



Studying Thermal Cracking Behavior of Vacuum Residue

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Abstract

In the oil industry, the processing of vacuum residue has an important economic and environmental benefit. This work aims to produce industrial petroleum coke with light fuel fractions (gasoline, kerosene, gas oil) as the main product and deasphalted oil (DAO) as a side production from treatment secondary product matter of vacuum residue. Vacuum residue was produced from the bottom of vacuum distillation unit of the crude oil. Experimentally, the study investigated the effect of the thermal conversion process on (vacuum residue) as a raw material at temperature reaches to 500 °C, pressure 20 atm. and residence time for about 3 hours. The first step of this treatment is constructing a carbon steel batch reactor its volume about 700 ml, occupied with auxiliary control devices, joined together with an atmospheric distillation unit. The amounts of light fuel fraction products are 2 vol. % for light gasoline, 4 vol. % for heavy gasoline 17 vol. % for kerosene and 24 vol. % for diesel oil. The second step was the treatment the residue matter from first step, in order to separate the petroleum coke matter from asphaltene matter by solvent deasphalting matter (propane) to prepare deasphalted oil (DAO). The amount of deasphalted oil is about 15 vol. %, leaving asphaltene with impurities to precipitate at the bottom of the reactor and these materials consist of the petroleum coke structure. The petroleum coke separate and calcined at approximately (1000 - 1100) °C, to eliminate the remainder of volatile matter from the industrial coke and reach to commercial property.

Keywords: vacuum residue, cracking, coking, distillation

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1- Introduction

The physical and chemical properties of crude oils are influenced by boiling point of constituents, it is therefore important to characterize the heaviest fractions of crude oils [1].

The conversion process is intended to minimize the production of heavy fractions from crude oil; the intended objective of conversion is to convert of all heavy products [2]. Atmospheric and vacuum residue units in petroleum refineries contains large amount of impurities (sulfur, nitrogen, metals and asphaltenes). The rate of conversion is limited by the presence of asphaltenes which tend to concentrate and precipitate in the heavy product cuts, thus rendering them unsuitable for consumption [3].

Asphaltenes are dark brown solids, usually leave carbonaceous matter on heating; they are made up of complex structure aromatic compounds consist of a number of benzene rings, known as polynuclear aromatic compound layers joined with saturated links, their molecular weights span a wide range, from a few hundred to several million [4].

They are found in the heavy petroleum cuts and their presence is undesirable they cause catalyst deactivation and coke deposition, besides causing environmental problems. Liquefied petroleum fractions are used in deasphalting residues process [5].

The presence of asphaltene and resins residue can create many problems in properties of light production; they lead to coke formation in products [6]. Resins are polar molecules in the molecular weight range of 500-1000; the resin molecules surround the asphaltene micelles and suspend them in liquid oil [1, 7].

The thermal cracking begins as soon as petroleum feed stock reaches about 400 to 420 °C [8, 9], the severity of the process depends on the temperature and the residence time [10, 11]. To eliminate all lights matter from industrial coke it must be calcined [12, 13].

Coking, in particular, is recognized not only for the marked reduction in heavy fuel oil produced but also as a method of producing additional light products.

Coke contains about 83% carbon and 6% hydrogen and balance with impurities [14, 15]. The major uses of industrial petroleum coke are as domestic fuel without calcining, manufacture of anodes, graphite, electrodes and manufacture of metals [16, 17].

Mori, et.al studied the effect of temperature range between (400-630) °C on heavy oil cracking, its specific gravity of 0.9 to 1.1 in batch reactor to produce light fractions and by product which heated to 800 – 1200 °C.

Syamsuddin, et.al studied the effect of temperature and type of catalyst of atmospheric crude oil residue in batch reactor at 350 °C for 3 hours residence time and the conversion reaches to 52-65 respectively and the gasoline yield reaches to 7 – 14. Lopes, et.al studied the transforms heavy oil to lighter crude oil at temperature 480- 540°C, the produces less sulfur content.

Kondo et.al studied the effect of temperature on vacuum residue cracking in batch reactor at 400-440 °C; the main products were coke. Del Bianco et.al studied the kinetic for thermal cracking of petroleum vacuum residue matter at 410-470°C and reaction reaches to 120 minute, the activation energy reaches to 14 kcal / mol.

