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Microwave Heating of Organic Solvents : Thermal Effects and Field Modelling

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Abstract : Superheating of ethyl and methyl alcohols (under microwave in a monomode cavity has been studied), in connection with field modelling. Non-even field distribution can seems to induce a lack of reproducibility in measurements and superheating.

INTRODUCTION

For the last several years, published results concerning the effects of microwave heating in organic reactions remain unclear. Particularly in the case of the Diels Alder cycloaddition the main problem encountered is the lack of reproducibility of the results. The model reactions that we have studied, under reflux of the solvent, have presented a rather broad dispersion of the experimental results whether done under microwave irradiation or not[1].

One of the basic problems in microwave heating concerns the question of the boiling point of liquid undergoing irradiation, and our objectif is to study this effect and to conclude about the reproducibility on chemical reactions.

Several years ago studies on the boiling point of polar liquids under microwave heating were carried out and many authors have establised that microwave heating seems to play a role in the physico-chemico properties of these solvents. Noteably Roussy *et al.*[2] have clearly established that the enthalpy of vaporization is the same under microwave and conventional heating, but that the rate of evaporation is dependent of microwave intensity.

Much work has been carried out on the evaporation of liquids under microwave heating by Lallemant's group which includes the authors : Abtal *et al.*[3,4] , Stuerga *et al.*[5-10], Steinchen *et al.*[11] and Courville *et al.*[12]. They have also shown that the rate of vaporization, and the temperature of both vapour and liquid at the liquid/vapour interface strongly depend on the experimental conditions and particularly on the absorbed microwave power[3,4]. We note that these experiments were carried out under reduced pressure, for a low microwave input power, and it has been shown that the nature of hydrodynamic behaviour of water and ethyl alcohol during evaporation induced by microwave heating results directly from the thermal dependency of the dielectric loss of the concerned solvents. Futhermore, Baghurst and Mingos have shown that organic solvents undergo superheating above their conventional boiling points in a microwave oven[13,14].

This has prompted us to further investigate the variation of the boiling point temperature of a liquid under a microwave field to that of a liquid under conventional heating : the modelling of the electric field in the reactor allows us to predict the variation of the two boiling point temperatures as a function of the intensity of the electric field absorbed by the solvent.

EXPERIMENTAL RESULTS

The study consists of a comparison of the boiling point temperature found when methyl and ethyl alcohols are heated under microwave and conventional heating. Futhermore the influence of the experimental conditions on the boiling point temperature has been investigated and the parameters have been studied boiling chips, thermal insulation of the reactor, silylation of the internal surface of the reactor and microwave input power.The temperature was measured by a fiber optic thermometer (Luxtron). Typical results are illustrated in figure 1 where we remark that after a rapid increase of the temperature, a plateau region at a constant temperature (±1° C range) is observed as the liquid begins to reflux. The temperature measured on the plateau region is considered to be the boiling point temperature. It can be seen that under conventional heating no superheating occurs and that the measured temperature is reproducible and corresponds, within experimental error, to the reported litterature data. This observation validates the method here used for the measurement of the boiling point temperature. Under microwave heating the temperature of the ethyl alcohol passes through a maximum before reaching its boiling point. At this point, the liquid undergoes minor explosions as the refluxing starts up. The temperature the drops down to the plateau that we consider to be the boiling point. This transient superheating can reach temperatures as high as 20° C and may persist for a few minutes (figure 1b). It has never been observed with methyl alcohol, and this is consistent with previous observations[13,14].The values of boiling point temperatures obtained as a function of the reaction conditions are reported in figure 2 and 3 for ethyl and methyl alcohol respectively. Experimental temperatures at the plateau region found under conventional heating (see entry 2) are compared to those found under microwave heating (see entries 3 - 7). The input power used is about 40 Watts.The study of the influence of microwave input power was carried out in a silylated quartz reactor without boiling chips as shown in entry 5 figure 3 and in entry 6 figure 2. The use of a treated reactor was decided by the fact that the silylation permits a better reproducibility of the results yet still maitains a considerable difference between boiling point temperatures found under microwave and under conventional heating. The results are illustrated for ethyl alcohol in figure 4, but similar results are obtained with methyl alcohol. The power increases from 100 to 800 watts and each measurement is run about ten times.

