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Types of reservoir fluids in the Polish Lower Paleozoic shale formations

In accordance with commonly used petroleum terminology [3, 6] which takes into account the characteristic properties and phase transitions of fluids occurring naturally in hydrocarbon reservoirs six types of hydrocarbon reservoir fluids were distinguished, namely: non-gasoline (dry) gas, gasoline (wet) gas, retrograde gas, volatile oil, black oil, heavy oil. As a result of tests conducted on reservoir fluid samples obtained from the wells performed in the Lower Paleozoic formations of the Baltic-Podlasie-Lublin Basin on PGNiG and Orlen Upstream concessions, on the basis of phase transitions, chemical compositions and physical properties, the types of reservoir fluids currently discovered in this type of reservoirs were described [5].

Key words: reservoir fluids, shale formations.

Rodzaje płynów złożowych z polskich dolnopaleozoicznych formacji łupkowych

Zgodnie z powszechnie stosowaną terminologią naftową [3, 6] uwzględniającą charakterystyczne właściwości i zmiany fazowe naturalnie występujących płynów w złożach węglowodorów wyróżniono sześć rodzajów węglowodorowych płynów złożowych, a mianowicie: gaz bezgazolinowy (suchy), gaz gazolinowy (mokry), gaz kondensatowy, ropę lotną, ropę (*black oil*), ropę ciężką. W wyniku przeprowadzonych badań próbek płynów złożowych, pozyskanych z pozytywnie wykonanych odwiertów w dolnopaleozoicznych formacjach basenu bałtycko-podlasko-lubelskiego na koncesjach PGNiG oraz Orlen Upstream, zdefiniowano w oparciu o zachodzące zmiany fazowe oraz skład chemiczny i właściwości fizyczne rodzaje płynów złożowych dotychczas odkrytych w tych utworach [5].

Słowa kluczowe: płyny złożowe, formacje łupkowe.

Introduction

In an attempt to estimate the recoverable hydrocarbon reserves in shale formations of the Lower Paleozoic in Poland, in the Report of the Polish Geological Institute [7] on the presented map (Fig. 1) the areas with natural gas and oil reservoirs were separated symbolically by a thermal maturity isoline of 1.1% Ro. It was also indicated that in reality, in broad borderland between these zones, both the oil, and dry and wet natural gas occur in varying proportions. Matrix rocks change their maturity starting in the east and going towards the west, ranging from immature rock or one that is too poorly developed to generate hydrocarbons, through the oil window, then the wet gas and dry gas windows [7].

Preliminary review of the current works related to unconventional systems of shale gas/shale oil in the Polish context revealed that in many regions closer attention should

be drawn to the possibility of occurrence of shale oil [1]. To identify the possibilities of hydrocarbon accumulations in shale formations the research is required which should also result in the risk assessment with respect to four categories: geochemical, geological, petrophysical and concerning reserves [2].

The presented publication contains provisional test results concerning the types of reservoir fluids obtained from successful wells (by PGNiG and Orlen Upstream) in the shale formations of Lower Paleozoic of the Baltic-Podlasie-Lublin Basin. The research work was accomplished as part of the ResDev Project executed within the Blue Gas – Polish Shale Gas program. At the present stage it is difficult to estimate exactly the quantitative ratios of particular phases of hydrocarbons which occur in the discussed shale formations, nev-

ertheless, the publication presents the types of hydrocarbon reservoir fluids encountered so far, adopting their classification

according to the commonly used oil terminology as a point of reference.

Types of reservoir fluids

Hydrocarbon reservoir fluids, in accordance with frequently used classification in the oil terminology [6] are divided into four groups:

- natural gas,
- retrograde gas-condensates,
- volatile oil (mixtures near the critical point),
- petroleum (black oil type).

Some of the authors [4] distinguish wet and dry gas in the group of natural gases.

Closer examination of characteristic properties and phase transitions of the fluids which naturally occur in hydrocarbon reservoirs allows to distinguish six types of hydrocarbon reservoir fluids [3], i.e.:

- dry gases,
- wet gases,
- retrograde gases,
- volatile oil,
- black oil,
- heavy oil.

They have been defined on the basis of phase transitions, in the described circumstances, in the following sequence:

- initial reservoir pressure and temperature parameters,
 - production at falling pressure in the reservoir,
 - separation on the surface
- and presented in the diagram (phase diagram) in the PT system.

