REVIEW

APPLICATIONS OF MOLECULAR DISTILLATION TECHNIQUE IN FOOD PRODUCTS

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ABSTRACT

There are several separation techniques -including conventional distillation- for extracting heat sensitive compounds from food products. However, some compounds may have high boiling points at which other compounds might be adversely affected. Vacuum application is also needed for such kinds of foods. Molecular distillation is an advanced vacuum distillation method performed by short-path evaporators. Distance between evaporator and condenser is extremely reduced which results in minimized pressure drop. Heat sensitive material meets heat for a short time under high vacuum, thus low or no decomposition occurs. This review aims to discuss the basics and uses of molecular distillation in foods.

- Keywords: molecular distillation, purification, separation, short-path, vacuum -

INTRODUCTION

Distillation is a simple physical separation process of liquid mixtures based on differences in boiling points of components in the mixture. Very first usage of distillation dates back to 1st century (FORBES, 1970). Further experiments leaded to new knowledge that is known as fundamentals of distillation now. In 1830, Aeneas Coffey - an Irish inventor - patented his distillation column (GAISER *et al.*, 2002). Coffey's column (a.k.a "continuous still", "patent still" or "Coffey still") achieved to reach higher concentrations of alcohol. In 20th century, some special distillation equipments and techniques were produced in correlation with increasing innovations in petrochemical industry. Especially in chemical and food research, demand for extracting compounds with high purity leaded to development of computer aided systems. Today, several distillation techniques are present for various purposes. Appropriate distillation method should be chosen depending on properties of liquid mixture and distillation equipment. Some of the specific distillation methods could be listed as:

- Repeated evaporation-condensation cycles, known as fractional distillation.
- Steam distillation of heat sensitive materials (Harwood and Moody, 1989)
- Vacuum distillation of heat sensitive materials under reduced pressure.
- Reactive distillation
- Azeotropic distillation
- Extractive distillation
- Catalytic distillation
- Molecular distillation, an advanced vacuum distillation method.

General information on molecular distillation

Pure substances have certain vapor pressure values related to vaporization temperature. These vapor pressure-temperature data are plotted to a P-T diagram, which is called "phase diagram". Fig. 1 demonstrates a sample phase diagram of any pure substance.

As seen in Fig. 1, vaporization temperature (or boiling point) decreases when the ambient pressure is reduced along the vaporization curve. This principle is the basis of vacuum distillation. Distillation of compounds, which may be decomposed at high boiling points and/or may be air-sensitive can be possible with vacuum distillation. Typically, there are two types of vacuum distillation:

- Simple vacuum distillation: applied when higher vacuum levels are not needed. Ex: rotary evaporators, Perkin triangle.
- High vacuum distillation: applied when higher vacuum levels are needed for separation. Purity of distillate is higher than those of other distillation techniques. Ex: thin film evaporators (TFE) and short-path distillation equipment (SPD).

According to SHI *et al.* (2007), distillation method can be called as molecular distillation if the distance between evaporator and condenser reaches to mean free path of a vapor molecule. Lei *et al.* (2005) described the mean free path, $< \lambda >$, with the following equation:

$$< \lambda > = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

where d (m) is the diameter of molecule, N_A is Avogadro constant (6.023×10^{23} mol^{-1}), P (Pa) is pressure, R is universal gas constant and T (K) is temperature. LUTIŠAN and CVENGROŠ (1995) defined molecular distillation as "the safest method to separate and purify thermally unstable compounds". SHI *et al.* (2007) pointed out that risk of thermal decomposition could be reduced with low temperature; as well oxidation could be prevented with air removal by vacuum. In addition, DE MORAES *et al.* (2006) drew one's attention to advantages of molecular distillation (e.g. avoiding toxicity, protect environment) that other chemical agent-based techniques do not have. LUTIŠAN and CVENGROŠ (1995) defined the main features of molecular distillation as; short time of exposure to heat, low evaporating temperature and a characteristic mass transfer. According to MARTINELLO *et al.* (2007), "small distance between evaporator and condenser" can also be defined as a feature of molecular distillation.

