



CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Biodegradable composites of polypropylene

Polypropylene (PP) is a thermoplastic material that is produced by polymerizing propylene molecules, which are the monomer units, into very long polymer molecules or chains as shown in Figure 2.1. PP is semitranslucent and milky white in color which provided excellent colorability. PP is one of the most widely used plastics that offer a good balance of thermal, chemical, and electrical properties, along with moderate strength and cost. PP is used in a great variety of applications such as fibers, films, sheets, packaging materials, and injection molded parts. Therefore, PP is present in various amounts in all types of waste derived from its usage: around 15% found in household waste; 10 to 15% present in commercial waste; 5 to 10% from shredded cars; less than 5% of electrical scrap (Brandrup *et al.*, 1996). An undesirable consequence of this widespread use of PP is the creation of tremendous waste materials which are environmentally concern.

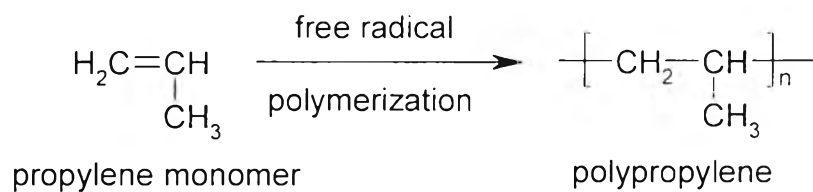


Figure 2.1. Polymerization of propylene into polypropylene.

PP can not be degraded by microorganisms under natural environment. One of the viable alternatives to accelerate the attack of microorganisms is the addition of natural polymers, like starch and cellulose to guarantee at least a partial biodegradation.

2.1.1 Starch

Starch is the natural, low cost and easily biodegradable polymer. It consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of α -D-glucose units. In amylose, these are α -(1,4)-D-glucose linked, whereas in amylopectin, about every twenty α -(1,4)-D-glucose unit are also α -(1,6)-linked forming branch-points represented in Figure 2.2 and 2.3, respectively (Aggarwal and Dollimore, 1995).

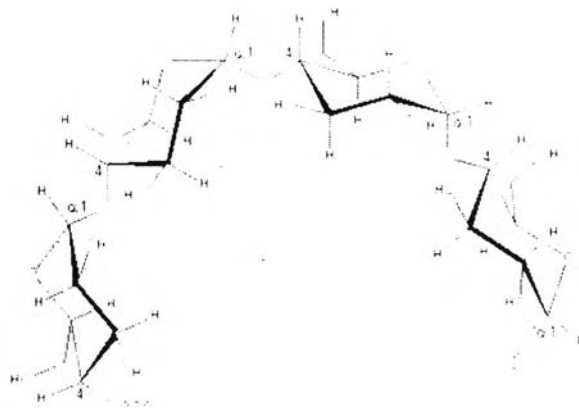


Figure 2.2. α -(1,4)-linkage of amylose.

