

## Initiation Effect of Local Heating in Hydro-Thermal Cracking of Resids

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The upgrading of heavy oils is attracting growing interest as a means of producing premium quality transportation fuels and other middle distillate products. Hydro-thermal cracking is one of the promising processes to obtain maximum middle distillate (kerosene + gas oil) from residual oils. This process and its reaction mechanism have been described elsewhere.<sup>1,2</sup> Hydro-thermal cracking of resid, which is the combination of thermal cracking and catalytic hydrogenation, is composed of the following elementary steps: (1) formation of free radicals proceeding *via* cleavage of C-C or C-X (heteroatom) bond;<sup>3,4</sup> (2) production of middle distillate proceeding *via*  $\beta$ -scission of free radicals;<sup>5</sup> (3) termination of free radical reactions and saturation of C=C bonds proceeding *via* catalytic hydrogenation.

High reaction temperature can simply accelerate the conversion of resid, but the selectivities of gaseous hydrocarbons and coke will be increased tremendously. We have demonstrated that adding some initiators, such as element sulfur and di-*tert*-butyl-peroxide, which might produce free radicals even at lower temperature, promoted the conversion of resids and increased the yield of distillate.<sup>2,6</sup> This paper presents our results on another initiation method, local heating by inside filament. The *in situ* measurement of free radical concentration during hydro-thermal cracking of Kuwait AR was carried out by ESR and reported elsewhere.<sup>7</sup> The *in situ* spin concentration (at  $g = 2.0035$ , which shows the signal of hydrocarbon free radical) was detected by using a quartz tube containing Kuwait AR at 2.0 MPa of hydrogen pressure and heating it at 5 K/min. The results showed that the spin concentration of free radicals increased with the increasing temperature probably due to the cleavage of C-C and C-S bond and leveled off at about 480 K, then it slightly decreased, and again increased very quickly at above 680 K. According to this trend, an inside filament was employed to realize higher-temperature zone at some limited space inside the reactor to initiate the formation of free radicals at lower reaction temperature. The experiment results proved that local heating effectively promoted the conversion of Canadian oil sand bitumen and Arabian VR.

Experiments were carried out in an autoclave reactor. The catalyst was 10%Ni/Al<sub>2</sub>O<sub>3</sub> (sulfided), which was prepared by impregnation method. The support used was Al<sub>2</sub>O<sub>3</sub> N613N (commercial support, Nikki). The reaction conditions were as follows: temperature 683-703 K; pressure 5.0 MPa; reaction time 30-60 min;

catalyst/oil ratio, 0.05. Feed oils were Canadian oil sand bitumen (residue content, 65.2 wt%) and Arabian heavy VR (residue content, 95.0 wt%). After having pressurized with hydrogen to the target pressure at room temperature, the reactor was heated and shaken up and down at a speed of 70 rpm during the whole reaction period to ensure an efficient contact with gas, liquid, and solid. Gaseous product was analyzed by gas chromatography (Shimadzu GC-8A) with active alumina column. Liquid product was separated by a distillation gas chromatography (Shimadzu GC-14A) with silicone OV-1 glass column into 5 components: naphtha (initial boiling point -443K), kerosene (443-503K), gas oil (503-616K), vacuum gas oil (616-798K) and residue (>798K). The amount of coke was determined as follows: after separated from oil, solid was Soxhlet extraction by toluene for 3 h, then dried at 393 K in vacuum (<10 mmHg) for 2 h, the amount of coke was the weight increment of catalyst. All the coke formed on the catalyst, the reactor wall (very few) and the filament were collected. The percentage of coke was on the feed oil basis. The material balances were  $100\pm 2\%$ ; The deviations in conversions were within 2%; The relative deviations in coke yields were less than 4%; The relative deviations in distillate yields were within 2%.

