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Study the Effect of Residence Time Parameters on Thermal Cracking Extract Phase Lubricating Oil

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Abstract

This work studies with produce of light fuel fractions of gasoline, kerosene and gas oil from treatment of residual matter that will be obtained from the solvent extraction process as by product from refined lubricate to improve oil viscosity index in any petroleum refinery. The percentage of this byproduct is approximately 10% according to all feed (crude oil) in the petroleum refinery process. The objective of this research is to study the effect of the residence time parameter on the thermal cracking process of the byproduct feed at a constant temperature, (400 °C). The first step of this treatment is the thermal cracking of this byproduct material by a constructed batch reactor occupied with control device at a selective range of residence time (duration of the reaction) 30, 45, 60 and 75 minutes respectively at a constant temperature (400 °C). The conversion of this byproduct by thermal cracking process reaches 90% for all these residence times. The second step for this study is distillation this cracked extract liquid by atmospheric distillation device, for these various residence times according to the ASTM-D86 method, to obtain light fuel fractions of gasoline, kerosene and gas oil,in volume percentages 15, 75 and 0 for residence time 30, 5, 60 and 25, for residence time 45, 5, 10, 75, for residence time 60 and (10, 60 and 20) for residence time 75, which separates according to its boiling point. The major physical and chemical properties for feed (extract phase) and cracking extract liquid with its light fuel fractions were experimentally calculated and the results refer to acceptable properties compared with other standard property.

Keywords: *Cracking, extract phase, feed liquid, residence time.*

1. Introduction

Crude oil is a complex liquid mixture that consist mainly of carbon and hydrogen and small amount of sulfur, oxygen, nitrogen and metals [1]. A petroleum refinery consists of many units such as a chemical separation (catalytic and thermal process) and a physical separation processes that consists of many units, like crude distillation, solvent de asphalting, solvent extraction, solvent de-waxing, and blending.

The solvent extraction process is used to treat luboil by solvent, like furfural, N-methyl pyrrolidone (NMP), which can dissolve the aromatic components in one phase (extract) and the rest of the oil in another phase (raffinate). The solvent is removed from both phases [1, 2].

The use of furfural for lubricating oil manufacture has been gaining in comparison with most other solvents. The yield of high viscosity index raffinate varies with the stock being treated [5]. When furfural (or other common solvent) is added to a heavy lubricating oil stock, two liquid phases (or layers) are produced; one (extract) which contains a relatively large amount of furfural with some asphaltic materials dissolved in it, and one (raffinate) which is lean in furfural but rich in high viscosity index oil [1]. The extracts have gravities in arrange of 4 to 13 API and slightly higher boiling ranges than the raffinates and they contain much more sulfur [6]. The extraction operation consists of a series of counter current contacts between oil and solvent, vertical packed towers are wider than settling tanks [6].

The general purpose of the solvent process is to separate a general group of materials or hydrocarbons from the oil. For example; propane de asphalting removes dark colored resinous materials, liquid sulfur dioxide extracts unsaturated and aromatic hydrocarbons from kerosene, and furfural treating produces lubricating oil of high viscosity index [1].

Speight 2015 Make combination between the temperature and residence time to get various conversions, he noticed that there ia a very small residence time when temperature high, similar to high residence time when temperature is low. The cracking temperatures are between 350 °C to 500 °C, the aromatic ring is estimated stable. Bianco et al 1993 studied the conversion reaction for the thermal cracking of vacuum residue (VR) at reaction time reaches to 120 minutes at 410 °C to 470 °C, the results which were obtained from this work were used as reference data for the study of residue thermal cracking. Kondo et al 2000 studied the thermal cracking for VR by using batch reactor at 400 °C to 440 °C and atmospheric pressure; He noticed the conversion of vacuum residue increased when the temperature of the reaction increased. Parkash 2003 viewed that the thermal decomposing for high molecular weight feed depends on many variables such as, temperature cracking, type of feed stock, residence time, and pressure.

