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Effect of vessel size and shape on experimental flammability limits of gases

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Abstract

The flammability limits of methane and propane have been measured using cylindrical vessels of various sizes and one spherical vessel. An ac discharge ignition method has been employed. For a cylindrical vessel of small diameter with a large height, the flammability limits are primarily determined by the quenching effect of the wall. For cylindrical vessels of smaller heights, the experimental flammability limits are affected by hot gas accumulation at the vessel ceiling, unburnt gas heating, self heating of the incipient flame by the reflection both from walls and ceiling, and the quenching effect of the walls. If the vessel size is large enough so that all these effects become negligible, the experimental values of flammability limits may approach to the values that would be obtained in free space. In order to approach this condition for a cylindrical vessel, it is desirable to use a container at least 30 cm in diameter and 60 cm in height. For comparison purpose, the measurement has also been done using ASHRAE type 12 l spherical flask.

Keywords: Flammability limits; Vessel size; Cylindrical vessel; Spherical vessel; Methane; Propane

1. Introduction

Regarding recent development of replacement chemicals for CFCs and HCFCs, one of the major concerns is the issue of flammability. If the newly developed substances are flammable, their usage implies concerns that did not arise with non-flammable gases. It may become necessary that the newly developed chemicals be classified according to their combustion hazard. The problem here is how to establish a way of characterizing the total

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combustion hazard of materials. Flammability limits may constitute one component in such characterization.

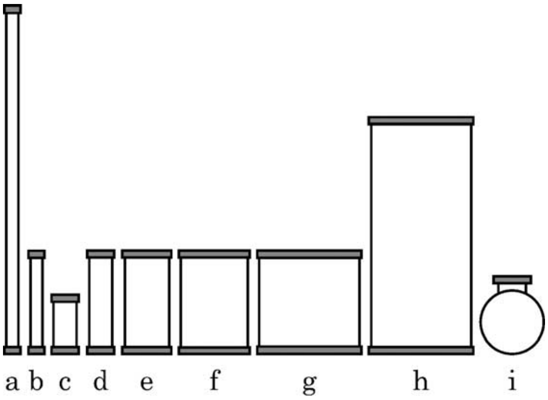
The method of measuring the flammability limits of gases has been known well for a long time [1]. However, in spite of the fact that measured flammability limits are strongly dependent upon the experimental apparatus and conditions with which they are measured, a standardized method for that measurement has not been established yet. Among other variables, the experimental flammability limits strongly depend on the size and shape of vessels as well as on the ignition source. Recently, we have investigated the effect of ignition source on the experimental flammability limits and determined the optimum conditions for the ac discharge method [2] as well as for the exploding wire method [3]. However, the effect of using different sizes and types vessels on the measurements is still not known clearly.

Coward and Jones [1] used a cylindrical vertical tube of 5 cm diameter and 150 cm height (USBM-type) to measure the flammability limits for a wide variety of gases and vapors. They used an electric spark or a small pilot flame as ignition source at the bottom end of the tube. Later, Zabetakis [4] has suggested that a tube diameter 5 cm is too small for measuring the flammability limits of halogenated hydrocarbons. In the ASTM E681 method [5], the gas mixture is contained in a spherical glass vessel of 5 l, and the ignition source is a match head at the center of the vessel initiated by heated nichrome wire. The method developed by BAM [6] employs a cylindrical vertical tube of 6 cm diameter and 30 cm height with ac spark ignition across a spark gap of 5 mm. De Smedt et al. [7] compared the experimental flammability limits of simple hydrocarbons obtained with a 20 l spherical vessel with the values obtained with DIN method. Leisenheimer et al. [8] measured flammability limits of flammable refrigerants in a cylindrical vessel of 3.5 l by using electrical capacitor discharge sparks. Heinonen et al. [9] investigated influences of some experimental conditions on the values of flammability limits measured with ASTM E681 test apparatus as well as with NMERI 8 l spherical vessel. Recently, ASHRAE [10,11] revised the ASTM E681 method for evaluating the flammability limits of flammable refrigerants. They decided to employ a 12 l spherical vessel.

In this paper, we report the result of a detailed study carried out to determine the optimum vessel size to be used for flammability limit measurements. Methane and propane were used as the combustible test gases. Cylindrical vessels of a wide variety of sizes were examined to investigate their influence on the flammability limits measurement. The ac discharge method was used as the ignition source throughout.

