP problem. Starting from a refinery case study, a 1.0% improvement in profit can be achieved using the simultaneous approach compared to the sequential approach. As a result, this method provides new insights into the refinery optimization problem. It can provide significant benefits to the refining industry.

Joly et al. (2002) developed nonlinear model for planning and mixed-integer optimization models for scheduling problems in petroleum refineries. Three applications were presented for scheduling problems, crude oil inventory management with several types of crude oil delivered exclusively by a single oil pipeline, optimization models intended to define the optimal production policy, inventory control, and distribution, and the planning model is extended to sequence decisions at the scheduling level in the liquefied petroleum gas (LPG). The scheduling problem was modeled as a MINLP because of the bilinear terms in viscosity. A rigorous MILP model derived from the previous nonlinear one proved efficient for planning and scheduling problems.

Alhajri et al., (2008) focus on an approach more realist to represent refinery production planning. The model proposed can predict the operating variables, cut-point temperatures in crude distillation, and conversion in the fluid catalytic cracking unit. The properties of the final products and market specifications are also included. The results show that the model provided an optimal operating strategy for the refinery. At the same time, meet product's properties and production rates. Quality give-away is also minimized hence resulting in considerable savings for the petroleum refinery.

Li et al. (2010) presents a refinery planning model that utilizes simplified nonlinear empirical models, including crude oil properties and product quality. The models are for crude distillation unit (CDU), fluidized-bed catalytic cracker (FCC), and product blending in the refinery. First, the CDU model is solved to determine the weight transfer ratios in distillation. The model for FCC fraction is solved to obtain the yields. Finally, the CDU and FCC models are integrated with NLP planning model. The models and case studies are implemented in GAMS.

Leiras et al. (2010) proposed a robust optimization methodology considering uncertainties in refinery processes. The uncertainties in saleable products, operating costs, product demand, and product yield were considered. The benefits of incorporating uncertainty in the different model parameters were evaluated in terms of the cost of ignoring uncertainty in the problem. The robust model offers advantages, and probability bounds of constraint violation were calculated to help the decision-maker make better choices regarding parameter choices to control robustness.

Alattas et al. (2011) emphasizes the production planning of a refinery being customarily developed as a linear model (LP). However, the nonlinearities of the original problem end up not being considered. Therefore, this article proposed a fractionation index model to add nonlinearity to the linear refinery planning models. The fractionation model is developed for the crude oil distillation, resulting in a simple model that optimizes the crude cuts and temperature. This approach predicted higher profit based on different crude purchase decisions.

Castillo et al. (2017) proposed a global optimization algorithm for solving oil refinery planning because nonlinear models are nonconvex, and traditional convex optimization techniques are not suitable if the global optimum is required. The formulation was a MINLP model. With relaxations in bilinear terms using McCormick, the problem results in a MILP model. Tight relaxations help to find a feasible solution to the original problem via a local nonlinear solver. The results compared the performance of two commercial solvers, BARON and ANTIGONE.

Unlike what is already published, this article interconnects production planning with hydrogen network management to produce hydrogen in a lean way and based on the existing network flexibility limitations. Initially, the model for the production planning was developed. Its resolution provides the used raw materials, the products and the hydrogen demand variation along a horizon. The hydrogen network is then re(designed) to achieve this variation with minimum cost. This is performed using a multi-scenario optimization model with a flexibility analysis in order to evaluate the feasible range of operation of the design. The elaboration of the multi-scenario model and the flexibility problem used in this work were developed and better described in Silva et al. (2021).

6.3 Refinery planning model

6.3.1 Refinery planning Problem Statement

The problem to be addressed for refinery planning can be stated as follows: given are (i) a set of crude oils *cr*, (ii) a set of oil cuts from distillation *cc*, (iii) a set of final products *cf*, (iv) a set of operating days in a month *t* and (v) a set of processes *p*, including distillation, hydrotreatment, catalytic reforming and delayed coking. The idea is to plan production based on the available oils and the required demand for final products. For this purpose, the intermediate processes between oil conversion and obtaining products should be considered: distillation, catalytic reform, hydrotreatments and delayed coking.

The oil derivates considered are liquefied petroleum gas (LPG_dd) from distillation, light naphtha (NL), heavy naphtha (NP), kerosene (K), light diesel (DL), heavy diesel (DP), light vacuum diesel (GLV), heavy vacuum diesel (GPV), and vacuum residue (RV).

For each crude oil is given the distillation yield for each distillation component *a(cr,cc),* the sulfur content *s(cr)* (% weight), density *d(cr)* and price *pr(cr,t).* The price used was reported as a parameter. However, its value is not fixed over time; it was considered price varying over time.

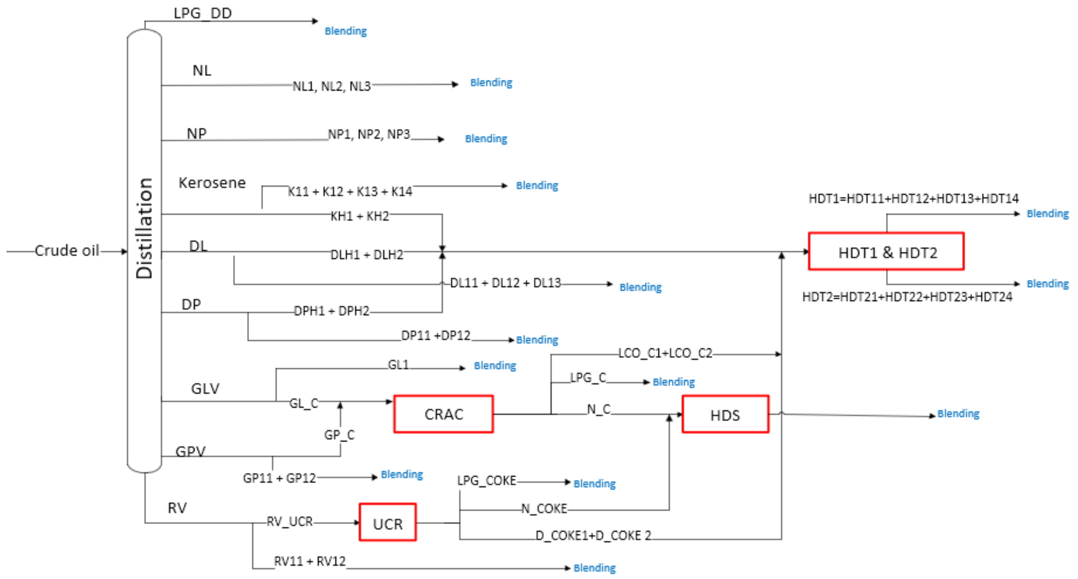
For the process units were considered the operating cost *op (p)*. Besides, the performance in removing sulfur in hydrotreatment units was necessary, and conversion of feed into products in catalytic reforming and delayed coking.

The final products considered are *LPG*, gasoline (GASO), petrochemical naphtha (NPTQ), diesel S-10 (S-10), diesel S-500 (S-500), fuel oil (OCB), asphalt (CAP), and jet fuel (QAV). For each final product was necessary the sales price *pf(cf)* and product quality specifications for products with sulfur content controlled *qs(cf)* (QAV, S10, S500, and OCB). These products are formed through blending with the different flowrates produced in refining.

A summary of the oil refining considered in this work is illustrated in Figure 6.1a. In this work, two diesel hydrotreatment units and one gasoline hydrodesulfurization unit were considered, in addition to a delayed coking unit and a catalytic cracking unit. The different crude oils are fed into the distillation unit, where the oil products are produced according to each yield. The LPG from distillation, light, and heavy naphtha flowrates are directed to the blending. The flowrate of light diesel, heavy diesel, and kerosene can go to the blending directly or pass through the hydrotreatment unit to remove sulfur. The light and heavy diesel flowrates can compose the blending and be fed into the catalytic cracking unit. In this process, cracked LPG, cracked naphtha, and light cycle oil are obtained. The vacuum residue can be part of the blending directly or feed the delayed coking unit, producing coke naphtha, coke diesel, and LPG. Hydro treatment units also process light cycle oil and coke diesel, and hydrodesulfurization unit processes coke naphtha and cracked naphtha to remove sulfur.

The final products are formed by mixing the different flowrates to achieve the specifications when necessary, as shown in Figure 6.1b.

a)



b)

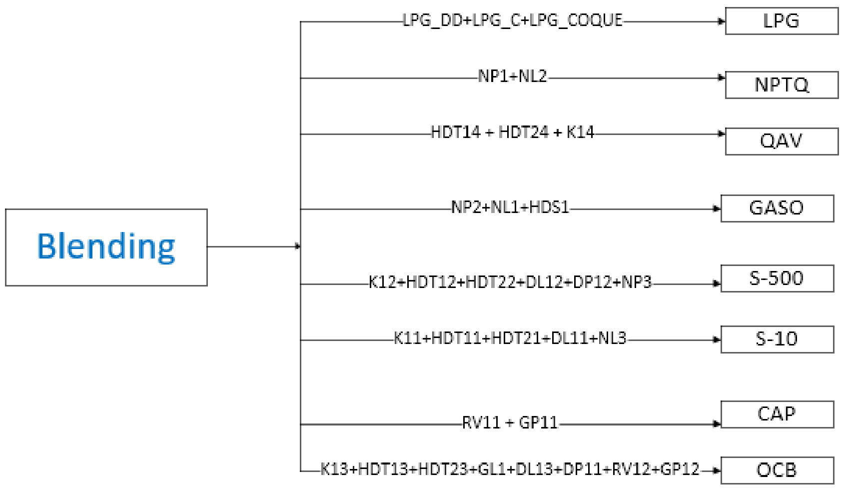


Figure 6.1: a) Oil refining scheme. b) Blending and formation of final products in a refinery.

6.3.2 Mathematical Formulation of the nonlinear planning model

The first material balance required is in the distillation unit, where crude oil is transformed into different fractions. The distillation material balance is described as follows:

$$u(cr,t) \times a(cr,cc) = z(cr,cc,t) \tag{6.1}$$

where $u(cr,t)$ are the flowrates of petroleum as a function of days, $a(cr,cc)$ are the yield of oil derivatives and $z(cr,cc,t)$ the quantity produced of each derivative as a function of oil and day. It is relevant to consider only the different derivatives regardless of the oil used since different types are processed.

$$\begin{cases} LPG_{DD}(t) = \sum_{cr} z(cr, 'LPG\_DD', t) \\ NL(t) = \sum_{cr} z(cr, 'NL', t) \\ NP(t) = \sum_{cr} z(cr, ' NP', t) \\ K(t) = \sum_{cr} z(cr, ' K', t) \\ DL(t) = \sum_{cr} z(cr, ' DL', t) \\ DP(t) = \sum_{cr} z(cr, ' DP', t) \\ GLV(t) = \sum_{cr} z(cr, ' GLV', t) \\ GPV(t) = \sum_{cr} z(cr, ' GPV', t) \\ RV(t) = \sum_{cr} z(cr, 'RV', t) \end{cases} \tag{6.2}$$

Where:
$LPG_{DD}(t)$ is the flow of LPG from distillation;
$NL(t)$ is light naphtha flowrate;
$NP(t)$ is heavy naphtha flowrate;
$K(t)$ is kerosene flowrate;
$DL(t)$ is light diesel flowrate;
$DP(t)$ is heavy diesel flowrate;
$GLV(t)$ is light vacuum diesel flowrate;
$GPV(t)$ is heavy vacuum diesel flowrate;
$RV(t)$ vacuum residue flowrate.

