New Methods for Characterization of Products from Micro-activity Testing (MAT) of Residue from Estonian Shale Oil

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Abstract

The utilization of fossil fuels is going through drastic changes due to growing transportation fuel consumption and stricter environmental regulations. Both will result in an increase in the proportion of diesel fuel produced from synthetic crude oils, which in turn will lead to the expanding of existing and the development of new processing technologies. Most of the crude oils used for fuel production consist predominantly of hydrocarbons and contain only relatively small amounts of sulphur, oxygen, and nitrogen. Shale oils, in contrast, can contain large amounts of organic sulphur and /or oxygen compounds. Therefore, during processing of shale oils, in addition to making fuels, there may be an opportunity to extract valuable chemicals. Knowledge of the physical and chemical properties of these hydrocarbon materials is very important for the development of technologies necessary to fully utilize these materials.

In this paper we discuss the possibility of increasing the utilization of Estonian shale oil by application of the fluid catalytic cracking (FCC) process to the atmospheric residue fraction boiling between 320 and 750°C. FCC, being the most common conversion process in the oil refining industry, uses micro-activity testing (MAT) as its research tool to test various feedstocks and catalysts. The main emphasis in this paper is on the development of characterization methodology to analyze mono- and di-hydric phenols in MAT products that are inherently produced in very small amounts (<2mL) and have a wide boiling range.

Introduction

Over the past 50 years, fluid catalytic cracking (FCC) has been the most important heavy gas oil conversion process. FCC generates products ranging from gases and light olefins, through naphtha to light cycle oil, and heavy cycle oil. In this paper we discuss the possibility of applying the FCC process (through the micro activity test - MAT) to the atmospheric residue derived from an Estonian shale oil. This oil is the source of fuel oils and synthetic gas, but it could also be a source of a number of chemicals such as antiseptic oil for wood impregnation, electrode coke, rubber softeners, casting binders, etc. The shale oil phenols are used as feedstocks for epoxy and other resins, and as glueing compounds, rubber modifiers, synthetic tanning agents, etc. The most valuable phenols are in the 200-360°C boiling range. Therefore, there is an interest in exploring the behavior of heavy residue in the cracking environment, particularly in terms of the production of phenols in the useful boiling range.

A characterization procedure described by Čherný et al. (1) was adopted as the basis of the new separation procedure developed here for quantification and identification of various fractions from the total liquid product from catalytic cracking of residue from an Estonian shale oil. The extrography procedure was replaced with open column chromatography, and the elution solvents were used in the order reported earlier (2). A different way of calculating the material balance was proposed for the full boiling-range material.

Experimental

The residual material derived from an Estonian shale oil was used as the feed for the macro-activity testing. Some properties of the feed and the total liquid product (TLP) are presented in Table 1. Simulated distillation curves are shown in Figure 1.

Table 1. Properties of feed and TLP from MAT testing of residue from Estonian shale oil

Feed		**Product**	
BP, ^{o}C	**%OFF**	**BP, ^{o}C**	**%OFF**
IBP (301.2^{o}C)	0.5	IBP (84.5^{o}C)	0.5
FBP (750.0^{o}C)	99.5	FBP (587.5^{o}C)	99.5
IBP-360°C	4.16	IBP-200°C	13.81
360-525°C	60.91	200-360°C	36.69
Density, g/mL	1.0660	Density, g/mL	1.0106

