

# Nonequilibrium Plasma Reforming of Greenhouse Gases Under Atmospheric Pressure by Using a Conventional Reactor

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## 簡便な非平衡プラズマ反応器による 温室効果ガスの大気圧下低エネルギー改質

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### Abstract

By using a conventional tubular reactor, nonequilibrium plasma reforming of greenhouse gases was carried out in low energy emission (below 12.5 W) under atmospheric pressure. Conversion of CO<sub>2</sub> increased to produce CO and O<sub>2</sub> according to increasing the output. By mixing CO<sub>2</sub> and CH<sub>4</sub> as a reactant feed, useful compounds such as ethane, ethylene (by way of methane coupling), and their partially oxidized compounds (ethanol, acetaldehyde, *etc.*). It is suggested the distance among electrodes, which is due to the thickness of the reactor wall, is very important to affect both the conversion of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) and the selectivity of product the useful chemicals.

**Key Words:** Conversion of greenhouse gases, Nonequilibrium plasma process, Conventional tubular reactor, From CO<sub>2</sub> and CH<sub>4</sub> to useful compounds

### 1. Introduction

As a critical global issue, increasing greenhouse gases deepens concerns about the pace of global warming<sup>1)</sup>. For sustainable society by significantly

reducing greenhouse gases, reduction of carbon dioxide (CO<sub>2</sub>) population in the atmosphere to account for enormous discharges is urgent<sup>2-3)</sup> because the greenhouse gases in the atmosphere

have certain property of absorbing infrared radiation. In 2010, the government of Japan approved the new CO<sub>2</sub> emission target, promising to reduce emissions by 25% by 2020 compared to the 1990 level. However, the reduction plan of the CO<sub>2</sub> failed virtually by a serious accident of Fukushima Daiichi Nuclear Power Station (F1NPS) due to the Great East Japan Earthquake in May 2011. As a result, the quantity of carbon dioxide emission increased after 2011 because of re-operation of the thermal power station<sup>4)</sup>. Even in Japan, it becomes essential to participate in a global approach for the reduction of the CO<sub>2</sub> emission immediately.

To provide a noble method for converting or immobilizing CO<sub>2</sub>, new chemical approach which can be accelerated with low energy is called for. But it has been energetically and economically difficult. Since CO<sub>2</sub> is chemically so stable that converting CO<sub>2</sub> needs considerable energy, high energy processes such as high temperature and/or pressure cannot be avoided for converting CO<sub>2</sub> to useful compounds (methane, methanol, syngas, *etc.*) even in catalytically major processes. On the other hand, the use of CO<sub>2</sub> feedstock can lead to the development of a new generation of useful and innovative chemical products with superior technical performance or unique properties in specific cases. If conventional decomposition of CO<sub>2</sub> (based on a fragmentation of the C=O bond) under low energy, a desired chemical process producing chemicals and fuels from CO<sub>2</sub> as a renewable carbon source will be acquired. It is one of an area to watch for one or more revolutions of the chemical industry in near future.

In the present study, we introduced a nonequilibrium plasma reforming of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>). By applying atmospheric pressure glow discharge, the greenhouse gases can activate to the radical intermediates under low energy field. The nonequilibrium plasma reactors employed in the present study are made easily by hand, and very simple and inexpensive. As reported in a previous paper<sup>5)</sup>, a conventional surface discharge tubular reactor can be applied

for direct conversion of greenhouse gases even under low energy emission below 20 W. By using this type of reactor, CO<sub>2</sub> can easily decompose according to the output under atmospheric pressure. Conversion of methane also proceeds more easily. At the same time, combination between nonequilibrium plasma process and catalytic one (plasma-catalysis), which can be achieved by filling the catalytic materials into the reactor, will be applied widely for converting greenhouse gases to useful chemicals<sup>6)</sup>. When a spherical material pellet is filled into the reactor, another type of reaction as a dielectric barrier discharge Plasma (DBD) reaction can be proceed.

