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Accelerate the Aging of Polymer as Energy-Saving Method Prior to the Pyrolysis Process

Jin Hu

Abstract

Pyrolysis technology has appeared a long time ago, but it has not been widely recognized and used in the area of waste plastic/rubber management. The key reason is that the high energy consumption of pyrolysis is the most important problem that plagues the further development of pyrolysis. Prior to the pyrolysis of waste plastics/rubbers, in addition to dehydration and drying can save part of the energy consumption of pyrolysis, in this study, we have first reviewed and discussed high irradiance exposure to artificially accelerate the aging process of waste plastics/rubbers as pretreatment. The results from our preliminary experiments show that the pyrolysis process of the plastic that has undergone UV accelerated aging was speed up, accordingly to achieve saving energy in thermal cracking.

Keywords: pretreatment, natural aging, artificially accelerated aging, energy saving

1. Introduction

Pyrolysis is the thermochemical decomposition of organic matter into non-condensable gases, condensable liquids, and a solid residual coproduct, biochar or charcoal in an inert environment (i.e., in the absence of oxygen) [1].

In a singular pyrolysis reactor, oxygen must be excluded otherwise more of the gas, oils, and char will burn, thereby losing products and reducing efficiency. Pyrolysis has historically been implemented to produce useful substances such as methanol, acetone, acetic acid, and creosote from wood in predominantly batch process retorts prior to petrochemical production routes [2].

Nowadays, pyrolysis has great potential to convert waste such as plastic/rubber/biomass into valuable products, such as fuels, power, heat and other valuable chemicals and materials to achieve maximum economic and environmental benefits. For instance, liquid oil produced from different types of plastic waste had higher heating values (HHV) in the range of 41.7–44.2 MJ/kg similar to that of conventional diesel. Therefore, it has the potential to be used in various energy and transportation applications after further treatment and refining [3].

Municipal Solid Waste (MSW) is mainly derived from the disposal of general waste streams that include green waste, food waste, and miscellaneous products (ie, leather, textile, metal scraps), which can be separated as noncompostable materials [4]. Although most MSW ends up in unsightly landfill sites, a significant quantity has been used to produce different value-added products such as compost, feedstuffs, and biogas [5].

Most mixed MSW technologies attempt to treat large quantities of heterogeneous mixed waste streams. This can be appealing to governments which do not want to source separate waste and seek a single, technological solution. However, the approach of looking for a technology fix for mixed waste treatment presents unique challenges, and is not as successful as more comprehensive source separation strategies. Gasification, pyrolysis and plasma arc technologies are most applied for homogeneous material streams. The heterogeneous nature of MSW is not well suited to this type of technology [6].

Andrew and Jumoke's review [7] has shown that when appropriate system boundaries are applied, a MSW pyrolysis plant for self-sustaining energy from waste is thermodynamically unproven, practically implausible, and environmentally unsound. No practical examples of a self-sustaining MSW pyrolysis plant, using either gas, oil, or char were found.

For homogeneous material streams, an approach of energy saving is pre-treatment of the waste, by removing wet organics and inert material while retaining the high-energy plastics in the waste stream. In the process of converting organic solid waste into energy, besides the major thermal cracking energy consumption, a variety of additional energy consumption would incur e.g. feedstock sorting, conditioning, drying, shredding, pyrolysis gas cooling/condensation, combustible gases cleaning…How to reduce the energy consumption in each link to achieve the ultimate goal of reducing total energy consumption and increasing energy efficiency in the entire process.

Moisture is present in all solid organic waste (even visibly dry material), existing at both surface and cellular level, therefore unless drying is set outside the system boundary it must be included in energy balances. Prior to the pyrolysis process occurs, removing this water from the solid organic waste is highly energy intensive due to the high latent and sensible enthalpy demands in both liquid and steam phases, and high enthalpy of vaporization [8]. These endothermic phenomena are known as parasitic enthalpy demand, and are well understood from extensive work with steam cycles. Therefore, dehydration and drying outside the pyrolysis system under controllable temperature and a good ventilation cycle are preference that has a much better effect than that in a relatively closed pyrolysis reactor and save more energy.

During the pyrolytic conversion, the process of transforming long-chain hydrocarbons into short-chain hydrocarbons needs an extraneous energy supply to drive the process so this is provided allothermally from electricity or by burning additional fuels. Generally speaking, catalytic pyrolysis is a major technique to obtain more oil or combustible gas at relatively low temperatures and low energy consumption. Apart from this, this study will first review the published experimental results of artificially speeding up the aging of raw materials for some common organic solid wastes under different conditions e.g. temperature, natural or artificial ultraviolet light. Second, to propose using this method in the pre-treatment of raw materials to reduce the energy consumption of thermal cracking from long-chain to short-chain, and finally shortening the thermal cracking time and reducing energy consumption.

2. Sources of solid waste

Polymer degradation can be caused by heat (thermal degradation), light (photodegradation), ionizing radiation (radio degradation), mechanical action, or by fungi, bacteria, yeasts, algae, and their enzymes (biodegradation). The deleterious

effects of weathering on polymers generally has been ascribed to a complex set of processes in which the combined action of UV light and oxygen predominant.

The overall light-initiated process in the presence of oxygen generally is referred to as oxidative photodegradation or photooxidation. A pure thermal effect in possible because oxygen is always present and so the process is thermaloxidative degradation [9].

