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Converting of Waste Crude Oil of East Baghdad Oil Field into Light Hydrocarbons Using Thermal Cracking Technology

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Abstract

East Baghdad oil field produces a lot of quantities of waste crude oil due to drilling and production processes activities. This waste is caused a negative impact on the environment and human health. In the present investigation, the collected waste crude oil of API= 13 was converted into light hydrocarbons via a thermal cracking reaction. The thermal cracking process was achieved in a batch reactor at temperatures ranging between 350-450°C in absence of oxygen. At each temperature, the reaction pressures varied between (1-6) kg/cm^2. Moreover, a continuous stirring of the reaction mixture inside the reactor was continued during the course of the thermal cracking process at a velocity of 96 rpm. The best yield of produced liquid hydrocarbon, gases, and coke at optimum conditions was 77.56 wt.%, 9.3 wt.%, and 13.14 wt.%, respectively. Actually, this process regards cheap, and simple with a high rate of liquid hydrocarbon production as well as environmentally beneficial.

Keywords: Thermal cracking; Environmental pollution; Waste crude oil; Hydrocarbon production; Oil field; Disposal pits.

تحويل مخلفات النفط الخام الناتجة من حقل شرق بغداد النفطي إلى هيدروكربونات خفيفة باستخدام تقنية التكسير الحراري

الخلاصة:

ينتج حقل شرق بغداد النفطي كميات كبيرة من نفايات النفط الخام نتيجة لأنشطة عمليات الحفر والإنتاج، وتسبب هذه النفايات تأثيرا سلبيا على البيئة وصحة الإنسان. في البحث الحالي، تم تحويل نفايات النفط الخام ذات API= 13 إلى هيدروكربونات خفيفة عبر تقنية التكسير الحراري. تمت عملية التكسير الحراري في مفاعل دفعي عند درجات حرارة تتراوح بين 350-450 درجة مئوية في غياب الأكسجين. وعند كل درجة حرارة تراوحت ضغوط التفاعل بين (1-6) كجم/ سم^2. علاوة على ذلك، استمر التحريك المستمر لخليط التفاعل داخل المفاعل أثناء عملية التكسير الحراري بسرعة 96 دورة في الدقيقة. أفضل إنتاج من الهيدروكربون السائل والغازات وفحم الكوك المنتج في الظروف المثلى كان 77.56% بالوزن، 9.3 بالوزن، و13.14 بالوزن، على التوالي. في الواقع، تعتبر هذه العملية رخيصة الثمن وبسيطة مع ارتفاع معدل إنتاج الهيدروكربون السائل بالإضافة إلى أنها مفيدة بيئياً.

1. Introduction:

In petroleum exploration and production processes, different environmental accidents occurred [1, 2]. In fact, these activities are caused by oil spill problems due to leaks in transportation pipelines, storage tank leaks, wells pre-drilling processes, and pre-production processes [3, 4]. The crude oil wastes will cause many negative impacts and problems for the environment, categories of living organisms in the world, and human health [5]. All crude oil wastes are toxic compounds that lead to pathological diseases. The general health impacts of these crude oil wastes comprise clear damage to the neuron cells, low immunity, eye diseases, respiratory diseases, and cancer [6, 7]. On the other hand, the release of crude oil wastes into the environment will cause fatal problems by settling these wastes on the soil area and plants, and even into living organisms leading to different diseases and then death [8, 9].

From an economic point of view, the use of crude oil wastes is an important challenge to convert low-value components into high-value ones. This point will contribute to more economic issues as well as probability via the production of fractions [10, 11]. Accordingly, the thermal cracking technique is usually applied to convert the residual oil to fractions under different operating conditions of temperature and pressure. Moreover, the catalytic cracking process is widely used to convert heavy hydrocarbons into light components [12, 13]. The process control system and catalyst costs make this technology complicated and require an efficient reactor operation system [14, 15]. Furthermore, applying of visbreaking method, coking, and thermal cracking techniques is regarded as more economical technology due to simple operation without using a catalyst or hydrogen gas. Also, the reaction pressure in these systems is low in comparison with that of the catalytic cracking process [16, 17].

