



# Experimental Study of Thermal and Catalytic Decomposition of PVC Wastes

Murtadha S. Al-Eissa\*, Riaydh S. Almukhtar, Bashir Y. Sherhan

Department of Chemical Engineering, University of Technology – Iraq

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### \*Corresponding Author:

Murtadha S. Al-Eissa

[che.17.901@student.uotechnology.edu.iq](mailto:che.17.901@student.uotechnology.edu.iq)

## Abstract

The excessive use of plastics in the last years is the challenge that has arisen in managing plastic wastes to avoid dangerous effects. Polyvinyl chloride is part of these wastes. It can be utilized to produce fuel-like petroleum fractions depending on pyrolysis, which is the thermal decomposition of plastics in the absence of oxygen. This work aims to reduce environmental pollution and reuse plastic waste as an alternative fuel source. A comparison of the thermal and catalytic processes under the optimum temperature 450 °C, pressure 20 bar, and residence time 1 hour in a semi-batch reactor with and without adding Pt/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Thermo-gravimetric analysis (TGA) analysis was made for PVC. Catalysts were characterized by X-RAY diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The liquid and gas products were analyzed by (GC/MS) to evaluate the quality of products. In the hydro-cracking reaction, most gas products were produced using NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, about 62.29 wt%. The aromatic and saturated-aliphatic in the liquid using NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts were 21.07 and 72.81 wt%. The aromatics and saturated aliphatic in the liquid product using thermal non-catalytic and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were 23.83 wt% & 63.52 wt% and 21.88 wt% & 64.01, respectively. The ratio of gasoline range components is the highest in the hydrocracking process on NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Using catalytic-hydrocracking on Pt/Al<sub>2</sub>O<sub>3</sub> gives the highest diesel range component. It was confirmed that the generated undesirable product seems was very few in the hydrocracking reactions compared to the thermal cracking reactions.

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## 1. Introduction

Plastics play an essential role in human life because many items are made of various types of plastics, ranging from packaging, films, covers, pipes, bags, and containers to buildings and a huge material in a wide range of applications. Plastics are several types like; low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), accounting for 74.2 percent of global plastic production [1]. Plastics are polymers that are natural or synthetic

molecules composed of a large number of smaller moieties, monomers, which react with one another to form a long chain. Polymers can be classified based on two major criteria: thermal activity and polymerization process. Polymer classification is important because the best way to degrade a given polymer is related to the properties of the plastic molecules [2]. Plastics are harmful; as a result, they never combine or bond with other materials. That is, plastics do not decompose normally. It takes thousands of years to decompose or degrade in the soil. Some plastics do not decompose at all. They may dispose of their waste in the ocean or a landfill. Accordingly, plastics are causing many harmful implications for humans, the atmosphere, and the environment on land and inside the oceans. Plastic production and use are increasing continuously. Thus, dominating this issue has become very crucial [2]. PVC waste is considered one of the most harmful plastic waste to the atmosphere because it contains chlorine and the process of converting it into useful products requires reducing toxic products and harmful acids to a minimum. PVC use accounts for 12% of total demand among these six major types of plastics, and it is in the 2<sup>nd</sup> among them. PVC's global plastics production capacity exceeded 61 million tons in the last few years. Global demand is expected to increase by around 3.2 percent per year in the coming years [1] [3, 4]. There are various applications of PVC as it is the main material of pipes and window profiles, followed by rigid films and cables and many uses in a wide range, especially in medical and industrial in our public life. During PVC processing, a wide variety of additives are also added, enhancing the mechanical properties of PVC products and broadening PVC applications. Even though durable PVC products have a longer service life than other plastics, they will ultimately become solid waste. It is an environmental problem because of its high chlorine ratio of about 56% and is non-biodegradable. The above points made it rank advanced among the most common types of the most considerable amounts of plastic wastes [1, 3]. Researchers are increasingly focusing on converting these highly toxic and harmful wastes into other new products that are useful and have fewer effects on the environment and health. The primary way for this object is the pyrolysis process, which has a significant advantage over other traditional ways in wastes management like landfilling, burning, and recycling. Pyrolysis is a thermal decomposition in the absence of oxygen. The pyrolysis process will break down polymer chains into low molecular weight compounds. The by-products of plastic pyrolysis could be used as fuels or chemicals. Two types of pyrolysis processes are known (i.e. thermal non-catalytic pyrolysis and catalytic pyrolysis) [2]. Jie Yu et al. examined various chemical recovery approaches for PVC, such as pyrolysis, catalytic dichlorination, and hydrothermal treatment, to resolve the energy problem and the effects of PVC environmental degradation. The dehydro-chlorination of PVC will catalyze and accelerate the pyrolysis process. Metal oxide catalysts, depending on their basicity (i.e. the number of hydrogen atoms replaceable by a base in a particular acid), behaved primarily as adsorbents for the evolved HCl or as inhibitors of HCl formation. While, zeolites and noble metal catalysts may create lighter oil, depending on the total number of acid sites and the number of accessible acidic sites. PVC decomposes in 3 stages: PVC was dehydro-chlorinated to form polyene in the first region less than 250 °C; polyene decomposed to low-molecular-weight compounds in the second region (250 - 350 °C), and polyene further decomposed to a considerable number of low molecular weight compounds in the third region at more than 350 °C [1]. Nisar et al. used thermo-gravimetry to study the pyrolysis action of polyvinyl chloride (PVC) in the presence of commercially available oxide catalysts. The pyrolysis was carried out at a rate of 5°C/min in a temperature range of 200-650 °C. The thermo-gravimetric properties in terms of maximum degradation temperature reduction and percent change in weight were investigated with a larger pore size and surface area, silica gel and alumina catalysts were found to be the most active materials in terms of lowering the overall degradation temperature and increasing the percentage of conversion, both alumina and silica had performed well [5]. Sharma et al. investigate the catalytic degradation of PVC in a fluidized bed reactor using three catalysts (Fe<sub>2</sub>O<sub>3</sub>, ZSM-5, and Pd/Al<sub>2</sub>O<sub>3</sub>) at temperatures ranging from 100 to 430 °C. It was decided to adsorb liberated chlorine on CaCO<sub>3</sub>. The effect of feed to catalyst ratio and temperature on maximum liquid yield was investigated. Using catalyst ZSM-5 at a 3:1 feed ratio, a maximum liquid yield of 12.17 wt% was obtained [3]. The pyrolysis of PVC in a batch reactor was studied by Vijayakumar et al, with a temperature range between 220 – 520 °C and with a heating rate of 10°C/min. Liquid oil obtained was of range 12 wt% to

