Impact of carbon dioxide on Ivanić oilfield in tertiary oil recovery phase

D. Novosel

ORIGINAL SCIENTIFIC PAPER

Current annual oil production in Croatia on more than 30 oilfields, amounts to a little more than 0.5 million t per year. In the last 50 years, the realized oil recovery factor from the oil reservoirs has on average amounted to 32.6% of original oil in place. The currently favourable oil price increases the need for higher oil recovery from existing oilfields through the implementation of tertiary oil recovery methods. As for Croatia, a 3% increase in the oil recovery factor from current oil reservoirs, obtained due to the implementation of tertiary oil recovery methods, increases annual oil production by 15 000 t. Although tertiary oil recovery methods (EOR methods) are becoming more common worldwide, carbon dioxide injection in oil reservoirs is the most implemented EOR method. Based on the laboratory test results of the applications of tertiary oil recovery methods on oil reservoirs in Croatia, the carbon dioxide injection process was chosen as an appropriate method for increasing oil production on the Ivanić oil field.

During the injection stage, carbon dioxide changes the state of the matter from liquid to gaseous or supercritical state. Unfortunately, the measured carbon dioxide injection results and laboratory test results differ. In situ measurements are very expensive and sometimes impractical; therefore, various approximations are taken into account with numerous equations of state. The aim was to approximate an equation of state on the measured data, for a wide range of *p,T* conditions, during a pilot project of carbon dioxide injection on the Ivanić oilfield reservoir. Among numerous cubic equations of state, van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, Peng-Robinson, Valderrama-Cisternas, Patel-Teja, Lawal-Lake-Silberberg and Matin and Hou equation of state. After comprehensive comparisons and analysis of the values measured and calculated for a wide range of *p,T* conditions during carbon dioxide injection on the Ivanić oilfield, some of equations of state were recommended for determinations carbon dioxide changes of state.

Key words: tertiary oil recovery phase, Ivanić oilfield, carbon dioxide injection, thermodynamic changes of states, equation of state, inversion curve

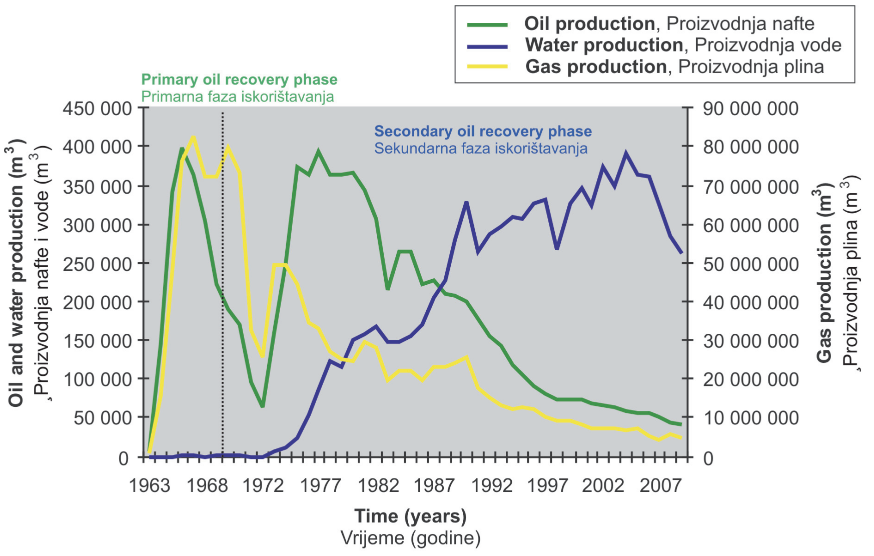
1. INTRODUCTION

Relatively low oil recovery or oil reserves remaining in the reservoir after primary and secondary phase of oil recovery triggered theoretical scientific and practical research of new enhanced oil recovery technologies. Tertiary phase of enhanced oil recovery methods (hereinafter EOR methods) is applied when secondary recovery methods reach the economic limit.[21] Carbon dioxide injection was used for the first time on Dewey Bartlesville field in Oklahoma, USA. Over last two years there have been around 300 EOR projects around the world. According to the recent data[1], carbon dioxide dominates in enhanced recovery methods (in 65% of EOR projects around the world and in 85% of projects in the USA).

Over last 50 years, 103 million m^3 of oil was produced in Croatia with an average recovery of 32.6% of original oil in place. Highly explored Pannonian Basin and abundant carbon dioxide sources (gas fields in Podravina, Šandrovac oil-gas field, Kopčevac locality) open perspective for application of enhanced oil recovery methods.[5,21] According to the laboratory research results[8] and numerical simulation, trial injection of carbon dioxide and water in alteration (hereinafter; pilot project) was performed on a restricted part of Ivanić oilfield from 2001 until 2006. After two alteration cycles of carbon dioxide and water injection, over 5000 m^3 of oil were produced from two production wells by the end of 2008. This confirmed the efficiency of carbon dioxide in enhanced oil recovery from reservoir.

During implementation of the pilot project, the injected carbon dioxide was injected in liquid state. Due to geothermal gradient, carbon dioxide has changed its aggregate state in the borehole. It was in liquid state at the wellhead and within a part of injection pipes, and then further in injection pipes it was like mixture phase while at the bottom-hole it was in the overheated area (carbon dioxide overheated vapor). Changes of carbon dioxide thermodynamic characteristics during injection are difficult to determine by measuring but they can be numerically defined by equations of state or real gas and vapor. Equations of state, according to their mathematical shape[6] can be cubic equations of state (that can be solved by volume) and polynomial (virial) equations of state. Among numerous cubic equations the following were randomly selected: van der Waals equation of state, Redlich-Kwong equation of state, Soave modification of Redlich-Kwong, Peng-Robinson equation of state, Patel-Teja equation of state, Lawal-Lake-Silberberg equation of state, Valderrama-Cisternas equation of state and polynomial Martin-Hou equation of state for the analysis of carbon dioxide thermodynamic characteristics changes. The exploratory approach to the issues of carbon dioxide state phase changes which occur during its injection into the reservoirs on Ivanić oilfield implied also the defining of pressure saturation and volume calculation under three injection conditions. KJS[18] computer program was used for comparing the calculation results for three selected carbon dioxide injection conditions with the measured data. During further considerations of carbon dioxide efficiency, carbon dioxide inversion pressure was calculated for considered three injection conditions in Iva-28 well according to the previously mentioned equations of state.

The obtained calculation results, i.e. deviation of calculated from measured values enables the decision on applying certain equations of state for analytic considerations of carbon dioxide injection during enhanced oil recovery on Ivanić oilfield.

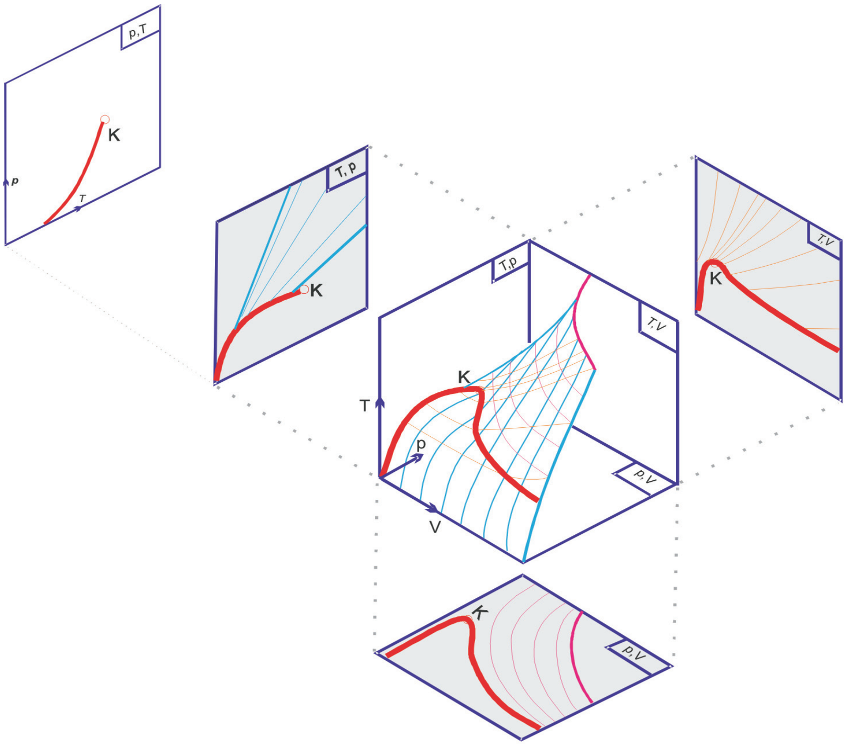


Source: Study on Hydrocarbons Reserves on Ivanić Exploitation Field (as of December 31, 2005), INA-Naftaplin files, 2006., data from table on page 41.
Izvor: Elaborat o rezervama ugljikovodika eksploatacijskog polja Ivanić (stanje 31.12. 2005.), Fond stručne dokumentacije INA-Naftaplin, 2006., podaci iz tablice na stranici 41.