The effect of different operating parameters conversion rates in the thermal cracking reaction usually depends on the specifications of feed crude oil. The operating temperature is the main variable in the thermal cracking process. Also, the reaction contact time is the key parameter in achieving an efficient ration rate [18]. Accordingly, it is important to understand the main properties of the applied oily sludge in the thermal cracking reactions. Ref. [19] investigated the specifications of oily sludge produced from a petroleum refinery by evaluating of alkanes, aromatics content, resins, and produced asphaltenes in the reaction mixture. Ref. [20] and Ref. [3] indicated that the increased viscosity of the crude oil waste with time in the emergency pit makes it difficult to handle or pump this material due to high energy consumption. Then, the cracking of crude oil waste to produce light fuel is the major goal in the petroleum industry. Accordingly, the use of thermal cracking will contribute to the reduction of environmental problems, economic benefits, and light fuel production. Ref. [21] analyzed the conversion values of crude oil (API=34) that reacted in the thermal and catalytic cracking units. The authors noted that in the two reaction systems, the production of gases, light olefins, and coke products is highly dependent on the reaction temperatures. Ref. [22] studied the influence of heating temperature on the quality of thermal cracking products (gaseous and liquids). The experimental work products were analyzed by using TGA and FTIR at different heating values. The authors noted that the heating rate represents the key factor in determining product quality.

The collection of crude oil wastes in a disposal pit required a deep understanding of the legal responsibility to treat these wastes. Moreover, all petroleum and gas sites must meet environmental regulations by reducing the sources of pollution [2, 23]. According to the literature review, there is a limited number of studies dealing with treating the collected crude oil wastes from the disposal pit. Therefore, the main objective of the present experimental work is to convert crude oil wastes into useful hydrocarbons using an efficient thermal cracking method under different operating conditions.

2. Material and Methods

2.1. Materials

Waste crude oil was collected from Midland Oil Company's disposal pit and used as the main raw material. The samples were collected at least one meter away from the edge of the pit and then transferred directly to the laboratory to be analyzed. Nitrogen with 99% purity was supplied from the factory in Al-Khaleej for industrial gas. The main properties of this feedstock are illustrated in Table (1). As can be seen from Table 1, the density of waste crude oil was measured using ASTM D5002, and it was equal to 0.9763 g/cm^3. Figure (1) presents some photographs of a disposal pit and a sample of waste crude oil in a laboratory for primary testing.

Table (1): Properties of the parent waste crude oil.

Property	Value
Density at 15 (g/cm^3)	0.9763
API	13
Salt content (ppm)	30
Water content (vol.%)	10
Sulphur content (wt.%)	5
Sediments (wt.%)	2

Fig. (1): Photographs illustrate the waste crude oil pit in petroleum site, and samples measurements at laboratory

2.2 Thermogravimetric analysis

The thermal stability and degradation temperature of the waste crude oil were obtained by using thermogravimetric analysis (TGA-STA, PT-1000, Linseys Company). The analysis started at an ambient temperature of 25 °C and then linearly increased to 800 °C at a rate of 15 °C/min in nitrogen (N_2) with a flow rate of 20 ml/min. The TGA curve was used to determine the thermal stability and degradation temperature of the crude oil. The TGA analysis was measured by the laboratories of the College of Education for Pure Science (Ibn Al-Haitham, Baghdad).

2.3 High-pressure thermal cracking apparatus

An autoclave-parr high-pressure semi-batch reactor of 300 ml size and cooling coil has been used for the thermal cracking of waste crude oil. Figure (2) shows the thermal cracking reaction system. The working pressure was measured using a pressure gauge by a stainless-steel tube mounted on the head of the reactor. The temperature was measured and controlled by a type K thermocouple with a 1/8" diameter that was inserted into the head thermowell and connected to the thermocouple socket on the control panel of the temperature controller. The temperature controller is near the reactor, leaving a space of at least six inches between the controller and the base of the reactor so the controller will not be affected by radiant heat. The reaction system included a cooling chiller to condense the produced liquid fuels. In addition, a nitrogen gas cylinder with a calibrated flow meter was connected to the stainless-steel reactor to lower the intensity of the reaction.

