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The H₂ potential of the Colombian coals in natural conditions

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ABSTRACT

Coal gasification to manufacture dihydrogen (H₂) has long been known as a surface process. Recent works have also highlighted the H₂ generating potential of the Organic Matter (OM). The evolution of OM generates H₂ all along the process but this gas is only expected to remain as free H₂ after the maturation and expulsion of the hydrocarbons (HC) which means at a high temperature of above 200 °C. In this paper we studied the potential of three different tertiary coals from Amaga, La Jagua de Ibirico and Barrancas, all located in Colombia. Their H₂ yields were studied using a pyrolyser and the kinetic of the H₂ generation were quantified. All the studied coals are immature to early mature as source rock (SR) with large TOC content, between 66 and 83%, and good H₂ potential. The highest values were found for the Barrancas area where the potential reached 25 mg H₂/g TOC. The temperature corresponding to the peak of H₂ generation is between 740 and 800 °C depending of the heating rate. This corresponds to the 200–300 °C for the H₂ kitchen, even if the H₂ generation starts before as already observed for continental organic rich source rock. Comparison with the other coals shows that H₂ potential is linear with TOC. In the Colombian coals, the H₂ yield in mg H₂/g of rock is around 1/4 of the TOC content. In average, these coals have so a H₂ yield about 10 000 mmol H₂/kg of rock, two orders of magnitude above the “best” olivines. It should nevertheless be kept in mind that the extrapolation of these laboratory data to sedimentary basins remains unconstrained and will need to be refined when well data and modelling tools are available.

1. Introduction

Until now, the dihydrogen, H₂, has been mainly manufactured from natural gas, coal and oil or is a by-product of the chemical industry. This situation is evolving with the emergence of decarbonized H₂ such as that produced by electrolysis (known as green H₂) and the natural H₂ from subsurface (known as white). Its use is also changing. Until now the H₂ has mainly been a raw material for fertilizers and other chemicals. Its potential as a fuel is now being tested, not only for rockets but also for everyday use in cars, buses or trains; its use in industry, particularly for decarbonizing certain processes, is also promising. This development calls for a major increase in H₂ production and various technologies and ideas are being tested. This article looks at the H₂ generated naturally from coal by the temperatures in subsurface and aims to compute the kinetic of these reactions and therefore the depth of H₂ kitchen in sedimentary basins.

1.1. Coal and H₂

1.1.1. Surface processes

The fact that heating coal generates a gas containing high level of H₂ has been known for over 200 years. The so-called “town gas” which refers to the gas that has been distributed for the lighting and then the heating since the first part of the 19th century in the cities was extracted from coal. Initially it was even produced by burning wood: Lebon invented the lighting gas in France in 1785 and built the first installation in Paris in 1801 [1]. Few years later, the English (Murdoch) and German (Winsor) scientists realized that coal gave better results and coal supplanted wood everywhere. The major advantage of gas over wood and coal is that it can arrive “on its own” through a pipe, whereas solid fuels have to be transported and supplied by workers.

Town gas could be a by-product of coke manufacture (Fig. 1A). But it is often manufactured for its own sake, it is the coal gasification process (Fig. 1B). This synthetic gas contains around 50% of H₂, 35% of methane and up to 10% of CO. It was gradually abandoned when large natural gas

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discoveries provided a better solution. Town gas contains CO which is a lethal gas. The switch to natural gas took place around 1950's in the US but only in the 1970's in UK. In some major Asiatic cities such as Hong Kong and Singapore, gas is still manufactured from coal. Today coal's ability to generate H₂ is used in surface processes. China which is the world's leading H₂ producer has generated 60% by coal gasification although the process of producing coke and thus coke oven gas still exists (Coke Oven Gas Hydrogen, Fig. 1A) [2]. At the world level this percentage is only 19% and the majority of H₂ comes from methane and water by steam methane reforming process.

1.1.2. Underground Coal Gasification (UCG) processes

In the early 20th century, many industrial towns were covered by thick clouds of smoke - a side effect of the Industrial Revolution, which was made possible by the use of coal. At that time, an eminent British scientist, Sir William Ramsay, ahead of his time, declared that the threat of smoke could be combated by ceasing to mine coal to burn it. He considered in-situ coal combustion and the use of the resulting syngas as a better solution to energy needs. Today, this process is known as "Underground Coal Gasification" (UCG). At the beginning of the 20th century, thinkers and politicians also saw this technology as a way of preserving the lives of miners [3] and many of the first pilots were done in Russia in the years 1925–1950 [4]. The problem of fumes diminished in the second half of the 20th century. This positive change was due to the replacement of coal by more harmless fuels (oil and gas). UCG, whose development in the 20th century was limited by the discovery of large oil and gas reserves, did not play a significant role in these improvements.

However, history tends to repeat itself, and the pollution over China's major cities indicates that the old problem of smoke is reappearing. In addition, much of the negative LCA (Life Cycle Assessment) of H₂ from coal is due to the extraction. If technically and economically feasible, the in-situ combustion should solve this problem. Coal mines are generally open-pit or near surface, the in-situ combustion also has the advantage to enabling deep coal seams to be mined. Countries that do not want to continue to exploit coal even though they have large reserves, such as USA [5] also develops pilots. Today China is taking the lead with many patents and more than 20 pilots since 1990.

These processes are also being closely examined in oil-sand-rich countries like Canada. Today, to manufacture light oils from bitumen,

one uses H₂ manufactured from gas. Including bitumen production, that makes 3 fairly dirty stages. In situ bitumen gasification process is therefore studied [6]. They make it possible to produce H₂ at less than 2 \$/kg [7].

1.2. Organic matter and gas

Organic matter maturation is known to follow the Arrhenius law [8] meaning that the rate of generation is only dependent on the time and temperature. The kinetic parameters being constant, it is possible to study reactions at high temperature, by applying a high rate of temperature gradient (1–25K/min), use these results to calculate what Mother Nature does in a few millions of years (at low gradients of 1–10K/My). As a result, pyrolyzers that heat organic matter at few hundred degrees in 20 min allow us defining the characteristics of a source rock that generates oil and gas between 100 and 150 °C in the range of 10⁶ years. It is used daily in the O&G industry to model fluids generation from the source rocks and to allow predictions of the accumulations. As coals are mined, their capacity to generate fluids at depth is less systematically studied.

Knowing that coals generate hydrogen at high temperatures in coke plants, as in UCG, we also can study their potential to generate this gas under natural conditions. This alternative to the water-rocks interaction (oxydo-reduction and radiolysis) to generate natural H₂ has been already proposed for the Songliao Basin in China [9] and for the Cooper basin in Australia [10]. Their conclusions are rather positive: in both cases the amount of H₂ that could be generated between 200 and 250 °C in the deepest parts of the basin by the buried coals and shale is significant: 4631 Gt of H₂ resources in the Songliao Basin [9] and 35 Gt in the Cooper Basin [10]. These two basins are oil and gas producing provinces.

The H₂ generation from OM is complex, H₂ plays a role in HC formation and the probability of this H₂ remaining as free gas is discussed in various papers [9,11]. Open pyrolysis most likely overestimates the H₂ yield by preventing certain reactions. Li et al [11] showed that in an open system pyrolysis the H₂ generation can start early, before 300 °C and exhibit various maxima. However, the pattern is simpler for coals which show a single peak of H₂ generation. In the present study in order to start developing a data base on the OM potential for H₂ generation, we sampled coal directly from 3 coal mines to investigate their potential,

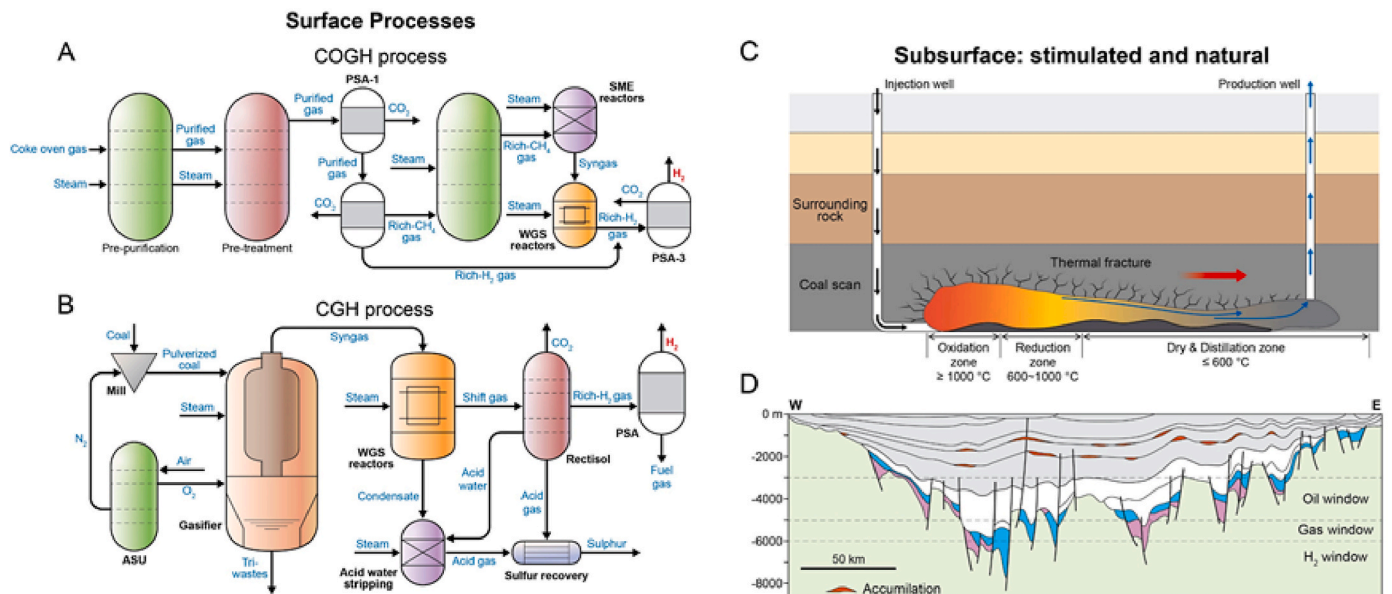


Fig. 1. Various ways to produced H₂ from coals, both in surface or in subsurface (A) COGH: coke oven gas-based H₂; (B) CGH coal gasification H₂; (C) Underground coal combustion – oxidation + pyrolysis (D) H₂ generation from late maturation of rich organic matter - pyrolysis.

and differences, as H₂ generating rocks. These coals are all Cenozoic and come from the 3 main mines in Colombia. Their H₂ potential was studied with a Rock Eval analyzer coupled with an H₂ detector. The kinetic order of the reaction was verified and the kinetic parameters studied. To begin, we summarize the conditions under which coals can generate H₂, high-temperature pyrolysis in the absence of oxygen, as studied with a Rock-Eval, being just one of them. We then present the new analyzer that has been developed. The second part of the article is a case study of the Colombian coals and we conclude with a comparison with already published values for the H₂ potential of organic matters.