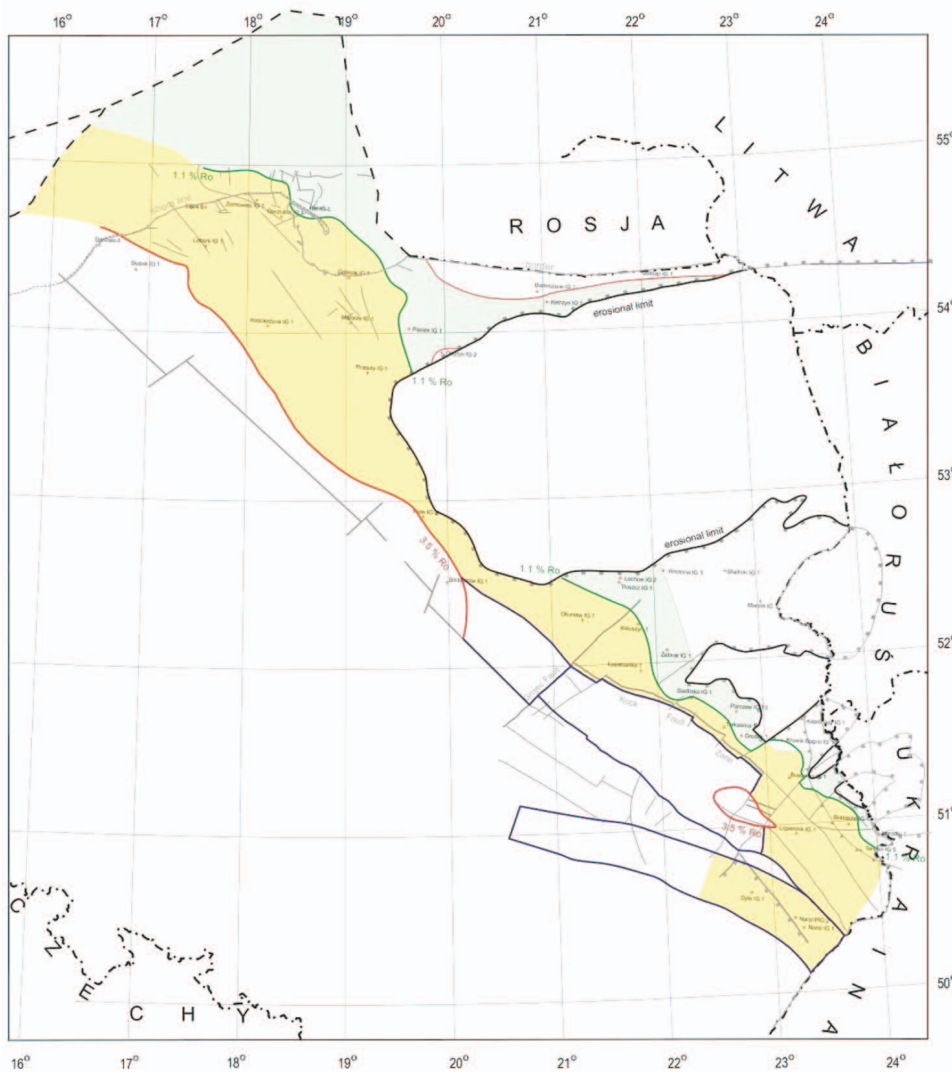


Fig. 1. The area qualified for calculation of natural gas reserves (yellow) and oil (green) in shale formations of the Lower Paleozoic, according to the Report of the Polish Geological Institute [7]

On account of the fact that the type of reservoir fluid is a factor which determines many decisions concerning the discovered reservoirs, it should already be defined at the phase of the initial development as it has an impact on the method of reservoir fluid sampling, the types and sizes of surface equipment, the calculational procedures for determining oil and gas in place, the techniques of predicting oil and gas reserves, the plan of depletion, and the selection of enhanced recovery method [4].

The production conditions during the flow of the reservoir fluid, starting from the primary reservoir parameters and finishing in the separation, were demonstrated in the subsequent phase diagrams. The reservoir parameters take the shape of an isotherm, as at the falling pressure caused by loss of the reservoir mass its temperature remains constant. In the diagrams, three points were marked as corresponding to the primary reservoir conditions, the parameters of surface separation and the critical point *K*. The discussed phases in the produced fluid change in respect of

pressure and temperature parameters (PT) along the curve connecting the reservoir conditions which are the geometri-

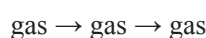
cal locus for points lying on the isotherm of reservoir conditions and the point of surface separation.

Dry gases

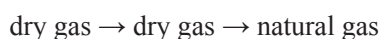
In the primary reservoir conditions and when the pressure is falling, dry gas always occurs as one gas phase, both in the reservoir and on the surface. In the entire course of production, on the route: reservoir – near-well zone – tubing – wellhead – surface separator, the composition of gas remains unchanged.

The history of dry gas production – from the initial reservoir conditions, through the well, up to the separation are presented in the notation:

general



actual



In the whole production process, the pressure path in the PT system which links the reservoir conditions with those prevailing in the separator does not cross the curve of dew points, therefore no liquid hydrocarbons can be obtained (Fig. 2).