During hydro-thermal cracking of heavy oil, the higher-temperature zone was realized by utilizing inside filament. The image of inside filament was depicted in Figure 1. The dimension and electric resistance were as follows: length 2-3 cm, diameter 0.16 mm, 53.76  $\Omega/\text{m}$ . The voltage and current charged in the filament were: 2-6 V, and 1-3 A. The power was supplied in pulse mode. The frequency was 10 second/ 3 min. The temperature difference between the surface of filament and the oil bulk was estimated to be about 323 K. This temperature difference might result in the higher concentration of free radicals. During the term of local heating, the temperature of the oil bulk increased about 3-5 K, and return to set point in 2 min. Because the filament was in very small size, and the time of power supplying was very short, the effect of filament on the temperature of the whole reactor (including oil) could be ignored.

The effects of local heating on hydro-thermal cracking of Canadian oil sand bitumen and Arabian heavy VR were listed in Table 1. The conversions were effectively enhanced in both feeds. When filament was employed, the conversion of bitumen was increased from 44.4 wt% to 54.8 wt% (runs 1 and 2), but the formation of coke was promoted slightly too. For Arabian VR, the conversion was increased from 38.2 wt% to 49.7 wt%, and distillate yield was increased from 38.2 wt% to 47.8 wt%. Obviously, local heating was an effective method to produce a higher-temperature zone at some limited space inside the reactor, which might accelerate the decomposition of hydrocarbon, resulted in the quick formation of free radicals near the surface of filament, therefore promoted the chain reactions, and reasonably enhanced the conversion of resids.

In order to study the effect of local heating further, a series of experiments in different reaction time (30-60 min) and temperature (683-703 K) were carried out. The experiment data were processed according to pseudo-first order reaction.

Resid = gas + distillate + coke

The Arrhenius plots were depicted in Figure 2, and the correspondent Arrhenius parameters (activation energy and pre-exponential factor) were listed in Table 2. When filament was utilized, the activation energy was lowered

from 43.1 to 30.0 kcal/mol (bitumen) and from 71.3 to 63.1 kcal/mol (Arabian VR). This should be attributed to the concentration increase of free radicals initiated by filament. At lower reaction temperature, the promotional effect of filament was more obvious than that in higher temperature. Bitumen was more sensitive to filament than Arabian VR. When using filament, the reaction temperature could be lowered about 15 K to obtain the same conversion level with absence of filament. The conversion of bitumen was easier to be enhanced by local heating. This might result from the structure difference of both feeds. The activation energy of both feeds in absence of filament heating had large difference, which partly presented the different effect of reaction temperature on the conversion of both heavy oils. The reason and the effect of local heating power (current, pulse time) will be reported in other paper.

Thus, the conversions of bitumen and Arabian VR were clearly promoted by local heating method during hydro-thermal cracking. This resulted from the higher-temperature zone near the surface of filament which accelerated the formation of free radicals and initiated the chain reactions. At lower reaction temperature, the higher conversion of resid could be realized by filament heating, and simultaneously lower the selectivity of gas and coke compared to obtaining the same conversion level at higher temperature.

## REFERENCES

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## FIGURE CAPTION

Figure 1. Image of inside filament and power control system

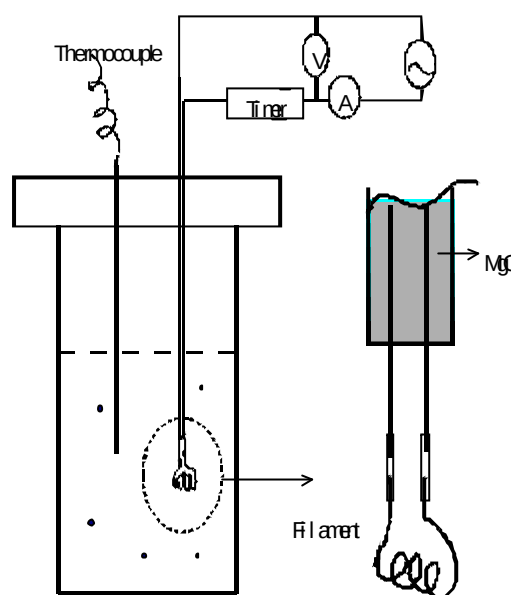


Figure 2. Arrhenius plots of resid hydro-thermal cracking

Feed: 10.00 g, catalyst 0.50 g, temperature: 683-703 K, pressure: 5.0 MPa, reaction time: 30-60 min. a: bitumen, absence of filament, b: bitumen, using filament, c: Arabian VR, absence of filament, d: Arabian VR, using filament.