2. Hydrogen-Eval principle

Natural H₂ may be generated in subsurface by various processes. Following the nomenclature introduced by Lévy et al. [12], the main reactions are the oxidoreduction of oceanic lithosphere (H₂_GR1) or iron rich sediment (H₂_GR2), the radiolysis (H₂_GR3) and the late maturation of organic matter (H₂_GR4). Quantification of the remaining potential for the H₂_GR1 and H₂_GR2 is based on the iron content and the characterization of the Fe²⁺ containing minerals. Today this characterization is still time-consuming and requires different levels of observation, from macro to micro. For the H₂_GR4 the characterization of the source rock, as usually performed for the oil and gas exploration, could be carried out rapidly using a pyrolyzer such as the Rock-Eval [8]. The process takes 20 min and requires just a few mg of rock, enabling measurement to be taken with good density across the entire thickness of the source rocks, particularly from cuttings. More than a hundred per well is not unusual. The overall principle of the pyrolyzer is to heat the sample at a given rate of temperature rise and to measure the generated effluents.

Concerning the H₂ potential of iron rich rocks (H₂_GR1 and H₂_GR2), given that the water/rock interaction, especially the oxidoreduction is temperature-depend, it may be possible to use a pyrolyzer to measure the H₂ generated. However, in the Rock-Eval the carrier gas used to heat the

sample and transport the generated HC is dry. It is a dried N₂ (Fig. 2). A first pilot has been done to inject in contrast wet N₂ and to measure the generated gas as a function of time and therefore temperature. Initial results were presented in July 2023 (Moretti et al., 2023) and a patent has been applied (N° FR2305855).

With regard to the H₂_GR4, the organic matter late maturation has been already studied with an open system pyrolyzer coupled with a GC to quantify the H₂ [9,11] and a yield of 20 mg H₂/gTOC was proposed for the Songliao SR, the TOC was low, 1.37%. In Australia, Malhstedt et al [10] proposed using half of this value for the Cooper basin SR which is a type I lacustrine SR with coal beds. Li et al. [13] also studied this H₂ generation from shale during a closed system pyrolysis; the oven temperature was limited to 600 °C and the curves clearly showed that it is not sufficient to study the complete evolution of OM. The H₂ generation starts to increase at 550 °C, but since the maximum is not reached at 600 °C, the potential cannot be calculated (see Fig. 2 in the [13] paper).

In order to determine the H₂ generating potential of the Colombian coals, an experimental Hydrogen-Eval prototype has been designed starting from a Rock-Eval 7 sulfur multi-gas (RE7S-MG). The RE7S-MG is the latest version of the Rock-Eval 7 enabling the detection of several new gases including methane, wet gas (based on butane detection) and water during pyrolysis [14]. Due to the high temperatures of H₂ generation during pyrolysis of organic matter, the oven used was the Rock-Eval 7 oxidation oven. This oven is made of ceramic and designed to withstand temperatures of up to 1200 °C. The carrier gas is still nitrogen. The detector used for hydrogen detection was a TCD (Thermal Conductivity Detector). Therefore, this detector is not only selective to the H₂, when using nitrogen as carrier gas, hydrogen is luckily one of the gases that best responds to TCD, along with helium. As helium is generated by radioactivity, and this reaction is slow, this gas is very unlikely to be generated and detected at the output of a pyrolyzer, but it's good to be aware of this selectivity. It is then possible to obtain hydrogen curves from the TCD. However, interferences are possible with

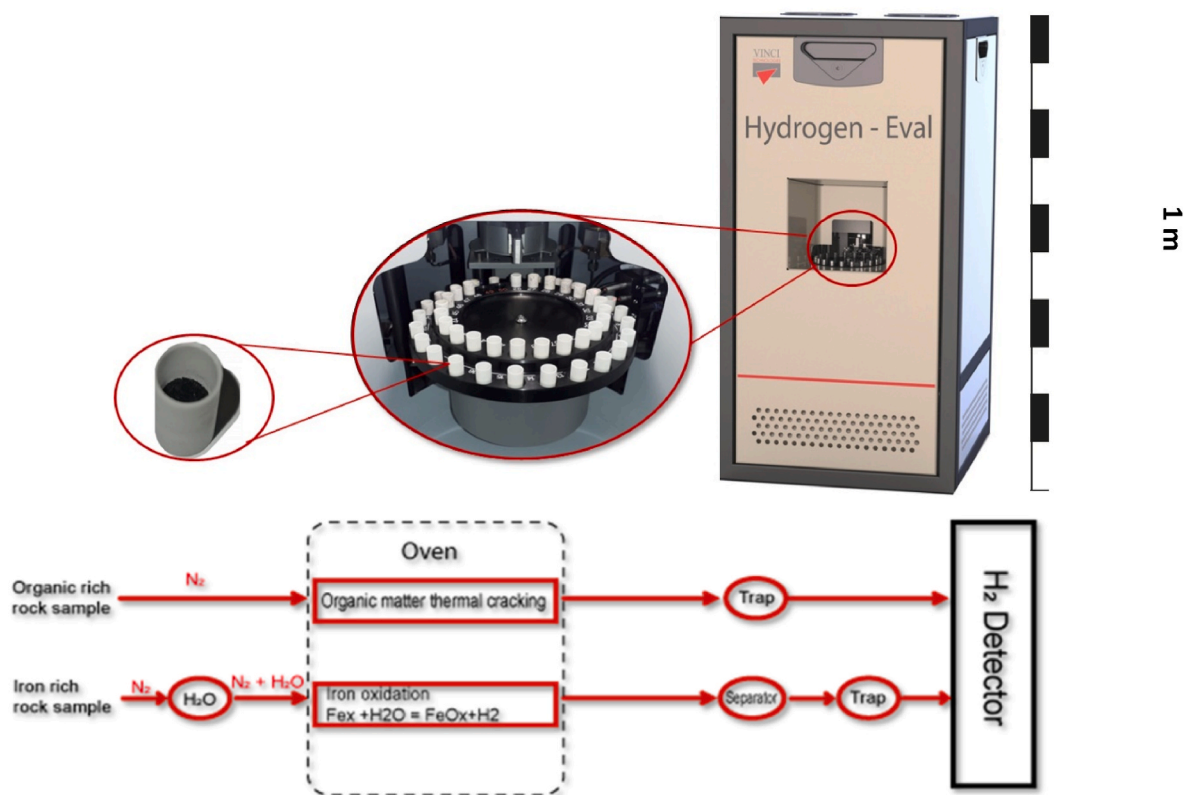


Fig. 2. Hydrogen Eval principle. As for the Rock Eval, a few milligrams of rock are placed in the crucible, which is heated in the furnace by a hot gas, dried nitrogen, to study the organic matter, and wet N₂ to study the reaction of oxidoreduction. The blend of generated fluids is then analyzed.

other gases such as gaseous hydrocarbons, CO₂, CO or water. For these reasons, certain chemical compounds need to be added to eliminate or at least to reduce these interferences. For the signal quantification, a H₂ specific calibration was performed using different concentration of H₂ inside a nitrogen matrix. Finally, an Elemental Analysis (EA) was carried out on one sample in order to validate Hydrogen-Eval quantification by performing analyses before and after 3 different pyrolysis steps.

3. H₂ from coal in natural context

Coals can generate H₂ through two reactions: (1) a low-temperature oxidation in presence of oxygen (usually air) and (2) high-temperature pyrolysis without oxygen.

3.1. Oxidation

Coal oxidation leading to spontaneous combustion it is a major hazard for underground coal mines [15]. The gas generation depends on temperature and coal rank. In the laboratory, the amount of H₂ released at 100 °C is about 15 ml 10⁻⁴ of H₂/g of coal for bituminous coal but only half of that for lignite. The rate of H₂ release increases by 2 orders of magnitude as the coal temperature rises from 60 to 200 °C [15]. In outcrops, this oxidation also leads to H₂ emanations and fires on the old slag heaps of abandoned mines. This oxidation is used to initiate to UCG and therefore increase the seam temperature, but the reaction cannot take place in an oxygen-free environment. On the other hand, mining activities can trigger this oxidation by bringing in air and therefore oxygen into the subsurface.

3.2. Pyrolysis

At higher temperatures, the coal pyrolysis generates some hydrocarbon, mainly methane, followed by H₂. This reaction requires no oxygen and can take place naturally in deep basins. We have quantified this with our new high-temperature Rock-Eval pyrolyzer coupled with an H₂ detector.

Initial tests were carried out to ensure that Arrhenius' law was adequate for H₂ generation, and that the methods used to deduce the characteristic parameters (content and kinetics) were valid. Fig. 3 shows the H₂ generation for different quantities of coal. Regardless of the method used (H₂ leak detector or TCD) the peak position of the H₂ generation maximum is independent of the quantity. The fact that the temperature of the H₂ generation peak is constant obviously has implications for the reaction kinetics, which we will investigate later. This linearity also implies that we can calculate a H₂ yield per g of rock, or per g of TOC.

During method development, we used two external commercial

detectors, the GA5000 and the VARIOTEC 460. These sensors have variable response times and measurement frequencies, making them unsuitable for continuous gas flow measurement. In addition, they have an internal pump, mandatory for the classical operating mode of soil gas measurement, but that requires dilution and correction when the H₂ flow already exists, as is the case at the pyrolyzer outlet. We have therefore chosen to calibrate the TCD (Thermal Conductivity Detector) curves with different hydrogen concentrations to be able to convert the TCD signal from mV to ppm of H₂ and the results presented below are as follows.

4. Coal in Colombia

In Latin America, Colombia boasts large reserves of high-quality bituminous coal, and the mining sector is active. Major open-pit operations, including those in La Guajira and Cesar, are in operation, as are underground mining operations in Antioquia [16]. For the purpose of this study, we sampled three coal provinces presented Fig. 4.

- (1) The Amagá Basin is situated in the northwestern Andes and resulted from tectonic interactions involving the South American, Caribbean, and Nazca Plates [17]. The studied coal sample comes from the "Carbones San Fernando S.A.S." mine located in the "Paso Nivel" sector within the municipality of Amagá, in the department of Antioquia. This municipality, positioned on the western flank of the Central Cordillera, is around 38 km from Medellín [18].

The Amagá Formation is a late Oligocene to mid-Miocene siliciclastic succession deposited across various sedimentary basins under a tropical climate [19]. The coal derived from this formation is classified as sub-bituminous [20].

- (2) La Jagua, Mine Calenturias and la Jagua, Cuervo Barco Formation, Paleocene

The La Jagua open-pit coal mine is located in the municipality of La Jagua de Iberico, in the department of Cesar, Colombia. The mine is owned by three companies: Carbones de La Jagua S.A., Consorcio Minero Unido S.A., and Carbones El Tesoro S.A [21]. The coal deposit was formed during the Paleocene-Eocene and is located in the La Jagua syncline. The coal from the mine is subbituminous [16].