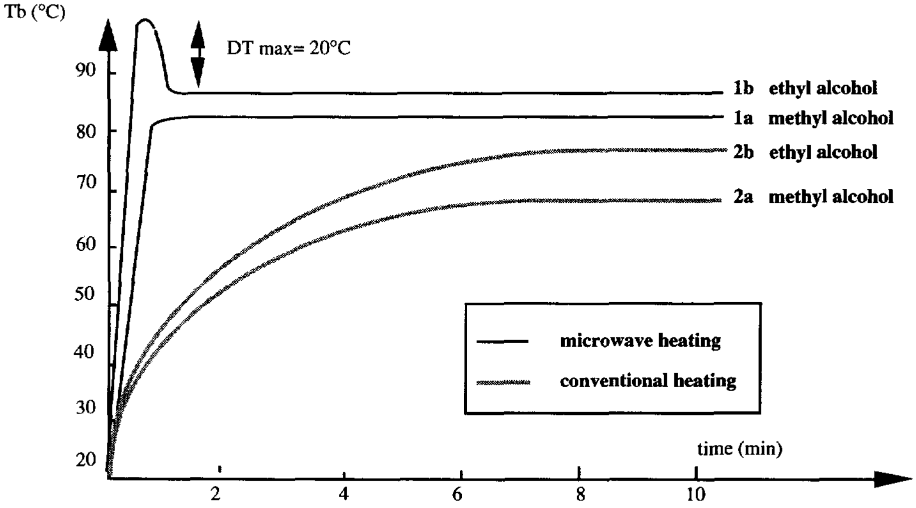

figure 1 : temperature profiles

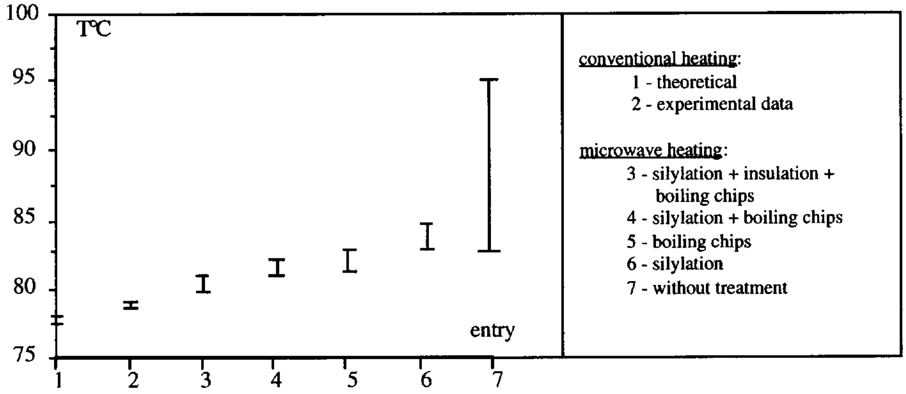

figure 2 : superheating of ethyl alcohol

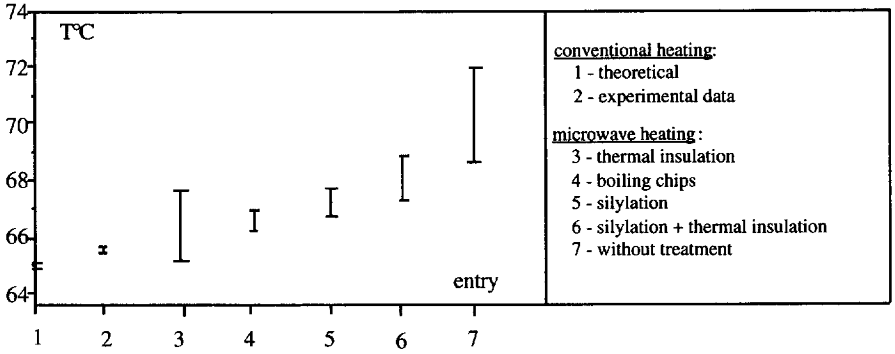

figure 3 : superheating of methyl alcohol

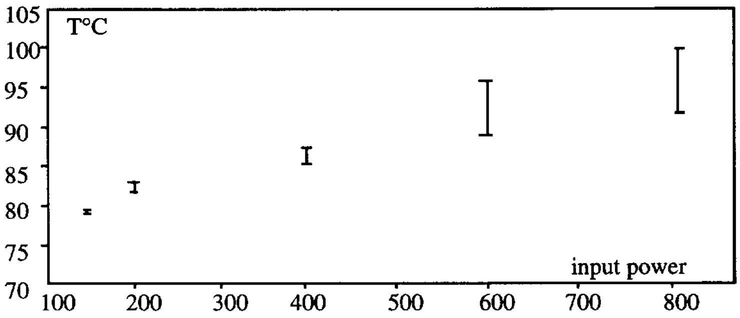

figure 4 : influence of the input power on the boiling temperature of ethyl alcohol

