

Carbon stable isotope analysis as a tool for tracing temperature during the El Tremedal underground coal gasification at great depth

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Abstract

The new opportunity given by the underground gasifier developed at Alcorisa in Spain (Province of Teruel) in the framework of an European experiment has promoted a better understanding of gasification in a natural reactor. The thermodynamical equilibria of gasification reactions and the repartition of the stable isotopes of carbon ($^{13}\text{C}/^{12}\text{C}$) in the produced gases have been used to monitor the process. An estimation of the temperatures inside the gasifier and at the exhaust has been performed. As shown by the isotopic balances, the tar formation is negligible or null and the pyrolysis zone spreads continuously. The study has confirmed the reality of the ^{13}C isotopic abundance measurements for the system CO/CO₂ as an indicator of the temperature inside the gasifier. During the gasifier expansion, the temperature at the exhaust decreases whereas the temperature inside the gasifier is practically constant showing a slight increasing trend. As pointed out by the data, the oxygen enrichment of the gasifying agent plays an important role on the estimated temperatures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gasification of coal; Modelling; Thermodynamics; Isotopic exchanges

1. Introduction

The well-known economical problem rising from the working of coal resources at great depth needs an effective alternative solution. For that reason, previous underground coal gasification experiments have been performed in the United States and in Europe, for instance at Thulin, Belgium [1]. In the framework of the THERMIE programme and financially supported by the European Commission and by Spanish, Belgian and UK organisations, new underground coal gasification (UCG) operations have been carried out at Alcorisa site (Teruel province), Spain, during summer and autumn 1997 [2]. The technical feasibility of UCG at 600 m depth demonstrated by the project is a significant improvement compared with previous low depth successful trials performed in the USA.

The experimental plant is summarised in Fig. 1. A first well, by which gasifying agents are injected, is an in-seam deviated well along which UCG takes place. A second well

intersecting vertically the end section of the in-seam deviated well serves for the recovery of the produced gases. Furthermore, a coiled tubing introduced inside the deviated injection well enables the Controlled Retraction of the Injection Point (CRIP) manoeuvre. Other details dealing with site geology, drilling, well completion and engineering activities are described elsewhere [3]. The two gasification operation phases, namely from 21 to 29 July 1997 and from 1 to 5 October 1997, are described by Chapel and Mostade [2]. The analysis of the results obtained from the Alcorisa gasifier is quite complex. On one hand, the flows at the inlet and the outlet of the gasifier are not accurately known due to the loss of gasifying agent and reaction products through the coal seam and the coal layer roof. On the other hand, the drastic experimental conditions prevailing inside the gasifier do not allow in situ measurements. Taking into account the experimental and theoretical uncertainties, a macroscopic description of the gasifier based on the thermodynamical equilibria is a rather satisfying approach due to the long residence times of the gases in the gasifier and to the high level of backmixing in the reactor as shown by helium tracer tests [4] and by simulation [5–7].

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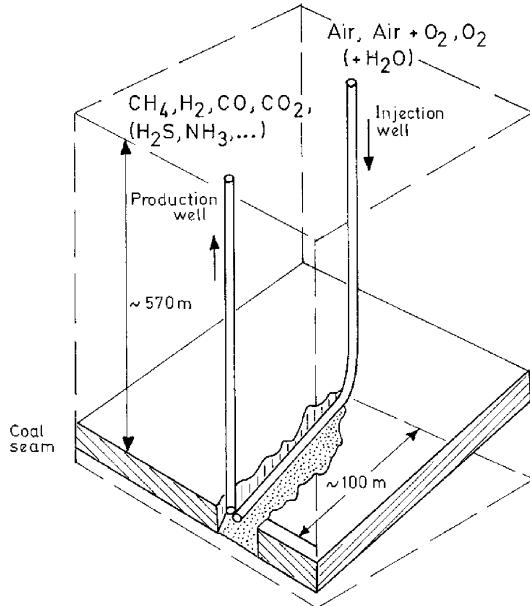


Fig. 1. Scheme of the underground gasification process.

A better understanding of the process needs additional information dealing with the in situ temperature and the mass balances. In a companion study concerning with the Thulin gasifier, the usefulness of the D and ^{13}C isotopic abundances determination in coal, gases and liquids recovered at the outlet for the in situ temperature estimation and the mass balances checking, have been successfully demonstrated [8–11]. For the present study, we have used such an indirect approach for the Alcorisa gasifier, taking into account isotopic and chemical equilibria data.

Despite stable isotope analysis were used in a similar way for in situ temperatures calculations at both Thulin and Alcorisa, a considerable difference related to the gasifier working procedure must be stressed. At Thulin, the gasification occurred by means of filtration through the coal seam and the composition of the produced gas allowed to separate between the contribution of pyrolysis and gasification [9]. At the contrary, since the gasification in Alcorisa occurred inside a cavity along a channel with a high backmixing rate [4], the gas produced by coal pyrolysis was involved in both combustion and gasification reactions.

