



Thermal Hydrogen Production from Petroleum Reservoirs Using Steam Reforming and In-Situ Catalyst Application: A Technical and Economic Analysis

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Abstract. Fluid and solid hydrocarbon reservoirs are one of the most important fossil energy sources in the world. However, due to the high emission of CO₂ and other greenhouse gases, the application of fossil energy is not sustainable. Nevertheless, the infrastructure of the existing oil reservoirs should also be part of the ongoing utilization of the resources; petroleum reservoirs can be used to produce green hydrogen through wet combustion. This technique enables the production of hydrogen or hydrogen-containing synthesis gas from depleted petroleum reservoirs. This paper gives a brief review of the existing literature, relevant patents, and experiments on the topic. A new type of catalytic hydrogen production from depleting oil reservoir is introduced. Hydrogen production capability and the economic feasibility are evaluated using data from the literature and the relevant process parameters. Finally, the application limitations of the new process in oil reservoirs are introduced and explained; the physical and chemical parameters which affect the applicability are discussed.

Keywords: Hydrogen generation · Depleted oil reservoirs · Enhanced oil recovery · In-situ combustion · Wet combustion · Air injection · Fossil energy

1 Introduction

In situ combustion is one of the thermo-chemical enhanced oil recovery methods, which are particularly suitable for heavy oils and oil sands. The method is based on the injection of air or other oxidant, which then leads to heat of reaction in the reservoir through combustion thus enhancing the oil recovery by improving the flow properties [1].

Hydrogen production measurements gave promising results in in-situ combustion tests both at core [2, 3] and field scales [4]. These results prove that hydrogen is produced in thermal processes in principle [5], and in particular in the in-situ combustion [4]. The effect is technically quantified at reservoir scale with a significant extent of up to 30% hydrogen in the gas phase [4]. The numerical evidence of these effects can be found in

this simulation study [6]. However, it should be admitted that to date, hydrogen formation has only been demonstrated in some cases rather as a byproduct of combustion, which was only measured for safety and tracer reasons.

Thermal hydrogen production is based on the principle of thermally induced reactions of hydrocarbons present in the reservoir. The thermal energy can be generated both as a side effect of steam flooding or in-situ combustion with high-pressure air injection. The methods for the recovery of hydrogen or synthesis gas from petroleum reservoirs are legally protected in the patents [7–10].

In principle, in chemical processes, the equilibrium reaction can be blocked by kinetic inhibition in certain temperature ranges. To eliminate this kinetic inhibition, catalysts can be used. In the case of in-situ combustion, the effectiveness of catalysts has already been proven [11]. The technology presented in this study differs from other methods in that the catalysts are to be introduced into the reservoir not for the combustion process, but for the formation of hydrogen from the decomposition reactions of the coke.

The technology in this paper formally represents a production variant of blue hydrogen. The climate impacts and the relevant emissions from the production of blue hydrogen and the resulting assessment with regard to the similarity with green hydrogen are dealt with in [12–15], among others. The topic is currently being intensively investigated but will not be elaborated further in this paper.

2 Investigation Methods

For the thermal process of hydrogen production, several potential well designs are possible. Important is to inject the air or the oxidizing agent from the deepest point and to allow the highest possible absorption of the resulting synthesis gases close to the sealing rock. Decisive factors include the highest possible permeability as well as formations free of faults and fractures. A heterogeneous permeability distribution would lead to unfavorable, uncontrolled fire courses, therefore homogeneous formations are advantageous. To enable the injection of a catalyst, an alternating injection of water and gas (i.e., air) must be carried out. The water is the carrier of the catalyst, which is mixed into the injected water in powdered form. The process thus resembles “wet combustion” due to the co-injection of water and gas.

The main reactions were defined by Murthy et al. for laboratory conditions [16] and by Hajdo et al. for the test field combustion [4]. The most important reaction with an impact on the hydrogen production is the coke gasification under steam conditions above 250 °C [4, 16]:



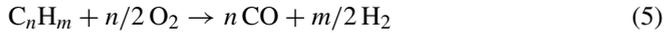
Murthy et al. estimated, that the following reaction leads to a water gas shift reaction inside of the coke zone, this could be observed in the really low amounts of CO produced in in-situ combustion field test [4]:



The methanation processes result in methane (CH₄) rather than H₂, methane is produced in field trials in similar quantities to hydrogen [4]. It is found that in core flooding experiments the methane production is more likely than the hydrogen production [2]:



The thermolysis or thermal cracking is the process, in which hydrogen is produced by thermal effects as discussed in Butron et al. [5]. However it should be mentioned that this accounts for maximum 10% of the produced hydrogen in total [4]:



Based on the above discussion and data presented, the requirements for a hydrogen-forming process in oil reservoirs can be formulated as follows:

- First, coke formation from crude oils must take place.
- The coke must react with water vapor without the influence of oxygen at a high-temperature range. This is to be justified by the fact that otherwise a combustion reaction of the coke or the formed hydrogen with the oxygen takes place.
- After the reaction, there must still be enough water vapor to produce a water gas shift reaction.
- The resulting hydrogen should migrate as quickly as possible to the production well(s) of the reservoir and be extracted there.

Figure 1 shows the process in seven steps, how hydrogen could be produced by combustion in petroleum reservoirs. Following steps can be helpful for the design of the process:

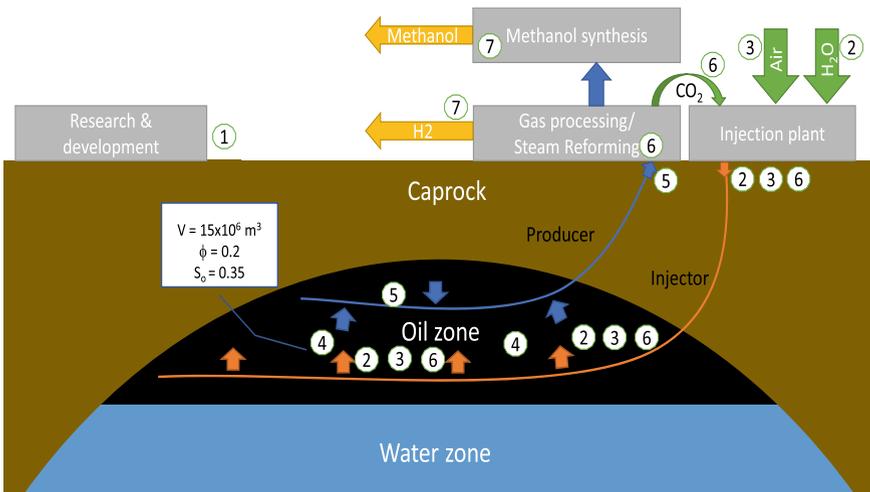


Fig. 1 Wet combustion illustration process

1. Numerical simulation

In this step, a model of the reservoir can be built based on history matches and existing production data. To calculate an in-situ combustion process, drill core tests as well as fluid sampling are necessary. These samples are aimed at the combustion properties and the lumping of the petroleum compounds to evaluate in-situ combustion reaction schemes using pseudo components. Based on this data, the process of in-situ combustion can be simulated in various thermal simulators such as CMG (Computer Modeling Group) Stars, Eclipse 300 and so on. The simulation is challenging, since in addition to the representative simulation of the four phases (water, oil, gas, and coke), each individual (pseudo) component must be considered in the context of its migration, convection, and an individual consideration of the respective component phase, especially for various gases and lighter oils must be made. Furthermore, the PVT (Pressure-Volume-Temperature) characterization of the frequently occurring mixtures represents a particular challenge.

2. Injection of water with catalyst

Ideally, the injection of hot water or steam is already conducted before the hydrogen production measurements. In this case, the reservoir can be taken over directly preheated. This method would have the advantage that, the injection of a powdered catalyst for the subsequent provision of hydrogen can already be started and mixed with the hot water. This is therefore meaningful because the method can be used in several cycles and the catalyst can reduce the activation energy towards the chemical equilibrium and thereby specifically reducing the kinetic inhibition of several gas phase reactions.

3. Injection of the oxidation agent (normally air)

This is followed by the injection of air or the treated air (this is characterized by a higher oxygen content, but this is also more energy-intensive to generate) or another agent of oxidation. Other oxidizing agents or strong heating agents are only suitable in the case of industrial waste or material and or energy flows that can no longer be used economically. This oxidizing agent is then injected into the reservoir and leads to oxidation of the crude oil and the associated developments of coke, thermal energy, water vapor and other combustion products. The key point here is that air injection itself is **not** the hydrogen-forming process. Rather, the contact with the oxidation component is very unfavorable for the hydrogen since hydrogen will react with the oxidation agent and thus release the desired chemical energy as heat of the combustion reaction.

