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Review

Catalytic and Noncatalytic in Situ Hydrogen Production from Heavy Oil: A Review of Experimental Studies

Mohamed Abdalsalam Hanfi, Olalekan Saheed Alade, Abdulkadir Tanimu, Mohamed Mahmoud, and Sulaiman A. Alarifi*

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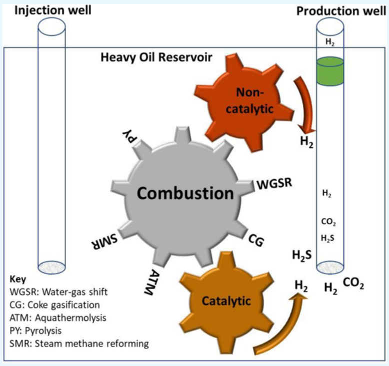
ABSTRACT: Hydrogen (H_2) offers a less carbon-intensive energy production method than natural gas. The potential of utilizing hydrogen at a large scale within the future energy mix to fuel the world opens the door to investigating hydrogen production from heavy and extra-heavy oil reservoirs. Various reaction mechanisms are involved in the in situ combustion gasification of heavy oil to produce sustainable and low carbon intensive hydrogen. In-situ catalytic hydrogen production involves injecting a catalyst into the reservoir or utilizing the in situ reservoir materials to catalyze the various reactions. Clay minerals and formation water were found to serve as in situ catalytic materials and enhance the in situ hydrogen production process. This work presents a comparative review of the catalytic and noncatalytic experimental studies carried out on in situ hydrogen production. The formation damage induced by the in situ combustion and its effect on hydrogen production was highlighted. In addition, the impact of the formation damage induced by the in situ combustion on the hydrogen production process is discussed. This study categorized the experimental studies conducted on the hydrogen production from heavy oil into catalytic and noncatalytic processes to highlight the effect of the synthetic and natural reservoir catalytic materials on in situ hydrogen production.



1. INTRODUCTION

Diminishing conventional oil reserves, continuous increases in energy demand, and climate change factors are expediting energy transition efforts. According to the International Energy Agency (IEA) report, fossil fuels such as heavy oil and extra-heavy oil are expected to be the dominant energy supply till 2035.[1] There is a substantial worldwide estimated original oil in place exceeding 6000 billion barrels of heavy and extra-heavy oil.[2] However, heavy oil characteristics lead to poor recovery processes and limited production flow.[3−7]

The term "Heavy" refers to the high density or specific gravity of the heavy oil compared to lighter oils, such as conventional oils. Specific gravity is measured in API degrees, where low values correspond to a higher specific gravity. Based on density and viscosity, crude oil is classified into (1) light oil which has API gravity higher than 22°, viscosity lower than 100 cP, and density lower than 934 kg/m^3. (2) Heavy oil has API gravity in the range of (10−22) °, viscosity higher than 100 cP, and density in the range of (934−1000) kg/m^3. (3) Extra-heavy oil (bitumen) has API gravity lower than 10°, viscosity higher than 10,000 cP, and density higher than 1000 kg/m^3.[8]

The challenging characteristics of heavy oil make it a potential target for hydrogen production. Hydrogen (H_2) is hailed as a clean energy carrier, producing only water as an emission when used in fuel cells. The physical characteristics of hydrogen are detailed in Table 1.

Hydrogen is naturally abundant in the compound form.[10−14] It is considered the lightest element that has a low energy density per unit volume. Currently, existing technologies offer multiple options for hydrogen production, storage, transportation, and utilization in diverse ways. Various sources of energy can be utilized for hydrogen production such as fossil fuel (oil, natural gas, and coal), nuclear, and renewables. Researchers reported the existence of hydrogen (H_2) naturally in different in situ environments with concentration above 10%.[15,16] Despite the discovery of natural H_2 in many locations, still there is a lack of comprehensive investigation into the characteristics and distribution of natural hydrogen in these environments.[17] The increasing global focus on adopting hydrogen as a clean energy solution is driven by two main points: First, no air pollutants or greenhouse gases are emitted from hydrogen utilization. Second, sources with low carbon

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Table 1. Physical Characteristics of Hydrogen as Compared with Fuels[a]

Property	Hydrogen	Comparison
Density (Gaseous)	0.089 kg/m^3 (0 °C, 1 bar)	1/10 of natural gas
Density (liquid)	70.79 kg/m^3 (−253 °C, 1 bar)	1/6 of natural gas
Boiling point	−252.76 °C (1 bar)	90 °C below LNG
Energy per unit of mass (Low heating value)	120 MJ/kg	3× that of gasoline
Energy density per unit of volume (ambient cond., Low heating value)	0.01 MJ/L	1/3 of natural gas
Specific energy (liquified, Low heating value)	8.5 MJ/L	1/3 of LNG
Flame velocity	346 cm/s	8× methane
Ignition range	4−77% in air by volume	6× wider than methane
Autoignition temperature (AIT)	585 °C	220 °C for gasoline
Ignition energy	0.02 MJ	1/10 of methane

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content such as biomass, renewables, and nuclear power can produce hydrogen.[18] The global demand for hydrogen is estimated to be around 70 million tonnes per year.[9] There are numerous options for hydrogen (H_2) production, categorized based on the raw materials used in renewable technologies and nonrenewable (conventional).[19−26]

Conventional technologies involve the use of fossil fuels and nuclear and renewable technologies that include wind, biomass, and solar. As a result of generating hydrogen from Naphtha, heavy oil, petroleum coke, and natural gas are the major feeds used for hydrogen production in petroleum.[27−32]

Various thermal recovery methods, commonly employed for extracting unrecovered hydrocarbon resources have the additional benefit of producing hydrogen as a byproduct. The characteristics of the reservoirs and hydrocarbons present allow for flexibility in selecting the most suitable method. In general, most of the thermal technologies such as in situ combustion and gasification techniques that are adapted for hydrogen production are part of a broader category of enhanced oil recovery (EOR) methods.[33,34] In the thermal recovery techniques, external sources of heat are introduced to the reservoir. These methods involved steam flooding,[35] Steam Assisted Gravity Drainage (SAGD)[36,37] and in situ combustion.[38,39]

Production of hydrogen from hydrocarbon resources is divided into surface operations and in situ operations. Surface operations refer to the refined oil and gas by petrochemical plants. While in situ operations are concerned with the reaction processes that occur in the reservoir such as in situ combustion and gasification.[40,41] The latest review studies[42,43] reviewed the literature on subsurface combustion and gasification related to hydrogen production. In addition, a techno-economic and lifecycle assessment were also presented.

In-situ hydrogen production entails generating hydrogen within the reservoirs through thermal cracking of hydrocarbons and reactions of hydrocarbons with water.[44−46] Hydrogen production from oil reservoirs is different from production from gas reservoirs in which the latter requires elevated temperature, this elevated temperature challenges the process. Once hydrogen is produced in the reservoir, downhole hydrogen membrane separators are employed to extract hydrogen to the surface while other gases such as CO_2 are sequestrated within the reservoirs as shown in (Figure 1).

In this study, depending on the materials involved in the in situ hydrogen production experiments and following the existing classification of the underground mechanisms of the heavy oil upgrading, we defined the in situ catalytic hydrogen production as any in situ reaction mechanisms that involve catalytic materials influence the crude oil gasification process and yield more hydrogen gas. These materials can be (1) natural materials that exist naturally in the reservoir such as water, quartz, and clay minerals; (2) synthetic materials which include any injected materials into the reservoir such as water-soluble catalysts, and oil-soluble catalysts.

It is important to highlight that the in situ catalytic process in this study is different from the in situ catalytic process that is used to describe the mode of the catalyst addition.

