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Modeling the temperature dependence of supercritical gas adsorption on activated carbons, coals and shales

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ABSTRACT

The recovery of natural gas from unconventional gas reservoirs such as shales and coal beds has increased significantly over the past few years. Since a majority of gas in these reservoirs is in an adsorbed state, knowledge of adsorption behavior of gases is essential for reliable gas-in-place estimates of these reservoirs. Further, some of these reservoirs also offer the potential for carbon dioxide sequestration. The existence of geothermal gradients in such reservoirs can affect the amount of gas. Since the temperatures in a reservoir are generally in the near-critical or supercritical region of the adsorbed gases, an adsorption model should be capable of reliable predictions of temperature dependence of adsorption in this region. To date, limited studies exist in the literature for modeling of temperature dependence of *supercritical* gas adsorption. In this work, we present a modification of the simplified local density (SLD) model to improve predictions of the temperature dependence of supercritical gas adsorption. Activated carbons were chosen as the reference adsorbents in the development of the modifications to the model since adsorption data on activated carbons are much more plentiful than data on coals and shales, for which data at multiple temperatures are extremely limited. Since activated carbons are simpler structural analogs of other carbonaceous adsorbents such as coals and shales, a model for activated carbons should serve as a basis for extension to the more complex coals and shales.

To undertake this study, a database was compiled that includes adsorption data at several temperatures for 11 gases on 18 activated carbons containing about 2600 data points. The database also included adsorption isotherms measured on six coals and six shales at multiple temperatures with a total of 670 data points.

The SLD model was modified by introducing a new temperature-dependence expression in the model. The modified SLD model was tested for its efficacy in describing the temperature dependence of near-critical and supercritical gas adsorption on the adsorbents contained in the above database. Results indicate that the modified SLD model is effective in modeling supercritical and near-critical gas adsorption. Further, the model was generalized to predict the temperature dependence of adsorption as a function of adsorbate and adsorbent properties. The generalized model was tested with an extended dataset and was found capable of predicting the temperature dependence with an average absolute deviation of 5%, in general.

The modified SLD model was tested with adsorption data on coals and shales at multiple temperatures. The model appears capable of describing the temperature dependence of adsorption on coals and shales with reasonable accuracy. We note, however, that the development of a completely generalized model requires additional experimental data on coals and shales and further model testing.

1. Introduction

Shale and coalbed methane reservoirs have become an important source of natural gas, and a significant portion of the gas in these reservoirs exists in an adsorbed state. Thus, knowledge of gas adsorption behavior over a range of pressures and temperatures is required to estimate the gas-in-place for these reservoirs. Further, some of these reservoirs can offer potential sites for CO_2 sequestration. Gases commonly encountered in these reservoirs are the natural gas components including carbon dioxide and nitrogen with the latter two being especially important in enhanced gas recovery and carbon dioxide sequestration. Since gas adsorption is temperature dependent, the presence of geothermal gradients in a reservoir affects the adsorption capacity of these gases. For example, in the Black Warrior basin the coal bed reservoir temperature varies from about 300 K to 325 K within the 0.3–1.8 km depth-range (Pashin and McIntyre, 2003). Thus, an accurate accounting for temperature dependence of gas adsorption is important

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Table 1
Database for pure-gas adsorption on activated carbons, coals and shales.