The objective of this work was to study the effect of the temperature on conversion process on (vacuum residue) to temperature reaches to 500 °C in order to production of industrial petroleum coke from vacuum residue matter with distillate fractions as a main production and de asphalted oil (DAO as a secondary production.

2- Experimental work

2.1. Materials

a. Vacuum residue

The heavy raw material, which was used as a raw material for production industrial petroleum coke in this work, was vacuum residue matter, which was obtained from the bottom of vacuum distillation tower of crude oil, whose major physical and chemical properties were listed in Table 1.

Table 1. The major physical and chemical properties of vacuum residue feed stock

Temperature Cut °C	Density gm./cc	API	Viscosity 100 °C cSt	Sulfur wt.% content	Conradson carbon index	Molecular weight gm/mol
540	1.048	3.5	4500	5.78	22.6	510

2.2. Procedure of the Work

a. Pyrolysis of Vacuum Residue

The process of thermal treatment for vacuum residue feed was performed in designed batch reactor as shown in Fig. 1, and Fig. 2. The reactor was made of carbon steel and its volume about 700 ml, this reactor contains two valves, the upper one was used for inlet raw materials and down was used for discharge product.

The reactor occupied with many auxiliary parts, like (electrical heater, thermocouple, timer, temperature controller, and hood).

The feed (vacuum residue) is introduced in the desired quantity (100 ml) in the reactor unit. The reactor was joined together with ASTM distillation unit which consist of (electrical and condenser) to eliminate part amount of volatile matter (gasoline, kerosene and gas oil) from feed, according to its boiling point with a temperature reaches to 350 °C and atmospheric pressure, in order to collect the volatility light petroleum fractions.

Firstly the reactor is heated with introduce nitrogen to remove the air from it, so that no explosive mixture forms with the stock vapors. The electrical heater used to heat the feed to desired temperature until 350 °C in the reactor unit and atmospheric pressure.

At temperature 30 °C separation of the distillate fractions begins, which increases as the temperature of the reactor rises to 350 °C. The volume of distilled fractions that obtained from this step is about 47%.

b. Coking of Asphaltene

When the temperature rises between 350 °C and 500 °C, for the residue which obtained from pyrolysis of vacuum residue step, the deasphalted oil (DAO) was formed.

The residual amounts in reactor (DAO, asphaltene and impurities) were treated with light petroleum solvent for extraction the remains oil.

Light paraffin such as propane in liquid form used to dissolve the deasphalted oil (DAO) its volume about 15 % from the feed stock and precipitate asphaltene with impurities.

Leaving last heavy distillate matter (asphaltene) to separate and precipitate with impurities, like (sulfur, nitrogen, salt, sediments, metals and others) in reactor its volume about 38 % from the feed stock (vacuum residue).

The thermal treatment for the precipitate asphaltene with impurities will be occurred at constant temperature 500 °C inside the reactor, which controlled by temperature controller and pressure about 20 atmosphere with residence time about 3 hours in order to production petroleum coke.

Additional heating used in coke reactor was needed to complete the coking process, dry and calcination the coke.

The petroleum coke calcined to temperature (1000 – 1100) °C to reduce the volatile matter to a very low level and complete the carbonization reactions in petroleum coke.

After completion of calcination, the temperature of the reactor lowered and the extraction of coke is begun.



Fig. 1. Laboratory batch reactor devices

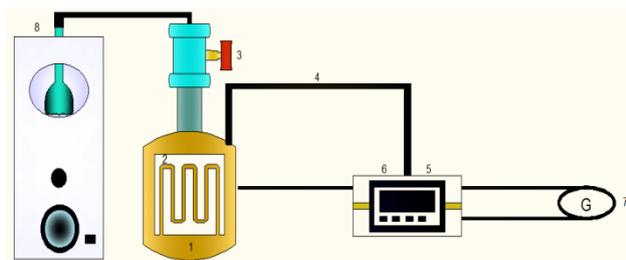


Fig. 2. Flow diagram of experimental batch reactor unit with controls system, 1-Reactor 2-Heater 3-Valve 4-Thermocouple 5-Timer 6- Temperature controller 7- Electrical source 8- ASTM D-86 unit

3- Results and Discussion

The structures of the compounds in petroleum, such as vacuum residue which have boiling points above 540°C are highly complex and consist of oils, resins, and asphaltenes related to solubility in propane or light other hydrocarbon.