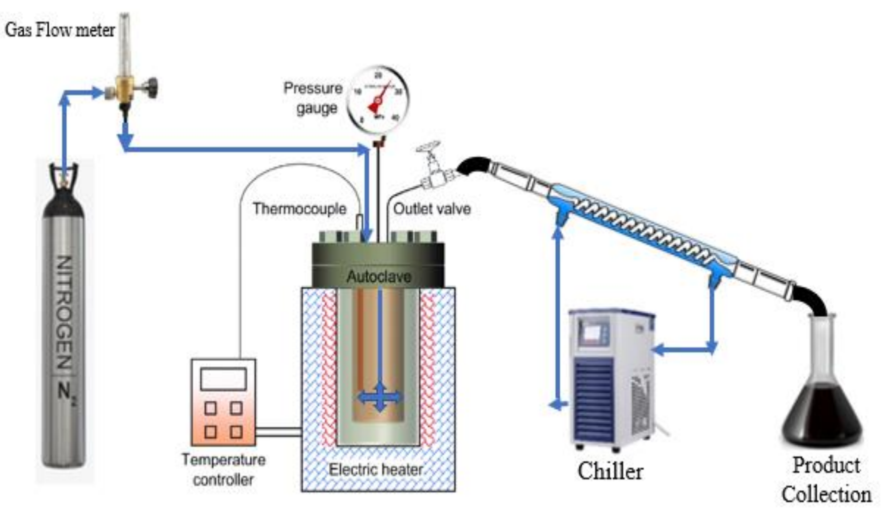

Fig. (2): Schematic of high-pressure thermal cracking apparatus.

2.4 The experimental procedure of thermal cracking reaction

The experimental runs of waste oil thermal cracking were carried out in the reactor using 150 ml of raw feedstock for each experiment. The chemical reaction was achieved in absence of oxygen gas. It is important to mention here that before any experiment, the nitrogen gas (99.8% purity) was feed into the reactor for 15 minutes to remove any traces of oxygen. The effect of operating temperature and pressure was carried out in the experimental work. The thermal cracking reaction was investigated at various temperature of 350, 400, and 450°C and pressure of 1, 2, 4, and 6 kg/cm^2. The heating rate value was kept constant at a rate of 15 °C/min. The reaction time was constant for each value of operating temperature. The reactor containing an internal stirrer (120 rpm). After purging the reactor with pure nitrogen gas for 15 minutes, it was heated to a reaction temperature in the range of 350–450 °C and an operation pressure in the range of 1–6 g/cm^3. In the range of 25–45 min, after the reactor's working temperature and pressure are attained, the produced fuel is cooled by a chilling system (condenser, chiller, gas separator). The condensable liquid fuel was dropped and accumulated in a conical flask to be weighed and sent for analysis, whereas the non-condensable vapors were vented to the atmosphere. The reactor cooled down at the end of each run, and the participating coke was measured. As for the calculation of the amount of gas produced, it was calculated as follows:

$$Produced\ gas = Feed - Produced\ liquid\text{-}\ Residue$$

3. Results and Discussion

3.1 The effect of temperature using Thermogravimetric analysis

Temperature is the main parameter affecting the thermal cracking, using the TGA analysis to find out the best temperature range in which the thermal cracking process takes place. Figure (3) shows the plot of weight/mass versus temperature curve for thermal decomposition of waste crude oil under a linear heating rate. The curve shows that the decomposition was a single-step degradation, the rapid loss of weight within the narrow range of temperature (150-220) ℃, due to a distillation process of the low boiling point of hydrocarbons [24], whereas the wide temperature range of the degradation was achieved within (350-450) ℃, related to the high temperature employed for the remainder of the waste crude oil. It is due to the formation of complex reactions such as the condensation of aromatic rings, the separation of alpha carbons and alkyl chains attached to naphthene rings and aromatic rings, and the ring-opening and dehydration of naphthene rings [13, 15].

