Production of value added olefins from catalytic pyrolysis of waste plastic straw

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Abstract

This study aims to find sustainable solutions for recycling plastic waste, with a focus on polypropylene, a commonly used material in plastic straw production. To achieve this, the pyrolysis of waste plastic straws (WPS) under inert conditions was carried out to generate olefins-rich gaseous products while significantly reducing carbon dioxide emissions. WPS was pyrolyzed in a fixed-bed reactor using ex-situ ZSM-5 and in-situ alumina-based catalysts. Proximate analysis and elemental analysis were conducted on the straw, while the characteristics of catalysts were evaluated for acidity using NH_3-TPD, specific surface area using BET, and metal oxide mass analysis using XRF to calculate the SiO_2/Al_2O_3 ratio. As a result of one-stage ex-situ catalytic pyrolysis (ESCP), ZSM-5(280) (Z280) showed the highest selectivity for gaseous olefins. Moreover, at one-stage in-situ catalytic pyrolysis (ISCP), the employment of Al-SBA-15 (S15) indicated the highest efficiency in the production of olefins-rich gas. Therefore, two-stage catalytic pyrolysis (TSCP) was carried out using Z280 and S15, further enhancement of gas yield and gaseous olefins selectivity. Meanwhile, the ex-situ coke yield in TSCP was lower than that produced in conventional ESCP. The lower coke yield leads to an extended lifetime of the ex-situ catalyst and enables stable and prolonged production of olefin gas. Overall, by the generation of gaseous olefins from plastic waste pyrolysis for waste plastic upcycling, a circular economy, a potential source for plastic production, and a reduction of carbon dioxide emissions can be established in plastic waste management and upcycling processes.

Keywords

waste plastic straw, two-stage catalytic pyrolysis, olefins, polypropylene

1. Introduction

The rate of solid waste emissions, particularly plastic waste emissions, has been increasing steadily. As much as 12 % of the world's total waste emissions are comprised of plastic waste. Every year, approximately 90 billion tons of plastic is utilized globally to manufacture goods, yet only 9 % of plastic is recycled [1]. The main components of plastic waste generated in urban areas are polyethylene (PE), polypropylene (PP), and polystyrene (PS) [2]. Polypropylene is a low-density thermoplastic polymer commonly used in the production of various plastic products due to its hardness, flexibility, heat resistance, and low density. It is also a major plastic used in the production of plastic straws. While waste plastic straws only account for a small portion of urban solid waste emissions, they are one of the primary sources of marine effluent microplastics [3].

Methods of treating plastic waste include landfill, physical recycling, and incineration. However, landfill requires physical space and can cause leachate problems [4], while plastic waste takes a minimum of 450 years to completely biodegrade [5]. Physical recycling is not a continuous process due to decomposition, and incineration generates air pollutants although it requires simple pretreatment.

Olefins such as ethylene and propylene are key components of plastics like PE and PP and play a crucial role in the petrochemical process. Alpha-olefin, one of the olefins, is a major raw material for plastic production and is produced through complex process technology that is expensive and generates carbon dioxide. The International Energy Agency predicts that plastic product production will double to 600 million tons by 2050 compared to 2010 levels, leading to increased environmental pollution from plastic use [6]. Therefore, environmental pollution caused by the use of plastic products can be expected to become more serious.

In response to the increase in plastic waste, environmentally friendly recycling methods have been developed. Pyrolysis and gasification reactions are methods that involve down-cycling waste into oil and gas products for fuel. Pyrolysis, in particular, is beneficial because it decomposes waste under anaerobic conditions, resulting in minimal carbon dioxide emissions. This study aims to pyrolyze waste plastics to produce gases with high olefin selectivity and additionally produce BTEXs oil. Traditionally, pyrolysis has focused on oil production, necessitating dechlorination in samples containing chlorine. In contrast, our study concentrates on producing olefin gas, thus obviating the need for dechlorination and increasing process value. It is economically beneficial to produce gas with high olefin selectivity and use it as an inexpensive raw material for plastic production, while also achieving waste plastic upcycling, which is beneficial to the environment. This approach will help create a circular economy by converting waste into new products, while also significantly reducing carbon dioxide emissions in the process of waste plastic treatment and production of plastic products.

