THAI process: Determination of the quality of burning from gas composition taking into account the coke gasification and water-gas shift reactions

Alex Turta [*], Punitkumar Kapadia, Claude Gadelle

A B S T R A C T

In the last 13 years, the Toe to Heel Air Injection (THAI) process has been piloted in six heavy oil reservoirs located in three countries.

In the THAI process, the production of upgraded oil along with the production of hydrogen is a proven and constant feature. Unlike the conventional **i**n-**s**itu **c**ombustion (ISC) process, THAI has a very extended, long zone for the chemical reactions, displaying a considerably longer residence time. In addition to primary reactions like high temperature oxidation and pyrolysis, reactions among the products of primary reactions, like coke gasification and water-gas shift reactions (WGSR) take place. Both in conventional ISC and in THAI, estimate of the burning quality can be made by calculating the apparent hydrogen-carbon ratio (H/C) from the composition of the produced gas. However, in THAI process some of the produced CO_2 is not due to oxidation process itself and, therefore, does not characterize the burning process; it is produced by coke gasification and WGSR.

An evaluation of this non-burning CO_2 is conducted, and a new method, taking into account this non-burning CO_2, is developed. This evaluation is based on a correlation between hydrogen and CO_2 generated by coke gasification and WGSR, in a simplified form. The method has been applied for the on-going Kerrobert THAI Project (in Saskatchewan, Canada), where CO% was close to zero, while H_2% remained high (2–4%)

H/C ratio calculated with the old methodology would provide a false impression of a better quality burning in the THAI process, sometimes resulting in unrealistically low H/C values. When using the new method, the calculated H/C ratio would slightly increase. Although slightly increased, it has never taken values higher than 2, confirming that in THAI process the intensity of low temperature oxidation reactions is considerably lower than that in the conventional ISC process.

1. Introduction

During the **T**oe-**T**o-**H**eel **A**ir **I**njection (THAI) process, along with physical changes, chemical changes are inevitable. These chemical changes are because of interaction of bitumen/heavy oil with injected oxygen and superheated steam. The chemical interaction among these reactants is complex and results in large number of multiple reactions, which consists of different combinations of series and parallel elementary reactions. For the conventional **i**n-**s**itu **c**ombustion (ISC) and to some extent in THAI, going upstream, these reactions can broadly be classified into following:

1. Low temperature oxidation (LTO) (Belgrave et al., 1993),
2. Aquathermolysis: Steam and bitumen/heavy oil chemical interaction (Hyne, 1986)

3a Pyrolysis: Thermal cracking of bitumen/heavy oil (Hayashitani and Bennion, 1977)
3b **W**ater **g**as **s**hift **r**eactions (WGSR), coke gasification and methanation reactions. Chemical interaction among the products of these three reactions also can happen (Hajdo et al., 1985). While the first two reactions generate hydrogen, the last one (methanation) consumes some of it.
4. High **t**emperature **o**xidation (HTO), (Kapadia et al., 2011)

The families of reactions mentioned here contribute to the production of coke, gas, and upgraded oil in different capacity, depending upon extent of reaction, which is function of temperature and pressure.

The amount of gas produced during aquathermolysis is less than 1% of the total gas produced during pyrolysis (Hyne, 1986) because of less severe conditions. Hence, effect of aquathermolysis can safely be

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neglected during THAI process, as other reactions are faster and dominating.

The amount of gas produced during pyrolysis is significant and it requires due consideration (Hajdo et al., 1985). For the conventional ISC (C-ISC) process applied for bitumen recovery, hydrogen produced during pyrolysis is not more than 5–6% of total gas produced (Hajdo et al., 1985, Hayashitani and Bennion, 1977; Hallam et al., 1989). Having known that most of the thermal cracking occurs immediately ahead of the ISC front, there is a likelihood that produced hydrogen would burn in the presence of oxygen to produce steam; also, some steam is produced by connate water vaporization, where oxygen concentrations may not be considerable. On the other hand, HTO reactions are in full bloom at the ISC front and contribute significantly to the production of carbon oxides.

Actually, both in C-ISC process and in THAI process the self-supporting capability of the ISC process is directly related to the generation of heat by the HTO reactions, as reflected by the production of carbon oxides (CO_2 and CO) in these reactions. Unlike the C-ISC process, THAI is a short-distance oil displacement process with a long zone for the chemical reactions taking place, hence, displaying a considerably longer residence time. In this zone, in addition to primary reactions like HTO and pyrolysis, reactions among the products of primary reactions, like coke gasification and water-gas shift reactions take place. In both processes, estimate of the burning quality can be made by calculating the apparent hydrogen-carbon ratio (H/C) from the composition of the produced gas. However, in THAI process some of the produced CO_2 is not due to oxidation process itself and, therefore, does not characterize the burning process. An evaluation of this non-burning CO_2 - produced by coke gasification and WGSR - is conducted, and a new method, taking into account this non-burning CO_2, is developed. The new method has been successfully applied for the on-going Kerrobert THAI Project (in Saskatchewan, Canada).

2. More in-depth analysis of the reactions occurring in ISC

2.1. General

A recent comprehensive simulation of the ISC with the generation of hydrogen used 25 reactions (Kapadia et al., 2013). In order to correctly consider all the assumptions and limitations, those equations are reproduced below (Figs. 1–3): It can be seen that:

➢ CO_2 is produced in aquathermolysis, pyrolysis, HTO and WGSR; most of it is produced via the 4 HTO reactions (See Fig. 3). At the same time, CO_2 can be consumed only in coke gasification reactions;
➢ hydrogen is produced in aquathermolysis, pyrolysis, coke gasification, and WGSR. H_2 is consumed in methanation reactions;
➢ CO is produced in aquathermolysis, pyrolysis, HTO and coke gasification. At the same time, CO is consumed in HTO and WGSR;
➢ H_2S is produced by aquathermolysis and pyrolysis

In reality, LTO reactions also produce some small amounts of CO_2 and CO, but they are neglected in the model (Fig. 3) (Kapadia et al., 2011).

It is known that in the conventional ISC (C-ISC) projects, which functioned in full HTO regime, the H_2 in the produced gas is extremely low almost NIL (less than 0.05–0.1%).

Exceptions are some special ISC application for bitumen recovery, where this percentage can be up to 5–6%, mainly when enriched-air is used for injection. Similarly, the C-ISC projects, which functioned in full HTO regime, showed that for high pressure ISC processes, the CO is very low, almost nil (0.2–0.4%) and only in low pressure ISC projects (pressure less than 4–6 MPa) the CO was higher, up to 1.5%.