3.1. Thermal Cracking Products

a. Atmospheric Distillation ASTM D-86 For Vacuum Residue

The results amount of distillation operation for vacuum residue which was needed to separate volatile matter, (gasoline, kerosene, and gas oil) from asphaltene and DAO, which are shown in Table 2.

Table 2. ASTM D-86 distillation for vacuum residue

Temperature °C	30	80	180	260	350
Volume %	0	2	6	23	47

The initial boiling point of vacuum residue is 30 °C at this temperature separation of the distillate fractions begins, which increases as the temperature of the reactor rises to 350 °C.

The volume of light gasoline fraction equal 2 vol.% until temperature equal to 80 °C, while the volume of heavy gasoline equal to 4 vol.% until temperature equal to 180 °C, also the volume of kerosene equal to 17 vol.% until temperature equal to 260 °C and the volume of diesel oil equal to 24 vol.% until temperature equal to 350 °C.

The mentioned results are accepted with those mentioned by [15]. The hardness and strength of industrial coke petroleum increase as the volatile matter was reduced.

b. Light Distillate Fractions

The main of physical and chemical properties for light petroleum cuts with residue (asphaltene and resin) that will be obtained after ASTM D-86 distillation of vacuum residue are shown in Table 3.

Table 3. The physical and chemical properties for light petroleum cuts and residue

Characteristics	Light gasoline	Heavy gasoline	Kerosene	Diesel oil	Residue
Cut °C	30 - 80	80 - 180	180 - 260	260 - 350	Over 500
Volume %	2	4	17	24	53
Density gm./cc	0.68	0.74	0.80	0.86	1.065
API	75.5	58.5	45	32	2
Viscosity (100 °C) cSt	0.8	1.5	1.6	1.1	2600
Molecular weight.	75	117	175	225	560
Sulfur content wt.%	0.05	0.1	0.5	3.35	5.9

The volume of all distilled fractions that obtained from this operation is about 47 vol. % and which is useful to use as automobile for gasoline cut and domestic uses for kerosene cut and diesel fuel for gas oil cut.

c. Deasphalted Oil (DAO)

The main physical and chemical properties of deasphalted oil (DAO) that will obtained after extraction operation by paraffin liquid (propane) for 53 vol.% of residue are shown in table 4.

Table 4. The main physical and chemical properties of deasphalted oil (DAO)

Yield vol.%	Density gm. / cc	Viscosity (100 °C)cSt	Sulfur content %	Conradson carbon%
15	0.973	120	1.06	8.5

The oil fraction in residue and the resin cut are soluble in propane but the asphaltene fraction is insoluble in propane.

The volume of DAO equal to 15 vol. % and the volume of asphaltene with impurities equal to 38 vol. % from the vacuum residue and these consist of the raw materials of industrial petroleum coke.

The DAO has low sulfur and removed with asphaltene and also the DAO used for production light fuel fractions (gasoline, kerosene and gas oil) by thermal cracking unit. The mentioned results are accepted with those mentioned by [3].

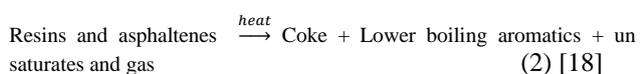
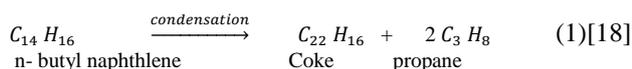
d. Industrial Petroleum Coke

The main physical and chemical properties of industrial petroleum coke which are obtained by solvent extraction process for residue are shown in Table 5.

Table 5. Analysis of calcined industrial petroleum coke

Volatiles matters wt.%	Moisture content wt.%	Ash content wt.%	Sulfur content wt.%	Density gm./cc	Trace Elements wt.%
0.75	0.9	0.38	3.65	2.06	0.25

Coke can be formed from the condensation of polynuclear aromatics such as n- butyl naphthlene.; Asphaltene and aromatic are desirable feed stock for a good yield of industrial petroleum coke. The hardness and strength of industrial petroleum coke increases as the volatile matter is reduced. The presence of high amounts of asphaltenes in crude oil can create many problems in refinery production; they lead to coke formation with all products. There is a decrease in volatile material with rising calcination and for most purposes devolatilization and dehydrogenation are complete at temperature 1100 °C. The mentioned results are accepted with those mentioned by [18, 19].



