

Co-Production of Liquid and Gaseous Fuels from Polyethylene and Polystyrene in a Continuous Sequential Pyrolysis and Catalytic Reforming System

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Abstract

This paper deals with the potential of using sequential pyrolysis and catalytic reforming process in a continuous system for the conversion of polyethylene and polystyrene into liquid and gaseous fuels using the HY-zeolite catalyst for the catalytic reforming of pyrolysis gas generated in a pyrolyzer. The effect of reforming temperature and the weight hourly space velocity on the product yields, liquid and gaseous compositions have been investigated for each feedstock. The experiments were carried out at the pyrolyzer temperature of 450 °C, the reforming temperature of 400, 450, and 500 °C and the weight hourly space velocity of 2, 3, and 4 g-sample g-catalyst⁻¹ h⁻¹. The results show that increasing the reforming temperature and decreasing the weight hourly space velocity have resulted in an increase of gaseous and solid products while the liquid product decreased. The maximum oil production for HDPE (70.0wt%) and PS (88.1wt%) were obtained at the pyrolysis temperature of 450 °C, the reforming temperature of 450 °C and the weight hourly space velocity of 4. The C₂, C₃ and C₄₊ gases (>75 mol %) were the main components of the gaseous and liquid products for HDPE. In case of PS, the C₂ and C₃ gases (>65 mol %) were the main components of the gaseous product. The high quality of gaseous products can be used as a fuel either for driving gas engines or for dual-fuel diesel engines.

Keywords: waste plastics, pyrolysis, catalytic reforming, fuels, zeolite

1. Introduction

Plastics are now becoming substantial materials in modern life and have wide range of applications. Plastic consumption has been growing rapidly in the last six decades due to their ability to be simply formed, its light weight together with non-corrosive behavior. The world's annual plastic consumption has increased about 20 times from 5 million tons in 1950s to nearly 100 million tons (United Nations Environment Programme [UNEP], 2009). A significant growth of the plastic consumption has resulted in an increased production of plastic wastes. Thus, plastic wastes have become a major stream in solid waste and caused significant environmental problems for nations worldwide. Disposing of plastic wastes by landfilling is not a suitable option due to slow degradation rates. The use of incineration technology has caused environmental problems since it generates several pollutants to the atmosphere. To minimize the environmental impact and to reduce damages caused by plastic wastes, they must be recycled and recovered. Therefore, alternative methods such as chemical or feedstock recycling which involves pyrolysis of plastics into fuel have been introduced not only for waste reduction but also for fuel production. This method has become very promising technology since plastics have a high calorific value of more than 40 MJ/kg which is similar to those of common liquid fuels such as gasoline, diesel, kerosene, etc.

Pyrolysis or thermal cracking involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500-800 °C (Aguado, Serrano, Miguel, Castro, & Madrid, 2007). These pyrolytic products can be divided into a gas fraction, a liquid fraction and solid residues (Buekens & Huang, 1998). Plastic wastes can be decomposed as a single feedstock or mixed with other materials such as coal and biomass (Ishaq et al., 2006). Co-pyrolysis of plastic and coal has indicated that there was

significant synergistic effect between plastic and coal, especially in the high temperature region (Zhou, Luo, & Huang, 2009). The thermal degradation of plastics may involve three different decomposition pathways (Aguado & Serrano, 1999) : (i) random scission at any point in the polymer backbone leading to the formation of smaller polymeric fragments as primary products, (ii) end-chain scission, where small molecules and long-chain polymeric fragments are formed, (iii) abstraction of functional substituents to form small molecules.

In many cases, several of these pathways occur simultaneously. However, the thermal degradation of plastics has a major drawback such as very broad product range and requirement of high temperature. These facts strongly limit their applicability and especially increase the cost of feedstock recycling for waste plastic treatment (Lin et al., 2010). Catalytic degradation therefore provides a means to address these problems. The use of catalyst is expected to reduce the reaction temperature, to promote decomposition reactions, and to improve the quality of the products.

Both homogeneous and heterogeneous catalysts have been used for studying the catalytic cracking of plastics by many researchers. In general, heterogeneous catalysts are the preferred choice due to their easy separation and recovery from the reacting medium (Aguado, Serrano, & Escola, 2006). A wide variety of heterogeneous catalysts have been tested by researchers such as zeolite, silica alumina, and FCC catalyst. Each catalyst has different structure and composition which affect the properties of the fuel products.

Catalytic degradation of plastic wastes has been investigated extensively by many researchers using zeolite-Y, ZSM-5, mordenite and silica alumina (Seo, Lee & Shin, 2003; Mikulec & Vrbova, 2008; Wang & Wang, 2011). The presence of catalysts promotes the chemical reaction resulting in the selectivity production of specific products with high added value. Direct catalytic cracking has been used widely due to several advantages, mostly in terms of the energy efficiency, the reaction temperature and the residence time. However, direct catalytic cracking of plastic waste suffers from a number of drawbacks which have prevented its commercial success. The first relates to difficulty to recover the catalyst after use, which increases the operational cost. Furthermore, direct contact with plastic wastes will make catalyst deactivate rapidly due to the deposition of carbonaceous matter and the poisoning effect of extraneous elements and impurities such as chlorine, sulfur and nitrogen containing species that may be present in the plastic wastes (Aguado et al., 2007). Therefore, separation of the catalytic reforming reaction from the pyrolysis stage can be applied to overcome these problems. This method has been firstly tested by Bagri and Williams (2002, 2004) for polyethylene and polystyrene using zeolite-Y and ZSM-5 catalysts. The use of other catalysts such as silica alumina and Al-MCM-41 have also been investigated by others (Wang & Wang, 2011; Miguel, Serrano, & Aguado, 2009). Preliminary assessment of plastic wastes valorization by using this method has been studied by Iribarren, Dufour & Serrano (2012). From a combined energy and environmental perspective, the results suggested the suitability of this system for plastic waste valorization. The energy performance of this system was deemed appropriate, based on the calculated cumulative energy demand and net energy ratio values.

The low thermal conductivity and high viscosity of plastics are the major problems for the cracking reactor design. Therefore, the reactor design becomes important parameter in feedstock recycling of plastics. Several reactor systems have been developed and used such as batch/semi batch, fixed bed, fluidized bed, spouted bed and screw kiln. Batch or semi-batch reactors have been used by many researchers because of its simple design and easy operation. However, it has a drawback in the stability of the process especially for large scale applications. Therefore, continuous flow operation is a suitable technique to study the degradation of plastics because the experimental data are obtained at steady state, that is, at a constant temperature, a constant pressure, and a constant amount of reactor content (Murata, Brebu, & Sakata, 2010).