12.79 wt% under 2 bar operating pressure [6]. A comparison between PVC liquid pyrolysis product and diesel fuel was made by Manickaraja et al, with and without catalyst. The yield obtained by this method was discovered to be 20 wt% higher than the yield obtained without the catalyst. The property test results were found to be roughly equal to those of diesel fuel, and the best blend for engine testing was discovered to be a 25% blend. It can be inferred that waste PVC oil may be used as a renewable fuel for internal combustion engines [7]. This study aims to examine the selection of the appropriate method for this degradation, to investigate the physical properties of the liquid products (i.e. petroleum derivatives), and to compare the quantity and components of the liquid and gaseous products from the used pyrolysis processes. In this study, the liquid and gaseous products from the two cracking processes were compared in the case of a catalyst (i.e. the catalytic hydrocracking process over monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and bimetallic NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts) and in the absence of a catalyst (i.e. the non-catalytic thermal process) to solve the problem of plastic accumulation and reducing harmful environmental effects by converting PVC wastes into oil derivatives with high value and considering this as an alternative to petroleum refining derivatives.

## 2. Materials

Waste PVC produced from pipes and electrical product of PVC was collected from industrial wastes in Baghdad. Hydrogen and Nitrogen gases with a purity of 99.9 % were supplied from the factory of Al-Khaleej for Industrial gases. Alumina (Al<sub>2</sub>O<sub>3</sub> with 99% purity) was obtained from Sigma Aldrich-Germany. Nickel (II) Nitrate (99% Ni(NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O, Mwt. 290), Ammonium Molybdate (NiMo) (99.6% (NH<sub>4</sub>)<sub>6</sub>MO<sub>4</sub>O<sub>24</sub>.4H<sub>2</sub>O, Mwt. 1235) and tetraammine platinum (II) nitrate (99.9 % purity Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, Mwt. 387.21) were all obtained from Sigma-Aldrich company.

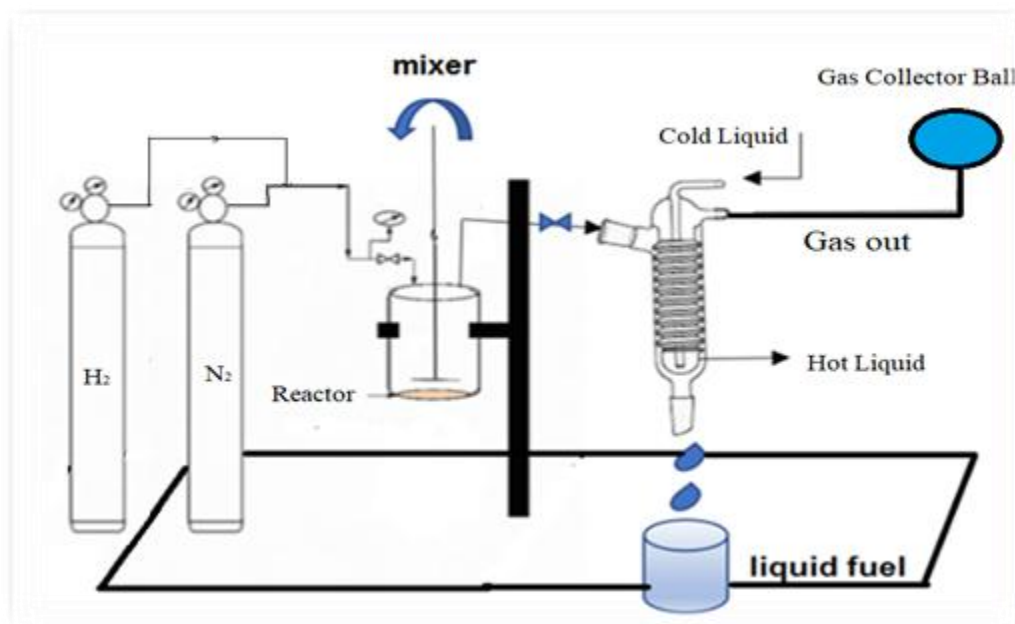
## 3. Characterization of PVC Feeds, Catalysts, and Products

TGA analysis was carried out for PVC using Universal V4.5A TA Instruments Company with high-temperature property providing TA universal software applied for data analysis. The crystalline structure of the prepared catalyst was investigated by the X-ray diffractometer with a 2θ range from 0° to 90° with a scan rate of 2 (deg/min) in the Nanotechnology and Advanced Materials Research Center, University of Technology. The prepared catalyst was also characterized by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) from (FEI Inspect S50, Holland) at the Applied sciences departments, University of Technology. The physical properties of the product liquid were tested by conventional methods according to "ASTM Petroleum Test Methods" of measuring viscosity, density, flash and pour points. The liquid and gas product compositions were investigated using a gas chromatography-mass spectrometer in the ministry of science and technology of the type (GCMS-QP2010 Plus, Shimadzu, Japan).

## 4. System and Experimental Method

The reactor, condenser, and gas separator systems were used to perform the tests in this study. Stainless steel experimental rig of the 0.3 L volume, semi-batch laboratory autoclave reactor type from parr company, USA has been used for this purpose. The PVC wastes were thermally and catalytically pyrolyzed to crack this polymer into gas, liquid, and solid char. In the beginning, the reactor was filled with either waste PVC or PVC and catalyst to do thermal or catalytic hydrocracking as needed. The reactor has an input line supplied with a needle valve to feed the desired gas before and during the operation. The gas will be nitrogen if thermal pyrolysis and hydrogen if catalytic hydrocracking. The output line is provided with a ball valve to discharge gases away from the reactor and trap them if needed to increase pressure inside the reactor. In addition, the reactor is provided with a mixer, pressure gauge with a limit of 25 bar, K-type thermocouple sensor, and it is surrounded by an electrical jacket 1000-W heater. A PID controller monitored the temperature inside the reactor. The reactor was followed by a cooling system which consists of a condenser, chiller, and gas separator to condense the high-temperature products from the reactor. A 1.2-m condenser was supplied with coolant from a chiller system. The

non-condensable vapours and gases were separated by a gas separator, and they were collected in rubber bags for examination later. The produced liquid was dropped and assembled in a container. Figure 1 shows a laboratory system that was used in this work.

