Properties of Co_2 Relevant To Sequestration – Density

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Carbon dioxide is an important industrial chemical in its own right, however, in recent years CO_2 has been implicating in the ongoing climate change. One of the proposals for dealing with anthropogenic carbon dioxide is to compress it and inject it into subsurface formations – the so-called CO_2 sequestration.

The design of the sequestration process requires accurate physical properties. This is the first in the series of papers on the properties of pure CO_2. The focus of this paper is the density of CO_2 from -20° to +250°C (-4° to 482°F) and for pressures up to 1000 bar (100 MPa, or 14,500 psia). This covers the range of temperatures and pressures from the low pressure flue gas state to the high pressures encountered in the storage reservoir. Furthermore, this includes the liquid, vapor, and supercritical regions.

INTRODUCTION

Carbon capture and storage (CCS) is a technology for capture and removal (sequestration) of atmospheric carbon dioxide, usually by storing it in the geosphere. The removal of CO_2 from the environment is a topical issue at present due to the almost universal consensus that exists in the scientific community about the effects of climate change[1], and hence interest in CCS is growing as a potential means of reversing climate change by removing the major greenhouse gas present in the atmosphere.

Holloway et al. outline the problems associated with carbon dioxide emissions as well as the methods of its artificial storage. Carbon is captured from industrial emissions sources and is then transported through pipelines or container shipment to a suitable storage site (Holloway et al., 2007). This means that the storage options available have to be narrowed down to ones with a certain level of retention capacity. In terms of a health hazards, the largest concern over CCS is the case of sudden, large releases of CO_2 escaping from storage sites into the biosphere. This could happen in the case of natural fracture at the surface of a storage site due to an excess in pressure build-up during carbon injection, or due to a well blowout: a sudden, explosive release of CO_2 from a reservoir into the atmosphere.

In order for the process of CCS to be viable, CO_2 storage sites need to be keenly regulated to ensure that escaping emissions are within set boundaries. This requires geological and hydro geological characterisation of the storage site as well as geological and reservoir modeling (Holloway et al., 2007). Geological models are used to project the feasibility of storage in saline rock formations. A good match between approximated models and observed results means that a high level of success can be expected in the site at hand.

In spite of the above, concerns do remain over the long term effectiveness of CCS. In particular, concerns over leakages at engineered carbon storage sites cannot be allayed until a significant amount of time has passed, since the oldest site is only 20 years old (Holloway et al., 2007). However, it should also be noted that the longer the carbon has been under the ground, the more likely it is to stay entrapped, as enhanced pore fluid pressure causes more and more CO_2 to migrate deep underground. The CO_2 is also likely to dissolve into the surrounding underground pore water as time goes by, increasing the density of the water and thereby causing it to sink further into the ground.

CCS techniques have thus evolved around the idea of maximized retention times. Of available storage sites, the best are found to be in areas of previously rich oil and gas fields as well as in deep saline formations. Layers of highly porous rock with an impenetrable layer of what is known as cap rock (World Coal, 2007) above them form ideal conditions for storage and retention. Depleted oil and gas fields have a natural geology which equips them to be gas retention sites. The stored CO_2 liquefies under the immense pressures of deep underground storage, and is then trapped within the porous spaces of the rock. There are different storage mechanisms involved with this trapping, including residual storage, dissolution storage, and mineral storage.

In order to design an efficient sequestration process, it is vital to analyze accurate data for the physical properties of carbon dioxide. This is the first in the series of papers on the properties of pure CO_2. The focus of this paper is the density of CO_2 from -20° to +250°C (-4° to 482°F) and for pressures up to 1000 bar (100 MPa, or

14,500 psia). This covers the range of temperatures and pressures from the low pressure flue gas state to the high pressures encountered in the storage reservoir. Furthermore, this includes the liquid, vapor, and supercritical regions.

REVIEW AND CORRELATION

The density data for carbon dioxide are plentiful. The first data measurements date back to the late 19th century with the work of Amagat. Although these data are quite old they are surprisingly accurate. From that data and through the first half of the 20th century there were several significant studies including the high pressure measurements of Michels et al. (1937) and Michels and Michels (1937) which were up to pressure greater than 3000 bar (30 MPa).

There have been many reviews of the density data over the years. Noteworthy reviews include: Vukalovich and Altunin (1965), Angus et al. (1976), and Span and Wagner (1996).

Equations of State

The cubic equations of state [such as those of Soave (1972) and Peng and Robinson (1976)] are very popular in the process industry. Their popularity arises from their relative simplicity combined with acceptable accuracy for VLE for many important systems. However they are not highly accurate for predicting densities, particularly in the high pressure and near-critical regions. Although they can be modified to improve the density, errors as large as 3% could be anticipated in any region of temperature and pressure and much higher in the two regions noted earlier.