In this paper, the sequential pyrolysis and catalytic reforming (SPCR) of polymer in a continuous system has been proposed to produce liquid and gaseous fuels over the HY-Zeolite catalyst. The fixed bed reactor was used as the pyrolysis reactor under the atmospheric pressure. Most of previous researches utilizing SPCR process have been done in a batch system. We introduced a continuous system utilizing SPCR process to produce liquid and gaseous fuels. Our proposed system will utilize all of products as fuels including liquid, gaseous and solid products. This novel system will utilize diesel fuel and gaseous products together for fueling a dual-fuel diesel engine to generate electricity. This power can be utilized for supplying the electricity to the plant itself and the excess power will be sent to outside of the plant. The solid products will also be investigated in terms of the energy content to assess the feasibility as a fuel for co-combustion with coal and biomass. The HY-Zeolite catalyst has been used by Bagri and Williams (2002, 2004). However, they studied only the effect of the reforming temperature. In this paper, we investigated not only the effect of the reforming temperature but also the effect of the catalyst loading on the liquid and gaseous products characteristics.

2. Materials and Methods

2.1 Materials

The feedstocks used for these experiments were high density polyethylene (HDPE) and polystyrene (PS) granules manufactured by Tosoh Co. in Japan. The catalyst employed in this study was commercial pelletized HY-Zeolite (CBV 780 CY) obtained from the Zeolyst International. The HY-Zeolite has $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 80, the unit cell size of 24.24 Å and the surface area of 780 m^2/g in the powder form. The diameter of the pellet was 1.6 mm which contains 20% of aluminum oxide.

2.2 Experimental Procedure

A schematic diagram of the experimental apparatus is shown in Figure 1. The apparatus was composed of a feeder, a pyrolyzer, a packed-bed catalytic reformer, a condenser, an oil collector and gas scrubbing bottles. The pyrolyzer and the reformer were made of stainless steel (SUS316) and covered with electric heaters. The pyrolyzer's inner diameter and height are 30 mm and 280 mm, respectively. The reformer's inner diameter and height are 45 mm and 550 mm, respectively. The reaction temperatures in both the pyrolyzer and the reformer were controlled with K-type thermocouples and heaters. A double-tube condenser was installed at the outlet of the reformer to separate gas and liquid products. The gas scrubbing bottles were installed after the condenser and isopropanol was used as the scrubbing absorbent to remove some light tar in the gaseous products.

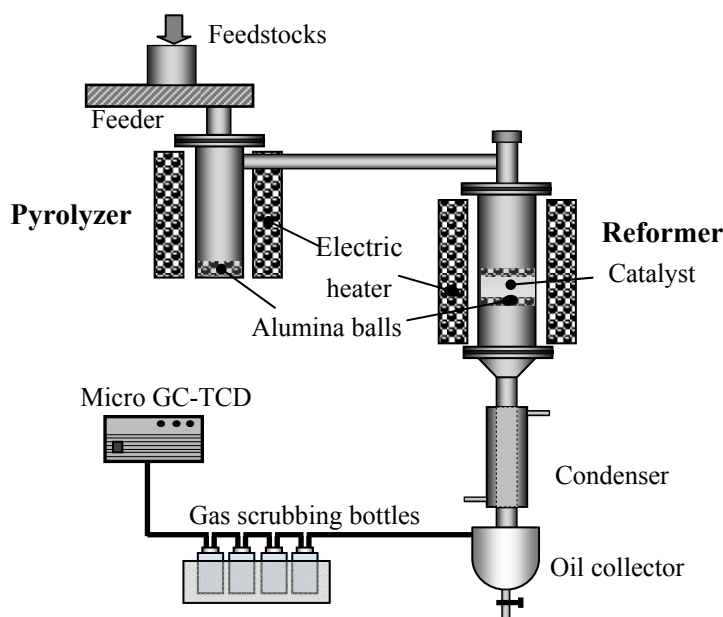


Figure 1. A schematic diagram of the experimental apparatus

In these experiments, after the pyrolyzer and the reformer heated up to the preset temperatures and air in the reactors was replaced with N_2 carrier gas, plastic granules were fed into the pyrolyzer at the feeding rate of 1 g min^{-1} . The feeding time of each experiment was 2 hours. The N_2 carrier gas flow rate was 1 L min^{-1} controlled by using a mass flow controller (Model CR-300, KOJIMA Instruments Inc. Kyoto, Japan). The catalyst was loaded into the reformer with the weight hourly space velocity (WHSV) range of 2, 3 and $4 \text{ g-sample g-catalyst}^{-1} \text{ h}^{-1}$. The calculation of WHSV is based on the equation below (Park et al., 2010):

$$WHSV = \frac{60 \times G}{W_{cat}} \quad (1)$$

where $G = \text{sample feed rate, g min}^{-1}$; and $W_{cat} = \text{weight of catalyst filled in the reformer, g}$.

The first experiments were carried out at the pyrolyzer temperature of $450 \text{ }^\circ\text{C}$, WHSV of $4 \text{ g-sample g-catalyst}^{-1} \text{ h}^{-1}$ and the reformer temperature of 400, 450, and $500 \text{ }^\circ\text{C}$. The second experiments were conducted at the pyrolyzer temperature of $450 \text{ }^\circ\text{C}$, the reformer temperature of $450 \text{ }^\circ\text{C}$ and WHSV of 2, 3, and 4 g-sample

g-catalyst⁻¹ h⁻¹. The gaseous and liquid products generated in the reformer were separated in the condenser and the liquid product was collected into the oil collector. The gas compositions were measured with a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Agilent Technologies Inc. USA).

2.3 Analytical Methods

The liquid product were analyzed by a gas chromatograph coupled with a mass spectrometer (GC-MS) (Agilent 6890N GC-MSD 5973N). The purpose of this analysis is to determine carbon atom number distribution and hydrocarbon type of the liquid products. The column was an HP5 (5% Ph-Me-Siloxane) capillary column, 30 m length with 0.25 mm diameter and 0.25 μm film thickness. Helium was used as the carrier gas. The temperature program used was, initial temperature of 30 °C for 5 minutes followed by a heating rate of 2 °C /min to 200 °C and then held at 200 °C for 5 minutes followed by a heating rate of 5 °C min⁻¹ to 300 °C and held at 300 °C for 10 minutes.

The composition of gases produced in the experiments was monitored by the GC-TCD every 6 minutes. Gas yields were calculated from Equation. (2)-(4) as follows (Park et al., 2010) :

$$F_{T, out} = F_{N_2, in} \times \frac{C_{N_2, in}}{C_{N_2, out}} \quad (2)$$

$$F_{i, out} = F_{T, out} \times C_{i, out} \quad (3)$$

$$Y_i = \frac{F_{i, out}}{G} \times \frac{1}{22.4} \quad (4)$$

where $C_{i, out}$ = gas i concentration in the outlet gas; $C_{N_2, in}$ = N₂ concentration in the carrier gas; $C_{N_2, out}$ = N₂ concentration in the outlet gas; $F_{i, out}$ = gas flow rate of i at the outlet, NI min⁻¹; $F_{N_2, in}$ = carrier gas flow rate (at the inlet), NI min⁻¹; and $F_{T, out}$ = total gas flow rate at the outlet, NI min⁻¹.

