

## **The Leidenfrost Reactor: A new general purpose direct-cooled reactor and its use for low temperature polymerizations**

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### Summary

Inspired by the Leidenfrost phenomenon a direct-cooled general purpose low-temperature reactor has been developed and its applicability for polymerizations was demonstrated. The Leidenfrost reactor is efficiently cooled by introducing relatively inexpensive liquid  $N_2$  ( $LN_2$ ) directly into the bulk of polymerization charges and the rapid evaporation of the coolant chills the system. The gaseous  $N_2$  generated provides an inert gas blanket that protects moisture and/or air sensitive charges. The installation of expensive cooling jackets or coils is superfluous and stirring is optional. The virtually complete recovery of cooling energy is possible. In the Leidenfrost reactor the  $LN_2$  heat sink is virtually in contact with the heat source so that the path of heat transfer is practically nil. Reactor fouling is eliminated which is of particular interest in butyl rubber manufacture. Constant temperature control is readily accomplished by regulating the input rate of the coolant and undesirable temperature jumps are suppressed. Continuous operation is possible. The operation of the Leidenfrost reactor is illustrated by the polymerization of isobutylene at  $-60^\circ C$ .

### Introduction

Cooling, particularly to cryogenic temperatures, is expensive and the cost of cooling energy can only rise in times ahead. Large or pilot scale cooling of chemical reactors is usually effected by means of external or internal cooling jackets or coils containing a circulating coolant. In laboratory practice reactors are conventionally externally cooled by immersion in a cooling bath containing the heat sink. Rapid stirring is mandatory in all these instances. Inherent major disadvantages of these types of conventional refrigeration are the high cost of refrigeration equipment (e.g., compressors, cooling jackets, or coil systems, coolants, stirrers), the necessarily incomplete utilization of cooling energy input and the tendency of reactor fouling (see later).

Cooling, particularly at cryogenic temperatures, of air- or moisture-sensitive exothermic reactions are further complicated by the need of inert atmospheres (nitrogen, argon) with a constant slight positive pressure to prevent backdiffusion. For example, Friedel-Crafts syntheses in general and cationic

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polymerizations in particular are typical reactions that require efficient sometimes cryogenic cooling under an inert atmosphere. Thus an elaborate dry-box system had to be devised (1) which is in constant use in our laboratories (2) for carbocationic polymerization research that requires cryogenic cooling and the exclusion of moisture.

The purpose of this paper is to describe the principle and application of a new type of inexpensive polymerization reactor that operates at low temperatures (from  $-180^{\circ}$  to  $-10^{\circ}\text{C}$ ) by injecting liquid nitrogen directly into the reaction medium. The instantaneous flash-evaporation of liquid nitrogen provides a large number of small bubbles (Leidenfrost phenomenon, see below) and thus efficient turbulent agitation (eliminating the need for special cooling equipment, stirrers). Further, the cooling energy input may be virtually completely recovered by controlling the evaporation, and the gaseous nitrogen generated in this process provides a blanket of inert atmosphere. The operation of such a "Leidenfrost reactor" is detailed and its use for polymerization is illustrated.

#### The Principle: The Leidenfrost Phenomenon

The memorable Leidenfrost phenomenon occurs when, for example, a drop of water falls on a hot-plate or  $\text{LN}_2$  is spilled on the floor: The liquid breaks up in numerous small droplets which vigorously move about until they completely disappear by rapid evaporation. Evidently due to the large temperature difference between the droplet and the relatively hot surface, a small portion of the liquid instantly vaporizes upon contact and the droplet vigorously rolls around on a cushion of vapor until the liquid completely evaporates. The heat of evaporation of  $\text{LN}_2$  (50 kcal/kg (3)) is mainly provided by the surface. Similarly, when  $\text{LN}_2$  is injected directly into the bulk of another liquid, the  $\text{LN}_2$  instantaneously evaporates accompanied by vigorous bubbling; the heat of evaporation is provided by the liquid medium and the temperature of the medium decreases in proportion to the amount of  $\text{LN}_2$  used. This principle has now been exploited for the design of an efficient low-cost multi-purpose reactor for carrying out reactions at low temperatures under an inert atmosphere.

