

# Investigation on hydrogen production through in-situ heavy oil gasification process under different atmospheres conditions

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## ABSTRACT

The in-situ production of hydrogen from hydrocarbon reservoirs offers a novel and cost-efficient approach, leveraging gasification and cracking reactions of fossil fuel sources. This study investigates the process of hydrogen production through heavy oil cracking under various atmospheric conditions, employing a kinetic cell apparatus. Additionally, this work pioneers the definition and computation method for hydrogen production efficiency, providing a quantitative framework to assess in-situ hydrogen generation performance during the later stages of heavy oil reservoir development. The outcomes of this research highlight that hydrogen generation transpires during the phases of pyrolysis and coke dehydrogenation reactions. Particularly noteworthy is that over 60% of the produced hydrogen originates from the coke dehydrogenation reaction range, prevailing at temperatures within 500–650 °C. In regard to the hydrogen production efficiency, when heavy oil samples are subjected to an air environment, it fluctuates within a range of 9.24–15.66%. This range is significantly lower compared to the nitrogen atmosphere, where efficiency varies from 12.26% to 28.65%. The inclusion of clay minerals serves as a natural catalyst, augmenting hydrogen generation rate and elevating efficiency to the peak value of 28.65%. This enhancement coincides with the maximum conversion rate of heavy oil, reaching 262.46 mL/g. Furthermore, the introduction of water substantially amplifies the overall mole count of hydrogen production, indicating its pivotal role in reducing the lower limit temperature for hydrogen generation from 400 °C to 300 °C.

**Keywords:** Heavy oil, Hydrogen, Hydrogen production, In-situ gasification technology

## NONMENCLATURE

### Abbreviations

ISG	In-situ gasification technology
ISC	In-situ combustion
LTO	Low temperature oxidation
FD	Fuel deposition
HTO	High temperature oxidation

## 1. INTRODUCTION

Converting fossil energy into clean and sustainable energy has been emerged as a prominent topic in energy development, capturing increasing attention from researchers in recent years [1-3]. Hydrogen, recognized for its high calorific value, is regarded as a gas fuel superior in energy content per unit mass compared to any other fuel types. The combustion of hydrogen only yields water as a byproduct, resulting in zero carbon emission. Currently, hydrogen production can be achieved through diverse methods, such as methane and biomass reforming, as well as from coal gasification, water electrolysis, and etc [4]. However, the promotion and large-scale application of various hydrogen production technologies are still limited due to the emission of a large number of greenhouse gases and high economic costs [5].

Gasification is a clean technology that converts fossil fuel to high-quality syngas with presence of gasifying agents [6]. By injecting air into the formation, hydrogen can be produced through the in-situ gasification process of heavy oil. The oxidation reaction of heavy oil varies with different environment temperature. The reaction of oxygen addition (also known as low temperature oxidation or abbreviation as LTO), oxidation cracking and high temperature oxidation (HTO) happen sequentially when the temperature increases to 150-250 °C, 220-340 °C, and 330-550 °C. The oxidation cracking reaction, which requires low or even oxygen free condition, takes precedence in the heavy oil upgrading process. This

reaction significantly contributes to the efficient utilization of oil and gas resources in the form of clean energy. The approach holds significant advantages in comparison to current industrial hydrogen production methods. The approach holds significant advantages in comparison to current industrial hydrogen production methods. Firstly, the oil reservoir is a natural underground reactor, and the material of hydrogen production is crude oil rather than processed fuel avoiding the waste of high-value-added products. In addition, this is a blessing for the heterogeneous heavy oil reservoir, which is difficult to develop, especially for abandoned tailings of heavy oil reservoirs with low oil recovery [7]. Secondly, generating and producing clean hydrogen directly from petroleum reservoirs, while leaving all carbon (including CO<sub>2</sub>) underground could avoid the emission of greenhouse gases. Thirdly, the cost of the technology could be potentially low by adapting existing oilfield infrastructures (e.g., wells and pipelines) [8]. Hence, hydrogen production directly from hydrocarbon reservoirs could be one of the energy-efficient and cost-effective ways.