2.2. Conditions favoring in-situ upgrading; THAI process

The generation of conditions in which high temperature is associated
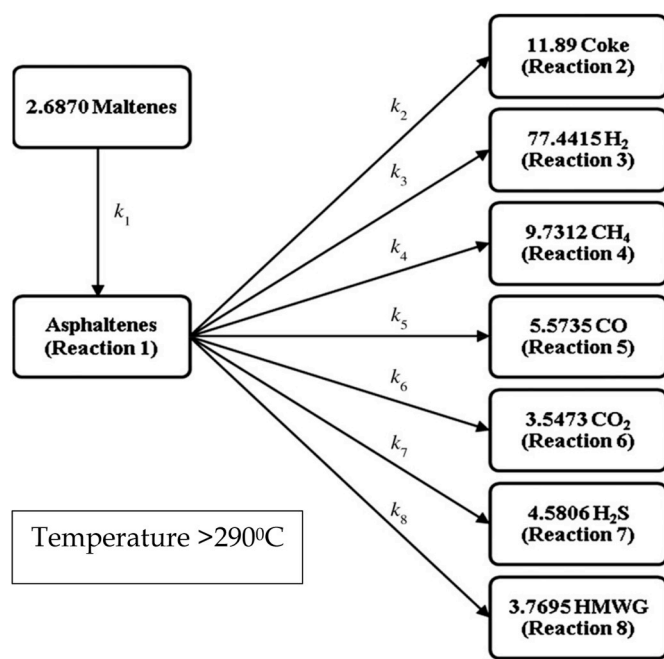

Fig. 1. Bitumen pyrolysis (thermal cracking) reaction scheme. Note: HMWG stands for. High molecular weight gas (a pseudo-component representing all C_{2+} combustible gases).
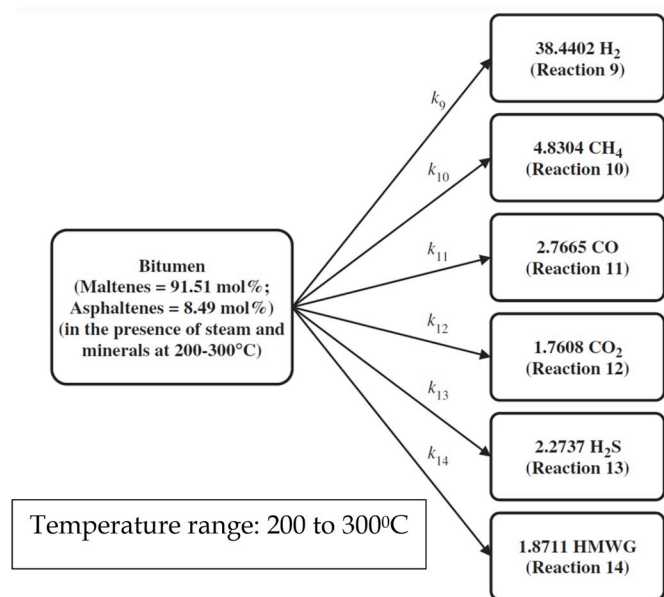

Fig. 2. Bitumen aquathermolisis reaction scheme (Kapadia et al., 2013). HMWG = high molecular weight gas (a pseudo-component representing all C_{2+} combustible gases).

with lack of oxygen is an important factor to favour the **w**ater **g**as **s**hift **r**eactions (WGSR) and coke gasification reactions. In oxygen deficient areas in reservoir (which may be purposely created by adapting the ISC process), the chances of progression of WGSR and coke gasification reactions can be high; for this case, actually, conditions are assumed for hydrogen generation reactions from Fig. 3 to prevail as compared to the reactions from Fig. 1. This is how some past field ISC processes inadvertently produced upgraded oil and H_2; in principal, they were pressure cycling ISC processes, with total interruption of air injection periods, and in these non-injection periods high temperature and lack of O_2 existed in some parts of reservoir. Therefore, periodic upgrading and H_2
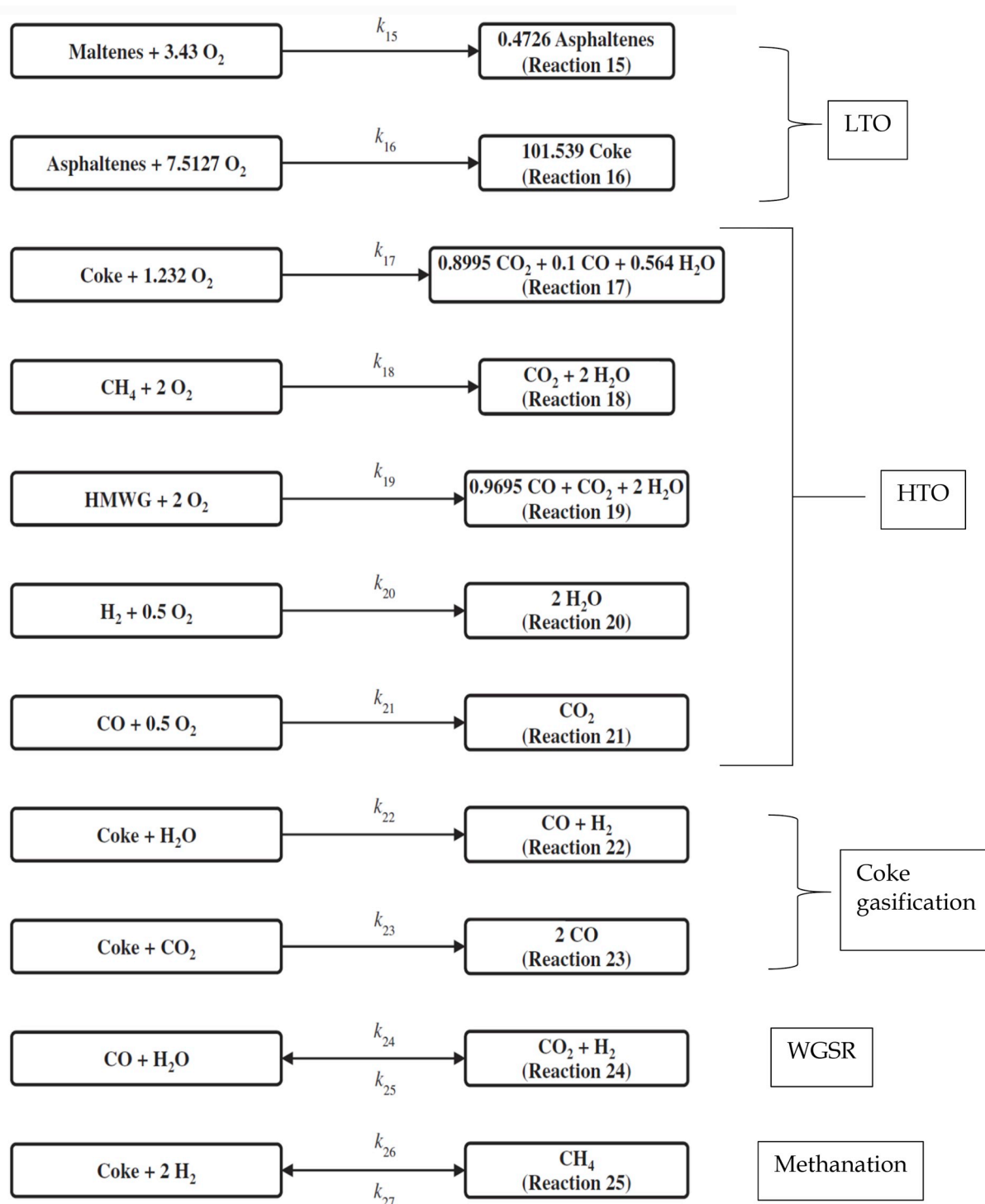
Fig. 3. Reaction schemes for LTO, HTO, coke gasification and water gas shift reactions (Kapadia et al., 2013). Note: HMWG stands for high molecular weight gas (a pseudo-component representing all C_{2+} combustible gases).

production occurred (Hajdo et al., 1985; Hallam et al., 1989).

