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OPTIMIZATION OF NMP EXTRACTION IN 1, 3-BUTADIENE PRODUCTION LINE

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Abstract: N-methylpyrrolidone is a powerful solvent for variety of chemical processes due to its vast chemical properties. It has been used in manufacturing processes of polymers, detergents, pharmaceuticals rubber and many more chemical substances. However, it creates large amount of residue in some of these processes which has to be dealt with. Many well known methods such as BASF in rubber producing units have tried to regenerate the solvent at the end of each run, however, there is still discarding of large amount of residue containing NMP, which over time, could cause environmental concerns. In this study, we have tried to optimize regeneration of the NMP extraction from butadiene production. It is shown that at higher temperatures NMP is separated from the residue with close to 90% efficiency, and the solvent residue proved to be the most effective with a 6: 1 ratio.

Introduction

N-methylpyrrolidone is a weak base and is an aprotic solvent with low volatility and toxicity (1).It is a powerful solvent for a wide range of chemicals, and Due to its thermal stability and its relatively high dielectric constant, it is extensively used in polymer industries (2,3).Its numerous advantageous qualities such as being environmentally friendly substance, non-carcinogenicity, non-corrosiveness, and low solvent loss have given a widespread use in pharmaceutical products(4), detergent industries, polymer and rubber producing plants (5,6), and many more usages are being found everyday. N-methylpyrrolidione is used in series of processes such as degassing, distillation, and solvent regeneration in rubber manufacturing as solvent for the extraction of 1,3-butadiene due to its high merit as a solvent, with the extractability of more than 99%; later the NMP and the residue is discarded or managed in a biologically equipped industrial waste treatment units which itself requires extra process and financial resources (5,6,7). Recently, however, efforts have been invested in reviewing and revising the current method. Our goal in this study was to find a way to extract NMP from the discarding residue of 1,3-Butadiene line to a higher percentage.

Experimental

Instruments and Reagents

All chemicals Methanol, Benzene, Toluene, Chloroform, Carbon tetrachloride, Xylene, ethyl acetate, n-Heptane, and petroleum ether used were from Merk, and the HPLC was from Shimadzo. A 25 cm. Shimadzo ODS column was used with the packing size of 5qm.Water was deionized by millipore milli-Q water purifier. The BD unit purpose is to separate 1, 3-Butadiene from the compounds with close boiling points with a 99% purity yields. This process is done with combination of distillation and extractions using NMP having 8.3% water content. Once the separation process is over, the un-evaporated residue from the solvent poses a great threat to the environment. Our first priority was to determine the amount of NMP in the residue then to devise a proper regeneration process and eventually a suitable discarding method.

RESULTS AND DISCUSSION

Extractions

The residue had some dissolution in various solvents such as water, Methanol, Benzene, Toluene, Chloroform, Carbon tetrachloride, Acetone, Xylene, Ethyl acetate, n-Heptane, and Petroleum ether which prompted further analyses of each solvent. First, the residue was dissolved in water, then liquid- liquid extractions proceeded using non-polar solvents. Extractions with Xylene produced three phases, thus rendering an unsuccessful extraction. The same procedures were used with Toluene, Ethyl acetate Methanol, and chloroform which all proved to be unacceptable where in each extraction, the amount of NMP entering the organic phase was too little or in a trace amount thus unsuccessful. The extraction with n-heptane, however, produced better results. Though NMP is sparingly soluble in n-heptane, the yield was exceptionally pure, therefore, we decided to further improve the extraction using different temperatures. Three different temperatures were determined to be used, at room, near the boiling point, and post boiling point.

Extraction at room temperature

10.0 grams of residue was mixed with 20.0 grams of n- Heptane at 25˚c. Only 1.05 grams residue was dissolved in n-Heptane. The dissolution formed two phases. The upper phase identified as E25˚c contained 23ml. (9.47gr.), and the lower phase $S_{25^{\circ}c}$ contained 3.5ml. (0.52gr.) n-heptane respectively.

Table1. N-heptane extraction of NMP at 25

Sample	Sample weight gr	%NMP weight in sample	% Impurities in sample	% n-Heptane in sample
$S_{25^{\circ}C}$	0.5185	91.80	0.66	7.54
$E_{25^{\circ}C}$	9.4713	6.01	0.04	93.95

shows the HPLC analyses of both phases, as it can be seen, the impurities present in both phases have been reduced in such a way that in the $S_{25^{\circ}c}$ phase, 0.66 and the $E_{25^{\circ}c}$ phase, 0.04% weight is present while the amount of NMP in $S_{25^{\circ}c}$ is 91.80 and in $E_{25^{\circ}c}$ is 6.01% weight. Therefore ,n-heptane has selectively separated NMP from the impurities.

