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Study the Effect of Catalyst -to- Oil Ratio Parameter (COR) on Catalytic Cracking of Heavy Vacuum Gas Oil

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ABSTRACT

This work deals with the production of light fuel cuts of (gasoline, kerosene and gas oil) by catalytic cracking treatment of secondary product mater (heavy vacuum gas oil) which was produced from the vacuum distillation unit in any petroleum refinery. The objective of this research was to study the effect of the catalyst -to- oil ratio parameter on catalytic cracking process of heavy vacuum gas oil feed at constant temperature (450 °C). The first step of this treatment was, catalytic cracking of this material by constructed batch reactor occupied with auxiliary control devices, at selective range of the catalyst –to- oil ratio parameter (2, 2.5, 3 and 3.5) respectively. The conversion of heavy vacuum gas oil which was obtained, reaches to (50, 70, 75 and 80) % for (2, 2.5, 3 and 3.5 catalysts -to- oil ratio parameter respectively. The second step for this study was distillation of this cracking heavy vacuum gas oil liquid by atmospheric distillation device for these several catalyst -to- oil ratio parameter, according to obtained light fuel cuts (gasoline, kerosene and gas oil). The percentage volume of light fractions at various COR are (7, 25 and 18) for COR 2, (10, 20 and 40) for COR 2.5, (10, 30 and 35) for COR 3 and (15, 30 and 35) for COR 3.5 which separates according to its boiling point. The light cuts were distilled by atmospheric distillation device in order to obtained distillation curve. The third step was study the major physical and chemical properties for feed (heavy vacuum gas oil) and catalytic cracking liquid of HVGO at various COR with its light fuel fractions, the results refers to acceptable properties compared with other commercial properties.

Key word. Catalytic Cracking Reaction, Heavy vacuum gas oil, Catalyst to oil ratio parameter

دراسة تأثير نسبة العامل المساعد الى الزيت COR على تفاعل التكسير الحراري بالعامل المساعد لزيت الغاز الفراغي الثقيل

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الخلاصة

يتعلق هذا البحث بتحضير مقاطع بترولية خفيفة (كازولين, كيروسين, كازاويل) وذلك من معاملة مادة ثانوية ناتجة من تصفية النفط الخام وهي زيت الغاز الفراغي الثقيل بواسطة تفاعل التكسير الحراري بالعامل المساعد لها.كمية هذه الماده الناتجه من

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عملية التصفيه للنفط الخام تتراوح بحدود 30 % من كامل كمية اللقيم الداخل (النفط الخام) الغرض من هذا البحث هو دراسة تاثيرنسبة العامل المساعد الى الزيت على التكسير الحراري بالعامل المساعد لمادة زيت الغاز الفراغي الثقيل عند درجة حرارة 450 °م .الخطوه الاولى من المعامله هي تصميم وتنفيذ مفاعل دفعي يتضمن العديد من الاجهزه المساعدة كانت النسب المختارة من COR (2, 2.5, 3,3.5) كان مقدار التحول لهذه الماده الثانويه يصل الى (50, 70, 75, 80) بالتسلسل.الخطوه الثانيه كانت تقطير السائل المتكسر لزيت الغاز الفراغي الثقيل بواسطة جهاز التقطير الجوي لهذه النسب المختلفه من COR لغرض الحصول على مقاطع وقود خفيفه (كازولين, كيروسين, كازاويل) حيث كانت النسب الحجميه لهذه المقاطع الخفيفه تتراوح بين (7, 25, 18) الى COR =2 و (10, 20, 40) الى COR =2.5 و (10, 30, 35) الى COR =3 و(15, 30, 35) الى COR =3.5 والتي فصلت اعتمادا على درجة الغليان لهذه المقاطع ولغرض الحصول على منحنى التقطير لها. وكانت الخطوه الثالثه هي دراسة اهم الخواص الفيزياويه والكيمياويه الى زيت الغاز الفراغي الثقيل وسائل التكسير الحراري له ولمختلف نسب COR مع المقاطع الخفيفه الناتجه من التكسير بالعامل المساعد وكانت النتائج تشير الى تقارب هذه المواصفات مع الخواص التجاريه.