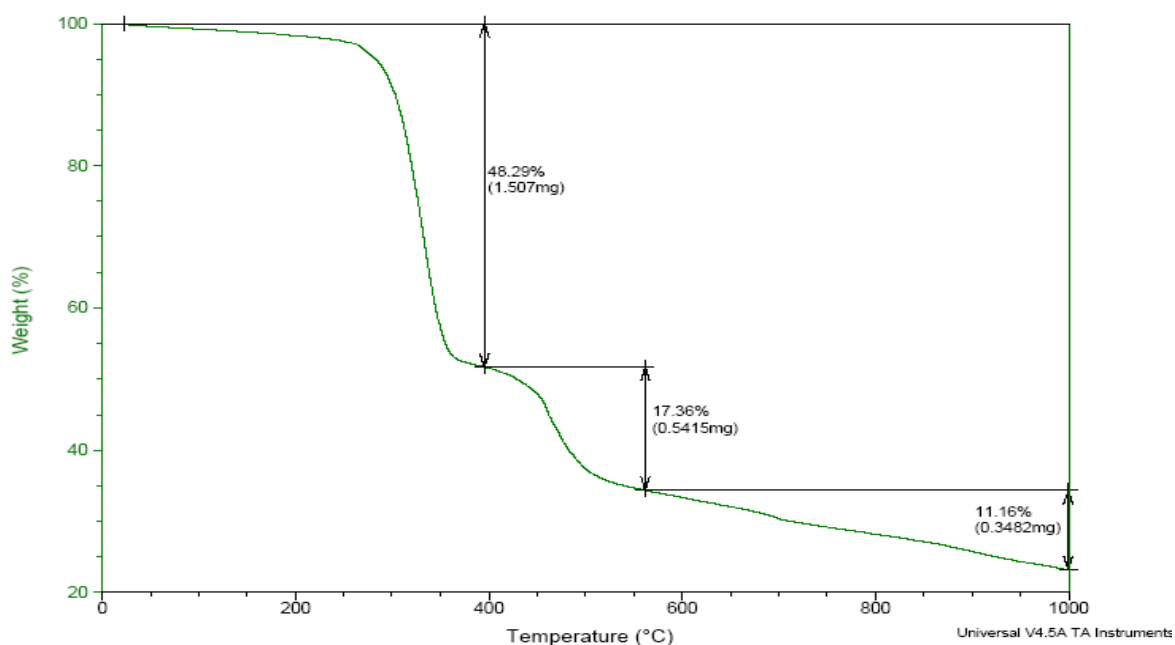


**Figure 1:** A sketch of the experimental system.

## 5. Results and Discussion

### 5.1. PVC Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) is a thermal analysis technique that measures the weight loss of material as a function of temperature in a controlled inert environment [8] [9]. TGA can demonstrate in the range when decomposition begins and ends at a material temperature with a heating rate of 10°C/min. Figure 2 shows TGA analysis for PVC.



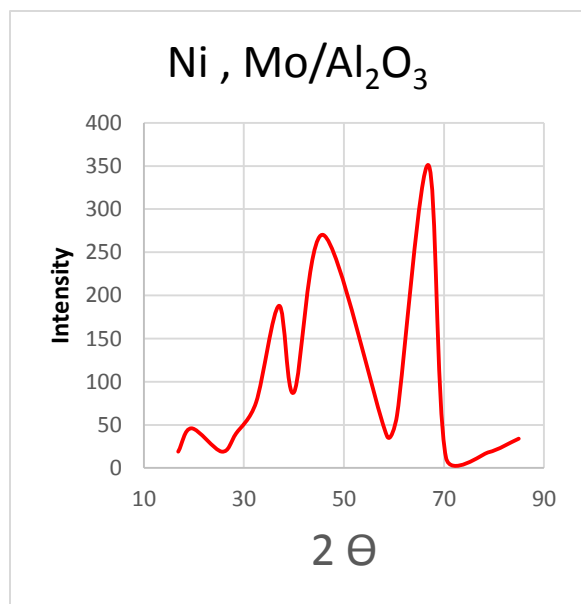
**Figure 2:** TGA for PVC plastic.

The weight loss in PVC defers from other plastics types. The decomposition can be divided into three regions instead of only two for polymers like PE, PP, or others. The first region of degradation is slightly decreasing weight because the moisture evaporates and impurities burn. In contrast, the second started at about 180-250 °C and ended at 375-390 °C and the third at 410-490 °C and continued to more than 550-1000 °C. It can be generally seen that more than 48% of weight loss was taken due to dichlorination of PVC since the chlorine gas was released at this temperature owing to breaking its weak bond within the polymer structure (i.e. dehydrochlorination due to the elimination of HCl molecules leaving behind longer polyene chains). Chlorine gas makes up a large part of polymer weight, reaching 56 wt% [1][3][10]. The other step also included the polymer decomposition that occurred (i.e. thermal degradation of the polyene sequences during this stage yielding volatile aromatic and aliphatic compounds).