However, in the THAI process the production of upgraded oil along with the production of hydrogen constitute a constant feature, not a periodic one. At this time, THAI is the first ever EOR process to produce underground upgraded oil and H2 on a constant basis. Unlike the conventional ISC process -which is a long-distance oil displacement process with short-distance chemicals reaction zone (including intensive oxidation) - THAI is a short-distance oil displacement process, but with a long-distance chemical reactions zone (including intensive oxidation).

Although LTO reactions can exist, THAI provides less favorable conditions for LTO reactions, as the O_2 molecules travel along an enlarged, very hot surface of the burning front. Estimate of the burning quality can be made in both processes (C-ISC and THAI) by calculating the apparent hydrogen-carbon ratio (H/C) from the composition of the produced gas. However, in THAI some of the produced CO_2 is not due to oxidation process, and therefore does not characterize the burning process. This work tries to evaluate it and develops a novel method for calculating the apparent H/C ratio, fully applicable to the THAI process.
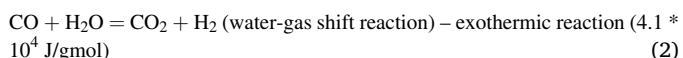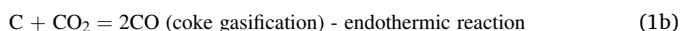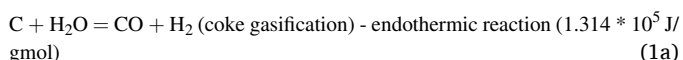
Hajdo et al., (1985) suggested that WGSR have significantly higher value of equilibrium coefficient and hence forward reaction rate above 400 °C. Hence, significant amount of hydrogen must come from WGSR, which consume carbon monoxide (assumed to be generated by coke gasification with water) to produce hydrogen and carbon dioxide; however, this carbon dioxide is not generated by oxidation and should not contribute to the characterization of the burning process. As far as the generation of methane during ISC is concerned, in the field this is extremely difficult to quantify, almost impossible; it is beyond our investigations at this stage.

3. Assumptions and limitations; the approach adopted

Unlike conventional ISC, in THAI process, two categories of coke can be formed, namely:

➢ Generated close to and burned at the fire front (in-situ coke)
➢ Leftover coke from HTO region or coke generated at high temperature areas (other than currently-present fire front location) and generally gasified because of absence of, or deficient oxygen environment; it may even be burned if oxygen is present (for instance at a sudden increase of air/oxygen flux)

As mentioned, in-situ coke may produce very little H_2, practically negligible. At the same time, at a high temperature, the non-in-situ coke is predominantly gasified if O_2 is not present (it has been already consumed), and steam and/or CO_2 is present; this way, H_2 is produced. There are many reactions producing H_2 but, as mentioned, it is believed that the major mechanisms are the coke gasification and WGSR (Hallam et al., 1989; Kapadia et al., 2011; 2012 and 2013). Simply represented, they are:

$C + H_2O = CO + H_2$ (coke gasification) - endothermic reaction ($1.314 * 10^5$ J/gmol)   (1a)

$C + CO_2 = 2CO$ (coke gasification) - endothermic reaction   (1b)

$CO + H_2O = CO_2 + H_2$ (water-gas shift reaction) – exothermic reaction ($4.1 * 10^4$ J/gmol)   (2)

Globally speaking, the endothermicity is higher when considering both reaction pairs (1 and 2); however, this will not constitute the topic of our analysis.

It is now well established that H_2 production occurs in the THAI process, but not (normally) in the conventional in-situ combustion (C-ISC) process; in THAI process these conditions may be found along the burning surface towards the horizontal section of horizontal producer.

In connection with the existence of these two categories of coke in the THAI process, the most important aspects to be clarified are:

➢ To evaluate how much CO_2 and CO are generated from the real burning process and how much are due to the coke gasification and WGSR; as a first approximation, this evaluation will be based on the amount of hydrogen in the produced gas
➢ To assess how accurately the apparent hydrogen/carbon ratio (H/C) can be calculated. The H/C ratio is a very important indicator of quality of burning; lower H/C values indicate higher peak temperature in the ISC front. In conventional ISC it is well established that all CO_2 recorded (from the produced gas) is generated by oxidation.

Therefore, considering the three major reactions presented in equations (1) and (2), we will try to estimate how much CO_2 does not come from pure oxidation (with the oxygen injected). However, it should be noted that equations (1a) and (2) will be accounted for separately from 1b to 2; in other words, the entire CO from eq (1a) or 1b will be consumed in eq (2). Therefore, the CO generated by gasification both with superheated steam and with CO_2 will be taken into account. In

general, the rate of coke gasification with CO_2 (eq. (1b)) is a lot lower than that with superheated steam (Kook, 2017); it is conducted at temperatures above 900 °C, which, generally, are out of the temperature range for ISC process; however just in case it may happen it will be accounted for.

Given the previous information, two categories of situations will be considered, namely:

1. The case of extremely low CO production (almost nil CO production)
2. The case of substantial CO production

As expected, for the first case our calculations will be almost correct, as CO will not have any erring effect; it can safely be assumed that all CO generated by eqs. (1a) and (1b) is used in eq (2); therefore, almost no CO appears in the produced gases. In the second situation, a further in-depth analysis of the errors involved should be done, and alternatively possible ways to account for, should be investigated; this has been beyond our scope, for the time being.

With a good approximation, the first case embodies the Kerrobert THAI pilot, where the CO% has been up to 0.2–0.4%, while the second case relates to the Whitesands, Athabasca THAI Pilot, where the CO% has been in the range of 0.5–5% (Ayasse et al., 2005; Turta et al., 2018 & website: www.insitucombustion.ca, 2019).

The approach adopted makes the assumption that no hydrogen is produced by aquathermolysis and pyrolysis; all H_2 is produced in coke gasification and/or WGSR. Also, it is known that methanation can decrease the H_2 production, but its effect cannot be determined; its effect has been neglected at this time.

At first, let us consider only the chemical equations (1a) and(2). This is done in order to simplify and make the calculation of a H/C (taking into account coke gasification by superheated steam and WGSR) possible. From equations (1a) and (2) it can be seen that if H_2 and CO are formed from coke gasification and WGSR - and assuming that all CO formed in eq (1a) reacts with steam to form CO_2 and H_2 - then the H_2 amount should be 2 times the amount of CO_2 produced. A similar analysis shows that this is also true for coke gasification with CO_2, i. e considering eqs (1b) and (2). It is assumed that the two reactions (either 1a and 2 or 1b and 2) can proceed simultaneously or consecutively with reaction from eq (1) being first, as temperatures for coke gasification are required to be higher than those for WGSR; given the temperature distribution in THAI process, it is assumed that the consecutive reactions will prevail. The amount of calculated H_2 can be slightly less than double amount of CO_2, if some extra CO_2 will be formed by WGSR with CO coming directly from HTO reactions. Alternatively, the amount of calculated H_2 can be slightly lower than double amount of CO_2, due to a consumption of some H_2 by methanation, or to other phenomena (producing H_2), as aquathermolysis and pyrolysis, for instance.