This study reviews the literature on hydrogen production from crude oil and aims to classify the existing experimental studies based on the materials utilized in these studies to catalytic and noncatalytic. None of the previous reviews provide such a classification of the in situ hydrogen production from crude oil. This comparative study provides the difference between the catalytic and noncatalytic experiments conducted to investigate the production of hydrogen from in situ heavy oil. In addition, the study covered the reaction mechanisms,

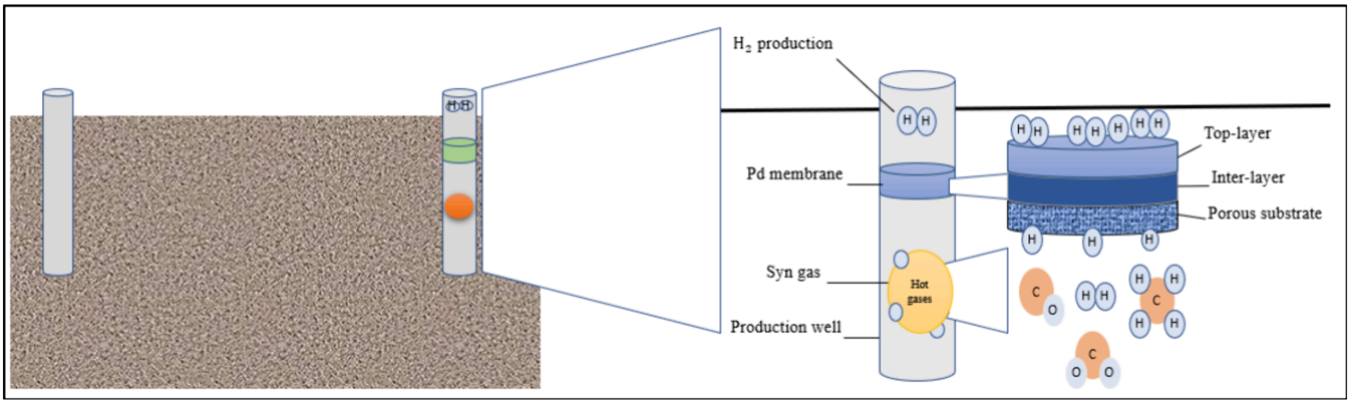

Figure 1. H_2 membrane separation from in situ syngas.

field techniques, and color coding of the hydrogen production process.

2. IN-SITU CATALYTIC AND NONCATALYTIC HYDROGEN PRODUCTION

2.1. In-Situ Catalytic Hydrogen Production. The in situ hydrogen production process involved similar reaction mechanisms involved in the in situ oil upgrading. Whereas the only difference is the final product of each process. In-situ reaction mechanisms such as catalytic cracking and catalytic aquathermolysis play an important role in the heavy oil upgrading process as well as hydrogen production. Shi et al.[47] reported the similarity between the different processes utilized for in situ hydrogen production and the processes performed in petroleum refineries. They concluded that in situ hydrogen production required minimal surface equipment compared to other in situ technologies utilized for upgrading heavy oil. Whereas, both processes involved the same reaction mechanisms but with different objectives.

Various technologies used for upgrading heavy oil such as in situ solvent addition, and in situ steam/catalyst addition can be implemented for in situ hydrogen production.

The conventional catalysts often used in the upgrading process may be classified into many categories, such as water-soluble catalysts, oil-soluble catalysts, amphiphilic catalysts, dispersion catalysts, and nanocatalysts.[48−52] These types of catalysts can also be utilized for in situ hydrogen production but need more investigation.

Yuan et al.[53] used microwave (MW) radiation as a heat source to investigate a complex of crude oil, water, and/or Fe catalysts in fragmented rock specimens. The Kirby sandstone was pulverized into particles with a diameter ranging from 0.25 mm to 0.425 mm (40−60 mesh). Subsequently, the samples were combined with catalysts, support materials, oil, and/or water to facilitate microwave heating during the tests. The rock sample used is uniform, with porosity ranging from 19% to 21%, permeability ranging from 70 to 85 millidarcy (mD), a matrix density of 2.2 g per cubic centimeter (g/cm^3), and an average grain size of 0.127 mm (mm). The density of the crude oil used in the studies is 0.86 g/mL. The oil composition study was obtained using gas chromatography−mass spectrometry (GC-MS). The ratio of hydrogen to carbon (H/C) is 1.81, while the weight percentages of carbon, hydrogen, and sulfur are 84.16%, 12.70%, and 3.14% respectively. The experiment showed that microwave heating efficiently and quickly raised the reactor's temperature, resulting in the generation of highly pure hydrogen in 2−3 min. During the trials, hydrogen was found to be the main component in the produced gas mixtures, with purity levels ranging from 45.81% to 63.49%. Water increases the total production of hydrogen in all the studies performed. In addition, hydrogen is produced via the water-gas shift process. The metallic minerals found in the rocks may act as natural catalysts, significantly improving the production of hydrogen and aiding microwave heating. Catalysts enhance the pace of chemical reactions and serve as highly active regions during microwave heating, hence facilitating the initial generation of hydrogen. The results indicate that placing catalysts near the downhole wellbore in reservoirs might potentially increase hydrogen production at lower temperatures, therefore enhancing the energy efficiency of MW heating.

Adam et al.[54] suggested a novel method of using microwave heating to facilitate subsurface, catalytic enhancement of heavy oil during the Toe-to-Heel Air Injection process. Touchstone Exploration Inc. Canada (formerly Petrobank) offers a dense oil with a specific gravity of 14.3 API and a viscosity of 880 cP. The catalyst used for catalytic upgrading was CoMo/γ-Al_2O_3, which is a hydrodesulfurization catalyst. The experiment included injecting a combination of 15 g of oil and 1.0 g of solid catalyst into a quartz reactor that was purged with nitrogen. The findings indicated that using the CoMo/γ-Al_2O_3 catalyst resulted in a significantly elevated hydrogen content (18.8%) in the generated gas, in contrast to the use of alumina alone, which yielded a mere 0.779%. Hydrogen is generated during the catalytic upgrading process via intricate processes, which include the catalytic dehydrogenation of naphthenes (cycloalkanes) and aliphatic hydrocarbons. This leads to the creation of aromatic compounds and olefins. The emission of olefinic gases throughout the process is evident from the existence of gaseous products such as ethene, propene, butene, and others.

Djimasbe et al.[55] studied the impact of newly developed catalysts on the production of hydrogen from extra heavy oil at the Tahe oil field located in China. The catalysts used in this study were composed of nickel (Ni), cobalt (Co), and nickel-cobalt (Ni-Co) alloys, which were supported by aluminum oxide. These catalysts were used in the presence of supercritical water (SCW). Before being used for oil upgrading via different processing methods, the catalysts obtained were subjected to characterization using a range of physical and chemical tests. This facilitated a thorough comprehension of their characteristics. In addition, these catalysts were assessed in the presence and absence of supercritical water (SCW) to investigate the impact of SCW on the upgrading process. The Agilent 7890A gas chromatography (GC) instrument, equipped with a flame ionization detector (FID), was used to analyze the carbon number distribution of the saturate fractions, as well as to assess the composition and yield of evolved gases during hydrothermal upgrading procedures. The SARA (Saturated hydrocarbons, Aromatics, Resins, and Asphaltenes) composition portion, which includes saturated hydrocarbons, aromatics, resins, and asphaltenes, was analyzed using the ASTM D 4124 method.[56] The aromatic fractions of both the heavy crude oil and upgraded oil samples were measured using gas chromatography/mass spectrometry (GC-MS). In addition, the resin and asphaltene fractions were analyzed using a Bruker AVANCE-III-HD-500 nuclear magnetic resonance (NMR) spectrometer, following the method given by Djimasbe et al.[57] Consequently, their findings indicated that the combination of supercritical water (SCW) and catalysts led to enhanced production of molecular hydrogen. Without the presence of SCW, the yield was 1.0598 mol.%, but it increased to 6.1320 mol.% when SCW was introduced. The highest achievable yield of 11.78 mol.% was obtained by combining supercritical water (SCW) with Ni-Co/Al2O3 catalysts. The results of our study suggest that the notable rise in hydrogen production while using supercritical water (SCW) and catalysts may be due to the activation of steam methane reforming and water-gas shift reactions during the upgrading procedure. In addition, the catalytic upgrading process showed outstanding effectiveness in eliminating heteroatoms by radical and oxidative mechanisms, as shown by a reduction in sulfur content from 1.84 to 1.35 wt. %.

