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## KINETIC STUDY OF HYDROCARBON LIQUID PRODUCTION VIA THERMAL AND CATALYTIC PYROLYSIS FOR LOW-DENSITY POLYETHYLENE

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**ABSTRACT:** - Pyrolysis process becomes an interesting technique to shrink the increasing amounts of the plastic waste. Iraqi kaolin clay has used as a catalyst for the pyrolysis of polyethylene plastic in order to produce the hydrocarbon liquid fuel. The pyrolysis process carried out for low-density polyethylene plastics in semi-batch open system reactor in a temperature range of 370 to 450°C.

Thermo-gravimetric analysis for the plastic presented the range of degradation was between 349 and 489 °C. The pyrolysis results show a remarkable increasing of the hydrocarbon liquid yield produced from the catalytic pyrolysis process by Iraqi kaolin compare with the thermal pyrolysis results. The kinetic study demonstrates that the pyrolysis temperature affected the catalytic production rate of hydrocarbon liquid more than the thermal process.

The characterization of the liquid hydrocarbon products by the Fourier Transform Infrared spectroscopy shows that alkanes were the main compounds in the produced hydrocarbon liquid while the x-ray diffraction indicated no sulphur in the produced hydrocarbon liquids. The ASTM distillation reported obvious increasing in the total light fractions (below 250 °C) for the catalytically pyrolysis reaction products.

Keywords: Polyethylene, Pyrolysis, Kaolin, Kinetic.

## **1- INTRODUCTION**

Plastic is one of the most widely used materials in our lives. Plastic has different properties like low thermal conductivity, resistance to chemicals, lightweight, energy efficiency and low cost. Plastic can produced in to varying thickness and forms. All of these factors lead to increasing the demand for plastic [1].

Plastic has become a needful part in our today's world so the production of plastics has increased with the growing population by an average of roughly 10% every year on a universal basis the fifties of the last century. The entire worldwide production of plastics increased from around 1.3 million tons (MT) in 1950 to 230 MT in 2009[2]. Also plastic are non-biodegradable materials; hence, the live cycle of most plastic materials ends at waste plastic facilities [3].

Generally, polyethylene (PE) is one of the largest commodity plastic material in the world. Polyethylene consists from two types: high-density polyethylene (HDPE) and low-density polyethylene (LDPE). HDPE has wide uses start from the rigid containers used as fuel tanks for vehicles to milk jugs, while LDPE uses include flexible films such as grocery and dry cleaning bags [4, 5].

Recycling of plastics is the most attractive method. It is one of the three methods for throwing away and minimization of waste plastic like incineration and landfill. Recycling is able to solve the problem of waste plastic. It divided to mechanical recycling (primary and

secondary) and feedstock recycling or chemical recycling. Feedstock recycling is try to convert waste plastic to its starting monomers by solvolysis include (glycolysis, methanolysis, ammonolysis and others) or to useful hydrocarbon fuel by thermolysis which include gasification, hydrogenation and pyrolysis [6].

Pyrolysis is thermal cracking reaction, which involves breaking bonds of the large molecular weight polymer carbon chains under oxygen free environmental and produces small molecular weight molecules [7]. The pyrolysis process can deals with all mixtures of wastes plastic consisting of various sorts of plastics without sorting or treatment [8].Pyrolysis has high capability to convert wastes plastic, even of small quantities, into useful hydrocarbons. It is becoming a promising alternative, in order to recover fuel oil and hydrocarbons feedstock [9, 10].

The main products of the pyrolysis process of wastes plastic is hydrocarbon gases, hydrocarbon liquids, solid and coke. The liquids can either be fuels for power generation stations and boilers [11], or as a feedstock for further refining processes to produce high quality fuels. The gases can used as fuel to generate the heat required for the pyrolysis reactor, or liquefied as fuels [12].Some types of plastics are suitable for pyrolysis process such as polyethylene, polypropylene, and polystyrene 950 ml of oil recovered from 1 kg of them [13].The coke deposits inside the pyrolysis reactors [14].Less than 1 wt. % of coke when about 80 wt. % of hydrocarbon liquid obtained from pyrolysis of polyethylene at 400 °C in semi-batch reactor with mixing [15].