2. Principles of isotopic exchanges analysis

Hydrogen, carbon, oxygen, nitrogen and sulphur are the main elements contained in the produced gases at Alcorisa. All these elements have different stable isotopes whose relative abundance between various molecules slightly varies with the chemical processes in which each element is involved. Usually stable isotopes are used as tracer when radioactivity problems rise or when the element has no radio-isotope with an half-life long enough (which is the case for nitrogen and oxygen). In these cases, the abundance

variations of the rare isotope used as tracer, connected with the different physico-chemical behaviour of isotopic molecules, are totally neglected. When stable isotopes have no tracer role, the relative small abundance variations of an element, measured accurately with a mass spectrometer, can be useful for the study of the mechanism of reactions involving the studied element. Despite the fact that many applications are well-known in chemistry, biochemistry and hydrology, this approach seems to be less used in the gas-coal reactions studies [12].

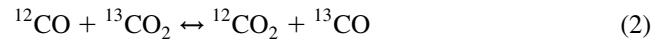
Considering R_i as the isotopic ratio between the number of heavy and light isotopes of the same element present in the molecule i, the isotopic abundance is thus defined by the common delta notation:

$$\delta = \left(\frac{R_i}{R_{\text{ST}}} - 1 \right) 10^3 \quad (1)$$

where R_{ST} refers to the isotopic ratio of the same two isotopes in a reference sample (V-PDB for ^{13}C , V-PDB is an international standard).

The isotopic abundance δ is directly proportional to the concentration of an isotope and can be used instead of absolute concentration in isotopic balances.

Although the isotopic exchange phenomena have been known for a long time, the kinetic data relative to these reactions are rather rare. Therefore, it is commonly admitted to consider that the isotope distribution complies with the thermodynamic laws and to neglect all phenomenon occurring outside equilibrium state. If we consider the following isotopic equilibrium:



The corresponding equilibrium constant is

$$\alpha = \frac{[^{13}\text{CO}]^{12}\text{CO}_2}{[^{12}\text{CO}]^{13}\text{CO}_2} = \left(\frac{R_{\text{CO}}}{R_{\text{CO}_2}} \right)_{\text{eq}} \quad (3)$$

Taking into account the relation between R_i and δ , as well as the small value of δ , α can be written:

$$10^3 \ln \alpha = \delta^{13}\text{C}_{\text{CO}} - \delta^{13}\text{C}_{\text{CO}_2} = \epsilon_{\text{CO-CO}_2}(T) \quad (4)$$

$\epsilon(T)$ so defined is called the isotopic fractionation.

For each isotopic exchange of an element between two molecules i and j, the equilibrium equation can be written

$$\epsilon_{ij}(T) = \delta_i - \delta_j \quad (5)$$

For pressures below 1 GPa, equilibrium is only temperature dependent [13]. Assuming that the isotope distribution should obey statistical thermodynamic laws, the isotopic fractionation factor, $\epsilon_{ij}(T)$, an absolute temperature function, is calculated using thermodynamical data collected by Richet et al. [14] and Bottinga [15].

Eq. (5) which gives the isotopic fractionation of an element is not sufficient for temperature estimation. The mass balance and the isotopic mass balance must also be verified in each zone of the reactor and in the whole reactor.

Namely, the following additional equations must be solved:

$$(\sum \nu Q)_{\text{in}} = (\sum \nu Q)_{\text{out}} \quad (\sum \nu Q\delta)_{\text{in}} = (\sum \nu Q\delta)_{\text{out}} \quad (6)$$

where Q is the molar flow of each molecular species containing the chemical element; δ is the isotopic abundance of the element, and ν is the number of this element in each molecular species.

3. The problem of Alcorisa gasifier modelling

In the case of the Thulin gasifier, the hypothesis of the existence of two separate reacting zones (a coal pyrolysis internal box and a residual char burning and gasification external box) was supported by experimental results; the produced gases being the sum of gases generated in each zone [9]. On the contrary, as already mentioned above, the Alcorisa gasifier can be described as a highly backmixed reactor [5–7] where the gas produced by coal pyrolysis is involved in the combustion and gasification reactions. As a consequence, the models developed for the experiment performed at Thulin cannot be used with the data obtained from Alcorisa. A thermodynamical model including the pyrolysis gas in the gasification area equilibrium is too complex and depending on too many parameters in comparison with the quality and quantity of experimental data.

As described further, the main isotopic thermometer is based on the repartition of ^{13}C in the couple $\text{CO}_2\text{--CO}$. Since these gases are produced in the combustion–gasification zone, the isotopic fractionation alone can be considered, in a first approximation, as a correct measurement of the exchange temperature of this zone.

4. Experimental

4.1. Sampling

The core samples recovered from several post-burn drillings consist of a mixture of matter and rubbles impregnated by drilling mud coming from the geological formations situated at the top of the cavity developed by the gasifier. The very low recovery rate of carbon does not allow significant isotopic abundance measurements.

The sampling of gases has been performed in a glass vessel connected on a pipe flushed by the produced gas. Practically, 10 glass vessels, labelled from 1 to 10, have been collected for isotopic analysis.

In order to record information about the virgin coal, 11 solid samples located at different depths have been taken as well.

4.2. Gas analysis

Between the well-head of the production well and their combustion in the incinerator, the gases pass successively through different units, namely a first expansion room, a

heat exchanger, a flowmeter, a sampling pipe for online gas analysis and a second expansion room. The heat exchanger is used to keep the produced gases in their gaseous state in order to allow accurate flow measurements and sampling.

The composition of dry gas and liquid fraction is obtained with the online gas analysis unit. These data allow the control of each operating phases during a test as well as the calculation of mass and heat balances.