4. Shut-in time

As part of the next step, hydrogen formation is to be improved by shut-in-time. This is advantageous if the resulting thermal energy as well as the existing components are sufficient for further hydrogen formation in-situ. However, the shut-in time should not last so long that other components such as methane increase, or the water phase condenses out again. This is particularly relevant because a condensed water phase leads

to a significantly lower relative permeability and a pressure loss in the transport of the remaining gas phase. Furthermore, the colder water phase is no longer suitable for the surface steam reforming operations.

5. Production phase

In the next step, the gas phase is to be produced. The production of the gas phase can be started after the shut-in time either with only a slight pressure reduction, to avoid too much liquid production or too high-pressure gradients. Furthermore, various publications and patents propose to selectively control hydrogen production through membranes in situ [10], but this is not a sound approach in the context of the high thermal loads of up to 800 °C in the reservoirs and the current costs of membrane technology.

6. Gas operation plant

In the gas operation plant the normal gas treatment is done isothermally. Normally, the gas is dried, but this would be disadvantageous here due to the need for water vapor. This is because of the steam reforming reactor, where the steam can be used for the reactions.

7. Hydrogen generation

After the production of the gas phase, hydrogen can be generated with the scheme shown in Fig. 2. For this purpose, it is also possible to operate steam reforming with conveyed carbon monoxide and other components. This would make it possible to use the extracted methane, which is in about the same desired deficiency as hydrogen, without causing CO₂ emissions. The CO₂ is then reinjected into the reservoir via a compression station. Obviously for CO₂ injection another well in already depleted areas of the field can be used. Also, the CO₂ can be reused in the context of a methanol-synthesis.

3 Technical Evaluation

The following approximations are based on the data from [3, 4, 6, 9, 10] and simulations and calculations in numerical and general models. Assuming a reservoir, as in Fig. 1, with a porosity of 20% and a residual oil saturation of 0.35, a formation of approx. 500 Nm³ hydrogen from 1 m³ crude oil can be assumed for the most optimistic case based on the discussion above. For a reservoir with a total volume of approx. 15 × 10⁶ m³, a crude oil quantity of approx. 1.05 × 10⁶ m³ can thus be assumed; the quantity of hydrogen formed can reach up to 525 × 10⁶ Nm³. In the case of the application of in-situ combustion, the extraction efficiency is correspondingly high, since in most cases a pure gas phase with high temperature can be extracted. A hydrogen feed efficiency of approx. 50% should therefore be assumed here, i.e., a feed of approx. 262 × 10⁶ Nm³ hydrogen would be optimally achievable. For other processes, in particular non-gasifying processes, the transport efficiency is correspondingly lower because of critical gas saturation as well as relative permeability.

