Separation of Nitrogen Heterocyclic and Homocyclic Compounds Contained in Atmospheric Residue by Solvent Extraction

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1. Introduction

The demand for heavy petroleum fractions have been shrinking recently, so that it is desired to convert these fractions into lighter fractions, for which the demands are relatively high. This conversion can be achieved by catalytic cracking [1]. Before this catalytic reaction, it is necessary and favorable to remove nitrogen heterocyclic compounds and polycyclic aromatic hydrocarbons in order to avoid catalytic poisoning etc. In this thesis, the solvent extraction using non-polar and polar solvent[2-6] was applied to the separation of the above compounds contained in the atmospheric residue, a petroleum heavy fraction obtained from the bottom of atmospheric distillation tower in the refinery.

2. Experimental

Table 1 shows the conditions of the extraction using non-polar solvent. The feed was atmospheric residue (AR), whose boiling range was 623 K~. Heptane etc. were used as non-polar solvents. After the feed and solvent were equilibrated under specified conditions, the liquid extract (solvent phase) and solid residue were separated from each other by filtration[2].

The conditions of the extraction by polar solvent are summarized in **Table 2**. The following mixtures were used as feeds: AR; the liquid extract from non-polar solvent extraction (Table 1) of AR (DAAR); heptane solution of vacuum gas oil (VGO) as a model for DAAR (MDAAR); etc. The VGO is the lighter fraction of two obtained from the vacuum distillation of AR, of which boiling range was 623~823 K. In some runs with polar solvent, the additive, such as, aluminum chloride, was used in the solvent in order to enhance the extraction [3]. After equilibration of feed and solvent phases, separatory funnel was used to separate the raffinate and extract.

The samples of the feed, extract, solid residue, and raffinate were analyzed by FT-ICR MS, chemical luminescence (JIS-K 2609), potentiometric titration. In FT-ICR MS analysis, more than ten thousands of heterocyclic and homocyclic compounds contained in AR or VGO were identified and quantified. The contents of total nitrogen and total basic nitrogen were determined by chemical luminescence and potentiometric titration, respectively.

3. Results and Discussions

The compositions of AR and VGO are given in Table 3. These heavy fractions mainly contained cyclic compounds and the contents of alkanes were quite low. The content of nitrogen compounds in AR was much higher than that in VGO. The content of nitrogen compounds with shorter side chain and more aromatic rings was higher.

A major part of AR dissolved in heptane, non-polar solvent to form the liquid extract, and the other small part remained as solid residue. The distribution ratio of component i, m'_i, in the non-polar solvent extraction was defined as,

$$m'_i = z_i / y'_i \tag{1}$$

where z_i was the mass fraction of component i in the solid residue, and y'_i was that in the liquid extract. **Figure 1** shows the effects of the number of carbon atoms in side chain and that of aromatic rings on m'_i in the extraction of AR by heptane. The m'_i decreased, as the side chain lengthed and the number of aromatic rings decreased. There was not clear difference of m'_i between nitrogen heterocyclic and homocyclic compounds. However, since the nitrogen compounds contained in AR was those with shorter side chain and more aromatic rings as mentioned above, the content of the nitrogen compounds in total

Table 1 Experimental conditions in extraction by non-polar solvent

Feed	AR
Mass of feed	0.02 kg
Solvent	heptane etc.
Mass ratio of solvent to feed	5
Temperature	303 K
Time	48 h

Table 2 Experimental conditions in extraction by polar solvent

| Feed	AR, DAAR[*], MDAAR[**], etc.
Mass of feed	0.13 ~ 0.24 kg
Solvent	aqueous solution of methanol
Additive to solvent	aluminum chloride etc.
Mass ratio of solvent to feed	1
Mass fraction of methanol	0.9
Mass fraction of additive	0, 0.027
Temperature	303 K
Time	48 h

[*] The extract from non-polar solvent extraction of AR.
[**] Heptane solution of VGO as a model for DAAR. The mass fraction of VGO in MDAAR was 0.33.