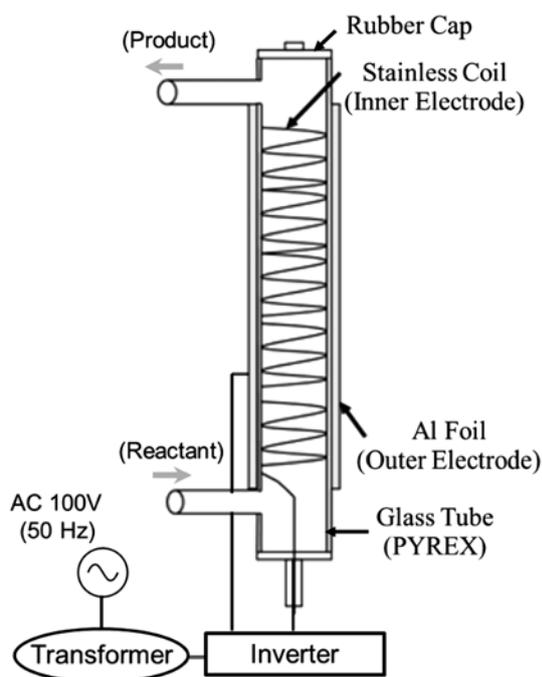
As a subject, it is difficult to control the selectivity of products over the nonequilibrium plasma reaction. For example, CO formation is dominant in nonequilibrium plasma reaction because decomposition of CO<sub>2</sub> (to CO+1/2 O<sub>2</sub>) and partially oxidation of CH<sub>4</sub> (by way of reacting O<sub>2</sub> from CO<sub>2</sub>) tend to proceed at the same time. To produce the useful chemicals such as ethane, ethylene (by way of oxidative coupling of methane) and partially oxidized compounds (alcohols, carboxylic acids, ketones, *etc.*), it is very important to achieve the selectivity control of the products by controlling the parameters on the nonequilibrium plasma reaction. In particular, the condition plasma-irradiated field onto the reactor strongly relates to the reactivity for converting. In this study, correlation between the reactor parameters and reactivity of CO<sub>2</sub> and CH<sub>4</sub> conversion to produce useful chemicals is studied by using several types of nonequilibrium plasma reactor.

## 2. Experimental

A surface discharge reactor, which consists of PYREX glass tube with branched pipes, a spiral stainless wire coil (as an inner electrode into the reactor tube, 0.35 mm of wire thickness), stainless foil tape (as an outer electrode), and terminal rubber cap, was used for the nonequilibrium plasma reaction. A spiral wire coil was set in contact with the inner wall of a glass tube as a

barrier, and stainless foil tape was set on the outer side of the tube as the ground electrode. Two electrodes are connected a high-voltage amplifier, which used a M-5 (100 V) inverter-type neon transformer (Lecip) *via* a power meter (3333 Power HiTESTER, Hioki) and variable voltage type transformer. Fig. 1 shows the outline of the nonequilibrium plasma reaction system in the present study.

Several types of tubular reactor were used in this study as summarized in Table 1. The parameters; (A) indicates the length of plasma filed, (B) indicates the internal diameter of tubular reactor, (C) indicates the thickness of the reactor wall (due to the distance among electrodes), and (D) indicates the number of turns in an inner electrode. As a dielectric barrier discharge Plasma



**Fig. 1** Outline of the non-equilibrium plasma reactor (for surface discharge plasma reaction under atmospheric pressure).

(DBD) reaction, spherical filler with *ca.* 2 mm diameter was filled into each reactor. The fillers are; silica-gel (Fujifilm-Wako), alumina for catalyst (Sumitomo Chemical), and water absorptive alumina (Union Showa).

