

STUDY ON LOW PRESSURE ADSORPTION OF BIOMETHANE FROM BIOGAS BY COAL ACTIVATED CARBON

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Abstract

A study on low pressure adsorption of biomethane purified from biogas by a commercial coal activated carbon (AC) was carried out. The adsorption mechanisms of biomethane at 80 and 90% CH₄ concentration were considered by Langmuir model and Dubinin-Astakhov model. The lower biomethane concentration was better adsorbed since the activated carbon gave higher affinity for CO₂ than that for CH₄. By Langmuir model, the limiting uptake of biomethane on the activated carbon (q_{max}) and the Langmuir's constant (K_L) increased with the decrease of the AC temperature. The value of q_{max} for 80% biomethane adsorption was in a range of 4.80-5.06 mmol/g_(AC) compared with a range of 2.98-3.23 mmol/g_(AC) for 90% biomethane adsorption. The value of K_L was in a range of 0.37-0.43 MPa⁻¹. For Dubinin-Astakhov equation, the structural heterogeneity parameter (n) for the coal ACs was investigated and found to be 1.48. The isosteric heat of adsorption for 80 and 90% biomethane were in a range of 5.56-9.76 kJ/mol.

Keywords: Biomethane adsorption, Activated carbon, Langmuir model, Dubinin theory.

1. Introduction

Biogas could be produced from organic matter by anaerobic bacteria. Generally, biogas component is mainly consisted of methane and carbon dioxide with percentages of about 60-70 and 30-40% by volume, respectively. Biogas could be taken as an energy source to generate electrical power by a gas engine. Due to the

Nomenclatures	
A	Adsorption potential, J/mol
E	Characteristic energy of the adsorption system, J/mol
H_{ad}	Isosteric heat of adsorption at specific loading, J/mol
K_L	Langmuir's constant, MPa ⁻¹
M_i	Molecular weight of gas in biomethane, g/mol
M_{wmix}	Molecular weight of biomethane, g/mol
n	Structural heterogeneity parameter
P	Equilibrium pressure, MPa
P_c	Critical pressure of gas, MPa
P_s	Saturation vapour pressure, MPa
q	Adsorbed biomethane per unit AC, mmol/g _(AC)
q_{max}	Limiting uptake of biomethane on the adsorbent, mmol/g _(AC)
\bar{R}	Universal gas constant, 8.1345 J/mol-K
T	Equilibrium temperature, K
T_c	Critical temperature of gas, K
W	Amount of uptake biomethane per unit AC, cm ³ /g _(AC)
W_{max}	Limiting uptake of biomethane by the adsorbent, cm ³ /g _(AC)
y_i	Mol fraction of gas in biomethane
Abbreviations	
AC	Activated Carbon
BET	Brunauer-Emmett-Teller
CBG	Compressed Biomethane Gas
D-A	Dubinina and Astakhov
D-R	Dubinina and Radushkevich

high concentration of CO₂ in the gas supply, the engine performance is rather low. The removal of carbon dioxide would result in higher energy intensity and a more steady combustion in the combustion chamber.

Biogas could be purified to get high CH₄ concentration and the upgraded gas is called biomethane. The compositions and properties of the biomethane are quite close to those of natural gas. In Thailand, the biomethane quality refers to the Announcement of the Department of Energy Business, Ministry of Energy (2014) on properties of natural gas for vehicle of which the methane must be higher than 82% [1]. The compressed biomethane used in vehicles and households is called compressed biomethane gas, CBG. The gas pressure is around 20 MPa thus the gas tank must be designed to withstand the high pressure then the cost due to gas compression and the cost of the storage tank are rather expensive. Then a technique of biomethane adsorption of which low pressure is needed could solve these problems.

Several researchers studied gas adsorption on activated carbon. Esteves et al. [2] studied natural gas and biogas adsorption by activated carbon made of coal. The temperature and the pressure were controlled at 0-325 K and 0-9 MPa, respectively. It was found that the activated carbon could properly adsorb all gases at any temperature and pressure. When the temperature was decreased, the amount of gas adsorption increased. Guan et al. [3] studied methane adsorption by compressed granular activated carbon from by-products of sucrose sugar

