IN-SITU HYDROGEN PRODUCTION FROM PETROLEUM RESERVOIRS VIA ELECTROMAGNETIC-ASSISTED CATALYTIC HEATING

Keju Yan, Qingwang Yuan*

Bob L. Herd Department of Petroleum Engineering, Texas Tech University

ABSTRACT

To address the escalating demands for decarbonization within the petroleum industry, a pioneering technology known as in-situ hydrogen (H_2) production via electromagnetic-assisted catalytic heating has recently been proposed for extracting clean H_2 directly from petroleum reservoirs. This study explores H_2 generation from hydrocarbon/water reactions in the presence of natural rock powders under electromagnetic irradiation. Real-time data on temperature profiles of rock samples, gas production, and concentrations of generated gases are monitored and recorded. Thermal Runaway (TR) phenomena are observed in both sandstone and shale rocks, occurring at 568°C for sandstone and 253°C for shale. Remarkably, upon TR occurrence, the post-TR sample can be efficiently reheated up to 600°C using significantly lower input power compared to fresh rocks. The findings also reveal that iron-based and other metal minerals in the sandstone rocks exhibit a noticeable natural catalytic effect in promoting CH_4 conversion to H_2, yielding over 70.0% H_2 concentration as temperature approaches 650°C. In terms of oil conversion to hydrogen, a concentration of 60.7 mol.% H_2 is achieved, accompanied by moderate percentages of CH_4 and C_2H_4, along with a minor amount of CO. Additionally, water proves to enhance H_2 generation via coke gasification within a temperature range of 330-580°C. Furthermore, throughout the experiments, negligible CO_2 and minor CO emissions are observed, underscoring the potential for a carbon-zero H_2 technology. The proposed technology holds promise in paving a new pathway for clean H_2 production directly from oil and gas reservoirs.

INTRODUCTION

Most existing hydrogen (H_2) technologies suffer either high cost (e.g., water electrolysis) or high greenhouse gas footprint (e.g., steam methane reforming). Meanwhile, the petroleum industry is facing increasing pressure towards decarbonization. Transforming the natural gas sector into a clean hydrogen supplier emerges as a pivotal solution to substantially curtail the greenhouse gas emissions in this decarbonization process.

A recent novel approach for in-situ hydrogen production from petroleum reservoirs is using electromagnetic (EM) -assisted catalytic heating, proposed by Yuan et al. (2022). The idea is to install an in-situ dipole antenna, comprised of standard oil field tubulars, to deliver EM energy into the formation. Instead of heating the entire reservoir, part of the formation around the wellbore will be heated. With artificial catalysts pre-placed in the targeted zone as well as the natural catalysts in reservoir rocks, this process can be more effective because catalysts can not only promote EM heating as they are good EM absorbing materials but also enhance hydrocarbon conversion to hydrogen. Once the required temperature is achieved in situ, a high concentration of H_2 will be generated from a series of reactions as hydrocarbons flow to the wellbore through the heated zone. Further, Since the entire process is a non-combustion approach, it can drastically suppress the generation of CO_2. With the assistance of downhole H_2 membrane separators, only high-purity H_2 will be extracted to surface, as shown in Fig. 1. This is therefore a carbon-zero technology. It does not necessitate the use of fresh water compared to water electrolysis and SMR, thus saving substantial water resources. Furthermore, the renewable energy (i.e., wind and solar) in South Central states, U.S. can be perfectly utilized for in-situ EM heating. These states have abundant hydrocarbon resources, negative wholesale price of renewable energy for 25% of all hours per year (Seel et al., 2021), and the highest water stress level (Connelly et al., 2020). All these factors and existing resources can collectively contribute to an even lower cost, cleaner hydrogen production.