- (3) Cerrejón mine, Guajira, Paleocene, sub-bituminous,

The Cerrejón Formation is located in the Cesar-Ranchería basin, bordered to the northwest by the Sierra Nevada de Santa Marta and to

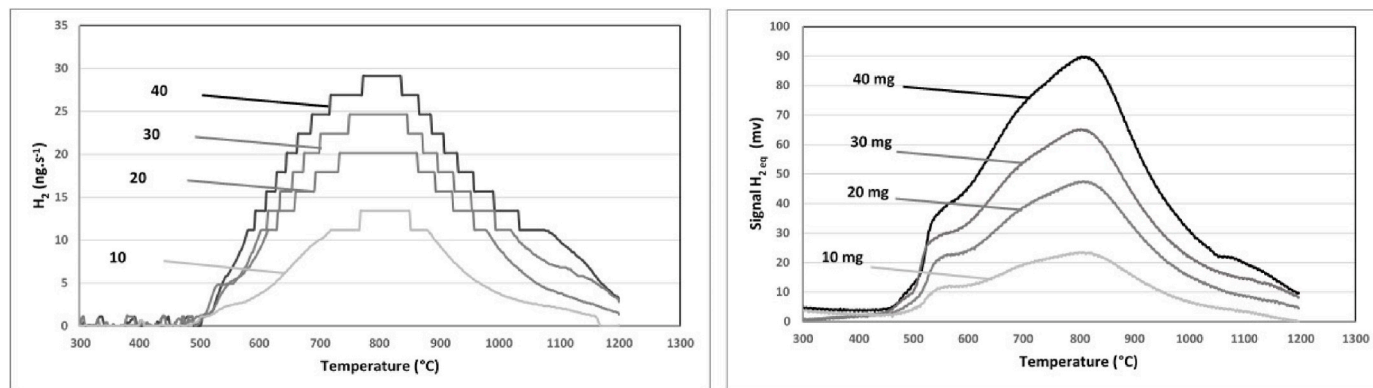


Fig. 3. H₂ generation from various masses of coal COA3 (from 10 to 40 mg). Left: measured from an H₂ detector (Variatoc) connected with a pyrolyzer. Right: FID. In both cases the pick ($T_{max\ H_2}$) is independent of mass. The different vertical scales will be discussed later. The steps on the Variotoc curves are due to the fact that the sensor operates in 2 ppm increments above 10 ppm.

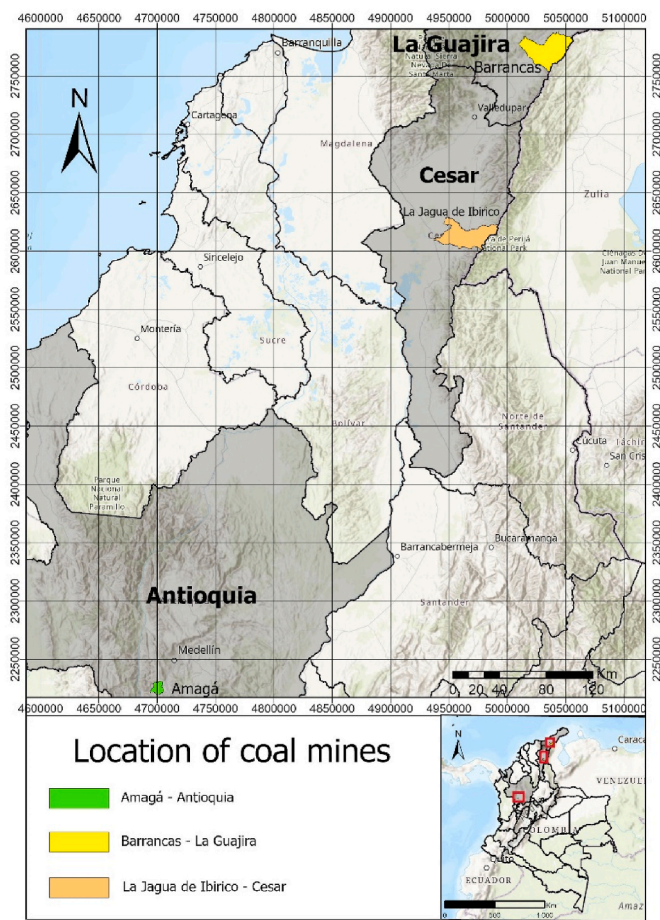


Fig. 4. Map of Colombia with the three studied coal rich areas.

the southeast by the Cerrejón Fault, which in turn borders the northwest of the Serranía de Perijá [22]. It is an open-pit mine, the coal deposit is Paleocene in age and of the subbituminous type [16]. The Cerrejón Formation is composed of approximately 80 coal seams [23], in contrast to other deposits where the number of seams is commonly around 10 (Australia; [24], South Africa; [25]).

5. Coals geochemical properties

Samples of these three coals were analyzed with the Rock-Eval 7 Sulfur device [26,27] at Vinci Technologies to determine the geochemical parameters (Table 1). Coal samples from the first two mines Antioquia (COA1) and La Jagua (COA2) are both largely immature as SR with a Tmax below 430 °C, which is the most accepted common limit for the oil generation. By contrast, the Cerrejon Fm coal (COA3) has started its maturation and is in the early oil generation window. All the coals studied are terrestrial coals and the associated kerogen is type III.

All the coal samples have a high TOC content (>65%) which is usual for coals (Table 1). Sample COA3 from the Cerrejon Fm even reaches the

Table 1
Characteristic of the studied coals.

Samples	S1 (mg/g)	S2 (mg/g)	Tmax (°C)	HI	OI	OMTP	TOC (%)	MINC (%)	Total S (%)	SI
COA1	2.2	172.1	410	267	8	3	66.5	0.1	0.5	4
COA2	1.7	164.4	426	235	4	3	70.4	0.01	0.6	1
COA3	3.3	309	441	372	4	3	83.1	0.02	4.8	9

S1 Quantity of HC generated/liberated before 300 °C. S2 Quantity of HC generated during the pyrolysis. HI Hydrogen Index, OI oxygen index, OMTP Organic Matter Type, TOC Total Organic Carbon, MINC Mineral carbon, Total S: percentage of sulfur in mass, SI Sulfur Index. See Ref. [28] for more details.

theoretical maximum TOC value for a rock sample, i.e. 83%. According to the S2 values, the hydrocarbon potential is important for all the samples but classical for coals. The COA3 sample, with a S2 value of 300 mg/g, is still notable with 30% of its weight, which can be convert into hydrocarbons.

Sulfur content is an important parameter to consider while performing kinetic studies of kerogens, and especially the origin of the sulfur whether it comes from mineral compound such as pyrite or from the organic matter itself. Indeed, the presence of sulfur can lower the Activation Energies and enable the generation of hydrocarbons at lower temperatures [29]. The coals studied all contain a small fraction of sulfur, with the exception of sample COA3 which contains almost 5% of sulfur.

The new functionality of the Rock-Eval allowing the analysis of dry gas (methane) and wet gas (hydrocarbons in the gaseous state under standard pressure and temperature conditions) was used to determine the capacity of these coals to generate HC as well as to be able to accurately determine oil, wet gas and dry gas windows. Results are presented in Table 2. They show that COA3 is the sample that produces the largest amount of hydrocarbons with 309 mg of HC per gram of rock, of which 32.6% is gas. This coal can therefore be considered an outstanding gas source rock. The other two coals have a lower petroleum potential but still very high for a source rock. Furthermore, although the two S2 values are quite similar, the COA2 coal produces almost twice as much gas as COA1 and more methane than COA3 in percentage terms. This makes COA2 a very good source rock for gas.

6. H₂ potential of the Colombian coals

6.1. H₂ yields

First set of experiments were done with a classical heating ramp of 25 °C/min. The H₂ production curves are presented Fig. 5 showing a generation of H₂ from all these coals.

The temperature at maximum generation, called Tpeak, is rather homogeneous between 738 and 786 °C which is not surprising since the maturity levels of these coals are quite similar. To compare with the Rock-Eval classical Tmax, as the heating rate was 25 °C/min, 39 °C must be subtracted. The H₂Tmax is therefore between 699 and 747 °C. The quantity of H₂ that could be generated, which we will call S₂H₂ by analogy with the HC, is 18 mg/g ± 2 mg/g of rock. It should be noted that the curve is wide, in the pyrolyzer, H₂ is generated continuously between 400 and 1200 °C (Fig. 5). At 1200 °C the H₂ generation is close to zero but not exactly null for two of the samples, but the pyrolysis oven cannot handle higher temperatures. The small underestimation of the S₂H₂ does not appear to reach 5 %, which is within the uncertainty range of such measurement. In addition, the TCD baseline can

Table 2
HC potential of the studied coals, in percentage of weighth.

	Dry Gas (%) (1)	Wet gas (%) (2)	Total HC Gas (%) (3), (1)+(2)=(3)	Total HC Liquid (%) (4), (3)+(4) = 100%
COA1	7.8	5.3	13.1	86.9
COA2	14.2	8.8	23	77
COA3	13.3	19.4	32.6	67.4

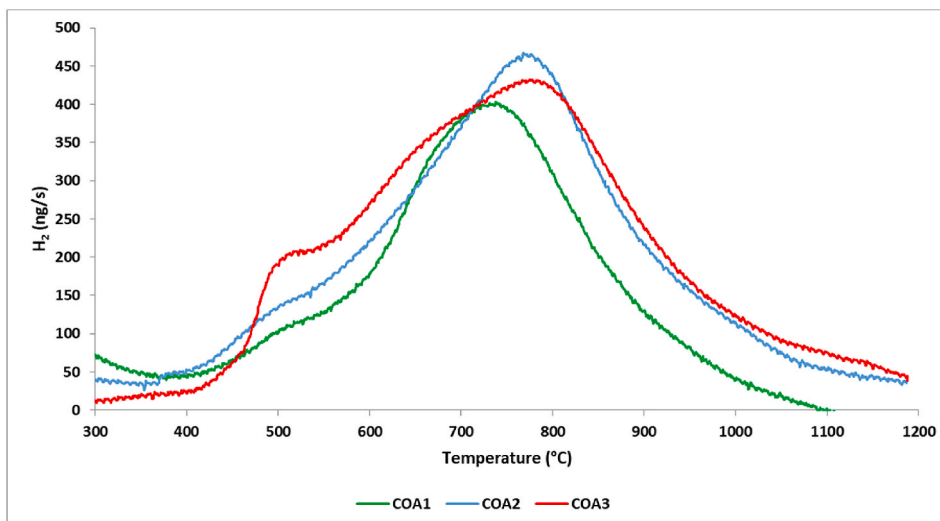


Fig. 5. Hydrogen curve for samples COA1–COA2–COA3 starting from 300 °C to 1200 °C with a heating rate of 25 °C/min. The graph data acquisition was performed with a TCD detector.

