Estimation of the Combustion Temperature Profile in a Romanian Oil Field

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Developing and producing of the heavy crude oil involved significant economic and technological challenges. The oil industry ability to prospect and capitalize the huge world heavy oil resources both economically and environmentally friendly will be crucial in helping meet future energy needs. Thermal oil recovery is one of the three types of techniques belonging to Enhanced Oil Recovery. It is applied for increasing the cumulative of crude oil that can be produced in an oil field. One of the oldest thermal oil recovery is in-situ combustion or fireflooding applied for the first time about 100 years ago. Despite in-situ combustion has not found widespread acceptance among operators like other thermal processes (such as steam injection), analysis of the successful projects indicates that the process is applicable to a wide range of oil reservoirs, especially to heavy crude oils. An important monitoring parameter of thermal oil recovery process is represented by thermal regime especially in heavy oil fields in which a high-temperature regime must be occur as the insitu combustion to be successful. In the paper the authors are using thermal analysis (thermogravimetric and thermodifferential analysis) for investigation of the thermal regime involved in the production process of an oil reservoir by in-situ combustion.

Keywords: heavy oil field, in-situ combustion, organic substance oxidation, thermal analysis, thermal regime modeling

Growing demand for crude oil worldwide (ca. 100 million barrels oil per day) [1] and decreasing in the production of conventional oil has led to consideration of alternative or insufficiently utilized energy sources in order to supplement short-term and long-term oil needs. An important oil source is representing by heavy oil and natural bitumen which promises to play a major role in oil industry in the near future. Heavy oil is often overlooked as a resource because of the difficulties and costs involved in its production and refining. Relative to the total world oil resources (fig. 1), more than six trillion barrels (ca. one trillion cubic meters) or more than two-thirds of the world's oil resources, are heavy and viscous crude oil. Huge heavy oil resources of the world represent an important global energy supplier, but require a high level of effort and expertise to economically developed and produced, and is a challenge for production and refining [2]. Many countries tend to increase their oil production, revising their estimated resources, testing new technologies and investing in infrastructure in order to ensure optimal production of heavy oil resources. The oil industry ability to develop and produce the world heavy oil resources both economically and environmentally friendly (lower rate of CO2) will be crucial in helping meet future energy needs. Over 30 countries are known to possess huge recoverable heavy oil reserves, the group being led by Venezuela, followed by Canada, United States and Russia. As energy demands grow, major conventional oil discoveries are rare and difficult to find, and the costs of discovering and producing conventional oil goes up, the economics of heavy oil will steadily improve [3-8].

Suplacu de Barcau heavy oil field is one of the largest Romanian oil field (162 MMbbls 2P) and it represents the most important oil field in the world operated by in-situ combustion (ISC). Suplacu de Barcau oil field it has been in operation for more than 45 years as a dry in-situ



combustion process (less than 1.40 MPa) of a heavy and viscous oil (2,000 mPa.s viscosity) in a very shallow reservoir (less than 180 m) using a small well spacing (50 to 100 m). The in-situ combustion process are operated using a linear combustion front propagated downstructure, starting from the uppermost part of the reservoir and going downdip [9-11].

Suplacu de Barcau structure is situated in the northeastern part of Pannonian Basin (North-West Romania) and it was formed by covering of the altered crystalline basement (paleorelief) by the Pliocene sedimentary suite. The structure looks like a slightly-folded monocline (fig. 2), East-West oriented, axially faulted by a major fault (Suplacu de Barcau fault). The wells spudded on the structure encountered deposits that belongs to the altered crystalline basement, Sarmatian, Pannonian (Pliocene) and Quaternary. The productive formation is represented by the Pannonian basal complex which transgressively overlying the Sarmatian or the altered crystalline basement. The basal complex (productive) is composed of slightly consolidates sands, saturated with heavy and viscous oil (2,000 mPa . s) and has a variable thickness between 5-7 m in the East side and 25-30 m in the North-West side. Both depth and thickness increase from the East to West and the North to South. [9-11]

