A NEW SCHEME FOR UPGRADING FUSHUN SHALE OIL

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ABSTRACT

Commercial practice of upgrading Fushun shale oil in 50 years was reviewed. In view of the situation that shale oil is now being used directly as boiler fuel,a new scheme for upgrading is proposed. Shale oil is first treated by exhaustive delayed coking to light fractions which were treated successively with dilute alkali,and sulfuric acid to recover the acidic and basic nonhydrocarbon components as fine chemicals and the remaining hydrocarbons,containing about 0.4 % N can thus be readily hydrotreated to obtain naphtha, jet fuel and light diesel fuel.This scheme is profitable and can be conveniently coupled into an existing petroleum refinery.

The current annual production of shale oil in China has dropped from 800,000 T to 180,000 T (90,000 T for each refinery in Fushun and Maoming), and will remain at this level in the near future. In late 1950's, shale oil once accounted for 20 % of total crude oil production. At that time,motor fuels made from shale oil had played an important role. Now the percentage has dropped to about 0.2 %, and the equipments once used to upgrade shale oil have been turned to refine petroleum crudes, resulting in the direct use of shale oil as boiler fuel. Clearly, such use of resource is economically unreasonable. In view of this situation, a new scheme which can be conveniently coupled into an existing refinery was investigated and proposed here.

A Brief Review of Commercial Practice and Research Works

Up to 1960,Fushun shale oil had been refined for more than 20 years. In Fushun Refinery No.1,it was first fractionated into several fractions,and the residual portion,being mixed with the cracking residuum, was sent to be coking. Straight run waxy fraction (after dewaxing) and heavy CGO were thermally cracked.All the light fractions obtained were treated with concentrated sulfuric acid, to produce motor gasoline and diesel fuels , the total yield was around 57 % [1]. In early 1950's, the Fushun Refinery No.3 had already produced motor gasoline and kerosene by hydrocracking a portion of light gas oil from shale oil[2]. Naphtha recovered from oil shale retort gas by an absorption process was also hydrotreated in Fushun Refinery No.3.

At the end of 50's,Fushun Refinery No.2 planned to upgrade shale oil according to a scheme including thermal treatment, hydrotreating and catalytic reforming[3]. However this refinery was turned to refine petroleum crude oil later.

Exhaustive delayed coking of shale oil to hydrocarbon gases, naphtha, light gas oil and coke was tested in industrial scale in late 50's in Fushun Refinery No.2, the yields were 10 %, 77% and 13% respectively[4], and hydrogenation of the light oil obtained under mild pressure was studied[5].

In 50's,high pressure hydrogenation of shale oil crude was studied in a pilot plant of semicommercial scale[6]. The products included diesel fuel, light lubricating oil stock, and wax, with total liquid yield of 97.3%,and NH_3 and H_2S as byproducts.

Presentation of the New Scheme

It has been widely accepted that shale oil is a kind of complementary and future energy source. Thus,since 50's, all studies over the world in upgrading shale oil have been directed to produce transportation fuels.Combination of high pressure hydrogenation and FCC is surely a promising scheme. But in our country, it does not seem to be economically feasible, because of the high investment and operational costs for a high pressure hydrogenation plant,especially the current production of shale oil is too low.

In view of the situation that current shale oil production is carried out in the petroleum refineries and it accounts for only a small portion of the petroleum crude refined, a new scheme to upgrade shale oil, which can be conveniently coupled into the existing refinery flow diagram, was investigated and proposed.Exhaustive delayed coking is the first step. The coking naphtha and light gas oil are first separately extracted successively with dilute alkali and dilute sulfuric acid to recover the acidic and basic nonhydrocarbon components, which are later refined to fine chemicals. The remaining oil, in which the nitrogen content has been reduced to around 0.4 %, can be mixed with coking naphtha and gas oil from delayed coking of petroleum residuum. The coking naphtha is now being hydrofined in Fushun Refinery No.2, and the coking gas oil hydrocracked in Fushun Refinery No.3 to produce naphtha, jet fuel and diesel fuel component.

Experimental

Experimental investigations[7] were mainly made on the extraction by alkali and acid, because the other steps, exhaustive coking and hydrotreating need no more research works. For coking naphtha,tests were carried out with separating funnels, while for coking gas oil, larger scale extractions were made to obtain larger quantities of fine chemicals for field application tests.

From the coking naphtha, by extraction with 5 % (vol.) of 10 % and 20 % NaOH solution, neutralization with acid and final distillation, 1.36 % (wt) of phenolic compounds including phenol, cresols and xylenols were obtained. On later extraction with 10 % H_2SO_4 and refining,1% (wt feed) of pyridines was obtained.

