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Research Article

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Separating dimethylbenzene and butyl acetate

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ABSTRACT

The recovery of dimethylbenzene and butyl acetate from industrial spent solvent by batch distillation was studied. The first experiment was the batch distillation of a pretreated material. The second experiment was a heterogeneous azeotropic batch distillation, and the final experiment involved removing the light and heavy parts of the industrial spent solvent oil and then separating dimethylbenzene and butyl acetate from the remaining mixture. Different types of batch distillation methods to distill from waste solvents gave different recoveries of butyl acetate and dimethylbenzenes, and the dimethylbenzene-rich fractions generally contained low concentrations of butyl acetate. Using a heterogeneous distillation process allowed the separation process to be achieved at a lower temperature than was required for the normal distillation process. Multiple distillations gave higher recoveries and concentrations of butyl acetate and dimethylbenzenes in the distillates, but obviously involved higher levels of energy consumption. The process used for a particular industrial application should be chosen to suit the actual requirements of the application.

Keywords: batch distillation; recovery; dimethylbenzene; butyl acetate

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INTRODUCTION

The discharge of industrial waste has recently increased sharply in Chinese cities, especially in cities in economically developed regions, so ensuring that hazardous waste is handled properly has become more important than ever [1]. Organic solvents, in particular, are widely used in different industries, and in Qingdao alone 6500–8000 t of recyclable waste organic solvents are produced annually. The automobile industry, as an example, uses a lot of valuable organic solvents in the processes of painting and cleaning cars [3,4]. A large number of aromatic substances are also used in the lubricant detergent recycling process [5]. A lot of waste oils from vehicles are rich in benzene, toluene, ethylbenzene, dimethylbenzene, and butyl acetate, but contain large ranges of organic impurities, are viscous, have complex compositions, are pungent, and can cause harm to the human nervous system and to ecological systems [6–9].

Waste organic solvents are, at the moment, generally incinerated, distilled, or processed using other methods, such as the dilution method [10–14]. Incineration involves the direct combustion of the waste oil and solvent using a strictly controlled combustion process. Non-compliance with the strict combustion process requirements results in the process producing polychlorinated dibenzo-p-dioxins and dibenzofurans and soot, and these can be more serious environmental problems than the waste oil and solvent being disposed. Incineration also involves high processing costs (about 3000–3500 yuan/t), so this method is not currently desirable from the point of view of the available technology and economic conditions. Recovering waste solvents using vacuum distillation and a fractionation cooling tower gives relatively good recoveries of the main components of solvent mixtures, but this method has two major shortcomings, in that it requires airtight vacuum distillation equipment that is expensive and that it consumes a great deal of energy. Diluting waste solvent in a lot of water is not only wasteful of water but it leads to large

amounts of polluted water being produced, so this method is not desirable. There are currently, therefore, no effective treatment methods for waste solvents produced by the automobile manufacturing processes used in China.
In the study presented here, we batch distilled waste oil that contained solvents, which had been produced in car manufacturing processes [15–16]. The aim was to recover dimethylbenzene and butyl acetate from the waste oil with high yields, so that these solvents could be reused. Using the batch distillation process could effectively decrease the amount of environmental pollution produced and lead to lower processing costs for waste oil.

EXPERIMENTAL SECTION

1.1 Materials and equipment

o-Xylene (1,2-dimethylbenzene), m-xylene (1,3-dimethylbenzene), p-xylene (1,4-dimethylbenzene), butyl acetate, benzene, and toluene (chromatographically pure) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). n-Heptane, 1-octane, and methylcyclohexane were obtained from the Tianjin Chemical Reagent Plant (Tianjin, China). Waste solvents were obtained from FAW–Volkswagen (Changchun, China).The batch distillation apparatus was obtained from Komen Technology Development Co., Ltd. (China). A 6890N gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) was used for the gas chromatographic analyses, and an AUY120 (Shimadzu Corp., Kyoto, Japan) electronic balance was used when appropriate.

