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PHYSICAL CHARACTERISTICS OF PRODUCTS FROM BONNY LIGHT CRACKING USING NOVEL CATALYST

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ABSTRACT

Petroleum remains the predominant source of industrial chemicals and the foremost supplier of global transportation fuels. However, the escalating global drive for cleaner automotive fuels has prompted scientists to pioneer advanced technologies for refining more environmentally friendly gasoline. In pursuit of this objective, a comprehensive investigation was conducted on the thermal and catalytic cracking of bonny light crude oil. The study focused on optimizing processing conditions, including variations in time and temperature. Specifically, the study employed synthetic Co-Mo supported on zeolite and commercial zeolite Y catalysts. The investigation encompassed an analysis of product yield distribution and alterations in the physical attributes of liquid products. Notably, the research revealed a propensity for higher liquid product yields and reduced residual product formation, particularly under more rigorous conditions. The study examined how temperature variations affected the key properties of the cracked oils. Parameters such as pour point, cloud point, viscosity, density, and API values exhibited an incremental trend with elevated temperatures. Furthermore, the study delved into the intricate interplay of temperature, residence duration, and hydrogen presence on the composition of the cracked oils. These findings contribute significantly to advancing our understanding of how different factors influence the outcome of oil cracking processes.

Keywords: Co-Mo, Zeolite, Density, Viscosity, Pour point

INTRODUCTION

Petroleum, often regarded as humanity's primary global energy source, has played an indispensable role in powering diverse transportation systems, encompassing automotive, marine, aviation, haulage, and more. In response to mounting pressures on fuel producers worldwide, there exists a compelling imperative to revolutionize both the composition and performance of fuels [1]. At its core, crude oil stands as a naturally occurring liquid manifestation of petroleum, predominantly comprised of hydrocarbons, and concealed beneath the Earth's surface [2]. Remarkably, human civilization has been cognizant of petroleum's monumental significance as the foremost global energy reservoir since time immemorial [3,4].

Petroleum, being a classification-defying ensemble of compounds, necessitates systematic categorization to extract meaningful insights [5]. In essence,

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hydrocarbons, marked by their multifarious molecular configurations predominantly comprised of hydrogen and carbon, form the bedrock of crude oil's composition and refined petroleum fractions. However, the complexity of crude oil extends far beyond hydrocarbons, encompassing a myriad of organic and inorganic elements, including sulphur, nitrogen, oxygen atoms, and a spectrum of metals such as iron, vanadium, nickel, and chromium [6]. This extraordinary diversity within petroleum's composition underscores the intricate challenges and profound opportunities that lie ahead as we endeavor to harness this invaluable resource to meet the ever-evolving energy demands of our modern world.

Different oil fields' crude oil has different physical and chemical characteristics. This is due to the crude oil's unique ratios of various molecular kinds, hydrocarbon sizes, and other elemental components [7]. The origin as well as the conditions of formation is vital in the context of crude oil's chemical composition. Generally, crude oil is a homogeneous multiplex or multi-component chemical mixture [8] of numerous distinct chemical components ,made up predominantly of about 95% hydrocarbons (organic compounds) [9] together with naphthenes, paraffins, and aromatics with minor components of non-hydrocarbons and small amounts of metals (such as nitrogen, sulphur as well as compounds of oxygen), resins and also asphaltenes (which are the high molecular weight constituent having relatively high atomic molecules with high level of metals), which are in physical equilibrium with each other in the form of colloid [10,11] that are processed into various petroleum fractions to give vital sources of energy, derivatives and chemicals for the petrochemical industry[12,8].The chemical utilization of crude oils and petroleum products experiencing swift increase has attracted studies to probe into the knowledge of the chemical composition, structure or framework and characteristics of their fractions [13]. The remaining components of crude oil included trace amounts of oxygen, nitrogen, sulphur, carbon dioxide, and metals like iron, vanadium, nickel, and chromium /9,2].The nitrogen occurs in the range of 0.01 to 2% as dissolved gas in the crude oil and oxygen occurs in distinct forms in oxygen-carrying resin-like materials [2].The physical attributes and chemical composition change from one reservoir to another as well as the different depths in the same oil well *[9]*. Owing to the complexity, to characterize and comprehend the chemical composition of crude oil, many analytical techniques with high resolving power are required, such as paraffinic chains, naphthenic structures, and aromatic structures [8].

The measurable attributes of crude oils that are quantifiable are termed the characteristics of crude oils. These properties change in accordance with the content of oil, the relative availability of the hydrocarbons group as well as the essential dependence on reservoir temperatures and pressures. The physical properties which are vital include the following: American Petroleum Institute (API) gravity, and viscosity, density, pour and cloud points and sulphur content (%). These vital parameters are utilized in the classification and specification of crude oil blends [14].

The stagnation in the development and adoption of new catalyst support materials since World War II is indeed noteworthy. While advancements have been made in catalytic processes, the reliance on traditional materials like alumina, silica, and carbon

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persists due to their familiarity, availability, and proven performance. However, these materials are not without their limitations. Alumina, for instance, can suffer from low surface area and limited thermal stability, while silica may exhibit poor mechanical strength and susceptibility to deactivation under certain conditions. Carbon, on the other hand, may be prone to oxidation and can present challenges in terms of controlling surface chemistry. Despite these drawbacks, the inertia in adopting new support materials could be attributed to several factors. Firstly, the rigorous testing and validation required for any new material to enter commercial use can be time-consuming and costly. Additionally, there may be a lack of incentive for industries to invest in the development of alternative support materials when existing options meet their immediate needs.

However, the landscape might be changing with increasing emphasis on sustainability, efficiency, and performance optimization in catalytic processes. This renewed focus could drive research and development efforts towards exploring novel support materials with enhanced properties such as higher surface area, improved thermal stability, and better resistance to deactivation. In recent years, there has been growing interest in materials like metal-organic frameworks (MOFs), zeolites, and various nanoparticle-based supports for catalysis. These materials offer unique structural and chemical properties that could potentially overcome the limitations of traditional supports. While they may not have yet achieved widespread commercial adoption, ongoing research and technological advancements could pave the way for their integration into industrial catalytic processes in the future. The present study is aimed at evaluating the efficiency of a new, highly efficient low cost catalysts in terms of the physical characteristics of the products after undergoing the cracking procedure. A Co-Mo/zeolite catalyst with Co and Mo loadings of 3 wt. % and 14 wt.%, respectively, previously synthesized and characterized[16] was used. Co-Mo catalyst supported on zeolite derived from the inexpensive locally available kaolin clay, utilized as support, was synthesized by impregnation method. The products of the thermal and catalytic process using both the synthesized material and a commercial catalyst were evaluated.

