



# Treatment of Waste Extract Lubricating Oil by Thermal Cracking Process to Produce Light Fractions

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## Abstract

This work deals with thermal cracking of three samples of extract lubricating oil produced as a by-product from furfural extraction process of lubricating oil base stock in AL-Dura refinery. The thermal cracking processes were carried out at a temperature range of 325-400 °C and atmospheric pressure by batch laboratory reactor. The distillation of cracking liquid products was achieved by general ASTM distillation (ASTM D -86) for separation of gasoline fraction up to 220 °C from light cycle oil fraction above 220 °C. The comparison between the conversions at different operating conditions of thermal cracking processes indicates that a high conversion was obtained at 375°C, according to gasoline production. According to gasoline production, noticed that sample (3) was the best due to their high gasoline product at thermal cracking, so another distillation will occur to obtain other composition and its volume present. Gasoline and kerosene conversion was 19 % and for light cycle oil 81% for the best one (sample 3).

*Keywords: thermal cracking, furfural extraction, lubricating oil.*

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## 1- Introduction

Extract lubricating oil is a totally rich aromatic content by-product of furfural extracting process. This process is applied in refinery crude oil process to control the cost of the final output and to develop the viscosity index of various kind of lubricating oil fractions. Normally extract lubricating oil has black color, which identified by high polycondensed aromatics and some lubricating oil fraction and also by high viscosity [1][2].

To reduce the aromatic compounds, different solvents like phenol ,furfural, cresol, sulfur dioxide, nitrobenzene, aniline, beta beta dichlor-ethyl ether, nitro-phenols, chlorinated phenols, pyridine, and many others, including mixtures of the foregoing with or without a modifying solvent [3] are used in extraction process that is applied to extract the lubricating oil. The used solvent is removed from the outputs after the extraction and that make the residual rich of aromatic material (aromatic extract lubricating oil).

According to the source of these compounds, these are described as residuum aromatic extracts (RAE) if the oil base stock produces in vacuum process and distillate aromatic extracts (DAE) if it produces in atmospheric distillation [1][2].

The applications of aromatic extract are relatively limited. The tires industry utilizes large quantities of an aromatic extract. On the other hand, plastic and rubber manufacture and asphalt blends utilize lower quantities[2] [4].

The thermal breakdown of high molecular weight component into low molecular weight outputs is one of the initial transformation operations applied in the petroleum manufacturers, it was improved in the early 1900s and the specific sources of the operation are unexplained [5].

It is a free radical chain reaction; a free radical is their mode of reaction that truly defines the product distribution through thermal cracking and it is referred to a group of atoms or just one atom holding an unpaired electron. Free radical reactions are so reactive.

When the free radical reacts with a hydrocarbon it creates a stabilized end output and a new free radical by removing a hydrogen atom [6].

Paraffins are hydrocarbons with the least thermal stability; the olefins created from the decomposition of paraffin are else reactive. The minimal readily decomposed hydrocarbons are naphthenes (cycloparaffins), their stability depending largely on any side chains present, but ring incision may happen, and dehydrogenation can lead to the production of unsaturated aromatics and naphthenes [7].

The most stable (refractory) hydrocarbons are aromatics, their stability depending on the stability and the length of side chains. In the reaction of condensation reactions for ring components very hard thermal decomposition of high-boiling raw materials is able to occur, producing a high ratio of coke [8].

The processes are based on the notes that the averages of the thermal breakdown progress at significantly greater averages in the case that in which the temperature of heating for petroleum fractions is in a surplus of 350°C (660F) [9][10].

In this work we study the characterizations of extract lubricating oil, the performance temperature for thermal cracking of extract lubricating oil at different operating conditions by batch laboratory unit and the characterizations of gasoline produced by thermal cracking and compare it with commercial gasoline and other fractions.

## 2- Experimental Work

### 2.1. Materials

#### a. Feed (Extract lubricating oil)

Extract lubricating oil produced from the extraction unit of lubricating oil stock in Al-Dora Refinery is utilized as a feedstock in this work.

The properties of three samples for extract lubricating oil are shown in Table 1.