In 1979, BP Resources Canada Ltd. stumbled upon a surprising discovery: emission gas mixtures from a heavy oil reservoir during an in-situ combustion (ISC) pilot yielded a 10-20% mole fraction of H<sub>2</sub> [9,10]. The reaction pathways responsible for hydrogen generation within heavy oil reservoirs are intricate and varied. Mechanisms such as thermal cracking or thermolysis, aquathermolysis, water-gas shift reaction, and coke gasification reaction have all been identified as contributors to the production of hydrogen gas during the in-situ combustion process [11,12]. Pyrolysis plays an important role in the heavy oil ISG process. During the 1920s, thermostatically closed reactors found application in investigating the pyrolysis reaction of crude oil. Henderson and Weber [13] examined the duration necessary for crude oil to undergo alterations in its physical characteristics across varying temperatures. They put forth the conjecture that through sufficient heating time or elevated pyrolysis temperatures, crude oil could undergo near-complete conversion into hydrogen, methane, and coke. Bunker et al. [14] conducted pyrolysis experiments on oil sands employing non-isothermal conditions within a temperature span of 25-625 °C. They observed significant quantities of hydrogen and methane generation, particularly at temperatures surpassing 500 °C. In another study, Kök et al. [15] employed a thermogravimetric analyzer coupled with a mass spectrometer (TGA-MS) system to scrutinize the gas resulting from heavy oil pyrolysis. Their findings

indicated that gas produced from low molecular weight cracking primarily occurred around 450 °C. Hayashitani et al. [16] introduced kinetic parameters for thermal cracking reactions for the first time, providing crucial data to support numerical simulations. To enhance the comprehensiveness of the thermal cracking reaction scheme, Kapadia et al. [17] incorporated an additional six reactions to account for the generation of gas components. It becomes evident that hydrogen can be produced via various reaction processes, including aquathermolysis, thermolysis, coke gasification, and the water-gas shift reaction, as reported by distinct researchers. Nevertheless, research on the hydrogen generation mechanism through the gasification process of heavy oil is even scarcer. Aspects like the lower limit temperature of hydrogen generation and the evolution of produced gas composition remain relatively unexplored.

In this study, we introduce the definition and calculation equation for the efficiency of producing hydrogen-rich syngas (comprising hydrogen and methane). This novel approach allows for a quantitative assessment of the effectiveness of in-situ hydrogen production through the gasification of heavy oil within the reservoir. For the first time, we undertake an extensive examination of hydrogen production performance from heavy oil under varying atmospheric conditions using a kinetic cell experiment apparatus. Our investigation delves into the impact of factors such as environmental conditions, clay minerals, and water content on the efficiency of generating hydrogen-rich syngas. These variables not only significantly influence the lower limit temperature of hydrogen generation but also shape the compositions of the resulting gas mixtures.

## 2. EXPERIMENTS

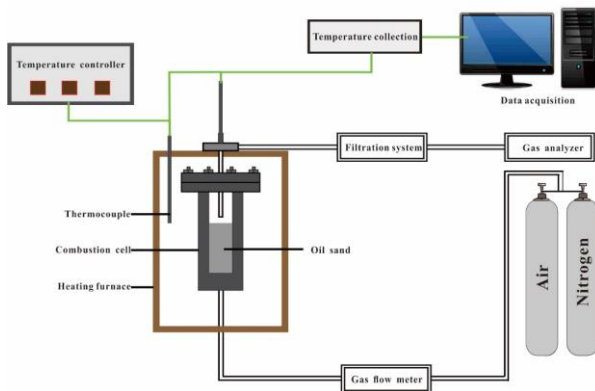
### 2.1 Materials and sample preparation

The heavy oil sample utilized in the experiments was obtained from the Caogu\* block of the Shengli oil field in Shandong province, China. Prior to conducting any experiments, dehydration was performed using an electric dehydration instrument (Petroleum Analytical Instrument Company, China). Viscosity measurements for the oil sample were conducted using the HAAKE RS6000 Rotor Rheometer (Thermo Scientific, Germany). The recorded viscosity value was 73.4 Pa·s at a shear rate of 10 s<sup>-1</sup> and a temperature of 30 °C. At standard ambient conditions, the density of the oil was determined to be 0.98 g/cm<sup>3</sup>. The heavy oil's atomic ratio (H/C) is 1.5, as

determined by employing an Elemental Analyzer (Flash EA 1112, American), following the ASTM D5291 standard. In the experiments, quartz sand particles with a mesh size ranging from 40 to 60 were employed. The clay minerals used consisted of approximately equal parts (50% each by weight) of kaolinite and montmorillonite.