Pu et al.[58] studied the in situ hydrogen generation from heavy oil by mimicking the in situ heavy oil gasification using

HPHT reactors. In this study, many parameters such as reaction time, temperature, oil−water ratio, and porous media were varied to investigate the possibility of hydrogen generation after steam stimulation. Three different temperatures 450, 500, and 550 °C were applied and each temperature was run for 2, 4, and 8 h. The results showed that the hydrogen started to be generated starting from 400 °C. Also, it found that as the reaction time and the water−oil ratio decreased the fraction of generated hydrogen increased.

He et al.[59] performed an experimental investigation on four distinct varieties of heavy and light oil. The research used a ramped temperature oxidation (RTO) device to replicate the oxidation process of crude oil in a high-pressure high temperature (HPHT) environment. Two distinct tubular reactors were used throughout the tests. One of the methods used was the utilization of an artificial sand-filling tube, wherein the tube was filled with a combination of quartz and coarse sand. Subsequently, heavy oil was injected into this combination. The second reactor is a stainless-steel tube reactor containing a genuine reservoir core. This setup was used to examine the mineral composition's impact on hydrogen production during the gasification of heavy oil. The findings indicate that the primary minerals and their intricate pore structure facilitate the production of hydrogen by reducing the injected oxygen, hence minimizing the consumption of the generated hydrogen. The investigations demonstrated that the reservoir core yielded a hydrogen concentration of (55−60 mol%), whereas the sand filling model only obtained 5−10 mol%. Crude oil has shown to be more advantageous than carbon in generating hydrogen owing to its lower temperature threshold for hydrogen production (about 500−550 °C compared to 700−750 °C for carbon). Additionally, the peak production of H_2 is seen within the temperature range of 750−800 °C. The coke gasification and water-gas shift reactions were the primary contributors to the production of hydrogen.

2.2. Noncatalytic Hydrogen Production.

Tang et al.[60] conducted a laboratory experiment to study the production of hydrogen from in situ crude oil gasification. Heavy and light crude oil were obtained from Chinese oil field. The experiment was performed by TG-MS in combination with characteristic spectrum analysis (ECSA). The different heating rates were set with an experimental temperature range between room temperature and 1000 °C. The results revealed that mass loss of the heavy oil was observed in the pyrolysis stage within the temperature range of (366−521 °C), while the mass loss of the light oil found to be in the drying stage at temperature range (30−366 °C). Regarding hydrogen generation, the heavy oil generated hydrogen during the drying, pyrolysis, and coking stages, whereas light oil generated hydrogen during pyrolysis and coking stages only. Also, it found that hydrogen can be generated from heavy oil more easily than light oil.

Yang et al.[61] investigated the processes involved in generating hydrogen from heavy oil by using a thermogravimetric analyzer (TGA) and a mass spectrometer (MS). The TGA-MS experiment was conducted under a continuous flow of nitrogen at a fixed rate of 50 mL/min, using three distinct heating rates of 5, 10, and 20 °C/min. Two stages have been described based on the temperature range: the physical stage occurs at temperatures ranging from 85 to 351 °C, while the chemical stage occurs between 528 and 900 °C. The chemical step comprises two distinct reactions: pyrolysis, which takes place at temperatures ranging from 351 to 528 °C, and coke dehydrogenation, which happens within the temperature range of 528 to 820 °C. Additionally, it was discovered that 80% of the overall hydrogen was generated by the process of coke dehydrogenation. According to their assertion, the coke generated in the pyrolysis phase was used as a fuel for the coke dehydrogenation phase, and the amount and quality of the coke principally rely on the asphaltene concentration. Yan et al. presented a kinetic model for the gasification of heavy oil based on TGA-MS measurements, which included three processes. The heavy oil is categorized into light and heavy constituents, with the light portion undergoing vaporization, while the heavy portion is used in the pyrolysis process. The reaction had a significant role in the production of hydrogen.

A summary of catalytic and noncatalytic hydrogen production from heavy oil studies is summarized and presented in Table 2.

3. ASSESSMENT OF HYDROGEN PRODUCTION IN LABORATORY EXPERIMENTS

The hydrogen production process from crude oil gasification is inherently complex, resulting in the production of a variety of gases that interact with one another. Several variations in the equipment type, injected fluids, flow rates, pressure, and temperature can be significant in experimental settings, making it inappropriate to assess hydrogen generation performance based solely on instantaneous hydrogen content. Evaluation of hydrogen A new concept is proposed by He et al.[59] to assess the efficiency of the experiment by a novel concept termed "hydrogen generation efficiency" (HGE). Hydrogen production efficiency (HGE) is then defined as the ratio of the volume of hydrogen generated to the volume of hydrogen consumed within a specified time (Δt), As illustrated in the following equation.

$$E_{hg} = \frac{\mathrm{H_2(Generated)}}{2\cdot \mathrm{O_2(Consumed)}}$$

Yuan et al.[53] introduced a set of metrics to evaluate the hydrogen generation from the original oil sample at each separate experiment. The proposed metrics can be summarized as follows:

- Ultimate hydrogen generation selectivity $= \frac{\text{total hydrogen produced (mL)}}{\text{initial crude oil weight (g)}}$
- Cumulative evolved H_2 volume $= \frac{\text{cumulative hydrogen produced from intial time to any time (mL)}}{\text{initial crude oil weight (g)}}$
- Ultimate hydrogen purity $= \frac{\text{total hydrogen produced (mL)}}{\text{total gas produced (mL)}}$

4. KINETIC MODELS FOR IN SITU HYDROGEN PRODUCTION

Okere et al.[62] developed a new SARA-based numerical model to simulate hydrogen production from heavy oil reservoirs. The new reaction scheme incorporated eleven SARA-based components and fourteen reactions. In addition, the mass balance in the SARA fractions was improved by modifying the stoichiometric coefficient of the reactions. The data used in the simulation model was derived from Marguerite Lake Project data. The results showed the variation in the hydrogen content analysis that changed with the injected gas. The constituents for the three gases used were 12%, 9%, and 0.3% for air, pure oxygen, and CO_2, respectively.

Kapadia et al.[63] introduced a kinetic model that investigates the feasibility of producing hydrogen from Athabasca bitumen. The proposed reaction scheme involved thermal cracking, oxidation/combustion, hydrogen production, and hydrogen consumption reactions. The hydrogen production rates estimated by the proposed reaction scheme and its kinetic constants were compared to empirical data obtained from experimental and pilot plant studies on the partial oxidation/combustion of fossil fuels documented in the literature. The findings suggest that the novel reaction scheme offers accurate assessments of Athabasca bitumen's ability to generate hydrogen. The accuracy of the model's predictions was confirmed by comparing them to data obtained from Athabasca bitumen pyrolysis and aquathermolysis tests, demonstrating a prominent level of agreement with the experimental findings. Afterward, the reaction model was examined to ascertain the most favorable temperature and pressure settings attainable in an in situ combustion process. The results revealed that the production of hydrogen from Athabasca bitumen reaches its highest levels within the temperature range of 320 to 380 °C, while maintaining a total pressure of 4 MPa. An in-depth analysis of the reactions revealed that the presence of thermal cracking and low-temperature oxidation leads to the production of a substantial quantity of coke, which in turn enhances the pace of hydrogen generation processes. Nevertheless, when the temperature surpasses this range, there is an increased consumption of coke due to high-temperature oxidation, leading to a reduced amount of coke available for hydrogen production. In summary, the findings of this novel kinetic model indicate that by maintaining operating parameters within the ideal range, hydrogen gas produced from the gasification of Athabasca bitumen might be a feasible and eco-friendly energy option.

5. HYDROGEN PRODUCTION COLOR CODING

Recently, assorted colors have been employed to indicate different energy sources, technology, and cleanness levels associated with hydrogen production.[64−66] In general, hydrogen may be brown or black, gray, blue, turquoise, pink, yellow, or green. Aqua, green, and blue are color codes that distinguish the technologies used to produce hydrogen from fossil fuels based on emitted carbon dioxide. "Blue" signifies hydrogen production with the implementation of CCUS (Carbon Capture, Utilization, and Storage), and "aqua" is coined for hydrogen production from in situ resources where no CO_2 is produced to the surface. On the other hand, "green" is used for hydrogen production from renewable resources. Nonetheless, there are no universally defined color standards for hydrogen derived from sources such as biomass, nuclear energy, or diverse forms of grid electricity.