Table 1. The physical and chemical properties of three samples for extract lubricating oil

Property	Number Of Extract		
	1	2	3
Molecular weight (gm/gmole)	144.42	143.6	136.54
Specific gravity	0.972	0.965	0.964
API	14.08	15	15.28
Mean average boiling point ( $T_b$ )	C	222	255
	K	495	491
Aniline point	C	78	71
	F	172	160
Diesel index	24.27	24.2	25.36
Cetane index	62.5	55.5	59
Refractive index	1.561	1.546	1.547
Sulfur content %	0.426	1.86	1.52
Aromatic content %	30.6	20.25	24.77
Paraffinic content %	33.125	23	28
Hydrogen content %	11.42	11.525	11.54
Heat content MJ/Kg	42.3	42.3	42.32

#### b. Distillation of Extract Lubricating Oil

Table 2 shows the ASTM (American Society for Testing and Materials) distillation of three samples of feed.

Table 2. The ASTM distillation of samples

Vol. %	Number of Extracts Temp. in C		
	1 IBP=140	2 IBP =86	3 IBP =140
5	156	176	146
10	178	182	160
15	172	178	166
20	190	194	196
25	194	198	171
30	198	205	194
35	216	240	190
40	210	210	222
45	214	230	262
50	220	156	256
55	210	198	164
60	234	200	190
65	238	246	244
70	250	260	166
75	248	266	250
80	252	270	254
85	258	278	256
90	262	287	260
95	268	296	262
100	272	305	264

Table 3 shows the true boiling point (TBP) of the three samples.

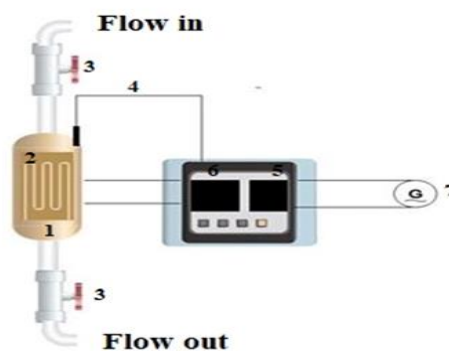
Table 3. TBP of three type of feed

Volume %	True boiling point °C		
	Sample (1)	Sample (2)	Sample (3)
0	110	60	110
10	162	166	143
30	193	201	189
50	223	157	260
70	259	269	165
90	275	301	273
95	280	304	274

### 2.2. The Experimental Unit

The thermal cracking experiments were carried out in batch laboratory unit. Fig. 1 shows the flow diagram of this unit, which includes:

1. Batch reactor (250 ml),
2. Temperature controller,
3. Thermostat couple type K,
4. Thermal insulator,
5. Valves fitting,
6. Electrical heater



1-Reactor 2-Heater 3-Valve 4-Thermostate couple  
5-Timer 6-Temperature controller 7-Electrical source

Fig. 1. Flow diagram of laboratory reactor unit

The reactor has a stainless steel tube with 5 cm inside diameter and 14 cm length and 250 ml volume.

It was heated by one heater insulated by the jacket and carried by the climb and controlled automatically by digital control.

The temperatures inside the reactor were measured by thermocouple fixed inside the reactor at the top.

### 2.3. The Experimental Procedure

105 ml of extract lubricating oil as a feed (1, 2 and 3) put in the batch reactor unit, that heated at a deferent temperature (325, 350, 375 and 400 °C) for four runs at residence time (30 minutes) for each run.

### 2.4 General Distillation

The common distillation of liquid products as a result of cracking was achieved according to ASTM D86.

## 3- Discussion

### 3.1. ASTM D-86 and TBP of the Feed (Extract Lubricating Oil)

The distillation curves for the three samples of feed extract were listed in (Fig. 2, Fig. 3 and Fig. 4).

As shown in Table 3 noticed that true boiling point distillation information gives an extra itemized description to extract lubricating oil volatility of. the initial boiling point (IBP) for TBP distillation test is minimum as well as its end boiling point (EP) is higher as compared with the test of ASTM because separation degree for it is much higher from that of the test of ASTM distillation.

The curve of TBP (sketch for normal boiling point (NBP) against sample distilled percent volume) is commonly utilized like a principle for description the extract lubricating oil for purpose of design and analysis.

