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Gasoline Fuel Production via Catalytic Cracking of Low-Density Waste Plastics Dissolved in Gasoil

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In the present work, catalytic cracking of low-density polyethylene (LDPE) dissolved in gasoil was investigated with a laboratory scale fluid bed reactor using commercial zeolite Y as catalysts for gasoline fuel production and waste plastics recycling. The liquid products chiefly consist of paraffins, isoparafins, olefins, naphthenes, and aromatics compounds. At a conversion of 75%, within gasoline pool (C_5-C_{12}), C_5 and C_6 were the principal components, and they accounted for approximately 25-30wt%, dependent of the catalyst applied. It is noted that hexane yield dominated around 50% of the total paraffins. The hydrothermal deactivated treatment (HDT) catalysts exhibit higher selectivity for i-C_5 in the isoparafins, but it shows lower selectivity for aromatic compounds in comparison with that obtained using equilibrium catalysts (ECAT) catalyst under the same condition, resulting from their different acidity density and strength. Most aromatic compounds are in the range of C_6-C_{10} with a benzene content less than 0.25wt%. The hydrocarbon composition of gasoline obtained from this work satisfied the current regulatory requirement of the commercial gasoline fuel. This work confirmed that simultaneous production of gasoline fuel and recycling of waste plastics by mixing a proper amount, i.e., 2.5 wt%, of LDPE with gasoil as feedstocks using the existed FCC technology is a highly practical route.

1. Introduction

Currently, a huge volume of plastic wastes is produced each year all over the world. These wastes generate serious environmental problems due to their low density, resistance to biological degradation, combustible nature, and a very large quantities, posing threats on aquatic life, ecosystems, and human health [Gall S.C. and Thompson R.C., 2015]. The plastic wastes can be chemically converted to high value combustible fuels [Nikles D.E., Farahat M.S. 2005; Li N. et al., 2022] or nanostructured carbon and hydrogen [Shoukat B. et al., 2024], using the catalysis technique. The produced C_1-C_4 gases are all valuable for petrochemical industries and the liquid fuels can be used directly as secondary energy to realize energy utilization of plastic waste [Nanda S. and Berruti F., 2020]. Heterogeneous catalysts take a key role in the catalytic cracking and reforming of plastics. Zeolites such as ultra-stable zeolite Y [Manos G., et al, 2001], ZSM-5 [Serrano D.P., 2002], zeolite beta [Aguado J., et al, 2000], H-ZSM-5 [Rojo-Gama D. et al., 2017], vision zeolite [Dragomir R.E., 2023], and mesoporous MCM-41 [Ortega D., et al, 2010] were investigated extensively and have proven to be particularly effective in polymer cracking and plastics conversion.

The main target of this work is to investigate the possibility of using low-density polyethylene (LDPE) dissolved in gasoil as feedstock for gasoline fuel production, which differs from the most previous investigations where pure plastics were used as reactants. Commercial fluid catalytic cracking (FCC) zeolite Y was used as catalyst and the catalytic evaluation was carried out on a laboratory scale FCC unit, aiming at utilization of the existed industrial FCC unit for gasoline production and plastic recycling in the future, minimising the infrastructure investment. The catalytic activity of different zeolites was comparatively evaluated by using pure gasoil and a

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mixture of 2.5wt% LDPE with gasoil as feedstock. Particular attention was paid to the influence of the surface acidity (acidity density, types, and strength) of the catalysts and catalyst/oil ratio on the gasoline yield and hydrocarbons distribution.

2. Experimental procedure

X-ray diffraction (XRD) patterns of the catalysts were obtained in a two-theta region between 4 and 50° with Cu *Kα* radiation (λ= 0.15418 nm) on a Siemens D500 diffractometer. The surface acidity of the catalyst samples was determined by means of TPD–NH_3 technique employing a Micromeritics 2900 analyzer.