pyrolysis at 1,373 K and compared with that by compressed carbon powder. The temperature and the pressure were controlled at 263 to 300 K and 0-4.2 MPa, respectively. It was found that the granular activated carbon could adsorb more methane. Blanco et al. [4] studied methane, carbon dioxide and hydrogen adsorption by monolith activated carbon made of coconut shell under pyrolysis. Gases were fed at temperature of 298 K and pressure in a range of 0-4.5 MPa and it was found that the suitable porosity for methane and carbon dioxide adsorption was in a range of 5-10 Å and the methane could be adsorbed around 1.0-4.0 mmol/g_(AC). Pitak [5] studied adsorption of biomethane at 80% methane by volume by three activated carbons at temperature of 288-298 K and pressure of 3-9 MPa, respectively. It was found that the activated carbons could adsorb the biomethane about 5.63-10.12 mmol/g_(AC) at temperature of 298 K and pressure of 3 MPa. Rahman et al. [6] also found that the amount of adsorbed methane was found to be higher than that compressed in a storage tank at the same pressure.

It could be seen that activated carbon has a high potential to be used as a biomethane adsorbent. In this study, adsorption of biomethane on coal activated carbon at low pressure [0-0.8 MPa(abs)] was carried out. This pressure is similar to that of the normal household LPG tank, then the biomethane could be used to replace the LPG for household cooking. The adsorption phenomena on the activated carbon were also investigated.

2. Method

The amount of biomethane adsorption by activated carbon could be calculated from Langmuir's equation [7] which is based on the assumption of a structurally homogeneous adsorbent. It could be described as

$$q = q_{max} \left[\frac{K_L P}{1 + K_L P} \right], \quad (1)$$

$$\text{or } \frac{1}{q} = \left(\frac{1}{q_{max} K_L} \right) \frac{1}{P} + \frac{1}{q_{max}} \quad (2)$$

where q is the adsorbed biomethane per unit AC (mmol/g_(AC)) at equilibrium temperature and pressure, q_{max} is the limiting uptake of biomethane on the adsorbent (mmol/g_(AC)), K_L is the Langmuir's constant (MPa⁻¹) and P is the equilibrium pressure (MPa).

From the above equation, q_{max} and K_L could be evaluated by correlating $1/q$ and $1/P$ from experimental data. $1/q_{max}$ is the intercept on the $1/q$ axis and $1/(q_{max} K_L)$ is the slope of the correlation curve.

Dubinin and Radushkevich (D-R) [7] also proposed a model for gas adsorption on microporous surface as

$$W = W_{max} \exp \left[- \left(\frac{A}{E} \right)^2 \right]. \quad (3)$$

Dubinin and Astakhov (D-A) [8, 9] modified the D-R equation which could fit the data accurately, and proposed the following model for adsorption of vapours and gases on nonhomogeneous carbonaceous solids with a wide pore size

distribution. The amount of adsorbed vapour could also be explained by Dubinin and Astakhov (D-A) equation [7- 9] which could be calculated by

$$W = W_{max} \exp \left[- \left(\frac{A}{E} \right)^n \right], \quad (4)$$

where A is the adsorption potential (J/mol), W is the amount of uptake biomethane per unit AC ($\text{cm}^3/\text{g}_{(\text{AC})}$), W_{max} is the limiting uptake of biomethane by the adsorbent ($\text{cm}^3/\text{g}_{(\text{AC})}$), E is the characteristic energy of the adsorption system (J/mol), n is the structural heterogeneity parameter which indicated trend of the heterogeneity surface.

A is also denoted as the specific work done in isothermal compression of a unit mass of vapour from pressure P to the saturation vapour pressure P_s and it could be given by [7]

$$A = \bar{R}T \ln \left(\frac{P_s}{P} \right) \quad (5)$$

where \bar{R} is the universal gas constant (8.1345 J/mol-K).

Then from Eqs. (4) and (5),

$$\frac{W}{W_{max}} = \exp \left[- \left\{ \frac{\bar{R}T}{E} \ln \left(\frac{P_s}{P} \right) \right\}^n \right]. \quad (6)$$

It could be seen that the term W could be rewritten in term of q in $\text{mmol}/\text{g}_{(\text{AC})}$ [6, 10] as

$$\frac{q}{q_{max}} = \exp \left[- \left\{ \frac{\bar{R}T}{E} \ln \left(\frac{P_s}{P} \right) \right\}^n \right]. \quad (7)$$

The equation is performed with the assumption that the vapour density in the porous medium is constant.