There are many different modes of polymer degradation. These are very similar since they all involve chemical reactions that result in bond scission.

2.1 Polypropylene

Polypropylene (PP), as a representative of modified plastics, is widely used in textiles, construction, and other industries, and can also be used to make fiber products, automotive plastic parts, woven bags, etc. Of these, PP is an attractive material for packaging due to its low cost, higher tensile strength, glossy and versatility [10].

However, since isotactic polypropylene is a spiral crystal and its unique molecular structure, its molecular chain is more susceptible to light, heat, oxidative degradation, and poor product cold resistance, resulting in its application range, especially as engineering materials and outdoor products are greatly restricted [11].

Gallo and co-workers have studied the natural weathering of both thin and thick polypropylene film samples [12–14]. The authors concluded that the degradation behavior of these PP films is different in its oxidation products and crystallinity. The structural rearrangement or chemical modification occurs mainly in a region nearer to the surface of the material during weathering. Hence, the thinner PP films were degraded easily than the thicker PP films or plates.

Rajakumar et al. [15] used mathematical models to predict attempted life time of PP. Their experimental and simulation results showed that the carbonyl growth is more affected by ultraviolet (UV) and cumulative total solar radiation for PP weathered during summer. The loss in tensile strength of PP weathered during summer is more dependent on the average temperature and the UV portion of the total solar radiation whereas, intensity of UV radiation has profound effect on the tensile strength of PP weathered during winter.

Meanwhile, the UV-induced degradation of PP has been investigated by many authors and reported in a number of reviews and research articles [16–18].

Ni et al. [19] have studied the effects of indoor temperature difference aging and ultraviolet light aging on the aging degree of PP samples by means of mechanical properties, capillary rheology and scanning electron microscopy.

Their experimental results show that the retention of elongation at break was 58.7% at 20°C and 6.7% at 100°C, respectively. And the greater the temperature difference, the faster the brittle fracture speed of PP and the greater the degree of fracture. The torque at a temperature difference of 100°C was reduced from 0.188 N·m to 0.099 N·m, the sample is degraded to a large extent and loses its value in use. The elongation at break under ultraviolet irradiation of 340 nm for 20 days was 15.3%, while under ultraviolet irradiation of 313 nm, which was 3.1%. The torque of PP samples aged under ultraviolet irradiation of 340 nm decreased from 0.188 N·m to 0.112 N·m for 20 days, while for samples under ultraviolet irradiation of 313 nm, the torque decreased to 0.084 N·m, respectively. At this time, the sample completely loses its use value. They concluded that different aging methods make different aging degrees for PP and the ultraviolet irradiation of 313 nm makes more serious aging for PP samples because of higher energy.

2.2 Polyethylene

According to the difference in production technology and physical and chemical properties, polyethylene molecules can be divided into low-density polyethylene (LDPE), high-density polyethylene (HDPE), medium-density polyethylene (MDPE) and linear low-density polyethylene (LLDPE) [20].

Among them, LDPE molecules are generated under high temperature and high-pressure conditions, and the reaction conditions are violent. The generated molecular chain has numerous branches, loose molecular arrangement, and relatively low crystallinity (that is, the percentage of crystalline regions in the polymer molecular chain), which is manifested as material density Small, poor strength, but with good flexibility, light transmission, and relatively easy to degrade; HDPE is produced by polymerization under lower temperature and pressure conditions through the action of a catalyst, with a few branches, dense molecular chain arrangement, and high molecular crystallinity. The material has high density, high mechanical strength, and the slowest degradation [21–23].

Polyethylene has a long molecular chain, large relative molecular mass, high crystallinity of the chain segment, strong hydrophobicity, and it is difficult to contact with biological or chemical substances or enter the microbial body to be catabolized; in addition, inside the polyethylene structural unit ($-[CH_2-CH_2]n-$), the physical and chemical properties of the CC and CH bonds of $[CH_2-CH_2]n$ are stable, and higher energy or force is required to break the molecular bonds. The relative molecular weight is large, the molecular chain is long, the chain segment is high in crystallinity, and the hydrophobicity is strong [24–27]; these determine that the polyethylene molecule is difficult to degrade, so the degradation process under natural conditions is very slow [24].

Albertsson et al. [28] tracked and monitored the 14CO$_2$ release of polyethylene film under soil landfill conditions through 14C labeling of polyethylene materials. The study found that the degradation rate of polyethylene film was only 0.2%~0.5% when buried in soil for 10 years. Ohtake et al. [29–31] further analyzed the surface molecular structure and molecular weight of polyethylene film and plastic bottles that have been buried in the soil for 32 years and calculated that the complete degradation of the polyethylene film with a thickness of 60 μm under the conditions of field soil landfilling is probably required 300 years.

The non-biological oxidative degradation of polyethylene refers to the oxidative cleavage of covalent bonds when the molecular chain of polyethylene is subjected to non-biological factors such as light, heat, and mechanical force higher than the energy of the covalent bond between the molecules. Under aerobic conditions, the process of rapidly reacting to generate unstable intermediate products such as peroxy or hydroperoxy, and further reacting to generate small molecules or low molecular weight substances such as aldehydes, ketones, acids, esters, carbon monoxide, etc. [32].

Chiellini et al. [33] analyzed the material molecular weight and surface properties and other indicators and confirmed that the decomposition rate of polyethylene film increased significantly with the increase of temperature (55, 70°C).