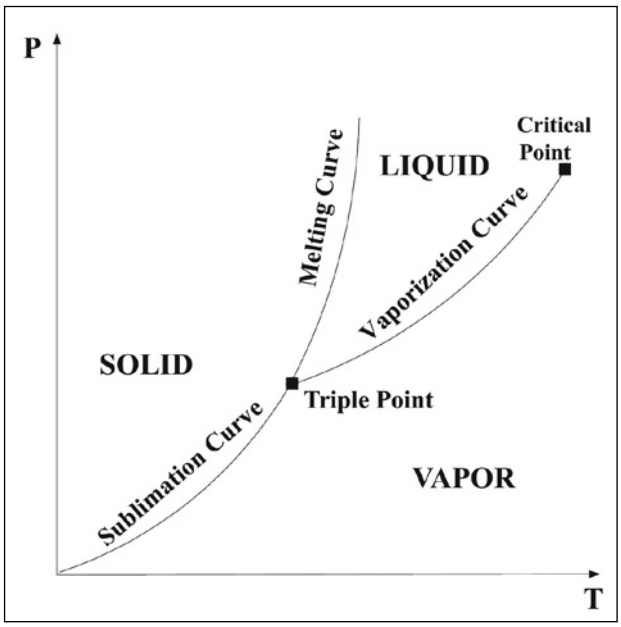

Fig. 1 - Sample phase diagram of any pure substance.

HIGH VACUUM AND MOLECULAR DISTILLATION EQUIPMENT

There are typically two types of evaporators used in high vacuum distillation, i.e. thin film evaporators (TFE) and short-path evaporators (SPE). These equipments have similar designs with few differences. In both evaporators, feed is agitated with a rotor-wiper system and high vacuum is produced by vacuum pumps. In TFE, operating pressure can be reduced to 1-100 mbar (UIC GmbH, 2014) and there is no other unit between vacuum and condenser (PILODIST, 2014). Fig. 2 shows an illustration of a TFE.

In SPE, condenser is placed in the centre of evaporator unit, so distance between boiling and condensation surface is extremely reduced and pressure drop is minimized. The operating pressure can be reduced up to 0.001 mbar. Distillation performed by a short-path evaporator is also called as "molecular distillation" (Buss-SMS-Canzler GmbH, 2014a; Buss-SMS-Canzler GmbH, 2014b; PILODIST, 2014; TECHNOFORCE, 2014). Fig. 3 shows an illustration of a SPE.

There are many parameters that can affect distillation yield and molecular evaporation rate. Molecular evaporation rate, k_i, can be calculated by Langmuir-Knudsen equation (ROSSI *et al.*, 2011):

$$k_i = \frac{P_{v_i}(T^S)}{\sqrt{2\pi R M_i T^S}}$$

where T^S is evaporation temperature, R is universal gas constant, M_i is molecular weight of evaporating component and P_{v_i} is vapor pressure of component. XU *et al.* (2002) describes the most important parameters of molecular distillation as evaporator temperature, flow rate, vacuum and wiper speed. Flow rate has an important effect on the contact time of the molecules with hot surface during evaporation. Higher flow rates reduce the residence times of molecules being vaporized. Wiper speed affects film thickness and viscosity. Feed becomes highly turbulent with intensive agitation, which leads to high heat transfer coefficients (Buss-SMS-Canzler GmbH, 2014c).

MOLECULAR DISTILLATION IN FOOD PROCESSING: SOME EXAMPLES OF RECENT STUDIES

Molecular distillation has many application areas in food industry. Some of these applications can be summarized as but not limited to: concentration of ω-3 fatty acids, distillation of monoglycerides from di- and triglycerides, concentration of tocopherols and tocotrienols (Buss-SMS-Canzler GmbH, 2014d), fractionation of squalene (SUN *et al.*, 1997), recovery of carotenoids (BATISTELLA and WOLF-MACIEL, 1998). As distillation is a separation process, studies about molecular distillation generally focus on either removal of undesired compounds or concentration of valuable compounds.