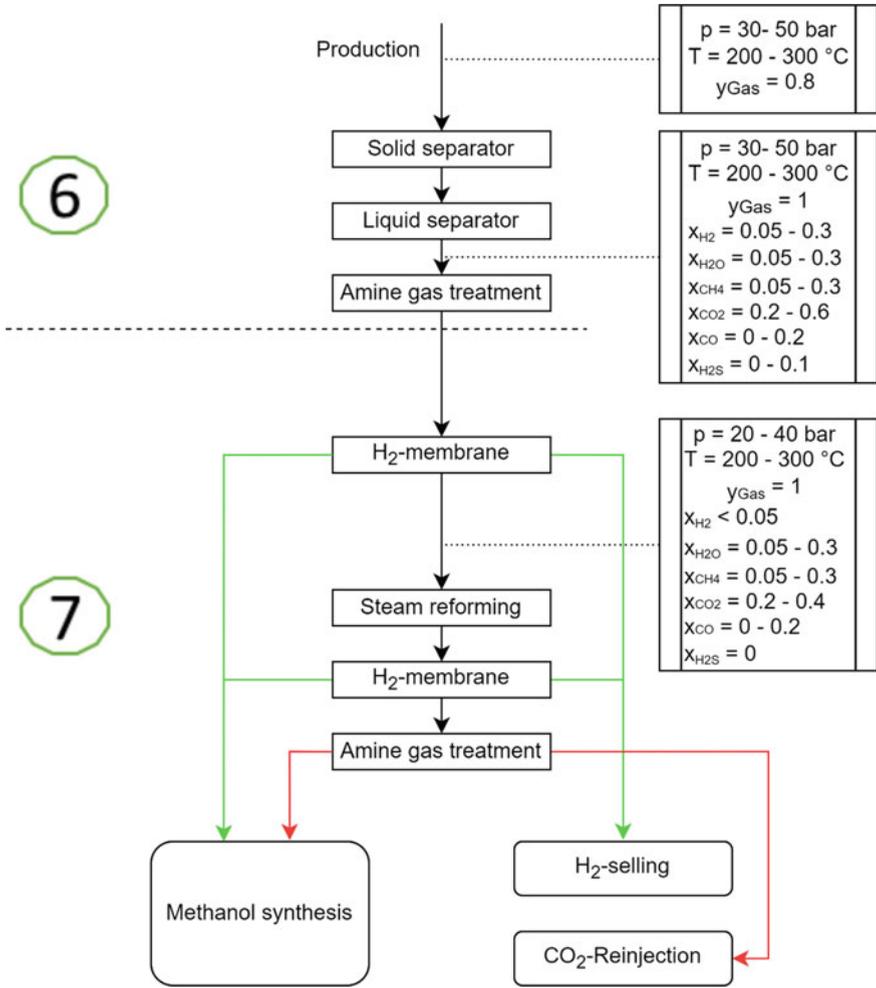


Fig. 2 Gas operation plant (6) and hydrogen generation (7) processes

Assuming a molar weight of the oil ($m_{m,oil}$) of 200 g/mol and a stock tank density (ρ_{oil}) (at norm pressure and norm temperature) of 700 kg/m³ (derived from [17–19]) the molar quantity of the oil stored in the reservoir (n_{oil}), can be calculated. This molar quantity of residual oil represents the potentially utilizable chemical energy inside the reservoir.

$$n_{oil} = V_{oil} * \rho_{oil} * 1000 / m_{m,oil} \tag{6}$$

$$n_{oil} = 3.68 \times 10^9 \text{ mol} \tag{7}$$

Based on this calculation, the upper and lower necessary amount of oxygen can be determined using reference values such as 30–50 mol oxygen per mol of oil and thus the

lower and upper amount of air to be injected. In this way, the total volume of air injection can be calculated as V_1 , this volume being calculated always at the surface pressure $p_1 = 1$ bar and has the isentropic coefficient $\kappa = 1.4$. The compression necessarily needs to exceed the reservoir pressure, which is the parameter the injection pressure p_2 is derived from. Using this, the necessary work for air compression $W_{V, Iso}$ can be determined on the basis of the necessary compression pressure via isentropic compression [20]:

$$W_{V, Iso} = \frac{p_1 V_1}{\kappa - 1} \left[\left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} - 1 \right] \quad (8)$$

The temperature reached by the compression $T_2(p_2)$ plays a significant role for the cooling capacity or further use of the energy. The temperature of the compressed medium is estimated by the inlet temperature of the compression T_1 and the pressure change in the compressor p_2 [20]:

$$T_2(p_2) = T_1 \cdot \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \quad (9)$$

For corrosion protection reasons, cooling must be conducted during compaction depending on the maximum injection temperature. However, this is not significant compared to the required compaction power. Assuming an overall electrical efficiency of 50%, this results in the electrical work per standard cubic meter of hydrogen, the compaction energy is the biggest variable cost factor.

Furthermore, the pumping and treatment of the gases must be conducted as part of the process, but this can be done with an addition of 100% on the expected energy quantity. In principle, gas compression is the most energy-intensive process; this is why the energy analysis is conducted on this basis.

4 Economic Evaluation

For the economic evaluation of the process, estimated values of the respective investment costs (CAPEX) and operating costs (OPEX) are listed in Table 1. The economic data are derived from existing studies [21–26] and adapted to the current situation. Unfortunately, there are not sufficient scientific publications on the economic parameters. Therefore, many values had to be adjusted to the necessary levels based on the intended project size.