The main objectives of the present work are to study the physical and chemical properties for the byproduct matter (extract phase), and to study the effect of several residence times (30, 45, 60, and 75) minutes on the thermal cracking of the extract phase by using a batch reactor, and to study the physical and chemical properties for the cracking extract phase liquid and its light fractions.

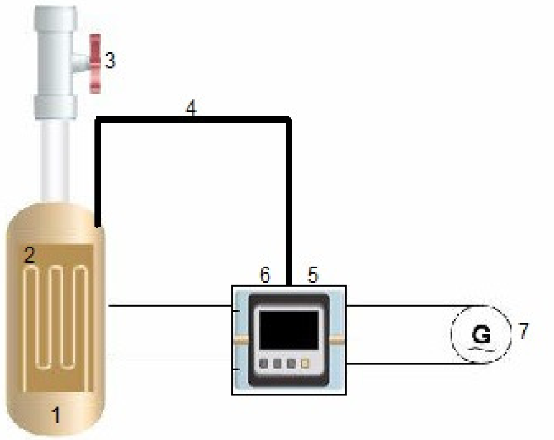
2. Experimental Work

2.1. Procedure of the Work

The process of thermal cracking for the extract phase feed was carried out in the designed batch reactor unit which in figures 1 and 2 its volume is about 300 cubic ml. occupied with many auxiliary parts, like an electrical heater, thermocouple, timer, temperature controller, and a hood. 100 ml of the feed (extract phase) will be put in the reactor. The controlled temperature inside the reactor was constant at 400 °C according to another research (was the best to conversion) and various residence time (30, 45, 60, and 75) minutes which is the period for reaction.

The distillation process of extract phase feed and cracked extract phase liquid were done in a distillation device which behaves as one tray and the distillation is done at atmospheric pressure. Distillation process on the byproduct mater (extract phase feed) and cracked extract phase liquid all these types of residences time will be done by the ASTM- D86 method. And finely, calculate the major properties of the extract phase feed and cracked extract phase liquid also light fuel cuts in order to compare it with commercial types and the possibilities of the use it in various usages.

Fig. 1. Experimental batch reactor unit with distillation unit.



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

Fig. 2. Flow diagram of experimental batch reactor unit with control system.

3. Results and Discussion

3.1. Atmospheric Distillation Method

The analysis of the extract phase and different cracked extract phase liquids, for all these ranges of residences time results are shown in table 1.

Table 1,
Atmospheric distillation for extract phase feed and various cracked extract feed.

Volume %	**Extract phase feed °C**	**The cracked extract liquid feed (°C)**			
		Residence time 30 minute	**Residence time 45 minute**	**Residence time 60 minute**	**Residence time 75 minute**
0	70	82	70	76	75
5	122	164	120	150	90
10	160	180	200	220	180
15	170	180	220	230	190
20	178	190	240	270	220
25	182	200	250	290	225
30	190	205	260	300	250
35	200	210	270	310	240
40	205	215	290	310	230
45	210	220	296	300	240
50	215	200	300	300	220
55	220	208	210	300	230
60	225	200	220	260	250
65	230	192	224	210	260
70	240	180	260	210	250
75	245	176	270	212	255
80	250	190	270	220	250
85	260	200	276	230	260
90	280	210	280	225	264
95					
Tave.	**217**	**195**	**260**	**251**	**233**

Table 1 represents the atmospheric distillation results for the extract phase feed and cracked extract liquid in deferent residence time of cracking feed in reactor and can be noticed from the above results. the cracking occurs in all selected residence times and the conversion of the extract phase feed reaches above 90% in all selected residence times but the best one is 30 minutes due to their high amount of gasoline product and summarized time for cracking extract phase feed.

3.2 Physical and Chemical Properties for Extract Phase

The physical and chemical properties of extract phase at 400 °C for different residence times (30, 45, 60, and 75) are shown in tables 2, 3, 4, and 5.

