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Run Octane Number (RON) Analysis of Gasoline Obtained from Catalytic Cracking of *n*-Hexadecane using Composite Fluid Catalytic Cracking Catalyst

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ABSTRACT

This study presents the Run Octane Number (RON) analysis of gasoline obtained from catalytic cracking of *n*-hexadecane using composite fluid catalytic cracking (FCC) catalyst. Composite FCC catalyst was formulated using as-synthesized zeolite Y and ZSM-5 anchored on support matrix made of activated alumina, metakaolin and silica sol. The as-prepared catalyst was characterized using X-ray diffraction, the composite catalyst performance at 400, 500 and 550 °C were 53.07, 73.17 and 88.85 %, respectively. The gasoline produced at 400 °C had paraffinic content of 53 %, olefin and aromatic content of 47 %. The gasoline produced at 500 °C had paraffinic content of 39 % olefin and aromatic content of 43 % while the gasoline produced at 550 °C had paraffinic content of 36 % olefin and aromatic content of 44 %. The gasoline obtained at 400 °C had the least RON value of 51.47 % whereas those obtained at 500 and 550 °C had RON values of 85.39 and 87.38 %, respectively. This study has shown that the optimum operating temperature was 500 °C and incorporation of ZSM-5 in FCC catalyst formulation improved the catalyst performance

KEYWORDS

Zeolite Y, ZSM-5, Fluid catalytic cracking catalyst, Catalytic cracking, Catalytic performance, Run octane number.

INTRODUCTION

The modern technological advancement is largely driven by energy availability, as this is informed by the continuous search not only for more energy sources but alternative energy sources as well. It was forecasted that by 2030 the world energy demand would have increased by 57 % [1]. The current global production of energy rest hugely on petroleum, and it is scarcely sufficient. The scarcity or insufficiency of petroleum today is vividly evident in the current energy politics of our modern day. Therefore, the relevance of petroleum and its strangle hold in the energy politics of the future is a reality that must be reckoned with. Gasoline, which is widely synonymous to petroleum in literal sense, is the most economically viable product of petroleum refining. Fluid catalytic cracking (FCC) process is the key refining process through which gasoline is produced [2-5]. The FCC process employs the use of catalyst made of zeolite, the common zeolite used in the formulation of FCC catalyst is the zeolite Y. Zeolites are crystalline microporous aluminosilicate minerals. They possess regular two or three dimensional structural patterns having internal voids made of uniform pores, cages, cavities and channels in molecular dimensional order; in the range of 3-10 ≈ [1,2]. They are also referred to as solid acids with fascinating chemisorption, high selectivity and thermal stability properties [3,4]. In addtion, they are referred to as molecular sieves due to their ability to selectively sort molecules primarily based on size exclusion criterion. Zeolite Y is a faujasite (FAU) member of zeolite family known for its famous catalytic performance and thermal stability. Among the industrially used zeolites, zeolite Y is the most widely employed in petroleum refining processes. It is widely used as catalyst in the fluid catalytic cracking (FCC) and hydrocracking processes [5-7]. ZSM-5, which means zeolite sieve of molecular porosity (or zeolite socony mobil)-5, (structure type MFI-mordenite framework inverted) is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. ZSM-5 is composed of several pentasil units linked by oxygen bridges to form pentasil chains [8,9].

Researchers have reported works regarding the performance of different catalysts in cracking of hydrocarbon feeds. The most popular of such works [10-12] are those involving FCC catalysts made of zeolite Y. In each of these works zeolite Y catalyst was used for catalytic cracking of different hydrocarbon feeds and different grade of fuels have been reported for the works. The current focus of research in this direction bothers on formulation of hierarchical FCC catalyst which is achieved by composite catalyst involving different framework type zeolites. This work studies the run octane number (RON) of the gasoline produced from the catalytic cracking of *n*-hexadecane at 400, 500 and 550 ºC using a composite FCC catalyst made of zeolite Y and ZSM-5. It gives deeper perspective of previous work [13] as this studied the RON property of the gasoline produced using the composite FCC catalyst made from zeolite Y and ZSM-5.

EXPERIMENTAL

Raw kaolin was collected from Kankara deposit at Kankara local Government area of Katsina state, Nigeria. Sodium hydroxide pellets (98%) and conc. H_2SO_4 (98%) were supplied by Sigma Aldrich Chemicals. Commercial zeolite Y was supplied by Zeolyst Company, lanthanum chloride and ammonium chloride were supplied by Fisher Chemical.

Synthesis of zeolite Y and ZSM-5: Zeolite Y was synthesized from Kankara kaolin as reported earlier [13] and ZSM-5 was synthesized from commercial chemicals as per reported method [14,15].