#### The Leidenfrost Reactor and Its Advantages

Figure 1 shows the scheme of a Leidenfrost reactor. To maximize the path-length of the ascending coolant bubble the reactor is preferentially cylindrical. It is desirable to lengthen the residence time of the  $\text{LN}_2$  in the reactor so that the bubble can completely vaporize before it reaches the surface of the charge. Under these conditions the cooling energy of the  $\text{LN}_2$  is most efficiently exploited. The rapid evaporation of the coolant, particularly when the temperature of the charge is above  $\sim -50^{\circ}\text{C}$ , causes strong foaming and thus agitation of the charge.

Since the heat source is the environment, the installing of expensive cooling surfaces (jackets or coils) becomes unnecessary and the desired temperature is maintained by controlling the input rate of the  $\text{LN}_2$ .

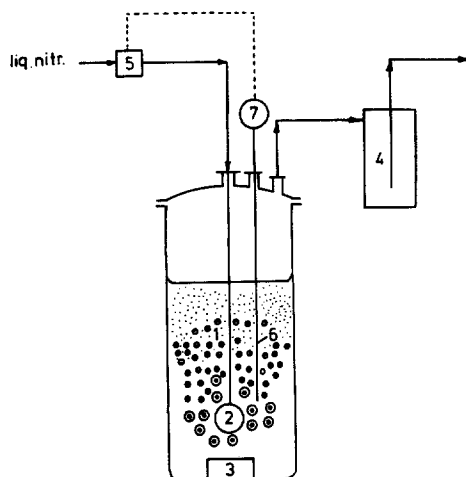
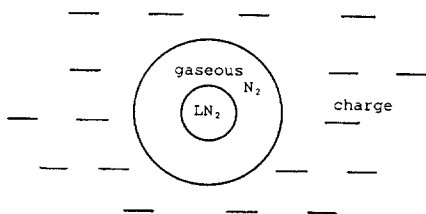


Figure 1. The Leidenfrost Reactor. 1. Reactor (3-5L Pyrex kettle) 2. Dispersion unit (glass bulb with 5 holes) 3. Stirrer (LABGLASS SPINSTAR LG-9558T) 4. Drop-trap 5. Magnetic valve (Gilmore 8263205LT) 6. Thermocouple (OMEGA HPS-RT-K-18G-12; 7. Regulator (OMEGA CN 7000)

A stream of  $\text{LN}_2$  is led into the charge by means of a glass tube ( $\sim 5$  mm ID) and is dispersed through a sparger, a hollow glass bulb ( $\sim 20$  mm D) with  $\sim 5$  holes ( $\sim 2$  mm). The efficiency of cooling is largely insensitive to the dispersion grade as long as a steady stream of  $\text{LN}_2$  is maintained. Too finely dispersed streams (e.g., by the use of porous glass frits) tend to cause freezing at the pores and thus clogging the inlets. The moment the  $\text{LN}_2$  hits the charge (whose temperature is usually much higher than that of the boiling point of  $\text{LN}_2$  ( $-196^\circ\text{C}$ )) the stream literally explodes into thousands of small bubbles composed of a  $\text{LN}_2$  core surrounded by a shell of gaseous  $\text{N}_2$ :



The  $\text{LN}_2$  droplet is insulated from the bulk of the charge so that freezing can be avoided. The formation of numerous bubbles decreases the average density of the charge which promotes agitation. Dissolution of  $\text{N}_2$  in the charge is of little importance since  $\text{N}_2$  may be considered an inert diluent.

The residence time of the  $\text{LN}_2$  droplet in the reactor may be extended by stirring or by the use of taller reactors (i.e., by scaling up). On the laboratory scale (3-5L) stirring is optional because of the strong boiling of  $\text{LN}_2$  provides sufficient agitation. In tall cylindrical industrial or pilot scale reactors (> 12L) stirring should increase the residence time of the ascending  $\text{LN}_2$  droplets and thus cooling is rendered more efficient. Indeed, larger Leidenfrost reactors are in general more efficient than smaller units in which the liquid  $\text{N}_2$  may reach the surface of the charge.