5.1. Blue Hydrogen.

Blue hydrogen is referred to hydrogen primarily generated from natural gas or coal by different processes such as reformation or coal gasification, accompanied by carbon capture and storage (CCS) technologies.[67] Among these methods, the most prevalent technique is the steam reformation of methane with CCS (derived from natural gas). The most common hydrogen production processes are illustrated in this section.

5.2. Aqua Hydrogen.

The internal processes involved in aqua hydrogen production are different from the ones involved

Table 2. Summary of Catalytic and Noncatalytic

Author	Study category	Research Emphasis	Type of oil	Reaction mechanism responsible for H_2 generation	Equipment	Findings
Hajdo et al.[103]	Catalytic	Experimentally investigate the flow and reaction mechanism responsible for hydrogen generation	Bitumen	Coke gasification, water-gas shift, thermal cracking	Combustion tube	The primary source of the produced hydrogen primarily stems from the coke gasification reaction, which generates both H_2 and CO. Subsequently, the water gas shift reaction enhances the hydrogen yield.
He et al.[59]	Noncatalytic	Study the hydrogen generation processes by injecting air/nitrogen and water	Heavy oil, light crude oil, and carbon powder	Carbon gasification and water-gas shift reaction	Tubular reactor	Hydrogen generation is primarily from coke gasification and the water-gas shift reaction. The optimal production of hydrogen occurred within the temperature range of 750 to 800 °C. In the case of the RTO experiment with the reservoir core, the highest hydrogen rate reached 55−60 mol%, whereas the sand-filling model only achieved 5−10 mol %.
Yang et al.[61]	Noncatalytic	Investigate the mechanisms of hydrogen generation using TGA-MS	Heavy oil	Pyrolysis and coke dehydrogenation	Thermogravimetric analyzer (TGA) and mass spectrometer (MS)	The experimental identify a two-stage process in the weight loss of heavy oil when subjected to temperatures ranging from 25 to 900 °C. The physical stage primarily involves the evaporation of lighter components. The chemical stage encompasses pyrolysis and coke dehydrogenation reactions. Notably, approximately 80% of the hydrogen is generated through the coke dehydrogenation reaction, occurring within the temperature range of 528 to 820 °C.
Tang et al.[60]	Non- catalytic	Investigate the mechanisms of hydrogen generation using TGA-MS	Heavy and light oil	Drying, pyrolysis, and coking	Thermogravimetric analyzer (TGA) and mass spectrometer (MS)	The results showed that the heavy oil generated hydrogen during the drying, pyrolysis and coking stages. Whereas the light oil generated hydrogen during pyrolysis and coking stages only.

in the blue hydrogen pathway. In subsurface hydrogen production, combustion is induced by an injection of oxygen gas or air into a reservoir containing hydrocarbons. The elevated temperature in the reservoir causes the mixture of oxygen and oil to ignite. Different ignition methods could be used if the autoignition temperature is not reached such as gas burners, chemical reactions, or electrical heaters. The heat generated from combustion triggers additional reactions (thermal cracking, aquathermolysis, water-gas shift reaction, and coke gasification) that result in the formation of hydrogen. At the production well, the implemented membrane selectively allows hydrogen gas to be produced while the other unwanted gases will be stored in the reservoir.

Collaboration between the University of Calgary and Proton Technologies devised an inventive technique to generate hydrogen from in situ oil sand. This approach involves the injection of oxygen or air into the heavy oil reservoirs, initiating an autonomous oxidation reaction that generates heat. At subsurface temperature of 350 °C, the oil will crack and some of the low boiling point gases will evolve. Despite the elevated temperature, the Presence of water, localized temperature, and the reservoir depth keep the process controllable. As a result of these reactions, hydrogen gases are produced through production wells while other gases are sequestrated in the reservoir.

5.3. Turquoise Hydrogen.

The production process of turquoise hydrogen relies on the pyrolysis process of methane. The pyrolysis of methane causes the generation of hydrogen gas and the formation of coke, as represented by reaction 1.[68]

$$CH_4 \rightarrow 2H_2 + C \tag{1}$$

A notable advantage of thermally cracking methane is the oxygen-free process, which suppresses the formation of carbon oxides. Solid carbon deposited in the process can be stored in various forms such as carbon nanotubes or carbon nanofibers.[69,70] The remaining amount of methane that is not reacting can be separated using a membrane, potentially raising the concentration of hydrogen in the produced gas up to 99% by volume.[70] The thermal cracking of methane results in a reduction in hydrogen production by 50% per mole of methane, while also consuming around 45.26% less energy when compared with steam methane reforming.[71] Table 3 summarizes the hydrogen production color coding related to oil and gas as a feedstock.

Table 3. Summary of Hydrogen Production Color Coding

Color Code	Production Method	Feed	Product
Blue Hydrogen	SMR/Gasification combined with CCUS	Fossil fuels	Low carbon Hydrogen
Aqua Hydrogen	In-situ gasification	Fossil fuels	Zero CO_2 emission
Turquoise Hydrogen	Thermal cracking	Methane	Solid carbon

6. FIELD TECHNIQUES AND REACTION MECHANISMS APPLIED FOR IN SITU HYDROGEN PRODUCTION

6.1. Field Techniques.

For the coming decades, fossil fuels are projected to continue being the prevailing energy source, hydrogen is almost supplied from fossil fuels. Consequently, considerable focus has been directed toward the efficient production of hydrogen from heavy and extra-heavy oils which constitute approximately 70% of the global oil reserves.[72]

6.1.1. In-Situ Combustion Gasification Process.

The in situ gasification (ISCG) technology applied for heavy oil involves a reaction of air and water at elevated temperatures in heavy oil reservoirs. ISG consists of various combinations of series and parallel reactions which is detailed in Section 5. ISCG aims to generate synthesis gas (H_2 and CO) from the heavy or immobile hydrocarbons and then deliver to the surface by production wells (Figure 2).

Gasification and carbonization are two processes that are involved in most of the in situ technologies.[73] ISCG relies on heat generation which can be achieved through combustion. ISC occurs in two distinct oxygen consumption, temperature, and ranges: (1) low-temperature oxidation (LTO) occurs in the range from 150 to 300 °C and it can be characterized by low oxygen consumption rates. (2) high-temperature oxidation (HTO) lies in the range from 380 to 800 °C and can be distinguished by high oxygen consumption rates. During combustion measurements and ahead of the combustion zone, the oil sand temperature increases through heat conduction. Thermal cracking takes place where no oxygen exists ahead of the combustion front whereas well a thin layer of coke will be generated. However, with the progression of the combustion front, any coke generated beyond the front in LTO-region ignites and fuels the front; this coke is mainly a product of resin and asphaltene components.[74] Additionally, the combustion process aids in diminishing the sulfur and heavy metals content which produces a lighter and superior-quality oil. Furthermore, maltenes converted to asphaltene while asphaltene converted to coke with the generation of hydrogen, methane, and carbon oxides by the influence of complex chemical reactions involved in the pyrolysis reactions.[75−79] In regions with low oxygen concentration, the process is dominated by LTO reactions, leading to the formation of oil compounds with high oxygen content and coke. Conversely, in areas with high oxygen concentration, high-temperature oxidation (HTO) reactions prevail, converting the coke that is produced from thermal cracking and LTO into carbon oxides.