2. Materials and methods

2.1. Feedstock

In this study, the straw samples used in the pyrolysis experiments were directly collected from domestically generated WPS. The collected WPS were washed and dried at room temperature for more than one day before being cut into cylindrical shapes with a length of less than 5 mm for use. To determine the moisture, volatile matter, fixed carbon, and ash contents of the WPS, an industrial analysis was performed using a thermogravimetric analyzer (TA instrument, TGA 55). To determine the carbon, hydrogen, oxygen, nitrogen, and sulfur contents, elemental analysis was conducted using an elemental analyzer (ThermoFisher Scientific, Flash EA 2000).

2.2. Catalysts preparation and characterization

The zeolite catalyst used in ESCP is ZSM-5, a commercial catalyst purchased in powder form from zeolyst. ZSM-5 with SiO_2/Al_2O_3 ratios of 30, 80, and 280 was used and calcined at 550 ℃ in air for 3 hours. Additionally, to increase the contact time between the catalyst and the reaction, pellets of 0.7-1.7 mm size were made and used.

The mesoporous catalysts used in ISCP are Silica-alumina (SA), S15, and Al-MCM-41 (M41). SA is a commercial catalyst purchased from Sigma-Aldrich, and M41 was provided by Chonnam National University. SA and M41 were calcined at 550 ℃ in air for 3 hours and used in powder form.

S15 was prepared by using SBA-15 as a support, which was purchased from ACS Material. SBA-15 was mixed with a solution of NaAlO2 in distilled water and stirred at 45 ℃ for 12 hours to allow NaAl to bind to the Terminal Hydroxyl group. The resulting catalyst was filtered and dried in an oven at 110 ℃ for at least 3 hours. The dried catalyst was then mixed with 1 M NH_4NO_3 solution and stirred at 50 ℃ for 2 hours, and the process was repeated 3 times with vacuum filtration. Finally, the catalyst was dried in an oven at 110 ℃ for over 12 hours and calcined at 550 ℃ in air for 5 hours to obtain S15 in powder form. For the alumina catalysts, XRF analysis was conducted to determine the weight ratio of metal oxides using ZSX Primus II (Rigaku, Japan), and the ratio of SiO_2 and Al_2O_3 was calculated from the analysis results.

To analyze the characteristics of the catalysts such as pore volume and specific surface area, BET measurements were carried out using a nitrogen adsorption-desorption analyzer (Belsorp mini X, MicrotracBEL). To remove any moisture or impurities inside the catalyst pores, ZSM-5 catalysts were pretreated under vacuum at 350 ℃ for more than 12 hours, and alumina catalysts were pretreated under vacuum at 150 ℃ for 6 hours. Afterward, the nitrogen adsorption-desorption amount was measured under liquid nitrogen (77 K) conditions.