1. INTRODUCTION

The purpose of catalytic cracking reaction is to convert high boiling petroleum feedstocks to lower boiling products by cracking the hydrocarbon in the feed. During cracking, the condensed type molecules, such as naphthalene or anthracene, are converted into lower molecular weight hydrocarbons. The main kinds of feedstock for catalytic cracking are fractions generally boiling within the range of 200 – 500 °C. The refiners employed amorphous or synthetic silica – alumina catalysts. After cracking of heavy vacuum gas oil, fractional distillation separates light fuels and unconverted oil. Crude oils are mainly constituted of hydrocarbons mixed with variable amounts of sulfur, nitrogen, and oxygen compounds. **(Speight, J.G. 1999)**. Crude oils are not used directly as fuels or as feedstock for the production of chemicals, this is due to the complex nature of the crude oil mixture and the presence of some impurities that are corrosive or poisonous to processing catalysts **(Speight, J.G. 1999)**. Crude oils are refined to separate the mixture into simpler fractions that can be used as fuels, lubricants, or intermediate feedstock to the petrochemical industries**. (Speight, J.G. 1999)**. Heavy vacuum gas oil (HVGO) is complex mixtures of high molecular weight compounds. They consist of aromatic, aliphatic and naphthenic hydrocarbons, typically having carbon numbers from C_{20} to C_{50}, together with asphaltenes and smaller amounts of heterocyclic compounds containing sulphur, nitrogen and oxygen. **(Alkilani.A. Haitham, et al., 2007)** Vacuum gas oils are high boiling point petroleum cuts (350-550°C). HVGO consists primarily of the residue from distillation or cracking units in there refinery. **(Pillion L. Z, 2005)**.The increasing demand for transportation fuels such as gasoline, kerosene and diesel has led to an increased value for the atmospheric residue as a feedstock for vacuum distillation and for cracking processes. **(Gary, J. H., and Handwerk, G. H 2001)**Treatment in any thermal process results in the formation of gases, gasoline, middle distillate fractions (kerosene and gas oil), heavy residual fractions, and coke. The yield, relation between the reaction product's and the properties of these products depend on many factors, but the main role is played by the composition of the feed stock, the temperature, pressure and duration of the reaction. **(Alan G. Lucas 2001).** Mohammed et .al 2013 study the catalytic cracking of vacuum gas oil at reaction temperature range 440 – 500 °C and weight hour space velocity range 10 – 25 $h^{-1}$the conversion at 500 °C and WHSV 10 h^{-1} was 50.2 % and gasoline yield was 24.8 %. Reagan 1968 studied the catalytic cracking wax at the reaction temperature range 470 – 500 and catalyst to oil ration 0.2 – 0.8 by zeolite catalyst and the conversion reaches to more than 85%. Lappas et.al 1986 study the catalytic cracking for wax at reaction temperature 460, 500, 538 and 565°C and catalyst to oil ratio 2 – 12 to produce light fuels and the conversions ranges from 70 to 90 wt.%. Mori et .al study the thermal cracking of heavy oil at the reaction temperature 400 – 630 °C to produce the light oil and cracking gas to form by product carbon. The objective of this research was to study the effect of different catalyst -to- oil ratio on catalytic cracking process of heavy vacuum gas oil feed at constant temperature (450 °C).

2. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Heavy vacuum gas oil (HVGO)

The raw material for this study was heavy vacuum gas oil matter, which was obtained from the unit of vacuum distillation of AL-Dura refinery, which was used as a feedstock in this work and its major physical and chemical properties were listed in table 2.

2.1.2 Catalyst

The catalyst that will be used for cracking heavy vacuum gas oil and other matters like (slack wax, vacuum residue, furfural extract oil,…etc.) was prepared by previous work, have some major properties were listed in table 1.

Table 1. Properties of catalyst.