The reactant gas mixture is; [i] CO<sub>2</sub> (15 mL/min)+Ar (30 mL/min), [ii] CO<sub>2</sub> (15 mL/min)+CH<sub>4</sub> (15 mL/min)+Ar (15 mL/min), or [iii] CO<sub>2</sub> (15 mL/min)+CH<sub>4</sub> (30 mL/min). For each case, the reactant gas mixture was fed into the reactor at a total flow rate of 45 mL/min under atmospheric pressure, and a high-voltage ac was applied across the electrodes at ambient temperature (without heating). Under stepwise increasing power output below 15.0 W (with 2.5 W step), nonequilibrium plasma reaction was performed for 20 min in each output step. In case of 15.0 W output for 20 min, temperature in center of the reactor was 53.0 degrees Celsius measured by thermography. After the plasma reaction, the product gas was analyzed by two TCD gas chromatographs (GC-8A, Shimadzu) equipped a Shincarbon-ST (3 m) column or Porapac-Q (2 m) +Gaschropack54 (3 m) connected columns. From the analytical results, Carbon-based conversion and selectivity were obtained.

### 3. Results and Discussion

Fig. 2 shows the reactivity of nonequilibrium plasma reforming of CO<sub>2</sub> and CH<sub>4</sub> by using (I)-(III) reactors. For CO<sub>2</sub>+Ar reactant (i), CO and O<sub>2</sub> was detected in all the reactors below 12.5 W output. In the case of type (II) reactor, highest CO<sub>2</sub> conversion is shown among (I)-(III) reactors. This result indicates that the reactivity for converting CO<sub>2</sub> is not depend on the turn number of coil (as an inner electrode) or a volume of plasma-irradiating field. For CO<sub>2</sub>+CH<sub>4</sub> reactant

**Table 1** Parameters of the plasma filed in tubular reactor for surface discharge plasma reaction.

Reactor	(A) Length / mm	(B) Diameter / mm	(C) Thickness / mm	(D) Turn number of coil	Volume / mL
I	177	7.0	1.5	30	6.8
II	184	9.0	1.5	40	11.7
III	198	12.0	2.0	45	22.4

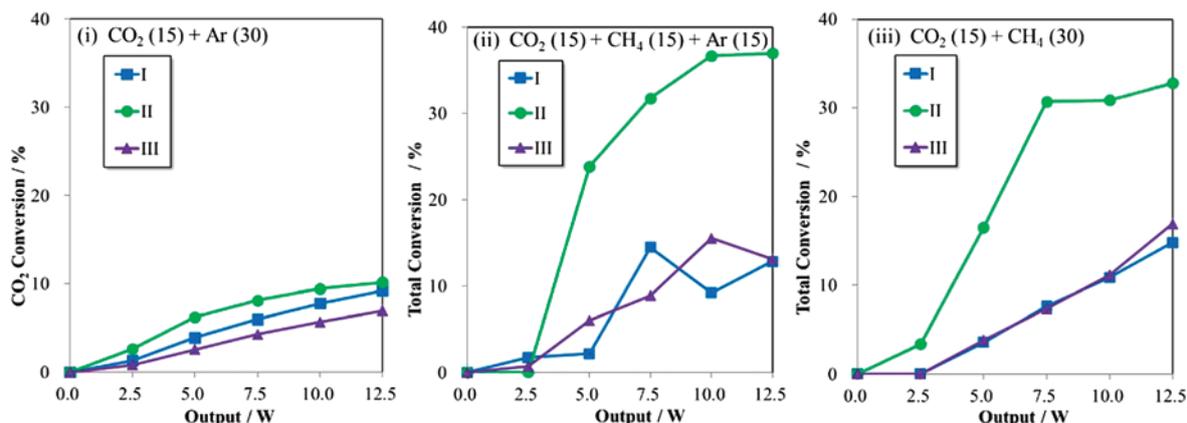


Fig. 2 Conversion of  $\text{CO}_2$  and  $\text{CH}_4$  by glow discharge vs. input power using (I)-(III) reactors without fillers.