Continuous research and development endeavors are focusing on the production of hydrogen from fossil fuels using CCUS technology. Compared to surface gasification methods, in situ combustion gasification has lower operational cost and the feedstock is well-distributed.[80]

6.1.2. In-Situ Combustion.

In-situ combustion (ISC) or fire flooding is a well-known method utilized for heavy oil upgrading and enhancement where the elevated viscosity presents difficulties in flowing and producing the oil using standard energy sources or alternative EOR methods. This process includes injecting air or oxygen to react with hydrocarbons. The reaction between the oil and the oxygen (exothermic reaction) generates a considerable amount of heat that facilitates the flow of the remaining unburned oil to the production wells by reducing the viscosity and enhancing the mobility.[81−83]

In contrast to steam injection methods, ISC employs compressed air, reducing the cost and the energy required to generate steam. Additionally, ISC does not require water recycling and results in significantly reduced greenhouse gas emissions. Spontaneous ignitions take place shortly after oxygen injection. Alternatively, manual heating may be required to initiate ignition if the combustion conditions are not satisfied. ISC (In-Situ Combustion) can be classified based on the ignition method into (1) traditional ISC and (2) high-

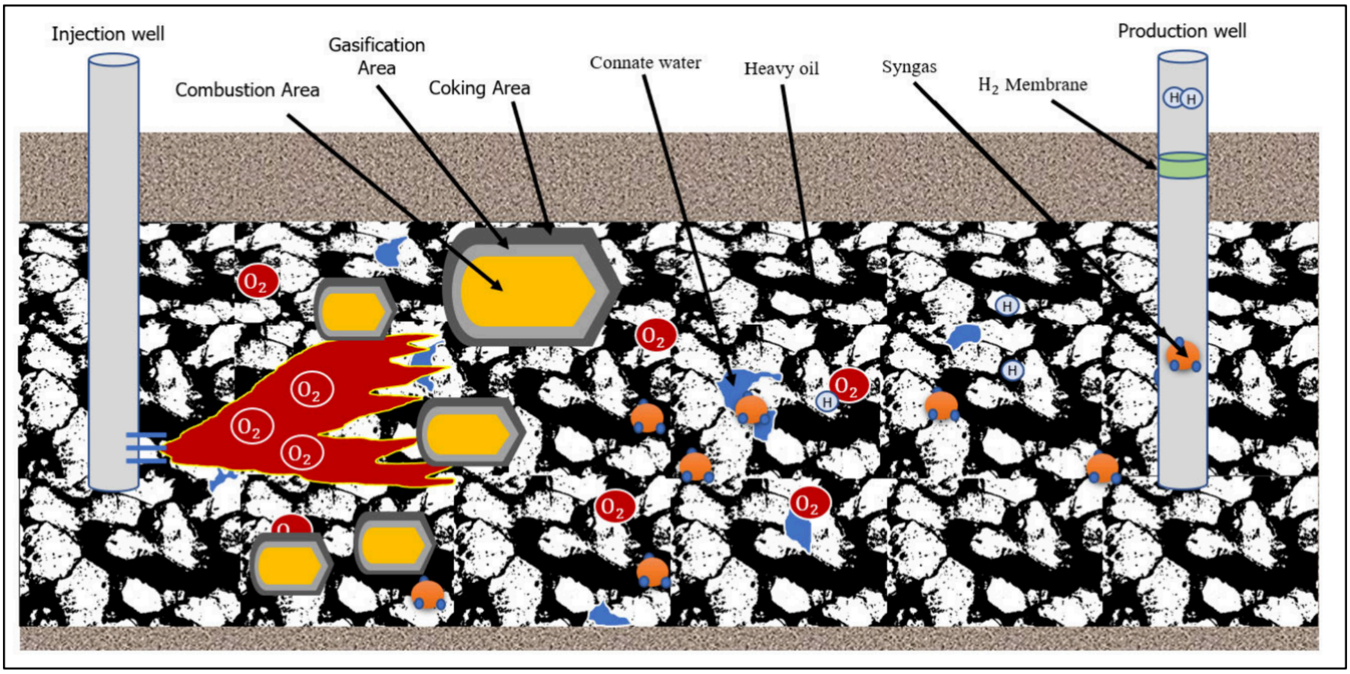

Figure 2. Hydrogen production through the ISCG process.

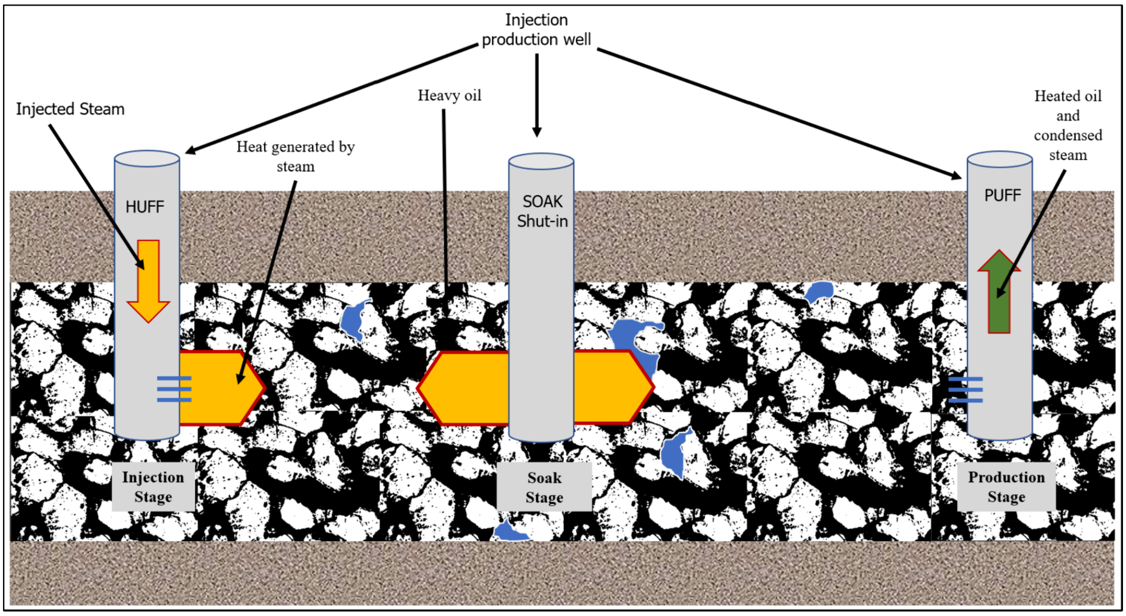

Figure 3. Process of cyclic steam injection.

pressure air injection (HPAI). Traditional ISC is a well-established method utilized since the 1940s.[84−89] In the traditional method, the crude oil is ignited either physically using an air burner, electric ignition, or chemically by chemical agent injection.[90−94] Reveres combustion refers to the ignition occurring at the production well, while in forward combustion the ignition is induced near the injection well.[95] When combustion temperatures exceed the autoignition temperature (AIT), the reactions involved become more intricate, including combustion and thermal cracking. Huang et al.[96] found that the autoignition temperature for ordinary oil is 243 °C at atmospheric pressure and can be reduced to 114.39 °C at 35 MPa. Changbin et al.[97] found that the ignition temperature of heavy oil falls in the range between 260 and 280 °C. The commonly used forward combustion process can be executed in either dry or wet forms. Steam and air are injected concurrently in the wet forward combustion process. This approach efficiently reduces fuel consumption and minimizes the amount of air needed for heating specific reservoir regions. On the other hand, the dry forward combustion process involves injecting only air to initiate the combustion of oil. Once ignited, a gas chamber comprising air and combustion gases forms, along with a combustion front. ISC involves the formation of distinct zones, each with varying temperatures and oil and water saturation, including the oil bank, water bank, steam zone, evaporation and visbreaking zone, cracking zone, combustion zone, and burned zone.[98,99] The burned zone is the part of oil that is consumed by combustion, filled

