*Arab Gulf J. scient. Res.* **2** (2), pp. 743-752 (1984)

# Delayed Coking of Spent Oil Distillate

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ABSTRACT A laboratory coking unit was designed and constructed for the experimental study of the delayed coking process of spent oil distillate. The yield and analysis of coke, gases and liquid products were obtained for each experiment. The study showed that spent oil distillate produced relatively low sulphur content coke and with no metals. Increasing the recycle ratio increases the coke yield and decreases the gas and gasoline yield and the olefins content of gasoline. The recycle ratio has a slight effect on the sulphur content of produced coke.

The yield and quality of products from delayed coking are greatly influenced by charge stock properties and operating conditions (Stormont 1969, Kutler *et al.* 1970 and Rose 1971). Principle charge stock properties that affect coke quality and yield are: specific gravity, Conradson carbon residue, boiling range, Watson characterization factor, sulphur content and metal content.

Many empirical correlations are reported, that relate coke yields with some properties of feedstocks, especially Conradson carbon residue for some different feedstock (Nelson 1952 and 1956, Wright 1958, Krasyukov and Sedov 1969). However, the abovementioned correlations do not apply for some other feedstocks (Mohammed *et al.* 1979). The sulphur content in the coke is a function of the sulphur content in the charge, however, it is difficult to generalize a relationship between these two variables (Kutler *et al.* 1970). It is important that an appreciable part of the sulphur in the feedstock goes into the coke (Ries 1975).

By increasing the recycle ratio, the yield or produced coke, gas, gasoline and light gas oil increases at the expense of heavy gas oil (Rose 1971).

## Experimental

*Feedstock*

The spent oil distillate with a boiling range 305-550°C was produced from mixtures of spent lubircating oil by vacuum distillation. The general specifications of original oil mixture and spent oil distillate are shown in Table 1. The yield of spent oil distillate composes 60.08 wt.% of the original spent oil mixture.

**Table 1.** General specification of original spent oil mixture and distillate.

| | **Original spent oil mixture** | **Spent Oil distillate** | **Test method** |
|---|---|---|---|
| 1. Specific gravity at 15.6/15.6 °C | 0.90245 | 0.88104 | ASTM D 1298, IP 18 |
| 2. Kinematic Viscosity, Cs | | | ASTM D 445, IP 71 |
| at 37.8 °C | 568.53 | | |
| at 98.9 °C | 5.61 | | |
| 3. Conradson carbon residue, wt.% | 4.25 | 1.24 | ASTM D 189, IP/3 |
| 4. Flash Point, °C | 110 | 141 | ASTM D 93, IP 34 |
| 5. Water content, wt.% | 1.21 | nil. | ASTM D 95, IP 74 |
| 6. Ash content, wt.% | 0.781 | 0.0021 | ASTM D 982, IP 4 |
| 7. Pour Point, °C | | −3.9 | ASTM D 97 |
| 8. Bromine number, mg Br/100 g | | 10.8 | ASTM D 1159 |
| 9. Sulphur content by X-ray spectroghraphy, wt.% | 1.4 | 0.78 | ASTM D 2622 |
| 10. Metals by AAS, ppm | | | |
| Cu | 15 | nil. | |
| Ca | 1147 | nil. | |
| Pb | 524 | nil. | |
| Ba | 295 | nil. | |
| Zn | 590 | nil. | |
| Fe | 107 | nil. | |
| Ni | 1 | nil. | |
| Al | 72 | nil. | |
| 11. Hydrocarbon Comp. wt.% by elution Chromatography: | | | |
| Aromatic | – | 17.8 | |
| Nonaromatic | – | 82.2 | |
| Olefinic | – | 8.1 | |

Compared to the original lubricating oil which has high metals (Ca, Pb, Zn, Cu, Fe, Al, Ba) and sulphur contents, the spent lubricating oil distillate contains no metals and has a lower sulphur content. Therefore, the lube distillate is quite suitable as feedstock for delayed coking.

*Laboratory Coking Unit*

The coking of spent oil distillate was carried out in a laboratory delayed coking unit (Fig. 1) with a stainless steel coke drum (I.D. 82 mm and length 300 mm). The coke drum is constructed on the same general lines as the laboratory size mini-coker developed at Marathon's Denver research centre (Allred 1973).

The feedstock is pumped from the reservoir (R) to the preheater (H) in which it is preliminary heated to about 350°C, it then entered the coke drum (D). The run proceeds until sufficient coke has been produced. The oil injection is then stopped and nitrogen is passed into the coke drum in order to strip hydrocarbon vapours from the coke, thus reducing the volatile matter of the coke. After that the coke calcination takes place at 600°C for 1 hr.