Table 3

H₂ potential of the Colombian coals, standard deviation and consistency of measurements.

Sample	S _{2H₂} (mgH ₂ /g of rocks)	±σ	Min	Max	Nb of analyses
COA1	15.7	1.2	14.6	17.2	5
COA2	17.9	1.3	15.9	19.5	5
COA3	20.1	1.2	18.1	21.7	9

sometimes not be fully constant throughout analysis and advanced baseline processing is required.

Analyses were repeated to ensure the quality of the measured S₂–H₂. The mean, minimum and maximum values for each sample are presented Table 3, together with the standard deviations. The H₂ production potential does not seem to be directly correlated with the hydrocarbon's potential (S₂ value from Rock-Eval). And the same applies for the wet and dry gas production values. These values cannot be extrapolated from the classical S₂ values measured by Rock-Eval.

6.2. Temperature dependency

Table 4 and Figs. 5 and 6 show that temperature values at the maximum (Tp) increase during thermal cracking of kerogen. This phenomenon, long well known for hydrocarbon production, can now be extended to H₂ production, which takes place at higher temperatures. For these 3 coals, the higher the Tp, the higher the Tp_{H₂}, but there is no mathematical evident correlation between both values: Tp_{H₂} cannot be extrapolated from the usual Tp measured by Rock-Eval. And the same applies for the Tp values of methane and butane.

Fig. 6 shows the evolution of the generation type through the temperature rise from the Cerrejón coal sample COA3. The HC peak is narrow and the results being presented in mass, ng/s, indicate a large amount of HC. The Tpeak is 479 °C which means 440 °C for the Tmax. As already stated this coal is early mature. The wet gas and dry gas have Tpeak respectively 34 °C and 80 °C higher. The H₂ peak is much broader and it spreads over more than 400 °C, even though the maximum is reached at high temperature (786 °C).

6.3. Quality control

The samples were pyrolyzed several times to check the repeatability of the measurements as shown in Table 3.

Additionally, to the Rock-Eval and Hydrogen-Eval analyses, the

Table 4

S₂ and Tpeak temperature for the HC and the various gases generated during the pyrolysis at 25 °C/min.

Sample	S _{2H₂} (mg/g)	Tp _{H₂} (°C)	S _{2Dry} gas (mg/g)	Tp _{Dry} Gas (°C)	S _{2Wet} gas (mg/g)	Tp _{Wet} Gas (°C)	S ₂ (mg/g)	Tp _{FID} (°C)
COA1	15.7	738	14.4	534	11.8	490	172.1	454
COA2	17.9	771	25.6	545	19.7	502	164.4	458
COA3	20.1	786	44	559	70.2	514	309	479

COA3 sample was analyzed with an Elemental Analyzer to determine the H₂ content and perform a mass balance on H₂ at different pyrolysis steps. To this end, the coal sample was pyrolyzed three times to a final temperature of 650 °C, 800 °C and 1200 °C respectively. At the beginning, the raw sample contained about 6.8%w of elemental hydrogen (Table 5). After a pyrolysis with a final temperature of 650 °C, this value has fell to 2.6% but due to the loss of weight from other elements (C, N, S, O) during the pyrolysis a normalization was done to compare the initial and final composition. After the normalization the amount of elemental hydrogen fell down from 100% to 22.7% during the pyrolysis. It means around 77.3% of the hydrogen initially present inside the sample was produced associated with carbon. Indeed, if we take the S₂ value of the COA3 sample (309 mg/g) multiplied by the proportion of hydrogen commonly used in the organic matter which is about 17% (and 83% for the carbon content) [30], we find a total of hydrogen about 5.25%w lost (percentage of elemental in total sample weight) which corresponds to a loss of 76.7% of the whole elemental hydrogen initially present into hydrocarbons mainly.

$$S_2 \times H \text{ content in the OM} = 309 \times 0.17 = 52.5 \text{ mg.g}^{-1} = 5.25\%w \quad (1)$$

This value is consistent with loss of elemental hydrogen found in the elemental analysis results. Nevertheless, the hydrogen curve shows that around 25% of the H₂ was produced before 650 °C which represent 0.5% w of the whole elemental hydrogen weight content in the coal (see S₂–H₂ table (4)).

$$S_{2H_2} \times \text{Proportion of H}_2 \text{ curve before } 650^\circ\text{C} = 20.1 \times 0.25 = 5 \text{ mg.g of rock}^{-1} = 0.5\%w \quad (2)$$

By chance the amount of elemental hydrogen which has not been pyrolyzed from the methane signal after 650 °C represent also 0.5% of the whole hydrogen. This can be computed with the S_{2Dry} Gas value

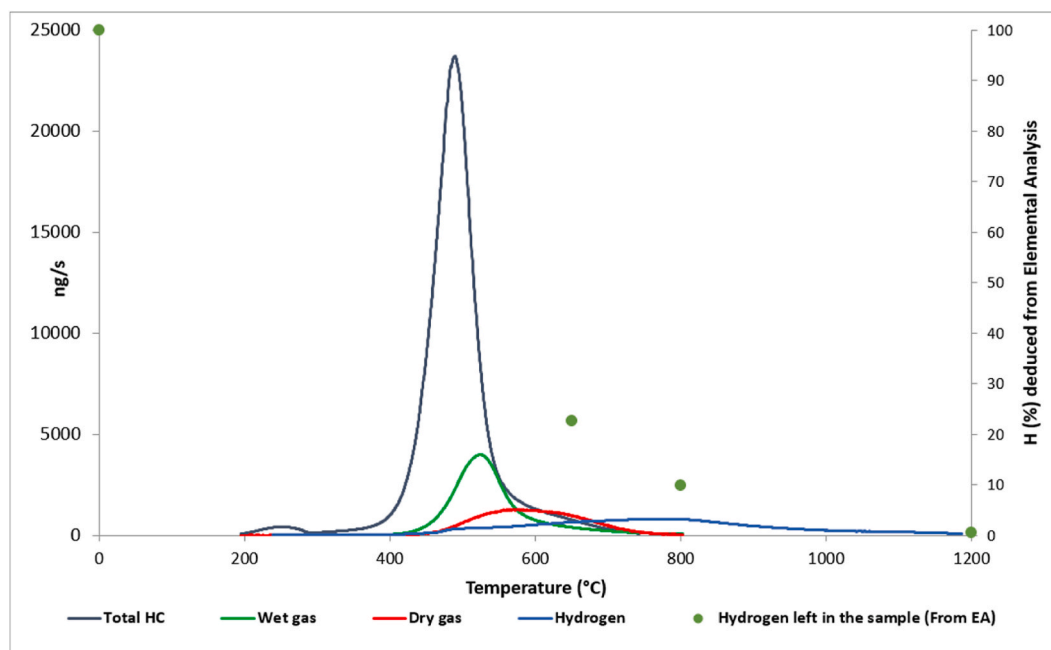


Fig. 6. Superimposition of Total Hydrocarbons curve (dark blue), wet gas curve (green), dry gas curve (red) and H₂ curve (light blue) as a function of temperature. The green circles represent the percentage of hydrogen measured by elemental analysis remaining inside the pyrolyzed coal, up to a final temperature of 650 °C, 800 °C and 1200 °C. The point at 100% and 0 °C corresponds to the percentage of hydrogen left before pyrolysis. These values were obtained from the elementary analysis of the COA3 coal sample (see numbers Table 5): on the bulk sample, and the residue of the coal samples pyrolyzed to 650 °C, to 800 °C and to 1200 °C (see section 6.3 for discussion). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 5

Hydrogen Elemental analysis results of the sample COA3 for the raw sample and the sample pyrolyzed with respectively a final temperature pyrolysis (FTP) of 650 °C, 800 °C and 1200 °C.

	Raw Sample	Sample after FTP of 650 °C	Sample after FTP of 800 °C	Sample after FTP of 1200 °C
Hydrogen Content (% weight)	6.84	2.59	1.14	0.04
Hydrogen Content left from initial raw sample (%)	100	22.7	9.9	0.6

(44 mg/g) and the proportion of the methane signal obtained after 650 °C (45%) multiplied by the proportion of elemental hydrogen inside the methane molecule.

$$S_{2CH_4} \times \text{Proportion of } CH_4 \text{ curve after } 650^\circ C \times \frac{4 \times M(H)}{M(CH_4)} = 44 \times 0.45 \times \frac{4}{16} = 5 \text{ mg.g of rock}^{-1} = 0.5\%w \quad (3)$$

Then after a pyrolysis stopped at 800 °C the EA shows an elemental hydrogen concentration left of about 9.9% which is fully consistent with the Hydrogen Eval result which predicts 0.78%w left in the rock sample which corresponds to 11.4% of the initial amount of hydrogen. At this temperature all the methane has already been generated. Finally the EA also confirms the Hydrogen Eval results showing 0.04% of hydrogen remains in the pyrolyzed sample at 1200 °C (Fig. 5).

To conclude, the EA, Hydrogen Eval and RE7S-MG results are fully consistent and the interferences seen on the TCD curves are neglectable on the quantification. Nevertheless, work on the H₂ detection will be done in the future to improve the accuracy of the Hydrogen Eval results.

7. Kinetic parameters

7.1. Determination of the kinetic order of the reaction

In addition to measure the potential of source rocks, the oil and gas industry has relied on laboratory experiments, such as Rock-Eval® analyses, to calculate the kinetic parameters of these pyrolysis reactions [8]. The methodology consists at maturing SR rapidly (within 10–20 min), at high temperatures (300–650 °C), and to calculate the A and E_a values of the Arrhenius equation. By applying these parameters into sedimentary basins conditions, it is possible to extrapolate the reaction at the geological times (millions of years) and temperatures (20–150 °C). Without claiming to represent elementary processes, this has greatly helped to simulate the maturation reaction of OM into oil and gas in the subsurface.

Before performing standard kinetics calculations on experimental curves, there is a first unknown parameter in the Arrhenius equation, which is never measured anymore in the O&G analyses: n, the apparent order of reaction. Actually, the order of reaction, n (see equation (1a)), is known, or assumed, to be equal to 1 for the production of HC from OM.

Using the new Hydrogen-Eval instrument, and applying the methodology presented, and mathematically demonstrated, in Appendix A of [31], the reaction order n of the reaction of transformation of organic matter into H₂ was checked. Sample COA3 was analyzed four times, using the same heating rate profile at 25K/min, but with different initial masses: 10, 20, 30 and 40 mg (see Fig. 3). Since the Tpeak is constant at 786 °C, whatever the weight of coal analyzed, this clearly indicates that the order of reaction of OM into H₂ is n = 1 order.

