Pyrolysis of Waste Polystyrene and High-Density Polyethylene

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1. Introduction

As the rate of consumption of plastic materials in the world is greatly expanded, more waste plastics are generated. In recent years, their generation amount in Korea becomes about four million tons per year, according to data from the National Institute of Environmental Research. The disposal of waste plastic is mostly achieved by conventional ways such as landfill or incineration. However, these methods have a problem of a social resistance due to the air pollution, soil contamination, and the economical resistance caused by an increase of a space and a disposal cost. Thus, the recycling of plastic wastes as a cheap source of raw materials has become a predominant subject over all countries. The development of technologies acceptable from the environmental and economical fields is one of the most important key factors.

Generally, the recycling methods are classified as the material recycling and chemical recycling. The former is one of the most conventional methods but is limited by difficulties in maintaining the high quality and adequate price of final products, in particular, for the mixture of plastic waste. Thus, application of other procedures such as chemical recycling and energy recovery is required (Al-Salem et al., 2009).

The chemical recycling, referred to as an advanced recycling technology, is included in a tertiary recycling. The process is converted from plastic wastes into smaller molecules corresponding to chemical intermediates through the use of heat and chemical treatment, such as liquids, gases and waxes. These chemical intermediates can be used as the fuel oil and feed stocks of petrochemicals processes, etc. The chemical recycling is described by the routes as follows (Kumar et al., 2011).

The chemical recycling can be mainly explained by the chemical recovery systems, which are classified as a heterogeneous and a homogeneous process. The chemolysis methods as homogeneous process utilize chemical agents as catalysts for depolymerization of polymers to obtain the products with low molecular wieghts. Chemolysis includes the processes such as glycolysis, hydrolysis, methanolysis and alcoholysis. On the other hand, heterogeneous processes are greatly described by gasification and pyrolysis. Gasification as partial oxidation (using oxygen or steam) can generate a mixture of hydrocarbons and synthesis gas (CO and H_2), which are dependent on the type of polymer, biomass, coal and co-mixture, and on quantity of and quality of resulting product.

Chemical Recovery Systems	Heterogeneous Process	Cracking	Thermal Cracking
			Catalytic Cracking
			Hydro Cracking
		Gasification	
	Homogeneous Process	Chemolysis	Methanolysis
			Glycolysis
			Alcoholysis
Energy Recovery Systems	Incineration Technology		

Fig. 1. Schemes of chemical recycling.

The pyrolysis involves the degradation of the polymeric materials by heating in the absence of oxygen. The method has the routes as the thermal cracking, catalytic cracking and hydro cracking. The recycling of waste plastics by thermal and catalytic degradation processes can be an important source producing alternative fuel oil from the view point of an economical aspect and contributing to the environmental protection from the view point of an environmental aspect (Demirbas, 2004). The method of pyrolysis takes advantage over the incineration and landfill methods because it is based on relatively simplicity into the oil for all thermoplastic mixtures without using the separation treatment for plastic type in the mixture and to lower the environment resistance for air pollutant and soil contamination.

In the pyrolysis, thermal degradation is a simple method for upgrading plastic waste into liquid product at medium temperature (400-600 $^{\circ}$C) in the absence of oxygen. However, this process requires relatively high energy consumption, due to a low thermal conductivity of waste plastic and to an endothermic reaction by degradation of waste plastic. Moreover, the oil obtained by pyrolysis of plastic wastes has a wide molecular weight distribution with poor economical value, which does not have a sufficient quality to use as alternative fuel oils (Marcilla et al., 2009). The pyrolysis of polyethylene with high proportion in mixed plastic produces much more unstable heavy compounds with high viscosity as low grade product (Marcilla et al., 2009; Lee & Shin, 2007). The characteristics of these products depend on the nature of plastic waste and process conditions.

The catalytic degradation process, based on the addition of catalyst, can be conducted at low temperatures and high quality products are obtained in a comparison with thermal

degradation process (Miskolczi et al., 2004). The most commonly used catalysts are (1) solid acid catalysts such as zeolite, silica-alumina, FCC catalyst and MCM-41, etc [Miskolczi et al., 2004; Lee et al., 2002; Garcia et al., 2005; Seddegi et al., 2002; Achilias et al., 2007; Miskolczi et al., 2006; Marcilla et al., 2005; Lin & Yang, 2007] and (2) bifunctional catalysts (Buekens & Huang, 1998). In the degradation of the polymer chain using acidic catalyst, the molecular weight of polymer chain could be rapidly reduced through cracking reaction and then carbonium ion intermediates would be rearranged by hydrogen and carbon atoms shifts with producing the isomers of high quality. In the case of bifunctional catalyst consisting of both acidic and metal material as reforming catalyst, the metallic sites catalyze hydrogenation/ dehydrogenation, while the acidic sites on the support catalyze the isomerization reaction. These reactions would improve the octane numbers of light hydrocarbons. Also, hydro-cracking involves the reaction with hydrogen over a bimetallic catalyst at moderate temperatures and pressures, which is focused on obtaining a high quality hydrocarbon product. These catalysts used in refinery hydro-cracking reaction for heavy hydrocarbons incorporate both cracking and hydrogenation.

With regards to the reactant used in this chapter, high-density polyethylene has a linear structure with no or little branching, while polystyrene is cyclic structure with relatively low degradation temperature. Polyolefinic and polystyrene polymers that have above 70% fraction in plastic waste are the major polymeric materials in a municipal plastic waste stream. In case of western Europe, polyethylene plastics make up over 40% of the total plastic content of municipal solid waste (Onwudili et al., 2009). These polymers consisting of mainly hydrogen and carbon atoms are so close to crude oil that the plastic waste would be processed by the reaction methods such as the thermal and catalytic cracking. In the pyrolysis process, polystyrene can be thermally degraded to the corresponding monomer or aromatics with its high selectivity at lower temperatures, whilst thermal degradation of polyolefinic polymers occurs at higher temperatures and lead to a complex mixture of aliphatic hydrocarbons.

This chapter presents the pyrolysis of both polystyrene and high-density polyethylene with different physiochemical properties and also the upgrading of low-grade oil product obtained by thermal degradation. Moreover, the effect of mixing of two plastics and catalyst addition for the pyrolysis would be explained by the yield for gas, liquid, solid products and the composition of liquid components, etc.