MATERIALS AND METHODS

The synthesis of the catalyst (Co-Mo/Zeolite) utilized for this study was discussed elsewhere. [15, 16]. The CoMo/zeolite catalyst was prepared using the impregnation method having synthesizing the zeolite from kaolinite clay(32)

Catalytic activity tests

Both the synthesized and commercial catalysts, zeolite Y (CBV100) were evaluated in a batch reactor. The experiments were conducted in a 400 ml stainless steel batch reactor. A 100 ml of feedstock made up of 75 g and 1g of catalyst was charged into the reactor, flushing and leak checked by pressurizing with nitrogen thereby creating an inert atmosphere and hydrogen gas was then introduced into the reactor. The heat required for the reaction was provided by a 75W heater connected with a thermocouple. The residence time measurement began from the point when the liquid temperature reached the desired temperature. The sample bottles were oven dried and properly labeled for the storage

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of the cracked product. The five reaction temperatures considered for this study were within 300 °C to 500 °C and the residence time varied from 5 minutes to 25 minutes. All data concerning the reaction conditions and the products yield are reported in the tables. During the reaction, the components present in the feedstock were cracked to yield gas, liquid and solid (coke), products

- ***Percentage yield (%yield)***

The percent yield of the desired product is defined as the amount of the particular product obtained from the bonny light oil feed after cracking reaction divided by the amount of bonny crude oil feed.

$$\text{Percentage Yield (\%)} = \frac{D}{F} \times 100 \qquad (1)$$

Where: D= amount of desired product (gas, solid and liquid product).

F =amount of crude oil feed.

The liquid collected after the cracking of crude oil over the Co-Mo/zeolite catalyst as well as the commercial zeolite Y and thermal cracking were subjected to physical measurements. The following physical properties were determined from the liquid products of cracking reactions; density, specific gravity, API, viscosity, pour point, and cloud point.

- ***APIgravity and Density measurement***

The feedstock and the liquid products produced were measured physically in line with ASTM D-1250 to assess their density and American Petroleum Institute (API) gravity, or how heavy or light a crude oil is in comparison to water.

50ml density bottle (empty) was washed, oven-dried, followed by weighing on an analytical weighing balance, this weight was recorded. The weight of 50ml of water in the density bottle was weighed and recorded. 50ml of the cracked liquid was transferred into the empty density bottle, weighed and recorded in triplicates. The average weight was determined, and the weights of the liquid products were obtained through arithmetic. The densities of the liquid products were determined using the relation below.

$$\text{Density (g/ml)} = \frac{weight\ of\ the\ liquid\ product}{volume\ of\ density\ bottle} \qquad (2)$$

The specific gravities were obtained using the relation below.

$$\text{Specific Gravity} = \frac{density\ of\ the\ liquid\ product}{density\ of\ water} \qquad (3)$$

The API value for each liquid product was determined using the relation below.

$$^{o}\text{API} = \frac{141.5}{specific\ gravity} - 131.5 \qquad (4)$$

- ***Viscosity measurement***

The viscometer with model number NDJ-8S was used to measure the viscosity of the cracked product samples making use of rotor 1 at a constant speed of 60RPM (revolution per minute). The liquid product (filtrate) (60ml) was poured into a beaker and the rotor attached to the viscometer was inserted into it. The viscometer was started and it stops automatically after the viscosity of the material has been determined. The readings were displayed in milli Pascal per seconds.

- ***Pour point***

The liquid product samples (10ml) were measured in a measuring cylinder; the test tube was placed into a beaker containing 50g of ice. Thermometer was used to monitor the temperature at

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which the oil begins to turn into semi solid (temperature at which the oil ceases to flow). The procedure was carried out three (3) times, for each sample of oil and the average was determined.

- ***Cloud point***

The liquid product samples (10ml) were measured in a measuring cylinder; the test tube was placed into a beaker containing 50g of ice. Thermometer was used to monitor the temperature at which the oil begin to thickens or show a cloudy appearance. The procedure was carried out three (3) times, for each sample of oil and the average was determined.

RESULTS AND DISCUSSION

The degree of cracking differs greatly, depending on the composition of the feedstock as well as the origin/location of the crude oil [17]. Only one light crude oil feedstock was studied; having an API gravity of 29.9 °API and viscosity of 8.00 mPa.s. However, the detailed properties of the feedstock used have been reported elsewhere [16]

Effects of reaction conditions

The principal characteristics of the liquid products obtained that are of much importance in any oil upgrading process includes: the overall product yield, API gravity, liquid product viscosity, and impurity removal [17]. The effects of reaction conditions, such as temperature, on thermal cracking, catalytic cracking using Co-Mo/Zeolite catalysts, and catalytic cracking using Zeolite Y catalysts, were therefore investigated in this section.

Effect of temperature on the mass balance

In addition to the degree of upgrading of the oil produced as measured by viscosity and API gravity analysis, the study on the temperature influence on the yield of liquid, gas, and coke deposited was investigated in both thermal cracking and upon the employment of catalysts. After deducting the masses of the oil produced and the solid deposited in the reactor, the mass of gas evolved during cracking reactions was determined to be the mass of oil remaining. The following equations were used to compute the mass balance of the three pseudo-products, liquid, gas, and coke, in terms of a percentage of the Bonny light crude oil [18,19]:

$$\text{Yield (wt \%)} = \frac{Wj}{Wf} \times 100 \quad (5)$$

Gas (wt %) = 100 - coke yield (wt %)- liquid yield (wt %)

Wf is the total weight of the Bonny light crude oil, and Wj is the weight of component j.