This observation seems obvious, but it is, to our knowledge, the first time that this has been measured and confirmed. It also provides further evidence that the production of H₂ from OM follows the same rules of unimolecular reactions as the production of oil and gas from organic matter. Indeed, following the Rice–Ramsperger–Kassel–Marcus (RRKM)

transition state theory of unimolecular reactions [32], the order of unimolecular reactions should be $n = 1$.

7.2. Calculation of kinetic of COA1 using Kissinger equation

The standard Arrhenius equation (1a) below can be used to describe mathematically the experimental curves obtained in the laboratory conditions, with $Q'(t)$ the rate of production of H₂, methane, butane, hydrocarbons at any time t during the analysis:

$$Q'(t) = -Ae^{-\frac{E_a}{RT}}Q(t)^n \quad \text{Equation 1a}$$

where $n = 1$ for the H₂ production.
and

$$Q(t) = Q_0 - \int_{t=0}^t Q'(t) \quad \text{Equation 1b}$$

with $Q(t)$ the concentration or mass of reactant (coal) at time t , and Q_0 the initial mass of sample at the start of the reaction (at $t = 0$).

Since the analysis is conducted using a non-isothermal profile, but with a constant heating rate, called β , in K/min, or °C/min, there is a 3rd equation driving the reaction in the instrument:

$$T(t) = T_0 + \beta t \quad \text{Equation 1c}$$

The coals were analyzed several times, at different heating rates to calculate the A and Ea parameters of the Arrhenius equation.

The COA1 kinetic parameters for oil and HC gas were acquired at 1, 2, 5, and 10K/min using the RE7MG instrument (beta version).

The Hydrogen-Eval was used to analyses the H₂ generated by the COA1 sample at 2, 5, 10, 20 and 25K/min.

The obtained curves are all bell-shaped, as expected since they follow the Arrhenius equation. As already discussed, there is a point which is the maximum, corresponding to the temperature called Tpeak (Tp), the derivative of this curve is zero at this point. By deriving equations (1a) and (1c), and applying

$$Q'(t) = 0, \text{ at the Tpeak point}$$

One gets the well-known Kissinger equation (see Ref. [28] for the mathematical demonstration of the Kissinger equation from the Arrhenius equation):

$$\ln\left(\frac{\beta}{Tp^2}\right) = \ln\left(\frac{AR}{Ea}\right) - \frac{Ea}{R} * \frac{1}{Tp} \quad \text{Equation 2}$$

This so-called Kissinger equation is so well known that it is an ASTM method [33], easily applicable with a spreadsheet, is a quite fast and inexpensive method to estimate the A and Ea values. It is not very robust since it uses only one point per curve. But it generally provides information as a first approach to kinetics analysis.

The Tpeak of each curve (FID, C4, C1 and H₂) is associated with the heating rate (β , in K/min, ie 1, 2, 5, 10, 20 and 25K/min), and it is possible to add all these points into a Kissinger plot, ie $\ln\left(\frac{\beta}{Tp^2}\right)$ vs $\frac{1}{Tp}$. If the reaction follows an Arrhenius equation, the points must be aligned on a straight line. The A and Ea values of the reaction can be estimated from the obtained slope and intercept.

Fig. 7 shows the results for the COA1 sample. As predicted by the theory, for each product, all the points are aligned for all heating rates (dashed lines), and it is possible to estimate easily the A and Ea values for each reaction from these straight lines. Furthermore, for each heating rate, the points of the different products are also aligned (along the solid black lines): this gives an interesting general picture. These results tend to show that H₂ generation, at least from the coal, is just the continuation of the natural maturation of OM, and the reaction that produces H₂ follows the same pathway than the one that produces oil and gas.

From the straight lines above, obtained in the Kissinger plot, using the laboratory data, it is possible to calculate in Table 6 below the A and Ea values.

The A and Ea values obtained by the RE7 and its additional module are rather low (1E8 - 1E12 range), compared to the expected 1E13 - 1E14

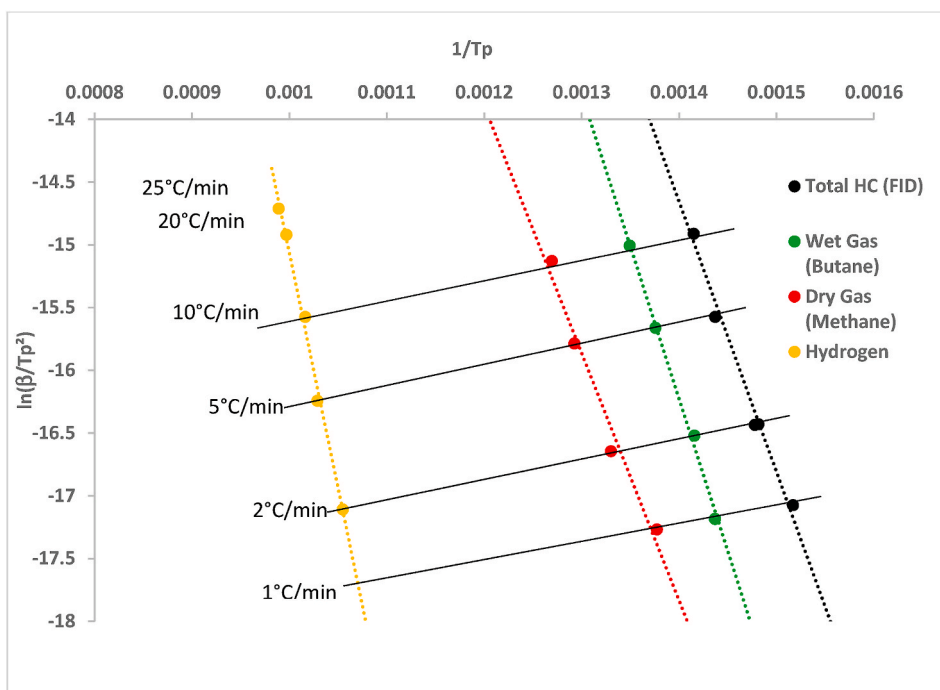


Fig. 7. Kissinger plot for the hydrogen, methane, butane and total HC (FID) reactions obtained with the Hydrogen-Eval and Rock-Eval 7 MG instrument at different heating rates on the COA1 sample. The black lines have been added to link the different reactants obtained at the same heating rates.

Table 6

Ea and A values for each reaction, calculated from the experiments at different heating rates, using the Kissinger method.

	slope	intercept	Ea, J/mol	A, Hz	Ea, Kcal/mol
FID (HC)	−21541.6	15.50	179097	1.16E+11	42.8
C4 (wet gas)	−24276.8	17.76	201837	1.25E+12	48.2
C1 (methane)	−19699.7	9.75	163784	3.37E+08	39.1
TCD (H ₂)	−37453.9	22.39	311392	1.98E+14	74.4

range [34]. This explains the low Ea values (40–50 kcal/mol), compared with the expected 45–55 kcal/mol values. But the Hydrogen-Eval instrument, yielded expected A values, which are in range with what the transition state theory says about unimolecular reactions [32]. The obtained high value of activation energy (Ea = 74.4 kcal/mol) is expected if the A = 1E14 value is valid.

7.3. Multi-kinetics (compensation A, Ea)

One advantage of the Kissinger equation is that it allows to calculate only one solution for the A and Ea values. While when trying to fit the experimental curves with the Arrhenius equation, with a set of A and Ea values, according to the classical Tissot and Espitalié approach, there is an infinity of solutions. It is indeed possible to fit any single curve with pre-exponential factors (A) with values of A = 1E8 or A = 1E20, even if there is no physical meaning for such values. By analyzing the same sample at different heating rates, it is possible to better constrain the choice of A and Ea solutions, among an infinite number of them. Another advantage of analyzing the same sample at different heating rates is to gain greater confidence when extrapolating the reaction process to the geological times and temperatures (see 7.4), especially when taking the time to go down to 1 or 2K/min.

One disadvantage of the Kissinger equation is that it allows to calculate only one single Ea value, a mean one, the one closer to the Tpeak. It does not describe the full process, from the beginning to the end of the reaction, it only calculates the Ea value close to the reaction maximum. Nevertheless, the Kissinger approach is a good tool for choosing which solution, among the infinite number of solutions in the conventional Tissot-Espitalié, approach makes sense.

To go one step further, we used the kinetics modules of Geoworks (Vinci-Technologies, France) to describe the H₂ curves obtained with the Hydrogen-Eval instrument, and we calculated a set of A values and of {Eai; xi} values to fit the curves.

Having found A values as low as 3.4E8 from the Kissinger equation for methane, the set of hydrogen generation curves at 25, 20, 10, 5 and 2K/min is used to calculate a set of {Eai; xi} values with initial A values ranging from 7E9, to 2E14 and to 1E19 Hz.

At this stage, there is an infinity of solution (here only three have been processed) to rebuild the experimental curves. It is not easy to pinpoint which one is the best.

7.4. Application to basin scale

What the Kissinger approach has to say about extrapolating these laboratory measurements to the geological conditions of sedimentary basins can be seen below (see Fig. 9).

The plot allows to estimate the temperature of ~50% of transformation ratio in the basin: a value of 120–130 °C is common for the production of oil in most basins (despite the unusually low A and Ea values found here). Using the same approach, H₂ would be produced at 50% of TR at 300 °C in the same basins (indeed, this approach is based in a single Ea value, due to the Kissinger simple model).

The Kissinger plot also shows how far the laboratory conditions are from the basin conditions.

But it does not show the full process. The usual kinetics approach used in the oil and gas industry, from Rock-Eval curves, was applied to the H₂ curves from the Hydrogen-Eval.

With Fig. 8, it was seen that whatever the pre-exponential factor ranging from A values as low as 7E9 to 2E14 and even 1E19 Hz, the recalculated (pink) curves at 5K/min were quite similar. Down to 3K/My, the curves are significantly shifted (see Fig. 10). With A = 2E14; the maximum temperature of production is found at 300 °C, as stated before. But what is interesting is that H₂ production starts at temperatures as low as 100 °C and ends at about 600 °C. The Tpeak is therefore maybe between 200 and 400 °C, which represents a huge difference in depth of the formation, but due to the high number of activation energies, production occurs a very long temperature range.

While the curves at 5K/min were similar using A = 7E9, 2E14 or 1E18 Hz, the curves are different at 3K/My: Tpeak is shifted by ~100 °C for each tested value. The A = 2E14 value being the value indicated by the Kissinger equation, the middle curve (and its associated TR% curve) is the most probable solution, applicable to the basin. In this case, maximum production occurs at 300 °C. It is interesting to note that whatever the kinetics parameters applied at 3K/My, there is a continuous production of H₂ from 100 to 600 °C, due to the high dispersion of Ea values. Lacustrine (type I) OM shows a unique activation energy, for oil and gas generation, since the organic matter is very homogeneous (lipids mainly). On the contrary, terrestrial OM (type III), like coals, always show a wider range of activation energies, because of the more diverse pools of organic matter. But such a dispersion of activation energies between 40 and 100 kcal/mol, for hydrogen generation, is quite unusual, and unexpected. This means that there is a wide range of initial organic bonds that break to yield hydrogen, typical of a type III OM for oil and gas production.