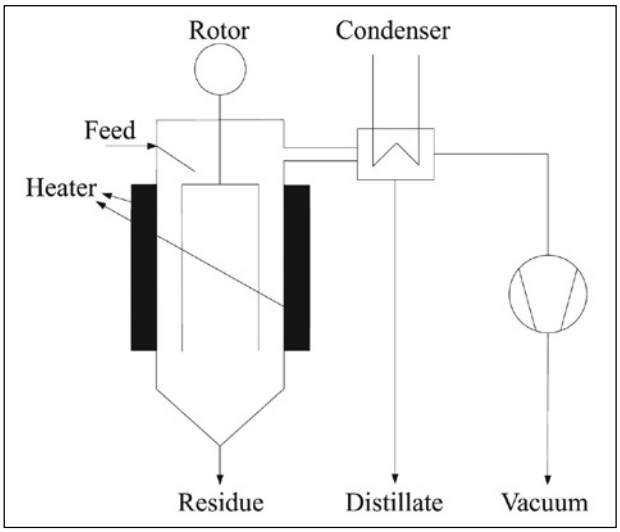

Fig. 2 - Illustration of a TFE unit.

Removal of undesired compounds

In a study about removal of cholesterol from butter and lard by using molecular distillation (LANZANI *et al.*, 1994), researchers reported that cholesterol content of lard was reduced from 988 ppm to 105 ppm in the residue after 2 hours of distillation under 10^{-4} torr pressure and 250°C evaporator temperature.

Molecular distillation can also be used for physical deacidification. MARTINS *et al.* (2006) separated free fatty acids (FFA) from vegetable oil deodorizer distillate. They achieved to reduce

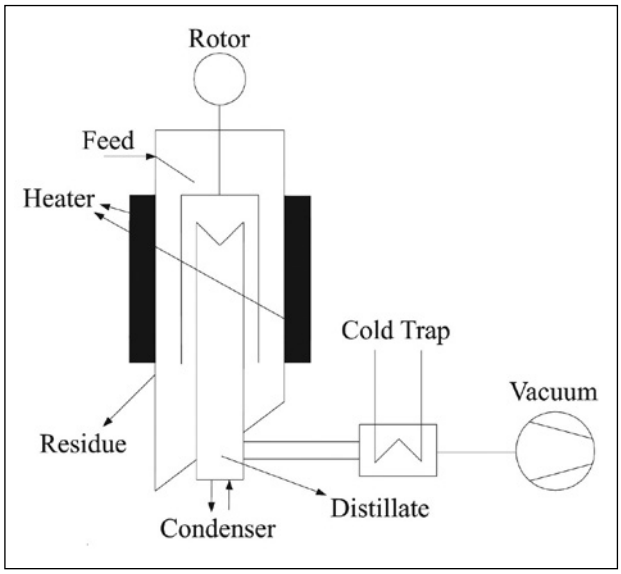

Fig. 3 - Illustration of a SPD unit.

FFA content to 6.4% from initial FFA content of raw material with 57.8% at 160°C evaporator temperature, under 10^{-6} bar pressure and 10.4 g min^{-1} feed flow rate. They also noted that concentration of tocopherol in residue stream was found 18.3%, while initial tocopherol concentration was 8.97%. FFA elimination was 96.16% and tocopherol recovery was found 81.23%.

WANG *et al.* (2010) aimed to separate FFAs and diacylglycerols (DAG) from enzimatically hydrolyzed soybean oil. They achieved to increase the removal of FFAs from 88.8% to 99.44% by increasing evaporator temperature from 125°C to 160°C, under 0.5-1.0 Pa process pressure, 200 mL h^{-1} feed rate and 300 rpm wiper speed.