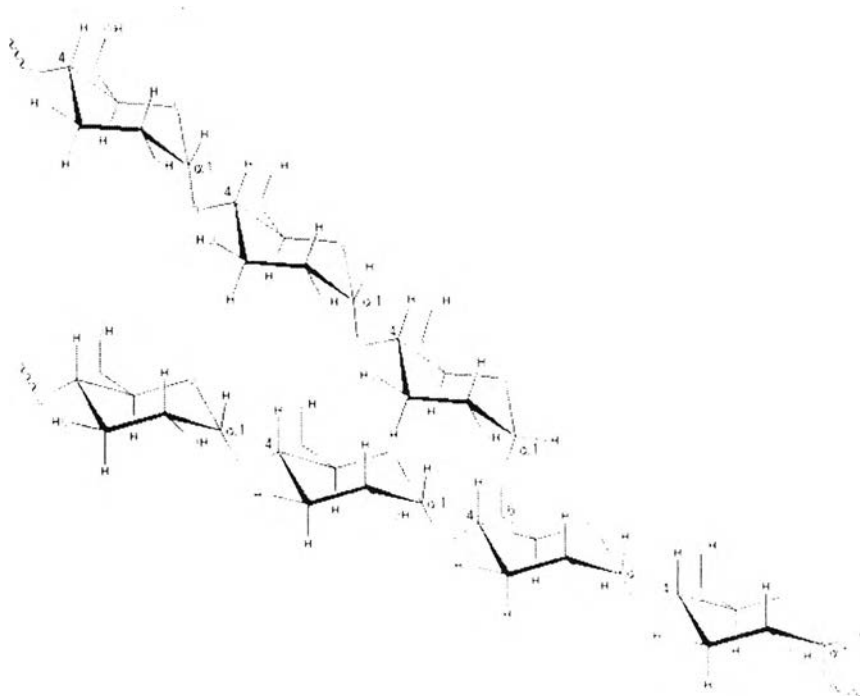


Figure 2.3. α -(1,6)-linkage forming branch-points of amylopectin.

Starch is already used as filler in polyolefins to allow the economical removal of polymer waste by biodegradation. The mechanical and rheological behavior and susceptibility to natural degradation of starch containing polymer systems depends on many factors such as content and properties of starch, blending and processing conditions of the polymer composites. Rule of thumb is that an increase of starch content in composition results in worsening of mechanical and rheological properties and the processability of the polymer systems. On the other hand, the most important factor is the continuity of the easily degradable starch phase. An increase of the content of the continuous starch phase improves the accessibility of the polymer matrix. Zuchowska *et al.*, (1997) studied the structure and properties of degradable polyolefin-starch blends. This study showed that the degradation susceptibility is determined by the type of polymer and the continuity of starch phase of the blend. But the rate of weight loss during soil ageing is significantly slow, and landfilling technique is not a suitable recycle solution because it is still not well established what the long-term effects of their degradation could lead to. (Pinto *et al.*, 1999)

2.1.2 Microcrystalline cellulose

Cellulose is found in plants as microfibrils in 2-20 nm diameter and 100-40000 nm long. These form the structurally strong framework in the cell walls. Cellulose is a linear polymer of β -(1,4)-D-glucose units as shown in Figure 2.4 (Shlieout *et al.*, 2002). The fully equatorial conformation of β -linked glucose residues stabilize the chair structure, minimizing its flexibility relative to the slightly more flexible α -linked glucose residues in amylose of starch.

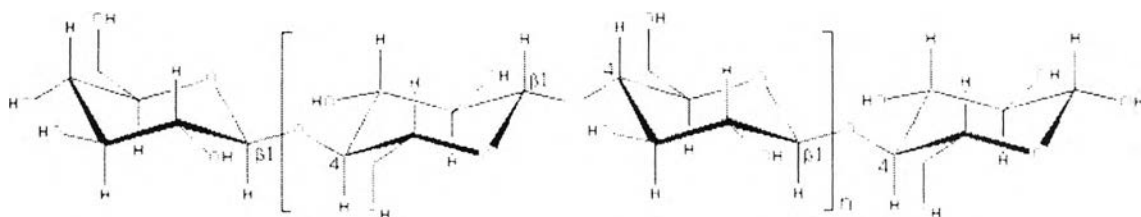


Figure 2.4. β -(1,4)-D-glucopyranose linkage of cellulose

Each cellulose microfibril exhibits a high degree of three-dimensional internal bonding resulting in a crystalline structure that is insoluble in water and resistant to reagents. The natural crystal is made up from cellulose I with all the cellulose strands parallel and no inter-sheet hydrogen bonding. If it can be recrystallized (e.g. from base or CS_2), cellulose I gives more stable cellulose II structure with an antiparallel arrangement of the strands and some inter-sheet hydrogen bonding. However, there are relatively weak segments of the microfibril with weaker internal bonding. These are called amorphous regions. The crystalline region is isolated to produce microcrystalline cellulose (MCC). MCC is prepared from native cellulose by controlled acid hydrolysis, which preferentially attacks amorphous regions, followed by neutralization with alkali to recovery MCC. This material is largely composed of aggregated bundles of crystallization of cellulose formed as porous particles (Levis, 2001). It is white, odorless, tasteless, and is insoluble in water, dilute acids and most organic solvents.