## 2.2 Experimental setup

The schematic diagram of the kinetic cell setup is illustrated in Fig. 1. The kinetic cell experiment device contains four integral units: a temperature control unit, an air flow rate control unit, a gas concentration measurement unit and a data logging & transportation unit. Within the temperature control unit, components such as an electric heater, k-type thermocouples (manufactured by OMEGA), and a heating jacket are integrated. The air flow rate control unit encompasses essential elements including compressed gas cylinders (nitrogen and air), a pressure regulator valve (Swagelok Company, US), a gas mass flow meter (Beijing Sevenstar Electronics Co. Ltd, China), and a pressure gauge. For real-time monitoring of the emission gas composition, a gas analyzer (Wuhan Cubic Optoelectronics Co. Ltd, China) was employed.



*Fig. 1 Schematic diagram of the kinetic cell experiment*

A total of six experiments, each involving distinct conditions, were designed as outlined in Table 1. These experiments were categorized into two groups: the first group (Exp.#1 to #3) and the second group (Exp.#4 to #6). The first group was conducted under a nitrogen atmosphere, while the second group was carried out in the presence of air. This division aimed to assess the influence of oxidizing gas on the hydrogen production efficiency of heavy oil. Furthermore, within each group of experiments, specific variations were introduced. Clay minerals were added to the oil sand in Exp.#2 & #5, whereas water was incorporated in Exp.#3 & #6. These additions were made to explore the respective impacts

of clay minerals and water on the efficiency of hydrogen production.

*Tab.1 Experimental conditions for hydrogen production of heavy oil under different atmospheres.*

No.	Atmosphere	Carrier type	Temperature, °C	Pressure, MPa
Exp.#1	Nitrogen	Quartz sand	RT-300-400-500-600	1
Exp.#2	Nitrogen	Quartz sand + clay minerals	RT-300-400-500-600	1
Exp.#3	Nitrogen	Quartz sand + water	RT-300-400-500-600	1
Exp.#4	Air	Quartz sand	RT-300-400-500-600	1
Exp.#5	Air	Quartz sand + clay minerals	RT-300-400-500-600	1
Exp.#6	Air	Quartz sand + water	RT-300-400-500-600	1

## 2.3 Kinetic cell experiments

The hydrogen generation through the in-situ gasification process of heavy oil under nitrogen and air atmosphere conditions was investigated through distinct kinetic cell experiments. To ensure temperature uniformity, multiple K-type thermocouples were strategically positioned within the cell and furnace, allowing for temperature measurement at various points. The experimental procedures are outlined as follows:

(1) Thoroughly mixing quartz sand particles with a mesh size of 40~60 and heavy oil in a mass ratio of 15:2.5. Subsequently, 15 g of the resulting mixture was accurately weighed and introduced into the cell. When involving clay minerals or water, they were blended with the heavy oil at a mass ratio of 1:1.

(2) Establishing connections among the experimental components as illustrated in Fig. 1. Ensuring the airtight seal of the kinetic cell and verifying the integrity of connection points.

(3) Introducing nitrogen gas or air into the kinetic cell at a controlled flow rate of 100 mL/min, and maintaining a backpressure of 0.5 MPa. For experiments conducted within a nitrogen atmosphere, it is imperative to ensure an oxygen concentration of less than 0.01% prior to commencing the tests.

(4) Initiating the experiment by incrementally raising the heat furnace temperature to 300 °C, 400 °C, 500 °C, and 600 °C, respectively, with a heating rate of 3 °C/min. Each target temperature is sustained for 0.5 hours, allowing the pyrolysis reactions to fully occur.