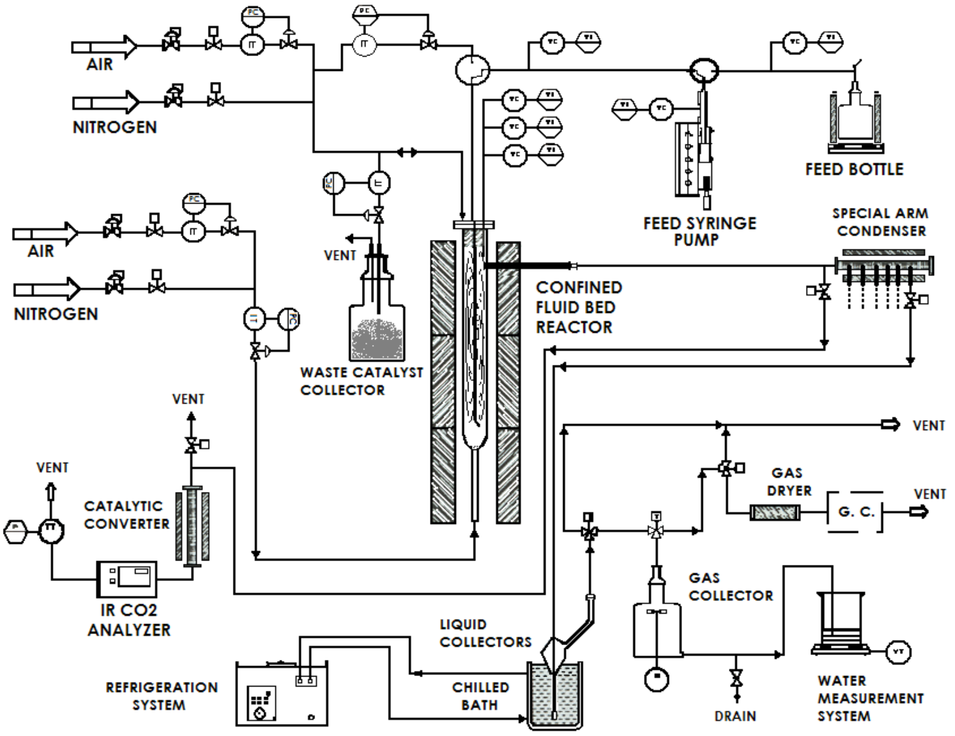

Figure 1. Diagram of the catalytic evaluation system.

The laboratory scale catalytic cracking reaction system is diagramed in Figure 1. The feedstock was injected by a gear pump and dispersed with nitrogen in the lower section of the reactor. The vapor feed rose through the reactor and contacted with the catalyst where reactions occurred to produce the respective products. Following the injection/reaction, catalyst was subjected to a stripping stage with nitrogen to remove the hydrocarbons occluded in the catalyst. The gaseous reaction products were accumulated and volumetrically quantified in a receptacle by displacement of water temperature and atmospheric pressure. The liquid product was recovered in a collecting glass in a bath of condensation. The experimental conditions (reaction temperature, injection time, catalysts to oil ratio, catalyst mass, and feedstock flow rate), are reported in Table 1.

Table 1: Experimental conditions of the catalytic cracking reaction

Reaction temperature, °C	520	520	520
Injection time, s	150	100	75
Catalysts to oil ratio, g/g	3	4.5	6
Catalyst loading, g	9	9	9
Feedstock flow rate, g/min	1.2	1.2	1.2

The liquid products were analyzed by GC-HP-6890 using hydrogen flame ionization detector, by which the distribution of the families of hydrocarbon compounds in the gasoline fraction or detailed analysis PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics) was determined. The gas collector system comprises a water storage vessel and a flue gas valve connected with a three-way glass. The total gas volume was measured by displacement of water. The gaseous product was also analyzed with a GC-HP-6890.