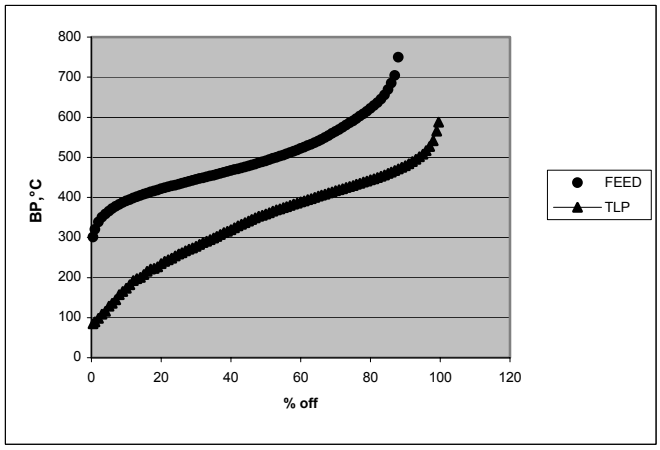

Figure 1. Simulated distillation of feed and TLP

The total liquid product (TLP) from the MAT was separated using the modified liquid chromatography method. This method was based on the extrography method described in the literature (1). The extrography column that was equipped with plunger pump and filled with basic alumina and silica in the original method was replaced with an open glass column (13.5-mm I.D. and a 450-mm length) filled with silica gel. Silica gel from Fisher Scientific (28-200 mesh) was activated for 12 h at 140°C. Its activity was adjusted by the addition of 4wt% water.

While in the original method, the analyzed sample was evenly distributed throughout the whole surface of the silica gel prior to extraction; in our modified method the total amount of TLP (0.7286 g) was applied on top of the column. The elution solvents were used in order of increasing polarity (2). Since TLP contained some of the material boiling below 200°C (13.81wt%), the calculation of material balance using gravimetric determination would not be suitable. Removal of solvents on vacuum rotary evaporator and vacuum dryer would result in the loss of light ends. In our case, the solution of each fraction was reduced to a known volume by using a mild rotary evaporation and a nitrogen gas sweep. The fractions were further analyzed by gas chromatograph-flame ionization detector (GC-FID). Quantification of fractions in the specified temperature intervals was performed by using the calibration standards prepared from previously separated fractions. All fractions were quantified only from 200°C, therefore the slight loss of the light ends encountered

during the nitrogen purge did not affect the results. The retention time calibration was performed by analyzing the normal paraffin standards at the identical conditions.

Results and Discussion

Micro activity testing of the material derived from an Estonian shale oil with IBP 301.2°C and FBP 750.0°C, yielded a product with IBP 84.5°C and FBP 587.5°C. From the simulated distillation data it was calculated that 13.81wt% of the material boiled below 200°C in the product. The yield of the material boiling between 200-360°C was 36.69wt%, while there was only 4.1wt% below 360°C in the feed. This temperature interval was important since it represented the fraction that might contain the phenolic compounds of interest, produced by cracking of heavy material.

The results of LC separation of TLP are presented in Table 2. The retention times for 200°C and 360°C were 5.727 min and 17.482 min respectively. The chromatograms of each fraction were integrated between these two points and the results were balanced with the results from the simulated distillation data.

According to the original method, the phenolic fractions are represented by fraction 4 (monohydric phenols) and fraction 5 (dihydric phenols). The GC-FID chromatograms of these fractions are shown in Figures 2 and 3.

Table 2. Results of LC separation of TLP from MAT testing of residue from Estonian shale oil

			200 - 360°C	200 - 360°C	IBP - 200°C	360°C - FBP	IBP - FBP
			GC-FID	SimDist	SimDist	Sum	Sum
Fr. No	Solvent	Designation	Recovery, wt%	wt%	wt%	wt%	wt%
Fr.1	Hexane	Saturates	2.3				
Fr.2	Toluene	Aromatics	24.6				
Fr.3	Chloroform	Esters+	0.6				
Fr.4	Chlor./Dieth.Ether	Monophenols	5.2				
Fr.5	THF/Methanol	Diphenols	3.3				
Fr.6	Methanol	Polars	0.7				
Total			36.7	36.7	13.8	49.5	100.0