Characteristics	Value
Average pore diameter A^o	9
Surface area, m^2/ gm.	230
Granular size, mm	3-8

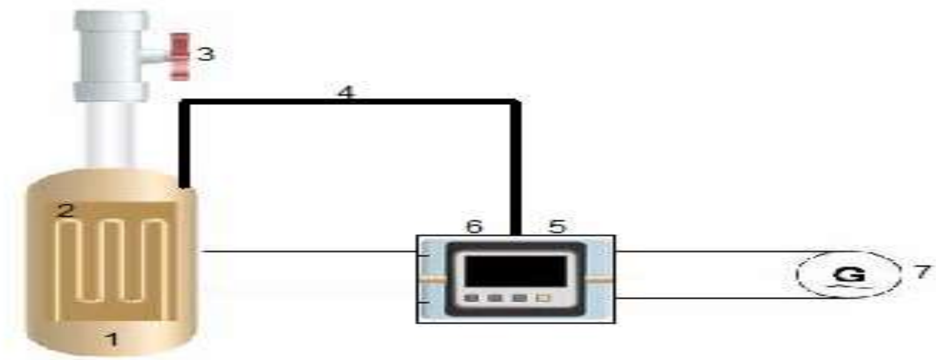
2.2. Procedure of the work:-

The process of catalytic cracking of heavy vacuum gas oil feed were carried out in designed batch reactor unit **Fig.1, and Fig.2**, made of carbon steel and its volume about 300 ml., which contain two valves, upper for inlet raw material and down for discharge product, occupied with many auxiliary parts, like (electrical heater, thermocouple, timer, temperature controller, hood).

The desired quantity (110 ml) of the (HVGO) fed in the reactor, which contains amount of prepared zeolite catalyst, used as catalytic cracking reaction with ratio of feed, and by several runs with various amount of catalyst -to- oil ratios (2, 2.5, 3 and 3.5) that will be used as variable parameter for catalytic cracking process. The cracking will be occurred with constant temperature at 450 °C inside the reactor which controlled by temperature controller and pressure about (80 – 90) atmosphere. The results of cracked HVGO liquid were listed in **Table 2.**

The second step is, distillation process that will be done by ASTM- D86 device; (which consist of heater, condenser, Flask) on the heavy vacuum gas oil feed and cracked liquid fuel and its light products to final distillation temperature is 350 °C and the results were listed in **table 2**. And finely calculate the major physical and chemical properties of the heavy vacuum gas oil feed and cracked HVGO liquid also its light fuel fractions (gasoline, kerosene and gas oil) in order to compare it with commercial types and possibilities of use it in various usages.

Figure 1. Laboratory batch reactor device.



[1-Reactor 2-Heater 3-Valve 4-Thermocouple 5-Timer 6- Temperature controller 7-Electrical source]

Figure 2. Flow diagram of experimental batch reactor unit with controls system.

3. RESULTS AND DISCUSSION

3.1. Atmospheric distillation (ASTM D-86 method)

The analysis of the heavy vacuum gas oil and different cracked HVGO liquid, for all these ranges of catalyst -to- oil ratio results are shown in **table 2.**

Table2. Atmospheric distillation for HVGO feed and cracked HVGO liquid feed at different catalysts -to- oil ratio.

Volume %	HVGO feed °C	The cracked HVGO liquid feed at different catalyst -to- oil ratio			
Conversion %		**2**	**2.5**	**3**	**3.5**
0	198	80	65	68	60
5	262	166	100	110	90
10	266	190	165	184	164
15	280	210	256	200	178

20	294	218	260	240	190
25	304	230	266	250	216
30	312	244	268	260	242
35	325	260	276	270	248
40	338	290	270	274	252
✓ **45**	**350**	308	276	282	264
✓ **50**		**350**	278	288	288
55			286	294	294
60			290	300	300
65			292	308	306
✓ **70**			**350**	344	318
✓ **75**				**350**	324
✓ **80**					**350**
Average temperature	**320** °C	**245** °C	**260** °C	**270** °C	**286** °C

Table.2. represents the atmospheric distillation results for HVGO feed and cracked HVGO liquid feed in deferent amount of catalyst -to- oil ratio of catalytic cracking fed in reactor.