(5) Monitoring and recording the temperature of the oil sand, effluent gas flow rate, and gas composition throughout the experiment for subsequent data analysis.

## 2.4 Methodology

Various metrics have been established to gauge the hydrogen production potential through in-situ heavy oil conversion:

a) Hydrogen Generation Efficiency ( $\eta$ ): Expressed as the ratio of elemental hydrogen within the hydrogen-rich syngas ( $N_h$ ) to the overall elemental hydrogen content in heavy oil ( $N_H$ ). The hydrocarbon compound mixture of heavy oil is symbolized by the chemical formula  $C_xH_y$ , and the parameters  $x$  and  $y$  can be ascertained using the Elemental Analyzer.

$$\eta = \frac{N_h}{N_H} \quad (1)$$

b) The hydrogen conversion rate of heavy oil ( $\theta$ ): the total volume of hydrogen-rich syngas production ( $V_H$ ) divided by the initial weight of the crude oil ( $m_o$ ). The calculation of the total hydrogen produced is carried out at the end of each experiment, once the reactions have finished. The ultimate hydrogen generation selectivity signifies the volume of hydrogen that can be generated per gram of crude oil.

$$\theta = \frac{V_H}{m_o} \quad (2)$$

c) Hydrogen yield ( $\varepsilon$ ): the total production of hydrogen rich syngas in the emission gas mixtures ( $V_H$ )/total production of the emission gas mixtures ( $V_g$ ) (%). The volume of gas is measured at lab conditions (25 °C, 1 atm).

$$\varepsilon = \frac{V_H}{V_g} \quad (3)$$

d) The average rate of hydrogen production ( $v$ ): the total hydrogen rich syngas production ( $V_{Hx}$ )/reaction time ( $\Delta t$ ).

$$v = \frac{V_{Hx}}{\Delta t} \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1 Variation of effluent gases concentration

The variation in effluent gas concentrations as temperature increases during the experiments is illustrated in Fig.2. The first row of Fig.2 displays the experimental outcomes conducted under a nitrogen gas environment. As an inert gas, nitrogen is acknowledged as a heat transfer medium. In the absence of oxidizing gases, heavy oil only undergoes pyrolysis reactions. The heavier components are subsequently cracked into lighter hydrocarbons as the temperature rises. This process is accompanied by the bond scissoring reaction

of C–C, C–H, and H–H bonds, leading to the formation of various free radicals, including hydrogen radicals, saturated hydrocarbon radicals, and unsaturated hydrocarbon radicals (both aromatic and non-aromatic). A portion of these free radicals engage in cross-bonding to produce new molecules. For instance, interactions like  $H\cdot + \cdot H \rightarrow H_2$  and  $H\cdot + \cdot CH_3 \rightarrow CH_4$  can take place. Moreover, the cycloalkane and its derivative aromatization through the dehydrogenation and polycondensation of low molecular weight hydrocarbons can generate a small number of hydrogen radicals and coke. The C–H bonds scissoring occurs when the temperature surpasses 500 °C, triggering the dehydrogenation of heavier components and rendering them more viscous with a lower H/C ratio. From these observations, it can be inferred that hydrogen is produced during both the pyrolysis and heavy component dehydrogenation stages.

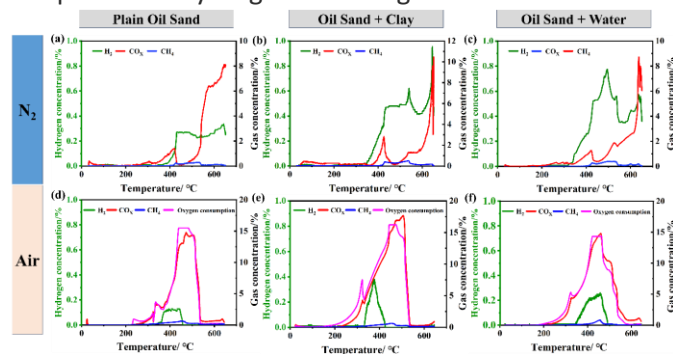


Fig. 2 Variation of effluent gas compositions versus temperature during each experiment.