(ii and iii), it is definite that type (II) reactor shows high conversion for  $\text{CO}_2 + \text{CH}_4$ . This result suggests that the factors of maximum reactivity for  $\text{CO}_2 + \text{CH}_4$  conversion are possibly include appropriate surface discharge condition, which is based on the distance between the electrodes and an effective volume of the reaction field. In fact, the turn number of coils as an internal electrode reflects the spread of plasma flame. But it is difficult for the plasma flame to reach the center (due to the core of cross-section circle in the reactor) of the reactor. Thus, the wide diameter of the reactor is not always effective for surface discharge plasma reactor even in large volume of

plasma irradiation. In addition, the distance of the electrodes due to thickness of wall in the reactor is very important because of spread of plasma flame. When  $\text{CO}_2$  and  $\text{CH}_4$  react, production of  $\text{H}_2\text{O}$  cannot be avoided. The produced  $\text{H}_2\text{O}$  surely inhibits the reactivity under a weak plasma flame. As a result, it is suggested that the factor of appropriate surface discharge condition includes the moderate distance of electrodes and spread of plasma flame at the same time. It may be estimated that the reason of maximum reactivity over type (II) reactor is due to the comfortable irradiation of surface discharged plasma flame.

Table 2 and 3 shows the product selectivity

**Table 2** Selectivity of the products by glow discharge vs. input power over (ii)  $\text{CO}_2 + \text{CH}_4 + \text{Ar}$  flow reaction using the (II) reactor without fillers.

Output (W)	Total Conv. (%)	Selectivity (%)									
		CO	$\text{CH}_3\text{OH}$	HCHO	HCOOH	$\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{CHO}$	$\text{C}_3\text{H}_8$
2.5	0.2	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
5.0	23.9	48.2	0.5	0.0	0.0	0.0	1.6	21.3	2.6	0.9	24.9
7.5	31.8	55.1	0.4	0.0	0.0	0.0	1.0	17.7	1.9	0.3	23.5
10.0	36.7	69.6	0.3	0.0	0.0	0.0	0.6	11.7	1.1	0.5	16.1
12.5	37.0	73.9	0.3	0.0	0.0	0.0	0.4	10.0	0.9	0.4	14.2

**Table 3** Selectivity of the products by glow discharge vs. input power over (iii)  $\text{CO}_2 + 2\text{CH}_4$  flow reaction using the (II) reactor without fillers.

Output (W)	Total Conv. (%)	Selectivity (%)									
		CO	$\text{CH}_3\text{OH}$	HCHO	HCOOH	$\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{CHO}$	$\text{C}_3\text{H}_8$
2.5	3.4	26.1	0.8	0.0	0.0	0.0	8.4	25.9	5.0	2.1	31.6
5.0	16.5	26.8	0.6	0.0	0.0	0.0	3.5	21.7	3.4	1.2	42.8
7.5	30.7	23.7	0.5	0.0	0.0	0.0	2.6	21.6	3.1	1.1	47.3
10.0	30.8	36.7	0.7	0.0	0.0	0.0	1.6	15.4	2.3	1.0	42.3
12.5	32.8	38.1	0.5	0.0	0.0	0.0	1.3	14.8	2.2	0.9	42.2

