

# Molecular Distillation of Thermally Supersensitive Liquids

W. A. FRANK and H. D. KUTSCHE

ENAE<sup>R</sup> GLASWERK SCHOTT & GEN., Mainz, W. Germany

► By using an all-glass apparatus with a special device to distribute the film of the liquid to be distilled, it is possible to distill and separate thermally supersensitive liquids up to a molecular weight of approximately 2000. The apparatus is briefly described. New results of distillation experiments are reported. The reasons for the unusual separating power at higher molecular weights are discussed.

**M**OLECULAR DISTILLATION is a process by means of which it is possible to distill thermally labile substances that would be decomposed if ordinary distillation processes were applied. To protect such materials from thermal destruction they are distilled at the lowest possible temperature in high vacuum. The physical and chemical principles of molecular distillation are well known. Different types

of apparatus are described in (2) and (5). An optimum seemed to be reached by the construction described in (3).

Many experiments have been carried out to improve the apparatus mentioned last. However, it was not possible to obtain a higher degree of separation power (1), nor was it possible to distill material with a molecular weight higher than 1200.

## EXPERIMENTAL

**Effect of Constructional Material and Design of Apparatus.** It is known that the pump fluids in metal oil diffusion pumps show a higher degree of decomposition than the same pump fluids used in pumps made of glass (4). This observation led us to the idea that an all-glass apparatus for molecular distillation should enable one to avoid catalytic decomposition of thermally sensitive materials. Highly durable borosilicate glass, which also has very good mechanical and thermo-

mechanical properties, seemed to be the best material from which to build an apparatus for molecular distillation. In contrast to other all-glass apparatus, a device had to be installed which spreads the liquid to a thin film and revolves the film continuously. Thus catalytic and thermal decomposition can both be avoided. The design of such an apparatus is shown in Figure 1.

The substance, degassed in the usual manner, flows down the outer surface of a cylinder which is heated from the inside. This cylinder is surrounded by a rotating coil. After a short flow-path the liquid is taken up by the coil which is closely fitted to the cylindrical heating element.

Coil and heating element are roughly match-ground. Thus the coil is able to spread out the liquid in the form of a smooth and thin film (Figure 2). During rotation of the coil the film of the liquid is continuously turned over because of the rough contact of both surfaces. Immediately afterward, the coil releases the evaporation surface again, so that the molecules of the lighter volatile constituent that have risen to the surface can evaporate. This procedure is repeated after every turn of the coil. If a suitable distillation temperature has been selected, the whole lighter volatile constituent will finally evaporate from the surface of the condenser without any unnecessary superheating taking place, while the residue drips off the heating cylinder and flows into the flask. The fact that the heating finger and coil are made of glass is of utmost importance, because thermolabile organic substances are catalytically cracked by glass only to a very insignificant extent.

**Dimensions of Apparatus.** All experiments mentioned in this article have been carried out with the apparatus shown in Figure 1. Supple-