2.2 Pyrolysis process

The usual ways to deal with plastic wastes are recycling, composting, landfilling, and incineration. However, they are not preferred solutions because of high energy consumption, risk of odor, no suitable place for disposal, emission of hazardous substance, respectively (Ren, 2002). Possible acceptable processes are converting these wastes into reusable products such as gasoline and heavy oil by pyrolysis process.

Pyrolysis is defined as the thermal decomposition of macromolecules by thermal energy under oxygen deficient conditions. This decomposition results in breaking of molecular bonds and fragmentation into small molecular species that related to constituents in their original material. The degradation of molecules which occurs during pyrolysis is caused by the dissociation of chemical bonds and the production of free radicals. Pyrolysis products from organic materials contain hydrocarbons, which may be utilized as fuel, recycle material and monomer.

The general processes to explain the behavior of these molecules are based on free radical degradation mechanisms. The way in which a molecule fragments during pyrolysis depends on the types of chemical bond involved and on the stability of the resulting smaller molecules. The carbon chain backbone of macromolecule such as in many synthetic polymers, may be expected to break apart in a random trends and is referred to as random scission. If all of the C-C bonds are about the same strength, such as in polypropylene, there is no reason for one to break more than others (Wampler, 1995). It would break apart into hydrocarbons, which may contain any number of carbons, such as methane, ethane, propane, etc. The random scission produces hydrocarbons with terminal free radicals, which may be stabilized by abstracts a hydrogen atom from a neighboring molecule or intramolecular radical transfer via six-membered ring intermediates (backbiting, as shown in Figure 2.5. This hydrogen transfer results in a saturated end, and creates another free radical in the neighboring molecule or produces intramolecular tertiary radicals, follows by beta scission to stabilize, which accounts for most of the polymer backbone degradation by producing an unsaturated end and a new terminal free radical. This process continues, producing hydrocarbon molecules which are saturated, or have one terminal double bond at each end as seen from Figure 2.6 (Wampler, 1995).

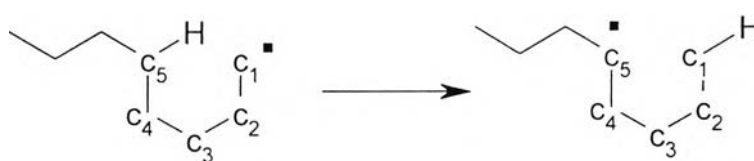


Figure 2.5. Intramolecular radical transfer via six-membered ring intermediates.