Tables 1.0 (a), (b) and (c) shows the mass balance of gas, liquid, and coke (obtained from thermal, catalytic cracking reactions using synthetic Co-Mo/zeolite catalyst, and catalytic cracking reactions using commercial zeolite Y catalyst) from which it can be seen that the lower temperature favors lower manufacture of gases and coke and more liquid products, which are obvious indications of a low extent (i.e. degree) of both thermal as well as catalytic cracking. The quantity of coke produced at 350°C, 5 minutes reaction time was 0.45 wt % compared to the 2.58 wt % at 450°C, 5 minutes, and the corresponding measured liquid were 84.95 wt % and 72.32 wt % respectively. The yield of the gases at the same temperature and time was 12.56 wt % and 25.19 wt

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%. The same trends were seen in the cracking process involving the use of the synthesized Co-Mo/zeolite and the commercial zeolite Y catalysts at the temperature and time under consideration. The quantity of coke produced at 350°C, and 5 minutes reaction time for cracking over the synthesized Co-Mo/zeolite was 0.80 wt % compared to the 1.64 wt % at 450°C, 5 minutes, and the corresponding measured liquid were 85.33 wt % and 55.71 wt % respectively. The yield of the gases at the same temperature and time was 13.33 wt % and 40 wt %. The quantity of coke produced at 350°C, and 5 minutes reaction time for cracking reactions over the synthesized Zeolite Y was 0.66 wt % compared to the 1.75 wt % at 450°C, 5 minutes, and the corresponding measured liquid were 86.67 wt % and 82.86 wt % respectively. The yield of the gases at the same temperature and time was 9.33 wt % and 14.29 wt %. The increased manufacture of gas and coke at higher temperatures was due to the increased catalytic cracking with temperature rise which is a similar trends earlier reported [18.19,16] in the distribution of the gas, liquid and coke during the cracking reactions.

Table 1.0: (a) Product yields from catalytic cracking using commercial zeolite, expressed as a percentage

Temp.(°C)	Time(mins)	Gas	Liquid products	Coke
300	5	6.67	93.33	0.89
350	5	9.33	86.67	0.66
400	5	14.29	85.00	0.41
450	5	14.29	82.86	1.75
500	5	42.67	46.67	2.26

Table 1.0 (b): Product yields from thermal cracking expressed as a percentage

Temp. (°C)	Time (mins.)	Gas	Liquid product	Coke
300°C	5	14.14	63.44	0.44
	15	17.24	75.86	0.88
	25	17.25	82.75	1.67
350°C	5	12.56	84.95	0.45
	15	18.92	78.38	1.49
	25	20.27	67.57	1.25
400°C	5	18.81	75.57	0.96
	15	19.67	79.75	0.58
	25	20.00	84.00	0.85
450°C	5	25.19	72.32	2.58

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	15	26.25	71.52	2.12
	25	31.25	62.50	2.59
500°C	5	20.55	76.71	2.62
	15	25.00	18.75	2.36
	25	81.25	12.50	2.26

Table 1.0 (c): Product yields from catalytic cracking using Co-Mo/zeolite expressed as a percentage.

Temp. (°C)	Time (mins.)	Gas	Liquid product	Coke
300	5	6.67	86.67	2.39
	15	6.25	92.50	0.75
	25	12.50	87.50	0.62
350	5	13.33	85.33	0.79
	15	6.67	86.67	0.71
	25	6.67	92.00	0.50
400	5	6.67	85.33	1.54
	15	6.67	84.94	1.40
	25	6.67	78.64	0.96
450	5	40.00	55.71	1.64
	15	25.00	71.27	1.40
	25	18.75	82.30	2.31
500	5	56.25	40.00	0.75
	15	88.24	11.25	1.36
	25	80.00	13.33	1.69

Effect of Hydrogen on Mass Balance

Table 1.0 (d) shows the mass balance of gas and liquid as well as the coke yields during the catalytic cracking process with the use of hydrogen gas at 350°C

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Without doubt, the yield of coke produced from the thermal cracking reaction was 0.66 wt. %, as seen in Table1.0 (a) which is lower than that obtained under hydrogen reaction media. Conversely, the yield of the liquid products increased by 11.04 wt. % above 76.96 wt. % obtained from the thermal cracking reactions. However, the liquid product yield from the addition of hydrogen gas to the feedstock upgrading processes can cause an increase of up to 20-25 volume percent greater than the yield from other processes. The hydrogenation of the fragments enhanced the yield of liquid product [17]

Table 1.0 (d): Mass balance of products; Reaction media: Hydrogen gas, reaction temperature: 350°C, catalyst: synthesized Co-Mo/zeolite.

Products	Co-Mo/Zeolite	Thermal
Liquid	88.00	76.96
Gas	8.89	17.25
Coke	0.67	0.66

°

API, density and relative density

The feed and generated oils' densities and API gravities (i.e., how heavy or light a crude oil is relative to water) were calculated [19]. It is a grade that regulates how easily crude oil can be transported through pipelines [20].The sulphur content and gravity of petroleum are the two most important properties that influence market value. Petroleum with a low sulphur concentration is especially recommended [21]. Additionally, the results for both catalysts showed that the density of the generated oils declined or decreased as temperature increased, indicating an increase in the feed conversion into lighter products at high temperatures [22]. The grade or quality of crude oils is determined by API gravity [23].

According to Adetoro and coworker, [23] petroleum samples with an API gravity of 20 or less are considered to be heavy petroleum, whereas samples with API gravity of 31 or above are generally considered to be light crude oils. The lighter the substance, the higher the API gravity value indicates. Light crudes typically have an API gravity of 38^{O}API or above, whereas heavy crudes are all crudes with an API gravity of 22^{O}API or lower. Bonny When compared to the API standard of 22°, the light petroleum used in this study has an API gravity of 29.9°, making it lightweight petroleum.

Temperature's impact on API gravity

The API gravity of the oils generated at various processing temperatures is displayed in Figures 1.0. It is a clear indication that the API gravity of the oil produced from the cracking reactions increased as the temperature of the reaction increases from 300°C, 5 minutes to 500°C, 5 minutes. There is a notable increase in the API gravity as seen for all the cracking process with the reactions over synthesized Co-Mo/Zeolite having better API gravities. This is likely due to the fact that during the reactions, the catalyst has not been deactivated and is still quite active. An initial API increase of 1.5 to 6 degrees was observed in the oil generated for the three samples at lower temperatures of 350 and 400 compared to the crude oil sample (feedstock).