The control of the process is ensured by several specific apparatus: a paramagnetic analyser for oxygen, a multi-channel infrared analyser for carbon monoxide, carbon dioxide and methane, an ultraviolet analyser for hydrogen sulphide and a gas chromatograph for hydrogen. A redundancy of these data is given by an online mass spectrometer which allows the analysis of Ar, He, C_2H_6 , C_3H_8 , NH_3 , and heavier hydrocarbons (C_4 , C_5 , $\text{C}_6 +$) content as well for mass balance calculations and further analysis of tracer tests.

4.3. Analytical method for the isotopic abundance measurement

4.3.1. Gaseous sample

The isotopic abundance measurements imply the quantitative separation as well as the collection of the involved gases. Taking into account that only the ^{13}C repartition in the $\text{CO}_2\text{--CO}$ couple is considered, gases containing carbon (CO , CH_4, \dots) must be oxidised to the CO_2 form for practical mass spectrometer analysis reasons. The $\delta^{13}\text{C}$ isotopic abundance is then measured using a mass spectrometer. The whole process from the gas separation to the isotopic measurements is described elsewhere [16].

Considering the various analytical problems due to the complexity of the gaseous mixtures or liquids recovered, the isotopic results are given with the following accuracy:

$$\begin{aligned} &\pm 0.1\% \text{ for } \delta^{13}\text{C}_{\text{CO}_2} \\ &\pm 0.2\% \text{ for } \delta^{13}\text{C}_{\text{CH}_4} \text{ and } \delta^{13}\text{C}_{\text{CO}} \\ &\pm 0.1\% \text{ for } \delta^{13}\text{C}_{\text{Coal}}. \end{aligned}$$

4.3.2. Solid samples

After grinding and homogenisation of coal samples, about 1 mg of sample is introduced in an elemental analyser connected by continuous flow to the mass spectrometer for $\delta^{13}\text{C}_{\text{CO}_2}$ measurements. This latter operation is performed three times for each sample.

5. Results

The operating conditions of the underground gasifier during gaseous samples collecting periods are given in Table 1. The inside gasifier pressure (P_R), considered as constant during these periods, is the arithmetic mean of the inlet and outlet pressures. The pressure values are determined by means of the well-head pressure, taking into

Table 1

Operating conditions during the gaseous samples collecting

Sample	Injection		Operating conditions				
	Date	Hour	$F_{\text{in}, \text{O}_2}$ (kmol/h)	$F_{\text{in}, \text{N}_2}$ (kmol/h)	F_{out} (kmol/h)	P_R (MPa)	r_{Ar}
1	26/07/97	19:50	7.6	12.2	30.0	4.80	0.68
2	27/07/97	9:55	7.6	12.2	48.4	4.75	0.74
3	27/07/97	18:55	7.6	12.2	29.3	4.68	0.66
4	28/07/97	9:00	7.6	12.2	29.6	4.75	0.67
5	28/07/97	18:45	7.6	12.2	23.2	5.10	0.54
6	29/07/97	9:00	7.6	12.2	16.3	5.12	1.27
7	2/10/97	18:00	22.3	17.1	120.0	5.12	1.21
8	3/10/97	9:50	22.3	17.3	68.1	4.96	0.74
9	3/10/97	16:00	26.8	1.4	60.5	4.89	0.67
10	4/10/97	7:44	30.0	18.1	62.8	5.06	0.72

account the weight of the gaseous column in the well. The recovery rate r_{Ar} , i.e. the quantity of injected gas recovered at the exhaust, is calculated from the argon mass balance [2].

The composition of the dry gas at the gasifier outlet, reported in Table 2, is deduced from the gas composition at the wellhead taking into account the N_2 quantity injected in the recovery well.

The coal composition, obtained by means of ASTM standard procedure, is shown at Table 3. Following the ASTM classification, the data can be considered typical of subbituminous coal of class C closed to the lignite rank.

The data plotted on the diagram of Fig. 2 show the mean $\delta^{13}\text{C}_{\text{Coal}}$ values for each sample of the virgin coal and the corresponding depth. It must be stressed the lowest ^{13}C content near the roof and the wall of the coal seam. The mean value for the coal seam, calculated without taking into account the two extreme $\delta^{13}\text{C}$ is equal to $-22.08\text{\textperthousand}$ ($\sigma = 0.32\text{\textperthousand}$). It is interesting to note that the isotopic value $\delta^{13}\text{C}$ of organic matter near the roof and wall of the coal seam are significantly lower than the mean isotopic value $\delta^{13}\text{C}$ of the virgin coal. Such a situation has also been observed at Thulin ($\delta^{13}\text{C}_{\text{Coal}} = -23.6\text{\textperthousand}$). The Alcorisa $\delta^{13}\text{C}_{\text{Coal}}$ ($-22.08\text{\textperthousand}$) is rather high if compared with the $\delta^{13}\text{C}_{\text{Coal}}$ values of European coals ($-23\text{--}24\text{\textperthousand}$) [17]. The

$\delta^{13}\text{C}_{\text{Coal}}$ values for non-European coals range between -25 and $-26\text{\textperthousand}$. The values from Alcorisa could result from ‘a cooking effect’ related to the intense tectonic movements the coal has been submitted to. The organic matter near the roof and the wall of the coal seam should have kept a lower value near the initial value of the coal before any transformation [17].

The ^{13}C isotopic abundances mean values of CO_2 , CH_4 and CO contained in the samples are reported in Table 4.