4. Case of practically very little or no CO production

4.1. Theory

This case represents very well the THAI Kerrobert Project). At the same time, it is adopted for our analysis, as it is the simplest case. Kerrobert is a conventional heavy oil with bottom water; the THAI pilot has been initiated as a secondary EOR method, when the primary recovery with vertical and horizontal wells led to an oil recovery of 1.2%, at a water cut of over 85% (Turta et al., 2018 & website: www.insitucombustion.ca, 2019).

In this case, theoretically, three different possibilities can be discussed, namely:

1. Only coke gasification
2. Only WGSR
3. Coke gasification and WGSR as consecutive reactions (eq (1a) followed by eq (2) or eq (1b) followed by eq (2))

For all three possibilities, assuming that produced hydrogen does not get consumed by methanation and or other phenomena, for the first possibility (only coke gasification) we would have a 1:1 proportion of H_2 and CO in the produced gases (the ratio $H_2\%/CO\%$ would be around 1 or slightly higher).

The percentages of H_2, CO and O_2 in the produced gas for the wells KP1 and KP2 Kerrobert are shown in Fig. 4a and b. It clearly shows that for both wells, in general, the H_2 percentage is always greater than CO percentages. However, for both wells two distinct periods can be separated, namely:

- First 1–1.5 year period, when CO% was up to 0.5%, therefore higher, sometimes being closer to the $H_2\%$
- Second long period (longer than 4 years), afterwards, when CO% was close to zero while $H_2\%$ remained high; the ratio $H_2\%/CO\%$ would be very high.

For the second possibility (only WGSR) it has to be assumed that the CO originates from the oxidation process (that one from pyrolysis is neglected). For this case from the WGSR (eq (2)) it results that CO forms CO_2; therefore this CO_2 is directly from burning, but via CO, therefore is not a non-burning CO_2. Consequently, this case is not to be analyzed. However, if CO is generated from a coke gasification (along with H_2) and all generated CO enters a WGSR, this is a case which can finally produce very little CO and a significant amount of H_2; this is just the case of the second long period described previously and the mechanism of H/C calculation will be analyzed further (as a third possibility).

For the third possibility (consecutive coke gasification and WGSR) -therefore for the second period - all in all, considering equations (1a) and (2), per 2 mol of water reacted consecutively in these two reactions, 1 mol of CO_2 will be formed for 2 mol of H_2 formed (one from first reaction and another from second reaction), while CO is only an intermediary product and does not appear in the final gas produced. The same (1 mol of CO_2 will be generated for 2 mol of H_2 formed) will
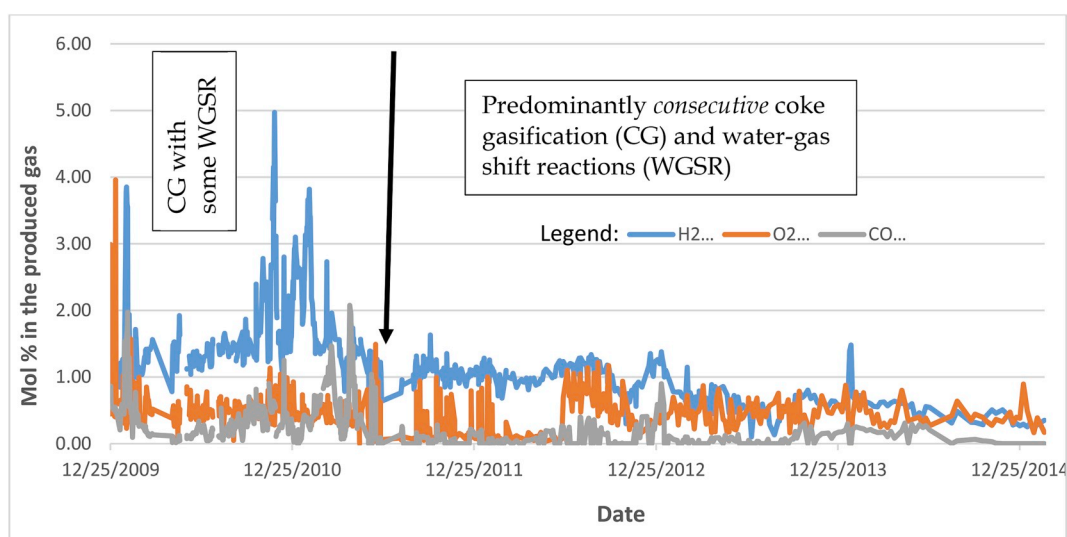
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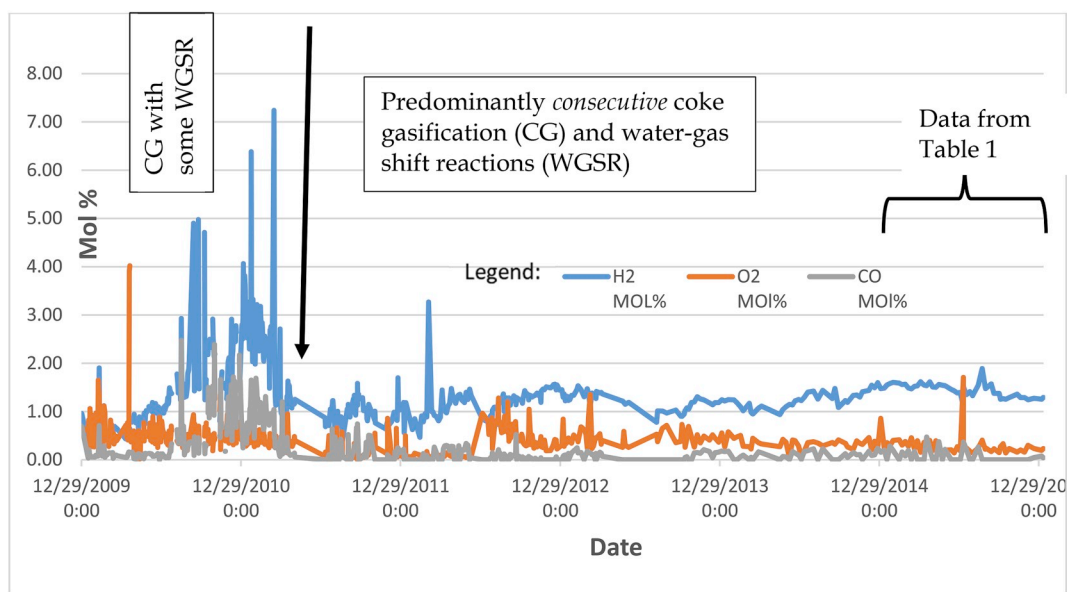
b

Fig. 4. a: Variation of hydrogen (H_2, carbon monoxide (CO) and oxygen (O_2) in the gas produced by KP1 well in Kerrobert THAI Project b: Variation of hydrogen (H_2, carbon monoxide (CO) and oxygen (O_2) in the gas produced by KP2 well in Kerrobert THAI Project.

happen when eqs. (1b) and (2) are considered.