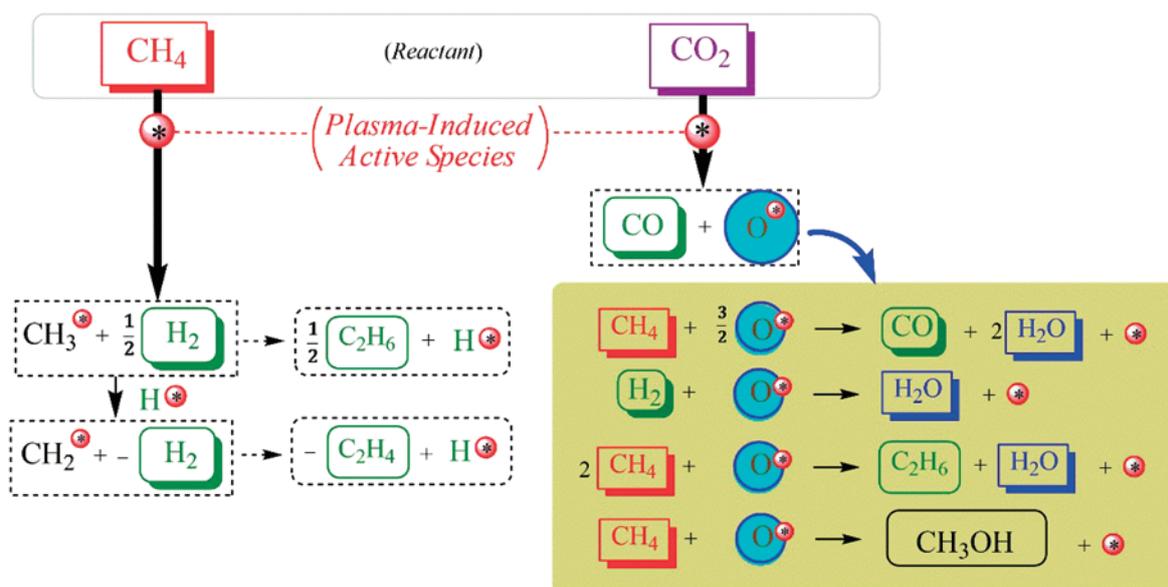
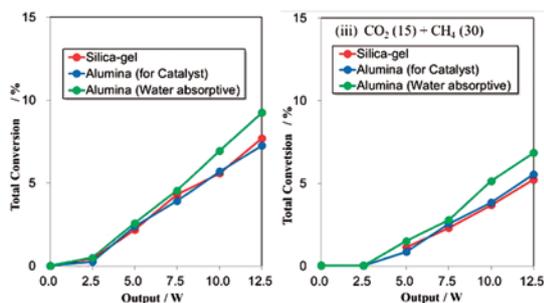


Fig. 3 Simplified conceptual diagram of plasma reaction process *via* radical-induced reactions.

against input power over (ii)  $\text{CO}_2 + \text{CH}_4 + \text{Ar}$  and (ii)  $\text{CO}_2 + 2\text{CH}_4$  flow reaction, respectively, using the (II) reactor without fillers. For the (ii)  $\text{CO}_2 + \text{CH}_4 + \text{Ar}$  reactant as shown in Table 2, formation of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  is remarkable along with the CO formation in the low output region (2.5-7.5 W). It is presumed that radicalization of  $\text{CH}_4$  occurs in an initial step, and dehydrogenated  $\text{CH}_x$  convert  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  by way of methyl radical species. In parallel, hydrogen react O species, which can be formed by  $\text{CO}_2$  decomposition, to form  $\text{H}_2\text{O}$ . Even in a low selectivity,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CHO}$  are formed as partially oxidized products from  $\text{C}_2\text{H}_6$ . They can possibly be formed by reaction between O- or OH-type radicals and  $\text{C}_2\text{H}_6$ . With increasing the output below 12.5 W, the CO selectivity increased while the selectivity of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  decreased. It suggests the proceeds of oxidation form  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  to form CO under high energy output region. For the (iii)  $\text{CO}_2 + 2\text{CH}_4$  reactant as shown in Table 3, formation of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  is definite with high selectivity in whole output region. It can be proposed that the rate of  $\text{CH}_4$  promotion (dehydrogenation to  $\text{CH}_x$  radicals) is higher than that of CO formation (by way of both  $\text{CO}_2$  decomposition and oxidation of  $\text{CH}_x$

species), and thus, in  $\text{CH}_4$ -rich reactant under low output below 7.5 W. Fig. 3 shows a simplified conceptual diagram of initial plasma reaction process *via* radical reactions. As an activation to plasma-induced species, activation of  $\text{CH}_4$  to  $\text{CH}_x$  species is relatively faster than  $\text{CO}_2$  decomposition to  $\text{CO} + 1/2 \text{O}_2$ . Formed  $\text{H}_2$  (from  $\text{CH}_4$  dehydrogenation) can easily react with  $\text{O}_2$  to produce  $\text{H}_2\text{O}$ , and react with hydrocarbon radical ( $\text{CH}_x$  and/or  $\text{C}_2\text{H}_x$ ) species to produce  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CHO}$  as minor produces.  $\text{CH}_3\text{OH}$  was hardly formed on the plasma reaction. It is suggested from the results of selectivity that a direct reaction between an ethyl radical and an oxygen radical occurs much easier than between methane and oxygen (or a methyl radical and a hydroxyl radical).