A major benefit of the Leidenfrost reactor is the ease and high rate it is able to compensate for sudden large temperature jumps. The area of the cooling surfaces in conventional reactors are necessarily limited and faster cooling can be achieved only by increasing the circulation rate of the coolant in the cooling jackets or coils. In these installations the maintenance of constant low temperatures may not even be possible in case of excessively rapid massive heat build-ups. In contrast, in the Leidenfrost reactor the area of cooling surfaces (number of  $\text{LN}_2$  droplets) can be virtually instantaneously increased in response to rapid temperature jumps by increasing the rate of coolant input. Also, the  $\text{LN}_2$  cooling "surface" is in virtual contact with the heat source so that the length of heat transfer is minimum. The flow rate of the coolant can be automatically regulated by connecting the input valve to a temperature sensing device (cf. Figure 1).

Another great advantage of the Leidenfrost reactor is that reactor "fouling" cannot occur. Fouling is the gradual accumulation of solids (i.e., polymer) on the cooling surfaces during operation which leads to a gradual reduction of cooling efficiency and ultimately to costly reactor shut-down. The cleaning of cooling surfaces is a cumbersome time-consuming operation. Fouling is quite common, for example, in butyl rubber manufacture where fouling necessitates the use of more than one (usually three) parallel reactors to ensure continuous operation: while one of the reactors is shut down for cleaning the rest are in operation.

Finally, the vaporizing liquid  $\text{N}_2$  also provides a blanket of inert gas which, particularly in smaller scale (pilot plant) operations, may be quite advantageous to protect moisture-sensitive charges.

The Leidenfrost reactor can readily be used in the continuous or semicontinuous mode. In continuous operations all the reactants and the liquid  $\text{N}_2$  are metered in simultaneously into the reactor and the effluent is collected by a suitable outlet system. In semicontinuous operations the product is allowed to accumulate in the reactor.

An equipment somewhat similar to the Leidenfrost reactor has been described (3), however, its use for the carrying out polymerization reactions has not been mentioned.

In sum, the directly-cooled Leidenfrost reactor is superior to conventional externally-cooled reactors in view of the following advantages:

1. Simplicity of design, inexpensive equipment, installation of cooling surfaces unnecessary.
2. Use of relatively inexpensive LN<sub>2</sub> coolant (by-product of oxygen production).
3. Complete recovery of cooling energy stored in LN<sub>2</sub> in the form of heat of vaporization is possible.
4. Vaporization of LN<sub>2</sub> yields environmentally unobjectionable non-polluting non-toxic gaseous N<sub>2</sub>.
5. The gaseous N<sub>2</sub> generated provides inert gas blanket and protects moisture- or air-sensitive reactions.
6. Ease of scale-up; larger units tend to operate more efficiently than smaller units.
7. Ease of constant temperature control; massive temperature jumps can be eliminated by automatically increasing coolant input.
8. Can be readily converted to continuous operations.
9. Eliminates fouling problems.
10. Stirring optional, may be useful in large (>100 L) reactors; boiling liquid N<sub>2</sub> provides agitation and a reduction of the average density of the charge.

In view of these characteristics the Leidenfrost reactor was adopted for the low temperature polymerization of isobutylene and copolymerization of isobutylene-isoprene (butyl rubber) charges.

#### Polymerization of Isobutylene by the Use of a Leidenfrost Reactor

A Leidenfrost reactor has been built of commercially available components and its operation tested by carrying out isobutylene IB polymerizations using a recently developed "living" initiating system i.e., dicumyl acetate/BCl<sub>3</sub> (4) and methylene chloride as diluent at -60°C. Figure 2 shows the flowsheet of the polymerization unit and the caption specifies the components used.

First diluent (CH<sub>2</sub>Cl<sub>2</sub>, 1500 mL) and initiator (DiCumAc, 1.37 g, 0.005 mole) were charged into reactor 1. The charge was cooled to -60°C and agitated by the direct introduction of LN<sub>2</sub> into the reactor. The coolant was delivered pneumatically from a LN<sub>2</sub> Dewar container 3 and its flow rate was automatically regulated by the magnetic off-and-on valve 5 connected to the temperature regulator-sensor 8. The charge was cooled from ambient to -60° in about 25 mins, and subsequently the temperature was maintained to ± 1°C.