Sulfur in feed stock though it increases petroleum coke yield, it forms complex with coke. The removal of sulfur from such product is rather impossible; calcination of coke again strengthens the bonds between sulfur and carbon.

4- Conclusions

This work study the production of industrial petroleum coke as a main product with light fuel fractions and de asphalted oil as aside production from thermal treatment of vacuum residue as a raw material, so the conclusions from this study are:

- Production of industrial petroleum coke and distillate fractions (gasoline, kerosene and gas oil) with deasphalted oil (DAO) can be obtained it, by thermal treatment process of secondary matter (vacuum residue)
- Possibilities uses of distillate fractions, gasoline for automobile, kerosene for domestic uses, and gas oil for diesel fuel uses according to its perfect property.
- The deasphalted oil (DAO) also used for production light fuel fractions, due to its heavy product, by thermal cracking operation unit.
- Coking, in particular, is recognized not only reduction in heavy fuel oil produced but also as a method of producing additional light products and distillates matter.
- The severity of the process depends on the temperature and the residence time, to eliminate almost all lights matter from industrial petroleum coke.

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دراسة سلوك التكسير الحراري على المتبقي الفراغي

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الخلاصة

تعتبر عملية معالجة المتقطر الفراغي عملية مهمة جدا صناعيا لانها ذات فائدة اقتصادية وبيئية, الغرض من هذا العمل هو انتاج الكوك البترولي الصناعي ومقاطع وقود خفيفة (كازولين, كيروسين وزيت الغاز) كنتاج رئيسي والزيت الخالي من الاسفلتينات كنتاج ثانوي من معالجة مادة ثانوية وهي متبقي التقطير الفراغي الناتج من اسفل برج التقطير الفراغي للنفط الخام. عمليا يهدف هذا العمل بيان تاثير التحول الحراري (التكسير الحراري) على (المتبقي الفراغي كمادة اولية) عند درجة حرارة تصل الى 500 م° وضغط (20) جو وزمن مكوث داخل مفاعل التكسير 3 ساعة. الخطوة الاولى للمعالجة كانت تصميم وتصنيع مفاعل للمعاملة الحرارية ذو دفعات حجمه بحدود 700 ملتر مصنوع من الكربون ستيل وملحق به مجموعة من الاجزاء المساعدة للسيطرة على ظروف التفاعل ومربوط على التوالي مع وحدة التقطير الجوي وذلك لتقطير المواد الخفيفة المتطايرة (الكازولين, الكيروسين, الكازويل) وفصلها عن الكوك البترولي الصناعي ولغاية درجة حرارة تصل الى 350 م° وضغط جوي واحد. وكان حجم المتقطر من المقاطع البترولية الخفيفة كالاتي: 2% حجم الكازولين الخفيف, 4% حجم الكازولين الثقيل, 17% حجم الكيروسين و24% حجم الديزل. الخطوة الثانية هي معالجة المتبقي الثقيل من الخطوة الاولى للمقطر الفراغي لغرض فصل مادة الكوك البترولي الصناعي الغني بالاسفلت والمخلفات عن الزيت منزوع الاسفلتين (DAO) وذلك باستعمال مذيبي بارافيني خفيف (البروبان) السائل حيث يتم اذابة الزيت وفصله عن مادة الاسفلت, حيث كان حجم هذا الزيت المفصول عن الاسفلتين 15% من حجم اللقيم تاركا الاسفلتينات والمواد الثقيلة الاخرى كالكبريت والمعادن المختلفة مترسبة في المفاعل. وهذه هي المكونات التركيبية للكوك البترولي النفطي الذي يفصل ويقسى الى درجة حرارة تصل الى 1000 - 1100 م° للتخلص من المواد المتطايرة الخفيفة الباقية في الكوك الصناعي واعطاء المواصفات التجارية اللازم توفرها في المواصفات المختبرية لانتاج الكوك الصناعي البترولي.

الكلمات الدالة: منقطر فراغي, تكسير, تكويك, تقطير