Fig. 1. Production of oil and solution gas in primary oil recovery phase on Ivanić oilfield
Sl. 1. Proizvodnja nafte i plina otopljenog u nafti u primarnoj fazi iskorištavanja Naftnog polja Ivanić

2. HISTORY OF OIL AND GAS PRODUCTIN ON IVANIĆ OILFIELD

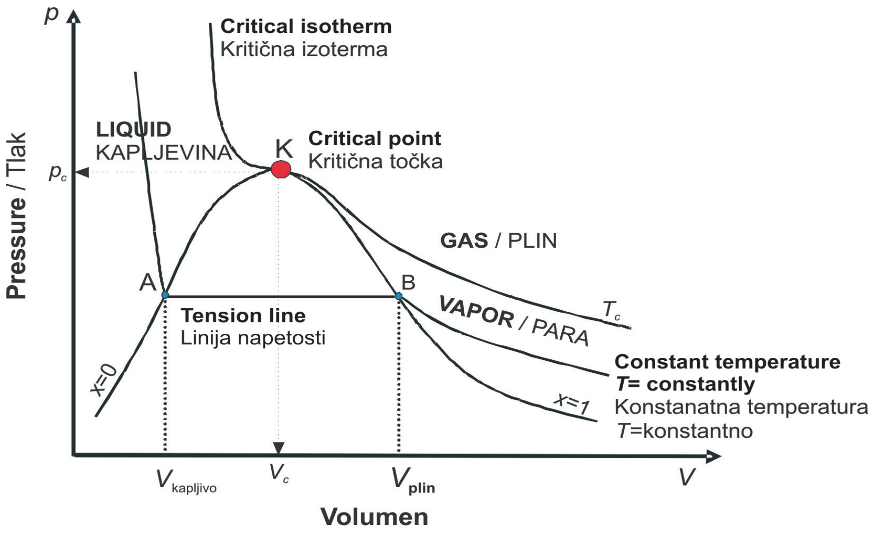
Commercial quantities of hydrocarbons were discovered in gamma reservoir sandstones on Ivanić oilfield during 1963. Oil and gas production on Ivanić oilfield started in November 1963 with only 5 production wells. The highest production was realized during primary oil recovery phase during 1966. Unfavorable impact of solution gas drive dominated the reservoir which directly affected oil recovery that should have been 18% while only 9.2% was recovered. Analysis of oil recovery process from oil reservoirs confirmed the impact of solution gas drive thus secondary methods of enhanced oil recovery were implemented to increase oil recovery. Water injection for pressure maintenance started in 1972. Peak oil production in secondary phase of oil recovery was recorded in 1977.[5] Figure 1 shows oil and gas production flow in primary and secondary oil recovery phase.



Source: GOLUB, M.: Mathematical Model of Gases and Vapors Thermodynamic State in Petroleum Mining, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 1993, p. 17.
Izvor: Golub, M.: Matematički model termodinamičkih stanja plinova i para u naftnom rudarstvu, Doktorska disertacija, Rudarsko geološko naftni fakultet Sveučilišta u Zagrebu, Zagreb, 1993., p. 17.

Fig. 2. Thermodynamic surface of real gases and vapors
Sl. 2. Termodinamička površina realnih plinova i para

Tertiary methods of enhanced oil recovery were applied in 2001.[13] Injecting of water started in a restricted part of gamma reservoir 2/4 where oil and gas production was stopped. Target was to increase the pressure in reservoir to minimal mixing pressure determined during laboratory research.[8] This was the beginning of pilot project. After two years of water injection, the measured pressure was 170 bar. There was no further pressure increase in the reservoir due to strong water environment. Pilot project continued under reservoir conditions that were favorable for mixing.[13] First cycle of carbon dioxide injection started in November 2003 after the construction of plant which consisted of two reservoirs for liquid carbon dioxide, two reciprocating pumps for carbon dioxide injection, surface pipelines and other measuring instrumentation equipment. Carbon dioxide in liquid state was transported by truck tanks at the temperature of: T = 255.16 K (t = -18 °C), and pressure of p = 18 bar.[14] It was injected into the well in liquid state. Due to the geothermal gradient of well, its aggregate state changed in injection pipes.



Source: BOŠNJAKOVIĆ, F.: Heat Science, first part, second edition, Tehnička knjiga, Zagreb, 1962, p. 112.
Izvor: BOŠNJAKOVIĆ, F.: Nauka o toplini, dio prvi, drugo izdanje, Tehnička knjiga, Zagreb, 1962., p. 112.

Fig. 3. Change of state and tension lines of pure substance depending on pressure and volume
Sl. 3. Promjena stanja i linija napetosti čiste tvari u ovisnosti o tlaku i volumenu

3. THERMAL CHARACTERISTICS AND PHASE CONDITIONS OF CARBON DIOXIDE

In the engineering practice, it is important to be familiar with thermodynamic states p,V,T of certain matter. It is especially significant during the implementation of enhanced recovery methods in a reservoir. Injection of carbon dioxide in tertiary phase of oil reservoir recovery causes changes in balance ratio, i.e. changes in its p,V,T characteristics. These changes occur in surface and underground well completion. They are very difficult to determine by measuring, however they can be calculated with the knowledge of mathematical, physical and chemical rules. Those are equations of state of gases and vapors that connect their mutually related basic thermodynamic state amounts (p,V,T), i.e. macroscopic characteristics of matter.[2,4] Experience has confirmed that pressure - p, volume - V and temperature - T are connected by the following equation:

$$f(p,V,T)=0 \qquad (1)$$

According to Bošnjaković[2], this equation is called thermal equation of state and is expressed in implicit shape and its mathematical shape is different for different substances. This equation is good for all aggregates states of substance, and can be expressed in explicit shape of one-component gases and their mixtures:

$$p=f_1(T,V),\ V=f_2(p,T) \text{ and } T=f_3(p,V) \qquad (2)$$

Thermodynamic surface of real gases represents mutual connection of thermodynamic state amounts - p,V,T and is presented in Figure 2:

Table 1. Pressure and temperature change measured data depending on well depth during carbon dioxide injection into Iva-28 well.

Measuring Depth m	Pressure bar	Temperature °C	
0	54.35	-18.00	**First condition**: CO_2 as liquid
50	60.26	-18.00	
100	60.25	-18.00	
150	69.87	-18.00	
200	75.43	-18.00	
250	80.25	-17.00	
300	85.26	-10.00	
350	89.89	-5.70	**Second condition:** CO_2 as mixture
400	94.53	-3.00	
450	98.97	0.00	
500	103.61	3.00	
550	108.24	5.00	
600	113.06	8.00	
650	117.14	10.00	
700	121.58	13.20	
750	125.85	15.60	
800	130.11	17.50	
900	138.27	18.00	
1 000	146.65	27.00	
1 100	155.04	31.00	
1 200	162.87	36.20	**Third condition**: CO_2 in overheated area
1 300	170.51	40.70	
1 400	178.33	45.20	
1 500	185.60	49.30	
1 550	189.33	51.40	
1 700	204.91	58.40	