After finishing the experiments, a small amount of solid residue was remained in the reactor. The coke formation also occurred in the catalyst. Different weight of the catalyst before and after the experiment was defined as coke. The weight of solid residue was calculated by the difference between the total feedstock weight and liquid, gaseous and coke weights.

The proximate and ultimate analysis were conducted for solid residue samples. The higher heating value (HHV) has been calculated using a modified Dulong's formula as a function of the carbon, hydrogen, oxygen and nitrogen contents as follows (Demirbas, 2010) :

$$\text{HHV (MJ/kg)} = 0.335 \text{ C} + 1.423 \text{ H} - 0.154 \text{ O} - 0.145 \text{ N} \quad (5)$$

where C is carbon content (wt.%), H is hydrogen content (wt.%), O is oxygen content (wt.%), and N is nitrogen content (wt.%).

3. Results and Discussions

The results obtained from the experimental investigation on the pyrolysis and catalytic reforming of HDPE and PS are presented and discussed in this section. The results focused on the effect of the reforming temperature and WHSV on the product yields, oil characteristics and gas composition for each feedstock.

3.1 Pyrolysis and Catalytic Reforming of HDPE

3.1.1 Effect of the Reforming Temperature

The effect of the reforming temperature on the product yields from the pyrolysis and catalytic reforming of HDPE is shown in Figure 2. It can be seen that the increase of the reforming temperature increased the yield of gaseous and coke products, whereas the yield of liquid products was decreased. The higher temperature led to the enhancement of the activity of the HY-zeolite catalyst and then cracked some relatively large-molecular liquid products into small molecular gaseous products. The increase of the coke was mainly originated from the following reasons; on the one hand, the coking reaction was easier to occur on the surface of the HY-zeolite at a higher reforming temperature (Neves, Botelho, Machado, & Rebelo, 2006). On the other hand, the HY-zeolite catalyst has a relatively large pore size and a large supercage with its crystallite, resulting in the formation and accumulation of coke on the internal and external surfaces of the HY-zeolite catalyst. The coke formation may not only prohibit heat transfer and cause operating problems in the reactor, but also lower the number of active

sites and the surface area of the catalyst and then lead to the increase of the operation cost (Al-Khattaf, 2002; Neves, Botelho, Machado, & Rebelo, 2007). Therefore, from the viewpoint of industrial application, it is a great importance to optimize the reaction conditions and clarify the deactivation behaviors of the catalyst.

Furthermore, the solid wax was produced in the condenser at the reforming temperature of 400 °C, which means that, at this temperature, the activity of the catalyst was not high enough and could not convert all of the pyrolysis gas into gaseous and liquid products. On the contrary, no wax formation was observed at the reforming temperature of 450 and 500 °C. In addition, the increase of the reforming temperature from 450 to 500 °C resulted in the increase of gaseous products and the decrease of liquid products.

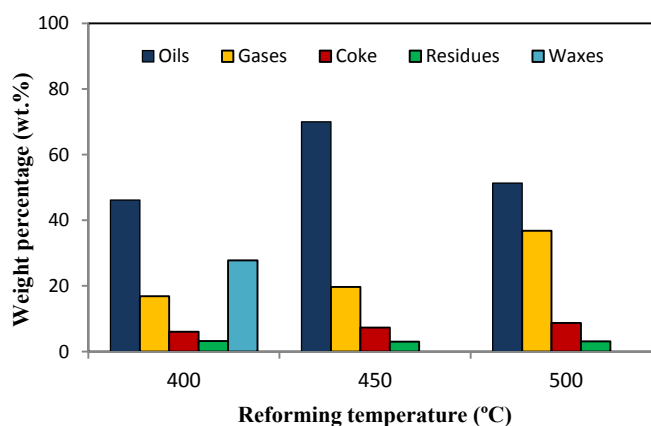


Figure 2. Effect of the reforming temperature on the product yields of HDPE at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

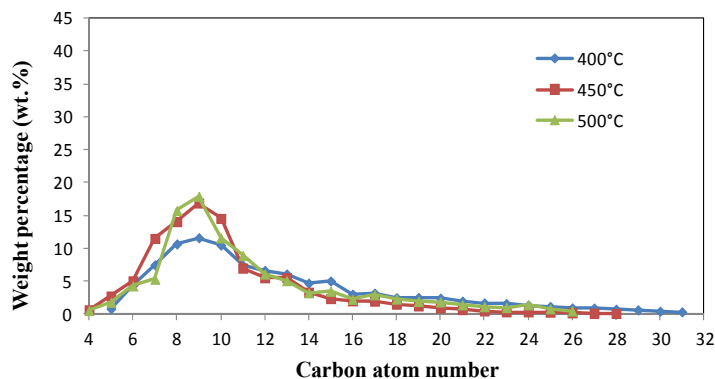


Figure 3. Effect of the reforming temperature on the carbon atom number distribution of liquid products of HDPE at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

The liquid hydrocarbon products generated from the SPCR process were characterized by their carbon atom number distribution and hydrocarbon types which will determine their potential application as a refinery feedstock and fuel. Figure 3 represents the carbon atom number distribution of the liquid products of HDPE produced by the SPCR process at the pyrolysis temperature of 450 °C, WHSV of 4 g-sample g-catalyst⁻¹h⁻¹ and at different reforming temperatures from 400 °C to 500 °C. It was notable that the gasoline like components (C₅-C₁₂) and kerosene like components (C₈-C₁₆) were the major components of liquid products. It was due to the relatively moderate acidity and a large pore size of the HY-zeolite catalyst as mentioned previously as well as the type and structure of polyethylene. In addition, the increase of the reforming temperature from 400 °C to 450 °C led to a marked increase in the proportion of light oil (C₅-C₁₂), as well as an obvious reduction in the amount of heavy oil hydrocarbons (>C₂₀), which was attributed to the fact that the higher reforming temperature enhanced the activity of the HY-zeolite catalyst and then led to intense catalytic cracking of the pyrolysis gas into smaller hydrocarbons (Aguado et al., 2007). However, when the reforming temperature increased from 450 °C to 500 °C, the change of the carbon atom number distribution of the liquid products was not significant. It could be the

consequence of the coking on the catalyst surfaces at a higher temperature. The formation of coke influenced catalyst activity by covering some of the active sites and blocking the channels which could make the inner active sites inaccessible for the reactant molecules (Miskolczi, Bartha, Deak, Jover, & Kallo, 2004 ; Uemichi, Hattori, Itoh, Nakamura, & Sugioka, 1998).

