

**EFFECTS OF PROCESS PARAMETERS ON RECOVERY OF BASE OIL  
FROM SPENT LUBRICANTS USING SOLVENT EXTRACTION METHOD**

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## ABSTRACT

Typically lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons and many others are sometimes used as base oils. Solvent extraction is the method to eliminate the usage of high temperature or hydrogenation process in re-refining the base oil from spent lubricant oil. The main objective of this study is to recover the base oil from spent lubricants using solvent extraction method. Besides that, the effect of different solvent, the retention time and the characteristics of the extracted base oil are also determined. The raw materials that being used were spent lubricant oil and two types of solvents. These solvents are hexane mixed with potassium hydroxide in isopropyl alcohol and N-vinyl-2-pyrrolidone (NNVP). During the experimental study, 200 ml of lubricant oil and 800 ml of solvents were mixed and leave to settle. After that, the mixture was filtered by vacuum pump to separate the sludge. Separation was continued using rotary evaporator to get the pure base oil. Then, the characteristics of the base oil for every mixture were analyzed. Results shows that the best solvent, is solvent 1 (Hexane + KOH + IPA) because it can recover more volume of base oil compare to solvent 2 (NNVP). Besides that, the best stirring time (retention time) for both solvent is 60 minutes. Solvent 1 is better than solvent 2 because it can recover higher volume of base oil compared to solvent 2 by 37%. As a recommendation for future work, in order to recover higher volume of base oil, the amount of potassium hydroxide (KOH) used must be increased.

## ABSTRAK

Minyak pelincir biasanya mengandungi 90% minyak asas (minyak bumi, disebut minyak mineral) dan kurang dari aditif 10%. minyak nabati atau cecair sintetik seperti dihidrogenasi poliolefin, ester, silikon, fluorocarbons dan banyak lagi kadang-kadang digunakan sebagai bahan asas. Pelarut ekstraksi adalah kaedah untuk menghilangkan penggunaan suhu tinggi atau proses hidrogenasi dalam menyempurnakan kembali minyak pelincir dasar dari minyak yang telah digunakan. Tujuan utama dari penyelidikan ini adalah untuk memulihkan dasar dari minyak pelincir yang dihabiskan dengan kaedah ekstraksi. Selain itu, kesan pelarut yang berbeza, waktu retensi dan karakteristik dari minyak asas diekstrak juga ditentukan. Bahan-bahan mentah yang digunakan adalah minyak pelincir dan dua jenis pelarut. Pelarut ini ialah heksana dicampur dengan kalium hidroksida dalam alkohol isopropil dan N-vinil-2-pyrrolidone (NNVP). Semasa ujikaji dijalankan, 200 ml minyak pelincir dan 800 ml pelarut yang dicampur dibiarkan untuk proses pemendapan. Setelah itu, campuran itu ditapis dengan pam vakum untuk memisahkan bendasing. Selepas itu, campuran tersebut dipisahkan dengan menggunakan penyejat untuk mendapatkan minyak asas. Kemudian, karakteristik minyak asas bagi setiap campuran dianalisis. Sebagai keputusannya, pelarut yang terbaik adalah pelarut 1 (Heksana + KOH + IPA) kerana dapat memulihkan isipadu minyak asas lebih banyak dibandingkan dengan pelarut 2 (NNVP). Selain itu, masa pengadukan terbaik (waktu retensi) untuk kedua-dua pelarut adalah 60 minit. Pelarut 1 dapat memulihkan isipadu minyak asas lebih daripada pelarut 2 sebanyak 37%. Sebagai cadangan bagi kerja yang akan datang, kalium hidroksida (KOH) yang digunakan harus ditingkatkan untuk memperolehi isipadu minyak asas yang lebih banyak.

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## LIST OF SYMBOLS

%	Percent
$^{\circ}\text{C}$	Degree Celsius
h	Hour
t	Tonne
rpm	Revolution per minute
mm	Millimeter
kg	Kilogram
ppm	part per million
mg	Milligram
ml	Milliliter
Min	Minute
$\text{Kg}/\text{M}^3$	Kilogram per Meter <sup>3</sup>

## GLOSSARY OF ABBREVIATIONS

KOH	Potassium Hydroxide
IPA	Isopropyl Alcohol
NNVP	N-vinyl-2-pyrrolidone
USEPA	Environmental Agency of United State of America
CSIRO	Commonwealth Science and Industry Research Organisation
MAE	Microwave Assisted Extractor
AAS	Atomic Absorption Spectrometer
SEF	Supercritical Fluid Extraction
PLE	Pressurized Liquid Extraction



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

A lubricant sometimes referred to as lube is a substance (often a liquid) introduced between two moving surfaces to reduce the friction between them, improving efficiency and reducing wear. It may also have the function of dissolving or transporting foreign particles and of distributing heat. One of the single largest applications for lubricants, in the form of motor oil, is protecting the internal combustion engines in motor vehicles and powered equipment (Boughton and Horvath, 2003).