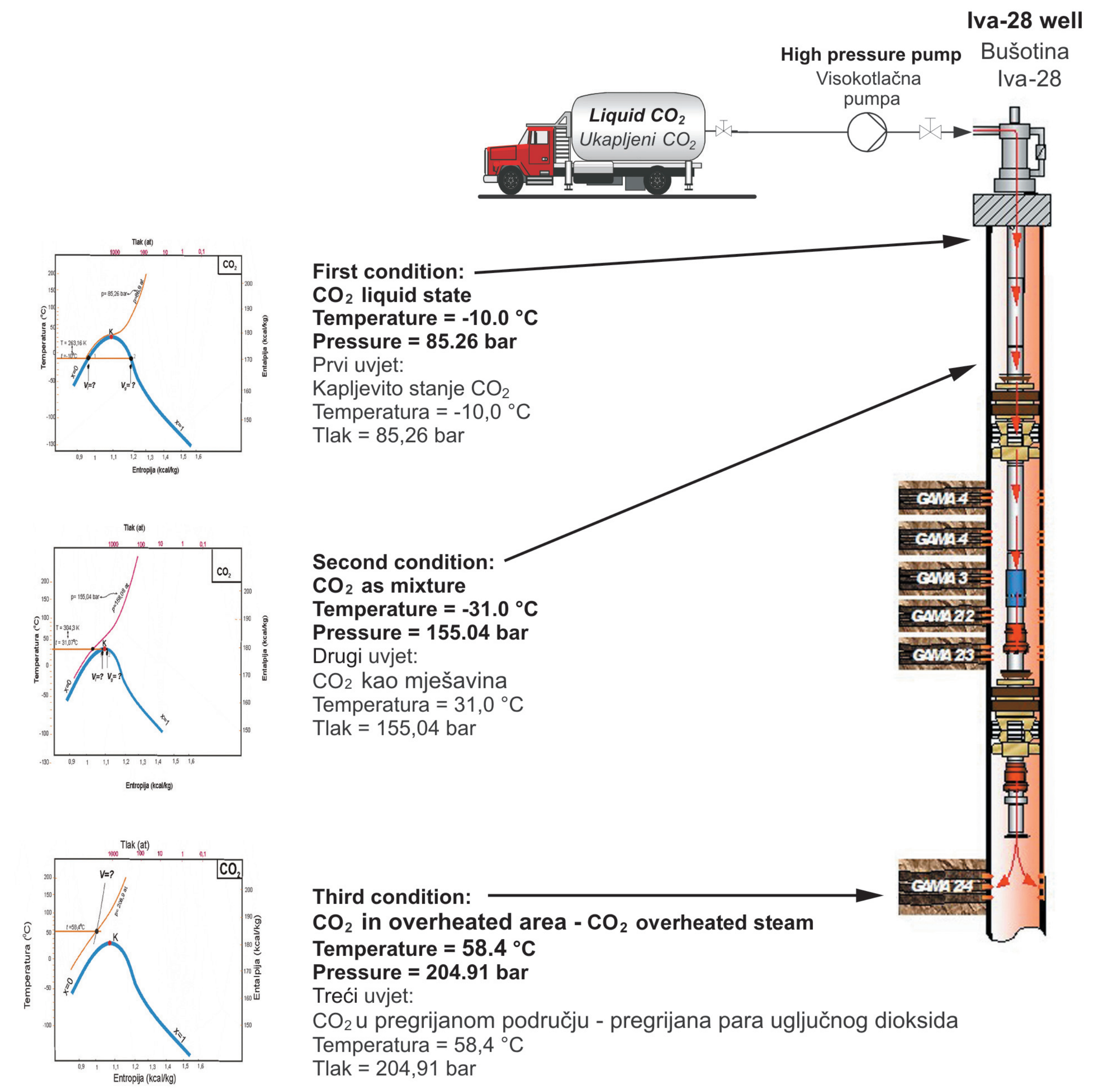
Source: NOVOSEL, D.: Initial Results of WAG CO_2 IOR Pilot Project Implementation in Croatia, SPE 97639, SPE, IIORC Asia Pacific, Kuala Lumpur, 2005., p.4.

$$\left(\begin{matrix} p \\ V \\ T \end{matrix} \right\} \begin{matrix} pV \\ VT \\ pT \end{matrix} \qquad (3)$$

but also enthalpy - *i* and entropy *s*: $^{i}/_{s}$. Graphical presentation of phases or phase diagram is a common way of presenting certain substance and the conditions where its phases exist. There are two types of diagrams mostly used presenting thermodynamic characteristics in thermodynamics:

p,V - where surfaces are presented by work or energy, and

T,s - where surfaces within a diagram are presented by heat



Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009, p. 11-13, 48-104.
Izvor: NOVOSEL, D.: Učinak ugljičnog dioksida u tercijarnoj fazi iskorištavanja naftnih ležišta polja Ivanić, doktorska disertacija, Rudarsko–geološko-naftni fakultet Sveučilišta u Zagrebu, Zagreb, 2009., p. 11-13, 48-104.

Fig. 4. Graphic review of considered conditions for carbon dioxide injection
Sl. 4. Grafički prikaz razmatranih uvjeta utiskivanja ugljičnog dioksida

Table 2. Review of selected equations of state

Two-parameter cubic equations of state		Equation constants for CO_2
Van der Waals (1873.)	$p = \frac{RT}{V-b} - \frac{a}{V^2}$	a = 3.658 281 bar m^6/kmol^2 b = 0.042 857 m^3/kmol
Redlich-Kwong (1949.)	$p = \frac{RT}{V-b} - \frac{a}{\sqrt{T}V(V+b)}$	a = 3.706 886 bar m^6/kmol^2 b = 0.297 05 m^3/kmol α = 1.092 004
Soave-Redlich-Kwong (1972.)	$p = \frac{RT}{V-b} - \frac{a}{V(V+b)}$	a = 3.706 886 bar m^6/kmol^2 b = 0.297 05 m^3/kmol α = 1.143 892
Peng-Robinson (1976.)	$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$	a = 3.964 909 bar m^6/kmol^2 b = 0.026 673 m^3/kmol α = 1.122 871
Three-parameter cubic equation of state		
Patel-Teja (1982.)	$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$	a = 4.319 800 bar m^6/kmol^2 , b = 0.022 877 m^3/kmol, c = 0.610 28 m^3/kmol α = 1.122 717 5
Four-parameter cubic equation of state		
Lawal-Lake-Silberberg (1983.)	$p = \frac{RT}{V-b} - \frac{a}{V^2+\alpha_L bV-\beta_L b^2}$	a = 4.856 928 bar m^6/kmol^2 b = 0.033 705 m^3/kmol α = 1.114 389 2 α_L = 2.810 637 β_L = 3.249 487
Valderrama-Cisternasa (1986.)	$p = \frac{RT}{V-b} - \frac{a}{V(V+b)+c(V-b)}$	a = 3.925 426 bar m^6/kmol^2 b = 0.027 17 m^3/kmol, c = 0.022 303 m^3/kmol α = 1.130 383 2
Polynomial equation of state		in Table 3.
Martin and Hou (1955./1959.)	$p = \frac{f_1}{V-b} + \frac{f_2}{(V-b)^2} + \frac{f_3}{(V-b)^3} + \frac{f_4}{(V-b)^4} + \frac{f_5}{(V-b)^5}$	

Table 3. Constants of Martin-Hou equation of state for carbon dioxide

Constant	First equation from 1955	Modified equation from 1959
T_c	31.01 °C	31.01 °C
p_c	73.7 bar	73.7 bar
V_c	0.002 156 363 m^3/kg	0.002 156 363 m^3/kg
z_c	0.276 71	0.276 71
m	14.0	14.0
β	3.25	3.25
T_b/T_c	0.80	0.80
n	-	1.70
y	-	3.50
b	0.007 495	0.007 495
A_2	-8.927 363 1	-8.927 363 1
A_3	0.189 078 19	0.179 486 21
A_4	-2.112 459 x 10^{-3}	-2.112 459 x 10^{-3}
A_5	-	7.017 835 x 10^{-6}
B_1 or R	0.243 81	0.243 81
B_2	5.262 476 x 10^{-3}	5.262 476 x 10^{-3}
B_3	-7.046 17 x 10^{-5}	-5.770 542 x 10^{-5}
B_5	1.956 559 3x 10^{-8}	1.023 511 x 10^{-8}
C_2	-150.975 87	-150.975 87
C_3	4.083 142 4	4.705 805
C_5	-	-4.55437 x 10^{-4}

Source: MARTIN, J.,J., KAPOOR,R.,M., DE NEVERS, N.: An Improved Equation of State for Gases, A.I.Ch.E. Journal, Volume 5, Number 2., 1959., p 160.

Real area for a certain substance can be illustrated by p,V diagram (Figure 3). As shown in Figure 3, liquid and gas exist at the same time from point A to point B. The line from point A to point B is called tension line while the area below is two phase area or saturated area.

Changes in thermodynamic characteristics of carbon dioxide during injection into a reservoir can be numerically defined by equations of state for real gases. According to mathematical shape[2,3] equations of state can be cubic ones (solvable by volume) and polynomial (virial) equations of state.[6] Equations of state for real gases are of great importance for petroleum mining.[6,7,17,21,26] The basic equation of state was made by J. D. van der Waals in 1873 and it represents the starting point for all analyses of thermodynamic characteristics changes.[25] After that, numerous scientists have proposed over hundred equations of state[3] and even today they are trying to derive new shapes. Eight randomly selected equations shall be compared on the example of carbon dioxide injection during a pilot program. Results obtained by use of equations of cubic shape by volume: van der Waals[25] (1873), Redlich-Kwong[20] (1949), Soave-Redlich-Kwong[22] (1972), Peng-Robinson[17] (1976), Valderrama-Cisternas[23] (1986), Patel-Teja[16] (1982), Lawal-Lake-Silberberg[10] (1983), and by polynomial (virial) equation of state: Martin and Hou[11,12] (1955/1959) were compared with measured values.

4. RESULTS OF VOLUME CALCULATION AND SATURATION PRESSURE AT CARBON DIOXIDE INJECTION INTO THE RESERVOIRS OF IVANIĆ OILFIELD

Change of pressure and temperature was measured in the wellbore of injection well (Iva-28)[13,15] during injection of carbon dioxide. The results of those measuring are presented in Table 1. As a random example, during consideration of phase state changes during the injection of carbon dioxide, three conditions from Table 1 shall be considered. Those conditions are graphically presented in Figure 4.[13,15] Analyses of those conditions of carbon dioxide injection during pilot project showed that within the injection well wellbore, carbon dioxide has changed its aggregate state from liquid at the wellhead to carbon dioxide in overheated area (carbon dioxide overheated steam) at the bottom-hole.