Table 3 Composition of AR and VGO (in mass fraction)

	heterocyclic compounds			homocyclic compounds
	N	NS	S	
AR	0.0332	0.048	0.556	0.3421
VGO	0.0072	0	0.4595	0.459
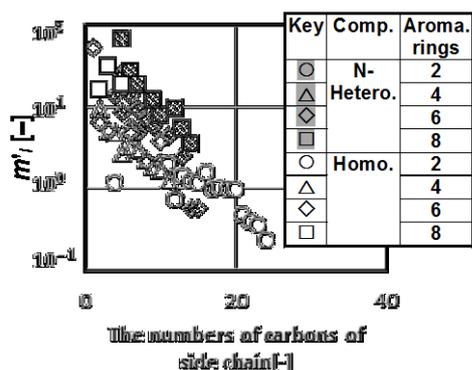
Fig. 1 m'_is of nitrogen heterocyclic and homocyclic compounds in AR extraction by heptane
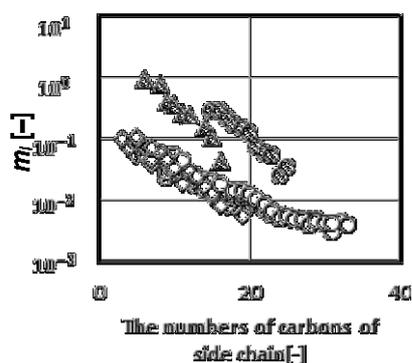
Fig. 2 m_is of nitrogen heterocyclic and homocyclic compounds in MDAAR extraction by aqueous solution of methanol

Table 4 Effect of aluminum chloride, AlCl$_3$, addition to polar solvent on m_i of total and basic nitrogens

	m_i [–]	
	without AlCl$_3$	with AlCl$_3$
Total nitrogen	0.4	0.4
Basic nitrogen	0.03	0.23

was reduced from 0.0813 in AR to 0.0796 (solvent free) in the liquid extract. The compounds with shorter side chain and more aromatic rings could be removed and the content of nitrogen compounds in total was lowered by non-polar solvent extraction of AR.

While it was difficult to conduct the direct extraction of AR by aqueous solution of methanol, polar solvent, in the range of this work, the extraction of DAAR, MDAAR, etc. could be carried out satisfactorily. The distribution ratio, m_i, was written as,

$$m_i = y_i / x_i \qquad (2)$$

with the mass fraction in the extract, y_i, and that in the raffinate, x_i, in the polar solvent extraction. In **Figure 2**, the m_is are plotted against the number of carbon atoms in side chain with the various numbers of aromatic rings, where MDAAR was extracted by aqueous solution of methanol, polar solvent. The m_is decreased with number of carbon atoms in side chain. The effects of the number of aromtic rings on m_is

were not obvious. The m_is of nitrogen heterocyclic compounds were larger than those of homocyclic compounds. The effects of aluminum chloride addition to the solvent on the m_is of total and basic nitrogens in the MDAAR extraction are shown in **Table 4**. The m_i of basic nitrogen with AlCl$_3$ in the solvent was higher than that without AlCl$_3$, while that of total nitrogen was not affected by AlCl$_3$ addition. The high affinity of aluminum ion with the lone pair of nitrogen atom in the basic nitrogen compound would enhance the dissolution of the nitrogen compound into aqueous solvent phase [3].

Based on the above experimental results, the following process was suggested. The AR is, first, extracted by non-polar solvent to remove nitrogen heterocyclic and homocyclic compounds with shorter chain and more aromatic rings as solid residue and to lower the nitogen compound content in the liquid extract to some extent. In the second, this liquid extract from the non-polar solvent extraction is extracted again by polar solvent to remove light nitrogen compounds. The raffinate after this polar solvent extraction mainly contains homocyclic compounds with longer side chain and less aromtic rings without nitrogen, which is an appropriate fraction for the downstream catalytic reaction.

4. Conclusions

The nitrogen heterocyclic and homocyclic compounds with shorter side chain and more aromatic rings contained in atmospheric residue could be removed and, thus, the total content of nitrogen compounds could be lowered by non-polar solvent extraction. The polar solvent could extract the nitrogen compounds selectively from the liquid extract obtained in the non-polar solvent extraction. According to these results, it was suggested to extract atmospheric residue with non-polar and polar solvents to provide an appropriate fraction for the downstream catalytic reaction operation.

Nomenclature

m_i = distribution ratio of i in polar solvent extraction, m'_i = distribution ratio of i in non-polar solvent extraction, x_i = mass fraction of i in raffinate phase in polar solvent extraction, y_i = mass fraction of i in extract phase in polar solvent extraction, y'_i = mass fraction of i in liquid extract in non-polar solvent extraction, z_i = mass fraction of i in solid residue in non-polar solvent extraction
<Subscripts>
i = component i

References

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