The second row of Fig.2 depicts the experimental outcomes under an air atmosphere. When the cracking reaction occurs in the presence of air, the introduction of oxygen not only renders the reaction scheme more intricate but also leads to a notable reduction in the production of lighter hydrocarbons and hydrogen. It has been documented by numerous researchers that LTO, which generally involves relatively lower oxygen consumption, predominantly occurs within the temperature range of 150 °C to 350 °C. During the initial phase of the LTO process at lower temperatures, heavy oil undergoes an oxygen addition reaction [18]. The branched and alkyl side chains present in hydrocarbons contain numerous active sites, making them susceptible to reacting with oxygen and giving rise to oxygen-containing polar compounds such as carboxylic acids, aldehydes, ketones, and alcohols [19]. These polar oxygen-containing compounds exhibit instability and engage in ongoing interactions with oxygen through two distinct mechanisms: decarboxylation and dehydrogenation reactions. The decarboxylation process

involves the cleavage of carbonyl and ether compounds into CO, while carboxyl compounds are converted into CO<sub>2</sub>. This process contributes to the substantial production of carbon oxides (CO<sub>x</sub>), which is generally used as an indicator of cracking reactions. As the temperature escalates to 350°C, the concentration of CO<sub>x</sub> gases exhibits the first peak, reaching a value of 5%. Subsequently, the CO<sub>x</sub> concentration curve experiences a valley, referred to as the fuel deposition (FD) stage, occurring within the temperature range of 350°C to 400°C. Studies have revealed that, during the FD stage, the primary occurrence of cracking reactions involving C–C bond cleavage predominantly involves aromatics, resins, asphaltenes, and heavily saturated hydrocarbons [20]. This stage results in the formation of coke, with a reduced H/C ratio, which covers the surface of sand particles. The H/C ratio experiences a decline with increasing duration throughout the FD process, which is also recognized as the dehydrogenation stage. The HTO process, which combusts coke as fuel, takes place when the ambient temperature escalates to the higher range of 450°C to 650°C. During this phase, a notably larger volume of CO<sub>x</sub> is generated, which exhibits a significant correlation with the main peak observed in the CO<sub>x</sub> concentration and oxygen consumption curves.

Furthermore, the findings from the experiments reveal noteworthy trends. The initial peak value of O<sub>2</sub> consumption and CO<sub>x</sub> emission, occurring at 350°C for Exp.#4 in the absence of clay minerals, marks the end of the LTO process. Subsequently, the concentration of O<sub>2</sub> consumption and CO<sub>x</sub> emission exhibit a diminishing trend during the FD stage, followed by a dip to valley values at 400°C. These concentrations then gradually increase throughout the HTO phase. In the case of Exp.#5, which involves the addition of clay minerals, the concentrations of O<sub>2</sub> consumption and CO<sub>x</sub> emission experience swift variations over a lower and narrower temperature range, forming a curve with a more pronounced peak after the LTO process. This observation indicates that the catalytic effect of clay minerals considerably diminishes the activation energy (E<sub>a</sub>) and augments the rate of fuel deposition, thereby facilitating the transition from the FD to HTO stage.

### 3.2 Reaction kinetics of hydrogen generation

Temperature is a recognized pivotal factor influencing the pyrolysis process and the subsequent changes in emission gas concentrations. As depicted in Fig.3, the impact of temperature variations on hydrogen generation through the heavy oil cracking process under distinct gas environments is demonstrated. The lower

temperature thresholds for hydrogen generation under different conditions are approximately 350 °C and 400 °C. These values correspond to the pyrolysis reaction within a nitrogen environment and the LTO process within an air environment. All experiments conducted under a nitrogen atmosphere (Exp.#1, Exp.#2, and Exp.#3) exhibit greater hydrogen production and a wider temperature range compared to those conducted in an air atmosphere (Exp.#4, Exp.#5, Exp.#6). These findings suggest that hydrogen molecules follow a preferential reaction pathway with oxygen, leading to a significant higher reaction rate. This phenomenon results in an extensive consumption of generated hydrogen. Consequently, it can be inferred that a higher quantity of hydrogen generation can be achieved when an environment devoid of oxygen or even oxygen-free conditions are provided.