It is also essential to evaluate the sulfur level in the derivatives. For this, the mass fraction of sulfur $(ys(t))$ in each of the streams above is defined as:

$$\begin{cases} ys_{LPG_{DD}}(t) = \frac{\sum_{cr} z(cr, 'LPG'_{DD}, t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'LPG'_{DD}, t) \times d(cr)} \\ ys_{NL}(t) = \frac{\sum_{cr} z(cr, 'NL', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'NL', t) \times d(cr)} \\ ys_{NP}(t) = \frac{\sum_{cr} z(cr, 'NP', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'NP', t) \times d(cr)} \\ ys_{K}(t) = \frac{\sum_{cr} z(cr, 'K', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'K', t) \times d(cr)} \\ ys_{DL}(t) = \frac{\sum_{cr} z(cr, 'DL', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'DL', t) \times d(cr)} \\ ys_{DP}(t) = \frac{\sum_{cr} z(cr, 'DP', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'DP', t) \times d(cr)} \\ ys_{GLV}(t) = \frac{\sum_{cr} z(cr, 'GLV', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'GLV', t) \times d(cr)} \\ ys_{GPV}(t) = \frac{\sum_{cr} z(cr, 'GPV', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'GPV', t) \times d(cr)} \\ ys_{RV}(t) = \frac{\sum_{cr} z(cr, 'RV', t) \times s(cr) \times d(cr)}{\sum_{cr} z(cr, 'RV', t) \times d(cr)} \end{cases} \tag{6.3}$$

where $s(cr)$ is the sulfur content of each crude oil e $d(cr)$ density since the flow rates are volumetric and the sulfur content is in mass %.

As mentioned, each fraction derived from crude oil can be either part of the blending or go through processing units as imposed by the equations (6.4).

$$\begin{cases} NL(t) = NL1(t) + NL2(t) + NL3(t) \\ NP = NP1(t) + NP2(t) + NP3(t) \\ K = K11(t) + K12(t) + K13(t) + K14(t) + KH1(t) + KH2(t) \\ DL = DL11(t) + DL12(t) + DL13(t) + DLH1(t) + DLH2(t) \\ DP = DP11(t) + DP12(t) + DPH1(t) + DPH2(t) \\ GLV = GL1(t) + GL_{C(t)} \\ GPV = GP11(t) + GP12(t) + GP_{C(t)} \\ RV = RV11(t) + RV12(t) + RV\_UCR(t) \end{cases} \quad (6.4)$$

Where:
$NL1(t), NL2(t), NL3(t)$ are flowrates of light naphtha directed to blending;
$NP1(t), NP2(t), NP3(t)$ are flowrates of heavy naphtha directed to blending;
$K11(t), K12(t), K13(t), K14(t)$ are kerosene sent directly to blending;
$KH1(t), KH2(t)$ are the kerosene flowrates sent for hydro treatment;
$DL11(t), DL12(t), DL13(t)$ are flowrates of light diesel that make up the blending;
$DP11(t), DP12(t)$ are flowrates of heavy diesel that make up the blending;
$DLH1(t), DLH2(t)$ are flowrates of light diesel that are sent to hydro treatment;
$DPH1(t), DPH2(t)$ are flowrates of heavy diesel that are sent to hydro treatment;
$GL1(t), GP11(t), GP12(t)$ are light and heavy vacuum diesel directed to the blending;
$GL\_C_{(t)}$, $GP\_C(t)$ are light and heavy vacuum diesel that feeds the cracking unit;
$RV11(t), RV12(t)$ are vacuum residue flowrate;
$RV\_UCR(t)$ are vacuum residue flowrate that feeds the delayed coking unit.

The material balance at the input of the processing units is then the sum of the mentioned flowrates (equation 6.5).

$$\begin{cases} CRAC(t) = GL\_C(t) + GP\_C(t) \\ HDT1(t) = KH1(t) + DLH1(t) + DPH1(t) + DIESEL\_COQUE1(t) + LCO\_C1(t) \\ HDT2(t) = KH2(t) + DLH2(t) + DPH2(t) + DIESEL_{COQUE2(t)} + LCO_{C2(t)} \\ HDS(t) = NAFTA_{C(t)} + NAFTA_{COQUE(t)} \\ UDAV(t) = sum\big(cr, u(cr, t)\big) \\ UCR(t) = RV\_ucr(t) \end{cases} \quad (6.5)$$

Where:
$CRAC(t)$ is the sum of flowrates submitted to cracking;
$HDT1(t)$ and $HDT2(t)$ are flowrates of each hydrotreatment unit;
$DIESEL_{COQUE1(t)}, DIESEL_{COQUE2(t)}$ are diesel flowrates from delayed coking;
$LCO_{C1(t)}, LCO_{C2(t)}$ are the flowrates of light cycle gas from catalytic cracking;
$HDS(t)$ is the sum of the flows in the hydrodesulfurization unit;
$NAFTA_{C(t)}$ and $NAFTA_{COQUE(t)}$ are the flowrates of cracked naphtha and naphtha from delayed coking, respectively;
$UDAV(t)$ is the sum of all crude oil processed in the distillation unit; and,
$UCR(t)$ the flowrate that feeds the delayed coking unit.

According to the performance of the processing units, their products are calculated as shown in equation 6.6. The cracking feed flow is converted 20% into cracked LPG

$(GLP\_C(t))$, 55% in cracked naphtha ($NAFTA\_C(t)$) and 10% in light cycle gas ($LCO\_C1(t) + LCO\_C2(t)$) (Farah, 1996).

$$\begin{cases} GLP\_C(t) = 0.2 \times CRAC(t) \\ NAFTA\_C(t) = 0.55 \times CRAC(t) \\ LCO\_C1(t) + LCO\_C2(t) = 0.1 \times CRAC(t) \end{cases} \tag{6.6}$$

The flowrate of the delayed coking is converted 13% to naphtha ($NAFTA\_COQUE(t)$), 5% in LPG ($GLP\_COQUE(t)$), and 40% in diesel ($DIESEL\_COQUE1(t) + DIESEL\_COQUE2(t)$) (Farah, 1996).

$$\begin{cases} NAFTA\_COQUE(t) = UCR(t) \times 0.13 \\ GLP\_COQUE(t) = UCR(t) \times 0.05 \\ DIESEL\_COQUE1(t) + DIESEL\_COQUE2(t) = UCR(t) \times 0.4 \end{cases} \tag{6.7}$$

In hydrotreatment units, there is no conversion, only sulfur removal. Therefore, these units' outflow makes up the blending (4 streams from the Hydrotreating Unit 1, 4 streams from the Hydrotreating Unit 2, and a stream from the Hydrodesulfurization).

$$\begin{cases} HDT1(t) = (HDT11(t) + HDT12(t) + HDT13(t) + HDT14(t)) \\ HDT2(t) = (HDT21(t) + HDT22(t) + HDT23(t) + HDT24(t)) \\ HDS(t) = HDS1(t) \end{cases} \tag{6.8}$$

As there is a mixture of flowrates before the processing units, it is important to define the sulfur content in each unit's inlet and outlet flowrate.

$$y_{CRAC}(t) = \frac{GL_{C(t)} \times ys_{GLV(t)} + GP_{C(t)} \times ys_{GPV}(t)}{CRAC} \tag{6.9}$$

$$y_{UCR}(t) = ys_{RV}(t) \tag{6.10}$$

In the catalytic cracking and delayed coking unit, the sulfur content is not changed, so it is the same value at the inlet and outlet. In the case of delayed coking, as there is no mixing, the vacuum residue stream's sulfur content is the same as the unit's sulfur content. The purpose of hydrotreating units is to remove sulfur, so it is necessary to define the sulfur fraction in the inlet and outlet flowrate.

$$\begin{cases} y_{HDT1}(t) = \dfrac{KH1(t) \times ys_K(t) + DLH1(t) \times ys_{DL}(t) + DPH1(t) \times ys_{DP}(t) + DIESEL\_COQUE1(t) \times y_{UCR}(t) + LCO\_C1(t) \times y_{CRAC}(t)}{HDT1(t)} \\ y_{HDT2}(t) = \dfrac{KH2(t) \times ys_{K(t)} + DLH2(t) \times ys_{DL}(t) + DPH2(t) \times ys_{DP}(t) + DIESEL\_COQUE2(t) \times y_{UCR}(t) + LCO\_C2(t) \times y_{CRAC}(t)}{HDT2(t)} \\ y_{HDS}(t) = \dfrac{NAFTA\_C(t) \times y_{CRAC}(t) + NAFTA\_COQUE(t) \times y_{UCR}(t)}{HDS(t)} \end{cases} \tag{6.11}$$

At the output of each unit, it is essential to inform the yield as a parameter to calculate the residual sulfur content.

$$\begin{cases} y_{HDT1\_}s(t) = y_{HDT1}(t) \times (1 - rhdt1) \\ y_{HDT2\_}s(t) = y_{HDT2}(t) \times (1 - rhdt2) \\ y_{HDS\_}s(t) = y_{HDS}(t) \times (1 - rhds) \end{cases} \tag{6.12}$$

where $rhdt1, rhdt2$, and $rhds$ are the yields of each hydrotreatment unit. With this, the final products can be formed by mixing the different flows listed above. The blending that forms each product is described below.

The LPG flowrate obtained is:

$$LPG(t) = LPG\_DD(t) + LPG\_C(t) + LPG\_COQUE(t) \tag{6.13}$$

The flowrate of petrochemical naphtha is:

$$NPTQ(t) = NP1(t) + NL2(t) \tag{6.14}$$

The gasoline flowrate is:

$$GASO(t) = NL1(t) + HDS1(t) + NP2(t) \tag{6.15}$$

The jet fuel flowrate is:

$$QAV(t) = HDT14(t) + HDT24(t) + K14(t) \tag{6.16}$$

The diesel S10 flowrate is:

$$S10(t) = K11(t) + HDT11(t) + HDT21(t) + DL11(t) + NL3(t) \tag{6.17}$$

The diesel S500 flowrate is:

$$S500(t) = K12(t) + HDT12(t) + HDT22(t) + DL12(t) + DP12(t) + NP3(t) \tag{6.18}$$

The fuel oil flowrate is:

$$OCB(t) = K13(t) + HDT13(t) + HDT23(t) + GL1(t) + DL13(t) + DP11(t) + RV12(t) + GP12(t) \tag{6.19}$$

