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## Evaluating H-Beta and H-ZSM-5 Catalysts in Heterogeneous Pyrolysis of Plastic Waste

Awatif Meelad<sup>1</sup>, Nadya AL Sbani<sup>2</sup>, Omar Sultan<sup>3\*</sup>,  
Takwa Mohammed<sup>4</sup>, Haifa Ergeg<sup>5</sup>, Jamila Alrtaimi<sup>6</sup>

<sup>1, 2, 3, 4</sup> Department of Chemical Engineering, Faculty of Oil, Gas,  
Renewable Energy Engineering, University of Zawia, Libya

<sup>5</sup> Department of Environmental Engineering, Faculty of Natural  
Resources Engineering, University of Zawia, Libya

<sup>6</sup> Higher Institute of Science and Technology, Zawia, Libya

n.alsbani@zu.edu.ly

### Abstract

This research investigates the application of pyrolysis technology for converting plastic waste into liquid fuel, focusing on three common types of plastics: polyethylene terephthalate (PET), high-density polyethylene (HDPE), and polypropylene (PP). Two catalysts, H-Beta and H-ZSM5, were employed, with H-ZSM5 undergoing acid treatment using hydrochloric acid (HCl) to enhance catalytic activity. A mixture of 60 g of the plastics, in a ratio of 20:20:20 g, was subjected to pyrolysis in an autoclave reactor without oxygen at varying temperatures (400, 425, and 450 °C). Product characterization was performed using gas chromatography-mass spectrometry (GC-MS). Results demonstrated the highest gas production of 54.3% at 400 °C with acid-treated H-ZSM5. For liquid fuel yield, the highest production was observed at 400 °C with H-Beta, yielding 42.9%, while acid-treated H-ZSM5 yielded 38.7% at 425 °C. These findings suggest that both catalysts significantly influence the efficiency of plastic waste conversion, offering a promising approach to sustainable fuel production from plastic waste.

**Keywords:** Plastic Waste, Pyrolysis, Autoclave reactor, Catalysts, Fuel.

## تقييم محفزات (H-Beta) و (H-ZSM-5) في التحلل الحراري غير المتجانس للنفايات البلاستيكية

عواطف ميلاد<sup>1</sup>، نادية السباني<sup>2\*</sup>، عمر سلطان<sup>3</sup>، تقوى محمد<sup>4</sup>، هيفاء الرقيق<sup>5</sup>، جميلة الرتيمي<sup>6</sup>

<sup>1, 2, 3, 4</sup> قسم الهندسة الكيميائية، كلية هندسة النفط والغاز والطاقة المتجددة، جامعة الزاوية، ليبيا

<sup>5</sup> قسم الهندسة البيئية، كلية هندسة الموارد الطبيعية، جامعة الزاوية، ليبيا

<sup>6</sup> المعهد العالي للعلوم والتكنولوجيا، الزاوية، ليبيا

n.alsbani@zu.edu.ly

### الملخص

يدرس هذا البحث تطبيق تقنية التحلل الحراري لتحويل النفايات البلاستيكية إلى وقود سائل، مع التركيز على ثلاثة أنواع شائعة من البلاستيك: البولي إيثيلين (PET) والبولي إيثيلين عالي الكثافة (HDPE) والبولي بروبيلين (PP). أيضا تم استخدام حافزان، هما (H-Beta) و (H-ZSM-5)، حيث خضع H-ZSM5 لمعالجة حمضية باستخدام حمض الهيدروكلوريك (HCl) لتعزيز نشاطه التحفيزي. خضع خليط من 60 غ من الأنواع الثلاثة للبلاستيك، بنسبة 20:20:20 غ، للتحلل الحراري في مفاعل أوتوكلاف في غياب الأكسجين عند درجات حرارة متفاوتة (400، 425، و 450 درجة مئوية). أُجريت توصيفات المنتج باستخدام كروماتوغرافيا الغاز - مطياف الكتلة (GC-MS). أظهرت النتائج أعلى إنتاج للغاز بنسبة 54.33% عند 400 درجة مئوية مع H-ZSM5 المعالج بالحامض. أما بالنسبة لإنتاجية الوقود السائل، فقد لوحظ أعلى إنتاج عند 400 درجة مئوية مع H-Beta، حيث بلغ 42.9%، بينما بلغ إنتاج H-ZSM5 المعالج بالحامض 38.7% عند 425 درجة مئوية. تشير هذه النتائج إلى أن كلا المحفزين يؤثران بشكل كبير على كفاءة تحويل النفايات البلاستيكية، مما يوفر نهجاً واعداً لإنتاج وقود مستدام من النفايات البلاستيكية.