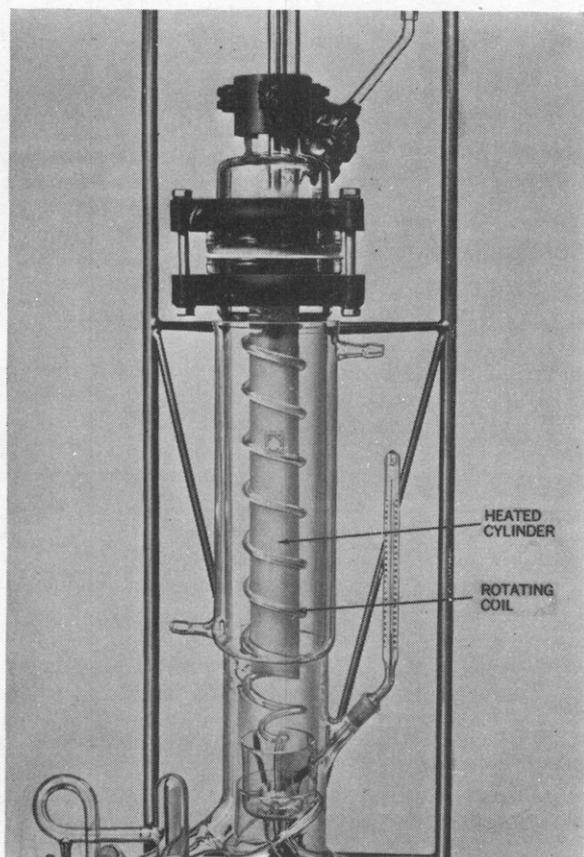


Figure 1. Main elements of apparatus

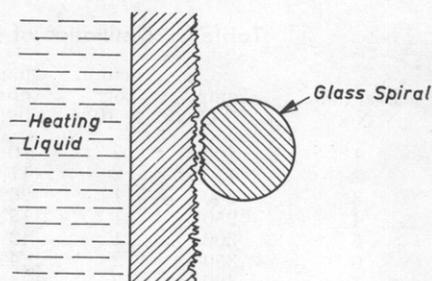


Figure 2. Principle of revolving film of liquid by rough-ground-glass surfaces of heater and coil (glass spiral)

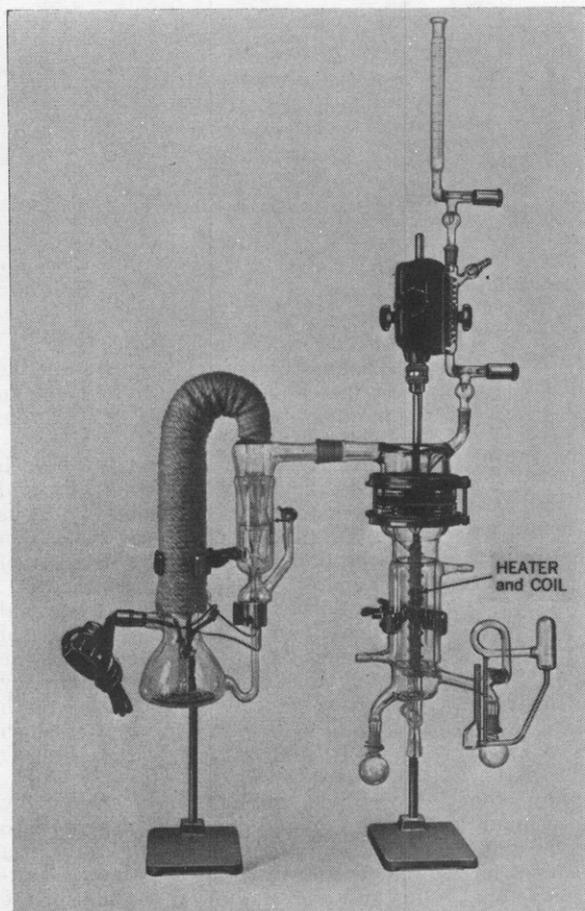


Figure 3. View of apparatus for distillation of small volumes

mentary parts such as vacuum equipment and thermometers are not described in detail.

The apparatus used has a maximum throughput of 1 liter per hour. However, two other modifications of the same apparatus have already been developed. One of them has a throughput of 0.1 liter per hour and allows distillation of very small amounts (5 ml.) of material (Figure 3). The other one has a throughput of 7 liters per hour. Figure 4 compares the sizes of the three types of apparatus mentioned. It shows the coils which distribute the film of the liquid on the heating element.

Although the development of the

large modification is not yet complete very interesting results concerning the distillation of thermally sensitive materials are anticipated with this apparatus too.

#### RESULTS OF DISTILLATION

The distillation results achieved with the apparatus described prove the validity of the considerations outlined above. The quality of the separation and distillation of liquids containing substances of a molecular weight up to

