LITERATURE REVIEW

Feedstock of tertiary recycling is the organic component of the polymer waste that can be converted into high-value refinery products such as naphtha, crude oil, or syngas. Feedstock recycling is essentially cleavage of waste plastic back into petrochemical feedstocks that can be used as raw materials in the production of new petrochemical and plastics, without any deterioration in their qualities and without any restriction regarding their applications. Tertiary recycling consists of three types of reaction such as thermal cracking, catalytic cracking, and hydrocracking.

Thermal cracking

Thermal cracking or thermolysis involves the use of high temperature to cleave the bonds in the backbone of the polymer (Schier, 1998). The main forms of feedstock recycling of polymers by thermolysis are shown in Figure 1. When this decomposition process is carried out in the absence of air, this is termed pyrolysis. When it is performed in hydrogen atmosphere, it is referred to hydrogenation. If it is carried out in the presence of a controlled amount of oxygen, then it is known as gasification. Depending on the conversion route employed, the end products vary in composition and quality.

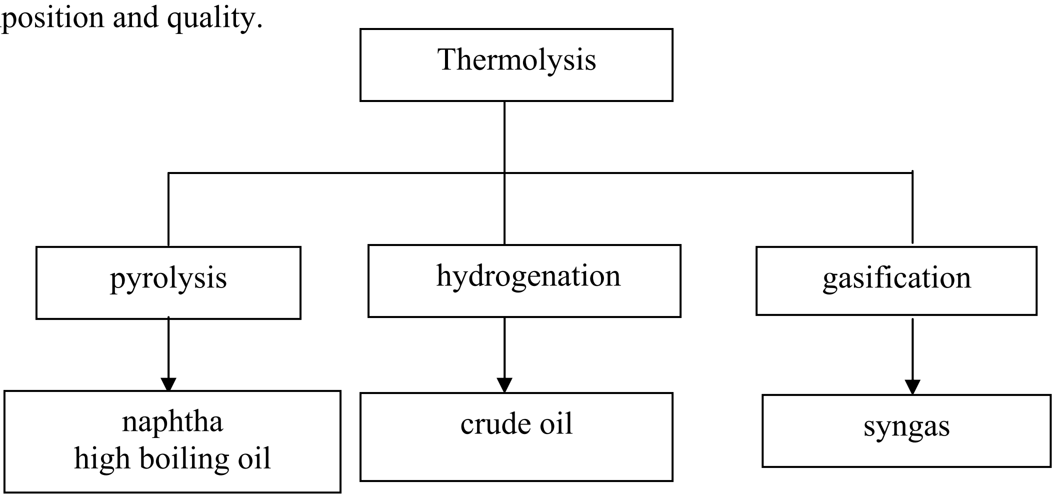


Figure 1 Overview of the main forms of feedstock recycling for waste plastics by thermolysis.

Source: Schier (1998)

Pyrolysis is carried out in a reducing atmosphere (i.e. in the absence of air) at temperature of up to 800^oC. In the pyrolysis process, plastic waste can be converted into petrochemical feedstocks such as naphtha, liquid and wax-like hydrocarbons and gases.

Pyrolysis is an excellent method for the recycling of heterogeneous materials such as mingled waste of automotive shredder residue. The thermal cracking of plastic waste has been conducted on an industrial scale by BASF. Due to the fact that the process is flexible and the design is simple, pyrolysis recycling can be economically viable.

Pyrolysis of plastic waste is conducted using a kiln which gives a high thermal efficiency of around 75-85%. The pyrolysis plant can convert plastic waste to pyrolytic oil and solid coke. Pyrolysis products may need further processing, such as refining of the light pyrolysis oils. Thus pyrolysis may be viewed as part of a multi-step process, rather than an integral system on its own.

Some general advantages of pyrolysis include:

- the energy consumption of the pyrolysis process is very low (for example, only a maximum of about 10% of the energy content of the waste plastic is used to convert the scrap into petrochemical products).

- the process can handle plastic waste which cannot be efficiently recycled by alternative means.

- the pyrolysis process operates without the need for air of admixtures of hydrogen, and does not involve elevated pressures.

Mechanism of thermal cracking

Thermal cracking processes generally proceed via radical pathways (Olah, 1995). The principal reactions of pyrolysis involve hydrogenation or dehydrogenation concurrently with fragmentation of the carbon skeleton. The process is initiated by carbon-carbon bond homolysis with formation of two free radicals as equation 1. The initially formed radicals may then abstract secondary hydrogen as shown in equations 2 and 3 since secondary hydrogens have lower bond strength than do the primary hydrogens. All secondary hydrogens are equivalent in their ease of homolysis in comparison with homolysis of primary hydrogen from methyl group. The intermediate radical may undergo C-C bond homolysis (β-scission) to form olefins as ethylene and propylene and a new alkyl group as shown in equations 4 and 5. Dis proportionation leads to a new olefin and an alkane with the same number of carbon atoms in equation 6.

$$CH_3(CH_2)_{14}CH_3 \longrightarrow CH_3(CH_2)_8\,CH_2CH_2\overset{\bullet}{C}H_2 \;+\; {\bullet}CH_2CH_2CH_2CH_3 \tag{1}$$

$$CH_3(CH_2)_8\,CH_2CH_2\overset{\bullet}{C}H_2 \;+\; CH_3(CH_2)_{14}CH_3 \longrightarrow CH_3(CH_2)_8\,CH_2CH_2CH_3 \;+\; CH_3(CH_2)_{11}\,CH_2CH_2\overset{\bullet}{C}HCH_3 \tag{2}$$

$${\bullet}\,CH_2CH_2CH_2CH_3 \;+\; CH_3(CH_2)_{14}\,CH_3 \longrightarrow CH_3CH_2CH_2CH_3 \;+\; CH_3(CH_2)_{11}\,CH_2\overset{\bullet}{C}HCH_2CH_3 \tag{3}$$

$$CH_3(CH_2)_8\,CH_2CH_2\overset{\bullet}{C}H_2 \longrightarrow CH_3(CH_2)_8\,\overset{\bullet}{C}H_2 \;+\; CH_2{=}CH_2 \tag{4}$$

$$CH_3(CH_2)_{11}\,CH_2CH_2\overset{\bullet}{C}HCH_3 \longrightarrow CH_3(CH_2)_{11}\,\overset{\bullet}{C}H_2 \;+\; CH_2{=}CHCH_3 \tag{5}$$

$$2\;{\bullet}CH_2CH_2CH_2CH_3 \longrightarrow CH_2{=}CHCH_2CH_3 \;+\; CH_3CH_2CH_2CH_3 \tag{6}$$