**الكلمات المفتاحية:** النفايات البلاستيكية، التحلل الحراري، مفاعل الأوتوكلاف، المحفزات، الوقود.

## 1. Introduction

The plastics industry has expanded recently, which has led to the widespread use of plastic products, which in turn has led to the production of about 400 million tons of plastic waste annually. If this trend continues, global production will reach 1,100 million tons by 2050 (Kumar et al., 2021). Therefore, it is necessary to search for solutions to this trend, such as reusing, recycling, and upcycling.

There are several methods for disposing of municipal and industrial plastic waste, including gasification, incineration, material recycling, chemical recovery, landfilling, and bioconversion, among others. (Abdel-Shafy and Mansour, 2018; Davidson et al., 2021). However, most of these disposal methods pose serious threats to the environment, for example, generating toxic substances through incineration, which cause serious health problems. Unless effective solutions are developed for the growing issue of plastic waste in the environment, the global community is likely to face significant ecological challenges that disrupt environmental balance. Moreover, this accumulation of plastic contributes to visual pollution. (Pilapitiya and Ratnayake, 2024, Verma et al., 2016).

One of the important plans is to convert this waste into alternative fuels using pyrolysis technology. This technology is considered one of the important upcycling technologies that protect the environment from emissions of gases that cause global warming (Nasution et al., 2022; Jung et al., 2023). Pyrolysis is a process that can not only solve the problem of plastic waste disposal but also create an alternative fuel (Sharuddin et al., 2016). Pyrolysis is a process that thermally decomposes long-chain polymer molecules into shorter, less complex molecules using heat and pressure, making it an effective method for plastic waste management. This process necessitates intense heat for a short period in the absence of oxygen (Kafle et al., 2023; Panda, 2011).

Plastic pyrolysis involves complex reaction mechanisms that vary depending on the type of plastic and process conditions. The cracking reaction consists of several key steps: initiation, where free radicals are generated; propagation, which involves the formation of products and secondary radicals, along with isomerization; and termination, encompassing processes such as recombination, disproportionation, and cyclization. Figure (1) illustrates the thermal cracking reaction mechanism of Polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene

(LDPE).(Rodriguez Lamar et al., 2021, Gornall, 2011, Locaspi, 2023)

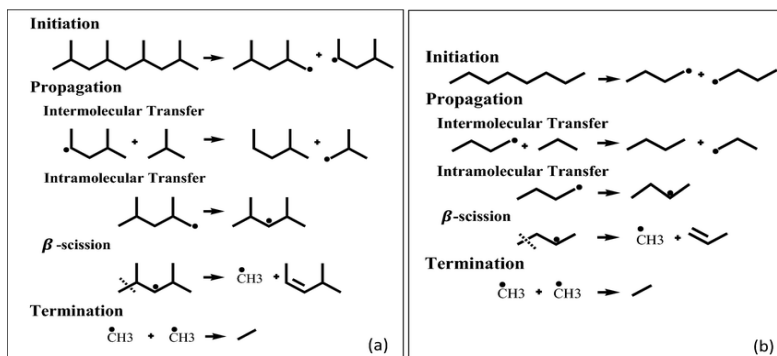


Figure (1) Reaction mechanism of thermal cracking (a) PP and (b) HDPE/LDPE.