Therefore, for the evaluation of how much CO_2 are generated from the real burning process and how much are due to the coke gasification and water-gas shift consecutive reactions, the amount of H_2 produced may be an indicator, although it may not be perfect. Assuming that the water-gas shift reactions consume entirely all CO from coke gasification and practically only CO_2 is formed - and recorded in the produced gas - it means that the CO_2 formed this way should be equivalent to the H_2 produced, in a certain proportion; as shown the equivalence $CO_2:H_2$ was 1:2. Furthermore, the H/C may be calculated more exactly after reducing the total CO_2 recorded, by subtracting the CO_2 corresponding to H_2 generation ($CO_{2coke-gas}$). This way one can adjust (reduce) the CO_2 percentage further used in calculation of H/C ratio, and this reduced value would be called CO_{2-burn}. This is necessary as the H/C ratio is supposed to characterize only the burning process.

As mentioned, for the time being we are going to deal only with cases where CO percentage is extremely low and it can be considered negligible. As shown, the simple case of practically NIL CO production has been almost a reality in the Kerrobert THAI process, except a first period immediately after ignition. Therefore, in this case it can be assumed that all the CO generated by coke gasification is used in the water-gas shift reaction, producing CO_2. This way, the attempt to estimate the $CO_{2coke-gas}$ and CO_{2-burn} has correct premises. Additionally, as mentioned, it is assumed that there is no H_2 generated by aquathermolysis or thermal cracking. Similarly, no H_2 formed in those two reactions (1 and 2) will be consumed in the reaction of H_2 with oxygen to form water or in a methanation reaction. The errors introduced by those assumptions, at this time are not estimated.

4.2. Examples of H/C calculations taking into account the coke gasification reactions and WGSR as consecutive reactions

As mentioned previously, the examples of H/C calculations and its use for the estimated of the quality of burning will be presented for the Kerrobert THAI Project, as in this case the CO% is extremely low, almost NIL.

For the production well KP2 in Kerrobert Project, the gas composition data for year 2015 is shown in Table 1a. In general, the CO percentage was less than 0.2%, although there were a few periods with high CO concentration (up to 0.6–0.9%). Further on, the data in Table 1a will be used. The recorded average composition was:

CO_{2-r} = 15.5%; CO = 0.05%; O_2 = 0.22; N_2 = 77%; H_2 = 1.4%; CH_4 = 3%; C_2^+ = 1% and H_2S = 0.4%

Where CO_{2-r} is percentage of CO_2, as recorded.

The daily gas production of KP2 is around 30,000 sm^3/day. The amounts of CO_2 and H_2 produced daily are:

CO_2 = 0.155 * 30,000 = 4650 sm^3/day

H_2 = 0.014 * 30,000 = 420 sm^3/day

From previous chemical equations (1) and (2), it results that 2 molecules (or moles) of H_2O participating in the consecutive reactions of coke gasification and water-gas shift reactions (WGSR), produce one molecule (or mole) of CO_2 and 2 molecules (or moles) of H_2.

Therefore, for a number "N" of H_2 molecules produced, "N/2" molecules of CO_2 are generated. In that case the CO_2 due to coke gasification and WGSR ($CO_{2coke-gas}$) will be:

$CO_{2coke-gas}$ = 420 *0.5 = 210 sm^3/day

Table 1

Kerrobert Project. Produced Gas Composition for Well KP2 during 2015 and January 2016). Picture from a computer display (Turta et al., 2018) Legend: AAHCR = Apparent atomic hydrogen-carbon ratio. CG=Coke gasification; WGSR=Water-gas shift reactions.

Time	KP2-Lab	H2 MOL%	O2 MOL%	N2 MOL%	CO MOL%	CH4 MOL%	CO2 MOL%	C2H6 MOL%	C3H8 MOL%	C4 MOL%	C5 MOL%	H2S MOL%	AAHCR	AAHCR corrected for CG and WGSR
/16 13:5!	Field. J. Elliott	1.27	0.31	76.87	0.01	3.93	15.58	0.77	0.45	0.26	0.14	0.463		
/16 11:4!	Field. J. Elliott	1.28	0.28	76.29	0.05	3.85	15.39	0.74	0.43	0.18	0.14	0.465		
/16 12.1(	Field. J. Elliott	1.26	0.19	76.22	0.01	3.87	15.65	0.75	0.46	0.27	0.14	0.474	1.137	1.35
/16 13:3:	Field. J. Elliott	1.28	0.23	76.51	0.04	3.59	15.59	0.71	0.44	0.28	0.14	0.464		
/16 10:4	Field. J. Elliott	1.25	0.19	76.49	0.08	3.76	15.52	0.75	0.47	0.29	0.15	0.467		
/15 10.1	Field. J. Elliott	1.27	0.23	76.90	0.05	3.90	15.17	0.68	0.38	0.24	0.12	0.440		
/15 13:1'	Field. J. Elliott	1.24	0.30	77.22	0.00	4.00	15.08	0.60	0.33	0.12	0.05	0.412		
/15 11.2(	Field. J. Elliott	1.27	0.16	76.45	0.00	3.85	15.16	0.57	0.32	0.18	0.06	0.420		
/15 10:3(	Field. J. Elliott	1.28	0.20	77.29	0.00	3.83	15.36	0.57	0.32	0.20	0.06	0.421		
/15 09:4(	Field. J. Elliott	1.35	0.16	77.28	0.00	3.19	15.87	0.60	0.38	0.26	0.14	0.447		
/15 15:3	Field. J. Elliott	1.28	0.23	77.49	0.00	3.75	15.22	0.53	0.31	0.18	0.06	0.392		
/15 10:2(	Field. J. Elliott	1.25	0.14	76.98	0.00	4.49	15.18	0.55	0.30	0.18	0.05	0.386		
/15 11.2:	Field. J. Elliott	1.26	0.33	77.05	0.00	4.12	15.23	0.55	0.31	0.19	0.07	0.391		
/15 13:0:	Field. J. Elliott	1.25	0.27	77.49	0.00	4.28	14.68	0.54	0.31	0.19	0.05	0.390		
/15 17.2	Field. J. Elliott	1.35	0.14	76.63	0.00	2.47	16.00	0.58	0.34	0.13	0.06	0.418		
/15 14:3(	Field. J. Elliott	1.35	0.23	76.02	0.00	3.58	15.31	0.51	0.28	0.17	0.05	0.399		
/15 10:4	Field. J. Elliott	1.57	0.17	76.78	0.00	3.60	15.55	0.56	0.32	0.18	0.75	0.419	1.17	1.39
/15 10.1(	Field. J. Elliott	1.45	0.24	75.80	0.00	4.20	15.18	0.47	0.25	0.10	0.05	0.388		
/15 09:5(	Field. J. Elliott	1.49	0.22	76.65	0.00	4.29	15.14	0.48	0.25	0.16	0.05	0.396		
/15 11:3(	Field. J. Elliott	1.86	0.40	76.63	0.00	2.44	15.93	0.44	0.25	0.16	0.05	0.422		
/15 14:4!	Field. J. Elliott	1.53	0.25	76.68	0.26	3.57	15.47	0.45	0.24	0.14	0.04	0.399		
/15 13:3(	Field. J. Elliott	1.32	0.14	77.06	0.00	3.66	15.68	0.43	0.24	0.14	0.04	0.410		
/15 10:4	Field. J. Elliott	1.42	0.18	77.78	0.00	4.02	15.60	0.44	0.24	0.12	0.00	0.402		
/15 17:3	Field. M. Wright	1.33	0.24	76.43	0.21	4.27	14.82	0.37	0.18	0.11	0.07	0.377		
/15 11:4!	Field. D. Tetarenko	1.48	0.21	76.28	0.36	3.52	14.62	0.38	0.22	0.12	0.07	0.375		
/15 11.4	Field. D. Tetarenko	1.10	1.69	76.72	0.31	3.12	14.62	0.38	0.22	0.12	0.07	0.375		
/15 13:5(	Field. M. Wright	1.37	0.18	76.45	0.00	3.49	15.13	0.44	0.23	0.12	0.06	0.406		
/15 09:1(	Field. D. Tetarenko	1.38	0.27	77.45	0.00	3.55	15.90	0.44	0.22	0.09	0.02	0.419	1.58	1.87
/15 12:3	Field. M. Wright	1.41	0.14	76.64	0.00	3.45	15.68	0.43	0.22	0.12	0.06	0.399		
/15 14.0	Field. D. Tetarenko	1.45	0.21	77.00	0.00	3.81	15.55	0.47	0.24	0.12	0.08	0.406		
/15 10.5	Field. D. Tetarenko	1.54	0.20	77.97	0.22	3.15	15.75	0.43	0.22	0.12	0.07	0.427		
	Average	1.32												