2. Basic pyrolysis

2.1 Reaction mechanism of high-density polyethylene and polystyrene

The pyrolysis is basically degraded for large hydrocarbons into smaller ones. From this process, the polymer is converted into paraffins and olefins, etc., with low molecular weights. Thermal degradation is accompanied with a free radical chain reaction. When free radicals react with hydrocarbons, new hydrocarbons and new free radicals are produced. Also, free radicals can decompose into olefins and new radicals. In the reaction mechanism by polymer type (Scheirs & Kaminsky, 2006), high-density polyethylene consisting of straight long carbon chains is pyrolyzed through the random-chain scission, which is broken up randomly into smaller molecules with various chain lengths. This product is obtained

with a wide distribution of molecular weight, including hydrocarbons with high boiling point and/or low valuable products like wax. Thus, this means that the addition of catalyst in the pyrolysis can be a more efficient method to produce high valuable products with mainly gasoline range components. On the other hand, pyrolysis of polystyrene with cyclic structure is occurred by both end-chain and random-chain scissions. This polymer is broken up from the end groups successively yielding the corresponding monomers, as well as its breakage randomly into smaller molecules of one or more benzene-ring structures. This product is monomer recovery with a high fraction.

2.2 Thermal and catalytic degradation (Scheirs & Kaminsky, 2006)

(a) Thermal and (b) catalytic degradation of heavy hydrocarbons can be comparatively described with the following items

(a) Thermal degradation

1. High production of C_1s and C_2s in the gas product.
2. Olefins less branched.
3. Some diolefins made at high temperature
4. Wide distribution of molecular weight in the liquid product (poor gasoline selectivity)
5. High fraction of gas and coke products
6. Relatively slow reactions.

(b) Catalytic degradation

1. Short in the reaction time and low in degradation temperature
2. High production of C_3s and C_4s in the gas product
3. Olefins as the primary products and more branched by isomerization
4. More C_5-C_{10} products in the liquid product (high gasoline selectivity)
5. Aromatics produced by olefin cyclization
6. More reactive for larger molecules
7. No reaction for pure aromatics
8. Paraffins produced by H_2 transfer
9. Product distribution controlled by the selection of a catalyst

2.3 Mass balance

To demonstrate the mass balance, it is essential to determine the product yield for gas, liquid and residue, and also the composition of liquid products at different conditions of the various operating parameters such as temperature, residence time and pressure. From this, it is required to mention the economical aspect. Raw materials in a pyrolysis process contain nonproductive constituents, such as moisture, inorganic material, etc. These loss factors have to take into a consideration for the establishment of mass balance. Generally, mass balance is established by input and output amount, based on 100% of feeding amount. In the pyrolysis process, the important operating point is controlled by the maximum of valuable products and minimum of sludge amount. Thus, the operating margin must reach a reasonable level for mass balance in the economic aspect.

3. Pyrolysis of pure waste high-density polyethylene and polystyrene

Although the catalytic degradation of polyethylene over a wide variety of catalysts have been tested, zeolites have proven effective by many researchers [[Miskolczi et al., 2004; Lee et al., 2002; Garcia et al., 2005; Seddegi et al., 2002; Achilias et al., 2007; Miskolczi et al., 2006; Marcilla et al., 2005; Lin & Yang, 2007; Buekens & Hunang, 1998]. Seo et al (Seo et al.,2003) reports that the product characteristics for both thermal and catalytic degradation of waste HDPE using various zeolites are relatively compared as the yields of gas, liquid and residue, and carbon number distribution of liquid products, as shown in Table 1. Yields of liquid were over 70% using all zeolites, with the exception of ZSM-5, as well as thermal degradation. However, the catalytic degradation was produced much more light hydrocarbons (C6-C12) than that of thermal degradation, and moreover ZSM-5 and zeolite Y were more effective than mordenite. ZSM-5 and zeolite Y have a unique three-dimensional micropore structure as well as a strongly acidic property, whereas mordenite has only a parallel one-dimensional pore structure with a restricted diffusion of reactant. Especially, ZSM-5 with a smaller pore size, rather than that of zeolite Y was more cracked into light hydrocarbons such as C_6-C_{12} components and gas products. Since the initially degraded materials on the external surface of catalyst can be dispersed into the smaller internal cavities of catalyst, they can be further degraded to the smaller size of gaseous hydrocarbons. These findings mean that the pore properties of catalyst are important factor in the degradation of heavy hydrocarbons.

Catalysts	Yield			Liquid fraction*		
	Liquid	Gas	Coke	C_6-C_{12}	C_{13}-C_{23}	$\geq C_{24}$
Thermal cracking	84.00%	13.00%	3.00%	56.55%	37.79%	5.66%
ZSM-5 (powder)	35.00%	63.50%	1.50%	99.92%	0.08%	0%
Zeolite Y (powder)	71.50%	27.00%	1.50%	96.99%	3.01%	0%
Zeolite Y (pellet)	81.00%	17.50%	1.50%	86.07%	11.59%	2.34%
Mordenite (pellet)	78.50%	18.50%	3.00%	71.06%	28.67%	0.27%

* wt% were determined by GC/MS

Table 1. Yields of liquid, gas and coke produced from thermal and catalytic degradation of waste HDPE with various catalysts at 450ºC (Seo et al.,2003).

In the characteristics of oil product, paraffin, olefin, naphthene and aromatic (PONA) distribution is one of the important factors which can determine the quality of oil product, as shown in Table 2. Oil product from thermal degradation of HDPE consists of 40.47wt% paraffins, 39.93wt% olefin, 18.50wt% naphthenes and a trace amount of aromatics. Relative to thermal degradation of HDPE, catalytic degradation is known to occur at a faster reaction rate and lead to subsequent reactions including isomerization and aromatization, as well as cracking reaction (Vento & Habib, 1979). Subsequent reactions proceeding through carbenium ion-type intermediate generated by acidic catalysts contribute to the greater formation of olefins and aromatics, as shown in Table 2.

Catalyst	Total-Paraffin	(Total-Paraffin)		Total-Olefin	Naphthene	Aromatics	Others[*]
		n-paraffin	i-paraffin				
Thermal cracking	40.75	40.47	0.28	39.93	18.50	0.68	0.14
ZSM-5(powder)	1.63	1.51	0.12	16.08	23.55	58.75	0.01
ZeoliteY(powder)	5.39	0.00	5.39	79.92	7.68	7.01	0.00
Zeolite Y(pellet)	25.10	20.68	4.42	49.28	12.05	8.43	5.14
Mordenite(pellet)	31.07	30.89	0.18	57.07	11.51	0.13	0.22

*Others mean hydrocarbons containing oxygen or unidentified organic compounds.

Table 2. Weight fraction of each PONA Group in oil products from thermal and catalytic degradation of HDPE with various catalysts at 450°C (Seo et al.,2003).