Typically lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc. Lubricants such as 2-cycle oil are also added to some fuels. Sulfur impurities in fuels also provide some lubrication properties, which has to be taken in account when switching to a low-sulfur diesel, biodiesel is a popular diesel fuel additive providing additional lubricity (Boughton and Horvath, 2003).

Non-liquid lubricants include grease, powders (dry graphite, PTFE, Molybdenum disulfide, tungsten disulfide, etc.), teflon tape used in plumbing, air cushion and others

Dry lubricants such as graphite, molybdenum disulfide and tungsten disulfide also offer lubrication at temperatures (up to 350 °C) higher than liquid and oil-based lubricants are able to operate. Limited interest has been shown in low friction properties of compacted oxide glaze layers formed at several hundred degrees Celsius in metallic sliding systems, however, practical use is still many years away due to their physically unstable nature (Inman, 2003)

Many companies spend billions of dollars worldwide on exploring, recovering and refining crude oil to obtain a quality lube oil stock. In addition, these companies then spend million dollars on research and development, and marketing of retail product. Then, after utilizing the oil in cars, trucks and machinery, the oil is basically thrown away. This can be considered waste of precious and non-renewable resource, where the thrown away used oil will finally destroy the human life.

Researchers have encourages to carry out an investigation to obtain the base oil from used lubricant oil because of the remaining molecular structure of base oil (Hess, 1979). Synthetic base oil can be produced in the laboratory, but due to environmental concern and operation cost, the researchers spend their energy and mind towards finding a suitable method to re-refine the base oil from spent lubricant oil. The most popular conventional method is the acid/clay treatment. However this method creates another environmental problem due to the production of acidic sludge. The replacement of sulphuric acid consumption with hydrogenation process to re-refine the base oil somehow creates another problem when it requires high temperature to operate optimally. Implementation of high temperature, however, destructs the base oil molecular structure, which can only remain until 320°C (Inman, 2003)

Solvent extraction method is the method to eliminate the usage of high temperature or hydrogenation process in re-refining the base oil from spent lubricant oil. This new method retained the structure of the base oil through the whole process. Theoretically, the presence of polar solvent segregates the particles from liquid phase, while slightly/non-polar solvent stabilizes the polymeric molecules for example polyolefins and other additives. The stable dispersion, which occurs in the

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presence of this two extracting solvent, is destabilized in the presence of flocculating agent. It is then removed in the form of sludge and may used as raw material to the ink industry. The best performance of solvent extraction method is high sludge removal and minimum of oil loss.

## **1.2 Problem Statement**

Spent lubricant oil is one of the abundant liquid wastes in the country that needs to be further treated. Currently, this liquid waste has been disposed of to the environment and creates a lot of problems. It dumped on the ground, down the sewers, or sent to landfills, where it finally either seeps into ground or floats on water surface. Spent lubricant that manages to migrate into soil or ground may come across the underground water sources. It forms a thin black film on water surfaces and this film blocks the sunlight penetration. It can cause aquatic plant will not be able to photosynthesize and therefore reduces the oxygen supply to marine life. Without oxygen, marine life cannot survive and finally interrupt the natural food chain where human being is the prior victim. So, we need to recover the spent lubricant to get the base oil. Solvent extraction is the best method to recover the base oil but we should choose the best solvent to get the high sludge removal and minimum of oil loss. Furthermore, we can commercialize the product that we gain and make it profitable.

## **1.3 Statement of Objectives**

The main objective of this study is to recover the base oil from spent lubricants using solvent extraction method. Besides that, the effects of different solvent, the retention time and the characteristics of extracted base oil are also determined.