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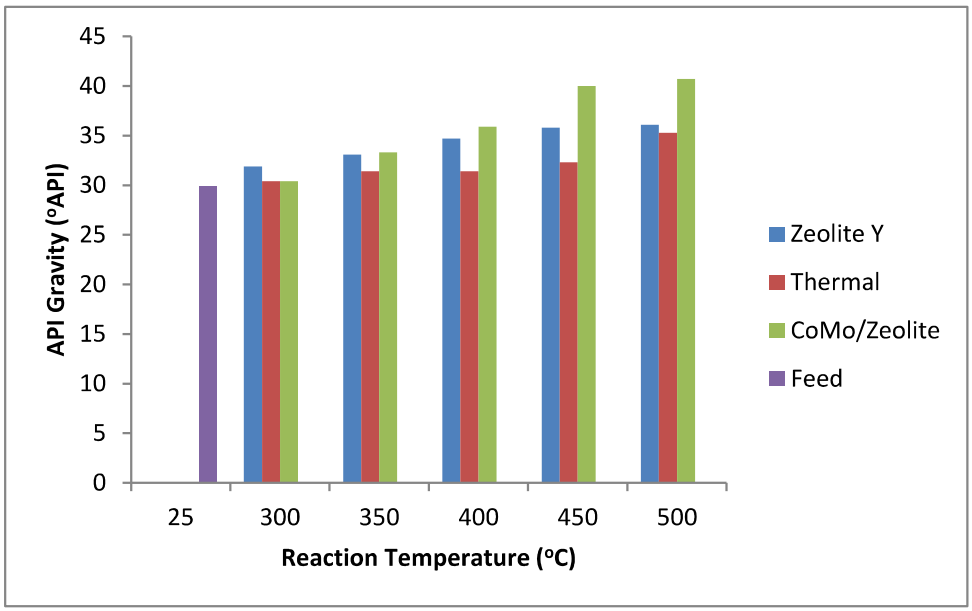


Fig. 1.0: The oil's API gravity created via thermal cracking, catalytic cracking, and commercial zeolite Y catalysts over synthetic Co-Mo/zeolite and reaction temperatures for five minutes.

The extent of upgrading appears to be influenced by temperature at higher temperatures in the raised zone, with a jump of roughly 2.4–10.1o at 450 °C for the three processes. The optimum cracking temperatures for the cracking processes were 450 °C and 500 °C, and further temperature increases result in increased coke deposition, necessitating reactor shutdown due to the reactor being filled with coke. As reported by Hart et al. earlier, these observed trends in API gravity were expected. A complete description of the crude oil and each of its constituents is required in order to determine the crude oil's refining value. However, two characteristics—API gravity (a measure of density) and sulphur content—are particularly important for the quick classification and comparison of crude oils. Oil's reluctance to flowing is referred to as viscosity. It is noteworthy because it demonstrates how easily oil flows, can be pumped, and can be atomized. Fuel oil viscosities change due to variations in the constituents' concentrations and various refining processes [21].

Viscosity

According to Akankpo and Essien [24], the viscosity of crude oil is a crucial physical property of petroleum that is important in the study of flow characteristics. This property governs and influences the movement of the crude oil via pipelines. By creating a force of friction between boundary walls and fluid particles, viscosity defies the motion [25]. Crude oil's viscosity varies depending on where it's derived from, the type it is, and how its chemical composition originates [26].

A high viscosity results in a pressure decrease in the pipelines, which increases the energy required to

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pump the fluid [27]. In order to analyze the viscosity of crude oil, the American Petroleum Institute gravity unit °API gravity) is frequently employed in the production of crude oil [27]. As displayed in table 1.1, according to an early work [24], the viscosities of crude oils increase with both a decrease in temperature and a fall in API gravity. It shrinks (thins) as the temperature rises. It's important because it shows how easily oil flows or is frequently pumped. In the production of crude oil, pipeline transit, and oil recovery procedures, viscosity and density play a critical role. Due to their great importance, these features should be carefully evaluated for reservoir simulation [28]. The reduced viscosity and higher API gravity value, a measure of the price of petroleum, were produced by the greater temperature. According to Akankpo and Essien [24], high API values indicate that the oil is light and can be moved readily through pipelines.

Table 1.1: The viscosities of thermal cracking and catalytic cracking liquid products

Temperature (°C)	Time (minutes)	Thermal cracking	Co-Mo/Zeolite
300	5	11.58	12.00
	15	12.96	13.50
	25	13.05	13.75
350	5	13.5	14.00
	15	14.65	14.85
	25	14.70	14.95
400	5	14.00	15.00
	15	15.40	16.25
	25	15.65	16.50
450	5	17.05	17.5
	15	17.20	17.45
	25	17.59	17.65
500	5	17.56	18.00

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	15	17.69	17.95
	25	17.85	18.50

Table 1.2: The viscosity of liquids during the catalytic process using Zeolite Y catalyst.

Temperature (°C)	Time (Minutes)	Zeolite Y
300	5	11.00
350	5	13.35
400	5	13.96
450	5	16.95
500	5	17.2