The curve shows that at their respective end-set temperatures, waste crude oil in the thermal cracking process left a large amount of solid residue that did not decompose even at 900 °C [17]. The weight loss of crude oil waste is slightly variable and is governed by the condensed reaction of aromatic nuclei, forming a precursor to the coke, the degree of condensation being much higher, and then being transformed into coke as the final residue [25].

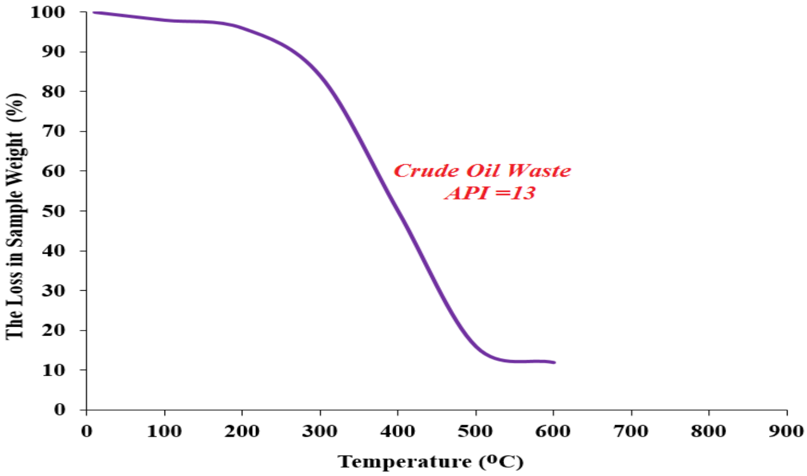

Fig. (3): The results of TGA analysis of parent waste crude oil (API=13)

3.2 Effect of Reaction time

The reaction time affects the yields of end products. Long cracking times are usually used for thermally cracking large particle sizes because increases in temperature or heating speed contribute to shorter reaction times [26]. The cracking of waste crude oil has been studied at different reaction times: 15 min, 25 min, 35 min, and 45 min. Figure (4) represents the effect of different values of reaction time at a steady reaction temperature of 350 °C, atmospheric pressure, and a heating rate of 15 °C/min. The liquid yield obtained from the thermal cracking increased gradually from 26.66% at 15 min to 33.47%, 38.65, and 40.37% at 25 min, 35 min, and 45 min, respectively. It is thought that a significant amount of time allows for the formation of gaseous products like methane, ethane, and CO_2 to react with other products and form substitutes for their primary structure. More time means more time to allow the product to interact [16].