The saturation vapour pressure (P_s), of a given isotherm temperature could be calculated by Dubinin and Astakhov's method [9] as

$$P_s = \left(\frac{T}{T_c} \right)^2 P_c ; \quad T > T_c \quad (8)$$

where P_c and T_c are the critical pressure, and the critical temperature of gas, respectively.

In this study, Langmuir's equation and D-A equation were taken for investigating biomethane adsorption by activated carbon. The properties of biomethane, such as critical temperature, pressure and density could be evaluated by REFPROP Program [11]. The molecular weight of biomethane for the calculation could be expressed as

$$Mw_{mix} = \sum y_i Mw_i, \quad (9)$$

where Mw_{mix} is the molecular weight of biomethane (g/mol), y_i is the mol fraction of gas in biomethane, Mw_i is the molecular weight of gas in biomethane (g/mol).

During adsorption, by assuming ideal gas-phase behavior, there is heat releasing which is called isosteric heat of adsorption. It could be calculated from Clapeyron's equation [12-14] as

$$H_{ad} = -\bar{R}T^2 \left(\frac{\partial \ln P}{\partial T} \right)_q, \quad (10)$$

where H_{ad} is the isosteric heat of adsorption at specific loading (J/mol), T is the temperature (K).

3. Experiment

In this study, 8x16 mesh granular coal activated carbon from Calgon Carbon Corporation, Belgium was used to study biomethane adsorption. The activated carbon properties were analysed by the technique of BET surface analysis. The data were given in Table 1.

Table 1. The BET surface analysis.

Sample	BET Theory (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter ((\AA)	Bulk density (g/cm^3)
Coal	1,418	0.916	12.92	50.02

Note: $\text{\AA} 1 = 0.1 \text{ nm}$

A stainless steel (SS 304) cylinder with an internal volume of $1.77 \times 10^6 \text{ mm}^3$ contained 891 g of activated carbon. There was cooling water feeding through a tube at the centre of the cylinder for temperature control during adsorption.

Figures 1 and 2 show the schematic diagrams of the biomethane adsorption container and the experimental setup.

Two concentrations of biomethane in the study were $\text{CH}_4:\text{CO}_2$ at 80:20% (80% biomethane) and 90:10% (90% biomethane). Each was compressed into a tank with a pressure of 10 MPa(g). The gas was fed into the activated carbon cylinder and the pressure was controlled by a pressure valve regulator.

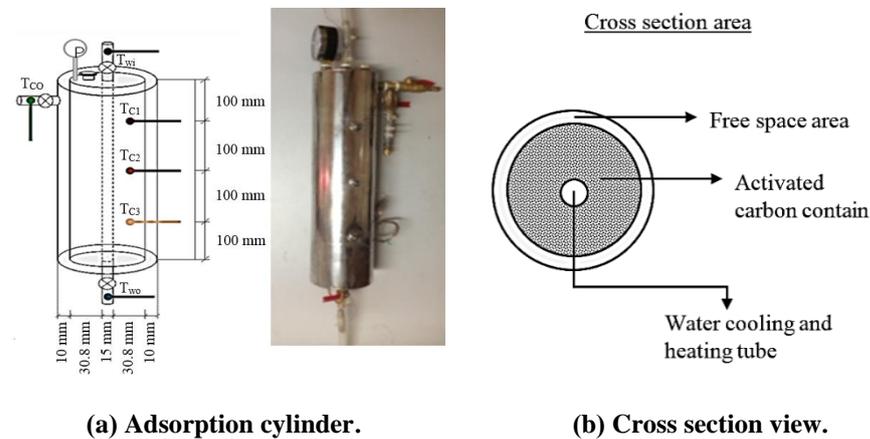


Fig. 1. The container for biomethane adsorption.

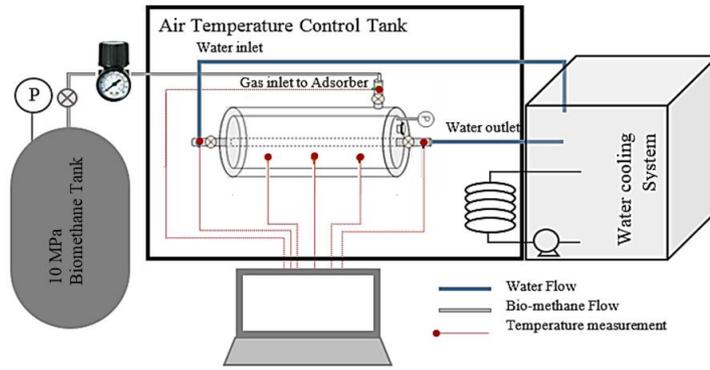


Fig. 2. A schematic diagram of the biomethane adsorption experimental setup.