6. Discussion

6.1. Argon and water content

The measured argon and water flow rates show the complex working conditions of the underground gasifier. The injected argon flow rate is systematically higher than the one recovered in the gasification products, gasifying agent and produced gases leaks through the coal seam and the roof deposit.

Despite the fact that the injected gasifying agent contains no water, the recovered water flow rate is very high. Moreover, the recovered water quantity at the outlet well is progressively much higher than the calculated one using

Table 2

Dry gas composition at the gasifier outlet, calculated liquid fraction and T_{chim} temperature

Sample	Dry gas composition					$(\text{H}_2\text{O})_{\text{eq}}$ (%)	T_{chim} (K)
	n_{CO_2} (%)	n_{CO} (%)	n_{CH_4} (%)	n_{H_2} (%)	$n_{\text{H}_2\text{S}}$ (%)		
1	29.5	4.0	10.7	14.7	6.0	23.0	959
2	30.7	3.2	10.7	7.5	6.5	27.0	948
3	30.0	3.0	8.2	15.1	6.4	21.0	946
4	30.1	2.9	7.5	14.8	6.0	24.0	946
5	29.8	2.9	8.6	14.6	6.3	30.0	944
6	28.6	1.8	5.9	13.1	6.1	39.0	926
7	32.6	14.2	16.2	17.2	8.7	44.0	1016
8	34.7	10.3	10.1	18.3	7.9	0.0	1012
9	36.7	8.4	10.4	20.5	8.4	22.0	1001
10	41.6	8.8	7.8	18.3	7.5	23.5	1001

Table 3

ASTM immediate and elemental analysis of coal (– not measured)

Sample	Depth (m)	Immediate analysis				Elemental analysis				
		Moisture (% mass)	Ash (% mass)	Char (% mass)	Volatile matter (% mass)	C (% mass)	H (% mass)	N (% mass)	S (% mass)	O (% mass)
1	528.3	31.8	14.4	30.6	23.2	69.6	4.7	0.6	7.5	17.6
2	528.6	20.4	39.1	21.6	18.9	61.3	4.3	0.7	–	–
3	529.0	29.9	13.3	33.2	23.6	68.1	4.5	0.6	7.0	19.8
4	529.4	28.6	11.9	33.9	25.6	71.1	4.6	0.5	–	–
5	529.9	28.5	12.1	34.1	25.3	71.7	4.6	0.5	–	–
6	530.2	27.5	16.3	32.5	23.7	70.5	4.4	0.6	6.4	18.1
7	530.4	32.5	9.4	32.3	25.8	73.0	4.7	0.5	–	–
8	530.7	26.6	14.7	33.3	25.4	69.9	4.4	0.5	–	–
9	531.0	31.3	7.9	35.1	25.7	74.3	4.6	0.5	–	–
10	531.4	24.9	16.5	32.9	25.7	71.1	4.7	0.5	6.0	17.7
11	531.9	29.5	7.7	35.1	27.7	73.4	4.7	0.4	46.5	–

thermodynamical equilibria from the dry gas composition. It may be concluded that significant amounts of water come from the roof clayey sand and that the progressive increase of the water quantity is not involved in the gasification process but is directly recovered at the production well.

6.2. ^{13}C isotopic abundances

The whole reactions of combustion, gasification and

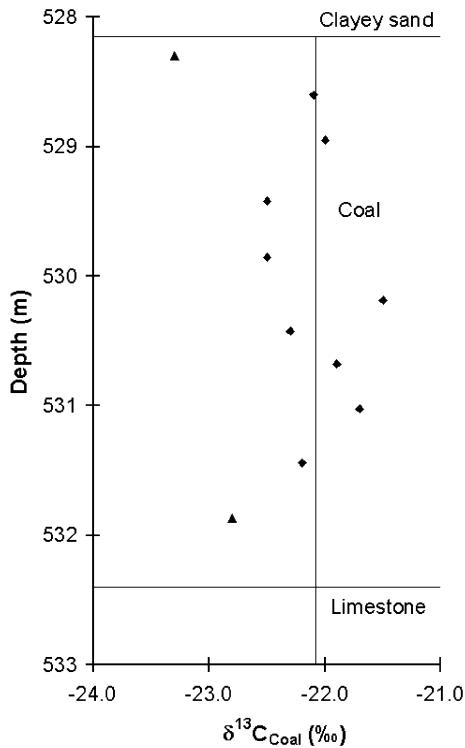
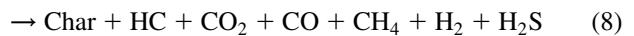
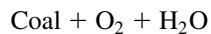


Fig. 2. Evolution of $\delta^{13}\text{C}_{\text{Coal}}$ with depth. ▲ samples near the roof and wall of the coal seam, ◆ samples taken in account for the $\delta^{13}\text{C}_{\text{Coal}}$ mean value calculation.

pyrolysis can be written as a global reaction:



where Char = residual coke, HC = hydrocarbons and the other organic compounds heavier than methane, in particular tars.