As the current $H_2\%$ is $H_2 = 1.4\%$, translated to percentage, the $CO_{2coke-gas}$ will correspond to approximately 0.7%. Consequently, the CO_2 due to pure burning will be:

$$CO_{2-burn} = CO_{2-r} - CO_{2coke-gas}$$

$$CO_{2-burn} = 0.155–0.007 = 0.148 \ (14.8\%)$$

Taking into account the gases not participating directly to the oxidation, the so-called foreign gases (FG = $H_2 + CH_4 + C_2^+ + H_2S$) for H/C ratio calculation (Sheng, 2013), equation (3) applies, where FG = 6.6%:

$$H/C = (1-(FG/100)) \{[106 / (CO_2+CO)] +$$

$$[2CO-5.06 \ (CO_2+CO + O_2)] / (CO_2+CO)\} \quad (3)$$

$$H/C = [106+2CO-5.06 \ (CO_2+CO + O_2)] / (CO_2+CO) \quad (4)$$

In the above equations it is automatically considered that the CO_2 recorded is due exclusively to oxidation reactions.

While in equation (3) the percentage as recorded are applied, when using equation (4) the normalized percentages of CO_2, CO and O_2 have to be used.

In order to switch to normalized percentages, from the recorded composition:

$CO_2 = 15.5\%$; $CO = 0.05\%$; $O_2 = 0.22$; $N_2 = 77\%$, we have:

$CO_2\% + CO\% + O_2\% + N_2\% = 93.4\%$ and 93.4 will be the new base for calculation of normalized percentages, i.e.:

$CO_2 = 15.5/93.4 = 16.6\%$; $CO = 0.05/93.4 = 0.054\%$; $O_2 = 0.22/93.4 = 0.236\%$ and

$N_2 = 77/93.4 = 82.44\%$, with 16.6 + 0.054+0.236 + 82.44 = 99.3%

Application of equation (3), or of equation (4) (using the normalized percentages, calculated), would give:

$H/C = 1.24$

In order to correct for the CO_2, which is generated by coke gasification and WGSR, for the calculation of a more representative H/C ratio, in equation (3), the average percentages of gases should be considered, as follows:

$CO_{2-burn} = 14.8\%$; $CO = 0.05\%$; $O_2 = 0.22$; $N_2 = 77\%$; $H_2 = 1.4\%$; $CH_4 = 3\%$; $C_2^+ = 1\%$, $H_2S = 0.4\%$ and $CO_{2coke-gas} = 0.7\%$. It is to be underlined that in equation (3), the percentage of $CO_{2coke-gas}$ will be considered along with hydrogen, methane, C_{2+} and H_2S, as being gas not taking part directly in the oxidation; therefore, the FG = 7.3%. Similarly, in calculation of normalized percentages the new base will take into consideration a reduced CO2 percentage (14.8%).

The calculated H/C ratio will be 1.49, as compared with 1.24, when the correction for coke gasification and WGSR was not considered.

This fully corrected value (1.49) is higher. Therefore, without correction for the coke gasification the value of H/C is smaller, which may artificially show a better quality of burning than in reality.

For a certain day, for example the day of February 4th, 2016 (the first record from Table 1a-highlighted in blue), the real composition is:

CO2-r = 15.58%; CO = 0.01%; N2 = 76.87%; O2 = 0.31; H2 = 1.27%; CH4 = 3.93%; C2+ = 1.62% and H2S = 0.463%. (total 100%)
With FG = 7.28%
In this case, H/C = 1.137.
In order to make the correction for coke gasification and WGSR:
As H2% = 1.27%, then CO2coke-gas = 0.635%
CO2-burn = 15.58–0.64 = 14.94%, and the modified composition (to account for correction) will be:
CO2-burn = 14.94%; CO = 0.01%; O2 = 0.31; N2 = 76.87%; H2 = 1.4%; CH4 = 3.93%; C2+ = 1.62%, H2S = 0.463% and CO2coke-gas = 0.64%.

In this case: FG = 7.28 + 0.64 = 7.92.
And the corrected for coke gasification and WGSR, H/C = 1.35.
Similar calculations for a day when the CO_2 was maximum (16%) and another day, when the CO_2 was minimum (14.62%) - highlighted in Table 1 - gave H/C values of 1.17 and 1.58, respectively, while with coke gasification and WGSR corrections these values increased to 1.39 and 1.87, respectively. It can be noticed that with or without correction, the values suggest a better burning quality, hence a higher peak temperature for the case when CO_2 was maximum.

Actually, this calculation - of the normal H/C ratio and of the H/C ratio corrected (for the coke gasification and WGSR) - has been done for the entire life project for both KP1 and KP2 wells. The difference between normal value of H/C ratio and the corrected one is not extremely high.

4.3. Interpretation of results, limitations and possible further developments

As shown, the production of hydrogen in THAI process can be used to evaluate the CO_2, which is not generated by oxidation, but in consecutive reactions of coke gasification and water gas shift. Taking into account this non-oxidation-generated CO_2 it was shown that the H/C ratio would slightly increase actually eliminating the error due to neglecting of the coke gasification and WGSR. Although increased, the H/C has never taken values higher than 2 showing that, generally, in the THAI process the intensity of LTO is considerably lower than in conventional ISC.

Above analysis suggests that there is a significant potential for coke gasification and water gas shift reactions to occur during THAI. It seems that the consumption of produced CO from the first reaction (coke gasification) can be directly related with the production of hydrogen through WGSR.

For a more in-depth look at the Kerrobert Project, the whole evolution in time, of the hydrogen and CO percentages in the produced gas for the well KP1 and KP2 is shown in Fig. 4a and b, respectively; in these figures, also, the O_2 percentage was added to the graph.

Inspecting Fig. 4a and b, the following conclusions can be drawn:

➢ It is confirmed that for both wells, always the $H_2\%$ is higher than the CO%; there is just an isolated exception for KP1 well in April 29, 2011 when CO% slightly exceeds $H_2\%$ (2% versus 1.8%). As a rule, $H_2\%$ never becomes zero, while CO% can be zero in many cases.