The effect of the reforming temperature on the distribution of the hydrocarbon types of liquid products from HDPE pyrolysis can be seen in Figure 4. It is well known that the thermal degradation of HDPE has been assigned to the random scission reaction which led to the formation of a large number of n-paraffin hydrocarbon species. The C-C bond is the weakest in the HDPE structure and during the degradation process, the stabilization of the resultant radicals after the chain scission leads to the formation of carbon double bonds in the structure in addition to n-paraffin (Williams & Slanery, 2007). Consequently, the major compositions of the liquid products of HDPE thermal degradation were n-paraffin and olefins. However, in the SPCR process, because of the reforming reaction process, it was found that there was a large number of iso-paraffin, naphthene and aromatic existed in the liquid products of HDPE. The reason for this could be that most zeolites including the HY-zeolite show an excellent catalytic effect on the cracking, isomerization and aromatization due to an acidic property and a micropore crystalline structure. The formation of aromatic compounds was related to both Brönsted and the Lewis sites on the catalysts, but reaction is probably more favorable on the Brönsted sites (Seo et al., 2003). In addition, during the aromatization reaction, a considerable number of hydrogen atoms are abstracted which subsequently accumulate on the catalyst surface, and then consumed in the hydrogenation of olefins. Moreover, the HY-zeolite adsorbed polar molecules strongly, which may also lead to a possible explanation for the increase of iso-paraffins at the expense of olefins (Marcilla, Beltran & Navarro, 2009 ; Manos & Garforth, 2000). Therefore, a lot of aromatics and iso-paraffins at the expense of the n-paraffins and olefins existed in the final liquid products.

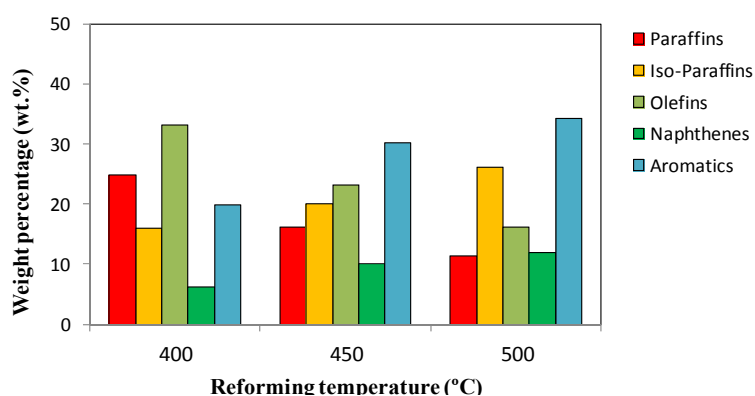


Figure 4. Effect of the reforming temperature on PIONA distribution of HDPE liquid products at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

Furthermore, Figure 4 also indicated that by the increase of the reforming temperature, the proportion of aromatics, iso-paraffins and naphthenes increased while the percentage of paraffins and olefins decreased. The reason is that, as mentioned above, the high temperature will increase the activity of the catalyst and lead to intense catalytic reforming. The reactions such as saturation, isomerization, cyclization, hydrogen transfer and the coking were at high severity (Murata, Brebu, & Sakata, 2009).

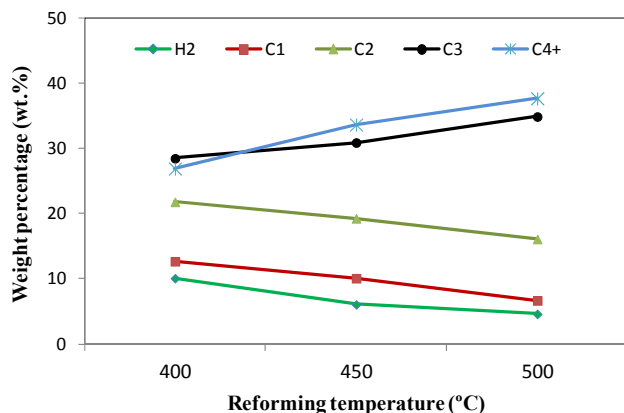


Figure 5. Effect of the reforming temperature on the gaseous product composition of HDPE at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

The gaseous product compositions of HDPE pyrolysis as a function of the reforming temperature is shown in Figure 5. The reforming temperature significantly affected the gaseous composition of the products. It was illustrated from Figure 5 that with the increase of the reforming temperature, there were significant changes of the gaseous compositions of the products. As the reforming temperature increase, the mol percentage of H₂, C₁ and C₂ gases were decreased whereas C₃ and C₄₊ hydrocarbons were increased. The increase of C₃ and C₄₊ hydrocarbons were resulted from the conversion of liquid products into gaseous products. In addition, more than 80 mol% of the final gaseous products was C₂, C₃, C₄₊ hydrocarbons; which originated from the relatively moderate acidity and large pore size of the HY-zeolite catalyst (Miskolczi et al., 2004 ; Audisio & Bertini, 1990 ; Chumbhale et al., 2005). In large scale application, the high quality of gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolysis reactor.

3.1.2 Effect of WHSV

In a continuous flow reactor, another parameter affecting the products distribution is the weight hourly space velocity (WHSV). Therefore, the effect of WHSV on the products yields, as well as the composition and physicochemical properties of gaseous and liquid products of HDPE was evaluated in this section at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C, respectively. It can be seen from Figure 6 that when both the pyrolysis temperature and the reforming temperature were fixed at 450 °C, with the increase of WHSV, the fraction of gaseous products decreased whereas the liquid products increased. This is due to the fact that increasing WHSV is equal to reducing the amount of catalysts and shortening the contact time. In addition, it was found that the effect of increasing the amount of catalyst (decreasing the WHSV) on the product yields have the similar trend with that of increasing the reforming temperature.