Equations and their constants are presented in Table 2 and Table 3. Comparison of the results is in fact deviation of calculated value from the measured one and is expressed in percentage.[3] Values for comparison of carbon dioxide were read from Thermodynamic tables[19] and are considered as measured values. According to pressure and temperature values from the first condition (Figure 4), carbon dioxide is in liquid state and is in real two phase saturated area. Volume at the lower boundary line or saturated liquid volume (V_l), volume at the upper boundary line or saturated vapor volume (V_g) and saturation pressure (p_{1g}) (Figure 3) for given temperature shall be calculated. Figure 5 on *T,s* graphically shows this injection condition. Numeric solutions according to selected equation of state are presented in Table 12.[15]

Numbers from the second condition (Figure 4) of carbon dioxide injection (carbon dioxide as mixture) were inserted in selected equations and values for volume (V_l) and (V_g) and carbon dioxide saturation pressure (p_{1g}) were calculated once again like for the first condition. Temperature from this condition (31.0 °C) is very close to critical temperature of carbon dioxide. The obtained results were compared to the measuring data and deviations were calculated.[3,15]

At the third injection condition which is overheated state at the bottom-hole of Iva-28 injection well, volume according to selected equations was calculated and

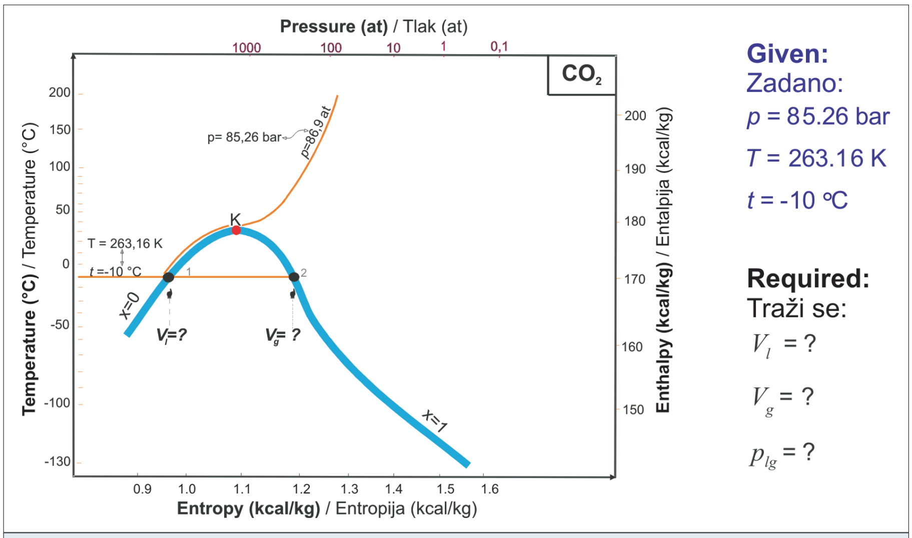


Fig. 5. Carbon dioxide volume and saturation pressure calculation for the first condition
Sl. 5. Grafički prikaz proračuna volumena i tlaka zasićenja ugljičnog dioksida za prvi uvjet

Table 4. Comparison of calculated values V_l, V_g, and p_{1g} of CO$_2$ and measured values for the given isotherm t = -10 °C

No	Equation of State	Calculated V_1	Measured V_1 from Thermodynamics Tables	Deviation from measured values	Calculated V_1	Measured V_1 from Thermodynamics Tables	Deviation from measured values	Calculated p_{lg}	Measured p_{lg}	Deviation from measured values
		m³/kmol	m³/kmol	%	m³/kmol	m³/kmol	%	bar	bar	%
1	van der Waals	0.072 838	0.044 846	-62.42	0.369 079	0.624678	40.92	40.21	26.46	-51.97
2	Redlich-Kwong	0.052 928		-18.02	0.515 509		17.48	30.86		-16.63
3	Soeve-Redlich-Kwong	0.050 595		-12.82	0.625 208		-0.08	26.61		-0.57
4	Peng-Robinson	0.044 596		0.56	0.623 944		0.12	26.28		0.68
5	Patel-Teja	0.036 247		19.17	0.711 283		-13.86	23.32		11.87
6	Laval-Lake-Silberberg	0.041 685		7.05	0.956 244		-53.08	18.29		30.88
7	Valderrama - Cisternas	0.040 721		9.20	1.181 681		-89.17	15.58		41.12
8	Martin-Hou	0.066 075		-47.34	0.438 877		29.74	32.65		-23.39

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009, p. 87-90.

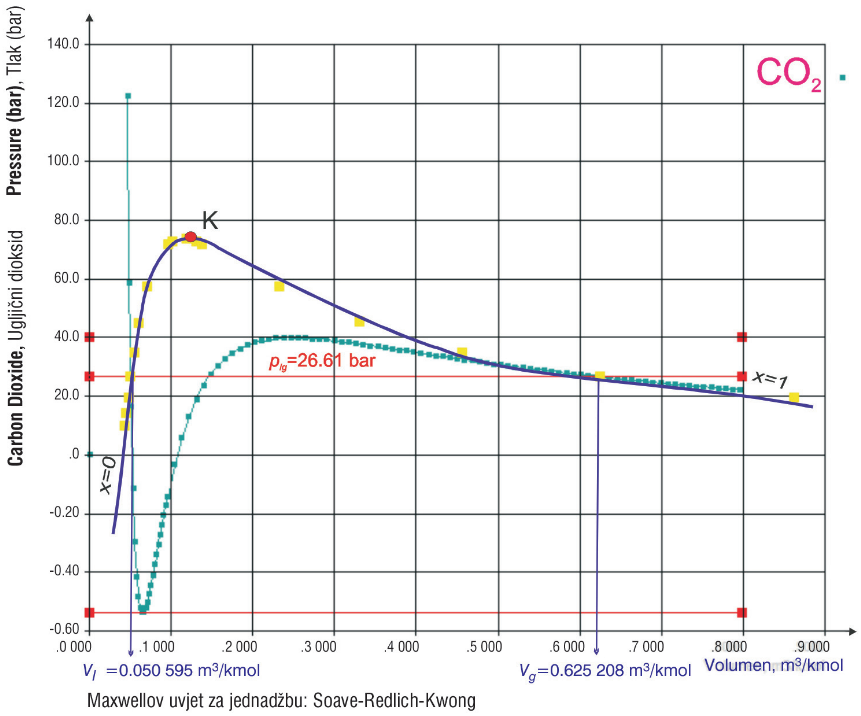
compared with the measured data. This volume was calculated with given pressure and temperature values for all three injection conditions from Figure 4. These values were compared with the volume calculated according to randomly selected equations of state and deviations were determined.[15]

Also, the volume was calculated according to selected equations of state and was compared to measured data,[9] i.e. with the volume calculated from measured pressure and temperature data during carbon dioxide injection into Iva-28 well (Table 1).[15]

FIRST CONDITION: → LIQUID STATE OF CARBON DIOXIDE

Comparative review of estimation results for seven chosen cubic equations and one polynomial equation of state is presented in Table 4 where the smallest deviations from measured values are marked in red.[15]

The lowest deviation of calculated volumes from the measured values was obtained by Peng-Robinson equation of state (0.56%). The closest results to this were those reached by Laval-Lake-Silberberg (7.05%) and Valderama-Cisternas (9.2%) equation of state. Results of other equations had much higher deviations. The lowest deviation of calculated volume from measured values was obtained by using Redlich-Kwong equations of state (0.08%) while Peng-Robinson equation of state also had exceptionally good result (0.12%). Other results differ from the measured values in very high percentages and are not satisfactory. Deviation of calculated values from measured values according to polynomial Martin-Hou equation of state for both calculated volumes is considerable (- 47.3% and 29.74%) and also not satisfactory. The line which crosses isotherm in three points (Figure 3) below the critical point between minimal and maximal pressure according to Maxwell's equal area rule determines the saturation pressure (p_{1g}) value. Results of carbon dioxide saturation pressure calculation for given isotherm are presented in Table 4. The lowest deviation for given isotherm was obtained with the use of Soeve-Redlich-Kwong (hereinaf-



Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009, p. 89.
Izvor: NOVOSEL, D.: Učinak ugljičnog dioksida u tercijarnoj fazi iskorištavanja naftnih ležišta polja Ivanić, doktorska disertacija, Rudarsko–geološko-naftni fakultet Sveučilišta u Zagrebu, Zagreb, 2009., p. 89.