(Rodriguez Lamar et al., 2021, Gornall, 2011, Locaspi, 2023)

This process can produce up to 45-50% liquid oil, 35-40% gases and 10-20% coal, productivity depends on several variables including temperature ranging from 300-500°C, pressure, types of plastic and catalysts that lower the required temperature and speed up the reaction (Harussani et al., 2022, Martynis et al., 2019, Wong et al., 2015, Xu et al., 2009), such as HZSM-5 zeolite, ZnO, silica, calcium carbide, alumina, magnesium oxide, zinc oxide, and ZSM-5 (Ratnasari et al., 2017). Pyrolysis yields about 45-50% liquid oil, 35-40% gaseous products, and 10-20% solid char. The productivity of thermal cracking is influenced by several factors, including temperature (ranging from 300 to 500 °C), pressure, the types of plastics, and the use of catalysts. Catalysts such as H-ZSM5 zeolite, zinc oxide (ZnO), silica, calcium carbide, alumina, magnesium oxide, and ZSM-5 are employed to reduce the temperature and accelerate the reaction (Ratnasari et al., 2017).

Hydrochloric acid treatment of H-ZSM5 zeolites has been shown to significantly alter their structural and catalytic properties. The treatment can induce mesopore formation, increase specific surface area, increase pore volume of the H-ZSM5 zeolite, and redistribute acid sites (Meng et al., 2020; Velichkina et al., 2021; Yang et al., 2020).

The produced liquid oil can be utilized in various applications, including as fuel for diesel engines, similar to diesel fuel. It can also serve as an alternative heavy fuel or as a raw material for resale in the petrochemical industry. Additionally, byproducts such as char

and gases can either be sold or further processed to enhance the overall value of the process (Damodharan et al., 2017; Almeida and Marques, 2016; Kafle et al., 2023). This research deals with the process of recycling plastics into fuel using catalytic pyrolysis technology. The effect of different temperatures and the use of different catalysts on the overall yield was studied using a mixture of PET, HDPE, and PP plastics. Catalytic pyrolysis is an environmentally sustainable approach that seeks to mitigate the release of greenhouse gases and reduce the accumulation of plastic waste in our environment. And convert this waste into usable fuel, which ultimately promotes a more sustainable future and addresses pressing environmental issues (Pawelczyk et al., 2022).

## 2. Materials and Methods

### 2.1. Materials

Plastic materials were collected from household waste and classified according to the plastic recycling code. Three different types of plastic waste (PP, HDPE, and PET) were considered in the experiments. H-ZSM5 and H-BETA catalysts from Catal International Ltd, were donated by the Libyan Petroleum Institute (LPI). The H-Beta zeolite catalyst was used as received.

### 2.2. Acid treatment of H-ZSM5 catalyst

9 gm of H-ZSM5 catalyst is placed in a 13.80 ml solution of distilled water to the impregnation of distilled water mixed with 0.01 ml/l of HCl (PH=4). Under reflux conditions, the mixture is heated at 60 °C with constant stirring for one hour. After this period, the impregnated H-ZSM5 zeolite was separated, and the product was filtered two to three times with distilled water. Following filtration, it was washed with distilled water to remove any to remove excess or free HCl. Finally, the H-ZSM5 catalyst was dried in an oven at 100 °C for one hour.

### 2.3 Experimental procedure

The reactions were carried out in a batch autoclave reactor, which consisted of a stainless-steel tubular reactor equipped with a programmable temperature controller. The size of the autoclave reactor is 1 L. The reactor is housed in the furnace. The maximum operating pressure of this reactor is 345 bar, whilst the maximum operating temperature is 500 °C. Figure (2) shows the Autoclave Batch Reactor.



Figure (2): Autoclave Batch Reactor

A set of 20g samples was prepared with varying percentage mixtures of PP, HDPE, and PET. The sample placed in the autoclave batch reactor was gradually heated over an hour at a rate of 10°C/min. The temperature was then maintained at the target temperature for 1 hour under a nitrogen blanket. All runs were conducted with a consistent reaction time of 1 hour. The experiments were conducted by heating the samples to thermal decomposition at different temperatures (400, 425, 450 °C) in an inert atmosphere. Table (1) displays the cracking temperature, catalyst type, and the PP/HDPE/PET ratio used in this study. Finally, the product obtained from the catalytic pyrolysis process was tapped into a container.

