REFERENCES:

[1]B. **Hileman**, C&E News, (1997), 75,46,8 and 75,50,9.

[2]J. Scheirs and W. Kaminsky "Feed stock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels" (2006) Edited by John Wiley & Sons, Ltd ISBN: 0-470-02152-7.

[3]Siauw .H. Ng, Hesham Seoud, Maria Stanciulescu, and Yoshikazu Sugimoto" Conversion of Polyethylene to Transportation Fuels through Pyrolysis and Catalytic Cra**cking"** Energy Fuels, 1995, 9 (5), 735-742, Publication Date (Web): 01 May 2002

[4]Ding .W, Liang. J, Anderson .L. L "Thermal and catalytic degradation of high density polyethylene and commingled post – consumer plastic waste, fuel process Techno" (1997) 51:47-62.

[5]Mohammad Farhat Ali,Mohammad Nahid Siddiqui,S.Halim Hamidd Redhwi" Study on the conversion of waste plastics /petroleum residue mixtures to transportation fuels" Mater Cycles waste Management (2004)6:27-34.

[6]Graforth AA, LinYH,Sharratt PN, Dwyer J "Production of hydrocarbon by catalytic degradation of high density polyethylene in laboratory fluidized –bed reactor "APPL Catal A:Gen ;169:331-(1998).

[7] Antonnio.Marcilla, M. Remedio, A.Garcia '' Degradation of LDPE/VGO mixtures to Fuel using a FCC equilibrium catalyst in sand fluidized bed reactor'' Applied catalysis A 2008: General (APCATA-11398; NO of page11.

[8] Prosper A.O., Banadda N., Zziwa A., Seay J., and Kiggundu N. '' Reverse engineering of plastic waste into useful fuel products", Journal of Analytical and Applied Pyrolysis, Vol. 130, March 2018, Page 285-293.

[9] Joppert N., Araujo da silva A., and Marques M. da costa, "Enhanced diesel fuel fraction from waste high-density polyethylene and heavy gas oil pyrolysis using factorial design methodology", Waste Management, vol. 36, Feb. 2015, page 166-176.

[10] Verma A., Aditya R., Quraishi M.A., Tirkey J.V., and Chandrabhan V., "Engine Fuel Production from Waste Plastic Pyrolysis (WPO) and Performance Evaluation in a CI engine with Diesel Blend" Journal of Materials and Environmental Sciences, 2018, Vol. 9, Issue 6, page 1712-1721

for H-ZSM5 at 450^{0}C cracking temperature. The drop of the mass loss curve (green line) is clear. This indicates that the carbon was oxidised to CO2. From fig 9, the exothermic peak appears on the heat flow started from 10 to23μV, the temperature ranged from 400C° to 500C°and the coke % is about 14.1%.

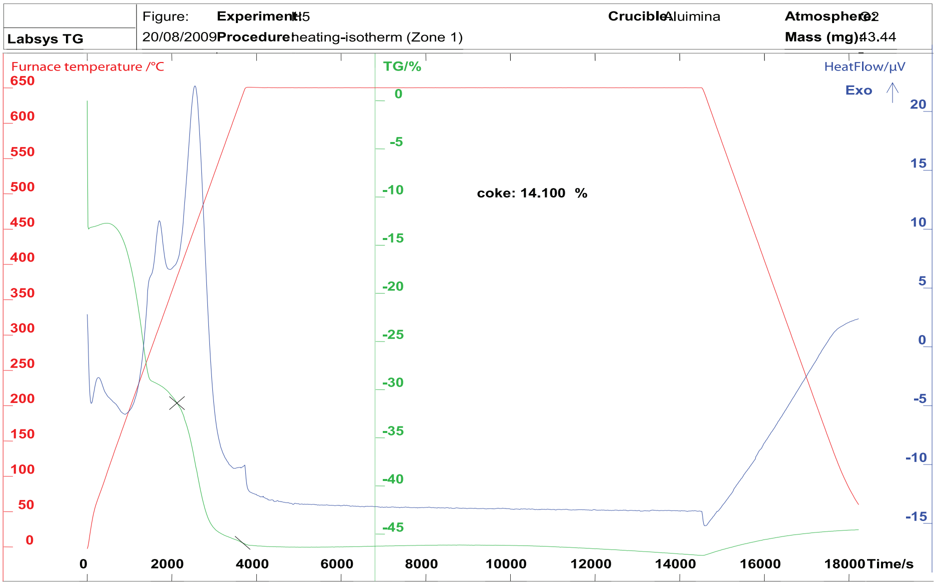

Fig 9 TGA of H-ZSM5 after reaction at 450C°

Conclusion:

The catalytic cracking of waste plastics blends with HGO is a feasible process by which they can be converted into liquid fuels or chemical feedstock. In liquid products, as the percentage of HDPE/PP increase the yield of gases, gasoline and coke are increased whilst the yield of [210+C^o] is decreased. In gas fraction, the selectivity leads to much higher values of LPG fraction versus dry gas. This fact clearly indicates higher generation of C3–C4 compounds than C1–C2 hydrocarbons, C3 formed more than C4 when used H-ZSM5 but C4 is more when H-BETA used. TGA is used to evaluate the quantity of the coke deposit on the catalyst surface and the analysis shows the H-ZSM5 produced more coke.

Acknowledgements

Thanks are due to Petroleum Research Center and National Oil Organization, Libya for their support and providing experimental facilities.

The influence of cracking temperature on the yield of gasoline using H-Beta and H-ZSM5 are given in figure 7. H-ZSM5 gives higher yield of gasoline than H-Beta, as well as higher yield of gas than H-BETA .This can be explained that the bimolecular reactions are more favoured in the presence of H-ZSM5 zeolite [6]. It is obvious that as the cracking temperature increase, the percentage of coke increase .Also with increase of the PP, HDPE ratio the percent of coke increase as shown in Fig 8. The quantity of coke deposited on the surface of catalyst found by thermal gravimetric technique. The deactivation of zeolites due to coke deposition is very important. When the amount of coke on the surface and in the pores increases, the number of available acid sites and the local diffusion possibilities decreases. Figure 9 shows the TGA curves