INTERPRETATION

Influence of the experimental conditions :

A set of experiments carried out at a given input power and microwave heating has shown that superheating is always observed and depends on the experimental conditions. Without a silyation treatment of the reactor, see entry 7, the temperature of the plateau region changes dramatically within the range of 82-97°C for ethanol and 69-73°C for methanol from one experiment to another, under apparently identical irradiation conditions (same input power setting, same tuning of the cavity). These temperatures changes occur randomly, although two or three consecutive runs may give identical results within experimental error (±1°C). The origin of this superheating effect has been discussed[13,14] and it has been concluded that the fiber optic thermometer gives a measurement of the bulk temperature while the boiling phenomenon, nucleation, occurs at the "cold" internal surface of the reactor. Our observations are in good agreement with those reported by Baghurst and Mingos, [13,14]although their apparatus used was quite different from ours. However, with the non-treated reactor, we have found a much smaller superheating effect (respectively 6°C and 12°C for methyl and ethyl alcohol) than that reported by Baghurst and Mingos[13] which was greater than 20°C. This observations corroborate that microwave heating results in “reversed heat transfers” (from the irradiated medium to the outside). Our reactor is small (10 ml) and located in a monomode cavity, while Baghurst *et al.*[13] used a much bigger reactor (200 ml) located in a modified domestic oven, which is a multimode cavity. Therefore, input power, electric field distributions obtained in the medium and heat loss are different. This can account for the observed differences in superheating found between the two works. Thermal insulation of the reactor gives somewhat similar erratic results but lowers the variations of the temperature under microwave and conventional heating as illustrated in figures 2 and 3 for ethyl and methyl alcohol respectively. This effect was expected and may be due to lower heat loss as the temperature of reactor’s wall is close to that of the liquid bulk. Reproduicibility of results is better for both solvents when the inner surface of the glass reactor is silylated, when boiling chips are added or when a combination of silylation, insulation and the boiling chips occurs (see entries 3, 4, 5, 6). The silylation decreases the wetting properties of the quartz and the boiling chips increase the number of nucleation sites. Moreover, in all these experiments superheating is significantly lower than with the non "treated", non insulated reactor.

Influence of microwave power :

The investigation of the influence of the input power on the temperature of the plateau region has shown that superheating increases with input power and simultaneously reproducibility decreases. The temperature corresponding to the plateau region results from an equilibrium between the dissipated energy and the heat loss experienced. It seems likely that the energy is dissipated faster than heat loss, and this can explain the observed increase of the superheating. The microwave power dissipated into heat in the medium is not homogeneous and the local temperature is partly a function of the input power.

The classical laws between the microwave power, the absorbed power and characteristics of the heated medium can be written as follows :

$$P_{abs} = P_{inp} - P_{out}$$

$$P_{abs} = \pi \nu \varepsilon_0 \varepsilon_r' \, tg\delta \, |E_{loc}|^2$$

where

- P_{asb} is the power absorbed by the medium (W m^{-3})
- P_{inp} and P_{out} are respectively the input and ouput powers (W m^{-3})
- ν is the frequency (Hz)

- ε_0 is the vacuum permittivity (Farad m^{-1})
- tgδ is the medium's ability to heat under microwave
- $\varepsilon_r = \varepsilon_r' (1 - j\, tg\delta)$ is the medium permittivity
- E_{loc} is the local electric field (V m^{-1})

All these observations prompted us to investigate the local electric field at a given time in a cavity containing different solvents and to compare the results found.

FIELD MODELLING AND DISCUSSION

This modelling of the electric field intensity absorbed by the solvent has been carried out using a finite elements method[15]. Dielectric values of ethyl and methyl alcohol necessary for the calculations were already determined.

