Implementation of Power-to-Gas to Reduce Carbon Intensity and Increase Renewable Content in Liquid Petroleum Fuels

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2017

AUTHOR'S DECLARATION

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

I would like to acknowledge the names of my co-authors who contributed to the research described in this thesis, these include:

- Dr. Azadeh Maroufmashat
- Dr. Michael Fowler
- Dr. Ali Elkamel
- Ushnik Mukherjee

The specific contribution made by the above co-authors is clearly defined at the beginning of respective chapters

ABSTRACT

Power-to-gas (PtG) is an emerging energy storage concept, which can transfer the surplus and intermittent renewable generated power into a marketable hydrogen, as well as providing other ancillary services for the electrical grid. In the case of Ontario, excess power is encountered during periods of low electricity demand as a result of substantial generation from baseload nuclear and increasing integration of intermittent renewable sources powering the electrical grid.

This thesis develops various simulation and analysis of Ontario's energy system to illustrate the use of PtG when its electrolytic hydrogen is employed in the gasoline production cycle to reduce the carbon intensity of the production process, and increase the renewable content of this traditional transportation fuel. The work includes a case study for a simulated refinery to evaluate the production cost and life cycle emission for different production scenarios, related to the deployment of polymer electrolyte membrane (PEM) electrolyzers to meet the refinery demand of hydrogen. Moreover, the study involves examining the use of the province surplus baseload generation (SBG) for which currently results in net exports to neighboring jurisdictions, and curtailed power generation capacity from wind and nuclear to meet the overall demand of the refining industry. Furthermore, a comparative assessment is conducted of blending 10% corn-ethanol and using electrolytic hydrogen supply via PtG on the 'well to wheel' (WTW) impacts of gasoline fuel, according to the metrics of total energy use, greenhouse gas emissions, and criteria air pollutants.

According to the study, it is found that steam methane reforming (SMR) provides a lower cost hydrogen as a result of the current low natural gas prices, even with stringent carbon-pricing policy. However, the electrolytic hydrogen production shows a potential to curb significant carbon emissions as a substitute for SMR hydrogen. At a single refinery level, the use of electrolytic hydrogen can be compared to eliminating as many as 35,000 gasoline passenger vehicles from the road when there is an installation of 130 PEM electrolyzer units (1 MW nameplate capacity per unit). Also, the analysis shows that PtG has the potential to supply the refineries within the province with the entire hydrogen demand with a fraction of the surplus power, particularly when making use of available seasonal storage at least for the next four years. Moreover, PtG is found to decrease 4.6% of the natural gas consumption on the gasoline cycle, and increase the renewable content of gasoline by extending the utilization of wind and hydro power. Furthermore, the deployment of electrolytic hydrogen results in minimizing gasoline carbon intensity by 0.5 gCO_2e per MJ of the fuel. When associated with the annual gasoline sales in Ontario, it can offer the reduction of 0.26 Megaton of greenhouse gas (GHG) emissions yearly. Moreover, PtG may contribute to lowering VOCs, NO_x, PM_{10} and $PM_{2.5}$ criteria air pollutants from gasoline cycle, which cannot be achieved with blending corn based ethanol.

Accordingly, the results of this thesis outline the benefits of using power-to-gas to mitigate the existing issue of surplus power generation. Utilizing the excess electricity to produce hydrogen for refinery end user also increases the utilization of CO_2 free energy and renewable content of gasoline within its life cycle production scheme.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Professor Michael Fowler for his immense support and guidance which helped me in all the time of research and writing of this thesis. I would also like to extend the appreciation to Professor Ali Elkamel who provided invaluable supervision and insights to ensure the success of my Master degree study.

I thank Dr.Azadeh Maroufmashat and Ushnik Mukherjee and the rest of my fellow research group for the collaborations and enlightenment throughout the course of research and surely for the great time spent together

I would like to thank my sponsoring company Saudi Aramco, which keeps developing their workforce at every stage of their career to meeting the energy challenges of tomorrow

Last but not least, I would like to thank my parents back home for their emotional support who I will be grateful forever for their love and compassion. Special thanks go to my wife, Bashayer, for her love, support, patience, and understanding.

DEDICATION

To my dear wife Bashayer and my little angels Sarah and Noor

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NOMENCLATURE

CRF	Capital Recovery Factor	LHV	Lower heating value
gCO_2	grams of carbon dioxide	g	Grams
kg	Kilogram	mg	Milligram
kWh	Kilowatt-hour	Kt	thousand tons
MWh	Megawatt hour	Mt	Mega-tons
GWh	Gigawatt hour	Wh	Watt-hour
kW	Kilowatt	W	Watt
MMscfd	Million Standard Cubic Feet per Day	m	Meter
MW	Megawatt	bbl	Oil Barrel
MMBtu	Million British Thermal Unit	L	Liter
MJ	Megajoule		
kJ	Kilojoule		
E10	gasoline with 10% ethanol content		
E0	gasoline with no ethanol content		

Chapter 1: Introduction

1.1 Background

Hydrogen has a broad range of industrial applications, as discussed thoroughly by Zhang et al. [1] and Ramachandran and Menon [2]. Oil refining and chemical industry constitute the largest segments of hydrogen consumption worldwide. The majority of the global hydrogen is consumed for ammonia production at 53% and 20% for oil refining while the remaining are for other industrial uses [3]. In refineries, hydrogen is primarily used in hydrotreating and hydrocracking processes. Hydrotreating is a catalytic process which involves the removal of sulfur and nitrogen impurities via hydrogen from the petroleum products. In hydrocracking process, hydrogen is used to upgrade the heavy gas oils which contain high boiling range hydrocarbons into more valuable low boiling streams such as gasoline and diesel.

The refining industry has experienced significant hydrogen demand shift in recent years due to several reasons. The primary factor is the stringent environmental regulation of sulfur content in petroleum fuels, driving the consumption of hydrogen up to meet the fuel quality legislation. Moreover, the markets have shifted into lighter fuels demand, pushing refiners to get more value from the bottom of the barrel through the petroleum cracking processes. Also, many refineries need to process heavier and sourer crude for which the hydrogen consumption highly depends on the density (API gravity), and the sulfur content of the processed crude. In addition, refinery operators have to reduce the level of aromatics in gasoline which entails restricting reforming severity and hence hydrogen production from the process. All these factors pose challenges to refineries to tackle the hydrogen balance issue while meeting growing demand and stricter quality of petroleum fuels.

Hydrogen can be produced from multiple sources in refineries. Figure 1 outlines a general hydrogen balance scheme in typical refineries. The catalytic naphtha reforming process is a significant source of hydrogen. The hydrogen is generated as a byproduct of the process used to convert heavy naphtha to a higher octane product called reformate, for gasoline blending. Also, the recovery of hydrogen rich off-gases through pressure swing adsorption (PSA) can be a good source of additional hydrogen when it is economical. The hydrogen is sent to various consumers in a refinery for treating and upgrading the petroleum products. However, the demand for these units usually surpasses the hydrogen available from naphtha reforming. Therefore, a hydrogen production facility is generally needed to meet the supply gap in the refinery. That source may come from an outside supplier or commonly steam methane reforming (SMR) is used as an on-site hydrogen production method.

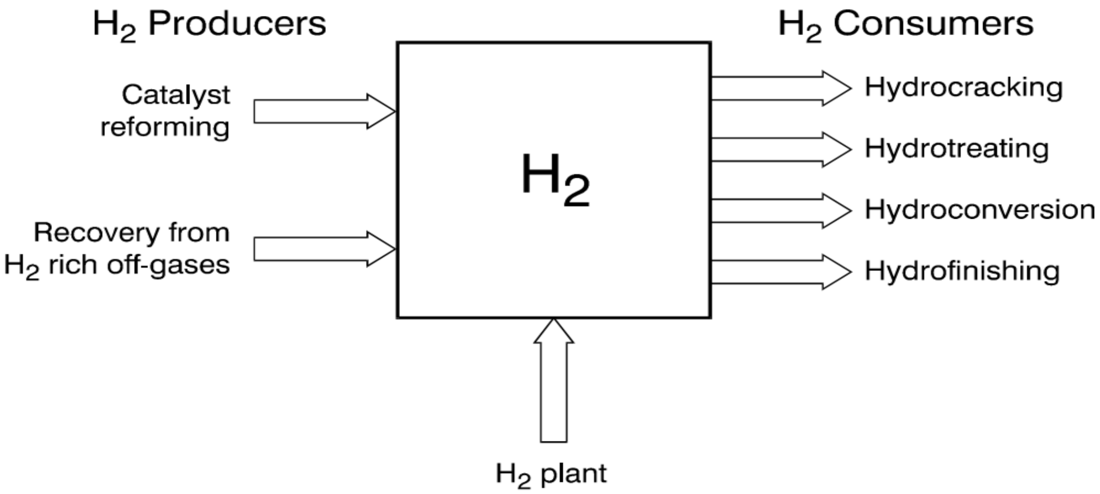


Figure 1. Schematic of refinery hydrogen balance [4]

Around 96% of the global hydrogen production comes from fossil fuels while electrolysis produces almost all of the remaining 4%. Methane or natural gas reforming meets nearly half of the world's demand followed by liquid hydrocarbons and coal at 48%, 30%, and 18% respectively [5]. Steam methane reforming (SMR) is a mature technology for the production of hydrogen and is the most used pathway to supply hydrogen for refining and chemical industries. In U.S., 95% of the total produced hydrogen comes from SMR technology [6]. In Canada, the refineries have a total hydrogen production capacity of 405 million standard cubic feet per day (MMscfd) [7], produced typically from the catalytic reforming and SMR processes [8].

SMR chemical reaction is an endothermic and catalytic, where methane or natural gas reacts with steam to form a synthesis gas comprised of hydrogen and carbon monoxide (CO), as described by Eqn. (1). Then, CO is further converted to carbon dioxide (CO_2) by reacting with steam in the water gas shift reactor (Eqn. (2)). Modern SMR processes are equipped with pressure swing adsorption (PSA) technology to purify the hydrogen rich gas from CO_2. The produced hydrogen comes with 99.9% purity which has multiple advantages for the hydrotreating and hydrocracking processes [9].

Steam methane reforming reaction: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ Eqn. (1)

Water gas shift reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$ Eqn. (2)

In spite of SMR maturity and low production prices, it emits significant greenhouse gas emissions which can be in the range of 11-13 kg of CO_2e per kg of hydrogen [10-12]. SMR is considered one of the main sources of CO_2 emissions in oil refineries which contribute nearly 4% of the global CO_2 emissions [13].

In contrary, hydrogen from an electrolysis technology (electrolytic hydrogen) has a significantly less carbon footprint when using an electrical grid powered mostly by nuclear and renewable energy sources. Ontario electricity grid is suited for green hydrogen production via electrolysis since the electricity grid is powered by mostly CO_2-free sources of electrical energy after phasing out the coal plants completely since 2014 [14]. The majority of Ontario power output, as shown in Figure 2, comes from nuclear and renewable sources (hydro, wind, solar and biofuel) which comprise about 90% from the total electricity supply. Nuclear and most of the hydroelectric with the variable wind and solar provide the baseload power generation, while the natural gas facilities are flexible that can vary the output based on the province demand for dispatchable power generation [15].

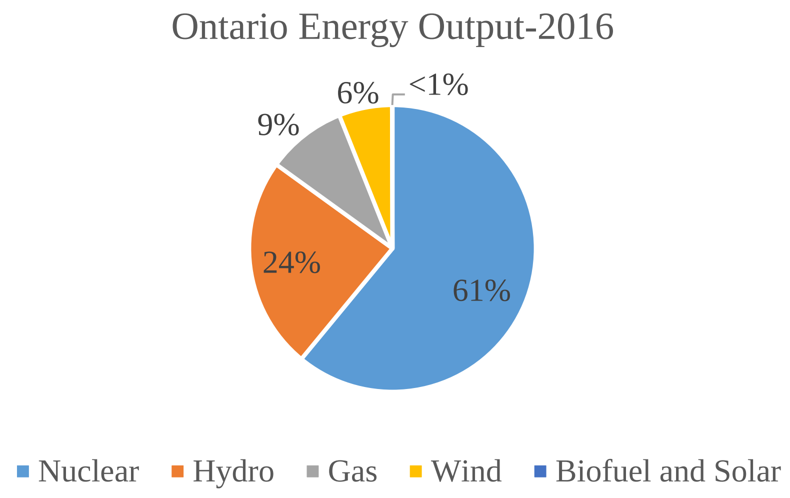


Figure 2. Ontario energy output by fuel type (Source: IESO, 2017)

In fact, the region often encounters periods of surplus baseload generation (SBG), when the supply from baseload nuclear and hydro (which is mostly baseload) with an intermittent wind and solar generation exceeds the region demand. As Ontario grid is interconnected with neighboring jurisdictions (Manitoba, Michigan, Minnesota, New York, and Quebec), the excess power is net exported to these provinces as low below cost pricing to maintain the grid reliability [16]. Managing the surplus also extends to curtailing the wind and nuclear electricity generation (i.e. shedding wind or heat). For instance, the total curtailed power from wind during 2015 was 733.5 GWh, which is about 7.5% of the total produced power from wind energy [17]. Also, the total energy lost from nuclear as a result of maneuvers and shutdowns due to SBG was 897 GWh, equivalent to 1% of the total generated power from nuclear in 2015 [17]. In addition, the period between April 2016 and March 2017 included a total of nearly 2,600 GWh energy curtailments from wind, nuclear and minor import cuts to manage the encountered SBG [18]. According to the recent outlook report by the Independent Electricity System Operator (IESO) [18] covering mid-2017 till end-2018, Ontario will continue experiencing SBG issue for which exports and energy curtailments are anticipated to balance the supply and demand. Furthermore, the surplus baseload is forecasted to continue beyond 2030 [19-21], that will be managed by implementing the existing mechanisms, which involve unfortunately losing a vital CO_2-free energy from nuclear and renewable sources. Therefore, there is a potential opportunity present in Ontario province to tap into the surplus clean power from baseload nuclear as well as hydro and wind generation to produce a 'clean' hydrogen via electrolysis (i.e. 'power to gas' or PtG). Thus, to meet a significant demand of the oil industry while minimizing the life cycle greenhouse gas (GHG) emissions and increasing renewable content of petroleum fuels while also enhancing the operability of the grid.

1.2 **Power-to-Gas**

Regions with large quantities of baseload nuclear and substantial component of intermittent renewable power generation, encounter challenges with matching generation and demand profiles. As a result, the use of electrical energy storage (EES) systems is encouraged to maintain the grid reliability while increasing the penetration of CO_2-free electrical generation sources.

Energy storage is defined as converting the electricity during low or off-peak demand into a storable form and converting it back to electricity during high peak demands or as needed [22]. Storing the energy can also be desirable during low generation cost and intermittent energy from renewables. There are various EES technologies, which can be classified based on the stored energy form into mechanical, electrochemical, electrical, thermochemical, thermal and chemical [23]. There are a number of academic journals [22-26] that provide an extensive technical review of multiple EES technologies and comparison of the characteristics of each technology. The evaluation criteria includes normally the cycle or 'round-trip' efficiency (%), capacity (MW), energy density (Wh per kg), power density (W per kg), power capital cost ($ per kW), energy capital cost ($ per kWh), response time, lifetime (years), cycle life (cycles), self-discharge, maturity and environmental impact. Each technology has its own characteristics while selecting the technology depends on the required applications. The applications include but not limited to power quality, grid stability/reliability, demand response, frequency regulation, peak shaving (and spinning reserve), seasonal storage, energy arbitrage, etc. For instance, pumped hydroelectric storage (PHS) and compressed air energy storage (CAES) technologies are the most common for high energy storage applications over other technologies such as flywheels, batteries, supercapacitors, etc. However, PHS and CAES require substantial capital investments while appropriate sites for the technologies construction are limited and take a long time to build [22, 24,26]. Furthermore, PHS is a net consumer of electricity (more electricity intake than generated) and also has some environmental issues [22,24,26]. Thus, there is a recognized need for more economic and environmental approach to storing a vast amount of power for an extended duration of time to increase penetration of renewables generation.

Power-to-gas (PtG) is an emerging energy storage technique that can potentially resolve the surplus power issue effectively. The concept refers to the conversion of the excess electricity during low-demand profiles to chemical energy that is hydrogen via electrolysis technology [27]. The electrolysis is a hydrogen production method which uses electricity to decompose the water into hydrogen and oxygen gas. The two commonly known electrolyzers technologies that exist in the market are alkaline and polymer electrolyte membrane (PEM) electrolyzers. The resultant hydrogen via electrolysis can have several pathways to different applications [28] as shown in Figure 3, part of which the consumption of hydrogen as a raw material by the petroleum industry [12,29,30]. Moreover, it can be injected into existing natural gas infrastructure to produce a cleaner mixture called hydrogen-enriched natural gas (HENG) [31, 32], and used in current applications without the need for additional modification. Furthermore, the hydrogen can be utilized to generate a renewable natural gas (RNG) after combining it with CO_2 stream from biogas in a methanation process [33,34]. Also, it is possible to be stored in a tank and withdrawn during high demand to produce electricity using a fuel cell [35] in an energy load leveling or energy arbitrage application [36,37]. Finally, the hydrogen can be consumed directly as a transportation fuel in fuel cell vehicles [38-40].

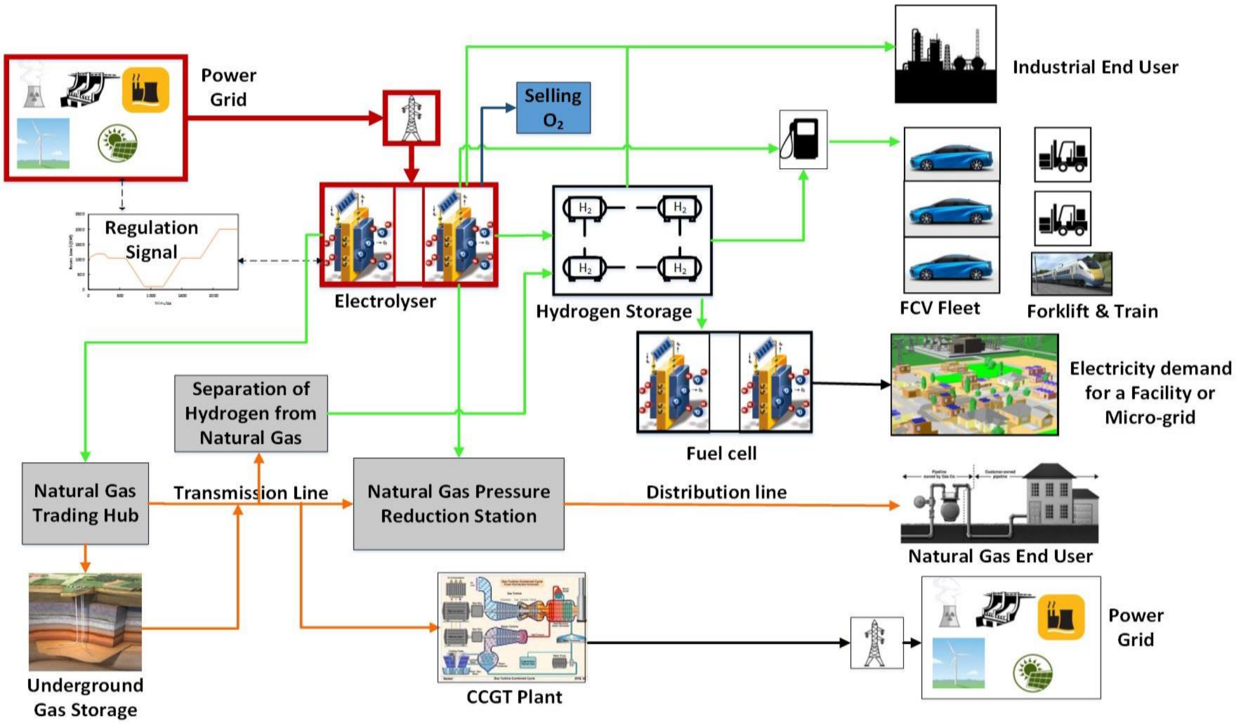


Figure 3. Illustration of Power-to-Gas Energy System [41]

Walker et al. [42] compare PtG with other energy storage mediums for different applications using an analytical hierarchy process. The study [42] find that PtG has the lowest total generation capacity cost ($ per kW) and energy storage cost ($ per kWh) compared to other storage alternatives. In addition, PtG has the highest energy density (kWh per m) and can provide storage for up to 7 years given Ontario gas storage infrastructure. Moreover, the Independent Electricity System Operator (IESO) has published a report [43] that identifies the current opportunities of energy storage technologies in the province of Ontario to alleviate surplus baseload generation (SBG). The report by the IESO [43] recognizes the technologies that are capable of taking the surplus electricity and convert it to another form of energy, like hydrogen from PtG concept, as the most adequate to managing SBG conditions and have more opportunities at least to the early 2020s.

1.3 Objectives of the Thesis

In this thesis, the author examines the feasibility of using electrolyzers to generate hydrogen for refinery operations via power-to-gas, when the pathway of hydrogen to end users is considered. Thus, to provide Ontario the potential to efficiently utilize the surplus clean power while decarbonizing and increasing the renewable energy content of traditional transportation fuels. This can act as a transitional solution and a cost effective way of reducing carbon emissions from the transportation sector without requiring major near-term investments in charging and refueling infrastructures for battery and fuel cell electric vehicles.

1.4 Outline of the Thesis

The thesis consists of three Papers which are arranged in separate chapters based on their implementations. In Chapter 2, the study performs an economic and life cycle emissions analysis between steam methane reforming and PEM electrolysis for the supply of required hydrogen to a refinery. The content was originally published in the International Journal of Hydrogen Energy under the title “Presenting the implementation of power-to-gas to an oil refinery as a way to reduce the carbon intensity of petroleum fuels” in June 2017. In Chapter 3, the study investigates the potential opportunity of the available surplus electricity in Ontario to meet the demand of industrial users including refineries. The content is going to be published soon in the conference proceedings of 2017 the 5th IEEE International Conference on Smart Energy Grid Engineering, August 14-17, 2017, Oshawa, Canada. In Chapter 4, a comparative assessment of blending 10% corn-ethanol and electrolytic hydrogen via power-to-gas on the life cycle of gasoline is developed to provide the incentives of including the electrolytic supply in the renewable fuels regulations as an alternative and complementary method to increase renewable content of gasoline. The chapter is based on submitted work to the Energies Journal which currently under review with the title “Evaluating the Incentives of Considering the Hydrogen Supply via Power to Gas in the Renewable Fuels Regulations of Petroleum Fuels”. Finally, Chapter 5 closes the thesis with the main conclusion and remarks with respect to works and recommendations for future research.

Chapter 2: Power-to-Gas Application to an Oil Refinery-Case Study

The following chapter is based on previously published work in the International Journal of Hydrogen Energy under the title "Presenting the implementation of power-to-gas to an oil refinery as a way to reduce carbon intensity of petroleum fuels" by "AlSubaie et al." on 29 June 2017. This thesis author specific contribution to this paper was to: "conduct the refinery processes simulations, integrate the electrolysis process into the overall simulation and analysis, complete the post simulation calculations and analysis, prepare all the graphics and results, and prepare the final manuscript and reviewer edits with direction from the project supervisors who are co-authors". This paper is co-authored by Dr.Azadeh Maroufmashat, a post-doctoral fellow, whom assisted with the development of the optimization routine, Dr. Michael Fowler and Dr.Ali Elkamel as supervisors who aided in editing the work.

2.1 Research Background

The emissions released from hydrogen production and oil refining, in general, are directly tied to the life cycle emissions of petroleum fuels. Figure 4 illustrates the life cycle of gasoline and diesel, usually referred to as Well-to-Wheel (WTW) analysis. It constitutes of crude extraction, crude transport, crude refining, petroleum fuels transportation and distribution, and finally vehicle consumption. While the direct emissions from vehicles have the biggest impact on the carbon intensity of gasoline and diesel, the crude extraction and oil refining also have a significant contribution. Keesom et al. [44] provide WTW analysis of gasoline and diesel for various crudes imported and processed in the United States. The majority of greenhouse gas (GHG) emissions come from vehicles fuel combustion with about 80% of emissions, while crude production, refining, transportations, and distribution constitute the other 20%. The large contribution from vehicles is apparent since a gasoline passenger car emits an average of 4.7 metric tons of CO_2 annually [45].

Several regulations were introduced in North America and Europe to reduce the carbon intensity of petroleum fuels on the life cycle basis. For example, California has set a 10% reduction target by 2020 under the Low Carbon Fuel Standard (LCFS) [46]. The European Union also has legislation, known as the Fuel Quality Directive (FQD), that aims to have 6% cut of the petroleum fuels carbon intensity by 2020 [47]. Meanwhile, Ontario province in Canada is also planning to introduce a similar regulation with 5% reduction of gasoline GHG pollution by 2020 [48]. Note all of these regulations are beyond the ones that enhanced vehicle fuel efficiency which reduce emission from the vehicle by lowering the amount of fuel consumed. The introduction of battery-electric (BEV) and hydrogen fuel cell (FCV) vehicles obviously can have the largest impact on reducing urban air pollution and carbon footprint of the transportation sector. Despite significant development in recent years, these technologies are still not commercially competitive with light-duty internal combustion (ICE) and diesel petroleum powered vehicles. Therefore, the regulations of reducing the carbon intensity of petroleum fuels are seen as a holistic approach towards decarbonizing the transportation sector in the short and medium term. Each stage of the fuel production life cycle in Figure 4 provides an opportunity to achieve the overall emissions reduction targets. The increased GHG free energy content in gasoline and diesel combined with fuel efficiency improvements in vehicles has the potential to reduce emissions in the current fleet of vehicles while BEVs and FCVs increase their market penetration.

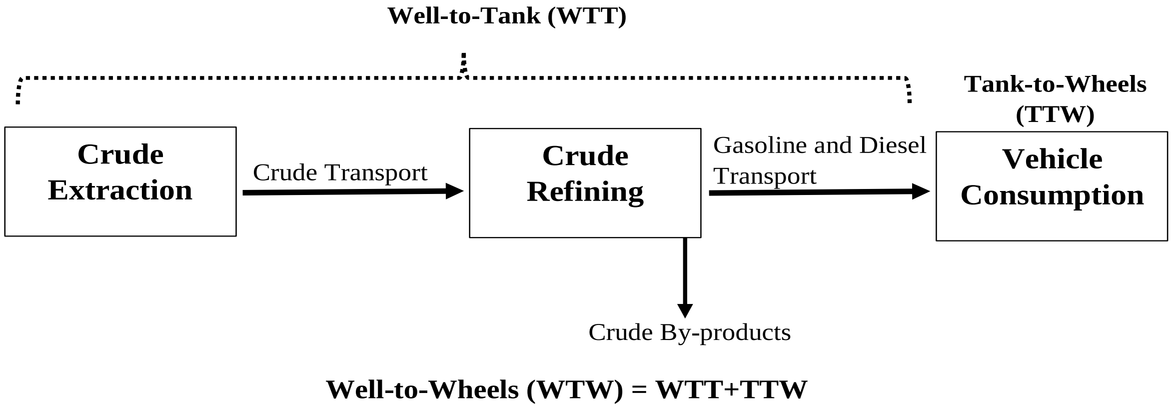


Figure 4. Gasoline and diesel life cycle

The aim of this chapter is to present one of the opportunities for crude refining sector to curb significant GHG emissions during production of petroleum fuels, and ultimately contributing to the carbon intensity reduction target. As such, it is proposed to use the surplus GHG free electrical power to generate hydrogen utilized in the petroleum manufacturing life cycle, then 'storing' the energy in liquid fuels.

Unlike Steam methane reformer (SMR), electrolysis produces hydrogen with no associated GHG emissions except when fossil fuels partly power the grid (e.g. Combined Cycle Gas Turbines). The energy mix powering the grid plays a key role in validating the use of electrolysis since it requires electricity. In Ontario, about 90% of the electricity generation came from GHG free energy sources, specifically nuclear and renewable energies (hydro, wind, biofuel and solar).

There exists only a limited number of available reports and academic journals that explore the use of electrolytic hydrogen for the petroleum industry. For instance, Walker et al. [29] examine the use of the power-to-gas concept to provide a hydrogen for potential bitumen upgrader in Sarnia, Ontario. Similarly, Olateju et al. [12] explore supplying hydrogen to a bitumen upgrading facility in western Canada but using the application of a dedicated large scale wind-hydrogen plant.