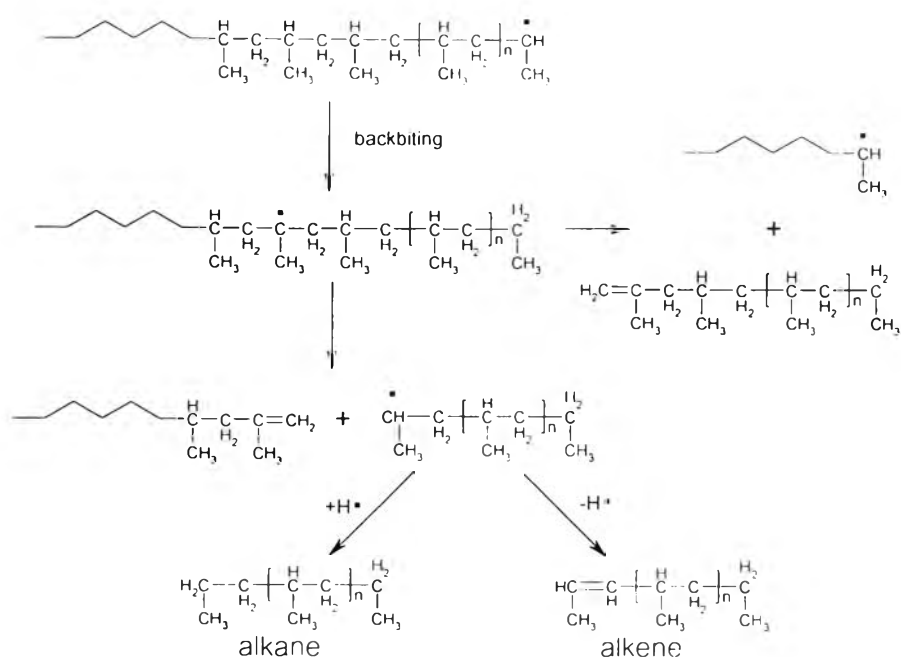


Figure 2.6. Saturated and terminal alkene products from free radical mechanisms.

Dialkenes formation in Figure 2.7 starts with a terminally unsaturated polymer chain from an internal tertiary radical via hydrogen abstraction of neighboring molecule or by main-chain cleavage followed by backbiting. Decomposition of polymer chain via beta scission leads to a series of α,ω -dialkenes. Another pathway leads to a secondary radical to alkene and diene oligomers (Lattimer *et al.*, 1995).

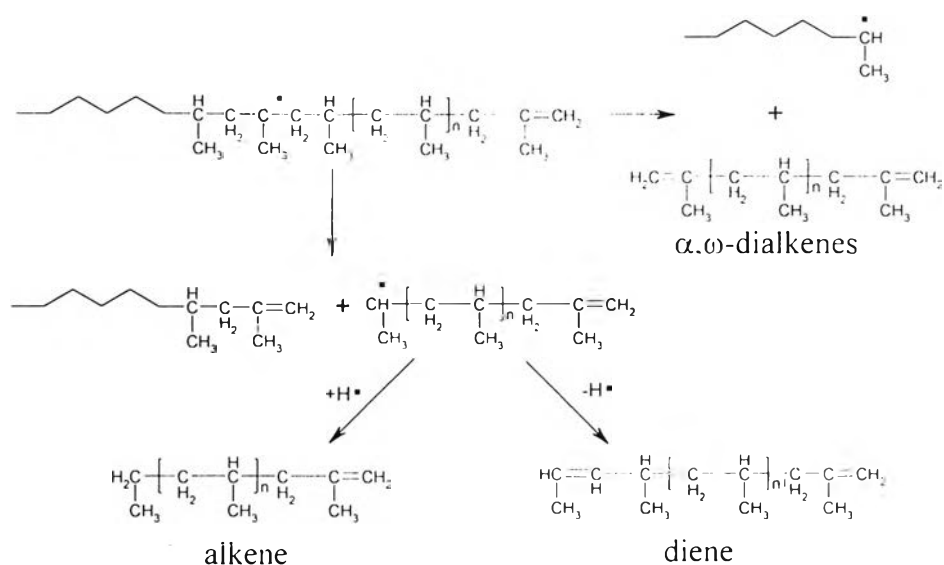


Figure 2.7. Diene and α,ω -dialkenes formation from terminal alkene products.

The pyrolysis process of PP has been studied by several authors in various compositions and parameters. Pinto *et al.*, (1999) investigated the effect of plastic waste composition on product yield by slow heating rate. They reported that end product yields and properties depend on the plastic waste composition. The presence of polyethylene increased alkane content, the presence of polypropylene favored alkene formation, while polystyrene led to higher aromatic content in the end product. Therefore, the desired end product can be obtained by varying plastic composition. Ciliz *et al.*, (2004) also studied slow pyrolysis conditions of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene. They suggested that the impurities consist of dirt and food residues led to higher amounts of gas yields.

Using virgin LDPE and PP for co-pyrolysis was also carried out at different carbon ratios (Ballice, 2002). The bond dissociation energy for the break up of LDPE was found to be greater than PP, indicated that PP should be easier to crack and could decomposed into pyrolysis products without any residues. On contrary, high-molecular weight waxy compounds remained in pyrolysis of LDPE. For LDPE/PP co-processing, no residue were obtained. It can be stated that pyrolysis products of PP react with heavier pyrolysis products of LDPE, leads to the radical degradation to give low-molecular weight hydrocarbons. But in LDPE-PP ratio of 1 to 3, pyrolysis products of PP is expected to be a poor solvent preventing further thermal degradation of LDPE, resulting in a wax formation.