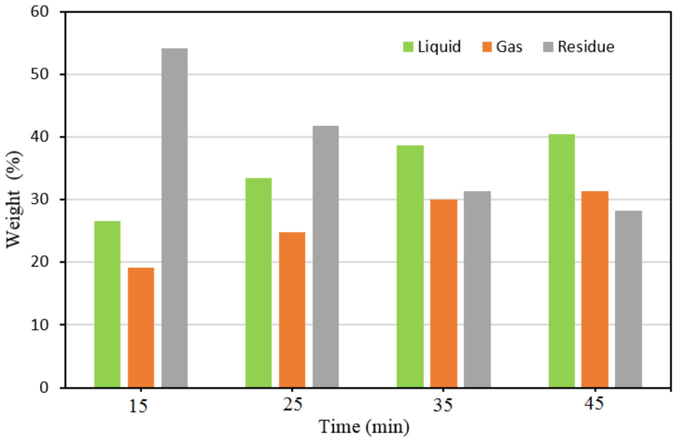

Fig. (4): Effect of reaction time on product distribution at 350°C

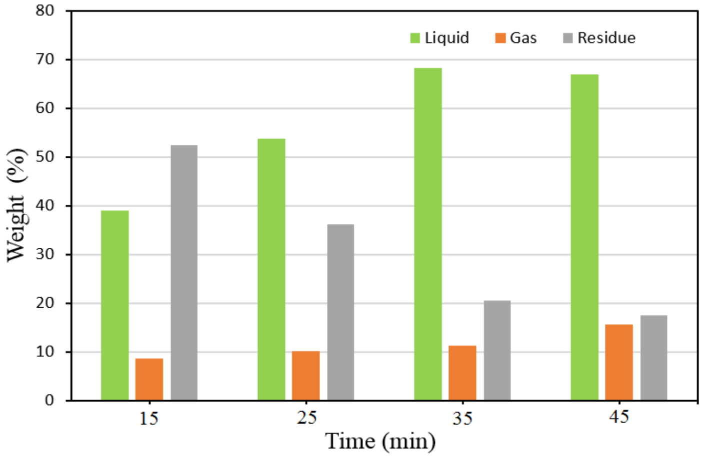

Fig. (5): Effect of reaction time on product distribution at 400°C

For a reaction temperature equal to 400 °C, the produced liquid was observed to increase significantly from 38.99% at 15 min to 53.67% and 68.3% when the reaction time was increased to 25 min and 35 min, respectively; however, a minimal decrease was noticed when the reaction time was increased to 45 min, as illustrated in Figure (5). As for the temperature of 450 °C, the liquid hydrocarbon yield increase slightly from 38.99% at 15 min to 56.89% at 25 min, as shown in Figure (6), However, it was observed that prolonging the reaction time to 35 min and 45 min led to a decrease in the amount

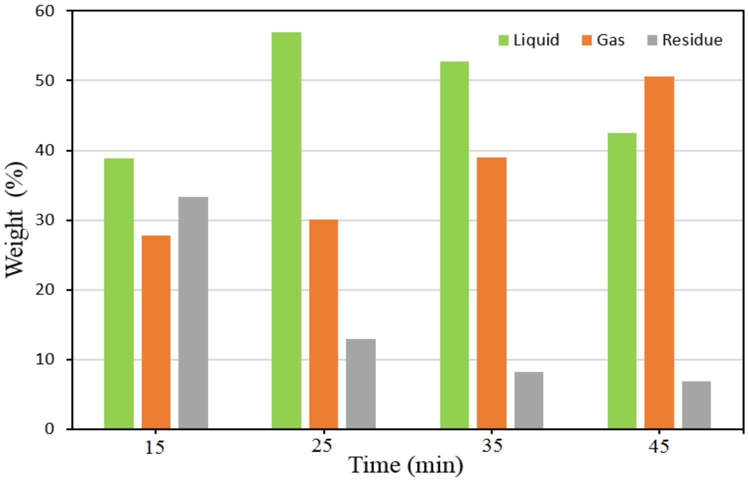

Fig. (6): Effect of reaction time on product distribution at 450°C

On the other hand, higher temperatures can encourage the liquid fuel's secondary cracking to produce the shorter-chain pyrolysis gas. As a result, gas production typically increases with increasing temperature and reaction time at a constant heating rate [7, 18]. As opposed to the residue decreasing as the aforementioned parameters were increased. The delay in reaction time reduces the degradation of primary products, resulting in thermal stable products such as lightmolecular-weight hydrocarbons and non-condensable gases [14, 20]. Higher rates of condensation and dehydrogenation processes may actually lead to an increase in the amount of polycondensed aromatic compounds in the cracked residue, making them more resistant at considerably shorter durations [27].

3.3 Effect of Pressure

To investigate the effect of high pressure on thermal cracking under constant heating rate and residence time. Thermal cracking of the feedstock was carried out at 350℃, 400℃ and 450℃ under 1kg/cm^2, 2kg/cm^2, 4 kg/cm^2, and 6 kg/cm^2 for each mention temperature degree. At reaction temperature 350 ℃, reaction time 45, and heating rate 15 ℃/ min, According to Figure (7) we can notice that the produced liquid hydrocarbons increase gradually from 40.37% at atmospheric pressure to 44.56% and 52.77% at 2 kg/cm^2 and 4 kg/cm^2 respectively, Whereas the gases decrease gradually from 31.43% at atmospheric pressure to 28.67%, 23.9% of 2 kg/cm^2 and 4 kg/cm^2 respectively. It is remarkable that with increasing pressure to 6 kg/cm^2 the amount of produced liquid decrease to 38.34%, In contrast to the amount of gas increased to 39.09%. We also note that the quantity of residue at reaction temperature of 350 ℃ and operating pressure of 1, 2, 4 and 6 kg/cm^2 decreases gradually.