Briassoulis et al. [34] used artificial heating and ultraviolet radiation to speed up the aging of the residual polyethylene mulch film and backfilled it into the soil to observe the decomposition of the mulch film in its natural state. The results show that the polyethylene film without artificial accelerated aging treatment is not degraded significantly after being buried in the soil for 8.5 years, but after high temperature (50°C treatment for 800 h) and ultraviolet radiation (under 35~45 W·m-2 ultraviolet radiation, the lamp irradiated at a distance of 25 cm for 800 h). The polyethylene film was backfilled into the soil for 8.5 years and then

completely decomposed into plastic micro-particles with a diameter of less than 1 mm, and the degradation process continued. The above results show that environmental factors such as light and heat can significantly promote the degradation reaction of polyethylene film.

Prakash Bhuyar et al. [35] selected plastic packaging sheet as LDPE sample (the low-density polyethylene) and garbage plastic sheet as HDPE sample (high-density polyethylene) for the degradation test under ultraviolet light. Such samples were placed in the Laminar Air Flow (LAF) under UV light of wavelength of 253.7 nm up to 30 days.

They found that the LDPE sheet after 30 days of UV-treated is more fragile and completely broken up into small parts compared to the LDPE sheet after 15 days of UV-treated. The longer the UV treatment applied to the LDPE sheet, the more crack and fragile the plastic sheet. The percentage weight loss for UV-treated LDPE was 87.5% for 30 days.

By comparison, they found HDPE sheet after 30 days of UV-treated is more crack and tear up into small parts compared to the HDPE sheet after 15 days of UV treated. The longer the UV treatment applied to the HDPE sheet, the more crack the HDPE sheet will be. The percentage weight loss for UV-treated HDPE was 21.6% for 30 days. This shows that the percentage weight loss for UV-treated LDPE is higher than the weight loss for UV-treated HDPE.

LU Lin et al. [36] have conducted the exposure test of medium density polyethylene (MDPE) for different time periods up to one year in Xisha (Paracel) Islands.

Their experimental results showed that during the aging period, the color abbreviation and hardness increased, while the gloss, the retention of tensile strength and that of elongation at break decreased. The aging evaluation showed a stepwise increasing tendency of aging rate with the extending of exposure time.

2.3 Polystyrene

Polystyrene (PS) is one of the most commonly used plastics at present. In recent decades, PS has been widely used through different ways of modification. Therefore, it is of important significance to study the aging behavior of PS. Polystyrene (PS) is a multipurpose polymer that is used in varied applications in rigid and foamed form. Polystyrene is manufactured by the addition polymerization of the styrene monomer unit. At room temperature, polystyrene is normally a solid thermoplastic, but can be melted at higher temperature for molding or extrusion, then resolidified. Styrene is an aromatic monomer, and polystyrene is an aromatic polymer [37].

PS is a widely used as thermoplastic. Its hardness, hydrophobic nature and chemical composition cause it to persist in nature without any decomposition for long period of time thus cause environmental pollution [38].

Polystyrene degrades very slowly in nature and the expanded polystyrene is not easily recyclable because of its lightweight and low scrap value. It is generally not accepted in curbside programs. Expanded polystyrene foam takes 900 years to decompose in the environment and has been documented to cause starvation in birds and other marine wildlife [39].

Shah et al. [39] have observed that the UV-irradiation having wavelength range of 365 nm has a profound effect on polystyrene sample. The reduction of the molecular weight of polystyrene shows the degradation of polystyrene macromolecules by irradiation. The increase in number of chain sessions per polymer with the increase irradiation time indicates in the increase in rate of degradation of polystyrene with irradiation time.

Zhang et al. [40] have conducted several UV accelerated weathering tests on PS samples in 4 different ways. They used UV 340 nm, irradiance 0.89 W/m^2. Among them, one way, the sample is unaged. The test method A, the sample was irradiated for 12 hrs at 60°C. The test method B, the sample was irradiated for 8 hrs at 60°C, then 4 hrs condensation at 50°C. The test method C, the sample was irradiated for 8 hrs at 60°C, then 3.75 hrs condensation at 50°C, 0.25 hrs water spray at ambient temperture (without irradiation) as the last step.

Zhang et al. [40] have investigated the thermogravimetric curve of PS samples which can reflect the aging degree of the sample because when the molecular weight decreases under the action of ultraviolet light, resulting in a corresponding decrease in the initial thermal decomposition temperature. The result is shown in the **Figure 1**. In the **Figure 1**, the PS sample aged by Method A has the lowest initial decomposition temperature, followed by B, and then C compared with unaged sample. It shows that the degree of influence of the three test conditions on the aging of the sample is method A>method B>method C. Their results show that UV radiation is the main factor for the chemical aging of PS, the temperature promotes the aging behavior, but humidity has little effect on the aging behavior.

2.4 Polystyrene foam

Polystyrene foam (EPS) is prepared by adding polystyrene (PS) resin as the main body and adding foaming agents and other additives. When EPS is exposed to the natural environment, under the influence of light, heat, oxygen, water, and other factors, the appearance will appear yellowing or even cracks, which will deteriorate its performance and shorten its service life...The aging behavior of EPS is the fundamental basis to determine service life and service environment.