On the basis of the isotopic fractionation $\epsilon(T)$ calculated by Richet et al. [14] and Bottinga [15] and on the basis of the ^{13}C mass balance, it can be deduced that the $\delta^{13}\text{C}$ for each molecular species have to follow the sequence:

$$\begin{aligned} \delta^{13}\text{C}_{\text{CO}} &< \delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{HC}} < \delta^{13}\text{C}_{\text{Coal}} < \delta^{13}\text{C}_{\text{Char}} \\ &< \delta^{13}\text{C}_{\text{CO}_2} \end{aligned} \quad (9)$$

The data of Table 4 verifies this inequality. Due to a lack of representative samples, the relation (9) has not been verified for the ^{13}C of tars (HC) and residual coke. It must be stressed that the inequality (9) has also been observed during the Thulin experiment [9]. This is particularly important, because it can be concluded that the shifts in isotopic

Table 4
Measured mean values of ^{13}C isotopic abundances for CO_2 , CH_4 and CO and calculated isotopic equilibrium temperature using Eq. (4)

Sample	$\delta^{13}\text{C}_{\text{CO}_2} (\text{\textperthousand})$	$\delta^{13}\text{C}_{\text{CO}} (\text{\textperthousand})$	$\delta^{13}\text{C}_{\text{CH}_4} (\text{\textperthousand})$	$T_{\delta^{13}\text{C}} (\text{K})$
1	-19.30	-27.9	-27.0	1175
2	-19.60	-30.0	-26.8	1060
3	-20.05	-29.9	-27.3	1090
4	-19.75	-28.8	-27.8	1145
5	-20.00	-29.2	-26.3	1130
6	-21.20	-27.4	-25.5	1390
7	-17.60	-24.8	-25.1	1295
8	-19.30	-26.4	-25.3	1300
9	-19.75	-26.1	-25.6	1370
10	-19.40	-25.9	-25.7	1360

abundance between gaseous compounds can be used a priori for the estimation of the isotopic equilibria temperature.

Previous work dealing with laboratory tests corroborate the results obtained from Alcorisa and Thulin but also point out their limits. It is of particular interest to keep in mind the following observations:

the inequality $\delta^{13}\text{C}_{\text{CO}} < \delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{CO}_2}$ is respected for gases produced during coal pyrolysis at Thulin [18,19];

the residual coke ^{13}C content increases during open system pyrolysis of various coal including the one from Thulin; $\delta^{13}\text{C}_{\text{Coal}} < \delta^{13}\text{C}_{\text{Char}}$ [8];

the ^{13}C content of the tars recovered at the surface decreases during Thulin experiment; $\delta^{13}\text{C}_{\text{HC}} < \delta^{13}\text{C}_{\text{Coal}}$ [8].

Considering the methane production, the following previous results must be recalled:

the methane produced during the pyrolysis of coal from Thulin is poorer in ^{13}C ($\delta^{13}\text{C}_{\text{CH}_4} = -28.5\%$) than the initial coal ($\delta^{13}\text{C}_{\text{Coal}} = -23.6\%$) [9];

the methane formed by water reaction with residual coke obtained by pyrolysis of the coal from Thulin shows an isotopic fractionation around -5% , very closed to the isotopic fractionation of pyrolysis methane [9].

As a conclusion, one cannot distinguish the methane produced by pyrolysis from that obtained by methanation on the basis of ^{13}C measurements only. Complementary investigations are needed [10].

6.3. Isotopic balances

At each time t of the gasification process, the ^{13}C content of the solid carbon must be distributed between the produced compounds.

The mass balance at time t is written:

$$(\sum n_i) \delta^{13}\text{C}_{\text{Char}} = \sum n_i \delta^{13}\text{C}_i \quad (10)$$

where

n_i = ratio of compound i (CO , CO_2 , CH_4 , HC) in the gaseous mixture,

$\delta^{13}\text{C}_i$ = isotopic abundance in ^{13}C of molecular compound i ,

$\delta^{13}\text{C}_{\text{Char}}$ = isotopic abundance in ^{13}C of solid carbon.

Table 5 shows the ^{13}C mass balances for each sample. The calculations were performed assuming that the solid carbon is virgin coal ($\delta^{13}\text{C}_{\text{Char}} = \delta^{13}\text{C}_{\text{Coal}}$) and that gasification products containing carbon are the gaseous CO , CO_2 and CH_4 . On this basis, the ^{13}C mass balances are verified as

Table 5

Mass balance calculations for ^{13}C and calculated $\delta\text{C}_{\text{Char}}$ isotopic abundances ($\sum n_i = n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{CH}_4}$ (see Table 2))

Sample	$\sum n_i$ (%)	Mass balance		Δ (%)	$\delta\text{C}_{\text{char}}$ (%)
		$(\sum n_i) \delta^{13}\text{C}_{\text{char}}$	$\sum n_i \delta^{13}\text{C}_i$		
1	44.2	-9.70	-9.76	0.06	-21.94
2	44.6	-9.84	-9.85	0.01	-22.06
3	41.2	-9.14	-9.10	-0.04	-22.19
4	40.5	-8.88	-8.94	0.06	-21.93
5	41.3	-9.07	-9.12	0.05	-21.96
6	36.3	-8.05	-8.02	-0.03	-22.18
7	63.0	-13.32	-13.91	0.59	-21.15
8	55.1	-11.96	-12.17	0.21	-21.71
9	55.5	-12.10	-12.25	0.15	-21.80
10	58.2	-12.35	-12.85	0.50	-21.22

shown by the data (Table 5). Indeed,

$$\begin{aligned} n_{\text{CO}} \delta^{13}\text{C}_{\text{CO}} + n_{\text{CO}_2} \delta^{13}\text{C}_{\text{CO}_2} + n_{\text{CO}_2} \delta^{13}\text{C}_{\text{CH}_4} \\ \approx (n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CO}_2}) \delta^{13}\text{C}_{\text{Coal}} \end{aligned} \quad (11)$$

with a difference Δ being between 0.01 and 6.59%.