The Benedict et al. (1940) equation of state, the BWR EoS, is a multi-constant equation well-known in chemical engineering circles for yielding high accuracy density estimates but also for being a little complicated to implement than a cubic equation of state.

In order to achieve higher accuracy one must use a multi-constant equation of state and in particular a "reference" equation of state. These equations have many adjustable parameters and are design for the highest degree of accuracy. For carbon dioxide the equation of state of Span and Wagner (1996) is the standard reference equation.

The reference equation of state of Span and Wagner (1996) was used in this study to generate plots of the density as a function of the pressure and the temperature and to generate detailed tables of the density.

DENSITY

Table 1 shows the density of saturate vapor and liquid carbon dioxide. The table is presented in increments of one Celsius degree until close to the critical point and from there smaller steps are taken. This table also gives the vapor pressure of CO_2 corresponding to the given temperature.

Table 2 gives the density over a wide range of pressure and temperatures. However the table is too large for his paper, but it can be downloaded from the website www.gasliquids.com. These are at a relative fine grid and should be highly useful for designs involving pure CO_2.

The plots of the density are appended to this paper. Larger sized plots are also available from the website www.gasliquids.com.

REFERENCES

1. Benedict, M., Webb, G.B., and Rubin, L.C., "An Empirical Equation of State for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures", *J. Chem. Phys.*, **8**, 334-340, (1945).
2. S. Holloway, J.M. Pearce, V.L. Hards, T. Ohsumi, J. Gale, "Natural emissions of CO_2 from the geosphere and their bearing on the geological storage of carbon dioxide", Energy 32 (2007) 1194–1201
3. Michels, A. and Michels, C., "Series Evaluation of the Isotherm Data of CO_2 between 0 and 150 degrees C. and up to 3000 atm." *Proc. R. Soc. Lond. A,* **160**, 348-357, (1937).
4. Michels, A., Bijl, A., and Michels, C., "Thermodynamic Properties of CO_2 up to 3000 Atmospheres between 25 and 150 degrees C", *Proc. R. Soc. Lond. A*, **160**, 376-384, (1937).
5. Peng, D.-Y. and Robinson, D.B., "A New Two-Constant Equation of State", *Ind. Eng. Chem., Fundam.* **15**, 59-64, (1976).

6. Soave, G. "Equilibrium Constants from a Modified Redlich-Kwong Equation of State", *Chem. Eng. Sci.*, **27**, 1197-1203, (1972).

7. Span, R. and Wagner, W., "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K and Pressures up to 800 MPa", *J. Phys. Chem. Ref. Data,* **25**, 1509-1596, (1996).

8. Vukaloicih, M.P. and Altunin, V.V., *Thermophysical Properties of Carbon Dioxide*, Collet's Publishers, London, UK, (1968). – Translation form Russian.

9. ———, World Coal Institute/IEA Greenhouse Gas R&D Programme – Storing CO_2 Underground, July 2007