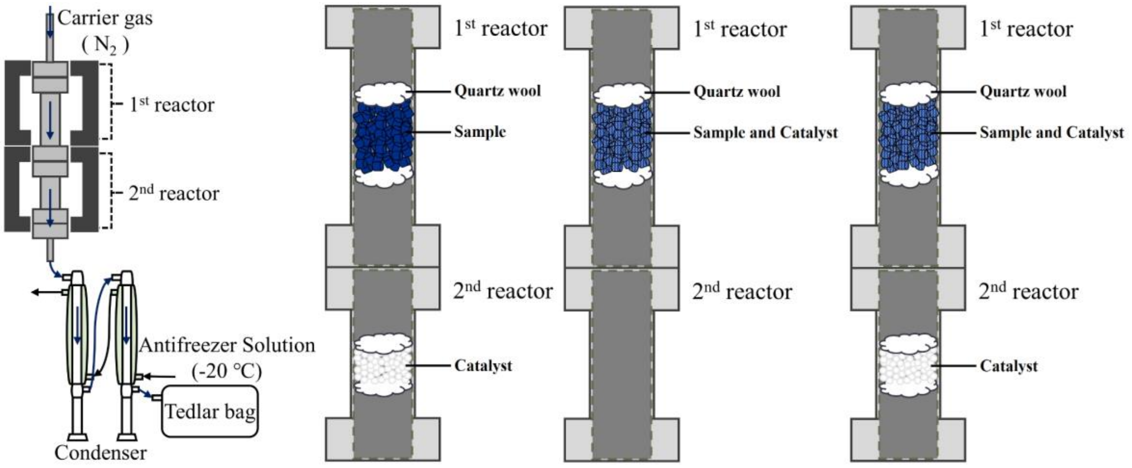
The surface acidity of the catalyst was measured using a chemical adsorption analyzer (BEL-CAT, MicrotracBEL). The sample was pretreated under a 30 mL/min He flow at 500 ℃ for 1 hour before the analysis. After lowering the temperature to 100 ℃, NH_3 adsorption was performed, and the physically adsorbed NH_3 was removed with a 30 mL/min He flow. After the temperature was raised to 650 ℃ at a rate of 10 ℃/min under a He flow of 30 mL/min, the desorption of NH_3 was analyzed using a thermal conductivity detector (TCD).

2.3. Fixed-bed pyrolysis experiments

In the case of non-catalytic pyrolysis and catalytic pyrolysis (CP) in this research, a fixed-bed pyrolysis reactor was used as shown in (Fig. 1 a). WPS pyrolysis experiments in this study were conducted within three sets: one-stage ESCP, one-stage ISCP, and two-stage catalytic pyrolysis (TSCP). ESCP and ISCP were initially implemented and a catalyst with high olefin selectivity at ESCP and a catalyst with high gas yield at ISCP were selected to use at TSCP. At the ESCP stage, 4 g of WPS and 2 g of ZSM-5 with different SiO_2/Al_2O_3 ratios were separately located in the 1st and 2nd reactors (Fig. 1 b), respectively, and the process was carried out at a temperature of 600 °C under 100 mL/min of N2 gas. At the ISCP stage, 4 g of WPS and 2 g of alumina catalysts were mixed and placed in the first reactor (Fig. 1 c), and the process was conducted under the same condition as ESCP. In the case of TSCP, the pyrolysis experiments were implemented in the same conditions as explained above (Fig. 4 d). The effect of TSCP with the addition of an in-situ catalyst was explained by comparing the results of non-CP, ESCP, and TSCP.

The yields of the main products of WPS including gas, oil, char, and coke were measured through the following procedure. Firstly, the weight percent (wt.%) of char and oil were measured simply considering their weights in the final products and the initial weight of the WPS (4 g). The quantity of carbon deposited on the catalyst surface (coke) was calculated by using a TG analyzer. Subsequently, the amount of gas yield was calculated from the difference in the initial WPS weight and the summation weight of oil, char, and coke.

The gaseous components were identified by gas chromatography (GC, GC-6000). For the analysis of H2, CO, CO2, and CH4, the GC was equipped with a thermal conductivity detector (TCD), while a flame ionization detector (FID) was coupled to GC to recognize the heavier hydrocarbons (≥CH4). In this study, Autochro 2000 software was applied to analyze data acquired from GC.



(a) (b) (c) (d)

Fig 1. The fixed-bed pyrolysis reactor: (a) the reactor, (b) ESCP, (c) ISCP, and (d) TSCP.