The asphalt flowrate is:

$$CAP(t) = RV11(t) + GP11(t) \tag{6.20}$$

Some of these products have the specified sulfur content, so this restriction should be included in the model for diesel s-10, diesel s-500, and fuel oil. The sulfur content of these products is defined as:

$$\begin{cases} y_{QAV}(t) = \frac{HDT14(t) \times y_{HDT1\_}s(t) \times d_{m_{HDT}} + HDT24(t) \times y_{HDT2\_}s(t) \times d_{m_{HDT}} \; K14(t) \times ys_K(t) \times d_{m_k}}{QAV(t) \times d_{QAV}} \\ y_{QAV}(t) \geq qs(QAV) \end{cases} \tag{6.21}$$

$$\begin{cases} y_{S10}(t) = \dfrac{\begin{gathered} K11(t)\times ys_{K(t)}\times d_{m_k} + HDT11(t)\times y_{HDT1\_s}(t)\times d_{m_{HDT}} + \\ HDT21(t)\times y_{HDT2\_s}(t)\times d_{m_{HDT}} + DL11(t)\times ys_{DL}(t)\times d_{m_{DL}} + NL3(t)\times ys_{NL}(t)\times d_{m_{NL}} \end{gathered}}{S10(t)\times d_{S10}} \\ y_{S10}(t) \geq qs(S10) \end{cases} \quad (6.22)$$

$$\begin{cases} y_{S500}(t) = \dfrac{\begin{gathered} K12(t)\times ys_{K(t)}\times d_{m_k} + HDT12(t)\times y_{HDT1_{s(t)}}\times d_{m_{HDT}} + \\ HDT22(t)\times y_{HDT2\_s}(t)\times d_{m_{HDT}} + DL12(t)\times ys_{DL(t)}\times d_{m_{DL}} + DP12(t)\times ys_{DP(t)}\times d_{m_{DP}} + \\ Np3(t)\times ys_{NP}(t)\times d_{m_{NP}} \end{gathered}}{S500(t)\times d_{S500}} \\ y_{S500}(t) \geq qs(S500) \end{cases} \quad (6.23)$$

$$\begin{cases} y_{OCB}(t) = \dfrac{\begin{gathered} K13(t)\times ys_{K(t)}\times d_{m_k} + HDT13(t)\times y_{HDT1_{s(t)}}\times d_{m_{HDT}} + HDT23(t)\times y_{HDT2_{s(t)}}\times d_{m_{HDT}} \\ HGL1(t)\times ys_{GLV}(t)\times d_{m_{GLV}} + DL13(t)\times ys_{DL(t)}\times d_{m_{DL}} + DP11(t)\times ys_{DP(t)}\times d_{m_{dp}} \\ RV12(t)\times ys_{RV}(t)\times d_{m_{RV}} + GP12(t)\times ys_{GPV}(t)\times d_{m_{GPV}} \end{gathered}}{OCB(t)\times d_{OCB}} \\ y_{OCB}(t) \geq qs(OCB) \end{cases} \quad (6.24)$$

where d is the respective density of each fraction, entered as a parameter in the model. The purpose of a refinery's production planning is to obtain the highest profit. Therefore, the objective function of this optimization problem is defined as:

$$profit = \sum_t vf\_sales(t) - \left(\sum_t u_{price}(t) + UDAV_{cost}(t) + HDT1_{cost}(t) + HDT2_{cost}(t) + HDS_{cost}(t) + CRAC_{cost}(t) + UCR_{cost}(t))\right) \quad (6.25)$$

$$vf\_sales(t) = LPG(t) \times pf + S10(t) \times pf + S500(t) \times pf + GASO(t) \times pf + NPTQ(t) \times pf + CAP(t) \times pf + OCB(t) \times pf + QAV(t) \times pf \quad (6.26)$$

$$u\_price(t) = \sum_{cr} u(cr,t) \times pr(cr,t) \quad (6.27)$$

$$\begin{cases} UDAV_{cost}(t) = UDAV(t) \times op \\ HDT1_{cost}(t) = HDT1(t) \times op \\ HDT2_{cost}(t) = HDT2(t) \times op \\ HDS_{cost}(t) = HDS(t) \times op \\ CRAC_{cost}(t) = CRAC(t) \times op \\ UCR_{cost}(t) = RV\_UCR(t) \times op \end{cases} \quad (6.28)$$

Where:
vf_sales is the total sales value of the products;
pf is the sales value of each final product;
$u\_price(t)$ is the total cost of crude oil;
$UDAV_{cost}(t)$ the total cost of distillation;
$HDT1_{cost}(t), HDT2_{cost}(t)$ and $HDS_{cost}(t)$ the total costs of hydrotreating;
$CRAC_{cost}(t)$ the total cost of the catalytic cracking unit;
$UCR_{cost}(t)$ the total cost of the delayed coking unit;
op is the cost of each processing unit depending on the quantity to be processed;
$pr(cr)$ is the cost of each crude oil type.

6.4 Mathematical programming approach for hydrogen networks

The use of mathematical programming for hydrogen network optimization is very recurrent. Through the development of linear (LP) and nonlinear (NLP) formulations, it is possible to represent the hydrogen network and its constraints. Hydrogen networks are composed by hydrogen sources (such as hydrogen-generating units - UGH), hydrogen-consuming units (typically hydrotreatment units), and hydrogen purification units (commonly Pressure Swing Adsorption – PSA units). In addition, other constraints as pressure level, compressor capacity, and existing lines and equipment units are considered in the optimization in the case of a redesign. The choice of the objective function is a crucial step. It is usually associated with minimizing operating costs or annual costs (including operating and capital costs). In this case, it may be necessary to install new equipment to improve the network performance, such as new lines, compressors, and even purification units. As new equipment can be considered, the problem then becomes MILP or MINLP. So, network management can be applied to an existing fixed topology or develop a new hydrogen network design through mathematical modeling.

As described in Silva et al. (2021), the formulation should describe the hydrogen network through material balance in the units, according to the hydrogen demand required by consumers. This demand may vary according to several factors, such as crude oil type and the demand for specific products.

Therefore, it is essential to consider the uncertainties during hydrogen network design to ensure that the resulting network will operate in all possible scenarios and operating conditions within the uncertainty region. In this case, the network is called flexible. In general, the term *flexibility* is defined as the ability of a process to function correctly under a specific range of uncertain conditions, and it is one of the most critical components in the operability of chemical plants (Grossmann and Floudas, 1987; Reza et al., 2016).

A systematic approach that represents an optimal design in the hydrogen network and the flexibility with which it needs to operate is vital to cost reduction and efficient resource usage. The hydrogen network is defined from a superstructure and modeled according to all constraints involved. The central differential in this work is the inclusion of different operating scenarios focused on the variation of the hydrogen demand of the consuming units. For this, a linear model (MILP) and a nonlinear model (MINLP) were developed based on mathematical programming to optimize the hydrogen network to find an optimal and flexible design.

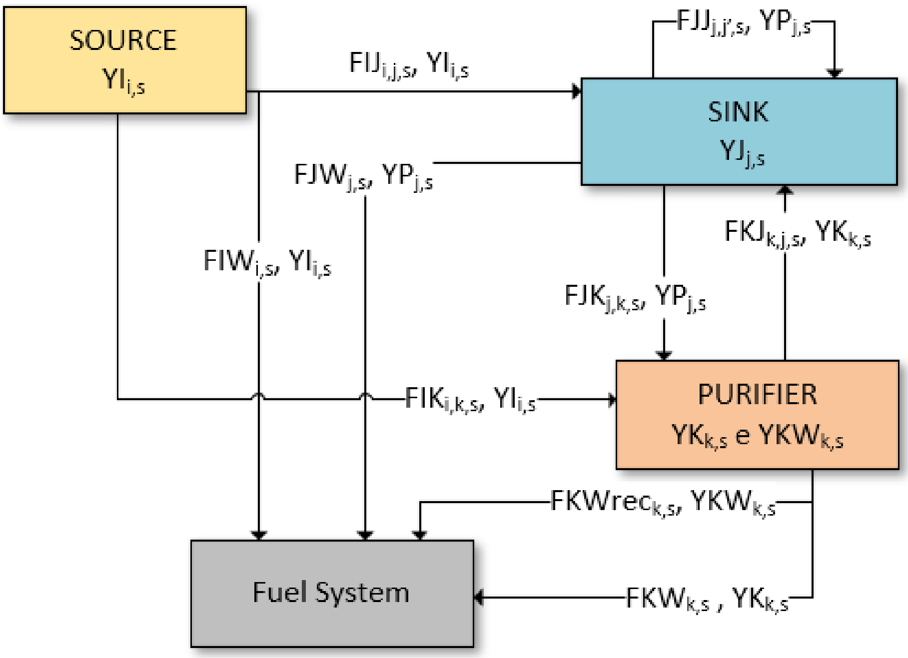
The MINLP problems are more challenging for solving because they combine the NLP and MILP models and their characteristics. However, they allow a more rigorous representation including several additional restrictions and hence they result in more realistic networks a. Linear modeling has advantages over nonlinear modeling, such as the guarantee of obtaining the global optimum, ease of resolution, and convergence. The initialization strategy, where the nonlinear model is initialized with the result obtained from the linear is a competitive alternative used to facilitate resolution and obtain even better results (SILVA et al., 2020).

6.4.1 Hydrogen Network Design - Problem Statement

The problem to be addressed in this paper can be stated as follows: (i) a set of sources i ϵ hydrogen sources (HS), (ii) a set of consumers j ϵ hydrogen consumers (HC), and (iii) a set of purifiers k ϵ hydrogen purifiers ($HP = OHP \cup NHP$), considering the existing purifiers, OHU, and the new purifiers, NHP , in each scenario given by the set of scenarios s ϵ scenarios (S). Figure 6.2 shows the two superstructures considered in this problem for the linear formulation (Figure 6.2a) and the nonlinear formulation (Figure 6.2b).

In the case of nonlinear formulation, there is still a set of compressors c ϵ hydrogen compressors ($HCP = OHCP \cup NHCP$), considering the existing compressors $OHCP$ and new compressors $NHCP$. In the nonlinear model, the compressors are considered independent units that may connect units that need compression, so the compressor's inlet and outlet pressure and the hydrogen composition in the compressor are variables. This model's only nonlinearity arises in the hydrogen balance in the inlet of the compressors' product flow /purity.

a)



b)

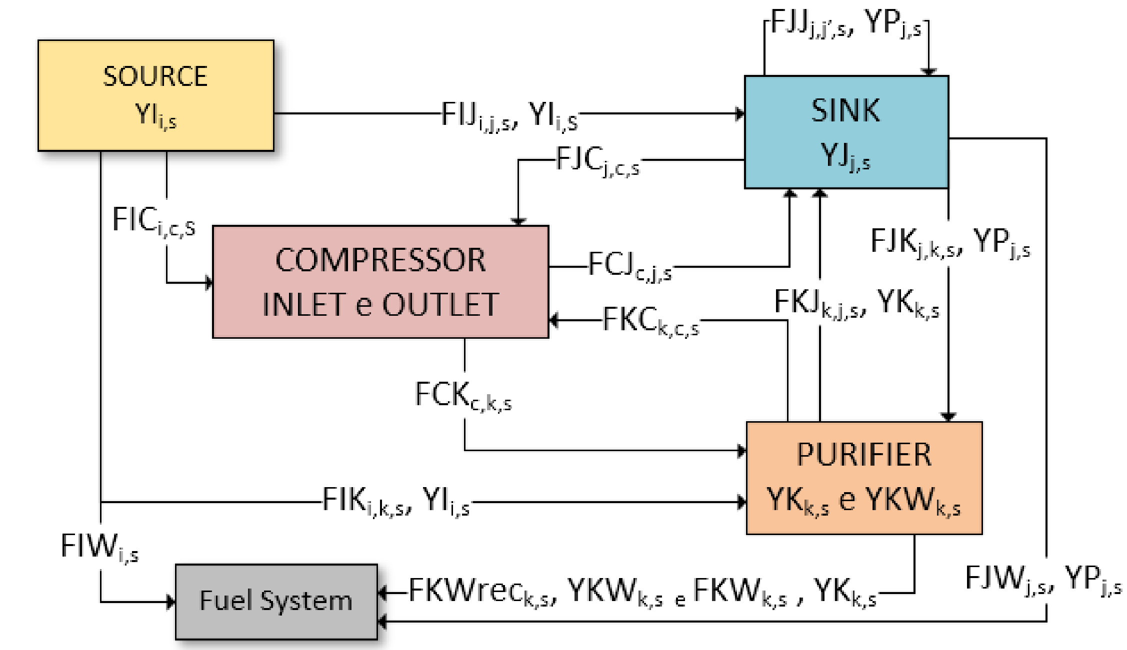


Figure 6.2: (a) Scheme of the Superstructure developed for MILP problem. (**b)** Scheme of the Superstructure developed for MINLP problem.