Figure (8) shows the bar graph of the thermal degradation at 400 ℃, 35 min, and a heating rate of 15℃ /min. The figure of liquid hydrocarbons increases from 68.3% at atmospheric pressure to 77.56% at 2 kg/cm^2. By contrast, the figure of gases and residue decrease gradually from 11.23%, 20.47% to 9.3%, 13, 14% at pressure 2 kg/cm^2 respectively.

For further increase in pressure to (4, 6) kg/cm^2 the percentage of produced liquid gradually decreases to reach 73.4% and 60.5%, respectively; however, the yield of gases and residue increases in the aforementioned pressure degrees to 13.22% and 13.38% (at 4 kg/cm^2) and to 24.5% and 15% (at 6 kg/cm^2) respectively.

The produced liquid hydrocarbons, gases, and residue yield% at 450 ℃, operating pressure 1, 2, 4 and 6 kg/cm^2, reaction time 25 min and heating rate 15 °C/min are illustrated in Figure (9). Overall, the amount of liquid product decreases from 55.89% at atmospheric pressure to 51.45%, 39.6% and 32.66% with pressure rising to 2,4 and 6 kg/cm^2 respectively.

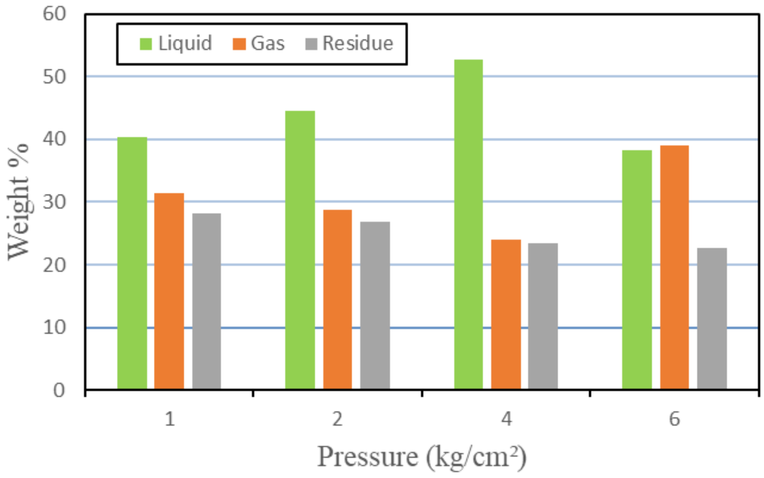

Fig. (7): Effect of thermal cracking pressure on product quality at 350℃.

However, the yield of gases increases from 26.23% at atmospheric pressure to 30.88%, 37.6 and 39.69% for rising operating pressure to 2,4 and 6 kg/cm^2 respectively. The subsequent breaking of the preformed products could account for the drop in liquid products and rise in gas production at higher temperatures; the same observations were also reported by Ref. [28]. Likewise, the ratio of residue increases from 16.88% to 17.67%, 22.8% and 27.65% at operating pressures 2,4 and 6 kg/cm^2 sequentially.