Additionally, the impact of clay minerals and water on the reaction kinetics governing hydrogen generation through in-situ heavy oil gasification was investigated under both air and nitrogen atmospheres. As illustrated in Fig. 3, the incorporation of clay minerals and water yields a notable reduction in the lower limit temperature range for hydrogen production, shifting it from 350–400 °C to 300–350 °C. The catalytic influence of clay minerals is underscored by a distinct decrease in activation energy (E<sub>a</sub>) as well as the lower limit temperature range for hydrogen generation [21]. Water presented in oil reservoir has different manner, including connate water, injected water, and water in residual oil zones (ROZs). Therefore, examining the role of water is essential in understanding the mechanism of in-situ generation of hydrogen through the gasification process of heavy oil in reservoirs with different formation water. Additional hydrogen is generated from water-gas shift and water-hydrocarbon shift reaction in the presence of water [22,23]. Therefore, clay minerals and water could improve the reactivity of the oil and reduce the low limit temperature range of in-situ hydrogen generation.

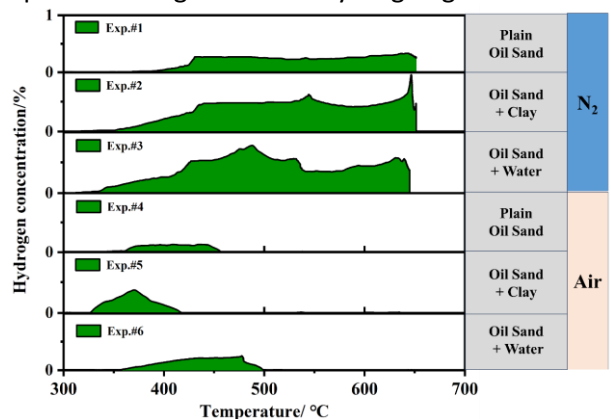




Fig. 3 Hydrogen concentration versus temperature during each experiment.

Fig. 4 depicts the percentage distribution of hydrogen production across different temperature ranges for each experiment. The temperature ranges of hydrogen generation under air and nitrogen atmosphere are 300–500 °C and 300–700 °C, respectively. In a nitrogen environment, hydrogen is generated during both the pyrolysis and coke dehydrogenation stages. Within a temperature range of 300–400 °C, the proportion of hydrogen production remains as only 1.12%–4.56%, owing to the low reactivity of heavy oil. However, between 400 and 500 °C, there is a notable upsurge in the proportion of hydrogen production, ranging from 25.49% to 30.47%. The coke generated during the pyrolysis stage serves as fuel for the subsequent coke dehydrogenation stage. Within the temperature range of 500–700 °C, a substantial amount of hydrogen is generated during the coke dehydrogenation stage. Notably, the proportions of hydrogen production from coke dehydrogenation were 71.91%, 71.66%, and 61.70% for Exp.#1, #2, and #3, respectively. As a result, the hydrogen production stemming from the pyrolysis reaction in a nitrogen atmosphere ranges from 27.10% to 38.05%, while the coke dehydrogenation reaction contributes to hydrogen production in the range of 61.70%–71.91%. Conversely, within an air atmosphere, the proportions of hydrogen generation are zero within the temperature ranges of 500–600 °C and 600–700 °C, attributed to the combustion of coke. Therefore, hydrogen generation only takes place during the cracking stage in an air environment, encompassing the temperature range of 300–500 °C.

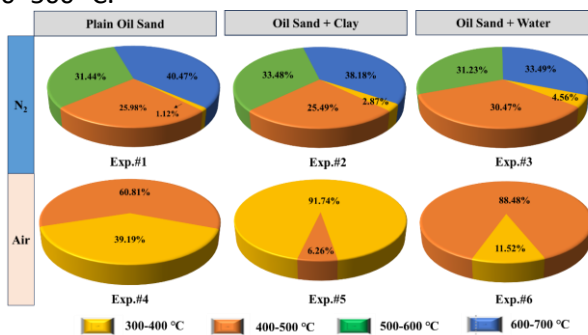


Fig. 4 Hydrogen generation percentage distribution within different temperature ranges.