Each source is given the maximum and minimum flowrate, the hydrogen composition, and the outlet pressure. Each consumer is given the inlet flowrate demand, pressure, composition, outlet purge flow, pressure, and composition. Each purifier is given the maximum flow capacity, the composition of purified flowrate and purge flowrate, the pressure of purification, and the hydrogen recovery. It is also considered a fuel system in which waste streams can be burned and used as fuel. The existing networks are also given the existing lines (unit connections), the distance between the units if informed, and the existing compressors (capacity and pressures) and purifiers.

The optimization problem is subject to material balances and process operating constraints. The global balance and hydrogen material balance are applied to all units involved. Besides, in PSA, it is necessary to take into account the purification efficiency of hydrogen recovery. Uncertainty was added to the parameter that calculates the hydrogen consumed, based on each consuming unit's required demand. Since the purity is constant, allowing flexibility in this parameter means that consumer demand and purge flow may vary. The uncertainty is then added to a percentage of interest on the nominal value.

For the retrofit case, process modifications are allowed to reduce the total operating costs (the objective function), despite the investment costs due to the installation of new pipelines, compressors, and possibly new purifiers. To consider the capital cost associated with new equipment, it was necessary to use constraint modeling through logical propositions and disjunctions, so binary variables and logical inequality equations were included in the model with binary parameters.

Because the objective function is to minimize the operational cost, it is necessary to identify its costs. Operating costs include the production of hydrogen, the cost of electricity used in compressors, the purifying units' operating cost, and the economic value corresponding to the fuel system's burning gas. It is also essential to consider the hydrogen network's annual total cost formed by the operating cost and capital cost. The capital cost includes the cost of new compressors, new purification units, and new pipelines. It is essential to highlight that the capital cost was calculated as an average cost, assuming the same probability of all scenarios. In the case of different probabilities, a weighted average should be considered. Each scenario's capital cost has an associated investment proportional to the flow rate.

The detailed description of the linear and nonlinear formulation and the entire equation system is described in our previous work (Silva et al., 2021). It should be noted that the two formulations are used, linear and nonlinear because a new methodology called Virtual Compressors was proposed combined with an initialization strategy. The initialization technique used was also validated in case studies of previous studies and consisted of the result obtained from linear optimization provided as initialization of nonlinear optimization. It improves the optimization problem's processing time and facilitates convergence (Silva et al., 2020). The limitation found in using the linear model instead of the nonlinear model is mixing different flowrates in the compressors before the units. As proposed and better described in Silva et al. (2020), this limitation can be mitigated using the Virtual Compressor Analysis technique (VCA). Thus, there is a reuse of existing compressors and a reduction in the cost of capital.

6.4.2 Flexibility

The flexibility of a network is related to its ability to operate under different conditions, including the operation scenarios used in multi-scenario optimization. Given the importance of the production and efficient use of hydrogen, it is essential that working with an optimal and flexible hydrogen network capable of operating under different scenarios. Scenarios are related to process uncertainties, in this case, uncertainties in hydrogen consumption in hydrotreatment units. Flexibility can be evaluated for either the original network or retrofit. The installation of new equipment and connections increases flexibility in this case.

The full definition and formulation of the problem to solve the degree of flexibility are detailed in (Silva et al., 2021). Swaney and Grossman (1985) proposed the solution of the optimization problem for the definition of the flexibility index :

$$F = \max\ \delta$$
$$\left\{ \begin{array}{l} s.t.\ \psi(d,\theta) = 0 \\ \quad \psi(d,\theta) = \min u \\ \quad s.t\ \ h_i\ (d,z,x,\theta) = 0 \\ \quad\quad g_j\ (d,z,x,\theta) \le u \\ \quad\quad T(\delta) = \{\ \theta \mid \theta^N - \delta\Delta\,\theta^- \le \theta\ \le\ \theta^N +\ \delta\Delta\,\theta^+\} \end{array} \right. \tag{6.29}$$

where F is the flexibility index (a positive scalar variable), δ is a positive auxiliary variable and $T(\delta)$ is a scaled hyperrectangle according to the uncertainty region. d are the design variables (binary), z are the independent variables (degrees of freedom), x are the dependent variables, θ are the uncertain parameters, and u is a scalar free auxiliary variable allowing the relaxation of the inequality constraints. $\psi(d,\theta)$ is the feasibility function for a given design (fixed d) and a given realization of the uncertain parameters (fixed θ). The T region is defined by the maximum ($\Delta\,\theta^{+}$) and minimum deviation ($\Delta\,\theta^{-}$) from the nominal conditions (θ^{N}) for each uncertainty parameter θ.

The geometric interpretation of the flexibility index is presented in Figure 6.3. The value of F corresponded to the maximum hyperrectangle centered in the nominal condition. It is scaled according to the uncertainty region that can be inscribed within the feasible region. For this illustration, the hyperrectangle $T(\delta = F)$ contains the region T, and hence, the region T is inside the feasible region. The flexibility index would return a value greater than one. For $F < 1$, $T(\delta = F)$ is contained in T, and the design is not flexible since some region of T cannot find feasible operation. For $F \geq 1$, $T(\delta = F)$ contains T (strictly the same hyperrectangle for $F = 1$), and the design reaches feasible operation for all T, so it is flexible.

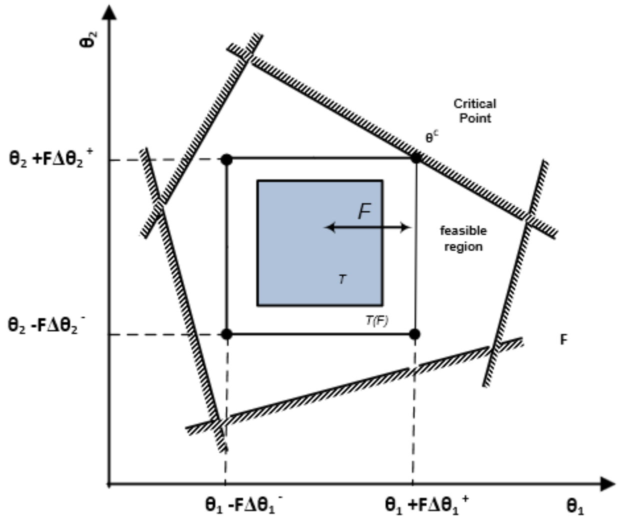


Figure 6.3: Geometric interpretation of feasibility index (Aragão, 2011).

The flexibility problem is solved for a fixed design, and its solution provides the maximum level of uncertainty in which the design can operate. Using the Vertex Enumeration strategy, this level is searched for all vertices direction. It is defined as the smallest one. This is the critical direction with a corresponding critical vertex. Since it is desired the operation within the uncertainty region, critical directions may be used to update the scenarios to the multi-period optimization problem to ensure the operation in these scenarios. This procedure will increase the cost of the design but also the level of flexibility.

6.5 Proposed framework

The methodology developed in this work can be divided into three components: production planning, multi-scenario optimization, and flexibility analysis. The objective is to interconnect all the steps to increase the refinery profit according to the efficient and economic hydrogen production to attend the varying demand. If some investment cost is allowed, the hydrogen network is redesigned to accomplish the hydrogen demand with minimum cost. On the order hand, the constraint imposed by the fixed network topology is taken into account the refinery production planning.

Following the description carried out in Section 3, production planning is based on the characteristics, and crude oils reported. The optimization, aiming at the highest profit, provides the amount processed in the hydrotreatment (HDT1, HDT2, and HDS) as one of the results, as shown in Figure 6.4a, step 1. It is necessary to use literature references to relate this information to the amount of hydrogen needed to remove sulfur from the products. According to Brasil et al. (2012), the typical operating ratios related to the amount of hydrogen ($H_2\ flowrate$) and hydrotreatment units flowrate ($HDT\ flowrate$) are described in Table 6.1.

Table 6.1: Volumetric ratio in hydrotreatment units.

	Volumetric ratio in CNTP
Direct distillation naphtha	$60\ \frac{H_2\ flowrate}{HDT\ flowrate}$
Kerosene	$80\ \frac{H_2\ flowrate}{HDT\ flowrate}$
Diesel	$140\ \frac{H_2\ flowrate}{HDT\ flowrate}$
Vacuum diesel	$210\ \frac{H_2\ flowrate}{HDT\ flowrate}$
Residue	$> 525\ \frac{H_2\ flowrate}{HDT\ flowrate}$

Once solve the production planning, the amount of hydrogen is calculated based on this information and the flowrates that make up the HDT, according to Figure 6.1b. Through the project's nominal value, it is possible to establish the time horizon variations. In addition to determining the most extensive and smallest variation found, the calculation of different scenarios is provided due to production planning.

Once the scenarios have been identified, it is possible to propose a network redesign, through multi-scenario optimization, that meets the required amounts of hydrogen identified. The goal is to obtain a competitive redesign in terms of operating cost, which justifies the investment and can meet greater demands, as shown in Figure 6.4a step 2. For this, the flexibility of redesign must also be analyzed (Figure 6.4a step 3).

Based on all the costs involved in managing the hydrogen network, annual operating costs are defined as:

$$C_{operating} = \frac{\sum_S (CH2I_S + CH2K_S + CH2C_S - CH2F_S) * t}{NS} \quad (6.30)$$

where NS is the number of scenarios, $CH2I_S$ is the cost of producing hydrogen based on the flow of UGH, $CH2K_S$ is the cost of hydrogen purification, based on the flow that processed in PSA, $CH2C_S$ is the cost of electricity related to the need for the use of compressors and $CH2F_s$ is the corresponding cost of burning the hydrogen surplus, based on the amount of hydrogen and methane in the fuel gas.

Parallel to this, it is necessary for an existing network design to verify the current network's uncertainty level by running the flexibility index problem, as shown in Figure 6.4b. The objective is to evaluate whether the original network can meet the hydrogen variation imposed by production planning. For this, the largest and the smallest variation of hydrogen consumption obtained is used. If the flexibility (F) obtained is less than 1, the current network cannot operate with the necessary hydrogen demands. In this case, the next step is to use the flexibility (F) obtained to limit the variation of hydrogen, forcing that a new production planning is obtained and that it can be established within the range in which the current network operates. To obtain the range of hydrogen variation supported by the current network, it is necessary to recalculate the hydrogen consumption served by the flexibility obtained.

With this, both the original network and the redesign can be evaluated for operational cost and flexibility (these results are represented in green and orange in Figure 6.4). Besides, the profit obtained in production planning is also an essential aspect of analysis. The most relevant is that the chosen hydrogen network, redesigned or original, can meet the demand imposed by production planning with the highest possible profit. Figure 6.4 summarizes the proposed framework.