Moreover, Hinicio and LBST firms had a recent report [30] that examines the impact of applying power-to-gas in France and German refineries to the European Fuel Quality Directive (FQD) reduction target. As presented in the report [30], the concept appears to curb a significant amount of emissions but with a higher production cost compared to SMR. Also, it could potentially reduce 2.83 million tons of CO_2 annually from both countries. The report quantified the emissions as those released from nearly 1,223 thousand gasoline driven passenger cars. On the other hand, Samaniego et al. [49] discuss the potential use of electrolytic hydrogen utilizing the excess hydro power in Ecuador for use in petrochemicals and oil refining industries. However, the examination of the deployment of power-to-gas at an individual refinery, to the knowledge of the authors, has not been published. Nor there is a publication considering the application to meet a particular demand of a refinery and integrating the electrolytic generation of hydrogen within a refinery model. Therefore, this chapter provides a further contribution to the power-to-gas field of study that concerns its application to the petroleum industry. It is also considered as an extension to AlSubaie et al. [50] work that examines the environmental benefits of supplying a refinery with 35 Million standard cubic feet per day (MMscfd) of hydrogen by polymer electrolyte membrane (PEM) electrolysis technology briefly. This work originates from building on the availability of excess power in Ontario to provide a renewable hydrogen to the oil refining industry. Certainly, introducing GHG free hydrogen to the crude upgrading and refining industry is considered one of the measures towards reducing the carbon intensity of petroleum fuels, and providing an effective storage concept for electrical energy in the near term.

The chapter organization starts with the methodology section that outlines the utilized models and correlations for this study. Subsection 2.2.1 goes over the developed model of a typical high conversion refinery using Aspen HYSYS simulation software. Subsection 2.2.2 discusses the

Mixed Integer Linear Programing (MILP) model used to provide optimized settings of the PEM electrolysis production system. Subsection 2.2.3 introduces available cost estimation correlations for SMR to perform the economic analysis. Then, the results and discussion section presents the simulation results of hydrogen network for a refinery processing 100,000 barrels (bbl) of crude per day as a study case. Furthermore, it quantifies the emissions reductions impact as a result of deploying PEM electrolyzers in a refinery to produce 25 MMscfd. It also compares the economics of the two production pathways, as illustrated in Figure 5, including a sensitivity analysis concerning natural gas and carbon prices. The analysis is conducted for five hydrogen production scenarios to meet the refinery demand as follow:

- Scenario 1: Total production for the refinery from SMR (Base case);
- Scenario 2: Total production for the refinery from PEM electrolysis;
- Scenario 3: Half production from PEM electrolysis and the other half by SMR;
- Scenario 4: Total refinery demand production from PEM electrolysis based on nuclear and renewable grid power; and,
- Scenario 5: Total refinery demand production from PEM electrolysis during low electricity prices (off-peak period).

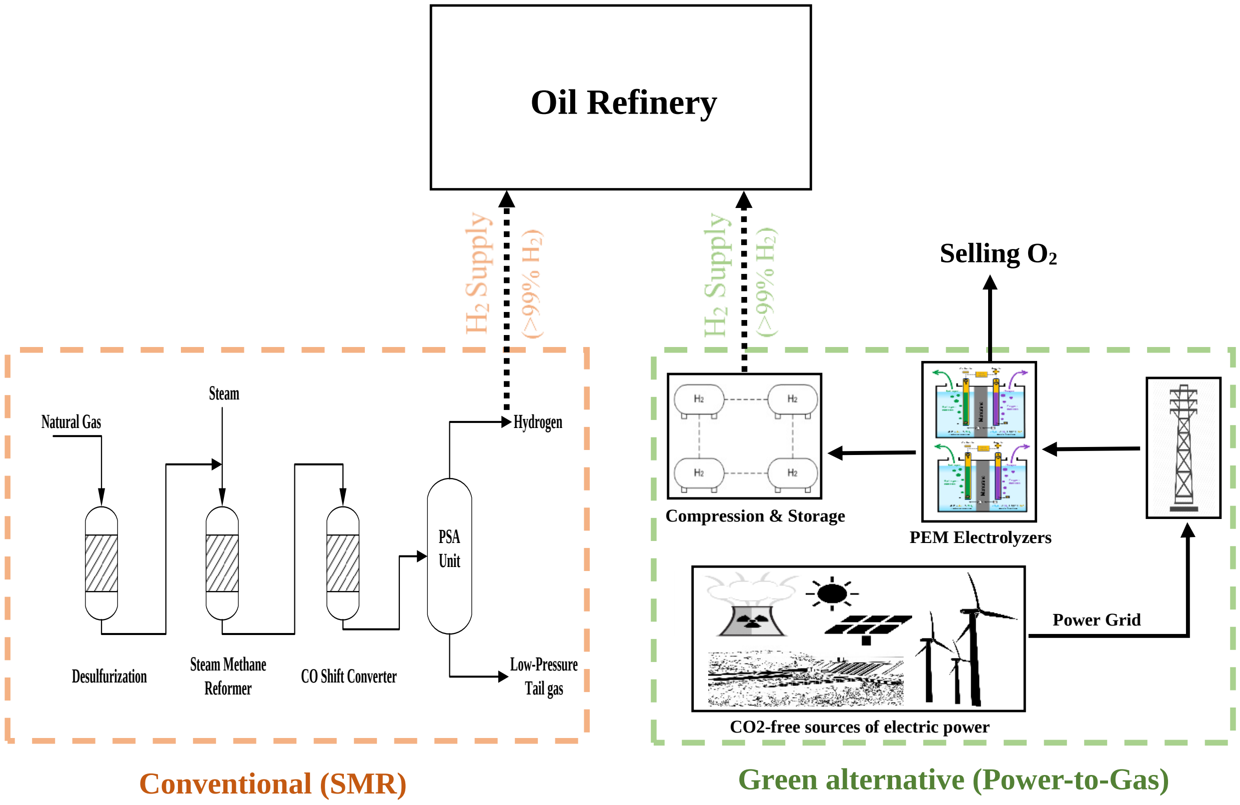


Figure 5. Hydrogen production pathways evaluated in this chapter

2.2 Methodology

2.2.1 Oil refinery Simulation

The study started with developing a model in Aspen HYSYS V8.8 process modeling and simulation software [51] to resemble a typical configuration of a high conversion refinery to generate hydrogen demand data for various blends of crude oil. The refinery simulation in Aspen HYSYS follows the block flow diagram provided in Figure 6. The simulation starts with selecting the desired crudes to be refined through the petroleum feeder. The blended crude is sent to a desalter using a 3-phase separator, where the desalted oil is sent later to a series of heat exchangers to increase its temperature. The hot stream enters the atmospheric column that separates it to major petroleum cuts based on their boiling range. Heavy naphtha, kerosene, and light gas oil out of the column are sent directly to naphtha (NHT), kerosene (KHT) and diesel (DHT) hydrotreaters respectively to treat the products from sulfur and nitrogen impurities using hydrogen. The heavy naphtha is further processed in a catalytic reforming unit (CCR) to increase the stream octane number for gasoline blending , where hydrogen is produced in conjunction with the reformate. The relatively thick product known as the atmospheric residue leaving the bottom of the column is sent to the vacuum distillation unit. The unit further separates it to useful gas oils that are sent to a fluid catalytic cracking (FCC) and a hydrocracker (HC) to produce more valuable refined products such gasoline and diesel. FCC naphtha or gasoline is further treated in the cracked naphtha hydrotreater (CNHT) to improve the sulfur quality of the gasoline pool. The off-gas from the top of the atmospheric column is combined with other refinery off-gases and sent to a gas processing unit to recover C3-C6 products and produce fuel gas for use within the plant. A complete summary of the processes operating variables as well as the unit models employed in Aspen HYSYS for the refinery simulation is found in Table 1. Furthermore, the Appendix section in this thesis provides more simulation background of the main processes and units in the developed refinery in Aspen HYSYS.

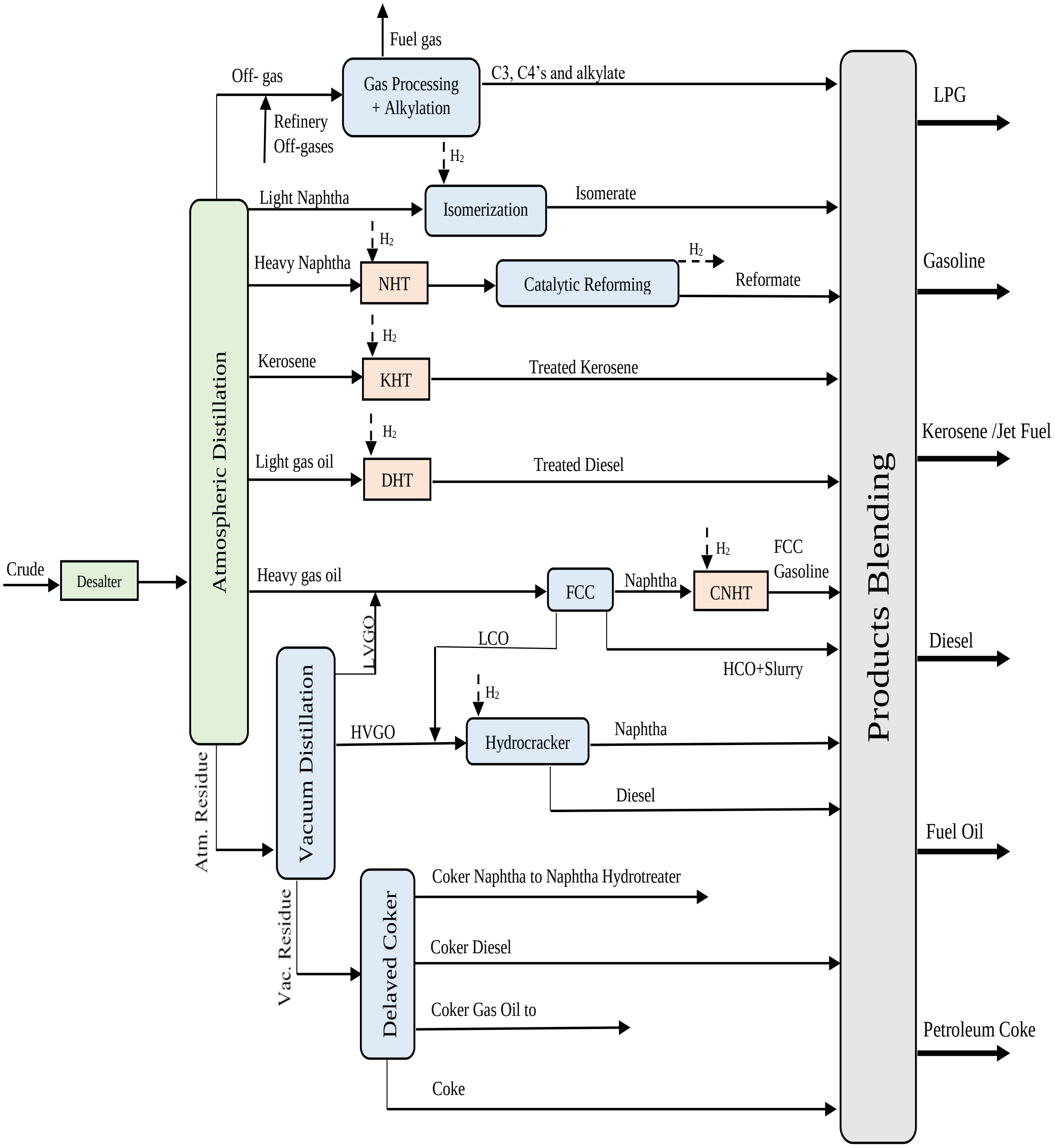
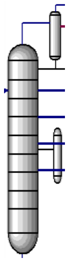
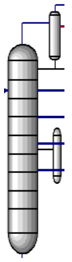
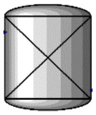
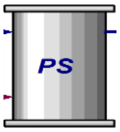
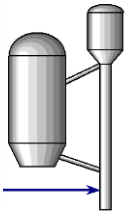
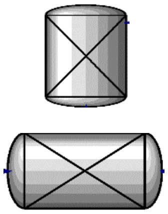
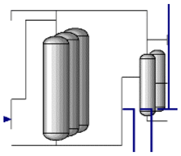
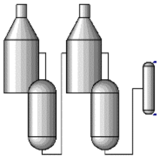
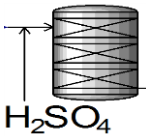


Figure 6. Block flow diagram of a high-conversion refinery

Table 1. Unit models summary used in Aspen HYSYS (V8.8) for the refinery simulation

			Fluid Package: Peng-Robinson		
Refinery Unit Operation	HYSYS Unit Model used	Model Palette	Feed Type and Characteristics	Feed Temperature and Pressure	Main Products
Atmospheric Distillation	Petroleum Distillation Column (20 theoretical stages)		Cold Lake Blend + Hibernia+ Bow River Heavy API= 29.73 Sulfur wt%= 1.45	387 °C 2.0 bar	- Off-gas -LSR - Heavy Naphtha -Kerosene -Light Gas Oil (LGO) -Heavy Gas Oil (HGO) -Atmospheric Residue
Vacuum Distillation	Petroleum Distillation Column (9 theoretical stages)		Atmospheric Residue API=13.78 Boiling Range: 350-700+ °C	400 °C 0.15 bar	-Off-gas -Light Vacuum Gas Oil (LVGO) -Heavy Vacuum Gas Oil (HVGO) -Vacuum Residue
Naphtha Hydrotreater	Naphtha Hydrotreater (NHT)		Heavy Naphtha Sulfur wt%= 0.04 Boiling Range: 50-200 °C	350 °C 16 bar	-Light Ends - Treated Heavy Naphtha
Kerosene Hydrotreater	Hydroprocessor Bed (HBED)		Kerosene Sulfur wt%= 0.17 Boiling Range: 150-260 °C	370 °C 34 bar	-Light Ends -Treated Kerosene
Diesel Hydrotreater	Hydroprocessor Bed (HBED)		LGO Sulfur wt%= 0.49 Boiling Range: 210-320 °C	380 °C 75 bar	-Light Ends -Treated Diesel
Delayed Coker	Petroleum Shift Reactor		Vacuum Residue API=6.4 Boiling Range: 540-700+ °C	504 °C 0.13 bar	-Light Ends -Coker Naphtha -Coker Diesel -Coker Gas Oil -Coke
Fluid catalytic cracking (FCC)	Fluid catalytic cracking (FCC)		Gas Oils (HGO+LVGO+ Coker Gas Oil) API= 22.32	250 °C 3.0 bar	-Light Ends - FCC Naphtha -Light Cycle Oil (LCO) -Heavy Cycle Oil (HCO) -Slurry

FCC Gasoline Hydrotreater	CatGas Hydrotreater (SHU) + CatGas Hydrotreater (HDS)		FCC Naphtha Sulfur wt%= 0.1 Boiling Range: C5-250 °C	SHU: 150 °C 27 bar HDS: 300 °C 28 bar	-Light Ends -Treated FCC gasoline
Hydrocracker	Hydrocracker (2 stage)		HVGO+LCO API=20.1	315 °C 130 bar	-Light Ends -Naphtha -Diesel -Bottoms
Catalytic Naphtha Reforming	Catalytic Reformer		Heavy Naphtha Boiling Range: 110-200 °C	410 °C 15 bar	-Net H2 -Light Ends -Reformate
Alkylation	H_2SO_4 Alkylation		Olefins+Iso-butane	-12 °C 1.0 bar	-Propane and Butane -Alkylate to gasoline blending

The hydrogen demand across the refinery hydrotreaters is estimated by modeling a typical configuration of the catalytic process found in literature as shown in Figure 7. The flow of the process starts with mixing the right ratio of total hydrogen, comprising of the recycle and the makeup, with a liquid feed stream. The mixed stream is then introduced to the hydrotreating reactor after it is heated to the required temperature for the reaction. The effluent from the reactor is cooled and sent to a separator at which the remaining hydrogen is sent for recycling, and the treated product is further forwarded to a distillation column to separate the light hydrocarbons and other gasses formed in the reaction from the desulfurized product. The separated hydrogen is first treated in amine scrubber to remove hydrogen sulfide (H_2S) contaminants, where the majority is compressed and sent back to the process, and the rest is drawn as a purge. The purge streams from the consumers are sent to the refinery fuel system where some can be routed to another user(s) depending on its hydrogen quality.

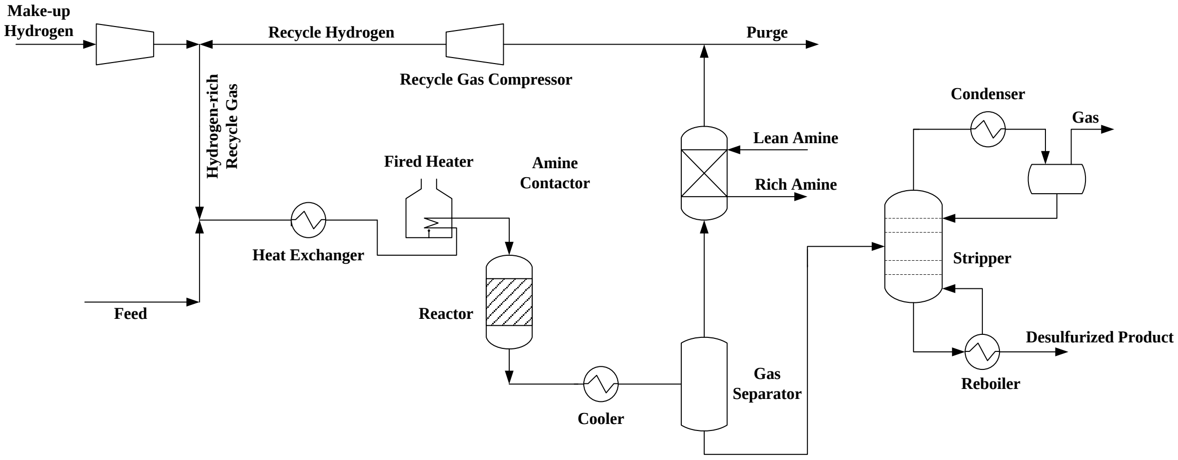


Figure 7. Schematic diagram of a typical hydrogen hydrotreater

Figure 8 shows a simplified hydrogen network for the simulated refinery. Hydrogen rich gas from the catalytic reforming and part of the purge gases from many consumers is being purified through pressure swing adsorption (PSA) units. This hydrogen is further combined with the additional hydrogen from the on-purpose hydrogen plant. The hydrogen is then compressed to various pressures depending on the requirement of each hydrogen consumer. However, the network design shown here does not convey an optimal utilization of the hydrogen sources available in a refinery. One can use further a hydrogen pinch analysis technique to develop an improved hydrogen scheme at which part of the purge streams may be cascaded with other hydrogen consumers.

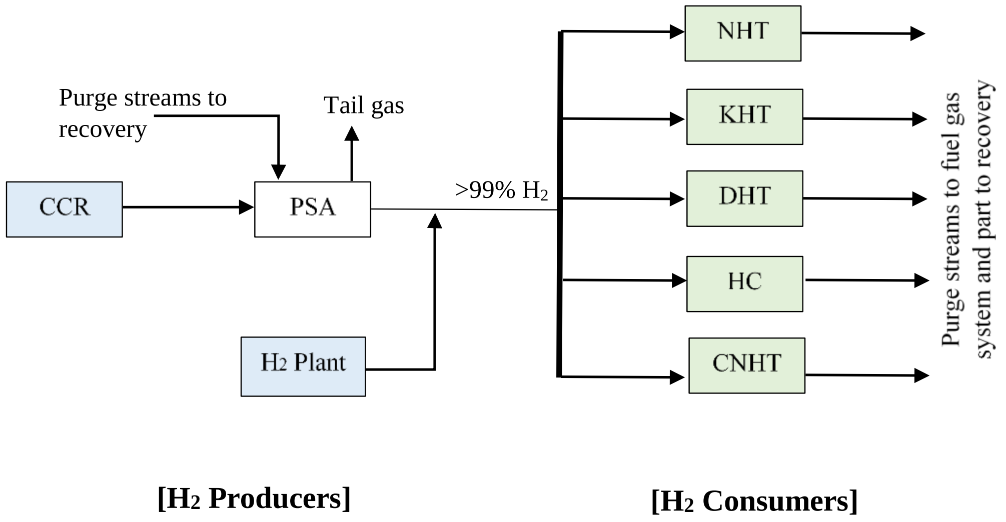


Figure 8. The hydrogen network design used in this chapter

2.2.2 Polymer Electrolyte Membrane (PEM) Electrolyzers Modeling

The second stage is the development of a mixed integer linear programming (MILP) optimization model. The aim of the model is to provide an optimum set-up of the electrolysis production system to meet the refinery hydrogen demand obtained from the Aspen HYSYS model. A Hydrogenics 1 MW nameplate capacity PEM electrolyzer module is used in the optimization model [52,53]. PEM electrolyzers are selected based on the given advantages of higher efficiency, compact mass-volume characteristics, and a high hydrogen purity when compared to its counterpart alkaline electrolyzers[54]. Besides, PEM electrolyzers have quicker ramp-up and ramp-down rates than alkaline electrolyzers[55]. Moreover, Hydrogenics PEM electrolyzers are designed for large scale applications with a hydrogen outlet pressure of 30 bar.

The optimization model is developed in the General Algebraic Modeling System (GAMS) [56], and the input is based on data collection of the year 2015. The set of inputs to the model include data for the refinery hourly hydrogen demand, the hourly Ontario electricity price (HOEP) and the hourly emission intensity of Ontario grid [57]. Also, the technical and cost information of the electrolysis system is incorporated.

The system is optimized to determine the optimal configuration and operating conditions for the electrolysis production system to meet the refinery hydrogen demand obtained from HYSYS model. The objective function is to minimize the annual total cost of the scheme, which includes capital, operation, and maintenance (O&M) expenses of the system. The capital cost includes the cost of the electrolyzers, compressors, and hydrogen storage tanks. These costs are amortized over a 20 year lifetime of the project with an interest rate of 8% (CRF is the amortization factor). The model decision variables are the number of electrolyzers, tanks, compressors (N_i) and variables related to the operating characteristics of the equipment, such as the hourly purchased electricity from the grid ($P_{grid}(h)$) and the operation of the storage tanks. Eqn. (3) presents the total annual cost formula.

$$Minimize\ Total\ cost = \sum_{\substack{i=Electrolyser,\\ Compressor,\\ Tank}} (C_{unit_i} . N_i . CRF + O\&M_i) + P_{grid}(h) \times (c_{elec}(h) + c_{trans}) + P_{compressor}(h) \times c_{elec}(h) \qquad \text{Eqn.(3)}$$

Where; C_{unit_i} is the unit capital cost of each equipment ($ per unit), c_{trans} is the charge fee for electricity transmission to the electrolyzer ($\$\ per\ kWh$), $c_{elec}(h)$ is the hourly price of electricity retrieved from IESO, and $P_{compressor}$ is the required electricity by the compressor. The capital cost data of the hydrogen compression and storage system is taken from literature [53]. A constant hourly hydrogen production is considered for the refinery. Furthermore, the technical information of the electrolyzer, compressor, as well as hydrogen storage tanks are presented in Table 2. The PEM electrolyzer considered for this work has a capacity of 1-MW with an efficiency of 76.7% that can generate a hydrogen with purity of 99.99% and at outlet pressure of 30 bar. The compressors of the system can increase the hydrogen pressure of the electrolyzers up to 172 bar for the hydrogen storage system, if needed. Also, each hydrogen tank has a fixed size of 89 kg, with a minimum and maximum inventory of 5.8 and 45.7 kmol, respectively. Note that the minimum inventory is the minimum capacity of the storage system and the maximum inventory is the maximum capacity of storage system. Moreover, the lifetime of the storage system is a 20-year [58].

Table 2. Technology information for the electrolytic hydrogen production

Electrolyzer		**Compressors for Tank Storage**		**Tanks for Hydrogen Storage**	
Maximum Capacity (kW)	1000	Output Pressure (bar)	172	Suction Pressure (bar)	20
System Efficiency (HHV) (%)	76.7	Capacity (kg/h)	42	Maximum Pressure (bar)	172
H2 Production(kg/Mw/hr)	19.4	Efficiency	0.65	Maximum Capacity (kg)	89
H2 outlet pressure(bar)	30	Power consumption (kWh/kmol)	3.3	Minimum Inventory (kmol)	5.8
H_2 purity	99.9%			Maximum Inventory (kmol)	45.7

The lifetime of the electrolyzer is assumed 10 years, and all replacement cost is considered as well in the capital cost of the project.

The levelized cost of hydrogen production (LCHP) is calculated based on the following (Eqn.(4)):

$$LCHP = \frac{Total\ cost}{\sum_{h=1}^{8760} H_{2_{production}} \times AF} \qquad \text{Eqn.(4)}$$

Where; AF is the availability factor

In addition, the model provides the total CO_2e emissions associated with producing the electrolytic hydrogen based on Ontario's grid emissions intensity. The annual total emission is calculated based on Eqn. (5).

$$Total\ Emission = \sum_{h} P_{grid}(h) \times EmF(h) \qquad \text{Eqn.(5)}$$

Where; EmF(h) is the hourly emission intensity of Ontario's electricity grid in kg CO_2e per MWh resulted from the total sources of electricity, which is estimated based on Eqn.(6).

$$EmF(h) = \frac{Nuclear\ power \times EF\ nuclear + Hydro\ power \times EF\ hydro + NG\ power \times EF\ NG + \cdots etc}{Total\ hourly\ power\ output} \qquad \text{Eqn. (6)}$$

Where; EF is the emission factor associated with each electricity source, which is obtained from Meier [59].

2.2.3 Steam Methane Reforming (SMR) Production Cost Estimate

Steam Methane Reforming (SMR) production cost is highly sensitive to the natural gas price. The cost of feedstock accounts for 52%-68% of the total cost of hydrogen production for large plants while about 40% for small plants [60]. The 2015 natural gas spot price at Henry Hub averaged \$2.62 per MMBtu, which was the lowest cost during the last 15 years [61]. According to U.S. Energy Information Administration (EIA) forecast, the prices will not see major fluctuation during the next 25 years ranging between 2.58-5.12 at 2015\$ per MMBtu [62]. As for Ontario province, the average natural gas price from the distributors was \$0.11 per m^3 or about \$3.07 per MMBtu in 2015 [63].

There are multiple correlations available in the literature to provide a fair estimate of the hydrogen cost from SMR. Bartels et al. [64] outline the use of two equations (Eqn. (7) and Eqn. (8)) for SMR production cost estimates obtained from Gray and Tomlinson [65] and Penner [66] respectively. Brinkman [67] has compiled SMR cost estimates from literature and provides a graph showing the relation of hydrogen cost (\$ per GJ) to natural gas prices (\$ per GJ). The costs from the figure can be approximated according to Eqn. (9).

$$\text{Hydrogen cost (1998\$ per MMBtu)} = 1.27 \times \text{NG price (\$/MMBtu)} + 0.985 \qquad \text{Eqn. (7)}$$

$$\text{Hydrogen cost (2006\$ per kg)} = 0.286 \times \text{NG price (\$/MMBtu)} + 0.15. \qquad \text{Eqn. (8)}$$

$$\text{Hydrogen cost (2002\$ per GJ)} = \text{NG price (\$/GJ)}/0.86 + 2.265 \qquad \text{Eqn. (9)}$$

However, the hydrogen costs from SMR has the economy of scale factor for which larger plants tend to have lower production costs and vice versa. The hydrogen cost estimates from the above correlations will be adjusted in this chapter to 2015$ using Chemical Engineering Plant Cost Index (CEPCI) value of 556.8 [68]. The availability factor (AF) of SMR plant is assumed to be 90% [60,67].

2.3 Results and Discussion

Table 3 shows Aspen HYSYS simulation results of the hydrogen network for a refinery having 100,000 bbl per day processing capacity. The crude blend consists from 65% Hibernia, 20% Cold Lake blend and 15% Bow River Heavy with 29.73 API and 1.45 wt. % of the sulfur content. All make-up hydrogen streams are assumed to be more than 99 vol%, given the existing of PSA units to increase the purity of hydrogen. The hydrogen plant shall produce around 25 MMscfd to meet the overall demand of the refinery. This demand is approximated by subtracting the consumers' intake minus the available hydrogen from other refinery sources.