Catalytic degradation using ZSM-5 with small size increases aromatic hydrocarbons up to 59wt%, as a shape selectivity of catalyst, which is mainly consisting of the alkyl-aromatics with one-benzene ring structure. ZSM-5 is superior to zeolite Y in terms of aromatic formation. Also, the hydrogen atoms in ZSM-5 catalytic degradation contribute to the formation of naphthenes with largely C_6-C_8 hydrocarbons. Paraffins and olefins contain mostly lighter hydrocarbons.

It has been demonstrated that rare earth exchanged zeolite Y is more active than silica-alumina as cracking catalyst (Lin&Yang, 2007; Onwudili et al., 2009), because zeolite can provide a greater acidic site density. Since zeolite Y has more favorable shape selectivity for aromatic formation than non-zeolite catalyst, some intermediate carbenium ion formed by acidic zeolite will choose a pathway to aromatic formation, and some will be left over as olefin. Thus, the oil product from zeolite Y was mostly consisted of C_6-C_9 molecules which would be produced as largely light olefins and some cyclics. Zeolite Y improved the formation of branched isomers by the isomerization of light olefins and in cyclic products, naphthenes and aromatics by cyclization were mostly consisted of C_6 and C_7-C_{10} molecules, respectively.

The oil product over mordenite, among zeolites, appeared differently from other zeolites. This product distribution was similarly shown with that of thermal degradation, rather than other zeolites. This contrasting result of both mordenite and other zeolites seems to be correlated with the crystalline pore structure. Since this physical property is adopted for greater diffusion, mordenite with large pore size of one-dimensional pore structure can provide a greater initial activity than zeolite Y, but it would tend to lose activity more rapidly with time on stream. Coke formation in mordenite is known to be significant in a literature(Chen et al., 1989). As the result, the lighter molecules were less formed in mordenite.

4. Pyrolysis of mixture of waste HDPE and PS

When the pyrolysis is conducted to obtain the oil product, the effects of the mixing of HDPE and PS are described in this section. For the catalytic degradation of two polymers with a different mixing proportions, the cumulative amount distributions of liquid products as a

function of reaction lapsed time are shown in Fig. 2. The experiments were performed with a stirred semi-batch reactor at a catalyst amount of 9.1 wt % and at a temperature of 400 °C with the same reaction temperature programming.

The cumulative amount distributions of liquid products clearly increase with an increase in the mixing proportions of PS against HDPE. These results are due to the fact that the increase of PS content in HDPE and PS mixture has much high yield of liquid product and high degradation rate. This means that pyrolysis of PS is predominant over the pyrolysis of HDPE in the mixture. According to the previous result (Lee et al.,2002), waste PS showed higher liquid yield and higher initial degradation rate in the catalytic degradation than waste PP and PE, because PS is mainly converted into stable aromatic components as liquid phase and also the low degradation temperature.
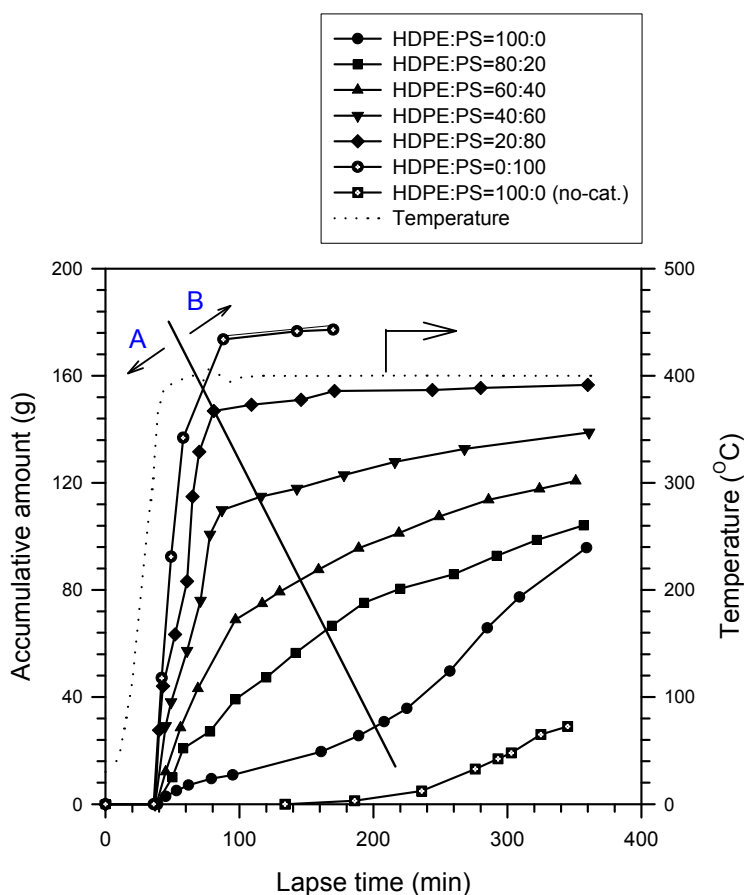
Fig. 2. Cumulative amount distributions of liquid products for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C. (A: Initial degradation region, B: Final degradation region) (Lee et al., 2004).

The slope of the cumulative amount of liquid product versus reaction lapsed time represents as the degradation rate of HDPE and PS mixtures which is needed to obtain liquid products. The initial liquid product was obtained at around 400 °C of reaction temperature. These can be classified as two region of initial (A; initial degradation region) and final (B; final degradation region) lapse time in the reaction time and were appeared as initial and final degradation rate with a function of PS content, as shown in Fig. 3. The initial degradation rates are exponentially increased with increasing PS content in the mixture, while the final degradation rates were also suddenly decreased with increasing PS content, due to the influence of HDPE in the mixture. These results show that the polymers studied do not react independently, but some interaction between samples was observed.
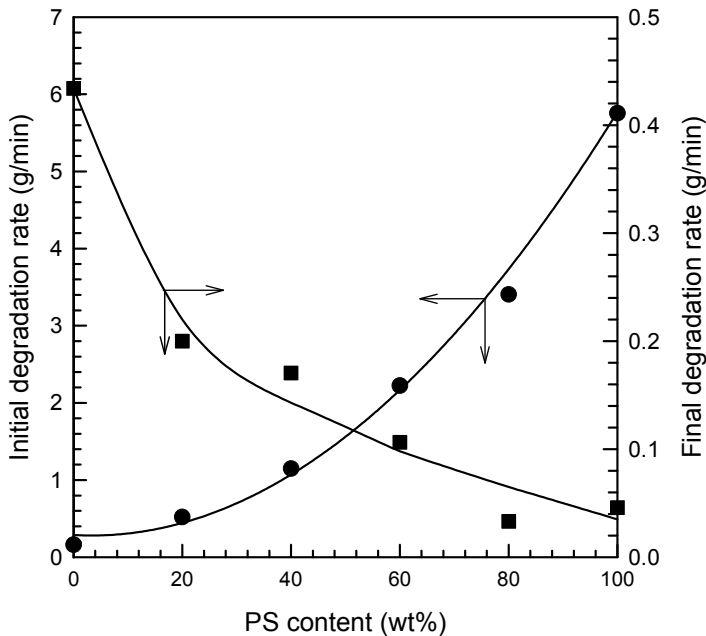

Fig. 3. Initial and final degradation rate as a function of PS content for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C (Lee et al., 2004).