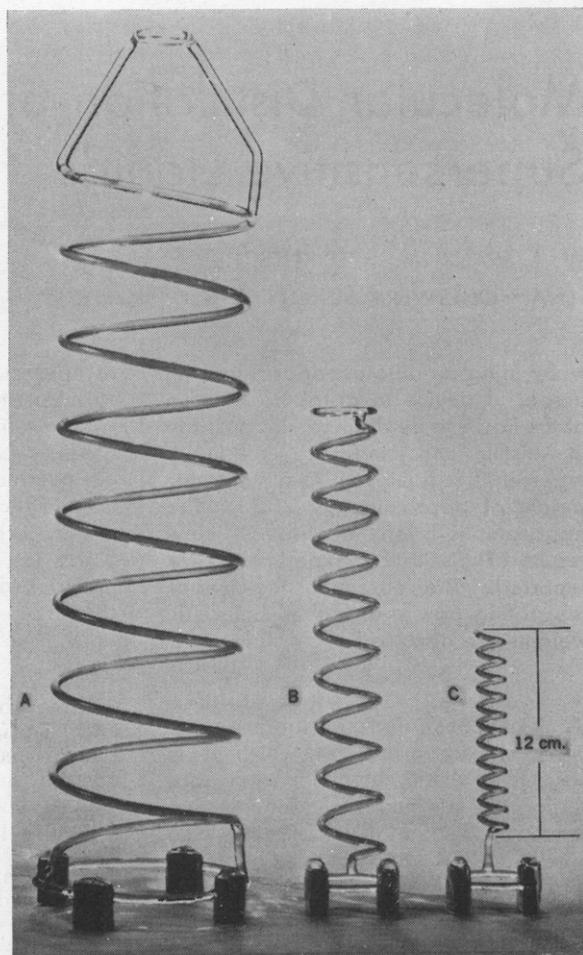


Figure 4. Comparison of sizes of coils for apparatus with throughput of 7 liters/hour (A), 1 liter/hour (B), and 0.1 liter/hour (C)

2000 is shown in Table I. The original material was a residue of petroleum oil. If this substance is distilled in one of the usual apparatus under a vacuum of 1 torr and an upper temperature of 230° C., a high amount of cracking occurs. By using our apparatus and under the conditions shown in Table I, it was possible to separate 97.4% of the whole product as distillate. It should be pointed out that the molecular weight of the eighth fraction distilled at a temperature of 450° C. is 1820.

A second example is given in Table II. It shows the results obtained with a glyceric oil. Very interesting in these results is the high resolving power of the apparatus. Before distillation the palm oil showed the following constants: acid number, 11.2; saponification number, 196.1; iodine number, 57.3. The high acid number of the first fraction indicates that here mainly free fatty acids are present. A small amount of free fatty acids can also be found in the second fraction containing the bulk of carotene which can be identified by its deep red color. After separation of fraction 1 and 2, amounting to only 7%, the palm oil is absolutely free from

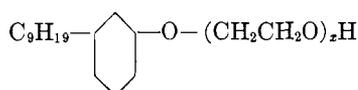
Table I. Distillation of a Residue of Petroleum Oil

Fraction No.	Temp., ° C	Vacuum torr $\times 10^{-4}$	Quantity of distillate, %	Total share, %	Molecular wt.	Refractive index $n_D^{17}$
1	100	2	10.15	10.15	362	1.4461
2	150	2	17.20	27.35	512	1.4482
3	200	1	26.70	54.05	634	1.4532
4	250	1	18.20	72.25	755	1.4587
5	300	1	13.60	85.85	1050	1.4646
6	350	2	4.40	90.25	1260	1.4681
7	400	2	4.10	94.35	1590	1.4720
8	450	4	3.05	97.40	1820	1.4742
Residue				2.60	2200	1.4784

acids. Fractions No. 3 and 4 contain the glycerides, higher-molecular unsaturated constituents being concentrated in the residue. The increase in the iodine number is caused by the higher vapor pressure of the saturated fatty acids compared with unsaturated ones of the same carbon number.

The results of a third experiment are given in Table III. The initial product was a material known as "Monoolein." According to the information given by the manufacturer it contains 38 to 42% glycerin monooleate and no more than 5% of free glycerin. The product is specified by the following numbers: acid number, 2.3; saponification number, 167.8; hydroxyl number, 248. According to the high hydroxyl number of 1771 the first fraction contains almost only free glycerin (hydroxyl number of glycerin, 1827.8). Fraction No. 2 contains according to the acid number of 123.2 mainly free oleic acid. According to the characteristic numbers of 3 and 4 and the residue, the components glycerin monooleate (saponification number, 157.3; hydroxyl number, 315), glycerin dioleate (saponification number 180.7; hydroxyl number, 90.4) and glycerin trioleate (saponification number 190.1; hydroxyl number 0) have been separated completely.

The fourth example is interesting from the analytical standpoint as well as from the standpoint of organic preparative chemistry. The experiments have been carried out with differently ethoxylated nonyl phenols. The general formula of these compounds is:



The amount of components with the index  $x$  follows a Gaussian error-curve with a maximum between 8 and 9. The position of the maximum depends

on the condition under which the compounds were formed. Details on the material used in our experiment are given in Table IV. Figure 5 shows that the distribution of the amount of the different fractions designated by the number  $x$  follows with good approximation the above mentioned curve.