Table 3. Hydrogen data from Aspen HYSYS

	Process	**Flow (MMscfd)**	**Flow (~Kg per hr)**
Hydrogen make-up to consumers	Naphtha Hydrotreater (NHT)	8.0	803.3
	Kerosene hydrotreater (KHT)	6.0	602.4
	Diesel hydrotreater (DHT)	12.0	1205
	Cracked naphtha hydrotreater (CNHT)	4.0	401.6
	Hydrocracker (HC)	30.4	3052
Hydrogen Sources	Catalytic Naphtha Reformer (CCR) and Purge streams combined after PSA	33.6	3381
	H_2 plant	25	2510

Starting with SMR as the base case, Table 4 shows the production cost estimates using Eqns. (7), (8) and (9) respectively. The average natural gas price of Ontario province in 2015 ($3.07 per MMBtu) was used, and the hydrogen costs were adjusted to 2015$. Since SMR is sensitive to natural gas prices, Figure 9 gives a range of hydrogen price across a range of natural gas price. Also, it shows the impact of having carbon pricing of $15, $50 and $100 per ton of carbon to the economy of SMR, based on the direct emissions from the unit at about 9 kg of CO_2e per kg of H_2 production [11].

Table 4. SMR cost estimates from Equations (7), (8) and (9)

	Equation	**Hydrogen cost (2015$ per kg)**
at a Natural gas price of $3.07 per MMBtu	(7)	0.94
	(8)	1.15
	(9)	1.13

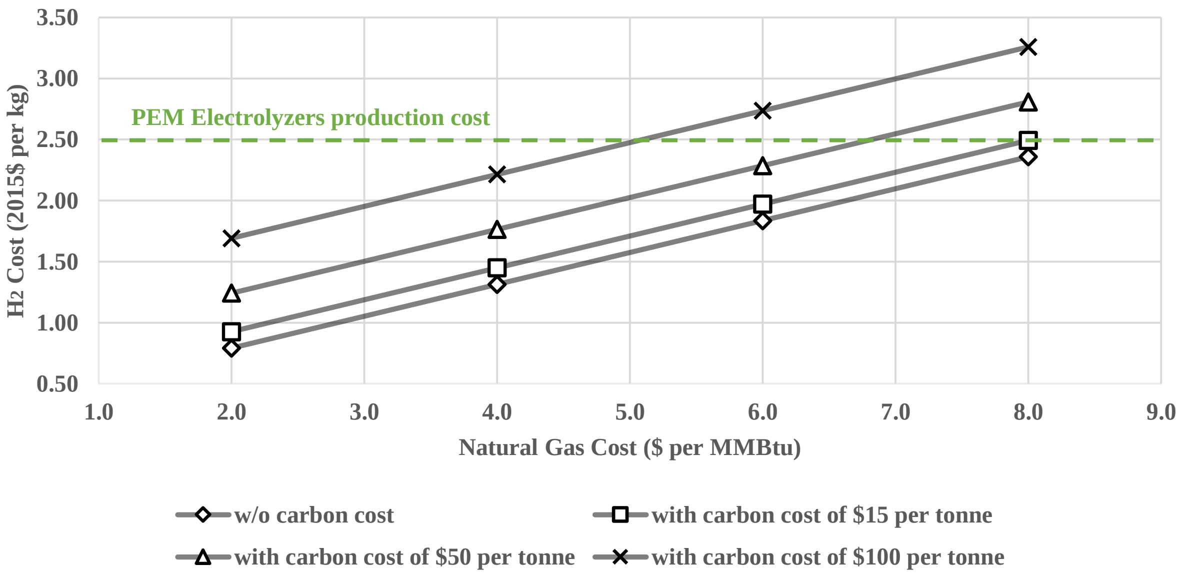


Figure 9. Sensitivity analysis of SMR cost estimates given natural gas and carbon price

Table 5 shows the economic and environmental comparison of producing 25 MMscfd (~2510 kg per hour) of hydrogen from SMR and PEM electrolyzers under five hydrogen production scenarios. The first scenario is total production (25 MMscfd) from SMR as the baseline. The second scenario is the production of the same quantity by the electrolyzers. The third assumes that the refinery has both systems and 50% of the demand is met by the electrolyzers. This scenario looks into the integration of the electrolyzers alongside SMR for a flexible production to the refinery processes while minimizing emissions. The fourth evaluates the output from the electrolyzers under the presumption that the grid is powered entirely by nuclear and renewable sources. The last scenario deals with the electrolyzers' operation time during off-peak periods when the hourly electricity prices are minimal, and store the excess produced quantity into storage tanks to continuously supply hydrogen to the refinery.

The third column in Table 5 lists the number of 1 MW PEM electrolyzers required for each scenario as generated by the MILP model. The fourth column provides the cost estimates of hydrogen production based on each setting. The last column provides the life cycle emissions in CO_2e for each case, at which the electrolysis emissions are associated with Ontario's electricity grid life cycle emissions intensity.

Table 5. Results summary of the studied scenarios

Scenario#	Hydrogen production scheme for the refinery	No. of 1 MW electrolyzers	Hydrogen Production Cost (2015$ per kg)	Life cycle CO_2e emissions (10^3 tons per year)
1	Total production from SMR	-	~ 1.1	235.1
2	Total production from electrolysis	130	2.5	71.1
3	Half production from electrolysis and the other half by SMR	65	1.8	153.1
4	Total production from electrolysis based on nuclear and renewables grid	130	2.5	13.6
5	Total production from electrolysis during low electricity prices (off-peak period)	427	5.9	36.0

Below is the discussion associated with each scenario:

Scenario 1: Total production for the refinery from SMR (Base case)

The annual life cycle CO_2e emissions from SMR production is calculated based on the below equation:

SMR annual emissions (tons of CO_2e) = H_2 production capacity (tons/year) × AF × SMR emissions per hydrogen production (tons of CO_2e/tons of H_2) Eqn. (10)

Where; AF is the availability factor, and the life cycle emissions ratio of SMR production is 11.88 kg of CO_2e per kg of H_2 as estimated by Spath and Mann [11]. Accordingly, the subject SMR emits 235.1 thousand tons (Kt) of the greenhouse gas emissions annually. Moreover, the plant produces the lowest hydrogen cost at an average of $1.1 per kg from equations (7-9) estimates with the absence of carbon taxation.

Scenario 2: Total production for the refinery from PEM electrolysis

The annual life cycle CO_2e emissions from PEM electrolysis production utilizing Ontario's electricity grid is 71.1 kt, as calculated by the MILP model using equations (5) and (6). The life cycle emissions are associated with Ontario's electricity sources for 2015 which constituted from 60% nuclear, 24% hydro, 10% natural gas and 6% wind. The electrolyzer operates at an availability factor (AF) of 99%, where the production from the electrolysis minimizes emissions by nearly 164 kt of CO_2e compared to SMR level. This has the same impact as removing 34,893 gasoline passenger vehicles from the road, based on 4.7 tons of CO_2 per car a year. The supply from the electrolysis will cost $2.5 per kg, calculated by equations (3) & (4) from the model. This production cost is higher than SMR provided that the natural gas price does not exceed $5 per MMBtu, even with a carbon price of $100 per ton. The horizontal line in Figure 9 illustrates the likely conditions at which hydrogen cost from electrolysis breaks even with SMR. Despite the higher cost of electrolysis, the government may mandate this scenario to ensure emission targets are achieved.

Note: the optimization model suggests using one tank (89 kg capacity) because the hydrogen is continuously supplied to the refinery.

Scenario 3: Half production from PEM electrolysis and the other half by SMR

The annual life cycle CO_2e emissions resulted from the integration of electrolysis and SMR into the refinery is 153.1 kt. The electrolyzer operates at availability factor of 99%, where this production mode minimizes emissions by about 82 kt of CO_2e compared to SMR level. This has the same impact as removing 17,446 gasoline passenger vehicles from the road. The combination set-up will roughly cost $1.8 per kg of H_2. This mode of production seems a good approach for a gradual utilization of electrolysis into refining processes. Also, it shows the potential benefits when integrating PEM electrolysis in a refinery when there is a need to expand the hydrogen production, instead of increasing SMR capacity. Therefore, this scenario not only has the advantage of achieving significant emission reductions, but it would also allow for a smaller or significantly less SMR equipment (this potential saving has not been considered).

Scenario 4: Total refinery demand production from PEM electrolysis based on nuclear and renewable grid power

The annual life cycle CO_2e emissions from PEM electrolysis production is 13.6 Kt, assuming the electricity grid is powered only by nuclear and renewable energy sources. Although these are clean energy sources, yet they still have a related life cycle emissions factors [59]. The electrolyzer operates at availability factor of 99%, where this scenario implies that around 80% of the grid emissions comes from the gas-fired plants. The cost is assumed to be indifferent than the second scenario, which is unlikely, under the presumption that the electricity price will not be affected by phasing out the gas-fired power plants.

Scenario 5: Total refinery demand production from PEM electrolysis during low electricity prices (off-peak period)

The annual life cycle CO_2e emissions from PEM electrolysis production during off-peak period is 36.0 kt. This setting was successful in reducing the emissions further in comparison to regular production in scenario 2. This is inevitable as the grid emissions intensity during off-peaks is lower since the power production from gas fired plants is ramped down. The average electricity price for large consumers in Ontario for the year 2015 was 1.43 and 2.08 cents per kWh during the off-peak and on-peak period respectively, as obtained from IESO. The electrolyzer operates at an availability factor of 80%, where the supply from the electrolysis during the off-peak period (7 P.M. to 7 A.M. weekdays) will cost $5.9 per kg of H_2. The reason for this higher cost is the need for a larger system with many storage tanks to accommodate the produced hydrogen during off-peak, and to continuously supply the demanded quantity during on-peak when the electrolyzers are not in a production mode. The cost of the capital settings outweighs the operating expenses reduction advantage associated with lower electricity prices. Though, if an underground seasonal storage of the hydrogen in salt caverns or depleted wells is considered, it would reduce the cost of this scenario significantly. The cost from scenario 5, however, has no delivery and handling charges because the hydrogen is sent directly to the refinery, unlike hydrogen supply to refueling stations. Nevertheless, the off-peak production mode must be further evaluated when there is access to an actual refinery demand data, as this paper assumes a constant demand during the operating year.

2.4 Conclusions

Steam methane reforming (SMR) and polymer electrolyte membrane (PEM) electrolyzers have been evaluated to supply 25 MMscfd of hydrogen to the Aspen-based simulation of an operating refinery for the production of gasoline and diesel. The study included production costs and life cycle emissions assessments based on five scenarios to meet the hydrogen demand of the refinery. The baseline (first) scenario was the conventional production from SMR while the rest scenarios deal with different operational scenarios for the electrolyzers from Ontario's electricity grid. The grid has a low average emission factor with a significant amount of baseload nuclear power and increasing amount of wind and solar power. The production cost estimates for SMR was $1.1 compared to $2.5 from PEM electrolysis. SMR remains a lower cost pathway to produce hydrogen under low natural gas prices. Low prices of natural gas provide a competitive advantage to SMR at this time, despite implementing stringent carbon pricing. Nevertheless, PEM electrolysis technology powered by clean energy sources was able to curtail significant carbon emissions from SMR level. It had a similar impact as potentially removing 34,893 gasoline passenger vehicles from the road, which can be compared to other emissions reduction initiatives. Though the production mode during off-peak has even larger emissions cut, it costs higher with $5.9 per kg of H_2 but with no delivery and handling charges required.

Chapter 3: Power-to-Gas Potential to Meet Ontario's Industrial Demand of Hydrogen

The following chapter is based on submitted work soon to be published in 2017 the 5th IEEE International Conference on Smart Energy Grid Engineering August 14-17,2017, Oshawa, Canada under the title "Exploring the Potential of Power-to-Gas Concept to Meet Ontario's Industrial Demand of Hydrogen" by "AlSubaie et al.". This thesis author specific contribution to this conference paper was to: "conduct the entire analysis, prepare all the graphics and results, and prepare the final manuscript and reviewer edits with direction from the project supervisors who are co-authors". This paper is co-authored by Dr. Michael Fowler and Dr.Ali Elkamel as supervisors who aided in editing the work. Also, Ushnik Mukherjee, PhD candidate, who is included to present the work in the subject conference.

3.1 Goal and Scope of the Study

There exist several studies in the literature regarding implementing power-to-gas (PtG) energy storage concept in the province of Ontario [29,31,35-39,42,50,69]. However, there is no current evaluation of the magnitude of Ontario's off-peak power to produce hydrogen from electrolysis for the industrial use such as oil refining and chemical industries, to the author's knowledge. Therefore, this chapter aims to explore Ontario's surplus electricity during off-peak to meet the industrial demand of hydrogen, typically met by SMR, in the province using PtG concept. However, the work will not attempt to cover the economic aspects of PtG; nor the possible implications on the operation of the electrical grid. The study will be limited to quantify the total amount of 'wasted' power in Ontario and divert it hydrogen production via power-to- gas. Then, the produced hydrogen is compared with the industrial demand of hydrogen in Ontario.

3.2 Methodology

Ontario's power transmission system consists of 10 geographical zones as shown in Figure 10. Toronto, Essa and Ottawa zones are load congested, at which limited opportunities for power-to-gas (PtG) exists at these zones [43]. However, the majority of the industrial hydrogen users in Ontario are located in the West zone while others are near the Niagara and East zones [8]. These zones among the remaining (Northwest, Northeast, Bruce and Southwest) are adequate for electrolytic hydrogen production since the technology can utilize the excess power generations in these zones [43]. Accordingly, this work will provide an estimate of the maximum hydrogen withdrawal from these geographical zones during off-peak periods.

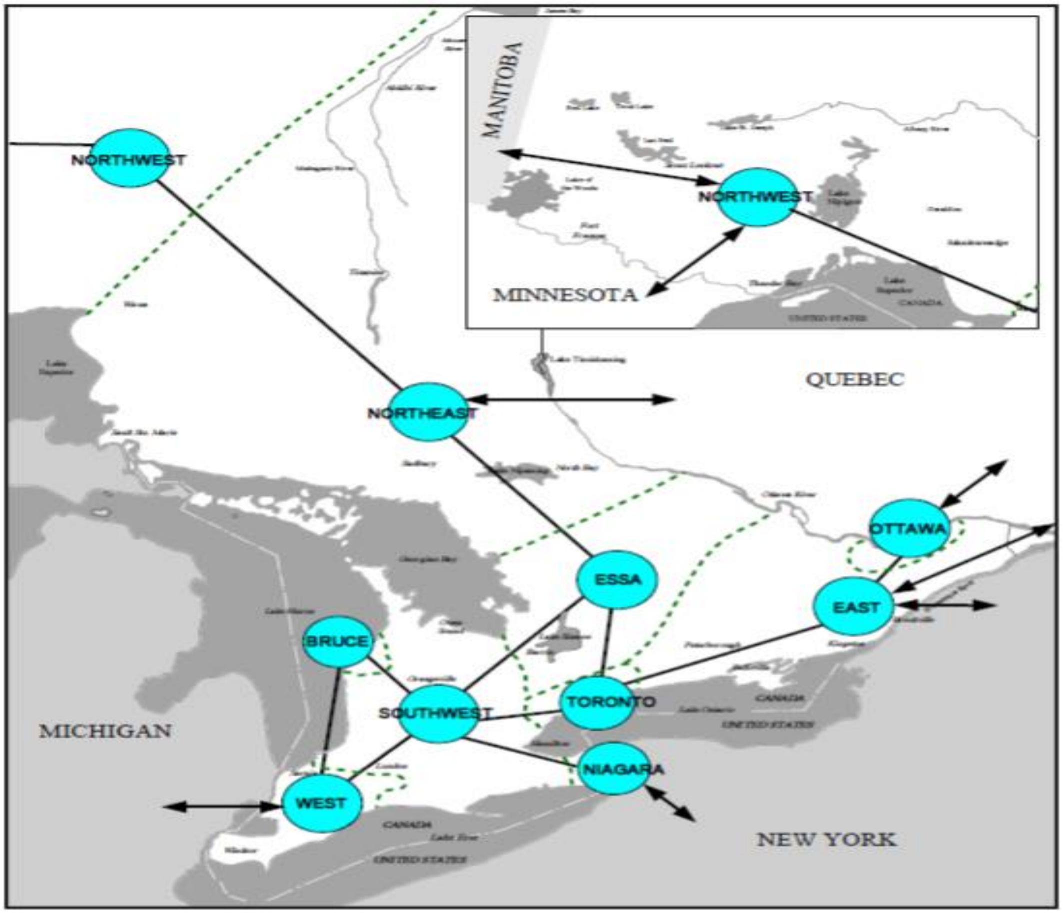


Figure 10. Ontario's power transmission system zones [43]

Table 6 presents an approximate of the total hydrogen production capacities available from SMR in Ontario. The data is collected based on the two surveys by Hunter and Deligiannis [8] and the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) [70]. The data in Table 6 includes the SMR plants production capacities from on-purpose captive (production by the user) and merchant (production from a company and sold to another).

The surplus power is estimated based on the combination of the net exported power to neighboring provinces during off-peak periods [57] and the curtailed power from wind and nuclear as well as import cuts [71]. Then, the study will convert the surplus power to hydrogen production via power-to-gas for the years 2014-2016 and compare it against the industrial demand from Table 6. Furthermore, the future of power-to-gas hydrogen production in Ontario will be evaluated during the next 15 years based on the SBG forecast [19-21] to quantify the required amount of electrolytic hydrogen to offset all SMR hydrogen in Ontario.

Table 6. SMR Captive and Merchant Production Capacities by Sector in Ontario

Sector (Industry)	**Production Capacity (MMscfd)**
Oil Refining	~ 124
Chemical	~ 84
Others	~ 14
Total	~ 223

With regard to the electrolysis technology, the most prevalent in the market are alkaline and polymer electrolyte membrane (PEM) electrolyzers. The full system specific energy consumption per a unit for both technologies can range from 5 to 6 kWh per Nm^3 of hydrogen [52,72]. The electricity consumption of 5.4 kWh per Nm^3 of hydrogen is assumed for the electrolysis unit in this study.

3.3 Results and Discussion

Table 7 shows the total amount of surplus power (in gigawatt hours) that went unused by the province during the previous three years (2014-2016), and when get diverted to hydrogen production (in millions standard cubic feet) via power-to-gas. The exported power to nearby jurisdictions constitutes about 80% of the total 'wasted' power since it is the major practice for managing the surplus generation. As for the electrolytic hydrogen production from Ontario's grid surplus power, it would have met the oil refining and chemical industry total hydrogen demand when comparing the results between Table 6 and 7. In addition, the annual hydrogen production from power-to-gas is found to surpass the oil refining SMR captive and merchant yearly production capacity by the range of 38-44%.

Table 7. The total amount of wasted power when diverted to hydrogen production via power to gas (electrolytic hydrogen)

	Year 2014	
	Power (GWh)	hydrogen production via power to gas (MMscf)
Exported Power	8,692	60,089
Curtailed Power	1,801	12,450
Total	10,493	72,540
	Year 2015	
	Power (GWh)	hydrogen production via power to gas (MMscf)
Exported Power	9,807	67,793
Curtailed Power	1,940	13,411
Total	11,747	81,204
	Year 2016	
	Power (GWh)	hydrogen production via power to gas (MMscf)
Exported Power	8,228	56,879
Curtailed Power	2,480	17,144
Total	10,708	74,024

Moreover, the monthly trend of surplus baseload generation (SBG) for the year 2014, 2015 and 2016 is presented in Figure 11, 12 and 13 respectively. The figures also include the electrolytic hydrogen in a million standard cubic feet per day (MMscfd) that could have been produced from SBG conditions during the studied years. The potential quantities of hydrogen are compared against total SMR captive and merchant production capacity of oil refining and all sectors combined in Ontario. As noticed in the figures, the encountered SBG is variable and can vary from similar seasons within the studied years. For instance, the dip of SBG at the beginning of 2014 was due to stronger demand during that colder winter season coupled with relatively less supply than the following years. In general, a gradual decrease of SBG is noticed during summer season (June – August) which may be due to higher electricity demand. Although occasionally there are periods of constricted electrolytic hydrogen production during lower SBG, about 2-3 months in each year, to match SMR daily production capacity of oil refining or chemical industry. Though, the current seasonal storage of depleted gas wells and salt caverns available in Sarnia and Windsor region can mitigate the variability of the technology production by storing the excess produced volume of hydrogen from electrolysis.

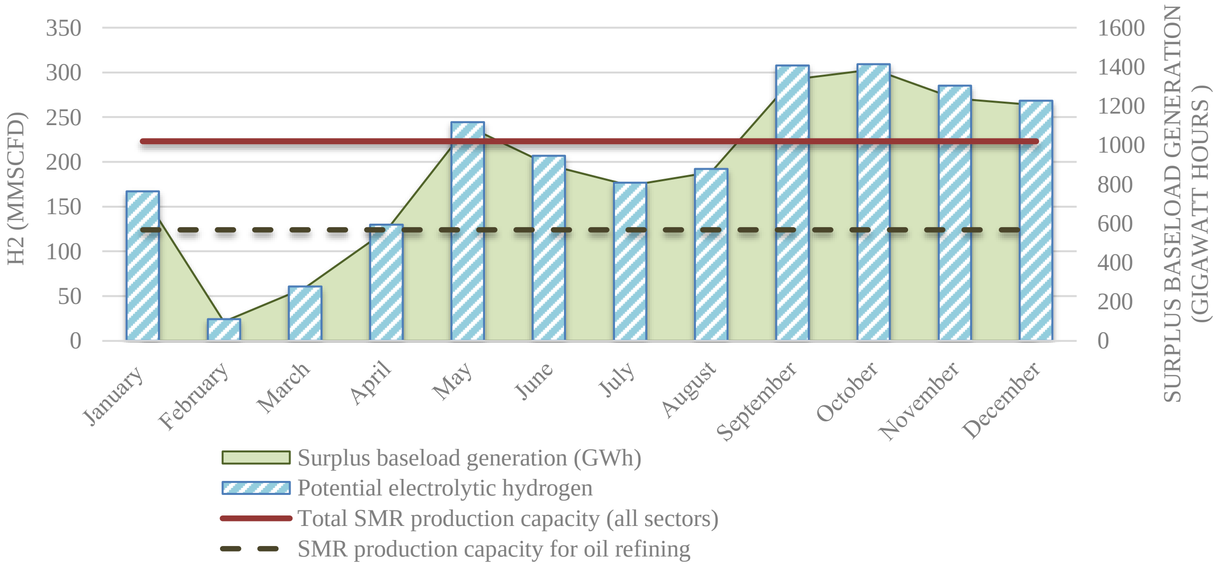


Figure 11.Ontario SBG and potential electrolytic hydrogen for the year 2014

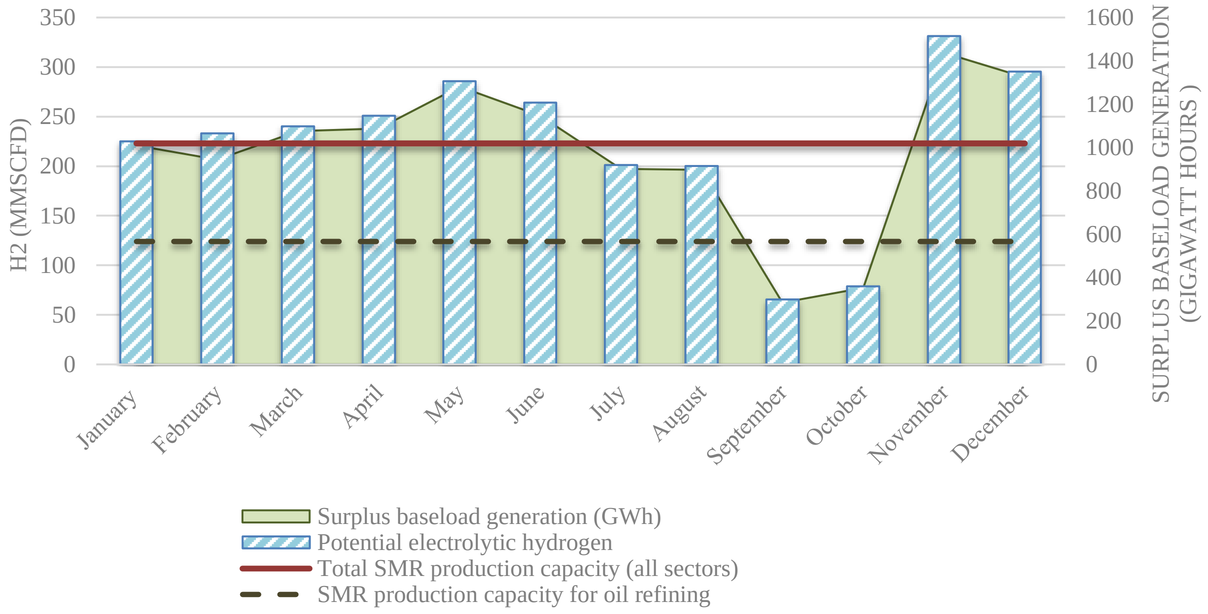


Figure 12. Ontario SBG and potential electrolytic hydrogen for the year 2015

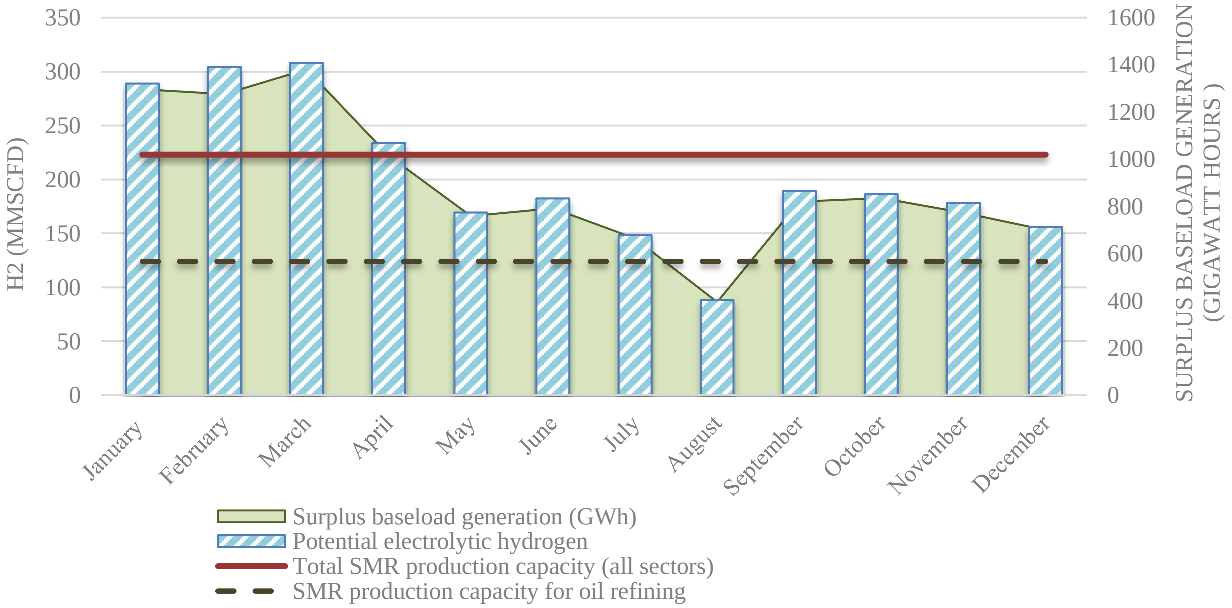


Figure 13.Ontario SBG and potential electrolytic hydrogen for the year 2016

Furthermore, Table 8 presents the yearly potential hydrogen production from electrolysis via power-to-gas from the surplus baseload generation estimate, and the percentage (%) offset it can offer to substitute SMR production from refineries as well as all industries combined. Also, the table highlights the annual hydrogen volume deficit from power-to-gas to counter all SMR production in the province according to the currently available outlook for the years 2017-2032 [20, 21]. Note that the demand for hydrogen is arbitrarily assumed in this study to be constant throughout the forecasted period. Also, Figure 14 provides the trend of the anticipated surplus power and the potential equivalent daily hydrogen production thru power-to-gas, for which it will continue to be significant during the next years. However, it is projected to be reduced beyond 2020 while the PtG hydrogen might be limited in the range of 35-78 MMscfd accordingly.

As a result, meeting the total industrial demand from electrolytic production utilizing only the surplus power appears not achievable particularly on 2021 and onwards. This is due to the uncertainty of SBG from Ontario grid which depends on several factors such as electricity demand, weather and planned nuclear refurbishments and outages as asserted by the Independent Electricity System Operator (IESO). Therefore, facilities applying electrolytic production may have need of consuming an additional load from the grid to meet their demand. At the same time, the production gap can also be used as incentives for the province to proceed with expanding renewable power supply.