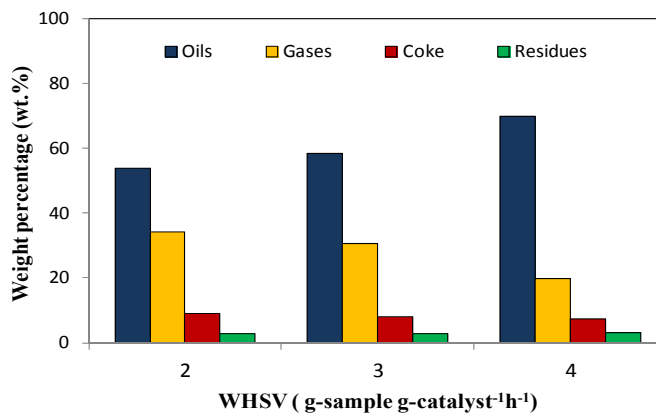


Figure 6. Effect of WHSV on the product yields of HDPE at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

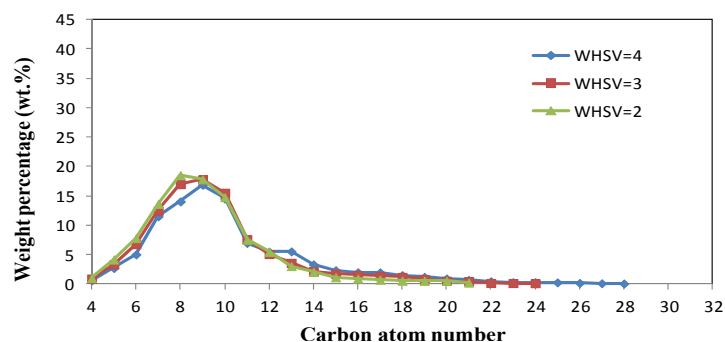


Figure 7. Effect of WHSV on the carbon atom number distribution of liquid products of HDPE at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

The effect of WHSV on the carbon atom number distribution of HDPE liquid products was investigated at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C. Figure 7 indicates that the decrease of WHSV (increase of the catalyst loading) resulted in the increase of the amount of light oil. Therefore, it was found that the effect of decreasing WHSV on the product yields of HDPE has similar trend with that of increasing the reforming temperature. As mentioned above, these results were due to the increase of the catalyst loading and the contact time, which could enhance the cracking reaction of the pyrolysis gas from relatively large-molecule hydrocarbons into small-molecule hydrocarbons. It was also observed from Figure 7 that the increase of WHSV increased the amount of heavy oil. However, light oil (C_5 - C_{15}) consisted of gasoline and kerosene fractions was the major component of liquid products, which is caused by the relatively moderate acidity and large pore size of the HY-zeolite (Luo, Suto, Yasu, & Kato, 2000).

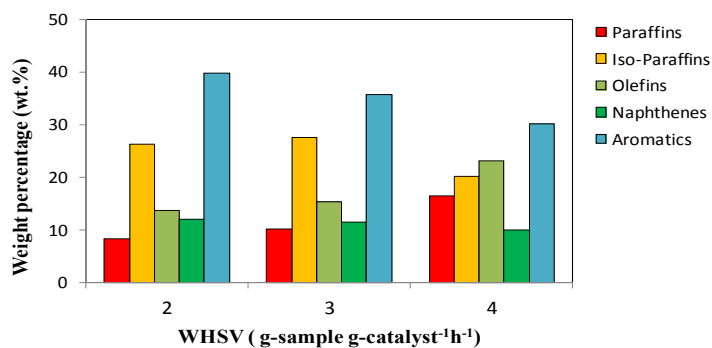


Figure 8. Effect of WHSV on PIONA distribution of HDPE liquid products at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

Figure 8 shows the effect of WHSV on the hydrocarbon type distribution of HDPE liquid products. The olefins, iso-paraffins and aromatics were the main type of liquid products. As discussed previously, on the one hand, the HY-zeolite catalyst could provide a large amount of acidic sites. On the other hand, because of its special pore size, the HY-zeolite catalyst has favorable shape selectivity for aromatic formation than non-zeolite catalyst, some intermediate carbenium ion formed by acidic zeolite would choose a pathway to aromatic formation, and some will be left over as olefin. Moreover, Figure 8 also indicates that when both the pyrolysis temperature and the reforming temperature were fixed at 450 °C, the decrease of WHSV led to the increase of the percentage of iso-paraffins, naphthene and aromatic at the expense of olefins and paraffins. This is due to the fact that a lower WHSV means larger amount of catalyst and longer contact time, which could promote the overcracking and secondary reaction such as aromatization, isomerization, etc. It can also be seen from Figure 8 that the increase of the reforming temperature and the decrease of WHSV have the similar trend on the hydrocarbon type distribution of HDPE liquid products (Luo et al., 2000).

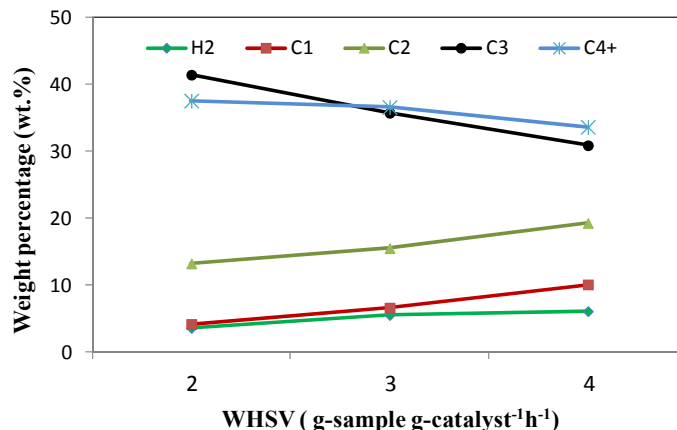


Figure 9. Effect of WHSV on the gaseous product compositions of HDPE at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

The effect of WHSV on the composition of gaseous products from HDPE pyrolysis was also investigated at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C. It is well known that the pore size is important for determining the size selectivity of reactants and products, which can enter and leave the active sites of the catalyst (Uemichi et al., 1998). When compared with other zeolite catalyst, such as HZSM-5, the HY-zeolite catalyst has a relatively large pore size, which may allow a little larger molecular gaseous products to leave the HY-zeolite catalyst. The results shown in Figure 9 illustrates that with the decrease of WHSV, the proportion of H₂, C₁ and C₂ gases decreased while the percentage of C₃ and C₄₊ gases increased, which proves the fact that the HY-zeolite catalyst has special selectivity for C₃ and C₄₊ gases. Therefore, the major gaseous products of the catalytic reforming of pyrolysis gas were C₃ and C₄₊ gases. When increasing the catalyst loading (lowering WHSV), the fraction of gaseous product increased and then the percentage of C₃ and C₄₊ gases increased at the expense of the H₂, C₁ and C₂ gases.

3.2 Pyrolysis and Catalytic Reforming of PS

3.2.1 Effect of the Reforming Temperature

Figure 10 shows the effect of the reforming temperature on the product yields from the pyrolysis and catalytic reforming of PS. It can be seen that PS produced higher liquid products and lower gaseous products compared with HDPE. The quantity of gaseous products was very few to serve as a fuel gas either for engine or for the SPCR process. It was related to the marked differences of molecular structure of HDPE and PS. Therefore, the degradation mechanism and thermal degradation products in the first thermal pyrolysis step are significantly different. The thermal degradation of HDPE consists of free radical formation and hydrogen abstraction steps whereas the thermal degradation of PS is a radical chain process including initiation, transfer and termination steps (Kiran, Ekinici, & Snape, 2000). The main composition of pyrolysis gas of HDPE flowing out from the pyrolyzer was wax while the major pyrolysis products of PS were stable aromatic components as liquid phase such as styrene, which have stable benzene ring structure and difficult to be converted into small molecular gaseous products (Pinto, Costa, Gulyurtlu, & Cabrita, 1999; Liu & Qian, 2000). However, these aromatic hydrocarbons were readily converted into coke existing on the internal and external surface of catalyst to make the catalyst deactivate.