3. Results and discussion

3.1 XRD analysis and TPD-NH_3 analysis

Figure 2A shows the XRD patterns of the fresh FCC zeolite, hydrothermal deactivated treatment (HDT) of FCC zeolite-Y, and equilibrium FCC catalyst (ECAT) zeolite catalysts. The XRD patterns of the HTD zeolite are very similar to the fresh FCC zeolite, and the crystalline structure remained almost unchanged, indicating its high hydrothermal stability after serious treatment. The XRD peaks at two-theta of 6.0, 10.4, 12.1, 15.3, 19.2, 20.3, 24.0, 27.0, 32.1, 34.3 ° corresponded to the reflection of (111), (220), (311), (331), (511), (440), (533), (642), (555), (840) and (664) planes of the zeolite Y [Mekki A., et al, 2020]. The crystallite sizes of the HDT catalysts were slightly large with high crystallinity as evidenced by the sharper XRD. The equilibrium FCC zeolite showed XRD peaks with lower intensity due to the fact that part of the ECAT particles was covered with coke materials. All the positions of the corresponding XRD peaks in ECAT slightly shifted toward the lower two-theta direction, with respect to those in the fresh zeolite, indicating that some carbon atoms dissolved into the lattice cell of the zeolite crystals [Rojo-Gama D., et al, 2017].

Figure 2B shows the TPD-NH_3 profiles of the three catalysts. Three types of acidity with different acid strength were observed on the fresh FCC catalyst as evidenced by ammonia desorption peaks at 100-400 °C, 400-600 °C, and 700-800 °C, respectively. However, two peaks with temperature maxima at 490 °C and 120 °C on HDT catalyst, and only one peak at 110 °C were observed on ECAT. The fresh FCC catalyst contains largest number of acid sites with weak, moderate, and strong acidity strength. For the HDT catalyst, the strong acidity disappeared. While, for the ECAT, only weak acid sites are present. The HDT catalyst contained 89 µmol NH_3/g acid sites with moderate strength and 217 µmol NH_3/g weak acid sites (Table 2). These results indicate that the number of acid sites and the acidity strength varied with hydrotreatment and thus will affect their catalytic activity.

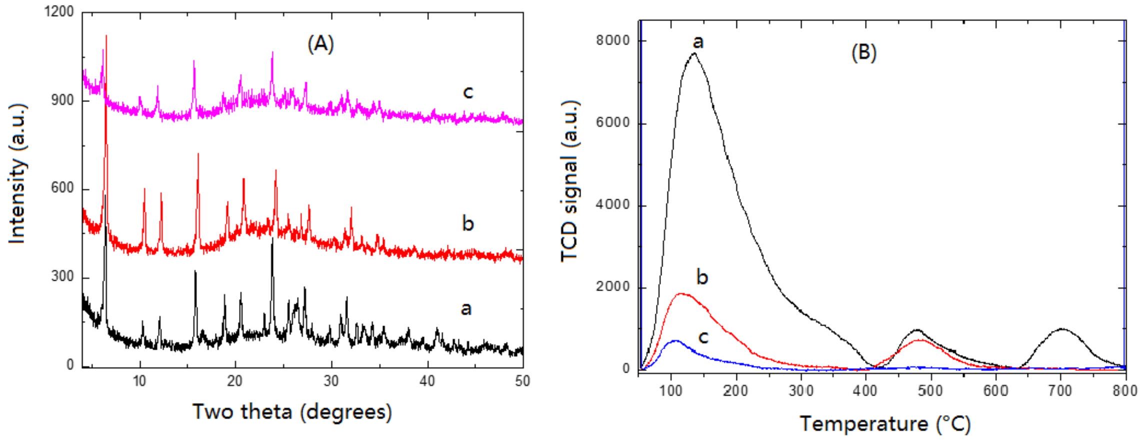

Figure 2: (A) XRD patterns of different zeolite catalysts; (B) TPD-NH_3 profiles of different catalysts. a: Fresh FCC zeolite; b: Thermal deactivated FCC zeolite; c: equilibrium FCC zeolite.

Table 2: Surface acidity data of the different catalysts obtained by TPD-NH_3 method.