Table 8. Surplus power forecast and amount to offset all SMR hydrogen in Ontario

Year	hydrogen production via power to gas	% offset from refineries SMR H_2	% offset from total industrial H_2 demand	Amount to offset all SMR hydrogen (MMscf)
2014	72,540	100%	89.1%	8,855
2015	81,204	100%	99.8%	191
2016	74,024	100%	90.9%	7,371
2017	59,382	100%	73.0%	22,013
2018	60,696	100%	74.6%	20,699
2019	44,174	97.6%	54.3%	37,221
2020	47,838	100%	58.8%	33,557
2021	15,831	35.0%	19.4%	65,564
2022	13,619	30.1%	16.7%	67,776
2023	15,209	33.6%	18.7%	66,186
2024	22,260	49.2%	27.3%	59,135
2025	17,766	39.3%	21.8%	63,629
2026	27,030	59.7%	33.2%	54,365
2027	17,421	38.5%	21.4%	63,974
2028	22,882	50.6%	28.1%	58,513
2029	12,858	28.4%	15.8%	68,537
2030	22,191	49.0%	27.3%	59,204
2031	19,011	42.0%	23.4%	62,384
2032	28,343	62.6%	34.8%	53,052

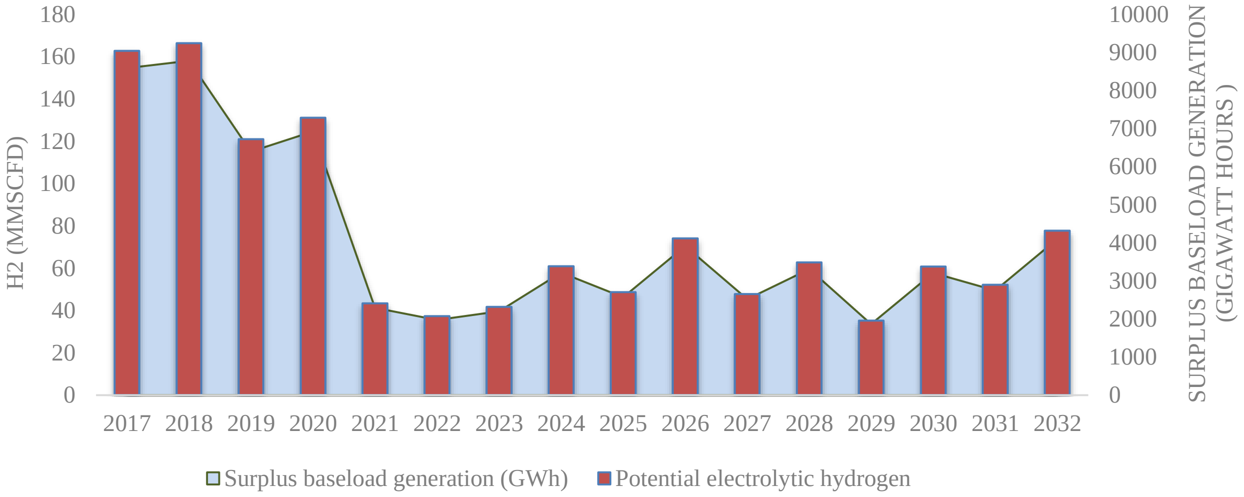


Figure 14.Ontario SBG and potential electrolytic hydrogen for the years 2017-2032

3.4 Conclusions

In this study, the surplus power in Ontario resulted from the off-peak net exports to neighboring jurisdictions plus wind and nuclear curtailments, was estimated for the past three years 2014-2016 as well as for the outlook of 2017-2032. The purpose was to compare the potential electrolytic hydrogen, as a result of deploying the power-to-gas concept, against Ontario’s industrial hydrogen demand that includes oil refining and chemical sector. The analysis showed that utilizing power-to-gas energy storage could potentially meet a significant demand for oil refining and chemical industry hydrogen demand that is typically met by steam methane reforming (SMR) at least for the next four years. However, the electrolytic production volumes beyond the year 2020 are yet tentative due to the uncertainty surrounding future electricity demand, weather and planned nuclear refurbishments and outages. For that reason, utilizing Ontario’s seasonal storage of depleted gas wells and salt caverns are required to provide an economical and a sustainable production during low surplus baseload generation from electrolysis to meet a significant industrial demand while minimizing greenhouse gas emissions.

Chapter 4: Power-to-gas Impact on the Life Cycle of Gasoline

The following chapter is based on work submitted to the Energies Journal which currently under review with the title "Evaluating the Incentives of Considering the Hydrogen Supply via Power to Gas in the Renewable Fuels Regulations of Petroleum Fuels" by "AlSubaie et al.". This thesis author specific contribution to this paper was to: "conduct the entire analysis, prepare all the graphics and results, and prepare the manuscript with direction from the project supervisors who are co-authors". This paper is co-authored by Dr. Michael Fowler and Dr.Ali Elkamel as supervisors who provided key insights throughout the course of this work and aided in editing the work.

4.1 Research Background

Biofuels are typically liquid fuels made from biomass. The use of biofuels in transportation fuels has been enacted in several regions in the world mainly to reduce the reliance on petroleum fuels and minimize greenhouse gas (GHG) emissions from the transportation sector. In U.S., the Renewable Fuel Standard (RFS) program was first introduced in the year 2005 and was expanded under the 2007 Energy Independence and Security Act (EISA) to post the renewable fuels volumes incrementally to 36 billion gallons by 2022 [73]. In Canada, the Renewable Fuels Regulations legislated late 2010 dictate gasoline producers and importers to blend renewable fuels with an annual average of no less than 5% of gasoline volumes [74]. Moreover, the European Union (EU) has requested each country within the union to have at least 10% of renewable energy share in the transport fuels by 2020 under the Renewable Energy Directive program [75]. Usually, ethanol and biodiesel are the most common used biofuels to meet such standards.

Ethanol fuel can come from different feedstocks such as corn, sugarcane and cellulose, with corn grain being the conventional feedstock for ethanol production in North America and Central

Europe [76]. However, corn-ethanol has an associated life cycle emissions depending on the production technology (e.g. Dry Mill or Wet Mill), fuel input (e.g. natural gas, coal or biomass), co-products credit (such as corn oil and distillers grains with solubles (DGS)) and land-use change effect, which apparently still a controversial subject among researchers. The carbon intensity (CI) estimates of corn-ethanol are varied in the literature between 31-177 in grams of carbon dioxide equivalent per megajoule of fuel (gCO_2e per MJ) [77-81]. Furthermore, Mullins et al. [82] expand the range of the carbon intensity to 250 gCO2e per MJ given the uncertainty surrounding corn-ethanol life cycle emissions. In contrast, the carbon intensity of gasoline from a conventional crude can range between 84-105 gCO_2e per MJ [77,83]. Thus, the environmental incentives of utilizing corn-ethanol in vehicles as an alternative fuel can be debated. For instance, Jaeger and Egelkraut [84] find that achieving U.S. corn-ethanol production target in 2025 has a less significant impact on CO_2 emissions and would only reduce the petroleum use by 1.75%. Moreover, DeCicco et al. [85] conclude that growing use of biofuels has an implication of a net increase in CO_2 emissions level rather. In addition, Hill et al.[86] and Jacobson [87] suggest that corn-ethanol fuel is linked to higher health impacts than conventional gasoline. Nevertheless, the shift to cellulosic ethanol can achieve the objective of emissions reduction than ethanol derived from corn [86]. However, as a second generation biofuel, the cellulosic ethanol industry is still emerging for a commercial scale production.

On the other hand, ethanol is blended with gasoline typically to 10% by volume, which is usually referred E10 (10% ethanol, 90% gasoline). The blend can increase the level of oxygen in gasoline (oxygenate agent) which promotes the combustion process reducing emissions at the tailpipe. Also, it increases the octane number of gasoline and the Reid vapor pressure but decreases the heating value of the fuel [88-90]. Corn-ethanol blend with a gasoline can also have some environmental concerns associated with some benefits. For instance, Niven [91] report the findings of various studies from the 1990s to early 2000s regarding E10, which primarily are: it decreases the tailpipe carbon monoxide (CO) and particulate matter (PM) emissions but increases acetaldehyde, ethanol and nitrogen oxide (NO_x) emissions; it poses a risk of contaminating the soil and groundwater since it increases storage tank corrosion; and it has 1-5% greenhouse gas (GHG) reduction compared to ethanol-free gasoline (E0). Furthermore, Kim and Dale [92] study the life cycle of corn-ethanol from dry milling process, and find the associated gasoline blend (E10) to reduce fossil energy use and GHG emissions but increase the acidification and photochemical smog mainly from the NO_x emissions during corn cultivation. Also, Hess et al. [93] analysis reveal the ethanol blend from corn to release additional criteria air pollutants of volatile organic compounds (VOCs), NO_x, particulate matter with size smaller than 10 micron (PM_{10}), particulate matter with size smaller than 2.5 micron ($PM_{2.5}$)and sulfur oxide (SO_x) except for CO, than E0. Moreover, Table 9 presents a comparative assessment of the tailpipe exhausts emissions for E10 versus E0 fuels in a spark-ignition (SI) engines from several studies since the early 2000s. It is apparent that researchers have a consensus that E10 lowers the CO, PM and hydrocarbons (HC) while increases acetaldehyde emissions. However, there seems a disagreement on whether E10 has a more or less CO_2, formaldehyde and NO_x emissions from the tailpipe exhaust. Accordingly, given the uncertainty of corn-ethanol environmental impacts in the short and long term, implies the need for more attractive, or complimentary, renewable fuel options that can influence the emissions released from the ‘cradle to grave’ use of petroleum fuels.

Table 9. Environmental impact of using E10 fuel in a spark-ignition (SI) engines

Source	CO_2	Formaldehyde	CO	NO_x	PM	HC	Acetaldehyde
Kim and Dale [94]	↓	↓	↓	↑	-	-	-
Najafi et al. [95]	↑	-	↓	↑	-	↓	-
Pang et al. [96]	-	↑	↓	↑	-	-	↑
Bayraktar [97]	-	-	↓	↑	-	-	-
Hsieh et al. [98]	↑	-	↓	↑	-	↓	-
Graham et al. [99]	NSD	NSD	↓	NSD	-	-	↑
Canakci et al. [100]	↓	-	↓	↓	-	↓	-
Storey et al. [101]	-	↓	↑	↓	↓	↓	↑
Costagliola et al. [102]	-	↑	↓	↑	↓	↑	↑
Maricq et al. [103]	-	-	-	NSD	↓	NSD	-
Turner et al. [90]	-	-	↓	NSD	-	↓	-
He et al. [104]	-	-	↓	NSD	-	↓	↑
Elfasakhany [105]	↑	-	↓	-	-	↓	-
Al-Hasan [106]	↑	-	↓	-	-	↓	-

↑: E10 has higher emissions than E0;↓: E10 has lower emissions than E0; NSD: no significant difference; - : not evaluated

Therefore, this study aims to introduce a novel approach to increase the renewable content of gasoline while minimizing its life cycle GHG emissions and well to wheel air pollution emissions as well. The idea stemmed from the utilization of an excess generated renewable or CO_2 free power during low demand to produce a 'clean' hydrogen via electrolysis (i.e. 'power to gas' or PtG), which can be then employed into the gasoline fuel production in an oil refinery. Refiners use mainly steam methane reforming (SMR) technology, which generates significant emissions during the production of the required hydrogen for the petroleum fuels hydrotreating processes. The advantages of substituting CO_2 free hydrogen for SMR hydrogen are:

- Reduces life cycle GHG emissions of petroleum fuels, and thus helps refineries to meet emission reduction targets;
- Aids in meeting the renewable energy content regulations of gasoline and diesel liquid fuels;
- Is complementary with the addition of ethanol or biodiesel to the fuel as it does not change the basic composition of the base fuel, so both ‘power to gas’ associated hydrogen, and bio-based additives can be employed to increase renewable energy content in the petroleum fuel in a complimentary fashion; and,
- There is no need to change fuel distribution equipment, nor the vehicle fleet itself, yet still achieve net emission reductions.

Accordingly, the objective of this work is to evaluate the impact of deploying power to gas concept for a renewable electrolytic hydrogen production on the life cycle of gasoline in accordance with the renewable fuels regulations. Thus, it will compare the renewable energy and environmental contributions of blending corn ethanol and implementing power to gas on a conventional gasoline fuel (E0). The study will use the case of Ontario province in Canada which has a potential to supply a green hydrogen from its grid which is powered by CO_2 free sources of electricity as it was detailed in the previous sections.

While the study in Chapter 2 presents the environmental incentives of implementing power to gas (PtG) to an individual refinery, the work does not evaluate its potential impact on the life cycle of gasoline. So, this chapter complements the previous study on PtG application at the refinery level by introducing the concept in the prospect of providing a renewable content to gasoline fuel like biofuels as well as reducing the petroleum fuel carbon intensity. This approach has not been investigated previously based on the life cycle of transportation fuel, according to the author’s knowledge. Note, there is a recognition that the renewable energy content of the overall well to wheel production of gasoline can be further improved with the introduction of PtG electrolytic hydrogen at the synthetic crude upgrader level and this has been outlined by Walker et al. [29], and it is not included in this analysis.

Accordingly, the chapter organization starts with the methodology section (4.2) that presents the carried life cycle assessment provided by the GREET® Model to achieve the objective of the study. Moreover, the results and discussion section (4.3) provides the well to wheel (WTW) analysis of the metrics: Total energy use (4.3.1); greenhouse gas emissions (4.3.2); and criteria air pollutants (4.3.3), for gasoline fuel according to the following scenarios:

i. Unblended gasoline (E0);
ii. Blended gasoline with 10% ethanol by volume (E10);
iii. Unblended gasoline (E0) with an electrolytic hydrogen production via power to gas (PtG) at the refinery level; and,
iv. Blended gasoline with 10% ethanol by volume (E10) and the base gasoline produced with an electrolytic hydrogen production via PtG at the refinery level.

4.2 Methodology

A life cycle assessment (LCA) will be established in this work to study the environmental impact of blending corn-ethanol and using electrolytic hydrogen from power to gas (PtG) concept as a renewable energy share in gasoline fuel. Consequently, the LCA will be performed using the latest GREET® Model (The Greenhouse gases, Regulated Emissions, and Energy use in Transportation Model) released in 2016 [107]. The LCA model is sponsored by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE), and regularly updated and maintained by Argonne National Laboratory. The model estimates the energy and emission impacts of various transportation fuels and vehicle technologies on the life cycle basis. Figure 15 shows the fuel and vehicle cycle considered in GREET model, where the well to pump (WTP) includes fuel production and transportation while the pump to wheel (PTW) is related to the direct consumption of the fuel by the vehicle. The sum of WTP and PTW results in the well to wheel (WTW) analysis of the fuel.

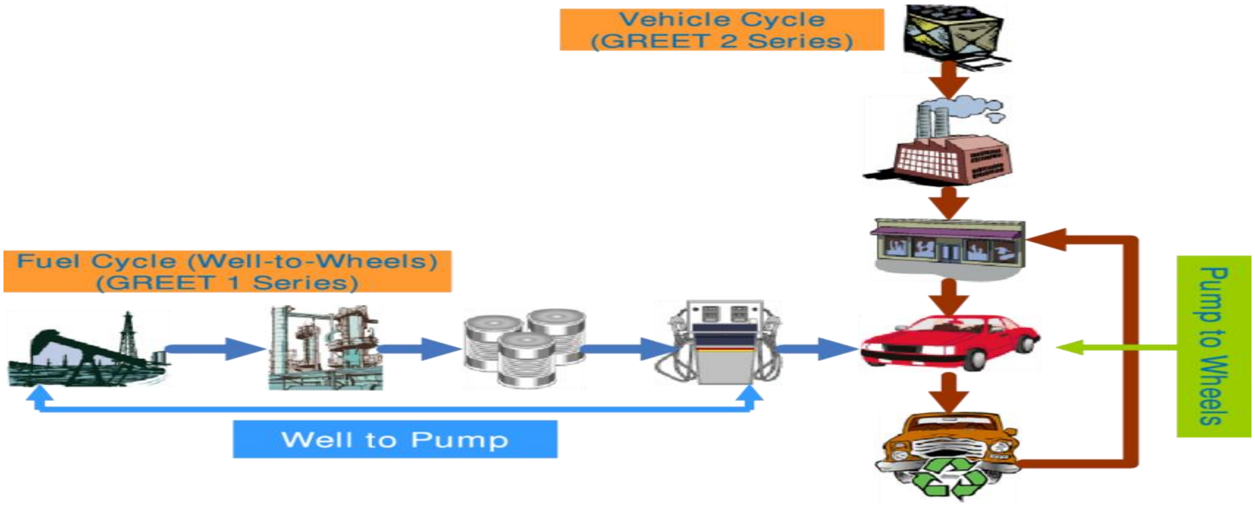


Figure 15. Life-cycle analysis of vehicle/fuel systems with the GREET model [117]

The greenhouse gases (GHG) emissions are based on CO_2-equivalent, which includes carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) according to their global warming potentials of 1, 25, and 298, respectively [108]. Furthermore, it encompasses the total emissions (from urban and rural emissions) of primarily six criteria pollutants, which are volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxide (NO_x), particulate matter with size smaller than 10 micron (PM_{10}), particulate matter with size smaller than 2.5 micron ($PM_{2.5}$), and sulfur oxides (SO_x). Moreover, GREET assesses the total energy use (from fossil and non-fossil sources), fossil fuel use (petroleum, natural gas, and coal combined) and also the consumption of petroleum, natural gas, coal and water on the well to wheel of the selected fuels.

The author is aware that GREET model is mainly developed to represent the U.S framework. However, it will still be used to provide a reasonable estimate of the impact of employing power to gas technology to the case of Ontario region in Canada with modification of the grid profile. The model has been selected since it is the most updated open source model available for fuel life cycle assessment (LCA) according to the author's knowledge. Although a program such as GHGenius model can perform similar LCA tasks based on Canada and U.S., the latest publicly released version of the model (GHGenius 4.03a) was in 2013 [109]. Note that even when both models run for the same pathway and location, they may not necessarily produce matching results based on the different default data and assumptions included in each model [110].

Therefore, GREET model will be used with some adjustments to the default model to provide similar conditions to the one in Ontario, which is related to crude oil slates, electricity mix (and associated grid emissions factor), ethanol and natural gas production profiles. As such these factors are outlined below:

4.2.1 Crude Oil Slates

Ontario refineries process different types of crude oil. The processed crude slates are 50% conventional light crude and about 25% conventional heavy crude while the remaining is synthetic crude [111]. However, GREET crude oil data includes the term 'conventional crude' without specifying whether the crude is light, medium or heavy. Accordingly, the default crude oil mix in the model is changed to 75% conventional crude and 25% synthetic crude. Furthermore, the majority (~ 90%) of the synthetic crude oil (SCO) upgraded from bitumen in Canada originates from mined bitumen whereas the remaining is based on in-situ bitumen [112], which is also adjusted in the model to reflect these shares.

4.2.2 Electricity Mix

Ontario's power generation is comprised of more than 90% of nuclear and renewable sources (hydro, wind, solar and biofuel) [113]. According to the Independent Electricity System Operator (IESO), the anticipated power generation outlook during the year 2017-2018 will consist of around 62% nuclear, 25% hydro, 7% natural gas-fired plants and the rest is mainly from wind power [71]. Therefore, in this work, a new pathway mix in the GREET model has been created to represent Ontario's electricity grid. Consequently, the electricity input source supplying the electrolysis technology as well as the refining and ethanol industry in the model is from the newly generated electricity pathway. Also, the power to gas (PtG) scenario will be based on the average emission factor from the developed electricity grid in the model. Accordingly, the life cycle emissions result of the electrolytic hydrogen via power to gas will be based on the carbon intensity of the Ontario grid, and is compared with steam methane reforming (SMR) in the analysis section.

4.2.3 Ethanol Industry

The majority of the ethanol industry in Ontario uses corn as a feedstock with the production technology of natural gas fired dry mill [114]. Accordingly, the study will be limited to the evaluation of corn-ethanol from dry mill technology with natural gas as the heat source.

4.2.4 Natural Gas

GREET includes the properties of Canadian natural gas among other selections of natural gas pathways. Therefore, all processes in GREET that involve natural gas input such as steam methane reforming (SMR) are changed to Canadian natural gas.

After all required adjustments completed, the objective of the study is now to perform well to wheel (WTW) investigation of the following scenarios:

i. Unblended gasoline (E0) produced and used in Ontario;

ii. Blended gasoline with 10% ethanol by volume (E10);

iii. Unblended gasoline (E0) with an electrolytic hydrogen production via power to gas (PtG) at the refinery level; and,

iv. Blended gasoline with 10% ethanol by volume (E10) with an electrolytic hydrogen production via PtG used in the gasoline production at the refinery level.

The analysis will consider the below metrics on the life cycle of gasoline production and use by an internal combustion engine vehicle (ICE) with a spark-ignition (SI):

- Total energy use;
- Greenhouse gas emissions (GHG); and,
- Criteria air pollutants (CO, VOCs, PM_{10}, $PM_{2.5}$, NO_x and SO_x)

4.3 Results and Discussion

4.3.1 Total Energy Use

The total energy use (kJ per MJ of fuel production and use) results are presented in Table 10 and Figure 16, respectively. The total energy consists of the fossil energy (petroleum and natural gas) and non-fossil energy (nuclear and renewables) consumption throughout the fuel cycle. The renewable energy includes the solar, wind, hydro and biomass energy usage during the well to wheel (WTW) of the studied fuels for gasoline vehicles. The considered gasoline fuel types in this study are: (i) unblended gasoline (E0); (ii) blended gasoline with 10% ethanol by volume (E10); (iii) E0 with an electrolytic hydrogen production via power to gas (PtG); and (iv) E10 with an electrolytic hydrogen production via PtG.

As for the fossil energy use, the use of 10% ethanol by volume can substitute 6.3% of the petroleum (gasoline) fuel in vehicles while PtG technology has no influence on the state of the fuel quality. Moreover, the utilization of PtG instead of steam methane reforming (SMR) in a refinery minimizes the consumption of natural gas on the gasoline cycle by 4.6%, unlike ethanol which also involves the use of natural gas as a heat energy during its production. Therefore, both ethanol and PtG can decrease the overall fossil energy for the production and use of gasoline as shown in the last scenario (iv) in a complimentary fashion. With regard to the non-fossil energy use, conventional gasoline production (i) has the least nuclear or electricity consumption since ethanol production and PtG technology consume additional electric power which is mainly derived from nuclear as the case of Ontario. On the other hand, the biomass energy of ethanol fuel can substantially increase the renewable energy content of regular gasoline while PtG can augment the renewable energy share from the extended use of hydro and wind power. Accordingly, PtG implementation for a hydrogen supply to the refining industry has a potential to be considered part of the renewable fuels criteria along with biofuels since both reduce the fossil energy use and increase the renewable share in the gasoline fuel.

Table 10. Energy use shares on well to wheel of studied gasoline types

Energy use (kJ per MJ of fuel produced and used)	**(i): E0**	**(ii): E10**	**(iii): E0 with PtG**	**(iv): E10 with PtG**
Petroleum	1092	1023	1092	1023
Natural Gas	193	209	184	200
Fossil	**1285**	**1232**	**1276**	**1223**
Nuclear	10	12	16	17
Renewable	7	87	10	89
Non-Fossil	**18**	**99**	**26**	**106**
Total Energy	**1303**	**1330**	**1302**	**1329**

Note: numbers may not add up due to rounding

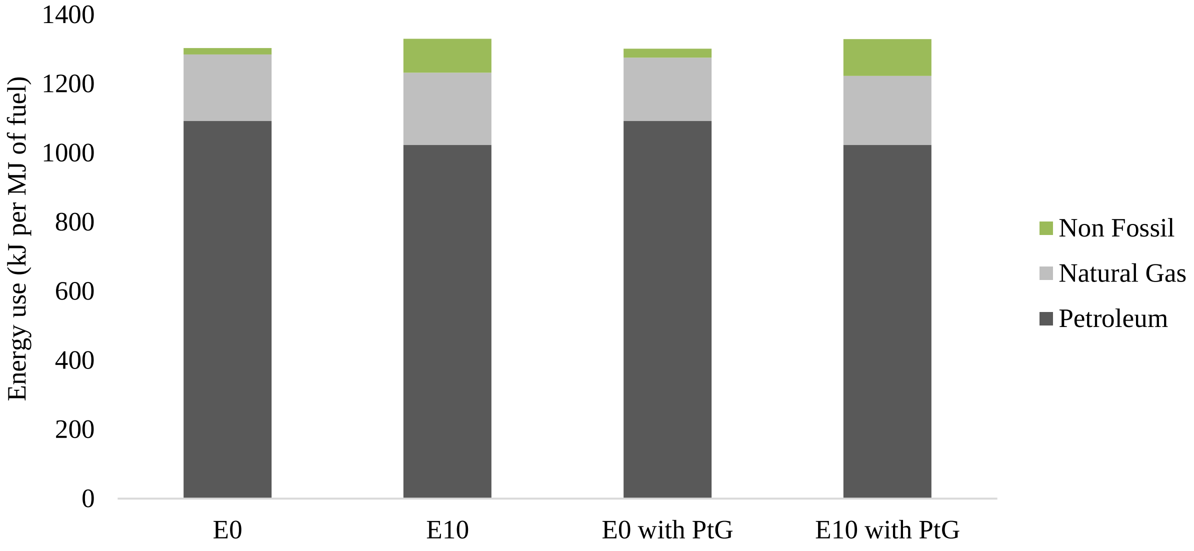


Figure 16. Total energy use per production and use of studied gasoline types

4.3.2 Life Cycle Greenhouse Gas (GHG) Emissions

The analysis starts with presenting the environmental influence of deploying electrolysis technology for hydrogen production instead of steam methane reformer (SMR). Figure 17 shows the life cycle emissions comparison of the two hydrogen production technologies obtained from the GREET model. SMR emits a considerable life cycle emissions of 11.3 of carbon dioxide equivalent (CO_2e) per kg of hydrogen. On the other hand, the electrolytic hydrogen production via power to gas (PtG) is responsible for a significantly fewer greenhouse emissions (GHG) of 1.6 kg of CO_2e per kg of hydrogen. Note that GREET model assumes generated power from wind and hydro has no associated carbon emissions while electrolysis related production emission is from gas-fired plants and nuclear generation. Therefore, the electrolytic production can have 85% of GHG reduction from SMR level as a result of utilizing Ontario's grid during low demand, which is supplied by a substantial integration of baseload nuclear and renewable sources of hydro and wind power. Consequently, the cleaner supply of hydrogen will entail reducing the carbon intensity of gasoline in the refining stage and hence on the life cycle of the fuel.

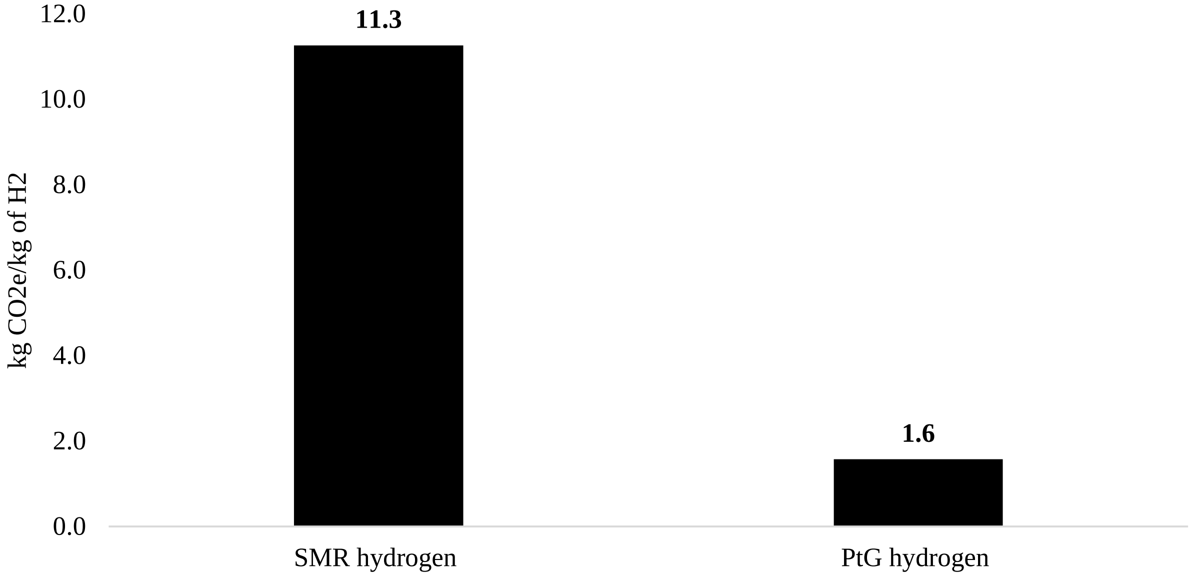


Figure 17. Life cycle GHG emissions of SMR and electrolysis from Ontario's electricity mix

Furthermore, the life cycle emission of gasoline fuel is presented in Figure 18 shows the effect of the corn-ethanol blend and electrolytic hydrogen use on the carbon intensity results of gasoline. The life cycle of the fuels in the figure comprises of well to pump (WTP) and pump to wheel (PTW) which the sum make up the well to wheel (WTW) result of each scenario. The columns in order from left to right presents, unblended gasoline (E0); blended gasoline with 10% ethanol by volume (E10); E0 with an electrolytic hydrogen production via power to gas (PtG); and E10 with an electrolytic hydrogen production via PtG. Note that the results include the account of biogenic CO_2, co-products credits (DGS and corn oil) and land use change associated with ethanol production.

