

CHAPTER II

LITERATURE REVIEW

2.1 Wax Overview

Wax is usually referred to a substance that is an organic, plastic solid at ambient temperature, and becomes a low viscosity liquid when heated (DeNavarre, 1962; Bennett, 1975; Bhargava, 1975; Dorgan, 1983). Wax can be categorized by its origin as follows (www.igiwax.com).

2.1.1 Natural wax

2.1.1.1 Animal Waxes: Beeswax, Lanolin, Tallow

2.1.1.2 Vegetable waxes: Carnauba, Candelilla, Soy

2.1.1.3 Mineral Waxes:

- Fossil or earth: ceresin, montan

- Petroleum: paraffin, microcrystalline

2.1.2 Synthetic wax (man-made)

2.1.2.1 Ethylenic polymers e.g. polyethylene & polyol ether-est

2.1.2.2 Chlorinated Naphthalenes

2.1.2.3 Hydrocarbon type, e.g. Fischer-Tropsch

2.2 Petroleum Wax

Petroleum wax is derived from crude oil, which normally consists of a complex mixture of hydrocarbons as the resultant products of the decomposition of tiny aquatic plants and animals that lived in the ancient seas millions of years ago. Therefore, another name of crude oil is fossil fuel. It is produced from the lube oil refining process, from which petroleum waxes are derived.

There are three categories of petroleum wax, paraffin wax, microcrystalline wax, and petrolatum. The properties of each wax are described as follows:

2.2.1 Paraffin Wax (Macrocrystalline Wax)

Paraffin wax derived from the light lubricating oil distillates, wax contains predominantly straight-chain hydrocarbons with an average chain length of 20 to about 50 carbon atoms (Saengarun, 1999).

2.2.2 Microcrystalline Wax

Microcrystalline wax is produced from a combination of heavy lube distillates and residual oils. It differs from paraffin wax in that it is poorly defined crystalline structure, darker color, and generally higher viscosity and melting point. Microcrystalline wax (sometimes also called micro wax) tends to vary much more widely than paraffin waxes with regarding to physical characteristics. Microcrystalline waxes can be ranged from being soft and tacky to being hard and brittle depending on the compositional balance.

2.2.3 Petrolatum

Petrolatum is derived from heavy residual oils and is separated by a dilution and filtering (or centrifuging) process. Petrolatum is microcrystalline in nature and semi-solid at room temperature.

2.3 General Properties of Paraffin Wax

Paraffin wax from petroleum is solid crystalline and a complex mixture of straight-chain hydrocarbons ranging from C_{20} to higher hydrocarbon molecule, that is $CH_3(CH_2)_nCH_3$ where $n \geq 18$ (Speight, 1999). It is generally non-reactive, non-toxic, colorless, good water barrier, and clean-burning fuel. It is a clearly defined crystal structure and tends to be hard and brittle. Its melting points are generally between 120 and 160°F.

Paraffin wax is widely used in many applications; such as treatment of paper and cardboard, binders and consistency regulators for ointments or creams in cosmetics industries, a viscosity regulated for adhesives, a release agent in electrical and electronics industries, and printing inks, as well as in food ceramic candle and pharmaceutical industries (Montserrat *et al*, 2005).

The processes employed for the production of wax are aimed at deoiling the wax. Two processes frequently used for deoiling the wax in actual operation are wax sweating and wax recrystallization (Speight, 1999):

2.3.1 Wax Sweating

Wax sweating was originally used in Scotland for the wax obtained from shale oil to separate wax fractions with various melting points. In a wax sweating process, a cake of oil-containing wax is slowly warmed to a temperature, at which the oil in the wax and the lower melting waxes become fluid and drip (or sweat) from the bottom of the cake, leaving a residue of higher melting wax. However, wax sweating can be carried out only when the residue wax consists of large crystals that have spaces between them, through which the oil and the lower melting wax can percolate. It is therefore limited to wax obtained from light paraffin distillate. Currently, wax sweating is still used to some extent but being replaced by the more convenient wax recrystallization process.

2.3.2 Wax Recrystallization

Wax recrystallization, like wax sweating, separates oil-containing wax into fractions. When a mixture of solvent and wax is heated, the wax dissolves completely. Then solution is cooled slowly to reach a temperature at which a crop of wax crystal is formed. These crystals will also be of the same melting point, and if they are removed by filtration, a wax fraction with a specific melting point is obtained. If the clear filtrate is further cooled, a second crop of wax crystals with a lower melting point is obtained. Thus, by controlling the crystallization temperature, the wax can be separated into a number of wax fractions, each with different melting points. This method of producing wax fractions is much faster and more convenient than wax sweating and results in much more complete separation of the various fractions. Furthermore, recrystallization can also be applied to the microcrystalline waxes obtained from intermediate and heavy paraffin distillates, which cannot be sweated. The process differs mainly in the use of different solvents. This process makes use of the different solubility of the wax fractions in the solvent, separating

wax as a solid that is crystallized from the oil solution as in solvent dewaxing process, which is also based on the same fundamental idea.