The catalysts (involving acid-catalysts silica-alumina, zeolite and non-acidic meso-pours silica catalysts) employed in pyrolysis usually accelerate the breakdown of high molecular weight compounds into smaller products for the purpose of improving selectivity and imparting certain desirable characteristics to the final product, such as volatility and flash point of liquid fuel [16, 17].

In batch reactor, the material fed either into batches for pyrolysis at the beginning of process or after all of the fed materials is processed. A semi-batch reactor removes the pyrolysis products continuously once they generated by a continuous flow of an inert gas (usually nitrogen) at reaction temperature. However, the feed materials added firstly before the pyrolysis process outsets. Secondary reaction may be occurring in the volatile product (e.g. oligomerization, cyclization, and aromatization). This reaction does not happen in batch reactors where secondary reactions are supposed to promote. Lower requirements for heating and cooling of semi-batch reactor are required due to the smaller volume of semi-batch reactors in comparisons to batch reactor [18].

The present work aimed to use a natural Iraqi kaolin clay as a catalyst in order to improve the pyrolysis reaction of LDPE to increase the yield of the hydrocarbon liquid fuel. Characterizations of the selected Iraqi kaolin clay intended. Then, thermo-gravimetric analysis (TGA) performed to understand the pyrolysis performance of LDPE. The best reaction conditions will attained to produce high hydrocarbon liquid yield and good quality by changing reaction temperature and reaction time. Finally, the produced hydrocarbon liquid will characterized.

## 2- RESEARCH DATA AND CALCULATION PROCEDURE

The apparatus used in the pyrolysis of wastes plastic consisted of semi-batch reactor made of carbon steel of 170 mm length, 90 mm inside diameter and 110 mm outside diameter. Thermo-couple (type K) with digital temperature recorder (model number) connected to the top of reactor 120 mm deep was used to measure the temperature inside the reactor. Figure 1 shows the schematic diagram of the semi-batch reactor.

The heat was supplied to the reactor by 3600 Watt external electrical heaters (1600 Watt heater in the bottom of the reactor and 2000 Watt heater surrounding the reactor) to get the required temperature for thermal and catalytic pyrolysis reaction (390 to 450 °C).

At the top end of the reactor, a tubing system connected with two gate-valves. All tubes had 6 mm in diameter and made from copper. Measured amount of nitrogen enters the reactor through one of the tubes located 100 mm inside the reactor with elbow shape, which has three holes to distribute the nitrogen from the bottom of reactor.

The condensate liquid products collected from the bottom of the condenser (450 mm length) and the gases product leaves the system at the top of the condenser.

At the beginning, the batch reactor cleaned with naphtha. 2.5 g of the natural kaolin clay (if catalytic pyrolysis essential) and 50 g of virgin LDPE pellets mounted to the clean reactor. The kaolin particle size was 1630 micrometer with surface area4.93  $m^2/g$ . The chemical compositions of the Iraqi kaolin brief in Table 1.

The virgin LDPE pellets with average particle size of 3 mm with density of 0.918 to  $0.934 \text{ g/cm}^3$  and melting point of 105 to 115 °C. The reactor closed and bolted tightly by ten nets (size 10 mm). Nitrogen supplied several times to purge the air out of the reactor (flashing the system triple for one minute each) before the experiment started.

The two electrical heaters were turned on to attain the required reaction temperature; the accuracy of temperature readings was about  $\pm 5$  °C and the time zero was recorded when the gases started to get out of reactor to the condenser. The chiller supplies the cooling water (at a temperature of 4°C) flows in condenser. The condenser was effective enough to drop the temperature of the pyrolysis product to less than 30 °C.