Starting with the WTP results, the unblended gasoline (E0) with the alteration to the electrolytic hydrogen production via PtG in an oil refinery has the least carbon intensity; because ethanol production from corn is also a carbon intense activity which explains the increase of emissions in the ethanol-blended gasoline (E10). The switch to an electrolytic hydrogen production method on the oil refining share in the WTP cycle (~ 45%), will result in minimizing the carbon intensity of gasoline production by at least 0.5 gCO_2e per MJ of fuel produced and used. Therefore, the electrolysis technology can slash 5% from an oil refinery total GHG emissions, which can be benefited by refinery operators subjected to either carbon regulation via cap-and-trade or carbon taxation. Although the electrolytic production appears to have an overall minor impact on gasoline cycle emission, it has a significant magnitude when compared to the total use of gasoline in cars. For instance, there are around 8 million vehicles in Ontario [115] with a net consumption of about 16,000 million liters of gasoline according to Statistics Canada in the year 2015 [116]. Consequently, lowering the gasoline carbon intensity by 0.5 gCO_2e per MJ of fuel will result in curbing 256 thousand tons (Kt) of GHG emissions annually[1]. The reduction impact can be equated to taking nearly 54,000 vehicles off the road, assuming a typical passenger car emits 4.7 tons of CO_2 per year [45]. Accordingly, there can be a substantial impact to the refinery operator or the

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[1] The annual emissions reduction calculation: $1.6 \times 10^{10}\ L\ gasoline \times \frac{32\ MJ}{L}\ (LHV) \times \frac{0.5\ gCO2e}{MJ\ gasoline} \times \frac{1\ ton}{1 \times 10^{6} g}$

province as a whole, without a need to change the current fleet of vehicles or fuel distribution systems (which both will take some time to change).

Additionally, the PTW in Figure 18 provides the emissions quantities associated with combusting E0 and E10 fuels on ICE vehicles. The results show that the combustion of E10 fuel releases a lower tailpipe GHG emissions than E0. The same figure also gives the fuel cycle (WTW) values from the sum of WTP and PTW of each studied gasoline option. Accordingly, the use of conventional gasoline (E0) has the highest GHG emissions (96.7 gCO_2e per MJ of fuel) when using neither ethanol nor electrolytic hydrogen content in the fuel. The GREET model suggests that ethanol blending with gasoline at 10% by volume has a relatively more impact in minimizing the carbon intensity of regular gasoline (95.66 gCO_2e per MJ of fuel) than electrolytic hydrogen via PtG (96.15 gCO_2e per MJ of fuel) despite the WTP reduction advantage. Fortunately, the PtG application can be utilized in conjunction with ethanol blending to curtail the gasoline cycle emissions further as shown for the last scenario (95.14 gCO_2e per MJ of fuel). Therefore, PtG can provide a further reduction in the gasoline carbon intensity without jeopardizing the ethanol blend standards.

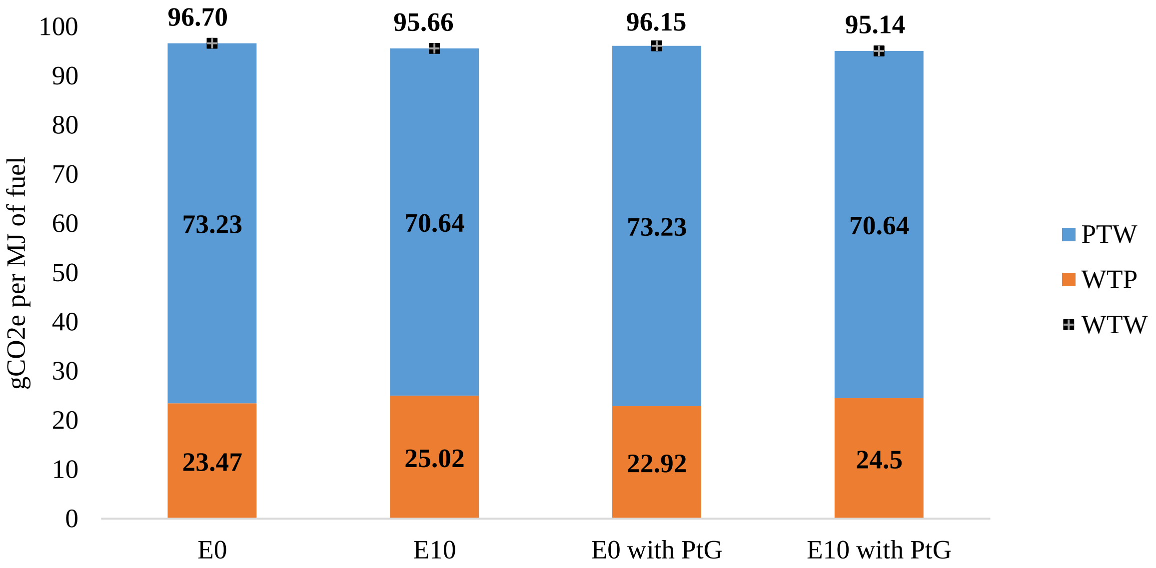

Figure 18.Life cycle GHG emissions of gasoline when employing corn-ethanol blend and power-to-gas electrolytic hydrogen from Ontario's electricity

4.3.3 Criteria Air Pollutants

Another important factor to consider in this study is the impact of the given renewable content scenarios on the air quality. Consequently, Figure 19 provide the well to wheel (WTW) results of each scenario for the volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x) , particulate matter with size smaller than 10 micron (PM_{10}) and particulate matter with size smaller than 2.5 micron ($PM_{2.5}$), respectively. Note that GREET model combines the urban and rural emissions for the total air emissions estimates.

According to the GREET model, E0 has lower air pollutants of VOCs, NO_x , PM_{10} and $PM_{2.5}$ than E10, while the use of PtG concept for hydrogen supply to refining processes improves the results of both fuels slightly. As for the CO release, it is predominantly coming from the fuel combustion stage at the vehicle (PTW). Therefore, GREET result of each scenario suggests almost no difference in the life cycle values of CO. Though, it is expected that blending ethanol with gasoline has a factor in minimizing the CO level from gasoline combustion as advocated by many researchers. Also, the sulfur oxides (SO_x) analysis indicates that E0 has a marginally better life cycle number, where PtG application has no apparent impact on both fuels. Note that GREET model assumes generated power from wind and hydro has no associated criteria air pollutants while electrolysis (PtG) related production pollutions is from gas-fired plants and nuclear generation.

As seen from the results, the impact on air quality must be taken into account when evaluating the life cycle of different biofuel blends to gasoline, besides greenhouse gas emissions; since corn-ethanol has an adverse impact on some air pollutants measures compared to conventional gasoline. On the other hand, PtG application can potentially reduce the air pollutions of gasoline production and hence influence its life cycle results marginally. Accordingly, PtG can be included in the renewable regulations of petroleum fuels to minimize any possible impact from various biofuels blends on the air quality.

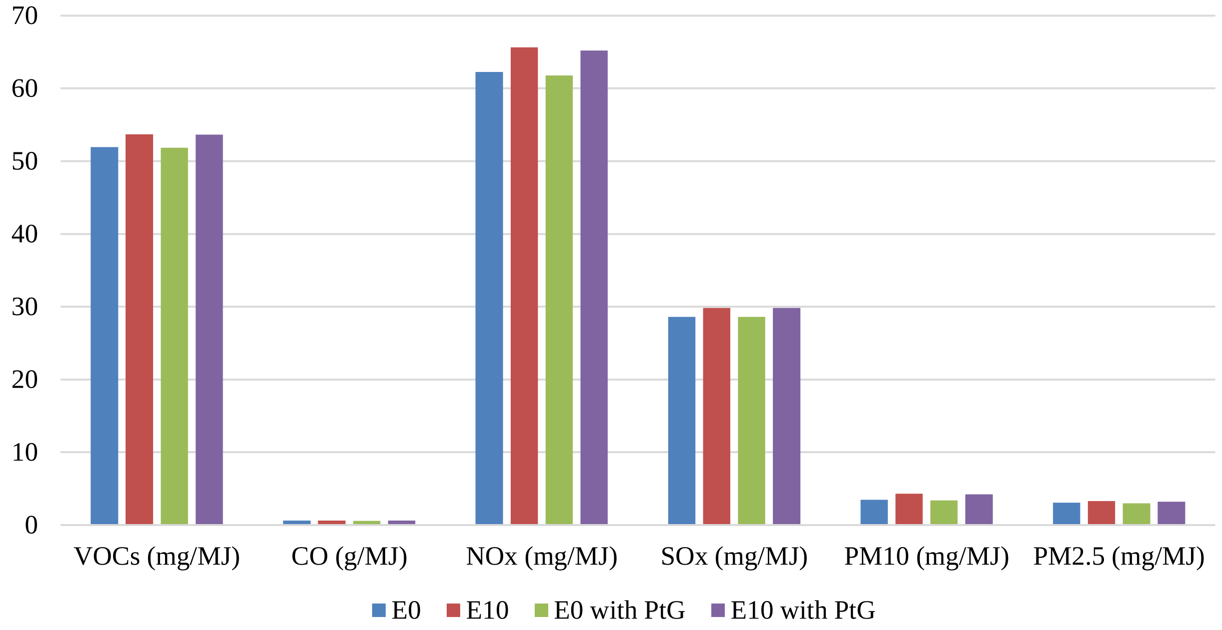

Figure 19. The WTW air pollutants result of gasoline when using corn-ethanol blend and power-to-gas electrolytic hydrogen from Ontario's electricity

4.4 Conclusions

The environmental benefits of using biofuels especially corn-ethanol for meeting the renewable regulations of petroleum fuels are still today a controversial subject but can provide a limited renewable content to the current fuels. This dispute has motivated researchers to continuously evaluate various fuels with different production technologies to achieve the target of dropping the greenhouse gas emissions from the transportation sector to address the climate change phenomena. Accordingly, this chapter uniquely introduced the emerging energy storage approach of 'power to gas' for a renewable hydrogen production to be acknowledged as part of the several enacted regulations to increase the renewable content of gasoline. Power to gas can harvest the excess clean power generated from nuclear and intermittent renewable energy during low electricity demand to produce green and renewable hydrogen from water electrolysis technology, which can be used for several applications including oil refining industry. Refinery operators commonly use the on-purpose hydrogen production method ,steam methane reformer, to meet their hydrogen demand, but the unit produces as well considerable carbon emissions as a co-product. In contrast, the electrolysis generated hydrogen from a clean power grid has a significantly fewer carbon emissions, and also serves as energy storage to enhance the operability of the grid. Accordingly, it can be considered as a potential replacement for steam methane reformer to meet refinery hydrogen demand while reducing the carbon footprint of gasoline production.

Therefore, this study evaluated the impact of electrolytic hydrogen production via power to gas on the life cycle emission of gasoline. The study considered the case of Ontario's electricity grid which faces regularly surplus baseload power generation from nuclear and renewable sources. The assessment included four scenarios for blending corn-ethanol and using renewable hydrogen from power to gas in the gasoline cycle. The analysis was performed using GREET model, which is a credible life cycle assessment method for transportation fuels. The comparative study was based on the metrics of total energy use, greenhouse gas emissions and criteria air pollutants on the well to wheel impact of gasoline fuel.

As for the fossil energy use, corn-ethanol was able to reduce the petroleum consumption by 6.3% while power to gas lowered the natural gas use by 4.6% from the conventional gasoline production cycle. Also, power to gas had extended the renewable energy content in gasoline when used in a complementary fashion with ethanol as a result of integrating additional utilization of the hydro and wind power from Ontario’s electricity grid. Hence, power to gas has the potential to support the objective of reducing fossil energy use and enhance the renewable contents in gasoline fuel. Furthermore, the electrolytic hydrogen through power to gas was capable of minimizing the greenhouse gas emissions from the refining stage by 5% and ultimately the gasoline carbon intensity by at least 0.5 gCO_2e per MJ of fuel produced and used. When compared to the total gasoline sales in Ontario, it had the impact of cutting nearly 0.26 Megaton (Mt) of greenhouse gas emissions annually or removing about 54,000 vehicles from the road. Thus, power to gas implementation with blending 10% corn-ethanol by volume had minimized well to wheel impact of gasoline from 96.70 to 95.14 gCO_2e per MJ of fuel produced and used. Additionally, power to gas was found to offer a slight improvement on the air quality measures of gasoline production especially with VOCs, NO_x, PM_{10} and $PM_{2.5}$ criteria air pollutants.

Chapter 5: Conclusion and Recommendations

5.1 Conclusion

Hydrogen is an essential commodity in the oil refining industry for the treatment of petroleum fuels. The demand of hydrogen is growing to meet the stringent environmental regulations of petroleum fuels, for which clean production methods are needed. Hydrogen is principally produced from the mature technology steam methane reforming (SMR), which has a drawback of releasing significant greenhouse gas emissions. The 'Power-to-Gas' concept, on the other hand, can produce green hydrogen through water electrolysis by utilizing Ontario's electricity grid which is powered mostly by CO_2-free sources. In addition, the province has a significant surplus of clean power which frequently get exported at a deep discount or curtailed (wind and nuclear production). Thus, power-to-gas is a novel energy storage concept which can also manage the surplus baseload generation issue encountered in the province through the production of hydrogen based on off-peak clean electricity. While power-to-gas has several recovery pathways to different applications, this study was focused on a single pathway that is the hydrogen consumption by industrial end users (e.g. oil refining).

In this work, the potential use of electrolytic hydrogen generation via power-to-gas concept for the oil refining industry has been examined. A concept of renewable and CO_2 free electrolytic hydrogen represents a near-term transition towards reduced greenhouse gases and increased renewable content of energy within traditional liquid transportation fuels. This is also an effective way to store or load level the increased intermittent renewable power.

The study presented in this thesis consisted mainly of three related aspects (presented in separate chapters) of implementing power-to-gas to the oil refining and ultimately the gasoline fuel cycle in Ontario province. The first study established a detailed analysis of the dynamic operation of electrolyzers to meet an individual refinery demand with the aid of Aspen HYSYS simulation and mixed integer linear programming models. It included evaluation of the deployment of polymer electrolyte membrane (PEM) electrolyzers based on Ontario's electricity grid to supply a refinery with 25 million standard cubic feet per day (MMscfd) of required hydrogen. The analysis assessed the associated life cycle emissions and production costs of the electrolysis and steam methane reforming (SMR) to meet the refinery demand under different production scenarios. Moreover, the second part of the study has evaluated the current opportunity in Ontario to meet a significant part of the industrial demand for hydrogen in the province upon implementing the power-to-gas technique to minimize SMR technology utilization. Thus, it capitalized on the encountered and forecasted surplus power in the province to quantify the potential hydrogen volumes that could be produced by embedding electrolysis units in the region's industrial zones. The last part of the study evaluated the incentives of considering the hydrogen supply via power-to-gas in the renewable fuels regulations of petroleum fuels. As ethanol or other biofuels are used by oil operators to meet the renewable fuel criterions for transportation fuels, these biofuels production are linked to an associate life cycle emissions while feedstocks are limited and heavily subsidized. Therefore, a comparison between involving renewable electrolytic hydrogen and blending ethanol content (made from corn grains) was performed. The analysis was based on the assessment of the metrics related to total energy use, greenhouse gas emissions, and criteria air pollutants on the life cycle of gasoline (per MJ of gasoline produced and used).

Below is summary of the key results and findings of the conducted work:

- Electrolytic hydrogen production via power-to-gas based on Ontario's electricity grid releases significantly less emissions than SMR. Thus, the emissions from refineries can be minimized with the full or partial replacement of SMR unit production at a refinery;

- The installation of 130 PEM electrolyzers units (1 MW nameplate capacity per unit) can supply a refinery with 60,000 kg of hydrogen per day at a levelized cost of $2.5 per kg of hydrogen, using some of the clean electricity being exported to neighboring jurisdictions as low below cost pricing or currently being curtailed, and would be the equivalent of removing about 35,000 vehicles from the road (without shifting to different vehicles technologies on the road and without changing any fuel distribution infrastructure). The hydrogen generated is injected into the present liquid fuel production processes and resulting fuel product is unchanged and used in the existing fleet of vehicles;
- The maturity of SMR coupled with the current low commodity prices of natural gas will maintain the technology to be a lower cost pathway to produce hydrogen in the short term, despite implementing stricter carbon pricing since the low cost of the natural gas dominates the cost of the technology production;
- The electrolytic hydrogen production during off-peak demand in the province offers the largest emissions cut for a refinery, though this option appears to have higher associated costs. Nevertheless, the produced hydrogen has no required handling charges as it is consumed directly by the refinery; and there is no requirement for any fuel cell vehicle market penetration or hydrogen distribution at this time;
- Implementing power-to-gas energy storage system in Ontario can have several advantages from actually managing surplus baseload generation (SBG) conditions to meeting major shares of the industrial demand for hydrogen typically met by SMR. However, the study was not able to confirm significant surplus baseload generations' presence beyond 2021 due to the currently available forecast by IESO which suggests that there is uncertainty surrounding future electricity demand, weather and planned nuclear refurbishments and outages;

- Given the uncertainty of SBG forecast as well as the potential rise in industrial demand, facilities implementing electrolytic production may require using an additional load from the grid to meet their hydrogen demand. Although, the hydrogen shortage from power-to-gas production may present at the same time an opportunity for the province to expand the penetrations of renewables generations since there is room to harvest the surplus by the industries hydrogen usage;
- In addition, utilizing the underground seasonal storage of salt caverns or depleted wells will minimize the variability and increase the reliability of electrolytic production as well as reducing the production cost of the technology;
- Electrolytic production via power-to-gas is found to decrease 4.6% of the natural gas consumption on the gasoline cycle, thus reducing the fossil energy use and increase the renewable content of gasoline by extending the utilization of wind and hydro power. Accordingly, it results in curbing 5% of the total refining emissions and subsequently minimizing gasoline carbon intensity by 0.5 gCO_2e per MJ of the fuel;
- When associated with the annual gasoline sales in Ontario, it can offer the reduction of 0.26 Megaton (Mt) of greenhouse gas emissions yearly which can be equated to removing as many as 54,000 vehicles off the road; and,
- Power-to-gas may contribute to lowering VOCs, NO_x, PM_{10} and $PM_{2.5}$ criteria air pollutants from gasoline cycle, which cannot be achieved with blending corn based ethanol.

Accordingly, the results of this work assert the recognition of renewable electrolytic hydrogen to be part of the solutions to the existing issue related to the excess clean power under-utilized by Ontario region, while also providing important opportunity to the refinery operators to minimize the industry emissions which can be benefited given existing carbon regulation via cap-and-trade or carbon taxation. Moreover, the outcome of this study endorse the inclusion of a power-to-gas concept in the renewable fuels regulations and encourage policymakers to include the subject method on the existing standards given its promising potentials.

5.2 Study Remarks and Recommendations

5.2.1 Remarks with respect to works

Electrolyzer's economics: The approach for the economic calculation of the PEM electrolyzer technology in the model was based on the associated capital and operating costs of installing a unit, and therefore the levelized cost of the technology is fixed regardless of the number of units installed. Consequently, the electrolysis was assumed to have no economy of scale in this study, but it will if this proposed number of electrolyzers is implemented. Moreover, the oxygen quantities produced from the electrolyzers were not considered as part of the economic calculation. If oxygen is being supplied to consumers with sufficient quantities, this will reduce the electrolyzers production cost and help the technology economics to be as competitive with SMR. In fact, oxygen enrichment in refining processes is being used and explored further to increase the capacity and efficiency of units like FCC, sulfur recovery plant, furnaces, and wastewater treatment plant. Therefore, electrolysis can also be a good venue to refiners for oxygen production when it is required in sufficient quantities.

SMR economics: Although SMR production cost estimates from the provided equations were close, the available correlations in literature are more than ten years old. Better costs estimate of SMR would be with the availability of recent assessments of the technology. The assessments must also take into account the scale of hydrogen production, as smaller plants tend to have higher production cost.

Refinery hydrogen demand: This work has assumed a constant daily demand of hydrogen by a refinery facility during the operating year to simplify the analysis, which may not be necessarily true given the dynamics of refining operations such as the need to process different types of crudes, change in production levels based on seasonal demand, which ultimately impacts the hydrogen production levels to equip with such requirements. Therefore, the availability of actual refinery data with showing the dynamic demand of the facility is preferred to provide a better optimization outcomes for the integration of electrolyzers units in the evaluated refinery.

Export power estimate: This work estimated the excess net exported power to neighboring jurisdictions during only off-peak demand as a conservative approach, however, the evaluation must involve comprehensive assessment of the net exported power including during regular demand, peak demand hours as well as off-peak demand.

Grid intensity factor: Since there is no 'official' data of Ontario's actual intensity factor, according to the author knowledge, the analysis carried in Chapter 2 involves the calculation of the grid intensity factor according to the emission factors for each energy source (including renewable sources such as hydro and wind) powering the grid. On the other hand, the analysis of Ontario's grid emissions factor was also calculated by GREET model in Chapter 4, for which the model assumes the generated power from wind and hydro to have no associated carbon emissions. Therefore, the life cycle emissions of electrolysis production (kg CO_2e/kg of H_2) based on Ontario's electricity grid is found different between the first study (Chapter 2) which is about 3.6 kg CO_2e/kg of H_2 and GREET estimates (Chapter 4) which is 1.6 kg CO_2e/kg of H_2 .

Industrial demand of hydrogen in Ontario: There is a very limited information on the industrial demand of hydrogen in Ontario province in the existing literature, according to the author knowledge, where the adapted survey may be relatively old. This might be due to the production rates being commercially confidential by companies.

5.2.2 Recommendations for future analysis

The following recommendation for future analysis are made:

- Involve the economy of scale in the economic comparison between both production technologies (e.g. SMR and electrolysis);
- Include oxygen selling profits in the overall economic evaluation of electrolysis technology, and potential for integration of oxygen in the refinery operation or the complimentary production of other products;
- When comparing partial replacement of SMR by electrolysis units, consider the potential saving as a result of using less SMR equipment or utilization in the economic comparison;
- A complementary work is needed to examine the aspects of implementing power-to-gas in the province related to potential capital investments and grid operation for the power-to-gas pathway of hydrogen supply to the industrial end users, which can be compared to the cost of other decarbonizing initiatives such as subsidies for electric vehicle and charging infrastructure;
- The use of additional life cycle assessment methods or models is recommended to provide overall insights on the discussed subject;
- Investigate the potential impact of SMR processing hydrogen enriched natural gas (HENG), which is a cleaner fuel, in the performance of the technology when the power-to-gas pathway of injecting electrolytic hydrogen in natural gas infrastructure is considered for which the hydrogen limit in the natural gas is 4-5%;

- Evaluate the life cycle improvement of gasoline as a result of the introduction of power to-gas electrolytic hydrogen at the synthetic crude upgrader level (depending on the electricity sources), since the overall well to wheel production of gasoline can be further improved; and,
- While this study evaluated the performance of power-to-gas and corn-ethanol on the life cycle of gasoline, it is suggested to carry further out similar analysis related to the use of power-to-gas electrolytic hydrogen and biodiesel blends in the petroleum diesel fuel life cycle.

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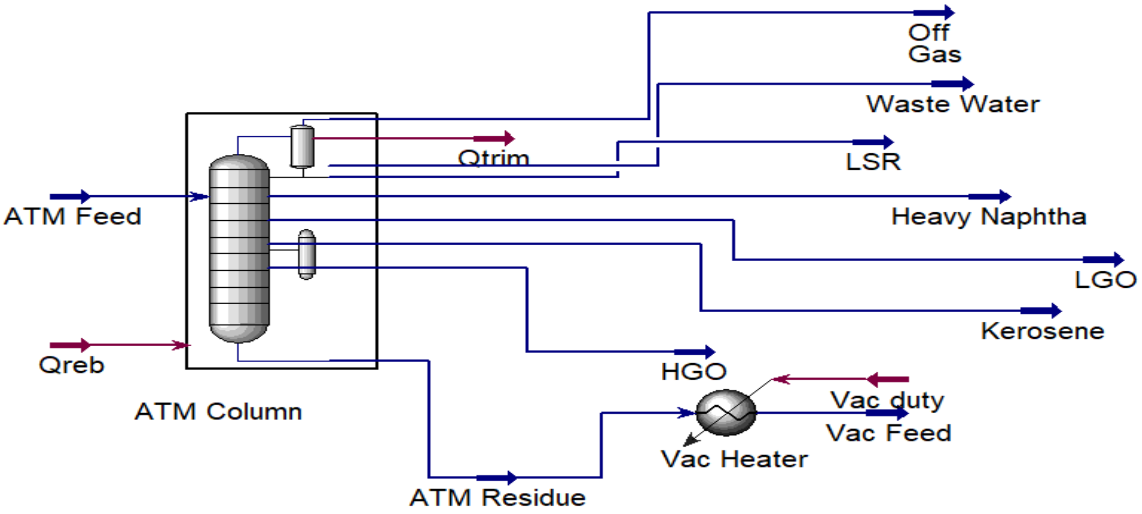
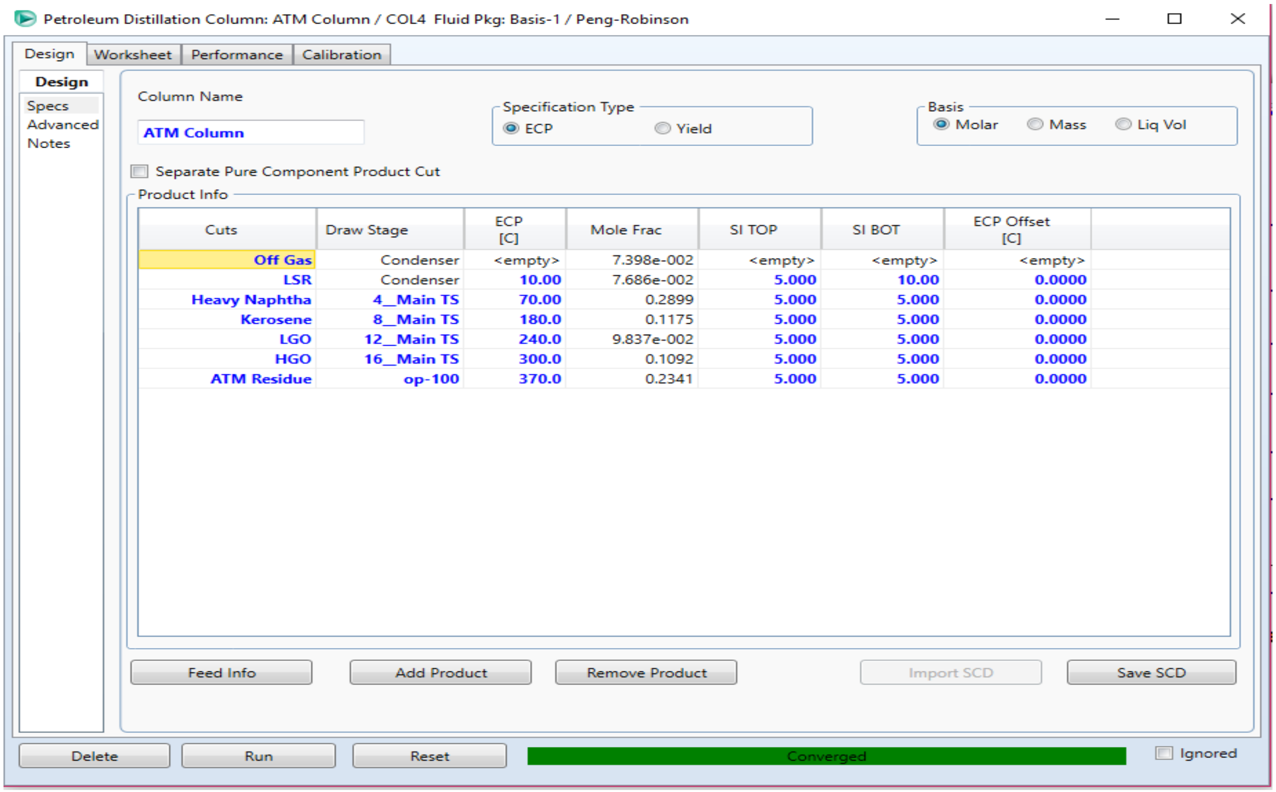
Appendix