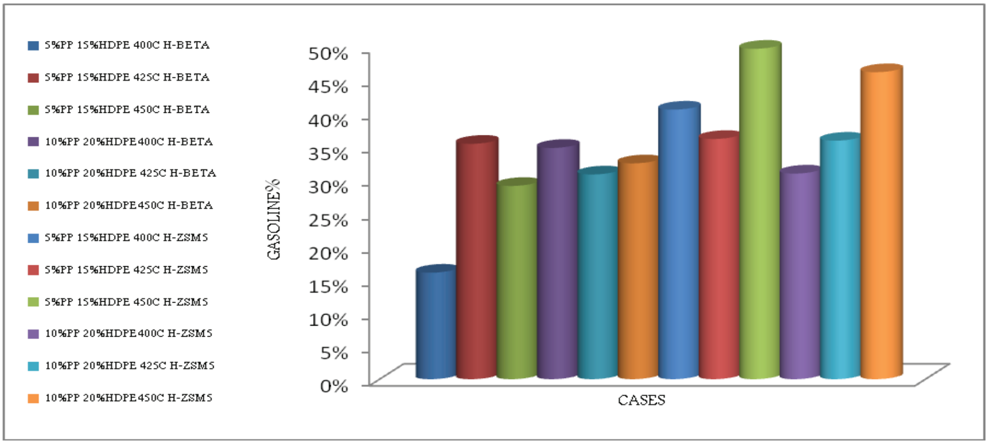

Fig: 7The effect of cracking temperature on the yield of gasoline

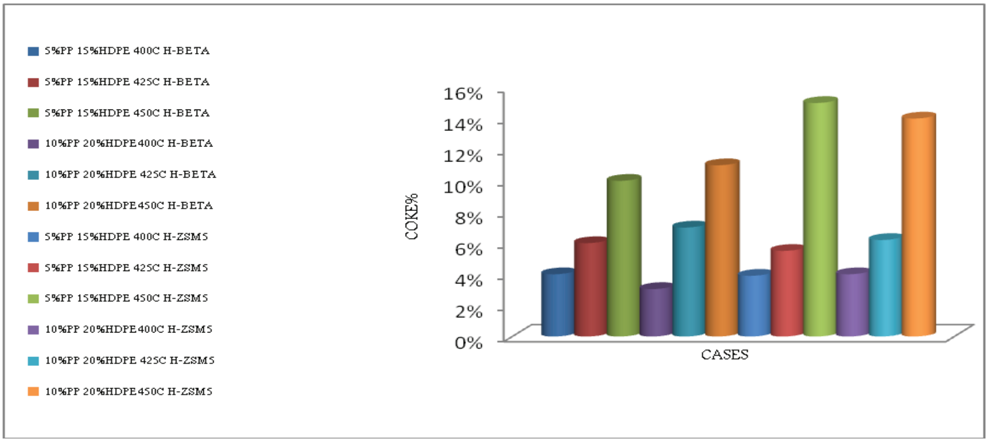

Fig: 8The effect of cracking temperature on the yield of coke.

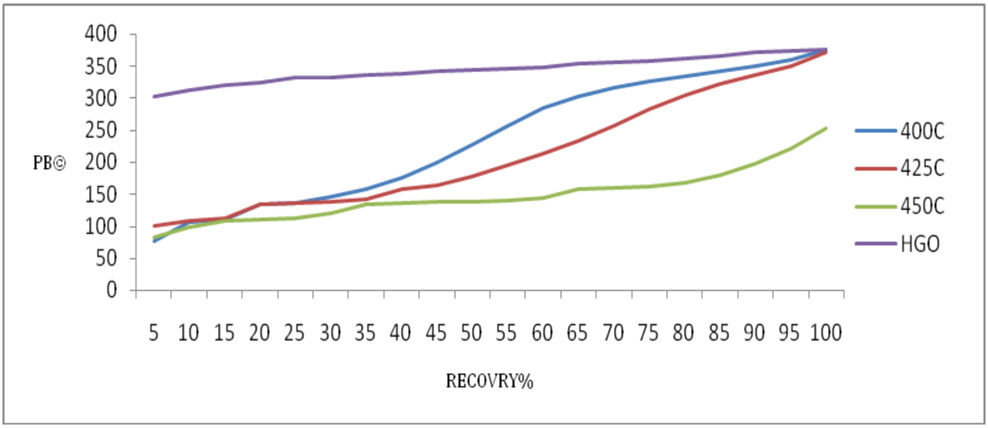

Fig4: The effect of cracking temperature and catalyst type on the boiling point distribution range of liquid products of 5%PP, 15%HDPE, and 80%HGO over H-ZSM5.

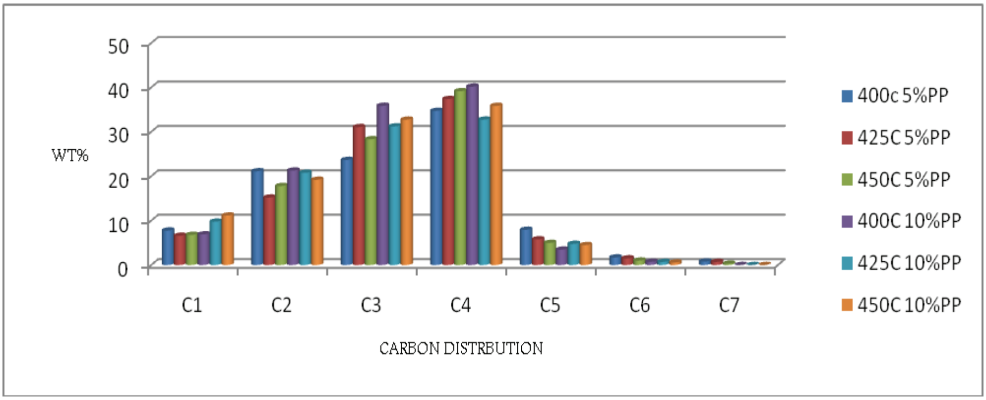

FIG: 5 Gas products from catalytic cracking over H-BETA.