In this simulation, the Oy axis corresponds to the direction of the electric field and the Oz axis to the direction of the wave's propagation as seen in figure 5.

A two-dimensional field modelling was made along the Ox and Oz axes of the wave guide. There is theoretically no field variation along the Oy axis because the reactor along this axis is considered to be an object of infinite dimension. The Ox axis admits a symmetrical electric field. The amplitudes of the electric field E were normalised as $|E| = 1$ at the entrance of the guide. As a consequence only the variations of $|E|$ along the Oz and Ox axis should be considered.

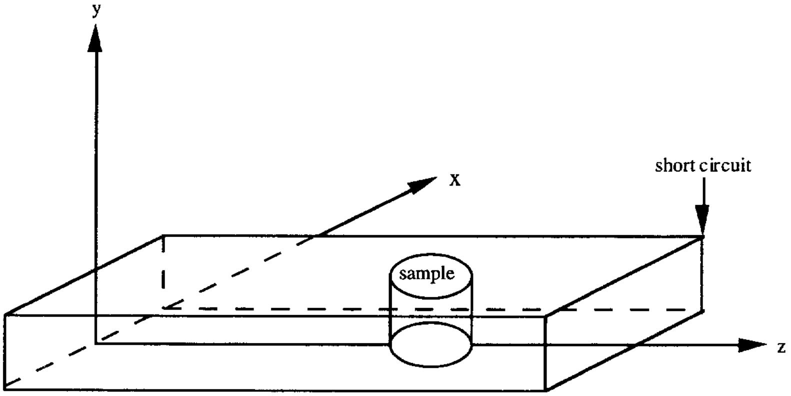

figure 5 : microwave cavity

Results and discussion :

Firstly, the electric field was calculated in the empty wave guide, then in the wave-guide containing the quartz reactor and lastly with the quartz reactor filled with ethyl or methyl alcohol. For the alcohol these experiments were carried out at two different temperatures : room temperature and boiling point temperature of the respective solvents. The presence of the reactor does not significantly change the field distribution in the guide. Figures 6 and 7 show the electric field distributions E(z) with or without solvent for ethyl and methyl alcohol respectively. In figure 8 is illustrated the electric field for both solvents near their boiling point temperatures. Figure 9 illustrates the electric field distribution E(x) for both solvents.