Yao et al. [41] have found: with increasing time of UV accelerated aging, on the molecular chain of EPS some coloring groups that turned the color of the sample surface yellow were produced. With increasing aging time, cushioning efficiency decreased. When aging time was more than 100 h, there was a tendency to lose cushioning property. With increasing aging time, molecular weight of EPS
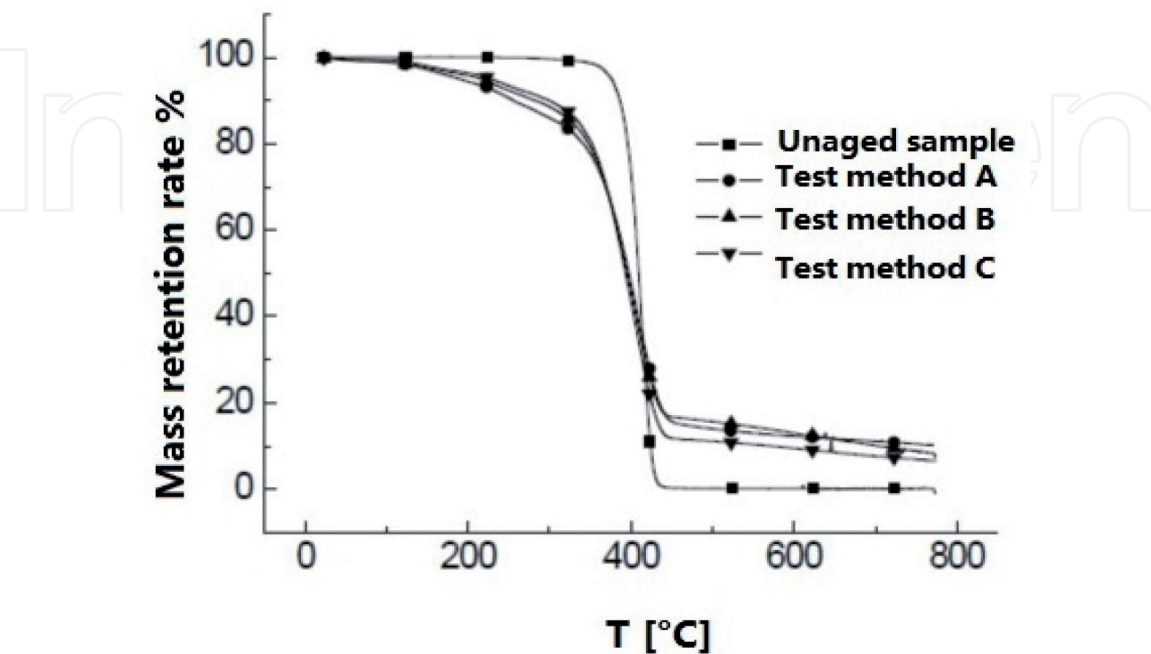

Figure 1.
TG curves of PS after UV aging test (regenerated figure from reference [40]).

decreased, the stability of the molecular structure of EPS was destroyed and photo-oxidative degradation occurs. The chemical degradation, resulting in molecular chain breaks and recombination phenomena, causing in the decline of mechanical properties.

2.5 Rubber

The rubber material is a polymer material with high elasticity and viscoelasticity. Among them, natural rubber (NR) is widely used in tires, conveyor belts, hoses, adhesive tapes, adhesives, sponges, and rubber products because of its excellent comprehensive properties. Production of various rubber products such as shoes, sports equipment, wires and cables, medical equipment, aircraft, and auto parts.

In the past 30 years, the average annual growth rate of global natural rubber consumption has exceeded 5%. The consumption has increased from 4.35 million tons in 1985 to 11.98 million tons in 2015 [42, 43].

In the actual storage and application process, rubber products are often in various environments and will be affected by oxygen, ozone, ultraviolet rays, and heat [44–47].

Weng et al. [47] have investigated Vulcanized natural rubber (NR) under quiescent thermal oxidation aging and high temperature fatigue loading with small strain amplitude. The vulcanized NR was simultaneously subject to high temperature (85°C) and cyclic loading. Under these conditions, their scanning electron microscope (SEM) images confirmed the appearance of nanoscale cracks and voids which are initiated by the combined impact of high temperature and cyclic loading. As the cracks evolve, nano-scale voids appear. They concluded that further evolution of the smaller voids leads to the larger spherical voids with their diameters varying between a few hundred nanometers and several microns.

In addition, seawater [48] will also affect rubber products. The above-mentioned various factors lead to the destruction of rubber composition and structure, gradually losing its original excellent performance, and even loss of use-value, the phenomenon of rubber aging [49]. "Aging" is a common problem of all polymer materials, especially natural rubber with unsaturated bonds on the major chain, which is more susceptible to aging by oxygen and free radicals. Once aging occurs, it will seriously affect its use value and application range, and even a major accident with dire consequences.

2.5.1 Aging mechanism of natural rubber

The aging process is: under the action of ultraviolet rays, the oxidation reaction of natural rubber starts from α-H, first is attacked by oxygen to generate hydroperoxide, and then further reacts to generate aldehydes and ketones, and at the same time the main chain is broken [50, 51]. The free radicals generated by chain scission may combine with double-free radicals, or they may be further attacked by oxygen to continue oxidation; in this process, double bonds addition reaction occurs, and the attack of free radicals on double bonds reduces the content of olefinic hydrogen. The early stage of the reaction is dominated by oxidative degradation, which is manifested as the surface of the aged sample is sticky, and cross-linking occurs in the later stage, the surface of the sample is dried and hardened, and cracks appear.