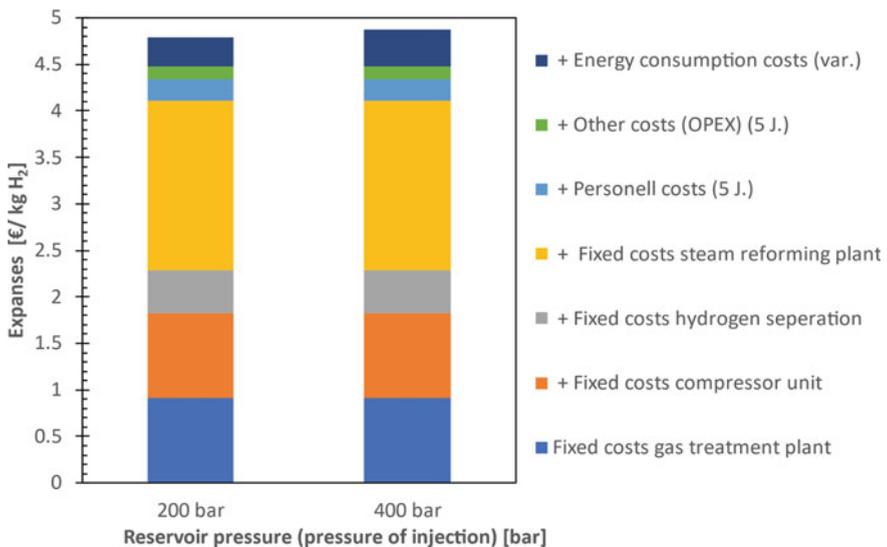
It is assumed that the wells as well as the pipeline infrastructure are existing, so there are no more costs for these initially. The steam reforming reactor for the improvement of the hydrogen yield with extraction of steam, CO and CH₄ is not considered necessary for the process. The steam reforming reactor is considered here in the context of economic efficiency, since it is used for hydrogen production; the methanol synthesis is given for information only.

If the costs for the process are given cumulatively over the respective reservoir pressure or two possible injection pressures per maximum recoverable hydrogen (see Fig. 3) it becomes clear that the process is economically feasible only if gas treatment plants

Table 1 Investment and operation cost

CAPEX		OPEX	
Compressors for air and CO ₂	10 Mill. €	Electrical energy (compaction, surface facilities)	0.1 €/kWh
Gas conditioning unit	10 Mill. €	Personnel costs	500 Tsd. €/J
Hydrogen separators	5 Mill. €	Others (Maintenance, etc.)	300 Tsd. €/J
Steam reforming reactor	20 Mill. €		
Methanol synthesis unit	20 Mill. €		

already exist at the surface. The energy costs as well as ongoing costs (maintenance, etc.) are of little importance with the assumed useful life of 5 years, the fixed costs for further process engineering plants represent the “game changer” aspect. The assumed utilization range is based on the capacity of the reservoir; after 5 years, it is presumed to be no longer energy-rich enough even for this process.

**Fig. 3** Investment, operation, and energy costs depending on reservoir pressure

5 Results

The results of the study are summarized in Table 2. Although the process itself has already been technically assessed at reservoir format, it still needs further research on sound (industrially meaningful) amounts of hydrogen production to be launched in energy

market. Furthermore, natural gas reservoirs are not usable and the process is limited to reservoirs, which do not have a gas cap. With respect to reservoir properties, the process can be applied over a wide range, but reservoirs with faults and fractures are not preferred.

The advantages and drawbacks as well as risks of the process are summarized in Table 3. The advantages are the continued use of the chemical energy remained in the reservoir as well as the production of hydrogen using cost effective basic materials in an existing infrastructure. The biggest advantage of the process over other hydrogen extraction processes from petroleum reservoirs is clearly the already proven functionality. The disadvantages of the process are the potential cost for generators and conversion. Applicable technical and business models are still open for discussion, as they have high risks for field investments due to the inaccuracies they contain. These risks are complex and cannot be ignored.

6 Discussion

The method shown and proposed here is based on few observations of reservoir engineering phenomena as well as previously unpublished patent applications. The model calculation, in which different parameters such as yield and costs are defined, is based on strong simplifications that have been adapted to reality by the introduction of efficiency and safety factors. This publication is therefore only intended to present an current state of research and the challenges and possibilities of application.

The literature review conducted is based on a keyword and secondary source-based approach, which is used throughout the paper. Furthermore, references are also made to standard works and technically recognized publications. The patent search is primarily based on an evaluation of the relevant IPC (International Patent Classification) classes as well as related and dependent patents. Furthermore, numerical simulations and experiences are used.

7 Conclusions

Based on previous knowledge of thermal hydrogen formation in petroleum reservoirs within the framework of EOR (enhanced oil recovery) processes, a novel process using catalysts is demonstrated and presented in the publication. This process is based on a modified in-situ combustion, which is better geared to hydrogen production using specific catalysts. To evaluate the method for further research, a preliminary calculation is conducted on generic reservoirs. This calculation shows that the process can produce hydrogen economically in the reservoirs properly screened, if necessary technical plants exist in the fields selected and if the individual process steps are conducted appropriately.