In the temperature range of 500-800°C methyl and ethyl radicals are the only stable radicals formed. Apparently all higher radicals decompose into alkanes and either methyl and ethyl radicals or atomic hydrogen. These then react via hydrogen abstraction to give methane, ethane and dihydrogen as in Figure 2. The overall result of thermal cracking is changed in hydrogen content and carbon skeleton. The reactions of methyl alkanes are also illustrative of the chemistry occurring.

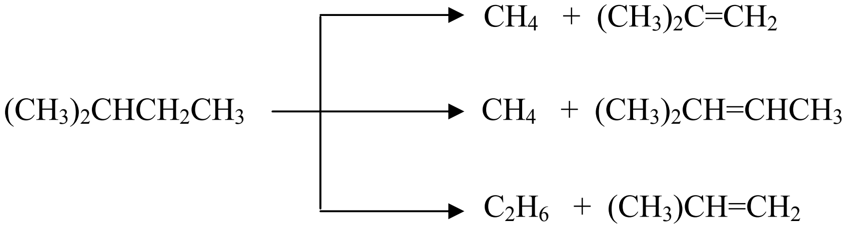


Figure 2 Reaction scheme of hydrogen abstraction.
Source: Olah (1995)

In cracking of alicyclic alkanes, the reaction proceeds by abstraction of a hydrogen atom followed by β scission. The cyclopentyl radical may undergo successive hydrogen abstraction to form cyclopentadiene.

Under certain conditions dehydrogenation is becoming an important reaction during pyrolysis, thermal dehydrogenation. However, only ethane is transformed to ethylene in high yield without cracking. Propane also gives propylene, but cracking to form methane and ethylene is significant. In general, lower molecular weight (hydrogen rich) alkanes undergo dehydrogenation with the hydrogen formed participating in hydrogen transfer reactions. In contrast, C-C bond rupture is the characteristic transformation of higher-molecular weight (more hydrogen-deficient) hydrocarbons. Paraffins most easily undergo thermal cracking. Olefins, cycloalkanes, and aromatics all exhibit decreasing order of ease of cracking. In each type higher-molecular-weight hydrocarbons are more reactive than hydrocarbons with lower molecular weight.

Thermal dehydrogenation of the saturated hydrocarbons only ethane and propane undergo practical dehydrogenation to yield the corresponding alkenes. All other higher homologs and cycloalkanes undergo cracking when treated at high temperature. Under pyrolytic conditions at temperature above 300°C, generally between 500-800°C, the pyrolysis reaction forms alkenes by carbon-hydrogen scissions as shown in equations 7 to 9.

$$CH_3CH_2CH_3 \longrightarrow CH_3\overset{\bullet}{C}HCH_3 + H\bullet \qquad (7)$$

$$CH_3\overset{\bullet}{C}HCH_3 \longrightarrow CH_2{=}CHCH_3 + H\bullet \qquad (8)$$

$$CH_3CH_2CH_3 + \overset{\bullet}{H} \longrightarrow CH_3\overset{\bullet}{C}HCH_3 + H_2 \qquad (9)$$

Dehydrogenation is the chief reaction when ethane is pyrolyzed. The reaction begins at about 485°C and is quite rapid at 700°C. At this temperature about 90% of the reacting ethane is converted to ethylene and hydrogen. The major industrial source of ethylene and propylene is the pyrolysis of hydrocarbon. Since there is an increase in the number of moles during cracking, low partial pressure favors alkene formation. Pyrolysis, therefore, is carried out in the presence of steam, which also reduces coke formation. Cracking temperature and residence time are used to control product distribution.

Very little skeletal rearrangement occurs via pyrolysis, a fact inherent in the failure of free radicals to readily isomerize by hydrogen atom or alkyl group migration. As a result, little branched alkanes are produced. Aromatization through the dehydrogenation of cyclohexanes and condensation to form polynuclear aromatics can take place. Additionally, olefin polymerization also can occur as a second process.

Many researchers have studied pyrolysis reaction for recycle of waste plastics for more than ten years. They attempted to find suitable conditions which can solve all waste plastic problems.

Kaminsky *et al.* (1996) pyrolyzed mixed plastics waste with low chlorine content in technical scale. The oil gave large amount of valuable aromatic oils.

Problematic pollutants, such as chloro-organic compounds and heavy metals, were absent. Gas product had a calorific value of 50 MJ/kg.

Kaminsky and Kim (1999) pyrolyzed mixed plastics in laboratory scale fluidized bed reactor to give aromatic oils and heat-providing gas. Aromatics, such as benzene, toluene, xylenes, and styrene, yield was 30-40% by weight.

Li *et al.* (1999) used a rotary kiln to pyrolyze municipal solid waste. They were interested in a gas product for heating fuel. The fast heating rate produced more gas product and provided less reaction time. The moisture content affected pyrolysis time because higher moisture content means that more heat is required for evaporation. Heating value of gas product was analyzed which it was in the range of 15-19 MJ/Nm^3.

Day *et al.* (1999) pyrolyzed three plastic types which were used in an electronic industry by the pyrolysis reactor connecting with gas chromatograph-mass spectrometry (Py-GCMS). Acrylonitrile-butadiene-styrene, polycarbonate and polyoxymethylene were selected and contaminated by copper and PVC. The results of the study suggested that both the presences of PVC and copper could influence the extent of degradation and the pyrolysis product distribution.