The product separated in the condenser to non-condensable gases leaves from the top of the condenser to get out of laboratory by fan. While, the liquid and wax collected from the bottom of condenser in sealed cylinder. The collected liquid and wax cooled to 16 °C and separated by vacuum pump in to liquid and wax.

The remaining solid in the reactor was kaolin clay and the coke formed during the reaction. The coke calculated by burned coke and catalyst (kaolin) mixture in oven at temperature 700  $^{\circ}$ C to get the amount of initial catalyst and know the weight of coke. Finally, the gas weight calculated by difference between initial weight of plastic and summation of liquid, wax and coke weight.

## **3- RESULTS AND DISCUSSION**

# **3.1** Thermo-gravimetric analysis and differential thermos-gravimetric analysis of the feedstock

Thermo-gravimetric analysis attained to study the performance of thermal degradation for LDPE. The TGA monitors the weight loss of 20 mg LDPE (under 35 ml/min of nitrogen flow rate) versus the temperature. The heating rate was 20 °C/min from surrounding temperature to 800°C. The weight loss of polyethylene verses temperature curve recorded to know the range of effective temperature for pyrolysis. Test carried out using thermo-gravimetric analyzer TGA (PC SERIIES TGA7).

As shown in Figure2, the LDPE decomposition started at 349°C and was complete at 489°C. The degradation temperature at which the original sample loses 50 % of its weight took place at about 457.49 °C. The second dotted curve represents the differential thermal gravimetric analysis (DTGA). Hypothetically, the peak of the DTGA represents the highest pyrolysis rate for the sample, whatever the product yields. The DTGA of only one peak indicates that there is only one-step of degradation.

#### **3.2 Distribution of pyrolysis products**

The thermal and catalytic pyrolysis products obtained versus different pyrolysis temperatures (370 to 450 °C). The time started to calculate when the first produce hydrocarbon vapor reach to the condenser. The time  $(t_f)$  stopped when no more vapors out from the reactor i.e. no more than hydrocarbon vapor appear. The product distributions for thermal and catalytic pyrolysis of LDPE summarized in Tables 2 and 3, respectively.

Generally, catalytic reaction finished during shorter time than non-catalytic. According to the collision theory, which is the most well-known theory that described the chemical reaction [19, 20], the increasing in reaction temperature causes a rise in molecules activities, which increase of the probability of impacts of the molecules that have more energy to react in the reaction mixture. Thus, higher temperature (430 and 450°C) gives shorter time of pyrolysis.

As the hydrocarbon liquid fuel is the desired product, the maximum yield of liquid, which is about 48.98 wt.%, are produced from the thermal pyrolysis of LDPE at 390 °C. during 38 minutes, while the approximately the same amount (49.60 wt. %) of hydrocarbon liquid fuel yields from catalytic reaction by the Iraqi kaolin in the same temperature but in lower reaction time (only 35 minutes).

At temperatures (410 and 430 °C), when the yield of the hydrocarbon liquid fuel via the thermal pyrolysis declining, remarkable increasing of the yield of the hydrocarbon liquid produced from the catalytic pyrolysis process by Iraqi kaolin has been observed (63.26 to 68.26 wt. %). This selectivity of the kaolin for improving the hydrocarbon liquid yield perhaps owing to the naturally present oxides such as  $Fe_2O_3$  and  $TiO_2$ . At higher temperature (450 °C) both of the hydrocarbon liquid yield from thermal and catalytic pyrolysis of LDPE are decreasing with remarkable increasing of the wax amount.

The expected yield of the hydrocarbon liquid fuel in open semi-batch reactor is less than that yield attained from the closed batch reactor. This decreasing of the liquid yield may be due to the absence of the polymerization reactions of the gases products, which carried out of the reactor with the inert gas.

This consequence is in good agreement of the reported results of the thermal pyrolysis of LDPE in closed batch reactor system. About 73 wt.% of hydrocarbon liquid fuel yield has been obtained only during only 10 minutes at 480°C. This increasing of the liquid yield was due to the polymerization reactions occurred in closed reactor, thus the less gas amount noticed in the final product [21].

