

Communication

Study on Removal of Nitrogen-Containing Heterocyclic Compounds Contained in Crude Methylnaphthalene Oil by Formamide Extraction

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Abstract: This study examined the effect of experimental factors and conditions on the removal of nitrogen-containing heterocyclic compounds (NCHCs) by performing equilibrium extraction using formamide or formamide aqueous solution as a solvent to remove NCHCs contained in crude methylnaphthalene oil (CMNO). The CMNO used as a raw material in this study contained three types of NCHCs (quinoline, isoquinoline, and indole) classified as group A, and six kinds of non-NCHCs (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, dibenzofuran, and fluorene) classified as group B. Increasing the volume fraction of water to the solvent before the extraction run increased the raffinate residual rate but conversely decreased the removal rate of group A. The increase in the volume fraction of solvent to feed before the extraction run and operating temperature decreased the residual rate of raffinate but conversely increased the removal rate of group A. Over the entire range of extraction conditions performed in this study, the removal rate of group A ranged from 10.8% to 70.7%. Considering that these experimental results were obtained using only a single stage of batch equilibrium extraction, the formamide extraction method applied in this study showed excellent performance in terms of the residual rate of raffinate and the removal rate of group A. Therefore, it was expected to be an alternative to the reaction extraction method using acids and bases applied so far to separate NCHCs in the distillation residue of coal tar.

Keywords: coal tar; crude methylnaphthalene oil; nitrogen-containing heterocyclic compounds; formamide extraction; removal; quality improvement



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1. Introduction

Crude methylnaphthalene oil (CMNO; approximately 10,000 tons/year in Korea) is produced as a distillation residue of naphthalene oil (bp 483–533 K) from coal tar after the recovery of crude naphthalene [1]. The CMNO used as a raw material in this study contains a total of 15.23 wt% of nitrogen-containing heterocyclic compounds (NCHCs): quinoline (QNL, 6.72 wt%), iso-quinoline (IQNL, 4.15 wt%), and indole (ID, 4.36 wt%). These NCHCs contained in CMNO, which are hazardous, flammable, and carcinogenic chemicals, are considered undesirable impurities of CMNO because they cause air pollution by NO_x generated from combustion, produce a very unpleasant odor, and deteriorate catalyst performance [1–3]; there are also many restrictions on the transportation and handling due to the harmfulness of CMNO. For the above reasons, improving the quality of CMNO by removing NCHCs contained in CMNO would be very significant. Meanwhile, the by-product discharged in the process of improving the quality of CMNO contains a large amount of very useful NCHCs, such as QNL, IQNL, and ID, which are used in the manufacture of drugs, perfumes, pesticides, dyes, and pigments [2–7]. Therefore, we believe that the study on improving the quality of CMNO by removing NCHCs contained in CMNO is very important in improving the quality of CMNO and utilizing the very useful resources contained in the by-products discharged from the process.

So far, the separation of NCHCs contained in the distillation residue of coal tar has been mainly achieved by reactive extraction using acids and bases; however, this method, which uses both strong alkaline (e.g., NaOH) solutions and acidic (e.g., H₂SO₄) solutions, has the disadvantages of high cost, corrosion of the metal separation apparatus, environmental pollution, and complicating the separation process because the separating agent cannot be regenerated [8,9]. Therefore, finding new alternative separation methods that are simpler and more efficient than reactive extraction is significant. Currently, to find an alternative to the reaction extraction method for removing NCHCs contained in distillation residues of coal tar, studies such as adsorption [10–12], supercritical extraction [1,4,8], extraction using ionic liquids [13–16], inclusion complexation [17,18], and organic solvent extraction [3,7,19–25] with a variety of organic solvents, including methanol, ethanol, and formamide, are in progress. Among organic solvent extractions, methanol extraction using CMNO, one of coal tar's distillation residues directly produced in the coal tar distillation industry, showed very high solubility of NCHCs and compounds other than NCHCs. As a result, the methanol extraction method was not satisfactory the separation between NCHCs and compounds other than NCHCs due to the low selectivity of NCHCs to non-NCHCs below 10 [7,21,25].