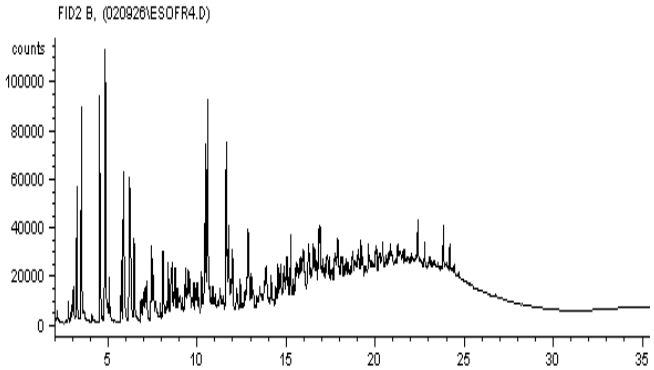

Figure2. GC-FID chromatogram of Fraction 4

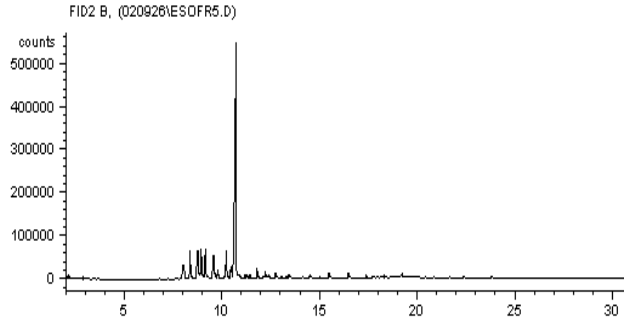

Figure 3. GC-FID chromatogram of Fraction 5

The combined phenolic fraction was the second largest (8.5wt%) after the aromatic fraction (24.6wt%). Both were analyzed by gas chromatography-mass spectrometry (GC-MS-equipped with mass selective detector from HP) with the library search option. Most of the peaks in Fraction 4 were designated as phenols with the largest peaks being cresols and 2,5-dimethyl phenol at 6.78 min, 6.86,min, 7.10,min, and 7.57, min. The rest of the chromatogram represents the variety of di- and tri-methyl phenols. There were no acids found in this fraction. Apparently, they decomposed during cracking. No clear assignments for peaks were given by the GC-MS in Fraction 5 due to a very low concentration of individual compounds. The largest outstanding peak was designated as phenol, 2,5-bis(1,1-dimethyl)-4-methyl.

Conclusions

Cracking of the residual material derived from an Estonian shale oil with a density 1.066 g/mL resulted in the production of a lighter liquid product with the density 1.0106 g/mL, and also resulted in quite a significant shift in the boiling point range. The starting material boiling between 301.2oC and 750oC was converted to a lighter material boiling between 84.5oC and 587.5oC.

The usefulness of this material in terms of the presence of phenolic compounds was verified by applying the separation technique, which was adapted from the original extrography method and modified into a simplified open column chromatography procedure. The new procedure was developed for analyzing the samples having a full boiling range.

The results of separation showed that useful phenols were produced as the result of catalytic cracking.

The project is ongoing and the full extend of catalytic cracking on the production of phenols and other streams at different conditions will be investigated, and the results will be published in future publications

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References

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(2) M.M. Boduszynski, R.J. Hurtubise and H.F. Silver, Anal. Chem., 1982, 54, 375.

Table 3. Peak assignments for Fraction 4 of TLP from MAT of Estonian shale oil

Peak RT,min	Assignation
5.70	phenol
6.78	phenol,2-methyl
6.86	phenol,2-methyl
7.10	phenol,3-methyl
7.57	phenol,2,5-dimethyl
8.03	phenol,2-ethyl
8.18	phenol,3,5-dimethyl
8.47	phenol,3-ethyl
8.60	phenol,2,3-dimethyl
8.84	phenol,2,4-dimethyl
8.99	phenol,2,3,6-trimethyl
9.32	phenol,2-ethyl-5-methyl
9.39	phenol,2-ethyl-6-methyl
9.47	phenol,3-(1-methylethyl)-
9.53	phenol,3-ethyl-5-methyl
9.77	phenol,2-(1-methylethyl)-
9.88	phenol,3,4,5-trimethyl
9.94	phenol,2,4,6-trimethyl
10.58	4-allylphenol
10.95	phenol, 3,5-diethyl
11.90	6-methyl-4-indanol
12.44	phenol, 4-(3-methyl-2-butenyl)-
13.06	1-naphthalenol
13.18	2-naphthalenol
14.33	1-naphthalenol,2-methyl
14.39	1-naphthalenol,3-methyl
14.64	1-naphthalenol,4-methyl
15.30	benzaldahyde, 2-chloro-6-fluoro-
15.48	1-naphthol, 5,7-dimethyl
16.37	2-hydroxy-1-naphthalenepropanol

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