2. Experimental apparatus and procedures

Fig. 1 shows a schematic diagram of the experimental vessels used to measure the flammability limits. They are cylindrical glass vessels of various sizes and an ASHRAE-type spherical glass vessel (12 l). The cylindrical vessels other than the largest one of 45 cm Ø × 100 cm and the tallest one of 5 cm Ø × 150 cm (USBM-type) were equipped with a relief valve at the top flange to relieve overpressure. The relief pressure was set at 10 psig unless otherwise stated. The 5 cm Ø × 150 cm vessel was equipped with an electromagnetic valve of approximately 2 cm in diameter at the bottom flange. The valve is made open just



a.	5cm ϕ X 150cm	(cylinder,	3 liter)
b.	5cm ϕ X 40cm	(cylinder,	0.8 liter)
c.	10cm ϕ X 20cm	(cylinder,	1.5 liter)
d.	10cm ϕ X 40cm	(cylinder,	3 liter)
e.	20cm ϕ X 40cm	(cylinder,	13 liter)
f.	30cm ϕ X 40cm	(cylinder,	28 liter)
g.	45cm ϕ X 40cm	(cylinder,	64 liter)
h.	45cm ϕ X 100cm	(cylinder,	160 liter)
i.	28cm ϕ	(sphere,	12 liter)

Fig. 1. Dimensions of explosion vessels used in this study.

before ignition in each experiment. The jumbo cylindrical vessel of 45 cm Ø × 100 cm had three actuator valves each 2.5 cm in diameter both at the top and bottom flanges. In the case of ASHRAE-type spherical vessel, no relief valve is attached but the plastic flange is fixed on the top by four springs. If the explosion occurs in the vessel, the top flange is lifted up against the springs by the overpressures to relieve the overpressure automatically. All the vessels had tungsten electrodes for ac spark ignition near the bottom. The 2 mm diameter tungsten electrodes were sharpened at the top and were at 7 mm apart. An ac electric spark was generated by a Neon transformer. A spark duration time of 0.15 s was used throughout this work. The conditions for spark ignition were established in our previous study [2].

All the vessels, except USBM-type one, were equipped with a fan for mixing the gas to prepare the sample mixtures in the vessels by the partial pressure method. An MKS baratron was used to measure gas pressures. The mixture was stirred with a fan in the vessel for 10 min and left quiet for 1 min before ignition. In the case of USBM-type vessel, the gases were mixed in a separate container and introduced into the vessel before ignition. For each experiment, the flame movement was recorded with a video camera. Where possible, the pressure change after ignition was recorded in the experiment.

Combustible gases used in the experiments were methane and propane. This is because they are typical hydrocarbon fuels and the exhaust gases resulting from these gases can be easily treated.

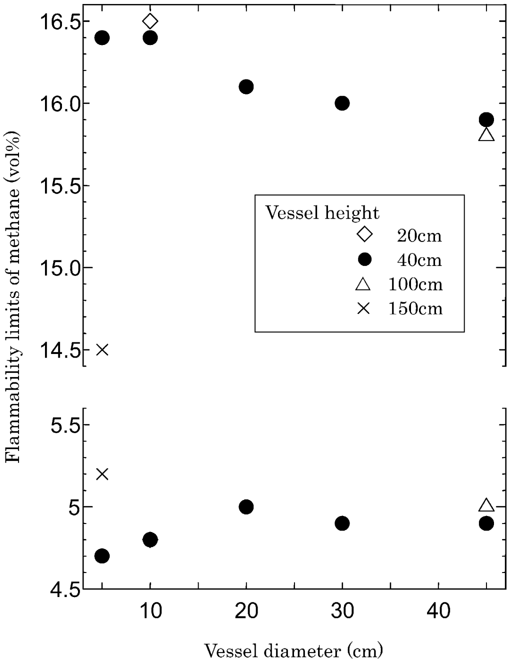


Fig. 2. Experimental flammability limits of methane measured in vessels of various sizes.