In a previous study [3], we investigated the recovery of NCHCs contained in wash oil, one of the distillation residues for recovering naphthalene oil in coal tar, using a mixture of formamide and water (MFW) as a solvent. The recovery results reported that MFW is an excellent solvent in terms of balance between solubility and selectivity of NCHCs. Therefore, this study examined the reduction of NCHCs contained in CMNO using MFW as a solvent. For this review, we performed equilibrium extraction using formamide or MFW as a solvent to examine the effect of experimental factors and conditions on the removal of NCHCs.

2. Experimental Section

2.1. Material

The raw material for this study, CMNO, was supplied by OCI Company Ltd. in Seoul, Republic of Korea. For the identification and quantitative analysis of each compound present in CMNO through gas chromatography (GC), we purchased standard reagents Naphthalene (NLT, 99% purity), QNL (98% purity), IQNL (97% purity), ID ($\geq 99\%$ purity), 2-methylnaphthalene (2MNLT, 97% purity), 1-methylnaphthalene (1MNLT, $\geq 95\%$ purity), biphenyl (BP, $\geq 99.5\%$ purity), dibenzofuran (DBF, 98% purity), and fluorene (FR, 98% purity) from Sigma-Aldrich Korea (Seoul, Republic of Korea). Formamide ($\geq 99.5\%$ purity), used as a solvent, was also purchased from the same place.

2.2. Method

First, formamide and tap water were mixed to make a solvent of a certain experimental concentration. Next, a 500 mL Erlenmeyer flask containing a certain amount of feed (F₀: CMNO) and solvent (formamide or MFW, S₀) was placed in a shaking water bath maintained at the experimental temperature, and shaking was started. After a certain period, the shaking was stopped and allowed to settle; the mass of each phase was measured after the extract phase, and the raffinate phase was separated using a 500 mL separatory funnel. The concentration of each compound contained in each phase was measured by GC analysis of each sample, to which a small amount of acetone (a diluting solvent for concentration measurement) was added to the extraction and raffinate phases. Analysis of two phases was performed using GC equipped with a flame ionization detector. Details of the analysis apparatus and conditions are presented in Table 1.

Table 1. Analysis apparatus and conditions.

Gas Chromatograph	HP 6890 (Hewlett Packard Co., Houston, TX, USA)
Column (19091Z-416)	Capillary column HP-1
length (m)	60
inner diameter (mm)	0.32
film (μm)	0.25
Carrier gas	N_2
split ratio (-)	0.025
the flow rate in column (mL/min)	1
Sample volume (μL)	1
Injection temperature (K)	523
Column temperature (K)	383–593
increasing rate (K/min)	0 (0–3 min) 5 (383–523 K) 14 (523–593 K)
Detector temperature (K)	593

2.3. Material Systems and Conditions

Table 2 shows the material systems and experimental conditions used in this study. As described above, CMNO and formamide or MFW were used as feed and solvent, respectively. The distribution equilibrium experiment was performed by changing the liquid-liquid contacting time (t), the operating temperature (T), the volume fraction of water to solvent before the extraction run ($y_{w,0}$), and the volume fraction of solvent to feed before extraction run (S_0/F_0).

Table 2. Experimental system and conditions.

System	
Feed crude methylnaphthalene oil (CMNO)	
Solvent formamide, the mixture of formamide and water (MFW)	
Experimental conditions	
Liquid-liquid contacting time, t (h)	24–96
Operating temperature, T (K)	277–343
Volume of total liquid (ml)	400
Volume fraction of water to solvent before extraction run, $y_{w,0}$ (-)	0–0.3
Volume fraction of solvent to feed before extraction run, S_0/F_0 (-)	1–9