Can noticed from the above results, the cracking will be occurs in all selected catalyst -to- oil ratio, but at different conversion according to amount of COR, So the conversion of HVGO reaches to 50% at COR equal to 2, also the conversion of HVGO reaches to 70 % at COR equal to 2.5 and the conversion of HVGO reaches to 75 % at COR equal to 3, but the best conversion is reaches to 80% at COR equal to 3.5, due to their high conversion and high amount of gasoline product as shown in **figure 7**.

Based on the maximum of the gasoline yield and middle distillate yield, it could be said that the best catalyst -to- oil ratio of catalytic cracking reaction is 3.5.

3.2 Physical and chemical properties for HVGO feed and catalytic cracking products.

The physical and chemical properties of HVGO at 450 °C for different catalyst to oil ratio (2, 2.5, 3 and 3.5) are shown in **tables 3, 4, 5 and 6**.

The properties of the catalytic cracking process for HVGO feed at 450 °C and at the catalyst -to- oil ratio of **2** are shown in **Table 3.**

Table3. Physical and chemical properties for HVGO feed and it fractions.

Property	ASTM D method	HVGO feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	ASTM D1298	0.973	0.9446	0.898	0.9554	0.973
API gravity	ASTM D1298	13.962	18.3	26.1	16.6	13.92
Mean average boiling point.° C	ASTM D86	320	245	156	244	330
Molecular weight	equation	228	169.4	118	166	238
Refractive index	ASTM D1218	1.5015	1.497	1.478	1.497	1.510
Viscosity 40 °C cSt	ASTM D445	50	6.5	4.5	4.5	5.6
Viscosity 100°CcSt	ASTM D445	5.2	1.9	1.5	1.6	1.5
Aniline point °C	ASTM D611	36	20	5	16	39
Flash point °C	ASTM D93	162	110	46	108	168
Hydrogen %	equation	13.36	12.3	12.6	11.8	11.6

Sulfur %	ASTM D129	2.754	3.055	2.011	3.1	3.585
Carbon %	equation	83.886	84.645	85.389	85.1	84.815
C/H		6.278	6.88	6.777	7.21	7.311
Aromatic %	equation	24.18	40.8	36.1	48.6	51.77

Heavy vacuum gas oil feed rich with undesirable components such as aromatics, oxygen, nitrogen, and sulfur. So, the physical and chemical properties of HVGO feed such as API gravity or specific gravity, density, viscosity and others properties are considerably influenced by high boiling point temperature for constituents, like these undesirable components that concentrated in HVGO feed, so it is important to characterize the heaviest fractions of HVGO feed in order to determine their properties as shown in **tables 3, 4, 5 and 6**. HVGO feed has high molecular weight so, has high ability to crack to produce light fractions like, gasoline, kerosene and gas oil. The cracking liquid product with lower mean average boiling point gives more gasoline yield until distillation temperature 350 °C, at a catalyst -to- oil ratio equal 3.5 and this correct for others COR, **but in different volume % content of gasoline, kerosene and gas oil, which separates according to its boiling point (IBP, 180 °C) for gasoline cut,(180, 250 °C) for kerosene cut and (250, °350 C) for gas oil cut, as shown in Table 2.**

On the other hand the properties of the catalytic cracking for HVGO feed at 450 °C and at the catalyst -to- oil ratio of **2.5** are shown in **Table 4.**

Table4. Physical and chemical properties for HVGO feed and it fractions.

Property	HVGO feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.973	0.948	0.9294	0.95	0.965
API gravity	13.962	17.76	20.75	17.45	15.13
Mean average boiling point.° C	320	260	165	250	360
Molecular weight	228	181	118	172	273
Refractive index	1.5015	1.491	1.480	1.483	1.496
Viscosity (40 °C) cSt	50	5.6	4.5	9	11
Viscosity (100 °C) cSt	5.5	1.75	1.5	2.3	2.5
Aniline point °F	36	24	-3	20	52
Flash point °C	162	120	52	112	190
Hydrogen %	13.36	11.9	12.1	11.8	11.7
Sulfur %	2.754	2.88	2.44	2.61	3.08
Carbon %	83.886	85.22	85.46	85.59	85.218
C/H	6.278	7.16	7.06	7.25	7.28
Aromatic %	24.18	47	43.93	48.63	50.2

Also the properties of the catalytic cracking for HVGO feed at 450 °C and at the catalyst -to- oil ratio of **3** are shown in **Table 5.**

Table 5. Physical and chemical properties for HVGO feed and it fractions.