3. Results and discussion

3.1. Experimental flammability limits in cylindrical vessels of different sizes

As shown in Fig. 1, a wide variety of cylindrical vessels have been examined. The experimental flammability limits of methane and propane obtained for different vessels are summarized in Figs. 2 and 3, respectively. To measure the effect of vessel diameter, vessels of diameter 5, 10, 20, 30, and 45 cm were examined using a constant vessel height of 40 cm. The maximum value of the experimental flammable range was measured with the smallest vessel diameter of 5 cm both for methane and propane. In general, it was found that the larger the diameter the narrower the experimental flammable range. This finding is quite the reverse of what had been expected before the experiments. As regards the vessel diameter, it had been thought that the quenching effect of the wall is the largest factor that determines the experimental flammability limits, and it had been expected that the larger the vessel diameter the wider the flammable range would be.

By observing the video pictures from the experiments, it was found that the flame instantly expands to the full vessel size from the point of ignition if the gas in the vessel is a near stoichiometric fuel–air mixture. As the concentration of gas approaches the flammability limits the combustion becomes weaker and in the vicinity of the flammability limits a thin incipient flame travels up toward the vessel top. The flame behavior at this stage is particularly important to determine the experimental flammability limits in the vessel.

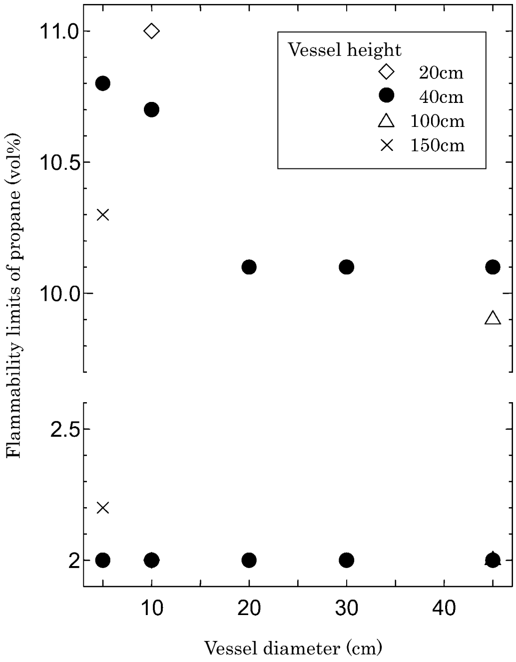


Fig. 3. Experimental flammability limits of propane measured in vessels of various sizes.

One of the characteristic features observed in the video pictures of flame propagation in near-limit mixtures is the turn-around of the incipient flame after its arrival at the vessel top. The thin incipient flame which reaches the vessel's top may or may not begin to turn back downwards. Whether or not this phenomenon occurs seems to be determined by a multiple factors. As the thin flame goes up from the point of ignition toward the top, the unburnt gas that fills the space surrounding the path of the thin flame is heated. At the same time, hot reacting gas is accumulated in the central region just beneath the top to produce a hot reaction zone. Then, suddenly a re-energized real flame may or may not be initiated in the hot reaction zone and start propagating downwards, engulfing the unburnt heated gas left in the space surrounding the initial flame path, and cause explosion. The occurrence of this phenomenon seems to be caused at least by two major factors: one is hot reacting gas accumulation which re-energizes the initial flame at the ceiling, and the other is unburnt gas heating which supports the downward propagation of the flame in mixtures of near-limit concentrations.

The explosion vessel described in DIN 51649 standard is of interest [6]. The size of this vessel is quite small, i.e. 6 cm in diameter and 30 cm in height. More interesting is the fact that the DIN method employs an open system: the vessel is open to the ambient air through a tube at the top of the vessel. Therefore, no accumulation of hot reacting gas can occur at the top of the vessel. In spite of this, the flammable range of methane measured in this apparatus is reported to be 4.4–16.5% [6], which is even a wider range than the value obtained in this study with a 10 cm Ø × 20 cm vessel. If the vessel diameter is small, the incipient flame may be substantially strengthened by the heat which is radiated from the incipient flame itself and reflected by the vessel walls. In a cylindrical vessel, the reflection occurs in such a way that the reflected radiation is focused on the central line of the cylinder. Note that the emitter of radiation is the most efficient absorber of the radiation from the emitter itself. Furthermore, it is probable that the incipient flame is supplied with more than enough energy from the ignition source in this case, because the DIN method employs ac spark ignition with neon transformer with spark duration of 0.5 s which is three times as long as 0.15 s recommended in the literature [2].