#### 3.3Kinetic of hydrocarbon liquid production

The kinetic of the hydrocarbon liquid production from pyrolysis of LDPE has been studied. The thermal pyrolysis study in the temperature range between 370 and 410 °C, however the catalytic pyrolysis studied in temperature range between 370 and 430 °C. The amount of produced hydrocarbon liquid versus time at different temperatures illustrated in Figures 3 and 4. Generally, higher temperature gives higher production amount of hydrocarbon liquid with shorter time. Actually, when the of hydrocarbon liquid increases the rate of the hydrocarbon liquid production was decreasing. Thus, the assumption of the rate of the production of the hydrocarbon liquid ( $r_L$ ) is inversely proportional with the amount of hydrocarbon liquid produced (L) to order n. The proposed production rate kinetic is:

$$r_L = \frac{dL}{dt} \propto \frac{1}{L^n} \dots (1)$$
$$r_L = \frac{dL}{dt} = \frac{k}{L^n} \dots (2)$$

Where k is the production rate coefficient (reaction constant). Integration of Equation (2) between any time and final time gives:

$$\int_{L}^{L_{f}} L^{n} dL = \int_{t}^{t_{f}} k dt \dots (3)$$

Where  $L_f$  is the amount of final production of the hydrocarbon-liquid obtained at stop time ( $t_f$ ) ( $L_f$  in Tables 2 and 3).

$$L_f^{n+1} - L^{n+1} = (n+1)k (t_f - t)... (4)$$

Assume *n* equal to 1, Equation (4) becomes:

$$L_f^2 - L^2 = 2k (t_f - t) \dots (5)$$

The plot of Equation (5) between  $L_f^2 - L^2$  versus  $(t_f - t)$  gives a straight line starting from the origin with slope of 2k. The plots for pyrolysis results thermally and catalytically shown in Figures 5 and 6.

The production rate coefficients (k) calculated from obtained slopes of Figures 5 and 6 at varies pyrolysis temperatures. The values of calculated k versus temperatures for the thermal and catalytic pyrolysis summarized in Table4.

Assume that the production rate coefficient effected by the temperature of the pyrolysis according to the Arrhenius law [19, 20]:

$$k = k_o e^{\left(\frac{-E}{RT}\right)}..(6)$$

Where: k is the production rate coefficient,  $k_0$  is the frequency factor, *E* is the activation energy, *R* is the universal gas constant and *T* is the temperature of the pyrolysis. To find the activation energy of the production rate, a plot of *ln k* versus *1/T* (Arrhenius plot) of Equation 5 gives a straight line, with slope of *-E/R*, and intercept equal to *ln k<sub>0</sub>* as shown in Figure7.The constants values of the Arrhenius equation (Eq. 6) for the thermal and catalytic pyrolysis of LDPE summarized in Table 5.Higher activation energy for the catalytic production rate of hydrocarbon liquid means more effected by pyrolysis temperature, this may be due to influence of the diffusion process around the kaolin particle in addition of the surface reaction by temperature.

#### 3.4 Characterization of the produced hydrocarbon liquids

The hydrocarbon liquid fuels produced collected from pyrolysis of LDPE open system semi-batch reactor at the finest temperature that gives the higher hydrocarbon liquid. The best conditions for the thermal pyrolysis step were 390 °C and 38 minutes, whereas were 430 °C and 10 minutes for the catalytic pyrolysis.

#### 3.4.1 Fourier transform infrared analysis

The FTIR analysis results shown in Figures 8 and 9.Generally, no major differences in FTIR spectra between the hydrocarbon liquids produced from thermal and catalytic pyrolysis. Similarly, FTIR spectra indicated that the structures of hydrocarbon liquid obtained from thermal and catalytic pyrolysis are very similar. The peaks between 2960 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> indicated the presence of CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> functional groups which are indicative of alkanes species. The presences of peaks in the region of 1350 to 1500 cm<sup>-1</sup> due to the deformation vibrations of C–H bonds confirm the presence [1, 21].