*Test Method*

The separation of light fractions is made in 5-plate Oldershaw column. The physical properties of feedstock and coking products including the produced coke

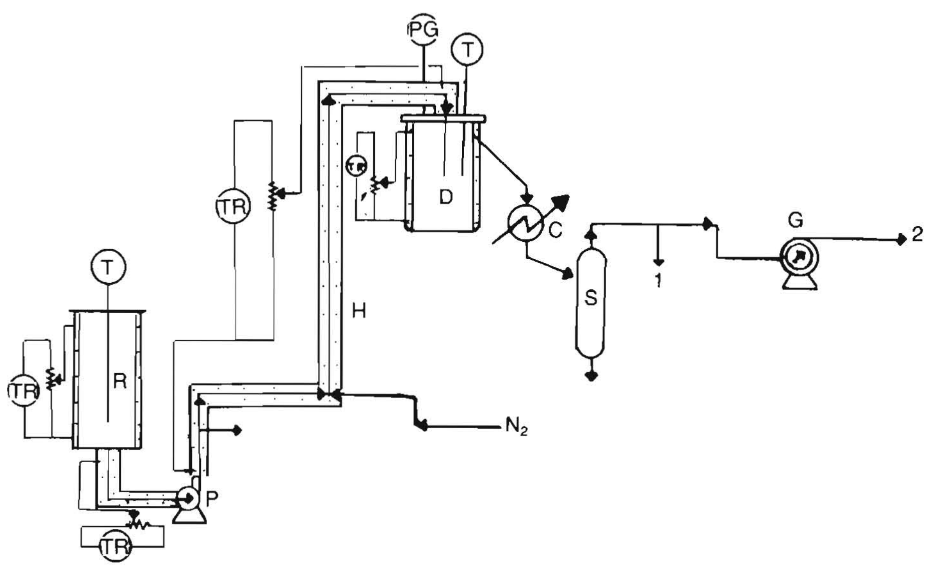


**Fig. 1.** Laboratory Coking Unit.
R- Reservoir, P-Flow pump, H-preheater D-Coke drum, C-Condenser, S-Separator, G-Gasmeter, T-Thermocouple, TR-Transformer, PG-Pressure gauge

are determined using ASTM. The metal content of spent lubricating oil and spent oil distillate are evaluated using PYE UNICAM SP-9 atomic absorption spectrophotometer. The yield of gases calculation is based on gas chromatography analysis. The gas is analyzed by gas chromatograph (PYE UNICAM 204). Sulphur content of spent oil, oil distillate and coking products are determined using the LAB-X100 of radio isotope excited X-ray fluorescence analyser. The hydrocarbon composition of spent oil distillate is determined by elution absorption chromatography (Hala *et al.* 1981).

## Results and Discussion

Initially the oil distillate was coked at 500°C, pressure 1.6 bar and LHSV (Liquid Hourly Space Velocity) of 0.062 $hr^{-1}$. Under these conditions only 1 wt.% of coke was produced, while the yield of gas and gasoline ($C_5$-160°C) were 16.82 and 4.73 wt.%, respectively. The sulphur content of the coke produced was 2.75 wt.%.

In order to increase the spent oil distillate conversion during coking, the coking temperature was increased to 520°C and the LHSV decreased to 0.055 $hr^{-1}$. The pressure was kept unchanged. The temperature increase, and the LHSV decrease, increased the coke and gasoline yields markedly. Coke, gas and gasoline increased from 1.0, 16.82 and 4.73 wt.% to 1.6, 21.36 and 16.96 wt.%, respectively. The sulphur in the coke only increased slightly (from 2.75 to 2.91 wt.%).

The liquid residue (305°C plus) was recycled and mixed with fresh feedstock, in order to increase the coke yield and modify the composition further.

To study the influence of recycle, a series of similar runs were carried out at 520°C, LHSV of 0.055 $hr^{-1}$ and pressure of 1.6 bar. The liquid products produced during the coking operation were collected and distilled to separate the residue (305°C plus) of distillation to be used as recycle. This residue was mixed with spent oil distillate in different recycle ratios.

The recycle ratios are plotted against the gas and gasoline yield (based on combined feed-fresh feed + recycle) in Fig. 2 and 3, which indicate that the gas and gasoline yield decrease as recycle ratio increases. This is because the recycled material is heavier than oil distillate and produces less gas and gasoline during coking, and it has higher thermal stability.