In-situ combustion is a thermal recovery technique which involved the injection of an oxidizing gas (air or

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oxygen-enriched air) in formation in order to enable burning of a part of the heavy oil in place to generate heat. The heat brings a reduction in viscosity of the crude oil leading to the improvement of the mobility and hence oil production rate and recovery. Typical combustion front (fig. 3) moves slow (some cm/day) through reservoir matrix (pores) by consuming the fuel as it moves ahead. The combustion zone is often a few centimeters in thickness and it has a temperature up to 700-800°C. The oil is driven toward the production well by a vigorous combustion gases drive and water drive (water of combustion and recondensed formation water) [6, 12-14].

In the in-situ combustion process it is encountered several chemical reactions which occur over different temperature ranges. The reservoir conditions and oil properties determine the rate of oxidation which leads to the formation of the combustion front. Generally, researchers divided the chemical reactions associated to in-situ combustion in three types:

1) low temperature oxidation (LTO) - the LTO reactions are developed in a heterogeneous media (gas/liquid) and generally results in production of partially oxygenated compounds and little or no carbon oxides; 2) medium temperature (fuel formation reactions) involve cracking/pyrolysis of hydrocarbons which leads to the formation of coke (a heavy carbon rich, low volatility hydrocarbon fraction);

3) high temperature oxidation (HTO) or combustion of the solid hydrocarbon residue (coke) - the HTO reactions are also heterogeneous (gas-solid and gas-liquid), in which the oxygen reacts with unoxidized oil, fuel and the oxygenated compounds to give carbon oxides and water. The transition from LTO to HTO reactions needs a significant level of heating or oil artificial ignition [6, 14-16].

The hydrothermal conditions that occur in front of and behind the combustion zone can facilitate chemicomineralogical transformations followed by new minerals forming. Most of the researches performed in the oil fields operated by in-situ combustion process agree that the bitumen is adsorbed on the mineral fraction and the in-situ combustion process produces a significant amount of iron oxide/hydroxide and reduces the quantity of kaolinite, illite and smectite clay [6, 11, 17-21].







Fig. 4. MOM Q-1500 D derivatograph

Experimental part

In order to evidence of the exothermic/endothermic transformations and to estimate the temperatures which rocks had been exposed in the in-situ combustion process were collected twelve rock samples from the wells spudded behind of the combustion front in the burned area. The samples were collected both in productive formations and in the subjacent crystalline basement (altered).

The rock samples collected from the burned area of the Suplacu de Barcau oil field (table 1) were subjected of the complex mineralogical study consist of optical microscopy, X-ray diffraction and thermal analysis (thermogravimetric analysis TG and thermodifferential analysis DTA).

For establish the rock type were manufactured thin sections from each sample and were performed optical microscopy observations with a Zeiss Amplival-type microscope belonging to the laboratory of Mineralogy in the Petroleum-Gas University of Ploiesti.

X-rays diffraction analyses (powders method) were performed at Prospectiuni S.A. Bucharest, Geological Analyzes Laboratory Division, using an HZG 4/A-type diffractometer with following measurement parameters: CuK α radiation, Ni filter, I = 1.54Å, 25 kV/15 mA, scanspeed 1°/min, measurement range (20) 0-70°.

Thermal analysis (thermogravimetric and thermodifferential analysis) were performed at Prospectiuni S.A. Bucharest, Geological Analyzes Laboratory Division, using an MOM Q-1500D-type derivatograph (fig. 4) with following measurement parameters: the amount of sample = 1 g; the linear heating rate = 10° C/min.; maximum heating temperature = 1000° C; thermocouple system PT-Pt/Rh; static air atmosphere.