OLLI *et al.* (2013) studied removal of organic pollutants in fish oils. Their SPD system, which has an evaporator temperature of approx. 220°C and operating pressure below 0.03 mbar, achieved to remove total amount of chlorinated pesticides (some of them are DDT and HCH) from 215.07 ng g^{-1} to 21.95 ng g^{-1}, corresponding to 89% reduction.

According to MEYER *et al.* (2011), total pesticide traces in rapeseed deodorizer distillate were dropped below 0.05 mg kg^{-1} from an initial content of 0.968 mg kg^{-1} by achieving more than 94.8% reduction. SPD evaporator temperature was set to 110°C, feed flow rate was 200 mL h^{-1} and pressures were between 0.006 and 0.01 mbar. Researchers stated that it would be a mistake to affirm that all types of pesticides were removed by using SPD according to this reduction data, because many different types of pesticides might be present before distillation and analysis of effects on specific compounds has to be performed.

Concentration and/or fractionation of compounds

BATISTELLA and WOLF-MACIEL (1998) studied the recovery of carotenoids from palm oil by using a molecular distillator and after a set of distillation trials, they achieved to increase carotene concentration to 19500 ppm from an initial feed concentration of 600 ppm under $9x10^{-5}$ torr pressure and 170°C evaporator temperature.

SUN *et al.* (1997) fractionated squalene from alkali-refined amaranth seed oil and their highest recovery of squalene was 67.8% with SPD conditions of 100 mtorr pressure and 180°C distillation temperature.

Campos *et al.* (2003) fractionated milk fat by SPD and recorded distillate yields (w/w) as a function of temperature. They observed that distillate yield was 0.3% at 125°C process temperature; however a 42.7% recovery was observed when process temperature was increased to 250°C, which meant a significant and positive effect of temperature on process efficiency.

SPD was performed on lemongrass essential oil by TOVAR *et al.* (2011) and researchers reported that they were able to increase citral concentration in distillate stream from 17.658 mg mL^{-1} to 33.576 mg mL^{-1} when evaporator temperature was increased from 60°C to 120°C with a feed flow rate of 1.5 mL min^{-1} and pressure of 5 Pa.

Mono and diglyceride (MDG) concentration and production are also possible with molecular distillation. FREGOLENTE *et al.* (2010) produced partial glycerides from soybean oil by using molecular distillation. Concentration of monoglyceride (MG) in distillate stream increased with elevated evaporator temperature. At 250°C with 10 mL min^{-1} feed flow rate, MG concentration was increased from initial feed value of 12.75% to 80.00% in distillate stream under 24 Pa operating pressure. They also pointed that lower flow rate increased recovery of MG, because molecules contacted with hot evaporator surface for a longer period of time. Recovery for any component is defined with following equation:

$$Recovery(\%) = 100\, x \frac{Distillate}{Feed}$$

ZHANG *et al.* (2013) studied effects of evaporation temperature, feeding rate, feeding temperature and wiper speed on concentration of ω-3 fatty acids by molecular distillation and optimized these parameters with response surface methodology (RSM). Researchers reported the optimum conditions as 110.4°C evaporator temperature, 78.7 mL h^{-1} feeding rate, 350 rpm wiper speed, 10 Pa operating pressure and 80°C feed temperature.

CONCLUSIONS

Separation techniques such as extraction, evaporation, distillation etc. are accepted as unit operations in food industry. Vacuum distillation is frequently used both in chemical and food industries; however simple vacuum distillation might not be capable of separation of heat-sensitive materials from food products. In that case, molecular distillation (short-path distillation) should be used for separation of these materials. Molecular distillation has been used more in pharmaceutical, chemical and petrochemical applications, but nowadays importance of molecular distillation has increasingly been understood in food industry. Separation, concentration and purification of commercially valuable food constituents can be easily performed by molecular distillation; furthermore, healthier food products can be produced by removal of some health damaging compounds such as excess cholesterol, organic pollutants. Authors expect an increasing trend in usage of molecular distillation in food industry when taking all these applications into consideration.

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