Catalyst formulation: Fluid catalytic cracking (FCC) catalyst was formulated by wet granulation method. The RE Y zeolite was supported with silica-alumina matrix. The matrix was made of activated alumina and metakaolin prepared as presented in previous works [16,17]. Silica sol was used as a binder. The percentage composition of the formulation was 30 wt % RE Y, 30 wt % metakaolin, 20 wt % activated alumina and 20 wt % silica sol. The components were mixed and granulated by thorough mechanical agglomeration so as to ensure even dispersion of the active ingredient-RE Y zeolite on the support matrix. The resulting granules were dried at 100 ºC for 6 h.

The XRD patterns of zeolite samples were recorded for 2 values of 5-50° using Pananalytical X'pert operated at continuous scanning speed of 5 º/min, generator settings of 10 mA, 40 kV and CuK_α node material.

Catalytic cracking of *n*-hexadecane: The formulated catalyst Y was used for catalytic cracking of a model petroleum oil using a fixed bed reactor. The reactor setup was as presented in previous work [14,18,19]. The reactor was equipped with an online GC-MS for online analysis of the gaseous product. The set-up also consisted of a condenser equipped with a high pressure liquid separator for collection of the liquid product for GC-MS analysis. The carrier gas was nitrogen connected *via* a mass flow controller (MFC), *n*-hexadecane was used as the model oil. The reaction conditions were 400-550 ºC, 2 bar, weight hourly space velocity (WHSV) of 3 h^{-1}, N_2 gas flow of 50 L/h.

RESULTS AND DISCUSSION

XRD: Fig. 1 shows the XRD patterns of fluid catalytic cracking (FCC) formulated from zeolite Y. The characteristic peaks at Bragg's angle (2θ) of about 6.2, 24.0, 26.7, and 31.0º [20-22] could be observed. The peak at 6.2º was the prominent, having intensity of 1600 counts, as it is the main characteristic peak of zeolite Y [20-22]. Other zeolite Y peaks such as those at 2θ values of 10.0, 11.7, 15.8 and 20.0º were largely in the background due to the presence of amorphous support matrix.

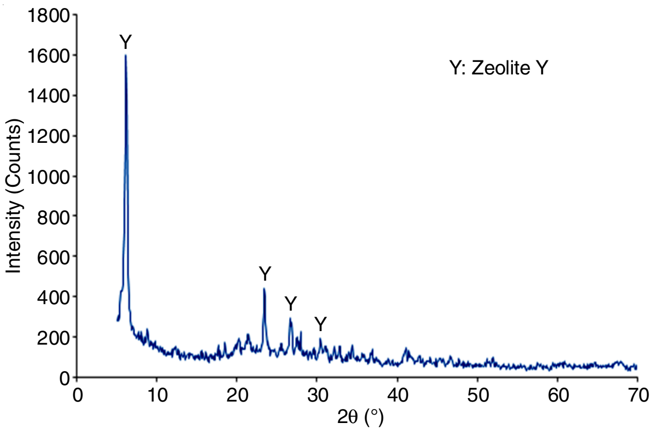

Fig. 1. XRD patterns of the FCC catalyst formulated using zeolite Y

Fig. 2 shows the XRD patterns of FCC catalyst formulated from zeolite Y + ZSM-5. It could be observed that the intensity of the characteristic peak of zeolite Y at 2θ value of 6.2º was 513 counts. The reduction in the intensity was due to the incorporation of ZSM-5, indicating reduction in the overall concentration of zeolite Y component of the catalyst. Other new peaks at 2θ values of 7.9 and 8.7º could be observed in the XRD pattern of the composite catalyst, these were due to the characteristic peaks of ZSM-5 [23].

Catalytic cracking: Fig. 3 shows the catalytic performance of the composite catalyst measured as the conversion at various reaction conditions. Generally, the catalytic performance increased with temperature progression; the performance at 400 ºC was 53.07 %, it increased by 38 % at 500 ºC, while at 550 ºC it increased by 67 %. The performance of the formulated catalyst at 550 ºC was 21 % higher than the performance at 500 ºC. Analysis of the gasoline selectivity (Fig. 4) further showed that even though the cracking conversion increased with temperature, the gasoline selectivity was not in consistent to this trend.