In our opinion the given examples show lower limits with regard to re-

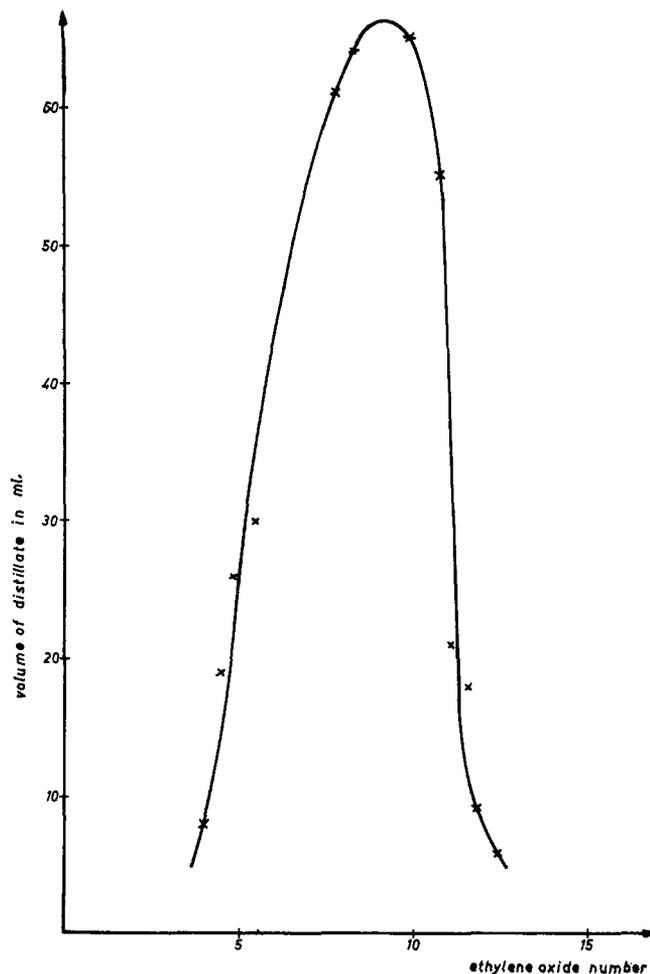


Figure 5. Distribution of fractions of mixture of ethoxylated nonyl phenols

Table II. Distillation of Glyceric Oil

Fraction No.	Temp., ° C. (° F.)	Amount in %	Acid No.	Saponification No.	Iodine No.	Color
1	140 (284)	4	194	202.1	61.7	Light yellow
2	200 (392)	3	0.4	184.3	48.55	Deep red
3	250 (482)	30	0	200.3	47.9	Yellowish
4	300 (572)	54	0	198.6	53.5	Pale yellow
Residue		9	0	186.4	79.3	Dark brown

Table III. Distillation of "Monoolein"

Fraction No.	Temp., ° C. (° F.)	Amount in grams	Acid No.	Saponification No.	Hydroxyl No.
1	80 (176)	13	0.3	3.1	1771
2	90 (194)	8	123.2	81	110
3	175 (347)	121	0.4	159	316
4	230 (446)	138	0	181.2	91.2
Residue		14	0	190.3	0.8

Table IV. Distillation of Differently Ethoxylated Nonyl Phenols

Fraction No.	Temp. in ° C. (° F.)	Amount in ml.	$x =$ ethylene oxide No.
1	120 (248)	8	4.0
2	135 (275)	19	4.5
3	150 (302)	26	4.9
4	165 (329)	30	5.5
5	180 (356)	61	7.8
6	195 (383)	64	8.3
7	210 (410)	65	10.0
8	225 (437)	55	10.8
9	240 (464)	21	11.1
10	255 (491)	18	11.6
11	270 (518)	9	11.8
12	350 (662)	6	12.4
Residue		2	19.2

solving power and thermal hazards. The state of development indicates possible further improvement in separating thermally supersensitive liquids.

#### ACKNOWLEDGMENT

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# Infrared Determination of Hydroxyl Content of Oxidized Polyethylene

DAVID E. KRAMM, JOHN N. LOMONTE, and JOSEPH D. MOYER

Washington Research Center, W. R. Grace & Co., Clarksville, Md.

► The hydroxyl content of oxidized polyethylene is determined by infrared analysis of the recovered polymer after quantitative acetylation with acetic anhydride. The analysis measures acetyl group content by use of the 1245-cm.<sup>-1</sup> C—O stretching vibration band typical of acetate esters, and equates this to the hydroxyl content. The method is standardized by the infrared spectrometric examination of polymers for which the hydroxyl content had been previously determined by acetylation with acetic anhydride-C<sup>14</sup> and subsequent radiochemical analysis. A simple titration, as used for standard acetylation analyses, cannot be used. Although the polymer can be dissolved at elevated temperatures for acetylation, when excess acetic anhydride is hydrolyzed and the temperature is lowered, the polymer is precipitated; this makes titration data unreliable. Also, the hydroxyl content is often quite low, making sample and blank titrations approach each other, an undesirable situation.