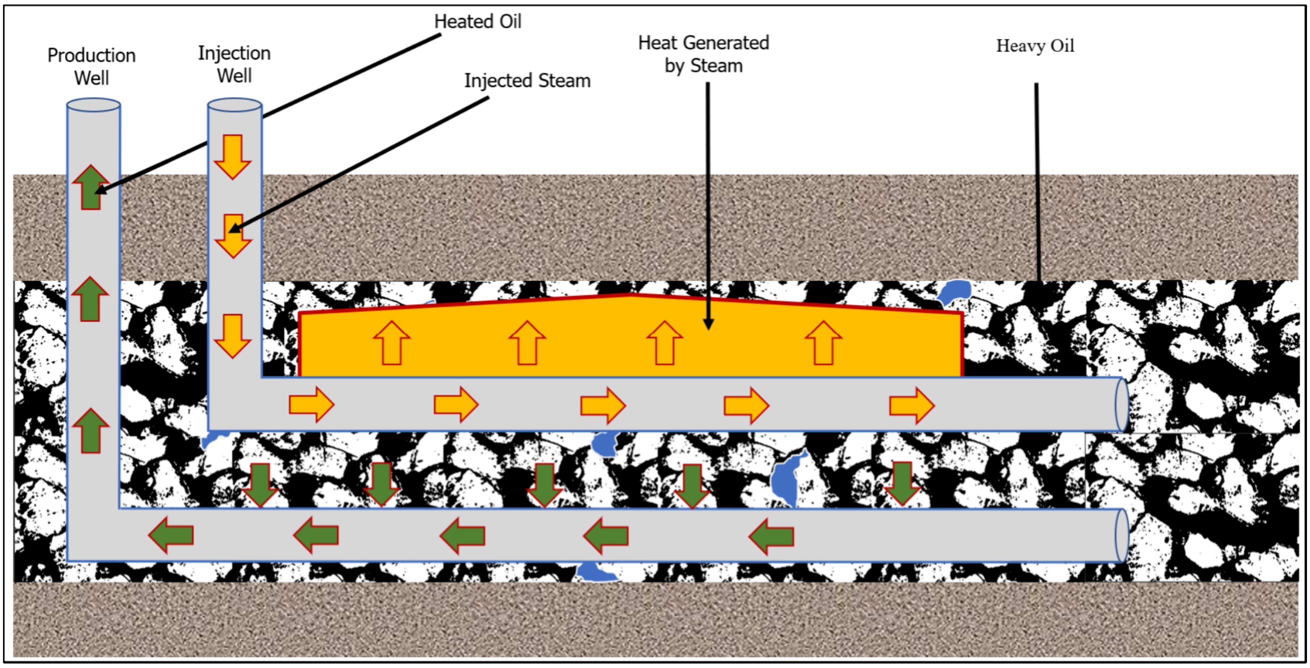

Figure 4. Schematic of steam-assisted gravity technique.

with air and some residual unburned organic solids. The elevated temperatures in this zone may lead to mineral alterations. Moving forward, the combustion front is the hottest region, at which oxygen and fuel react, resulting in high-temperature oxidation in addition to water and evolved carbon oxides. The fuel, often called "coke," is formed through cracking and pyrolysis in the zone just ahead of the combustion front. Downstream from the front, we have the cracking/vaporization zone where the residual oil is left behind the steam plateau. In this zone, the crude undergoes modification due to the high combustion process temperature. Light components vaporize and mix with the original crude downstream. Moving further, the steam plateau displaces most of the oil in front of it, and the immobile oil undergoes steam-distillation.

The temperature at which the steam reaches a plateau is contingent upon the partial pressure of water in the gas phase, potentially leading to mild thermal cracking of the initial oil, known as visbreaking, which reduces its viscosity. A water bank forms at the leading edge of the steam. The oil saturation increases with the decreasing temperature and saturation of the water bank gradually. In the oil bank region following the water bank, most of the oil displaced by heating from upstream, including light components resulting from thermal cracking exists in this region. Experimental research has confirmed that in situ combustion produces hydrogen as a byproduct in the gas products accompanied by other gases through chemical reactions,[100] the hydrogen and hydrocarbon gases did not exceed 2.7% of the product gases.[101] Field data supports this finding, showing that a significant amount of hydrogen, approximately 16% in syngas, is generated during the process.[102] Hence, the knowledge obtained from hydrogen generation techniques both at the surface and subsurface levels can hold significant value in progressing the study and practical implementation of hydrogen generation and production within in situ combustion methods.

6.1.3. Cyclic Steam Injection (CSI). Cyclic Steam Injection, also known as "Huff 'n Puff," is a thermal recovery technique that entails the intermittent injection of steam through the well to heat the reservoir near the wellbore area.

In this method, the injection and production are achieved through the same well. The process consists of three stages: injection, soaking, and production which aim to enhance the production rate as illustrated in (Figure 3).

Steam is injected at a pressure of 1 MPa and in the temperature range of 200−300 °C into the reservoir for a specific period to mobilize the reservoir oil by raising its temperature which results in viscosity reduction. Once enough steam has been introduced, the well is temporarily closed, allowing it to soak the reservoir for several days, a phase known as the soaking stage.

This soaking process increases the reservoir temperature due to steam injection and subsequently reduces the oil viscosity. Thereafter, the well is reopened, and the production stage commences initially through natural flow and later with artificial lift mechanisms. As the reservoir temperature gradually returns to a level causing a reduction in the oil flow rate, another cycle is initiated, and this repetition continues until the production reaches an economically viable level.

This technique is applied for hydrogen production in combination with other techniques to induce the set of reactions that contribute to the produced hydrogen as discussed in a study conducted by Hajdo.[103]

6.1.4. Steam Assisted Gravity (SAGD). This method was pioneered by Roger Butler in the 1970s as a method for recovering Alberta bitumen.[104,105] In this technique, the pay zone is accessed through a pair of horizontal wells with one well positioned 4−6 m higher than the other. Usually, the upper well serves as an injector where the oil around is heated and mobilizes toward the production well, as depicted in (Figure 4).

At the steam-oil interface, a steam chamber is created by the injected steam and gradually expands to displace heated oils with the condensed water into the production well. This process minimizes the tendency for steam to flow directly to the production well, thereby reducing or even eliminating the bypassing of the reservoir, resulting in significantly improved sweep efficiency.

6.2. Reaction Mechanisms for In-Situ Hydrogen Production.

6.2.1. Pyrolysis. Pyrolysis (also known as thermal cracking or thermolysis) is a conventional method for generating hydrogen in situ. This process entails thermally breaking down hydrocarbons in a free-oxygen environment, yielding hydrogen and solid carbon as a reaction product. It is important to mention that the carbon generated during the pyrolysis of oil/gas can engage in a carbon gasification reaction, resulting in extra hydrogen production. Unlike other processes, pyrolysis does not involve water or air, so it does not lead to the formation of CO or CO_2. Given the endothermic characteristics of reactions based on pyrolysis, this process is more practical in in situ conditions compared to surface operations. As a result, the overall emission of CO_2 to the surface is minimized and trapped within the reservoir. The pyrolysis reaction is represented by reaction 2.

$$C_nH_m \xrightarrow{\text{heat}} nC + \frac{m}{2}H_2 \tag{2}$$

During the 1970s and 1980s, geochemists had the belief that liquid hydrocarbons would entirely turn into gas when exposed to a temperature of 149 °C.[106,107] However, subsequent researchers argued that crude oil remains stable and will not be cracked and transformed into natural gas unless subjected to higher temperature conditions, ranging from 160 to 200 °C, whereas Hyne et al.[108] stated that the dominance of thermal cracking reactions becomes apparent at temperatures above 320 °C when it comes to breaking down heavier molecules, resulting in the creation of lighter molecular fractions in the form of gas and liquid components, alongside the deposition of condensed material known as coke. Several simulation experiments were conducted to investigate the factors that could potentially influence the transformation of crude oil into gas, including mineral catalysis, Thermal Sulfate Reduction (TSR), pressure, and geological background (heating history).[109−113] Among these factors, mineral catalysis within the reservoir has garnered significant attention.

Shuai et al.[114] investigate the role of the formation water (brine) to enhance the crude oil cracking to gas. They found that the gas yields increased significantly as well as the yield of the produced hydrogen gas.