Williams and Williams (1999) converted low density polyethylene back to petrochemical feedstock to make the virgin plastic or refined fuels. The main gas products were alkene. The aromatic content in oil depended on reaction temperature. The wax produced from the pyrolysis of LDPE was a very pure aliphatic with no aromatic species presented that could be used as feedstock of cracker in petrochemical process.

Esperanza *et al.* (1999) decomposed waste vanish based on polyurethane. Carbonmonoxide and carbondioxide were the main components of the gas fraction. Benzene and naphthalene were the main components of the condensable volatile fraction. The kinetic study showed three decomposition steps. The reaction orders of all these steps were in the range of 0.5-3.

Karaduman *et al.* (2001) studied polystyrene flash pyrolysis in free-fall reactor under vacuum. The liquid yield maximized around 750^{o}C and styrene yield at 825^{o}C. Solid product was not obtained at high reaction temperature. Therefore, this reactor which has shorter reaction time could prevent secondary reaction.

Palafox and Chase (2001) operated pyrolysis reaction in a new semibatch apparatus using the microwave induced pyrolysis process. The products were similar with other techniques but microwave process was successfully used to treat aluminum/polymer laminate as an example of real waste. This process could recover aluminum and this metal showed as clean and shiny.

Wong and Broadbelt (2001) studied pyrolysis of polypropylene, polystyrene and their binary mixture. They found that the conversion of binary mixture was higher than the average of conversion for the individual cases. Synergistic effect was shown in this mixture.

Karaduman *et al.* (2002) used solvent-assisted in thermal degradation of polystyrene wastes. The liquid yield was almost double and total conversion was exceeding 95%. Toluene as solvent gave more selectivity in ethyl benzene than cyclohexane.

Ciliz *et al.* (2004) concerned the effect of impurities on pyrolysis product. The impurities in PP waste led to higher amount of gas yield that showed increasing of cracking activity. The composition of oil showed that the polyaromatic content was not affected by contaminant.

Catalytic cracking

Catalytic cracking is important and widely used in refinery process for converting heavy oils into more valuable gasoline and lighter products (Matar, 1994). The light products are important feedstocks for petrochemical industry. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because more gasoline having a higher octane and less heavy oils and unsaturated gases are produced. This is due to the effect of catalyst, which promotes isomerization and dehydrocyclization.

Products from catalytic cracking units are more stable due to lower olefin content in the liquid products. This reflects a higher hydrogen transfer activity, which leads to more saturated hydrocarbons than in thermal cracked products from delayed coking units.

The feeds to catalytic cracking units vary from gas oils to crude residues. Heavier feeds contain higher concentration of basic and polar molecules as well as asphaltenes. Examples are basic nitrogen compounds, which are readily adsorbed on the catalyst acid sites and lead to instantaneous albeit temporary deactivation. Polycyclic aromatics and asphaltenes contribute strongly to coke formation. These feed stocks are often pretreated to decrease the metallic and asphaltene contents. Hydrotreatment, solvent extraction, and propane deasphalting are important treatment processes. Excessive asphaltene and aromatics in the feed are precursors to carbon formation on the catalyst surface, which substantially reduces its activity and produces gasoline of lower quality.

Cracking catalyst

Acid-treated clays were the first catalysts used in the catalytic cracking process, but have been replaced by synthetic amorphous silica-alumina, which is more active and stable. Incorporating zeolites (crystalline alumina-silica) with the silica/alumina catalyst improves selectivity towards aromatics. These catalysts have both Lewis and Bronsted acid sites that promote carbonium ion formation. An important structural feature of zeolites is the presence of holes in the crystal lattice, which are formed by the silica-alumina tetrahedral. Each tetrahedron is made of four oxygen anions with a -2 oxidation state that is shared between two silicon atoms, two aluminum atoms or aluminum and a silicon cation.

Four oxygen anions in the tetrahedral are balanced by the +4 oxidation state of the silicon cation, while the four oxygen anions connecting to the aluminum cation are not balanced. The result is -1 net charge, which should be balanced by metal cation such as Na^+, Mg^{2+}, or H^+.

Bronsted acid sites in HY-zeolites are mainly originated from protons that neutralize the alumina tetrahedral. When HY-zeolite is heated to temperatures in the range of 400-500^oC, Lewis acid sites are formed. Zeolites as cracking catalysts provided higher activities and better selectivities toward middle distillates than amorphous silica-alumina catalysts. This is attributed to a greater acid sites density and a higher adsorption power for the reactants on the catalyst surface.

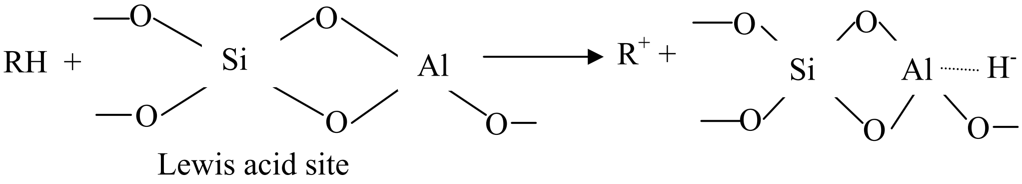
The higher selectivity of zeolites is attributed to its small pores, which allow diffusion of only smaller molecules through their pores, and to the higher rate of hydrogen transfer reactions. However, the silica-alumina matrix has the ability to crack larger molecules. Aluminum distribution in zeolites is also important to the catalytic activity. An imbalance in charge between the silicon atoms in the zeolite framework creates active sites, which determine the predominant reactivity and selectivity.

Deactivation of catalysts occurs due to coke formation and to poisoning by heavy metals. In general, there are two types of catalyst deactivation, reversible and irreversible. Reversible deactivation occurs due to coke deposition. This is reversed by burning coke in the regenerator. Irreversible deactivation results from a combination of four separate but interrelated mechanisms: zeolite dealumination, zeolite decomposition, matrix surface collapse and contamination by metals.