Effect of temperature on viscosity

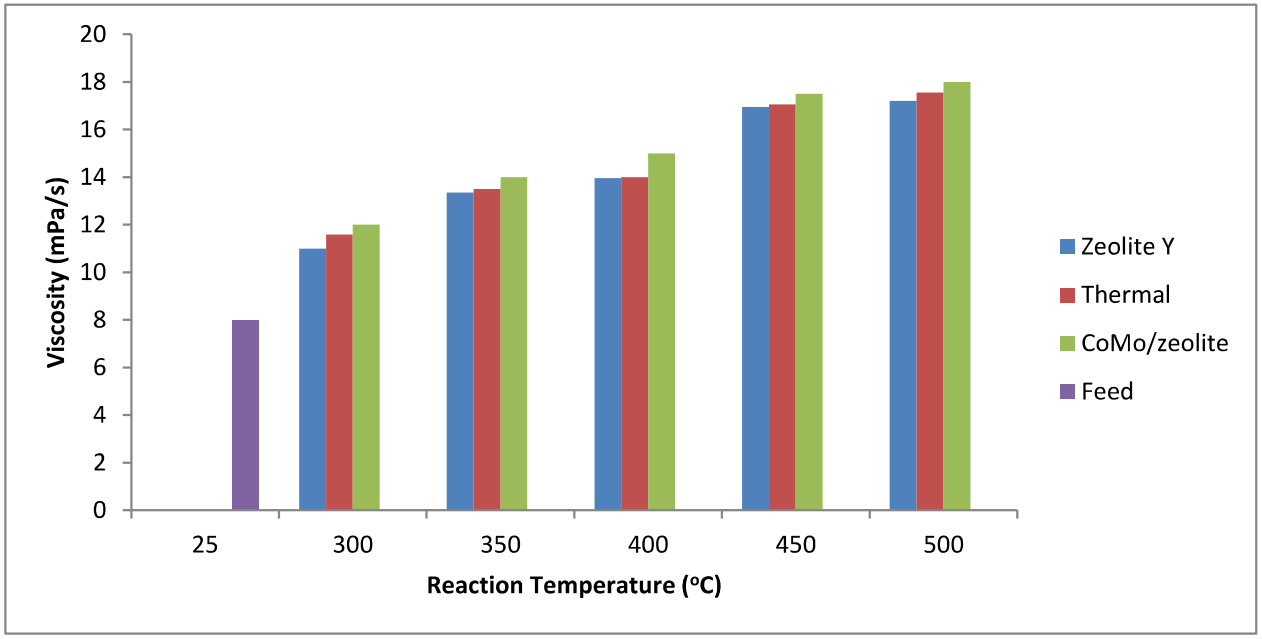


Fig. 1.1: Viscosity of produced oils during the thermal, catalytic over the synthesized Co-Mo/zeolite and commercial zeolite Y catalysts at reaction temperatures at 5 minutes.

Figure 1.1 displays the viscosity of the oil generated as a function of time and reaction temperature. In comparison to the viscous Bonny light crude oil feed, which can be seen in this figure, the viscosity of the fractured oil has been significantly reduced, with a noticeable reduction at temperatures above 400 °C.

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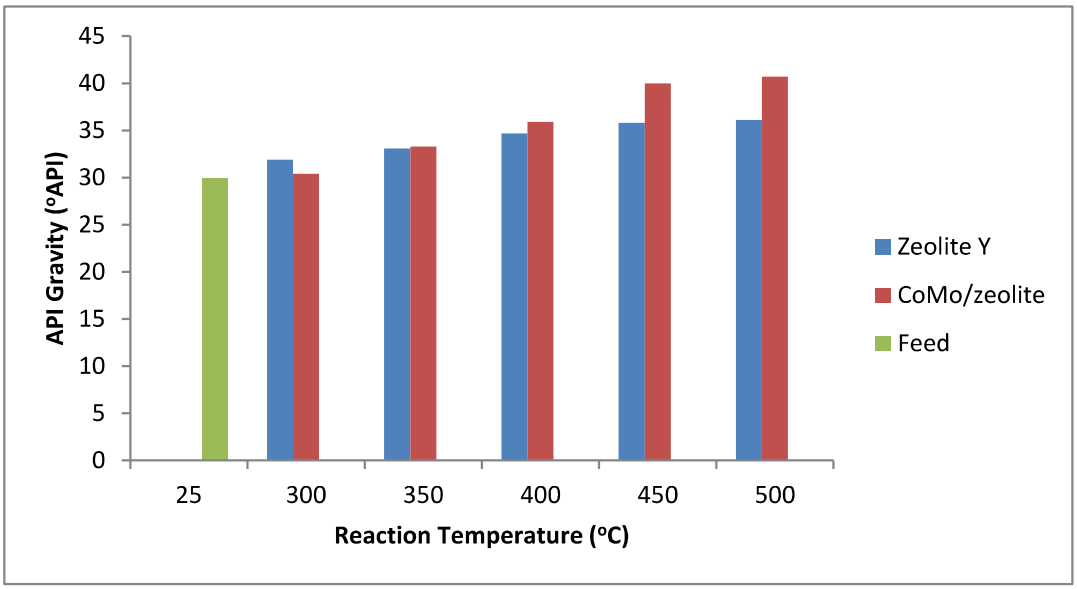
At 400, reaction temperatures and 5 minutes for thermal and cracking processes over Zeolite Y catalyst, the viscosity reduction of the oil produced were almost the same, found to be 13.96 and 14 mPa/s respectively, from the base value of 8.00 mPa.s for the feedstock. Note that the high values imply thinness of the produced oil samples. These values corresponded to about 2 times higher than the viscosity of the feedstock. At 300, and 500 ^{o}C reaction temperatures and 5 minutes for catalytic cracking over the synthesized Co-Mo/zeolite, the average viscosity of the oil produced reduced significantly with values of 12.00, and 18.00 mPa.s respectively, from the base value of 8.00 mPa.s for the feedstock. Note that the high values imply thinness of the produced oil samples. These values corresponded to about 1.5 and 2.3 times higher than the viscosity of the feedstock. The extent of reduction of the viscosity, which was about 55% increases in the value of viscosity compared to the viscosity of the feedstock at 500 ^{o}C in the presence of Co - Mo/zeolite, is a representation of a major step in the upgrading of crude oil. The viscosities of the oil produced at the reaction temperatures at 5 minutes for cracking over the commercial zeolite Y, were seen to have reduced compared to that of the feedstock. The oil produced was less viscous than the feedstock with viscosity of 8.00 mPa.s. In general, it is evident that as the temperature increases there were corresponding decrease in the viscosity of each product, appearing to approach an asymptotic limit [.5]. The reduction in the stress encountered during crude oil production, transportation, etc, due to the cracking of the oil, can be achieved. Crude oil with high viscosities could cause pipeline pressure drop and decrease in flow rate, these liquid products posses increased flow rate because of their low viscosities [24]. The data obtained for the viscosities of the liquid products which is temperature and pressure dependent can assist reservoir engineering, scientists and design operations.[26]. The results of the viscosity indicate that whenever the temperature is raised, there is a correspondent decreases in the viscosity thus indicating an inverse correlation between the temperature and the viscosity [28].