### 3.3 Comparison of hydrogen production efficiency

Table 3 outlines the pertinent metrics employed to assess the performance of hydrogen generation across each experiment. Notably, the hydrogen generation

efficiency, the hydrogen conversion rate of heavy oil, and the hydrogen yield within a nitrogen atmosphere (Exp.#1 to #3) substantially surpass those observed within an air atmosphere (Exp.#4 to #6). The diminished performance in the air atmosphere is attributed to the consumption of hydrogen generated through heavy oil gasification, ensuing from its reaction with oxygen. Moreover, the average hydrogen production rate within a nitrogen atmosphere ranged from 3.10 to 6.28×10<sup>-3</sup> mL/s, markedly outperforming the corresponding figures within an air atmosphere, which ranged from 0.32 to 0.89×10<sup>-3</sup> mL/s. Within the nitrogen atmosphere, the rate of hydrogen generation exhibited an upward tendency as temperature increased. In contrast, within the air atmosphere, hydrogen generation was characterized by low or even zero rates at higher temperatures, which is a consequence of the combustion reaction of heavy oil.

Tab.3 Analysis for hydrogen production metrics under different atmospheres.

No.	η, %	θ, mL/g	ε, %	V, ×10 <sup>-3</sup> mL/s				
				300-400	400-500	500-600	600-700	over all
E1	12.25	112.56	12.54	0.08	3.43	4.03	4.89	3.11
E2	28.65	262.46	20.35	0.82	6.69	8.60	8.90	6.25
E3	10.49	100.80	25.00	1.30	7.60	7.78	8.47	6.29
E4	9.24	60.64	4.83	0.44	0.78	0	0	0.32
E5	15.66	105.16	7.22	1.86	0.15	0	0	0.55
E6	4.67	33.39	8.94	0.38	3.10	0	0	0.89

Regarding the hydrogen yield, the heavy oil reaction within the nitrogen atmosphere remains incomplete, leading to a diminished total gas production. Consequently, there is a pronounced prevalence of hydrogen-rich syngas. Morphological examination, as depicted in Fig.5, reveals that within the air atmosphere, the oil coating on the surface of quartz sand particles is thoroughly combusted. This combustion leaves behind residual solid particles exhibiting a spectrum of colors, ranging from white to yellow-brown.

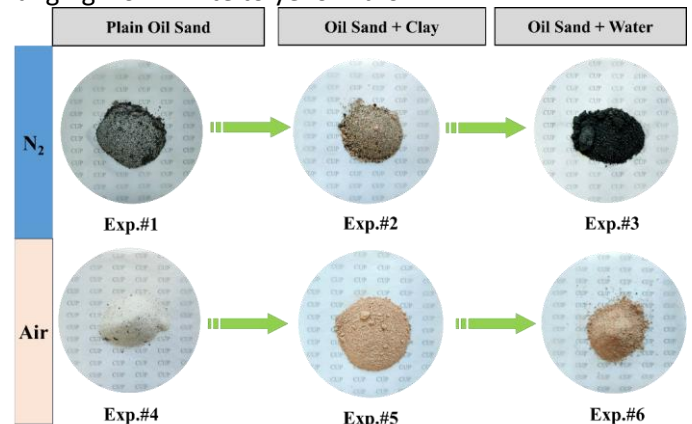


Fig. 5 Oil sand morphology after the experiments.

However, when considering the reaction of the oil sand mixture within a nitrogen atmosphere, the heavy oil primarily undergoes a cracking process. This process generates substantial coke films and solid particles, which adhere to the sand particles.