The plotting of coke yields, based on combined feed, against recycle ratios is shown in Fig. 4. The coke yield increases as recycle ratio increases. This is because of increasing Conradson carbon residue as recycle ratio increases (Fig. 5) and because of relatively easy polymerization and polycondensation of high molecular weight hydrocarbons which constitutes a considerable part of the recycle.

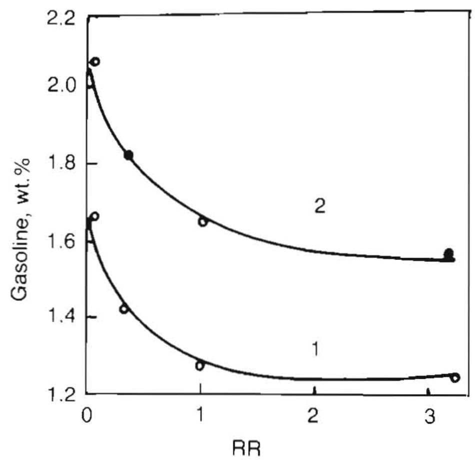


**Fig. 2.** The effect of recycle ratio on gasoline yield.
1. On feed 2. On liquid product

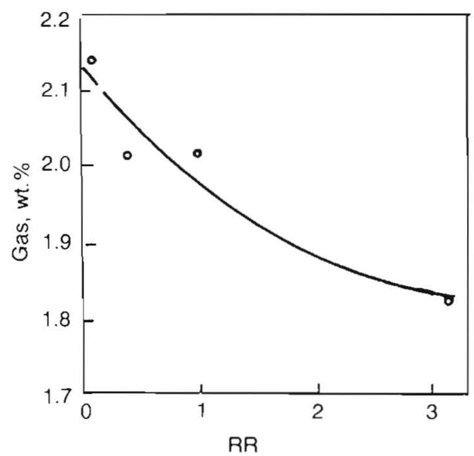


**Fig. 3.** The effect of recycle ratio on gas yield.

It is discovered that the sulphur in the coke produced increases slightly with increasing recycle ratio, as shown in Fig. 6, and with increasing sulphur in feed, as shown in Fig. 7.

A plot of increase of sulphur percent in the coke, related to sulphur in feed, against recycle ratio is shown in Fig. 8. Note that the percent sulphur increase in the coke produced without recycle is 1.68 wt.% and when recycle is used the sulphur increase is lowered and finally remains constant.