Effects of synthesized Co-Mo/Zeolite catalysts and Zeolite Y.

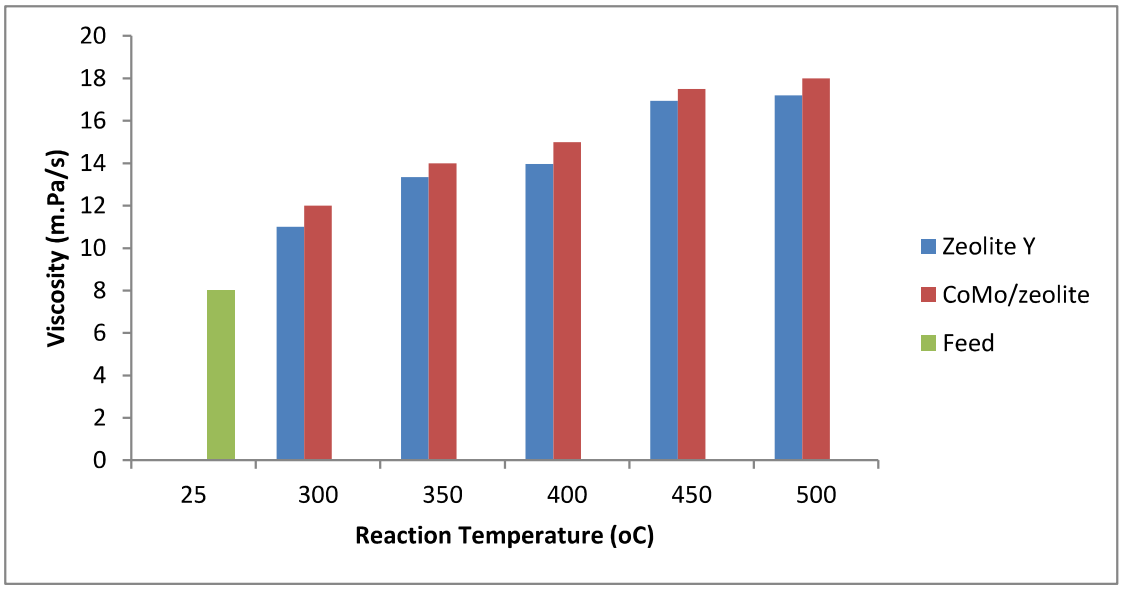
The acidic sites of the support execute cracking reactions, while the metal sites of the catalyst improve hydrogen-dehydrogenation performance. The commercial catalyst's catalytic performance was compared to that of the synthesized Co-Mo/zeolite..

Impact of synthetic Co-Mo/Zeolite and Zeolite Y-catalysts on API gravity and viscosity

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(a)



(b)

Fig. 1.2: Effect of Zeolite Y and synthesized Co-Mo/zeolite catalysts on produced oil (a) API gravity and (b) viscosity.

The API gravity and viscosity of the oil made with the synthetic Co-Mo/zeolite and zeolite Y catalysts are shown in Figure 1.2 as functions of temperature. The oil produced from the cracking reactions over the synthesized Co-Mo/zeolite catalyst was better with a mean API gravity of 36.06 °API with increase compared to zeolite Y with a mean API gravity of 34.32 °API, which indicated a further 1.74 °API gravity increase using the synthesized Co-Mo/zeolite catalyst.As predicted, the oil created by the cracking reaction over a synthetic Co-Mo/zeolite catalyst showed a further drop in API gravity of 1.74 and a viscosity reduction of more than 90% from the oil generated when zeolite Y catalyst was utilized. In

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addition to cracking processes by the acid sites, hydroconversion also had a significant role in the change in API and decrease in viscosity. As opposed to the zeolite Y catalyst, the synthesized Co-Mo/zeolite catalyst enhanced hydrogen uptake by free radicals to speed up hydrogenation reactions [17], while molybdenum provided inherent activity for the reactions of hydrodesulphurization (HDS) [29]. The molybdenum metal's concerted action, which enhanced the catalytic activity of this catalyst, is responsible for the synthetic Co-Mo/zeolite catalyst's superiority over zeolite Y. As long as the two metals in the catalyst are chemically bonded together and do not separate into individual metals, this coordinated effect is maintained. Additionally, it was discovered that molybdenum metal initiated faster and was more active than nickel metal, which helped to explain the catalyst's high activity [17]

Effect of Hydrogen

Impact of Hydrogen on API gravity

By breaking the C-C, C-S, and C-N bonds of species with high molecular weight, under the inclusion of hydrogen at elevated pressure and in the presence of a typical catalyst, catalytic cracking, which occurs in the presence of hydrogen gas, converts the hydrocarbon content of the oil into simpler molecules. These species are then hydrogenated, which transforms them into hydrocarbons with decreased molecular weight. As said, hydrogen encourages the saturation of olefins and aromatics, aids in the elimination of the precursors of free radical coke formed during the cracking reactions, and raises the hydrogen-to-carbon ratio of the oil produced. The output of these events can eventually result in the detachment of a heteroatom, which can results to coke and subsequent deactivation of catalyst [22].