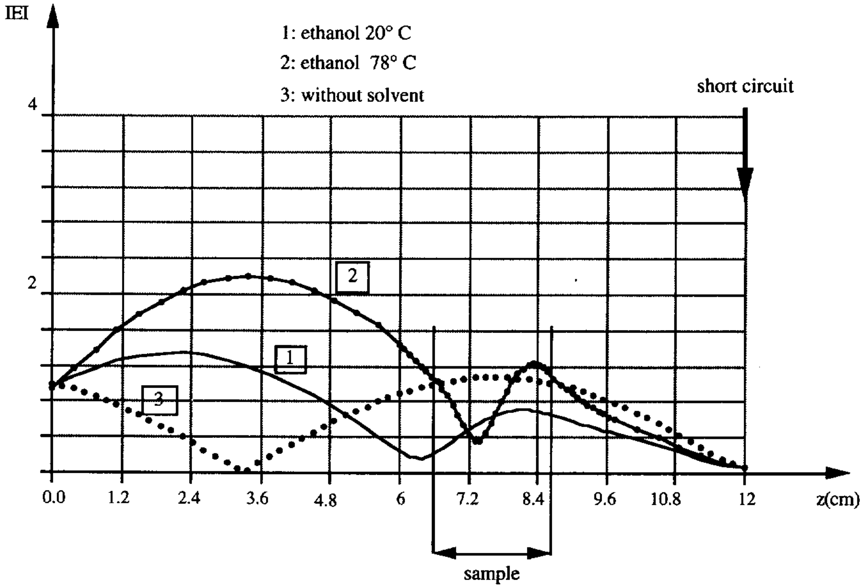

figure 6: field modelling with ethyl alcohol along the oz axis of the waveguide

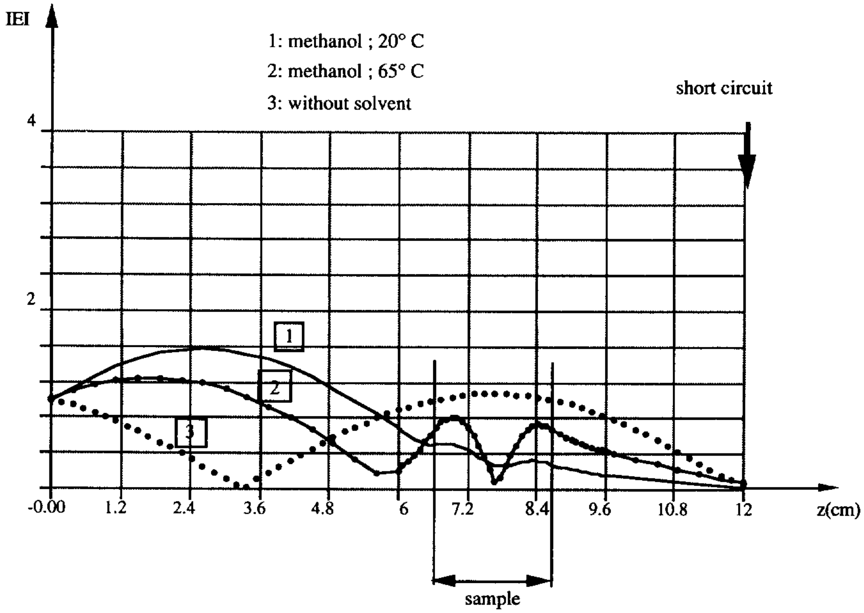

figure 7 : field modelling with methyl alcohol along the oz axis of the waveguide

It can be seen that with a small reactor placed in a monomode waveguide the field intensity is far from being homogeneous in the liquid and strongly depends on the nature of the solvent as well as on the temperature. As the dissipated energy is proportional to the square of the electric field's amplitude the energy distribution and dissipated power change from one point to another in the guide. This heterogeneity of the observed power which changes with time, induces the formation of hot and cold zones in the medium. Unfortunately the time response of the temperature probe is extremely long with respect to the heterogeneity and therefore the measured temperature is an average value.

The input power increase, induces a greater heterogeneity of the electric field and this phenomenon can explain the reason for the decrease of the reproducibility with the increase of the input microwave power.

From the mean values of the electric field it is possible to calculate the ratio of the absorbed power between ethyl and methyl alcohol . At the boiling temperature, this ratio (Pabs(ethyl alcohol) / Pabs (methyl alcohol)), is about 5. It is in good agreement with the fact that superheating is greater for ethyl alcohol than for methyl alcohol, and this in general because with a great input power an increase of superheating occurs.

It is quite clear that microwave heating, due to the direct energy (heat) dissipation occuring inside the reaction mixture, is different from conventional heating[13]. "Hot spots" have been observed at the surface of liquids, with an Infra-Red camera[3], but they could also occur in the solution bulk if the energy dissipation due to dielectric loss inside the reaction mixture is faster than heat transfer.

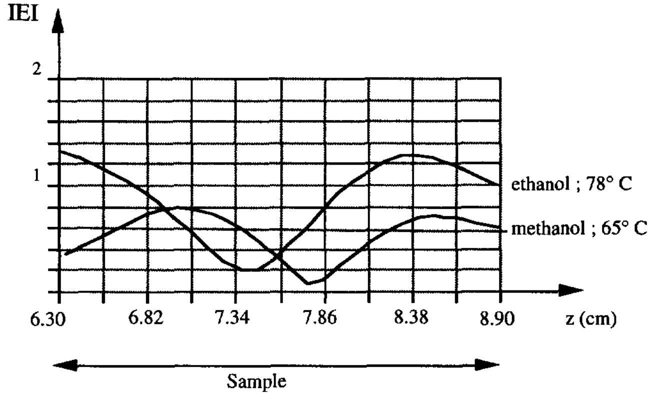

figure 8 : field distribution inside the reactor with ethyl and methyl alcohol

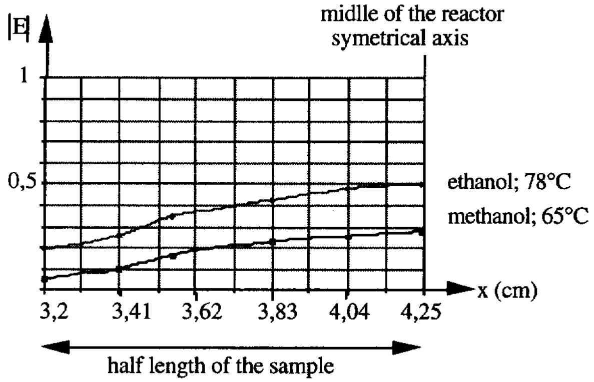

figure 9 : field distribution inside the reactor with ethanol and methanol along the Ox axis

