INFLUENCE OF QUINOLINE ON PERFORMANCE FCC CATALYST AND ADDITIVES FOR CRACKING OF N-Hexane

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ABSTRACT

In this research paper deals with effect of nitrogen compounds like Quinoline, Nitrogen compounds over the past 40 years not understand well. So studies performances of nitrogen compound were effect on fluid catalytic cracking catalyst and additives are reported in this present work. Actually nitrogen compound is two types likes basic and none basic. Both types of nitrogen compound concentration effect on the performance of fluid catalytic cracking of n-hexane and Vacuum Gas Oil (VGO). Active side of the catalyst were deactivated by strong adsorption of nitrogen compounds to use of alkali treated ZSM-5, Gasoline Sulfur Reduction (GSR) additives with Y-zeolite catalyst. Then, this process of fluid catalytic cracking of nitrogen compounds produces higher yield of olefins compared with untreated Y-zeolite catalyst.

Key words: Additives, Cracking, FCC catalyst, n-Hexane, Quinoline, Y-zeolite.


1. INTRODUCTION

Converting the middle distillate to lighter produced of fluid catalytic cracking, and also the fluid catalytic cracking is the secondary process and heart of the refinery. Catalyst design is the high level of metal contaminates, its challenge high conversion and good selectivity. So cracking is the break of high molecules to small molecules in the presence of an acid catalyst. The solid acid catalysts are the silica and alumina or Y-Zeolite are promoting the opposite charge of breaking bond yielding in carbonation and gives the very unstable hydride anion. The free radical localized of carbon followed by the position of C-C bond scission [1]. The catalytic cracking main product is liquefied petroleum gas (LPG), gasoline, heavy gas oil (HGO), diesel, heavy cycle oil (HCO) and coke. Y-zeolite is the heart of a fluid catalytic cracking process [2]. And made up by Si-O-Al atoms.

The specific pore structure of a fluid catalytic cracking catalyst calculated the acceptability of active side [3]. So the acid site are two types in process first are donate protons can bronsted acid site and Lewis site can accept electrons [4]. The reaction is takes
place only the Bronsted acid side only and matrix materials of ore in Lewis site. And extra result of aluminum framework is available in Lewis acids site [5].

1.1. ZSM-5
Pentasil zeolite family is belonged to ZSM-5, and ZSM-5 are using the increase of octane or maximization of LPG. It is the stable zeolite with certain alumina below than 10%. Its specific pores in the range of 5.49Å diameter [6]. The long-chain selectivity is lower octane range of normal paraffin’s molecules. Then its pore is undergoing continuous cracking, and zsm-5 is responsible to give high yield of olefins. ZSM-5 is two types additives use in catalytic cracking. Higher activity is the first type of additives then produce of the higher yields of light olefins, with reducing gasoline yield and less cracking activity means that lower yield of light olefins and increase the yield of gasoline. It’s found that tends to straight chain molecules isomerize to branched hydrocarbons [7].

1.2. Gasoline Sulfur Reduction Additives
Over the 40% refinery gasoline contributes of FCC catalyst unit. The FCC gasoline contains sulfur compounds like thiophene and benzothiophene. Accordingly 2% to 10% of FCC feed sulfur in gasoline [8]. The major constituent of gasoline is thiophene compounds. And higher boiling range gasoline is benzothiophene. So it is hydrogen transfer of required conversion of hydrogenation by thiophene. Then after H-donor before cracking as shown below:

\[
\begin{align*}
\text{R} & \quad \text{S} \quad \text{HT} \quad \text{Cracking} \quad \text{R-C}_4 + \text{H}_2\text{S} \\
\end{align*}
\]

It is to release H₂S from cracking sulfur species in the process by using gasoline sulfur reduction (GSR) additives. The additive varies from 10 to 25 wt% of total FCC catalyst. The feed and product vary by based of additives.

1.3. Nitrogenous Compounds
Naphthenes, alkanes and aromatic a part from the hydrocarbon constitute by crude oil and other constituent by crude oil is metal, nitrogen and sulfur compounds. The vacuum gas oil contains around to approximate 25 to 30% of nitrogen compounds available in the crude oil. Normally crude oil at occurs high molecular weight of nitrogen compounds.

The nitrogen compounds of small and medium molecular weight with define structure of quinoline, isoquinoline, pyridine, and acridine that all are present in crude oil and called basic nitrogen compounds. The none basic include is pyrrole, carbazole, and indole. In this paper basic nitrogen compounds like quinoline were taking five different concentrations. So the basic nitrogen compound (Quinoline) model n-hexane of fluid catalytic cracking are effect on the catalyst and additives and also discusses vacuum gas oil with concentration of nitrogen compounds to effect to catalyst and additives. The reasons that active site of the catalyst are deactivated by high strong adsorbed nitrogen compounds.
2. EXPERIMENTAL WORK

2.1. Materials
Nitrogen compounds (Quinoline) and solvent n-hexane (~ 99.7%) of GR grade and commercial equilibrium catalyst (E-catalyst) and additives (Octane booster (ZSM-5) and gasoline sulfur reduction additives in the form of powder taken from the refinery.