Using a Co-Mo/zeolite catalyst at a reaction temperature of 450 ^{o}C and a residence duration of 15 minutes, the effect of hydrogen on API gravity was investigated. Figure 1.0 depicts how the addition of hydrogen affected the API gravity of the oil that was produced. It is clear that the addition of hydrogen increased the API gravity of the oil produced when compared to thermal cracking reactions. When hydrogen was employed as the reaction medium, the average increase in API gravity was 10.1 ^{o}API as opposed to the Bonny Light Crude oil feedstock's 29.9 ^{o}API [17]. Co-Mo/zeolite is a typical metal and acidic bifunctional catalyst that promotes both hydrogenation and hydrocracking. The metal-containing sites encourage hydrogen addition to the acidic support sites, accelerating cracking events by a carbocationic mechanism. . Cracking reactions occurring over a hydrodesulphurization or hydrotreating catalyst; Co-Mo/zeolite, takes place through varying steps. Outsized molecules are split into smaller pieces, releasing fragmented free radicals that combine with hydrogen radicals to stabilize hydrocarbon chains and end the process. The active chains would be seen to continue reacting with one another in the absence of hydrogen, leading to the formation of compounds with higher molecular weight through polymerization, an increased yield of coke, as well as negative effects on the viscosity and API upgrading of the produced oil.. C-C, C-S, and C-N bonds are broken during hydrocracking processes, resulting in chains of free radical hydrocarbons. The termination of the active chains of these free radicals is a crucial step that is made possible by the attachment of hydrogen and results in the viscosity

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reduction of the generated oils. The free radicals produced during thermal or catalytic cracking events are extremely unstable, and hydrogen typically stabilizes them. However, an increase in hydrocracking and hydrogenation processes has previously been linked to API changes, which is consistent with the findings described here [18]

Pour and cloud points

The cloud points of the liquid products obtained from thermal and catalytic cracking over the synthesized sulphided Co-Mo/zeolite catalyst had temperature limit that is above the least expected annual mean temperature (>18°C) which is an indication that Nigeria is a tropical region with the exception of liquid products obtained from the cracking processes over the commercial catalyst which is an indication that deposition of wax can be prevented in this region with ease. However, from this Figures 1.3 a and b, it is seen that the pour points of the liquid products samples are beneath the ambient temperature mostly for the onshore pipeline equipments in the Niger Delta area. A critical observation of the figure indicated that liquid products from thermal cracking and catalytic cracking reactions over Co-Mo/zeolite catalyst has the lowest pour points while liquid products from cracking reactions over thermal process has the highest pour point which indicated that liquid products from zeolite Y and catalytic cracking over Co-Mo/zeolite catalyst contained the highest paraffin content with liquid products from the reactions over thermal process having the lowest paraffin content [30].

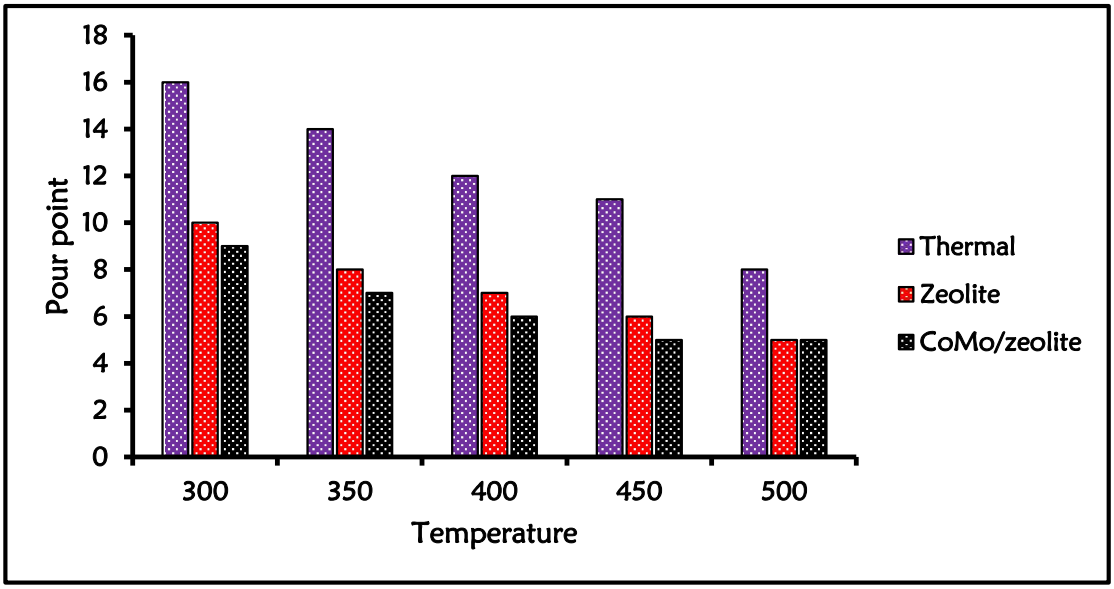


Fig.1.3 (a): Effect of temperature on pour point

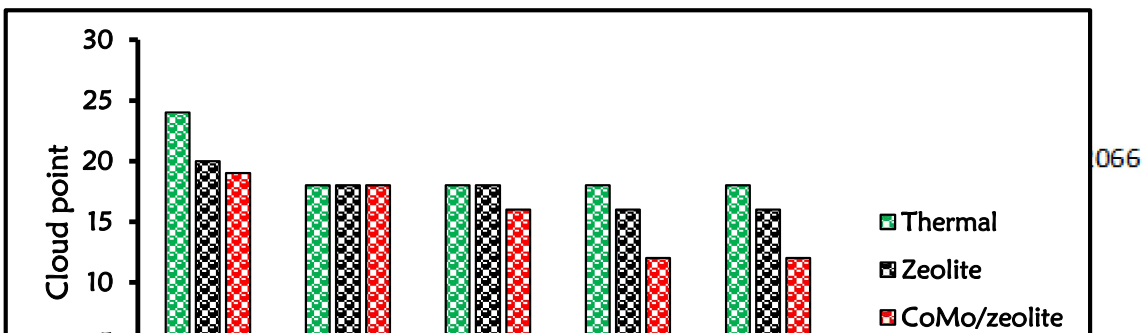


Fig.1.3 (b): Effect of temperature on cloud point

The deposition of wax reduces with a rise in the temperature difference. The cloud as well as the pour point temperatures is affected by the quantity of paraffin wax present in the samples of crude oil. There is high tendency of wax deposition in crude oils having high paraffin wax content than those with lower paraffin wax since wax can readily bundle up when there is high content than when there is a lesser content. The quantities of paraffin wax contained in a crude oil sample directly influence the rate at which crude oil reaches its cloud and pour point. Densities, specific gravities as well as the viscosities are factors that determine the pour and cloud point of crude oil samples. There is an existed relationship between specific gravity and density. In the same vein, the specific gravity also affected the viscosity since a denser fluid will be more viscous. Since cloud and pour point is affected directly by viscosity, the higher density, specific gravity and viscosity of the oil sample caused a great tendency in the oil reaching its pour and cloud points as demonstrated in figure 1.3 a and b respectively [30]. The low viscosities and pour points obtained for the liquid products makes the crude suitable as fuel in industrial furnaces and refineries, since the high viscosities and pour points of petroleum render it unsuitable as fuel in industrial furnaces and refineries [31].