## 1.4 Research Scopes

The research scopes for this study are:

- i) To study the effects of different solvent used; hexane + sodium hydroxide + isopropyl alcohol and N-vinyl-2-pyrrolidone (NNVP) on base oil characteristics.
- ii) To study the effects of different retention time at 30 min, 60 min and 90 min on base oil characteristics.
- iii) To characterize the extracted base oil ; density, viscosity, flash point and metal content of the base oil.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

Lubricant oil is the most important liquid that is used in almost every vehicles and machines. The oil is used to ensure the smooth performance and prolong the good condition of vehicles and machines. Basically, the main ingredient of lubricant oil is the base oil, which is refined from crude oil or synthesized in laboratory. Base oil mixed with additives to enhance the ability of the oil to act as a layer between contact surfaces. The origin of base oil is the crude oil, which is non-renewable resource. However, base oil molecular structure remains at initial condition although is has gone through particular usage in vehicles. Thus, re-refining the used oil after consumption, with intention to recover the base oil is a big potential in overcoming the shortage of lubricant oil sources in the future. Moreover, re-refining reduce the contribution of the used oil, which is one of the carcinogenic sources, in polluting the environmental, especially the water sources, and disrupting the marine life. Therefore, re-refining of the base oil from the spent lubricant oil is considered a tremendous contribution to the saving of crude oil resources as well as to the well being of environmental and human being.

## 2.2 Lubrication Oil

Lubrication oil is obtained either by refining or by residual fractions directly from crude oil. Process of the refining crude oil consist two stages. First is the light products refining which operates above the atmospheric pressure and the second is the refining of lubricating oils and waxes. Modern lubricating oil is made of base stock or base oil (71.5-96.2%), blended with few parts per million (ppm) of chemical additives according to its grade and specific duty. For lubrication, additives are added to fulfill the specific requirement. There are three major roles of additives. First is to impart new, useful and specific properties to lubricant oil. Second is to enhance present properties and third is to reduce the rate of undesirable change that take place during its service life (Lim, 2000). Each lubricant oils consisted at least one type of additives, or nearly 30 percent of weight of additives. Table 2.1 shows comparison of a typical lubricating oil obtained from Gergel (1992).

**Table 2.1 :** Comparison of a Typical Lubricating Oil (Gergel, 1992)

Ingredients		Weight %
SAE 30 or 40 base oil stock		71.5-96.2
Additives	Metallic detergent	2.0-10.0
	Ashless dispersant	1.0-9.0
	Oxidation inhibitor	0.5-3.0
	Antioxidant/antiwear	0.1-2.0
	Friction modifier	0.1-3.0
	Pour point depressant	0.1-1.5
	Antifoam	2-15 ppm

Additives are blended up to 3.8-28.5% of the weight. Metallic detergent is added at 2.0-10.0% to neutralize the deposits formation from combustion of high sulfur fuel or acidic combustion material, which also help to prevent the deposition of lacquer resulting from oxidation. An example of metallic detergent that usually added is magnesium sulfonates. Dispersant (1.0-9.0%), is blended with base stock to



disperse or suspend sludge formation during usage, such as polymeric succinimides and polyesters. 0.5-3.0% of zinc dithiophosphate is introduced into the base oil by of weight as the oxidation inhibitor. It helped the base oil to form a film layer to prevent acid from reaching the metal surface (Gergel, 1992). Esters or acidic (0.1-2.0%) performs as the antiwear to reduce the effect of wear and friction. Friction modifier and antifoam are added at 0.1-3.0% and 2-15 ppm, respectively. Antifoam collapses the small bubbles into big bubbles, which tend to rise and collapse at the surface. Pour point depressant for example methacrylates polymer is mixed into the oil at 0.1-1.5%. It helps to inhibit the formation of wax crystal structure, which preventing the oil flow, during usage at low temperature.

### 2.3 Base Oil

Base oil is the base component of lubricant oil. It is the basic requirement in lubricant engine oil. Generally, there are three types of base oil; mineral oils, modified oils and synthetic oils. Mineral oil is a selected fraction of crude oil with some components remained in order to improve the oil performance. Virtually, the molecules in the mineral oil are the similar molecules in the crude oil. Base oil from modified oil, is produced from the selected fraction of the refining process that went through a severe treatment carrying some of the molecules to rearrange, such as hydrocracked or hydrotreated base oil. It still contained most of the molecules that present in the original crude oil. Finally, synthetic base oil, which is synthesized by chemical reaction of limited number of well-define components. The main purpose is to meet targeted performance, such as exceptional low temperature behavior. This is obtained by the nature of synthetic molecules or the absence on unwanted components that usually exist in mineral oils. Moreover, the price of synthetic base oil is higher compare to conventional lube oil due to the complex process of manufacturing and pure chemicals of raw material as opposed to refine oil. (Petronas, 1999).