2.4 Solvent Dewaxing

All solvent dewaxing processes cool a mixture of feed oil and solvent to a temperature low enough to cause crystallization of wax and subsequent separation of the solid phase. They are some dewaxing properties concerned (McKetta, 1992). It requires high solvent power at low temperature for oils, but a very low solubility for wax, and a low melting point, well below the filtration temperature.

The methods are essentially alike in that the waxy oil is dissolved in a solvent, which the oil is kept in the solution. The wax is separated as crystals when the temperature is lowered. The process is different in the use of the solvent. Commercially used solvents are naphtha, propane, sulfur dioxide, trichloroethylene, and ethylene dichloride (Speight, 1999).

General selection of solvent are low cost, high thermal and chemical stability, low boiling points, low latent heat of vaporization, and low specific heat, uncorrosivity, and unotoxicity (McKetta, 1992).

To optimize the dewaxing properties of the solvent, a mixture of two solvents is used, such as ethylenedichloride-benzene (Barisol), methyl ethyl ketone-benzene (Benzol), methyl-n-butyl ketone and methyl-n-propyl ketone (McKetta, 1992). Most use of solvent mixture for dewaxing process known as the MEK process is a mixture of toluene and methyl ethyl ketone (MEK). The toluene is a good solvent for hydrocarbons and quite high solubility for wax. In order to minimize the wax solubility, MEK is added, because the solubility of hydrocarbons in MEK is quite low. If too much MEK is present in the toluene/MEK feed oil mixture, an oily liquid phase will also separate (McKetta, 1992).

There are two main disadvantages of the solvent dewaxing process. Firstly, the operating costs for the process are high, and secondly, the pour point that can be achieved is limited by the high cost of refrigerating to very low temperatures. Therefore, considerable researches have been carried out to find the other process for purification of wax.

More recently, supercritical fluid (CO₂) extraction is reported as a potential process for wax purification (Crause and Nieuwooudt, 2003), and are widely accepted for extraction, purification, recrystallization, and fractionation operations in many industries (Siti Machmudah *et al*, 2006). The diffusivity of supercritical carbon dioxide is one to two orders of magnitude higher than other fluids, which permits rapid mass transfer, and results in a larger extraction rate than that obtained by the conventional organic solvent extraction. Moreover, CO₂ is nontoxic, abundantly available at relatively low cost, and low critical temperature and pressure ($T_c = 31.1^\circ\text{C}$, $P_c = 7.4 \text{ MPa}$) (Irvan *et al*, 2006). In this process, the oil-containing wax is brought into contact with supercritical CO₂ mixed with some cosolvents. Then, the fractionation of wax can be obtained.

2.5 Supercritical Fluid Extraction

2.5.1 Physical-Chemical Properties of the Supercritical Fluids

A pure supercritical fluid (SCF) is any compound at a temperature and pressure above the critical point (www.andrew.cmu.edu). Above the critical temperature of a compound, the pure gaseous component cannot be liquefied regardless of the pressure applied. The critical pressure is the vapor pressure of the gas at the critical temperature. In the supercritical environment, only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximately liquids, as well as the transport properties common to gases.

2.5.2 Phase diagram of supercritical CO₂

By increasing the pressure of the CO₂ gas above the critical point (Figure 2.1), it is possible to give liquid-like densities and solvating strengths (www.sunny.vemt.bme.hu). Near the critical point, the density of the gas will increase rapidly with increasing pressure, here, the solubility of many compounds is several orders of magnitudes greater than predicted from the classical thermodynamics of ideal gases. As the average distance between molecules decreases, non-ideal gas behavior will begin to govern the interactions between the

solvent and the sample accounting for a tremendous enhancement in solubility. In supercritical region, solvating strength is a direct function of density, which in turn is dependent on the system pressure (at constant temperature). Solvating strengths can be fine-tuned by minutely adjusting the pressure and/or temperature, using the solvent anywhere in the range of ideal gas to nearly pure liquid. Because of the non-compressibility of liquids, this phenomenon is unique to supercritical fluids. It is even possible, by adding small quantities of co-solvent, to customarily design a supercritical fluid for a specific application.