Fig. 6. Graphic review of calculated saturation pressure and volume according to SRK equation for t = -10 °C
Sl. 6. Grafički prikaz izračunatog tlaka zasićenja i volumena po SRK jednadžbi za t =-10 °C

Table 5. Comparative analysis of the recent calculation and measured carbon dioxide volume for given conditions t =-10 °C, p = 85.26 bar

No	Equation of state	Calculated V (m³/kmol)	Read V from Thermodynamics Atlas (m³/kmol)	Deviation from the volume from Thermodynamics Atlas (%)	Measured V from HDM (m³/kmol)	Deviation from measured value (%)
1	van der Waals	0.067 472	0.044 01	-53.31	0.043 122 7	-56.47
2	Redlich-Kwong	0.049 656		-12.83		-15.15
3	Soeve-Redlich-Kwong	0.047 957		-8.97		-11.21
4	Peng-Robinson	0.042 444		3.56		1.57
5	Patel-Teja	0.034 880		20.75		19.11
6	Laval-Lake-Silberberg	0.041 103		6.61		4.68
7	Valderrama - Cisternas	0.039 546		10.14		8.29
8	Martin-Hou	0.048 722		-10.71		-12.98

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009., p. 91.

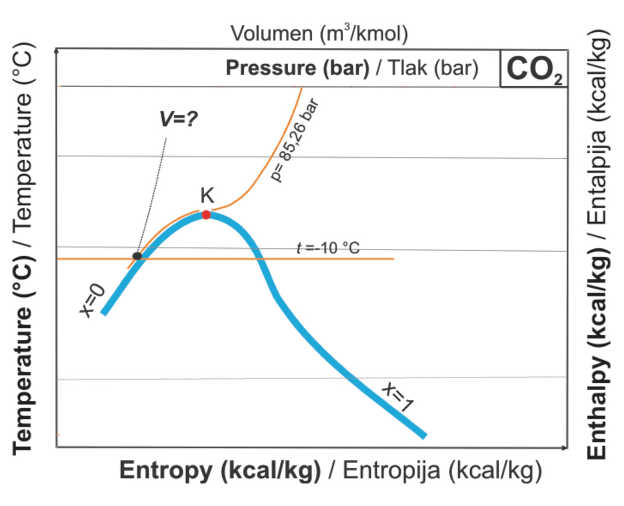
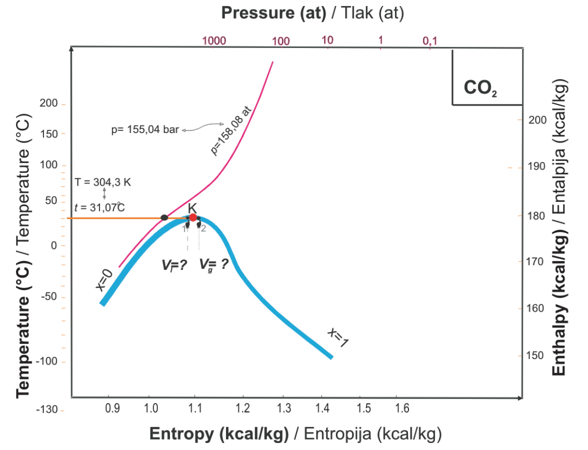


Fig. 7. Graphic review of carbon dioxide volume calculation for t = -10 °C, p = 85.26 bar
Sl. 7. Grafički prikaz proračuna volumena ugljičnog dioksida za t = -10 °C, p = 85,26 bar

ter: SRK) and Peng-Robinson equation of state (-0.57% and 0.68%). The explanation of this result is in the fact that parameters of this equation of state are not defined only by critical pressure and critical temperature but also by acentric factor. Graphic review of the results from Soeve-Redlich-Kwon equation of state is given on p,V in Figure 6.[15]

Calculated values of carbon dioxide volume for given conditions are compared to the volume (Figure 7) read from Thermodynamics Atlas[9] and the volume calculated from measured data of pressure and temperature change (hydrodynamic measuring, hereinafter HDM) at the depth of Iva-28 well[13] . Calculated volume values for given conditions t = -10 °C, p = 85.26 bar and their deviations from the volume obtained by hydrodynamic measurement are presented in Table 5.

The lowest deviation obtained by comparison of calculated measured volume values was reached with the use of Peng-Robinson equation of state (3.56% and 1.57%). Satisfactory result was also obtained by volume calculation according to Laval-Lake-Silberberg equation of state (4.68% and 6.61%) while other results are not satisfactory (deviation from the measured value is over 5%. Result obtained by solution of Martin and Hou polynomial equation of state (-10.71% and 12.98%) are not satisfactory either.



Given:
Zadano:
p = 155,04 bar
T = 304,3 K,
t = 31,0 °C

Required:
Traži se:
V_l = ?
V_g = ?
p_{lg} = ?

Fig. 8. Graphic review of carbon dioxide volume and saturation pressure calculation for the second condition
Sl. 8. Grafički prikaz proračuna volumena i tlaka zasićenja ugljičnog dioksida za drugi uvjet

SECOND CONDITION: → CARBON DIOXIDE AS MIXTURE

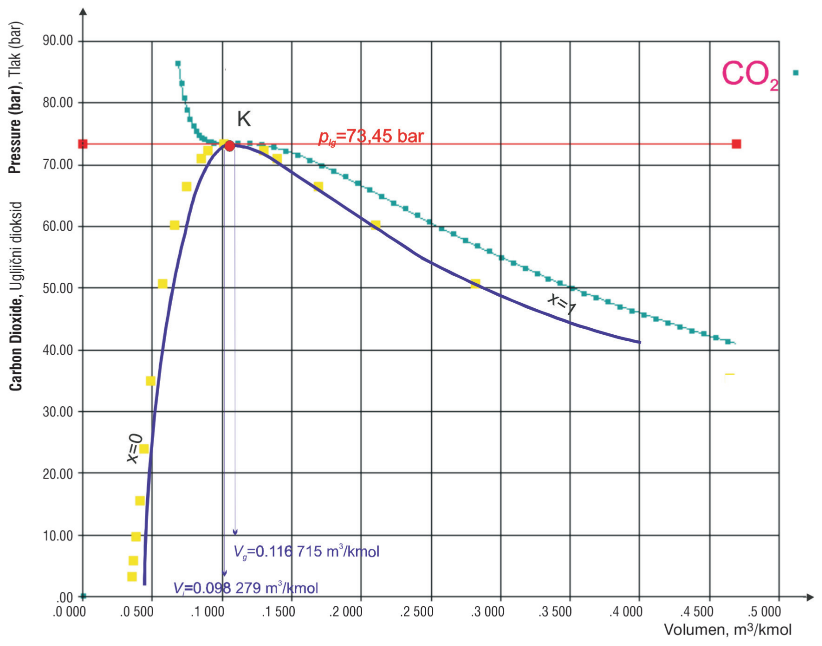
Review of calculation results for selected equations of state and deviations of these values from the measured ones is presented in Table 6.

The lowest volume deviation on the lower boundary line from measured values (Table 6) was obtained with the use of Valderama-Cisternas (hereinafter: VC) equation of state (-3.58%). The lowest volume deviation of carbon dioxide dry saturated vapor from the measured values was obtained with the use of Patel-Teja equation of state (-4.06%). Satisfactory results

Table 6. Comparison of calculated values V_l, V_g and p_{1g} of carbon dioxide and measured values for given isotherm = 31.0 °C

No	Equation of State	Calculated V_1	Measured V_1 from Thermodynamics Tables	Deviation from measured values	Calculated V_1	Measured V_1 from Thermodynamics Tables	Deviation from measured values	Calculated p_{1g}	Measured p_{1g}	Deviation from measured values
		m³/kmol	m³/kmol	%	m³/kmol	m³/kmol	%	bar	bar	%
1	van der Waals	0.125 346	0.094 885 56	-32.10	0.131 946	0.094 885 56	-39.06	73.72	73.51	-0.29
2	Redlich-Kwong	0.110 369		-16.32	0.118 490		-24.88	73.7		-0.26
3	Soeve-Redlich-Kwong	0.109 968		-15.90	0.118 927		-25.34	73.69		-0.24
4	Peng-Robinson	0.101 131		-6.58	0.109 910		-15.83	73.69		-0.24
5	Patel-Teja	0.089 544		5.63	0.098 738		-4.06	73.68		-0.23
6	Laval-Lake-Silberberg	0.089 290		5.90	0.099 105		-4.45	73.65		-0.19
7	Valderrama - Cisternas	0.098 279		-3.58	0.116 715		-23.01	73.45		0.08
8	Martin-Hou	0.089 094		6.10	0.099 259		-4.61	73.69		-0.24

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009., p. 92-94.



Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009, p. 94.
Izvor: NOVOSEL, D.: Učinak ugljičnog dioksida u tercijarnoj fazi iskorištavanja naftnih ležišta polja Ivanić, doktorska disertacija, Rudarsko–geološko-naftni fakultet Sveučilišta u Zagrebu, Zagreb, 2009., p. 94.