In the presence of natural additives, Jakab *et al.*, (2000) studied slow heating pyrolysis process of wood-derived materials such as wood flour, lignin, cellulose and charcoal mechanically mixed with PP. Their aim is to understand the pyrolytic behavior of the mixture of these components occurring in waste. The wood-derived materials decomposed at lower temperature than that of PP. Thus, char formed from wood influences the degradation process of PP, which leads to the lower decomposition temperature. Gas chromatography/mass spectrometry (GC/MS) analysis of pyrolysis products also revealed that char promotes the formation of low molecular weight products due to the reactions of primary radicals.

In 2002, *Sharypov et al.*, also investigated the effect of reaction conditions and mixture composition of wood biomass such as beech wood, pine wood, microcrystalline cellulose, and hydrolytic lignin co-pyrolysis with synthetic polymer such as polyethylene and polypropylene on the degree of mixture conversion as well as on the yields of pyrolysis products. They found that the origins of biomass, as well as the type of polymers, play an important role in the pyrolysis products' distribution. The results suggested that the olefinic products from PP thermal conversion react with products from biomass, resulting in the depolymerization pathways of PP, leads to the increasing formation of light fractions. The tacticity of PP also has an influence on the pyrolysis products due to the degree of polymerization.

The pyrolysis experiment can be performed by thermogravimetric analysis (TGA) in order to assess the thermal behavior of the plastic samples (Demirbas, 2004). TGA is a method used to study the weight loss characteristics of a polymer when a sample is heated over a temperature range or held isothermally at a temperature. TGA requires a sensitive balance and a well-controlled furnace to maintain a specified temperature. Data collected during a TGA experiment includes time, temperature, and sample weight. Figure 2.8 shows that TGA can be linked to other modules such as gas chromatography and mass spectrometry to characterize the degradation products given off by the sample, resulting in some evaluation of the degradation mechanism.

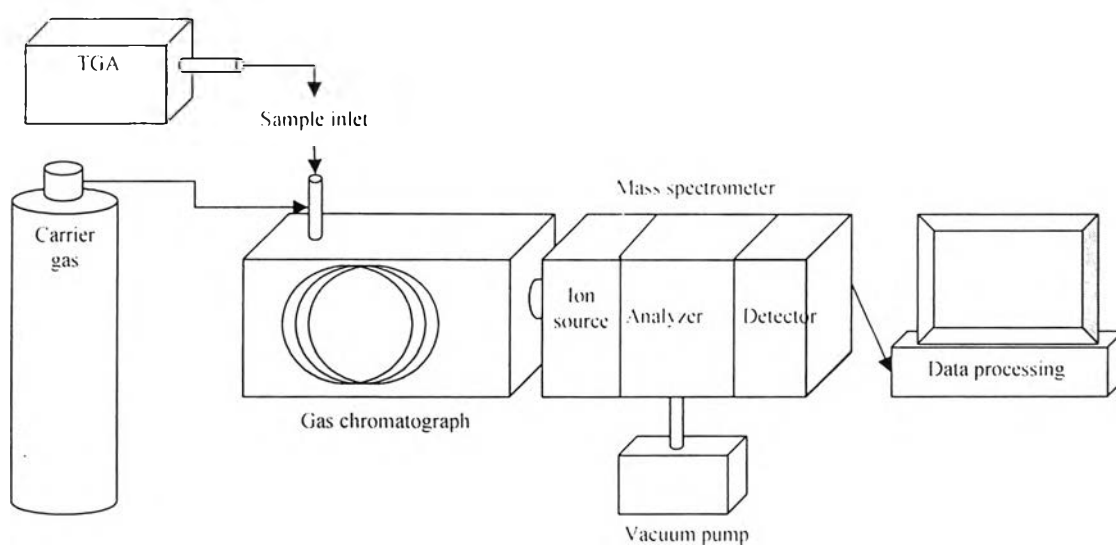


Figure 2.8. TGA-GC-MS systems.