The properties of the thermal cracking process for extract phase feed at 400 °C and residence time 30 minute are shown in table 2.

Table 2,
Physical and chemical properties for extract phase feed and its fractions.

Property	Extract phase feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.965	0.826	0.79	0.83	0.86
API gravity	15.2	39.8	47.6	38.98	33
Mean average boiling point.° C	217	195	155	219	310
Density gm. / cm^3	0.966	0.821	0.786	0.826	0.855
Molecular weight	142	204	130	171	247
Refractive index	1.547	1.504	1.479	1.503	1.528
K-factor	10.7	11.6	11.7	11.31	11.24
Viscosity (40 °C) C.st	125.1	3	4	2	5.8
Viscosity (100 °C) C.st	8	1.3	1.5	0.8	1.9
Aniline point °F	50	120	120	130	166
Pour point °C	-9	-7	-----	------	-----
Cloud point °C	-12	-12	-----	-----	-----
Flash point °C	89	74	45	90	150
Fire point °C	93	79	50	94	155
Refractivity intercept	1.06	1.093	1.086	1.09	1.1
Hydrogen %	11.52	13.61	14.15	13.55	13.1
Sulfur %	1.28	1.26	0.28	0.54	0.44
Carbon %	87.20	85.87	85.57	85.9	86.46
C/H	7.58	6.3	6.05	6.34	6.6
Aromatic %	53	20.27	11.8	21.21	28.26

The extract phase feed is rich with undesirable components such as aromatics, oxygen, nitrogen, and sulfur, so the physical and chemical properties of extract phase 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 are concentrated in extract phase feed, so it is important to characterize the heaviest fractions of extract phase feed in order to determine their properties as shown in table 2, 3, 4, and 5. The extract phase feed has high molecular weight so it has a high ability to produce light fractions like, gasoline, kerosene and gas oil. The cracking liquid product with lower average boiling point gives more gasoline yield as at residence time 30 minutes and this is correct for others residence times 45, 60 and 75 minutes as shown in table 1 but in different volume percentages content of gasoline, kerosene and gas oil.

On the other hand, the properties of the thermal cracking process for extract phase feed at 400 °C and residence time 45 minutes were shown in table 3.

Table 3,
Physical and chemical properties for extract phase feed and its fractions.

Property	Extract phase feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.965	0.81	0.77	0.82	0.85
API gravity	15.2	43.19	52.26	35.24	34.97
Mean average boiling point.° C	217	229	162	235	305
Density gm. / cm^3	0.961	0.806	0.766	0.815	0.845
Molecular weight	142	181	140	175	245
Refractive index	1.547	1.500	1.493	1.515	1.498
K-factor	9.7	11.67	11.71	11.57	11.30
Viscosity (40 °C) C.st	125.1	3	7.5	5.8	5.8
Viscosity (100 °C) C.st	8	1.3	2.1	1.9	1.9
Aniline point °F	50	155	135	150	170
Pour point °C	-9	-18	-----	-----	-----
Cloud point °C	-12	-21	-----	-----	-----
Flash point °C	89	97	50	102	151
Fire point °C	93	100	54	106	155
Refractivity intercept	1.06	1.097	1.11	1.04	1.075
Hydrogen %	11.52	13.85	14.45	13.7	13.25
Sulfur %	1.45	1.42	0.15	0.54	0.757
Carbon %	87.03	85.73	85.4	85.76	86
C/H	7.58	6.19	5.91	6.26	6.49
Aromatic %	53	16.51	7.1	18.86	25.9

Also the properties of the thermal cracking process for the extract phase feed at 400 °C and residence time 60 minutes were shown in table 4.

Table 4,
Physical and chemical properties for extract phase feed and its fractions.