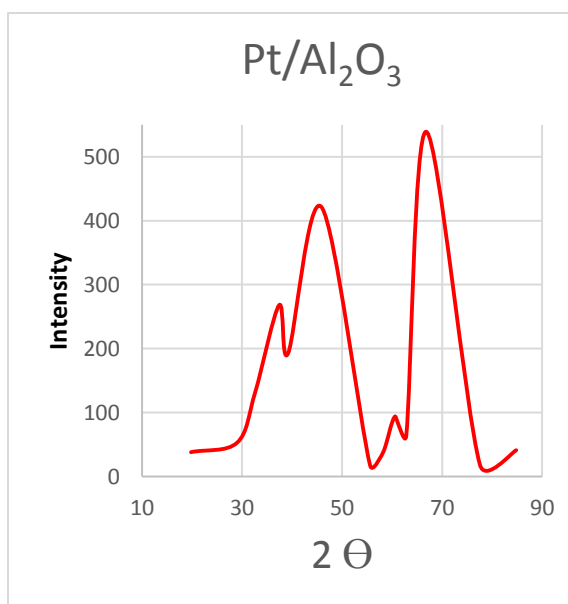
## 5.2 Catalyst Characterization

### 5.2.1. XRD Analysis

XRD was used to determine the materials crystalline structure of the two catalysts. The results of the XRD analysis are shown in Figures 3 and 4. It can be seen, three high diffraction peaks at a 2 theta angle of 67°, 46°, and 37° of each catalyst pattern, suggesting the crystalline structure of Alumina, which is the main supported content, and these results are in good agreement with the literature [11],[12],[13]. Furthermore, platinum, molybdenum, and nickel metals loaded onto alumina support can cause low-intensity peaks compared to alumina peaks when used alone [14]. The XRD patterns for the prepared catalysts, however, do not appear to have a well-defined peak of the metal support content due to the small percentage and small particles of loaded metals as documented [15], which should appear after 15 percent of the metal loading to be clear [16]. The synthesized catalyst has weak peaks in the XRD pattern, indicating small metal particle sizes and high metal dispersion. Increased dispersion of the metals (i.e. Pt, Ni, and Mo) inside the catalyst framework contributes to the formation of more active sites and the adsorption of more hydrogen, which improves the catalyst's operation and stability, as already reported [14][13].



**Figure 3:** XRD pattern of Ni, Mo / Alumina catalyst.



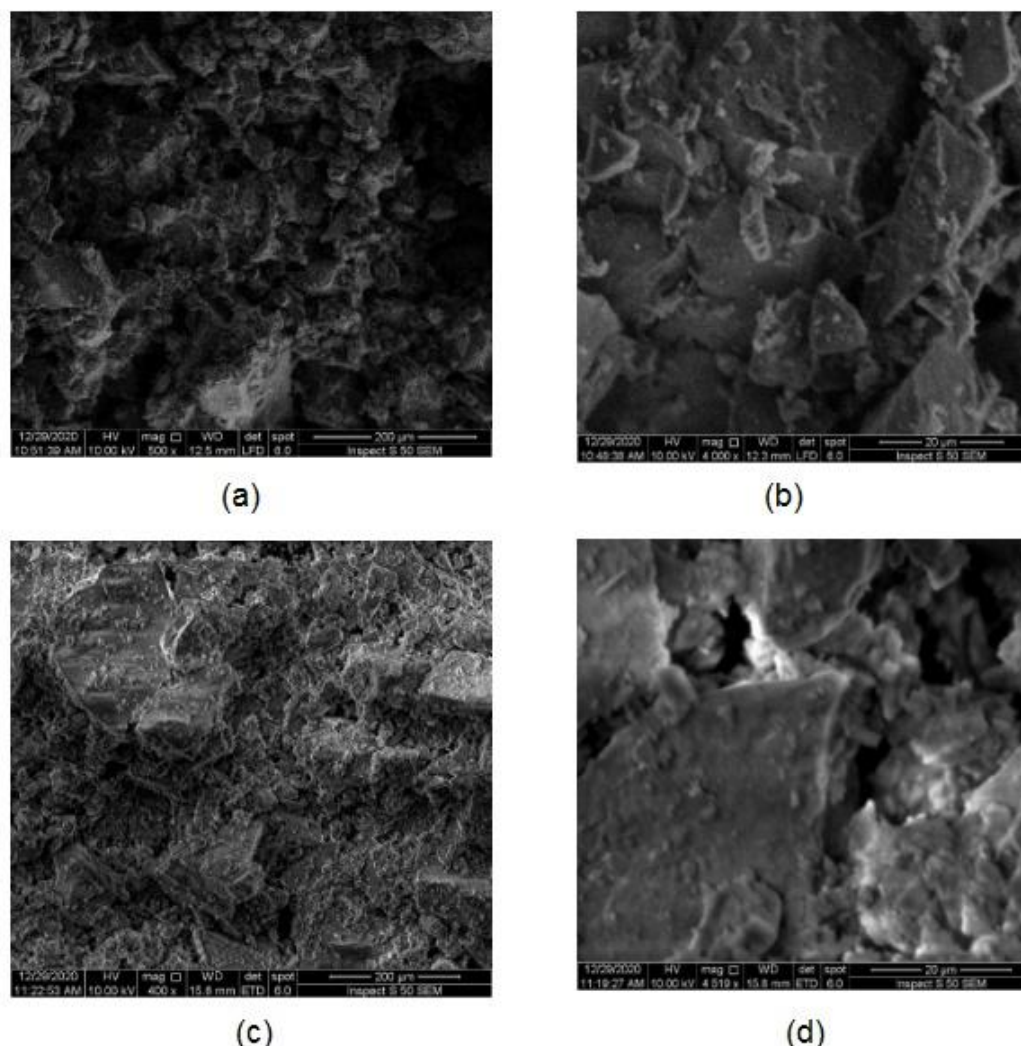
**Figure 4:** XRD pattern of Pt / Alumina catalyst.

### 5.2.2. SEM and EDX Analyses

Figure 5-a, b, c, & d displays the SEM images of the two forms of catalysts after wet impregnating Alumina with metals at various magnifications. It can be seen that the structural morphology is prominent, having sharp and



segregate edges, which agrees with other published results [17][9]. This finding, combined with the EDX results, indicates that the metals are distributed uniformly on the alumina support phase. The first catalyst has a metal ratio of 6.73 weight percent Mo and 1.37 weight percent Ni, while the other has a metal ratio of 0.21 weight percent Pt. It demonstrates that the metal was successfully loaded onto the alumina surface.