It is necessary to investigate the method in more detail regarding its further applicability and to assess hydrogen via detector measurements in existing in-situ combustion operations. This would provide further information about the extraction of hydrogen or methane as a further reaction product.

Table 2 Results of the study

Parameter	Process evaluation	Explanation
Technical feasibility	☑	The technical feasibility was proven by [4]
Technology readiness level (TRL)	3–5	The technology is still in research based on laboratory tests and numerical simulations
Economic feasibility	☑	With existing infrastructure and knowledge, it can be economically feasible
<i>Reservoir types</i>		
Petroleum reservoirs with primary gas cap	☒	The injected oxidation agent will otherwise directly migrate to the top of the reservoir and will not give the aimed result
Depleted petroleum reservoirs without gas cap	☑	
Bitumen reservoirs	☑	
Gas reservoirs	?	Research is ongoing, but the energy in place is small
<i>Reservoir properties</i>		
Depth (m)	400–3000	The depth is limited by the injection pressure
Faulted/fractured reservoirs	☒	In faulted and/or fractured reservoirs the burning is not controllable
Permeability (mD)	> 50	Lower permeability for air injection
P (bar)	–	No limitation
T (°C)	25–150	Depending on reservoir temperature, the ignition is an autoignition or artificial
S _o	> 30%	High oil saturation is necessary for a sufficient hydrogen yield
S _w	> 20%	Water vapor is one of the most influencing factors, without water the process is not feasible
Carbonate matrix	?	Effect of fractures and geochemical interactions needs to be investigated
Silicate matrix	☑	

Table 3 Pro, cons, and risks of the process

Pros	Cons	Risks
<ul style="list-style-type: none"> • Utilization of remaining fuel(oil) as raw material • Hydrogen and synthesis gas yield • Air and water as favorable raw materials (environmental friendly) • Existing infrastructure • Reduced amortization costs • Process feasibility proven! 	<ul style="list-style-type: none"> • Compression effort • Retrofitting expenses • Gas separation/treatment needs • Potential corrosion 	<ul style="list-style-type: none"> • Irregular combustion (peak temperatures) • Geomechanical damage • Lack of further research • Licensing and approval procedures (less experience) • High temperature and material corrosion • Side reactions

References

1. Fazlyeva, R.R., Mallory, D.G., Moore, R.G., Mehta, S.A., Cheremisin, A.N.: Screening in situ combustion applicability for a heavy oil candidate reservoir with an accelerating rate calorimeter. In: Day 2 Wed, October 23, 2019, Moscow, Russia (2019)
2. Gutiérrez, D., Mallory, D., Moore, G., Mehta, R., Ursenbach, M., Bernal, A.: New paradigm in the understanding of in situ combustion: the nature of the fuel and the important role of vapor phase combustion. In: Day 2 Tue, April 26, 2022, Virtual, Apr 2022
3. Hallam, R.J., Hajdo, L.E., Donnelly, J.K., Baron, P.R.: Thermal recovery of bitumen at wolf lake. *SPE Reserv. Eng.* **4**(02), 178–186 (1989). <https://doi.org/10.2118/17022-PA>
4. Hajdo, L.E., Hallam, R.J., Vorndran, L. (eds.): *Hydrogen Generation During In-Situ Combustion* (1985)
5. Butron, J., Bryan, J., Yu, X., Kantzas, A., (eds.): *Production of Gases During Thermal Displacement Tests* (2015)
6. Kapadia, P.R., Kallos, M., Chris, L., Gates, I.D., (eds.): *Potential for Hydrogen Generation during In Situ Combustion of Bitumen* (2009)
7. Larter, S.R., Head, I.M., Jones, D.M., Erdmann, M., Wilhelms, A.: *Process for Stimulating Production of Hydrogen from Petroleum in Subterranean Formations*, EP1765529 (A1), EP EP20050747248 20050527, 28 Mar 2007
8. Parsley, A.J., Stouthamer, C.: *Tertiary Oil Recovery Combined With Gas Conversion Process*, EP1417395 (A1), EP EP20020767334 20020806, 12 May 2004
9. Strem, G.D., Gates, I.D., Wang, J.: *In-Situ Process to Produce Synthesis Gas from Underground Hydrocarbon Reservoirs*, PH12020551480 (A1), PH PH20201551480 20200904, 6 Sep 2021
10. Wang, J., Gates, I.D.: *In-Situ Process to Produce Hydrogen From Underground Hydrocarbon Reservoirs*, JOP20180074 (A1), JO JOP20180074 20180806, 6 Feb 2020
11. Yuan, C., et al.: Potential of copper-based oil soluble catalyst for improving efficiency of in-situ combustion process: catalytic combustion, catalytic in-situ oil upgrading, and increased oil recovery. In: Day 3 Tue, October 15, 2019, Mishref, Kuwait, Oct 2019
12. Domínguez, S., Cifuentes, B., Bustamante, F., Cantillo, N.M., Barraza-Botet, C.L., Cobo, M.: On the potential of blue hydrogen production in Colombia: a fossil resource-based assessment for low-emission hydrogen. *Sustainability* **14**(18), 11436 (2022). <https://doi.org/10.3390/su141811436>
13. Howarth, R.W., Jacobson, M.Z.: How green is blue hydrogen? *Energy Sci Eng* **9**(10), 1676–1687 (2021). <https://doi.org/10.1002/ese3.956>