3. Results and Discussions

3.1. Gas Chromatogram of CMNO

Figure 1a shows the gas chromatogram of CMNO and the names of each compound identified using standard reagents. The peak numbers 2, 3, and 4, respectively, represent three kinds of NCHCs (QNL, IQNL, and ID) classified as group A, and the peak numbers 1 and 5 to 9, respectively, represent six kinds of non-NCHCs (NTL, 2MNLT, 1MNLT, BP, DBF, and FR) classified as group B. The gas chromatogram showed that the CMNO used in this study contained a relatively small amount of group A compared to group B. The composition of each compound contained in CMNO is presented in Table 3. The compositions of QNL, IQNL, and ID, the target compounds to be removed in this study, in CMNO were 6.72, 4.15, and 4.36 wt%, respectively, and group A, which summed these three kinds of NCHCs, was 15.23 wt%.

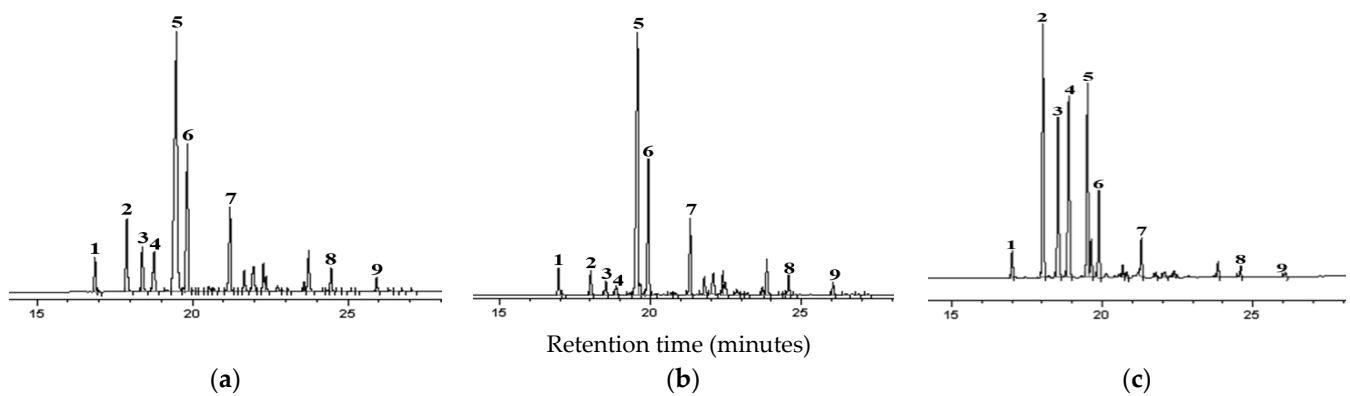


Figure 1. Gas chromatograms of (a) feed (CMNO), (b) raffinate phase, and (c) extract phase. Peak numbers; 1: naphthalene (NTL), 2: quinoline (QNL), 3: iso-quinoline (IQNL), 4: indole (ID), 5: 2-methylnaphthalene (2MNTL), 6: 1-methylnaphthalene (1MNTL), 7: biphenyl (BP), 8: dibenzofuran (DBF), and 9: Fluorene (FR). Extraction conditions: $y_{w,0} = 0.1$, $S_0/F_0 = 9$, $T = 303$ K, and $t = 72$ h.

Table 3. Compositions of compounds Contained in CMNO.

		Compound	Composition (wt%)
Group A	Heterocyclic Nitrogen Compounds (NCHCs)	Quinoline (QNL, C ₉ H ₇ N)	6.72
		Iso-quinoline (IQNL, C ₉ H ₇ N)	4.15
		Indole (ID, C ₈ H ₇ N)	4.36
Group B	Non-Heterocyclic Nitrogen Compounds (Non-NCHCs)	Naphthalene (NTL, C ₁₀ H ₈)	2.88
		2-Methylnaphthalene (2MNTL, C ₁₁ H ₁₀)	38.93
		1-Methylnaphthalene (1MNTL, C ₁₁ H ₁₀)	15.11
		Biphenyl (BP, C ₁₂ H ₁₀)	8.03
		Dibenzofuran (DBF, C ₁₂ H ₈ O)	1.92
		Fluorene (FR, C ₁₃ H ₁₀)	1.13
Others			16.77