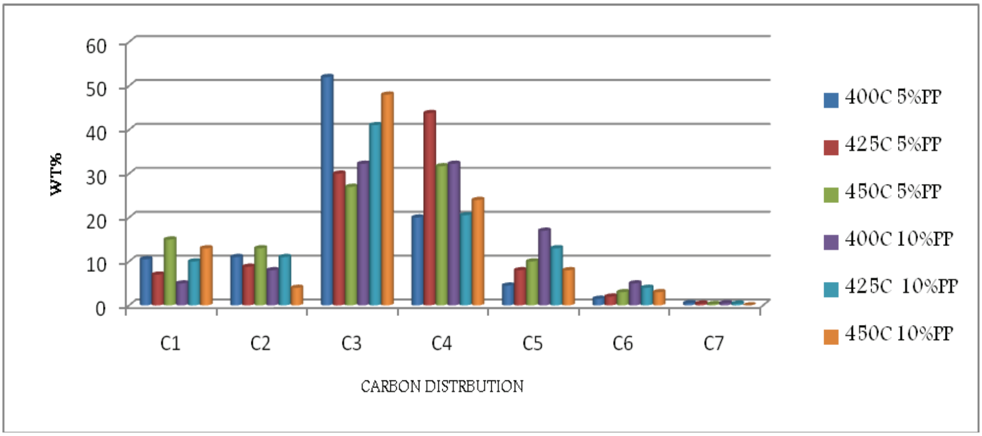

FIG: 6 Gas products from catalytic cracking over H-BETA.

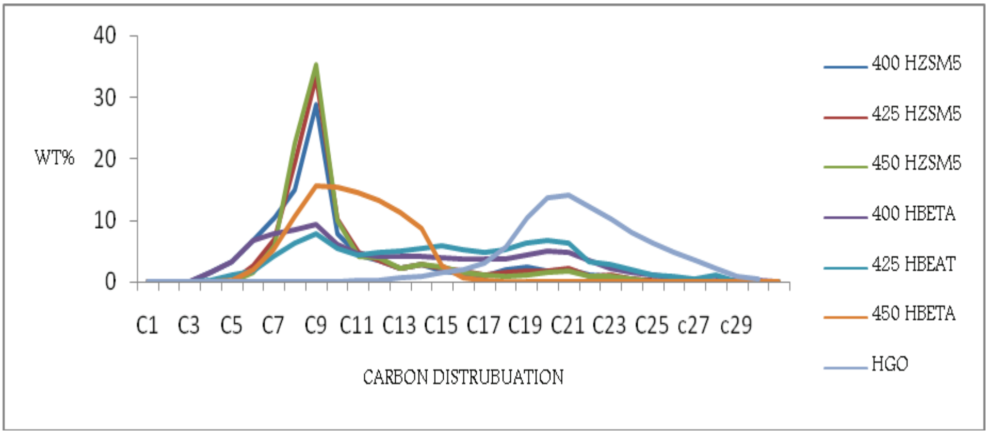

Fig: 1 Carbon distribution of feedstock (HGO) and reaction products from catalytic cracking of 5%PP/15%HDPE/80%HGO using H-ZSM5,H-BETAcatalyst

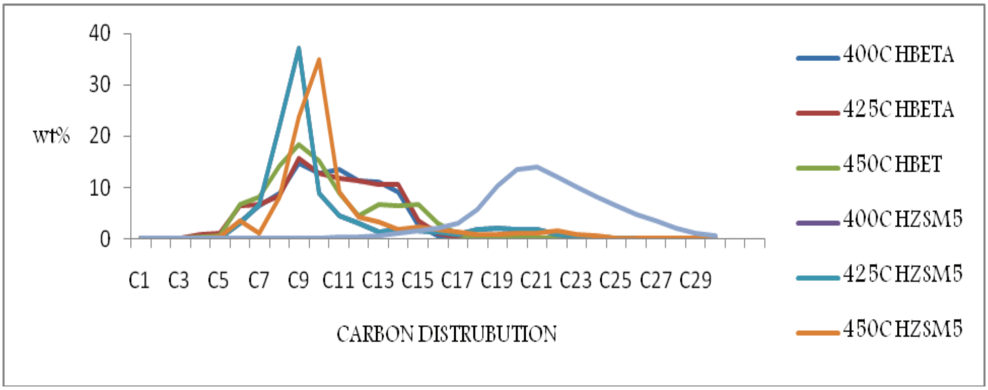

Fig: 2 Carbon distribution of feedstock (HGO) and reaction products from catalytic cracking of 10%PP/20%HDPE/70%HGO using H-ZSM5 ,H-BETA catalyst.