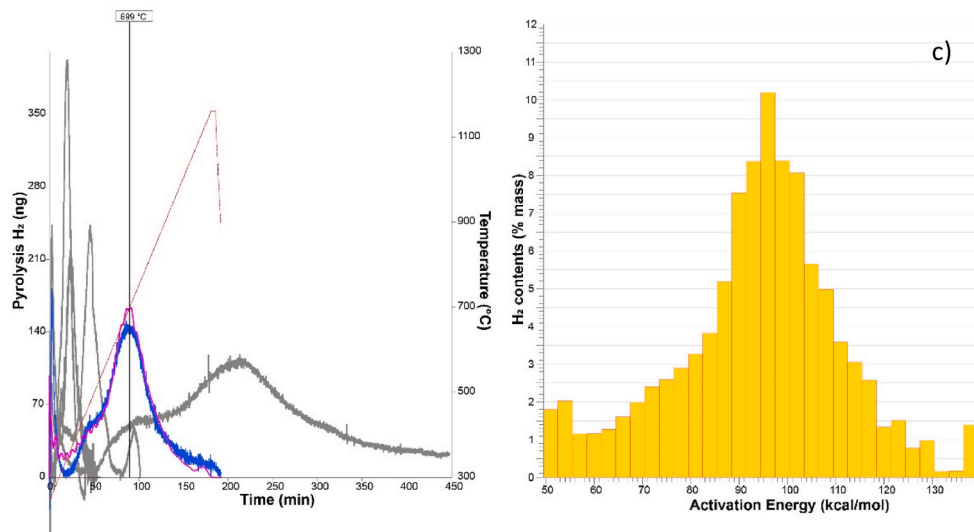
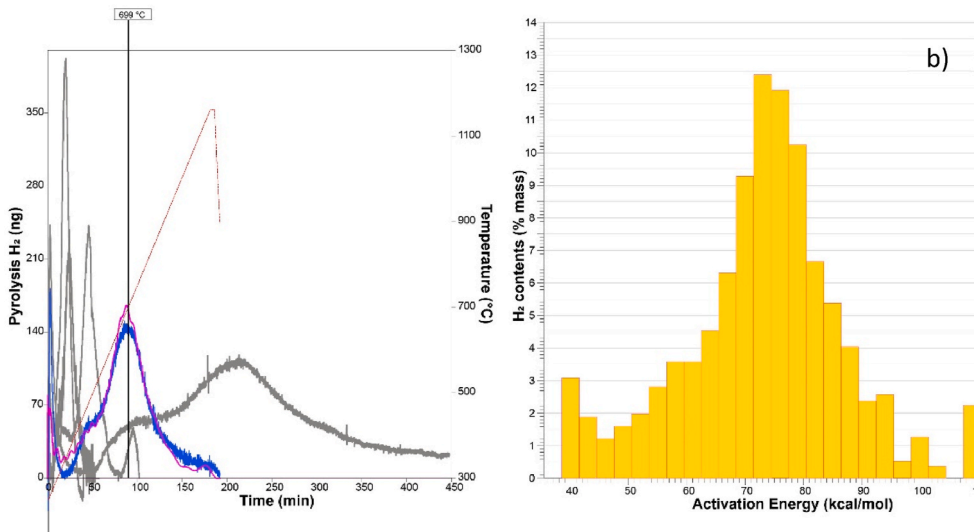
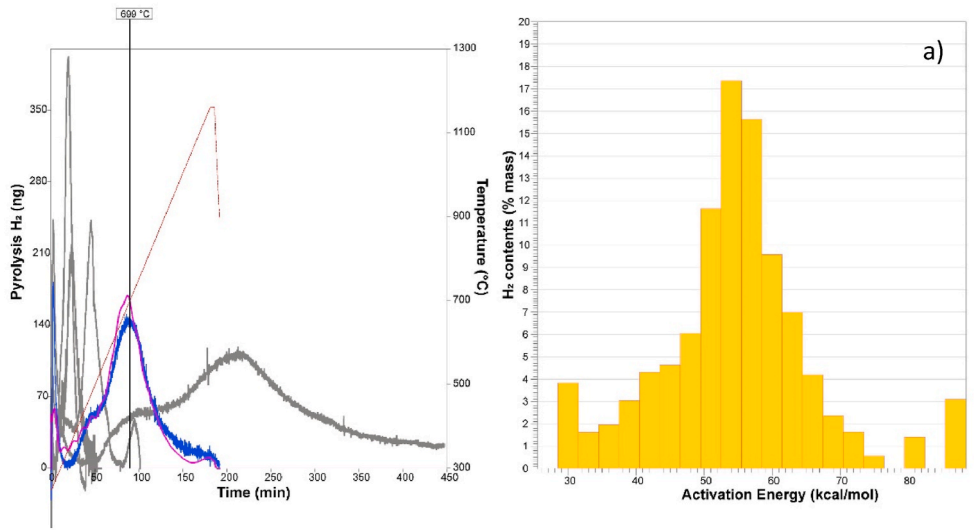
8. Discussion

8.1. Laboratory versus basin & open, close, semi closed pyrolysis

Pyrolyzers such as the Rock Eval are open systems and the carrier gas, nitrogen, is dry. As a result, their representativeness in relation to the natural process has always been questioned. The role of water and the fact that part of the HC produced remains in the SR is a priori neglected. The purpose of this article is not to enter into this 50-year old debate [35], which our modest work will certainly not be able to bring to a close. Open pyrolyzes have a huge advantage: they are quick and easy to set up. In the HC world, they have been widely used to quantify SR heterogeneity, maturity and residual potential. Maybe all the figures are “wrong”, but when used in basin models, they can predict where an accumulation will be found, and even to some, extent the chemistry of the fluids that will be found. That is what they are asked to do, so they are useful. The mesh size in basin modeling software is several meters thick and tens or even hundreds of meters wide, so we need a global approach that may differ from the description of the sequence of chemical reactions that takes place on a small scale. The use of basin modeling software in H₂ exploration is in its infancy, with only two publications to our knowledge [36,37], but they are promising. Our approach is part of this macro approach.

8.2. H₂ yield of the organic matter

The amount of H₂ that can be generated from coals, and other organic matter, at high temperatures has been quantified in the context of surface processes and UCG. In this study, we attempt to quantify it



(caption on next page)

Fig. 8. Calculation of Ea values different initial hypothesis regarding the A value (with a step calculation of 3 kcal/mol); 8a: A = 6.8E9 yields a maximum Ea around 56 kcal/mol; 8b: A = 2E14 yields a maximum Ea at 74 kcal/mol (in accordance with Kissinger); 8c: a value of A = 1E19 yields a maximum Ea around 96 kcal/mol. In pink, the recalculated curves for 5K/min, in all three cases, the three sets of data can reproduce the experimental curve, in blue, while only one set of data is true and would give good estimation at the geological times. The red curves correspond to the temperature curve (constant rate of T increase). The pink curve is the recalculated curve for 5K/min (based from the calculated A and Ea values): the three sets of data can reproduce the experimental curve at 5K/min, in blue, while only one set of data is true and would give good estimation at the geological times. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

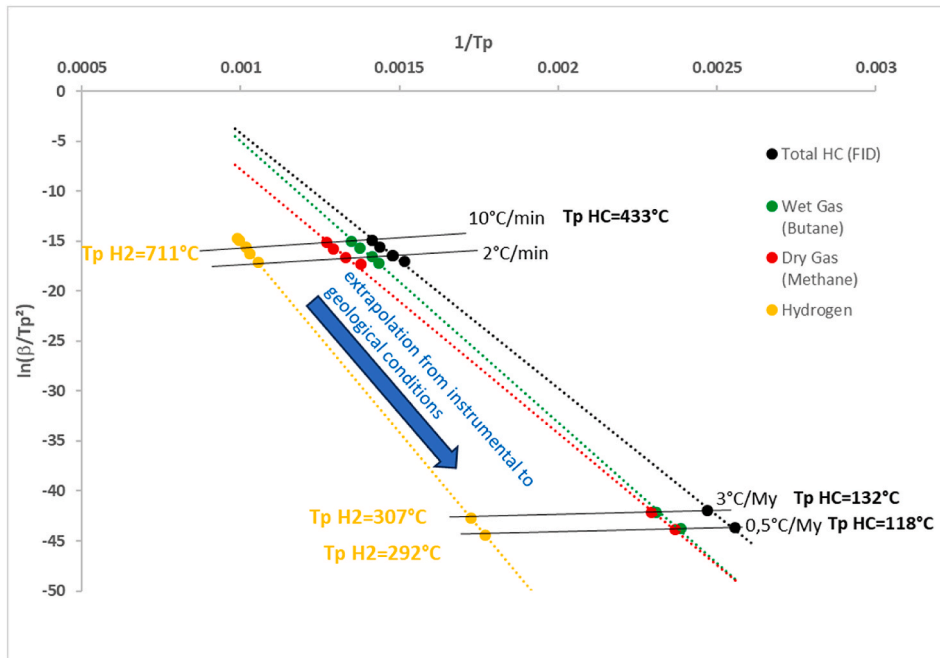


Fig. 9. Kissinger plot (with all points of the above Fig. 7), with calculated points corresponding respectively to heating rates of 5.7×10^{-12} °C/min and 1×10^{-12} °C/min in order to simulate a subsiding basin with a temperature profile of 3 °C/My and 0.5 °C/My.