2.2. Catalyst Characterization
The American society for testing and materials (ASTM) methods (ASTM D-390-88) were using to characterize catalyst and additives sample. Characterize method were used to FCC catalyst fresh and steamed particle. So ASTM procedure is a Micro Activity test Technique for fresh and deactivated catalyst. There was using basic fixed bed of reactors to 2 grams of the catalyst, at a temperature range are 390-450°C, catalyst/ ratio 3 and with operate continuous vapors of liquid feed 60 minutes [9].

2.3. Catalytic Reaction Study
Firstly set up is the glass bench scale reactor shown figure 1. Then total amount of the catalyst is 2 grams and additives sample were taking to cracking fixed bed glass reactor. The model nitrogen compounds like quinoline were different concentration with positive displacement pump at the rate of 0.14 ml/min. The reaction was taking by fixed temperature at 490°C and atmospheric pressure for 60 min. The collective product was in weight. Firstly, there was a blank sample of n-hexane (without nitrogen compounds to treats as base case). Hydrogen of flow rates 25 ml/min was used experiment as carrier gas. The base case feed and product use of analysis by gas chromatographic analyzer [10]. Some little reaction for selected amount of catalyst and additives sample, as pilot scale runs was conducted in PCPLC controlled fixed fluid bed reactor in FCC ACE pilot unit supplied by M/S Xytel, USA. The vacuum gas oil was available known amount of nitrogen compounds and this called premixed industrial VGO feed. The reaction runs were performing out at the fixed ratio of the catalyst/oil at temperature and pressure. IR analyzer was estimated coke by online, the gas product analyzed by gas chromatography (HP-6890) supplied by M/S AC analytical. And SIM, DIST (HP-6890) was analyzed of liquid product supplied by AC analytical the Netherlands.

Figure 1 Experimental Glass reactor set up used for studying catalytic cracking of model compounds.

3. RESULT AND DISCUSSION

3.1. Nitrogen Adsorption−Desorption
Brunauer–Emmett–Teller (BET) is on the basis method used to the obtained surface area, the specific pore size and distribution size and determine by the barrette. The particle size analyzer by (Mastersizer 2000, U.K.), and desorption of ammonia was characterized to acid site density. Herein determine the quinoline adsorption by infrared spectra. The IR transmitted spectroscopy where detection of quinoline absorbed on the catalyst at different type of amount
of the acid site. Quinoline adsorption were obtained out by catalyst on the evaluated for 1 hour at room temperature and atmospheric pressure [11]. The resolution of spectrometric at 6500 cm\(^{-1}\) of the spectra were tested and recorded. The catalyst performance on the quinoline was influence of the catalyst to create the acidic nature as acidic property. The characterized of acidity was conducted by the NH\(_3\)-TPD measurement. The temperature programmed desorption profile of zeolite and additives catalyst can be substitute in to two factors in figure 2, and low temperature factor from 40 to 280\(^\circ\)C in weak acid and higher temperature factor from 280 to 490\(^\circ\)C for stronger acid. The weak and stronger acid was determined and comparison with ZSM-5 additives and weak acid of Y-zeolite, then strong acid increase by amount 20%.

![Figure 2 NH\(_3\)-TPD profile](https://example.com/figure2.png)

### 3.2. Catalyst and Additives (Physico-Chemical Properties)

<table>
<thead>
<tr>
<th>Catalyst/additives</th>
<th>Total S.A (m(^2)/g)</th>
<th>M SA (m(^2)/g)</th>
<th>Mi SA (m(^2)/g)</th>
<th>Mi PV (cc/g)</th>
<th>TPV (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-cat</td>
<td>178</td>
<td>132</td>
<td>48</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
<td>GSR</td>
<td>180</td>
<td>143</td>
<td>30</td>
<td>0.01</td>
<td>0.18</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>188</td>
<td>118</td>
<td>65</td>
<td>0.11</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Shown the (Fig. 1), the experiment setup of nitrogen compounds like Quinoline with n-hexane was taking out in a glass reactor at 490\(^\circ\)C Temperature and atmospheric pressure condition about 60 minutes. The survey of literature, there was assumed that in fluid catalytic cracking reaction of quinoline, affecting of gaseous products compare than liquid product. Gas and liquid product analysis were not done; reaction was taking only based on weight of liquid yield. The monitoring the yield of liquid, if quinoline is available and quinoline not available in feed under the constant reaction condition. The experimental results are given in figure 3 to 5.