3.2. Checking of Time to Reach Equilibrium

To confirm the time to reach equilibrium, we analyzed the raffinate and extract phases recovered by liquid-liquid contacting between CMNO and MFW ($t = 24, 48, 72, 96$ h) under a constant experimental condition. We found that the composition of the two phases recovered at $t = 72$ and 96 h was almost identical. Therefore, the equilibrium reaching time of the system used in this study is within 72 h, so the entire distribution equilibrium experiment was performed in liquid-liquid contact for $t = 72$ h.

3.3. Definition of Equations

The residual rate of raffinate (RRR), the removal rate of group A (RRGA), the distribution coefficient (m_i) indicating the degree of solvency of component (or group) i , and the selectivity ($\beta_{i,j}$) suggesting the degree of separation efficacy between component (or group) i and a reference component (or group) j were calculated using the following definition equations.

$$RRR = \frac{\text{mass of raffinate phase}}{\text{mass of feed}} \times 100\%$$

$$RRGA = \frac{\text{mass of group in feed} - \text{mass of group A in raffinate phase}}{\text{mass of group A in feed}} \times 100\%$$

$$m_i = \frac{\text{mass fraction of component (or group) } i \text{ in extract phase}}{\text{mass fraction of component (or group) } i \text{ in raffinate phase}}$$

$$\beta_{ij} = \frac{\text{distribution coefficient of component (or group) } i}{\text{distribution coefficient of a reference component (or group) } j}$$

3.4. Removal Performance of Group A

Figure 2a–c, respectively, shows the effect of the volume fraction of water to solvent before extraction run ($y_{w,0}$) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) m_{GA} and m_{GB} , which are distribution coefficient of group A (GA) and group B (GB), and selectivity of group A in reference to group B ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). From (a), as $y_{w,0}$ increases, RRR increases while RRGA decreases. This is thought to be a tendency caused by an increase in the polarity of the extract phase as $y_{w,0}$ increases. In the range of $y_{w,0}$, RRR and RRGA, respectively, were 95.9% to 99.1% and 10.8% to 19.1%. From (b), we can see that the increase in $y_{w,0}$ increases the polarity of the extract phase, which decreases m_{GA} and m_{GB} but conversely increases $\beta_{GA,GB}$. Additionally, the fact that m_{GA} is much larger than that of group B shows that the polarity of group A is greater than that of group B. According to $y_{w,0}$, $\beta_{i,2MNTL}$ was reviewed to confirm the degree of separation between all the compounds identified using GC in this study. As predicted from the tendency of m_{GA} , m_{GB} , and $\beta_{GA,GB}$, according to $y_{w,0}$, of (b), we can see that the $\beta_{i,2MNTL}$ of each NCHC of group A increased with increasing $y_{w,0}$, but that of each non-NCHCs of group B showed almost constant values regardless of $y_{w,0}$. The $\beta_{i,2MNTL}$ of each NCHC obtained in the $y_{w,0}$ range of this study was approximately 3–5 times greater than that obtained from methanol extraction using wash oil [7,21,25]. In all compounds identified, $\beta_{i,2MNTL}$ showed the following order: ID > QNL = IQNL > NTL > BP > DBF > 2MNTL = 1MNTL > FR. Given the balance between RRR and RRGA, according to $y_{w,0}$, we thought an extraction that maintained $y_{w,0} = 0.1$ would be favorable for removing group A from CMNO using MFW as a solvent.