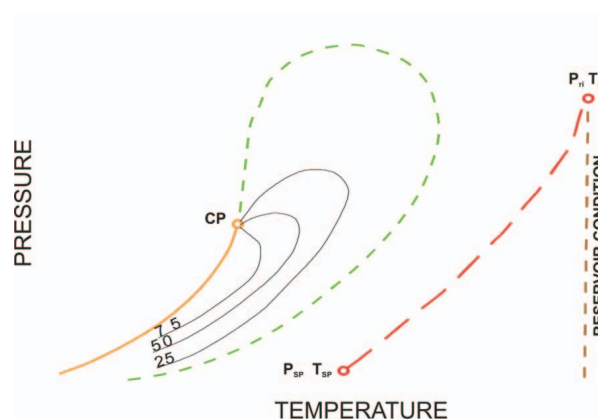


Fig. 2. Dry gas phase diagram, CP – critical point, continuous envelope line – the curve of saturation pressure, broken envelope line – the curve of dew points

So far, no non-gasoline dry gas has been discovered in any of the discussed wells in the Lower Paleozoic formations.

Wet gases

One characteristic feature of wet gas is that both in primary conditions and over the production period, in the reservoir and in the well, there is one gas phase. It is only in the surface conditions, as a result of considerable fall in temperature and pressure that the pressure path in the phase diagram crosses the curve of dew points and liquid phase appears, in the form of condensate, which is separated in the surface separators (Fig. 3).

The description of phase transitions of wet gas during the gas flow from primary conditions, through the well, up to the separator is shown below:

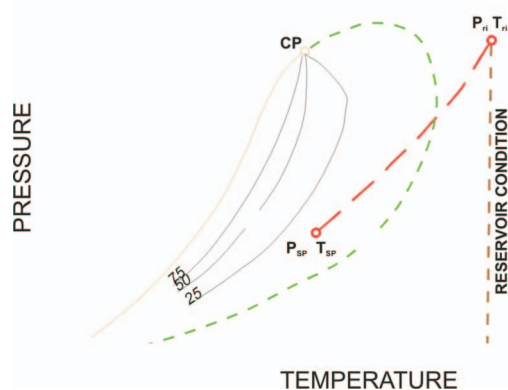
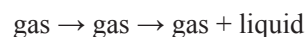


Fig. 3. Phase diagram of typical wet gas



which corresponds to the production conditions:



The whole period of wet gas production is characterized by constant value of condensate density and the gas-oil ratio. Depending on the composition of wet gas in the reservoir, the characteristic quantities take the following values:

- condensate density between $600 \div 720 \text{ kg/m}^3$,
- gas-oil ratio above $20\,000 \text{ Nm}^3/\text{m}^3$,
- condensate – colourless.

A typical example of wet gas from the shale formations of the Lower Paleozoic is the gas whose chemical composition was presented in Table 1. It is sulphur-free gas with a high content of hydrocarbons, low content of nitrogen and carbon dioxide.

The phase diagram of wet gas obtained from one of the boreholes which offer access to Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin was shown in Fig. 4.

Table 1. Chemical composition of wet gas from shale formations, where ρ_o – density of the liquid condensed in the process of separation, i.e.: $P = 60$ bar, $T = 20^\circ\text{C}$ [5]

Composition of reservoir liquid [%mol] at:	
$P_{reserv.} = 265.0$	bar
$T_{reserv.} = 90.0$	$^\circ\text{C}$
He	0.144
N_2	3.575
CO_2	0.151
C_1	84.304
C_2	5.970
C_3	3.334
iC_4	0.467

ect. Table 1

Composition of reservoir liquid [%mol] at:	
nC_4	0.995
iC_5	0.280
nC_5	0.291
C_6	0.268
C_7	0.128
C_8	0.076
C_9	0.008
C_{10+}	0.008
C_{10+} Mol. Weight	19.58
$\rho_{(PT)}$	735.9 kg/m^3