The ^{13}C mass balance (Eq. 10) allows the calculation of the char $\delta^{13}\text{C}_{\text{Char}}$ isotopic abundance (Table 5).

During the first gasification step (21–29 July), the ^{13}C isotopic abundances of virgin coal and char are practically identical, $\delta^{13}\text{C}_{\text{Char}} \approx \delta^{13}\text{C}_{\text{Coal}}$.

It can be concluded that, during the first gasification step, combustion and gasification reactions start from the ignition in a virgin coal area, which was expected, and that the only reaction products containing carbon are CO , CO_2 and CH_4 . The tars formation is probably negligible and the pyrolysis zone must not be very large.

During the second gasification step (1–5 October), the ^{13}C isotopic abundances of char calculated from the mass balance are higher than those measured for the virgin coal, $\delta^{13}\text{C}_{\text{Char}} > \delta^{13}\text{C}_{\text{Coal}}$. Such a difference could be explained by the production of heavier hydrocarbons (HC) poorer in ^{13}C as observed at Thulin [8]. However, at Alcorisa, no important organic liquids have been recovered at the surface. If we consider that these liquids remain inside the gasifier, they must be finally gasified with the advance of the gasification front. Eventually, all the carbon is recovered in the gaseous products $-\text{CO}_2$, CO , CH_4- . As a consequence, this hypothesis cannot be retained.

As already quoted above, the ^{13}C content of char increases during the coal pyrolysis [8]. Since the pyrolysis zone extends progressively, it can be supposed that in the case of Alcorisa gasifier, the combustion and gasification reactions of the second gasification phase, ignition, start in a zone containing already pyrolysed coal. At Thulin, the mass balance calculations lead to the same conclusion: the progressive enrichment of char during the growing of the gasifier [11]. This hypothesis has been confirmed by the analysis of char samples recovered by post-burn corings. It has been observed $\delta^{13}\text{C}_{\text{Char}} > \delta^{13}\text{C}_{\text{Coal}}$ [8]. Unfortunately,

no significant char samples have been recovered for analysis at Alcorisa and the $\delta^{13}\text{C}_{\text{Char}}$ variations calculated for each gasification phase are not significant.

Nevertheless, it must be stressed that the injection point has been retracted during each gasification phases thus probably compensating the pyrolysis effects, leading to an approximately constant isotopic composition of the gasified carbon.

6.4. Calculated temperature from chemical equilibrium

The combustion and gasification reactions can be described by the following chemical reaction system:

$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	Combustion reaction, exothermic
$\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$	Boudouard's reaction, endothermic
$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}$	Vapogasification reaction, endothermic
$\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$	Hydrogasification reaction, exothermic

The first equation is considered as complete and irreversible whereas the three others are considered reversible and at equilibrium despite the fact that, practically, the hydrogasification reaction equilibrium is never reached. The resolution of the system is difficult because the equations outnumber the unknown variables. In principle, all compositions are known, the temperature and the water fraction being the only unknown variables.

For practical reasons, the system is simplified and only two equations are simultaneously considered.

Model 1: Boudouard's reaction: $\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$ and shift reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$

Model 2: Shift reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ and methane reforming reaction: $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$

In both cases, the equilibrium temperature (T_{chim}) is calculated using the chemical equilibrium and resolving the obtained system, considering temperature and water fraction inside the gasifier as unknown variables.

The equilibrium temperatures calculated from model 1 (Shift + Boudouard) and from model 2 (Shift + reforming) are quite similar but the calculated temperature from model 1 is systematically lower than the one from model 2. The difference between the two temperatures is lower than 50 K. The T_{chim} temperatures calculated for model 2 are reported in Table 2. Fig. 3a and b show the evolution of the calculated temperature (model 2) during the first (21–29 July 1997) and the second (1–5 October 1997) gasification phase, respectively.

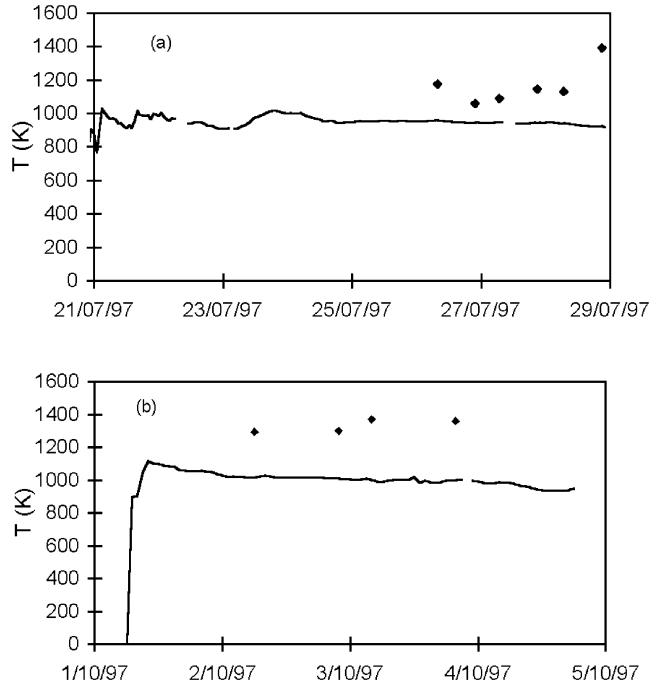


Fig. 3. (a) Evolution of T_{chim} (—) and $T_{\delta^{13}\text{C}}$ (◆) during the first gasification phase. (b) Evolution of T_{chim} (—) and $T_{\delta^{13}\text{C}}$ (◆) during the second gasification phase.

