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Thermal hydrogen production from depleted reservoirs: A reservoir-engineering and economic consideration

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ABSTRACT

The subsequent use of depleted oil reservoirs is one of the merging topics for the E&P industry due to the high capital amortization and actually missing reuse prospects. It is claimed that using such reservoirs for hydrogen production might be lucrative due to the emerging demand for sustainable and green hydrogen respectively green energy. The idea behind the processes is to economically utilize the chemical-microbial energy remaining in the residual oil. This paper first discusses the possibilities of further utilization of depleting oil reservoirs in principle, focusing on microbiological and thermal hydrogen production.

We demonstrate that the microbiological processes for the conversion of nutrients and/or oil to hydrogen are technically possible, but they are not economically feasible simply due to material balance considerations. The thermal process for hydrogen extraction is based on a modified in-situ combustion, in which gas production with high proportions of methane and hydrogen is forced by the alternating injection of (treated) air and steam. The process is technically feasible and - under certain conditions concerning fixed costs and market prices - also economical. This basic technical effect has already been proven in field tests in up to 20 $\%_{mol}$ hydrogen in the produced gas phase for a depleted bitumen reservoir. Similar effects were also found in other thermal tests on drill cores with up to 50 $\%_{mol}$ hydrogen.

We further investigate the technical and economical boundary conditions of the thermal hydrogen production process from depleting oil reservoirs. Based on these conditions, process designs are defined and evaluated based on recent publications, patents, and simulations. Considering the current state of knowledge as well as the results of the reservoir engineering investigations, the industrial applicability is shown and discussed. The workflow for the process application is presented. It starts with the laboratory evaluation, which is based on the knowledge of the physical - determination by oil sample testing with correlative history matching - and chemical - determination by combustion tests in drill cores with simulative accompaniment - behavior of complex component and phase mixtures enabling the mathematical description of related phenomena in porous media. In preliminary tests, upscaling is applied to generic reservoirs by means of successive coupling of the results of reservoir models with huff-and-puff tests.

EXTENDED ABSTRACT

Introduction

The exploitation of oil reservoirs takes place in primary, secondary and tertiary production phases. However, even after this intensive exploitation of the oil reservoir, a significant fraction of the oil (30-80% of the OOIP) usually remains within the reservoir. Because of this, there are currently many reservoirs that are at the limit of depletion or have already been depleted. The further use of these reservoirs therefore plays a key role for the oil and gas industry.

Feasible options for depleted oil reservoirs are abandonment (termination of production and quit), use for geothermal applications (normally not feasible due to technical restrictions), CO_2 storage and utilization (CCU and CCS, normally more feasible in depleted gas reservoirs), and further use of the residual chemically bound energy content of the reservoir through hydrogen production. The hydrogen production is characterized by the fact that a further use of the reservoir for energy supply as well as the surface facilities and the further existing infrastructure is made possible.

This work intends to provide a short review of the potential ways of producing hydrogen from depleting and/or depleted oil reservoirs. In this context, thermal hydrogen production is presented and evaluated as the only technical and economical method. Based on this, the paper shows the further path of the methods investigation to achieve an application in the large-scale field.

Methods for producing hydrogen from depleting oil reservoirs

In general, there are three methods to produce hydrogen from depleting oil reservoirs. While the thermal method for hydrogen production is based on adjusted partial oxidation reactions (POXY), the microbiological methods are based on the metabolization of nutrients and in case of the biogeneration on the metabolization of oil.

The thermal generation of hydrogen is based on the generation of a high temperature in the reservoir. This temperature leads to reactions, which are producing hydrogen or synthesis gas [1]. Therefore, in most cases an in-situ combustion or high-pressure-air-injection is applied to the reservoir [2, 3]. The main advantage of the thermal generation of hydrogen is that the method is already demonstrated in the reservoir format [4, 5]. The method is legally protected for the hydrogen production through in-situ membranes [6], synthesis gas production [7] and as extended EOR measurement [8]. The method will be introduced in detail in the following chapter.

The biogeneration of hydrogen is based on the metabolization of triggering nutrients and the oil present in the reservoir, as suggested and discussed by various references [9–11]. The method is due to the existing (indigenous) bacteria in the reservoir and the fact that the most of bacteria is found in the water phase limited. Therefore, the efficiency of the method is strongly depending on the interfacial contact between the oil and gas phase. To make the process more efficient the application of surfactants is suggested. But still, due to the restrictions by the biochemical reaction rates, the method is highly uneconomically. It is affirmed that this disadvantage can be solved by increasing metabolization offer of the oleic compounds. So far, the hydrogen yield of the process is as low as 0.004 kg H_2/kg glucose [12–14]. The method is protected as a subprocess of general EOR processes [15].