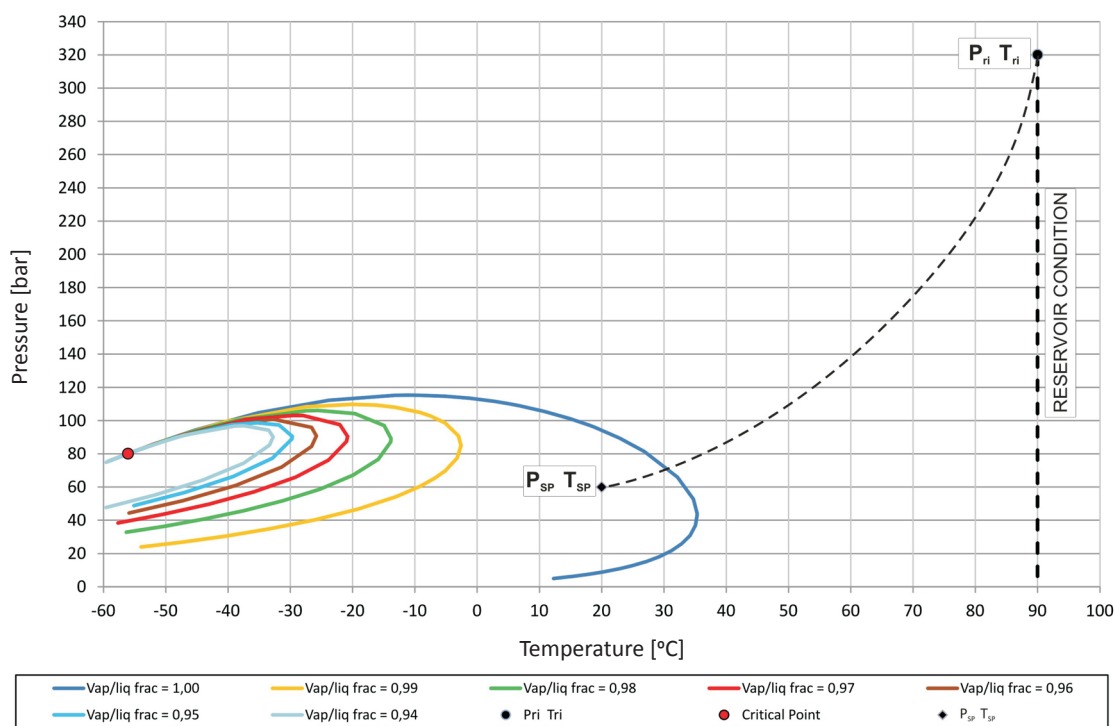


Fig. 4. Phase diagram of wet gas from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin. The production line linking the reservoir conditions and separation on the surface crosses the curve of dew points, the depletion isotherm is outside the dew points envelope in the entire period of production [5]

Retrograde Gases

In the primary reservoir conditions, retrograde gas occurs in one gas phase which is maintained with the decreasing pressure until it reaches the dew point pressure value (Fig. 5). When the pressure falls below the dew point, condensation of the liquid in the reservoir will take place and the reservoir fluid will be represented by two phases: condensate and natural gas. The liquid condensing from the gas will remain in the porous space – usually with no possibility of recovery it to the surface. Maintaining the reservoir pressure in the near-

well zone above the dew point pressure (e.g. by reinjection of gas deprived of heavy hydrocarbons into the reservoir, the so-called gas cycling) will prevent retrograde condensation and loss of heavy hydrocarbon components in the reservoir. At a considerable drop in pressure, the process of condensation of heavy hydrocarbons may begin at the bottom of the well and then, at appropriate rate of elevation in the tubing, condensate (already in the form of gasoline) will be produced in the surface separators.

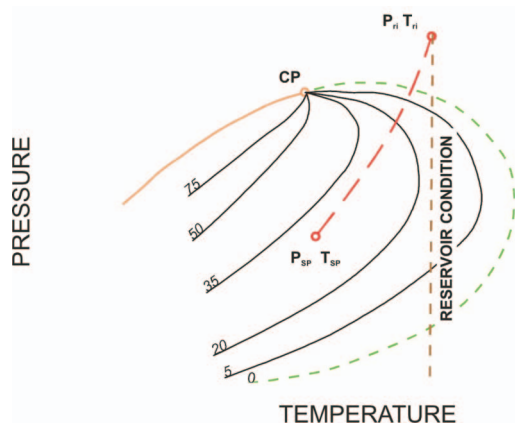


Fig. 5. Phase diagram of typical retrograde gas

A characteristic feature of this type of fluids is the location of the point of primary reservoir conditions situated on the right, in close vicinity of the critical point.

The history of phase transitions of retrograde gas over the production period from the primary reservoir conditions, through the well, to the separator runs in the following way:

gas \rightarrow gas + liquid \rightarrow gas + liquid

while in a more complex notation:

retrograde gas \rightarrow wet gas + condensate \rightarrow
natural gas + condensate

Production of retrograde gas in the period when only one gas phase occurs in the reservoir is characterized by:

- constant primary gas-oil ratio ranging from $600 \div 25\,000 \text{ Nm}^3/\text{m}^3$ [4],
- constant density of the condensate on the surface, reaching $700 \div 780 \text{ kg/m}^3$.

The increased value of the gas-oil ratio is associated with production of condensate in the reservoir and practically only wet gas flows to the surface. The condensate obtained in the separator is colourless or yellow.

An example of retrograde gas from the Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin is the chemical composition demonstrated in Table 2.

This is sulphur-free gas of high ethane and heavy hydrocarbon content, low content of nitrogen and carbon dioxide. A little higher nitrogen content than previously may be related to the use of nitrogen to stimulate the inflow of deposit fluids.

The phase diagram of retrograde gas obtained from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin was presented in Fig. 6.

