

## Structural change analysis of pyrolysis fuel oil with increasing heat treatment temperature using nuclear magnetic resonance

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### Introduction

Pyrolysis fuel oil (PFO), which is the by-product of petroleum refining process, is one of the most promising carbon precursors because it consists of various aromatic compounds. In the reforming process of pitch from petroleum residues, various reactions such as distillation, cracking reaction, polymerization, and condensation occur. But, due to the complexity of the petroleum residues, it is difficult to find out the structural changes during the pitch manufacturing process. Herein, we prepared the petroleum pitches and volatile matters by heat treating PFO at various temperature and investigated the structural changes among them by comparing their <sup>1</sup>H-NMR spectra.

### Materials and Methods

Pyrolysis fuel oil (PFO, Yeochun NCC Co., LTD, South Korea) was heat treated to obtain volatile matters (VMs) and heavy fractions (HFs). For heavy fraction preparation, 150 g of PFO was placed into 500 mL batch-type glass reactor and then heated to various temperatures ranging from 280 °C to 360 °C, with the ramp rate of 5 °C/min. The heat treatment was carried out for two hours, and during heat treatment, nitrogen gas was injected to maintain an inert atmosphere inside the reactor. At the same time, the volatile matters generated by the preparation of heavy fraction were obtained. The prepared VMs and HFs were subjected to structural analysis. For <sup>1</sup>H-NMR analysis, 1 wt% of sample was dissolved in 0.75 ml of chloroform-d (99.96 atom %D, 0.03 % (v/v) TMS, Aldrich Co., USA). The structural analysis was carried out by quantitative analysis according to the comparison of characteristic peak area of <sup>1</sup>H-NMR spectra.

### Results and Discussion

**Figure 1** is the <sup>1</sup>H-NMR spectra for the heavy fraction samples. According to the spectra, peaks for 1 ring aromatic compounds detected at the chemical shift of 6.3-7.2 ppm was not found in HF280 sample, indicating that 1 ring aromatic compounds were totally removed from feedstocks before 280 °C. 2 ring aromatic compounds, the peaks of which detected in 7.37, and 7.72 ppm is gradually decreased with increasing temperature, and after 320 °C, these chemicals seem to be mostly removed. **Figure 2** is the <sup>1</sup>H-NMR spectra for the volatile matter samples. Same as heavy fraction, peaks for 2 ring aromatic compounds are gradually decreased. The peaks for aliphatic sidechain attached to aromatic compounds are detected at 3.2 and 3.7 ppm. These peaks were not detected before 300 °C but were detected after 320 °C due to the decomposition of the aliphatic sidechain caused by cracking reaction.

## Conclusions

In this study, heavy fractions and volatile matters were separated from pyrolysis fuel oil at various heat treatment temperatures. According to the  $^1\text{H-NMR}$  spectra, 1-2 ring aromatic compounds were gradually eliminated with increasing temperature. Moreover, the temperature after 320 °C, peaks for aliphatic hydrocarbons were dramatically decreased which indicates the cracking reaction occurs.

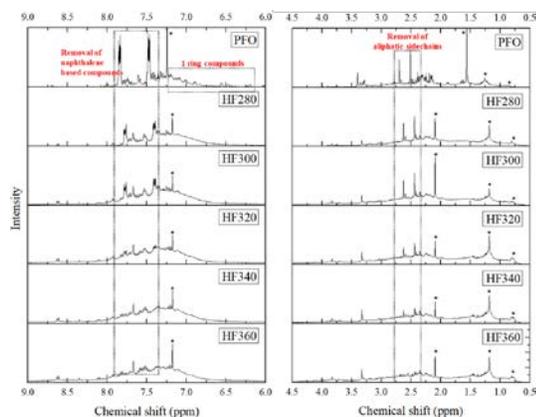


Figure 1.  $^1\text{H-NMR}$  spectra of pyrolysis fuel oil and heavy fraction.

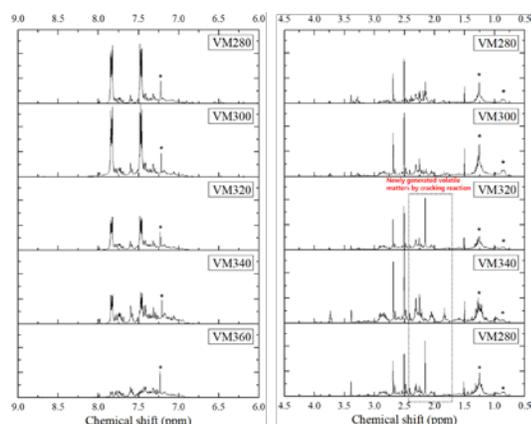


Figure 2.  $^1\text{H-NMR}$  spectra of volatile matters.

## References

- [1] S. L. Silva, A. M. S. Silva, J. C. Ribeiro, F. G. Martins, F. A. D. Silva, and C. M. Silva, Chromatographic and spectroscopic analysis of heavy crude oil mixtures with emphasis in nuclear magnetic resonance spectroscopy: A review, *Anal. Chim. Acta.* 707, 18 (2011).
- [2] J. G. Kim, J. H. Kim, B. -J. Song, Y. P. Jeon, C. W. Lee, Y. -S. Lee, and J. S. Im, Characterization of pitch derived from pyrolyzed fuel oil using TLC-FID and MALDI-TOF, *Fuel.* 167, 25 (2016).
- [3] P. Álvarez, N. Díez, C. Blanco, R. Santamaría, R. Menéndez, and M. Granda, An insight into the polymerization of anthracene oil to produce pitch using nuclear magnetic resonance, *Fuel.* 105, 471 (2013).