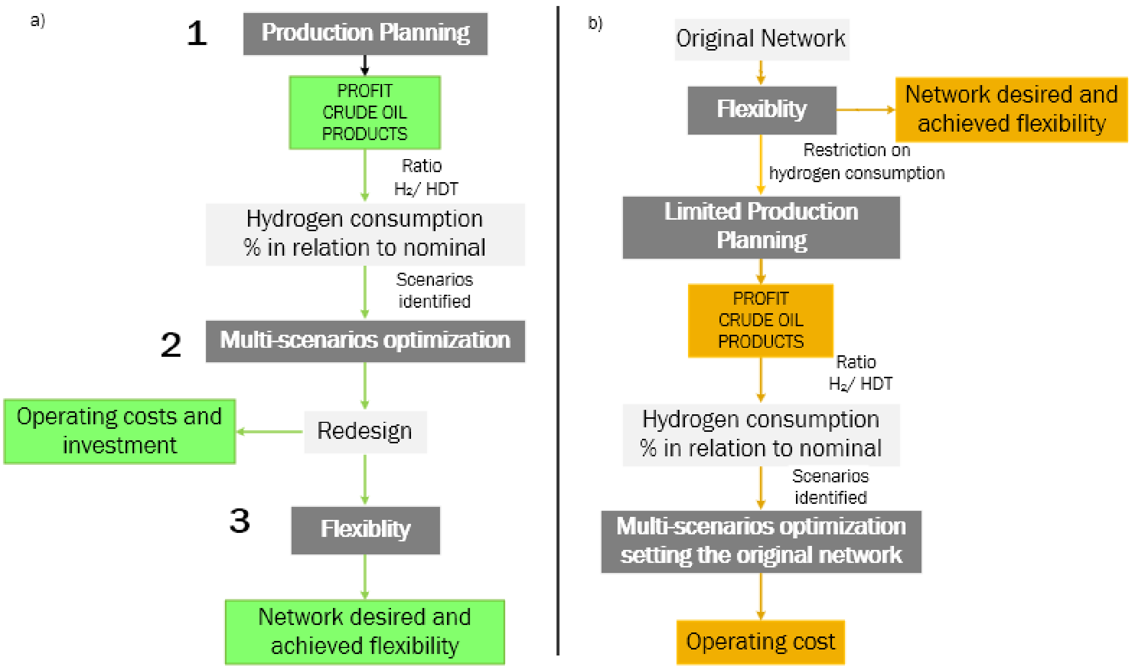


Figure 6.4: Summary of the proposed methodology. a) Methodology developed for the redesign. b) Methodology applied to the existing network.

6.6 Results

The proposed systematic approach was validated using a real case study of a Brazilian Refinery. The production planning and mathematical programming models were implemented in the modeling system GAMS on a 3.6 GHz Intel® Core ™ I7 CPU. In mathematical programming models, the solver used to solve the MILP model was CPLEX and MINLP, BARON. The solver used in the NLP model for production planning is also

BARON (GAMS, 2019). Other solvers such as CONOPT and SBB were tested, but the most satisfactory results were obtained with the selected solvers.

As described in section 6.3, the refinery model chosen to develop production planning in this case study has a distillation unit (UDAV), a cracking unit (CRAC), a delayed coking unit (UCR), two diesel hydrotreatment units (HDT 1 and 2) and a gasoline hydrodesulfurization unit (HDS). The hydrogen network responsible for providing the hydrogen for HDT 1, 2, and HDS units has two hydrogen sources and two purification units, as shown in Figure 6.5. For reasons of confidentiality of the information, the values of pressure, purity and flows were omitted in the figures.

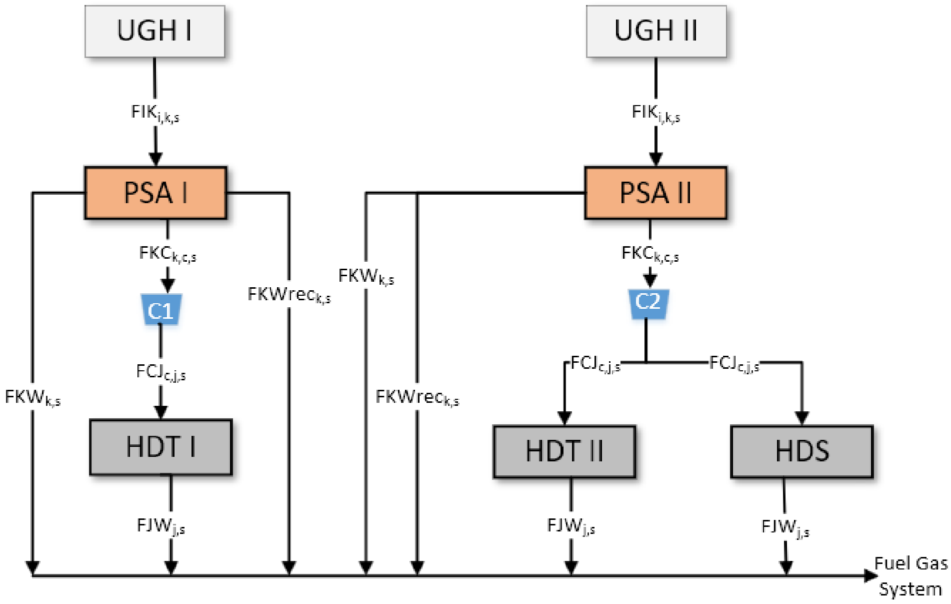


Figure 6.5: Existing hydrogen network in Brazilian refinery.

6.6.1 Methodology developed for the redesign

<u>5.1.1 Production planning</u>

The parameters informed for solving the optimization problem are described in Tables 6.2, 6.3, 6.4, and 6.5. The time horizon chosen was 30 days.

Table 6.2: Information about selected crude oils. Source: Bueno (2003).

Crude oil	Sulfur Content (% weight)	Density (kg/L)
Albacora	0.44	0.9
Bonny light	0.14	0.9
Marlim	0.77	0.9
Condensado Argelino	0.002	0.9
Roncador	0.585	0.9
Lula	0.35	0.9

Table 6.3: Derivatives yield for each selected crude oil and density. Source: Farah (1996).

	Albacora	Bonny light	Marlim	Condensado Argelino	Lula	Roncador	Density (kg/L)
LPG (%)	2	1	0	3	1.5	2	0.75
Light Naphtha (%)	6	10	4	42	10	2.5	0.8
Heavy Naphtha (%)	6	8	4	39	12	14	0.8
Kerosene (%)	18	27	14	10	12	12	0.8
Light Diesel (%)	10	25	9	4	12	12	0.8
Heavy Diesel (%)	10	6	9	1	12	6.4	0.8
Light vacuum diesel (%)	13	4	14	0.5	10	14.2	0.9
Heavy vacuum diesel (%)	13	14	14	0.5	8	8.9	0.9
Vacuum residue (%)	22	5	31	0	22.5	28	1.0

Table 6.4: Information about the final products needed for optimization. Source: ANP (2020).

Final products	Price ($/bbl)	Product quality specifications- sulfur content (% weight)	Density (kg/m³)
LPG	50	-	-
GASO	30	-	-
NPTQ	70	-	-
QAV	51	0.3	800
S10	43	0.001	840
S500	43	0.05	840
CAP	60	-	-
OCB	36	1	1001

Table 6.5: Performance in removing sulfur from hydrotreating units. Source: Farah (1996).

	Sulfur removal (% vol)
HDT I	0.997
HDT II	0.997
HDS	0.99

In the production planning model described in section 6.3, some limits and restrictions are necessary to solve the optimization problem. The upper limit of the sulfur content in the final products follows the specifications required by the ANP (% weight), and the lower limit was chosen by the authors (ANP, 2020).

$$\begin{cases} y_{QAV}(t) \leq qs(QAV) \\ y_{QAV}(t) \geq 0 \end{cases} \quad (6.30)$$

$$\begin{cases} y_{S10}(t) \leq qs(S10) \\ y_{S10}(t) \geq 0 \end{cases} \quad (6.31)$$

$$\begin{cases} y_{S500}(t) \leq qs(S500) \\ y_{S500}(t) \geq 0 \end{cases} \quad (6.32)$$

$$\begin{cases} y_{OCB}(t) \leq qs(OCB) \\ y_{OCB}(t) \geq 0 \end{cases} \quad (6.33)$$

The upper processing limit in the distillation unit and other units is defined below in bbl/day (Barros, 2014; Petrobras, 2019). The lower limit was chosen.

$$\{UDAV\ (t) \leq 198400\ bbl/day \quad (6.34)$$

$$\begin{cases} HDT1(t) \geq 20000\ \ bbl/day \\ HDT1(t) \leq 35000\ \ bbl/day \end{cases} \quad (6.35)$$

$$\begin{cases} HDT2(t) \geq 33000\ \ bbl/day \\ HDT2(t) \leq 40000\ \ bbl/day \end{cases} \quad (6.36)$$

$$\{HDS(t) \leq 30000\ \ bbl/day \quad (6.37)$$

$$\begin{cases} UCR(t) \geq 5000\ \ bbl/day \\ UCR(t) \leq 17000\ \ bbl/day \end{cases} \quad (6.38)$$

$$\begin{cases} CRAC(t) \geq 12000\ \ bbl/day \\ CRAC(t) \leq 46000\ \ bbl/day \end{cases} \quad (6.39)$$

ANP database provides the monthly production at each refinery [3]. The upper limit of the final products is defined in Table 6.6. These data correspond to May/2020. For this, new variables corresponding to the sum of the final products over time were created.

$$\begin{cases} GASO = \sum_t GASO(t) \\ QAV = \sum_t QAV(t) \\ S10 = \sum_t S10(t) \\ S500 = \sum_t S500(t) \\ CAP = \sum_t CAP(t) \\ NPTQ = \sum_t NPTQ\ (t) \\ OCB = \sum_t OCB(t) \\ LPG = \sum_t LPG(t) \end{cases} \quad (6.40)$$

Table 6.6: Production limit of petroleum products. Source: ANP (2020).

Final products	Upper limit (bbl)	Lower limit (bbl)
LPG	363,226	242,151
GASO	1,272,240	848,160
NPTQ	215,760	143,840
QAV	115,940	77,293
S10	772,520	515,013
S500	1,706,249	1,137,493
CAP	172,595	115,063
OCB	95,641	63,760

The model has 3699 single equations and 4749 single variables, and the time resource usage for the solution was 41 minutes. The initialization of the quantity of products was performed based on the values of Table 6.6, considering daily values. The capacities of the processing units were initialized with values close to the upper limit, $HDT1(t)$=33000, $HDT2(t)$ =38000, $HDS(t)$ =30000, $CRAC(t)$ =46000, $UCR(t)$ =17000. The production planning optimization results are mainly the oil types chosen among the informed ones, their daily flows, the daily flow of products, the daily flow processed in the HDT's and HDS, and the profit. The optimization using the parameters and constraints listed above provided a locally optimal response, and the profit obtained was 4.7812x10^7 \$/day. The crude oils chosen were Bonny Light, Algerian, and Marlim.