3. Results and discussion

3.1. WPS properties

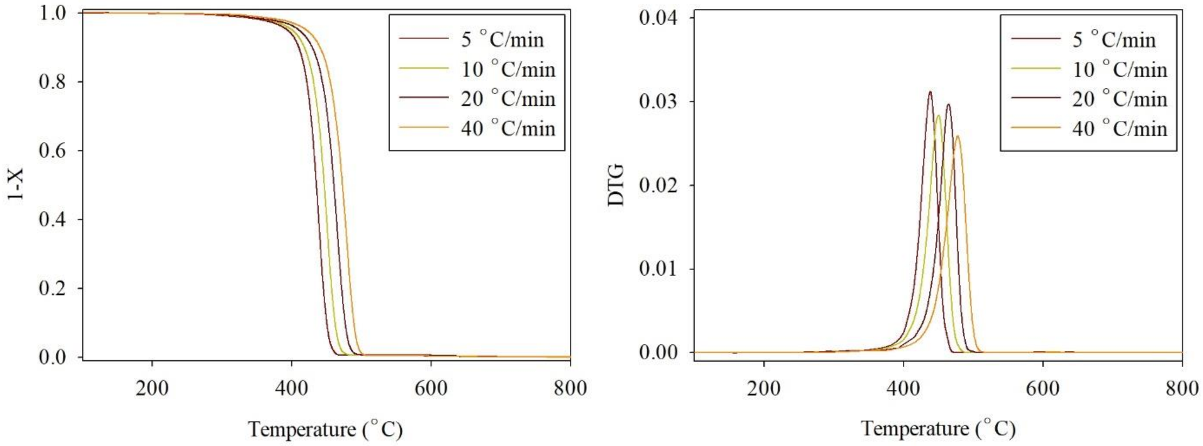
Table 1 indicates the results of the proximate analysis and the elemental analysis of WPS. The elemental analysis was conducted on an ash-free basis, and the weight ratios of C, H, N, and S were measured. The weight ratio of O was calculated by subtracting the sum of the weight ratios of the other elements from 100. WPS was confirmed to be completely dry at room temperature without any presence of moisture, consisting mostly of volatile components with trace amounts of N but mostly composed of C and H.

Table 1. The results of the proximate analysis and the elemental analysis of WPS.

Sample	WPS	
Proximate analysis (wt. %)	Moisture	0.0
	Volatile	99.7
	Fixed Carbon	0.0
	Ash	0.3
	Sum	100
Elemental analysis[a] (wt. %)	C	85.7
	H	14.1
	O	0.0
	N	0.2
	S	0.0
	Sum	100

[a] Dry and ash-free basis.

Fig. 2 shows the non-catalytic TG curve and derivative TG (DTG) curve of WPS at 5, 10, 20, and 40 ℃/min. WPS was decomposed over a narrow region of temperatures between 380 ℃ and 510 ℃, and its maximum decomposition temperature was about 440 ℃.



(a) (b)

Fig 2. Non-catalytic TG curve and DTG curve: (a) TG curve, and (b) DTG curve.

3.2. *Characterization of catalysts*

Table 2 indicates the BET surface areas, total pore volumes, and micro pore volumes of ZSM-5 catalysts. The SiO_2/Al_2O_3 ratios, BET surface areas, total pore volumes, and meso pore volumes of the alumina catalysts are shown in Table 3.

Table 2. Physical properties of ZSM-5 catalysts.

Ex-situ Materials	S_{BET} m^2g^{-1}	V_{total} cm^3g^{-1}	V_{micro} cm^3g^{-1}
ZSM-5(30)	422	0.33	0.17
ZSM-5(80)	468	0.30	0.21
ZSM-5(280)	390	0.21	0.18

Table 3. Physical properties of alumina catalysts.