**D**ETERMINATION OF HYDROXYL content in oxidized polyethylene by standard infrared spectrometric techniques is difficult, if not impossible, because of the proximity of other absorption bands. The use of integrated absorption, which has been useful in this type of system (3, 4), is precluded not only because the band is not resolved but because suitable model compounds are not available. Figure 1 shows the spectrum of a typical oxidized polyethylene. From this spectrum it can be seen that the hydroxyl band which would be located at about 3300 cm.<sup>-1</sup> is completely lost in the shoulder of the C—H stretching band in the 2900-cm.<sup>-1</sup> region. It will be shown that hydroxyl groups are indeed present by the ability to acetylate them and

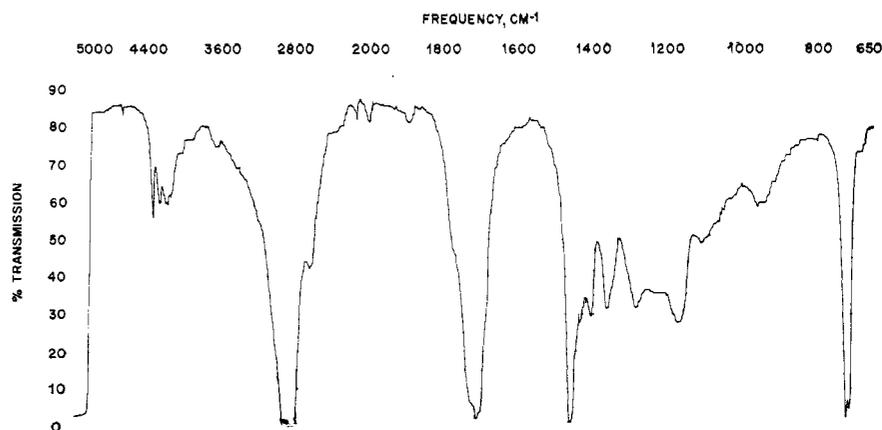


Figure 1. Infrared spectrum of a typical oxidized polyethylene

that this acetylation is free of side reactions.

By acetylation of the polymer and examination of the infrared spectrum (Figure 2), it has been found that hydroxyl content can be estimated in the acetylated product from the absorption at 1245 cm.<sup>-1</sup> arising from the C—O stretching vibration band of acetate esters (1). The procedure is standardized by an absorptivity constant,  $\alpha$ , obtained from measurements with polymers of known hydroxyl content. The known hydroxyl content of these polymers is determined by reaction with acetic anhydride-C<sup>14</sup> followed by radiochemical analysis (2).

#### EXPERIMENTAL

**Apparatus.** The radiochemical counting was done with a windowless, gas-flow counter made by Nuclear Measurements Corp. The infrared spectra were recorded on a Beckman IR-4 spectrophotometer using the following instrumental conditions: operating mode, double beam; slits, 1.5 × standard; filter period, 2 seconds; scan speed, 80 cm.<sup>-1</sup> per minute.

**Acetylation Procedure.** To an accurately weighed, 1-gram sample of oxidized polyethylene in a 500-ml. iodine flask is added 200 ml. of reagent grade xylene, 15 ml. of dry pyridine (less than 0.05% water), and 2 ml. of acetic anhydride. A Teflon-covered stirring bar is added, and the mixture is heated to reflux on a hot plate with magnetic stirring, and allowed to reflux for 3 hours. The sample is cooled and 50 ml. of methanol containing 10% water (by volume) is added. The sample is mixed vigorously and allowed to stand for 20 minutes to let the polymer coagulate. The precipitated polymer is collected by gravity filtration on No. 42 Whatman paper and allowed to air-dry for an hour. The sample is then dried in a vacuum oven at 50° C. for 3 hours.

**Radiochemical Analysis.** Several samples of oxidized polyethylene are acetylated with acetic anhydride-C<sup>14</sup>. The absolute specific activity of a purified derivative, *N*-acetyl-C<sup>14</sup>-*p*-toluidine is determined by a liquid counting procedure (5). The reagent has a specific activity of 0.648  $\mu$ c. per millimole.

The recovered polymer is molded into plaques and counted, and the count is