6.2.2. Aquathermolysis. Aquathermolysis is also known as hydrous pyrolysis, the term "aquathermolysis" was proposed by Hyne et al.[115] Heavy oil reacts with water in a free-oxygen environment. Hyne depicted the generated lighter hydrocarbons, CO_2, H_2, CH_4, and H_2S from the reaction of heavy oil and steam (reaction 3).[116−118] Compared to high-temperature thermal cracking, aquathermolysis reactions are nondestructive. This process plays a significant role in upgrading crude oil through desulfurization, viscosity reduction, and hydrocracking.

$$\begin{aligned}&RCH_2CH_2SHCH_3 + H_2O\\&\quad \rightarrow RCH_2 + CO_2 + H_2 + H_2S + CH_4\end{aligned} \tag{3}$$

During this process, heavy oil reacts with steam under a temperature range of (473−573) °K, which breaks the weak C-S single bond, reducing the sulfur content and enhancing the quality of the crude oil leading to the formation of light aromatics and saturated hydrocarbons. In hydrocracking, heavy crude oil undergoes several reactions involving cracking, hydrogenation, and isomerization at elevated temperatures.[119] After the initial upgrading via aquathermolysis, further refining occurs through distillation and extraction, utilizing the elevated temperatures and phase differences. Steam removes the light components in the gas phase by distillation when the mixture's boiling point is lower than that of the heavy oil.[120−122] Consequently, the separated components (light and medium components) displaced the production well. In general, aquathermolysis reactions are typically slow due to heat loss and steam sweep efficiency. Thus, catalysis was introduced to promote the breakdown of single and double bonds of the carbon with heteroatoms (C−S, C−N, C−O, C−C, C═S, C═N, C═O, and C═C).[116,123] After the sulfur is eliminated, the heavy oil molecule becomes susceptible to cracking. As a result, the total volume of gas produced through aquathermolysis on a laboratory scale is quite insignificant compared to the stimulated bitumen by steam.

6.2.3. Steam Methane Reformation. Steam methane reforming (SMR) is a chemical process in which natural gas (methane) reacts with steam.[124] The SMR process has three primary stages: syngas generation (reaction 4), water-gas shift (WGS) reaction (reaction 5), and gas purification or methanation (reaction 6). Syngas is generated by the catalytic reaction of hydrocarbons with steam at moderate temperatures.[125,126] The syngas is then sent via a heat recovery system and into a WGS reactor, where the reaction between carbon monoxide and steam produces more hydrogen and carbon dioxide as a secondary product. Subsequently, the gas mixture obtained is subjected to either a CO_2 removal or pressure swing adsorption procedure to acquire H_2 gas of exceptional purity. To avoid deactivation of the nickel-based reforming catalyst caused by coke formation on its surface, a desulfurization step may be carried out before the reforming process, depending on the sulfur concentration of the feedstock.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{6}$$

6.2.4. Coke Gasification. Coke gasification refers to the process in which coke, the residual product generated after pyrolysis, reacts with steam or carbon dioxide to produce hydrogen (H_2) and carbon monoxide (CO) as defined by reactions 7 and 8.

$$C + H_2O \rightarrow CO + H_2 - 31.4\ \text{kcal/mole} \tag{7}$$

$$C + CO_2 \rightarrow 2CO - 41.2\ \text{kcal/mole} \tag{8}$$

The in situ combustion (ISC) process includes the release of thermal energy, which improves the flow of the unburned part of crude oil and helps it to drain toward the production well.[127,128] The coke (defined as toluene insoluble residue) is regarded as the main fuel at the burning front in the in situ combustion (ISC) process,[129] which is formed because of the cracked heavy oil within the reservoir. Formed coke may undergo either oxidation or pyrolysis. Multiple studies have

Table 4. Summary of Hydrogen Production Reaction Mechanism

Reaction Mechanism	Hydrogen Production Temperature	Reaction
Thermal cracking (Pyrolysis, Thermolysis)	>320 °C	$C_nH_m \xrightarrow{\text{heat}} nC + \frac{m}{2}H_2$
Aquathermolysis	200−320 °C	$RCH_2CH_2SHCH_3 + H_2O \rightarrow RCH_2 + CO_2 + H_2 + H_2S + CH_4$
Steam Methane Reforming	800−900 °C	$CH_4 + H_2O \rightarrow CO + 3H_2$ $CO + H_2 \rightarrow CO_2 + H_2$
Coke Gasification	528−900 °C	$C + H_2O(\text{steam}) \rightarrow RCH_2 + CO + H_2 - 31.4\ \text{kcal/mole}$ $C + CO_2 \rightarrow 2CO - 41.2\ \text{kcal/mole}$
Water Gas-Shift Reaction	379−439 °C	$CO + H_2O \rightarrow CO_2 + H_2 + 9.8\ \text{kcal/mole}$

examined the characteristics of different forms of coke and have determined that the coke yield from oxidation is higher than that obtained from pyrolysis. Liu et al.[130] revealed that the coke formed by oxidation is five times that formed by pyrolysis. Additionally, it was discovered that the oxidized coke was produced at a lower temperature compared to the temperature needed for the formation of pyrolyzed coke.[131−133]

Researchers have determined that the amount of coke produced during a pyrolysis reaction is influenced by the content of resins and asphaltene in the crude oil since these are the primary factors contributing to coke production. Furthermore, they inferred that under circumstances of increased temperature and pressure, the greater the concentration of aromatics and CCR (carbon residue) value, the greater the quantity of coke produced.[134]

6.2.5. Water Gas Shift Reaction (WGS). The water gas shift reaction (WGSR) has been used for hydrogen synthesis since 1780, however, its practical implementation was not explored until the early 20th century. The composition of water gas (synthesis) mostly comprises hydrogen (H_2) and carbon monoxide (CO). The water gas shift reaction involves the interaction of carbon monoxide with steam to produce hydrogen and carbon dioxide. (reaction 9).

$$CO + H_2O \rightarrow CO_2 + H_2 + 9.8\ \text{kcal/mole} \tag{9}$$

Reaction 9 has a mild exothermic character, and its equilibrium constantly diminishes with increasing temperature. From a thermodynamic perspective, the reaction is more favorable at lower temperatures. However, at higher temperatures, the reaction rate becomes more significant due to kinetic factors, and any changes in pressure do not affect the reaction. The water gas synthesis (WGS) process is important for producing hydrogen without carbon monoxide and for controlling the ratio of H_2/CO.[135] Hydrogen generation techniques may be categorized into two groups: those that use catalysts and those that do not. Within the realm of catalytic techniques, additional classification may be made based on either the temperature at which the reaction occurs or the type of catalyst used. High-temperature shift (HTS) reactions often take place within the temperature range of 320 to 450 °C, while low-temperature shift (LTS) reactions are carried out at temperatures ranging from 200 to 250 °C. The water-gas shift reaction (WGSR) may occur without the need for catalysts when carbon monoxide (CO) is exposed to a supercritical water environment.[136−138] In an experimental investigation conducted by the researcher group,[136] they examined the noncatalytic water-gas shift reaction (WGSR). They evaluated this reaction under certain circumstances, including a CO/H_2O ratio of 0.03 and temperatures ranging from 653 to 713 K. In this work, the researchers calculated the rate constant for the first-order reaction of the water-gas shift reaction (WGSR). Table 4 presents a summary of reaction mechanisms related to the generation of hydrogen in its original location.

7. FIELD PILOT TEST

Most of the previous research that documented the quantity of generated hydrogen was specifically intended for enhanced oil recovery (EOR) purposes. Researchers have lately focused on the production, extraction, and transportation of hydrogen from underground formations to surface facilities. The ability to produce hydrogen directly from underground hydrocarbons in their original site can provide a substantial and plentiful new source of hydrogen to fulfill future needs. By enhancing hydrogen generation within economically depleted reservoirs, these reservoirs may be converted into easily accessible high-pressure chambers for hydrogen production and storage. Various reaction mechanisms have been tested for producing hydrogen from natural gas such as methane cracking, catalytic steam methane reforming (SMR), autothermal reforming, and partial oxidation. Throughout the SMR process, the production of each kilogram of hydrogen results in the emission of around 10 kg of CO_2. The primary chemicals that take place within the gas reservoir are methane cracking, water-gas shift reaction, and steam methane reforming. These reactions occur at temperatures over 500 °C and are aided by a catalyst composed of metallic elements.[139,140] This is following the forward reactions (10, 11, and 12) described below:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 - 206\ \text{kJ/mol} \tag{10}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 + 41\ \text{kJ/mol} \tag{11}$$

$$CH_4 \leftrightarrow C + 2H_2 - 75\ \text{kJ/mol} \tag{12}$$

Hajdo et al.[103] examined the process of producing hydrogen on-site from heavy oil reserves located in eastern Alberta. The research investigated the reaction mechanisms responsible for producing hydrogen, specifically focusing on five processes: (1) thermolysis, (2) aquathermolysis, (3) coke gasification, (4) water-gas shift reaction, and (5) methanation. Eight combustion tube experiments were performed on homogenized and unhomogenized repacked core materials, following the experimental protocols outlined by.[141] The experimental findings revealed that the primary processes responsible for hydrogen generation are coke gasification and water-gas shift reactions.

$$C + H_2O = CO + H_2\ (\text{coke gasification}) \tag{13}$$

$$CO + H_2O = CO_2 + H_2 \text{ (water − gas shift reaction)} \quad (14)$$

The field data shows that hydrogen production ranged from 10 to 20 mol% in most of the wells. Most hydrogen was created by the coke gasification process, while no contribution was recorded from the aquathermolysis process.