The dark fermentation of nutrients to hydrogen is based on the idea of generating a biochemical reactor inside the reservoir [16, 17]. But the evaluation of the reactions resulted that the related reactions even in an ideal reactor with a complete metabolization cannot produce hydrogen economically; even the costs for the necessary nutrients are more than ten times higher than the potential earnings by the hydrogen formation for the ideal case [14]. Because the process is dependent of the microbiological energy source, the process cannot be further improved.

Thermal hydrogen production from depleting oil reservoirs

For the thermal process of hydrogen production air or the other oxidizing agent (oxygen) is injected from the deepest point of a well adjacent to the reservoir of interest to allow the highest possible recovery of the resulting synthesis gases close to the sealing rock. Decisive factors for the success of the process include the highest possible permeability as well as formations free of faults and fractures. A heterogeneous permeability distribution would lead to unfavorable, uncontrolled fire progression, therefore homogeneous formations are advantageous. To enable the injection of a catalyst, an alternating injection of water/steam and gas (i.e., air) must take place. The water is the carrier of the catalyst, which is added to the injected water in powder form. The process is thus similar to "wet combustion", since water and gas are injected simultaneously. The main reactions of the process are defined by Murthy et. al. (2014) for laboratory conditions [18] and by Hajdo et. al. (1985) for the test field combustion [5]. The most important reaction with an impact on the hydrogen production is the coke gasification under steam conditions above 250°C [5, 18]:

$$C + CO_2 \leftrightarrow 2\,CO \tag{1}$$

$$C + H_2O \leftrightarrow CO + H_2 \tag{2}$$

Murthy et. al. (2014) 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 [5]:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{3}$$

The methanation processes result in methane (CH_4) rather than H_2. Methane is produced in field trials in similar quantities to hydrogen [5]. It is mentioned that in core flooding experiments the methane production is more likely than the hydrogen production [19]:

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

The thermolysis or thermal cracking is the process, in which hydrogen is produced by thermal effects [1]. However, it should be mentioned that this represents at most 10% of the total hydrogen produced [5]:

$$C_nH_m + n/2\,O_2 \rightarrow n\,CO + m/2\,H_2 \tag{5}$$

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 takes place.
- The coke reacts 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 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:

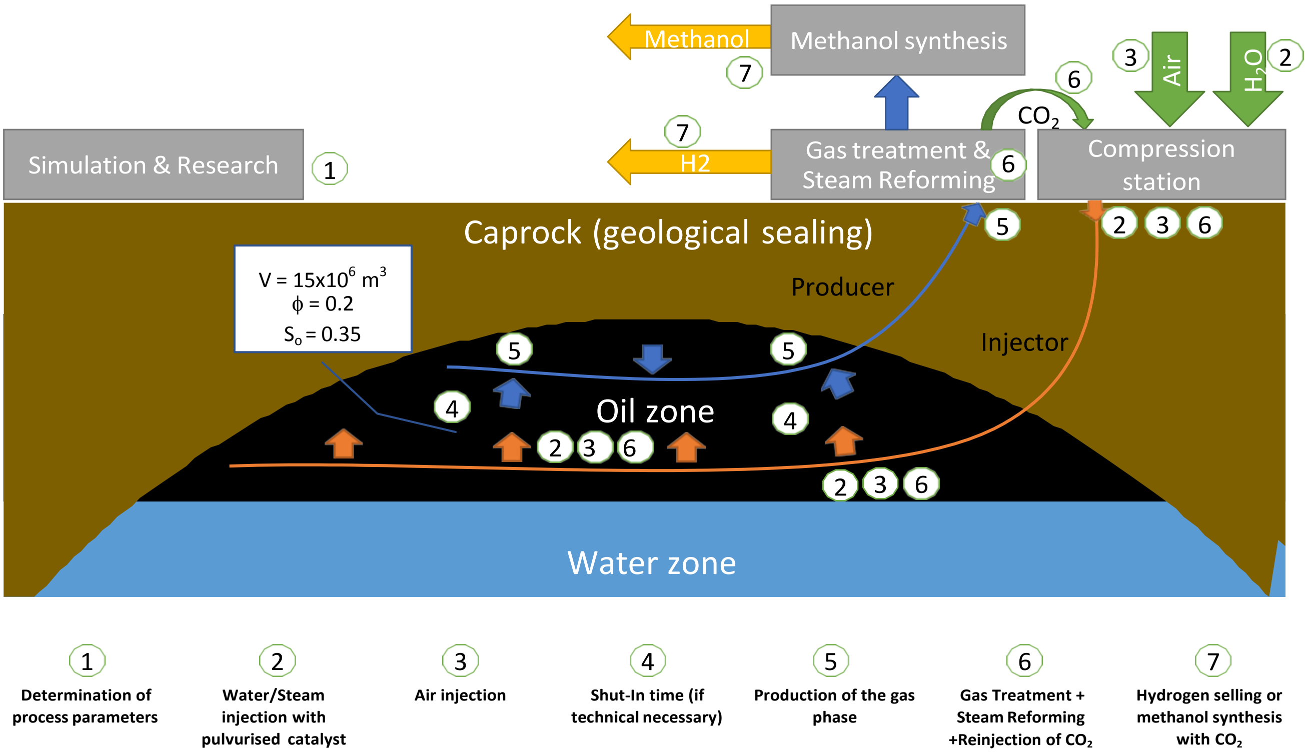

Figure 1. Process description of the thermal hydrogen production at the generic reservoir model

The process starts with the research on the process as well as simulations (1) of the field specific application. Based on the results of (1) steam and/or water with a pulverized catalyst is injected deep into the reservoir (2). This step is followed by the injection of (enriched) air or another oxidation agent (3). A shut-in time should be allowed based on the results of the simulation and the corresponding well data (4). To avoid a decrease in relative permeability, the water vapor should not condensate in the reservoir. The production (5) is started with small rates, due to fact that the gas phase recovery in the reservoir is preferred. As a result of the application, extended oil production can be expected due to the high temperatures of in-situ combustion, even for reservoirs previously considered depleted (by usual enhanced oil recovery (EOR) methods) reservoirs. The main surface process steps are the standard treatment of the produced fluids (6) and the special treatment for the hydrogen recovery in step (7).

Technical evaluation

For the assumption of a reservoir, as in Figure 1, with a porosity of 20% and a residual oil saturation of 35%, a formation of about 500 Nm^3 hydrogen from 1 m^3 crude oil can be assumed for the most optimistic case based on the values explained above [14]. For a reservoir with a total volume of approx. 15 x10^6 m^3, an oil quantity of approx. 1.05 x10^6 m^3 can be assumed, the amount of hydrogen formed would then be 5.25 x10^8 Nm^3. In the case of the application of an in-situ combustion, the recovery efficiency is correspondingly high, since usually a pure gas phase with high temperature can be achieved. Here, therefore, a recovery efficiency of the hydrogen of about 50% could be applied, i.e., a recovery of about 2.63 x10^8 Nm^3 hydrogen would be feasible in the case of optimal heat efficiency. In other methods, in particular non-gasification processes, the recovery efficiency is correspondingly lower because of critical gas saturation and relative permeability.

Assuming a molar weight of the oil of 600 g/mol and a bulk density of 850 kg/m^3, the molar quantity of the oil can be calculated:

$$n_{Öl} = V_{Öl} * \rho_{Öl} * 1000/m_{m,Öl} = 1.49\ x10^9\ mol \tag{6}$$

Based on this, the upper and lower necessary amount of oxygen can be determined on the basis of guideline values such as 30-50 mol of oxygen per mole of oil and thus the lower and upper amount of air to be injected. This can be used to determine the necessary work on the basis of the necessary compression pressure over the isentropic compression [20].

For corrosion protection reasons, cooling must be carried out during compression depending on the maximum injection temperature. However, this is not significant compared to the necessary compaction performance. The assumption of an overall electrical efficiency of 50% results in the electrical work per standard cubic meter of hydrogen.

In addition, the process must include extraction and treatment of the gases produced, but this should only be done at a 100% markup on the expected amount of energy. Basically, gas compressions represent the most energy-intensive processes here, so the energetic consideration is mainly made about it.

Economic evaluation

Table 1 gives an overview of relevant capital expenses (CAPEX) and operational expenses (OPEX). Unfortunately, there are not sufficient scientific publications on the economic parameters. It is assumed that the wells as well as the pipeline infrastructure are existing (see last line), 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 CH_4 are 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.