Fig. 9. Graphic review of calculated saturation pressure and volume according to V_C equation for t = 31 °C
Sl. 9. Grafički prikaz izračunatog tlaka zasićenja i volumena po V_C jednadžbi za t = 31 °C

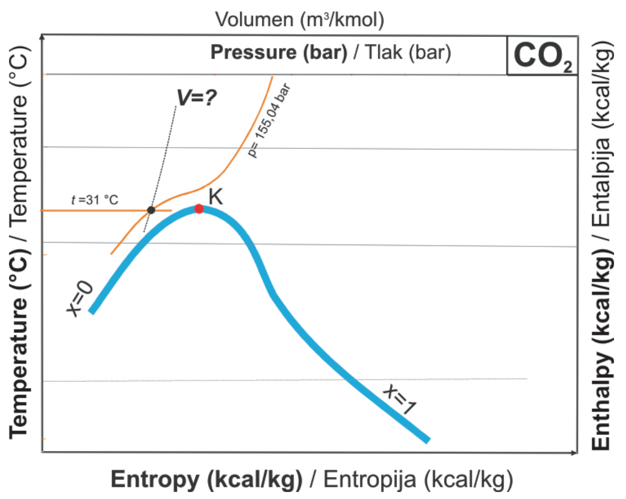


Fig. 10. Figure 10. Graphic review of carbon dioxide volume calculation for t = 31 °C, p = 155.04 bar
Sl. 10. Grafički prikaz proračuna volumena ugljičnog dioksida za t = 31 °C, p = 155,04 bar

were obtained also with the use of Laval-Lake-Silberberg equation of state (-4.45%) and Martin-Hou equation of state (-4.61%). Deviations of calculated saturation pressure results from measured values are small, ranging from 0.08% to -0.29%. The lowest deviation was obtained with the use of Valderama-Cisternas equation of state (0.08%). The highest deviation, just like for the first condition, was obtained with the use of vdW equation of state. Figure 9 gives graphic review of Maxwell's condition and saturated pressure calculation for the given isotherm according to VC equation of state.[15]

Figure 10 shows temperature and pressure data from the second condition of carbon dioxide injection: t = 31 °C, p = 155.04 bar on T,s diagram. Table 7 presents calculated volume values for given conditions and their deviation from the volume read from Thermodynamics Atlas[9] and from the one obtained by hydrodynamic measuring.

Results analysis from Table 7 determined that the smallest deviations were obtained according to Valderama-Cisternas (3.59% and -4.79%) and Laval-Lake-Silberberg equation of state (-0.18% and 7.75%). Satisfactory result was obtained by volume calculation according to Peng-Robinson equation of state (5.12% and -3.03%). Calculated carbon dioxide volume obtained by Martin-Hou equation of state can also be graded as satisfactory as its deviation from the compared volumes was 2.28 % and -6.12%.

THIRD CONDITON: → CARBON DIOXIDE IN OVERHEATED AREA - CARBON DIOXIDE OVERHEATED STEAM

Graphic review of the third condition for injecting into Iva-28 injection well- carbon dioxide overheated steam is presented in Figure 11. Table 7 shows comparative review of volume calculation results for carbon dioxide overheated steam for selected equations of state.[15]

Deviation of carbon dioxide volume calculated values in overheated area from the volume read in Thermodynamics Atlas[9] is the highest just like for the first two considered conditions according to van der Waals equation of state (-13.99% and -29.97%). The lowest deviation of carbon dioxide volume calculated values from the one read in Thermodynamics Atlas was obtained through Laval-Lake-Silberberg equation of state 1.03%. Satisfactory result was obtained also with Redlich-Kwong and Soeve-Redlich-Kwong equation of state (-2.19%). Comparing the calculated volume with carbon dioxide volume calculated on the basis of HDM measuring shows that the lowest deviation was obtained with the use of Patel-Teja equation (3.59%) and the result similar to this one was obtained with Martin-Hou equation of state (3.63%).

Table 7. Comparative analysis of the results for calculated and measured carbon dioxide volume for given conditions t = 31 °C, p = 155.04 bar

No	Equation of state	Calculated V (m^3/kmol)	Read V from Thermodynamics Atlas (m^3/kmol)	Deviation from the volume from Thermodynamics Atlas (%)	Measured V from HDM (m^3/kmol)	Deviation from measured value (%)
1	van der Waals	0.072 716	0.055 892 7	-30.10	0.051 467	-41.29
2	Redlich-Kwong	0.058 982		-5.53		-14.60
3	Soeve-Redlich-Kwong	0.058 978		-5.52		-14.59
4	Peng-Robinson	0.053 029		5.12		-3.03
5	Patel-Teja	0.045 580		18.45		11.44
6	Laval-Lake-Silberberg	0.051 559		7.75		-0.18
7	Valderrama - Cisternas	0.053 932		3.51		-4.79
8	Martin-Hou	0.054 617		2.28		-6.12

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009., p. 95.

Table 8. Comparative analysis of calculated and measured carbon dioxide volume results for given conditions t= 58.4 °C, p = 204.91 bar

No	Equation of state	Calculated V (m^3/kmol)	Read *V* from Thermodynamics Atlas (m^3/kmol)	Deviation from the volume from Thermodynamics Atlas (%)	Measured V from HDM (m^3/kmol)	Deviation from measured value (%)
1	van der Waals	0.075 252	0.066 015	-13.99	0.057 900 97	-29.97
2	Redlich-Kwong	0.064 903		-2.19		-12.09
3	Soeve-Redlich-Kwong	0.067 460		-2.19		-16.51
4	Peng-Robinson	0.061 598		6.69		-6.39
5	Patel-Teja	0.055 822		15.44		3.59
6	Laval-Lake-Silberberg	0.065 333		1.03		-12.84
7	Valderrama - Cisternas	0.071 137		-7.76		-22.86
8	Martin-Hou	0.055 801		15.47		3.63

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009., p. 97.

5. RESULTS OF INVERSION PRESSURE CALCULATION DURING CARBON DIOXIDE INJECTION INTO IVANIĆ OILFIELD RESERVOIRS

Carbon dioxide inversion pressure according to the equations of state from Table 2 shall be considered as a part of effect study from thermodynamics point of view. Inversion curve for carbon dioxide on Figure 12 is marked in green. Three considered conditions for carbon dioxide injection are drawn on *T,s* diagram (points 1, 2 and 3) and are located right from inversion curve where the gas is chilled and where the temperature change according to pressure is positive. Considering the fact that injection data are drawn in the diagram which was published in Technical System[9] units (diagram of this type in IS units has not been published yet in our country), during its use it is necessary to apply the following conversion coefficients:

- atmosphere (at) x 0.980 389 = bar
- kcal/kg x 4.186 8 = J/kg

In further consideration of carbon dioxide effect, carbon dioxide inversion pressure was calculated and calculation results are presented in Table 9.

The lowest deviation of calculated values from the measured ones for the first condition were obtained by using van der Waals equation of state (-5%). During consideration of the second condition, all equations of state ob-