**Table 1: Operating Conditions**

Runs	Catalyst	Weight g/g	Temperature (C)	PP: HDPE: PET
1,2,3	H-ZSM5	1.25	400, 425 and 450	1:1:1
4,5,6	H-BETA	1.25	400,425 and 450	1:1:1

### 3. RESULTS AND DISCUSSION

#### 3.1 Productivity of H-Beta and H-ZSM5 Catalysts

The reaction products collected from the outlet of the batch reactor were classified into gases, liquid hydrocarbons, and ash. Figure (3) shows samples of the obtained products. The results obtained from using the H-Beta catalyst display that the highest gas yield was 32.6 g, attaining a productivity of 54.3% at 450 °C, as shown in Figure (4). At 425 °C, the gas yield was 29 g (48.3%), and at 400 °C, it was 23.5 g (39.2%)

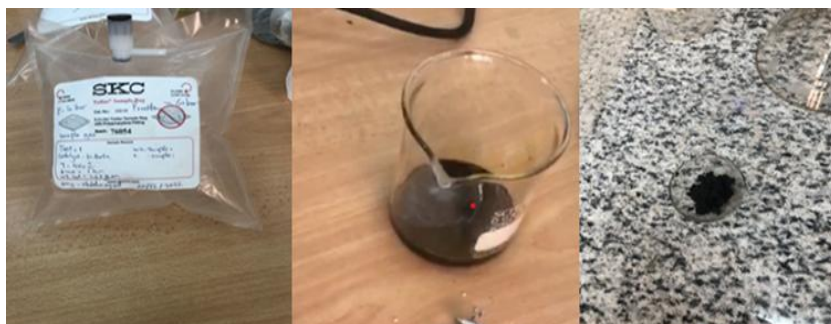


Figure (3): Output samples (liquid, gas, and Ash).

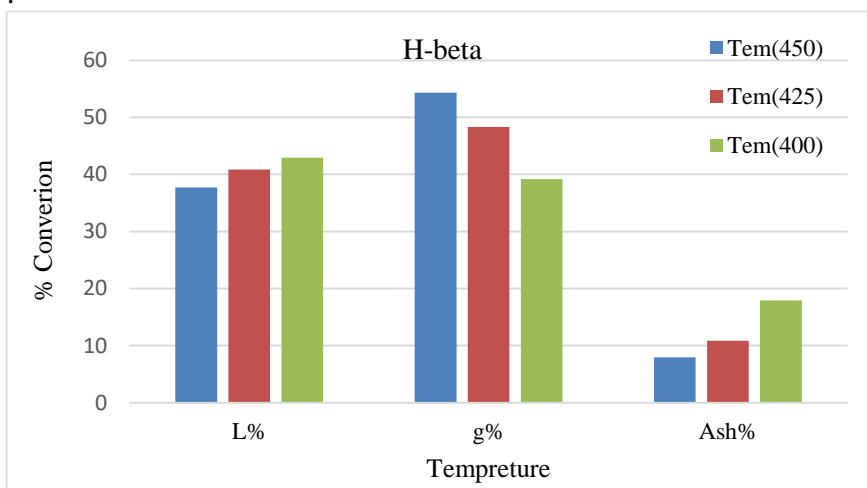


Figure (4): The relationship between the conversion and the temperatures with catalyst H-Beta.