Property	Extract phase feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.965	0.82	0.8	0.84	0.87
API gravity	15.2	35.84	41.37	32.95	27.14
Mean average boiling point.° C	217	251	170	240	315
Density gm. / cm^3	0.961	0.814	0.796	0.835	0.864
Molecular weight	142	198	141	186	249
Refractive index	1.547	1.521	1.505	1.527	1.532
K-factor	9.7	11.69	11.339	11.334	11.447
Viscosity (40 °C) C.st	125.1	2	24	9	7.5
Viscosity (100 °C) C.st	8	0.6	3.6	2.35	2.1
Aniline point °F	50	160	140	158	165
Pour point °C	-9	-15	-----	-----	-----
Cloud point °C	-12	-18	-----	-----	-----
Flash point °C	89	113	56	105	158
Fire point °C	93	118	60	110	162
Refractivity intercept	1.06	1.114	1.107	1.1095	1.1
Hydrogen %	11.52	13.7	14	13.4	12.96
Sulfur %	2.15	2.13	0.32	0.84	0.86
Carbon %	86.32	85.76	85.68	85.76	86.18
C/H	7.58	6.26	6.12	6.4	6.65
Aromatic %	53	18.86	14.16	23.56	30.45

Also the properties of the thermal cracking process for extract phase feed at 400 °C and residence time 75 minutes were shown in table 5.

Table 5,
Physical and chemical properties for extract phase feed and its fractions.

Property	Extract phase feed	The cracking liquid product	Gasoline product	Kerosene product	Gas oil product
Specific gravity	0.965	0.835	0.795	0.83	0.86
API gravity	15.2	34.36	47	38.98	33
Mean average boiling point.° C	217	233	165	225	295
Density gm. / cm^3	0.961	0.830	0.79	0.827	0.855
Molecular weight	142	182	133	173	242
Refractive index	1.547	1.510	1.483	1.500	1.550
K-factor	9.7	11.35	11.367	11.36	11.449
Viscosity (40 °C) C.st	125.1	3.5	38	45	29
Viscosity (100 °C) C.st	8	2.7	4.5	1.9	4
Aniline point °F	50	152	130	140	100
Pour point °C	-9	-21	-----	-----	-----
Cloud point °C	-12	-24	-----	-----	-----
Flash point °C	89	116	52	95	145
Fire point °C	93	120	58	100	150
Refractivity intercept	1.06	1.095	1.088	1.0865	1.1225
Hydrogen %	11.52	13.47	14.07	13.55	13.1
Sulfur %	1.65	1.64	0.39	0.55	0.7
Carbon %	86.82	86.06	85.54	85.9	86.2
C/H	7.58	6.39	6.08	6.34	6.58
Aromatic %	53	22.77	13.06	21.21	28.23

3.2 Effect of Temperature on Volume Extract Phase

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

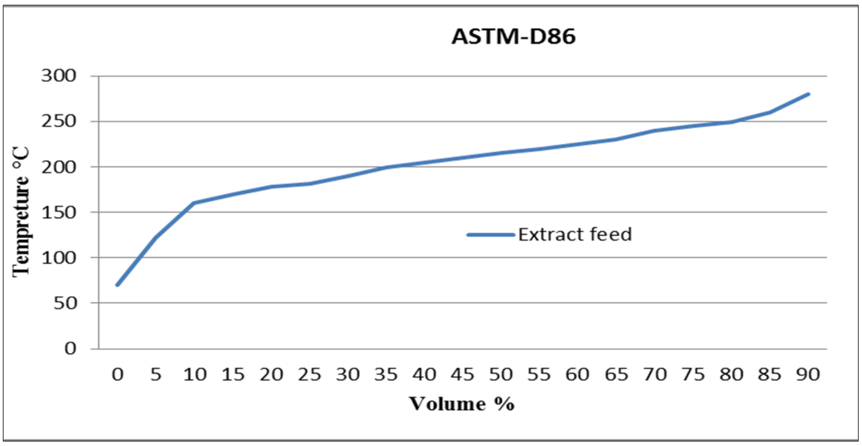


Fig. 3. Atmospheric distillation for extract phase feed.