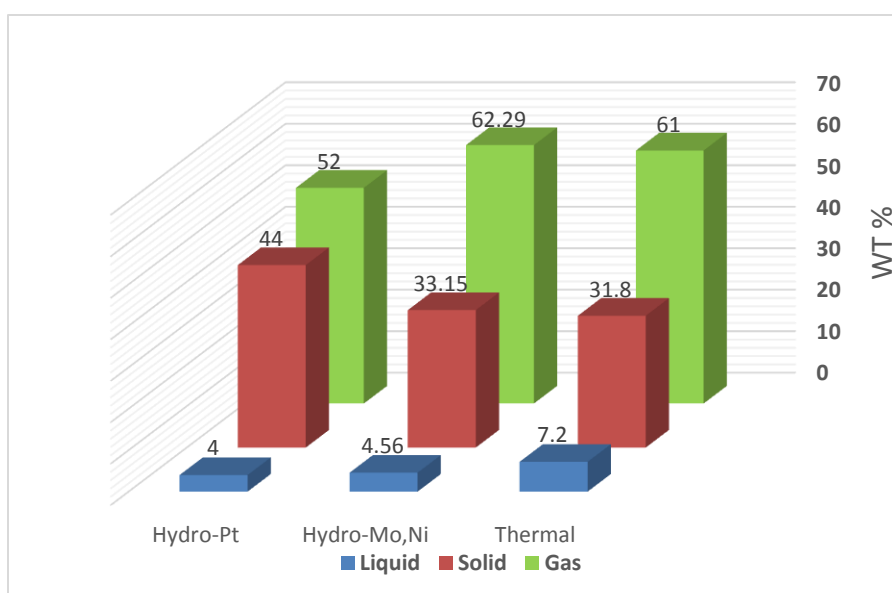


**Figure 5:** (a) & (b) SEM images for Ni, Mo / Alumina catalyst and (c) & (d) SEM images for Pt / Alumina catalyst.

### 5.3. Experimental Pyrolysis Process

The choice of operating conditions was based on the minimum proportion of solid residue that was produced from the pyrolysis process, if the amount of solid residue is small led to easy separation and recovery of the catalyst remaining in the reactor. So, several experiments were conducted to locate this optimum operating condition. It was found that a temperature of 450 °C and a pressure of 20 bar for an hour give the lowest possible percentage of semi-solid residue and the least possible agglomeration of the remaining materials produced in the reactor. In this way, the catalyst can be extracted and reused again in the following pyrolysis process after regeneration (i.e. reactivation by heating the spent catalyst under airflow and high temperatures to remove the coke accumulated on its surface as a result of the cracking reaction). Quantities of gas, liquid, and solid residue were produced in different weight ratios through the laboratory experiments. The ratio of the liquid was about 7.2% by weight in non-catalytic thermal cracking reaction, while it was found about 4 and 4.56 wt% when using Pt/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts in hydro-cracking reactions, as clearly shown in Figure 6. Although the amount of liquid fuel, resulting from the thermal decomposition process of plastic in the absence of the catalyst

appears to be high compared to the decomposition in the presence of the catalyst, it is harmful to the environment due to the amount of hydrochloric acid produced in it, as will be explained in detail later. On the other hand, the gas ratio was about 61 wt% in the thermal reaction and about 62.29 and 52 wt% throughout the hydrocracking reactions over NiMo/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. The proportion of the gas product is much higher than that of the liquid product owing to higher temperature and pressure inside the reactor, which leads to further cracking of long-chain bonds into smaller of lower molecular weight and also due to PVC dichlorination under these severe conditions, which leads to cracking of weak chlorine bond in the polymer structure that will produce hydrochloric acid and chlorine gas as it was previously reported [1]. It was also observed that the gaseous products decreased by about 10% by weight when using the platinum-loaded alumina catalyst with an increase in the percentage of the remaining solids on its surface by about 11% by weight, this result due to the indication that the rate of the hydro-cracking reaction on the surface of this type of catalysts is slower compared to the nickel & molybdenum-loaded alumina catalyst as the latter is more active in such kind of reaction. Finally, the residue ratios were found to be 31.8, 33.15, and 44 wt% in thermal reactions without catalyst and hydro-cracking over NiMo/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, respectively.



**Figure 6:** The spectra of products for all types of reactions.

#### 5.4. Physical Properties of Liquid Product

As shown in Table 1, the liquid formed from the pyrolysis process was seen in different colors with a slight difference in density and viscosity. Because of the high temperature and pressure conditions used in this work, therefore the density of the liquid product is assumed to be lower. The orange color of the liquid products from the thermal cracking process can usually be attributed to the increase in the amount of hydrochloric acid in it, and the color usually tends to be yellowish-green. The API-gravity was calculated to be 65.0 in non-catalytic thermal cracking and 70.6 and 59.7 in hydro-cracking over NiMo/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. Whereas the liquid products of the reaction can be classified as being within the limits of light crude oil, which has an API-gravity higher than 31.1 degrees (i.e. less than 870 kg/m<sup>3</sup>). An increase in the API value indicates that more cracking happened to the liquid hydrocarbons led to an increase in transport characteristics of the produced oil [2]. The API value can be relied upon in determining the quality of crude oil and its mixture of hydrocarbons, which contain a wide variety of molecular weights. Although the value of the API does not take into account the actual chemical composition of the crude, it is very important when determining the market

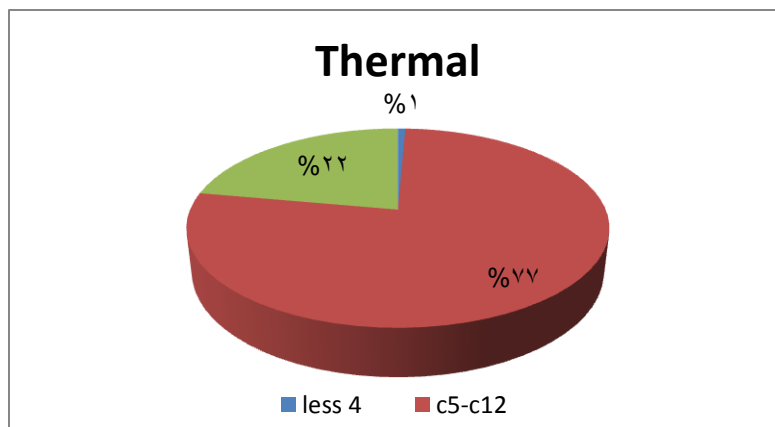
value of crude oil in terms of its classification according to ease of transportation and refining. In addition, the viscosity of the light crude oil produced shows a match with the result of the density calculation as well as the products of the non-catalytic thermal test shows a slightly higher value of the kinematic viscosity than that from catalytic hydrocracking. Furthermore, the results of flash point demonstrate that the catalyst efficiency follows the trend:  $\text{NiMo}/\text{Al}_2\text{O}_3 < \text{Pt}/\text{Al}_2\text{O}_3 < \text{non-catalytic thermal cracking}$ . The pour point results track the same context as the flashpoint results. These results confirm that the light liquid petroleum product from the reactions of recycling spent PVC-polymers has excellent flow characteristics under specific conditions.