From the coking gas oil,by treating it with 0.1 % (vol.) of 5 % NaOH, followed by treating the extract with petroleum naphtha to remove the dissolved basic nonhydrocarbons and occluded oil, and neutralization with acid, the yield of final product naphthenic acids after distillation under reduced pressure was 0.44 % (wt),with purity of 90 %. Then a 180-330°C crude phenolic product of 45 % purity was obtained in 2.56 % (wt) yield by extraction with 5 % (vol.) of 10 % NaOH, neutralization with acid followed by vacuum distillation. This product was proved to be useful as a component of sand aggregating agent in the oil well to prevent it from coming into the well tube. When the alkali treated gas oil was further extracted with 4.5 % (vol.) of 10 % H_2SO_4, followed by neutralization and vacuum distillation,two final products,a 200-300°C fraction (yield 2.8 % (wt)) and a 300-330°C fraction (yield 1.1% (wt)) mainly consisting of heavy pyridines and quinolines,were obtained,with purity of 95.6% and 92.5 % respectively. These products were proved to be useful as corrosion inhibitor, especially for oil well tubing to retard corrosion by HCl.

The alkali and acid pretreated oil fractions then mainly consisted of hydrocarbons, which could be directly mixed with coking naphtha and gas oil respectively from delayed coking of petroleum vacuum residuum in the same refinery, because the nitrogen content of the pretreated gas oil had been reduced from 1.0% to 0.45% . As a result,the N content of the petroleum CGO would rise from 0.10 % to 0.16 %,which would not cause any significant effect on the hydrocracking catalyst.

A flow diagram is shown in Fig.1 for upgrading 100,000 T/year shale oil.

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                  ___Hydrocarbon gas + Loss
                  |     10.5 % (10,500 T)
                  |
                  |___Naphtha 12.5__|Dilute alkali and|
                  |   % (12,500 T)  |acid extraction  |
                  |   ______________________________|
                  |   |--Light phenols 1.86 % (230 T)
                  |   |--Pyridines 1.0 % (125 T)____________
                  |   |--Raffinate (11,900 T)--|Hydrofining|
                  |   |--Loss (445 T)               |
                  |                              Naphtha
                  |                             (11,700 T)
                  |
                  |___Light gas oil 64.6__|Dilute alkali and|
                  |    % (64,600 T)       |acid extraction  |
Crude shale       |    ____________________________________|
oil (100,000 T)   |   |--Naphthenic acids,0.44 %(284 T)
      |           |   |--Crude phenolics,2.51 % (1,610 T)
  ____|____       |   |--Pyridines and quinolines,3.9 %
  |Delayed|       |   |  (2,440 T)
  |coking |       |   |--Raffinate (59,500 T)-|Hydrocracking|
                  |   |              ______________________|
                  |   |             |--Naphtha 15% (8,700 T)
                  |   |             |--Jet fuel 53% (32,100 T)
                  |   |             |--Diesel fuel component
                  |   |             |  30 % (17,500 T)
                  |   |             |--Gas + loss 2 % (1,190 T)
                  |   |
                  |   |--Loss (766 T)
                  |
                  |
                  |___ Sump Oil 2 %
                  |    (2,000 T)
                  |___ Coke 10.4 %
                       (10,400 T)
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Fig.1 A new scheme for upgrading Fushun shale oil

Thus, from 100,000 T Fushun shale oil, the final product distribution will be:

Light transportation fuel	70,000 T
Naphtha	20,400 T
Jet fuel	32,100 T

Diesel fuel	17,500 T
Petrochemicals	4,690 T
Coke	10,400 T
Total	85,490 T

Besides, there would be around 10,000 T hydrocarbon gases, which can be used as fuel,or as the raw material for hydrogen manufacture. Shale oil coke was low in sulfur, and is excellent for higher grade electrode manufacture and is also useful in chemical industry.

The estimated gain per ton shale oil was estimated to be around 100 yuan RMB.

Another scheme to upgrade shale oil, which might be considered, is that the naphtha and gas oil pretreated as mentioned above may be mixed and hydrofined,and the hydrofined oil may be used as the feedstock for steamcracking to produce light olefins, such as ethylene, propylene, butenes and butadiene,with ethylene yield around 24 % as shown by microreactor tests. By using such a scheme,shale oil can be fully upgraded to petrochemicals.

Summary

1. A new scheme for upgrading Fushun shale oil, which can be conveniently coupled into the existing petroleum refinery, was proposed.

2. From 100,000 T/year shale oil,the final production rate of light transportation fuels will be around 70,000 T/year, which is much greater than that from same amount of petroleum vacuum residuum, when treated by delayed coking and hydrotreating. Besides there will be produced 4,690 T/year petrochemicals and 10,400 T/year coke of superior quality.

3. By upgrading with the new scheme,gain per ton shale oil is estimated to be around 100 yuan RMB. which is much greater than that, when the shale oil is directly used as boiler

fuel.

4. The same scheme will be applicable also to Maoming shale oil.

REFERENCES

[1] Hou, Xianglin; chief editor, " China Shale Oil Industry " (in Chinese) , Petroleum Industry Publishing Co., P.193, 1984

[2] ibid. P.191

[3] ibid. P.193

[4] ibid. P.212

[5] ibid. P.196

[6] ibid. P.196

[7] "Studies on Schemes for Upgrading Fushun Shale Oil" (in Chinese), Unpublished File of Fushun Research Institute of Petroleum and Petrochemicals, 1986.