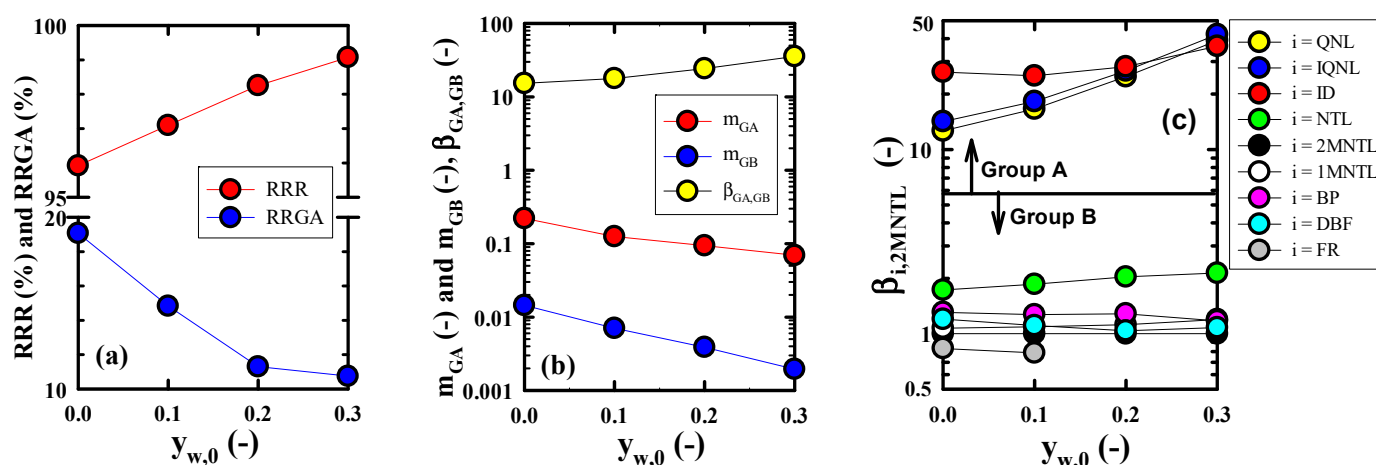


Figure 2. Effect of volume fraction of water to solvent before extraction run ($y_{w,0}$) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) distribution coefficient of group A (GA) and group B (GB) (m_{GA} and m_{GB}), and selectivity of GA in reference to GB ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). 2MNTL: 2-Methylnaphthalene. Extraction conditions: $S_0/F_0 = 1$, $T = 303$ K, and $t = 72$ h.

Figure 3a–c, respectively, shows the effect of the volume fraction of solvent to feed before extraction run (S_0/F_0) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) m_{GA} and m_{GB} , which are distribution coefficient of group A (GA) and group B (GB), and selectivity of group A in reference to group B ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). An increase in S_0/F_0 resulted in a decrease in RRR and an increase in RRGA. This tendency is caused by a chemical change, such as salvation between the NCHCs and a solvent by S_0/F_0 change [22,25]. When $S_0/F_0 = 1$ and 9, RRR decreased from 97.1% to 81.3%, but RRGA increased sharply from 14.8% to

70.7%. Through this, it is expected that if the raffinate phase recovered by $S_0/F_0 = 9$ is washed with water (to remove formamide contained in a small amount in the raffinate phase), it can be used as a CMNO with improved quality. It can be seen from (b) that as S_0/F_0 increased, m_{GA} and m_{GB} showed a weak increase trend and then decreased, but $\beta_{GA,GB}$ showed a slight increase trend as S_0/F_0 increased. The $\beta_{i,2MNTL}$ of each NCHC in group A increased with increasing S_0/F_0 , while that of each non-NCHC in group B was almost constant regardless of S_0/F_0 . Considering the balance of RRR and RRGa per the unit volume of solvent, according to S_0/F_0 , it was considered that extraction in $S_0/F_0 = 1$ using MFW as a solvent would be advantageous for removing group A in CMNO.