2.3 Apparent kinetic parameters determination

The derivation of kinetic data in the study of polymer decomposition using TGA has received much attention in recent years. Common approach to determine the apparent kinetic parameters is the weight loss behavior during material decomposition and to use the Arrhenius equation to fit the weight loss data to provide the kinetic parameters (Yang *et al.*, 2001). The basic rate equation is

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2.1)$$

The above equation expresses the rate of conversion ($\frac{d\alpha}{dt}$) at a constant temperature as a function of the rate constant (k) and the function of the conversion (α). In the case of polymer degradation, it is assumed that the rate of conversion is proportional to the concentration of material that has to react (Alvarez and Vazquez, 2004) so

$$f(\alpha) = (1 - \alpha)^n \quad (2.2)$$

The temperature dependence of the rate constant (k) is described by Arrhenius equation:

$$k = k_0 \exp(-E_a / RT) \quad (2.3)$$

The combination of these equations (Eq. 2.1, 2.2, and 2.3) give the following relationship:

$$\frac{d\alpha}{dt} = k_0 \exp(-E_a / RT) \cdot (1 - \alpha)^n \quad (2.4)$$

Where:

- k_0 : pre-exponential factor (rate constant at infinite temperature)
- E_a : activation energy (kJ/mol)
- R : universal gas constant (8.3136 kJ/mol K)
- T : temperature (K)

α : conversion of the reaction ($\frac{W_0 - W}{W_0 - W_x}$), W_0 is initial weight of the sample, W is sample weight at any temperature, and W_x is final sample weight.

n : reaction order

The conventional method to determine the Arrhenius parameters (E_a, k_0, n) is based on the Friedman's differential technique which uses the logarithmic Arrhenius equation as:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k_0 - \frac{E_a}{RT} + n \ln(1 - \alpha) \quad (2.5)$$

From Eq. 2.5, the activation energy can be directly obtained from the slope of the linearly regressed line of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$.

For non-isothermal data obtained at a constant heating rate ($\beta = \frac{dT}{dt}$) Eq. 2.4 can be rewritten as:

$$\beta = \frac{k_0(1-\alpha)^n}{d\alpha/dT} \exp(-E_a/RT) \quad (2.6)$$

The isoconversional method developed by Ozawa (1970) based on Eq.6:

$$\ln \beta = \ln\left(\frac{k_0(1-\alpha)^n}{d\alpha/dT}\right) - \frac{E_a}{RT} \quad (2.7)$$

This equation involves measuring the temperatures corresponding to fixed values of conversion (α) from experiments at different heating rate (β). The activation energy is obtained from the linearly regressing the plot of $\ln \beta$ against $\frac{1}{T}$ (Girija *et al.*, 2005).

To obtain the other kinetic parameter (k_0, n), Eq 2.4 can be rearrangement and written as

$$\left[\frac{(d\alpha/dt)}{\exp(-E_a/RT)} \right] = k_0 \cdot (1-\alpha)^n \quad (2.8)$$

By taking natural logarithm on both sides of Eq 2.8, the equation was in the new form of:

$$\ln \left[\frac{(d\alpha/dt)}{\exp(-E_a/RT)} \right] = \ln k_0 + n \ln(1-\alpha) \quad (2.9)$$

The plot of $\ln \left[\frac{(d\alpha/dt)}{\exp(-E_a/RT)} \right]$ versus $\ln(1-\alpha)$ is a straight line with slope equal to n and an intercept equal to $\ln k_0$ (Gersten *et al.*, 2000).

2.4 Characterizations of pyrolysis products

2.4.1 Gas chromatography

Gas chromatography (GC) is a dynamic method of separation and detection of volatile organic compounds and has chosen as an attractive method to analyze the complex mixture of pyrolysis products. GC involves the partitioning of gaseous solutes between an inert carrier gas as mobile phase and a stationary liquid or solid phase. Figure 2.9 is the major compartments of GC consist of gases, injection port, column, detector, and data acquisition system.