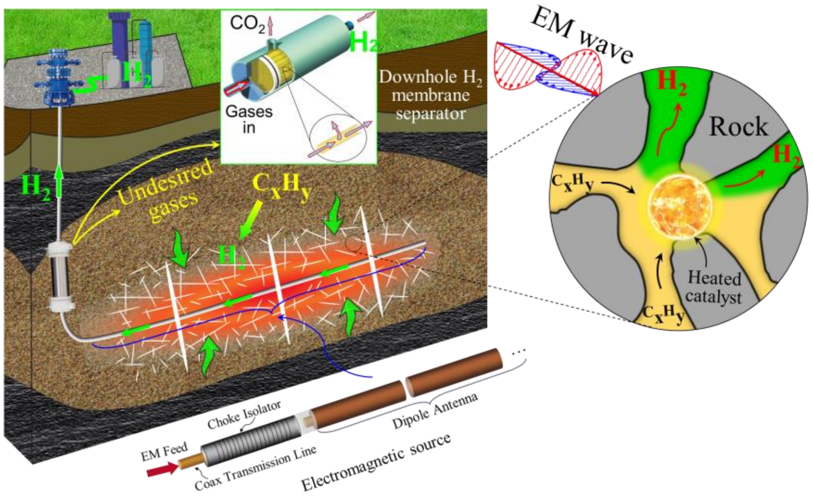


Figure 1 – Schematic of EM-assisted catalytic heating for in-situ hydrogen production from petroleum reservoirs

Research has shown that maximum 66 mol.% H_2 can be generated from crude oil in the presence of artificial catalysts (Yuan et al., 2021). It is also reported that methane (CH_4) conversion in both bulk shale and shale powders is higher than that in quartz samples under non-catalytic conditions, demonstrating the shale rocks' positive role in CH_4 cracking (Yan et al., 2022). While in the presence of sandstone rocks under catalytic condition, a concentration of 91 mol. % H_2 is obtained from CH_4 cracking under microwave irradiation (Yan et al., 2023b). A numerical simulation based on the Allen-Cahn phase field interface tracking method indicates that the hydrogen generation can occur across the entire target formation with minimal deformation of the hydrocarbon formation when this technology is applied at a reservoir scale (Ramsay, 2022).

While recent experimental findings have underscored the considerable promise of the proposed technology, several critical knowledge gaps persist. First, comprehending the heating capabilities of various natural rock types is paramount, given that in-situ hydrogen production inevitably entails EM interactions with rocks during the heating process. However, the energy consumption during EM heating remains unclear, as does the potential hydrogen yield from hydrocarbons. Secondly, the parameters governing hydrogen production via EM heating—such as the initial temperature of hydrogen generation, concentrations, flow rates, etc.—for different oil and gas compositions beneath various types of rocks, remain largely unknown.

Furthermore, water was not considered as a feedstock in most of the existing experiments using the electromagnetic-assisted catalytic heating approach, regardless of surface or subsurface conditions. However, in subsurface petroleum reservoirs, there is always a certain content of water in the form of free water or connate water. Therefore, it is crucial to understand the detailed situations and reactions when water and hydrocarbon coexist in rocks. However, it is unclear how much hydrogen will be generated from petroleum and water when the two feedstocks serve as hydrogen donors.

In this work, we perform microwave/electromagnetic-assisted catalytic heating experiments in a purpose-designed microwave reactor system in the presence of two types of rock powders: sandstone and shale. Rock heating performance under microwave irradiation is investigated during the process. Methane, shale oil, and water are used as three hydrogen donors to mimic the various practical conditions of petroleum reservoirs. The real-time gas composition of the produced gases is monitored by an online gas analyzer, therefore obtaining in-depth understanding on the relationship between temperature and composition of generated gases in the flow-through experiments. Through lab-scale experiments, this study endeavors to elucidate further technical uncertainties and mechanisms of in-situ hydrogen production using EM-assisted catalytic heating, with the goal of enhancing its feasibility.

EXPERIMENTAL

1. Materials

The materials utilized in this experiment include San Saba sandstone, Mancos shale (from Kocurek Industries, Inc.), quartz sand, silicon carbide (SiC, Sicat Catalyst), water (H_2O), and Fe_2O_3 particles (purity ≥ 99%, 50 nm particle size, Sigma-Aldrich Inc.). Pure quartz sample is employed as a reference case. The rock samples are crushed into particles ranging 38-100μm in diameter. To minimize the impact of free water presenting in the rock, the samples are subjected to a drying process in an oven at a temperature of 80°C for 24 hours. A 20-weight percentage (wt.%) of SiC is added to the rock samples to easily control the temperatures based on its excellent EM-absorbed ability.