This section provides more simulation background of the main processes and units in the developed refinery in Aspen HYSYS for the purpose of this thesis.

a. Atmospheric Crude Column





Petroleum Distillation Column: ATM Column / COL4 Fluid Pkg: Basis-1 / Peng-Robinson

Column Name: ATM Column

Specification Type: ● ECP ○ Yield

Basis: ● Molar ○ Mass ○ Liq Vol

☐ Separate Pure Component Product Cut

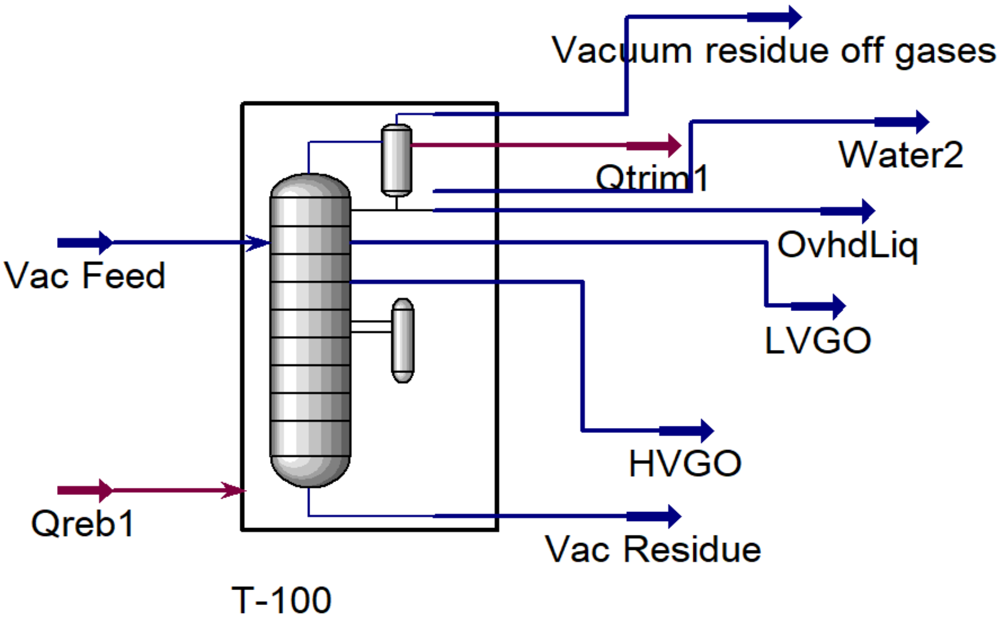
Product Info

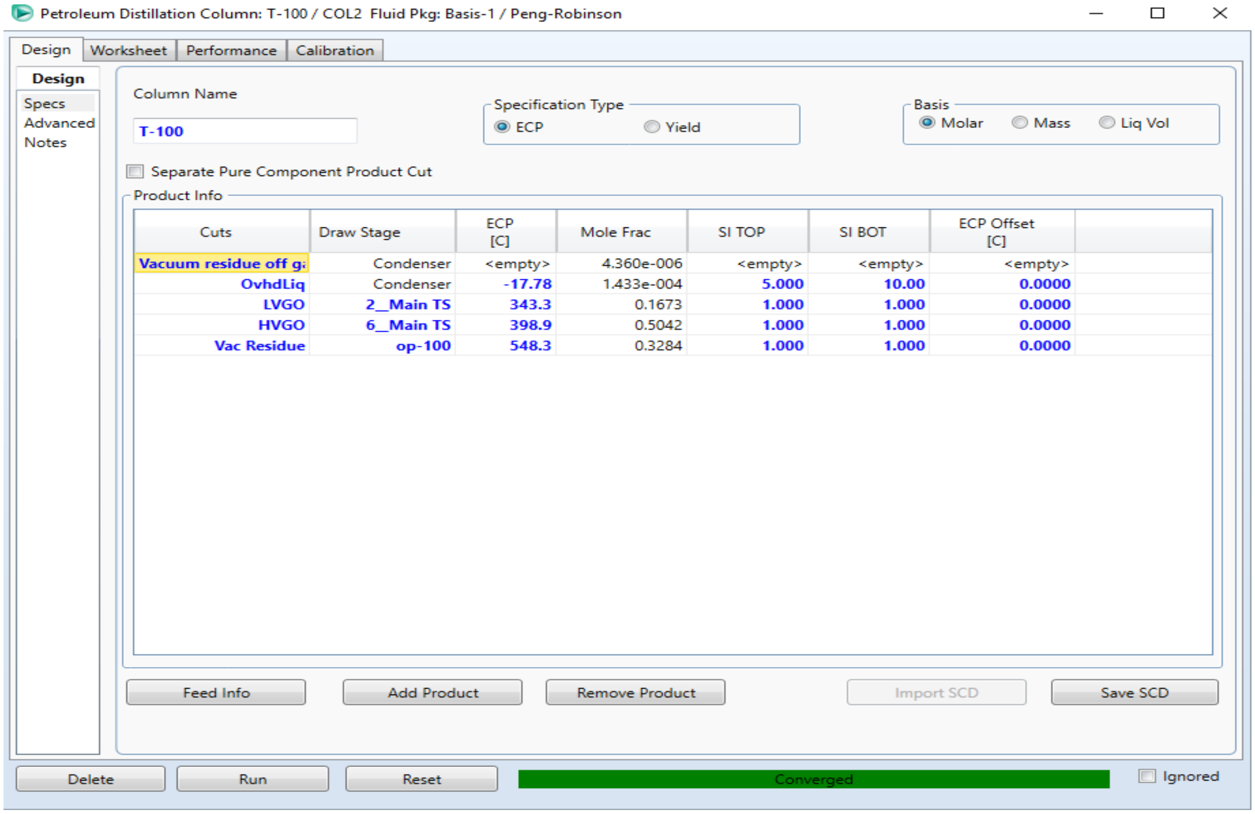
Cuts	Draw Stage	ECP [C]	Mole Frac	SI TOP	SI BOT	ECP Offset [C]
Off Gas	Condenser	<empty>	7.398e-002	<empty>	<empty>	<empty>
LSR	Condenser	10.00	7.686e-002	5.000	10.00	0.0000
Heavy Naphtha	4__Main TS	70.00	0.2899	5.000	5.000	0.0000
Kerosene	8__Main TS	180.0	0.1175	5.000	5.000	0.0000
LGO	12__Main TS	240.0	9.837e-002	5.000	5.000	0.0000
HGO	16__Main TS	300.0	0.1092	5.000	5.000	0.0000
ATM Residue	op-100	370.0	0.2341	5.000	5.000	0.0000

Converged

☐ Ignored

b. Vacuum Tower





Column Name: T-100

Specification Type: ● ECP ○ Yield

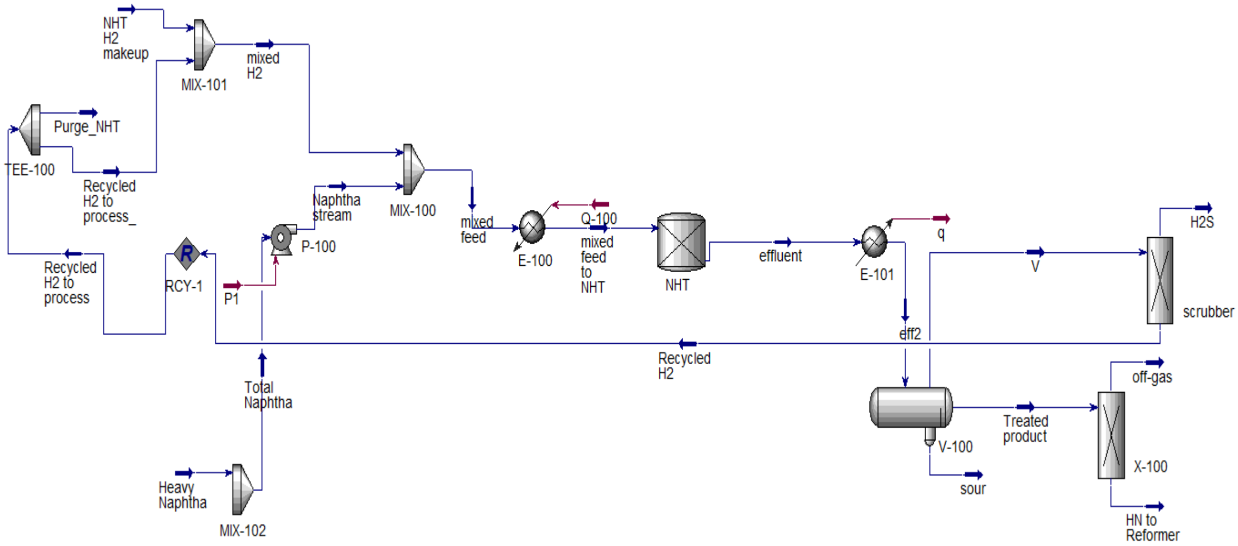
Basis: ● Molar ○ Mass ○ Liq Vol

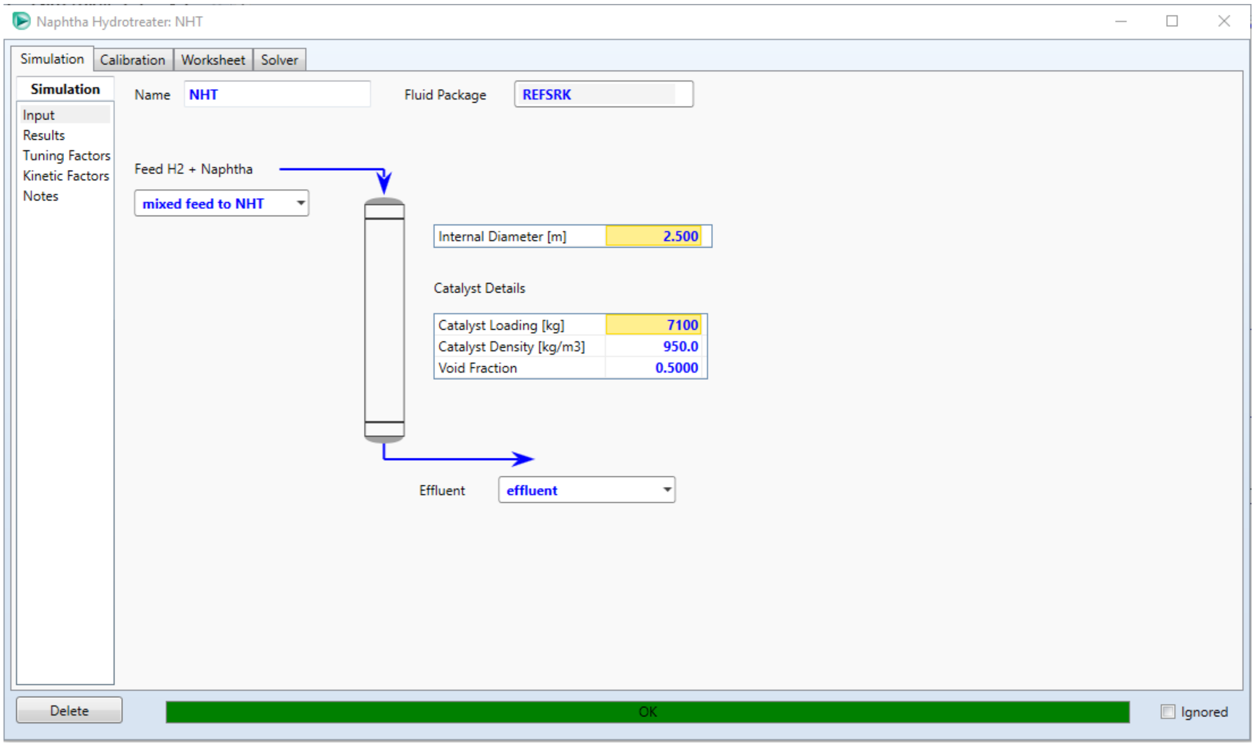
☐ Separate Pure Component Product Cut

Product Info

Cuts	Draw Stage	ECP [C]	Mole Frac	SI TOP	SI BOT	ECP Offset [C]
Vacuum residue off g:	Condenser	<empty>	4.360e-006	<empty>	<empty>	<empty>
OvhdLiq	Condenser	-17.78	1.433e-004	5.000	10.00	0.0000
LVGO	2__Main TS	343.3	0.1673	1.000	1.000	0.0000
HVGO	6__Main TS	398.9	0.5042	1.000	1.000	0.0000
Vac Residue	op-100	548.3	0.3284	1.000	1.000	0.0000

c. Naphtha hydrotreater (NHT)





Name: NHT

Fluid Package: REFSRK

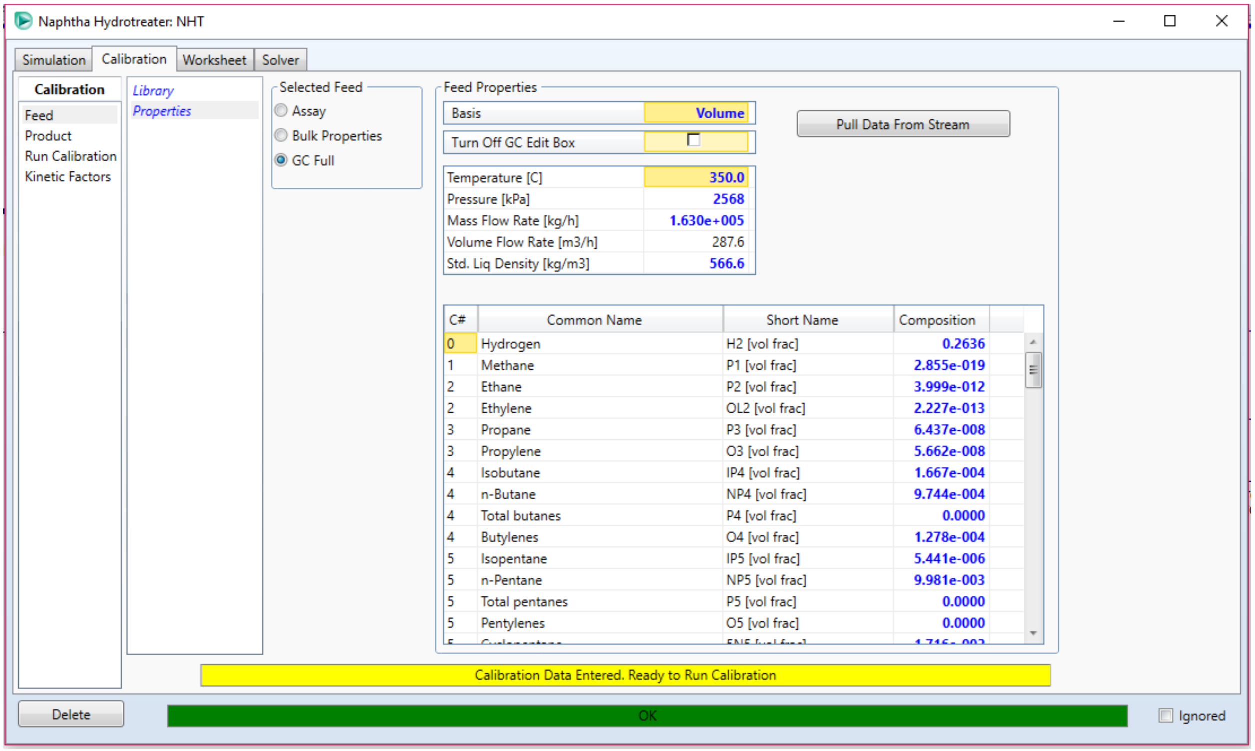
Feed H2 + Naphtha: mixed feed to NHT

Internal Diameter [m]	2.500

Catalyst Details

Catalyst Loading [kg]	7100
Catalyst Density [kg/m3]	950.0
Void Fraction	0.5000

Effluent: effluent



Selected Feed
○ Assay
○ Bulk Properties
● GC Full

Feed Properties

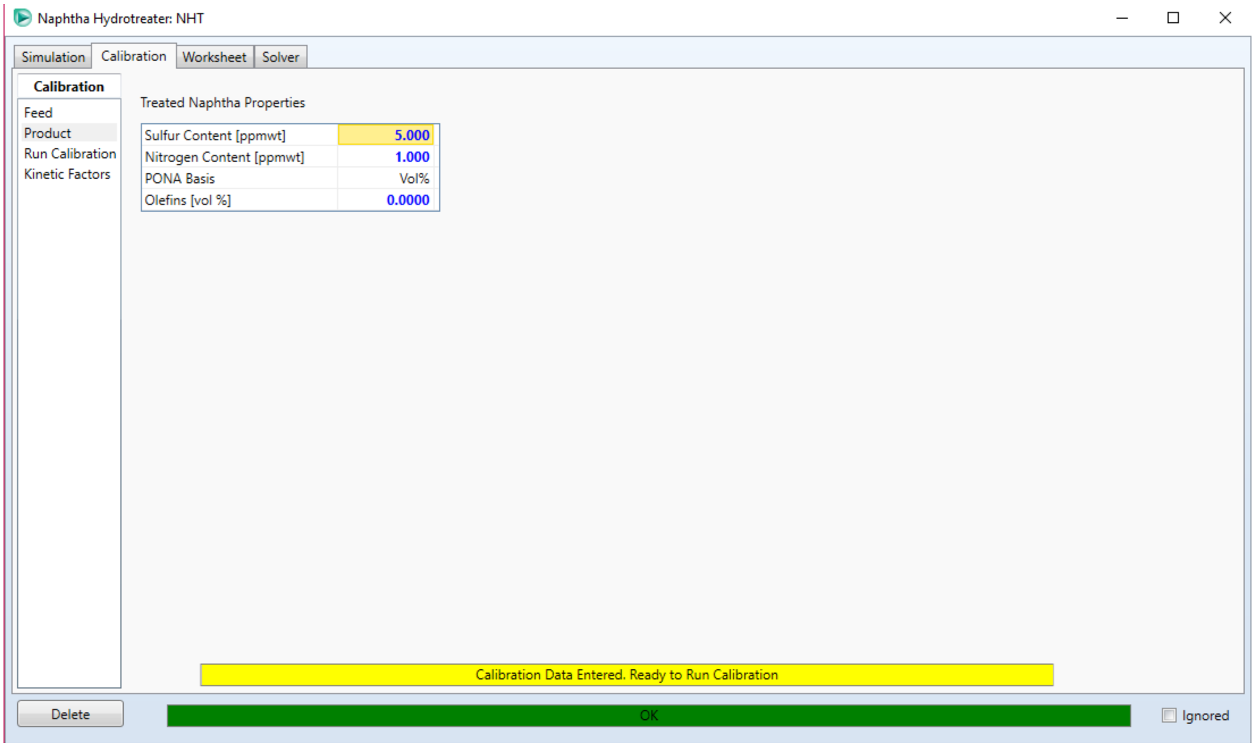
Basis	Volume
Turn Off GC Edit Box	☐

Temperature [C]	350.0
Pressure [kPa]	2568
Mass Flow Rate [kg/h]	1.630e+005
Volume Flow Rate [m3/h]	287.6
Std. Liq Density [kg/m3]	566.6

C#	Common Name	Short Name	Composition
0	Hydrogen	H2 [vol frac]	0.2636
1	Methane	P1 [vol frac]	2.855e-019
2	Ethane	P2 [vol frac]	3.999e-012
2	Ethylene	OL2 [vol frac]	2.227e-013
3	Propane	P3 [vol frac]	6.437e-008
3	Propylene	O3 [vol frac]	5.662e-008
4	Isobutane	IP4 [vol frac]	1.667e-004
4	n-Butane	NP4 [vol frac]	9.744e-004
4	Total butanes	P4 [vol frac]	0.0000
4	Butylenes	O4 [vol frac]	1.278e-004
5	Isopentane	IP5 [vol frac]	5.441e-006
5	n-Pentane	NP5 [vol frac]	9.981e-003
5	Total pentanes	P5 [vol frac]	0.0000
5	Pentylenes	O5 [vol frac]	0.0000

Calibration Data Entered. Ready to Run Calibration

OK



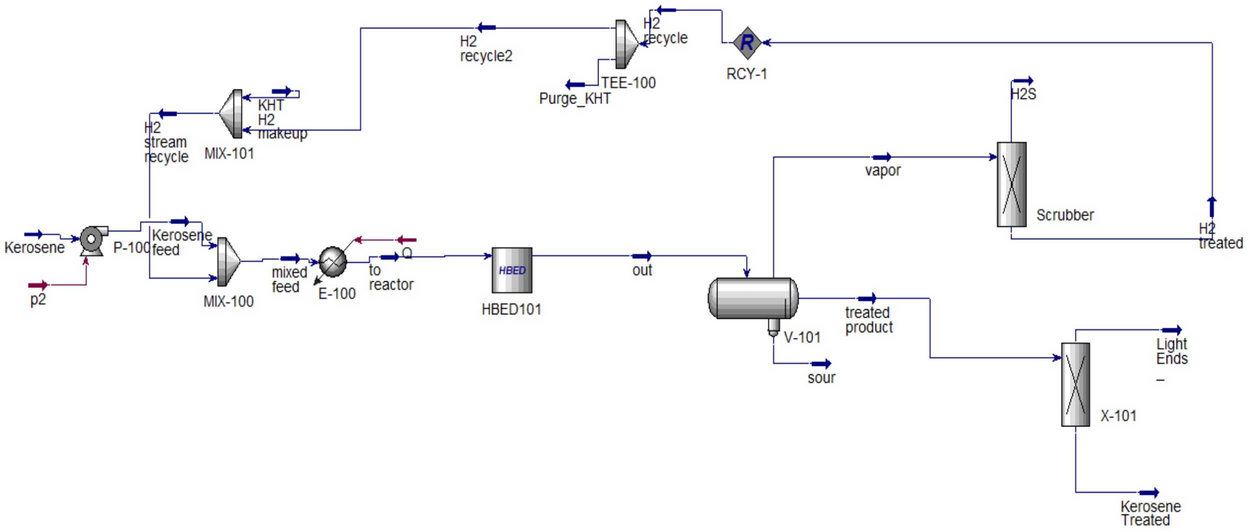
Treated Naphtha Properties

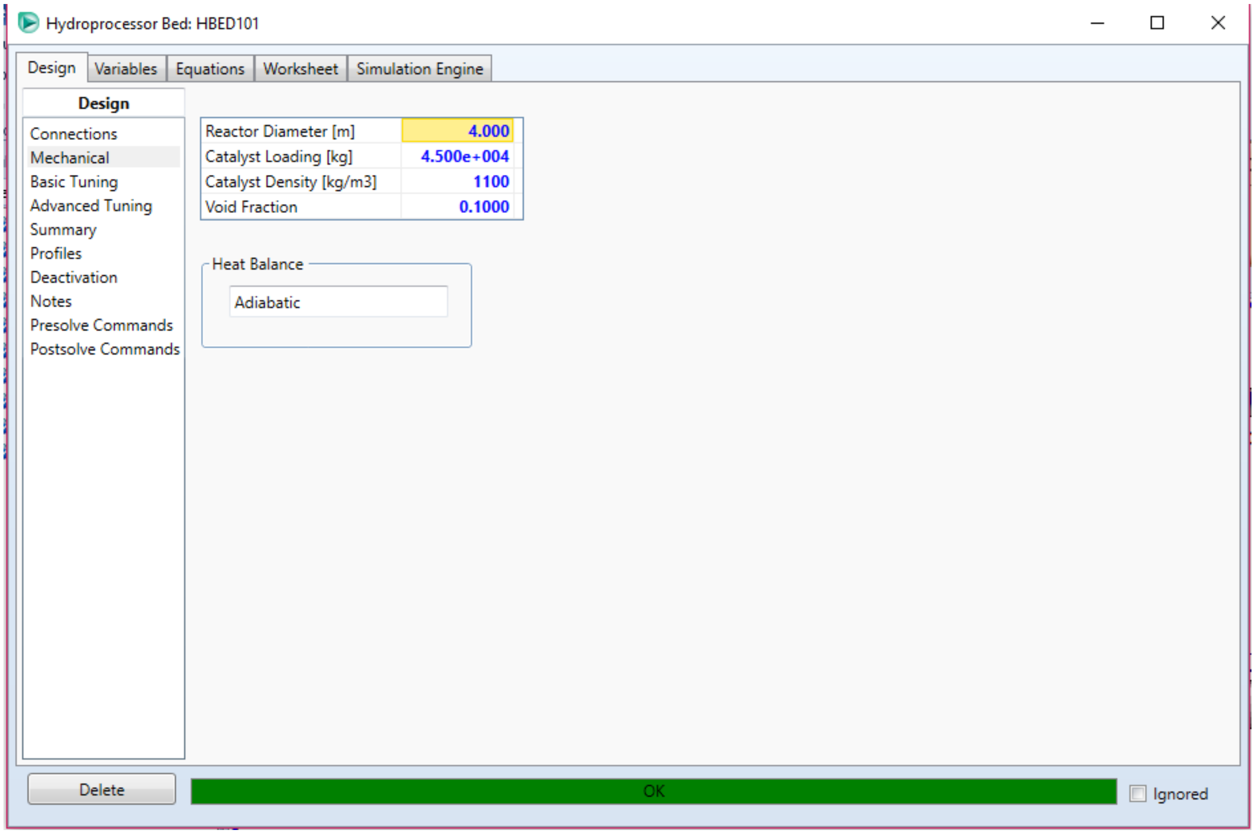
Sulfur Content [ppmwt]	5.000
Nitrogen Content [ppmwt]	1.000
PONA Basis	Vol%
Olefins [vol %]	0.0000

Calibration Data Entered. Ready to Run Calibration

OK

d. Kerosene Hydrotreater (KHT)