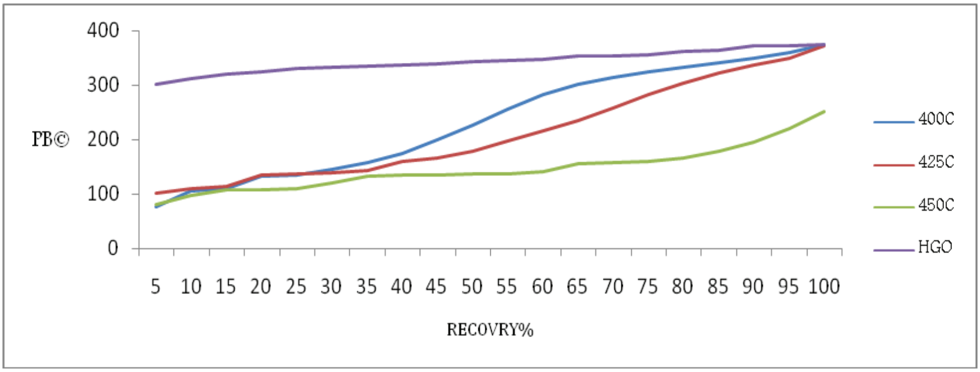

Fig: 3The boiling point distribution of liquid products of 10%PP, 20%HDPE and 70%HGO over H-ZSM5.

Table: 3 Product distributions of PP/HDPE/HGO.

Feed stock	%Gas	%Gasoline	%Coke	%.Total con
5%PP15%PE80%HGO H-BETA 400C	16%	16%	4%	36%
5%PP 15%PE 80%HGO H-BETA 425C	29%	35.37%	6%	70.37%
5%PP 15%PE 80%HGO H-BETA 450C	30%	29.04%	10%	72.04%
5%PP 15%PE 80%HGO H-ZSM5 400C	16.1%	38.4%	3.9%	58.4%
5%PP 15%PE 80%HGO H-ZSM5 425C	27.12%	39.6%	5.5%	72.22%
5%PP15%PE 80%HGO H-ZSM5 450C	37%	44.544%	15%	96.15%
10%PP 20%PE 70%HGO H-BETA 400C	27.45%	34.75%	3.05%	65.25%
10%PP 20%PE 70%HGO H-BETA 425C	33%	30.77%	7%	70.77%

Feedstock and Reaction Products Analysis: –

The reaction products collected from the outlet of the batch reactor were classified into gases, liquid hydrocarbons, and coke deposited on the catalyst surface. The feedstock and liquid reaction products were subjected to detail analysis using GC, and SimDist techniques whilst, gas products were identified using GC technique. Thermal gravimetric analysis (TGA) was used to quantify the carbon deposited on the catalyst. The yields of reaction products, gases, liquid and coke obtained from the catalytic cracking of different ratio of HGO/HDPE/PP at 400, 425 and 450^{0}C are given in table 3.The results demonstrate the yield of gases (C_1-C_4), gasoline (IBP-210), distillate(210C^{o+}) and coke using both H-Beta and H-ZSM5 catalysts with different percentage of HDPE. It is clear from this table that both reaction temperature and percentage of HDPE have strong influence on the yield. As it can be seen from this table that the highest conversion achieved was 46% at 450^{0}C cracking temperature with 20% HDPE using H-ZSM5 catalyst.