Ling Ding et al. [52]'s 1H-NMR and FT-IR absorption spectroscopy experimental results proved that the products obtained in the aging process of natural rubber in artificial ultraviolet light aging and natural aging are roughly the same. They found that natural rubber has poor resistance to ultraviolet light aging, and its molecular structure changes significantly when exposed to ultraviolet light for 2 h. Under

natural aging conditions, the structure of natural rubber changes significantly after 30 days. Artificial UV aging for 7 days is equivalent to the effect of natural aging for 3 months.

3. Experimental setup

Because of the very slow degradation of polymer materials under natural conditions, therefore researchers from various countries have developed various artificial accelerated aging test methods to study the aging mechanism of polymer materials. The fluorescent ultraviolet lamp aging test has a high acceleration rate, and the aging resistance of the material can be obtained in a short time. It is one of the most commonly used artificially accelerated aging test methods for polymer materials.
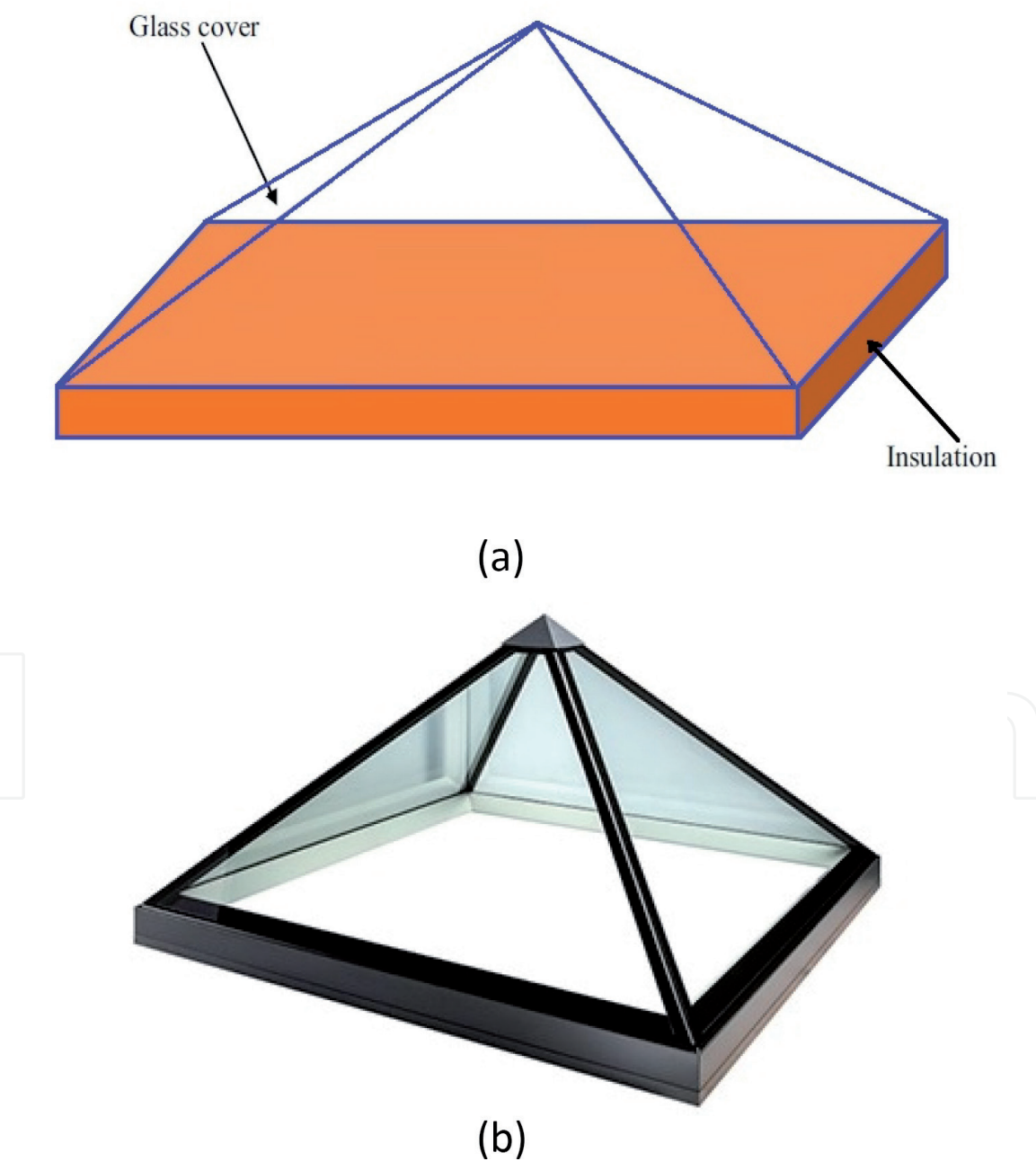

(a)

(b)

Figure 2.
a. a schematic diagram of the square pyramid test bench. b. the pyramid skylight structures.

In this study, we verify the effect of UV accelerated aging on pyrolysis through comparative experiments.

3.1 Raw materials

PP, PE, PS, EPS, Natural rubber sheets and PP granules for test are from Polyrocks Chemical Co., Ltd., Guangdong, China.