Before testing, the activated carbon was heated at temperature of 373 K and vacuumed at least 12 hours for degassing. After that the biomethane was fed to the activated carbon cylinder of which the temperature and the pressure were controlled at the ranges of 283-298 K and 0-0.8 MPa(abs), respectively. In the experiment, the container was weighed before and after adsorption. The amount of the adsorbed biomethane on activated carbon could be calculated by

$$n_{ad} = n_{total} - n_{sp} , \quad (10)$$

where n_{ad} is the adsorbed biomethane (mol) on activated carbon at equilibrium pressure and temperature, n_{total} is the total biomethane (mol) in the container at equilibrium pressure and temperature and n_{sp} (mol) is the biomethane in the free space volume in the container.

The biomethane in the free space volume could be calculated at equilibrium pressure and temperature as

$$n_{sp} = \frac{PV_{sp}}{RT} , \quad (11)$$

where P is equilibrium pressure (Pa), V_{sp} is free space volume in the container (m^3), T is temperature (K).

4. Results and Discussion

4.1. Biomethane adsorption

The 80 and 90% biomethane adsorptions by coal activated carbon (coal AC) at adsorption temperature and pressure of 283-298 K, 0-0.8MPa presented in Langmuir isotherm could be shown in Fig. 3.

It could be seen that the shapes of the isotherms were similar to monolayer adsorption or Type I adsorption isotherm as that reported by Rios et al. [15]. As the pressure difference between the gas in the container and that in the AC micropores increased, higher amount of adsorbed biomethane on activated carbon could be achieved. Then the adsorbed biomethane on activated carbon increased

when the pressure in the container increased and the AC temperature decreased. In addition, the coal activated carbon has a higher affinity to CO₂ than that for CH₄ [16]. Better CO₂ adsorption was better than CH₄ adsorption for average pore diameter of 12.92 Å as reported by Garcia-Perez et al. [17].

The quantity of adsorbed biomethane from experiment was about 0.78-1.10 mmol/g_(AC) which was in a range as that reported by Blanco et al. [4] for adsorbing pure methane (99.995% purity) on AC. From Langmuir model, the limiting uptake of biomethane on the adsorbent (q_{max}) and the Langmuir's constant (K_L) could be evaluated by correlating $1/q$ and $1/P$ from Eq. (2) and experimental data in Appendix A. The results were shown in Table 2.

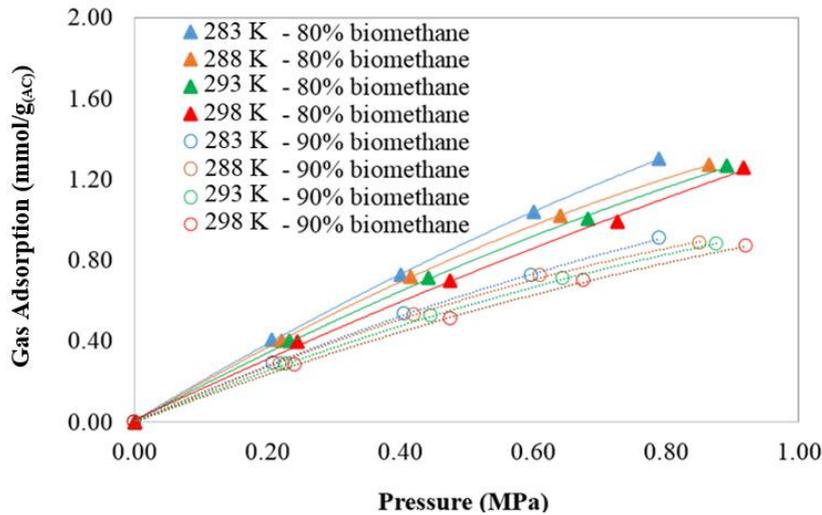


Fig. 3. Adsorption Isotherm of biomethane adsorption on coal activated carbon for 80:20 and 90:10% by volume; biomethane: CO₂ at 283-298 K.

Table 2. The limiting uptake (q_{max}) and the Langmuir's constant (K_L) of biomethane adsorption on the activated carbons.