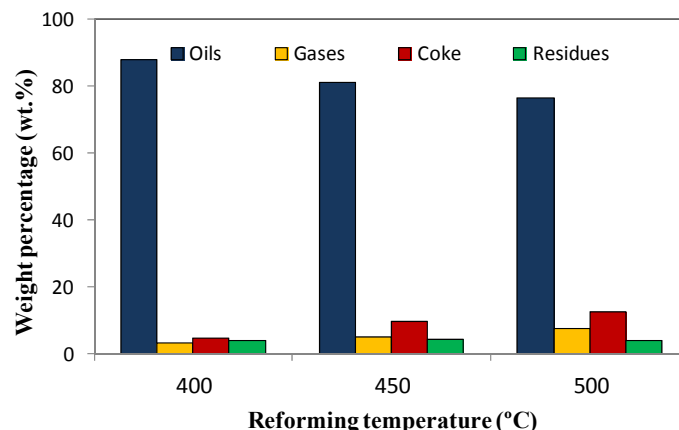


Figure 10. Effect of the reforming temperature on the product yields of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

The effect of the reforming temperature on the carbon atom number distribution from the pyrolysis and catalytic reforming of PS is shown in Figure 11. It indicates that when the pyrolysis temperature and WHSV were fixed at 450 °C and 4 g-sample g-catalyst⁻¹h⁻¹, respectively, the increase of the reforming temperature significantly affected the carbon atom number distribution of the liquid products of PS derived from the SPCR process. In addition, the C₆-C₈ and C₁₄-C₁₆ were the main compositions (80wt%) of liquid products derived from PS decomposition, which means the liquid products composition of PS was simpler than that of HDPE. Furthermore, as the increase of the reforming temperature from 400 °C to 450 °C, the proportion of C₆ (benzene) and C₇ (toluene) increased while the proportion of C₈ (styrene monomer and ethylbenzene) and C₁₄-C₁₆ (styrene dimer and polycyclic aromatic hydrocarbon) decreased. This is due to that a higher temperature would enhance the activity of the HY-zeolite and then improve the oligomerization and the hydrogen transfer reaction, which gave increase of the formation of monoaromatic hydrocarbon with a smaller molecular weight (Zhang et al., 1995; Onwudili, Insura, & Williams, 2009). However, when the reforming temperature increased from 450 °C to 500 °C, the changes of the carbon atom number distribution of the liquid products of PS was not significant because of the coking formation on the catalyst surfaces at a higher temperature. As mentioned previously, aromatic species have a greater predisposition to be involved in pathways to coke formation because of their ability to easily involve themselves in hydrogen transfer and cyclisation reactions. The analysis of pyrolysis oils derived from polystyrene have been shown to be very high in aromatic compounds and the composition is dominated by the presence of styrene (Williams & Bagri, 2004), consequently, leading to high char formation on the external and/or internal acid sites and then resulted in marked catalyst deactivations, compared with that of HDPE. Therefore, at the reforming temperature of 500 °C, the catalytic performance of the HY-zeolite is not as efficient as the reforming temperature of 450 °C.

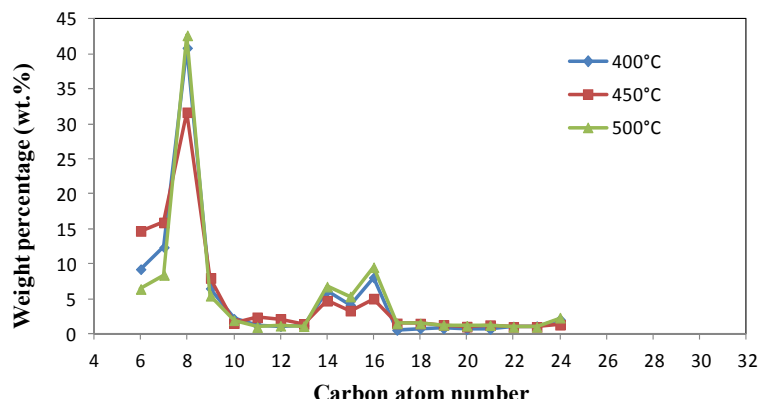


Figure 11. Effect of the reforming temperature on the carbon atom number distribution of liquid products of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

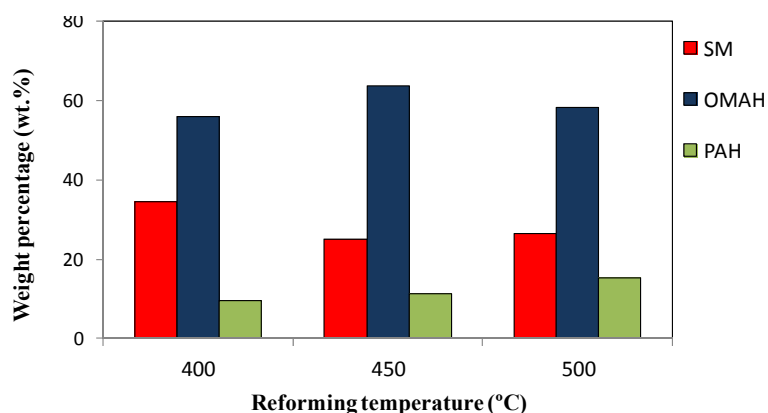


Figure 12. Effect of the reforming temperature on SM, OMAH and PAH distribution of PS liquid products at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹ (SM: styrene monomer; OMAH: the other monocyclic aromatic hydrocarbon except styrene monomer; PAH: polycyclic aromatic hydrocarbon)

Figure 12 shows the effect of the reforming temperature on the hydrocarbon type distribution of liquid products from PS pyrolysis. It can be seen that when the pyrolysis temperature and WHSV were fixed at 450 °C and 4 g-sample g-catalyst⁻¹h⁻¹, respectively, with the increase of the reforming temperature, the distribution of styrene monomer (SM), the other monocyclic aromatic hydrocarbon (MAH) and polycyclic aromatic hydrocarbon (PAH) had an obvious change, which means that the effect of the reforming temperature on the liquid products of PS was significant.

In contrast to HDPE, PS can be thermally depolymerized at a relatively low temperature. The thermal degradation of PS is a radical chain process including initiation, transfer and termination steps in the open reaction system, which led to obtain the styrene monomer with high selectivity. Styrene has a wide range of application in the chemical industry, e.g., in the manufacturing of plastics, synthetic rubber, resins, and insulators. Williams and Williams (1999) have reported that uncatalyzed pyrolysis of polystyrene has been shown to produce 83wt% conversion to a low viscosity oil which consisted mainly of styrene and a gas yield and char yield of less than 5wt% each.