Viscosity

The viscosity of crude oil is a vital property (i.e. physical property) of petroleum essential in the studying of flow characteristics [24]; a property that controls and effects the movement of the crude oil via the pipelines. Viscosity brings defiance to the motion by giving rise to friction force between boundary walls and fluid particles [25] The origin, type and the nature of its chemical composition contributes to the variation in the viscosity of crude oil [26]. A high viscosity causes a correspondent increase of pump energy as it generates pressure drop in the pipelines [27]. The American Petroleum Institute gravity unit (°API gravity) is majorly used in the manufacture of crude oil to study the viscosity of crude oil *[*27] The viscosities of crude oils increase with decrease in API gravity and also increase with decrease in temperature *[24].* It decreases (thins) with increasing temperature. It's significant because it indicates the convenience at which oil flows or is often pumped. Viscosity and density are very vital in crude oil manufacture, transportation via pipelines, as well as recovery processes of oil. These properties are

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of high importance and thus should be assessed precisely for simulation of the reservoir. [28]. The higher temperature resulted to the lower the viscosity, as well as the higher the API gravity value which is an indicator of the price of the petroleum. High API values means the crude is light and may be easily transported in pipelines.*[24]*.

Effect of temperature on viscosity

The viscosity of the oil produced as a function of time at the temperature of reactions is shown in Figure 1.4. From this Figure, significant reduction of viscosity of the cracked oil can be seen in comparison to the Bonny light crude oil feed which is viscous; with pronounced reduction at temperatures above 400°C. At 400°C, reaction temperatures and 5 minutes for thermal and cracking reactions over Zeolite Y catalyst, the viscosity reduction of the oil produced were almost the same, found to be 13.96 and 14 mPa/s respectively, from the base value of 8.00 mPa.s for the feedstock. Note that the high values imply thinness of the produced oil samples.

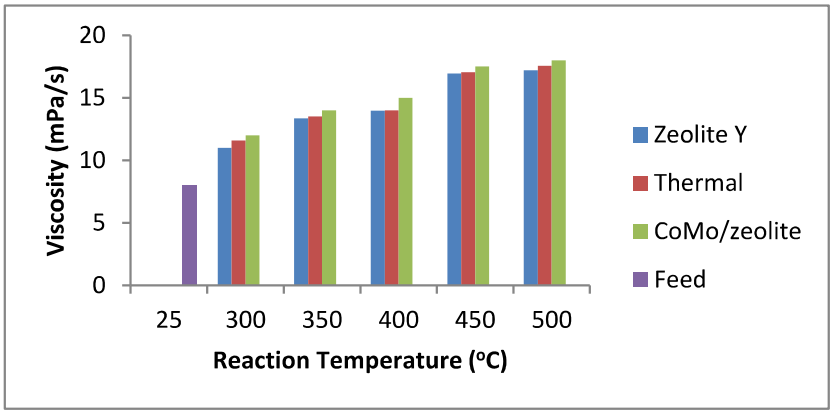


Fig. 1.4.: Viscosity of oil produced from thermal cracking, catalytic cracking over the synthesized Co-Mo/zeolite and commercial zeolite Y catalysts at reaction temperatures at 5 minutes.

These values corresponded to being about 2 times higher than the viscosity of the feedstock. At 300°C, and 500°C reaction temperatures and 5 minutes for catalytic cracking over the synthesized Co-Mo/zeolite, the average viscosity of the oil produced reduced significantly with values of 12.00, and 18.00 mPa.s respectively, from the base value of 8.00 mPa.s for the feedstock. Note that the high values imply thinness of the produced oil samples. These values corresponded to about 1.5 and 2.3 times higher than the viscosity of the feedstock. The extent of reduction of the viscosity, which was about 55% increases in the value of viscosity compared to the viscosity of the feedstock for the case of 500°C in the presence of Co-Mo/zeolite catalyst, is a representation of a significant step in the upgrading of crude oil. The viscosities of the oil produced at the reaction temperatures at 5 minutes for catalytic cracking over the commercial zeolite Y catalyst, were seen to have reduced compared to that of the feedstock. The oil produced was less viscous than the feedstock with viscosity of 8.00 mPa.s. In general, it is evident that as the temperature increases there were corresponding decrease in the viscosity of each

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product, appearing to approach an asymptotic limit [5]. The reduction in the stress encountered during crude oil production, transportation, etc, as a result of cracking of the oil, can be achieved. Since crude oil with high viscosities causes pipeline pressure drop and decrease in flow rate, these liquid products possess increased flow rate because of their low viscosities [24*]* The data obtained for the viscosities of the liquid products which is temperature and pressure dependent can assist reservoir engineering and design operations [27]. The results of the viscosity indicate that whenever the temperature is raised, there is a correspondent decreases in the viscosity thus indicating an inverse correlation between the temperature and the viscosity [28].

CONCLUSION

The developed Co-Mo/zeolite catalyst from inexpensive clay improved the cracking of crude oil with better features. The study found that, especially in more demanding circumstances, there was a tendency toward greater liquid product yields and decreased residual product development. The study looked at how the main characteristics of the cracked oils were impacted by temperature changes. Pour point, cloud point, viscosity, density, and API values were among the parameters that showed a gradual increase with higher temperatures. The study also examined the complex interactions between temperature, residence time, and hydrogen content that affect the cracked oils' composition. These discoveries greatly advance our knowledge of the ways in which various parameters affect the results of oil cracking operations.

Co-Mo/zeolite catalyst is recommended as an alternative to traditional industrial catalysts since it significantly improved and enhanced oil output and produced fuel that is environmentally benign.

Compliance with ethical standards
Conflict of interest

The authors declare that there is no conflict of interest.

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