In-situ Materials	SiO_2/Al_2O_3	S_{BET} m^2g^{-1}	V_{total} cm^3g^{-1}	V_{meso} cm^3g^{-1}
Silica-Alumina	5.6	549	0.77	0.76
Al-SBA-15	8.5	334	0.66	0.64
Al-MCM-41	28.6	943	0.87	0.80

Fig. 3 shows the NH_3-TPD profiles of the six catalysts, where the peak area in the graph of each catalyst represents the amount of acidity. ZSM-5(30) (Z30) and ZSM-5(80) (Z80) exhibit two peaks at 220 ℃ and 420 ℃, respectively. The first peak corresponds to weak acid sites, while the broad peak at 420 ℃ suggests the presence of strong acid sites, revealing that the densities of both types of acid sites are higher in the case of Z30 compared to those of Z80. Moreover, the NH_3-TPD pattern of Z280 shows two peaks at 180 ℃ and 380 ℃, but both peaks are not distinct, indicating a low density of acid sites at elevated SiO_2/Al_2O_3 ratios. In the case of the alumina catalysts, only one peak relevant to weak acid sites is observed at around 200 ℃ for each catalyst, where SA and S15 showed a significantly higher density of weak acid sites compared to that of M41.

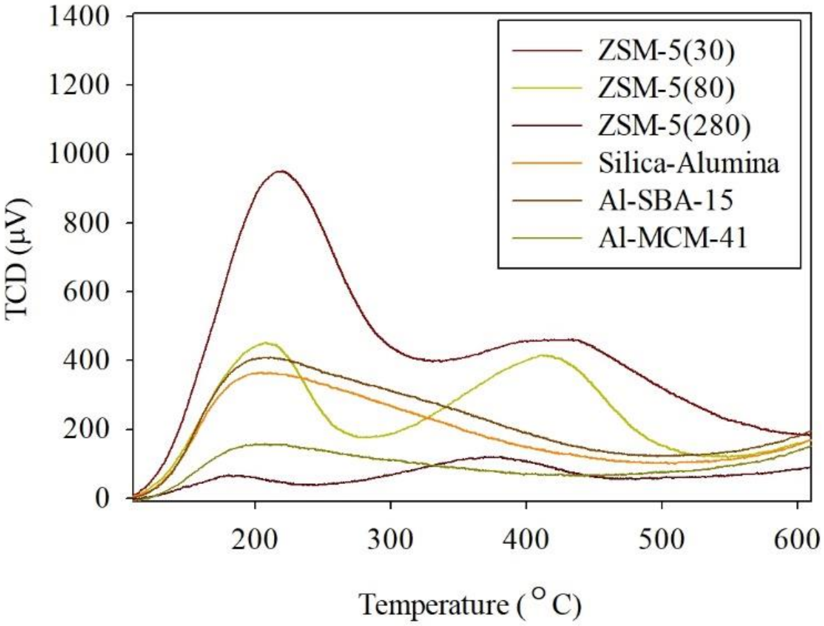
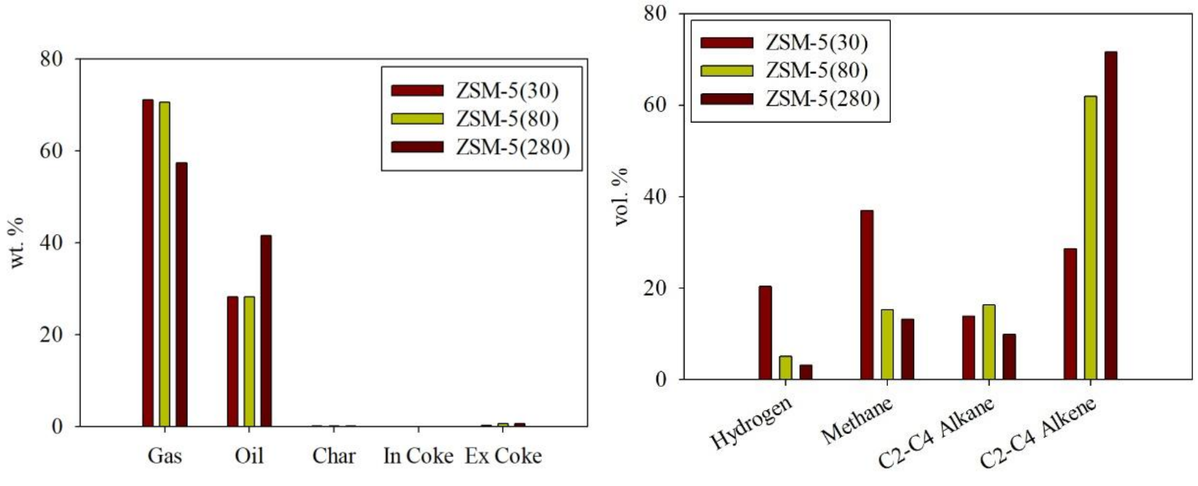