On the other hand, it is to be noted that among the explosion vessels used in the present study a USBM-type vessel of 5 cm in diameter and 150 cm in height has been found to yield by far the narrowest flammable range. Since the vessel is so high, it is not easy for the incipient flame to reach the vessel's top, the flame suffering from the quenching effect of the walls. Comparison of the result for tests in this vessel with the ones in other vessels may highlight the importance of the ignition energy in the flammability limits measurement. During the time the incipient flame travels upward along the central line of the tube, the flame may be given support by heat reflection from the walls as described above. However, at the initial stage of propagation, the flame cannot receive the supporting power of the vessel's top surface as described above. Therefore, the extra energy initially imported to the gas mixture as ignition energy from the spark may gradually be lost to the ambient, and eventually the flamelet will disappear. We may not be able to observe the flame propagation in this type of vessel unless a strong enough mixture is prepared that can overcome the quenching effect of walls all the way to the ceiling even after the excess energy originally given by the ignition source is completely lost away in the ambient.

Fig. 4 shows the behavior of incipient flame in 15.9% methane–air mixture for a time period of approximately 0.6 s starting from the moment of ignition in vessels of various sizes. The observations in four different vessels are shown: 20 cm Ø × 40 cm, 30 cm Ø × 40 cm, 45 cm Ø × 40 cm, and 45 cm Ø × 100 cm.

According to the data in Fig. 4(a), the vertical movement of the incipient flame does not vary much from vessel to vessel. As seen in Fig. 4(b), however, the growth of horizontal size (width) of the incipient flame in the vessel of 45 cm Ø × 100 cm is a little different from that in the other vessels. After about 0.4 s from ignition, the flame width seems to cease growing in this vessel while it continues to grow further in the other vessels. In particular, if the comparison is made between the two vessels of the same diameter 45 cm but different heights, 40 and 100 cm, such effects as the hot gas accumulation, unburnt gas heating, and self strengthening of the incipient flame do not give rise to any difference in the pattern of flame propagation in the two vessels up to this stage of propagation. On the other hand, the height of the flamelet approximately 20 cm above the ignition point at this stage is much lower than the top (100 cm) of the taller vessel. This result suggests that if the top is much lower than 100 cm, heat reflection at the top helps the incipient flame to keep growing.

Hot gas accumulation at the top as well as the heat reflection may be reduced if the vessel height is increased. This difference in vessel made the result obtained with the 45 cm Ø × 100 cm vessel different from that obtained with the 45 cm Ø × 40 cm vessel. The value obtained with the latter vessel was indeed wider than the former. Thus,

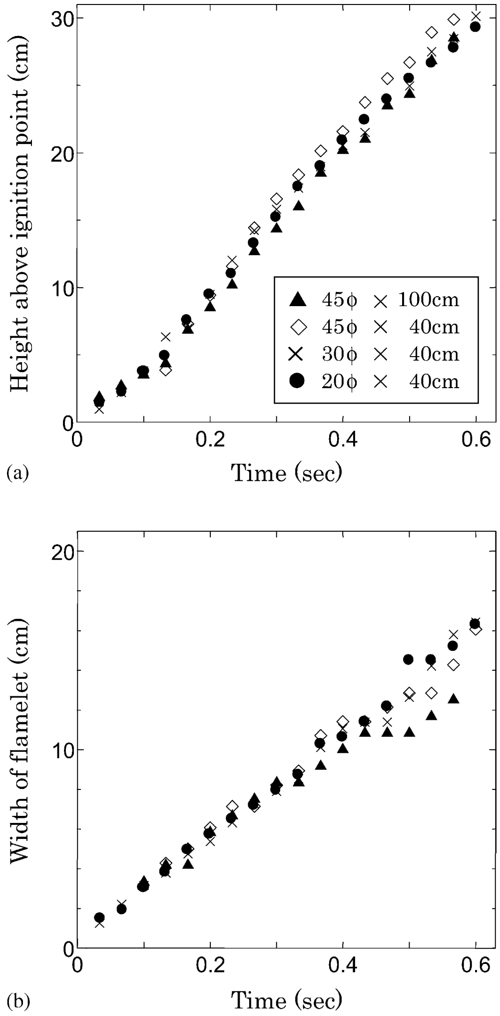


Fig. 4. Behavior of incipient flamelet after spark ignition of 15.9% methane–air mixture in cylindrical vessels: (a) vertical movement and (b) horizontal width of the incipient flamelet.