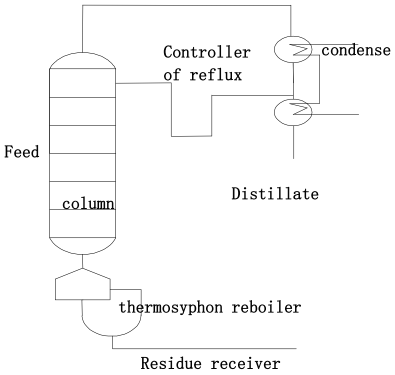

Fig. 1 Schematic diagram of the distillation column

1.2 Experimental methods

1.2.1 Preparation of standard solution

Different amounts of the analytes were weighed accurately using an electronic balance so that standard solutions with eight different concentrations could be prepared. The standards were analyzed by gas chromatography to give a calibration curve for each analyte.

1.2.2 Simple distillation

The waste solvent that was used had a complex composition, so the first process it was subjected to was ordinary distillation to remove impurities and provide colorless and transparent materials for the distillation tests.

1.2.3 Ordinary batch distillation

The waste solvent (300–400 mL) was distilled and the condensate was collected. The bottom of the distillation column was heated, and the temperatures at different measurement points in the distillation column were automatically recorded using a computer.

1.2.4 Heterogeneous distillation

An amount of water appropriate to the chosen oil to water volume ratio was added to the feedstock and an otherwise ordinary distillation was performed. The performance of the method was evaluated from the changes in the temperature over time. The mass and volume of the sample and distillates were measured, and a heptane internal standard was added to the distillate fractions to allow them to be quantitatively analyzed by gas chromatography.

1.2.5 Multiple distillation

The raw material was distilled at a low and a high temperature with the intention that only the dimethylbenzenes and butyl acetate would be distilled. The experimental conditions were the same as used for the ordinary distillation.

1.3 Analysis

The samples were analyzed using an Agilent 6890N gas chromatograph equipped with an HP-5 chromatography column. The gas chromatograph settings were chosen by taking setting from the literature [17–22] and modifying them to make them appropriate to the waste product that we used. The oven temperature program started at 60 °C and increased at 3 °C/min to 70 °C , which was held for 1 min, then increased at 2 °C/min to 80 °C, which was held for 2 min, then finally increased at 50 °C/min to 150 °C. The total run time was 13.73 min.. The injector temperature was 200 °C and the volume injected was 0.2 µL. The mobile phase was hydrogen, which was used at a flow rate of 40 mL/min. The air flow rate in the detector was 450 mL/min, and the detector temperature was 250 °C. An internal standard quantification method was used.

RESULTS AND DISCUSSION

2.1 Composition of the waste oil containing solvents

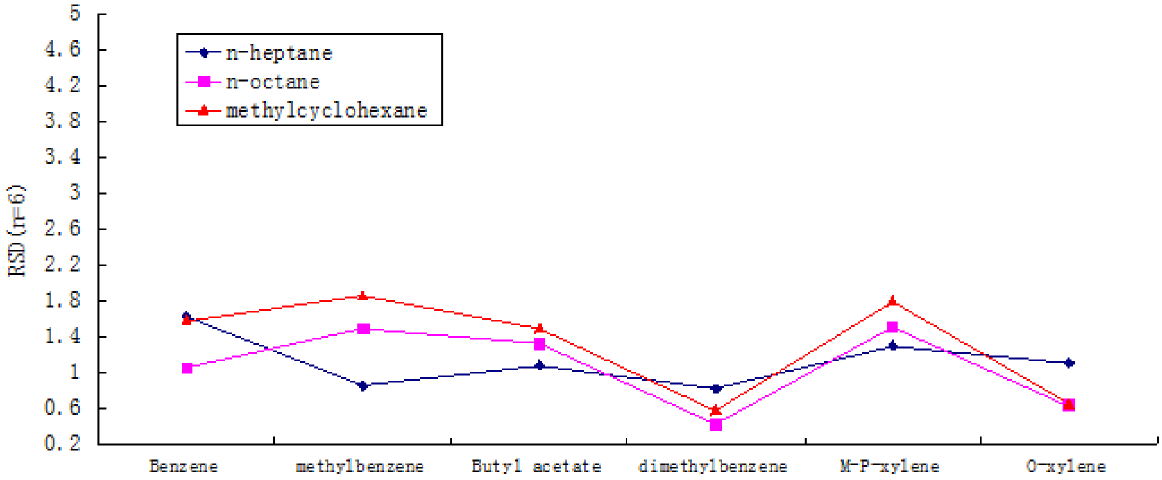

Fig. 2 Relative standard deviations of the solvent concentrations determined using three different internal standards