Results and discussions

The diagnosis of rocks collected from burned area of Suplacu de Barcau oil field resulted from optical microscopy study of thin sections is presented in table 1. It can be noticed the predominance of the siliciclastic rocks with carbonate cement, except 4B and 5B samples collected from the altered crystalline basement.

In the optical microscopy study of thin sections were observed interesting aspects in the rocks texture resulted

Sample code	Sampling point	Rock diagnosis				
1B	K30 well	Lithic greywacke				
2B	K20 well	Quartz sand poorly compacted				
3B	K30 well	Lithic subgreywacke				
4B	K20 well	Quartz-chlorite-micaceous schist				
5B	K20 well	Quartz-chlorite-micaceous schist				
6B	K8 well	Lithic sandstone with carbonate cement				
7B	K30 well	Lithic greywacke				
8B	K40 well	Lithic subgreywacke				
9B	K30 well	Lithic greywacke				
10B	K8 well	Lithic greywacke				
11B	K40 well	Lithic sand				
12B	K30 well	Quartz-lithic sand				

from the in-situ combustion (these are presented by means of microphotographs), such as:

a) the gradual stages of transformation (burning) of the organic substance (fig. 5);

b) the presence of secondary pellicles (by circulation) of the bitumen on the walls of the pores (fig. 6);

c) the presence of the microlenses of organic substance of circulation (fig. 7 and 8), lying on schistosity planes of the rocks from the altered crystalline basement, subjacent to the productive formation.



Fp

Fig. 5. The gradual stages of burning of the organic substance (So) (Q=quartz, C=calcite, LC=calcite cement, M=muscovite). (N II, 40x) [11]

Fig. 6. Secondary pellicles (by circulation) of the bitumen on the walls of the pores. (N II, 40x) [11]

Fig. 7. Microlenses of organic substance (So) of circulation in the schistosity planes of the crystalline basement rocks (Q=quartz, Fp=plagioclase feldspar, B=biotite). (N II, 40x) [11]

Fig. 8. Microlenses of organic substance (So) of irculation in the schistosity planes of the crystalline basement rocks (Q=quartz). (N II, 40x) [11]

Table 1DIAGNOSIS OF THE ROCK SAMPLES COLLECTEDFROM BURNED AREA INVESTIGATED BY OPTICALMICROSCOPY [11]

Sample	ple Mineralogical composition (%)									
code	Quartz	Feldspars	Micas	Kaolinite	Montmo-	Illite	Chlorite	Carbo-	Other	
					rillonite			nates	minerals	
1B	50	10	5	-	10	-	-	10	tobermorite	
									and C2S	
2B	60	5	10	10	-	-	-	-	tobermorite	
3B	50	-	-	-	10	-	-	25	okenite	
4B	50	5	-	-	5	10	5	10	tobermorite	
5B	50	10	5	-	5	-	10	5	okenite and	
									C2S	Table 2MINERALOGICAL
6B	50	5	5	-	5	-	-	25	iron	COMPOSITION OF
									hydroxide	SAMPLES COLLECTED FROM
7B	45	15	5	-	-	5	-	15	tobermorite	BURNED AREA
									and C2S	INVESTIGATED BY X-RAYS
8B	55	10	5	-	-	5	-	10	tobermorite	DIFFRACTION [11]
									and C2S	
9B	60	10	5	-	-	-	5	10	tobermorite	
									and C2S	
10B	45	5	-	-	-	5	5	25	tobermorite	
11B	45	10	5	-	-	5	-	20	tobermorite	
12B	55	5	5	-	-	5	5	10	tobermorite	

Mineralogical composition of the rock samples collected from burned area was obtained following investigations by X-rays diffraction analysis (table 2).

The thermal analysis performed on the rock samples collected from burned area of the oil field consists of thermogravimetric analysis (TG) and thermodifferential analysis (DTA). Interpreting of the thermal analysis of the twelve samples was correlated with investigations performed by optical microscopy and X-rays diffraction. The weight loss curve (TG), the thermodifferential curve (DTA) and the temperature changes (T) were recorded as a function of time.