For liquid fuel, the highest production was at a temperature of 400 °C, which was 25.74 g, with a productivity rate of 42.9 %. It was followed by 425 °C, which produced 23.5 g (40.8%), and the lowest yield was at 450 °C, with 22.6 g (37.7%). As shown in Figure 5, the



lowest coke productivity was at 450 °C, at 7.9% (4.75 g), while the highest ash productivity was 10.75 g at 400 °C. These results indicate that the optimal temperature for the H-Beta catalyst was 450 °C, as it produced the lowest amount of coke

Figure (5) illustrates the result of using H-ZSM5 as a catalyst. The highest gas yield was obtained at a temperature of 400 °C, where it reached 32.44 g with 54.3 %. The lowest amount of gas was produced at 425 °C, which was 27.86 g (46.4 %). At a temperature of 450 °C, the gas was 29.9 g (49.8%). The highest liquid fuel production was 23.24 g at 425 °C, equivalent to a productivity of 38.7%. At 450 °C, the yield decreased to 22.7 g. This result is similar to that at 425 °C, where the productivity was 37.8%. The lowest liquid yield was obtained at a temperature of 400 °C, with 17.06 g (28.4%)

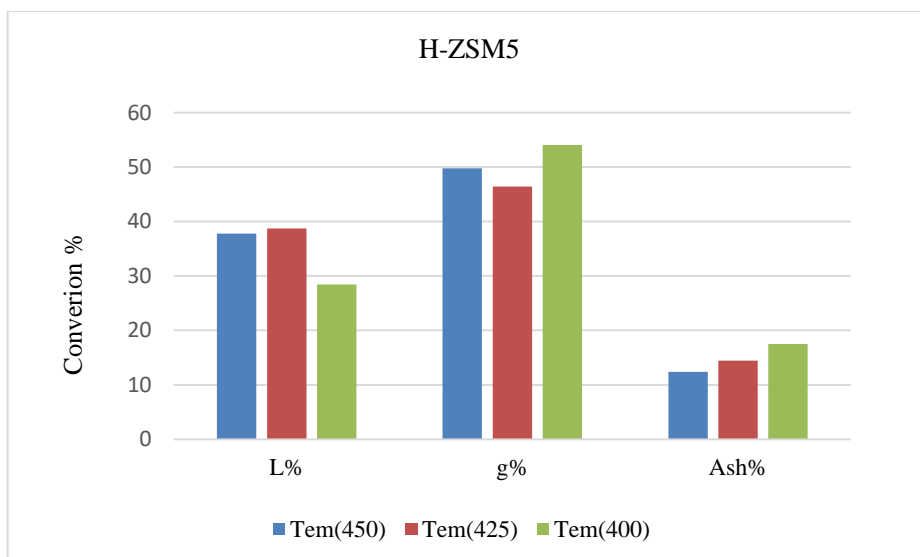


Figure (5): The relationship between the conversion rates at different temperatures using H-ZSM5 Catalyst.

For coke production, the result was the opposite. The highest production was at 400 °C, followed by 450 °C, with the lowest production at 425 °C, showing a productivity percent of 17.5%, 14.8%, and 12.4%, respectively. This indicates that using H-ZSM5 as a catalyst at 450 °C resulted in the lowest coke production. Hence, it can be concluded that 450 °C is the optimum temperature for minimizing coke production.



### 3.3 CHARACTERIZATION OF PRODUCTS

#### 3.3.1 Analysis of gas products

Based on the results shown in Figure 6, methane was the highest gas produced from plastic pyrolysis, followed by ethane and propane. The amounts of isobutane, neopentane, n-pentane, and isopentane were minimal, with n-butane at only 10.8% at 400 °C. The percentage of methane produced was 42.6% when using H-ZSM5 at 400 °C, compared to 27.6% at 425 °C. At 400 °C, methane production was nearly identical for both catalysts, with H-ZSM5 at 19.8% and H-Beta at 19.7%.

Likewise, when using H-ZSM5 at 450 °C, ethane production was 16.7%, compared to just 4.1% with H-Beta at the same temperature. At 425 °C, ethane production was 10.07% with H-Beta while it was 8.7% with H-ZSM5. At 400 °C, the yield of ethane with H-ZSM5 was 10.3%. Propane productivity reached 11.04% at 400 °C. The remaining gases (isobutane, neopentane, n-pentane, and isopentane) constituted a minor fraction of the gas, with concentrations ranging from 0.09% to 2.5%.