Figure 2 shows the relative standard deviations (RSD) that were found for the concentrations of the solvents that were analyzed using three different internal standards (n = 6 for each internal standard), n-heptane, n-octane, and methylcyclohexane. All of the RSD were within an acceptable range. It can be seen that that RSD were different for different analytes, and that the RSD found using the three internal standards were similar for butyl acetate and dimethylbenzene, and that the RSD for the different analytes varied less using n-heptane as an internal standard and more using n-octane as an internal standard.

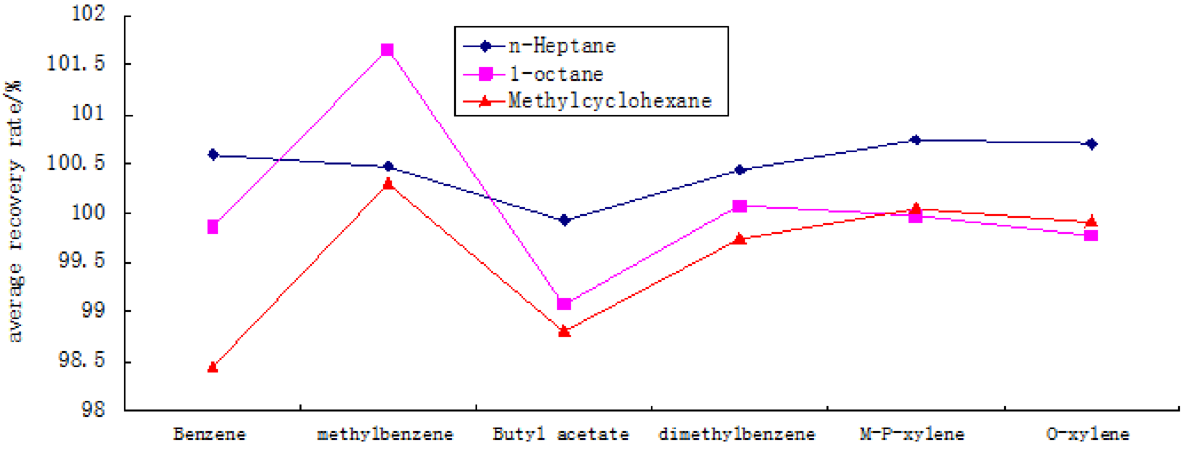

Fig. 3 Analyte recoveries achieved using three different internal standards

The average recoveries of the solvents that were analyzed, determined using three different internal standards, are shown in Figure 3. It can be seen that the method gave acceptable recoveries for each analyte using each internal standard. The recoveries of the different analytes varied less than using n-heptane as an internal standard than using the other two internal standards, indicating that the analytical method was more stable using n-heptane as an internal standard than using the other internal standards. A comprehensive analysis of Figures 2 and 3 showed that n-heptane was the best internal standard to use in the analytical method. The correlation coefficients (R^2) for the standard curves for the analytes, using n-heptane as an internal standard, were 0.9998–1.000.

Table 1 Composition of the spent solvent that was analyzed

Ingredient	Benzene and toluene	Butyl acetate	Dimethylbenzenes	Other components
Content / %	6.92	36.65	42.24	14.19

A waste solvent oil was analyzed after it had been through the simple distillation process, which gave a colorless oil. The complex components were analyzed by gas chromatography, and the concentration of each component in the waste oil was calculated. The crude distillation of each batch of waste oil gave a slightly different composition because of variations in the samples that were taken.