Adsorbate	Adsorbent	Adsorbed Temperature (K)	q_{max} (mmol/g _(AC))	K_L (MPa ⁻¹)
80:20%v/v; biomethane:CO ₂	Coal	298	4.80	0.37
		293	4.87	0.39
		288	4.96	0.40
		283	5.06	0.43
90:10%v/v; biomethane:CO ₂	Coal	298	2.98	0.37
		293	3.05	0.39
		288	3.21	0.39
		283	3.23	0.41

From Table 2, it could also be seen that the amount of biomethane adsorption in term of q_{max} at lower methane concentration was higher than that at high methane concentration. When the adsorption temperature decreased, the q_{max} value and the K_L value increased.

4.2. Dubinin and Astakhov (D-A) result

From D-A model (Eq. (6)) with various operating conditions, the relation between the adsorbate surface loading, $\ln(q)$ and the term $(T\ln(P_s/P))^n$ was performed. The characteristic energy of adsorption (E), the structural heterogeneity parameter (n), and the limiting uptake of biomethane on the adsorbent (q_{max}) at 283-298 K could be shown in Fig. 4 and Table 3. It could be noted that n value at 1.48 was suitable to fit the experimental data.

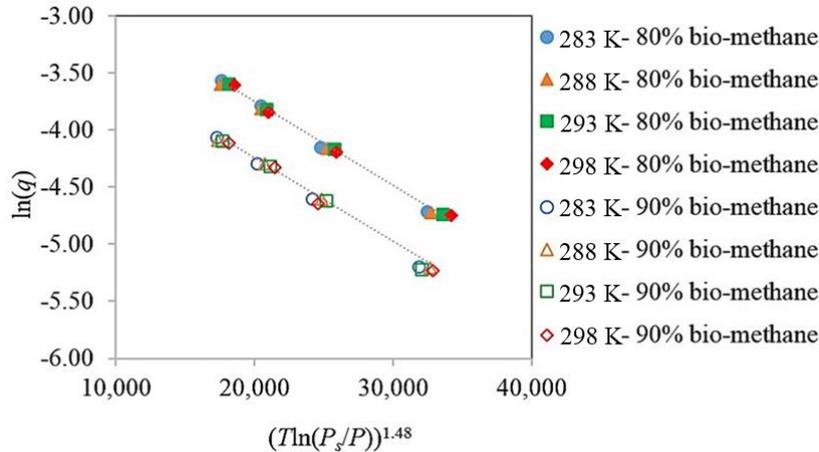


Fig. 4. The relation between $\ln(q)$ and $(T\ln(P_s/P))^{1.48}$ for 80:20 and 90:10% by volume; biomethane: CO₂ adsorption by coal activated carbon.

Table 3. The structural heterogeneity parameter (n), the characteristic energy of adsorption (E), and limiting uptake of biomethane on the adsorbent (q_{max}) for D-A model.

Biomethane	Type of AC	BET Surface (m ² /g)	D-A model			Langmuir model	Reference
			n	E (kJ/mol)	q_{max} (mmol/g _(AC))	$q_{max\,avg}$ (mmol/g _(AC))	
80:20%v/v; biomethane:CO ₂	Coal	1,418	1.48	5.34	4.63	4.92	This study
90:10%v/v; biomethane:CO ₂	Coal	1,418	1.48	4.88	3.39	3.12	This study
99.9995%v/v CH ₄	MaxsorbIII	3,140	1.33	5.26	18.16	N/A	[9]
99.9995%v/v CH ₄	ACF (A-20)	2,206	1.37	5.64	10.56	N/A	[9]
Pure CH ₄	Calgon AC	N/A	2.41	8.96	0.88	N/A	[13]
Pure CH ₄	AAC-1	801	2.57	9.80	1.3	N/A	[14]

From Fig. 4 and Table 3, it could be found that the average limiting uptake of biomethane on the adsorbent (q_{max}) at temperature of 283-298 K from Langmuir model and q_{max} from D-A model were quite similar.

With the n values for coal at 1.48, the characteristic energy of adsorption (E) were 5.34 and 4.88 kJ/mol for 80 and 90% biomethane adsorption, respectively which was in a range as that reported by [9]. It could also be noted that the micropores in our activated carbon are heterogenous since the n value is rather low [7].

4.3. Isotheric heat of adsorption

The isotheric heat of adsorption represents the energetic heterogeneity of a solid surface, it is a measurement of the interaction between adsorbate molecules and adsorbent [12]. The isotheric heat of adsorption could be calculated from the Clapeyron equation. From the experimental data, the isotheric heat of adsorption for 80 and 90% biomethane adsorption by coal was in a range of 5.56-9.76 kJ/mol which was in a range of those reported in the literatures [5, 12]. The isotheric heat of adsorptions for biomethane were shown in Fig. 5.