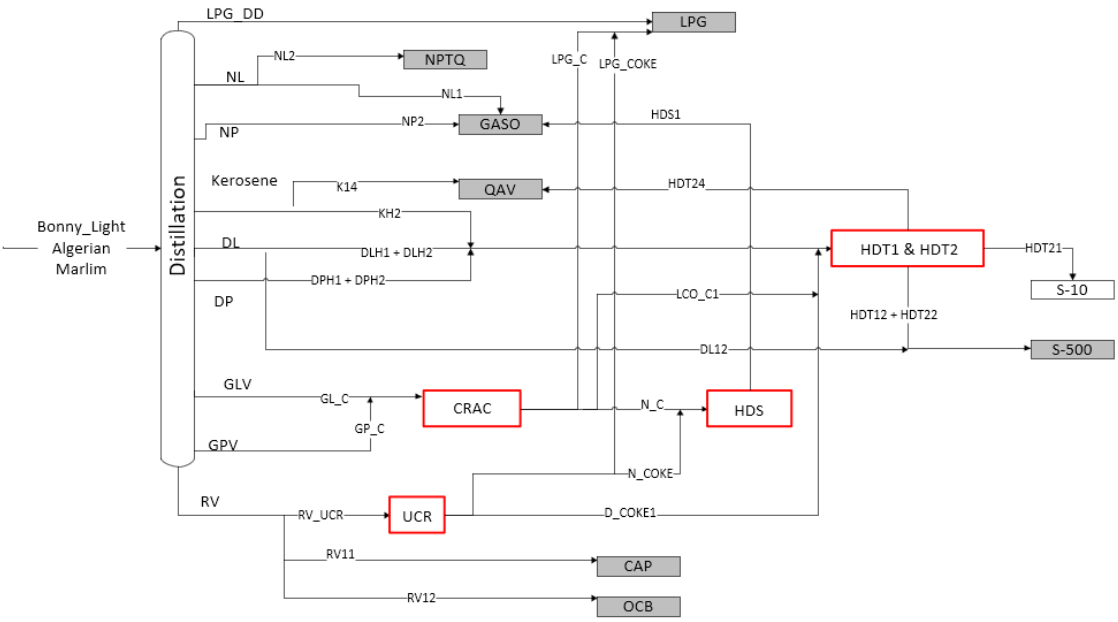
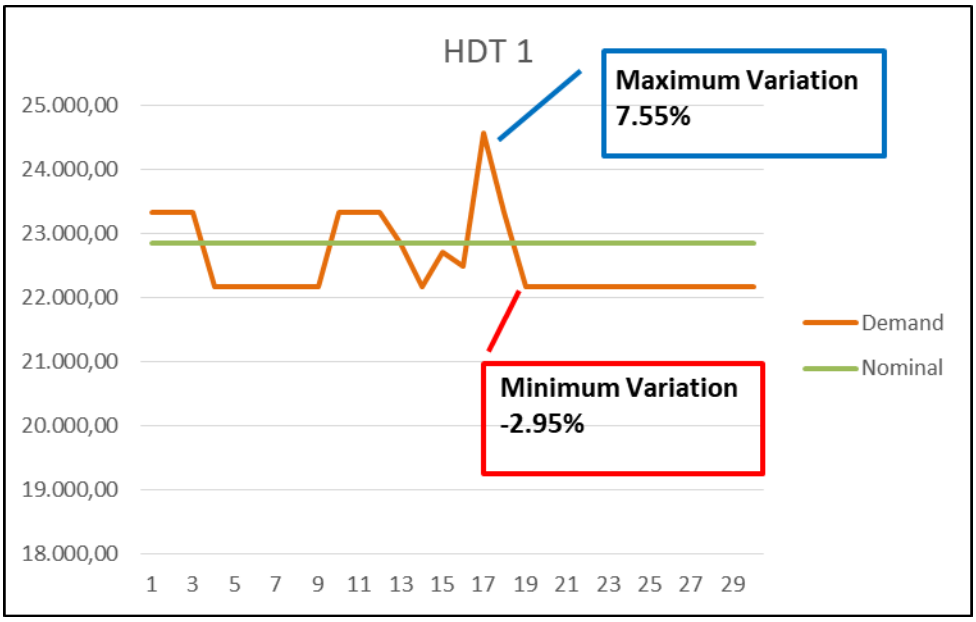


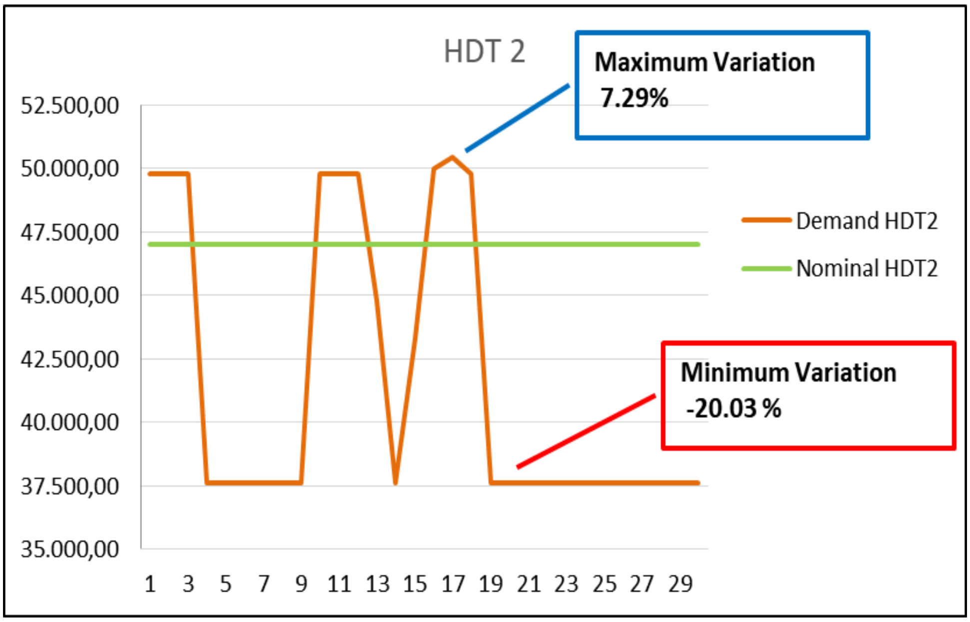
Figure 6.6: Production planning optimization results in terms of blending.

Using the relationship reported in Table 6.1, it was possible to calculate the amount of required hydrogen over the 30 days from the flowrates directed to the HDT's and HDS (Figure 6.7). A nominal value was calculated to obtain the maximum and minimum hydrogen variation, referring to the production planning solved only for one day of operation. For this, the information in Table 6.6 was considered daily and not monthly, with the other parameters listed above. Through this daily planning, it was possible to obtain the hydrogen demand in HDT's and HDS, which was considered as the nominal value for the following analyses.



a)

b)



c)

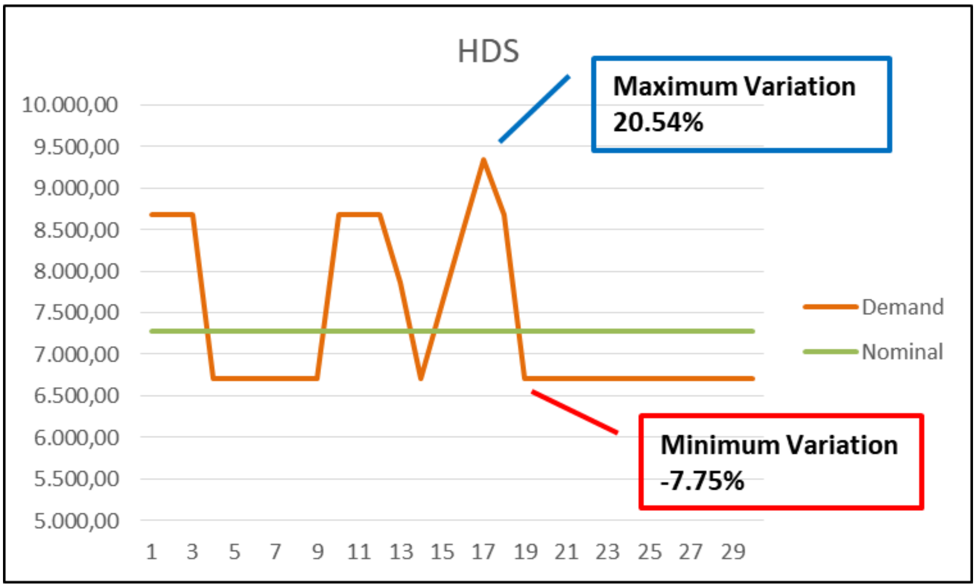


Figure 6.7: Hydrogen demand in Nm^3/h over the 30 days and maximum and minimum variation in relation to the nominal. a) HDT1. b) HDT2. c) HDS.

6.5.1.2 Multi-scenarios optimization

It was possible to determine the most significant positive and negative variation concerning the nominal one through the demands obtained. The variation was then applied to the project's nominal value, thus obtaining the hydrogen demand through the correct nominal. The different operating scenarios were identified over the 30 days, based on hydrogen demand in the three different consumers and their frequency. The frequency in which scenarios are repeated over the period is important for the cost calculation to be proportional, that is, this frequency is considered when calculating the costs and profit of production planning. It is shown in Table 6.7.

Table 6.7: Scenarios obtained in production planning.

		HDT2	HDT1	HDS	
Scenarios	**NOMINAL (Nm^3/h H_2)**	39,015.00	19,507.00	5,814.00	Frequency
	Scenarios 1 **(Nm^3/h H_2)**	31,198.36	18,932.12	5,363.65	3.80
	Variation %	-20.03	-2.95	-7.75	
	Scenarios 2 **(Nm^3/h H_2)**	35,956.14	19,401.89	6,100.44	0.20
	Variation %	-7.84	-0.54	4.93	
	Scenarios 3 **(Nm^3/h H_2)**	37,160.60	19,520.82	6,286.95	0.20
	Variation %	-4.75	0.07	8.13	
	Scenarios 4 **(Nm^3/h H_2)**	41,498.51	19,215.29	6,785.55	0.20
	Variation %	6.37	-1.50	16.71	
	Scenarios 5 **(Nm^3/h H_2)**	41,859.68	20,979.78	7,473.58	1.60
	Variation %	7.29	7.55	28.54	

Through mathematical programming, the mass balance between the units involved was performed, including the necessary pressure constraints, as described in session 6.4.1. For the resolution of the MILP and MINLP model in the multiscenario version, the parameters of the case study network, pressure and purity were used, in addition to the scenarios identified in Table 6.7. This optimization aims to obtain a redesign of the hydrogen network by minimizing the operational cost but allowing investment in new pipelines. The parameters used and the entire equation system are detailed in (Silva et al., 2021).

First, the linear model was solved, and its solution was used as initialization for the nonlinear model (MINLP). MINLP formulation has 4144 single equations, 2026 single variables, and 1223 discrete variables. The resource usage was 4940 seconds. The solver used was the Baron and the solution obtained is an optimal solution. This redesign includes the installation of 3 new pipelines. Figure 6.8 shows the proposed redesign. The redesign included new lines with recycle in the compressors and interconnection between PSAI and HDS. The redesign's operating cost is 32.724 million $/year, and the corresponding cost of the new lines depends on the distance between units. However, it has been estimated at 0.014 million $.

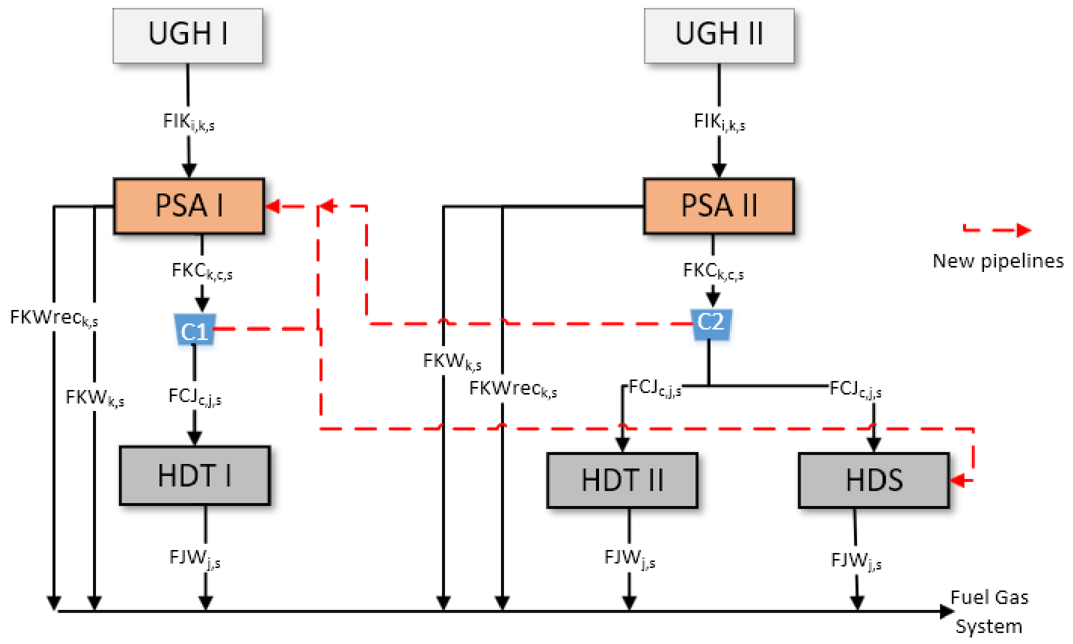


Figure 6.8: Redesign obtained through multi-scenario optimization.