The commercial pyrolysis process yields the pyrolytic oil from the reactor at short contact time of 1-2 hours. It is necessary to know the characteristics of product oil in initial degradation region of Fig. 2. For these results, the distribution of liquid paraffin, olefin, naphthene and aromatic (PONA) products is presented in Fig. 4. Hydrocarbon group compositions of degraded products are strongly dependent on chemical properties of plastic type in plastic waste. As PS is included in the mixture, even though it is low or high, the pyrolysis of this mixture greatly improves the formation of aromatics, whereas the olefins produced by pyrolysis of polyolefins mainly has a much low fraction. This can be explained by the fact that the acceleration of aromatic products stems from the aromatic fragments of PS degradation as well as the cyclization of paraffinic and olefinic intermediates in FCC

catalyst containing zeolite. Both the degradation of plastic mixture and the characteristics of oil product obtained are significantly influenced by plastic type in the mixture, as well as zeolite type in the catalyst.
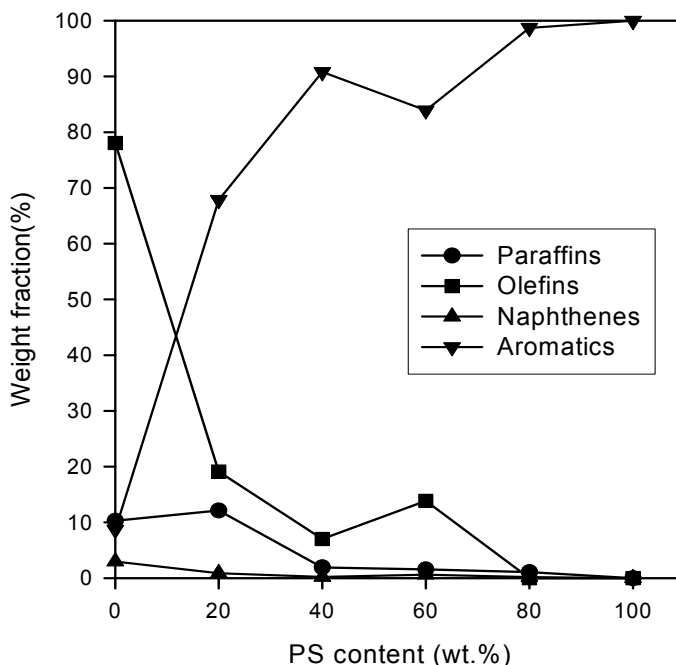

Fig. 4. The distribution of liquid paraffin, olefin, naphthene and aromatic (PONA) products for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst in the initial degradation time is presented with a function of PS content (Lee et al., 2004).

5. Pyrolysis of municipal plastic waste

Pyrolysis is a suitable process for thermoplastics like polyethylene and polystyrene. For a small mixture of polyvinyl chloride (PVC) and polyethylene terephthalate (PET) included in municipal plastic waste (MPW), an issue of environment and operation problems occurs in pyrolysis process. Thus, the removal of PVC and PET in MPW may be conducted by separation methods such as water separation, because of relatively high density of PVC and PET in a comparison for polyethylene and polystyrene with specific gravity 1.2 or less. Also, after the pretreatment of MPW, the inorganic materials contained with very low content are deposited in solid carbon residue during the pyrolysis. The MPWs are classified as low MPW(<1.0), medium MPW(1.0-1.1) and high MPW(1.1-1.2), based on the specific gravity 1.2 or less. The pyrolysis corresponding to three type MPWs is conducted.

Table 3 shows the yields of liquid, gas and residue products obtained by the pyrolysis of three different MPWs at a stirred batch reactor of 1.1 liter volume size, under the same experimental conditions. From these results, the product distribution is clearly different

over various samples of MPW. Basically, the yield of liquid products in all samples is 75% or over. Note the corresponding liquid yields is in the following order; medium MPW >> low MPW > high MPW. Especially, the medium MPW shows highest liquid yield with about 90%. On the contrary, the order of gas and residue yield shows reverse relationship. It can be explained by the result that the plastic type contained in each MPW separated by a difference of specific gravity is an important key on the product distribution obtained. Lee et al. (Lee et al., 2002) have reported the influence of plastic type on liquid, gas and residue yield for pyrolysis of plastic wastes. The pyrolysis of polystyrene, due to the structure of stable benzene-ring, shows higher liquid yield and lower gas yield than that of polyolefinic polymer (PE, PP) with a straight hydrocarbon structure. Polystyrene is less cracked to gas product of 5 carbon numbers or less. Hence, the product distribution is strongly dependent on the plastic type including in municipal plastic wastes.

Sample (S.G..)	Liquid yield (wt%)	Gas yield(wt%)	Residue (wt%)
Low MPW (<1.0)	80.9	11.1	8.0
Medium MPW(1.0-1.1)	89.8	2.9	7.3
High MPW (1.1-1.2)	76.0	9.7	14.3

Table 3. Product yields obtained from pyrolysis of various MPWs at 400°C (Lee, 2007).

As the characteristics of liquid product, the paraffin, olefin, naphthene and aromatic (PONA) components, etc are compared over three different MPWs, as shown in Table 4. Also, their carbon number distributions are plotted in Fig. 5, respectively. These showed a peculiar product distribution, due to the chemical nature and structure of plastic type in MPW.

Product Composition	Sample (S.G.)		
	Low MPW (<1.0)	Medium MPW (1.0-1.1)	High MPW (1.1-1.2)
Paraffins	4.61	1.82	0.06
Olefins	75.93	0.02	0.10
Naphthenes	6.08	0	0.46
Aromatics	11.97	97.19	22.24
Phenols	0.25	-	17.05
Nitro-aromatics	0.15	0.97	1.88
Aldehydes	1.01	-	-
Methylesters	0	-	58.21
<C_{13}	92.89	92.05	99.13
C_{13}-C_{24}	7.01	7.95	0.87
>C_{24}	0.10	0	0

Table 4. Liquid product composition obtained from pyrolysis of various MPWs at 400°C (Lee, 2007).