2.2 Simple batch distillation

The pretreated raw material described above was used in batch distillation experiments using reflux ratios (R =L/D) of 3, 4, 5, 6, and 7. The dimethylbenzene and butyl acetate components were separated at a specific temperature at an R of 6.

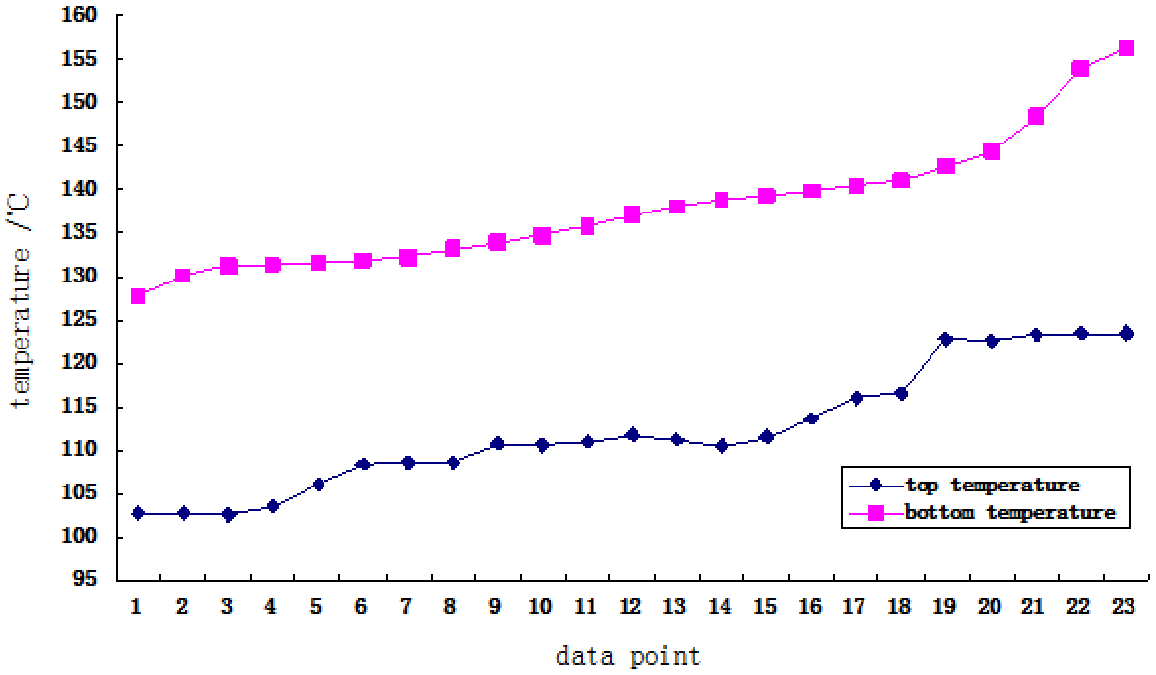

Fig. 4 Temperatures at the top and bottom of the cooling tower during the batch distillation process

Figure 4 shows the temperatures at the top and bottom of the cooling tower at each sampling time point during the batch distillation, and it can be seen that the temperature at the bottom of the tower was between 127.8 and 156 °C and the temperature at the top of the tower ranged from 102.6 to 123.5 °C. The dimethylbenzenes and butyl acetate will be removed from the waste solvent in these distillate temperature ranges. The temperature at the top of the tower was essentially constant when the first three samples were taken, and large amounts of benzene and toluene and other light components were removed in these fractions. The temperature at the top of the tower increased rapidly from the fourth to the sixth samples, and the composition of the distillate changed greatly over these samples. The temperature at the top of the tower changed little from sampling points six to fourteen, but the trend in the changes in the temperature changed slightly between sampling points nine and fourteen, indicating that the main components in the distillate remained constant but that the relative contributions of individual components changed. The temperature at the top of the tower at sampling time point fourteen, and the distillate composition also changed at this point, becoming dominated by 1,4-dimethylbenzene and butyl acetate. The temperature at the top of the tower increased rapidly at sampling point nineteen, indicating that at this time the distillate was dominated by dimethylbenzenes.