6.5.1.3 Flexibility

The next step was to evaluate the proposed redesign's flexibility to identify the demand met by this network. For this, it is necessary first to define hydrogen consumption and its formulation in the flexibility problem. The hydrogen consumption ($H_2\_c_V$) is defined according to the equation:

$$H_2\_c_V = H_2\_cn_j * \left(1 + VI_{V,j} * \delta\right) \tag{6.41}$$

$H_2\_cn_j$ is the nominal hydrogen consumption, and δ is a positive auxiliary variable used for the flexibility problem. For each vertex, a given identifier, a flexibility problem is solved, and the Flexibility level (F) is set as the smallest value obtained among all the subproblems, i.e., $F = \min_k F_k$. The vertices (V) are defined as a set with 2^{Np} vertices, where Np is the number of uncertainties parameters θ and these vertices compose the vertex identifier $V_{V,j}$. In this example, there are 3 consuming units, so there are 8 vertices that make up the matrix ($VI_{V,j}$), thus obtained critical vertices are illustrated in Table 6.8.

Table 6.8: Critical vertices for different consumers.

Vertex (V)	**Consumers (j)**		
	HDT I	HDT II	HDS
H_{2cn_j} **(Nm³/h H_2)**	**19,507.00**	**39,015.00**	**5,814.00**
(1)	**(+1)** $H_2\_cn_j *$ (1+0.0755)	**(+1)** $H_2\_cn_j *$ (1+0.0729)	**(+1)** $H_2\_cn_j *$ (1+0.2854)
(2)	**(-1)** $H_2\_cn_j *$ (1-0.0295)	**(-1)** $H_2\_cn_j *$ (1-0.2003)	**(-1)** $H_2\_cn_j *$ (1-0.0775)
(3)	**(+1)** $H_2\_cn_j *$ (1+0.0755)	**(+1)** $H_2\_cn_j *$ (1+0.0729)	**(-1)** $H_2\_cn_j *$ (1-0.0775)
(4)	**(+1)** $H_2\_cn_j *$ (1+0.0755)	**(-1)** $H_2\_cn_j *$ (1-0.2003)	**(-1)** $H_2\_cn_j *$ (1-0.0775)
(5)	**(+1)** $H_2\_cn_j *$ (1+0.0755)	**(-1)** $H_2\_cn_j *$ (1-0.2003)	**(+1)** $H_2\_cn_j *$ (1+0.2854)
(6)	**(-1)** $H_2\_cn_j *$ (1-0.0295)	**(+1)** $H_2\_cn_j *$ (1+0.0729)	**(+1)** $H_2\_cn_j *$ (1+0.2854)
(7)	**(-1)** $H_2\_cn_j *$ (1-0.0295)	**(-1)** $H_2\_cn_j *$ (1-0.2003)	**(+1)** $H_2\_cn_j *$ (1+0.2854)

(8)	**(-1)** $H_2\_cn_j *$ (1-0.0295)	**(+1)** $H_2\_cn_j *$ (1+0.0729)	**(-1)** $H_2\_cn_j *$ (1-0.0775)

To solve the flexibility problem, the nominal value of hydrogen consumption is reported as a parameter. The hydrogen network is fixed according to the redesign proposed in Figure 6.8. The lowest flexibility value found in one of the eight vertices corresponds to the network's flexibility, which was 1.381 (F=1.381). It means that the redesigned network can meet demand higher than the percentage of variation in Table 6.8, because F>1. With this value, it is possible to determine the variation in the demand for hydrogen, through equation 6.41, as shown in Table 6.9.

Table 6.9: Demand for hydrogen met with the redesigned network.

	Maximum variation met %	**Minimum variation met %**
HDT2	10.07	-27.67
HDT1	10.43	-4.07
HDS	39.42	-10.70

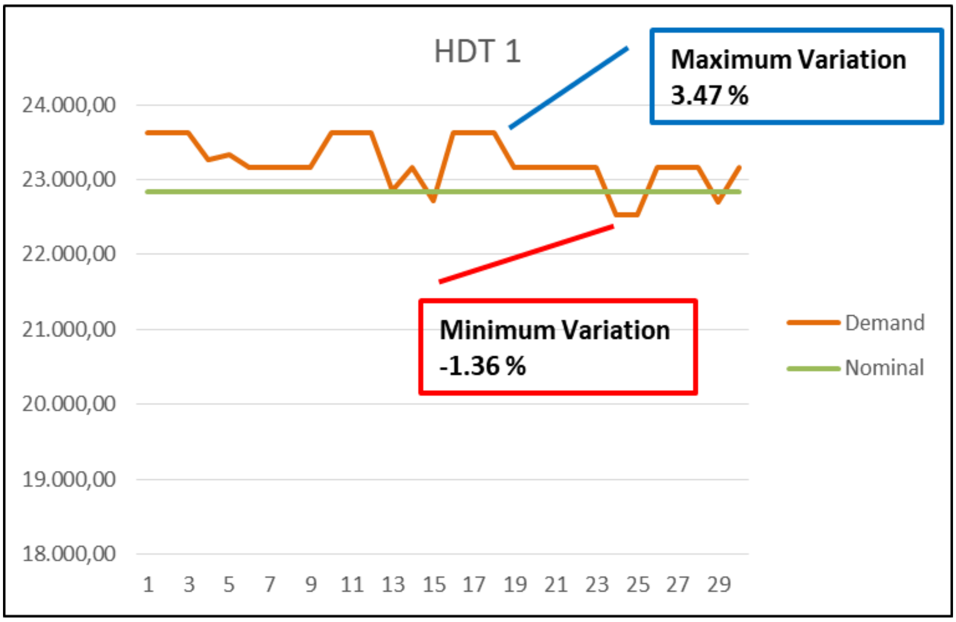
6.6.2 Methodology applied to the existing network

6.5.2.1 Flexibilty and limited production planning

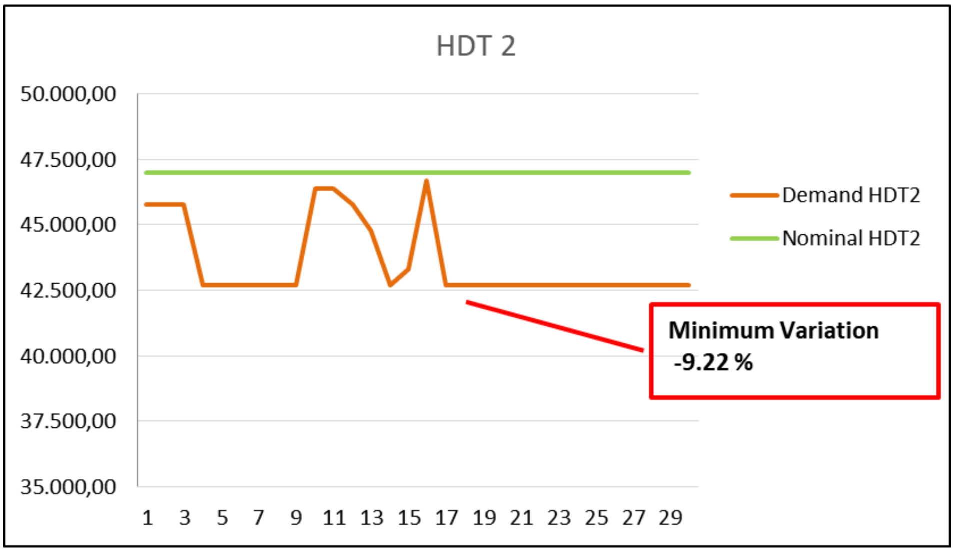
With the same data from Table 8, the flexibility problem for the original network was also calculated. The flexibility of the original network illustrated in Figure 6.5 is 0.46. Because this value is less than 1, according to the problem modeling, it indicates that the original network cannot operate with the demand variations obtained in production planning. However, it is essential to know what demand the original network can operate. For this, new planning was carried out, called production planning with restriction, where hydrogen demand was limited by the multiplication of nominal demand by the flexibility of the network obtained and by the values of Table 6.8 ($VI_{V,j}$).

The new restricted production planning uses Bonny Light, Marlim, Algerian, and Roncador oils. The profit obtained is 4.6480 x 10^7 \$/day, 2.78% lower than the profit obtained in the first resolved production planning. With this, a new hydrogen demand varying over the 30 days was obtained, according to Figure 6.9. It was possible to determine the most significant positive and negative variation in relation to the nominal one through the obtained demands.

a)


HDT 1
Maximum Variation
3.47 %
Minimum Variation
-1.36 %
24.000,00
23.000,00
22.000,00
21.000,00
20.000,00
19.000,00
18.000,00
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29
Demand
Nominal

b)


HDT 2
50.000,00
47.500,00
45.000,00
42.500,00
40.000,00
37.500,00
35.000,00
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29
Demand HDT2
Nominal HDT2
Minimum Variation
-9.22 %

c)

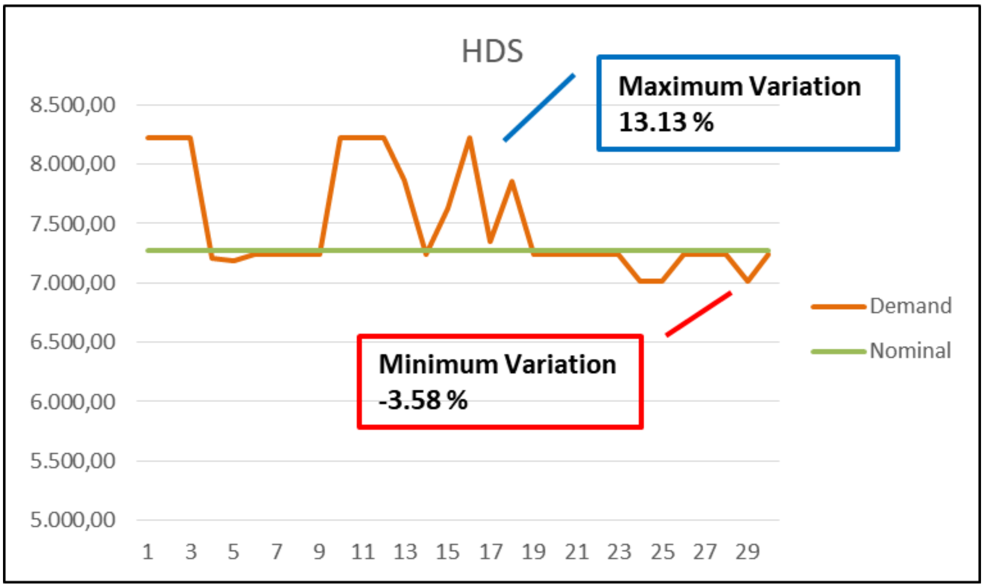


Figure 6.9: Hydrogen demand in Nm³/h over the 30 days and maximum and minimum variation in relation to the nominal for production planning with restriction. a) HDT1. b) HDT2. c) HDS.