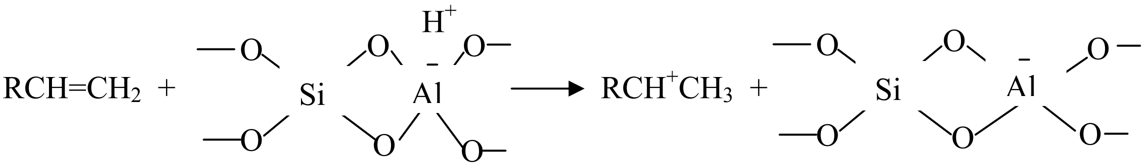
Mechanism of catalytic cracking

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lives and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions. The following reactions illustrate different ways by which carbonium ions may be generated in the reactor:

1. Abstraction of a hydride ion by Lewis acid site from a hydrocarbon



2. Reaction between a Bronsted acid site (H^+) and an olefin



3. Reaction of a carbonium ion formed from step 1 or 2 with another hydrocarbon by abstraction of a hydride ion

$$R^+ + RCH_2CH_3 \longrightarrow RH + RCH^+CH_3$$

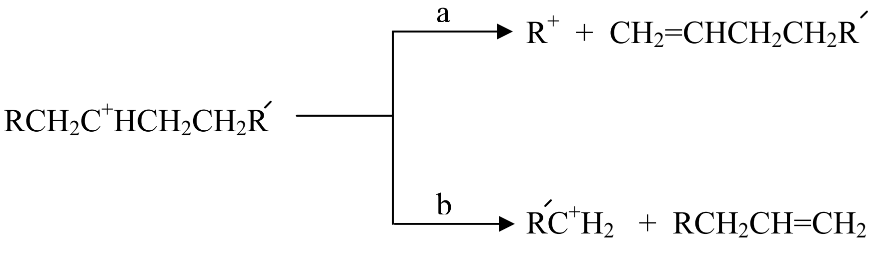
Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary carbon, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming. This isomerization reaction is responsible for a high ratio of branched isomers in the products.

The most important cracking reaction, however, is the carbon-carbon beta bond scission. A bond at a position beta to the positive-charged carbon breaks heterolytically, yielding an olefin and another carbonium ion.

$$RCH_2C^+HCH_3 \longrightarrow R^+ + CH_2{=}CHCH_3$$

The new carbonium ion may experience another beta scission, rearrange to a more stable carbonium ion, or react with a hydrocarbon molecule in the mixture and produce paraffin.

The carbon-carbon beta scission may occur on either side of the carbonium ion, with the smallest fragment usually containing at least three carbon atoms. For example, cracking a secondary carbonium ion formed from long chain paraffin could be represented as follows:



If R is H in the above example, then according to the beta scission rule (an empirical rule) only route b becomes possible, and propylene would be a product:

$$CH_3C^+HCH_2CH_2R' \longrightarrow CH_3CH{=}CH_2 + {}^+CH_2R'$$

The propylene may be protonated to an isopropyl carbonium ion:

$$CH_2{=}CHCH_3 + H^+ \longrightarrow CH_3C^+HCH_3$$

An isopropyl carbonium ion cannot experience beta fission (no C-C bond beta to the carbon with the positive charge). It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propylene by eliminating proton. This could explain the relatively higher yield of propylene from catalytic cracking units than from thermal cracking units.

Aromatization of paraffins can occur through a dehydrocyclization reaction. Olefinic compounds formed by the beta scission can form a carbonium ion intermediate with the configuration conductive to cyclization. During the cracking process, fragmentation of complex polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins. These compounds can be a source of C_6, C_7 and C_8 aromatics through isomerization and hydrogen transfer reactions.

Coke formed on the catalyst surface is thought to be due to polycondensation of aromatic nuclei. The reaction can also occur through a carbonium ion intermediate of the benzene ring. The polynuclear aromatic structure has a high C/H ratio.

Hydrocracking

Hydrocracking is a thermal process (>350°C) in which hydrogenation accompanies cracking. Relatively high pressure (100-200 psi) is employed, and the overall result is usually a change in the character or quality of the products (Speight, 1991). The wide range of products possible from hydrocracking is the result of combining catalytic cracking reaction with hydrogenation. The reaction is catalyzed by dual-function catalysts: the cracking function provided by acid catalyst and metal catalyst gives hydrogenation function.

All the initial reactions of catalytic cracking occur, but some of the secondary reactions are inhibited or stopped by presence of hydrogen. The methyl groups attached to secondary carbons are more easily removed than those attached to tertiary carbon atoms, whereas methyl groups attached to quaternary carbons are the most resistant to hydrocracking.

The effect of hydrogen on naphthenic hydrocarbon is mainly that of ring scission followed by immediate saturation of each end of the fragment produced. The ring is preferentially broken at favored positions, although generally all the carbon-carbon bond positions are attached to some extent. Aromatic hydrocarbons are resistant to hydrogenation under mild conditions, but under more severe conditions the main reactions are conversion of the aromatic to naphthenic rings and scissions within the alkyl side chains. The naphthenes may also be converted to paraffins. Polynuclear aromatics are more readily attacked than the single-ring compounds, the reaction proceeding by a stepwise process in which one ring at a time is saturated and then open.

Catalytic cracking and hydrocracking were used for feedstock recycling because they could control the selectivity of product. Therefore, the researchers studied the type of catalyst which provided desirable product.

Ding *et al.* (1997) converted plastic waste into transportation fuel over bifunctional catalysts. Hydrocracking reaction was used for cracking with metal and acid catalyst. Nickel on silica alumina gave oil with better quality than a commercial premium gasoline since it contained more isoparaffins and less aromatics.

Joo and Guin (1998) upgraded liquid product from plastic pyrolysis. They obtained gasoline yield 46-53%. The composition of product showed higher paraffins, lower aromatics, olefins and nitrogen, which indicated favorable gasoline from an environmental viewpoint.

Garforth *et al.* (1998) pyrolyzed high density polyethylene over different catalysts using laboratory fluidised bed reactor. This work confirmed that initial cracking must be confined to the external surface, the resultant initial cracked products are then degraded further within the pore. Two types of zeolite were studied, HZSM-5 and HMOR, product in the C_3-C_5 range was over 80%.