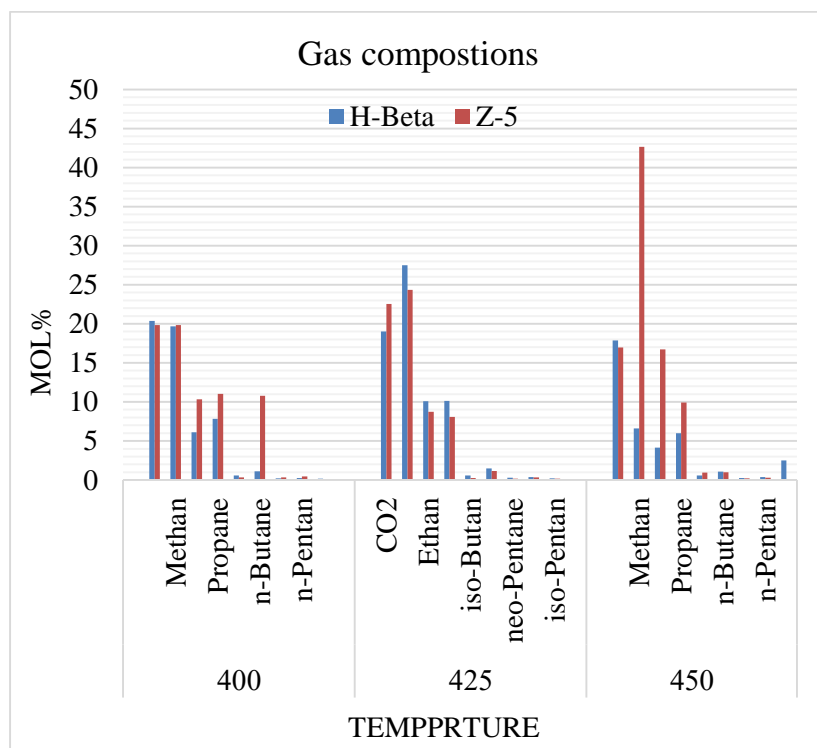


Figure (6): Gases produced using H-Beta and H-ZSM5 catalysts at different temperatures

At 425 °C using an H-Beta catalyst, methane production was the highest at 27.48%, followed by propane and then ethane, while the other gases were negligible. At 400 °C with the same catalyst, methane production was 19.65%, again followed by propane and ethane, with minimal production from the remaining gases. When using H-ZSM5 at 400 °C, methane production was 19.84%, followed by propane and ethane, with the remaining gases nearly non-existent. At 400 °C, both catalysts showed similar gas production, with only slight differences.

### 3.3.2 Liquid Products Analysis

The liquid phase products generated from the catalytic pyrolysis of plastic waste over H-Beta at temperatures of 400, 425, and 450 °C were characterized and the resulting carbon number distribution is illustrated in Figure 7. The carbon number distribution of the liquid products was found to be influenced by temperature, ranging from C3 to C35 at 400 °C, C4 to C28 at 425 °C, and C4 to C35 at 450 °C.

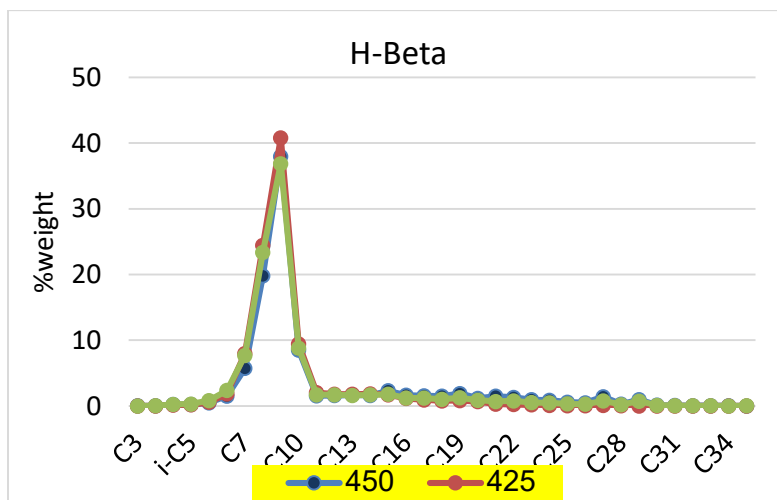


Figure (7): The relationship between hydrocarbon distribution and the temperatures at catalysts Z-Beta.