Extraction at near the boiling point

10.0 gram residue was refluxed in 20.0 gram n-heptane at 70˚c for three hours. As expected, more residue material about 4.08 grams was dissolved in n-heptane at higher temperature. Again two different phases were identified, the rich organic phase $E_{70^{\circ}c}$ containing 19.32 gram n-heptane and NMP rich $S_{70^{\circ}c}$ containing 1.11gr. The $E_{70^{\circ}c}$ phase was allowed to form two phases itself as the temperature lowered to ambient. The newly formed two phases of $E'_{70^{\circ}c}$ (18.26gr.) and $S'_{70^{\circ}c}$ (1.06gr.) were also analyzed using HPLC

Table2. N-heptane extraction of NMP at 70 °C

Sample	Sample weight gr	%NMP weight in sample	%Impurities in sample	%n-Heptane in sample
$S_{70^{\circ}C}$	1.1086	85.85	0.75	13.40
$\acute{S}_{70^{\circ}C}$	1.0641	85.51	0.17	14.32
$\acute{E}_{70^{\circ}C}$	18.250	9.2	0.01	79

It can be seen from the table that the amount of impurities in extracted material is lower than the residue. The impurities in $S_{70^{\circ}c}$ phase is 0.75 weight percent whereas the NMP in the sample $S_{70^{\circ}c}$ and $S'_{70^{\circ}c}$ are similar in amount to the residue. Therefore, the n-Heptane has selectively extracted NMP from the residue.

Extraction at post boiling point

Again in this stage, 10.0 gr. residue was mixed with 20.0 gram n-heptane, and the mixture was refluxed at 100˚c. Since n-heptane boils at 98.42˚c, a condenser was used to insure a successful condensation back to the solution. In this condition, About 6.43 gram residue was dissolved in the solvent, and the phases of $E_{100^{\circ}c}$ (21.86 gr.) and $S_{100^{\circ}c}$ (0.58 gr.) were identified. At lower temperature, $E_{100^{\circ}c}$ phase itself was divided to two other NMP and n-heptane rich phases, $E'_{100^{\circ}c}$ and the $S'_{100^{\circ}c}$ with 17.38 and 4.48gr.respectively,

Table3. N-heptane extraction of NMP at 100 °C

Sample	Sample weight gr	%NMP weight in sample	%Impurities in sample	%n-Heptane in sample
$S_{100^{\circ}C}$	0.5795	89.12	4.41	6.74
$\acute{S}_{100^{\circ}C}$	4.4794	90.89	1.18	7.93
$\acute{E}_{100^{\circ}C}$	17.2297	6.59	0.08	93.33

shows the HPLC analyses for $S'_{100^{\circ}c}$, $S'_{100^{\circ}c}$ and $E''_{100^{\circ}c}$ in which the amount of impurities have been reduced dramatically. The impurities in $S_{100^{\circ}c}$ which holds the highest amount is 4.41 percent weight and the $S'_{100^{\circ}c}$ phase which holds most efficient extraction contains1.18percent weight impurities. The amount of NMP in $S_{100^{\circ}c}$ and $S'_{100^{\circ}c}$ are similar, therefore, it can be said that n-heptane is very selective toward NMP and doesn't extract impurities.

Table 4. Summary of the NMP extraction in n-heptane in different temperatures.

Extraction temperature °C	NMP efficiency	Total efficiency	%sample extraction	%NMP by weight
25	5.53	10.49	0.5185	9.80
70	21.64	40.79	2.1723	85.68
100	53.26	64.23	5.0589	90.69

Shows the summary of the different temperatures used. As it can be seen with the increase in temperature more of the residue is dissolved in n-heptane also more NMP is extracted which results in the increase of the efficiency of the process.

Optimization of the extraction by increasing solvent residue ratio

Once the optimum temperature was determined, it was necessary to determine the effect of solvent residue ratio on the efficiency of the extraction. Four sets of weight percent rations 1:1, 2:1, 4:1, 6:1 were prepared in such a way that 10 gr. residue and equal or increasing amount of n-heptane were mixed at 100c.There was no separate phase formation as previous sections, however, as the mixture cooled phases began to form. The results are summarized in table5.

Table 5. n-heptane extraction of NMP in different ratios.

Solvent residue ratio	NMP efficiency	Total efficiency	Weight of extracted sample	%NMP by weight	%Impurity by weight
2:1	53.26	64.28	5.0589	90.69	1.55
4:1	47.66	77.73	4.4521	92.23	0.59
6:1	30.43	83.38	3.2001	82.28	0.37
8:1	25.27	85.29	3.0101	81.15	0.31
9:1	20.18	86.97	2.9862	80.27	0.28

As it evident from the table, with the increase in solvent, total efficiency is also increased, however, because the NMP solubility in n-heptane is constant at set temperature, by the reduction in temperature, the NMP rich phase is reduced, therefore, the more solvent is used the more NMP remains in solvent thus reduces NMP weight percent which is our goal. However, at higher solvent-residue ratio, this process renders inefficient with an intangible reduction in total efficiency and NMP weight percent. Therefore, a 6:1 solvent ratio seems to be optimum, and since this ratio tends to hold the highest acceptable total efficiency, and since the separation of NMP and n-heptane both having two very different boiling points, this method could save large amount of very valuable solvent.

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