(a)   (b)
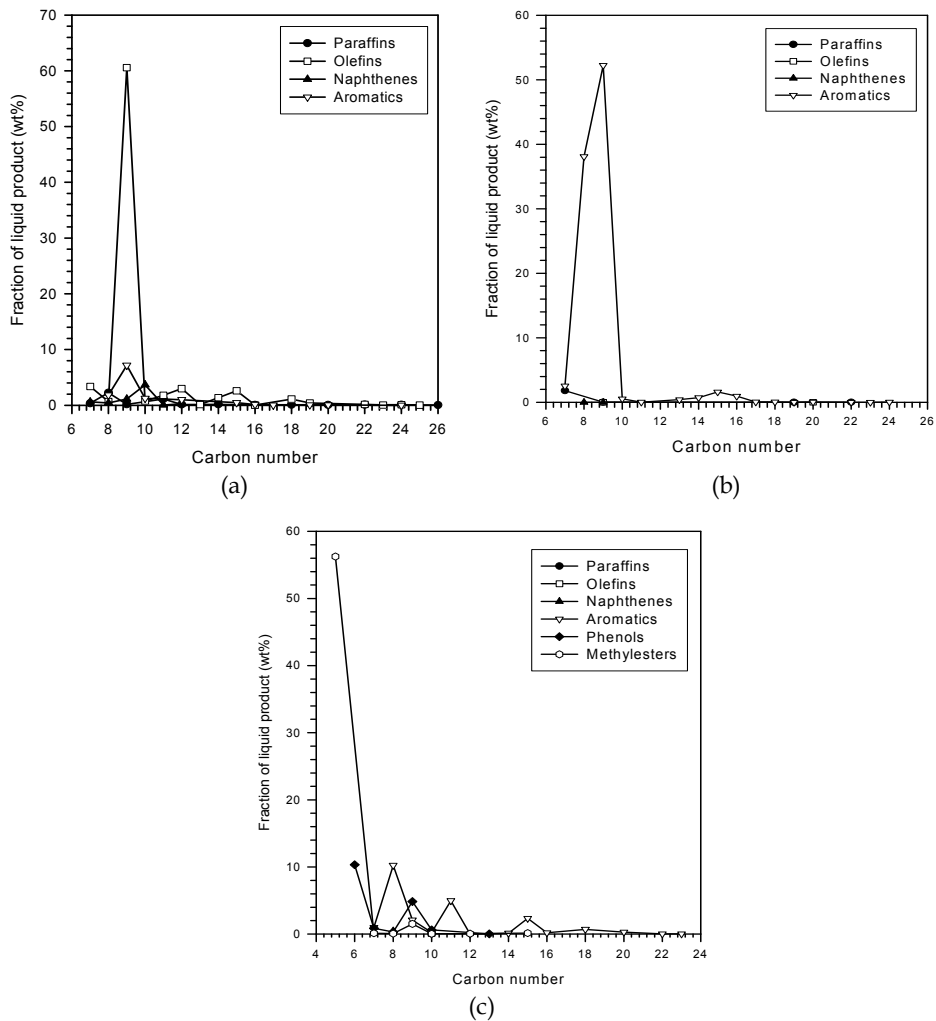

(c)

Fig. 5. Carbon number distribution of liquid paraffin, olefin, naphthene and aromatic products obtained from pyrolysis of MPW at 400ºC (specific gravity : <1.0(a), 1.0-1.1(b), 1.1-1.2(c)) (Lee, 2007).

In the case of low MPW sample, the fractions of liquid paraffin, olefin, naphthene and aromatic products are about 5%, about 76%, about 6% and about 12%, respectively. Primary liquid product is olefin components and secondary is aromatic components. In the liquid product, naphthene and paraffin components are produced with a little amount. This means that low MPW mainly consists of PP polymer, among polyolefinic polymers, with relatively low degradation temperatures and high olefin fraction of liquid product in pyrolysis process (Lee et al., 2002). Also, aromatic products show 10% or more, because of including a little PS in low MPW. These results were demonstrated by the

carbon number distribution of liquid PONA products over the case of low MPW, as shown in Fig. 4(a). Main liquid product was light olefin component with 9 of carbon number. This result was consistent with that of Sakata et al.(Sakata et al., 1999), who produced much more light hydrocarbon with 9 of carbon number from thermal degradation of PP at relatively low degradation temperature.

On the other hand, medium MPW showed highest fraction of liquid product with about 90% and lowest fraction of gas product, among three samples. In liquid product, aromatic components showed about 97% fraction and the rest was less than 2% fraction, respectively, as shown in Table 4. Moreover, phenol, aldehyde and methylester components in liquid products were not appeared and only nitro-aromatic products showed less than 2% fraction. It can be explained by the results that plastic type contained in medium MPW is mostly consisting of polymers with benzene-ring structures, especially PS among these polymers. This result can be reflected by carbon number distribution of liquid product, as shown in Fig. 4(b). Here, carbon number distribution was very short, mainly ranged from 8 to 9, as aromatic components. This result show a similar tendency in a comparison with that of Demirbas study (Demirbas, 2004), which is mainly consisting of 50-60% fraction of styrene and 10-20% fraction of C_5-C_8 hydrocarbons.

For pyrolysis of high MPW sample, the distribution of liquid products shows about 58% fraction in methylmethacrylate component, about 22% fraction in aromatic components and about 17% fraction in phenol components, as a main liquid product. However, straight hydrocarbon and naphthene components mainly obtained from pyrolysis of polyolefinic polymers are produced with very little amount (Lee et al., 2004). This result indicates that high MPW sample did not almost contain polyolefinic polymer type, and was mostly consisting of PMMA and then a little PS. This is demonstrated by the carbon number distribution of liquid products, as shown in Fig. 4 (c). Note the main product is methylmethacrylate monomer, producing from the pyrolysis of PMMA (Smolders & Baeyens, 2004).