Fig 3. NH_3-TPD results of catalysts.

3.3. *Investigation of catalytic activity in pyrolysis*

3.3.1. *One-stage Ex-situ catalytic pyrolysis*

According to the ESCP result (Fig. 4 a) of WPS, the gas yield increased as the acidity of the catalyst increased. This is because the heavy hydrocarbons of WPS adsorbed on the acid sites of ZSM-5, and then protonated to carbenium ions, which promote the cracking of the molecule, therefore the WPS decomposed into smaller materials as the acidity increases [7]. Furthermore, a comparison of the gas component selectivity (Fig. 4 b) showed that Z30 had a high selectivity for hydrogen and methane, while Z280 had a high selectivity for C2-C4 olefin gases. Therefore, it was determined to use Z280, which had the highest olefin gas selectivity in the ESCP, for the TSCP process.

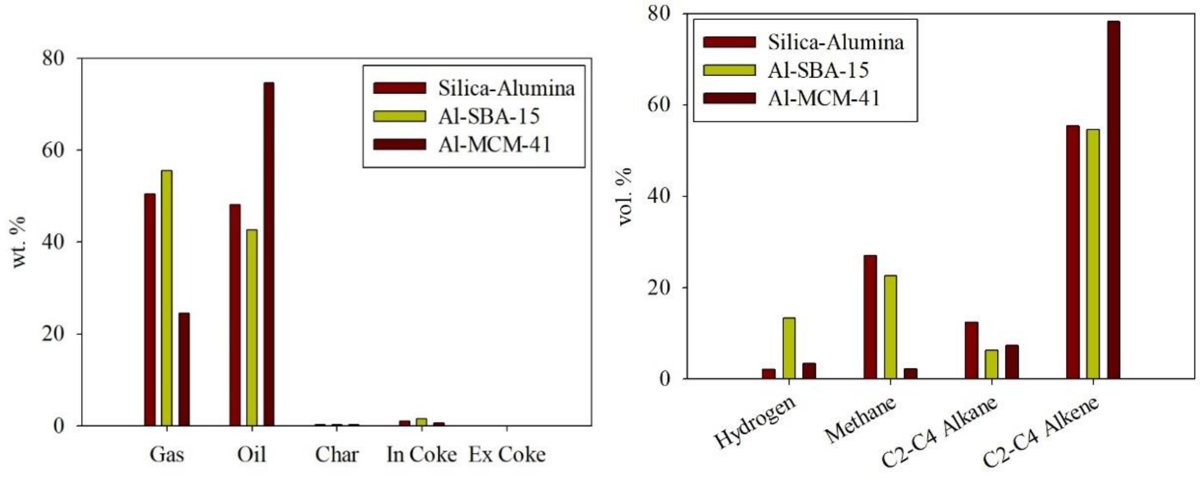


(a) (b)

Fig 4. Pyrolysis products yield and the selectivity of gas components of ESCP: (a) ESCP products yield, and (b) ESCP gas components selectivity.

3.3.2. *One-stage In-situ catalytic pyrolysis*

As shown in (Fig. 5 a), when using alumina catalysts, the results of ISCP were the highest in gas yield when using S15, followed by SA and M41. However, the highest selectivity toward C2-C4 olefins was acquired using M41 (Fig. 5 b). Considering that the olefin gas yield of M41 was low due to the low gas yield produced over this catalyst, S15 was determined as the best catalyst to obtain both the olefin-rich gaseous products.