Property	HVGO feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.973	0.93	0.8826	0.935	0.964
API gravity	13.962	20.65	28.82	19.83	15.285
Mean average boiling point.° C	320	270	170	244	350
Molecular weight	228	194	128	171	248
Refractive index	1.5015	1.488	1.477	1.4865	1.508
Viscosity (40 °C) cSt	50	6.2	4.5	5	5.8
Viscosity (100 °C) cSt	5.5	1.9	1.6	1.7	1.8
Aniline point °F	36	34	15	22	48
Flash point °C	162	126	56	108	183
Hydrogen %	13.36	12.1	12.8	12	11.6
Sulfur %	2.754	2.678	1.7	2.745	3.5
Carbon %	83.886	85.22	85.5	85.255	84.9
C/H	6.278	7.04	6.68	7.1	7.32
Aromatic %	24.18	43.93	32.96	45.5	51.76

Also the properties of catalytic cracking for HVGO feed at 450 °C and at the catalyst –to- oil ratio of **3.5** are shown in **Table 6.**

Table 6. Physical and chemical properties for HVGO feed and it fractions.

Property	HVGO feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.973	0.93	0.869	0.959	0.962
API gravity	13.962	20.65	31.33	16.1	15.59
Mean average boiling point.° C	320	286	165	240	360
Molecular weight	228	208	128	162	275
Refractive index	1.5015	1.500	1.476	1.490	1.508
Viscosity (40 °C) cSt	50	6	5.5	5.8	6.4
Viscosity (100 °C) cSt	5.5	1.85	1.75	1.85	1.9
Aniline point °F	36	39	19	14	52
Flash point °C	162	138	52	105	190
Hydrogen %	13.36	12.1	12	11.7	11.6
Sulfur %	2.754	3.078	1.194	2.9	3.437
Carbon %	83.886	84.822	86.8	85.4	84.96
C/H	6.278	7.01	7.23	7.3	7.32
Aromatic %	24.18	43.93	45.5	50.2	51.76

As shown from **Tables (3, 4, 5 and 6)** the physical and chemical properties for fuel fractions (gasoline, kerosene, and gas oil) which are product from treatment heavy vacuum gas oil at various catalyst -to- oil ratio and constant temperature 450 °C, acceptable for commercial uses due to their similar property with commercial one. So can said, success will be occur to convert secondary product mater HVGO to another light fuel fractions (gasoline, kerosene and gas oil) which are produced from crude oil, and which is useful to use as automobile for gasoline cut and domestic uses for kerosene cut and diesel fuel for gas oil cut.

Table 7. Some properties of commercial light fractions.

Light fraction	Specific gravity	Flash point °C	Viscosity 40 °C sCt	Final boiling point (°C)	Cetane number
Gasoline	0.775	2	0.9	190	---
Kerosene	0.81	38	1.5	258	---
Gas oil	0.85	54	5.6	350	53

3.3 Effect of temperature on volume heavy vacuum gas oil distillation

In order to study the effect of the temperature on the process with the accumulated volume percentage HVGO was studied with increasing of temperature of the process.