2. Setup

The microwave reaction system used in this study consists of several key components, including: 1) microwave generating unit (Sairem Ltd.), as described in Yan et al., 2023a; 2) purpose-built reactor unit. The reactor unit is made up of an E-field cavity, a quartz tube, and two gas flow meters that control the flow rate of methane (CH_4) and argon (Ar) respectively; and 3) a real-time data logging system. An online gas analyzer (Extrel MAX300 IG) can measure the produced gas molar composition within 5 seconds, even at extremely low concentrations of 10 parts per million (PPM). An infrared (IR) pyrometer (2.3 μm spectral range, Micro-Epsilon) is also mounted to the reactor to provide a measured temperature of the sample surface during the experiments.

3. Method and Process

The rock sample is carefully introduced into the center of the quartz tube and then placed into the cavity followed by the examination of hermetic sealing to the system. To eliminate the original air in both the samples and the system, a flow rate of 60 standard cubic centimeters per minute (sccm) of Ar gas is purged for 15 minutes to ensure an inert environment. Ar is used as a carrier gas to eliminate oxygen in the reactor prior to the experiments.

After that, for the experiments using *methane* as hydrogen donor, both CH_4 and Ar are continuously flowing through the sandstone rock samples at a flow rate of 30 sccm under microwave irradiation.

For the experiments using *shale oil* as the hydrogen feedstock, 0.20 grams of shale oil is saturated with shale rock samples, which will be left at least 8 hours to ensure the oil fully dispersed into the samples. Then a constant flowrate (60 sccm) of Ar will be introduced as the carrier gas to take the generated gases to the gas analyzer during the heating process.

As to the experiments with *water* (H_2O) involved, 0.40 grams of H_2O is fully saturated into the spent sandstone rock samples for 4 hours before microwave heating. The generated gases are also carried by the constant flowrate of Ar to gas analyzer for detection.

RESULTS AND DISCUSSIONS

1. Rock Heating Performance under EM Irradiation

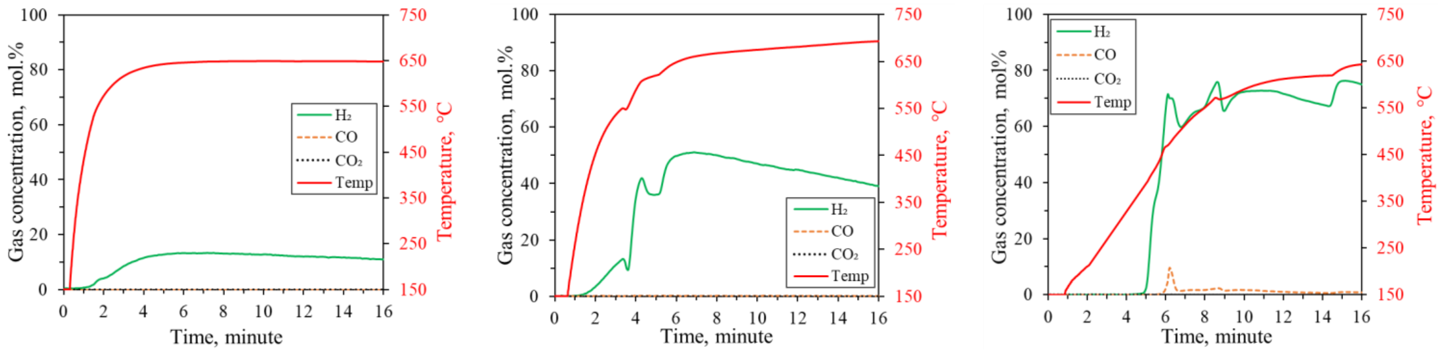
Achieving the necessary temperature for hydrocarbon conversion to hydrogen is paramount. Therefore, determining whether rock samples can be heated to a sufficiently high temperature via electromagnetic heating is crucial for in-situ H_2 production. To validate this, three powder samples—pure quartz, pure sandstone rock, and pure shale rock—are subjected to microwave heating in an Ar gas environment.