6.5. Temperature estimation from ^{13}C isotopic abundances

Practically, the three molecular couples are $\text{CO}_2\text{--CO}$, $\text{CH}_4\text{--CO}$ and $\text{CO}_2\text{--CH}_4$ with the related thermometers, respectively,

$$\begin{aligned} \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CO}} &= \epsilon_{\text{CO}_2\text{--CO}}(T) \\ &= 6602987/T^2 + 7514.4/T - 2.6 \end{aligned} \quad (12)$$

$$\begin{aligned} \delta^{13}\text{C}_{\text{CH}_4} - \delta^{13}\text{C}_{\text{CO}} &= \epsilon_{\text{CH}_4\text{--CO}}(T) \\ &= -665197/T^2 + 4969/T - 1.5 \end{aligned} \quad (13)$$

$$\begin{aligned} \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4} &= \epsilon_{\text{CO}_2\text{--CH}_4}(T) \\ &= 7268183/T^2 + 2545.3/T - 1.0 \end{aligned} \quad (14)$$

The graphic $\epsilon(T)$ of the $\text{CH}_4\text{--CO}$ couple displays a very low slope (Fig. 4). As a consequence, small variations of $\delta^{13}\text{C}_{\text{CH}_4} - \delta^{13}\text{C}_{\text{CO}}$ due to the measurements inaccuracy lead to high variations of the equilibrium temperature. Thus, the $\epsilon_{\text{CH}_4\text{--CO}}(T)$ thermometer must be rejected. The $\text{CO}_2\text{--CO}$ couple is a well-known thermometer. Using equilibrium experiment between CO_2 , CO and C carried out at 1073 K and atmospheric pressure, Létolle et al. [10] showed that the $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CO}}$ difference slowly tends towards a stable value close to the theoretical one, whereas the chemical equilibrium is rapidly reached. The authors also stress the role of solid carbon in the exchange, the production of CO_2 and CO by combustion and gasification instead reactions

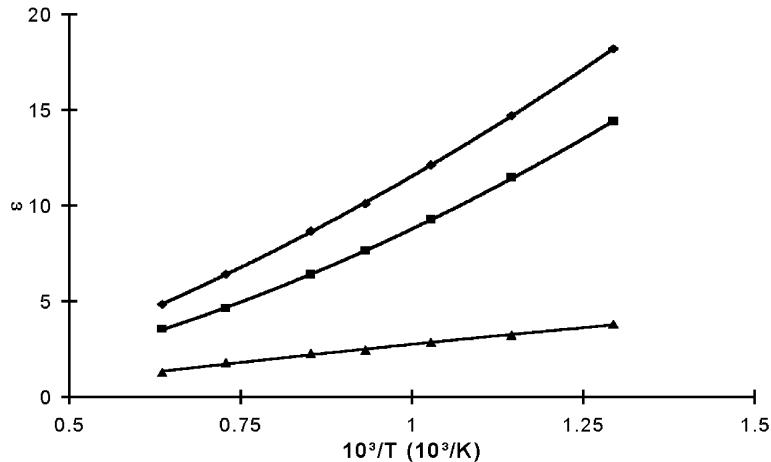


Fig. 4. Theoretical ^{13}C isotopic fractionation calculated in terms of temperature. $\diamond: \epsilon_{\text{CO}_2-\text{CO}}(T)$, $\blacksquare: \epsilon_{\text{CO}_2-\text{CH}_4}(T)$, $\blacktriangle: \epsilon_{\text{CH}_4-\text{CO}}(T)$.

and not by pyrolysis, and the reliability of the couple CO_2-CO as a thermometer of the gasification zone. The fact that the temperature calculated from ^{13}C isotopic abundances of CO_2 and CO is higher than the one obtained from the chemical equilibrium is interpreted by the authors as a consequence of the isotopic exchange kinetics being slower than the chemical kinetics.

The CO_2-CH_4 couple does not give good temperature estimations. Indeed, the experimental study carried out by Létolle et al. [10] shows that the $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ difference evolves towards more and more positive values. Moreover, the methane produced inside the gasifier can result either from the direct carbon methanation by vapour and/or formed hydrogen or from the coal pyrolysis. Thus, it is impossible to know a priori if the equilibrium between the isotopes of CO_2 and CH_4 produced by hydrogasification and pyrolysis can be reached before the gaseous products leave the gasifier.

In order to solve, even partly, the question of the methane production (direct methanation or coal pyrolysis), Dufaux et al. [11] performed heavy water tracer test at Thulin, the result of which strongly suggests a CH_4 production by direct methanation from coal. Unfortunately, no heavy water test data are available for the Alcorisa gasifier due to technical circumstances of the experiment.

Finally, the chemical and isotopic equilibria allow the definition of two temperature estimators having an actual physico-chemical sense.