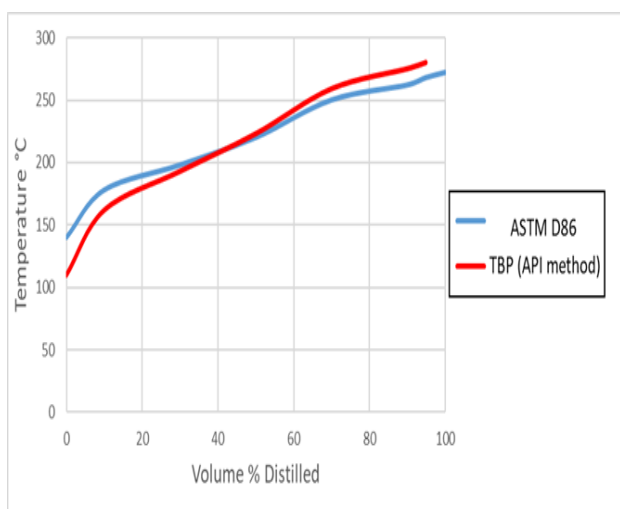


Fig. 2. ASTM D86 and True boiling point of sample (1)

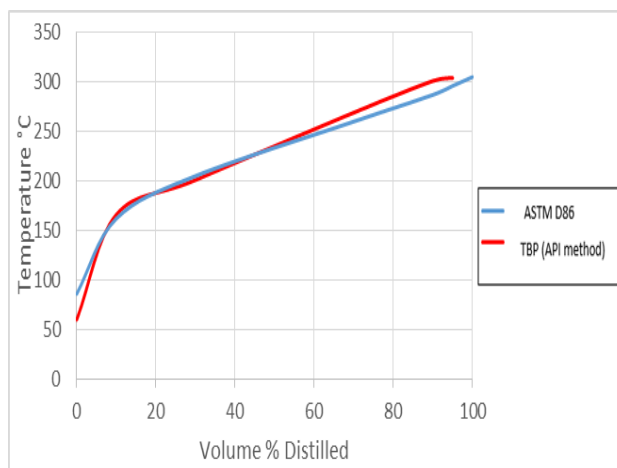


Fig. 3. ASTM D86 and True boiling point of sample (2)

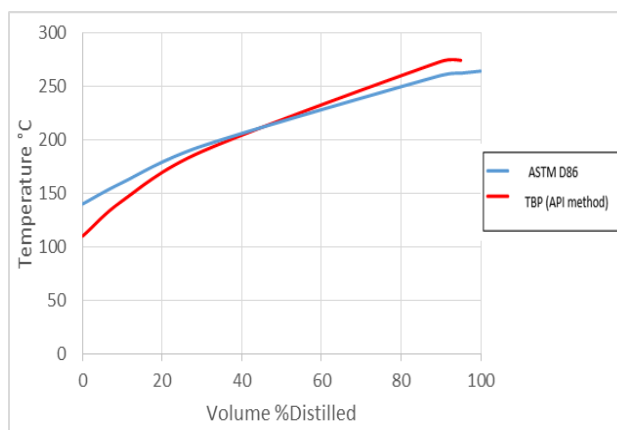


Fig. 4. ASTM D86 and True boiling point of sample (3)

### 3.2. Thermal Cracking

The temperature effectiveness on the thermal cracking of three feed of extract lubricating oil which carried out by batch laboratory unit in order to obtained light fractions (gasoline and light cycle oil) were studied.

Table 4, Table 5 and Table 6, Fig. 5, Fig. 6 display the thermal decomposition outcomes at temperatures (325,350,375and 400) for each of the three samples (sample 1,2 and 3) respectively.

The percentage of gasoline (% Gasoline) was calculated by the amount of distilled gasoline by ASTM distillation per 100 ml of the cracked liquid.

Table 4. Material balance of thermal cracking of sample (1)

Temperature (C)	Volume (ml) liquid of extract cracking	ASTM D.86	
		Vol. of gasoline fraction at 220 °C	Vol. of light cycle oil at 220 °C
325	100	11	89
350	100	13	87
375	100	15	85
400	100	10	90

Table 5. Material balance of thermal cracking of sample (2)

Temperature (C)	Volume (ml) liquid of extract cracking	ASTM D.86	
		Vol. of gasoline fraction at 220 °C	Vol. of light cycle oil at 220 °C
325	100	12	88
350	100	14	86
375	100	16	84
400	100	11	89

Table 6. Material balance of thermal cracking of sample (3)