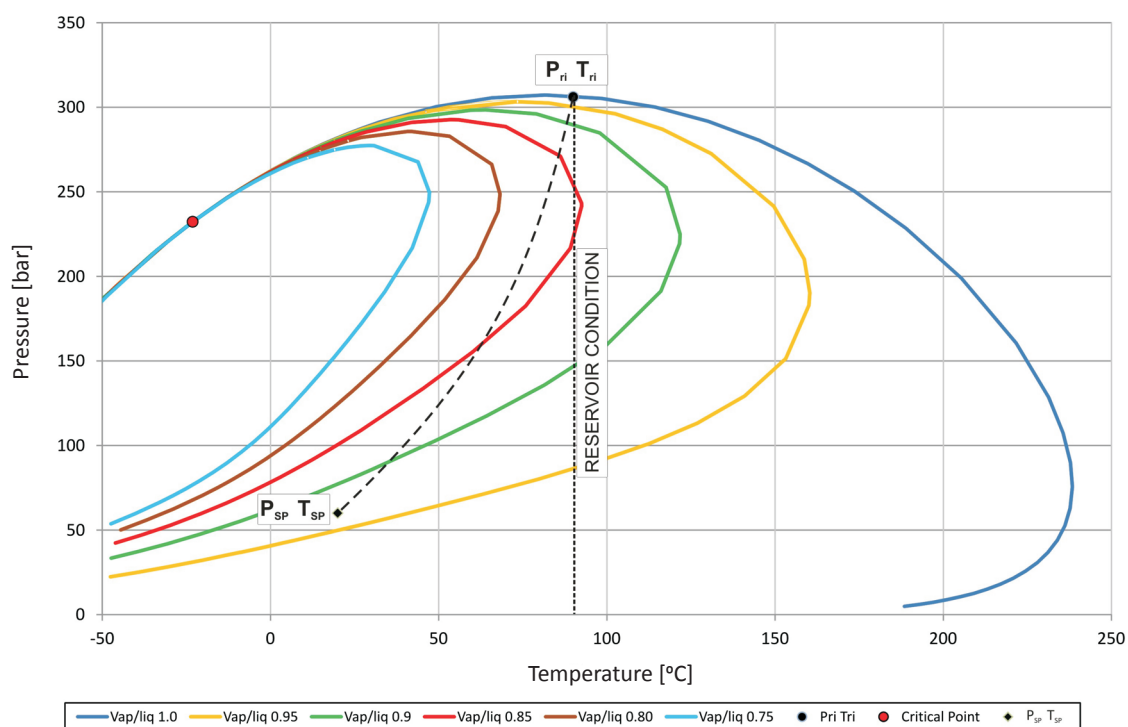


Fig. 6. Phase diagram of retrograde gas from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin.

The point denoting primary reservoir conditions is located on the dew point line and lower pressure contributes to condensation of liquid phase in the reservoir [5]

Table 2. Chemical composition of retrograde gas from the shale formations, where ρ_{20} – condensate density in the conditions is: $P = 1$ bar, $T = 20^\circ\text{C}$ [5]

Composition of reservoir fluid [%mol] at:	
$P_{reserv} = 303.0$	bar
$T_{reserv} = 90.0$	$^\circ\text{C}$
He	0.206
H ₂	0.100
N ₂	6.000
CO ₂	0.619
C ₁	55.431
C ₂	23.621
C ₃	4.512
iC ₄	0.473

ect. Table 2

Composition of reservoir fluid [%mol] at:	
nC ₅	1.461
iC ₅	0.354
nC ₅	0.593
C ₆	1.051
C ₇	1.233
C ₈	1.075
C ₉	0.899
C ₁₀₊	2.372
C ₁₀₊ Mol. Weight	161.77
GOR	2231 Nm ³ /m ³
ρ_{20}	773.1 kg/m ³

Petroleum

Petroleum as reservoir fluid in primary conditions of development is manifested as one-phase fluid. In conditions of the reservoir temperature, from the primary reservoir pressure to saturation pressure, i.e. crossing the bubble point curve, it is oil unsaturated with gas (Fig. 7). During

the production process it is advisable not to allow for pressure reduction in the reservoir below the curve of saturation and to use of enhanced oil recovery methodes to maintain one-phase flow. The surface separator yields gas and oil of the initial gas-oil ratio.

Phase transitions of oil, with production from primary reservoir conditions, through the well, to the separator run as follows: In general

$$\text{liquid} \rightarrow \text{liquid} + \text{gas} \rightarrow \text{liquid} + \text{gas}$$

as phase transitions in the reservoir

$$\text{oil} \rightarrow \text{oil} + \text{retrograde gas} \rightarrow \text{oil} + \text{wet gas}$$

The oil – as defined by the phase transitions described above was divided with reference to properties into:

- volatile oil,
- black oil,
- heavy oil.

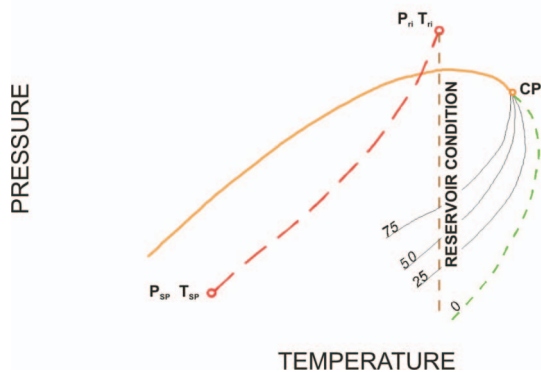


Fig. 7. Phase diagram of unsaturated oil

Volatile oil

Volatile oil, in the primary conditions of reservoirs development is characterized by:

- constant initial gas-oil ratio of values ranging between 350÷600 Nm³/m³,
- initial density of the separator oil, of constant value of 780÷820 kg/m³,
- colour of the oil – yellow, orange, green.