Masuda *et al.* (1999) used nickel and rare earth metal exchanged Y-zeolite to produce high quality gasoline from polyethylene cracking in steam atmosphere. Metal transported hydrogen from steam to hydrocarbon. Strong acid catalyst showed excessive cracking in steam atmosphere leading to high yield of liquid product and this catalyst did not present deactivation.

Vitolo *et al.* (2001) upgraded wood pyrolysis oil by HZSM-5. The catalyst was recycled for upgrading and regenerating repeatedly. In catalytic process, coke and tar were obtained as undesirable by-products. The regeneration of catalyst reduced the effectiveness of the catalyst due to the disappearance of a significant amount of acid sites.

Karagoz *et al.* (2003) studied coprocessing of municipal waste plastics with vacuum gas oil over various types of catalyst and under hydrogen atmosphere. They concerned the amount of chlorine and sulphur in liquid product. Co on activated carbon provided no chlorine compound in liquid hydrocarbon product and cracking activity.

Polyvinyl chloride (PVC)

Polyvinyl chloride (PVC) is a type of commodity plastics which presents in waste stream. The structure has chlorine group in side chain of polymer which is produced from vinyl chloride monomer by polymerization reaction. The PVC can be divided in two types as rigid and flexible PVC. The rigid PVC is non-plasticizer which is used in construction. The other type is plasticized PVC or flexible PVC.

They are mixed with plasticizer to reduce rigidity. Both rigid and flexible PVC are widely used in many applications.

Applications of polyvinyl chloride

Since Polyvinyl chloride has good properties, therefore, it has been used in many applications (Sarvetnick, 1969).

1. Electrical insulation

The applications for PVC in electrical insulation were during the late 1930's. It replaced vulcanized rubber because it was non-flammability, low cost, ease of extrusion, abrasion resistance, lack of sensitivity to moisture and chemical and excellent aging and weathering.

2. Foams

The major portion of vinyl foam goes in to yard goods such as flooring, upholstery, accessories and apparel. These large volume applications also use solid vinyl compositions. Vinyl foams have good aging characteristics and physical properties in comparison to other materials. They are resistant to hydrolysis, oxidation, mildew, chemicals, solvents and oils. They are non-flammable and have excellent resistance to tear and abrasion. Complicated shapes may be produced in molds. The flexible foams are characteristically not highly resilient, a property which is used advantageously in many applications such as textiles, flooring and padding.

3. Coating

Vinyls may be formulated to produce coatings with excellent resistance to water, alkalis, acids, alcohols, oil and aliphatic hydrocarbon. Weathering and aging are outstanding. The coatings are non-flammable, tough and flexible with low moisture vapor transmission and water absorption. These latter factors are considered to be vital for protection against corrosion. The durability of vinyls permits less frequent recoating, which is important in applications where recoating is expensive.

4. Packaging

The volume of PVC used in packaging represents approximately 5% of total consumption. The most rapidly growing applications are blow molded bottles and flexible and rigid film. The increasing importance of PVC in the packaging field is attributed to the excellent moisture, gas and odor barrier properties. Vinyls have good aging properties and are non fogging.

5. Building applications-rigid PVC

This category is expected to grow to become one of the largest application areas for PVC. PVC compositions have excellent weathering properties, strength and impact resistance as well as low cost when properly formulated. Applications include pipe, siding, trim, window frames, door frames, louvers, shutters, roofing, glazing, building panels, rain gutters, downspouts and awnings.

Chemical recycling of PVC

Waste PVC can be oxidized in oxygenated NaOH solution at temperatures in the range of 150-260^{o}C and at elevated pressure to give oxalic acid, a mixture of benzenecarboxylic acids and CO_2. It was found that the yield of oxalic acid increases with increasing NaOH concentration until 15 M. One ton of scrap PVC can yield 600 kg of oxalic acid which is a valuable intermediate in the chemical industry (Scheirs, 1998). Moreover, there are many chemical reactions to apply for PVC recycle.

Uddin *et al.* (1999) studied dechlorination of chlorine compounds in polyvinyl chloride mixed plastics. They investigated suitable sorbents to provide highest chlorine removal. The iron oxide which was used for chlorine sorbent decreased chlorine content in oil by 70%.

Horikawa *et al.* (1999) recovered chlorine gas by fixing it on metal oxide which was changed to metal chloride. After that, the metal chlorides were calcined under oxygen atmosphere to recover chlorine gas and to regenerate the metal oxide. Cobalt oxide can recover about 90% chlorine gas from pure PVC.

Akimoto *et al.* (2002) studied hydrothermal reaction for dechlorination and denitrogenation of municipal-waste-plastics using solution of alkaline metal hydroxide. Under hydrothermal condition, the chlorine content in the product oil was nearly 0 ppm.

Lu *et al.* (2002) studied pressurized hydrolysis dechlorination in an autoclave reactor. The chlorine was removed by 95-98% at 240^{o}C. The most important factor which affected the efficiency of dechlorination is reaction temperature.

Tang *et al.* (2003) degraded PVC-containing plastic mixture by thermal and catalytic reaction. The reaction was carried out by semibatch operation. The purpose of this research was to determine a suitable sorbent for chlorine removal. In catalytic degradation using Al-Zn composite catalyst, Zn showed a good effect on the fixation of HCl and significantly decreased the chlorine content in the oil. There was only 2.7% of Cl in liquid fraction. Al gave catalytic cracking activity for providing high amount of low boiling point fraction.

Zhou *et al.* (2004) studied degradation and dechlorination of PVC-containing mixed plastics by Al-Mg composite catalyst. Chlorine could be reduced by 73%. They suggested that Al-Mg be effectively used for catalytic degradation and dechlorination of chlorine-containing plastics to produce high quality and low chlorine content liquid products.

