Fuel Processing Technology 124 (2014) 115–122

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Upgrading of Estonian shale oil heavy residuum bituminous fraction by catalytic hydroconversion

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ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form 18 February 2014
Accepted 21 February 2014
Available online 17 March 2014

Keywords:
Hydroprocessing
Hydropurification
Hydrocracking
Dephenolation
Heavy shale oil
Hydrogenated oil

ABSTRACT

Possibilities for upgrading of the Estonian shale oil rectification residuum boiling above 360 °C by hydroconversion were studied for the first time with the aim to maximize the fractions boiling below 360 °C and between 275–360 °C.

The single- and two-step hydroprocessing were performed in a 500 cm^3 periodic autoclave under the range of temperatures 340–420 °C, duration 40–240 min, and the hydrogen initial pressure 6.4-7.5 MPa. Three types of catalysts foreseen for hydropurification (KGU-950, KF-848), for hydrocracking (GO-30-7, KF-1015, KC-3210) and for universal purpose (DN-3100 Th) were added in the quantity of 10% per the residuum. The effectiveness of the treatment was evaluated by yields of oil, gas, coke and water, by boiling curves, elemental composition, and group composition (hydrocarbons, aromatics, polyaromatics, low-polar heterocompounds and high-polar heterocompounds) of the hydrogenated oil, by FTIR spectra and GC/MS analysis, and by composition of the gases formed.

Any characteristic of the hydrogenated products depended on the complicated co-effects of the pyrolysis conditions, temperature, time and catalysts. So, there was no unique solution for the best conditions and catalysts for the best total result. The highest yield of the fraction boiling below 360 °C obtained was 82.7%.

1. Introduction

The increasing demand for liquid fuels and their rising prices have revived interest in shale oil. The world oil shale reserves are estimated to exceed 4.8 trillion barrels of recoverable oil [1].

The oil obtained by semicoking of Estonian Kukersite oil shale, is known as an unstable, extremely complex mixture of compounds and is specific one by its high content of oxygen. Therefore, the oil and even its distillation fractions are unsuitable for exploitation as a feedstock for motor fuels without visbreaking, stabilization and removing of the heteroatoms.

Recent advances in the production of high quality transportation fuels have been focused on the upgrading technologies of high boiling fractions of crude oils and residua by hydroprocessing. Unfortunately, a general upgrading scheme suitable for all heavy oil refineries is absent because there are many factors to take into consideration like: chemical and physical properties of the heavy oil and residua, available catalysts, local needs, as well as refinery configuration and prices of products [2]. Laboratory-scale research of shale oil upgrading has been studied intensively in the US, Estonia, Russia, Israel, Australia, Brazil, China, Near East countries and elsewhere [3–9].

In spite of the opening of the first industrial oil shale liquefaction factory in Estonia as early as 1924 [10], and advancing the oil distillation technology temporally by several modifications of the retorting units (tunnel ovens, shaft retorts, solid heat carrier varieties up to efforts to use for heating of fluidized bed oil retorts the circulating hot ash from the fluidized bed incineration of the semicoke and shale oil), neither the oil nor its distillation fractions have been hydroprocessed industrially. Extensive analysis and pilot plant testing of the Estonian shale oil obtained in Enefit Oil and Gas to upgrade the oil to Euro V diesel were conducted in Haldor Topsoe A/s in Denmark [11].

A comprehensive review of the previous investigations on the theory and practice of Estonian shale oil formation and its laboratory upgrading was given by Luik in [12]. The lion's share of oil shale was used for the production of electricity, the minor part for production of

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http://dx.doi.org/10.1016/j.fuproc.2014.02.018
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heating oil. Now, considering the large reserves of oil shale as high syncrude potential in Estonia, the elaboration of the possibilities and perspectives of employing the shale oil as synoil has again become relevant.

Catalytic hydrotreatment of different distillation fractions of Kukersite oil was studied by Luik [13–18] in a laboratory batch autoclave using Co–Mo and Ni catalysts. The fraction “heavy mazute” (heavy gas oil) boiling over 320 °C gave 90–91% of refined oil whereas the content of hetero-compounds decreased from 66.1 to 24.9%, and iodine number from 84 to 43.

Hydrotreating of the oil shale thermobitumen [19] under conditions 400 °C, 5 MP, 60 min. resulted 19.8% of gas and water and 76.9% of benzene soluble oil from the totally soluble in benzene initial matter whereas the content of hetero-compounds decreased from 90 to 66.7% and content of liquid hydrocarbons increased from 10 to 34%.

Noteworthy longer durations, 8 to 56 h, and higher hydrogen pressure, 15.0 MPa, were applied by Chishti and Williams [20] for hydroprocessing at 400 °C of the Kimmeridge Clay shale oil. With increasing duration the content of three and four ring polyaromatic hydrocarbons decreased; and the content of single ring and two ring ones increased. Concentration of nitrogen and sulfur containing three and four ring aromatic hydrocarbons in the oils was reduced with increasing hydrotreatment time to reach negligible concentrations after 56 h.

The heavy residuum bituminous shale oil fraction boiling above 360 °C obtained as a result of industrial semicoking of Kukersite makes up roughly 50% of the total oil and its further utilization is limited to coke production only [21]. The data concerning upgrading of the heavy residuum into liquid fuels are absent.