Temperature (C)	Volume (ml) liquid of extract cracking	ASTM D.86	
		Vol. of gasoline fraction at 220 °C	Vol. of light cycle oil at 220 °C
325	100	14	86
350	100	16	84
375	100	19	81
400	100	13	87

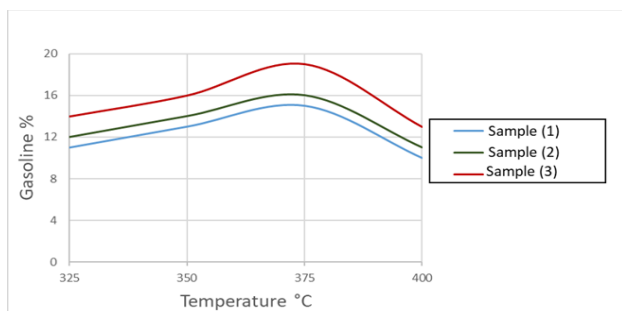


Fig. 5. Gasoline % produced from three samples by thermal cracking

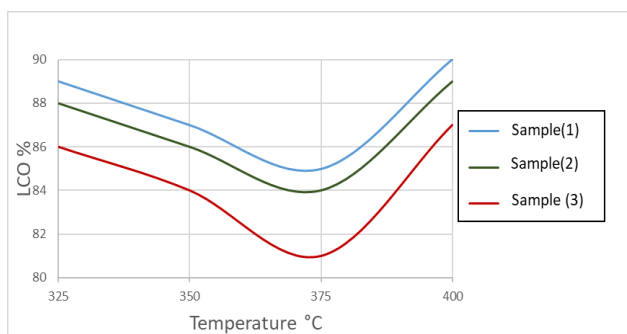


Fig. 6. Light cyclic oil % produced from three samples by thermal cracking

As shown in the above tables and figures, transformation of extract lubricating oil rises by temperature rising. This may be attributed to the increase of temperature which accelerates intermolecular motion, assists the transformation of reactants into new compounds [11].

The conversion of gasoline increases by increasing the temperature until it reaches 375 °C that at this temperature the conversion of gasoline reaches the best. After this temperature, higher temperature decreases the conversion of gasoline.

On the other side, the light cycle oil (LCO) decreases by temperature due to the increases in conversion with temperature increasing until it reaches 375°C, that at this temperature the conversion of LCO reaches the minimum. By furthermore increasing in temperature after 375 °C the yield of light cycle oil will increase because of the decreasing in conversion of gasoline because the gasoline will be cracking at this temperature.

Production of unsaturated gasoline is the elementary step for extract lubricating oil decomposition and this product is commonly the required output. Yet, the produced gasoline perhaps go under furthermore reaction which will be either oligomerization or cycloaddition for the compounds into dehydrogenated outputs as well as coke or subjected to side decomposition, which is commonly indicated to over decomposition, into gases component [11].

Furthermore, precipitated coke, as well as light side outputs, is produced by partly conversion of gasoline that produced like an intermediate output. Each of these compounds minimizes the productivity of gasoline in the case of high amount of transformation for the extract lubricating oil. Commonly, the transformation amount regulates in an amount equal to that of the highest gasoline in order to prohibit the incidence of this process of decay that damage the profit of the process [12].

The mentioned results are accepted with those mentioned by Reagan [13].

As a comparison between the three samples, the production of gasoline increase in the (sample 3) and decrease in sample (1), as shown in Fig. 5.

On the other hand, the production of light cycle oil (LCO) is largest in sample (1) and minimum in sample (3), as shown in Fig. 6.

As shown in Table 1, there is not any extract lubricating oil sample that is constant in all of the properties and just change in one of the mentioned properties, so according to that the study of the effect of the different kind of extract lubricating oil sample on the production of gasoline is complicated.

Certainly, the structure, as well as the productivity of gasoline, is highly respected for the kind of raw material. And so on, hydrotreated or paraffinic feedstocks yield higher gasoline as compared with non-hydrotreated or aromatic feeds. At high transformation for the feed, the presence of aromatics is favorable for the produced gasoline and these are our explanation agree with Lappas et al. [14].

At thermal decomposition of deferent raw materials, the content of saturated compound raises the reactivity of feedstock which also declines with the rising in the content of aromatic. Higher transformation in thermal decomposition also occurs due to the minimum aromatic and higher hydrogen and saturated content. All of that make sample (3) gives higher productivity of gasoline. [15].