Carbon distribution of feedstock HGO and reaction products from catalytic cracking of 5%PP, 15%HDPE and 80%HGO and 10%PP, 20% HDPE and 70%HGO at different cracking temperature using both H-Beta and H-ZSM5 are shown in figures1 and 2. The most dominate hydrocarbon present in feedstock is C_{20}. As the cracking temperature increase the light products formed increased when 5%, 15% and 10%, 20% of PP, HDPE receptivity blended with HGO over H-BETA. The liquid products were distributed in the range of (n-C_5-C_{29}), where the main product present was C_9 except for 10%PP, 20%HDPE 70%HGO over H-ZSM5 where the main product was $C_{10.}$

The liquid products from 70%HGO, 20%HDP and 10%PP over both of catalysts were lighter than that from 80%HGO, 15%HDPE and 5%PP over both of catalysts as shown in Fig 3, 4. It ranged from 80 c^{o} to 224 c$^{o\,o}$ at first ratio. In general, the greatest change at 450 C^{o} over H-ZSM5 and all factors has effect on the conversion. Figures 5 and 6 refer to the composition of gas products from the catalytic cracking of the HGO/HDPE/PP blend. The main products were C_3 and C_4 in all cases, as the cracking temperature change. The small effect occurs on the percentage of C_1 and C_2 and the yield of $C_{5,}$ C_6 decreases.

ket. All runs were made at reaction time of 1 hr and at temperatures of 400, 425, and 450C. The Catalytic cracking of gas oil blended with HDPE, PP with different ratios were studied .Table 2 shows the cracking temperature, catalyst type and the ratio of HGO/HDPE/PP selected in this research.

Table 1: Property data of heavy gas oil

Test method	Test description	Unit	Results
ASTMD1298	SPECIFICGRAVITY AT60/60F	-	0.8731
ASTMD1298	Density at15C	Kg/L	0.8727
ASTMD1298	API Gravity	-	30.57
ASTMD611	Anline Point	C	83
ASTMD975	Diesel index	-	55.45
	Anline Gravity	-	5545
	Refractive index at 20C	-	1.4895
	Total acidity	Mg KOH/g	0.058
ASTM D976	Cetane index	-	55.4
ASTMD2887	IBP-FBP	C	275-375

Table: 2 Operating conditions used in current study

Runs	Catalyst	Temperature	PP:HDPE:HGO
1,2,3	H-BETA	400^{0}C, 425^{0}C,450^{0}C	15%80%:5%
5,6, 4	H-BETA	400^{0}C,425^{0}C,450^{0}C	70%:20%:10%
7,8,9	H-ZSM5	400^{0}C,425^{0}C,450^{0}C	80%:15%:5%
10,11,12	H-ZSM5	400^{0}C,425^{0}C,450^{0}C	70%:20%:10%

of polypropylene at 5 wt.% and polystyrene at 10% and 25 wt.%. Thermal cracking of polypropylene produced mainly oleffines and iso-paraffines from polystyrene. Styrene monomer was the major product formed where catalytic cracking was carried out and the formation of gasoline increased with temperature for all cases. The product distribution for binary system using plastic and petroleum residue using Ni Mo/Al_2O_3, ZSM-5, FCC and hydro cracking catalysts provided high yield of liquid fuels in the boiling range 100^o-480^{o}C, gases and coke[5] .[Antonio Marcilla et al., 2006] investigated the thermal degradation of blends of different percentages of low-density polyethylene in vacuum gas oil carried out in fluidized bed reactor over FCC equilibrium catalyst, the result showed a high selectivity to production of iso-butane and iso – pentane in the volatile compounds as well as the aromatic the liquid products .Due to these advantages this research may provide meaning about the recovery of catalytic degradation of waste plastics with hydrocarbons gasoline-range. Several researchers have studied the effect blending oil catalyst [8],[9], and [10]. **Materials:**

Polymers used in this study are high density polyethylene [HDPE, Mn=8500] and polypropylene [PP, Mn=7500]. Petroleum Libyan gas oil derived from the Hamada, Feil and Shrara fields is supplied by Zawia Oil Refinery Company and its properties are listed in table 1.