The goal of this work was the upgrading by catalytic hydroconversion of the heavy bitumenous oil boiling above 360 °C to the liquid fuel boiling below 360 °C. For this purpose, the effect of hydroprocessing conditions on the yield and characteristics of the upgraded liquid products was studied in a laboratory batch autoclave.

2. Experimental

2.1. Materials and reagents

The shale oil heavy residuum bituminous fraction boiling above 360 °C (called later as “initial oil”) was an industrial fraction produced by VKG, the biggest oil shale processor in Europe [22].

The six Mo–Co- and/or –Ni catalysts on the alumina support with three purposes tested in this work are given in Table 1.

All the Akzo Nobel catalysts were activated by presulfiding of the oxides before use by feeding sulfur containing light gas oil and hydrogen.

2.2. Hydroprocessing procedure

The single- or two-step hydroprocessing of the initial oil and of the dephenolated residuum was conducted in a rocking 500 cm^3 batch autoclave with varying hydrogenation conditions. The products obtained in the first stage of hydropurification and in the second stage of hydrocracking at an elevated temperature after addition of a cracking catalyst were separated by filtration, extraction, distillation, and drying. The liquid products were characterized by their yield, phenol content, fractional composition, and elemental and group composition.

Table 1
Applied catalysts.

Type	Producer	Purpose
KGU-950	OAO AZKiOS, Irkutsk, Russia	Hydropurification
GO-30-7	OAO AZKiOS, Irkutsk, Russia	Hydrocracking
DN-3100 Th	Shell Chemicals LP, US	Universal
KF-848	Akzo Nobel, Netherlands	Hydropurification
KF-1015	Akzo Nobel, Netherlands	Hydrocracking
KC-3210	Akzo Nobel, Netherlands	Hydrocracking

Here and in succeeding Tables the hydrocracking catalysts are highlighted with 50% gray color, the hydropurification catalysts are not highlighted, and the universal catalyst or the mixes of the hydropurification and -cracking ones are highlighted with 25% gray color.

The reactor was provided with controlled heating system connected with an inside thermocouple, a manometer, and inlet and outlet valves. About 50 g of the initial oil or the dephenolated residuum, 10% of catalyst per the residuum, and hydrogen up to the pressure 6.4–7.5 MPa (at ambient temperature) were charged. The initial reaction time was taken when the nominal temperature (340–420 °C) was attained. The current temperatures and pressures were recorded. After the duration prescribed (40–240 min) the autoclave was cooled down to room temperature, the residual pressure was registered, and the samples for gas analysis were taken. After that, the autoclave was opened, and the solid phase (catalyst applied and coke formed) was separated from the hydrogenated oil by filtration through a filter paper. The filtrate was analyzed. The solid residuum in the filter cake was washed with benzene, dried and weighed. Benzene was evaporated from the washing filtrate in a vacuum rotator and the residuum obtained was considered in calculation of the total yield of liquid products.

2.3. Methods of analysis

Phenols were determined by their weight after separation by alkali dephenolation of the initial oil according to the five different extraction procedures described below in Section 3.1.

The alkali-extracted phenols were re-extracted after acidification of the phenolate solutions with diethyl ether. The total phenols were weighed after diethyl ether evaporation.

Water-soluble phenols were determined analogously, by water extraction of the initial oil diluted with benzene.

Asphaltenes were estimated by weight after dissolution of the samples in benzene (1:10), precipitation of asphaltenes by addition of *n*-hexane (1:50), and their filtration on the next day.

Boiling range of the oils recovered was estimated by Engler distillation.

Chemical group composition of the liquid products was estimated by adsorption thin-layer chromatography. For this aim, 300–500 mg of the oil was fractionated on the 2 mm high silica gel (Fluka 60 μm) spread on a plate 24 × 24 cm, and eluted with *n*-hexane: The following fractions of hydrocarbons (HC) and hetero-compounds (Het) were separated: aliphatic hydrocarbons (AlHC), monoaromatic hydrocarbons (MAHC), polyaromatic hydrocarbons (PAHC), low-polar hetero-compounds (LPHet) and high-polar hetero-compounds (HPHet), and weighed after their desorption with diethyl ether and desiccation.

Functional group composition was characterized by a Fourier transform infrared (FTIR) spectrometer “Interspect 2020 FT-IR”.

The GC/MS analysis was conducted on a Shimadzu QP 2010 Plus using 30 m capillary columns ZB-5 and HP-5MS.

Gas composition was analyzed by gas chromatography (Chrom 5).

Content of H_2S and NH_3 in the gases diluted with an excess of hydrogen were below sensitivity of the chromatographic methods. Therefore their yield was estimated by bubbling of the gas formed through alkali and acidic solutions followed by iodometric titration of sulfide ions and photometric measurement of ammonia content with Nessler reagent.

Ultimate analysis of C, H, S, N and O in oil was conducted on “Elementar Vario EL” analyzer.

3. Results and discussion

3.1. Phenolic compounds

In the previous works concerning hydrotreatment of Kukersite oil fractions [13–18], as a rule, the first stage has been separation of