From Table 1, API for each one of the extract lubricating oil samples indicate that these samples are heavy and from the mean average boiling point of each one of these samples that mentioned in Table 1, we can indicate the composition of oil fractions from the theoretical table of heavy fuel oil, Table 7 [16] and discover theoritacally that sample (3) of extract lubricating oil will give the largest amount of gasoline and that agree with practical part in this work. In Table 7 the fractions are characterized as amixture of psedo-component acording to their boiling point ranges (Tb) and each psedo-component is characterized by average boiling point corresponds to unknown actual compounds (paraffins, naphthenes, aromatic).

Table 7. Composition of oil fractions for heavy fuel oil [16]

Oil fractions	Tb (°C)	Content(wt.%)
C8-C12 (Paraffins)	69-230	4.3
C13-C25 (Paraffins)	230-405	10.1
C6-C12 (Cycloparaffins)	70-230	1.4
C13-C23 (Cycloparaffins)	230-405	3.4
C6-C11 (Aromatics)	80-240	1.8
C12-C18 (Aromatics)	240-400	4.3
C9-C25 (Nephteon)	180-400	0
Residuals	>400	74.7

According to that and from the data in Table 1 we can discuss the production of each extract lubricating oil sample:

#### Sample (1):

Molecular weight analysis: comparative high Molecular weight (144.42 gm/gmol) which means heavier compounds more than saturated paraffins.

Composition: high aromatics (30.6%) will cause a decrease in the performance of catalytic cracking.

Mean average boiling point (Tb) analysis: less saturated compounds that is why comparatively low boiling point (222 °C).

#### Sample (2):

Molecular weight analysis: high Molecular weight (143.6 gm/gmol) which refers to higher Molecular weight compounds.

Composition: comparatively low aromatics (20.25 %) but also low paraffins (23 %).

Mean average boiling point (Tb) analysis: More saturated hydrocarbons that are why comparatively high boiling point (255°C), but the overall low percentage of paraffin only 23%.

#### Sample (3):

Molecular weight analysis: comparatively low Molecular weight (136.54 gm/gmol) and high boiling point (248°C) shows more amount of saturated hydrocarbons.

Composition: significant paraffins (with high BP (248°C) and Low MW (136.54 gm/gmol)) shows more saturated paraffins (28%) may be there, comparatively very low aromatics (24.77%) which can favor Cracking

Mean average boiling point (Tb) analysis: high boiling point and low MW shows high paraffins(saturated) HC.

### 3.3. The Possibility of Extract Lubricating Oil Cracking Uses

The chemical composition of the produced gasoline using thermal cracking was tested by utilizing the differentiates in the composition and concentrations of five groups that are Paraffins, Isoparaffins, Olefins, Napthenes and Aromatic which called PIONA test.

PIONA composition for gasoline that produced is done in Oil Research and Development Center and described in Table 8.

Table 8. The chemical compositions of cracked gasoline produced from sample (3) at 375 °C

PIONA analysis	Total Mass%
n-Paraffins	9.3
Naphthenes	4.34
Iso paraffins	30.1
Aromatics	17.59
Olefin	22.66
Oxygenated	15.13

Table 8 shows that the obtained gasoline in our practical part has low olefins content in compared with gasoline produced by Esgair [17], who explained that the olefins content in yielded gasoline is 34.1%. The reason for that may be hydrogen transfer reactions growing that in which olefins with naphthenes reaction produce paraffins as well as aromatics. Naphthenic components are able to react with olefins yielding aromatics as well as paraffins because these compounds are hydrogen donors.

Since the extra reactive bonds are the double bonds are more reactive which simply polymerized as well as oxidized causing the production varnishes, as well as gums, injection nozzles and valves of automobiles, will be blocked due to the gasoline high olefin content [18].

It also can be noticed that gasoline which formed from this thermal decomposition has a lot of aromatics as well as isoparaffins and that cause high research octane number (RON) for this product. Toluene, 1,3-dimethylbenzene, and isobutyl benzene are the aromatic compounds that present in produced gasoline and those have high RON which is 111, 115, and 112 RON, respectively for each of them while isoparaffin compounds have high octane numbers (85-100) [19].

Baker et al. [20] noticed that the research octane number fundamentally respected on the content of aromatic, Fig. 7 explain this relation, and he also determined the chemical composition for decomposed gasoline obtained from various raw materials.