The DTA curve of sample 1B (fig. 9) show a lowly exothermic peak in the temperature range 100-220°C (accompanied by weight loss on the TG curve) due to oxidation reaction of the organic substance and two endothermic peaks, one less expressed at 560°C and the other between 700-870°C. The endothermic peak from 560°C it is assigned to loss of the OH groups from the clay minerals lattice, while the stronger endothermic peak between 700-870°C is a consequence of decomposition of the carbonates. The lowly developed exothermic peak between 100 and 220°C, assigned to the organic substance oxidizing of sample 1B, and the weak endothermic effect, specific to clay minerals dehydroxylation, pleads for the idea the rock was subjected to the temperature higher than 350-400°C.

In DTA curve of sample 2B (fig. 10) can be observed a lowly developed endothermic peak between 50-100°C

accompanied by weight loss on TG curve due to water loss in the phyllosilicates lattice, followed by a strong exothermic peak at 300-400°C assigned to the oxidation of the organic compounds and by a second endothermic peak, widely developed, at 520-560°C due to loss of the OH groups from the clay minerals lattice (kaolinite). On the DTA curve of sample 2B, the endothermic presence suggests that temperature in the combustion area was lower than the dehydroxylation temperature characteristic to clay minerals. More than that, the reduced persistence of the organic substance marked by the lowly developed exothermic peak at 300-400°C pleads for situating the temperature between 300 and 350°C.

DTA curve of sample 3B (fig. 11) evidenced three endothermic peaks doubled by loss weight on TG curve. The first endothermic peak of 120-150°C it is due to loss of the OH groups from the clay minerals lattice. The second endothermic peak, low developed, at 560°C can be assigned to dehydroxylation of the clay minerals. The last endothermic peak between 700-825°C is due to decomposition of the carbonates. Absence of any exothermic effect due to the oxidation of the organic substance and the very low endothermic effect at 560°C caused by the dehydroxylation of the clay minerals in sample 3B suggest that temperature reached in the combustion area was around 450-500°C. Such a temperature may cause the total oxidizing of the organic compounds and the complete dehydration followed by montmorillonite net collapse up to 9.70Å, having no influence on the carbonate minerals.

DTA curve of sample 4B (fig. 12) evidenced a first exothermic peak, lowly and widely developed, between 100-220°C and other stronger exothermic peak at 300-325°C which can be assigned to oxidation reaction of organic substance. Also, the curve shows two endothermic peaks, first peak lowly developed at 560°C caused by the loss of OH groups of the clay minerals lattice, and the other peak at 750-900°C due to decomposition of the carbonates (calcite). Persistence of organic substance reflected by the exothermic peak from 320°C on sample 4B's DTA curve and also the characteristic effect of clay minerals dehydroxylation from 560°C suggest the setting of temperature the rock was exposed to between 150 and 200°C.

DTA curve of the sample 5B (fig. 13) show an exothermic peak, lowly and widely developed, in the temperature range 100-350°C assigned to oxidation of the organic substance encountered in the schistosity planes of the analyzed rock. Also can be observed a lowly developed endothermic peak at 550-560°C (doubled by weight loss on TG curve) due to the loss of OH groups of the clay minerals lattice; another endothermic peak, widely and lowly developed between 620-700°C also due to dehydroxylation of the clay minerals and to the presence

of calcium silicates hydrate; and a last endothermic peak also lowly developed between 840-900°C due to decomposition of the carbonates. The presence on sample 5B's DTA curve of the effects characteristic to dexydroxylation of the clay minerals (550-560°C and 620-700°C) and decomposition of the carbonates (840-900°C) and also the existence of exothermic effect in 100-350°C interval assigned to the bitumen oxidizing (even if they are weakly expressed, but we have a sample taken from the altered crystalline basement) suggest that temperature the sample had been exposed to did not exceed 150-200°C, temperature not allowing the total oxidizing of the organic substance from the schistosity plans.