For the pure quartz sample, the temperature only reaches a maximum of 73°C within 20 minutes. However, when sandstone and shale rocks are subjected to microwave heating, their temperatures rapidly escalate after 15.6 minutes and 3.4 minutes, respectively, along with sudden changes in their heating rates (An et al., 2024). This phenomenon is reported as Thermal Runaway (TR) in reservoir rocks (Yan et al., 2024). The TR manifests at 568°C for sandstone and 253°C for shale. Evidently, the shale sample is considerably easier to heat compared to the sandstone sample. Another intriguing observation emerges from the process: Once TR occurs in either sandstone or shale samples, substantially less input power is required to reheat the post-TR samples to a same temperature compared to heating the fresh samples. This means the heating efficiency for post-TR rock samples has been significantly improved during the TR process.

These findings highlight the feasibility of electromagnetic heating in the reservoirs for achieving the desired temperatures for oil and gas conversion to hydrogen. Utilizing the TR phenomenon can enable a substantial reduction in energy input which will significantly reduce the cost of in-situ hydrogen technology as well.

2. Natural Catalytic Hydrogen from Methane Cracking in Sandstone

To gain insights into the hydrogen production resulting from methane cracking within sandstone rocks, a reference experiment is carried out using a sample consisting of 80 wt.% quartz and 20 wt.% SiC, in comparison to that with the same ratio of sandstone and SiC. Another comparative experiment using a sample consisting of 80 wt.% quartz, 15 wt.% SiC and 5 wt.% Fe_2O_3 nanoparticles is also conducted to further investigate the catalytic role of iron particles. A flow rate of 30 sccm CH_4 is used for providing the feedstock for the reaction, while the same flow rate of Ar gas is also deployed to quantitively calculate the flow rate of the generated gases in the experiments.



(a)

(b)

(c)

Figure 2 – Gases generated from different rock samples: (a) 80 wt.% Quartz + 20 wt.% SiC; (b) 80 wt.% Quartz + 15 wt.% SiC + 5 wt.% Fe_2O_3; (c) 80 wt.% Sandstone + 20 wt.% SiC.

From the results of gas concentration as depicted in Fig. 2, the produced gases from methane cracking in the three samples are mainly H_2 and minor CO. For the quartz sample (Fig. 2a), there is an approximate 13 mol.% H_2 can be produced when the temperature is approaching 650°C. In contrast, when adding 5 wt.% Fe nanoparticles into the quartz sample, Fig. 2(b) shows that a peak H_2 concentration of 50 mol.% is produced at the same temperature level. This means the Fe nanoparticles play a positive role in catalyzing the CH_4 cracking.

Strikingly, for the sandstone sample, the H_2 production is even higher than the quartz sample with iron catalyst, with an over 70 mol.% H_2 concentration when the temperature approaches 650°C as shown in Fig. 2(c). Since the total iron content measured in the sandstone is 1.06 wt.%, which is lower than that in the quartz sample with 5 wt.% Fe_2O_3, it is not sufficient to simply attribute the higher H_2 production to the iron element in the sandstone. In other words, although the Fe element in the sandstone indeed has a catalytic effect for hydrogen generation, other elements and minerals may also be involved in the reactions, resulting in a more efficient methane cracking and a higher H_2 concentration in the sandstone samples than those in the quartz sample with 5 wt.% Fe_2O_3.

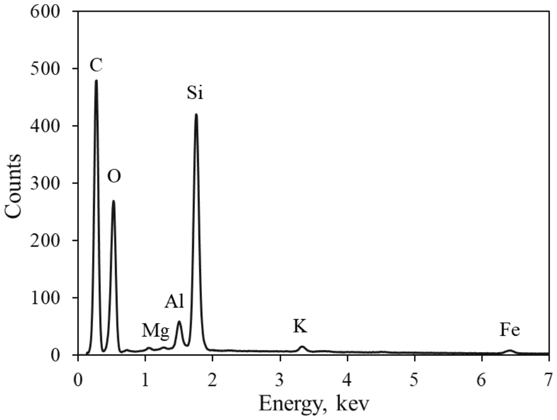


Figure 3 – EDX results of the fresh sandstone sample

To gain deeper insights into the natural catalytic effect of sandstone in methane cracking, we conducted energy dispersive X-ray spectroscopy (EDX, Hitachi S-4700) analysis on sandstone particles. The EDX results in Fig. 3 indicate that apart from the main content of SiO_2, there are also metal elements such as Fe and K presented on the surface of the rock samples. These metal elements have shown strong catalytic effect in methane cracking, hydroamination and hydrogenation reactions as demonstrated in previous research (Zhou et al., 2018; Yao et al., 2020).