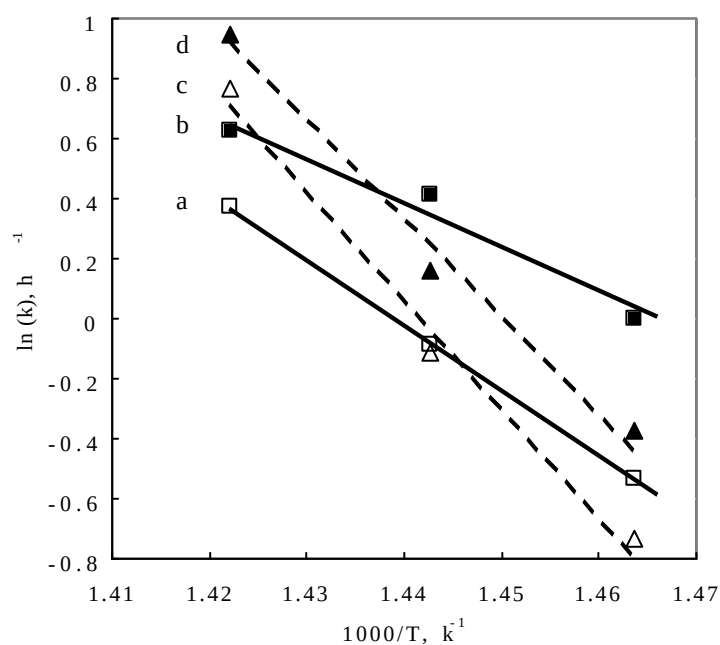


Table 1 Results of local heating effect

| run number                 | 1    | 2    | 3    | 4    |
|----------------------------|------|------|------|------|
| filament <sup>a</sup>      | non  | yes  | non  | yes  |
| feed                       | B    | B    | A    | A    |
| conversion, % <sup>b</sup> | 44.4 | 54.8 | 38.2 | 49.7 |
| yield, wt%                 |      |      |      |      |
| H <sub>2</sub> S           | 1.1  | 1.4  | 0.5  | 0.5  |

|                                |      |      |      |      |
|--------------------------------|------|------|------|------|
| C <sub>1</sub> -C <sub>4</sub> | 1.7  | 2.3  | 2.1  | 2.3  |
| naphtha                        | 2.9  | 5.0  | 4.2  | 4.5  |
| kerosene                       | 3.6  | 5.2  | 3.9  | 5.0  |
| gas oil                        | 15.3 | 17.8 | 9.0  | 11.5 |
| vacuum gas oil                 | 38.7 | 38.1 | 21.1 | 26.8 |
| residue                        | 36.3 | 29.5 | 58.7 | 47.8 |
| coke                           | 0.4  | 0.7  | 0.5  | 1.6  |
| distillate <sup>c</sup>        | 60.5 | 66.1 | 38.2 | 47.8 |

<sup>a</sup> current = 3A, power on 10 second per 3 min. <sup>b</sup> conversion (wt%) = (1-residue in product/residue in feed)\*100%. <sup>c</sup> distillate (wt%) = naphtha + kerosene + gas oil + vacuum gas oil. Temperature = 683 K, pressure = 5.0 MPa. Feed 10.00 g, catalyst 0.50 g.

Table 2 Resid hydro-thermal cracking Arrhenius parameters

|                         | bitumen |          | Arabian VR |          |
|-------------------------|---------|----------|------------|----------|
|                         | non     | filament | non        | filament |
| E, kcal/mol             | 43.1    | 30.0     | 71.3       | 63.1     |
| ln (A), h <sup>-1</sup> | 31.2    | 22.1     | 51.7       | 46.0     |

Feed: 10.00 g, catalyst 0.50 g, temperature: 683-703 K, pressure: 5.0 MPa, reaction time: 30-60 min

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