DTA curve of sample 6B (fig. 14) it is marked by a series of exothermic and endothermic peaks, strongly or weakly developed. The first exothermic peak, lowly and widely developed, is encountered between 100-200°C and is assigned to the low temperature oxidation reaction of the organic compounds. This is followed by two stronger exothermic peaks at 320-330°C and respectively at 390-400°C, both effects due to oxidation reaction of high temperature (HTO) of organic compounds. On the DTA curve can be observed also endothermic peaks, first peak at 560°C due to the loss of OH groups of the clay minerals lattice, and the second peak at 680-720°C due to decomposition of the carbonates. The strongly developed



Fig. 9. Derivatographof sample 1B [11]



Fig. 12. Derivatograph of sample 4B [11]

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Fig. 10. Derivatograph of sample 2B [11]



Fig. 13. Derivatograph of sample 5B [11]

Fig. 11. Derivatograph of sample 3B [11]



Fig. 14. Derivatograph of sample 6B [11]

exothermic peaks from 320 and 400°C on sample 6B's DTA curve due to bitumen oxidizing support the idea that the combustion area's temperature did not exceed 120-150°C.

DTA curve of sample 7B (fig. 15) show a series of exothermic and endothermic peaks. Thus are encountered a wide exothermic peak between 100-160°C, a well-developed exothermic peak between 300-400°C, a lowly endothermic peak at 560°C, and a well-developed endothermic peak between 750-840°C. Stronger exothermic peak between 300-400°C it is assigned to oxidation reaction of organic substance and endothermic peak from 560°C correspond to dehydroxylation of clay minerals. Endothermic peak relative well developed from 750-840°C is due to decomposition of the carbonates. On sample 7B's DTA curve, the presence of the organic substance, marked by the exothermic peak from 300-400°C, leads to the setting of the temperature highest limit to 250°C.

DTA curve of sample 8B (fig. 16) show a widely developed exothermic peak around 100°C and other two stronger exothermic peaks, first peak at 330°C and the second peak at 380°C, both assigned to the oxidation reactions of the organic substance. Also on the DTA curve can be observed a small endothermic peak at 560°C due to dehydroxylation of the clay minerals. Finally, there is a strong endothermic peak between 680-890°C assigned to decomposition reaction of the carbonates. Considering the results of sample 8B's DTA curve, it is reasonable to admit that the temperature reached at into the combustion area is analogue to that of the previous sample, not exceeding 250-300°C.

DTA curve of sample 9B (fig. 17) reveals the presence of two exothermic peaks and two endothermic peaks. Exothermic peaks are developed between 100-200°C (lowly developed) due to low temperature oxidation reaction of the organic compounds and respectively at 320-330°C (strong developed) also due to oxidation reaction of the organic substance. The first endothermic peak is encountered at 550-560°C due to the loss of OH groups of the clay minerals lattice. The second endothermic peak developed between 700-850°C it is assigned to decomposition reaction of the carbonates. The strong exothermic peak from 320°C, caused by the organic components in sample 9B oxidizing, plead for the idea that the combustion area temperature did not exceed 250°C, not enough for the total oxidation of rock's organic substance.

On the sample 10B's DTA curve (fig. 18) it can be observed three exothermic peaks, all peaks assigned to oxidation reaction of the organic substance. The first exothermic peak widely and lowly developed between 100-200°C due to LTO reaction; the second well developed exothermic peak at 340-350°C and the third exothermic



Fig. 18. Derivatograph of sample 10B [11]





peak at 400°C due to HTO reactions of organic substance. There are two endothermic peaks, the first lowly developed at 560°C due to dehydroxylation reaction of clay minerals, and the second endothermic peak developed between 730-840°C assigned to decomposition of the carbonates. Persistence of the organic substance marked by the exothermal from 350°C and respectively from 400°C on sample 10B's DTA curve suggest the setting of combustion area's temperature highest limit to 250°C.