The results of product distribution shown in Table 3 can be expected to be extremely attractive to approach the purpose of effective use of greenhouse gases at low energy. To enhance the yield of useful chemical compounds, several ceramic fillers were attempted to insert into the tubular reactor for DBD-like reaction. The filler with *ca.* 2 mm diameter used in this study is silica-gel, alumina for catalyst, and water absorptive alumina. The total conversion due to  $\text{CO}_2$  and



**Fig. 4** Conversion of CO<sub>2</sub> and CH<sub>4</sub> by glow discharge vs. input power using (I) reactors inserted a various ceramic fillers.

CH<sub>4</sub> by glow discharge vs. input power using the (II) reactor inserted each filler is shown in Fig. 4. For total conversion, inserted reactor with filler becomes quite lower than the reactor without filler. The major reason is a residence time of plasma irradiation: The volume of plasma field in the case of without filler (empty) and inserted with filler is 11.3 and 3.0 mL, respectively. Therefore, contact time in the plasma field is quite different from each other. Among the filler inserted into the reactor, water absorptive alumina shows relatively high conversion. In this case, unique selectivity is exhibited. Table 4 and 5 shows the product selectivity against input power over (ii) CO<sub>2</sub>+CH<sub>4</sub>+Ar and (ii) CO<sub>2</sub>+2CH<sub>4</sub> flow reaction, respectively, using the (II) reactor

inserted water absorptive alumina fillers in the reactor. It is noted that high selectivity of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> is definite. Because the surface discharge is enhanced, it is suggested that the insertion of the filler promotes the methane conversion to methyl radicals. On this plasma reaction condition, a subject is the enhancement of total conversion as well as high selectivity due to hydrocarbons and partially oxidized ones.

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**Table 4** Selectivity of the products by glow discharge vs. input power over (ii) CO<sub>2</sub>+CH<sub>4</sub>+Ar flow reaction using the (II) reactor inserted water absorptive alumina fillers in the reactor.

Output (W)	Total Conv.(%)	Selectivity (%)									
		CO	CH <sub>3</sub> OH	HCHO	HCOOH	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> CHO	C <sub>3</sub> H <sub>8</sub>
2.5	0.5	47.9	0.0	0.0	0.0	0.0	19.0	33.1	0.0	0.0	0.0
5.0	2.6	39.9	0.7	0.0	0.0	7.1	10.8	29.6	4.6	2.6	4.8
7.5	4.6	41.2	0.5	0.0	0.0	5.9	8.7	29.6	4.7	2.2	7.2
10.0	7.0	42.0	0.5	0.0	0.0	4.8	6.9	29.5	4.5	2.3	9.4
12.5	9.3	40.7	0.5	0.0	0.0	3.9	5.7	32.0	5.0	1.8	10.3

**Table 5** Selectivity of the products by glow discharge vs. input power over (iii) CO<sub>2</sub>+2CH<sub>4</sub> flow reaction using the (II) reactor inserted water absorptive alumina fillers in the reactor.

Output (W)	Total Conv.(%)	Selectivity (%)									
		CO	CH <sub>3</sub> OH	HCHO	HCOOH	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> CHO	C <sub>3</sub> H <sub>8</sub>
2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	1.5	27.6	0.7	0.0	0.0	8.8	13.5	30.6	4.9	2.4	11.5
7.5	2.8	29.8	0.7	0.0	0.0	7.2	11.6	32.4	5.2	2.4	10.8
10.0	5.1	28.1	0.6	0.0	0.0	6.0	10.0	34.5	7.4	3.4	10.0
12.5	6.9	25.8	0.5	0.0	0.0	5.0	8.3	34.5	11.1	4.2	10.7