Figure 12 also indicates that there were a large number of ethylbenzene, benzene, toluene, m-xylene, methyl styrene, indan, ethyl methylbenzene and methylbenzene (monocyclic aromatic hydrocarbon), as well as naphthalene, 2-methylnaphthalene, dimethylnaphthalene, phenanthrene, methylnaphthalene and pyrene (polycyclic aromatic hydrocarbon) existed in liquid products of PS. This is mainly due to the presence of relatively moderate acid sites of the HY-zeolites which have the potential to reduce the activation energy of the C-C bond and to hydrogenate the pyrolysis gas into all kinds of aromatic hydrocarbons. As can be seen in Figure 12, considerable amounts of monocyclic aromatic hydrocarbons, such as benzene and ethylbenzene, were formed by the catalytic reforming process. These products are attributed to the further cracking and hydrogenation of styrene yielded from the pyrolyzer, which resulted in a decrease of the fraction of styrene in the final oil products. Styrene monomer and polycyclic aromatic hydrocarbons were still main components in the final liquid products of PS, and they might be formed by β -scission of the C-C bond in the polystyrene main chain. Moreover, the increase of the amount of PAH could be related to an increase of intramolecular hydrocarbon transfer at a higher reforming temperature (Zhang et al., 1995).

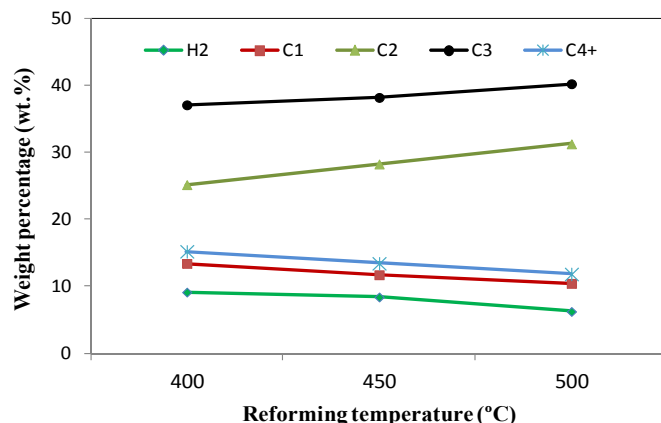


Figure 13. The effect of the reforming temperature on the gaseous product composition of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst⁻¹h⁻¹

The gaseous product composition of PS pyrolysis as a function of the reforming temperature is shown in Figure 13. It can be seen that C₂ and C₃ gases (>65 mol %) were the main components of gaseous products, which originated from the relatively moderate acidity and large pore size of the HY-zeolite catalyst (Miskolczi et al., 2004). As the reforming temperature increase, the mol percentage of H₂, C₁ and C₄₊ gases were decreased whereas C₂, C₃ and hydrocarbons were increased.

3.2.2 Effect of WHSV

Figure 14 illustrates the effect of WHSV on the product yields of PS pyrolysis in SPCR process. It can be seen that the fraction of liquid products of PS was higher than that of HDPE while the proportion of gaseous products of PS was much lower than that of gaseous products of HDPE, which means that although increasing the amount of catalysts is equal to increasing the contact time and then improved the overcracking reactions of pyrolysates produced from the pyrolyzer, it was still difficult to reduce the activation energy to break the stable benzene ring structure of the aromatic hydrocarbons of the pyrolysis gas into smaller molecular gaseous products (Murata et al., 2009). Furthermore, when compared with that of HDPE, the higher concentration of aromatic hydrocarbons in the pyrolysis gas of PS also led to more formation of coke on the internal and external surfaces of the HY-zeolite, which led to the increase of the proportion of the solid products. It was mainly due to the fact that, as mentioned previously, the aromatic hydrocarbons especially unsaturated and polyaromatic compounds such as styrene monomer and indan and naphthalene derivatives were formed as major products in the degradation of polystyrene and then they were readily converted into coke (Uemichi et al., 1998).

The carbon atom number distribution of PS as a function of WHSV is illustrated in Figure 15. The carbon atom number distribution of PS was dominated by C₆-C₈ with the weight fraction of more than 70%. This fraction was mainly composed of benzene, methylbenzene, ethylbenzene and styrene, which are valuable chemical feedstock and fuel used in our daily life and modern industry. In addition, there are also certain amount of C₁₄-C₁₆ aromatic hydrocarbons existed in the PS oil, which were mainly consisted of some potentially harmful polycyclic aromatic hydrocarbons (Lee, Yoon, & Park, 2002). Therefore, if the oil derived from PS would be used as combustion fuel oil, it should remove these harmful polycyclic aromatic hydrocarbons in advance. Consequently, it is preferable to recycle the PS oil as chemical crude materials rather than as fuel oil, compared with that of HDPE (Joo & Guin, 1997).

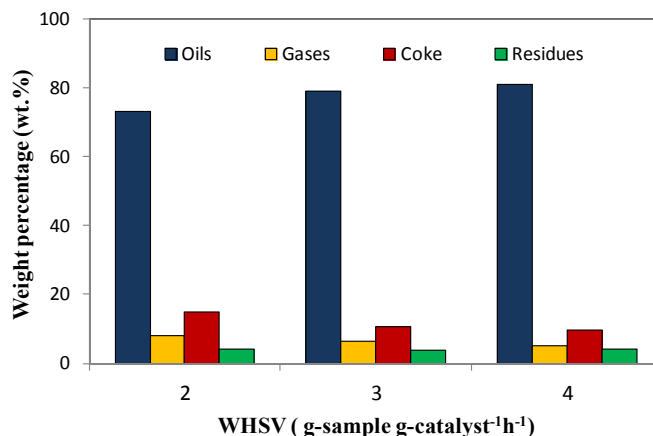


Figure 14. Effect of WHSV on the product phase distribution of PS at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

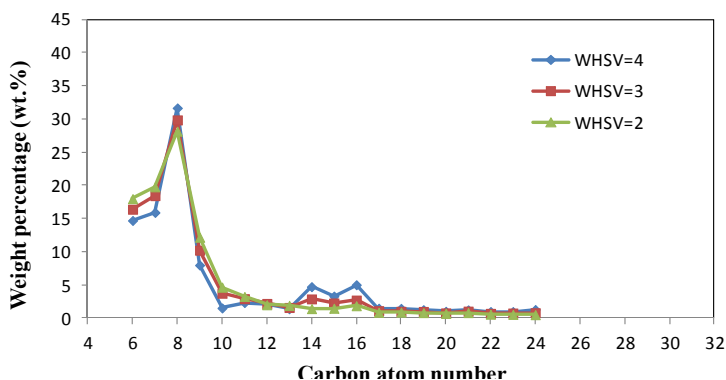


Figure 15. Effect of WHSV on the carbon atom number distribution of liquid products of PS at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