**Table 1:** Physical properties of liquid product.

No. of test	Operation type	Output color	Density (g/cm <sup>3</sup> )	API-gravity	Viscosity (cSt)	Pour point °C	Flash point °C
1	Thermal	Orange	0.72	65.0	2.54	-8	71
2	NiMo/Al <sub>2</sub> O <sub>3</sub>	Yellow	0.70	70.6	2.23	-11	68
3	Pt/Al <sub>2</sub> O <sub>3</sub>	Yellow	0.74	59.7	2.40	-10	70

### 5.5. Characterization Results of Liquid Product

The liquid products from three experiments were also investigated using chromatography-mass spectrometry as the components of this liquid are similar to the hydrocarbon components of petroleum [18] [19] [20] [21]. Figures 7, 8, and 9 are shown the components of the mixture liquid product concerning the number of carbon atoms depending on GC-MS results. A gasoline range hydrocarbons of (C<sub>5</sub> – C<sub>12</sub>) [22] [23] and diesel fuel in the range of (C<sub>13</sub>–C<sub>28</sub>) [23] [24]. It can be seen that the catalytic hydrocracking using NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst appears to break down large hydrocarbon molecules from waste PVC into smaller molecules, and this was not applied in the case of using Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, which gives a lower performance. The results of GC-MS also showed that the ratio of gasoline range components is higher in the hydrocracking process over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst and reaches about 93 wt% with only 6 wt% of diesel, while in the hydrocracking process over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, it was found that the ratio of gasoline range components is 73 wt% and the diesel range ratio is 27 wt%. On the other hand, when thermal cracking is used, the ratio becomes 77 and 22 wt% for gasoline and diesel, respectively.

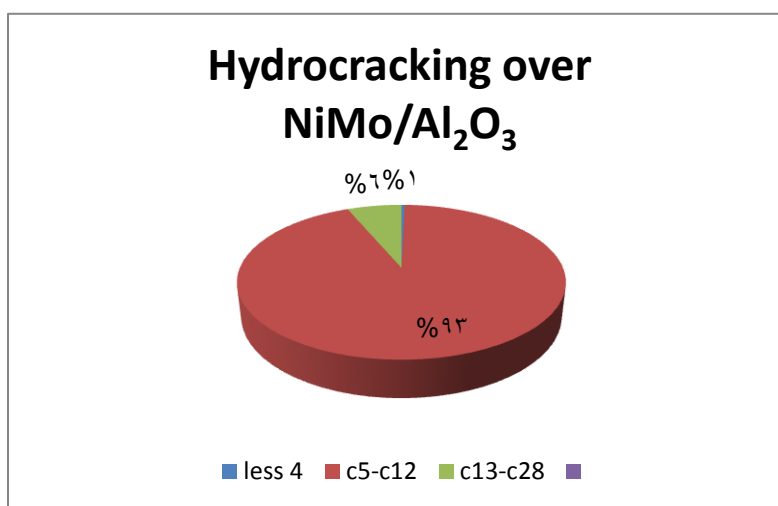


**Figure 7:** Thermal cracking components.

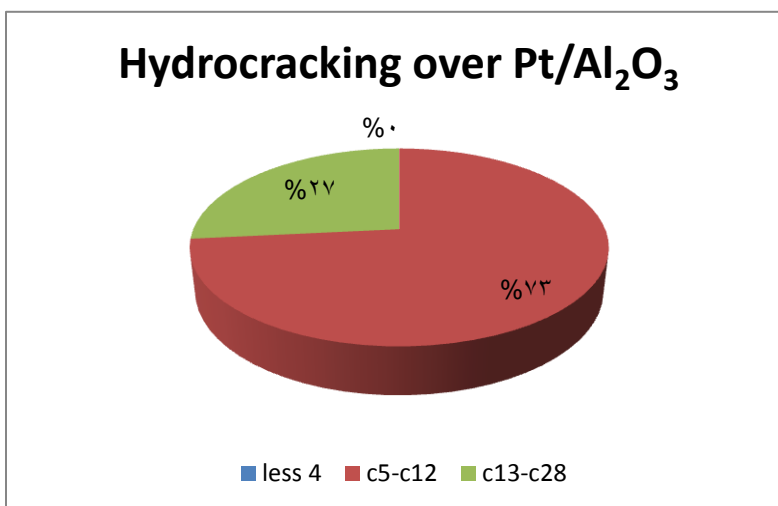
From another point of view and as illustrated in Table 2, the saturated aliphatic compounds reach a ratio of 72.81 wt% by using NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, while it was found to be approximately 64 and 63.5 wt% over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and thermal cracking, respectively. This means that the hydrocracking process can give more stable saturated composition products than the thermal cracking process, taking into account that NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst gives the best products results than Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. This result can be attributed to the emergence of acidic



cracking sites with the presence of two types of metal sites, namely molybdenum and nickel, for the hydrogenation and dehydrogenation reactions within this catalyst and that may catalyze the hydrocarbons of unsaturated aromatic compounds in the presence of hydrogen and convert them into a saturated aliphatic compound. The largest amount of aromatics, about 23.83 wt%, was also found in the liquid product of thermal cracking, and this ratio was 21.07 and 21.88 wt% for NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst and Pt/Al<sub>2</sub>O<sub>3</sub>, respectively. Additionally, there are small amounts of other hydrocarbons such as alcohols and ketones that may come from the reaction of the hydrocarbons with fillers or colorants that have been added as additives throughout the manufacture of the final PVC plastic products, which was referred to in Table 2 under title others.



**Figure 8:** catalytic hydrocracking components over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst.



**Figure 9:** catalytic hydrocracking components over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 2:** The proportions of hydrocarbons product in the liquid phase.