Figure 3 shows the relationship between the T &V% distillation curve for the extract phase feed. By this distillation curve, can calculate the mean average boiling point for the extract phase feed its equal to 217° C and by this temperature with specific gravity can calculate the molecular weight by empirical equation and other properties which listed in tables 2, 3, 4 and 5.

Distillation curve for extract phase feed and extract feed cracked in various residence times

Figures 4, 5, 6 and 7 show the relationship between the temperature and volume percentages distillation curve for the extract phase feed and extract feed cracked in 30, 45, 60 and 75 minutes respectively.

The average boiling point temperature for the extract phase feed cracked in (30, 45, 60 and 75) minutes are 195, 229, 251 and 233°C respectively as shown in figures 4, 5, 6 and 7. That means, when this temperature is low, this cracked feed contains high amount of light fractions (gasoline, kerosene and gas oil) than another residence time cracking. The percentage volume of light fractions in various residence times are; 15, 75 and 0 for residence time 30, 5, 60 and 25 for residence time 45, (5, 10, 75) for residence time 60, and (10, 60 and 20) for residence time 75 minutes which separates according to its boiling point as shown in table 1.

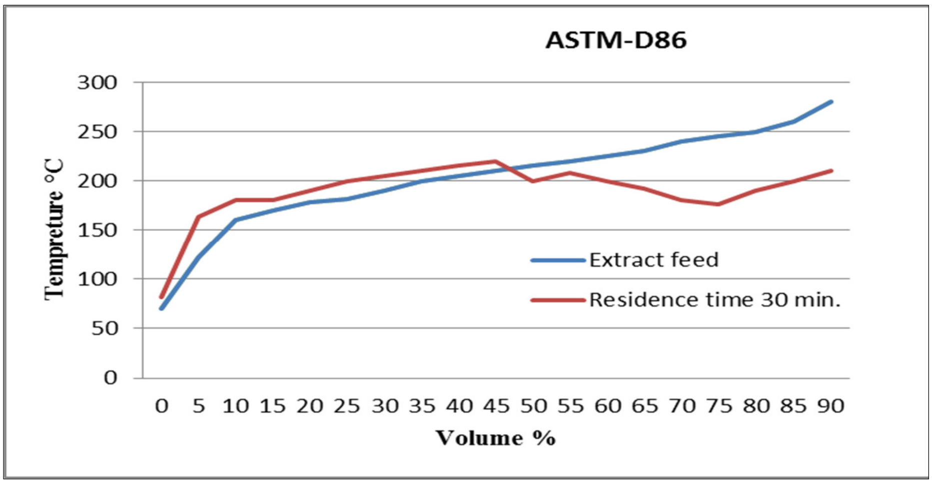


Fig. 4. Atmospheric distillation for extract phase feed and extract feed cracked in 30 minutes.

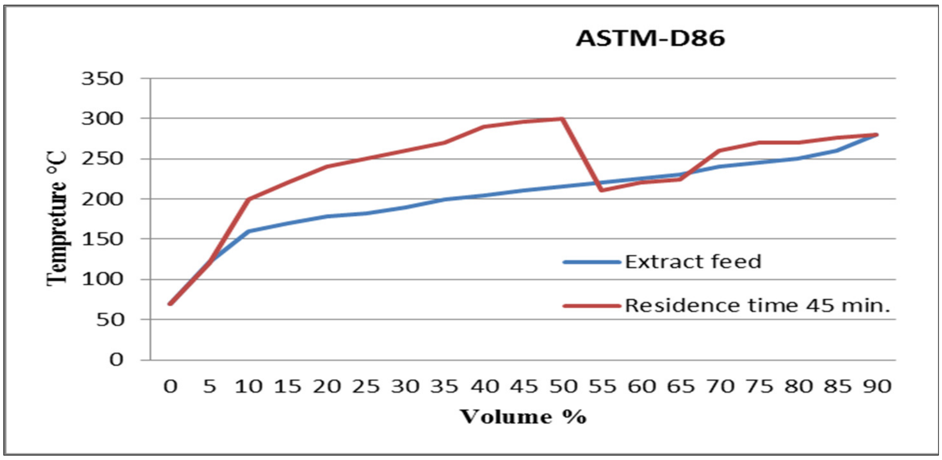


Fig. 5. Atmospheric distillation for extract phase feed and extract feed cracked in 45 minutes.