The results obtained using the H-Beta catalyst indicate that the liquid products contain a high percentage of aromatic and branched hydrocarbons. The gasoline and diesel ranges are classified as C5-C12 and C13-C20, respectively. The results showed that gasoline production was 89.08% at 425 °C and 83.65% at 450 °C, with the lowest value at 400 °C at 77.38%. For diesel, the highest percentage

was at 400 °C, reaching 13.41%, while at 425 °C and 450 °C, the percentages were 9.70% and 8.21%, respectively. Hydrocarbon compounds with carbon chains longer than C20 were present in small quantities at all temperatures.

Figure (8) presents the results using the H-ZSM5 catalyst. The range of hydrocarbons was consistent across all pyrolysis temperatures, extending from n-C4 to C34. The results indicated that the highest percentage of gasoline was 93.88% at 450 °C, while at 400 °C and 425 °C, the percentages were 83.85% and 80.51%, respectively. The lowest percentage of diesel was 4.09% at 450 °C, whereas at 400 °C and 425 °C, it remained constant at 12.6%. These results indicate that higher temperatures promoted cracking reactions, leading to increased gasoline production while reducing the formation of heavy hydrocarbons. However, a notable trend was observed where a decrease in the percentage of heavier hydrocarbons (C+20) with increasing temperature. This suggests that the catalyst effectively promotes cracking reactions, breaking down larger molecules.

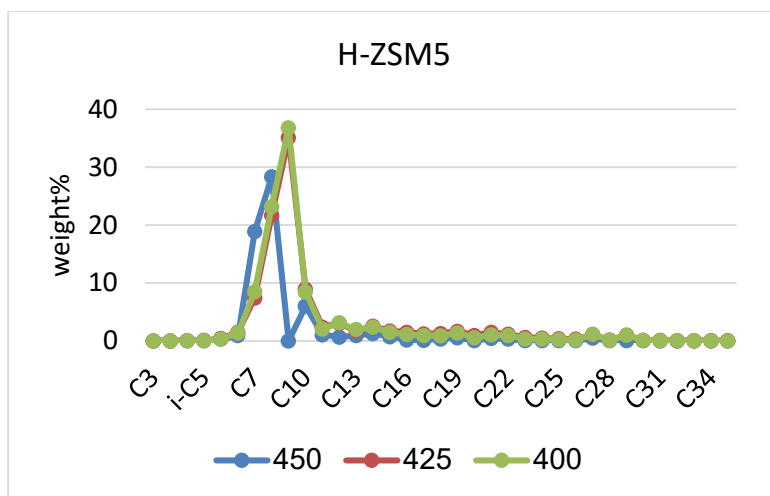


Figure (8) The relationship between hydrocarbon distribution and the temperatures at the catalyst H-ZSM5.

#### 4. Conclusion

This study investigates the thermal and catalytic degradation of plastics through the pyrolysis process and examines the effect of temperature on the final products. The results indicate that temperature is a significant operating parameter in pyrolysis, as it controls the cracking reactions of the polymer chain. Additionally, the required operating temperature depends on the preferred

product. If gaseous products are desired, higher temperatures should be used; however, if liquid products are preferred, lower temperatures are recommended. The products obtained from used plastics (PET, HDPE, and PP) are gases, liquids, and ash. The highest gas yield of 54.3% was achieved with H-ZSM5 at 400 °C, while the maximum liquid yield of 42.9% was obtained with H-Beta. The fuel liquids contained the most important petroleum products, gasoline, and diesel, and the percentage of gasoline was 93.88 % with H-ZSM5 at 450 °C. These findings demonstrate the potential of catalytic pyrolysis as an effective method for upcycling plastic waste. By converting plastic waste into valuable fuels and chemicals, this technology offers a sustainable solution for managing plastic pollution and reducing environmental impact.

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