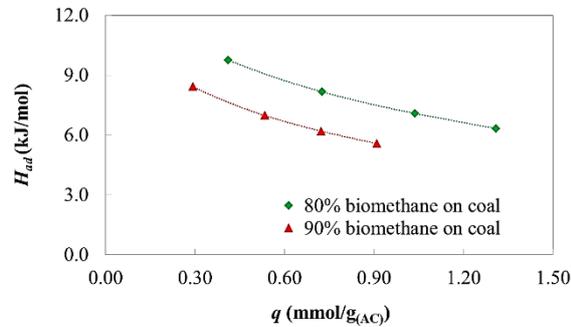


Fig. 5. The isotheric heat of adsorption for biomethane with the amount of adsorbed biomethane.

It could be noted that the isotheric heat of adsorption is a measure of the interaction between adsorbate molecules and adsorbent molecules. At the beginning, the adsorption occurred easily on the activity surface and highest adsorption heat was obtained. As the adsorbed amount increased, the adsorption at the surface was less active and the isotheric heat of adsorption also became low. In the Fig. 5, the isotheric heat of adsorption for biomethane decreased, when the amount of gas adsorption increased. The results were similar to those of Ning et al. [12].

5. Conclusions

This research could be concluded that the adsorbed biomethane by activated carbon increased when the pressure increased, and the temperature decreased. The 80% biomethane was better adsorbed since the activated carbons had higher affinity for CO₂ than that for CH₄.

The amount of biomethane adsorption and Langmuir's constant increased when the temperature decreased. The values of q_{max} for 80 and 90% biomethane adsorption by coal were in a range of 4.799-5.056 and 2.983-3.229 mmol/g_(AC), respectively. The value of K_L was in a range of 0.367-0.428 MPa⁻¹.

From Dubinin-Astakhov equation for biomethane adsorption, the structural heterogeneity parameter (n) for coal was 1.48.

The isotheric heats of adsorption for 80 and 90% biomethane by coal activated carbon were in a range of 5.56-9.76 kJ/mol. The heat of adsorption decreased when the adsorbed amount of biomethane increased.

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Appendix A

The experimental data for 80:20 and 90:10% by volume of biomethane adsorption on coal activated carbon at temperature of 283-298 K, Pressure of 0-0.8 MPa.

80:20% by volume biomethane:CO ₂				90:10% by volume biomethane:CO ₂			
Temp(K)	Pressure (MPa)	mmol/g _(AC)	g/g _(AC)	Temp(K)	Pressure (MPa)	mmol/g _(AC)	g/g _(AC)
283.00	0.000	0.000	0.000	283.00	0.000	0.000	0.000
282.50	0.206	0.412	0.009	282.75	0.210	0.290	0.006
282.75	0.401	0.725	0.016	282.75	0.410	0.530	0.010
283.35	0.601	1.037	0.022	283.40	0.600	0.720	0.014
283.00	0.789	1.302	0.028	283.20	0.790	0.910	0.017
288.00	0.000	0.000	0.000	288.00	0.000	0.000	0.000
287.15	0.222	0.405	0.009	288.00	0.220	0.290	0.005
287.15	0.416	0.721	0.016	287.80	0.420	0.530	0.010
287.15	0.641	1.021	0.022	288.60	0.610	0.720	0.014
288.00	0.864	1.271	0.028	288.00	0.850	0.890	0.017
293.00	0.000	0.000	0.000	293.00	0.000	0.000	0.000
293.00	0.233	0.402	0.009	293.70	0.230	0.290	0.005
293.00	0.443	0.712	0.015	292.50	0.450	0.520	0.010
293.00	0.681	1.007	0.022	293.70	0.650	0.710	0.013
293.40	0.891	1.266	0.027	293.45	0.880	0.880	0.017
298.00	0.000	0.000	0.000	298.00	0.000	0.000	0.000
298.15	0.246	0.397	0.009	298.20	0.240	0.280	0.005
297.55	0.475	0.699	0.015	298.10	0.480	0.510	0.010
297.40	0.726	0.990	0.021	297.80	0.680	0.700	0.013
298.00	0.916	1.260	0.027	298.00	0.920	0.870	0.016