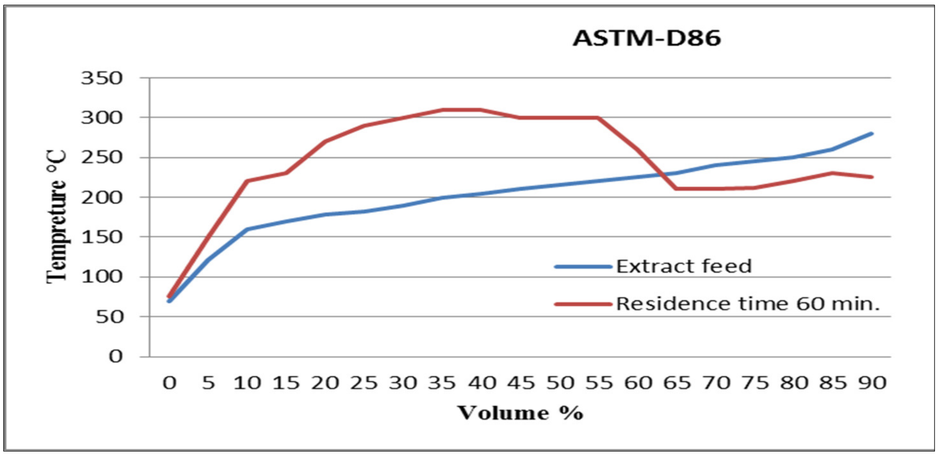


Fig. 6. Atmospheric distillation for extract phase feed and extract feed cracked in 60 minutes.

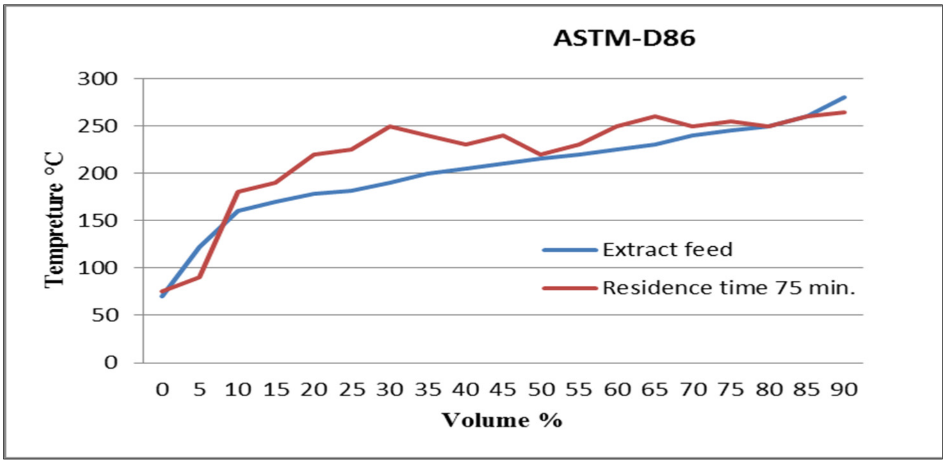


Fig. 7. Atmospheric distillation for extract phase feed and extract feed cracked in 75 minutes.

As shown in table 1, by various residence time 30, 45, 60, and 75 minutes, ability to convert extract feed phase to another light benefit fuel fractions in high conversion, which reaches more than 90% and in different amount of the light fraction products according to their boiling point (IBP, 180 °C) for the gasoline cut, (180, 250 °C) for the kerosene cut, and (250, °350 C) for the gas oil cut, but the more economic one is 30 minutes residence time due to their high amount of gasoline cut production (15, 75 and 0) and summarized of time cracking reaction.