➢ For both wells, for the first period after initiation of ISC, CO% was higher (0.5–1.5%) than afterwards, when it was less than 0.3%; $H_2\%$ was also higher in this first period (up to 3–4%), but it stabilized at around 1% (range 0.5%–1.5%) in the second period. Therefore, both H_2 and CO production was higher in the first period. To some extent this can be related to the existence of more **l**ow **t**emperature **o**xidation (LTO) reactions during and immediately after ignition operation.

➢ It can be speculated that in the first period the stand-alone coke gasification reactions, on one hand, and consecutive reactions of coke gasification and water-gas shift reactions, on the other hand, co-existed; this led to a ratio of $H_2\%/CO\%$ between 1 and 5, with value around 1 characterizing the predominance of coke gasification reactions - alone, without or very few other reactions. The second period, however, can be easily characterized by existence of predominant consecutive reactions of coke gasification and water-gas shift reactions, leading to the almost zero CO% and high values of $H_2\%$ (ratio of $H_2\%/CO\%$ extremely high in several cases infinity - see Table 1). It is speculated that this difference may be due to the fact that the burning surface is relatively small in the first period, but increases considerably in time; in line with that, the residence time of CO increases significantly in the second period, and the WGSR have by far higher probability to happen on a considerably bigger hot surface.

➢ In this first period of high CO% and H_2%, it was noticed that sometimes, spikes of CO lead to spikes in H_2 production, otherwise these parameters are not very correlated. For instance, for well KP1 the highest H_2% recorded were 3.85%, 4.97% and 3.82% at the dates of January 26, 2010, November 19, 2010 and January 28, 2011, respectively. At these dates, the CO% were 1.6%, 0.61% and 0.25%, such way not showing a clear correlation between individual H_2 and CO values (considered independent of time), although it shows that CO% decreased in time, as the hot burning surface became bigger and bigger.

➢ For the same first period, for well KP2 the highest H_2% recorded were 4.9%, 4.98%,4.71 and 7.42% at the dates of September 11 and 22, 2010, October 6, 2010 and March 14, 2011, respectively. At these dates, the CO% were 0.4%, 0.5%, 0.33 and 1%, this, not showing a correlation between individual H_2 and CO. and even a clear trend of decrease of CO in time. However, it has to be pointed out that at those dates the H_2S had an extremely high value, respectively 2.7%, 1.84, 1.74% and 1.2% (12,000 ppm), as compared to the normal range of 0.4–0.6%; a weak correlation between H_2 %

and H_2S% may exist. These very high values may suggest the existence of very high peak temperatures, as it was shown that, in SAGD, H_2S production increases with increasing temperature in the SAGD chamber (Kapadia et al., 2012). At this time, it is not known if a correction for H_2 due to H_2S production is necessary; in other words, it is not known if H_2S production causes additional hydrogen to be generated, or, even more plausible, hydrogen consumption is increased. It seems to be a difficult task; it may be worthwhile to be approached, in a separate project.

The Chinese investigators reported that in their field THAI pilot, a spike in hydrogen heralded an increase of the peak temperature in the ISC front (Guan, 2017). Therefore, it may be that higher H_2% are associated with higher peak temperatures.

There are essential differences between wells KP1 and KP2 performances, as in the last two years (2013–2014) the H_2% decreased continuously in KP1 (up to as low as 0.5%), while stayed in the range of 1–1.5% in KP2. The decrease of H_2% in KP1 was due to a continuous and pronounced decrease of air injection rate from approx. 36,000 sm^3/day
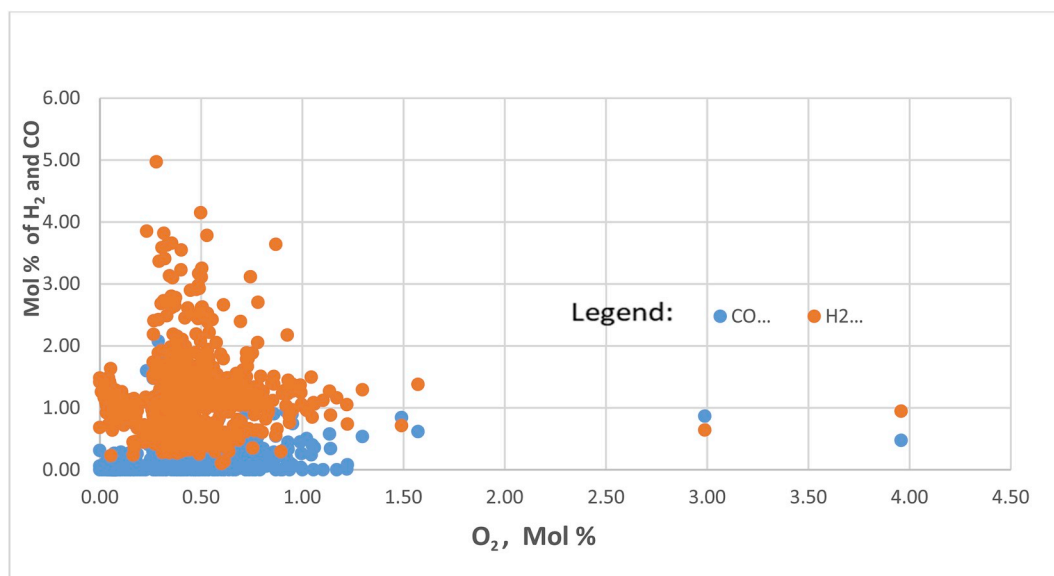
a
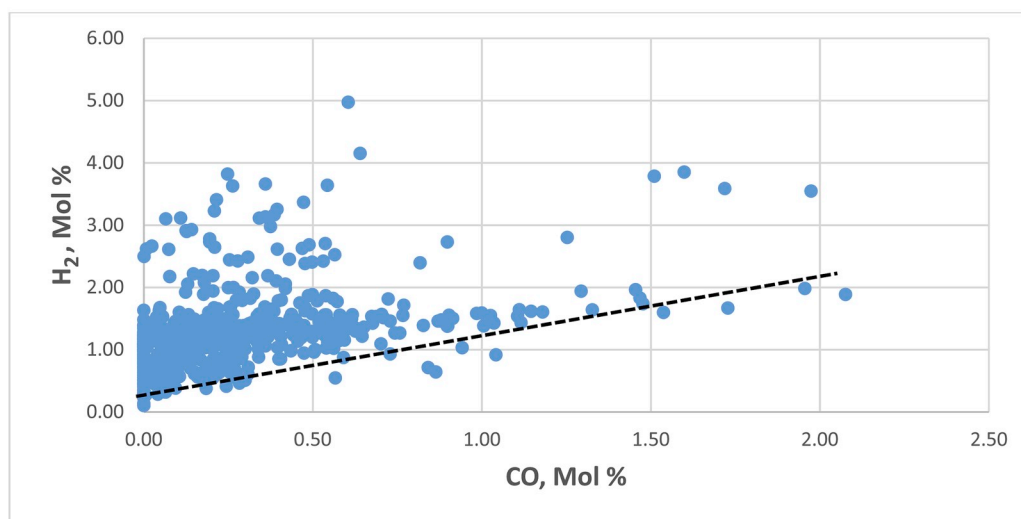
b

Fig. 5. a: Well KP1 Kerrobert. Correlation of the hydrogen (H_2) and carbon oxide (CO) with the oxygen (O_2) in the gas produced. b: Well KP1 Kerrobert. Attempt to correlate the H_2 percentage with CO percentage, for low percentages of O_2 in the produced gas (for $O_2<1$%) i. e for all points located left in Fig. 5a.

to approx. 12,000 sm^3/day in this period for the well pair KA1-KP1 (Turta et al., 2018). This led to a slight decrease of the burning quality (hence of the decrease of peak temperature in the ISC front) as indicated by the H/C ratio pronounced increase in that period. Indirectly, this would support the correlation of H$_2$ production with the value of maximum peak temperature of the ISC front, as found by the Chinese researchers.