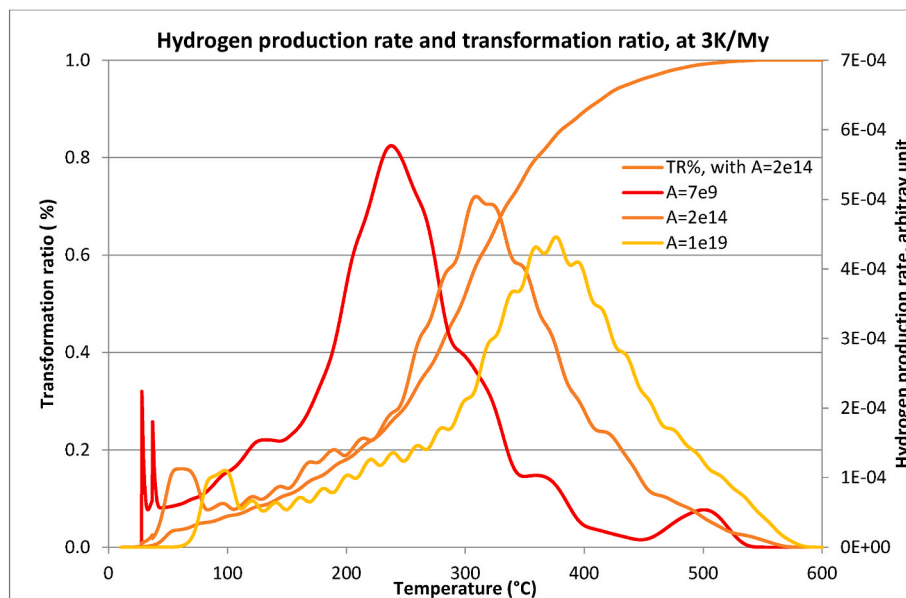


Fig. 10. One transformation ratio curve (left y axis) and generation rate curves (secondary axis) for hydrogen generation at 3K/My, using the three different A values tested above.

under normal burial and thermal gradient conditions, as a natural resource in sedimentary basins. Up to now the measurements have been carried out using a variety of analytical protocols as no commercial

instrument is yet available. However, even the heating ramps are different and the H₂ measurements done with different tools (repetitive sampling followed by GC measurements for [9,11] and continuous

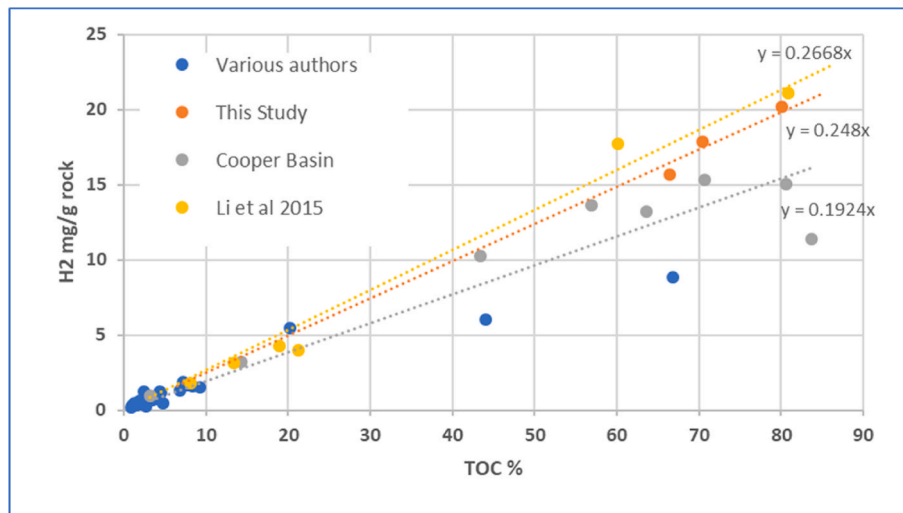


Fig. 11. Comparison of the H₂ yields computed in this study (orange) and the ones published in the literature. Li et al [11], Horsfield et al. [9], Mahlstedt et al. [10], Borham et al. [37] (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

measurement in this study), the results are coherent and allow to propose some order of magnitude.

Fig. 11: one may first notice a strong dependence of the H₂ yield on the TOC content. Coals have a much higher potential than the OMs with a lower TOC content. The studied Colombian coals are rather homogeneous with H₂ yields in mg/g of rock of ¼ of the TOC (orange dots and lines on Fig. 11). Data from the two coals studied by Li et al. [11] are rather similar, although these coals are older (yellow dots, Upper Carboniferous, TOC = 81% for the richest and Lower cretaceous, TOC = 60% for the second one). The Li et al. samples also include marine and

lacustrine shales that follow the same trend despite their lower TOC content. The other data from the Boreham's, Mahlstedt's and Horsfield's papers are more scattered [9,10,37]. It could be due to the fact that these samples were not immature. In the case of the Songliao Basin they have a maturity ranging from Tmax = 500 °C to about 650 °C at 5800 m [9].

8.3. Comparison with other H₂ generating rocks

The world's natural H₂ resources are an open question, as data is still lacking. The number of wells dedicated to H₂ exploration is low and they

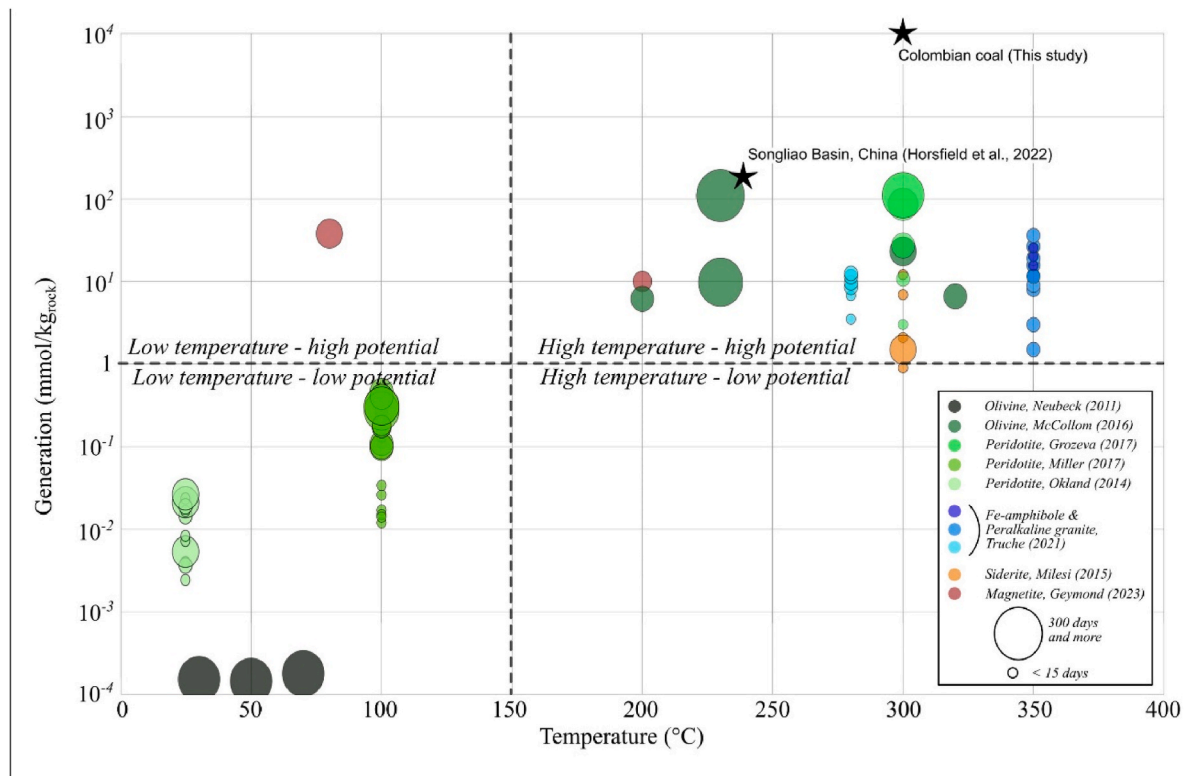


Fig. 12. H₂ yields of various generating rocks, green and blue circle mantle and oceanic lithosphere, red magnetite, black coals. In case of oxidoreduction the circles diameters are proportional to the duration of the experimentation. For the coals, the temperature corresponds to the one due to the burial, this late maturation requires millions of years. Modified from [12] (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

target reservoirs, or H₂ flow zone, rather than generating rocks. Moreover, the reactions that generate H₂ are numerous and take place on different timescales, from slow (radiolysis) to fast (reduction of water by iron rich minerals). At high temperature, around 250–300 °C, the mid oceanic vents as well as the lab experiments prove continuous and rapid generation of H₂ by serpentinization. At temperatures lower than 100 °C, H₂ could also be generated in less than a month by oxidation of iron oxides such as magnetite [38,39]. In this case, the explorationists may consider producing a flow of H₂, as is the case for the steam within some geothermal fields. Natural radioactivity, and hence radiolysis, on the other hand, is a very slow process and a reservoir and a good seal will be required to generate an accumulation. Maturation of OM is also a fairly slow process, although it is much faster than radioactivity as temperature rises, and thus refers to this second system in which a reservoir and a seal are mandatory to expect economic production.

A synthesis of the redox H₂ generating potential of various rocks expressed in mmol_{H2}/kg of rock have been published by Ref. [12]. Values range from 10⁻⁴ to 10² mmol_{H2}/kg_{rock} over a wide range of temperature. The values measured for the coal in the present study, very similar to the ones measured by other authors as shown Fig. 11, are between 8 × 10³ and 10⁴ mmol_{H2}/kg_{rock} with a reaction between 200 and 400 °C. If we upgrade the previous compilation (Fig. 12) it highlights that the potential of coals to generate H₂ is much larger than the yield of all other generating rocks associated with Fe oxidation, by at least one order of magnitude and sometimes two. In the case of a triggered reaction, whether by in situ coal combustion or by water injection into iron-rich rock, these results raise the question of whether the latter is likely to ever be more efficient. The UCG looks more promising. A similar process, the H₂ generation via in-situ gasification of heavy oil is also studied and could result quite efficient for a low cost H₂ generation [40].

8.4. Implication for the natural H₂ global resources

It has been published that the annual generation of H₂ by the two most studied reactions (serpentinization and radiolysis) should be of the same range with the total reaching 23 Mt/year [41–43]. As these reactions are mainly limited by the availability of water, the authors propose to estimate an annual flow. The H₂ budget from Fe oxidation of unconventional Fe-bearing sedimentary and volcanic facies (such as banded iron formations or granites) has not yet been assessed in details yet but it will certainly increase these numbers drastically since the surface of the Archean and Neoproterozoic cratons is enormous (see Ref. [12] and maps therein).

Considering the OM late maturation or even just the coals, the additional H₂ resource will not be renewable and it should be more accurate to speak about resources, fossil resource, and not about annual rate of generation. It is difficult to estimate the volume of coal which is, or has been at the right depth to generate H₂. Since the coal is mined, its volume is only estimated fairly close to the ground, and the low market price of coal does not justify deep mines as it may exist for some other minerals. Nevertheless, some values have been published: the resource estimates for the Songliao Basin alone are more than 4600 Mt [9] and 160 Mt for the coals of the Cooper Basin [10].

For the north Colombia's mines (sample COA3) which covers 700 km², coal reserves are 3 10⁹ t, which means that the coal from this region may have generated, or may generate, 60 10⁶ t of H₂. The switch from a resource to a reserve always entails a change in order of magnitude, and we do not claim that as much H₂ will be found in this basin, but the potential of OM to generate H₂ must be taken into account. Deeply buried coals not accessible to mining are sometimes not even mapped. Nevertheless, we can conclude that all the data acquired in recent years point to very substantial resources of H₂. This gas could be an alternative for decarbonizing our industry.

CRediT authorship contribution statement

Isabelle Moretti: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nicolas Bouton:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Jérémy Ammoual:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Alejandra Carrillo Ramirez:** Writing – review & editing, Resources.