14. Noussan, M., Raimondi, P.P., Scita, R., Hafner, M.: The role of green and blue hydrogen in the energy transition—a technological and geopolitical perspective. *Sustainability* **13**(1), 298 (2021). <https://doi.org/10.3390/su13010298>
15. Ocko, I.B., Hamburg, S.P.: Climate consequences of hydrogen emissions. *Atmos. Chem. Phys.* **22**(14), 9349–9368 (2022). <https://doi.org/10.5194/acp-22-9349-2022>
16. Murthy, B.N., Sawarkar, A.N., Deshmukh, N.A., Mathew, T., Joshi, J.B.: Petroleum coke gasification: a review. *Can. J. Chem. Eng.* **92**(3), 441–468 (2014)
17. Barillas, J., Dutra, T.V., Mata, W.: Reservoir and operational parameters influence in SAGD process. *J. Petrol. Sci. Eng.* **54**(1–2), 34–42 (2006). <https://doi.org/10.1016/j.petrol.2006.07.008>
18. Briggs, P.J., Baron, P.R., Fulleylove, R.J., Wright, M.S.: Development of heavy-oil reservoirs. *J Pet Technol.* **40**(02), 206–214 (1988). <https://doi.org/10.2118/15748-PA>
19. Gozalpour, F., Ren, S.R., Tohidi, B.: CO₂ Eor and storage in oil reservoir. *Oil Gas Sci. Technol. Rev IFP* **60**(3), 537–546 (2005). <https://doi.org/10.2516/ogst:2005036>
20. Baehr, H.D., Kabelac, S.: *Thermodynamik: Grundlagen und technische Anwendungen*, 16th edn. Springer, Berlin, Heidelberg (2016). [Online]. Available: <http://nbn-resolving.org/urn:nbn:de:bsz:31-epflicht-1486485>
21. Recovery performance and economics of steam/propane hybrid process: OnePetro, 2005
22. Subsurface Hydrogen Generation: Low Cost and Low Footprint Method of Hydrogen Production: OnePetro, 2022
23. Esteban, M., Romeo, L.M.: Techno-economics optimization of H₂ and CO₂ compression for renewable energy storage and power-to-gas applications. *Appl. Sci.* **11**(22), 10741 (2021)
24. Nodwell, J., Moore, R.G., Ursenbach, M.G., Lareshen, C.J., Mehta, S.A.: Economic considerations for the design of in-situ combustion projects. *J. Can. Pet. Technol.* **39**(08) (2000)
25. Nordio, M., Wassie, S.A., van Sint Annaland, M., Pacheco Tanaka, D.A., Viviente Sole, J.L., Gallucci, F.: Techno-economic evaluation on a hybrid technology for low hydrogen concentration separation and purification from natural gas grid. *Int. J. Hydrogen Energy* **46**(45), 23417–23435 (2021). <https://doi.org/10.1016/j.ijhydene.2020.05.009>
26. Bauer, J.F., Amro, M., Alkan, H.: Wasserstoffproduktion aus ausgeförderten Kohlenwasserstofflagerstätten: Eine lagerstättentechnische und wirtschaftliche Betrachtung. *DGMK/ÖGEW-Frühjahrstagung*, vol. 2022, pp. 160–180