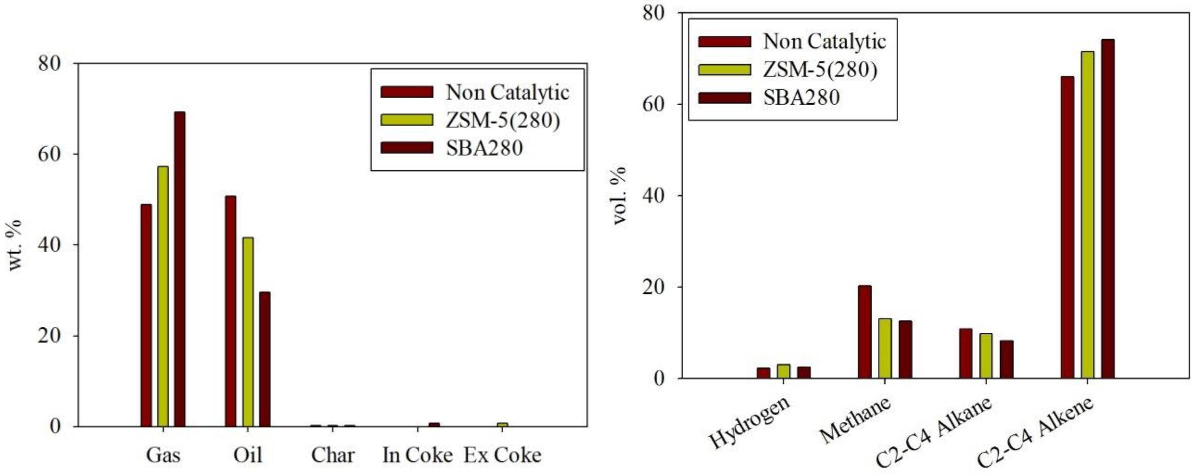


(a) (b)

Fig 5. Pyrolysis products yield and the selectivity of gas components of ISCP: (a) ISCP products yield, and (b) ISCP gas components selectivity.

3.3.3. *Two-stage catalytic pyrolysis*

TSCP was conducted using Z280 as an ex-situ catalyst and S15 as an in-situ catalyst, and the results (Fig. 6) were compared with the results of Z280 in ESCP and those of non-CP. As a result, the gas yield and olefin gas selectivity were the highest when using TSCP, and the ex-situ coke yield was lower than ESCP. This suggests that the oil was primarily decomposed into smaller intermediates over in-situ catalyst and was further cracked into gaseous products over ex-situ catalyst, leading to an increase in gas production. In addition, due to the use of ZSM-5 with low acid sites by ex-situ catalyst, oligomerization of components produced through in-situ catalysts did not occur due to mitigated dehydrogenation and cyclization reactions resulting in low selectivity for monocyclic aromatic hydrocarbons and high selectivity for olefins [8].



(a) (b)

Fig 6. Pyrolysis products yield and the selectivity of gas components of TSCP: (a) TSCP products yield, and (b) TSCP gas components selectivity.

4. Conclusion

In this study, the pyrolysis of WPS was performed at three different catalytic modes to produce the olefins-rich gaseous products. It was found that the lower the acidity of ZSM-5 in ESCP, the higher the selectivity for gaseous olefins. The synthesized S15 catalyst in this study exhibited better cracking activity and had the highest gas yield among the alumina catalysts used in ISCP. Concurrent employment of Z280 and S15 in TSCP further enhanced the gas yield and the selectivity of gaseous olefins due to the synergetic effect of suitable porosity and low acidity. This phenomenon is ascribed to producing smaller products with a micro-pore size while a low rate of oligomerization reactions. In addition, it was confirmed that the coke yield of the ex-situ catalyst in TSCP was lower than that in ESCP, indicating that the lifetime of the ex-situ catalyst was extended, and the production of gaseous olefins could be maintained for a long period.

Acknowledgement

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