PVC provided toxic products when it was thermally decomposed. McNeill *et al.* (1995, 1998) studied PVC thermal degradation and investigated polychlorinated hydrocarbon from PVC pyrolysis. HCl was the major fraction as much as 53%. 10%

of Cl atoms remained in the polymer after HCl evolution. The chlorinated hydrocarbon accounted for 1.75% of the liquid fraction and for 0.14% of the polymer. Dioxin, toxic compounds, were found in tar, a low volatility fraction, in PVC pyrolyis product. Yonezawa *et al.* (1999) determined mutagenic substances in pyrolysate from PVC, and suggested that mutagenic substances be found from burning PVC.

This research studies an alternative method for chlorine reduction by using nitrogen compounds in waste material to capture chlorine from PVC. The pyrolysis of nitrogen compounds or bio-wastes have been studied widely more than ten years because they need to reduce these wastes and obtained high heating values byproduct.

Bagreev *et al.* (2001) pyrolyzed fertilizer product from municipal sewage sludge. The pyrolyzed product derived from simple carbonization showed surface area up to 140 m^2/g. Therefore, it had a potential to be used as an adsorbent after it was treated to increase surface area.

Inguanzo *et al.* (2002) studied pyrolysis of sewage sludge produced by Spanish urban wastewater treatment plant. Solid product had relatively low heating values compared with those of other fuels. In liquid product, the organic fraction had heating value nearly the same as conventional fuels. These products had a potential for used as a fuel.

Shen and Zhang (2003) recovered oil from pyrolysis of activated sludge. The structure of bio-oil was investigated. It was made up of a group of aromatic clusters with one to three aromatic rings connected by long straight chain hydrocarbons with hydroxyl groups.

Shinogi and Kanri (2003) proposed a challenge way for disposing and recycling waste products in Japan. They pyrolyzed plant wastes, animal waste, and human waste and studied physical and chemical properties of the pyrolyzed products. The carbonized products were porous materials that can improve soil physical properties as soil amender and used as a low cost adsorbent. However, animal waste gave lower both physical and chemical properties than the others.

Islam *et al.* (2004) pyrolyzed scrap tire, waste plastic and waste paper in a fixed bed reactor. Liquid products were analyzed and their properties as fuels compared with petroleum-derived products. The liquid products had no sulfur and nitrogen and similar properties with fuel oil. From the results, pyrolyzed oil from scrap tire and waste plastic can be potential energy sources because they had heating values near liquid hydrocarbon fuels.

Corrosion problem was a result of pyrolysis of PVC. Cattle manure or cow solid waste was of interest for chlorine reduction from PVC pyrolysis. Shinogi and Kanri (2003) studied pyrolysis of various types of waste including cattle manure. The results showed pyrolysis of cattle manure gave products with poor properties. In this work, cattle manure was chosen for HCl reduction.

Many researchers studied kinetics behavior of thermal decomposition for identification and quantitative determination of the pyrolysis products. They tried to have more understanding about the pyrolysis mechanism in order to minimize toxic products.

The theory and kinetics approach of pyrolysis

The kinetics behavior of copyrolysis between PVC and cattle manure is of interest to understand the effect of cattle manure on the copyrolysis reactions. There are many methods to study kinetics behavior of PVC.

Marcilla and Beltran (1995) studied kinetics of PVC decomposition under nitrogen atmosphere by applying two kinetic models to dynamic thermogravimetric data. This work divided the decomposition of PVC to two stages. The first stage of PVC decomposition can only fitted satisfactorily when a model based on two parallel reactions was used. The second stage can be correctly predicted by a model based on single reaction.

Marongiu *et al.* (2003) presented an initial attempt at describing PVC thermal degradation through a semi-detailed and lumped kinetic model. They showed the mechanism of 40 species and 250 pseudocomponents from PVC degradation. The presence of the two steps mechanism was correctly predicted both in quantitative terms and in the temperature ranges.

The second part of this research studies the kinetics behavior of copyrolysis of PVC and cattle manure by isoconversional method (Gao, 2003). The differential of Arrhenius equation was integrated for reaction under dynamic condition.

$$\frac{d\alpha}{dt} = Ae^{-E/RT} f(\alpha) \tag{10}$$

In Equation 10, E represents activation energy, A is the pre-exponential factor of Arrhenius equation, and R is the gas constant. The degree of conversion is defined as $\alpha = 1 - \frac{m - m_{char}}{m_0 - m_{char}}$. Mass of PVC and cattle manure mixture at time (t), at initial and mass of remaining char are m, m_0 and m_{char}, respectively.

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} e^{-E/RT} dT = \frac{AE}{\beta R}\frac{e^{-x}}{x^2}h(x) \tag{11}$$

Where $x = \frac{E}{RT}$. β is linear heating rate and lists of f(α) and g(α) at various kinetic models are shown in Table 1. The temperature integral in equation 11 was expressed by the fourth Senum and Yang approximation (Flyn, 1997).

$$h(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{12}$$

The maximum rate was obtained by differentiation of equation 10, put it to zero and rearranged to equation 13.

$$-\frac{1}{d\,f(\alpha)/d\alpha}=\frac{A}{\beta}\frac{RT_{\max}^{2}}{E}\exp\left(-\frac{E}{RT_{\max}}\right)=\frac{1}{f'(\alpha_{\max})} \tag{13}$$

Combining equation 11 with equation13 gives

$$g(\alpha_{\max})\times f'(\alpha_{\max})=-h(E/RT_{\max}) \tag{14}$$

Table 1 Basic model of solid reaction

Model	f (α)	f' (α)	g(α)
An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-(1/n)}$	$(n-1)[-\ln(1-\alpha)]^{-1/n}-n[-\ln(1-\alpha)]^{1-(1/n)}$	$-[\ln(1-\alpha)]^{1/n}$
Rn	$n(1-\alpha)^{1-(1/n)}$	$(1-n)(1-\alpha)^{1/n}$	$1-(1-\alpha)^{1/n}$
D2	$-[\ln(1-\alpha)]^{-1}$	$-(1-\alpha)^{-1}[-\ln(1-\alpha)]^{-2}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	$(3/2)(1-\alpha)^{(2/3)}[1-(1-\alpha)^{1/3}]^{-1}$	$[1/2-(1-\alpha)^{-1/3}][1-(1-\alpha)^{1/3}]^{-2}$	$[1-(1-\alpha)^{1/3}]^{2}$
D4	$(3/2)(1-\alpha)^{(1/3)}[1-(1-\alpha)^{1/3}]^{-1}$	$[-1/2-(1-\alpha)^{-2/3}][1-(1-\alpha)^{1/3}]^{-2}$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
F1	$1-\alpha$	-1	$-\ln(1-\alpha)$
Fn	$(1-\alpha)^{n}$	$-n(1-\alpha)^{n-1}$	$[1-(1-\alpha)^{1-n}]/(1-n)$