3.2 Experimental apparatus

Ultraviolet light has a wavelength of 10 to 400 nm. Among such ultraviolet rays, the part with a wavelength of 10 to 300 nm is absorbed by the atmosphere. The ultraviolet rays with a wavelength of 300 to 400 nm have a destructive effect, and their light energy is very large.

Various plastics are affected in different wavelength areas. The most influential wavelengths are 325 nm for polyester; 318 nm for polystyrene; 300 nm for polyethylene; 310 nm for polypropylene; 310 nm for polyvinyl chloride resin; and 322 nm to 364 nm for vinyl chloride-vinyl acetate copolymer [53].

UVA-340 can perfectly simulate the sunlight spectrum in the critical short-wavelength range, and the wavelength range is 315-400 nm. Its luminescence spectrum energy is mainly concentrated at the wavelength of 340 nm. UVA-340 fluorescent ultraviolet lamp can well simulate the short-wave ultraviolet (<365 nm) part of the spectrum. UVA-340 nm lamp was used in this study, with power 100w, lamp intensity: 30 mW/cm^2, made by Shenzhen Anhongda Optoelectronics Technology Co., Ltd.
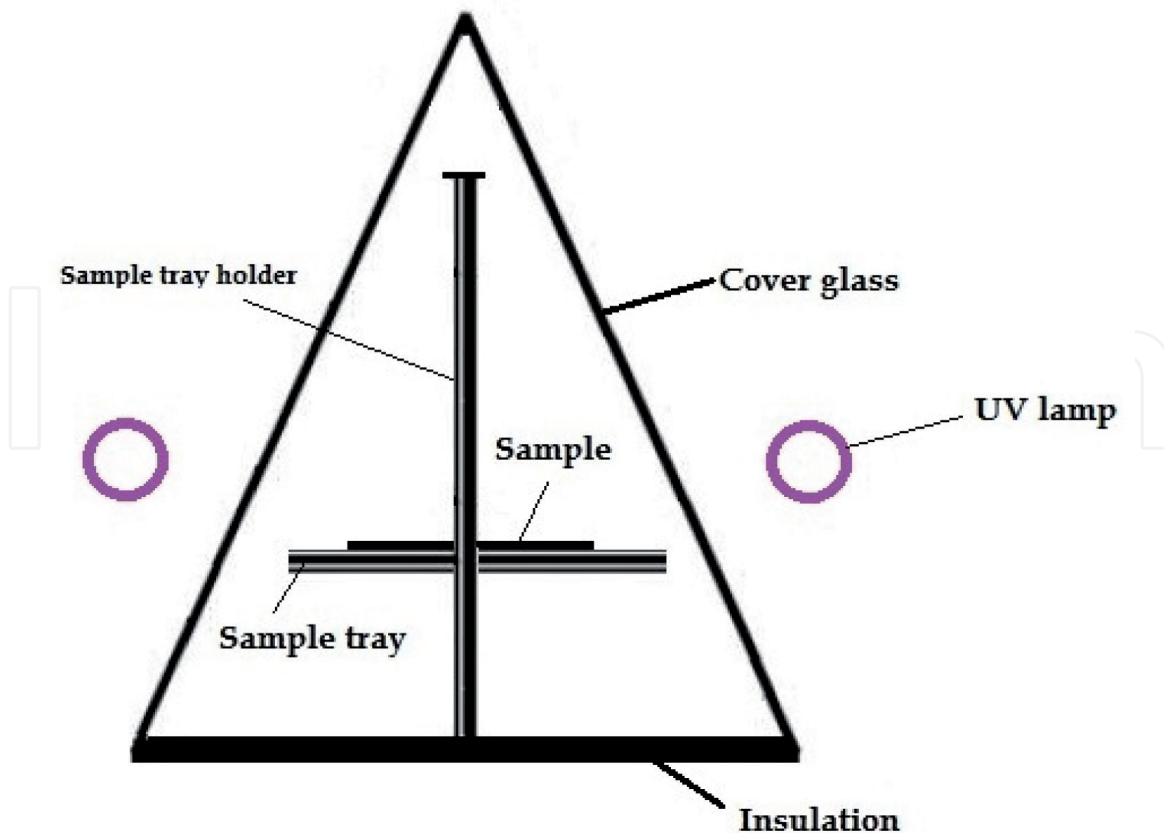

Figure 3.
Sectional view of the test bench.

Sample	Thickness (mm)	Photo
PP sheet	4	
PE sheet	4	
PS sheet	4	
EPS foam sheet	4	
Natural rubber sheet	4	
PP Granules	N/A	

Table 1.
Samples for aging test.

As pyramid skylight has relatively higher Standard Visible Transmittance (Tvis) average than the most of other skylight [54].

Based on this, we choose two identical pyramid skylight structures (single-glazed with clear glass) as the experimental platform to receive the light source as shown

in **Figure 2a** and **b**. Pyramid skylight was manufactured by Guangzhou Fineland Windows & Doors Co., Ltd.

A sample tray holder is placed in each pyramid skylight structure, and each sample tray is divided into multiple grids, which can separate different samples for simultaneous experiments, as shown in **Figure 3**.

3.3 Sample preparation

Cut PP, PE, PS, EPS, Natural rubber raw materials to prepare two sets of identical samples. Each sample size is 50 mm × 40 mm, the average thickness is 4 mm. PP granules 6 kg (**Table 1**).

4. Experimental results and discussion

For comparative testing, the samples will be performed simultaneously under two different conditions.