6. Upgrading of pyrolysis oil with low quality

6.1 Constant stirred tank reactor

Pyrolytic oil is mainly composed of heavy hydrocarbons with low quality, as well as light hydrocarbons. Heavy hydrocarbons must be cracked to light hydrocarbons, in order to use as the fuel oil. The degradation experiment of pyrolytic oil is conducted by a heating rate of 10OC/min up to 420OC/min and then holding time of 5 hours at that temperature. The effects of degradation temperature and holding time at high degradation temperature on pyrolysis process are investigated. When the pyrolytic oil is degraded in a stirred semi-batch reactor with a bench scale under the condition of degradation temperature programming, the low degradation temperature (at 420 OC or below, short lapse time) only distills each hydrocarbon with the corresponding boiling point within the pyrolytic oil, while at high degradation temperature and long lapse time heavy hydrocarbons are much more decomposed into light hydrocarbons like gasoline ranged components and also a little middle hydrocarbons., as a pattern of GC (gas chromatography) peaks shown in Fig. 6.
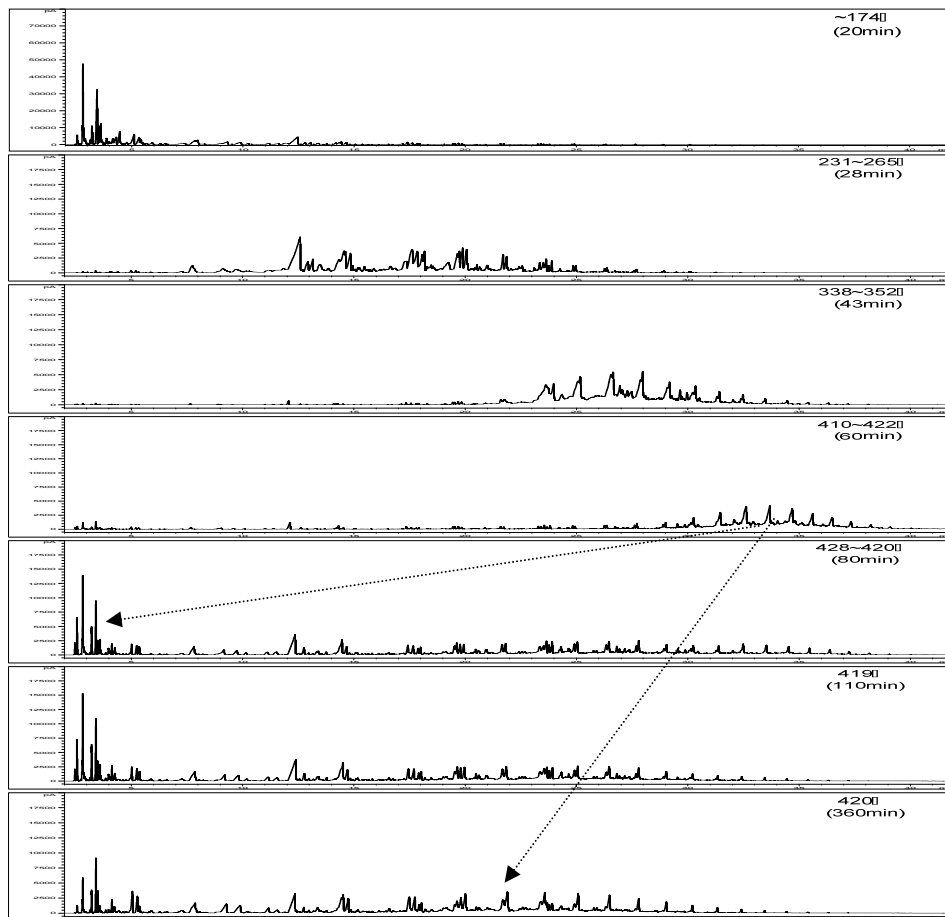
Fig. 6. GC peaks of product oils for thermal degradation of raw pyrolytic oil under degradation temperature programming (Lee, 2009).

Also, the catalytic degradation of pyrolytic oil using powder type FCC catalyst as a commercial cracking catalyst is investigated by a stirred tank reactor. The purpose of the catalytic degradation is to identify the possibility for utility of spent FCC catalyst as a waste catalyst, as well as the application of fresh FCC catalyst. A simple pyrolysis and catalytic degradation using spent or fresh FCC catalyst are compared by cumulative amount distribution of liquid product as a function of lapse time of reaction, as shown in Fig. 7. When a little catalyst (10%) is quickly loaded in the reactor at $420^{O}C$, the cumulative yield of liquid product is improved by the effects of catalyst, due to more cracking of heavy hydrocarbons into liquid product. Also, the cumulative yield distribution from catalytic degradation using both spent and fresh FCC catalysts is slightly deviated. This shows that spent FCC catalyst, compared to fresh FCC catalyst, has an effective result on the pyrolysis process.
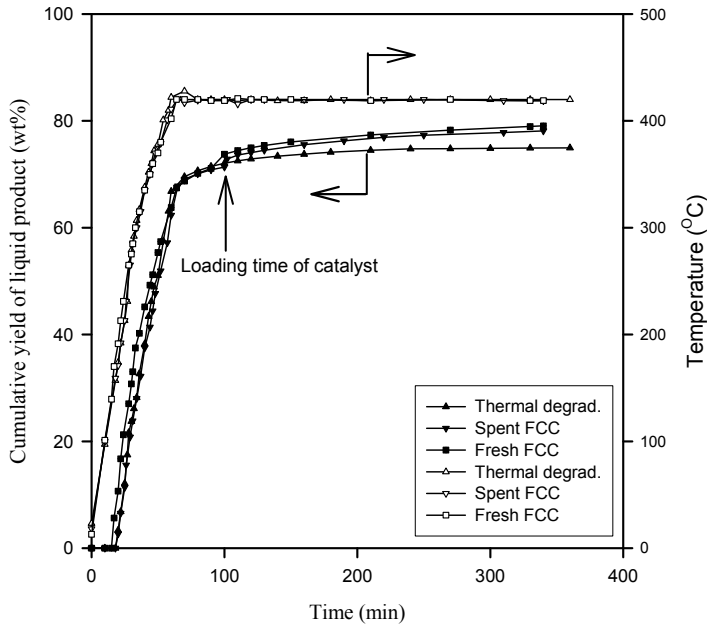
Fig. 7. Cumulative yield distribution of oil product for thermal and catalytic degradation of pyrolytic oil (Lee, 2009).

6.2 Fixed bed reactor

In chemical recycling, the pyrolysis process of plastic wastes by the use of commercial rotary kiln reactor can be taken into a consideration as an efficient method. From this system, municipal plastic waste as a reactant is converted into gas product, oil product (liquid product+wax) and residue. Among pyrolytic oil, the wax oil with a high proportion has a low value for a practical use in industrial companies and moreover difficulty to supply it as an alternative fuel oil, due to its high viscosity and low quality, etc. The SIMDIST (simulated distillation) curves, as the boiling point distribution, over the pyrolysis wax oil and the commercial oils (gasoline, kerosene and diesel) are shown in Fig. 8. The pyrolysis wax oil has much higher boiling point distribution, ranging from approximately 300°C to 550°C, compared to those of commercial oils. It mainly consists of paraffin components and a very wide carbon number distribution ranging from an approximate carbon number of 10 to a carbon number of nearly 40 (Lee, 2012).