The butyl acetate concentrations and the dimethylbenzene concentrations in the samples that were collected are shown in Figures 5 and 6, respectively. When the temperature at the top of the tower was 109 °C (before complex components were distilled), the distillate contained small amounts of butyl acetate, dimethylbenzenes, and light components, and the butyl acetate concentration in the distillate increased as the temperature increased, whereas the dimethylbenzene concentrations initially decreased as the temperature increased.

The butyl acetate concentration in the distillate, when an R of 6 was used, reached a steady state at 88.7–90.5% when the temperature at the top of the column was 109–112 °C, corresponding to sampling points nine to fourteen, and this corresponded with the temperature changes that are shown in Figure 4. The dimethylbenzene concentrations in the distillate remained unchanged until the temperature at the top of the tower reached 111.5 °C, when the butyl acetate concentration began to decrease and the dimethylbenzene concentrations began to increase. The dimethylbenzene concentrations had increased to >90% when the temperature at the top of the tower had reached 122 °C, and the dimethylbenzene concentrations had reached a steady state at 95–98% when the temperature at the top of the tower had reached 122.6–123.5 °C. The butyl acetate concentration in the distillate at this time had decreased to about 1.2%.

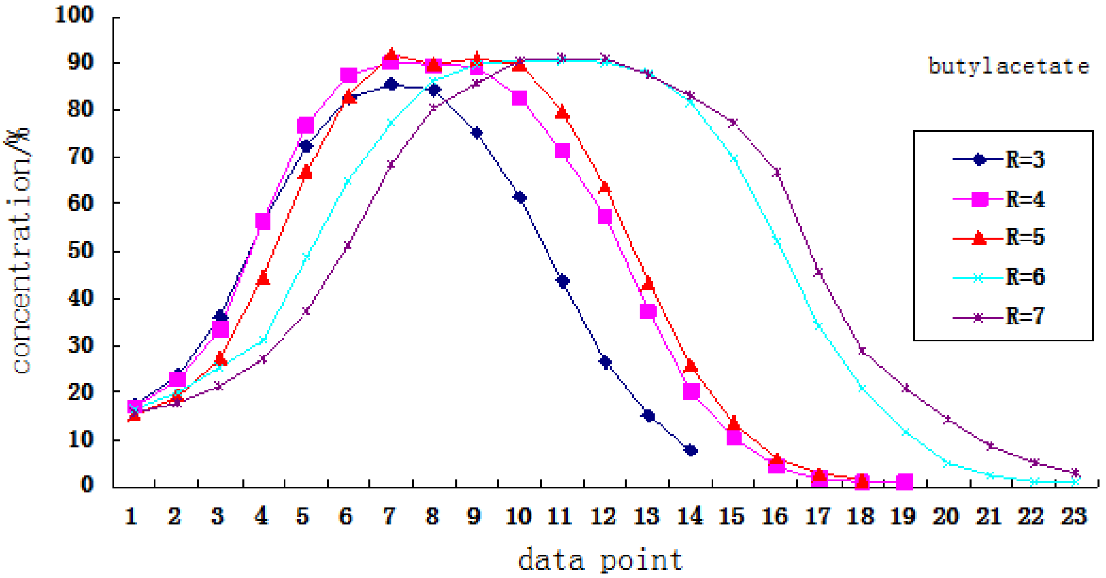

Fig. 5 Butyl acetate concentration in the distillate collected at each sampling time point when batch tests at different reflux ratios (R) were performed