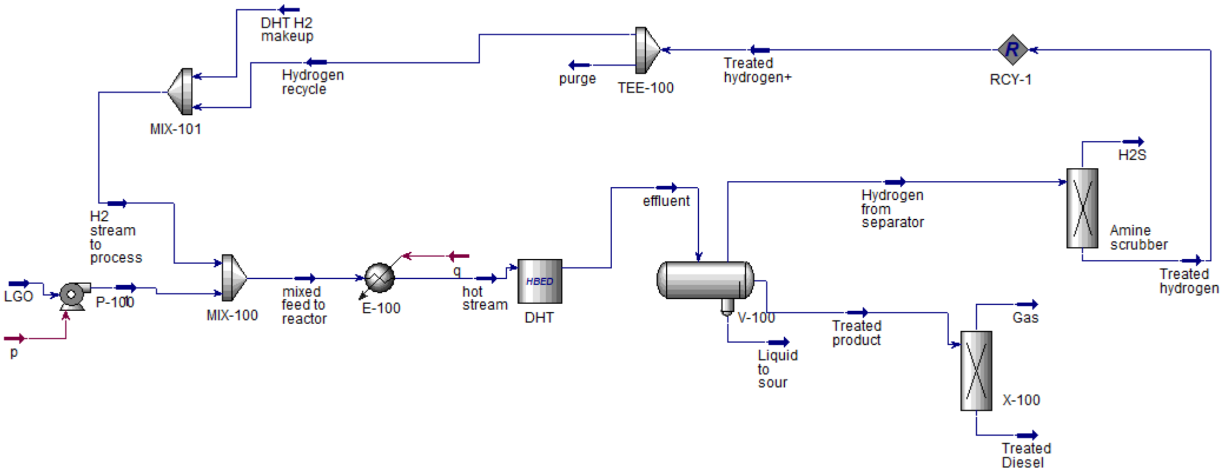


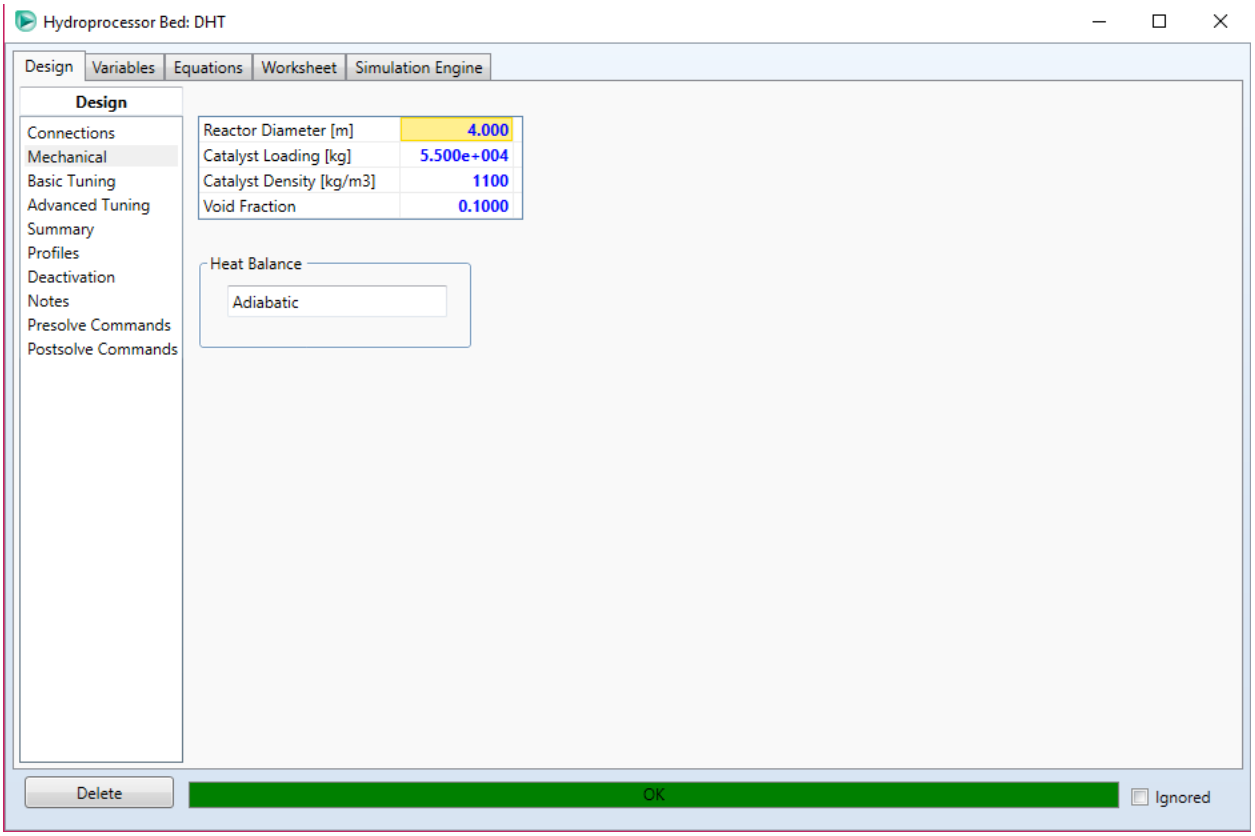


Reactor Diameter [m]	4.000
Catalyst Loading [kg]	4.500e+004
Catalyst Density [kg/m3]	1100
Void Fraction	0.1000

Heat Balance: Adiabatic

e. Diesel Hydrotreater (DHT)





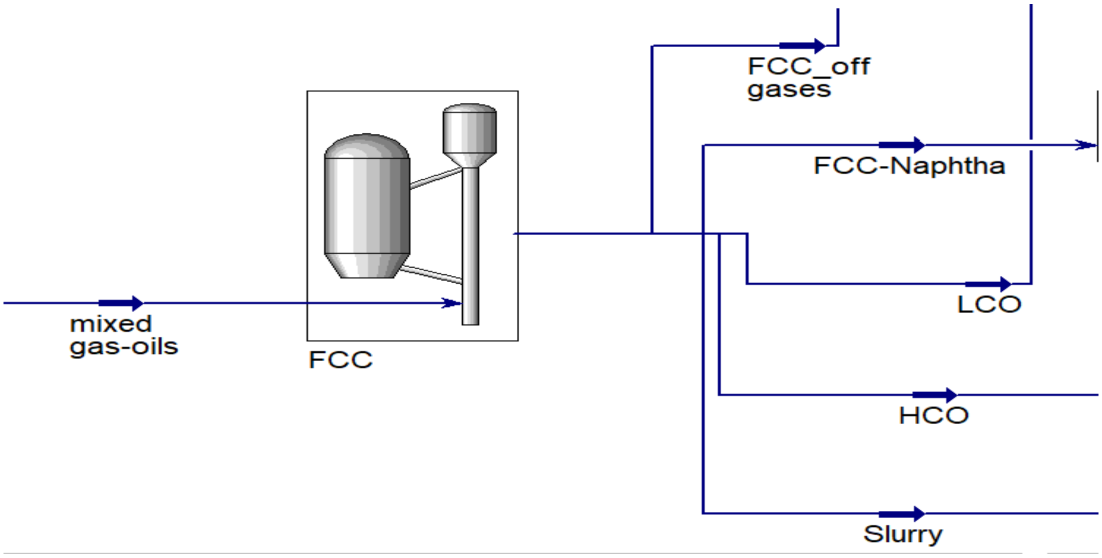
Hydroprocessor Bed: DHT

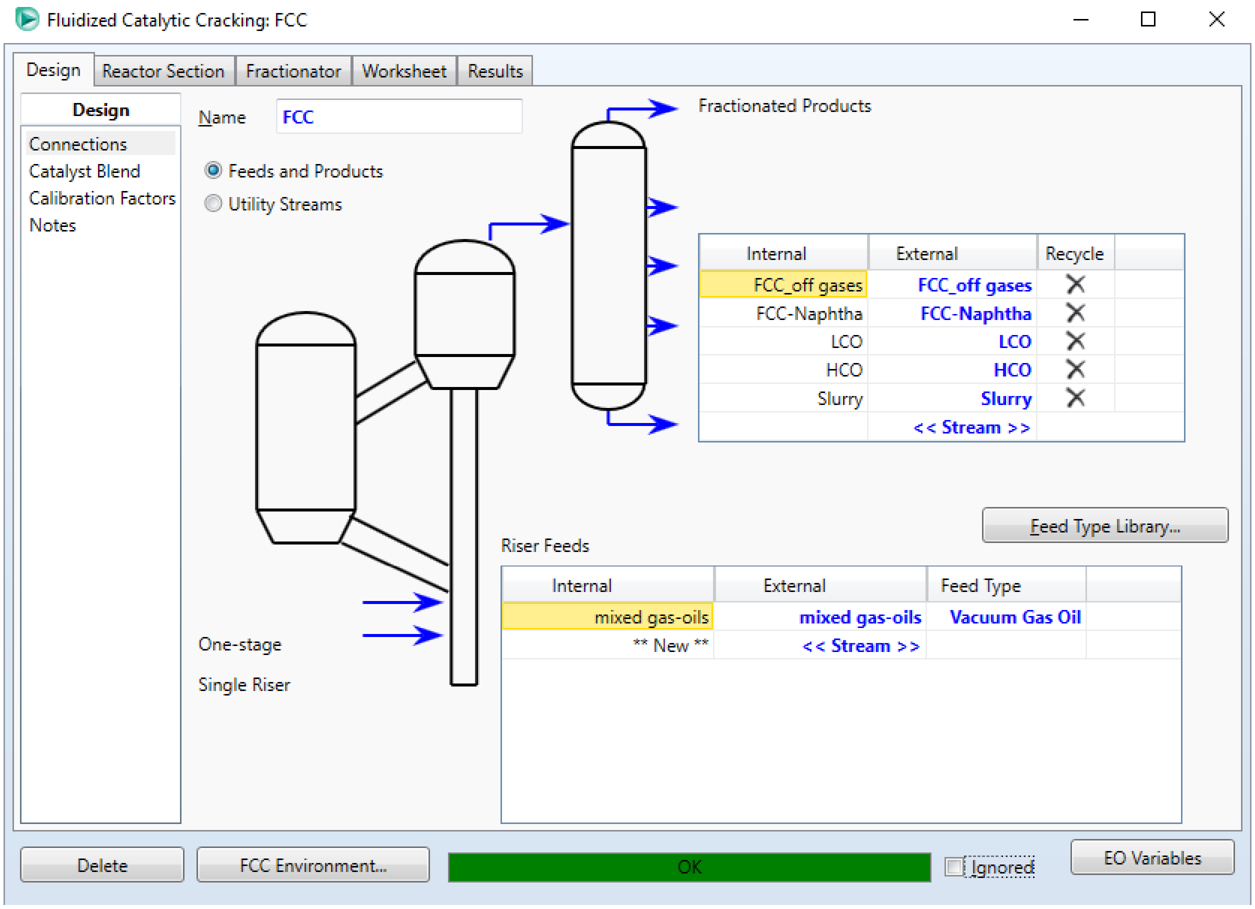
Reactor Diameter [m]	4.000
Catalyst Loading [kg]	5.500e+004
Catalyst Density [kg/m3]	1100
Void Fraction	0.1000

Heat Balance

Adiabatic

f. Fluid catalytic cracking (FCC)





Name FCC

● Feeds and Products
○ Utility Streams

Fractionated Products

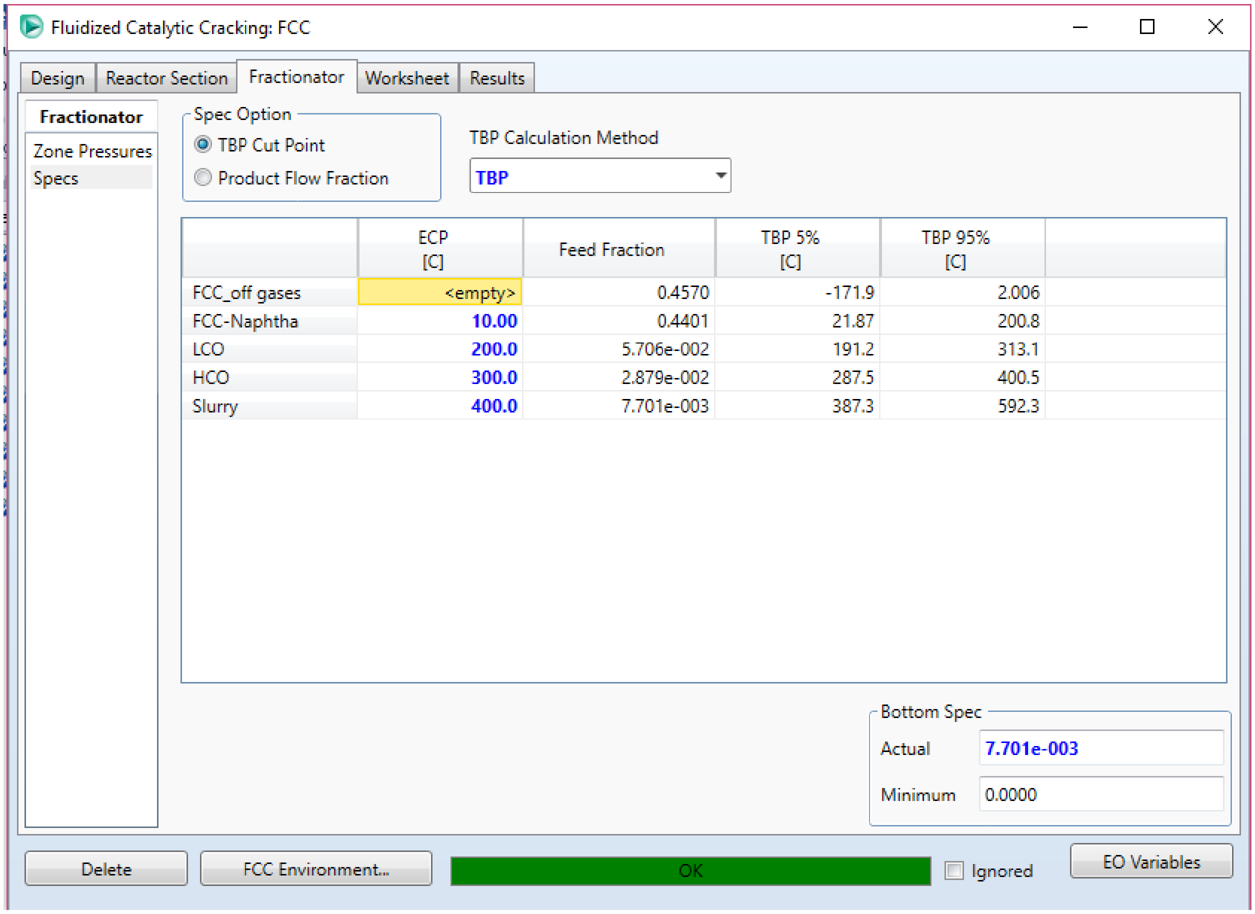
Internal	External	Recycle
FCC_off gases	FCC_off gases	☒
FCC-Naphtha	FCC-Naphtha	☒
LCO	LCO	☒
HCO	HCO	☒
Slurry	Slurry	☒
	<< Stream >>	

Riser Feeds

Internal	External	Feed Type
mixed gas-oils	mixed gas-oils	Vacuum Gas Oil
** New **	<< Stream >>	

OK

☐ Ignored



Spec Option
● TBP Cut Point
○ Product Flow Fraction

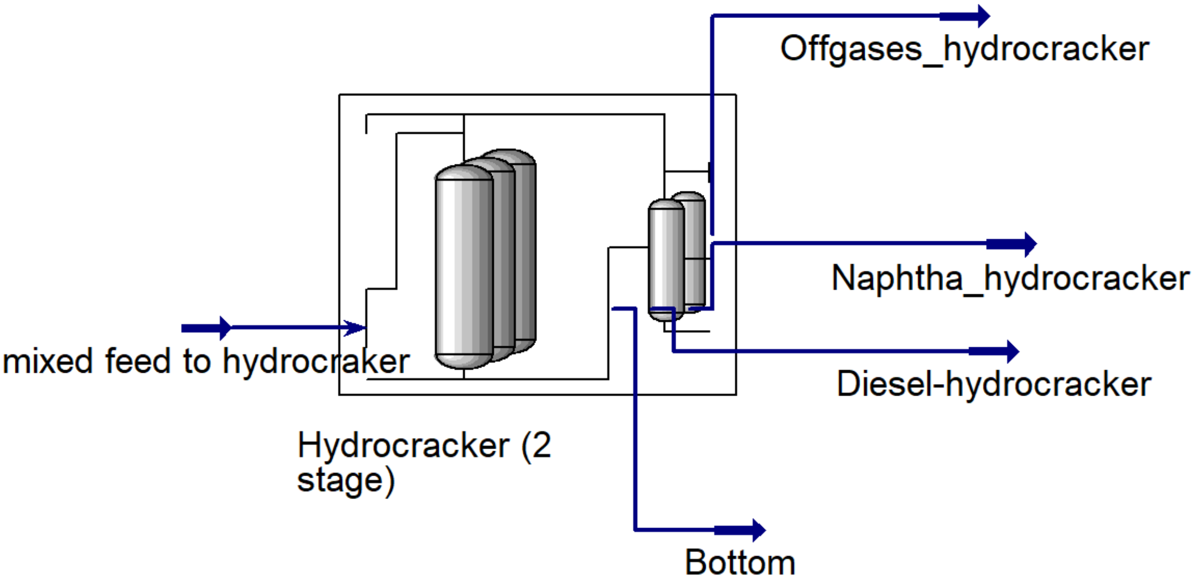
TBP Calculation Method: TBP

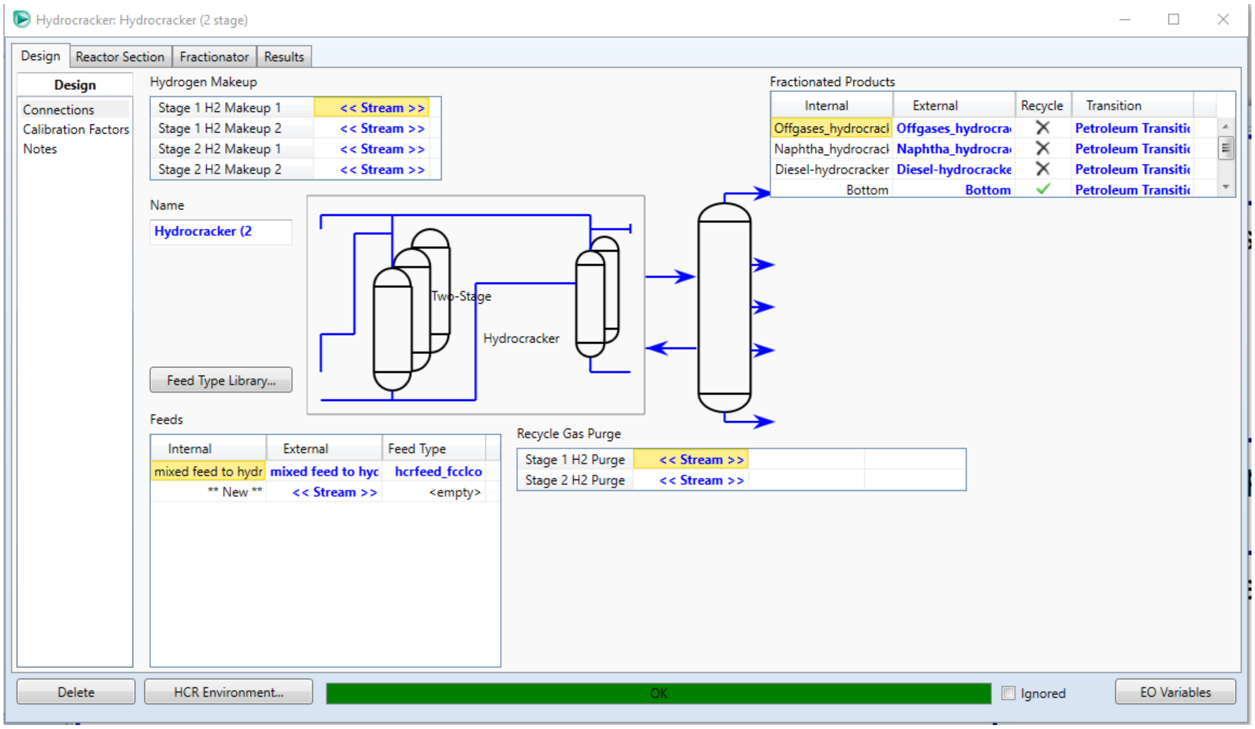
	ECP [C]	Feed Fraction	TBP 5% [C]	TBP 95% [C]
FCC_off gases	<empty>	0.4570	-171.9	2.006
FCC-Naphtha	10.00	0.4401	21.87	200.8
LCO	200.0	5.706e-002	191.2	313.1
HCO	300.0	2.879e-002	287.5	400.5
Slurry	400.0	7.701e-003	387.3	592.3

Bottom Spec
Actual 7.701e-003
Minimum 0.0000

☐ Ignored

g. Hydrocracker





Hydrogen Makeup

Stage 1 H2 Makeup 1	<< Stream >>
Stage 1 H2 Makeup 2	<< Stream >>
Stage 2 H2 Makeup 1	<< Stream >>
Stage 2 H2 Makeup 2	<< Stream >>

Name: Hydrocracker (2

Fractionated Products

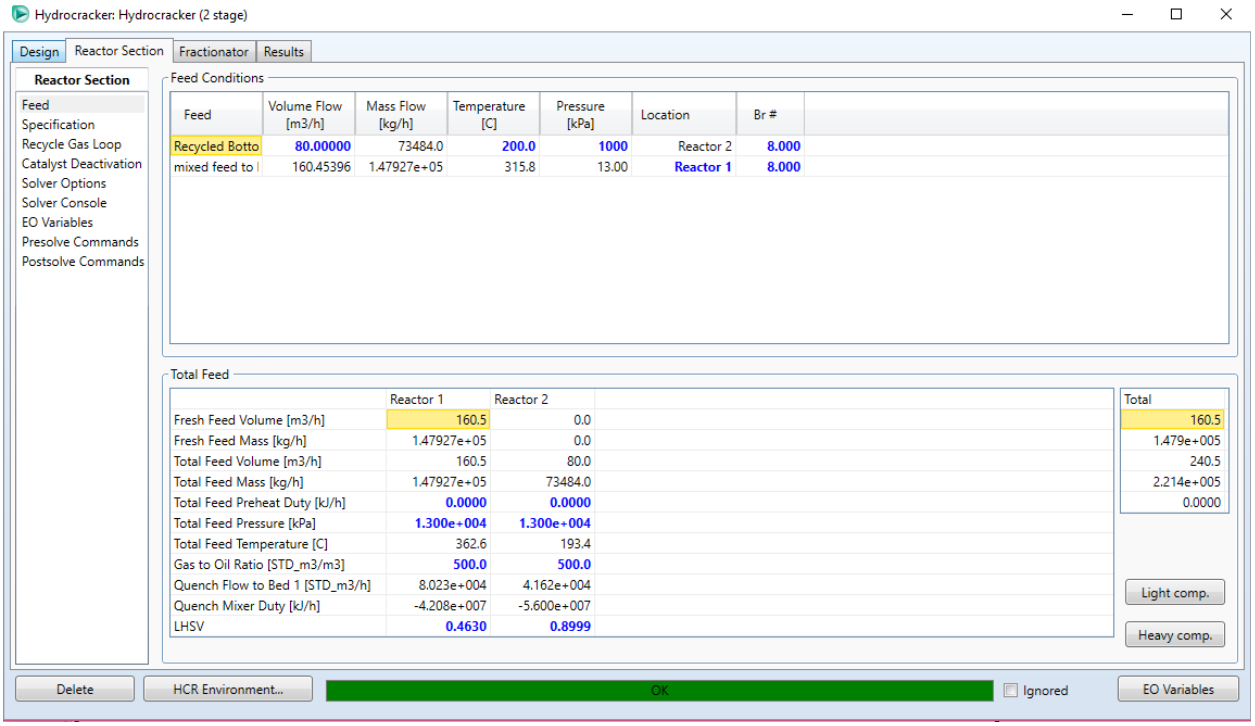
Internal	External	Recycle	Transition
Offgases_hydrocracl	Offgases_hydrocra	✕	Petroleum Transitic
Naphtha_hydrocracl	Naphtha_hydrocra	✕	Petroleum Transitic
Diesel-hydrocracker	Diesel-hydrocracke	✕	Petroleum Transitic
Bottom	Bottom	✓	Petroleum Transitic

Feeds

Internal	External	Feed Type
mixed feed to hydr	mixed feed to hyc	hcrfeed_fcclco
** New **	<< Stream >>	<empty>

Recycle Gas Purge

Stage 1 H2 Purge	<< Stream >>
Stage 2 H2 Purge	<< Stream >>



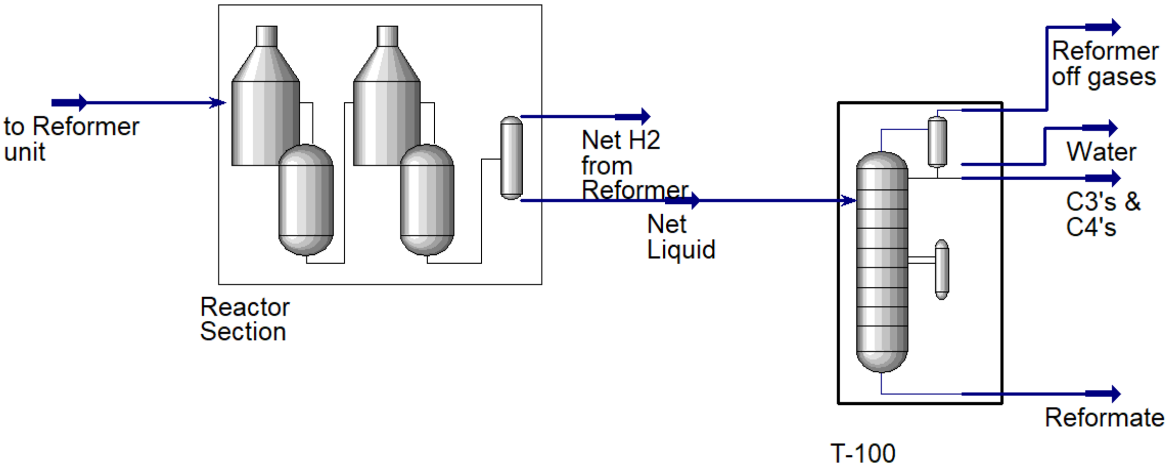
Feed Conditions

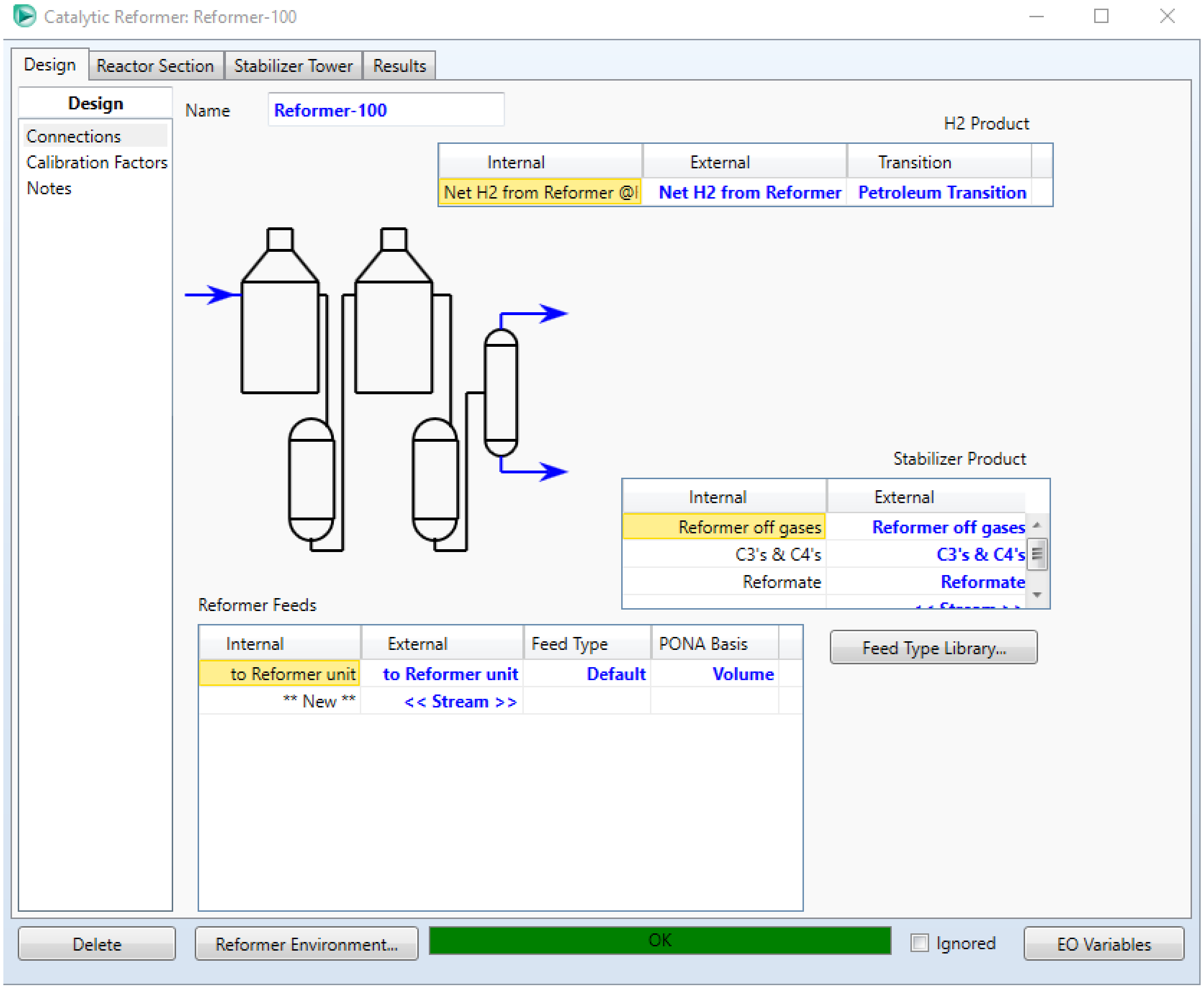
Feed	Volume Flow [m3/h]	Mass Flow [kg/h]	Temperature [C]	Pressure [kPa]	Location	Br #
Recycled Botto	80.00000	73484.0	200.0	1000	Reactor 2	8.000
mixed feed to I	160.45396	1.47927e+05	315.8	13.00	Reactor 1	8.000