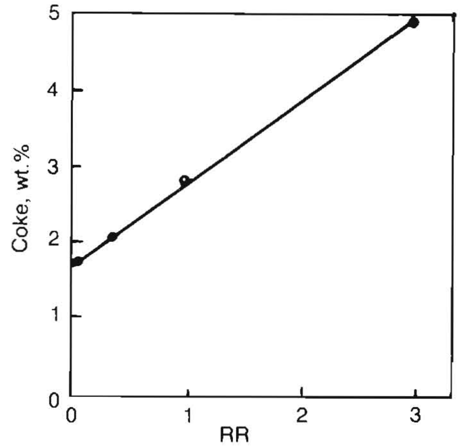


**Fig. 4.** The effect of recycle ratio on coke yield.

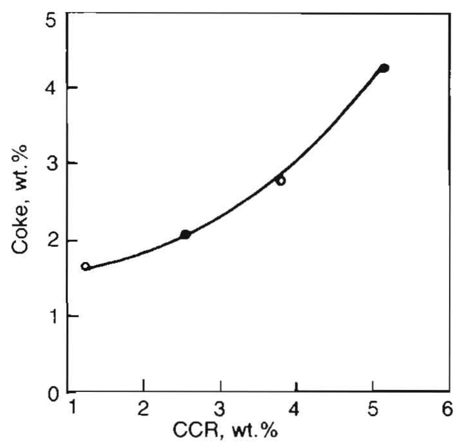


**Fig. 5.** Relation between the feed Conradson carbon residue and the coke yield.

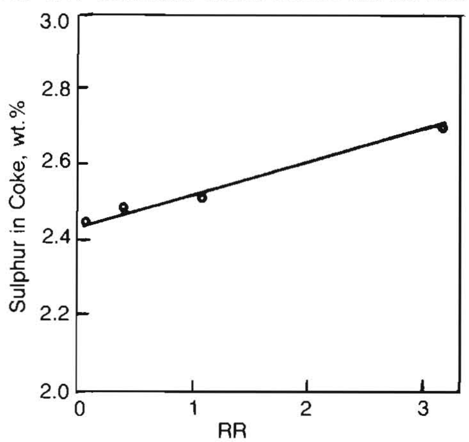


**Fig. 6.** The effect of recycle ratio on sulphur in coke.

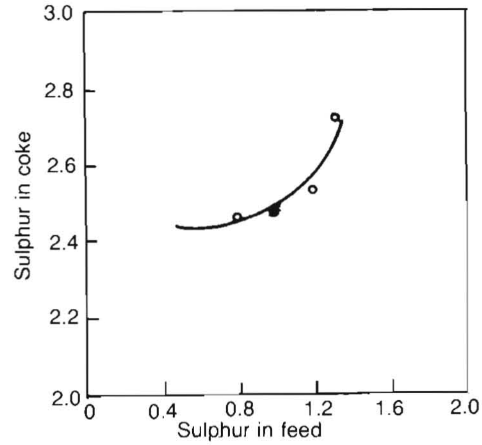


**Fig. 7.** Relation between Sulphur in feed and Sulphur in coke.

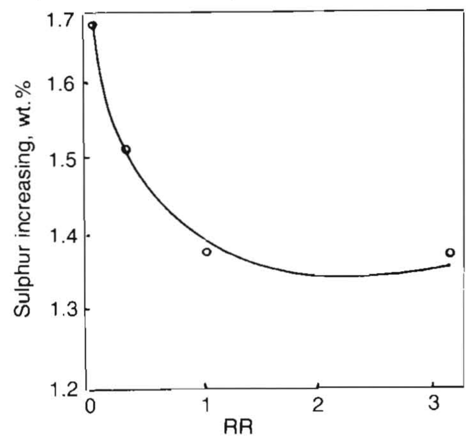


**Fig. 8.** Relation between recycle ratio and sulphur increase of coke.

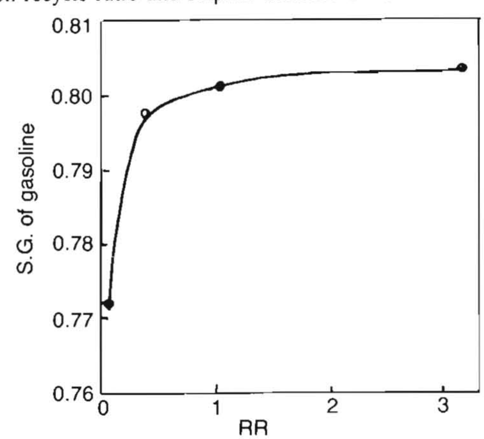


**Fig. 9.** The effect of recycle ratio on gasoline specific gravity.

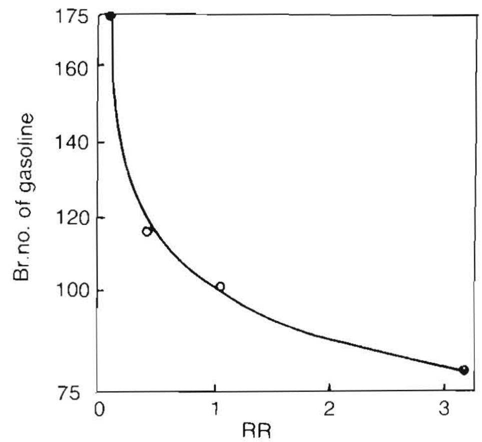


**Fig. 10.** The effect of recycle ratio on bromine number of gasoline.

The presence of recycle residue in the feedstock increases the quantity of high molecular weight hydrocarbons, especially aromatic hydrocarbons, in the combined feed. These hydrocarbons contribute to the formation of gasoline by cracking reactions during coking process. Therefore, the recycle ratio increase results in an increase in the specific gravity and a decrease in the bromine number of the produced gasoline as shown in Figures 9 and 10. The recycle ratio above 1.0 has no effect on the specific gravity of gasoline.

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*(Received 25/09/1983;*
*(in revised form 08/02/1984)*

# التفحيم المتباطىء لمقطر الزيت المستهلك

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لقد تم تصميم ونصب وحدة تفحيم مختبرية لدراسة عملية التفحيم المتباطىء لمقطر الزيت المستهلك. لقد تم حساب النواتج من الغاز والسائل والفحم لكل تجربة. بينت الدراسة أن الفحم الناتج يحتوى على نسبة واطئة من الكبريت نسبيا ولا يحتوى على معادن. إن رفع نسبة الإرجاع تزيد من الفحم الناتج وتخفض من نسبتي الغاز والغازولين الناتجين وكذلك تخفض من نسبة الأوليفينات في الغازولين. تؤثر نسبة الإرجاع تأثيراً طفيفاً على المحتوى الكبريتي للفحم الناتج.