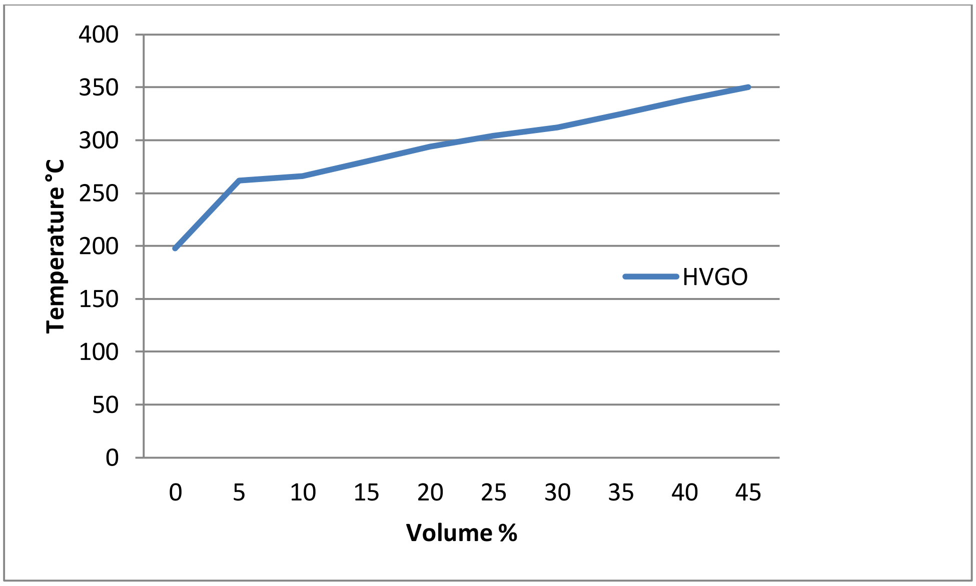


Figure 3. Atmospheric distillation for HVGO feed.

Fig. 3 shows the relationship between the temperature and volume distillation curve for HVGO feed. By this distillation curve, can calculate the mean average boiling point for HVGO feed its equal 320 °C and by this temperature with specific gravity, can calculate another property for example molecular weight by empirical equation and other properties which listed in **Tables 3, 4, 5 and 6**, and then to compare it with commercial product to know the benefit of this work.

3.4 Distillation curve for heavy vacuum gas oil feed and HVGO cracked at various catalysts –to- oil ratio

Fig.s 4, 5, 6 and 7 shows the relationship between the temperature and volume % distillation curve for HVGO feed and HVGO feed cracked in 2, 2.5, 3 and 3.5 catalyst -to- oil ratio respectively. The mean average boiling point temperature for HVGO feed cracked in (2, 2.5, 3 and 3.5) catalyst -to- oil ratio equal to (245, 260, 270 and 286°C) respectively as shown in **Fig.s 4, 5, 6 and 7**, that's mean, when this temperature is low it means, this cracked feed have high content in light fractions (gasoline, kerosene and gas oil) than another COR ratio cracking. The percentage volume of light fractions in various COR ratio are (7, 25 and 18) for COR ratio 2, (10, 20 and 40) for COR ratio 2.5, (10, 30 and 35) for COR ratio 3 and (15, 30 and 35) for COR ratio 3.5 which separates according to its boiling point (IBP, 180 °C) for gasoline cut,(180, 250 °C) for kerosene cut and (250, °350 C) for gas oil cut, as shown in **Table 2**.