Total Feed

	Reactor 1	Reactor 2	Total
Fresh Feed Volume [m3/h]	160.5	0.0	160.5
Fresh Feed Mass [kg/h]	1.47927e+05	0.0	1.479e+005
Total Feed Volume [m3/h]	160.5	80.0	240.5
Total Feed Mass [kg/h]	1.47927e+05	73484.0	2.214e+005
Total Feed Preheat Duty [kJ/h]	0.0000	0.0000	0.0000
Total Feed Pressure [kPa]	1.300e+004	1.300e+004	
Total Feed Temperature [C]	362.6	193.4	
Gas to Oil Ratio [STD_m3/m3]	500.0	500.0	
Quench Flow to Bed 1 [STD_m3/h]	8.023e+004	4.162e+004	
Quench Mixer Duty [kJ/h]	-4.208e+007	-5.600e+007	
LHSV	0.4630	0.8999	

h. Catalytic Naphtha Reforming





Name: Reformer-100

H2 Product

Internal	External	Transition
Net H2 from Reformer @I	Net H2 from Reformer	Petroleum Transition

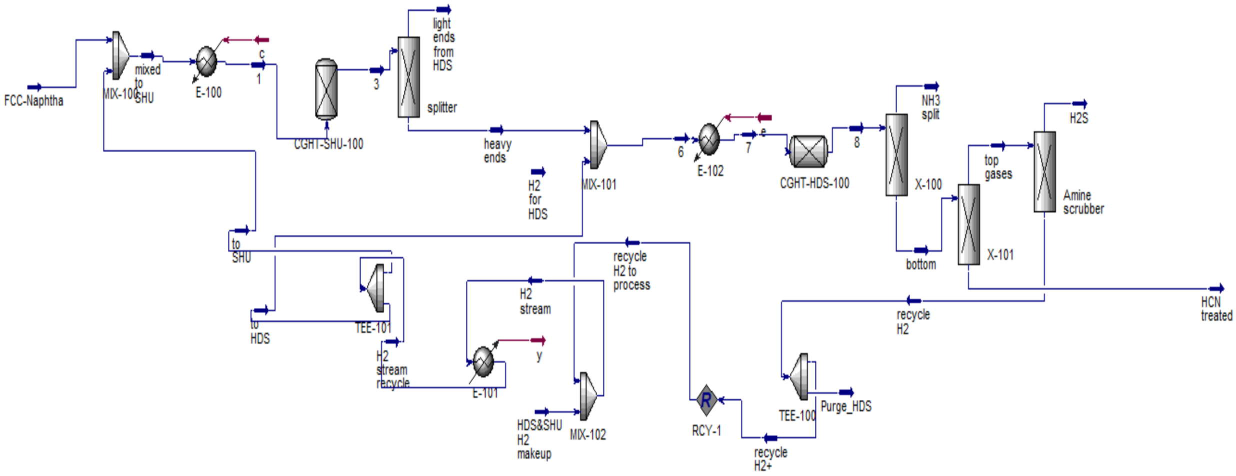
Stabilizer Product

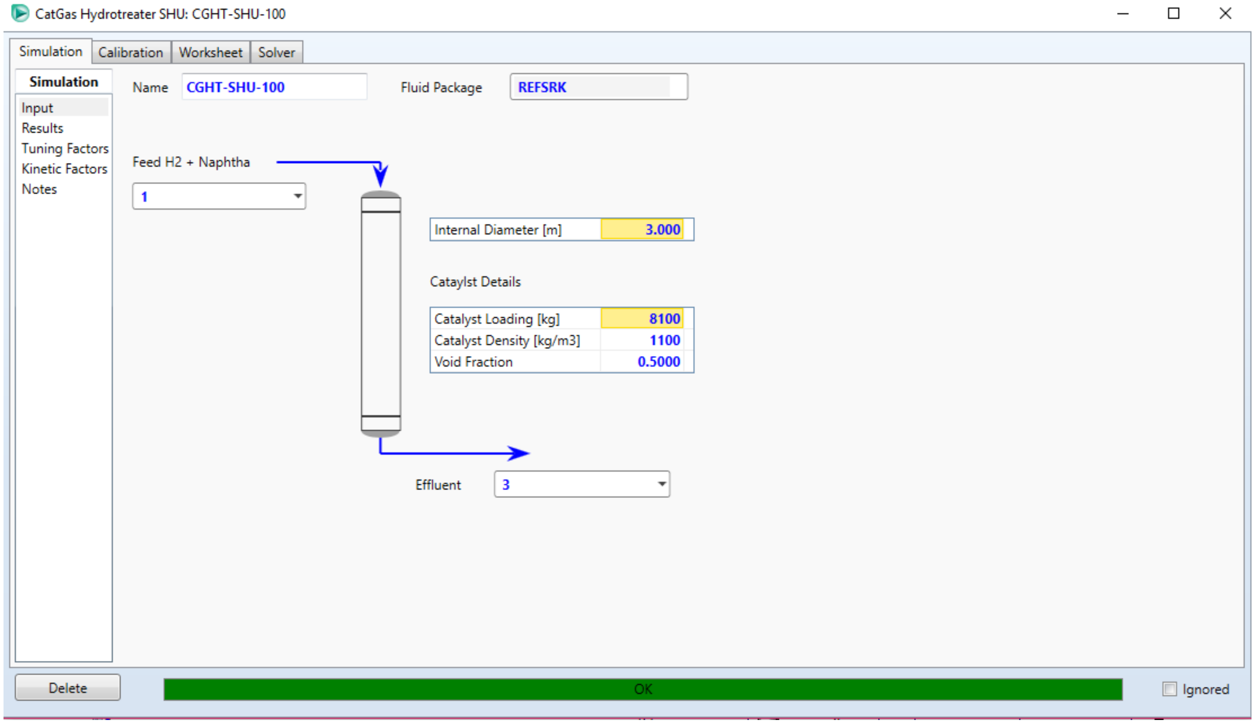
Internal	External
Reformer off gases	Reformer off gases
C3's & C4's	C3's & C4's
Reformate	Reformate
	<< Stream >>

Reformer Feeds

Internal	External	Feed Type	PONA Basis
to Reformer unit	to Reformer unit	Default	Volume
** New **	<< Stream >>		

i. FCC Gasoline Hydrotreaters (HDS and SHU)




CatGas Hydrotreater SHU: CGHT-SHU-100

Name: CGHT-SHU-100

Fluid Package: REFSRK

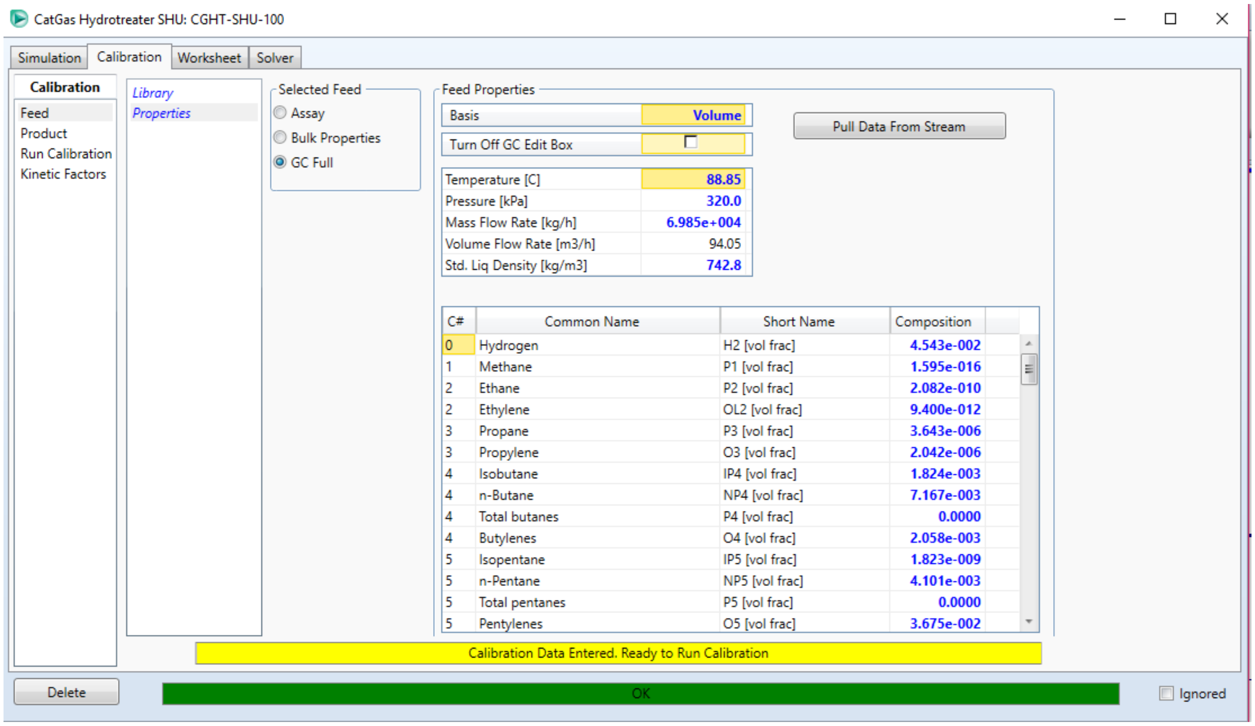
Feed H2 + Naphtha: 1

Internal Diameter [m]	3.000

Cataylst Details

Catalyst Loading [kg]	8100
Catalyst Density [kg/m3]	1100
Void Fraction	0.5000

Effluent: 3



CatGas Hydrotreater SHU: CGHT-SHU-100

Selected Feed
- ○ Assay
- ○ Bulk Properties
- ● GC Full

Feed Properties

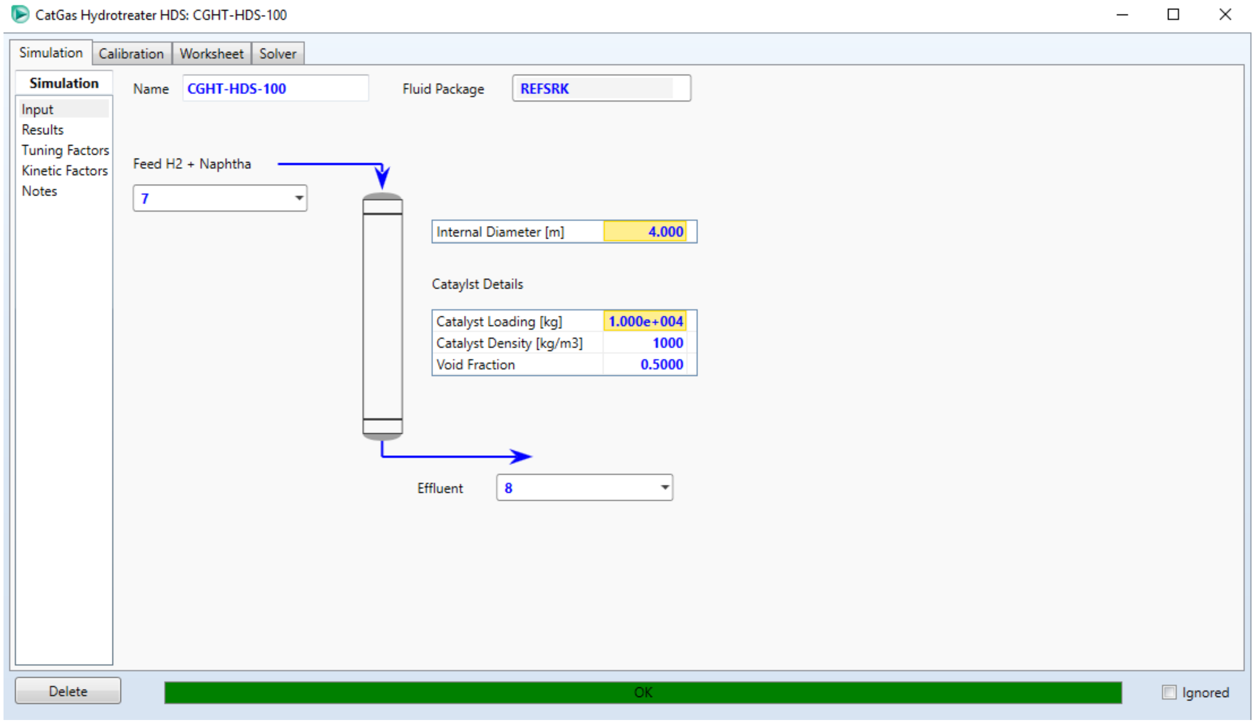
Basis	Volume
Turn Off GC Edit Box	☐

Temperature [C]	88.85
Pressure [kPa]	320.0
Mass Flow Rate [kg/h]	6.985e+004
Volume Flow Rate [m3/h]	94.05
Std. Liq Density [kg/m3]	742.8

C#	Common Name	Short Name	Composition
0	Hydrogen	H2 [vol frac]	4.543e-002
1	Methane	P1 [vol frac]	1.595e-016
2	Ethane	P2 [vol frac]	2.082e-010
2	Ethylene	OL2 [vol frac]	9.400e-012
3	Propane	P3 [vol frac]	3.643e-006
3	Propylene	O3 [vol frac]	2.042e-006
4	Isobutane	IP4 [vol frac]	1.824e-003
4	n-Butane	NP4 [vol frac]	7.167e-003
4	Total butanes	P4 [vol frac]	0.0000
4	Butylenes	O4 [vol frac]	2.058e-003
5	Isopentane	IP5 [vol frac]	1.823e-009
5	n-Pentane	NP5 [vol frac]	4.101e-003
5	Total pentanes	P5 [vol frac]	0.0000
5	Pentylenes	O5 [vol frac]	3.675e-002

Calibration Data Entered. Ready to Run Calibration

OK



CatGas Hydrotreater HDS: CGHT-HDS-100

Name: CGHT-HDS-100

Fluid Package: REFSRK

Feed H2 + Naphtha: 7

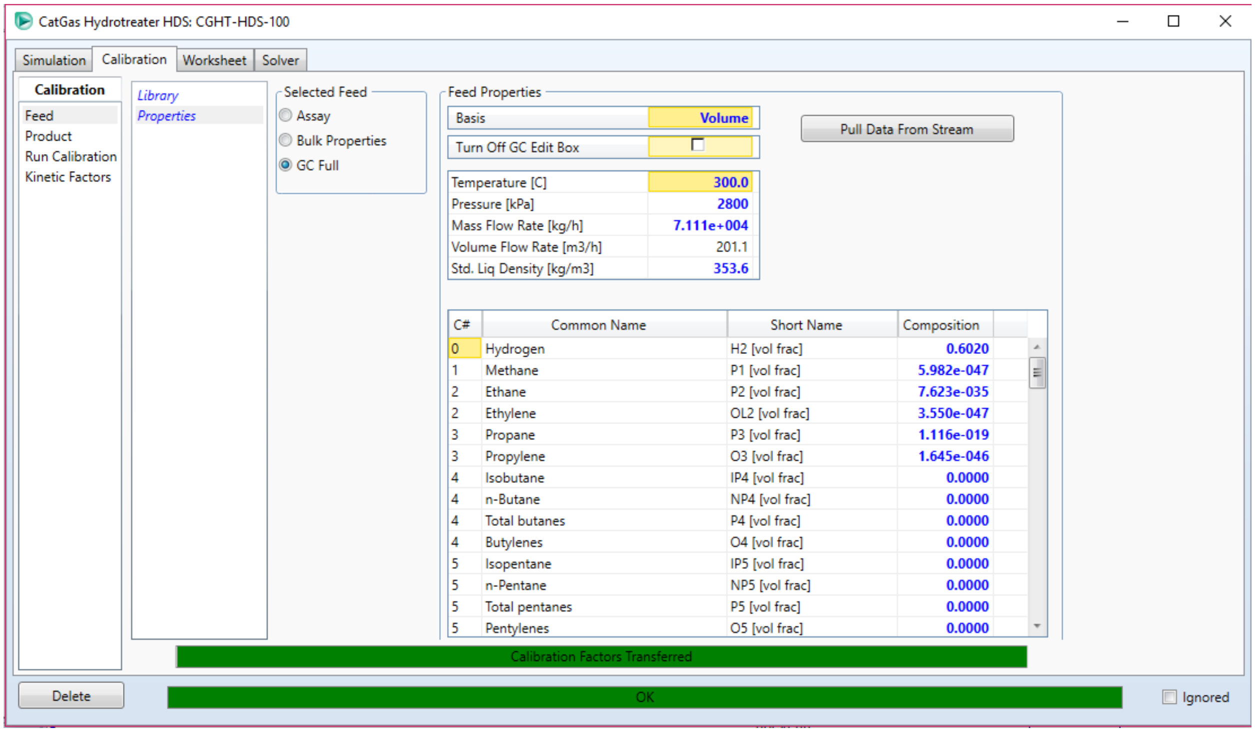
Internal Diameter [m]	4.000

Cataylst Details

Catalyst Loading [kg]	1.000e+004
Catalyst Density [kg/m3]	1000
Void Fraction	0.5000

Effluent: 8

OK



Selected Feed
○ Assay
○ Bulk Properties
● GC Full

Feed Properties

Basis	Volume
Turn Off GC Edit Box	☐

Temperature [C]	300.0
Pressure [kPa]	2800
Mass Flow Rate [kg/h]	7.111e+004
Volume Flow Rate [m3/h]	201.1
Std. Liq Density [kg/m3]	353.6

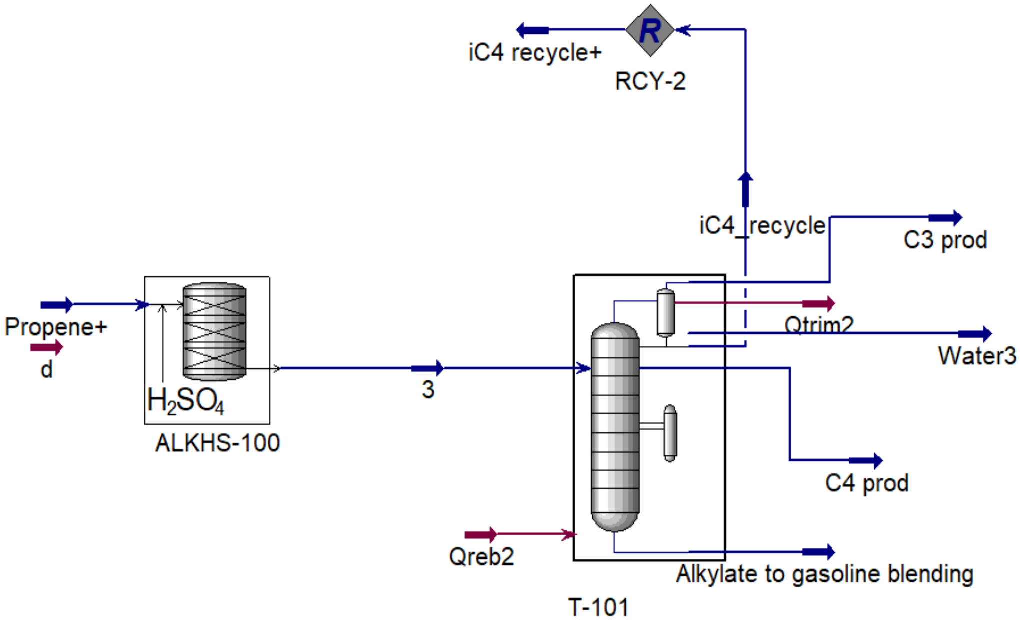
C#	Common Name	Short Name	Composition
0	Hydrogen	H2 [vol frac]	0.6020
1	Methane	P1 [vol frac]	5.982e-047
2	Ethane	P2 [vol frac]	7.623e-035
2	Ethylene	OL2 [vol frac]	3.550e-047
3	Propane	P3 [vol frac]	1.116e-019
3	Propylene	O3 [vol frac]	1.645e-046
4	Isobutane	IP4 [vol frac]	0.0000
4	n-Butane	NP4 [vol frac]	0.0000
4	Total butanes	P4 [vol frac]	0.0000
4	Butylenes	O4 [vol frac]	0.0000
5	Isopentane	IP5 [vol frac]	0.0000
5	n-Pentane	NP5 [vol frac]	0.0000
5	Total pentanes	P5 [vol frac]	0.0000
5	Pentylenes	O5 [vol frac]	0.0000

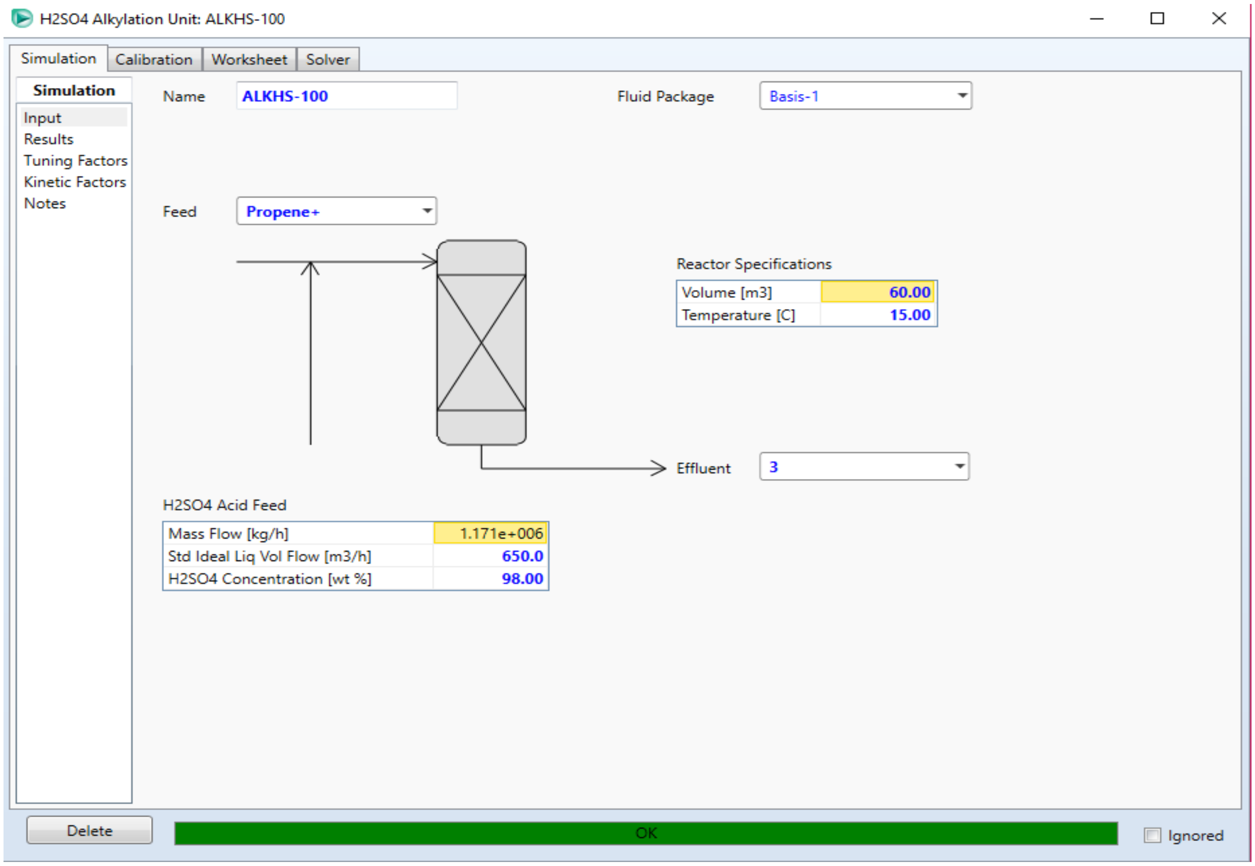
Calibration Factors Transferred

OK

☐ Ignored

j. Alkylation





Name: ALKHS-100

Fluid Package: Basis-1

Feed: Propene+

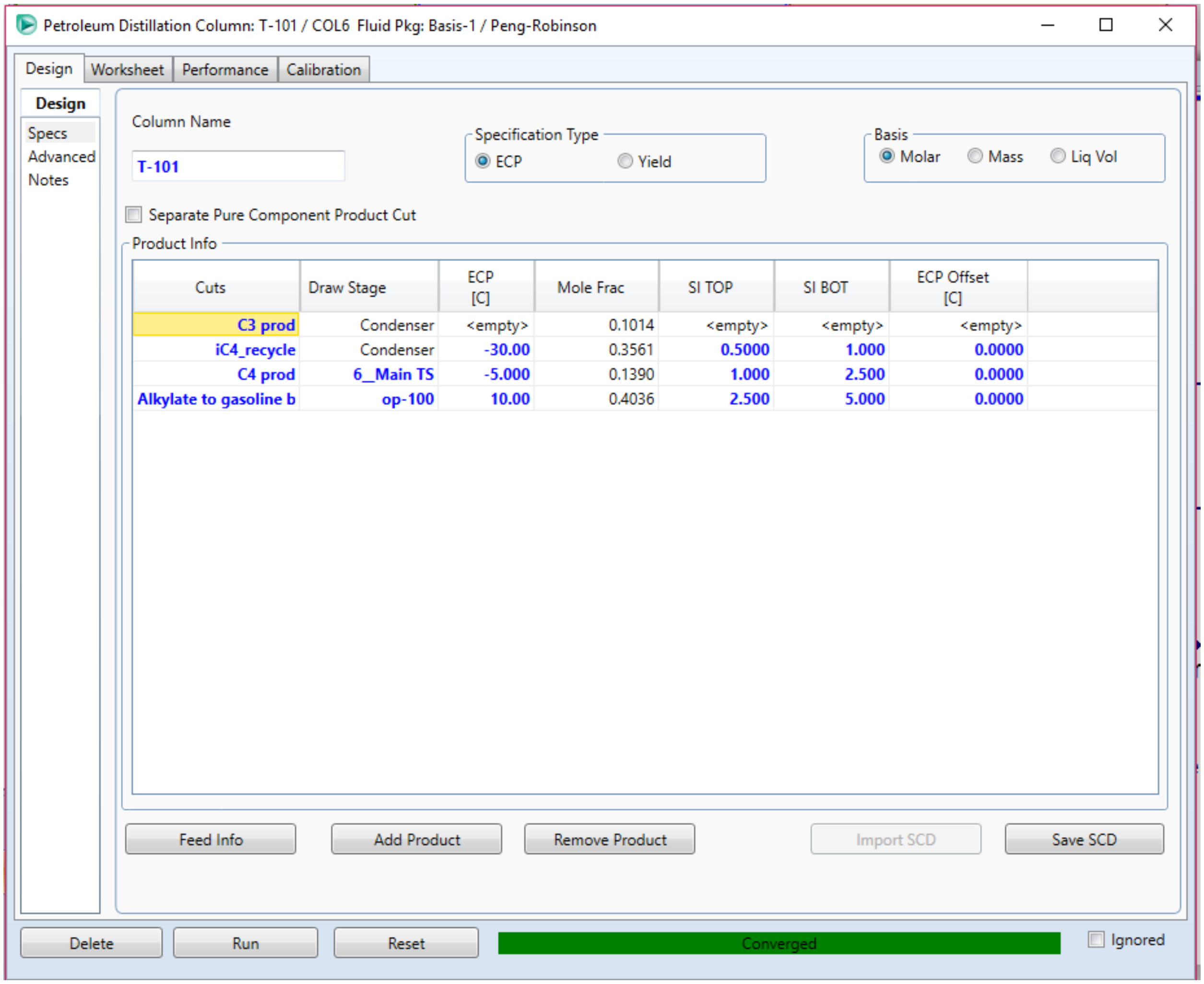
Effluent: 3

Reactor Specifications

Volume [m3]	60.00
Temperature [C]	15.00

H2SO4 Acid Feed

Mass Flow [kg/h]	1.171e+006
Std Ideal Liq Vol Flow [m3/h]	650.0
H2SO4 Concentration [wt %]	98.00



Petroleum Distillation Column: T-101 / COL6 Fluid Pkg: Basis-1 / Peng-Robinson

Column Name: T-101

Specification Type: ● ECP ○ Yield

Basis: ● Molar ○ Mass ○ Liq Vol

☐ Separate Pure Component Product Cut

Product Info

Cuts	Draw Stage	ECP [C]	Mole Frac	SI TOP	SI BOT	ECP Offset [C]
C3 prod	Condenser	<empty>	0.1014	<empty>	<empty>	<empty>
iC4_recycle	Condenser	-30.00	0.3561	0.5000	1.000	0.0000
C4 prod	6__Main TS	-5.000	0.1390	1.000	2.500	0.0000
Alkylate to gasoline b	op-100	10.00	0.4036	2.500	5.000	0.0000