Volatile oil is called a "near-critical" fluid, i.e. its critical point on the phase diagram is located close to the point which describes the primary reservoir conditions.

In the reservoir, with falling pressure, in occurrence of two phases, the gas and fluid significantly change their volumes at intense gas and oil flow to the surface, which results in:

- higher gas-oil ratio,
- lower density of the separator oil,
- as a result, condensation of gasoline which may even make up over a half of the surface tank.

So far, no light oil was encountered in the Lower Paleozoic formations of the Baltic-Podlasie-Lublin Basin.

Black oil

Black oil, in the initial conditions of one-phase flow is characterized by:

- constant gas-oil ratio of values below $350 \text{ Nm}^3/\text{m}^3$,
- constant oil density ranging from $800\div 900 \text{ kg/m}^3$,

Table 3. Chemical composition of unsaturated black oil from shale formations, where ρ_{20} – oil density at: $P = 1 \text{ bar}$, $T = 20^\circ\text{C}$ [5]

Composition of reservoir fluid [%mol] at:	
$P_{\text{reserv}} = 310.0$	bar
$T_{\text{reserv}} = 84.0$	$^\circ\text{C}$
He	0.111
H ₂	0.053
N ₂	1.464
CO ₂	0.066
C ₁	45.979
C ₂	8.220
C ₃	4.048
nC ₄	1.606
nC ₅	1.736
C ₆	0.944
C ₇	2.653
C ₈	4.329

- dark colour; black, brown, red, green.

One of the characteristic features is also high content of “heptanes plus” fraction – above 20%, an indication of a large quantity of heavy hydrocarbons.

ect. Table 3

Composition of reservoir fluid [%mol] at:	
C ₉	3.763
C ₁₀	3.271
C ₁₁	2.844
C ₁₂	2.472
C ₁₃	2.149
C ₁₄	1.868
C ₁₅	1.624
C ₁₆	1.412
C ₁₇	1.227
C ₁₈	1.067
C ₁₉	0.927
C ₂₀	6.166
C ₂₀₊ Mol. Weight	369
GOR	$161 \text{ Nm}^3/\text{m}^3$
ρ_{20}	807.8 kg/m^3

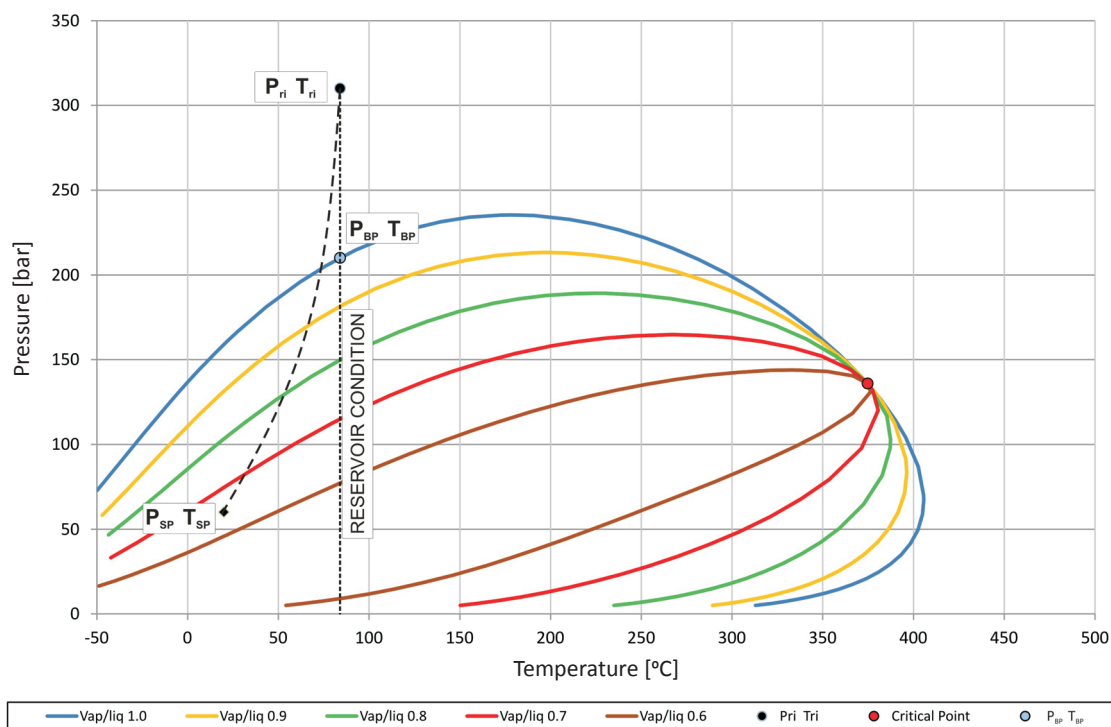


Fig. 8. Phase diagram of black unsaturated oil from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin. The production line which connects the reservoir conditions and surface separation crosses the bubble point line and enters the two-phase region. The critical point of the mixture is located far to the right of the point of initial reservoir conditions [5]

- As a consequence of two-phase flow during production:
- the gas-oil ratio increases,
 - oil density at the initial stage of deposit exploitation will be decreasing, and then it will be rising.