Source: Gao (2002)

From Table 1, nth-order of reaction, f(α) = (1- α)^n, was used as kinetic model. The equation 14 was turned to equations 15 and 16.

$$1-\alpha_{\max}=\left[1-\frac{n-1}{n}h(E/RT_{\max})\right]^{1/(n-1)} \quad n\neq 1 \tag{15}$$

$$-\ln(1-\alpha_{\max})=h(E/RT_{\max}) \qquad n=1 \tag{16}$$

The $\alpha_{\max}$ at various n determined by equations 15 and 16 are shown in Table 2 and compared with isothermal degradation measurement which was used to determine kinetic parameters. From equation 17, Arrhenius equation was integrated to equation 18.

$$f(\alpha)=(1-\alpha)^{n}=\left(\frac{m-m_{char}}{m_0-m_{char}}\right)^{n} \tag{17}$$

$$\frac{(m-m_{char})^{1-n}}{1-n}=\frac{(m_0-m_{char})^{1-n}}{1-n}-kt \tag{18}$$

Table 2 The theoretical values of α_{max} of n^{th}-order reaction at various reaction orders

n	α_{max}	n	α_{max}	n	α_{max}
1.1	0.56-0.60	2.1	0.43-0.47	3.1	0.35-0.37
1.2	0.55-0.58	2.2	0.42-0.46	3.2	0.34-0.36
1.3	0.53-0.57	2.3	0.41-0.45	3.3	0.33-0.35
1.4	0.51-0.55	2.4	0.40-0.44	3.4	0.32-0.34
1.5	0.50-0.54	2.5	0.39-0.43	3.5	0.31-0.33
1.6	0.49-0.53	2.6	0.38-0.42	3.6	0.30-0.32
1.7	0.47-0.51	2.7	0.37-0.41	3.7	0.29-0.31
1.8	0.46-0.50	2.8	0.36-0.40	3.8	0.28-0.30
1.9	0.45-0.49	2.9	0.35-0.39	3.9	0.27-0.29
2.0	0.44-0.48	3.0	0.34-0.38	4.0	0.26-0.28

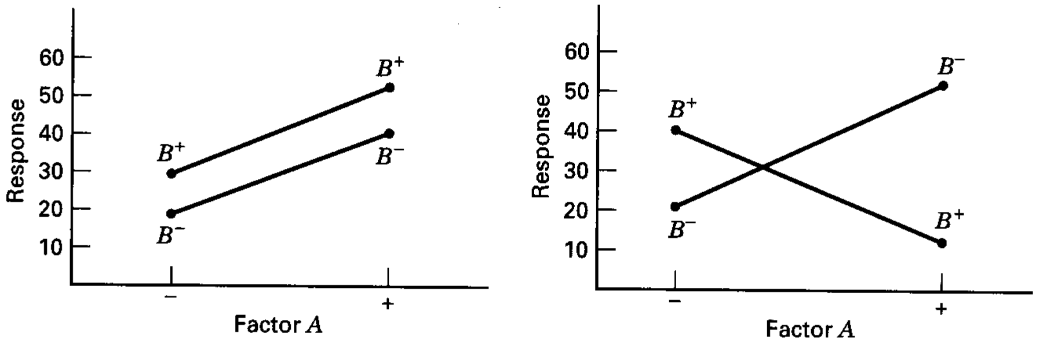
Note: Normally, ordinary reactions have E/RT_{max} = 15-70

Design of experiment

This research used statistical method to design the experiment. Factorial design method and response surface and contour plot by Box-Behnken model method were used to screen unaffected factor and to optimize experimental condition, respectively. Therefore, this section presents the theory of these statistical methods (Montgomery, 2001).

Factorial design

Factorial design is widely used in experiments involving several factors where it is necessary to study joint effect of the factors on a response. The effect of a factor is defined to be the change in response produced by a change in the level of factor. This calls a main effect because it refers to the primary factors of interest in the experiment. In some experiments, we may find that the difference in response between the levels of one factor is not the same as all levels of the other factors. When this occurs, there is an interaction between the factors. It may be illustrated graphically. Figure 3 shows the response data against factor A of both levels of factor B. B$^-$ and B$^+$ line which represent factor B at low and high levels are approximately parallel as show in Figure 3(a), indicating a lack of interaction between factor A and B but it is not parallel as shown in Figure 3(b), factors A and B have interaction.



(a) (b)

Figure 3 The factorial experiment (a) without interaction, and (b) with interaction

Note: B- was low level of factor B

B+ was high level of factor B

There is another way to illustrate the concept of interaction. Suppose both design factors are quantitative, then, a regression model of the two factor factorial experiment could be written as

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \varepsilon$$

Where y is the response, β is the coefficient whose value is determined, x_1 is a variable that represents factor A, x_2 is a variable that represents factor B, and ε is a random error term. The variables x_1 and x_2 are defined on a code scale from -1 to +1 (the low and high levels of A and B), and x_1x_2 represents the interaction between x_1 and x_2

The advantages of factorial designs can be easily illustrated. They are more efficient than one-factor-at-a-time experiments. Furthermore, a factorial design is necessary when interactions may be present to avoid misleading conclusions. Finally, factorial design allows the effects of factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions.