Consequently, there are two categories of base oil. First is paraffinics and second is naphthenics. Paraffinics base oil is high in alkanes with proportion of

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straight chain saturated hydrocarbons, has high viscosity index and adequate low temperature properties. However, it requires an aromatic removal and dewaxing during production process. Meanwhile, naphthenics contain high proportion of closed-ring methylene groups (Petronas, 1999), wax-free or little-wax content, has low pour points and more limited range in crude oil compares to paraffinics.

Normally, base oil is manufactured by simple distillation of petroleum crude oil. The quality of the base oil improved by additional of very simple processing such as acid treatment or filtration method, to remove less desirable component for example wax, aromatics and asphalt. The base oil was manufactured in large quantities with interrelationship between other process streams in modern refinery (Weinstein, 1974). Solvent extraction is then used in modern refinery to replace acid treatment method due to environmental consideration, with the main purpose of improving the oil's oxidation stability, viscosity index and additive response.

## 2.4 Used Oil

Used oil is defined as any semi-solid liquid used product consisting totally or partially of mineral oil or synthesized hydrocarbons (synthetic oil), oily residues from tanks, oil-water-mixtures and emulsions which comes from various sources such as lubricating, hydraulic, heat transfer and electrical insulating. (Mortier *et al.*, 1992).

Besides that, it also defined as oil from industrial and non-industrial sources, which has been used for lubricating or other purposes and has become unsuitable for its original purpose due to the presence of contaminants or impurities, or the loss of original properties due to physical contaminants and chemical reactions occurring during its use (Lim, 2000).

Generally, used lubricant oil comes from two major sources. Industrial used lubricant oil for metal working, hydraulic lube oil, turbine and circulating lube oil,

which is easy to recycle, and can be generated as lubricant oil without sophisticated treatment to achieve the standard requirement. Engine oil, hydraulic and gear oil contributed to the amount of automotive used lubricant oil, which need specific treatment to produce re-refined base oil (Mortier *et al.*, 1992).

From Environmental Protection Agency of United State of America (USEPA) regulatory, used oil is defined as any oil that has been refined from crude oil or any synthetic oil that has been used and a result of such use is contaminated by physical or chemical impurities. Table 2.2 shows used oil obtained from USEPA's Definition.

**Table 2.2 :** Used oil by USEPA's Definition

Used Oil is	Used Oil is Not
<ul style="list-style-type: none"> <li>• Synthetic oil-usually derived from coal, shale or polymer-based starting material</li> <li>• Engine oil-typically includes gasoline and diesel engine crankcase oils and piston-engine oils for automobiles, trucks, boats, airplanes, locomotives and heavy equipments.</li> <li>• Transmission fluid</li> <li>• Refrigeration oil</li> <li>• Compressor oils</li> <li>• Metal working fluids and oils</li> <li>• Laminating oils</li> <li>• Industrial hydraulic fluid</li> <li>• Copper and aluminium drawing solution</li> <li>• Electrical insulating oil</li> <li>• Industrial process oils</li> <li>• Oils used as buoyants.</li> </ul>	<ul style="list-style-type: none"> <li>• Waste oil that is bottom clean-out waste from virgin fuel storage tanks, virgin oil spill cleanups or other oil that have not actually been used</li> <li>• Products such as kerosene and antifreeze</li> <li>• Vegetable and animal oil, even when used as a lubricant</li> <li>• Petroleum distillates used as solvents</li> </ul>

## 2.5 Solvent Extraction Method

Liquid-liquid extraction, also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another liquid phase. Liquid-liquid extraction is a basic technique in chemical laboratories, where it is performed using a separator funnel. This type of process is commonly performed after a chemical reaction as part of the work-up.

In other words, this is the separation of a substance from a mixture by preferentially dissolving that substance in a suitable solvent. By this process, a soluble compound is usually separated from an insoluble compound. Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, the processing of perfumes, and other industries.