Catalysts: The following two catalysts were used as a catalytic material for the cracking of gas oil blended with HDPE and PP. These catalysts are:

1. H-ZSM-5[Na/ZSM-5 sample with Si/Al ratios of about 40 was exchanged with 1 M NH_4NO_3 solution].
2. H-Beta the H-BETA zeolite catalyst was used as received.

Method:

The reactions were carried out in Batch autoclave reactor consists of a stainless steel tubular reactor with programmable temperature controller obtained from the Parr Scientific, USA. The size of autoclave reactor is 1 L. The dimension of this reactor is 19 cm in length with 9 cm in diameter. The reactor is housed in furnace. The maximum operating pressure of this reactor is 345 bar whilst, the maximum operating temperature is 500^{o}C. The reactor with 25g feed was gradually heated via a 50 minute temperature ramp at the rate of 10 C^0/min and temperature was kept at 400 C for 1 h under the nitrogen blan-

Introduction

Plastics have become common materials of our everyday life and many of their properties such as durability, versatility and light weight can be significant factor in achieving sustainable development. However plastic applications also contribute to growing amount of solid waste generated as plastic products are often used only once before disposal. Most countries give attention to pollutants in the air such as carbon dioxide, nitrogen oxides and other greenhouse gases as climate change has been definitively libelled as global problem [1]. The recycling of plastic wastes is gaining increasing importance and classify to primary, secondary, tertiary, and quaternary recycling. Tertiary recycling is converting the waste plastics into original feedstock by Pyrolysis. Slow pyrolysis is one promising method for the treatment of mixed and contaminated plastic wastes and it can be thermally or catalytically treated. The advantages of catalytic cracking processes compared with simple thermal treatments are lowering of the reaction temperature, and shorter residence times. In the case of polyolefin's, the products derived from the catalytic cracking contain mainly cyclic, branched and aromatic hydrocarbons, which increase the quality of the potential fuels [2]. A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation deactivating the catalyst over time. The cost of catalysts also influences their selection and commercial viability. A few studies on the catalytic conversion of polymers co processing with coal and petroleum fractions were performed. The conversion of poly ethylene blended with oil (VGO) to transportation fuels via catalytic cracking was examined by that blended of VGO and 5 and 10 wt.% high density polyethylene were thermally and catalytically cracked in fixed bed reactor at 510°C[3] . Thermal cracking led to low conversion of VGO but the conversion of poly ethylene was over 50% by assuming that VGO gave the same overall product distribution as when poly ethylene was not present. The gasoline yields were in range 42-54% for all conditions studied, increasing with the catalyst to oil ratio,[4] performed similar study of catalytic and thermal cracking of polypropylene and polystyrene dissolved in refinery light cycle oil (LCO) a commercial cracking catalyst based on a REY Zeolite was used. The runs were carried at 1 bar at temperature range of 450°C to 550°C for thermal cracking and 500°C to 550°C for catalytic cracking with a catalyst to feed ratio of 6 by weight. The feeds were made up

Experimental Study of Catalytic Cracking of Waste Plastics

Blend with Heavy Gas Oil (HGO)

***Eng.Basma Tunsi *Eng. Asia Meshrghi *D. Mawaheb Derdar**

Abstract.

Due to the ever increasing concerns about waste plastics found in the world. The main aim of recycling is transformed waste plastic from land fields to oil productions. In present study catalytic cracking of waste plastics blend with heavy gas oil (HGO) was investigated using H-ZSM5and H-BETA. Reaction systems that were studied included high density polyethylene HDPE and polypropylene blend with HGO. Reactions were carried out in one liter micro autoclave reactor under different conditions of weight, temperature and type of catalyst. The optimum conditions were 2.5% catalyst by weight of total feed stock, one hour residence time, studying at atmospheric pressure and three selected temperatures 400C°, 425C°, and 450C°. The product distribution for the system [plastics and HGO] provided promised results of high yield of liquid [gasoline] up to 210C°, gases and small amount of heavy oils. From results were found highest conversion achieved was 45% at 450^0C cracking temperature with 20% HDPE using H-ZSM5 catalyst. In addition, the catalyst H-ZSM5 has been given higher than H-BETA at all selected temperature rang.

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