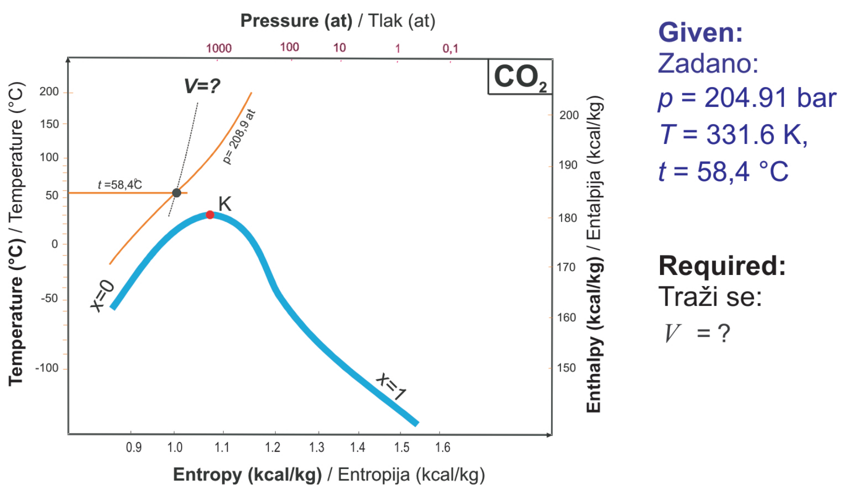
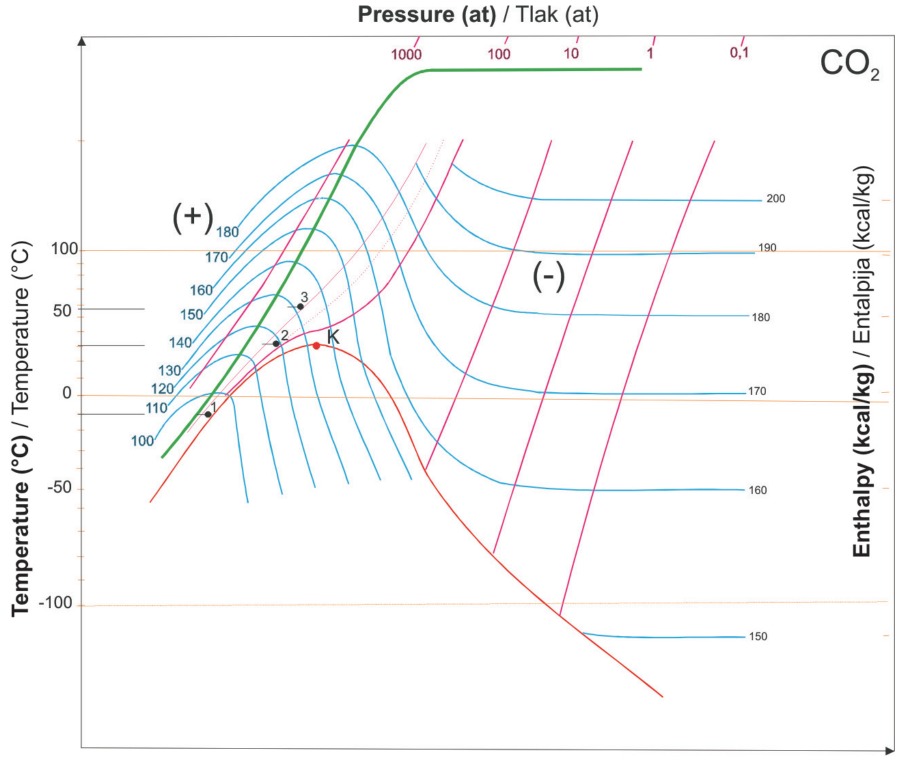


Fig. 11. Graphic review of carbon dioxide volume calculation for the third condition
Sl. 11. Grafički prikaz proračuna volumena ugljičnog dioksida za treći uvjet



Source: GOLUB, M.: Mathematical Model of Thermodynamic States of Gases and Vapors in Petroleum Engineering, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 1993, p. 93. (redrawn by: D. Novosel)
Izvor: GOLUB, M.: Matematički model termodinamičkih stanja plinova i para u naftnom rudarstvu, Doktorska disertacija, Rudarsko – geološko – naftni fakultet Sveučilišta u Zagrebu, Zagreb, 1993., p. 93. (precrtao D. Novosel)

Fig. 12. Inversion curve of carbon dioxide baffling with the data on carbon dioxide injection into Iva-28 well

Sl. 12. Inverzijske krivulja prigušivanja ugljičnog dioksida s podacima utiskivanja ugljičnog dioksida u bušotinu Iva-28

tained high deviations from the measured values. The lowest deviation was obtained by using van der Waals equation (45.89%), although this obtained deviation is too high. For the third condition (injection well bottom-hole), when carbon dioxide is in an overheated area, the best result was obtained through Laval-Lake- Silberberg equation of state (-2.65%). Deviations of certain equations of state depend on the conditions from which equation of state constants were derived. All equations of state are derived from van der Waals equation of state. Equation of state constants are determined with three critical properties: p_c, T_c, V_c. Van der Waals[25] has in his research on critical properties relations in critical point defined the coefficient of deviation of real from ideal gas in critical point z_c in the amount of 3/8 (0.375). Certain authors of equations of state define various values of z_c. According to Redlich-Kwong and Soeve-Redlich-Kwong equation of state, value z_c = 0.333 and according to Peng-Robinson is z_c = 0,307. Constants of van der Waals equation are defined with two critical properties, i.e. three combinations of these state properties: p_c, T_c, V_c. Authors of new versions of equations of state expand van der Waals principle of corresponding states by third criterion. This is acentric factor, ω or correction of equation of state due to non sphericity and polarity of molecules. This factor in equation of state describes the change in attracting molecules as temperature function $a(T)$. All this represents conditions from which the authors of equations of state have derived constants. They

Table 9. Comparison of calculated carbon dioxide inversion pressure and measured inversion pressure for the three considered conditions

No	Equation of State	Inversion pressure for t=-10 °C and p=85.26 bar (bar)V_1	Measured inversion pressure (bar)	Deviation from measured inversion pressure (%)	Inversion pressure for t=31.0 °C and p=155.04 bar (bar)	Measured inversion pressure (bar)	Deviation from measured inversion pressure (%)	Inversion pressure for t=58.0 °C and p=204.09 bar (bar)	Measured inversion pressure (bar)	Deviation from measured inversion pressure (%)
1	Van der Waals	94.5	90	-5.00	189.4	350	45.89	244.8	550	55.49
2	Redlich-Kwong	489.2		-443.56	558.8		-59.66	604.3		-9.87
3	Soeve-Redlich-Kwong	507.9		-464.33	583.6		-66.74	633		-15.09
4	Peng-Robinson	563.9		-526.56	648.9		-85.40	704.6		-28.11
5	Patel-Teja	666.7		-640.78	769.5		-119.86	837.5		-52.27
6	Laval-Lake-Silberberg	451.3		-401.44	519.7		-48.49	564.6		-2.65
7	Valderrama - Cisternas	600.1		-566.78	697.2		-99.20	761.4		-38.44
8	Martin - Hou	15.4		82.89	73.7		78.94	111.3		79.76

Source: NOVOSEL, D.: Impact of Carbon Dioxide on Ivanić Oilfield in Tertiary Recovery Phase, Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 2009., p. 105.

are derived from various conditions, thus the results in Table 9 show deviations.

6. ANALYSIS AND COMPARISON OF CALCULATION RESULTS WITH THE COMMENT ON CARBON DIOXIDE EFFECT FROM THERMODINAMIC POINT OF VIEW

During the procedure of determining carbon dioxide thermodynamic characteristics during its injection on pilot project, the results obtained from cubic equations of state and polynomial equations of state were compared. The preformed analysis shows that, for carbon dioxide liquid state, Peng-Robinson and Soeve-Redlich-Kwong equation of state obtained best results in calculating volume in real two-phase area, i.e. for saturation pressure calculation. Under the conditions when carbon dioxide was mixture in injection pipes (carbon dioxide temperature was very close to critical temperature) the best result for calculating volume in real two-phase area, i.e. for saturation pressure calculation, was obtained according to Valderama-Cisternas equation. Results obtained from Martin-Hou equation of state do not differ considerably from the ones obtained from Valderama-Cisternas equation. During volume calculation for the third condition (carbon dioxide overheated steam), the best result was obtained from Laval-Lake-Silberberg equation of state.

Calculated inversion pressure was compared to measured inversion pressure from Thermodynamics Atlas.[9] The lowest deviation for the first two considered deviations was obtained from van der Waals equation (5%) and (45.9%). The lowest deviation for the third considered condition was obtained from Laval-Lake-Silberberg equation of state (-2.65%).

Based on the performed comparison, a conclusion can be made on the use of certain equations of state. Peng-Robinson equation of state was used in numerical simulation for calculation of oil-carbon dioxide phase balance under mixing condition in Ivanić oilfield reservoirs. This equation was developed to be used in petroleum mining and is used very often. Peng-Robinson equation of state was also used in numerical simulation of pilot project.[8,21] HDM measuring[13,14] confirmed mixing conditions between injected carbon dioxide and oil at the very bottom-hole of Iva-28 well.

Before the pilot project, Iva-11 and Iva-19 production wells were closed due to high water content in the produced liquid. After the first cycle of carbon dioxide and water injection on Iva-11 production well, the production of liquid increased with lower water content in liquid and consequently, higher oil production. During the second cycle of carbon dioxide injection, the oil production increased simultaneously on both wells. The wells produced the total of 5 000 m^3 of oil during those two cycles. During the pilot project phase, wells were producing oil eruptively,[13,15] which confirms the successful impact of oil expulsion mechanism under mixing conditions. This also means that injected carbon dioxide was constantly in contact with oil within the reservoir and due to phase balance change, was dissolving in oil. The conclusion is that the choice of Peng-Robinson equation of state for calculating oil - carbon dioxide phase balance system under mixing conditions in Ivanić oilfield reservoirs was a good choice.

7. CONCLUSION

From thermodynamic point of view, this paper analyses the changes in carbon dioxide phase states which occur during its injection. Petroleum engineering requires measuring. They are either expensive or difficult to perform due to, for example, pressure, temperature or big well depth. When there are no measured data, analytical solutions are helpful.