The difference of the feed plastic that fed to the pyrolysis reactor effects on the chemical groups found in the pyrolysis products. Kumar [1], pointed out that the hydrocarbon liquid produced from thermal pyrolysis of waste HDPE in batch reactor consist mostly of alkane and alkenes with carbon number ranges between 9 and 24.

In addition, the type of reactor may play importantly effect on the final composition of the hydrocarbon liquid produce from pyrolysis process. Paul and Williams [22], testified that the oil produced from thermal pyrolysis of polyethylene in fixed bed reactor that consist from aromatic and aliphatic species such as alkanes and alkenes. The FTIR spectrometry reported by Shubber [21]shows similar structure of alkenes and aromatic in the hydrocarbon liquid fuel obtained from thermal pyrolysis of the two types of polyethylene (LDPE and HPDE) in closed batch reactor at 480 °C contain similar structure of alkenes and aromatic.

#### 3.4.2 Characterization properties and ASTM simple distillation

The characterization carried out for the hydrocarbon liquids that produced at the best operating conditions that yield the highest amount of liquids. These operation conditions were 430 °C and 10 minutes of the catalytic pyrolysis for LPDE and 390°C and 38 minutes of the thermal pyrolysis. The measuring of the specific gravity, kinematic viscosity, flash point, pour point and Sulphur content summarized in Table6. The characterization properties of the produced hydrocarbon liquids are in good agreement with the results of hydrocarbon liquids via pyrolysis found by Miller el al.[5], Abbas and Shubber [23], Parwar and Lawankar [24] and finally results by Abbas and Mohamed [25]. Commonly, polyethylene plastics does not contain Sulphur and water in the monomer (ethylene) which composed of only carbon and hydrogen. Parwar and Lawankar [24] established that the Sulphur content of obtained oil from the catalytic pyrolysis of mixture waste plastic is 0.002 wt. %.

Standard test method for distillation (ASTM-D86) carried out for hydrocarbon liquids produced from thermal and catalytic pyrolysis of LDPE in order to determine the amount of different fractions, as a primarily forecast of the evaluation. Figure10 shows the accumulative volume of produced hydrocarbon liquid fuels versus fraction temperature ranges. The initial boiling points were 109 °C for the hydrocarbon liquid produced catalytically contrasted with 87 °C for the hydrocarbon liquid produced thermally.

Both hydrocarbon liquids have the same fractions distribution with total light fractions (below 250 °C) of about 57 Vol. % for the produced hydrocarbon liquid catalytically versus 54 Vol. % for the hydrocarbon liquid produce by thermal pyrolysis. Liquid hydrocarbons with these fractions are rich sources for generating treasured petroleum fraction such as gasoline, kerosene, and gasoil. These results are in a good agreement with Miller el al. [5] and Abbas and Shubber [23].

## 4. CONCLUSIONS

- 1. TGA analysis of the virgin LDPE shows a single step degradation started at 349°C, completed at 489°C and the original sample lost 50% of its original weight at degradation temperature about 457.49 °C.
- 2. The maximum liquid hydrocarbon yield by thermal pyrolysis of LDPE (49.60wt.%) produce at 390 °C. during 38 minutes.
- 3. Used of Iraqi kaolin as a heterogeneous catalyst for the pyrolysis of LDPE improved the yield of the hydrocarbon liquid to the range of 63.26 to 68.26 wt. % in the pyrolysis temperature range between 410 and 430 °C.
- 4. The suggested kinetic model prove that he rate of the hydrocarbon liquid production is inversely proportional with the amount of hydrocarbon liquid produced.
- 5. The coefficients value of the production ratein creased from 9.28 to 19.86 (wt.%)<sup>2</sup>/minutes with the temperature rising from 370 to 410 °C and activation energy of about 69.76 kJ/mol for the thermal pyrolysis of LDPE.
- 6. The coefficients value of the production rate for catalytic pyrolysis by Iraqi kaolin increased from 7.86 to 124.89(wt.%)<sup>2</sup>/minutes with temperature between 370 and 430 °C and the catalytic pyrolysis activation energy was160.94 kJ/mol.
- 7. Nil Sulphur contains were recorded for all liquids produced by thermal and catalytic pyrolysis of LDPE.