Liquid-liquid extraction is possible in non-aqueous systems: In a system consisting of a molten metal in contact with molten salt, metals can be extracted from one phase to the other. This is related to a mercury electrode where a metal can be reduced, the metal will often then dissolve in the mercury to form an amalgam that modifies its electrochemistry greatly. For example, it is possible for sodium cations to be reduced at a mercury cathode to form sodium amalgam, while at an inert electrode (such as platinum) the sodium cations are not reduced. Instead, water is reduced to hydrogen. A detergent or fine solid can be used to stabilize an emulsion, or third phase.

In solvent extraction, a distribution ratio is often quoted as a measure of how well-extracted a species is. The distribution ratio ( $D$ ) is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, and a large number of other parameters. ( $D$  is related to the  $\Delta G$  of the extraction process).

which is often expressed as the logarithm. See partition coefficient for more details. Note that a distribution ratio for uranium and neptunium between two inorganic solids (zirconolite and perovskite) has been reported. In solvent extraction, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the more polar solvent, and the less polar solutes in the less polar solvent. In this experiment, the nonpolar halogens preferentially dissolve in the nonpolar mineral oil.

## 2.6 Atomic Absorption Spectrometer

In analytical chemistry, atomic absorption spectroscopy is a technique for determining the concentration of a particular metal element in a sample. The technique can be used to analyze the concentration of over 70 different metals in a solution. Although atomic absorption spectroscopy dates to the nineteenth century, the modern form was largely developed during the 1950s by a team of Australian chemists. They were led by Alan Walsh and worked at the CSIRO (Commonwealth Science and Industry Research Organisation) Division of Chemical Physics in Melbourne, Australia.

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It relies therefore heavily on Beer-Lambert law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

As the quantity of energy (the power) put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being

measured. In order to analyze a sample for its atomic constituents, it has to be atomized. The sample should then be illuminated by light. The light transmitted is finally measured by a detector. In order to reduce the effect of emission from the atomizer (e.g. the black body radiation) or the environment, a spectrometer is normally used between the atomizer and the detector.

The technique typically makes use of a flame to atomize the sample, but other atomizers such as a graphite furnace or plasmas, primarily inductively coupled plasmas, are also used.

When a flame is used it is laterally long (usually 10 cm) and not deep. The height of the flame above the burner head can be controlled by adjusting the flow of the fuel mixture. A beam of light passes through this flame at its longest axis (the lateral axis) and hits a detector.

A liquid sample is normally turned into an atomic gas in three steps:

1. Desolvation (Drying) – the liquid solvent is evaporated, and the dry sample remains
2. Vaporization (Ashing) – the solid sample vaporises to a gas
3. Atomization – the compounds making up the sample are broken into free atoms.

The radiation source chosen has a spectral width narrower than that of the atomic transitions. Hollow cathode lamps are the most common radiation source in atomic absorption spectroscopy. Inside the lamp, filled with argon or neon gas, is a cylindrical metal cathode containing the metal for excitation, and an anode. When a high voltage is applied across the anode and cathode, gas particles are ionized. As voltage is increased, gaseous ions acquire enough energy to eject metal atoms from the cathode. Some of these atoms are in an excited states and emit light with the frequency characteristic to the metal. Many modern hollow cathode lamps are selective for several metals. Atomic absorption spectroscopy can also be performed by lasers, primarily diode lasers because of their good properties for laser absorption

spectrometry. The technique is then either referred to as diode laser atomic absorption spectrometry (DLAAS or DLAS), or, since wavelength modulation most often is employed, wavelength modulation absorption spectrometry.

## 2.7 Microwave Extractor (MAE)

In recent years, MAE has attracted growing interest, as it allows rapid extraction of solutes from solid matrices by employing microwave energy as a source of heat, with extraction efficiency comparable to that of the classical techniques. The partitioning of the analytes from the sample matrix to the extractant depends upon the temperature and the nature of the extractant. Unlike classical heating, microwaves heat the entire sample simultaneously without heating the vessel; thus, the solution reaches its boiling point very rapidly, leading to a very short extraction time. Microwave energy causes molecular motion by migration of ions and rotation of dipoles. Dipole rotation refers to the alignment of molecules in the solvent and samples that have dipole moments. As the field decreases, thermal disorder is restored resulting in the release of thermal energy. At 2.45 GHz (the only frequency used in commercial systems), the alignment of the molecules followed by their return to disorder occurs  $4.9 \times 10^9$  times per second, which results in rapid heating (Ahmed, 2003).