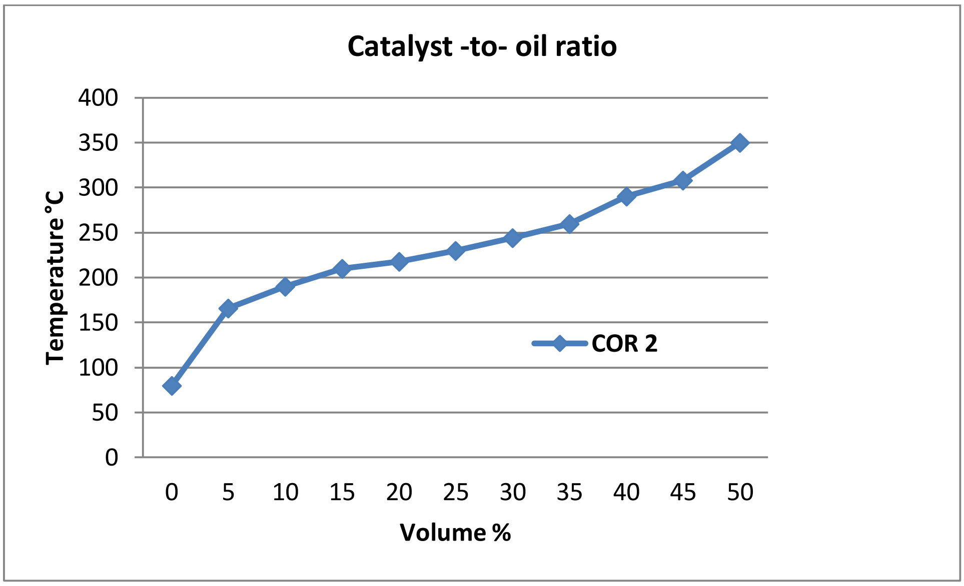


Figure 4. Atmospheric distillation for HVGO feed cracked at the catalyst -to- oil ratio of 2**.**

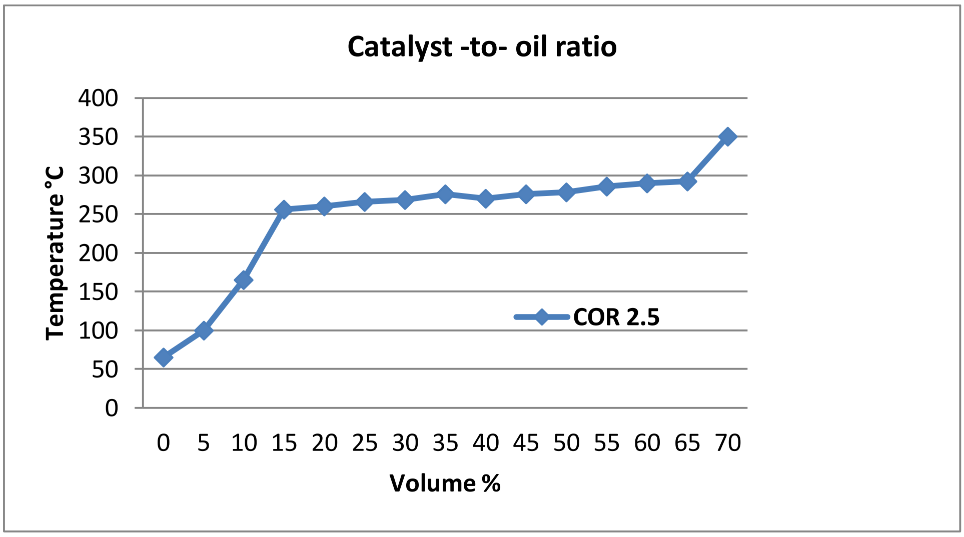


Figure 5. Atmospheric distillation for HVGO feed cracked at the catalyst -to- oil ratio of 2**.5**.