Table 4. Chemical composition of black oil, saturated, from shale formations, where: ρ_{20} – oil density in the conditions: $P = 1 \text{ bar}$, $T = 20^\circ\text{C}$

Composition of reservoir fluid [%mol] at:	
$P_{reserv} = 260.0$	bar
$T_{reserv} = 85.0$	$^\circ\text{C}$
He	0.239
N ₂	2.458
CO ₂	0.563
C ₁	41.112
C ₂	7.982
C ₃	5.572
iC ₄	0.642
nC ₄	3.668
iC ₅	0.662
nC ₅	3.973
C ₆	3.861
C ₇	4.039
C ₈	3.711

In subsequent phase diagrams, examples of black unsaturated oil were shown and two examples of saturated oil, with tables illustrating the chemical composition of the fluid in reservoir conditions (to C₂₀₊).

ect. Table 4

Composition of reservoir fluid [%mol] at:	
C ₉	2.556
C ₁₀	2.301
C ₁₁	1.538
C ₁₂	1.397
C ₁₃	1.268
C ₁₄	1.151
C ₁₅	1.045
C ₁₆	0.948
C ₁₇	0.861
C ₁₈	0.781
C ₁₉	0.709
C ₂₀	0.644
C ₂₁₊	6.320
C ₂₁₊ Mol. Weight	425.2
GOR	189 Nm ³ /m ³
ρ_{20}	823.0 kg/m ³

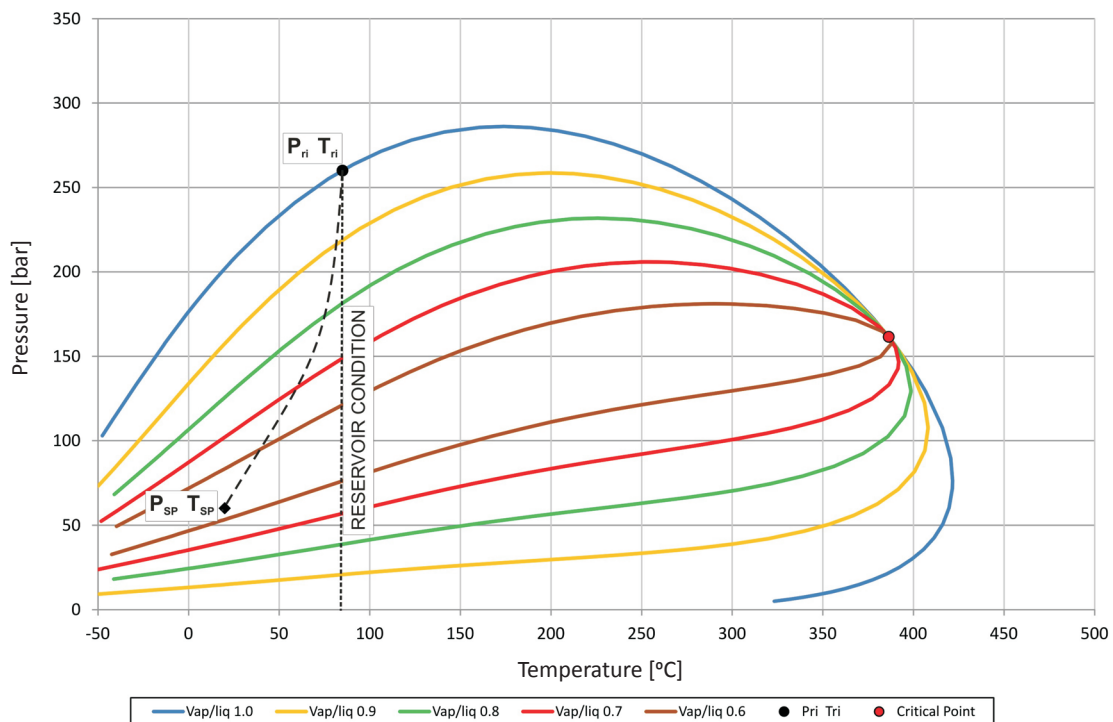


Fig. 9. Phase diagram of black oil, saturated, from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin. The production line which connects the initial reservoir conditions and surface separation begins at the bubble point line and enters the two-phase region. Critical point of the mixture is located far to the right of the point of initial reservoir conditions [5]

Table 5. Chemical composition of black oil from shale formations, where ρ_{20} – oil density in conditions: $P = 1 \text{ bar}$, $T = 20^\circ\text{C}$