These observations offer a plausible explanation for the natural catalytic effect facilitated by sandstone particles: 1) Metal particles or catalytic minerals dispersed randomly within the sandstone powders serve as catalysts for methane cracking; 2) Reactions occur in the presence of these natural catalysts when the required temperatures are attained under microwave heating. Consequently, methane undergoes cracking, yielding carbon and hydrogen. The solid carbon produced then precipitates around the catalytic minerals, while the presence of metal particles dispersed on the surface of sandstone particles also leads to the formation of some carbon nanotubes; 3) The large surface area of sandstone particles may enhance CH_4 cracking under microwave irradiation, thereby contributing to the catalytic process.

3. Hydrogen Production from Shale Oil in Shale Rocks

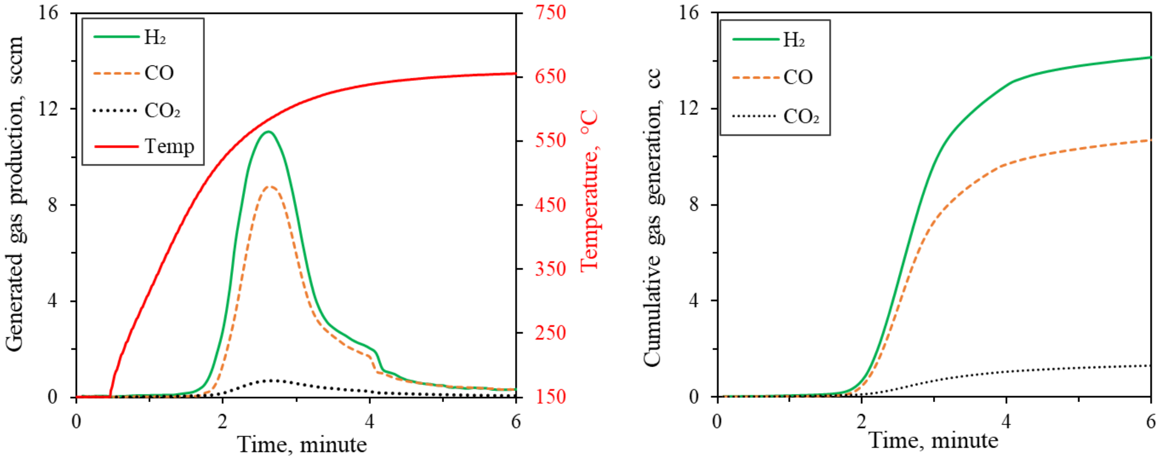
The results in our previous research show that H_2 dominates the gas generation in both the first-round and the second-round heating when utilizing 0.20 grams of oil as hydrogen donor (Yan et al., 2024). H_2 production commences at a measured temperature of 420°C. A certain amount of methane (CH_4) and ethylene (C_2H_4) is also generated alongside the H_2 production. Furthermore, carbon monoxide (CO) begins to be generated at higher temperatures, typically over 500°C, while carbon dioxide (CO_2) remains minimal or negligible; and a small amount of light hydrocarbon gases (C_2-C_4) is also produced during the heating.

Notably, there is a significant disparity in the flow rates of H_2 produced in the two-round experiments, as well as the cumulative gas production (Yan et al., 2024). These substantial hydrogen reductions in flowrate and cumulative volume suggest that the natural catalysts become deactivated over time. The deactivation can be attributed to carbon deposition on the surface of rock particles which hinders the natural catalytic effect during the process.

Regarding gas concentrations of the total gases generated in the two cycles, the second-round experiment reveals a significant 12.7% reduction in H_2 and a notable 20% increase in CO compared to the first-round heating. This provides another piece of evidence for the inefficiency and deactivation of natural catalysts over time.

