HYDROTREATING OF LIQUID PRODUCTS FROM COLD LAKE BITUMEN OBTAINED IN THE WRITE PROCESS

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Abstract

The WRITE process is a new emerging thermal cracking technology for the conversion of heavy oils and bitumen to synthetic crudes. The distillate products of any thermal bitumen processing, including the WRITE process, contain unsaturated compounds such as olefins and di-olefins. It is desirable to remove or convert these materials to saturated compounds before they reach refineries for processing. Hydrotreating of WRITE distillate products (-250°C) containing a significant amount of olefins and di-olefins was performed in a batch autoclave using spent commercial $NiMo/Al_2O_3$ hydrotreating catalyst. It was shown that at relatively mild conditions all di-olefins were converted to olefins or saturated compounds, but conversion of olefins required higher severity. Hydrotreating reactivity of WRITE products was compared with that of coker naphtha.

Introduction

When heavy hydrocarbons such as bitumen are subjected to thermal treatment for the production of synthetic crude, in the absence of hydrogen (to cap the intermediate free radicals) a significant amount of olefins and di-olefins are formed through free radical disproportionation reactions. The analytical procedures such as FIA and bromine number, developed for the determination of the olefin content for refinery products, are not suitable for crudes. In both of these methods components such as aromatics interfere with analyses, resulting in erroneous results.

Most existing and emerging upgrading technologies for conversion of heavy oils and bitumen to transportation fuels are based on thermal processes like visbreaking, coking and pyrolysis. These processes are performed in the absence of catalysts and hydrogen where a significant amount of unsaturated products are produced. Among those unsaturated compounds there are products such as conjugated di-olefins that are very reactive and can polymerize and form coke in different parts of a refinery. Although compounds with isolated olefinic bonds form in higher concentration than di-olefins during thermal reaction, they are less reactive. In the presence of oxygen, olefins can form hydroperoxide and initiate a free radical chain reaction. Due to their high reactivity, these materials can form sediment and sludge during fuel storage and the refining processes.

The WRITE process (Western Research Institute Thermal Enhancement) is a new thermal process for heavy oil conversion that is currently under review by a number of producers in Alberta. It is expected that the liquid products from this process will contain some olefins and di-olefins. The presence of these unsaturated materials in synthetic crudes has raised some concerns related to their stability during storage, pipelining and subsequent processing in refineries. The pipeline specification for the olefin content in crude is set by CAPP (Canadian Association for Petroleum Producers) at <1% by volume. Another pipeline specification, which is indirectly related to the olefin content of crude, is based on the bromine number of the –250°C cut and is set at <10 $gBr_2/100g$.

The objectives of this preliminary research are: 1) to investigate hydroprocessing conditions at which the –250°C distillate fraction products obtained from Cold Lake bitumen in the WRITE process meet pipeline specifications for bromine number (<10 gBr2/100g); 2) to compare hydrotreating reactivity of the –250°C distillate fraction from the WRITE process with fluid coker naphtha at the same reaction severity.

Experimental. Hydrotreating experiments were carried out in a 300 mL stirred tank autoclave equipped with a catalyst basket. In a typical experiment, about 104 g of feed (coker naphtha or WRITE –250°C distillate fraction) was placed in the reactor. A spent commercial $NiMo/Al_2O_3$ hydrotreating catalyst (18.6 g) was used in all experiments. The reaction temperature and hydrogen partial pressure used in these experiments are shown in Table 1. When the internal temperature of the autoclave was 5°C below the set point, the yield period time was begun. The autoclave furnace was turned off 60 minutes from this time. After the reactor cooled down to room temperature, the gas contents of the autoclave transferred to a gasbag; the gas volume in the bag was measured and the content was analysed by gas chromatography. The reactor was opened and the liquid contents were removed and analyzed for bromine number and diene content (UOP-326-82).