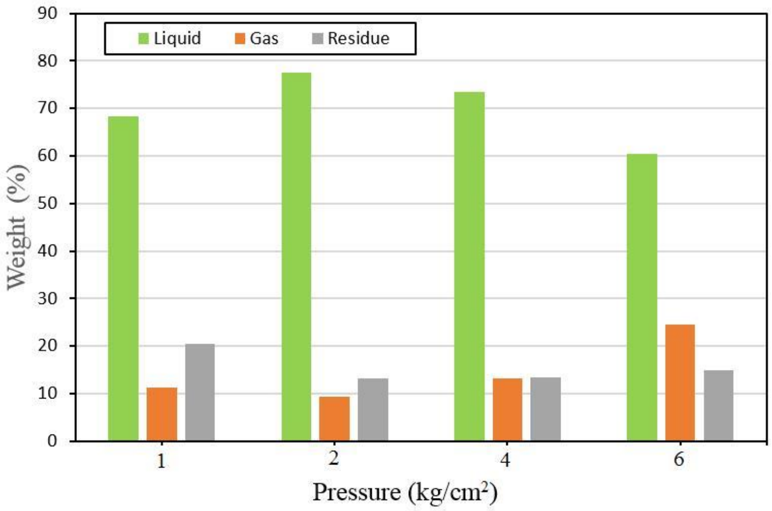

Fig. (8): Effect of thermal cracking pressure on product quality at 400℃.

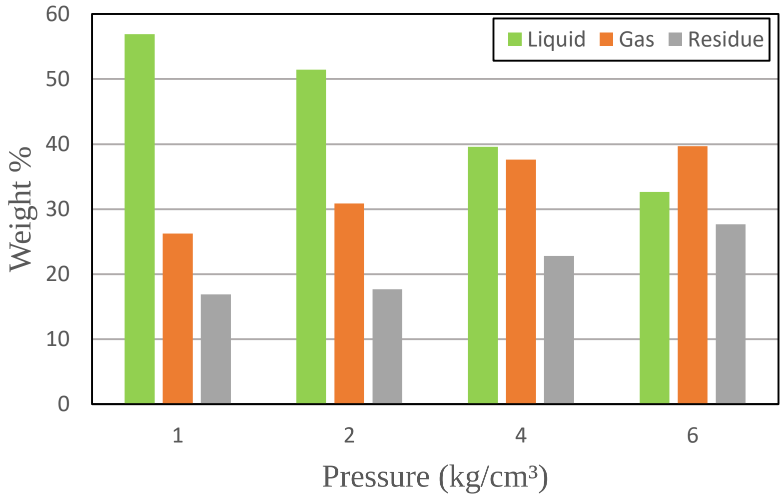

Fig. (9): Effect of thermal cracking pressure on product quality at 450℃.

Long-chain compounds may increase over time due to the fact that crude oil and its derivatives that spend longer in the reactor breakdown and produce heavier products than those that are produced early in the process [29].

Since lighter compounds had a shorter residence time in the reactor and evaporated and flowed out quickly, the reaction pressure significantly affected the distribution of the product. It is explained by enhanced C-C bond breakage at higher temperatures, resulting in lighter hydrocarbons with shorter carbon chains [2, 30].

It is important to mention here that the API gravity measurement was performed at the best conditions (350℃, 4 kg/cm^2 and 45 min), (400℃, 2 kg/cm^2 and 35 min), and (450℃, 1 kg/cm^2 and 45 min). At 350℃, 4 kg/cm^2, the API value clearly increased with the increasing operating pressure, and it was equal to 25.9, likewise, at 400℃, 2 kg/cm^2, which was equal to 31.3. However, the further increasing in temperature and pressure led to a reduction in the API value, it was evident that at the temperature 450℃ and 1 kg/cm^2, the API was equal to 27.2. This is attributed to the high decomposition of long-chain hydrocarbons to form large quantities of light hydrocarbons in the gas phase.

4. Conclusions

The present investigation succeeds in solving important two cases in petroleum sites, which are the environmental and economic issues due to the collection of waste crude oil in these sites. Accordingly, the thermal cracking technique was carried out efficiently to convert waste crude oil (API=13) into liquid and gaseous fuels. The reaction was achieved at different operating temperatures and pressures. The results indicated that the reaction temperature and pressures are the chief two operating parameters that determine the conversion rate of waste crude oil into useful hydrocarbons. Then, based on the evaluation of produced fuel quality, it was noted that the best thermal cracking temperature and pressure were 400°C and 2 kg/cm2, respectively in which liquid fuel was 77.56%. Accordingly, the overall rate of production yield of the thermal cracking process at the best operating conditions was 90.3%. The results of the present investigation provided a clear solution to the collected waste crude oil in the petroleum site (in an disposal pit). Moreover, it contributed to providing fuel with low operating cost and simple operation.

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