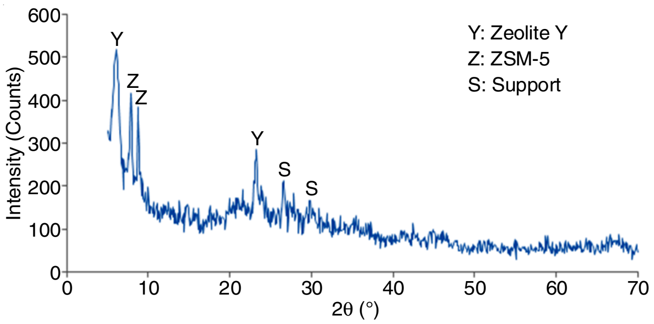

Fig. 2. XRD patterns of FCC catalyst formulated using zeolite Y + ZSM-5

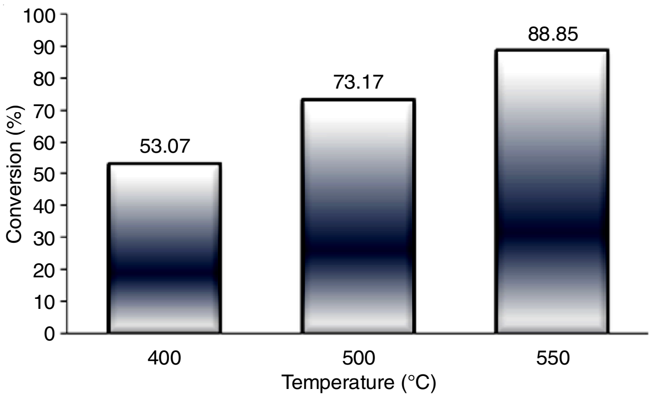

Fig. 3. Reaction conversion of the catalytic cracking of *n*-hexadecane at different temperatures

Fig. 4 shows that the highest gasoline conversion was at 500 °C, having conversion of 81.3 % followed by 400 °C having conversion of 76.6 % and the least gasoline conversion was 67.5 % at 550 °C. Hence, the increase in the performance at 550 °C over 500 °C resulted mainly due to the increase in other bye-products [18] at 550 °C compared to 500 °C.

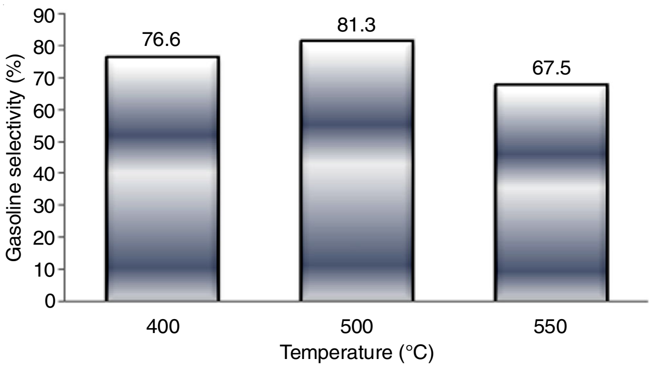

Fig. 4. Gasoline selectivity of catalytic cracking of *n*-hexadecane at different temperatures

Fig. 5 shows the hydrocarbon composition of gasoline obtained at various temperatures. The gasoline obtained at 400 °C was richer in paraffins than olefins and aromatics. The paraffinic content was 40 % higher than the aromatic content, and 477 % higher than the olefinic content. In contrary, the gasoline obtained at 500 and 550 °C were richer in aromatic than paraffins and olefins. At 500 °C, the aromatics were 10 % higher than the paraffinic contents and 130 % higher than the olefinic contents, while at 550 °C the aromatics were 22 % higher than the paraffinic content and 124 % higher than the olefinic content.

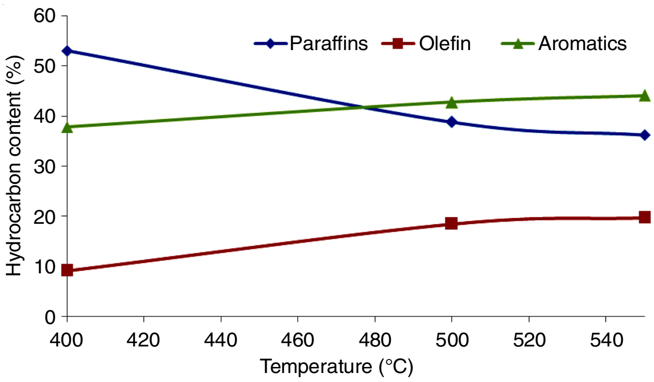

Fig. 5. Hydrocarbon composition of gasoline obtained at different temperatures

The octane number of gasoline depends on both the carbon number and molecular structure of the constituent hydrocarbon of the fuel. Table-1 presents the various hydrocarbon constituents of the gasoline obtained at various temperatures and the octane number of gasoline obtained.