## **5. REFERENCES**

- 1. S. Kumar, "Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis", *Brazilian Journal of Chemical Engineering*, 28 (4), 2011.
- 2. Plastics The Facts, "An analysis of European plastics production, demand and waste data 2014/2015", September 2015.

- 3. I. Ofoma, "Catalytic Pyrolysis of Polyolefins", M. Sc. Thesis, Georgia Institute of Technology, Department of Chemical Engineering, 2006.
- 4. S. Kumar, A. K. Panda and R. K. Singh, "A review on tertiary recycling of high-density polyethylene to fuel" *Resources, Conservation and Recycling*, 55, pp. 893–910, 2011.
- 5. S. J. Miller, N. Shah and G. P. Huffman, "Conversion of waste plastic to lubricating base oil", *Energy and Fuels*, 19(4), pp.1580-1586, 2005.
- 6. M. N. Siddiqui and M. F. Ali, "Catalytic Co –Liquefaction of Model and Waste Plastics", in *Proceedings of 15<sup>th</sup> Saudi –Japan joint Symposium*, Dhahran, Saudi Arabia, 2005.
- 7. J. Stepek and H. Daoust, Additives for Plastics, Berlin: Springer-Verlag, 1990.
- 8. J. Scheirs and W. Kaminsky, "Converting Waste Plastics into Diesel and Other Fuel in Feedstock Recycling and Pyrolysis of Waste Plastics", John Wiley and Sons, Ltd., 2006.
- 9. J. F. Mastral, E. Esperanza, C. Berrueco and J. Ceamanos, "Fluidized Bed Thermal Degradation Products of HDPE in an Inert Atmosphere and in Air-nitrogen Mixtures" *Journal of Analytical and Applied Pyrolysis*, 70, pp. 1-17, 2003.
- 10. A. Demirbas, "Pyrolysis of Municipal Plastic Wastes for Recovery of Gasoline-Range HC", *Journal of Analytical and Applied Pyrolysis*, pp. 97-102, 2004.
- 11. Y. Koreda and Y. Ishihara, "Novel Process for Recycling Waste Plastics to Fuel Gas Using a Moving Bed Reactor," *Energy and Fuel*, 20, pp. 155-158, 2006.
- 12. A. Okuwaki, "Feedstock recycling of plastics in Japan", *Polymer Degradation and Stability*, 85, pp.981-988, 2004.
- 13. P. V. Thorat, S. Warulkara and H. Sathonea, "Pyrolysis of waste plastic to produce Liquid Hydroocarbons", *Advances in Polymer Science and Technology: An International Journal*, 2013.
- 14. B. Z. Tyminski and K. Wolinski, "Degradation of Polyolefin Wastes into Liquid Fuels", *NUKLEONIKA*, 51(1), pp. 89-94, 2006.
- 15. K. H. Lee, N. S. Noh, D. H. Shin and Y. Seo, "Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst", *Polymer Degradation and Stability*, 78, p. 539, 2002.
- 16. Y. Sakata, M. A. Uddin and A. Muto, "Degradation of PE and PP into Fuel Oil by Using Solid Acid and Non-acid catalysts", *Journal of Analytical and Applied Pyrolysis*, 51, pp.135-155, 1999.
- 17. R. B. Williams and B. M. Jenkins, "Evaluation of Conversion Technology Processes and Products," *Broad Meeting, University of California*, pp.21-22, 2004.
- 18. Y. Uemichi and T. Suzuki, "H-gallosilicate-catalyzed degradation of polyethylene into aromatic hydrocarbons using different types of reactors", *Chemistry Letters*, p. 1137, 1999.
- 19. O. Levelspiel, "Chemical Reaction Engineering", 3<sup>th</sup> edition, John Wiley and Sons, 1999.
- 20. J. M. Smith, "Chemical Engineering Kinetics", John Wiley and Sons, 2014.
- 21. S. D. A. Shubber, Pyrolysis of thermal plastic waste for production of fuel –like hydrocarbons, Baghdad Iraq: M.Sc. Thesis, Chemical Engineering Department, Collage of Engineering University of Baghdad, 2007.
- 22. T. Paul and Willaims, "Yield and Composition of Gases and Oils/Waxes from the Feedstock Recycling of Waste Plastic", Energy and Resources Research Institute, Houldsworth Building, University of Leeds, Leeds, UK, 2006.
- 23. A. S. Abbas and S. D. A. Shubber, "Pyrolysis of high density polyethylene for the production of fuel like liquid hydrocarbons",*Iraqi Journal of Chemical and Petroleum Engineering*, 9(1), pp. 23-29, 2008.