Natural aging experiment: A set of 5 sheet samples and 2 kg of PP granules were placed on the sample tray in one of the pyramid skylight structure. Under natural conditions, they were directly exposed to solar radiation. Because the pyramid skylight structure is closed, the impact of moisture on the material is not considered. The experiment time is 12 consecutive days.

Ultraviolet aging experiment: Place another set of 5 sheet samples and 2 kg of PP granules on a sample tray inside of another pyramidal skylight structure, and place them in a dark environment at a controlled constant temperature of 22°C. Four ultraviolet lamps were placed outside the four inclined triangle sides of the pyramid skylight structure. The position of the UV light source is higher than the sample tray and the distance between the sample and the ultraviolet lamp is 10 cm, as shown in the **Figure 3**. The sample was receiving 100% UV light for 12 consecutive days.

The rest 2 kg of PP granules are without any aging treatment.

4.1 Aging test results and discussion

The appearance changes of two groups of samples under different aging test conditions are shown in **Table 2**. In 12 days of natural aging, the color of PP sheet, EPS sheet, Natural rubber sheet and PP granules did not change. The PE sheet and PS sheet only turned yellow very slightly. It can be seen that the surface aging of the material is not obvious in the short-term irradiation of natural light. Normally, the aging test under natural conditions takes months up to years to see the obvious aging effect.

While under 12 consecutive days of UV light irradiation, PP granules very slightly turned yellow; PP sheet, EPS foam sheet turned light yellow; Natural rubber sheet turned yellow; PE sheet and PS sheet severely yellowed. Obviously, UV light has a significant influence on the aging of Natural rubber, PE and PS.

4.2 Pyrolysis test results and discussion

The pyrolysis experiments were conducted in a fully automatic 5 kW electromagnetic induction heating pyrolysis system, which was manufactured by Greenlina SA, Switzerland as shown in **Figure 4**. Under exactly the same experimental conditions without using any catalysts, three pyrolysis experiments were carried out on 2 kg PP granules without any aging treatment, 2 kg PP granules that had undergone natural aging and 2 kg PP granules that had been aging by

Polymer sample	Color before experiment	Color after natural aging	Color after UV aging
PP sheet	Milky	Milky	Light yellow
PE sheet	White	Very slight yellowing	Severe yellowing
PS sheet	Transparent	Very slight yellowing	Severe yellowing
EPS foam sheet	White	White	Light yellow
Natural rubber sheet	White	White	Yellow
PP granules	Milky	Milky	Very slight yellowing

Table 2.
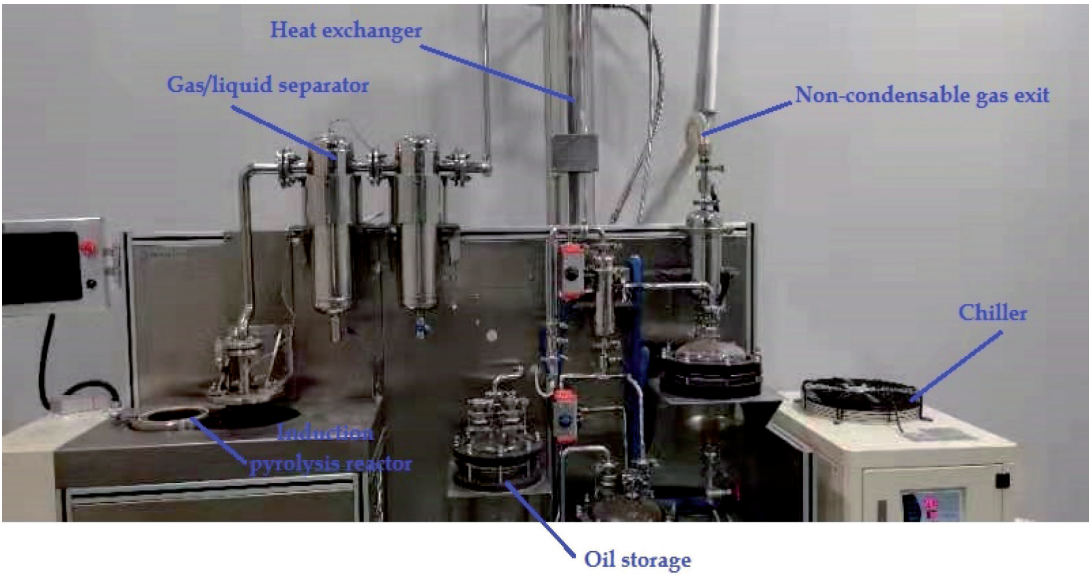*Experimental results of two different aging methods.*

Figure 4.
Fully automatic electromagnetic heat induction pyrolysis system.

ultraviolet light respectively. The ambient temperature in the experiment was 27±0.5°C. The setting temperature of the chiller used for condensation was 3°C, and the start-up time of the chiller was completely the same in the two tests. The set temperature of the heating jacket on the separation tank was 120°C, and the heating jacket started to heat at the beginning of the experiment for both tests.