Figure 16 shows the effect of WHSV on the hydrocarbon types of PS liquid products at both the pyrolysis temperature and the reforming temperature of 450 °C. It can be observed that monocyclic aromatic hydrocarbons including the styrene monomer were the major component of liquid products of PS. As discussed above, the possible reason was that the presence of the HY-zeolite would improve the hydrogenation reaction, the oligomerization reaction and the β -scission reaction, which would convert the styrene monomer produced from the fast pyrolysis of PS in the pyrolyzer into benzene, methylbenzene and ethylbenzene (monocyclic aromatic hydrocarbon), as well as naphthalene, 2-methylnaphthalene, phenanthrene (polycyclic aromatic hydrocarbon), etc. In addition, the increase of the catalyst loading (decreasing WHSV) enhanced above conversion trend and then led to the increase of polycyclic aromatic hydrocarbon and other monocyclic aromatic hydrocarbon at the expense of styrene monomer. The derived PS oil could be mixed with other kinds of derived oil to improve their RON number, because of the high concentration of aromatic hydrocarbon of PS liquid products (Serrano, Aguado, & Escola, 2000).

The effect of WHSV on the composition of PS gaseous products was also investigated at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C. As mentioned above, decreasing WHSV was nearly equal to increasing the amount of catalysts and increasing the contact time, which improved the overcracking of liquid products into more small molecular gaseous products. The results shown in Figure 17 illustrates that by the decrease of WHSV, the proportion of C₂ and C₃ of PS increased, which means that the HY-zeolite catalyst had special selectivity of C₂ and C₃ gases for PS. This result was consistent with some previously published reports. For instance, Puente and Sedran (1998) also reported a marked increase in C₂ and C₃ gases for the catalyzed pyrolysis of polystyrene compared to the thermal pyrolysis. Williams and Bagri (2004) also reported that C₂ and C₃ gases were the major composition of the gaseous products when employing the HY-zeolite as the catalyst to recycle the polystyrene into valuable fuel and chemical feedstock in a batch system.

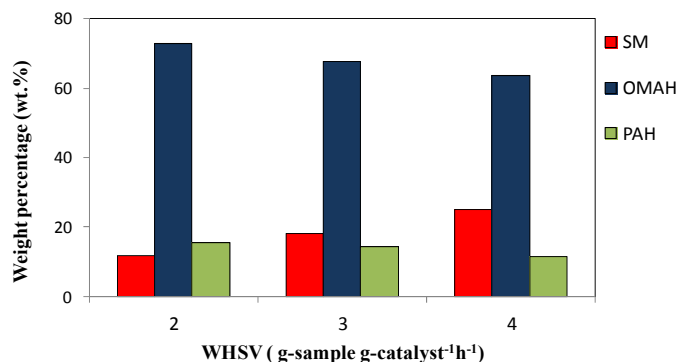


Figure 16. Effect of WHSV on SM, OMAH and PAH distribution of PS liquid products at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

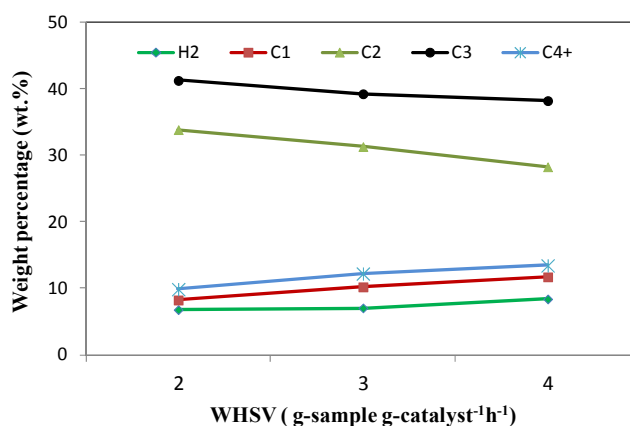


Figure 17. Effect of WHSV on the gaseous product compositions of PS at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

3.3 Solid Residues

The proximate analysis and ultimate analysis of the solid residues produced from the pyrolysis of HDPE and PS are shown in Table 1. It can be seen that the solid residue from HDPE has a higher ash content than that of PS. This might be due to the different additives which normally used in plastics materials. The moisture content of HDPE solid residue was also higher than that of PS solid residue. The higher content of ash in HDPE solid residue will absorb more moisture constituent from the atmosphere. The results also show that the solid residues produced from plastics pyrolysis have higher heating value than those of biomass. The higher heating value (HHV) of PS solid residue was higher than that of HDPE residue due to less content of ash in PS solid residue. Therefore, they can be used as a fuel either for blending with biomass and coal or for single fuel.

Table 1. Proximate and ultimate analysis of solid residues (wt.%)

Solid residues	Proximate analysis			Ultimate analysis						HHV** (MJ/kg)
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	O*	
HDPE	3.09	19.14	57.99	19.78	65.88	2.01	1.50	0	10.83	23.04
PS	0.91	37.44	57.28	4.37	91.14	4.09	0.09	0	0.31	36.29

* calculated by difference.

** calculated using a modified Dulong's formula.

4. Conclusion

A sequential pyrolysis and catalytic reforming process in a continuous system has been successfully tested for the conversion of HDPE and PS into liquid and gaseous fuels using the HY-zeolite catalyst for the catalytic reforming of pyrolysis gas generated in a pyrolyzer. The effect of the reforming temperature and WHSV on the product yields, the liquid characteristics and the gaseous composition have been investigated for both HDPE and PS samples. There were significant influences of the reforming temperature and WHSV on the products yields for both HDPE and PS. Increasing the reforming temperature and decreasing WHSV have resulted in an increase of gaseous and solid products while the liquid product decreased. The maximum oil production for HDPE (70.0wt%) and PS (88.1wt%) were obtained at the pyrolysis temperature of 450 °C, the reforming temperature of 450 °C and WHSV of 4.

C₂, C₃ and C₄₊ gases (>75 mol %) and valuable aromatic and branched species in the light oil range (C₅-C₁₅) (>70wt %) were the main components of the gaseous and liquid products for HDPE, which were attributed to the molecule structure of HDPE, as well as the relatively moderate acidity and large hole size of the HY-zeolite catalyst. In case of PS, C₂ and C₃ gases (>65 mol %) were the main components of the gaseous product. However, the quantity of gaseous products was very low to serve as a fuel gas either for engine or for the SPCR process. In addition, the liquid products of PS consisted of mostly monocyclic aromatic hydrocarbon, such as styrene and benzene, as well as lower concentrations of potentially harmful polycyclic aromatic hydrocarbons. The high quality gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolysis reactor.

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