Monomer (isobutylene, 23.5 g, 0.42 mole) and coinitiator (BCl<sub>3</sub>, 14.6 g, 0.12 mole) were vaporized from the evaporators 7 and condensed into the jacketed dropping funnels 2. When the working temperature is under -50°C the off-gas exiting gaseous N<sub>2</sub> provides sufficient cooling to liquefy the monomer and initiator. However, if the temperature is higher than ~ -50°C, a trap 6 should be used. The exiting cold N<sub>2</sub> gas cools the trap 6 below the dew point and thus prevents moisture back-diffusion from the atmosphere. The use of drying tubes is unnecessary (indeed they may create problems by increasing the pressure in the reactor).

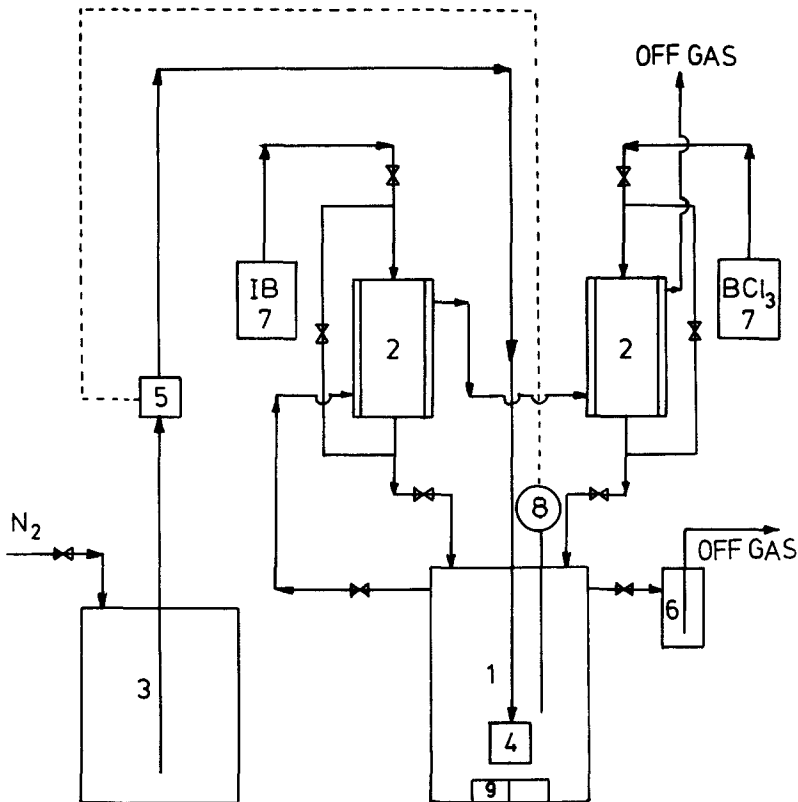


Figure 2. Flowsheet for the Polymerization of Isobutylene Using the Leidenfrost Reactor. 1. Reactor 2. Jacketed dropping funnels 3. Liquid nitrogen tank 4. Dispersion unit 5. Magnetic valve 6. Droptrap 7. Evaporators 8. Thermocouple and regulator

After the liquefied IB is introduced into the reactor the polymerization is started by rapidly adding the liquefied BCl<sub>3</sub> coinitiator to the charge. Polymerization occurs instantaneously and is perceived by a faster boiling of the liquid N<sub>2</sub>. In contrast to conventional operations, a temperature jump was not observed. After the desired polymerization time (15 mins) the reaction is quenched by the addition of prechilled methanol (100 mL) through one of the dropping funnels 2. The characteristic pale yellow color of the active polymerization charge is instantaneously discharged. After a few additional minutes the feeding of LN<sub>2</sub> is discontinued and the charge is allowed to warm to ambient. The routine polymer work-up procedure has been described (2,4).

In the above specific example conversion was 100%, with PIB  $\bar{M}_n = 8200$  and  $\bar{M}_w/\bar{M}_n = 2.4$ . According to <sup>1</sup>H NMR spectroscopic analysis the expected aromatic initiator residue

(resonance at 7.2 ppm) has been incorporated into the PIB chain. The Leidenfrost reactor is now routinely used in our laboratories for a large variety of polymerizations.

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