Composition of reservoir fluid [%mol] at:	
$P_{\text{reserv}} = 303.0$	bar
$T_{\text{reserv}} = 90.0$	$^\circ\text{C}$
He	0.034
H ₂	0.013
N ₂	4.629
CO ₂	0.423
C ₁	35.231
C ₂	14.414
C ₃	9.277
iC ₄	1.290
nC ₄	3.468
iC ₅	1.272
nC ₅	1.549
C ₆	2.431
C ₇	2.950

ect. Table 5

Composition of reservoir fluid [%mol] at:	
C ₈	3.407
C ₉	2.359
C ₁₀	1.992
C ₁₁	1.691
C ₁₂	1.215
C ₁₃	1.106
C ₁₄	1.007
C ₁₅	0.917
C ₁₆	0.835
C ₁₇	0.761
C ₁₈	0.693
C ₁₉	0.631
C ₂₀₊	6.403
C ₂₀₊ Mol. Weight	415.7
GOR	228 Nm ³ /m ³
ρ_{20}	820.0 kg/m ³

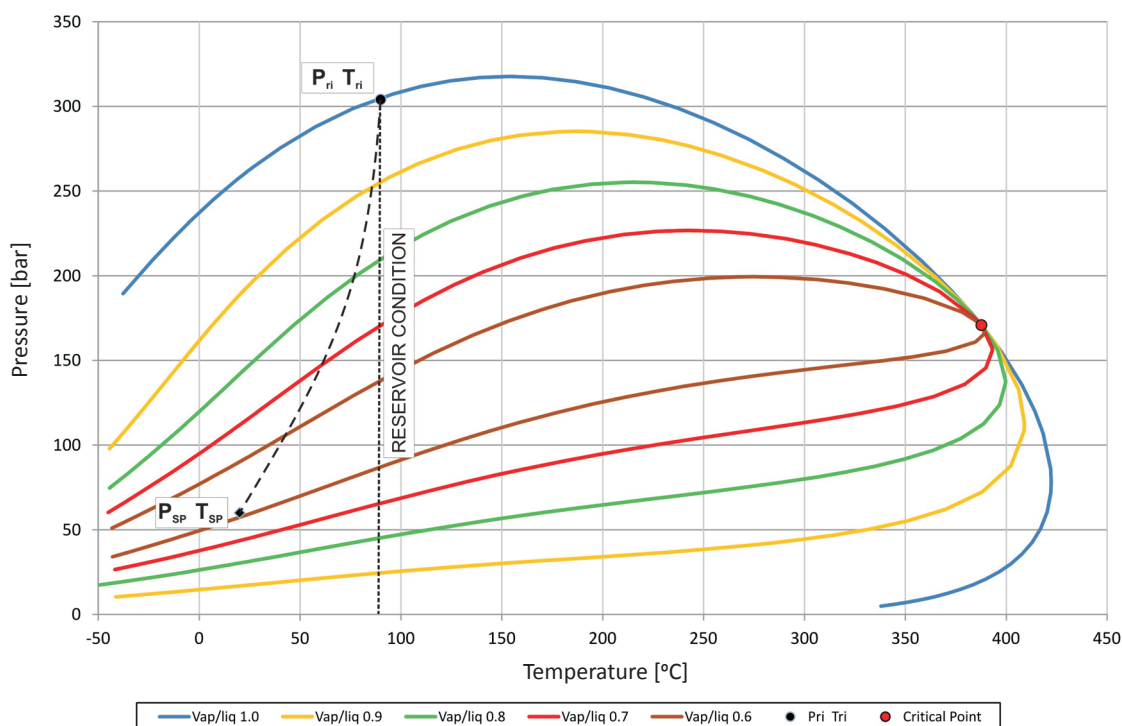


Fig. 10. Phase diagram of saturated black oil from Lower Paleozoic shale formations of the Baltic-Podlasie-Lublin Basin. The production line which links the initial reservoir conditions and surface separation begins on the bubble point line and enters the two-phase region. The critical point of the mixture is located far to the right of the point which describes the primary reservoir conditions [5]

Heavy oil

One of the qualities of heavy oils is very low gas-oil ratio, and often these are oils completely degassed. The transition

from the primary reservoir conditions through the well, to the separator may be noted in the following way:

in general form

liquid → liquid → liquid

and in the reservoir

oil → oil → oil

Heavy oil is characterized by black colour and density above 880 kg/m^3 , at times reaching the values almost corresponding to the density of water.

So far, no heavy oil was discovered in the Lower Paleozoic formations of the Baltic-Podlasie-Lublin Basin.

Summary

On the basis of currently performed research, as part of the project *Determination of the composition, phase properties and PVT parameters of reservoir fluid* (Blue Gas Program) carried out at the Oil and Gas Institute – National Research Institute, basic types of reservoir fluids were identified. The samples were taken from successful wells performed in the

Baltic-Podlasie-Lublin Basin which provide access to the reservoirs of Lower Paleozoic (Ordovician, Silurian period). In the six-category group of reservoir fluids; dry gas, wet gas, retrograde gas, volatile oil, black oil-type and heavy oils, the presence of wet gases, retrograde gases and black oils were found, both unsaturated and saturated.

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