Thus, the catalytic upgrading of low-grade pyrolysis wax oil is conducted by a fixed bed reactor, as a continuous gas-phase reaction using zeolite. The distribution of liquid product, gas product and coke over several types of commercial zeolite catalysts is listed in Table 5. Five commercial zeolite catalysts (ZSM-5, zeolite Y and mordenite, with or without clay or alumina as a supporter) used have their unique and different physicochemical properties.
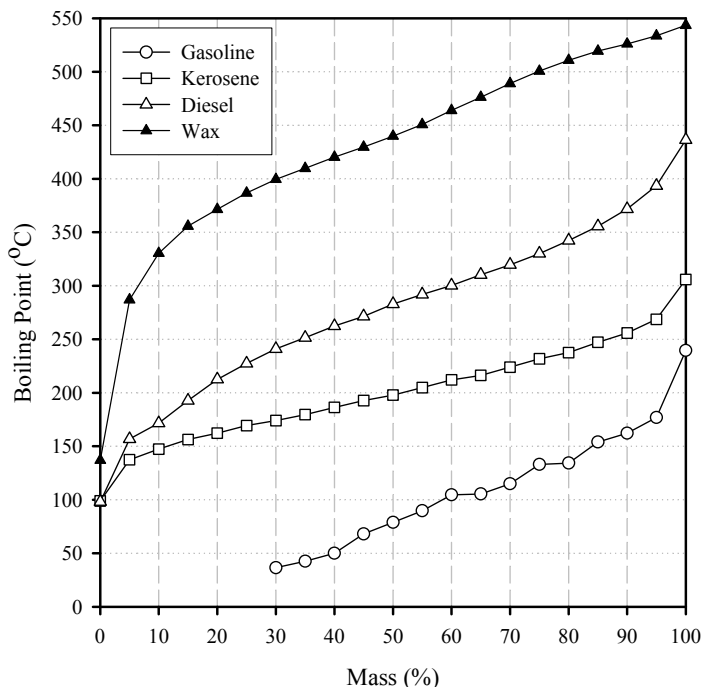
Fig. 8. Boiling point distribution as a function of mass fraction for pyrolysis wax oil and commercial oils (Lee, 2012).

Items	Liquid(wt%)	Gas(wt%)	Coke (wt%)
ZSM-5 (HZ30)	47.18	51.04	1.78
Zeolite Y (HY80)	66.98	28.95	4.08
Zeolite Y(80%)+Clay(20%) (HYC8)	74.12	22.95	2.93
Mordenite(80%)+Clay(20%) (HMC11)	92.12	7.72	0.16
Mordenite(80%)+Alumina(20%) (HMA6)	82.59	15.11	2.3

Table 5. Product distribution for catalytic upgrading of pyrolysis wax oil at 450°C, 1hr (Lee, 2012).

The order of the zeolite for the catalytic degradation of pyrolysis wax oil to gas products is ZSM-5 > zeolite Y > mordenite. ZSM-5 catalyst with a three-dimension pore structure shows the highest activity to gas product at nearly 50%. On the other hand, the catalyst containing mordenite with a one-dimensional pore structure shows the lowest conversion of heavy hydrocarbons into gas product. This indicates that the catalyst of zeolite type plays an important role in the catalytic degradation. As the effect of supporter, the distribution of gas products and coke with both pure zeolite Y and zeolite Y(80%)+clay(20%) shows a slight difference. The catalyst containing clay has low fraction of gas product and coke, compared to pure zeolite Y. The case of mordenite with a different supporter (clay or alumina) also shows a slight difference in the product distribution. It is concluded that the adequate

design of both zeolite as a role of main reaction and supporter is a major key to determine the product distribution.

This result can be also sufficiently illustrated by the distribution of the liquid paraffin (normal/iso), olefin (normal/iso), naphthene and aromatic (PONA) products according to zeolite catalysts, as shown in Table 6. Raw pyrolysis wax oil is composed of predominantly normal paraffins and small amount of normal olefins. Among zeolites, ZSM-5 shows the

Items	Paraffins (wt%)			Olefins (wt%)			Naphthenes (wt%)	Aromatics (wt%)
	N-	Iso-	Total	N-	Iso-	Total		
Raw wax	70.7	-	70.7	8.0	-	8.0	-	-
HZ30	2.4	0.5	2.9	-	-	-	17.7	76.8
HY80	12.5	28.5	41.0	6.4	7.5	13.9	9.4	30.2
HYC8	12.2	25.6	37.9	5.5	8.4	13.9	11.9	28.7
HMC11	71.8	-	71.8	8.2	1.6	9.8	0.6	1.8
HMA6	61.3	-	61.3	7.0	10.2	17.2	2.2	8.7

Table 6. Composition of liquid paraffin, olefin, naphthene and aromatic products for catalytic upgrading of pyrolysis wax oil at 450°C, 1hr (Lee, 2012).
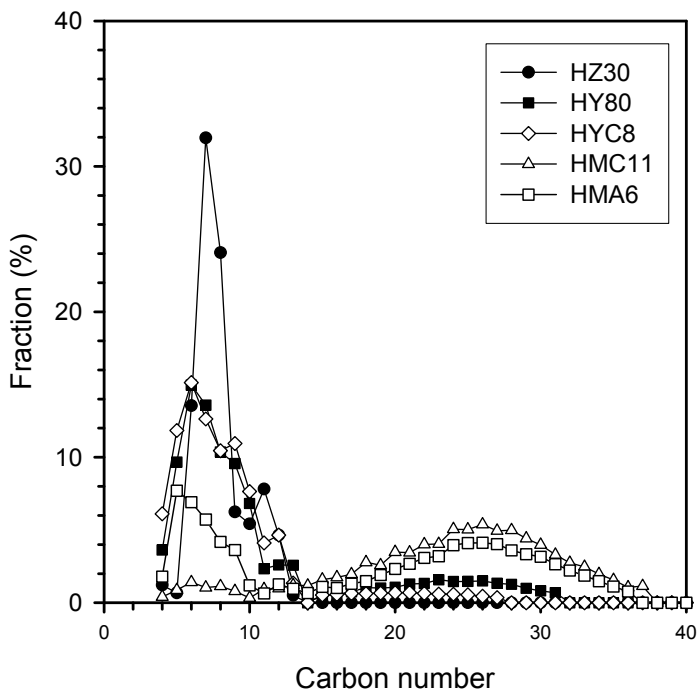