The 2^k factorial design

Factorial designs are widely used in experiment involving several factors where it is necessary to study the joint effect of the factors on a response. The 2^k factorial design is a special case of the general factorial design that is important because it is widely used in research work and also because they form the basis of other designs of considerable practical value. The most importance of these special cases is that of k factors, each only two levels. These levels may be qualitative or quantitative values. It is assumed that (1) the factor is fixed, (2) the design is completely randomized, and (3) the usual normality assumptions are satisfied.

The 2^k design is particularly useful in the early stages of experimental work, when there are likely to be many factors to be investigated. It provides the smallest number of runs with which k factors can be studied in a complete factorial design. Consequently these designs are widely used in factor screening experiments.

The method of analysis that we have presented thus far may be generalized to the case of a 2^k factorial design, that is, a design with k factor each at two levels. The statistical model for a 2^k design would include k main effect and interaction between factors. For 2^k design the complete model would contain 2^k-1 effects. The notation introduced earlier for treatment combination is also used here.

Hypothesis of factorial design was developed from fixed effects model. It was used for testing the equality of the treatment means. The appropriate hypotheses are

$$H_0: \mu_1 = \mu_2$$

$$H_1: \mu_1 \neq \mu_2$$

In the effect model, the treatment mean had two components such that $\mu_i = \mu + \tau_i$. μ is an overall mean so that

$$\frac{\sum_{i=1}^{a} \mu_i}{a} = \mu$$

This definition implies that

$$\sum_{i=1}^{a} \tau_i = 0$$

That is, the treatment or factor effects can be thought of as deviations from the overall mean. Consequently, an equivalent way to write the above hypotheses is in term of the treatment effect τ_i that

$$H_0\text{: } \tau_1 = \tau_2 = 0$$

$$H_1\text{: } \tau_i \neq 0$$

The test of equality of treatment mean and the test that the treatment effect is zero are similar. This research used statistical method to determine significant effect of each factor, therefore, null hypothesis had to be rejected and alternative hypothesis which showed a significant effect of a factor was accepted.

The general approach to the statistical analysis of the 2^k design is summarized in six steps that:

1. Estimate factor effects
2. Form initial model
3. Perform statistical testing
4. Refine model
5. Analyze residuals
6. Interpret results

A computer software package is usually employed in analysis process. The first step is to estimate factor effects and examine their signs and magnitudes. This gives the experimenter preliminary information regarding which factors and interactions may be important, and which direction these factors should be adjusted to improve the response. In forming the initial model for the experiment, we usually choose the full model, that is, all main effects and interactions, provided that at least one of the design points has been replicated. Then in step 3, we use the analysis of variance to formally test for significance of main effect and interaction. Step 4, refine model, usually consists of removing any no significant variables from the full model. Step 5 is the usual residual analysis to check for model adequacy and to check assumptions. Sometimes model refinement occurs after residual analysis, if we find that the model is inadequate or assumptions are badly violated. The final step usually consists of graphical analysis-either main effect or interaction plots, or response and contour plots.

This research studied four factors: heating rate, reaction temperature, ratio of PVC:cattle manure, and reaction time. The factors were analyzed by 2^k factorial design which they had 2 levels as low value (-) and high value (+) for calculation.

Ratio of PVC: cattle manure	1:1	(-)
	1:5	(+)
Reaction temperature	250^{o}C	(-)
	450^{o}C	(+)
Heating rate	1^{o}C/min	(-)
	5^{o}C/min	(+)
Holding time	0 min	(-)
	60 min	(+)

There are four factors to be studied, therefore, sixteen experiments were needed in 2^k factorial design as shown in design matrix in Table 3. However, the matrix will be operated randomly.

Table 3 The design matrix of 2^4 factorial design

Standard order	PVC: cattle manure	Reaction temperature (^oC)	Heating rate ($^oC/min$)	Holding time (min)
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	+	-
6	+	-	+	-
7	-	+	+	-
8	+	+	+	-
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+

Response surface and contour plot

Fitting and analyzing response surface is greatly facilitated by the proper choice of an experimental design. When selecting a response surface design, some of the features of a desirable design are as follows:

1. Provides a reasonable distribution of data points throughout the region of interest.
2. Allows model adequacy, including lack of fit, to be investigated
3. Allows experiments to be performed in blocks
4. Allows designs of higher order to be built up sequentially
5. Provides an internal estimate of error
6. Provides precise estimates of the model coefficients
7. Provides a good profile of the prediction variance throughout the experimental region
8. Provides reasonable robustness against outlier or missing values

9. Does not require a large number of runs
10. Does not require too many levels of the independent variables
11. Ensures simplicity of calculation of the model parameters

This research used Box-Behnken model to fit response surface and contour plot. It is a type of second-order model as shown below.

$$\hat{y} \ = \ \beta_0 + \beta_i \sum_{i=1}^{n} x_i + \beta_{ij} \sum_{i=1}^{n} \sum_{j=1}^{m} x_i x_j + \beta_{ii} \sum_{i=1}^{n} x_i^2 + \varepsilon$$

Box and Behnken have proposed some three-level designs for fitting response surfaces. These designs are formed by combining 2^k factorials with incomplete block designs. The result is usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable.

The research optimized three factors: heating rate, reaction temperature, and ratio of PVC: cattle manure using Box-Behnken model. The model consists of fifteen experiments made of low, high and center values. The design matrix is shown in Table 4.

Ratio of PVC: cattle manure	1:1	(-)
	1:3	(0)
	1:5	(+)
Reaction temperature	250°C	(-)
	350°C	(0)
	450°C	(+)
Heating rate	1°C/min	(-)
	3°C/min	(0)
	5°C/min	(+)

Table 4 The design matrix of Box-Behnken design

Standard order	PVC:cattle manure (X_1)	Heating rate (^{o}C/min) (X_2)	Reaction temperature (^{o}C) (X_3)
1	-	-	0
2	+	-	0
3	-	+	0
4	+	+	0
5	-	0	-
6	+	0	-
7	-	0	+
8	+	0	+
9	0	-	-
10	0	+	-
11	0	-	+
12	0	+	+
13	0	0	0
14	0	0	0
15	0	0	0