Table 1. Investment and operation cost

CAPEX	**OPEX**
Air compression	
Compressors for air & CO_2 Conversion costs	Electrical energy for compaction Maintenance costs for the compressor station Personnel costs Consumables
Gas treatment & Hydrogen production	
Hydrogen separators Steam reforming reactors (Methanol synthesis unit)	Electrical energy Heat energy Maintenance Personnel costs
Others	
Raw material utilization costs Consulting Research	Legal costs General administration
Assumed already existing infrastructure	
Wells (being more effective in horizontal directions, should be considered in most of the cases) Completion (mostly to be considered, as OPEX) General allowance for raw materials extraction (as OPEX) Gas treatment unit (as CAPEX)	

Application limitations

The general evaluation of the process is provided in **table 2**. Although the process itself has already been technically evaluated in the form of a reservoir application, more research is needed, particularly with respect to (industrially viable) quantities of hydrogen to be offered to the 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.

Table 2. Results of the study

Parameter	**Process evaluation**	**Explanation**
Technical feasibility	☑	The technical feasibility was proven [5].
Technology readiness level (TRL)	3-5	The technology is still in research. R&D focuses on laboratory tests and numerical simulations.
Economic feasibility	☑	Assuming infrastructure and knowledge are already existing, it can be economically feasible.
	Reservoir types	
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 cause of the energy in place therefore hydrogen yield is insignificant.
	Reservoir properties	
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	Higher permeability is needed for the alternating injection of high rates of water/steam and air.
P (bar)	-	No limitation
T (°C)	25 – 150	Depending on the temperature of the reservoir, ignition takes place as self-ignition or artificially.
S_o	>30%	High oil saturation is necessary for 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	☑	

Workflow for the process application

In the following a workflow for a complete feasibility study of the process is presented. This complex task cannot be considered by an analytical approach but must be solved by a combination of experimental and numerical simulations in addition to reservoir data. The following steps must be taken in the order as provided in **table 3**.

Table 3. Investigation design in six steps

1

Chemical sampling

In order to correctly estimate the properties of the oil, especially for chemical processes. In general, this is already available for depleted reservoirs.

2

Core heating and combustion tests including complete gas chromatography

The core testing provides data for the numerical tuning and relevant reaction parameters in porous media. Accurate imaging of the p-T conditions and the injected media are essential. Furthermore, to register higher-value gases and evaporating petroleum components, it is necessary to perform complete gas analysis.

3

Adjustment of parameters and kinetics based on the measured values in 3.

Based on the experimental data, the simulations can be further improved. This includes in particular the reaction kinetics, which describes both the various reaction products and the heat of reaction. Without these values, a simulation of the reservoir is only possible under severe restrictions, especially because of the geomechanically safety as well as the drilling integrity. Furthermore, an accurate estimation of necessary target temperatures is only possible within the framework of previously carried out sampling and measurements.

4

Simulation of relevant operations-based parameters from 4.; verification of geomechanically safety and well integrity

Based on the data from the core tests, the individual processes for the reservoir are upscaled and implemented into the reservoir model. A central part of the process review is studies on geomechanically stability and well integrity.

5

Execution of reservoir trials

The simulated process is carried out at the reservoir in interest at pilot scale. The aim is to validate and adapt the data of previous steps. In particular, it should also be emphasized here that in the context of combustion processes, further oil production can be expected in addition to the production of synthesis gases due to the high temperatures reached and the associated chemical and physical processes.

6

General evaluation model of economic and technical feasibility at field scale

Based on the field pilot carried out and the resulting database, a field model for technical and economic evaluations of the process is to be established.

Results

In the paper, hydrogen production from depleted oil reservoirs is evaluated and presented in a general sense. Thermal hydrogen production is identified as the only technical and economically feasible process. Therefore, this process is further evaluated in terms of technical and economic parameters. The complex procedure up to the applicability in the field has been shown. The knowledge of the method as in-situ combustion, which is a frequently used method for heavy oils, has a simplifying effect here.

Discussion

The methods presented in the paper are subject to the usual limitations of their assumptions and methods. These include the use of the generic reservoir model and the approximate calculation of chemical and physical processes. The evaluation of all proposed methods for hydrogen production from depleted hydrocarbon reservoirs including quantification of hydrogen yield is planned for a next publication.

Conclusion

The paper starts with the introduction of several methods for producing hydrogen from depleting oil reservoirs. Therefore, the thermal method, based on a modified in-situ combustion, the biogeneration, which is based on the fermentation of oil components to hydrogen, and the dark fermentation of nutrients is introduced. But only the thermal method is economically feasible, so the paper focuses on that.

The thermal method is introduced by a preferrable process design and a generic model. Based on that the application limits are shown. Also, the CAPEX and OPEX of the process are shown as a qualitative model. The paper ends with the path for the industrial application of the method.

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