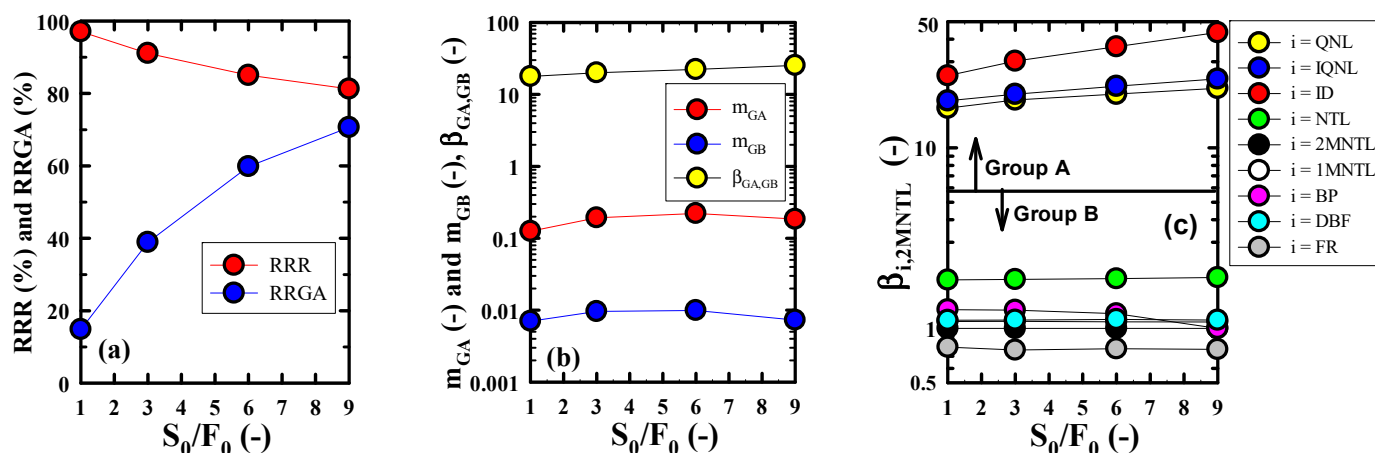


Figure 3. Effect of volume fraction of solvent to feed before extraction run (S_0/F_0) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) distribution coefficient of GA and GB (m_{GA} and m_{GB}), and selectivity of GA in reference to GB ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). 2MNTL: 2-Methylnaphthalene. Extraction conditions: $y_{w,0} = 0.1$, $T = 303$ K, and $t = 72$ h.

Figure 4a–c, respectively, shows the effect of the operating temperature (T) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) m_{GA} and m_{GB} , which are distribution coefficient of group A (GA) and group B (GB), and GA in reference to GB ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). As the operating temperature increased, RRR decreased, but conversely, RRGa increased. The operating temperature increased, the molecular movement of all compounds in CMNO became active, and the movement to the extraction phase through the liquid-liquid interface increased, reducing RRR; on the contrary, it showed a general extraction tendency to increase RRGa. From the results of examining the effect of operating temperature on m_{GA} , m_{GB} , $\beta_{GA,GB}$, and $\beta_{i,2MNTL}$ shown in (b) and (c), it was determined that room temperature operation could be used to remove NCHCs from CMNO.

Figure 1b,c show the gas chromatograms of the raffinate phase and the extract phase recovered through equilibrium extraction under constant conditions ($y_{w,0} = 0.1$, $S_0/F_0 = 9$, $T = 303$ K, $t = 72$ h), respectively. The gas chromatogram of the raffinate phase in (b) differed significantly from that of CMNO in Figure 1a, as the peak height of each NCHC of the raffinate phase was greatly reduced as many NCHCs were extracted. From differences in these gas chromatograms, it was possible to reconfirm the effect of removing NCHCs in CMNO by formamide extraction in this study. On the contrary, comparing the gas chromatogram of the extract phase with that of CMNO revealed a significant increase in the peak height of each NCHC compound of group A due to formamide extraction; still, the peak height of the six types of non-NCHCs of group B was greatly decreased. Compared to CMNO, the extract phase recovered from formamide extraction contained many useful NCHCs used to manufacture drugs, perfumes, pesticides, dyes, and pigments, as mentioned in the introduction. If NCHCs (especially ID) can be purified to high purity

by recovering the formamide extract phase and adopting an appropriate post-treatment process, this is thought to be very meaningful in terms of recycling resources.