Of course, for both wells, only building and analyzing separate representations for O$_2$–H$_2$ and O$_2$–CO, on the one hand, and then making a final attempt for a correlation H$_2$–CO it may be possible to find how the O$_2$ in the produced gases may have an influence (if any) on the strength of the CO–H$_2$ correlation. As a first step further processing of complete data from Fig. 4a and b were done, as suggested, and the results for well KP1 - which had the largest O$_2$ variation - are provided in Fig. 5a and b. The results for KP2 are very similar to those for KP1.

From Fig. 5a and b three conclusions can be drawn:

➢ Fig. 5a confirms that H$_2$% never takes a zero value.
➢ As seen in Fig. 5a, when O$_2$ is higher than 1–1.3%, both CO% and H$_2$% are less than 1%. In this case, there is little interest for the new method to be applied, as H$_2$ percentage is very small; non-burning CO$_2$ should also be very small. The figures for CO and H$_2$ are exactly halved for well KP2
➢ As seen in Fig. 5a, up to an O$_2$% of 1–1.3% the maximum values of H$_2$% (possible to be reached), - as outlined by an interrupted line - are generally decreasing as O$_2$% increases (an inverse correlation between H$_2$ and O$_2$ percentages); for the same conditions, the CO remain at a lower level (less than 2%). The full trend for the CO % values cannot be seen on Fig. 5a.
➢ For all the points from Fig. 5a - having O$_2$ < 1% - a correlation between H$_2$% and CO% was investigated in Fig. 5b. It can be seen that CO% does not seem to correlate with H$_2$. However, a weak direct correlation seem to exist between the minimum values of H2% (possible to be reached) - as outlined by an interrupted line - and the CO% values. This conclusion (lack of CO–H$_2$ correlation in case of KP1 well for O$_2$ <1%) was easily confirmed for the gas analyses of KP2 well (Fig. 6), which shows a similar pattern for the distribution of the points.

5. Conclusions

1. After summarizing the possible reactions in in-situ combustion process that can produce CO, H$_2$ and CO$_2$, on the basis of these reaction pathways, taking into account the coke gasification and water gas shift reactions, a novel method to calculate the apparent hydrogen-carbon (H/C) ratio for Toe to Heel Air Injection (THAI) process is proposed. In principle, the method is based on the determination of the CO$_2$, which is not generated by oxidation, and this CO$_2$ is calculated based on the H$_2$ produced from coke gasification and water gas shift reactions

2. The novel method was applied for Kerrobert THAI Project. According to the predominance of coke gasification and water gas shift reactions, two main periods could be distinguished. A first period, after the initiation of the in-situ combustion front, when stand-alone coke gasification reactions, and consecutive coke gasification reaction and water-gas shift reaction seemed to co-exist, while after this period, for the rest of the project, consecutive coke gasification reactions and water-gas shift reactions seemed to predominate and led to almost NIL CO content in the produced gas. The newly developed method was applied for the second period.

3. After applying the new method, it was found that the H/C increases, but it still shows that in the THAI process the low temperature oxidation (LTO) reactions are insignificant.

4. In the Kerrobert Project the H$_2$ content never becomes zero and it is always higher than CO content. It was found that O$_2$% higher than 1% cause both CO and H$_2$ to be low, less than 1%. For O$_2$% lower than 1%, H$_2$% can be up to 5%, while the CO% can be up to 2%; in this case the maximum values of H$_2$% (possible to be reached) are generally decreasing as O$_2$% increases (an inverse correlation exists); for the same conditions, the CO remain at a lower level. Furthermore, for lower O$_2$ percentages (less than 1%) it seems that a correlation between CO and H$_2$ percentages does not exist. However, a weak direct correlation seem to exist between the minimum values of H$_2$% (possible to be reached) and the CO% values. The complexity of the THAI execution in the presence of bottom water may cloud, to some extent, some of the correlations.

5. The developed method has the limitation that the effects of CO and CO$_2$ produced by pyrolysis and aquathermolysis were not accounted for. Also, it was not determined if there is an effect related to the production of H$_2$S on the H/C estimate in the THAI process. Finally,
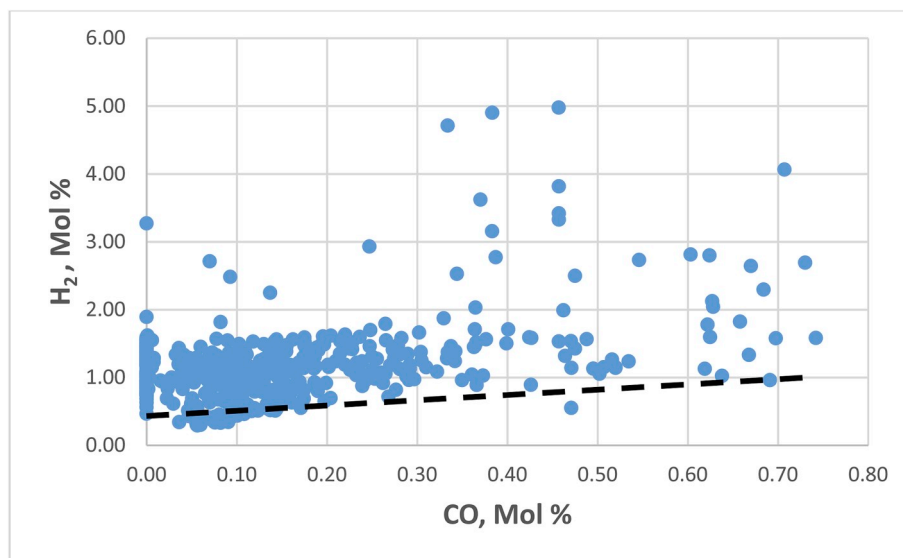

Fig. 6. Well KP2 Kerrobert. Attempt to correlate the H$_2$ percentage with CO percentage, for low percentages of O$_2$ in the produced gas (for O$_2$<1%). Note: An extremely weak correlation may exist for CO%<0.3%.

the consumption of hydrogen by methanation process should be considered, as well, at least from a theoretical point of view.

6. More work is necessary to consolidate the results, and extend them to the first period, immediately after the initiation of ISC. Also, it is necessary to better define the potential errors and the scope for the method application. The proposed method will provide an important tool for the evaluation of the former, current and future THAI projects, and thus contribute to the development of this novel ISC process.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2019.106638.

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