Catalysts	T_{max} (°C)			Acidity (µmol NH_3/g)			Total acidity (µmol NH_3/g)
	Peak I (weak)	Peak II (moderate)	Peak III (strong)	weak	moderate	strong	
Fresh zeolite	150	480	700	1860	98	97	2055
HDT zeolite	120	480		217	89		306
ECAT zeolite	110			78			78

3.2 N_2 adsorption-desorption isotherms

Table 3 shows the textural properties of the ECAT and HDT zeolites. The surface area of the commercial ECAT catalyst shows 14% lower than that of the HDT zeolites. Its pore volume and pore diameter are also smaller in comparison with HDT zeolites. This is because ECAT zeolites are partially deactivated due to the deposition of carbon or coke-like materials and metals. These deposits may diminish the pore volume by blocking some pores, and thus decrease its pore diameters, pore volume and surface area.

Table 3: Textural properties of the ECAT and HDT zeolites.

Catalysts	ECAT zeolite	HDT zeolite
Total surface area (m^2/g)	160	186
Surface area of zeolite (m^2/g)	119	142
Surface of matrix (m^2/g)	41	44
Pore volume (cm^3/g)	0.1	0.2
Pore diameter (Å)	36.4	46.3

3.3 Catalytic activity

Because the fresh FCC catalyst was rapidly coked in the reactor and deactivated in a very short time, we did not evaluate its catalytic activity. The catalytic activity of ECAT and HDT catalysts were comparatively evaluated with different feedstocks. The first test was carried out using pure gasoil as feed; and the second test was performed using a mixture of gasoil with 2.5wt% of LDPE. By using the same catalyst, conversion varied in a narrow range, no matter gasoil or mixture of gasoil with 2.5wt% LDPE was used, indicating that addition of low-density polyethylene into the feedstock of gasoil did not significantly change the catalytic conversion. As shown in Figure 3A, the ratio of catalyst weight (W) to oil mass (W/O at g/g) significantly influences on the oil conversion. For the two catalysts, oil conversion almost linearly varied with the values of W/O. However, HDT catalyst was more active than ECAT as evidenced by a conversion approximately 6.5% higher than that achieved with ECAT. The catalytic activity is related to surface acidity of the catalysts. The HDT catalyst contains both weak and moderate strong acid sites, and the number of acid sites is greater than that present on the ECAT catalyst. Catalyst with stronger acidity and a greater number of acid sites favored the cracking reactions, thus the HDT catalyst exhibited higher catalytic activity. Under the present condition, approximately 80 % of the conversion was achieved using HDT catalyst at an injection time 75s.

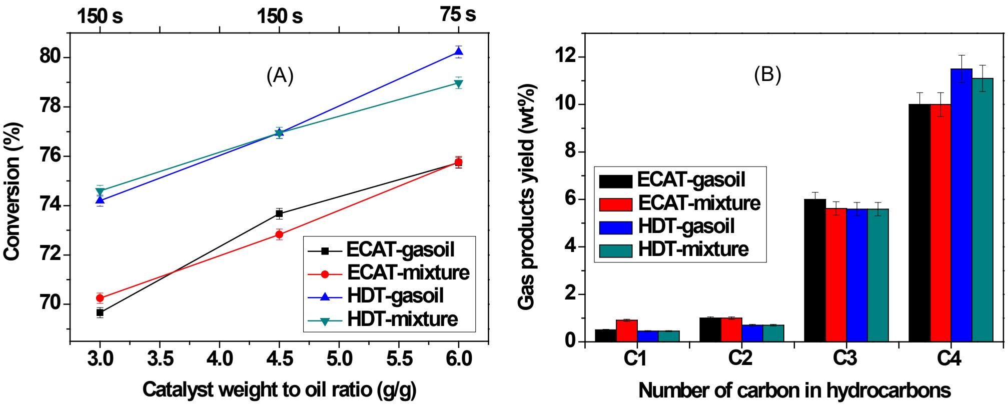

Figure 3: (A) Conversion of gasoil and gasoil-LDPE as a function of W/O at 520 °C; (B) Gas product yields as a function of carbon number inn hydrocarbons at a conversion of 75%.