Operation Type	Aromatics wt%	Saturated Aliphatic wt%	Unsaturated Aliphatic wt%	Others wt%
Thermal	23.83	63.52	9.68	2.97
NiMo/Al <sub>2</sub> O <sub>3</sub>	21.07	72.81	0.45	5.67
Pt/Al <sub>2</sub> O <sub>3</sub>	21.88	64.01	1.88	12.23

### 5.6. Gas product characterization results

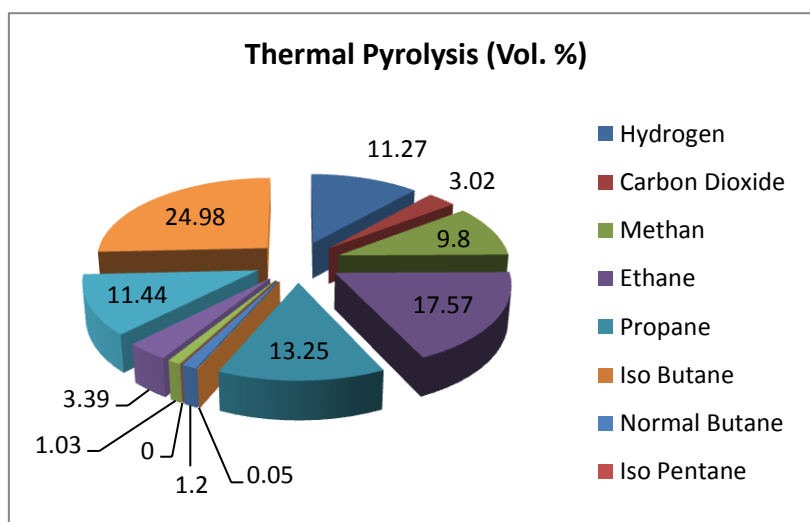
After condensation and liquid separation, the remainder of the non-condensing gas leaving the separator was collected with a rubber ball and subsequently analyzed by gas spectrometry (GC). As mentioned earlier during this study (Section 5.1), the decomposition of PVC has been begun up to 250 °C with dehydro-chlorinated and continued to decompose until 400 and 500 °C. Consequently, the gas collection was begun far from 250 °C, when the temperature reached 400 °C, to ensure that almost all hydrogen chloride and chloro-compounds were excreted. Table 3 shows the percentage of product gases components. Hydrogen gas yield in thermal pyrolysis recorded a ratio of 11.27 vol% while its volumetric ratio in hydrocracking over NiMo/Alumina and Pt/Alumina was 39.21 and 38.35 %, respectively, and this is due to the hydrogen amount inside the reactor formed for the period of hydrogenation/ dehydrogenation reactions. On the contrary, about nitrogen gas, it can be seen in thermal pyrolysis, the volume ratio of nitrogen was 11.44%. In contrast, the percentage ratio of nitrogen was much lower in the hydrocracking and catalytic reactions over NiMo/Alumina and Pt/Alumina, where it was within the range of 0.36 and 0.42 vol%, respectively. This can be attributed to the fact that the decomposition process of the plastic in the absence of the catalyst takes place in the presence of nitrogen-free of oxygen, while hydrogen plays the primary role in the cracking reactions in the presence of the catalyst.

**Table 3:** The proportions of hydrocarbons Product in the gas phase.

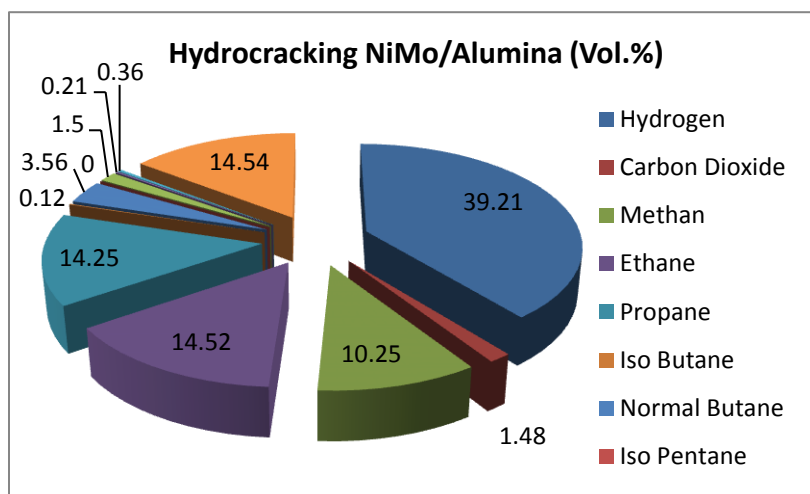
Resulting Components	Thermal Pyrolysis (Vol. %)	Hydrocracking NiMo/Alumina (Vol.%)	Hydrocracking Pt/Alumina (Vol. %)
Hydrogen (H <sub>2</sub> )	11.27	39.21	38.35
Carbon Dioxide (CO <sub>2</sub> )	3.02	1.48	0.93
Methane (CH <sub>4</sub> )	9.80	10.25	16.33
Ethane (C <sub>2</sub> H <sub>6</sub> )	17.57	14.52	15.36
Propane (C <sub>3</sub> H <sub>8</sub> )	13.25	14.25	14.39
Iso Butane (I-C <sub>4</sub> H <sub>10</sub> )	0.05	0.12	0.09
Normal Butane (N-C <sub>4</sub> H <sub>10</sub> )	1.2	3.56	4.48
Iso Pentane (I-C <sub>5</sub> H <sub>12</sub> )	0	0	0
Normal Pentane (N-C <sub>5</sub> H <sub>12</sub> )	1.03	1.5	0.05
Oxygen (O <sub>2</sub> )	3.39	0.21	0.24
Nitrogen (N <sub>2</sub> )	11.44	0.36	0.42
Hydrogen chloride (HCl)	24.98	14.54	13.36
Total	100	100	100

In addition, regarding the burnable hydrocarbons like methane, ethane, propane, and pentane in output gas, as shown in Figures 10, 11, and 12, the produced methane was found to be 9.8 vol% from thermal non-catalytic pyrolysis. It was increased to 10.25 and 16.33 vol% using NiMo/Alumina and Pt/Alumina, respectively. The ethane showed an opposite behaviour from methane which was 17.57 vol% in a thermal, and it was decreased to 14.52 and 15.36 vol% by using NiMo/Alumina and Pt/Alumina in catalytic hydrocracking, respectively. A significant amount of propane appeared in the product gas compared with the small proportions of both pentane and butane, which was 13.25, 14.25, and 14.39 vol% in non-catalytic process, catalytic process over NiMo/Alumina, and Pt/Alumina, respectively. This different behavior can be attributed to the difference in the reaction mechanism in both cracking processes, as the free radical mechanism of ( $H^\cdot$ ) is predominated throughout the thermal cracking reaction, which involves random disruption of chemical-bound between neighboring carbon atoms. While in catalytic cracking, the uniform cracking of hydrocarbons on the surface of the catalyst follows the rule of *beta*-scission (i.e. carbonium ion mechanism) has occurred in which the