The run octane number (RON) of gasoline was evaluated using eqn. 1:

$$\text{RON} = \sum V_i B_i^{ON} \quad (1)$$

where V_i is the fraction of the ith component of the gasoline, B_i^{ON} is the contribution of the ith component towards the fuel octane number. Values of B_i^{ON} used for the various hydrocarbon constituents of gasoline are obtained from Ghosh *et al.* [24].

The olefinic and aromatic contents of a gasoline are the octane boosting components of gasoline [24,25]. It would be observed that the total octane boosting components of gasoline obtained at 550 °C was 63.75 %, whereas that of 500 °C was 61.20 % and that of 400 °C was 46.97 %.

The gasoline obtained at 400 °C had the least RON value of 51.47 % whereas those obtained at 500 and 550 °C had RON values of 85.39 and 87.38 %, respectively. The optimum operating temperature was at 500 °C since the RON at 500 and 550 °C are close, the marginal difference cannot compensate the substantial temperature increase from 500 to 550 °C.

Conclusion

The gasoline obtained at 400 °C using the composite catalyst was richer in paraffins than olefins and aromatics, while the gasoline obtained at 500 and 550 °C were richer in aromatic and olefins than paraffins. The gasoline obtained at 400 °C had the least RON value of 51.47 % whereas those obtained at 500 and 550 °C had RON values of 85.39 and 87.38 %, respectively. The catalytic performance of the formulated composite catalyst at 550 °C was 21 % higher than the performance at 500 °C and 67 % higher than the performance at 400 °C. The optimum operating temperature was 500 °C, this is consistent with the finding of previous work [18] and this study has shown that incorporation of ZSM-5 in the FCC catalyst formulation has improved the catalyst performance and gasoline selectivity at the optimum temperature by 33 and 30 %, respectively.

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TABLE-1
RUN OCTANE NUMBER (RON) ANALYSIS OF GASOLINE PRODUCED AT VARIOUS TEMPERATURES

	Hydrocarbon contribution		V_i (%) at variable temperature		
	Type	B_i^{ON}	400 °C	500 °C	550 °C
Paraffin	*n*-C_4	94	0.20568928	2.47751938	2.68252081
	i- C_4	102	0	1.30465116	1.27348395
	n- C_5	62	0.85922684	2.52325581	2.48196591
	i-C_5	92	0.60393873	2.31782946	3.17241379
	Cyclo-C_5	100	0.3646973	0.46511628	0.49544193
	Cyclo-C_6	82.5*	1.38402626	2.39825581	1.56956005
	n- C_6	24.8	0.97680525	0.91317829	0.66841062
	i-C_6	91.8*	0.66958425	1.92139535	2.40142687
	n- C_7	0	0	0	0
	i-C_7	86.2*	0.81735959	2.4724031	1.52037257
	Cyclo-C_7	86.7*	0.63238512	1.41139535	1.15118906
	n-C_8	-15	-1.21444201	-0.27325581	-0.26753864
	i-C_8	66.3*	0	0.79662791	0.84090369
	Cyclo-C_8 naphthenes	55	0	0.81007752	0.61038446
	n-C_9	-20	-1.32749818	-0.24031008	-0.24970273
	i-C_9	55*	0	0.44767442	0.30519223
	Cyclo-C_9 naphthenes	35	0	0.05426357	0.06242568
	n-C_{10}	-30	-1.53172867	-0.25581395	-0.29131986
	i-C_{10}	48.3*	1.69102845	0.48674419	0.59346017
	n-C_{11}	-35	-1.63384391	-0.3255814	-0.31906461
	i-C_{11}	43.3*	0.15791393	0.26852713	0.21452636
	n-C_{12}	-40	-2.62582057	-0.49612403	-0.28537455
	i-C_{12}	40*	0.11670314	0.27906977	0.4914784
Olefin	*n*-C_4=	98.7	0.21597374	2.60139535	2.67972652
	n-C_5=	96.5*	0.3519329	6.35852713	7.47750694
	n-C_6=	95*	4.43471918	4.01356589	4.59373761
	n-C_7=	90	3.08533917	3.48837209	3.04994055
	n-C_8=	90	0.4595186	1.04651163	0.89179548
Aromatics	C_6 aromatics	102.7	1.72290299	1.03496124	2.01492271
	C_7 aromatics	118	14.2873815	13.2178295	13.469679
	C_8 aromatics	112	21.6484318	20.7503876	21.2857709
	C_9 aromatics	110	4.25237053	9.16666667	9.83154974
	C_{10} aromatics	109	0.63603209	3.46434109	2.31133571
	C_{11} aromatics	105	0.2297593	0.44767442	0.29131986
	C_{12} aromatics	102	0	0.03953488	0.36385256
	RON		51.4703866	85.3866667	87.3832937

*Represents the average B_i^{ON} of various isomers of hydrocarbon.

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