if both the height and diameter become large enough, all of the hot gas accumulation, unburnt gas heating, self strengthening of the flame, and heat reflection at the vessel top as well as the quenching effect of the walls may become small. Conversely, if both the height and diameter of vessels become small, all the foregoing effects may become large, and the flame encouraging power may supercede the quenching effect to enlarge the experimental flammable range. In addition, it should be emphasized that all these effects will be exaggerated if the ignition energy is in excess. Thus, it is essential to adopt the appropriate ignition condition for the correct measurement of flammability limits as well [2,3].

3.2. Additional experiments in jumbo cylindrical vessel

As stated, it is anticipated that the experimental values of flammability limits may approach one which might be obtained in the free space in an extremely large vessel. In connection with this prediction, the flame propagation behavior in the jumbo cylindrical vessel of 45 cm Ø × 100 cm was studied in more detail.

This aforementioned vessel was of glass and had three actuator valves, each 3 cm in diameter both on the top and bottom flanges. In the experiments, some or all of the actuator valves were opened just before ignition so that the overpressure resulting from the explosion was relieved to the ambient. Three different experiments were performed: (1) all six actuator valves were opened to the ambient before ignition, (2) only the three valves at the top were open, and (3) only the three valves at the bottom were open. The result is that practically the same experimental values of flammability limits have been obtained for all three cases, the obtained values being 5.0–15.8%. This is a remarkable result because, in general, the experimental values of flammability limits are extremely sensitive to this type of changes in the experimental condition. This experiment shows clearly that the present vessel size is large enough to measure the experimental flammability limits yielding results that are practically equivalent to what would be obtained in free space. In other words, in this vessel we can observe the flame propagation which is practically free either from the disturbance of vessel walls or from the disturbance of limiting height of the vessel top.

Table 1 is a summary of the observations made of flame propagation in methane–air mixtures in the jumbo cylindrical vessel. As stated, the observed value of flammable range of methane in this vessel is 5.0–15.8%. However, whether the flame can propagate in the mixture or not is very clear. Once the gas concentration enters into the flammable range, an explosion occurs. Reproducibility of the occurrence or non-occurrence is very clear indeed. Just outside the flammable range, the initial flamelet grows to a certain size but eventually fails to propagate and disappears. The size and the height up to which the initial flame can grow seems to be determined solely by concentration. In the lower limit region of methane, the initial flame reaches a height of approximately 20 cm above the ignition point and its

Table 1
Behavior of incipient flame in near-limit mixtures of methane in air observed in a jumbo vessel

Methane concentration (vol.%)	Lower limit region						Upper limit region				
	4.84	4.95	4.97	4.99	5.01	~	15.79	15.82	15.85	15.89	16.04
Explosion (○), non-explosion (×)	×	×	×	○	○	○	○	○	×	×	×
Max height traveled above ignition point (cm)	18	22	24	–	–	–	–	–	30	29	26
Maximum width of flamelet (cm)	6	10	13	–	–	–	–	–	12	10	9
Time up to the moment of quenching (s)	0.3	0.4	0.5	–	–	–	–	–	0.5	0.5	0.5
Ratio of maximum and initial pressures	1.00	1.01	1.01	>1.78	>1.92	–	>1.98	>2.14	1.01	1.01	1.01

Table 2
Behavior of incipient flame in near-limit mixtures of propane in air observed in a jumbo vessel

Propane concentration (vol.%)	Lower limit region						Upper limit region				
	1.89	1.99	2.02	2.05	2.08	~	9.81	9.87	9.92	9.98	10.05
Explosion (○), non-explosion (×)	×	×	×	○	○	○	○	○	×	×	×
Max height traveled above ignition point (cm)	14	21	28	–	–	–	–	–	62	46	46
Maximum width of flamelet (cm)	4	6	8	–	–	–	–	–	21	21	18
Time up to the moment of quenching (s)	0.3	0.5	0.5	–	–	–	–	–	1.3	1.0	0.9
Ratio of maximum and initial pressures	1.00	1.00	1.01	>1.35	>1.38	–	>1.76	1.14	1.01	1.01	1.01

horizontal size just before extinction is about 10 cm. The resulting overpressure is negligibly small. At the upper limit region, a similar thing happens and the initial flame reaches a height of approximately 30 cm above the ignition point. The time to reach the extinction point for these cases is approximately 0.5 s.