Gasoline yielded in this work has a research octane number (RON) that was measured by the equation of Fig. 7 (Aromatics = 2.436RON - 191.9), which was 86 for thermal cracking.

Finally, it is able to utilize the gasoline that yielded by the decomposition of extract lubricating oil as a useful requisite gasoline for regular and premium automobile gasoline yield because the minimum research octane number of regular and premium Iraqi gasoline are 85 and 90, respectively [21].

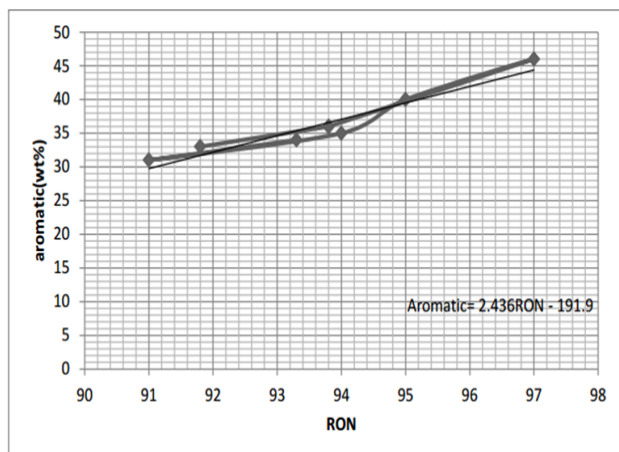


Fig. 7. Relation between RON and aromatic content for cracked gasoline [21].

Table 9 shows the characteristics of produced gasoline produced by thermal cracking and required properties of this fraction.

Table 9. The characteristics of produced gasoline

Characteristics	Value	
	Thermal cracking	Iraqi commercial value[21]
Specific gravity, 15.6 °C/15.6 °C	0.81	0.775
API gravity	43.191	51.00
Net heat, MJ/ kg.	10995	11000
Octane number	86	85

The gasoline has an octane number identical to the required.

#### 4- Conclusions

Uses of the raw material for this project (Extract lubricating oil) are almost limited but it has the ability to crack because of its high molecular weight so we can crack it to produce gasoline, kerosene, gas oil and lubricating oil. Study of the effect of thermal cracking on the extract lubricating oil in a batch laboratory reactor show that increasing of reaction temperature from 325°C to 375°C gives higher conversion and as a based on the maximum of the gasoline yield, it could be said that the best cracking temperature was 375°C and sample (3) gives more gasoline yield.

Gasoline yield increase in the run of 375 °C where it is 19 ml for thermal cracking, after this temperature the yield decrease because the gasoline itself will crack and light cycle oil yield increase in the run of 400 °C where it is 87 ml for thermal cracking.

From the PIONA analysis, the produced gasoline has high research octane number because it has high aromatics and isoparaffins. This means that it is possible to use gasoline for the automobile.

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## معالجة المتبقي من مستخلص زيوت التزيت باستخدام التكسير الحراري لإنتاج مقاطع خفيفه

### الخلاصة

يتعامل هذا البحث مع التكسير الحراري لثلاث نماذج من مستخلص زيوت التزيت الناتج من وحدة الاستخلاص باستخدام الفيرفرال لزيوت التزيت في مصفى الدورة. تمت عملية التكسير الحراري بمعدل درجات حراره 325–400° س و تحت الضغط الجوي باستخدام مفاعل مختبري. تم تقطير سائل التكسير الناتج من العملية باستخدام (ASTM D -86) و ذلك لعزل الكازولين عند درجة حرارة تصل الى 220°س عن المقاطع الاخرى في درجات حرارة اعلى من 220° س . لقد بينت المقارنه بين نسب التحويل في الظروف المختلفه للتكسير الحراري ان افضل نسبة تحويل كانت عند درجة حرارة 375° س اعتماداً على الكازولين الناتج . كما بينت المقارنة بين الكازولين الناتج من النماذج المختلفه ان النموذج (3) كان الافضل في انتاج الكازولين بالتكسير الحراري لذا تم اجراء عملية تقطير اخرى للناتج من النموذج لعزل المقاطع الاخرى عن الكازولين . نسبة التحويل للكازولين كانت 19% و لبقية المقاطع 81% بالنسبة للنموذج الافضل (نموذج 3).