Adsorbent	Adsorbate	Pressure range (MPa)	Temperature range (K)	BET surface area (m^2/g)	NDP*	Reference
Dataset for activated carbons						
PCB	CH_4	0.1–3.7	296–480	1150	65	Ritter and Yang (1987)
	CO_2	0.2–5.8				
	CO	0.1–1.3				
	H_2S	0.3–6.7				
Norit-RB1	CH_4	0.1–0.8	294–350	1100	128	Van Der Vaart et al. (2000)
	CO_2					
Nuxit-Al	CH_4	0.01–0.6	293–363	1200	447	Szepesy (1963)
	C_2H_2	0.001–0.1				
	C_2H_6	0.01–0.7				
	C_2H_4	0.01–0.6				
	C_3H_8	0.01–0.7				
	C_3H_6	0.01–0.8				
	nC_4H_{10}	0.001–0.1				
Columbia Grade L	CH_4	0.02–1.5	311–478	1152	272	Ray and Box (1950)
	N_2	0.03–1.5				
	C_2H_2	0.01–0.1				
	C_2H_6	0.01–1.5				
	C_2H_4	0.01–1.5				
	C_3H_8	0.01–0.7				
	C_3H_6	0.01–0.1				
BPL	CH_4	0.01–3.8	213–301	988	233	Reich et al. (1980)
	CO_2	0.003–3.84				
	C_2H_6	0.001–1.71				
	C_2H_4	0.001–1.70				
F30/470	CH_4	0.44–6.0	303–383	993	154	Berlier and Frère (1997)
	N_2	0.39–6.0				
F30/470	CO_2	0.05–2.5	288–328	993	113	Frère and De Weireld (2002)
LAC	C_3H_8	0.001–0.1	273–343	1011	102	Mofarahi et al. (2003)
	C_3H_6					
Carbotech	CH_4	0.006–3.4	300–318	885	32	Martin et al. (2011)
KT	CH_4	0.6–3.4	300–318	668	31	Martin et al. (2011)
Maxsorb II	CH_4	0.1–1.2	281–343	2768	126	Wang et al. (2010)
Templated carbon	CH_4	0.05–4.6	263–303	1500	71	Chen et al. (2011)
	C_2H_6	0.02–2.0				
Maxsorb III	CH_4	0.06–2.4	263–303	3140	128	Loh et al. (2010)
Columbia Grade G	CH_4	0.1–13.8	283–343	1157	141	Payne et al. (1968)
	nC_4H_{10}	0.003–0.8				
	C_3H_8	0.001–1.4				
JX101	CH_4	0.01–1.0	283–313	1500	107	Qin Wu et al. (2005)
External dataset for activated carbons used for validation						
Coconut shell-derived carbon	CH_4	0.1–9.3	235–333	3106	122	Zhou et al. (2000)
	N_2	0.5–9.0	198–298		61	
F-400	CO_2	0.14–9.4	303–318	850	116	Humayun and Tomasko (2000)
CNS-201	CH_4	0.01–6.8	243–333	2000	62	Dundar et al. (2012)
CO-64	N_2	0.01–6.6	153–298	1150	135	Dundar et al. (2012)
Dataset for coals						
Pocahontas	CH_4	1.4–13.8	308–328	N/A*	20	Sakurovs et al. (2008)
	N_2		298–328		20	
	CO_2		308–328		20	
Illinois-6	CH_4	14–13.8	308–328	N/A	20	Sakurovs et al. (2008)
	N_2		298–328		20	
	CO_2		308–328		20	
Beulah Zap	CH_4	14–13.8	308–328	N/A	20	Sakurovs et al. (2008)
	N_2		298–328		20	
	CO_2		308–328		20	
Hulun Buir	CH_4	2.5–19.1	308–328	N/A	41	Li et al. (2010)
	CO_2	3.8–24.2			80	
Pingdingshan	CH_4	3.0–19.7	308–328	N/A	43	Li et al. (2010)
	CO_2	5.2–24.6			71	
Jingcheng	CH_4	1.2–19.0	308–328	N/A	48	
	CO_2	3.6–24.6			67	
Dataset for shales						
WIC7145	CH_4	0.07–12.5	318–358	6.7	26	Rexer et al. (2014)
WIC7155		0.05–13.0		4.3	28	Rexer et al. (2014)
HAR7038		0.02–12.0		N/A	25	
HAR7060		0.06–13.5		N/A	14	
HAD7090		0.05–12.8		25.1	23	
HAD7119		0.07–13.8		21.0	29	
Total					3321	

* NDP is number of data points and N/A denotes not available.