6.5.2.1 Multi-scenarios optimization

With the scenarios identified, the operational cost of the original related comparison network was calculated. The operating cost for the original network is 36,743 million $/year. This cost is 12.28% higher than the redesign cost, so the 3 new pipelines' investment is paid in a concise time.

To solve the original network's flexibility problem, the nominal value of hydrogen consumption is reported as a parameter. Also, the original hydrogen network is fixed according to the network illustrated in Figure 6.5. Table 6.10 shows the percentages of variation in the identified vertices.

Table 6.10: Critical vertices for different consumers.

Vertex (V)	**Consumers (j)**		
	HDT I	HDT II	HDS
$H_{2_{cn_j}}$ **(Nm³/h H_2)**	**22,836,57**	**47,008.78**	**7,272.03**
(1)	**(+1)** $H_2\_cn_j *$ (1+0.0347)	**(+1)** $H_2\_cn_j *$ (1+0.0)	**(+1)** $H_2\_cn_j *$ (1+0.1313)
(2)	**(-1)** $H_2\_cn_j *$ (1-0.0136)	**(-1)** $H_2\_cn_j *$ (1-0.0922)	**(-1)** $H_2\_cn_j *$ (1-0.0358)
(3)	**(+1)** $H_2\_cn_j *$ (1+0.0347)	**(+1)** $H_2\_cn_j *$ (1+0.0)	**(-1)** $H_2\_cn_j *$ (1-0.0358)
(4)	**(+1)** $H_2\_cn_j *$ (1+0.0347)	**(-1)** $H_2\_cn_j *$ (1-0.0922)	**(-1)** $H_2\_cn_j *$ (1-0.0358)
(5)	**(+1)** $H_2\_cn_j *$ (1+0.0347)	**(-1)** $H_2\_cn_j *$ (1-0.0922)	**(+1)** $H_2\_cn_j *$ (1+0.1313)
(6)	**(-1)** $H_2\_cn_j *$ (1-0.0136)	**(+1)** $H_2\_cn_j *$ (1+0.0)	**(+1)** $H_2\_cn_j *$ (1+0.1313)
(7)	**(-1)** $H_2\_cn_j *$ (1-0.0136)	**(-1)** $H_2\_cn_j *$ (1-0.0922)	**(+1)** $H_2\_cn_j *$ (1+0.1313)

	(-1)	(+1)	(-1)
(8)	$H_2\_cn_j *$ (1-0.0136)	$H_2\_cn_j *$ (1+0.0)	$H_2\_cn_j *$ (1-0.0358)

The lowest flexibility value found in one of the eight vertices corresponds to the network's flexibility, which was 3.162 (F=3.162). It means that the original network can meet the demand higher than the percentage of Table 6.10 variation because F>1. With this value, it is possible to determine the variation in the demand for hydrogen, through equation 6.41, shown in Table 6.11.

Table 6.11: Demand for hydrogen met for original network.

	Maximum variation achieved %	**Minimum variation achieved %**
HDT2	0	-29.14
HDT1	10.97	-4.30
HDS	41.52	-11.31

Comparing the redesign with the original network, the redesign justifies its investment in 3 new pipelines, as it has an operating cost of about 12% lower. Besides, this network's flexibility shows that it is possible to operate with variations higher than the original network, being +10% and - 27% for HDT2, +10% and -4% for HDT1 and +39% and – 10% for HDS, compared to the nominal value.

6.6.3 KPI for evaluating the process

The information obtained in sections 6.5.2 and 6.5.3 shows that it is possible to evaluate hydrogen use within the refinery, making it an economic indicator (Equation 6.42). Production planning provides profit and information on the hydrogen demand required in fuel hydrotreatment processes. This information feeds multi-scenario modeling, which provides a redesign based on the lowest operating cost. This redesigned network provides maximum use of hydrogen and has an associated investment cost. Suppose it is not interesting to make investments in the network, in this case, it is possible to operate with the original network, and it also has a profit from the production planning it can meet. Thus, a KPI (Key Performance Indicator) can be used to assess whether it is worth investing in the redesign over a time horizon. This indicator is based on the profit obtained by the production planning that the reproject can achieve, considering the investment cost (annualized) and the profit obtained by the production planning with the original network. For the annualization of the investment, a period of 5 years with an interest rate of 5% was considered.

$$KPI_{H_2} = \frac{profit - annualized\ investment}{profit\ from\ original\ network} \tag{6.42}$$

If the KPI_{H_2} is close to 1, the actual network and the redesigned network operate similarly, not being observed the relevance of the investments proposed by the redesign. If the KPI is greater than 1, then reproject has a significant impact, making more profit even with the necessary investments.

In this work, the profit obtained in first production planning was \$4.7812 x 10^7/day, and the restricted planning profit due to the current network was \$4.6480 x 10^7/day. In addition, the investment of new lines was estimated at \$ 0.014 x 10^6, which was annualized. In this case, the investment cost is meager compared to the profits, resulting in $KPI_{H_2} = 1.03$, which means that it is worth investing due to its associated profit.

6.7 Conclusions

In this work, a methodology was proposed to combine the production planning to plan the amount of hydrogen needed in the hydrotreatment units, in refineries. For this, a nonlinear model of generic production planning and easily adaptable to other structures was developed. It is possible to relate the load of the hydrotreatment units, which is one solution of the optimization problem, with the amount of hydrogen required and the profit obtained in planning.

Besides, a MINLP formulation was used for multi-scenario optimization of hydrogen networks to evaluate whether the original network could meet the calculated hydrogen demand or propose a network redesign with an associated investment cost. It was also essential to evaluate both the original network and the redesign's flexibility, which allows determining which variations in hydrogen demand are supported by both networks.

The proposed methodology was possible to evaluate the original network and the redesign in terms of the profit of production planning, the network's operational cost, and flexibility, integrating the production planning of a refinery with the production schedule and its demand for hydrogen and incorporating the feedback of the process, being possible to optimize. All model implementations were made in GAMS, and project data from a Brazilian refinery were used, which increases the scientific appeal and contribution of this work.

It was possible to reduce the operating cost by approximately 12% through the redesign, and the profit obtained was almost 2.9% higher then original network. This redesign network flexibility is 1.38. These results were found for production planning; with more data, it is possible to increase the refinery's competitiveness by investing in the redesign, or it is still possible to analyze which other designs would be interesting to invest. As the network studied is small, few variations in the network would be necessary.

The methodology developed proved to be an excellent tool to assist in production planning and evaluate how much can be operated with the existing or redesigned network. In addition, the proposed KPI can be applied as process monitoring or for evaluating data for decision making on whether or not to invest in the hydrogen network.

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Capítulo 7 – **Considerações finais**

Neste capítulo são descritas as principais conclusões obtidas no desenvolvimento deste trabalho e sugere futuras pesquisas na área.

7.1 **Conclusões**

O hidrogênio tem papel importante na indústria do refino de petróleo, visto que é o insumo necessário para adequar o teor de enxofre nos combustíveis, cumprindo assim a legislação ambiental vigente. Nos últimos anos esta demanda vem crescendo devido a utilização de petróleos mais pesados, com maior teor de enxofre e também pela restrição no teor de enxofre permitido nos combustíveis. Por isso, uma gestão eficiente do hidrogênio tem impacto significativo no lucro das refinarias. Através do planejamento de produção e a integração com o gerenciamento de redes de hidrogênio, é possível obter a relação entre a capacidade das unidades de hidrotratamento e do consumo de hidrogênio, considerado como uma incerteza na otimização e reprojeto de redes de hidrogênio.

No Capítulo 2 foi feito uma revisão dos principais conceitos envolvidos nesse trabalho, facilitando o entendimento e também foi feito um levantamento dos trabalhos já publicados sobre o assunto.

As duas primeiras contribuições desta Tese são a formulação nominal dos modelos MILP e MINLP para reprojeto de rede de hidrogênio, totalmente descritas e avaliadas com diferentes restrições. O Capítulo 3 e 4 são fundamentais para o gerenciamento de hidrogênio, pois neles foi descrita toda a modelagem realizada através da proposição de uma superestrutura genérica e validada com diversos exemplos da literatura e também com dados reais de uma refinaria. Além disso, no Capítulo 4 foram propostas metodologias que facilitaram a resolução do modelo não linear, como a estratégia de inicialização e a redução do custo de capital através da técnica dos compressores virtuais. Foi concluído que a formulação não linear fornece resultados melhores e mais realistas de reprojeto de redes de hidrogênio quando utilizado estas duas propostas.

No Capítulo 5 se viu a necessidade de tornar ainda mais realistas a otimização de redes de hidrogênio, através da inserção da incerteza, do tipo variabilidade, no consumo de hidrogênio nas unidades de hidrotratamento. Além da extensão do modelo para versão multicenário, ainda foi proposto uma metodologia para avaliação da flexibilidade da rede de hidrogênio, informação importante para garantir operabilidade da refinaria. Essas etapas foram combinadas na proposição de uma metodologia para a obtenção de um (re)projeto ótimo, com mínimo custo e flexível (capaz de atender a variabilidade no consumo de hidrogênio). A metodologia se mostrou eficiente e foi ilustrada com dois estudos de caso, um da literatura e outro com dados reais de projeto de uma refinaria.

No Capítulo 6 foram unidos todos os conceitos anteriores com a ideia de estimar previamente a quantidade de hidrogênio através do modelo de programação matemática desenvolvido para o planejamento de produção da refinaria. Para isso, um modelo não linear foi proposto com base em determinados petróleos e produtos. Como resultado da otimização, é possível obter a quantidade de hidrogênio em um determinado período. É fundamental que esta informação se conecte com a capacidade de produção do hidrogênio e flexibilidade da rede, garantindo a operabilidade da refinaria. Outra informação importante é que, o planejamento de produção também pode ser otimizado baseado nas restrições impostas pela capacidade da rede de hidrogênio, o que mostra que todas as etapas desenvolvidas se complementam e podem ser aplicadas e comparadas tanto para a rede existente quanto para avaliar a relevância de reprojetos.

Por fim, através da integração do planejamento de produção e do reprojeto ótimo e flexível da rede de hidrogênio, garante-se o uso eficiente do recurso hidrogênio dentro da refinaria atendendo o planejamento de produção ótimo aumentando o retorno econômico do processo com menores custos e impactos ambientais na produção de hidrogênio.

7.2 Sugestões para trabalhos futuros

Como sugestão de ideias adicionais que podem ser trabalhadas:

Utilização da metodologia de gerenciamento de redes de hidrogênio, através dos modelos descritos, em outro estudo de caso que não seja hidrogênio, como por exemplo reutilização de água ou energia.

Utilização de mais dados históricos operacionais, para poder comparar quanto a rede original é capaz de produzir de hidrogênio e caso feito o reprojeto, quanto seria economizado em termos de custo operacional e aumento de hidrogênio fornecido.

Utilização dos KPIs propostos para nortear a operação de uma de rede hidrogênio em uma refinaria os integrando no dashboard de acompanhamento operacional da empresa.

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