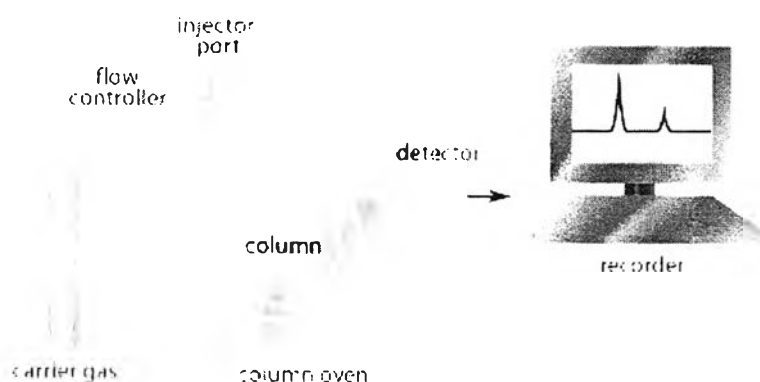


Figure 2.9. Gas chromatograph compartments

Helium is one of the most commonly used gases to carry the sample through the system. Increase the flow rate of carrier gas results in shorten the retention time. Injection port is the next major component to introduce the sample into the carrier gas stream. A split injection port is designed to allow only small fraction of sample volume into the column because of a limited sample capacity of the capillary column. Many split injection port can also operate in a splitless mode. In the splitless mode most of the sample is allowed to the column. This technique is suitable for samples with trace concentration. The third major component is column for separation of the components in the sample mixture. The more narrow the diameter and length, the greater the column efficiency to separate sample. The fourth major component of GC is the detector that senses the presences of components separated from the column and convert that information to the signal. The most commonly used detector is flame ionization detector (FID) because it responds to any type of hydrocarbon component. When hydrocarbon components burn in a flame, producing ions that are collected and converted into a current signal. As the components are separated and reach the detector, the signal increases and the detection or retention time of each peak is recorded and translated into a chromatogram by data acquisition system.

Gas chromatography is a well-established method in the analysis of pyrolysis products. Identification of pyrolysis-gas chromatography (PY-GC) is based either on the comparison with known chromatograms or the detailed analysis of pyrolysis products such as the combination with mass spectrometry.

2.4.2 Gas chromatography-mass spectrometry

Gas chromatography can separate volatile compounds with great resolution, but it cannot identify them. So mass spectrometry (MS) coupled with GC can provide detailed structural information of separated compounds.

In the first part of the MS, the ionizer which is an electron beam causes the components to gain a positive charge. This process causes further breakdown of the individual components. Each component has a unique fragmentation pattern. The sub-components then enter a magnetic region where they are focused and sent to a detector. Components with a lighter atomic mass enter the magnet set up and will be sent to the detector first. At the detector, the component transfers their charges which then activates a recorder capable of registering atomic mass, based on the mass/charge ratio, and identify the concentration of the particular component in the sample.

2.4.3 Elemental analysis

Elemental analysis on carbon, hydrogen and nitrogen is performed to characterize and prove the elemental composition of an organic sample to determine the empirical formula of the compound. The sample under test is weighed in tin capsule. The sample is then placed into the reactor chamber where excess oxygen is introduced before. At about 990 °C the material is mineralized and carbon monoxide is formed at this temperature. The complete oxidation is reached at a tungsten trioxide catalyst which is passed by the gaseous reaction products. The resulting mixture should consist of CO₂, H₂O, NO_x and some excess O₂ passes the catalyst. The product gas mixture flows through a silica tube packed with copper granules. In this zone, remaining oxygen is bound and NO_x are reduced to N₂. So the leaving gas stream consists of CO₂, H₂O and

N_2 . The gas mixture is passed to a gas chromatographic system. The individual components are then separated and elemental mass percentage of element in the sample is measured by thermal conductivity detector, TCD.