During the extraction of oils from plant materials, MAE allows the migration of the compounds out of the matrix by selective interaction between microwaves and free water molecules present in the vascular systems, leading to localized heating and boiling of water. As the system expands, the cell walls rupture, allowing essential oils to flow towards the organic solvent. This process is different from classical solvent extraction, where the solvent diffuses into the matrix and extracts the components by solubilization. Moreover, in MAE, a wider range of solvents could be used, as the technique is less dependent on a high solvent affinity (Ahmed, 2003).

The application of microwave energy to the sample may be performed using two technologies which are closed vessels under controlled pressure and temperature, a process referred to as pressurized MAE (PMAE) or open vessel under atmospheric pressure, referred to as focused MAE (FMAE). The most commonly used closed system, the CEM MES 1000, allows extraction of 12 samples simultaneously under controlled temperatures. The main drawbacks of such a system are: loss of more volatile solutes if the temperature inside the vessel rises rapidly; and, the vessels need to be cooled to room temperature after extraction and before they can be opened, thus increasing the overall extraction time. In open systems, as extractions proceed under atmospheric pressure, the maximum possible temperature is determined by the boiling point of the solvent. Sample heating is carried out homogeneously and efficiently. The most commonly used system is the Prolabo Soxwave 100. Losses of vapor are prevented by the presence of a reflux system on top of the extraction vessel. The system offers increased safety of sample handling compared to extraction in a pressurized, closed vessel, and a larger sample may be extracted in such a system than in a closed vessel system (Ahmed, 2003).

MAE seems to be a viable alternative to conventional extraction techniques for a variety of solid matrices, either spiked or containing native compounds. Moreover, MAE offers great reductions in time and solvent consumption, and increased sample throughput. Optimization of MAE conditions is rather easy, because there are few parameters (matrix moisture, nature of solvent, time, power and temperatures in closed vessels), and it is cheaper than other modern techniques, such as SEF and PLE. On the other hand, selectivity may be less, so a clean-up procedure may be required before analysis. For some applications, a filtration step only is needed, whereas, for others, SPE, GPC or additional LLE steps may have to be carried out. Although most existing applications of MAE deal with solid samples, the results from liquid matrices are promising, suggesting that this field of application will expand in the near future (Ahmed, 2003).

Even though dried plant material is used for extraction in most cases, but still plant cells contain minute microscopic traces of moisture that serves as the target for microwave heating. The moisture when heated up inside the plant cell due to



microwave effect, evaporates and generates tremendous pressure on the cell wall due to swelling of the plant cell. The pressure pushes the cell wall from inside, stretching and ultimately rupturing it, which facilitates leaching out of the active constituents from the ruptured cells to the surrounding solvent thus improving the yield of phytoconstituents. This phenomenon can even be more intensified if the plant matrix is impregnated with solvents with higher heating efficiency under microwave (higher  $\tan \delta$  value). Higher temperature attained by microwave radiation can hydrolyze ether linkages of cellulose, which is the main constituent of plant cell wall, and can convert into soluble fractions within 1 to 2 min. The higher temperature attained by the cell wall, during MAE, enhances the dehydration of cellulose and reduces its mechanical strength and this in turn helps solvent to access easily to compounds inside the cell (Vivekananda Mandal *et al.*, 2007).

In order to study cell damage during the MAE experiments, tobacco leaf samples were examined by scanning electron microscopy. Scanning electron micrographs of the untreated sample, heat-reflux extraction sample and MAE sample revealed that there were no structural difference between heat-reflux extraction and those of untreated samples, except few slight ruptures on the surface of the sample. However, the surface of the sample was found greatly destroyed after MAE. This observation suggests that microwave treatment affects the structure of the cell due to the sudden temperature rise and internal pressure increase. During the rupture process, a rapid exudation of the chemical substance within the cell into the surrounding solvents takes place. This mechanism of MAE based on exposing the analytes to the solvent through cell rupture is different from that of heat-reflux extraction that depends on a series of permeation and solubilization processes to bring the analytes out of the matrix. Destructive changes in the plant tissue of fresh orange peel due to microwave treatment was also observed using scanning electron micrographs. These changes in the plant tissue due to microwave heating gave a considerable increase in the yield of extractable pectin. Furthermore, the migration of dissolved ions increases solvent penetration into the matrix and thus facilitates the release of chemicals. Evidence has also been presented that during the extraction of essential oils from plant materials, MAE allows the desorption of compounds of interest out of the plant matrix. This occurs due to the targeted heating of the free