- 24. H. R. Parwar and S. M. Lawankar, "Waste plastic Pyrolysis oil Alternative Fuel for CI Engine A Review", *Research Journal of Engineering Sciences*, 2(2), pp. 26-30, 2013.
- 25. A. S. Abbas and F. A. Mohamed, "Production and Evaluation of Liquid Hydrocarbon Fuel from Thermal Pyrolysis of Virgin Polyethylene Plastics", *Iraqi Journal of Chemical and Petroleum Engineering*, 16 (1), pp. 21-33, 2015.

Component	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	Na <sub>2</sub> O	TiO <sub>2</sub>	Others	Loss of ignition
Weight percent (%)	50.84	0.96	33.3	0.09	1.34	0.81	12.66

**Table (1):** The chemical composition of kaolin clays

Tamparatura °C	Liquid (L <sub>f</sub> ),	Wax,	Gas,	Coke,	<b>B</b> eaction time (t.) min
Temperature, C	wt. %	wt. %	wt. %	wt. %	Reaction time (tf), inn.
370	31.88	41.84	24.28	-	40
390	48.98	24.47	26.53	0.02	38
410	46.42	9.87	43.68	0.03	35
430	25.81	47.77	26.42	-	12
450	9.00	67.37	23.63	-	11

Table (2): Product distribution of the thermal pyrolysis

Table (3): Product distribution of the catalytic pyrolysis

Temperature, °C	Liquid (L <sub>f</sub> ), wt. %	Wax, wt. %	Gas, wt. %	Coke, wt. %	Reaction time (t <sub>f</sub> ), min.
370	35.29	16.35	48.26	0.10	40
390	49.60	17.3	33.01	0.09	35
410	63.26	6.16	30.57	0.01	30
430	68.26	10.52	21.22	-	10
450	15.30	61.22	23.48	-	10

Table (4): Production rate coefficients for thermal and catalytic pyrolysis of LDPE

Temperature (°C)	Thermal pyrolysis	Catalytic pyrolysis
	k, ((wt.%) <sup>2</sup> /min.)	k, ((wt.%) <sup>2</sup> /min.)
370	9.28	7.86
390	15.71	18.90
410	19.86	25.86
430	-	124.89

Table (5): Constants values of the	e Arrhenius equation (	Eq. 6) for the therma	l and catalytic
	pyrolysis of LDPE		

Arrhenius equation constant	Thermal pyrolysis	Catalytic pyrolysis
$k_o$ , ((wt.%) <sup>2</sup> /minutes)	$4.51*10^{6}$	8.43*10 <sup>13</sup>
E, kJ/mol	69.76	160.94

Property	Catalytic pyrolysis	Thermal pyrolysis	Test method
Specific gravity, -	0.8577	0.8479	ASTM D-941
Viscosity, cSt	2.49	2.85	ASTM D-445
Flash point, °C	33	36	ASTM D-93
Pour point, °C	5	15	ASTM D-97
Sulphur, wt. %	Nil	Nil	X-ray diffraction method

Table (6): Characterization properties of	f the hydrocarbon liquid fuels
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Figure (1): Schematic diagram of the experimental apparatus.