![Figure 3 Effect of basic nitrogen compound (Quinoline) on cracking of n-hexane in presence of base FCC E cat](https://example.com/figure3.png)
3.3. Thermal Gravimetric Analysis

TGA Instruments was using the carried out thermal gravimetric analysis (Mettler Toledo, Universal V3). This experiment was taken by activated and deactivated amount of the sample is heated in a pre-programmed with reference in required atmosphere (N2/He/Air) and the changes of weight with temperature and time. To verify the nature of coke deposition and its amount with different level of nitrogen compound dosing in feed was studied using TGA technique.
Few spent catalyst samples were examined to investigate the weight change. It clears seen the weight change from TGA curve (Figure 6 to 9). The coke deposited on spent catalyst is 2.25 wt%. Complete coke burn is taking place at 650°C. If gasoline sulfur reduction additives are used in reaction, then coke deposited 1.05 wt%. The coke deposited higher than base case in seen (figure 5). It was found that total coke deposited in basic compound is more than none basic nitrogen compounds. Coke burning in none basic compounds is easier than the basic compound containing feed during cracking reaction, comparison of (figure 7, 8, 9), GSR and ZSM-5. Coke deposited on the catalyst is more in case of GSR additives compare then zsm-5 additives (figure 8). The reaction is taken by 520°C temperature and fixed amount of catalyst.
The ratio of 6.5 of the catalyst/oil with quinoline as shown the result in table 2. The vacuum gas oil feed and the product line is chocked. If uses of Quinoline above of 500ppm. The activity of the catalyst is deactivated of presence quinoline, then after 100ppm of quinoline using in the fluidized bed reactor get good result of gasoline.

Run conditions: catalyst weight: 6.5g; temperature: 490° C; Cat/Oil: 6.5.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Base</th>
<th>5% ZSM5</th>
<th>15% GSR</th>
<th>100ppm Quinoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conv.</td>
<td>66.270</td>
<td>70.660</td>
<td>81.750</td>
<td>67.880</td>
</tr>
<tr>
<td>Coke</td>
<td>3.628</td>
<td>3.805</td>
<td>8.724</td>
<td>3.446</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>1.854</td>
<td>3.022</td>
<td>2.334</td>
<td>1.666</td>
</tr>
<tr>
<td>H₂</td>
<td>0.054</td>
<td>0.064</td>
<td>0.050</td>
<td>0.063</td>
</tr>
<tr>
<td>LPG</td>
<td>26.468</td>
<td>30.816</td>
<td>27.640</td>
<td>24.791</td>
</tr>
<tr>
<td>Gasoline</td>
<td>34.320</td>
<td>33.021</td>
<td>43.050</td>
<td>37.981</td>
</tr>
<tr>
<td>LCO</td>
<td>14.936</td>
<td>14.140</td>
<td>10.564</td>
<td>14.901</td>
</tr>
<tr>
<td>HCO</td>
<td>3.1890</td>
<td>2.880</td>
<td>1.680</td>
<td>3.272</td>
</tr>
<tr>
<td>CLO</td>
<td>15.605</td>
<td>12.309</td>
<td>6.003</td>
<td>13.942</td>
</tr>
</tbody>
</table>

It can be noticed from the plots that the higher the amount of liquid lowers the conversion and lower the amount of liquid higher the conversion. Its compared to base case [12]. Effects of basic (quinoline) model compounds on activity of FCC were studies using model compounds. The studies were conducted at three different concentration (500, 1000 and 1500 ppm) ranges, catalyst used (plant E-cat) for all these experiments is the same. It is clear from the results that of nitrogen compounds inhibit the cracking activity of FCC catalyst. The extent of activity loss is more in case of basic nitrogen compounds [13]. The second set of cracking runs were conducted in fixed fluid bed reactor unit. Total nine experiments were conducted in this unit using VGO feed (IBP 350oC - FBP 550oC) with and without nitrogen compounds [14]. It is known from the literature that nitrogen compounds poison the catalyst forming coke precursors [15].

4. CONCLUSIONS
Basic nitrogen compound like (quinoline) has a strong effect on conversion and product. Many results show the performance of Quinoline concentration is more significant factor in fluid catalytic cracking. Its catalyst indicates that poisonous of catalyst by basic nitrogen compounds (Quinoline) can be reversibly absorbed on to the acid side. The hydro carbon catalytic cracking reaction was affecting on nitrogen compounds and that the noticed presence of Y-zeolite/ZSM-5 as octane booster and gasoline sulfur reduction. And the several base case catalyst studies shows that basic nitrogen compounds limit is less than 500 ppm.

REFERENCES
Influence of Quinoline on Performance FCC Catalyst and Additives for Cracking of N-Hexane