This meant determining saturation pressure, calculation of volume for injection and calculation of saturation pressure for three injection conditions. Randomly selected equations of state were used: van der Waals, Redlich-Kwong, Soave-Redlick-Kwong, Peng-Robinson, Patel-Teja, Laval-Lake-Silberberg, Valderrama and Cisternas and Martin and Hou equation of state. Calculated deviations from the measured values for considered carbon dioxide injection conditions brings us to conclusion on the use of Peng-Robinson, Valderrama-Cisternas and Lawal-Lake-Silberberg equation of state for in situ conditions. Injection of carbon dioxide into reservoir caused mixing of carbon dioxide and oil. Peng-Robinson equation of state was used in numerical simulation of Ivanić oilfield tertiary oil recovery for calculating oil-carbon dioxide phase balance in reservoir. Based on the results obtained in this study, Peng-Robinson, Valderrama-Cisternas and Lawal-Lake-Silberberg equations of state can be used for future calculations.

Symbols:

a,b,c,d	constants of gas equations of state
a_c	constants a of Redlich-Kwong equation of state in critical point
$a(T)$	parameter of Soave-Redlich-Kwong equation dependent on temperature $a(T)=a_c\,\alpha$
$A_1,B_1,A_2,B_2,C_2,A_3,B_3,C_3,A_4,B_5$	characteristic constants of Martin and Hou equation of state
A_C,B_C,C_C,D_C	characteristic constants of Valderrama and Cisternas and Lawal-Lake-Silberberg equation of state
f_1,f_2,f_3,f_4,f_5	temperature functions of Martin and Hou equation of state
i	enthalpy, J/mol
m	critical temperature line inclination on pressure and temperature diagram
m_c	parameter of Valderrama and Cisternas equation of state dependent on acentric factor
m_s	parameter of Soave-Redlich-Kwongove equation of state dependent on acentric factor
n	substance quantity, mol
k	constant in Martin and Hou equation of state, $k=5.475$
p	pressure, Pa
p_c	pressure in critical point, Pa
p_{1g}	saturation pressure, Pa
R	universal gas constant, Pa m^3/mol K
s	entropy, J/mol K
t	temperature, °C
T	absolute temperature, K
T_b	Boyle temperature, K

T_c	absolute temperature in critical point, K
V	volume, m³/mol
V_c	volume in critical point, m³/mol
V_g	vapor volume, m³/mol
V_l	liquid volume, m³/mol
y	ratio of curve inclination of reduced saturation density and inclination of critical isotherm
z	deviation coefficient for real gas
z_c	deviation coefficient in critical point
Ω_w	constant of Laval-Lake-Silberberg equation dependent on acentric factor
α	parameter of Soave-Redlich-Kwong equation of state dependent on temperature
α_L	parameter of Laval-Lake-Silberberg equation of state
β	Martin Hou characteristic constant in
β_L	characteristic parameter of Laval-Lake-Silberberg equation of state
ω	acentric factor

LITERATURE

1. **Annual EOR Survey**, Oil & Gas Journal, Houston, April 2002., p.15, April 2004., p. 16., April 2006., p. 17.
2. BOŠNJAKOVIĆ, F.: **Nauka o toplini I**, Tehnička knjiga, Zagreb, 1962. 345 pp., IV izdanje, 1970., p. 25-40, 87-88, 108-130.
3. BUDIN, R.: **Mogućnost primjene Van der Waalsove jednadžbe u kemijskom inženjerstvu**, doktorska disertacija, Kemijsko - tehnološki fakultet Sveučilišta u Zagrebu, Zagreb, 1974., p. 10, 20. - 65.
4. DIN, F. : **Thermodynamic Functions of Gases Volume 1, Ammonia, Carbon Dioxide and Carbon Monoxide**, Butterworth & Co.(Publishers) Ltd. , London, 1962., p. 77,102 - 103, 106.
5. DOMITROVIĆ, D., ŠUNJERGA, S., JELIĆ-BALTA, J.: **Numerical Simulation of Tertiary CO_2 Injection at Ivanić Oil Field Croatia**, SPE 89361, SPE/DOE, Fourteenth Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 2004., p. 1-8.
6. GOLUB, M.: **Matematički model termodinamičkih stanja plinova i para u naftnom rudarstvu**, Doktorska disertacija, Rudarsko-geološko-naftni fakultet Sveučilišta u Zagrebu, Zagreb, Hrvatska, 1993., p. 9, 89 - 105.
7. GORIČNIK, B.: **Termodinamika ugljikovodika**, Skripta Rudarsko - geološko - naftnog fakulteta Sveučilišta u Zagrebu, Zagreb, 2003., p. 27- 42 , 67 - 86.
8. GORIČNIK, B., DOMITROVIĆ, D.: **Laboratorijska istraživanja primjenjivosti CO_2 procesa na naftnim poljima u Republici Hrvatskoj**, Naftaplin 1/2003, Hrvatska udruga naftnih inženjera i geologa, Zagreb, 2003., p. 5 - 6, 8-9, 10.
9. KOLIN, I.: The Evolution of the Heat Engine - Thermodynamics Atlas 1, Longman Group Ltd., London, p. 1972. 34.
10. LAWAL, A., S., VAN DER LAAN, E.,T., THAMBYNAYAGAM, R.,K.,M.: Four-Parametar Modification of the Lawal-Lake-Silderberg Equation of State for Calculatin Gas-Condensate phase Equilibrica, SPE 14269, Presented at the 60th Annual Technical Conference, Las Vegas, 1985.
11. MARTIN, J.,J., HOU, YU-CHUN.: **Development of an Equation of State for Gases**, A.I.Ch.E. Journal, Volume 1, Number 2., 1955., p. 142 , 144,148.
12. MARTIN, J.,J., KAPOOR,R.,M., DE NEVERS, N.: **An Improved Equation of State for Gases**, A.I.Ch.E. Journal, Volume 5, Number 2., 1959., p. 159 - 160.
13. NOVOSEL, D.: **Initial Results of WAG CO_2 IOR Pilot Project Implementation in Croatia**, SPE 97639, SPE, IIORC Asia Pacific, Kuala Lumpur, 2005., p.4.
14. NOVOSEL, D.: **Termodinamički kriteriji utiskivanja ugljičnog dioksida u nafto polje Ivanić**, Nafta (2), Znanstveni časopis Hrvatskog Nacionalnog naftnog komiteta, Hrvatska Akademija Znanost i Umjetnosti, Zagreb, 2007., p. 83 - 93.
15. NOVOSEL, D.: **Učinak ugljičnog dioksida u tercijarnoj fazi iskorištavanja naftnih ležišta polja Ivanić**, doktorska disertacija, Rudarsko-geološko-naftni fakultet Sveučilišta u Zagrebu, Zagreb, 2009., p. 11-13, 48-104.
16. PATEL, N.,C., TEJA, A.,S.: **A New Cubic Equation of State for Fluids Mixtures**, Chemical Engineering Science, volume 37.,1982. p. 463-473.
17. PENG, D.,Y., ROBINSON, D.,B.: **A New Two-Constant Equation of State**, Industry and Enginerring Chemistry Fundamentals, volume 15. 1976. p. 59 - 65.
18. PRNIĆ, Ž.: **Upute za korištenje programa KJS za izračunavanje termodinamičkih svojstava, IMI - Instromont inženjering**, Zagreb, 2008.
19. RAŽNJEVIĆ, K.: **Termodinamičke tablice**, Svjetlost, Sarajevo, 1989. , p. 186. - 21.
20. REDLICH,O., KWONG, J.N.S.: **On the Thermodynamics of solutions V. An Equation of State. Fugacities of Gaseous Solutions**, Chem. Review 44, volume 2, 1949., p. 233 - 244.
21. SEČEN, J.: **Metode povećanja iscrpka nafte**, Ina Industrija nafte d.d.-Segment djelatnosti za istraživanje i proizvodnju nafte i plina - Naftaplin, Zagreb, 2006., p. 3,5,121,241,327, 404-410.
22. SOAVE, G: **Equilibrium Constants from a Modified Redlich-Kwong equation of state**, Chemical Engineering Science, 1972., p. 1197.
23. VALDERRAMA, J.,O.: **The state of the Cubic Equations of State**, Industrial Engineering Chemistry Res., Volume 42, 2003., p. 1603-1618.
24. VALDERRAMA. J., O., CISTERNAS, L.,A.: **A Cubic Equation of State for Polar and Other Complex Mixtures**, Fluid Phase Equilibrium, volume 29., 1986., p. 431-438.
25. WAALS, V.D., : **Die continuitades Gasformirgen und Flusingen Zustandes**, Johan Ambrosius Bart Verlag, Leipzig 1881., p. 148.
26. ZELIĆ, M.: **Termodinamika fluida pri protjecanju u tubingu**, Nafta 34 (4-5), Zagreb, 1983., p. 231.

❖

Author:

Dubravko Novosel, Ph.D. of technical sciences, INA-Industrija nafte, Oil and Gas Exploration and Production, South-east Europe E&P Sector, Expert, Šubićeva 29, 10000 Zagreb,
e-mail: dubravko.novosel@ina.hr