The products consist of gases and liquid. As shown in Figure 3B, the gaseous products consist of CH_4, C_2H_6, C_3H_8, and C_4H_{10}. The yield of gas product exhibits an increasing tendency: $C_4H_{10} > C_3H_8 > C_2H_6 > CH_4$. The high yields of C_3 and C_4 are valuable for petrochemical industries. However, in this work, more attention was paid to the yield of liquid products, particularly gasoline fuel (C_5-C_{12} hydrocarbons).

3.4 Production distribution in liquid products

In liquid products, gasoline accounts for approximately 51%; the yield of individual hydrocarbon within C_5-C_{12} generally decreases as the carbon number increases, as shown in Figure 4A. It is noted that paraffins, isoparaffins, oleffins, cycloalkanes, and aromatics are formed at different concentration. These results indicate that cracking, isomerization, dehydrogenation, cyclization reactions took place during the FCC process. Among the gasoline components, at a conversion 75%, C_5 and C_6 cuts are the principal products, and they account for approximately 25-35 wt% where C_5 cuts dominate with different catalysts. When HDT catalyst was used and a mixture of gasoil and 2.5wt% LDPE was the feedstock, the yield of C_7-C_{12} compounds were 0.6-1.2% greater than that obtained using pure gasoil as feedstock.

As shown in Figure 4B, n-C_5 and n-C_6 are the main components that representative approximately 50wt% of the straight-chain paraffins. Using different catalysts, with or without LDPE, product distributions are quite similar. Figure 4C shows the compounds of isoparaffins where the highest yield was isopentanes. The higher isomerization selectivity was achieved on the HDT catalyst. After mixed with 2.5wt% LDPE, the selectivity of i-C_5 was slightly enhanced when HDT catalyst was used, which is different from ECAT on which the selectivity decreases by using the mixed feedstock. This may be related to their different acidity density and strength. HDT catalyst exhibits a greater number of acidity and higher acidity strength; these may favour the isomerization reaction. Figure 4D shows the olefins yield distribution. Total olefins account for approximately 10wt% in the products in which 80% are $C_5^=$ hydrocarbons, which is slightly higher than the concentration of olefins in a typical gasoline. Naphthenes or cycloalkanes are important part of all liquid refinery products because they have high octane number. In the liquid products of the present experiment, Figure 4E, naphthenes are approximately 3%. It generally fits well the commercial gasoline compositions. Aromatics are around 20% (Figure 4F). It is interesting to find that the HDT catalyst shows higher selectivity to aromatics using mixed feedstock than using pure gasoil feed; approximately 15% increment was achieved. Naphthenes and aromatics have high octane numbers; therefore, they are a very important component in the gasoline fuel.