CONCLUSION

The main observations that can be be made from this work are :

- The boiling point temperature of solvents under microwave heating depends on the experimental conditions. These include noteably the dissipated power, the volume of the reactor and its surface/ volume ratio which induces a variation of heat loss, the number of nucleation sites and the surface properties of the reactor.

- An increase of the input power induces a poorer reproducibility due to a greater heterogeneity of the electric field.

Monitoring of experimental conditions appears to be of crucial importance for chemical reactions under microwave heating, especially when the reactions are carried out at solvent reflux. The non conventional thermal effects on chemical reactions as the Diels Alder reaction yet studied, under homogeneous conditions remain unclear (as already mentioned, the problem is quite different under heterogeneous conditions).

It is quite clear that further progress will rely on better handling of the experimental conditions, in particular of accurate measuring of the input and absorbed powers, and of better tuning of the monomode microwave guide.

As a consequence a fundamental question arises: what is the real meaning of temperature measurement under microwave heating? The importance of this point is crucial when comparative kinetic studies using microwave or conventional heating are carried out.

EXPERIMENTAL

Microwave device : The microwave system consists of two main parts. First of all, the magnetron working at a frequency of 2.45 GHz and the secondary waveguide, giving a TE_{10} mode propagation. The waveguide is fitted with : an EH tuner forthe minimization of the reflected power ; a circulator and a water load to absorb the reflected power and to protect the magnetron and a directional coupler equipped with two probes connected to a Hewlett Packard 438A wattmeter, in order to measure input and reflected power.The microwave device is depicted in figure 10.

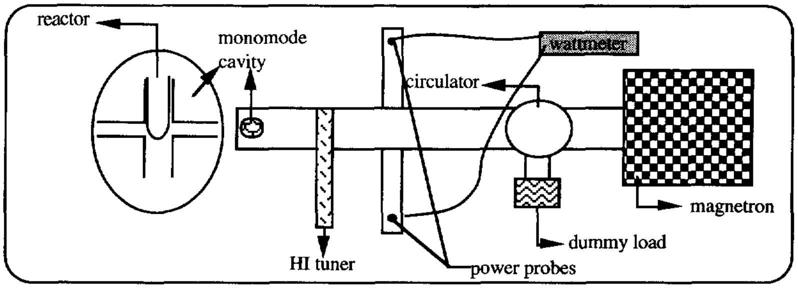

figure 10 : microwave device

The reactor having a diameter of 3 cm is located $\lambda/4$ cms away from the short circuit, and is protected by brass tubing in order to avoid a leakage of waves. The reactor is dipped into the waveguide through a teflon guide which assures correct positioning.

The microwave heating is carried out in a test tube (internal diameter 20 mm), fitted with a condenser. Experiments are run at atmospheric pressure. The temperature is measured with a fiber optic probe (Luxtron) connected to a bravo 286 computer. In a typical run, 10 ml of ethyl alcohol (ethyl alcohol absolu, Prolabo rectapur, % cpg 99,5) or methyl alcohol (prolabo rectapur, % cpg 99) are introduced into the reactor (previously washed with acetone, then rinsed with the alcohol in question, and dried with filtered air). The regularly calibrated fiber optic probe is inserted into a quartz capillary tube in order to protect it, and is then passed through the condenser. It is located in the middle of the reactor. One must check that when inserting the probe into the capillary tube it does not change the measurement of the temperature.
The silylation of the reactor is done by refluxing a mixture of 5ml of dimethyl dichlorosilane, 5ml of chlorotrimethyl silane, 2ml of triethylamine in carbon tetrachloride as the solvent for 4 hours. The boiling chips are dried in an oven before use. Thermal insulation is achieved by inserting the reactor into a polystyrene jacket.

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