Hallam et al.[142] reported BP Canada's Wolf Lake started the commercial extraction of bitumen by cyclic steam stimulation. For more than twenty years, this technique has been used to extract bitumen from the Wolf Lake region. Cyclic steaming was used as a preliminary measure to raise the temperature of the reservoir, facilitating a smooth transition to high-temperature combustion using oxidative techniques. The proportion of H_2 in the gases generated is as high as 25%.

Turta et al.[143] described the first field implementation of the Toe-To-Heel Air Injection (THAI) technique. This novel in situ combustion approach uses vertical air injection wells in combination with horizontal production wells. The in situ combustion (ISC) technique was started by preheating the injection wells using steam during an early phase. Immediately after, the injection of air followed. The elevated temperatures in the formation near the injection locations caused spontaneous combustion, leading to the formation of ISC fronts.

The gas composition recovered from the producer well revealed that hydrogen accounted for around 2−5% of the overall mixture. At times, this proportion increased to a maximum of 15%.

Ifticene et al.[144] reported that ISC THAI was implemented in two field projects for bitumen recovery and produced hydrogen with the produced gases. The first field project was conducted by Petrobank Energy and Resources in 2006. The concentration of the hydrogen in the produced gas reached 10 mol.%. In the second project, the hydrogen concentration produced was 7 mol.%.

8. CURRENT RESEARCH CHALLENGES AND FUTURE PERSPECTIVE

Various laboratory-based studies and field pilots have shown the possibility of using in situ upgrading technology to produce hydrogen gas from heavy oil reservoirs. However, there is still a significant gap that must be bridged before this technology can be economically implemented on a large scale in the industry. Currently, there are several obstacles confronting the practical implementation of in situ hydrogen production technology, which directly affect its economic feasibility.

8.1. Membranes. Separation and purification are crucial steps for hydrogen to be utilized as an energy carrier in most cases. In-situ hydrogen separation from associated gases evolved during the in situ gasification process is a vital objective. Presently, hydrogen purification techniques encompass three approaches: pressure swing adsorption,[145,146] cryogenic distillation,[147,148] and membrane separation.[149] In the hydrogen separation process, significant attention is directed toward advancing supported Pd composite membranes. Dense metal membranes based on Pd provide an effective means of purifying hydrogen from a high-temperature gas mixture, achieving purities exceeding 99.9999%. For in situ catalytic production of heavy oil, Hydrodesulfurisation (HDS) catalysts prepared from Ni, Co, and Ni-Co alloys supported by aluminum oxide show superior performance when utilized in thermal methods. Catalysts are prepared ex-situ then introduced into the reservoir by mixing them with steam or superheated water as a suspension. Similarly, unsupported nickel-based catalysts can be delivered into the reservoir in the form of a water solution containing precursor materials like nickel nitrate, oxalate, acetate, oleate, ammonium salts, and metal-containing acids. These precursors are easily decomposable at temperatures attainable in the reservoir due to thermal stimulation, leading to the formation of nickel (Ni) or nickel oxide (NiO) particles.

These membranes are typically created by applying a thin Pd membrane layer onto a porous substrate. The presence of this porous substrate serves to enhance the membrane's mechanical durability. Moreover, the composite Pd membrane allows for a reduction in the thickness of the dense Pd metal layer, resulting in enhanced permeability while conserving precious Pd metal resources. However, there are limitations associated with such membranes can be summarized as follows:

- Dense metals have a propensity to develop a stable oxide layer under normal environmental conditions.
- At higher temperatures, metallic membranes like titanium and vanadium exhibit reduced hydrogen permeability and tend to form layers of metal oxides that hinder their H_2 separation efficiency.
- The elevated CO level evolved from the water gas shift reaction affects the pd-based membrane performance.
- No-selective intercrystalline pores of some membranes such as zeolite and the thermal stability of the inner deposits limits their application for the in situ separation process.
- Inflated cost of membranes is one of the crucial issues that needs to be accounted for and reduced which affects the capital cost of the production process.
- HDS catalysts needed a high and maintainable temperature of around 425 °C.

8.2. Reservoir-Related Challenges. The primary methods employed for in situ hydrogen production in heavy oil reservoirs are typically thermal methods for EOR application. These methods include ISC as a primary process to generate heat that triggers gasification reactions. For instance, serious in situ challenges should be considered. The implementation of thermal methods for in situ hydrogen production can cause various types of formation damage due to the interaction between the injected fluids and the reservoir's rock and formation water. Clay minerals expansion, fine migration, and asphaltene deposition are probable types of formation damage that can be caused by the injection of steam and hot water into the reservoir. These different types of formation damage reduce the reservoir permeability and porosity.[150]

Zhang et al.[151] reported formation damage associated with the thermal method applied for heavy oil recovery. They categorized the formation damage based on the formation damage mechanisms into chemical mechanism, mechanical mechanism, and thermal mechanism. The formation damage caused by thermal methods impedes the migration of the produced hydrogen gas to the production well.

Coke deposition during in situ combustion is considered one of the formation damage mechanisms that block the pore throat and obstruct the flow of the injected oxidant or even the produced hydrogen gas.[152]

8.3. Perspectives. To advance clean hydrogen generation, several key strategies can be implemented. First, supportive policies, incentives, and regulations are crucial to facilitate the deployment and commercialization of clean hydrogen generation. Second, funding collaborated research can accelerate the development and enhancement of hydrogen generation from in situ reservoirs. Third, the development of advanced monitoring and modeling techniques can provide real-time insights into hydrogen generation processes. Lastly, incorporating high resolution imaging and real-time sensors within laboratory experiments can provide more precise and informative results.

9. CONCLUSION

This comprehensive review explores the production of environmentally friendly hydrogen from heavy oil and bitumen reservoirs. It delves into the intricate processes and mechanisms involved, encompassing both catalytic and noncatalytic methods. Key chemical reactions identified in most research include coke gasification, water-gas shift reaction, cracking, and aquathermolysis. These processes play a pivotal role in transforming heavy hydrocarbons into hydrogen.

The article provides a detailed analysis of in situ hydrogen production techniques, covering laboratory and field-scale pilots. It examines the challenges and potential solutions associated with these methods, such as temperature optimization, catalyst selection, and process efficiency.

Furthermore, the review highlights the potential environmental benefits of hydrogen production from heavy oil and bitumen. Hydrogen can serve as a cleaner alternative to fossil fuels, reducing greenhouse gas emissions and contributing to a more sustainable energy future.

Despite the promising potential, several challenges remain to be addressed. These include the development of cost-effective technologies, the efficient separation of hydrogen from other gases, and the long-term sustainability of the resource base.

■ AUTHOR INFORMATION

Corresponding Author

Sulaiman A. Alarifi − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia;* orcid.org/0000-0003-3643-4014; Email: salarifi@kfupm.edu.sa

Authors

Mohamed Abdalsalam Hanfi − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia*

Olalekan Saheed Alade − *Center for Integrative Petroleum Research (CIPR), King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-1657-9737

Abdulkadir Tanimu − *Interdisciplinary Research Center for Refining and Advanced Chemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-7541-0042

Mohamed Mahmoud − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-4395-9567

Complete contact information is available at:
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