Results and Discussions

The WRITE process is a new thermal processing technology that is currently being considered for the conversion of bitumen from oil sands to liquid fuels (1). Products from processing Athabasca bitumen, in the WRITE process, were shown to be relatively stable during 4 weeks storage at 43°C, in spite of having high olefinic content. Furthermore, the distillate products were compatible with most Alberta crudes (2). The refiners wish to receive feedstocks with no olefins or di-olefins content and discount streams that are high in such components. There are two options for removing unsaturated compounds from petroleum feedstocks. Olefinic compounds can be either extracted and used as petrochemical feedstock (3) or hydrotreated to form stable hydrocarbons.

In the present work it was decided to investigate the feasibility of hydrotreating the WRITE distillates (-250°C fraction) to produce products that were acceptable by refineries in terms of the olefin and di-olefin contents. Since a limited quantity of WRITE product was available, only a series of batch autoclave hydrotreating runs were performed to investigate the optimum conditions for the removal of olefins and di-olefins. We plan to carry out an extensive hydrotreating study using bench-scale continuous operation when larger quantities of distillates are available. For the purposes of comparison with the hydrotreating reactivity of the WRITE liquid products, we also selected a fluid coker naphtha and performed hydrotreating with the same catalyst and under similar reaction conditions.

Analysis of feedstocks and hydrotreated products from the coker naphtha and the WRITE feedstock (-250°C fraction) are shown in Table 1. Two analytical tests, namely diene number (UOP-326-82) and bromine number (ASTM D-874), were used to determine the degree of saturation of the unsaturated compounds after hydrotreatment. In the absence of more accurate analytical methods for quantitative determination of unsaturated compounds (olefins and di-olefins), we used the existing analytical methods to follow the directional changes in the properties of the distillate as a function of hydrotreating severity.

The analysis shown in Table 1 indicates that the coker naphtha had higher diene as well as higher bromine numbers compared to the WRITE feed.

The higher reactivity of dienes compared to olefins is clear for both feedstocks as these materials are converted to olefinic or saturated compounds at the lowest hydrotreating severity employed. The diene concentration in coker naphtha changed from 13.9 $gI_2/100g$ in the feed to 0.5 $gI_2/100g$ in the product at a reaction temperature of 200°C. Similar results were obtained in hydrotreating the WRITE feed. The diene concentration changed from 4.2 $gI_2/100g$ in the feed to 0.0 $gI_2/100g$ in the hydrotreated products at the same reaction temperature. The conversion of isolated olefinic double bonds to saturated compounds required higher temperature and hydrogen pressure compared to the dienes conversion. The data in Table 1 also show that at lower reaction severity the saturation of olefinic compounds in the coker naphtha, as determined by bromine numbers, is faster than that in the WRITE feed. However, at higher reaction severity olefins in the WRITE feed are hydrogenated faster than those in coker naphtha.

Table 1. Properties of Feedstocks and Hydrotreating Products

Feed	Temp. and H_2 Partial *P*	Diene $gI_2/100g$	Bromine # $gBr_2/100g$
Coker Naphtha feed		13.9	84.2
WRITE feed		4.2	53.3
Coker Naphtha	*200°C/500psi*	0.5	76.7
WRITE feed	*200°C/500psi*	0.0	50.0
Coker Naphtha	*300°C/700psi*	0.07	50.8
WRITE feed	*300°C700psi*	0.0	27.4
Coker Naphtha	*350°C/1000psi*	0.3	19.7
WRITE feed	*350°C/1000psi*	0.0	9.0

Conclusions

This study demonstrated that it is possible to convert olefins and di-olefins, produced during the thermal reaction of Athabasca bitumen in the WRITE process, by mild hydrotreating. It was shown that the hydrotreating reactivity of WRITE distillates (-250°C) was comparable to that of fluid coker naphtha.

Acknowledgement. This project was funded by WRI through the US Department Energy (USDOE). Partial funding for NCUT has been provided by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council (ARC) and the Alberta Energy Research Institute (AERI).

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