As shown in figure 3, by the distillation curve for the extract phase feed, the average boiling point can be calculated, and this property will used to calculate other properties for example molecular weight, and then to compare it with commercial product to find the benefit of this work.

As shown from tables 2, 3, 4, and 5 the physical and chemical properties for fuel fractions (gasoline, kerosene, and gas oil) which are products from treatment extract feed phase, are acceptable for commercial uses due to their similar property with a commercial one. So it can be said, success will be occur when converting the byproduct matter (extract phase) to another light fuel fraction which can be used as gasoline for automobiles, also it can be used domestically for kerosene, diesel fuel, and for gas oil.

4. Conclusions

-The ability of thermal cracking for heavy byproduct matter (extract phase) in different residence time and constant temperature 400 °C but the best one was 30 minutes for economic consideration.

- Possibilities obtained light fuel fractions (gasoline, kerosene, and gas oil) from byproduct matter (extract phase) with acceptable properties according to standard properties.
- Possibilities to use these light products for automobile for gasoline and domestic uses for kerosene and diesel fuel for gas oil.

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دراسة تاثير زمن المكوث على التكسير الحراري لمادة الاكسترات المتخلفة من استخلاص زيوت التزييت

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الخلاصة

يتعلق هذا البحث بامكانية انتاج مقاطع وقود خفيفة (كازولين ،كيروسين ،كازاويل) من معالجة مادة فائضة هي مادة المستخلص الناتجة من عملية الاستخلاص بالمذيب لزيادة معامل اللزوجة لزيوت التزيت الناتجة من عملية تكرير النفط الخام. نسبة هذه الماده العرضية (طور المستخلص) هي بحدود ١٠% من اللقيم (النفط الخام) الداخل الى وحدات التكرير وتركيبها الكيمياوي يحتوي على العديد من المواد النافعة مثل (مواد عطرية، زيت، مذيب وغيرها الكثير...) والتي هي سبب انخفاض معامل اللزوجة للزيوت.الغرض من هذا البحث هو بيان تاثير زمن المكوث لهذه المادة في مفاعل دفعي على التكسير الحراري لهذه المادة العرضية وعند درجة حرارة ثابته ٤٠٠ م° وزمن مكوث متعدد. المرحلة الاولى من هذه المعالجة هي دراسة اهم الخواص الفيزياوية والكيمياوية لهذه المادة ومن ثم اجراء التكسير الحراري لها في مفاعل دفعي تم تصميمه لهذا الغرض ومجهز كذلك باجزاء سيطرة مساعدة (حرارة، زمن) وكان زمن المكوث المختار (فترة التفاعل) (٣٠. ٤٥، ٦٠، ٧٥) دقيقه وعند درجة حراره ثابته ٤٠٠ م°. حيث كان مقدار التحول لهذه الماده العرضية بواسطة التكسير الحراري يزيد على ٩٠% لجميع هذه الاوقات.

المرحلة الثانية كانت دراسة بعض الخواص الفيزياوية والكيمياوية الهامة للسائل الناتج من عملية التكسير الحراري وكذلك اجراء عملية التقطير الجوي له تبعا ASTM-D86 وذلك للحصول على مقاطع وقود خفيفه (كازولين، كيروسين، كازاويل) والمفصولة على اساس درجة الغليان لها وحساب كميات هذه المقاطع الخفيفه وقياس بعض الخواص الفيزياوية والكيمياوية الهامة لهذه المقاطع. وكانت النتائج تشير الى تقارب المواصفات الفيزياوية والكيمياوية مع تلك القياسية وبالتالي امكانية الاستخدام وحسب المقطع كوقود للسيارات للكازولين وللاستخدام المنزلي للكيروسين او كوقود ديزل للمركبات.