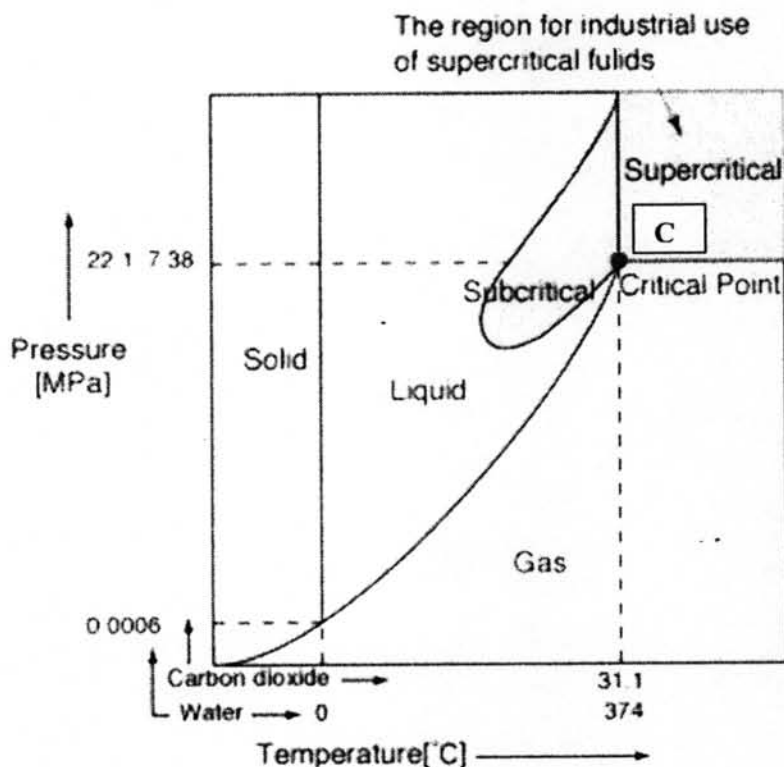


Figure 2.1 Phase diagram of carbon dioxide. (www.andrew.cmu.edu)

The critical point (C) is marked at the end of the gas-liquid equilibrium curve, and the shaded area indicates the supercritical fluid region. It can be shown that by using a combination of isobaric changes in temperature with isothermal changes in pressure, it is possible to convert a pure component from a

liquid to a gas (and vice versa) via the supercritical region without incurring a phase transition.

2.5.3 The behavior of supercritical fluid

The behavior of a fluid in the supercritical state can be described as that of a very mobile liquid. The solubility behavior approaches that of the liquid phase, while penetration into a solid matrix is facilitated by the gas-like transport properties. As a consequence, the rates of extraction and phase separation can be significantly faster than conventional extraction processes. Furthermore, the extraction conditions can be controlled to affect a selected separation. Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature. The dissolving power of a SCF increases with an isothermal increase in density or an isopycnic, i.e. constant density, increase in temperature. In practical terms, this means that a SCF can be used to extract a solute from a feed matrix as in conventional liquid extraction. However, unlike conventional extraction, once the conditions are returned to ambient, the quantity of residual solvent in the extracted material is negligible.

The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar), the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible. In a SCF, however, the solvating power of the supercritical fluid is highly dependent on its temperature and pressure (Larry, T.T, 1996). And the solute solubilities of up to several orders of magnitude greater than those predicted by ideal gas law behavior have been reported (Jit Kang, Lim).

The dissolution of solutes in supercritical fluids results from a combination of vapor pressure and solute-solvent interaction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure.

Although the solubility of volatile solids in SCFs is higher than in an ideal gas, it is often desirable to increase the solubility further in order to reduce the

solvent requirement for processing. The solubility of components in SCFs can be enhanced by the addition of a substance referred to as an entrainer, or co-solvent. The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a co-solvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid.

Co-solvents also provide a mechanism, by which the extraction selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of co-solvents. A factor that must be taken into consideration when using co-solvents is that the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

Some studies showed that use of supercritical fluid extraction with co-solvents can enhance the percent recovery of wax. Montserrat Lopez-Mesas (Montserrat *et al*, 2005) studied the extraction of wool wax from wool scour wastes by using supercritical fluid extraction at 80°C and 250 atm with co-solvents having different polarities, i.e. methanol, toluene, acetone, and n-hexane, and observed an increase of the efficiency of extraction. The result shows that the more non-polar co-solvent is the more effective. To study the effect of the amount of co-solvent, the system with methanol as co-solvent was chosen. When the amount of added methanol was increased, the recovery of the wool wax was also found to increase, and maximum recoveries were found when 2.5-3.0 ml was added (per 2.0 g of wool wax). At higher conditions, the efficiency decreased due to the overload of the cartridge.