Fig. 9. Carbon number distributions of product oil for catalytic upgrading of raw pyrolysis wax oil at 450°C (Lee, 2012).

highest fraction of aromatic products through the cyclization of light paraffins and olefins. Aromatic products are mainly C_6, C_7 and C_8 components of benzene, toluene, xylene and ethylbenzene, as shown in Fig. 9, due to shape selectivity of ZSM-5. The case of zeolite Y mainly used in a commercial cracking process like FCC process and the hydrocracking process shows also different PONA pattern. Zeolite Y has the highest fraction of branched hydrocarbons with high octane number and also high fraction of aromatic products in the liquid products, which mainly produces gasoline ranged components in liquid product. However, the catalysts containing mordenite with a one-dimension pore structure shows a PONA distribution similar to raw pyrolysis wax oil and also has a wide carbon number distribution ranging from approximately 10 to 40, as shown in Fig. 9. The catalysts contained mordenite do not sufficiently crack for pyrolysis wax oil into light hydrocarbons, as its relatively low activity.

7. References

A. Demirbas, Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons, J. Anal. Appl. Pyrolysis, 72 (2004) 97-102

A. Marcilla, J. C. Garcia-Quesada, S. Sanchez, R. Ruiz, Study of the catalytic pyrolysis behavior of polyethylene-polypropylene mixtures. J Anal Appl Pyrolysis 74 (2005) 387-392.

A. Marcilla, M. I. Beltran, R. Navarro, Thermal and catalytic pyrolysis of polyethylene over HZSM-5 and HUSY zeolites in a batch reactor under dynamic conditions, Applied Catalysis B : Environ., 86(2009) 168-176

D. S. Achilias, C. Roupakias, P. Megalokonomos, A. A. Lappas, E. V. Antonakou, Chemical recycling of plastic wastes from polyethylene and polypropylene. J Hazard Materials, 149 (2007) 536-42.

G. Buekens, H. Huang, Catalytic plastic cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes, Resources, Conversion and Recycling, 23(1998) 163-181

J. A. Onwudili, N. Insura, P. T. Williams, Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time, J. Anal. Appl. Pyrolysis, 86(2009) 293-303

J. Scheirs, W. Kaminsky, Feedstock recycling and pyrolysis of waste plastics: Converting waste plastics into diesel and other fuels, John Wiley & Sons, Ltd(2006)

K.-H. Lee, N.-S Noh, D.-H. Shin, Y.-H Seo, Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst, Polymer Degradation and Stability, 78(2002) 539-544

K.-H. Lee, D.-H. Shin, Y.-H. Seo, Liquid-phase catalytic degradation of mixtures of waste high-density polyethylene and polystyrene over spent FCC catalyst.-Effect of mixing proportions of reactants, Polymer Degradation and Stability, 84(2004) 123-127

K.-H. Lee, D.-H. Shin, Influence of plastic type on pyrolysis of waste thermoplastics into oil recovery, J. Korea Soc. Waste Management, 21 (2004) 646-651

K.-H. Lee, Pyrolysis of municipal plastic wastes separated by difference of specific gravity, J. Anal. Appl. Pyrolysis, 79(2007) 362-367

K.-H. Lee, D.-H. Shin, Characteristics of liquid product from the pyrolysis of waste plastic mixture at low and high temperatures: Influence of lapse time of reaction, Waste Management 27(2007) 168-176

K.-H. Lee, Thermal and catalytic degradation of pyrolytic oil from pyrolysis of municipal plastic wastes, J. Anal. Appl. Pyrolysis, 85 (2009) 372-379

K.-H. Lee, Effect of zeolite type on catalytic upgrading of pyrolysis wax oil, submitted to J. Anal. Appl. Pyrolysis 94 (2012) 209-214

K. Smolders, J. Baeyens, Thermal degradation of PMMA in fluidised beds, Waste Management, 24 (2004) 849-857

N. Y. Chen, W. E. Garwood, F. G. Dwyer, Shape-selectivity catalysis in industrial applications, Marcel Dekker Inc, New York, 1989

N. Miskolczi, L. Bartha, G. Deak, B. Jover, D. Kallo, Thermal and thermo-catalytic degradation of high-density polyethylene waste, , J. Anal. Appl. Pyrolysis, 72 (2004) 235-242

N. Miskolczi, L. Bartha, G. Y. Deak, Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts. Polym Degrad Stab 91 (2006) 517-26.

P. B. Vento, E. T. Habib, Fluid catalytic cracking with zeolite catalysts, Marcel Dekker Inc, New York, 1979

R. A. Garcia, D. P. Serrano, D. Otero. Catalytic cracking of HDPE over hybrid zeolitic-mesoporous materials. J Anal Appl Pyrolysis 74 (2005) 379-86.

S. Y. Lee, J. H. Yoon, J. R. Kim, D. W. Park. Degradation of polystyrene using clinoptilolite catalysts. J Anal Appl Pyrolysis 64 (2002) 71-83.

S. M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW) : A review, Waste Management, 29(2009) 2625-2643

S. Kumar, A. K. Panda, R. K. Singh, A review on tertiary recycling of high-density polyethylene to fuel, Resources, Conversation and Recycling, 2011,

Y. Sakata, M. A. Uddin, A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts, J. Anal. Appl. Pyrolysis, 51 (1999) 135-155

Y.-H. Seo, K.-H. Lee, D.-H. Shin, Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis, J. Anal. Appl. Pyrolysis 70(2003) 383-398

Y. H. Lin, M. H. Yang, Catalytic pyrolysis of polyolefin waste into valuable hydrocarbons over reused catalyst from refinery FCC units, Appl Catal A: General 328 (2007) 132-139.

Z. S. Seddegi, U. Budrthumal, A. A. Al-Arfaj, A. M. Al-Amer, S. A. I. Barri. Catalytic cracking of polyethylene over all-silica MCM-41 molecular sieve. Appl Catal A: General 2002; 225:167-76.
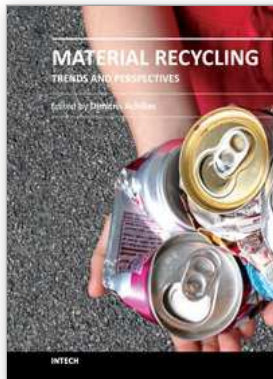
Material Recycling - Trends and Perspectives

Edited by Dr. Dimitris Achilias

The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

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