Figure (3): Produced hydrocarbon liquid versus time at different temperatures via thermal pyrolysis of LDPE



Figure (4): Produced hydrocarbon liquid versus time at different temperatures via catalytic pyrolysis of LDPE



Figure (5): Plot of Equation (5) for the thermal pyrolysis of LDPE at different temperatures



Figure (6): Plot of Equation (4) for the catalytic pyrolysis of LDPE at different temperatures



Figure (7): Arrhenius plot for the production rate thermally and catalytically.



Figure (8): FTIR for liquid produced from thermal pyrolysis of LDPE



Figure (9): FTIR for liquid produced from catalytic pyrolysis of LDPE



Figure (10): Accumulative volume percent versus fraction range of hydrocarbon liquid fuel

#### Abbreviation

ASTM	Standard test method
DTGA	Differential thermo-gravimetric analysis
FTIR	Fourier transform infrared spectroscopy
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
MT	Million tons
PE	Polyethylene
TGA	Thermo-gravimetric analysis

#### Nomenclature

Ε	Activation energy (J/mol)
k	Production rate coefficient ((wt.%) <sup>2</sup> /min.)
$k_o$	Frequency factor of the production rate coefficient ((wt.%) <sup>2</sup> /min.)
L	Percent of hydrocarbon liquid produced (wt. %)
$L_{f}$	Final percent of hydrocarbon liquid produced (wt. %)
n	Order of the production rate (-)
R	Universal gas constant (8.314 J/mol. K)

- $r_L$  Production rate of hydrocarbon liquid (wt. %/min.)
- *T* Temperature of pyrolysis (°C or K)
- *t* Pyrolysis time (min.)
- *t<sub>f</sub>* Time to produce final percent of hydrocarbon liquid (min.)

## دراسة حركية إنتاج المواد الهيدر وكربونية السائلة عبر التحلل الحراري والمحفز للبوليإيثيلين منخفض الكثافة

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## الخلاصة

تعتبر عملية التحلل تقنية مثيرة للاهتمام و ذلك لتقليص الكميات المتزايدة من النفايات البلاستيكية. أستخدم طين الكاؤولين العراقي كعامل محفز في التحلل لبلاستك البولي أتلين منخفض الكثافة لغرض إنتاج وقود هيدروكاربوني سائل من مفاعل شبه- دفعوي في درجات حرارة تراوحت بين 370 و 450 درجة مئوية.

وجد من التحليل الحراري الجاذبي للبلاستيك إن مدى حرارة التحلل تراوح بين 349 و 489 درجة مئوية. و بينت نتائج التحلل المحفز بواسطة الكاولين العراقي زيادة ملحوظة في السائل الهيدروكاربوني المنتج من عملية التحلل مقارنة مع نتائج التحلل الحراري. وضحت دراسة حركية التحلل إن درجة الحرارة تؤثر بصورة أكبر على معدل إنتاج السائل الهيدروكاربوني بواسطة التحلل المحفز.

تم تقييم المنتجات الهيدروكربونية السائلة و بينت نتائج الفحص بطيف "فوري به تحويل الأشعة تحت الحمراء" أن الألكانات هي المركبات الرئيسية في السائل الهيدروكاربوني المنتج و نتائج حيود الأشعة السينية تشير إلى عدم وجود الكبريت في السوائل الهيدروكربونية المنتجة. التقطير القياسي للسوائل الهيدروكاربونية المنتجة أشارت إلى زيادة واضحة في مجموع المقاطع الخفيفة (أقل من 250 درجة مئوية) لنواتج من عملية التحلل المحفز.