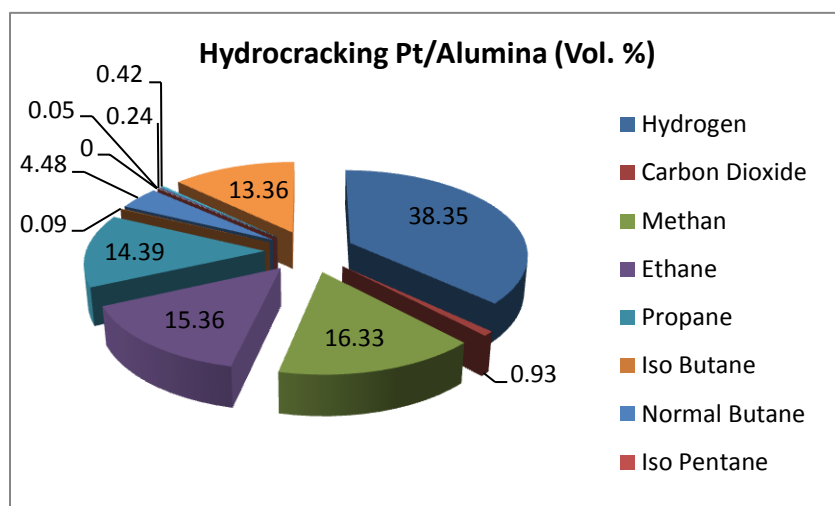
conventional carbon-carbon bonds rupture at pre-determined locations within the hydrocarbon molecule rather than randomly (i.e., uncertain definite location) as in the thermal cracking, and that may lead to more complex reactions that cause the occurrence of more cracking and saturation of hydrocarbons and reduce unwanted by-products. Furthermore, other gases like carbon dioxide and oxygen appeared due to plastic additives like colourants, fillers, etc., which may contain these elements. Hydrogen chloride also appeared with a ratio of 24.98, 14.54, and 13.36 vol% in the output product of thermal and hydrocracking over NiMo/Alumina and Pt/Alumina, respectively. This ratio was expected to appear due to the non-released amount that stayed in the reactor from the first decomposition stage, and this finding confirms what was previously mentioned that the presence of the catalyst and hydrogen significantly reduces the number of undesirable substances such as hydrogen chloride, which cause corrosion of the reactor walls and systems pipes, as well as causing the catalyst to wear out and reduce its life and activity during the reaction. The presence of a small number of chlorine compounds in petroleum derivatives from the decomposition of PVC is a very important advantage as it relates to the ability to use these products safely as direct fuel away from the health and environmental risks of harmful chlorine compounds [25].



**Figure 10:** Spectra of hydrocarbons produced in the gas phase from non-catalytic Thermal cracking.



**Figure 11:** Spectra of hydrocarbons produced in the gas phase from catalytic hydrocracking over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst.



**Figure 12:** Spectra of hydrocarbons produced in the gas phase from catalytic hydrocracking over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

## 6. Conclusions

The use of severe conditions of 20 bar and 450 °C in the pyrolysis process of PVC was led to a decrease in the amount of liquid yield and increased the gas products. GC–MS analysis of liquid produced from the catalytic hydrocracking with the presence of bimetallic NiMo/Al<sub>2</sub>O<sub>3</sub> gives the highest percentage of gasoline range component (C<sub>5</sub> – C<sub>12</sub>) than using monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and/or thermal cracking attributed to the appearance of acidic cracking sites with the presence of two types of metal sites, namely molybdenum and nickel, for the hydrogenation and dehydrogenation reactions while using of catalytic hydrocracking by Pt/Al<sub>2</sub>O<sub>3</sub> gives the highest percentage of diesel range component (C<sub>13</sub>–C<sub>28</sub>). The ratio of gasoline range components in the hydrocracking process over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst reaches about 93 wt% with only 6 wt% of diesel, while in the hydrocracking process over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the ratio of gasoline range components is 73 wt% and the diesel range ratio is 27 wt%. On the other hand, when thermal cracking is used, the ratio becomes 77 wt% and 22 wt% for gasoline and diesel, respectively. Most of the gas was produced in a non-catalytic thermal reaction, which is about 62.29 wt%, while the largest amounts of saturated aliphatic, about 72.81 wt%, were found in the liquid product of NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The aromatics hydrocarbon compounds reach a ratio of 23.83 wt% by using the thermal cracking, while it was found to be approximately 21.07 wt% and 21.88 wt% over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst and Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, respectively. The liquid products of the reaction can be classified as being within the limits of light crude oil. The results of density, viscosity, flash point, and pour point of the produced oil show that the catalyst efficiency follows the trend: NiMo/Al<sub>2</sub>O<sub>3</sub> < Pt/Al<sub>2</sub>O<sub>3</sub> < non-catalytic thermal cracking. These results reinforce the hypothesis that the oil produced from the spent plastic recycling process is high quality and has excellent flow characteristics. Finally, GC-MS analysis of the gas produced from the decomposition of PVC during the presence and/or absence of the catalyst showed that it contains burnable gases such as methane, ethane, propane, butane, and pentane in different proportions. The reason for this is mainly due to the difference in the cracking reaction mechanism between the two processes. The percentage of hydrogen produced from cracking reactions in the presence of the catalyst was very high. It was 39.21 wt% for NiMo/Al<sub>2</sub>O<sub>3</sub> and 38.35 wt%, while the percentage of nitrogen produced from cracking reactions in the absence of the catalyst was excessive less than 1wt % for the two catalysts, while it was 11.44 wt% for the thermal cracking process. It was confirmed that the generated undesirable product such as hydrogen chloride (HCl) was very little in the hydrocracking and catalytic reactions compared to non-catalytic thermal cracking reactions where the percentage was much higher because all the hydrogen produced due to the cracking of hydrocarbons turns into harmful acidic components.

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## Conflict of Interest

The authors declare that they have no conflict of interest.

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