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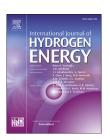
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## Presenting the implementation of power-to-gas to an oil refinery as a way to reduce carbon intensity of petroleum fuels

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#### ABSTRACT

Hydrogen plays a crucial role in refining industry to meet the growing demand and stringent quality of produced gasoline and diesel. Steam methane reforming (SMR) is commonly used by refiners for on-purpose hydrogen production. However, despite being a mature and efficient technology, SMR has a considerable carbon emissions footprint that adds to the carbon intensity of petroleum fuels. Therefore, this paper examines utilizing Ontario province electricity grid that is based mostly on CO2-free sources of electric power to generate hydrogen by electrolysis using the concept of 'power-to-gas'. Consequently, the study evaluates the deployment of a series of 1 MW nameplate capacity polymer electrolyte membrane (PEM) electrolyzers to produce 25 MMscfd of hydrogen for a refinery, instead of the conventional pathway based on steam methane reforming. It assesses the production costs and life cycle emissions for five production scenarios to meet the hydrogen demand of the refinery. Aspen HYSYS and mixed integer linear programming models are employed for the purpose of this study. Steam methane reforming provides a lower cost hydrogen under low natural gas prices, even with stringent carbon-pricing policy. However, the renewable electrolytic hydrogen production method shows a potential to curb significant carbon emissions from steam methane reforming level, increasing the CO<sub>2</sub> free energy and renewable content of the gasoline and design within the life cycle production scheme. This power-to-gas hydrogen production can be compared to eliminating as many as 34,893 gasoline passenger vehicles from the road. Accordingly, supplying electrolytic hydrogen to a refinery by a grid powered from clean energy sources is considered a good venue for providing decarbonization of petroleum fuels.

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#### Introduction

Hydrogen has a broad range of industrial applications, as discussed thoroughly by Zhang et al. [1] and Ramachandran

and Menon [2]. The main consumers of hydrogen are oil refining and petrochemical industries. In refineries, hydrogen is primarily used in hydrotreating and hydrocracking processes. The refining industry has experienced significant hydrogen demand shift in recent years due to several reasons.

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#### Nomenclature

bbl Oil Barrel

CRF Capital Recovery Factor gCO<sub>2</sub> grams of carbon dioxide

kg Kilogram kWh Kilowatt-hour

MMscfd Million Standard Cubic Feet per Day

MW Megawatt

MMBtu Million British Thermal Unit

MJ Megajoule

The main 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. All these factors pose challenges to refineries to tackle the hydrogen balance issue while meeting growing demand and stricter quality of petroleum fuels.

Around 96% of the global hydrogen production comes from fossil fuels while almost all of the remaining 4% is produced by electrolysis. 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 [3,4]. 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 petrochemical industries. In U.S., 95% of the total produced hydrogen comes from SMR technology [5]. 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 Eq. (1). Then, CO is further converted to carbon dioxide (CO2) by reacting with steam in the water gas shift reactor (Eq. (2)). Modern SMR processes are equipped with pressure swing adsorption (PSA) technology to purify the hydrogen rich gas from CO<sub>2</sub>. The produced hydrogen comes with 99.9% purity which has multiple advantages for the hydrotreating and hydrocracking processes [6].

Steam methane reforming reaction :  $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ 

(1)

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

The major drawback of SMR is the significant release of  $CO_2$  emissions associated with producing the hydrogen. The life cycle emissions from the process are estimated by Spath and Mann [7] to be 11.88 kg of carbon dioxide equivalent ( $CO_2$ e) per kg of  $H_2$ . The study shows that the hydrogen plant is responsible for almost 75% of the life cycle emissions. Collodi and Wheeler [8] suggest a range of 9–12 kg of  $CO_2$  per kg of  $CO_2$  depending on the type of feedstock used. The emissions resulted from hydrogen production and oil refining, in general, are directly tied to the life cycle emissions of petroleum

fuels. Fig. 1 illustrates the life cycle of gasoline and diesel, usually referred to as Well-to-Wheels (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. [9] 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% [9]. The large contribution from vehicles is apparent since a gasoline passenger car emits an average of 4.7 metric tons of CO<sub>2</sub> annually [10].

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) [11]. 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 [12]. Meanwhile, Ontario province in Canada is also planning to introduce a similar regulation with 5% reduction of gasoline GHG pollution by 2020 [13]. 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 major 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 Fig. 1 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.

Moreover, ethanol or other biofuels are used by oil companies to meet the renewable fuel standards for transportation fuels. However, ethanol production can have an associated life cycle carbon emissions while feedstocks are

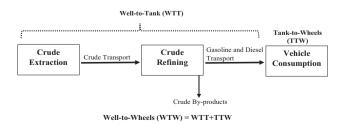


Fig. 1 – Gasoline and diesel life cycle.

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