The T_{chim} temperature calculated on the basis of the chemical equilibrium and gaseous compositions probably corresponds to the temperature at the outlet of the gasifier. During the first gasification phase (Fig. 3a), T_{chim} temperature reaches 1004 K and then displays a slight continuous decrease with the increase of gases residence time and gasifier volume [4] and, as a consequence, with the progressive removing of the gasifier outlet from the injection point. During the second phase (Fig. 3b), immediately after the burning, T_{chim} starts from a high value (1016 K) and, again, decreases slowly with the increasing of the gasifier

volume. The temperature difference between the two gasification phases is a direct consequence of the gasifying agent composition: the higher the oxygen content (second gasification phase) is, higher the temperature is. On the contrary, the faster temperature decrease observed in the second gasification phase is an indirect effect of the gasifying agent flow rate increase.

At a rough guess, the cavity volume increases proportionally to the oxygen flow rate. Since the loss of heat depends on the cavity volume and water influx, the increase of the gasifying agent flow rate is not sufficient to keep the higher temperature level in the gasifier.

Concerning the meaning of $T_{\delta^{13}\text{C}}(T_{\text{CO}_2-\text{CO}})$ temperature, calculated from $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CO}}$ using Eq. (4), the two possible assumptions in the absence of any available theoretical or experimental data on isotopic kinetics can be stated as follows:

1. $T_{\delta^{13}\text{C}}$, higher than T_{chim} , may indicate either the isotopic equilibrium ‘quenching’ or the temperature at the exit of the hot area. However, this latter hypothesis cannot explain the hot spot observed with sample 6 (1390 K).
2. The gaseous state isotopic exchanges $^{13}\text{C}/^{12}\text{C}$ between CO_2 and CO imply the presence of carbon from char. Practically, the isotopic exchange takes place when the Boudouard’s reaction shifts to the right. Thus, $T_{\delta^{13}\text{C}}$ can be also indicative of the temperature at which char-deposition reactions start. The error on $T_{\delta^{13}\text{C}}$ was estimated to be 25 K.

As shown in Table 4, the $T_{\delta^{13}\text{C}}$ temperature of the first gasification phase is approximately constant with a value of about 1100 K, but drastically increases at the end of the experiment, reaching a hot spot of about 1400 K. The second gasification phase is characterised by a higher $T_{\delta^{13}\text{C}}$ temperature (~ 1300 K) which displays an increasing trend with the development of the process. The higher oxygen content during this latter gasification phase is responsible for the $T_{\delta^{13}\text{C}}$ temperature higher than the one

estimated for the first experiment. The increase of the agent flow rate probably explains the $T_{\delta^{13}\text{C}}$ increasing trend observed during each experimental phase.

7. Conclusions

The experience clearly shows that indirect techniques are an interesting solution for the temperature data characteristics of an underground coal gasifier. Indeed, direct temperature measurements — thermocouples, optical fibres — can be envisaged only at the surroundings of the gasifier in order to avoid captors destruction. The Alcorisa experiment is thus a new opportunity to contribute to the improvement of the indirect technology approach.

Practically, the indirect method used in this work deals with chemical and isotopic equilibria, considered from chemical composition and ^{13}C isotopic abundances of the produced gases.

From the temperature point of view, two significant parameters can be defined, namely T_{chim} and $T_{\delta^{13}\text{C}}$.

The T_{chim} parameter, calculated using gas compositions, is probably indicative of the temperature at the gasifier outlet. The $T_{\delta^{13}\text{C}}$ parameter, estimated from ^{13}C distribution between CO and CO_2 , is a second value of gasification zone temperature which may inform about the regression temperature of Boudouard reaction, thus indicating the temperature at which char-deposition starts.

The comparison of both T_{chim} and $T_{\delta^{13}\text{C}}$ behaviour during the two gasification phases carried out at Alcorisa leads to useful informations. On one hand, T_{chim} is appreciably lower than $T_{\delta^{13}\text{C}}$ suggesting that the gasification process still continues at low temperatures, of the order of 1023 K — such an hypothesis is plausible since the gas–solid contact surface is quite large and the residence-times are sufficiently long. It is also worth noting that large amounts of CO and H_2 produced at high temperature disappear due to the equilibrium shift of Boudouard reaction ($\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$) and vapogasification reaction ($\text{C} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}$). On the other hand, the T_{chim} temperature decreases during each gasification phase due to the progressive gasifier development whereas the $T_{\delta^{13}\text{C}}$ temperature slightly increases owing to the progressive increase of gasifying agent flow rate. Finally, the higher the oxygen content of the gasifying agent (as in the case of the second gasification phase) the higher the T_{chim} and $T_{\delta^{13}\text{C}}$ temperatures.

Besides the temperature estimation of the underground gasifier, the isotopic approach also allows isotopic mass balances analysis. For the experience performed in Alcorisa, the isotopic mass balances based on ^{13}C confirm the negligible heavy compounds production, in particular tars, at the beginning of the process and also show an extension of the pyrolysis zone during the second phase of gasification.

The methane origin (from direct methanation, pyrolysis

or both), which cannot be identified from isotopic mass balances based on ^{13}C , must be determined by means of heavy water tracer tests [11].

Therefore, taking into account the lack of experimental and theoretical data as already noticed for the Thulin gasifier results which is an handicap, one can state that the use of stable isotopes as thermometers and mass balance checking for underground gasification of coal is a quite promising indirect method.

Acknowledgements

The authors are grateful to the European Coal and Steel Community for financial support (Coal Research Project 7220/EC/210 and 7220/ED/221).

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