Declaration of Competing Interest

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. Two of the authors work for Vinci Technology, the company that is starting to develop the Hydrogen Eval. This allowed us to use the prototype, but had no influence on the presentation and interpretation of the results.

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References

- [1] Lebon P. Thermolampes ou poêles qui chauffent, éclairent avec économie, et offrent, avec plusieurs produits précieux une force motrice applicable à toute espèce de machine. <https://www.livresanciens.com/livres/lebon-thermolampe-s-poeles-qui-chauffent-eclairent-avec-economie-1801-936;1801>.
- [2] Li J, Cheng W. Comparative life cycle energy consumption, carbon emissions and economic costs of hydrogen production from coke oven gas and coal gasification. *Int J Hydrogen Energy* 2020;45. <https://doi.org/10.1016/j.ijhydene.2020.07.0790360-3199>.
- [3] Lenin VI. A great technical achievement: Pravda No. 91. 1913. April 21.
- [4] Klimenko. Early ideas in underground coal gasification and their evolution. *Energies* 2009;2:456–76. <https://doi.org/10.3390/en20200456>.
- [5] Burton E, Friedmann J, Upathy R. Best Practices in Underground Coal Gasification. Livermore: LNL; 2019. p. 119.
- [6] Kapadia P, Kallos M, Gates I. Potential for hydrogen generation from in situ combustion of Athabasca bitumen. *Fuel* 2011;90(2011):2254–65.
- [7] Olateju B, Kumar A. Techno-economic assessment of hydrogen production from underground coal gasification (UCG) in Western Canada with carbon capture and sequestration (CCS) for upgrading bitumen from oil sands. *Appl Energy* 2013;111:428–40.
- [8] Tissot B, Espitalié J. Thermal evolution of organic matter in sediments: application of a mathematical simulation. *Petroleum Potential of Sedimentary Basins and Reconstructing the Thermal History of Sediments Oil & Gas Science and Technology - Rev. IFP* 1975;30(No.5):743–78.
- [9] Horsfield B, Mahlstedt N, Weniger P, Misch D, Vranjes-Wessely S, Han S, Wang C. Molecular hydrogen from organic sources in the deep Songliao Basin, P.R. China. *Int J Hydrogen Energy* 2022;47(38):16750–74. <https://doi.org/10.1016/j.ijhydene.2022.02.208>.
- [10] Mahlstedt N, Horsfield B, Weniger P, Misch D, Shi X, Noah M, Boreham C. Molecular hydrogen from organic sources in geological systems. *J Nat Gas Sci Eng* 2022;105:104704. <https://doi.org/10.1016/j.jngse.2022.104704>.
- [11] Li X, Krooss BM, Weniger P, Littke R. Liberation of molecular hydrogen (H₂) and methane (CH₄) during non-isothermal pyrolysis of shales and coals: systematics and quantification. *Int J Coal Geol* 2015;137:152–64. <https://doi.org/10.1016/j.coal.2014.11.011>.
- [12] Lévy D, Roche V, Pasquet G, Combaudon V, Geymond U, Loiseau K, Moretti I. Natural H₂ exploration: tools and workflows to characterize a play. *STET* 2023;78:27. <https://doi.org/10.2516/stet/2023021>.
- [13] Li X, Krooss BM, Weniger P, Littke R. Molecular hydrogen (H₂) and light hydrocarbon gases generation from marine and lacustrine source rocks during closed-system laboratory pyrolysis experiments. *J Anal Appl Pyrol* 2018;126:275–87. <https://doi.org/10.1016/j.jaap.2017.05.019>.
- [14] Bouton N, Espitalié J. Method and device for continuous analysis of gaseous hydrocarbons and H₂S in samples of petroleum products. patent WO/2020/157389. <https://patentscope.wipo.int/search/fr/detail.jsf?docId=WO2020157389&fid=EP344322903>; 2019.
- [15] Wang Y, Wu J, Xue S, Wang J, Zhang Y, Tang Y. Hydrogen production by low-temperature oxidation of coal: exploration of the relationship between aliphatic C-H conversion and molecular hydrogen release. *Int J Hydrogen Energy* 2017;42. <https://doi.org/10.1016/j.ijhydene.2017.08.040>.

- [16] Gómez Rojas OP, Blandón A, Perea C, Mastalerz M. Petrographic characterization, variations in chemistry, and paleoenvironmental interpretation of Colombian coals. *Int J Coal Geol* 2020;227. <https://doi.org/10.1016/j.coal.2020.103516>.
- [17] Lozano E, Zamora N. Servicio geológico colombiano, ANEXO B compilación DE LA CUENCA DE amagá-CAUCA-patfa. 2014.
- [18] Dulcey Torres SA. Trabajo de tesis: ACTUALIZACIÓN DEL SISTEMA DE GESTIÓN DE SEGURIDAD Y SALUD EN EL TRABAJO SG-SST LA MINA CARBONES SAN FERNANDO UBICADA EN EL MUNICIPIO DE AMAGÁ, DEPARTAMENTO DE ANTIOQUIA. Universidad Pedagógica y Tecnológica de Colombia; 2016.
- [19] Silva-Tamayo JC, Lara M, Salazar-Franco AM. Oligocene – miocene coal-bearing successions of the Amagá Formation, Antioquia, Colombia: sedimentary environments, stratigraphy, and tectonic implications. In: Gómez J, Mateus-Zabala D, editors. *The geology of Colombia, volume 3 paleogene – neogene*. Servicio geológico colombiano, publicaciones geológicas especiales, 37; 2020. p. 331–53. <https://doi.org/10.32685/pub.esp.37.2019.11>. Bogotá.
- [20] Fuentes Chica R, Molina Escobar J, Blandón Montes A. Parámetros explosivos para muestras de carbón (Antioquia – Colombia). *Revista Ingenierías Universidad de Medellín* 2018;17(33):19–38. <https://doi.org/10.22395/rium.v17n33a1>.
- [21] Díaz Borrego LD. Geomecánica del macizo rocoso PRESENTE en el bloque 5 del SINCLINAL la jagua, la jagua de ibirico -cesar. 2017.
- [22] Morón S, Montes C, Jaramillo C, Bayona G, Sánchez C. CICLICIDAD en la formación cerrejón. *Bol Geol* 2007;29(1):1–10.
- [23] Ajiaco Castro FS. Evaluación del comportamiento térmico de carbones del Cerrejón, carbones coquizantes y sus mezclas en la producción de coque metalúrgico. 2011.
- [24] Holdgate RG. Geological processes that control lateral and vertical variability in coal seam moisture contents Latrobe Valley (Gippsland Basin) Australia. *Int J Coal Geol* 2005;63:130–55.
- [25] Selley RC. African basins. In: Hsu KJ, editor. *Series editor), sedimentary basins of the world, 3*. Amsterdam: Elsevier; 1997. p. 269–317.
- [26] Wattripont A, Bouton N, Espitalié J, Antonas R. Rock-eval sulfur & GEOWORKS software. Proceedings of the first EAGE/IFPEN conference on sulfur risk management in exploration and production; ruail-malmaison. 2018. <https://doi.org/10.3997/2214-4609.201802756>. France, Sept 18–20.
- [27] Espitalié J, Lamoureux-Var V, Bouton N. *The rock-eval method, principles and applications*. 2023 [chapter 8], ISBN: 978-1-394-25622-8.
- [28] Baudin, F. *The rock-eval method, principles and application*, ISBN 978-1-78945-153-5.
- [29] Lewan MD. Sulfur radical control on petroleum formation rates. *Nature* 1998;391:164–6.
- [30] Behar F, Beaumont V, De B, Penteado HI. *Rock-eval 6 technology: performances and developments*. 2001.
- [31] Baudin F, Bouton N, Wattripont A, Carrier X. Carbonates thermal decomposition kinetics and their implications in using Rock-Eval analysis for carbonates identification and quantification. *Sci Tech Energy Trans* 2023;78:2023. <https://doi.org/10.2516/stet/2023038>.
- [32] Henriksen Niels E, Hansen Flemming Y. *Theories of molecular reaction dynamics: the microscopic foundation of chemical kinetics*. 2019. ISBN 9780198805014.
- [33] ASTM E2890-21. Standard Test Method for Determination of Kinetic Parameters and Reaction Order for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger and Farjas Methods. <https://doi.org/10.1520/E2890-21>.
- [34] Waples DW, Nowaczewski VS. Source-rock kinetics. <https://siriusdummy.files.wordpress.com/2013/11/perspective-on-sr-kinetics-ss.pdf>. [Accessed 8 March 2024].
- [35] Landais P, Montoux M. Closed system pyrolysis: an efficient technique for simulation natural coal maturation. *Fuel Proc Technol* 1988;20:123–32.
- [36] Prinzhofer A, Cacas-Stentz MC. Natural hydrogen and blend gas: a dynamic model of accumulation. *Int J Hydrogen Energy* 2023;48(57):21610–23. <https://doi.org/10.1016/j.ijhydene.2023.03.060>.
- [37] Boreham CJ, Edwards DS, Feitz AJ, Murray AP, Mahlstedt N, Horsfield B. Modelling of hydrogen gas generation from overmature organic matter in the Cooper Basin, Australia. *APPEA J* 2023;63(2):S351–6. <https://doi.org/10.1071/AJ22084>.
- [38] Neubeck A, Duc NT, Hellevang H, Oze C, Bastviken D, Bacsik Z, Holm N. Olivine alteration and H₂ production in carbonate-rich, low temperature aqueous environments. <https://doi.org/10.1016/j.pss.2014.02.0140032-0633/&2014>; 2014.
- [39] Geymond U, Briole T, Combaudon V, Sissmann O, Martinez I, Duttine M, Moretti I. Reassessing the role of magnetite during natural hydrogen generation. *Front Earth Sci* 2023;11:1169356. <https://doi.org/10.3389/feart.2023.1169356>.
- [40] Song P, Li Yin. Simulation of hydrogen generation via in-situ combustion gasification of heavy oil. <https://doi.org/10.1016/j.ijhydene.2023.09.248>; 2024.
- [41] Sherwood Lollar B, Onstott TC, Lacrampe-Couloume G, Ballentine CJ. *The contribution of the Precambrian continental lithosphere to global H₂ production*. *Nature* 2014;516:379e82.
- [42] Zgonnik V. The occurrence and geoscience of natural hydrogen: a comprehensive review. *Earth Sci Rev* 2020;203. <https://doi.org/10.1016/j.earscirev.2020.103140>.
- [43] Worman SL, Pratson LF, Karson JA, Schlesinger WH. Abiotic hydrogen (H₂) sources and sinks near the Mid Ocean Ridge (MOR) with implications for the seafloor biosphere. *Proc Natl Acad Sci USA* 2020;117(24):13283–93. <https://doi.org/10.1073/pnas.2002619117>.