Table 2 summarizes the observations for propane–air mixtures. For propane, there is no difficulty in determining whether or not the flame can propagate in the mixture. Once the gas concentration enters the flammable range, an explosion occurs. The flammability limits of propane were 2.0–9.9%. Just below the lower limit, the initial flamelet grows to an approximate size of 5 cm and reaches a height of approximately 20 cm above the ignition point. The resulting overpressures are negligibly small. In the upper flammability limit region, the initial flame grows to a size of approximately 20 cm and reaches a height of 50 cm or more. The lifetime of the initial flame just outside the flammability limit is approximately 1 s in this case which is longer than that in the lower flammability limit region.

As stated, one of the important things concerning the phenomena that occur in the jumbo vessel is that the result is the same as would occur in free space. For methane–air mixtures, for example, the incipient flame which cannot grow into normal flame can grow approximately 10 cm and to a height of 20–30 cm. For the upper flammability limit region of propane, the non-propagating incipient flame can grow to as much as 20 cm and ascend to a height of 50 cm or more. It is desirable that the size of the explosion vessel used in the flammability limit measurements be large enough so as not to disturb the movement of incipient flames inside the vessel. Then, the size of cylindrical vessel should be at least 20 cm in diameter and probably 60 cm in height. Considering the result in Figs. 2 and 3, the vessel diameter of 30 cm is preferable.

3.3. *Experimental flammability limits in a spherical vessel*

In addition to the cylindrical type vessels, we have examined an ASHRAE-type spherical vessel to measure the flammability limits of methane and propane. The inner diameter of the vessel is 28 cm and the volume is 12 l, which is about the same as that of the cylindrical vessel of 20 cm in diameter and 40 cm in height. In ASHRAE's method, the determination of the flammability limits is made by observing the flame movement referring to an empirical criterion of 90° fan as measured from the point of ignition to the walls of the vessel [10,11]. If the flame is seen to override the 90° fan, the mixture is determined to be flammable and vice versa. This criteria are said to be obtained from a comparison of the results from the 12 l vessel and a big tube apparatus of 200 l vessel [12].

From measurements in the ASHRAE-type vessel, the value of 5.0–15.7% has been obtained for the flammability limits of methane. Similarly, the flammability limits of propane were found to be 2.0–10.1%. We have also carried out pressure measurement at early stages after ignition in the ASHRAE-type vessel to determine the flammability limits. From the rising point of the pressure in the vessel, the flammability limits of methane were found to be 5.0–15.9%, which is a larger range than obtained by the flame observation method. The flammability limits of propane were 2.0–10.3%. At any rate, the values of methane and propane obtained with the ASHRAE-type vessel are close to and can be taken as a reasonable approximation to the values obtained in the jumbo vessel.

4. Conclusion

We have carried out flammability limit measurements of methane and propane using various explosion vessels. As a result, we concluded that for a cylindrical vessel of 5 cm in diameter and 150 cm in height the flame quenching effect is the one that determines the flammability limits. For vessels of relatively small height, the flammability limits is determined by at least three factors in addition to the quenching effect of the vessel walls: (1) the hot gas accumulation just beneath the ceiling, (2) the unburnt gas heating during the time the initial flame travels up to the ceiling, and (3) the strengthening of the incipient flame by the heat radiated from the flame itself and reflected at the walls and ceiling of the vessel. For vessels of ordinary size, the total of these effects tends to surpass the quenching effect of walls to widen the experimental flammable range. However, as the vessel diameter and the height are increased they gradually become small. Eventually, all these effects including the flame quenching effect may become negligibly small and the experimental flammability limits converge to a certain value, which one would obtain if one can measure the flammability limits in the free space.

One of the fundamental questions is how small an experimental vessel can be made in order to economize but still proving experimental condition practically equivalent to that in the free space. If a cylindrical vessel is used, it is desirable that the diameter should be at least 30 cm and the height at least 60 cm.

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