Table 1 Density (kg/m³)of Saturated Carbon Dioxide

| Temp (°C)	Press (bar)	Liquid	Vapor	Temp (°C)	Press (bar)	Liquid	Vapor
-20	19.70	1031.7	51.70	9	43.92	868.4	130.7
-19	20.31	1027.0	53.40	10	45.02	861.1	135.2
-18	20.94	1022.3	55.15	11	46.15	853.6	139.8
-17	21.58	1017.6	56.96	12	47.30	845.9	144.7
-16	22.24	1012.8	58.82	13	48.47	837.9	149.8
-15	22.91	1008.0	60.73	14	49.66	829.7	155.1
-14	23.59	1003.1	62.70	15	50.87	821.2	160.7
-13	24.29	998.1	64.73	16	52.11	812.4	166.7
-12	25.01	993.1	66.81	17	53.37	803.3	172.9
-11	25.74	988.1	68.97	18	54.65	793.8	179.6
-10	26.49	982.9	71.18	19	55.96	783.8	186.6
-9	27.25	977.7	73.47	20	57.29	773.4	194.2
-8	28.03	972.5	75.83	21	58.65	762.4	202.3
-7	28.82	967.1	78.26	22	60.03	750.8	211.1
-6	29.63	961.7	80.77	22	60.03	750.8	211.1
-5	30.46	956.2	83.36	23	61.44	738.4	220.6
-4	31.30	950.6	86.03	24	62.88	725.0	231.1
-3	32.16	945.0	88.79	25	64.34	710.5	242.7
-2	33.04	939.2	91.65	26	65.84	694.5	255.9
-1	33.94	933.4	94.60	27	67.36	676.4	271.0
0	34.85	927.4	97.65	28	68.92	655.3	289.1
1	35.78	921.4	100.8	29	70.51	629.4	312.0
2	36.73	915.2	104.1	29.5	71.32	613.3	326.6
3	37.70	909.0	107.5	30.0	72.14	593.3	345.1
4	38.69	902.6	111.0	30.2	72.47	583.5	354.3
5	39.70	896.0	114.6	30.4	72.80	572.0	365.3
6	40.72	889.4	118.4	30.6	73.13	557.7	379.1
7	41.77	882.5	122.3	30.8	73.47	537.4	399.2
8	42.83	875.6	126.4	30.98	73.77	467.6	467.6
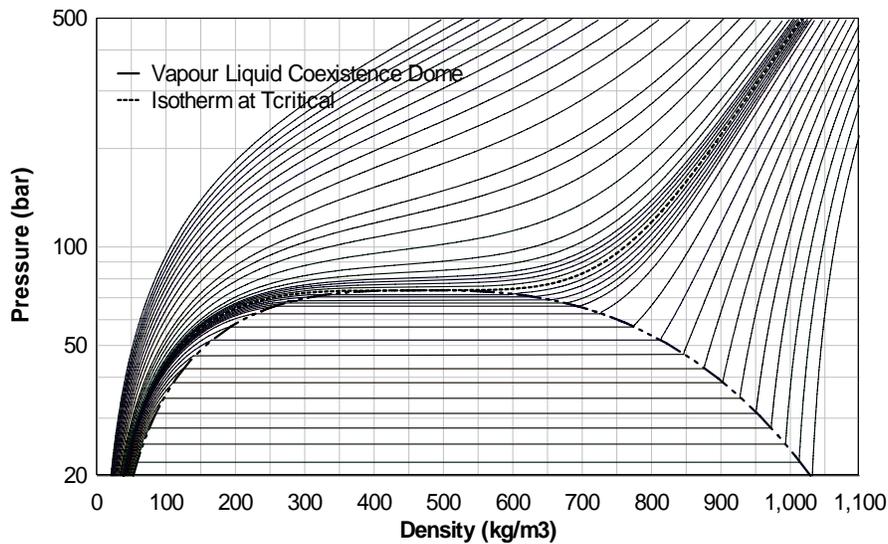
Fig. 1 Isotherms are displayed for the temperature range of 20°C to 250°C. They are arranged at intervals of 4°C from -20°C to 24°C, followed by 26°C, 27°C, 28°C, 29°C, 30°C, the critical isotherm 30.978°C, 32°C, 33°C, 34°C, 35°C, 37°C, 40°C and 46°C. From 46°C to 70°C, values are spaced at 8°C. From 70 to 230°C Isotherms are separated by a difference of 16°C as the values crowd closer together at this high temperature range. Finally the 250°C curve is plotted at the far left of the chart.
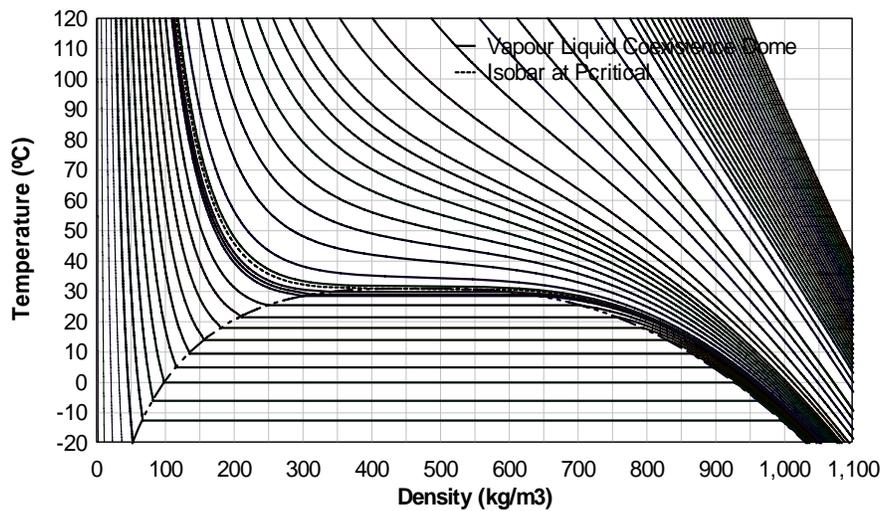

Fig. 2 Isobars are displayed for the pressure range of 1 to 1000 bar. They are arranged at intervals of 5 bar from 1 bar to 70 bar, followed by 70, 71, 72, the critical isobar at 73.77 bar, and 75. After this Isobars are arranged at intervals of 10 bars between 80 and 160 bar, and 20 bar between 260 and 200 bar. Isobars between 200 and 520 bar are separated by 40 bar intervals and, finally, from 520 to 1000, the isobars are displayed at differences of 20 bar, up until 1000 bar.

Isobars of Carbon Dioxide

Isotherms of Carbon Dioxide