4. Water Enhancement for Hydrogen Generation

Our previous work shows that water indeed plays a positive role in generating additional H_2 (Yan et al., 2023b), however, it seems water does not significantly contribute to CH_4 cracking or steam methane reforming during the water-involved experiments. The water enhancement for hydrogen generation most likely results from the gasification reaction ($C + H_2O \rightarrow CO + H_2$), which can easily happen at lower temperatures compared to reactions like methane cracking ($CH_4 \rightarrow C + 2H_2$) and steam methane reforming ($CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$).



(a)

(b)

Figure 4 – Gas generation from 0.40g H_2O in the spent sample (80 wt.% Sandstone + 20 wt.% SiC): (a) real-time flowrate; (b) cumulative gas over time.

To further verify the increased production of H_2 through coke gasification reaction, an additional test was carried out by saturating 0.40 grams of water (H_2O) into the spent sandstone sample after methane cracking. To mitigate interference from other reactions, only pure Ar gas was introduced into the experimental reactor at a flowrate of 60 sccm, ensuring an inert environment as well as serving as a carrier gas. Theoretically, the reactants present in the sample encompass only water and the carbon deposited from the preceding methane cracking reactions. Fig. 4 depicts the real-time data illustrating the generated gas flowrate and cumulative gas production over time.

It is evident from the experiment that H_2 and CO are the primary products, aligning with the outcomes expected from the coke gasification reaction. In the presence of H_2O, H_2 generation initiates around 350°C, reaching its peak flowrate of 11.1 sccm at 580°C. On the other hand, CO generation commences at 500°C, peaking at 587°C with a flowrate of 8.8 sccm. Notably, the production trend of CO closely mirrors that of H_2. However, it's essential to highlight that the flow rate of CO consistently remains lower than that of H_2 throughout the process. Additionally, a minor amount of CO_2 is generated alongside CO production, which may be attributable to the water-gas shift reaction (WGSR, $CO + H_2O \rightarrow CO_2 + H_2$). Fig. 4(b) demonstrates the cumulative volume of generated gases in the reaction are 14.1 cc (54%), 10.6 cc (41%), and 1.3 cc (5%) for H_2, CO, and CO_2, respectively.

These observations suggest that the supplementary H_2 primarily arises from coke gasification, followed by the water-gas shift reaction. Another advantage of coke gasification is its potential to assist in removing deposited solid carbon from the rock surface, thereby aiding in mitigating the deactivation of the natural catalytic effect. The feasibility of coke gasification to facilitate the reactivation of the catalytic effect is worthy of exploration in future investigations.

CONCLUSIONS

This study conducted lab-scale microwave-assisted catalytic heating experiments to investigate hydrogen production from oil and gas in the presence of reservoir rocks, with water (H_2O) also utilized as a hydrogen donor to explore its enhanced role in hydrogen generation. The key findings are summarized below:

1) The shale sample is considerably easier to heat compared to the sandstone sample under microwave heating. Thermal Runaway (TR) phenomena occur in both sandstone and shale rocks,

manifesting at 568°C for sandstone and 253°C for shale. Leveraging TR could substantially reduce energy input for in-situ hydrogen production from petroleum reservoirs.

2) Iron-based minerals and other minerals in sandstone demonstrate a noticeable natural catalytic effect, promoting methane conversion to H_2, yielding over 70.0% H_2 concentration as temperature approaches 650°C.
3) Hydrogen production from shale oil in shale rock initiates at 420°C, while CO generation occurs at higher temperatures (over 500°C). Oil conversion primarily yields H_2 with a concentration of 60.7 mol.%, followed by a moderate percentage of CH_4 and C_2H_4 and a small amount of CO.
4) Water demonstrates an enhanced role in hydrogen production primarily through coke gasification reactions within a temperature range of 330-580°C.
5) CO_2 generation remains negligible throughout the experiments, suggesting the potential for a carbon-neutral and cost-effective technology for in-situ H_2 production from both new and depleted petroleum reservoirs.

ACKNOWLEDGEMENT

This work is supported by a generous gift from The CH Foundation and the Matejek Family Faculty Fellowship. K.Y. thanks the support from the Distinguished Graduate Student Assistantship and the Graduate Research Support Award at Texas Tech University. The authors also thank ConocoPhillips for donating the gas analyzer and Mr. Cecil Millikan for technical support during the experimental process. The authors appreciate the assistance for experiments from Mr. Baizheng An.

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