DTA curve of sample 11B (fig. 19) reveals three exothermic peaks: first peak, widely developed between 100-200°C due to LTO reactions, the second strong peak at 350°C and the third peak at 400-420°C due to HTO reactions. Also can be observed two endothermic peaks, the first lowly developed at 560°C due to dehydroxylation of clay minerals, and the second endothermic peak developed between 740-850°C due to decomposition of the carbonates. The strongly developed exothermal peaks on sample 11B's DTA curve from 350°C and 400°C, caused by bitumen oxidation, support the idea that the combustion area temperature did not exceed 250°C.

On the DTA curve of the sample 12B (fig. 20) can be noticed several exothermic peaks and one endothermic peak. The exothermic peaks are developed at the following temperatures: 180-190, 260-270, 340-350, 400, 660°C; all exothermic peaks assigned to the oxidation reactions of the organic substance. The endothermic peak is encountered at 700-760°C. Can be observed an exothermic effect, stronger and widely developed whose peak temperature is 400°C. The endothermic effect wide and of the low intensity between 700-760°C can be assigned decomposition of the carbonates. The decomposition of the carbonates in the small amounts can take place in the temperature range 700-760°C. The stronger developed peak from 400°C on sample 12B's DTA curve caused by the organic substance oxidizing, speaks for the idea that the combustion area temperature did not exceed 200-250°C, considering the negligible effect upon the organic substance, otherwise at least partially oxidized at temperatures higher than 250°C.

In the most of the samples collected from the burned area of the Suplacu de Barcau oil field analyzed by thermal methods was evidenced the presence of organic substance by exothermic oxidation processes of the organic substance. The presence of the organic substance in the samples from the burned area, swept by combustion front, offers clues on the types of the oxidation reactions of the organic substance/bitumen and a thermal regime which organic substance had been exposed in the in-situ combustion process. The temperature values inferred by thermal analysis interpretations of the rock samples collected from the burned area of the Suplacu de Barcau oil field allowed the modeling of the reservoir thermal regime and building of a cross-section with distribution of the izotemperature zones in the productive formation (fig. 21).

Conclusions

The reservoir rocks of Suplacu de Barcau oil field (Romania) which is operated by in-situ combustion are exposed to variable temperatures in the range 150-500°C, which is proved by the exothermic/endothermic transformations observed as a result of the thermal analysis study of the rock samples collected from the burned area of the reservoir.

Exothermic effects from around 350°C met on the main part of the DTA curves of the sample rocks collected by burned area of the oil field studied are due to the oxidation reactions of the organic substance and support the setting of the temperature at approx. 250-300°C for almost the entire reservoir. This temperature (250-300°C) does not allow the total oxidation of the organic substance in the reservoir rock, instead may cause, considering that the reaction speed increases as temperature increases, noticeable chemico-mineralogical transformations of the *sensitive* minerals.

Optical microscopy study of thin sections pointed out interesting aspects in the rocks texture (these are presented by means of microphotographs) resulted from the in-situ combustion, such as: the gradual stages of transformation (burning) of the organic substance; the presence of secondary pellicles (by circulation) of the bitumen on the walls of the pores; the presence of the microlenses of organic substance of circulation, lying on schistosity planes of the rocks from the altered crystalline basement, subjacent to the productive formation.

The researches carried out are expensive and requires specialized and authorized equipment. The collecting and selecting of the rock samples, the sample preparation for investigation by optical microscopy, X-rays diffraction and thermal analysis, processing and interpretation of the measurements of the analysis methods mentioned can be performed only by qualified personnel.

The performed investigations brings an important comtribution to the knowledge of the physico-chemical mechanisms of oil fields operated by in-situ combustion. Consequently, the obtained results can also be used for other oil fields operated in similar conditions, in order to modeling the thermal regime.

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Manuscript received: 14.03.2018