Molecular Distillation

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THE technique of molecular distillation has developed in recent years into an useful tool in research and in industry. It is a new means available for analysis of various components present in oils. According to Hickman[1], the process is a revolution in the technology of oils, fats and waxes which hitherto have been considered undistillable. The technique has grown from a laboratory application to an industrial process like the separation of vitamin A from fish liver oils which was begun in 1932 by the British Drug Houses, Ltd., in England and about the same time by the Eastman Kodak Co., in the U.S.A.

The principle of molecular distillation[2] is very simple. It consists of the transfer of vapour from the warmer surface of the liquid to the cooler surface of a nearby condenser, the space between the two being evacuated sufficiently (about 10^{-3} mm. or higher) to prevent any obstruction of the vapour. The distance between evaporator and condenser is considerably less than the mean free path of the molecules at the vacuum maintained. Hence, the molecules leaving the evaporating surface directly lodge on the condensing surface, before colliding with each other or rebounding back in the mass.

The concept of molecular distillation was put forward by Langmuir[3] in 1916. He devised a pump that gave more efficient evacuation than was possible previously. One of the first applications of this idea was the separation of isotopes of mercury by Brönsted and Hevesy[4] in 1922. Successful application of the principle to organic materials was made by Burch[5] who developed an apparatus in which the most refractory oil could be refined by molecular distillation.

The principle of molecular distillation, as it is understood, was demonstrated by Burch[5], Washburn[6], Waterman[7] and others. The earliest amongst the molecular stills were the pot stills where only a small amount (less than 20 ml.) of the material could be distilled. These stills of Burch[5], Washburn[6], Waterman[7], Hickman[8], Nelson and Haller[9], Carothers[10] and others were in operation since about 1929 in laboratories throughout the world. Progesterone[11] was separated from an extract of pig's ovaries in a tiny pot still. Farmer and Van den Heuvel[12] investigated the marine fatty acids using a glass pot still. Vitamin K was separated by Dam[13] in a pot still and by Almquist[14] in a compound tube still. Similarly calciferol[15] was distilled from ergosterol in a tubular still.

The pot and tube stills were followed by the cyclic falling film still designed by Hickman[2]. In the latter, a thin film of the material being distilled flows by gravity over a heated evaporating cylinder surrounded by a cold glass cylinder. Several workers have studied the concentration of vitamin A from shark liver oil[16-18] and whale liver oil[19]. Patel and Sreenivasan[16] obtained a thirty-fold concentration of vitamin A from Indian shark liver oils using a cyclic falling film still. These authors separated the saturated and unsaturated fatty acids from molecularly distilled fractions and studied their characteristics. Cyclic falling film stills have also been employed on an industrial scale for the production of vitamin A, vitamin D[20] and vitamin E[21]. Vitamin A concentrates could be obtain-

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ed in a pure form and in unsaponified condition, in potencies up to 5,00,000 units/gm. These ester concentrates can be saponified and redistilled to produce pure vitamin A alcohol with a potency greater than 3,000,000 units/gm[22].

In 1941, the cyclic falling film stills were entirely replaced by 32 inch centrifugal stills[23]. The latter employ centrifugal force to whirl the liquid in a thin layer across the surface of a heated plate held in front of a cooled condenser. The thermal exposure in a cyclic falling film still is perhaps 100 times less than in a pot still; whereas in the centrifugal still the exposure may be from 100 to 10,000 times less. Hickman[24] has described commercial molecular distillation using a 5 ft. centrifugal still. This design with rotors 5 ft. in diameter and an active distilling area of 5 yds., evaporating 30 lbs. an hour at a pressure as low as a micron were put into service in the laboratories of Distillation Products, Inc., N.Y.

In a comprehensive review, Hickman[1] has surveyed the history, evolution, design and scientific accomplishments of molecular stills discussing the relative still performance. He deals with the applications of molecular distillation and the elimination curve technique.

Embree[25] has published an excellent review on the application of the technique of molecular distillation to natural oils and fats. According to him, molecular distillation cannot be carried out with oils that contain more than traces of phosphatides and mucilaginous matter. Embree[25] concludes that the free fatty acids, odouriferous material and unsaponifiable matter could be effectively separated from animal and vegetable oils. The review deals with the triglyceride fractionation data of linseed[26], castor[27], corn[28], soyabean[28], cotton-seed[29], menhaden[30] and other oils. The results presented indicate that there is no fractionation of the triglycerides. The initial fractions are potent in free fatty acids, sterols and unsaponifiable matter. These concertrates can thus be obtained without saponification of the oil which might otherwise alter the property of the natural constituents.

Bhat, Kane and Sreenivasan[31] molecularly distilled sesame, karanja, undi and malkanguni oils in a cyclic falling film still and studied the concentrates of unsaponifiable matter. Sesamin and karanjin were isolated from the concentrates of sesame oil and karanja oil respectively. The fractionation of the antibacterial principle of Undi oil (*Calophyllum inophyllum, Linn*) using the same still was reported[32] earlier.

Haller[33] *et al.* molecularly distilled sesame oil and the fractions obtained were separately added to pyrethrum insecticide and tested against house flies. Wachs[34] studied the separations of sesamolin from sesame oil and mono-glycerides from technical mixture by molecular distillation. The molecular still is effective for separating mono-glycerides from a mixture of mono-, di- and tri- glycerides. Kuhrt[35] *et al.* using a 5-inch centrifugal still obtained pure mono-glycerides (92-97%) from a commercial monoglyceride mixture of hydrogenated vegetable oil, cotton-seed oil and soyabean oil.

Recent reports indicate that molecular distillation could be employed for deodorization of fats[36] and deacidification of coconut oil[37].

There is no doubt that this useful technique of molecular distillation will be employed more and more for the production of new and improved materials and for information concerning lipids generally.

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