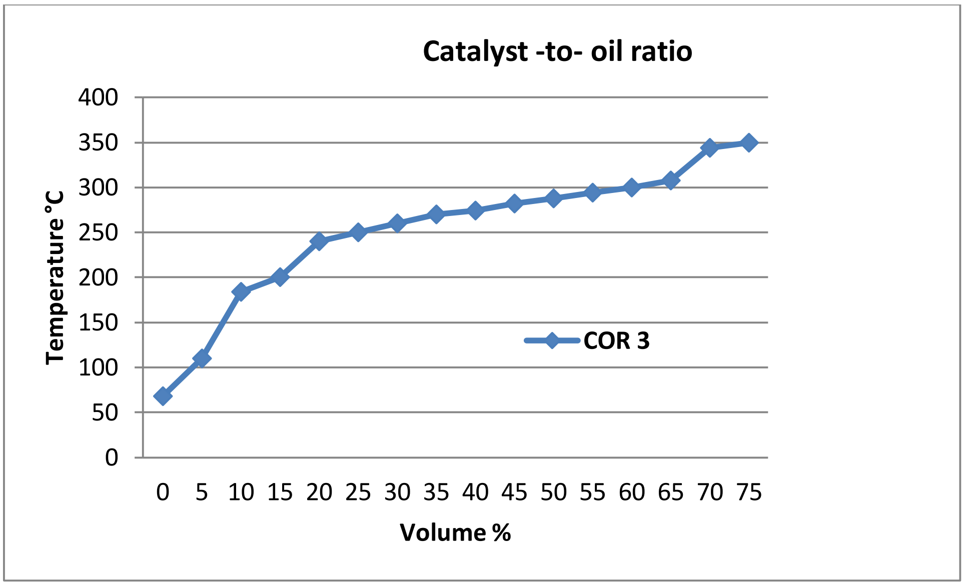


Figure 6. Atmospheric distillation for HVGO cracked at the catalyst -to- oil ratio of 3.

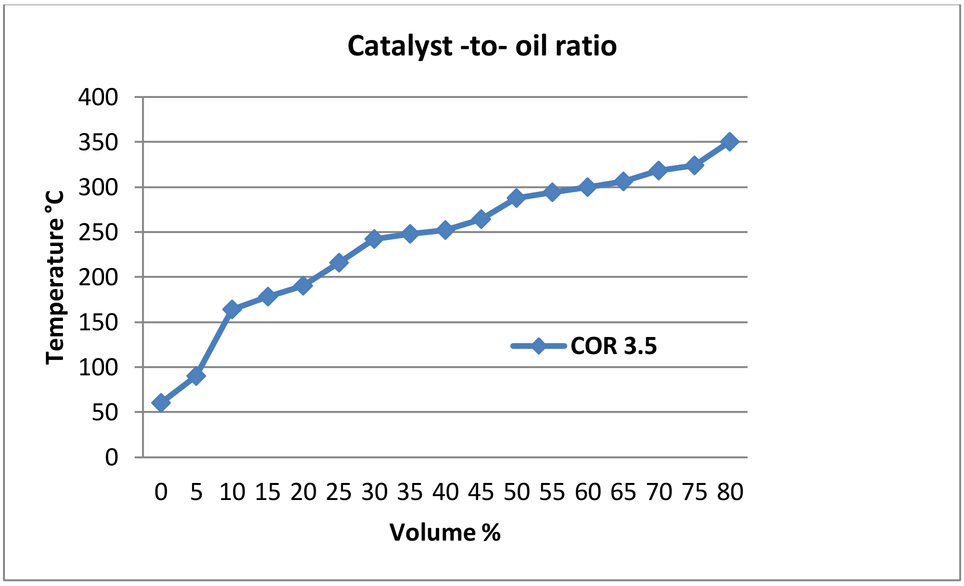


Figure7. Atmospheric distillation for HVGO feed cracked at the catalyst -to- oil ratio of 3.5.

As shown from **Table 2**, by various catalyst to oil ratio (2, 2.5, 3 and 3.5) ability to convert HVGO as a feed to another light benefit fuel fractions in high conversion, which reaches to more than 80% and in different amount of the light fraction products according to their boiling point (IBP, 180 °C) for gasoline cut,(180, 250 °C) for kerosene cut and (250, °350 C) for gas oil cut, but the more economic one is 3.5 of catalyst -to- oil ratio due to their high conversion 80% and high amount of light cut production (15, 30 and 35).

4. CONCLUSIONS

1- The ability of catalytic cracking for secondary product matter, heavy vacuum gas oil (HVGO) at different catalyst -to- oil ratio and constant temperature 450 °C and pressure about 90 atmosphere and period reaction time about to 30 minute but the best one was at COR ratio equal 3.5 for economic consideration (conversion and amount of light fractions).

2- Possibilities to obtained light fuel fractions (gasoline, kerosene, and gas oil) from catalytic cracking of secondary product matter (HVGO) with acceptable properties products according to standard properties.

3- Possibilities to use these light products to automobile for gasoline cut and domestic uses for kerosene cut and diesel fuel for gas oil cut.

5. ABBREVIATION

HVGO	Heavy Vacuum Gas Oil
COR	Catalyst –to-Oil Ratio
ASTM	American Society for Testing and Material
WHSV h^{-1}	Weight Hour Space Velocity
IBP (°C)	Initial Boiling point

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