Fig.6 shows the hydrogen production efficiency of heavy oil under both atmospheric conditions. The efficiency attained within the air atmosphere ranges from 9.24% to 15.66%, which is notably lower in contrast to the nitrogen atmosphere's range of approximately 12.26% to 28.65%. Evidently, experiments featuring the incorporation of clay minerals (such as Exp.#2 and #5) exhibit superior hydrogen production efficiency when compared to the reference experiments conducted without clay minerals. Among all six experiments, Exp.#2 boasts the highest efficiency value at 28.65%.

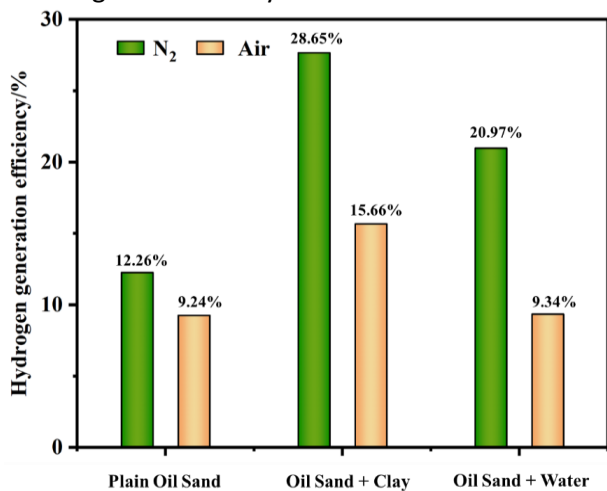


Fig. 6 Comparison of hydrogen generation efficiency in the experiments.

The rationale behind these findings can be summarized as follows: Firstly, the catalytic influence of clay minerals substantially diminishes the activation energy required for reactions, thereby augmenting the rate of hydrogen generation[24]. Secondly, clay minerals feature intricate pore structures and expansive specific surfaces [25], leading to reduced contact frequency between oxygen and combustible gases. This reduction significantly curtails hydrogen consumption. For scenarios devoid of water, such as Exp.#1 and Exp.#4, the hydrogen production efficiency varies between 9.24% and 12.26%. In contrast, under aqueous conditions (Exp.#3 and Exp.#6), the efficiency ranges from approximately 9.34% to 20.97%. This observation suggests that water addition facilitates the water-gas shift reaction process and enhances the reaction rate between water and hydrocarbons.

#### 4. CONCLUSIONS

In this study, a systematic exploration was conducted to assess the impact of air atmospheres on in-situ hydrogen generation through the gasification process of heavy oil. This investigation provides valuable insights for potential modifications in enhancing the underground upgrading performance of late-stage heavy oil reservoirs. The key conclusions drawn from this research are as follows:

(1) Temperature Variation and Reaction Pathways: the analysis of temperature variation elucidates that under a nitrogen environment, hydrogen is generated through both pyrolysis and coke dehydrogenation reactions. The latter, specifically the coke dehydrogenation reaction, constitutes over 60% of total hydrogen generation and occurs within the temperature range of 500–650 °C. Conversely, hydrogen is exclusively produced during the cracking stage when an air atmosphere is employed, spanning a temperature range of 300–500 °C.

(2) Hydrogen Production Efficiency: among the kinetic cell experiments conducted, the hydrogen production efficiency within an air atmosphere ranges from 9.24% to 15.66%. This efficiency is significantly lower compared to the nitrogen atmosphere, which yields efficiencies ranging from 12.26% to 28.65%. These findings imply that creating a "hypoxic" environment or incorporating non-oxidizing gases could potentially enhance the hydrogen production efficiency of heavy oil.

(3) Influence of Clay Minerals and Water: initial findings suggest that the addition of clay minerals and water positively influences hydrogen generation. The introduction of clay minerals and water advances the lower limit temperature for hydrogen production from 350–400 °C to 300–350 °C. This indicates that these additives have the potential to lower the threshold temperature for effective hydrogen generation.

Overall, this study sheds light on the complex interplay between different gas atmospheres and their impact on in-situ hydrogen generation from heavy oil. The insights gained from this investigation offer a foundation for potential strategies to optimize hydrogen production efficiency and the operational conditions within heavy oil reservoirs.

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## DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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