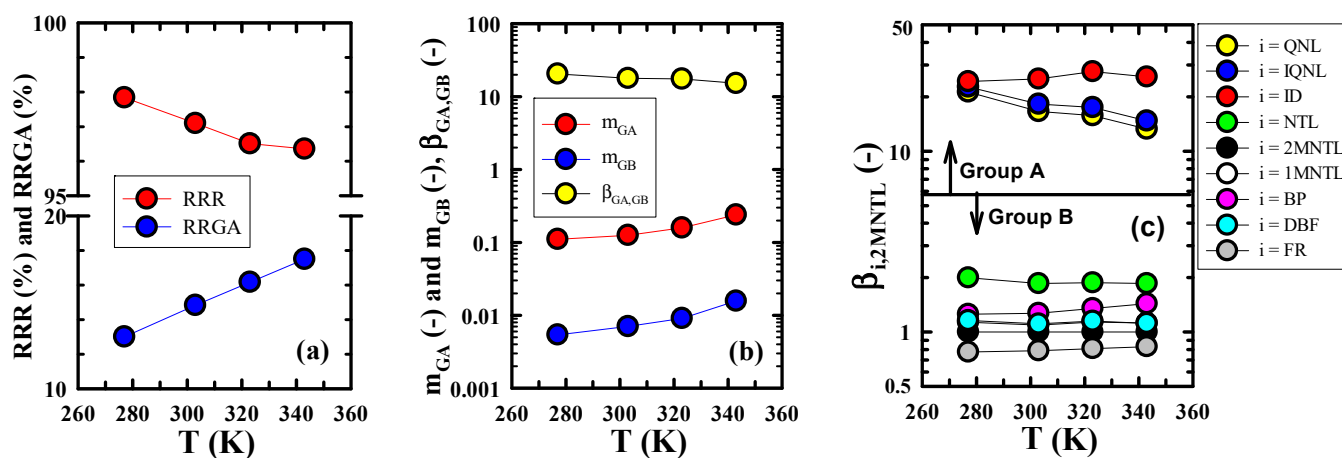


Figure 4. Effect of operating temperature (T) on (a) residual rate of raffinate (RRR) and removal rate of group A (RRGA), (b) distribution coefficient of GA and GB (m_{GA} and m_{GB}), and selectivity of GA in reference to GB ($\beta_{GA,GB}$), (c) selectivity of compound i in reference to 2MNTL ($\beta_{i,2MNTL}$). 2MNTL: 2-Methylnaphthalene. Extraction conditions: $y_{w,0} = 0.1$, $S_0/F_0 = 1$, and $t = 72$ h.

From the results of this study, which comprehensively examined the effects of experimental factors and conditions on the removal of group A contained in CMNO, we considered $y_{w,0} = 0.1$, $S_0/F_0 = 1$, and $T = \text{room temperature}$ to be the optimal experimental conditions. In addition, considering that these experimental results obtained through this study were obtained using only a single stage of batch equilibrium extraction, it is expected that very high removal efficiency of group A can be obtained from CMNO if formamide extraction is performed using the multi-stage continuous extraction apparatus of the tower type with large liquid-liquid contact area under an optimal extraction condition.

4. Conclusions

To improve the quality of CMNO, this study performed distribution equilibrium between CMNO and formamide, or a mixture of formamide and water, to investigate the effects of experimental parameters and conditions on the removal of NCHCs in CMNO. When extraction operation was performed under the experimental conditions of $y_{w,0} = 0.1$, $S_0/F_0 = 1$, and $T = 303$ K, the very excellent removal efficiency of NCHCs in CMNO was achieved. The formamide extraction method applied in this study showed excellent performance in terms of the residual rate of raffinate and the removal rate of group A (NCHCs), so it was expected to be an alternative to the reaction extraction method using acids and bases applied so far to the separation of NCHCs in the distillation residue of coal tar.

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Data Availability Statement: The data presented in this study are available within the article (tables and figures).

Conflicts of Interest: The author declares no conflict of interest.

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