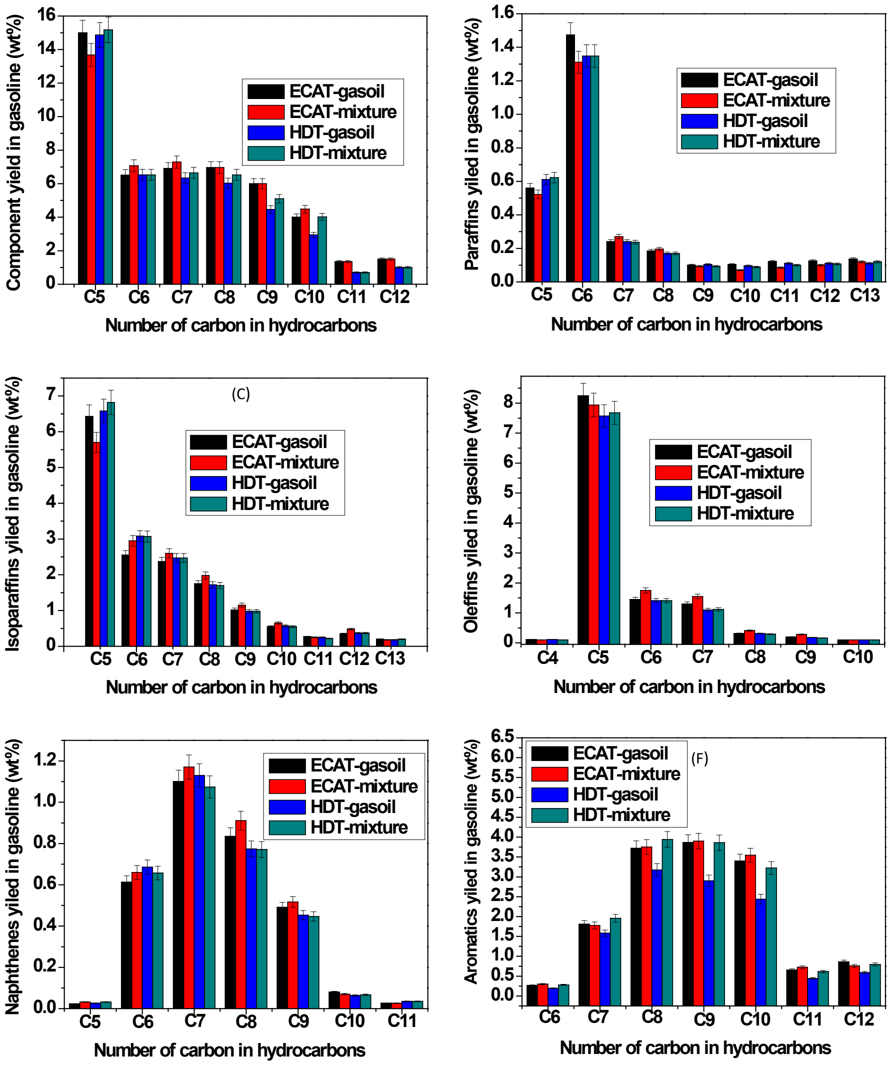

Figure 4. Production yield distribution as a function of carbon number at 75% of oil conversion.
(A) Component yield in gasoline; (B) Paraffins; (C) Isoparaffins; (D) Oleffins; (E) Naphthenes; (F) Aromatics.

The product distribution is a comprehensive result of several reactions involving cracking, isomerization, dehydrogenation, and cyclization during the reaction process, which is related to the surface acidity, textural properties, crystalline structure of catalysts, and the feedstock composition. After adding 2.5wt% LDPE into the gasoil feedstock, some reactions were promoted at an expanse of others, affecting the final product selectivity. The detail investigation of reaction mechanism will be reported in a separated paper.

The typical commercial gasoline consists of 4-8% (by volume) alkanes, 2-5% alkenes; 25-40% isoalkanes, 3-7% cycloalkanes, 1-4% cycloalkenes, and 20-50% total aromatics (0.5-2.5% benzene). The hydrocarbon composition of gasoline obtained from this work satisfied well the current regulatory requirement of the commercial gasoline fuel. Amongst the constituents of gasoline, benzene is known as a human carcinogen [Patton A.N., et al, 2021]. Therefore, its content is strictly limited to no more than 0.62 vol% in gasoline. In the present work, C_6 aromatics in the liquid products is less than 0.25 vol%. Therefore, benzene concentration in gasoline is lower than its household value.

4. Conclusions

This work confirmed that simultaneous production of gasoline fuels and recycling of LDPE waste plastics utilizing FCC zeolite catalyst is a highly practical technique route. When 2.5wt% LDPE was mixed with gasoil as feedstock, 70 to 81% conversions were achieved, depending of different catalysts and the catalyst to oil ratio. The HDT catalyst presented higher catalytic activity and selectivity to gasoline; whereas the ECAT showed a major selectivity to olefins in the liquid fraction. 50 to 54wt% of the products in liquid fuel are in gasoline range where the principal hydrocarbons were C_5 olefins (15wt%) and isoparafins (12wt%), respectively. The aromatics C_8 to C_{10} account for 20wt%; C_6 parafinas are only 3wt%, and C_7 naphtenes are approximately 2wt%. It is noteworthy that, when 2.5wt% LDPE was mixed with gasoil, an increase of aromatic C_8 - C_{10} was achieved using HDT catalyst with respect to that achieved using gasoil feedstock only. The hydrocarbon composition of gasoline obtained from this work satisfied the current regulatory requirement of the commercial gasoline fuel.

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