It is not difficult to see from the **Table 3** that without the aid of catalyst, under the same experimental conditions, there is not much difference in oil yield between the two different treatments of PP granules and the granules without any aging treatment. However, the PP granules that have undergone UV accelerated aging began to produce pyrolysis oil after about 17 minutes, and it took about 60 minutes to complete the entire pyrolysis process. The naturally aged PP granules started to produce pyrolysis oil after about 24 minutes, and it took about 77 minutes to complete the entire pyrolysis process. While the PP granules without aging treatment started to produce pyrolysis oil after about 25 minutes, and it took about 78 minutes to complete the entire pyrolysis process. Considering of reasonable deviation, short-term natural aging samples hardly improve the oil generation time and the time required to complete the entire pyrolysis process comparing with the sample without aging. Nevertheless, we have noticed that the pyrolysis (from long chains to short chains) of PP plastic granules after UV accelerated aging becomes much easier and faster. In other words, less energy was consumed to complete the entire pyrolysis process.

Sample	Mass (kg)	Set Power (kW)	Set Temperature (°C)	Time to start oil production (min)	Complete pyrolysis time (min)	Oil production (g)
PP granules (without aging)	2	4	350	~25	~78	1632
PP granules (Natural aging)	2	4	350	~24	~77	1640
PP granules (UVaging)	2	4	350	~17	~60	1657

Table 3.
The comparison test of pyrolysis.

Figure 5.
The pyrolysis oil of PP plastic granules.

Component	Aromatic %	Non-aromatic %
C_5-C_9	6.48	18.4
C_{10}-C_{13}	2.35	7.10
>C_{13}	13.18	52.49

Table 4.
Component in liquid fraction obtained from pyrolysis of PP granules using GC–MS analysis.

The pyrolysis-oil (**Figure 5**) from PP granules was analyzed by GC–MS (as shown in **Table 4**). The identified compounds were categorized according to the length of their carbon chain: C5–C9, C10–C13 and C>13. Those molecules with a chain length of C5–C9 represents to light hydrocarbons (gasoline fuel), which generally contain hydrocarbons between C5 and C9, while C>13 correspond to the heavy oils.

It was observed that pyrolysis of PP granules mainly yielded non-aromatic hydrocarbons with carbon number C>13 around 52.49% and aromatic hydrocarbons with carbon number C>13 around 13%. For PP granules, the resulting oils are mostly aliphatic hydrocarbons (alkanes and alkenes) with carbon number more than C13, which makes it suitable for use in diesel engines.

Compounds	Ratio (%)
C_9H_{18}	15.35
$C_{23}H_{46}$	15.18
$C_{18}H_{36}$	8.84
$C_{15}H_{30}$	8.68
$C_{12}H_{24}$	4.12

Table 5.
The most abundant compounds present in oils from the pyrolysis of PP granules as detected by GC–MS analysis.

The most abundant compounds present in oils from the pyrolysis of PP granules are present in **Table 5**. Pyrolysis of PP granules produced an oil containing C_9H_{18} (15.35%), $C_{23}H_{46}$ (15.18%), $C_{18}H_{36}$ (8.84%), $C_{15}H_{30}$ (8.68%) and $C_{12}H_{24}$ (4.12%).

5. Conclusions

Through review, we found that the heterogeneous nature of MSW is not well suited to gasfication/pyrolysis technology due to high energy consumption and low energy efficiency. Pyrolysis is suitable for homogeneous material streams (e.g., Waste plastics/rubber after sorting; numerous studies have shown that the short-term accelerated aging of polymers under a specific wavelength of artificial ultra-violet light is equivalent to the results of long-term natural aging of polymers.

In this study, 12 days of natural aging has almost no effect on the appearance of the experimental samples. While the artificial accelerated aging by the aid of 340 nm ultraviolet light in 12 days has a significant effect on the appearance of the experimental samples.

In the comparative pyrolysis experiments of PP granules under the same experimental conditions, the pyrolysis results confirmed that the PP granules undergone UV accelerated aging were faster than the short-term natural aging PP granules in the time of oil producing and completing the entire pyrolysis. The time was reduced about 1/4, thereby reducing total energy consumption. The performance of the PP granules undergone short-term natural aging is consistent with the performance of the PP particles that have not undergone any aging treatment, which confirms the short-term natural aging does not help the energy consumption of thermal cracking.

Pyrolysis is a high energy-consuming treatment method. In addition to the use of catalysts to greatly reduce the cracking temperature, it is recommended to use ultraviolet light to artificially accelerate the aging of the raw materials at the same time when the raw materials are dried/dehydrated in the pretreatment stage.

This additional pretreatment step can speed up the thermal cracking reaction, reduce energy consumption and increase thermal efficiency which has been confirmed by lab-scale experiments. While in some remote or power-deficient areas, it is not realistic to implement UV light to artificially accelerate aging during the pretreatment of raw materials. Where conditions are available, for large-scale pyrolysis production, there are currently many unknown factors such as: how much additional investment is needed as an additional step of pretreatment; the optimal irradiation frequency and intensity of artificial UV light for universal/mixed polymers; the shortest and most effective aging time required for artificial aging; the overall energy consumption of artificially accelerated aging by UV light; the overall energy saving during the pyrolysis after this pretreatment; whether it is cost-effective if the

investment required for UV sped up aging compared with the benefits brought by energy-saving…all need to be further verified in the future study.

6. Outlook

SEM experiment of the sample after accelerated aging under ultraviolet light is need to carry out; at present, only the energy consumption comparison tests of PP plastic granules pyrolysis have been done due to time limitation. In the near future, more energy consumption comparison tests of different types of materials pyrolysis need to be carried out. Large scale experiments need to be carried out to estimate overall energy consumption and efficiency.

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Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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