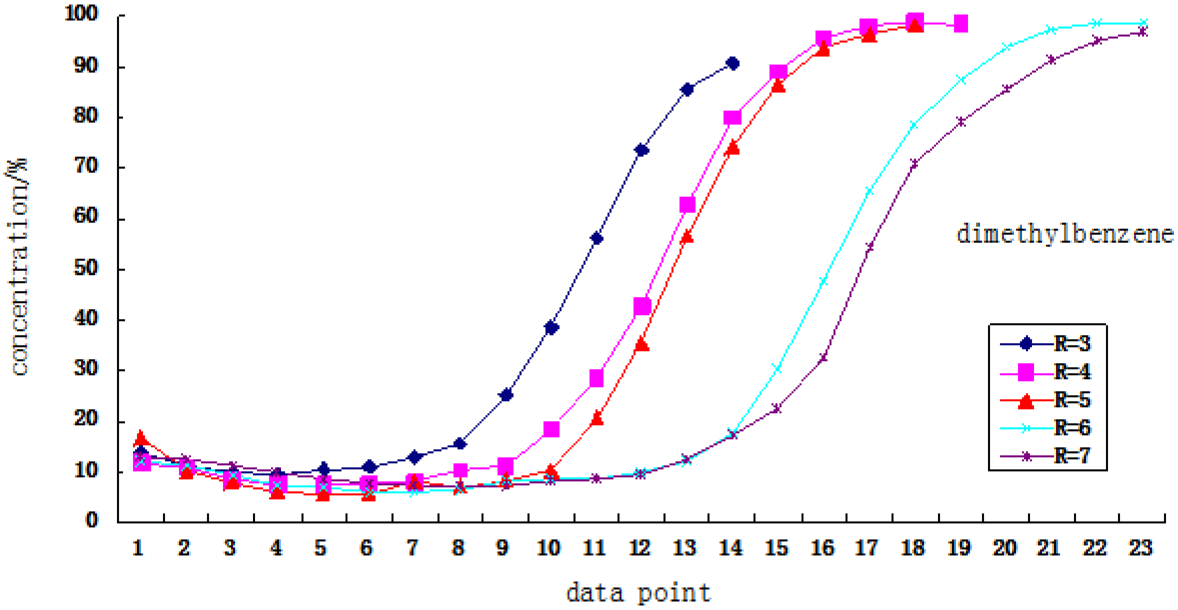

Fig. 6 Dimethylbenzene concentrations in the distillate collected at each sampling time point when batch tests at different reflux ratios (R) were performed

The effect of the reflux ratio on the dimethylbenzene and butyl acetate yields and contents in the distillate are shown in Tables 2 and 3, respectively.

Table 2 Effect of the reflux ratio on the product yield

Reflux ratio / R		3	4	5	6	7
Yield / %	Dimethylbenzene	95.1	95.01	94.8	90.32	90.8
	Butyl acetate	98.6	98.6	97.5	97.3	96.7

Table 3 Effect of the reflux ratio on the product concentration in the distillate

Reflux ratio / R		3	4	5	6	7
Concentration in the distillate / %	Dimethylbenzene	85–90.7	95.6–98.8	94–98.2	94–98.5	95–97
	Butyl acetate	82.7–85.4	89.03–90.03	89.7–91.8	89.7–90.6	90.6–91

It can be seen from Table 2 and 3 that increasing the reflux ratio decreased the dimethylbenzene and butyl acetate recoveries. This would have been because increasing the reflux ratio increased the amount of time taken for the distillation process to occur. The dimethylbenzene recovery decreased particularly noticeably when the reflux ratio was increased from 5 to 6. The separation of dimethylbenzenes and butyl acetate improved as the reflux ratio was increased to 4, and below that they were poorly separated.

2.3 Heterogeneous batch distillation

Table 4 Temperatures at the top of the cooling tower and in the reactor region of the tower during the heterogeneous batch distillation process

Oil–water ratio	Top temperature range / °C	Tower reactor temperature range / °C
2:1	87–89.2	85.8–103
3:1	86.5–89.5	90.5–111
4:1	87–117	83–145

From Table 4, it can be seen that the temperature at the top of the cooling tower was 86.5–89.5 °C when the oil–water ratio was 3:1. When the water content was lower (using an oil–water ratio of 4:1), the later part of the distillation process was similar to the process achieved in the ordinary distillation process, and the temperature at the top of the cooling tower was relatively high.

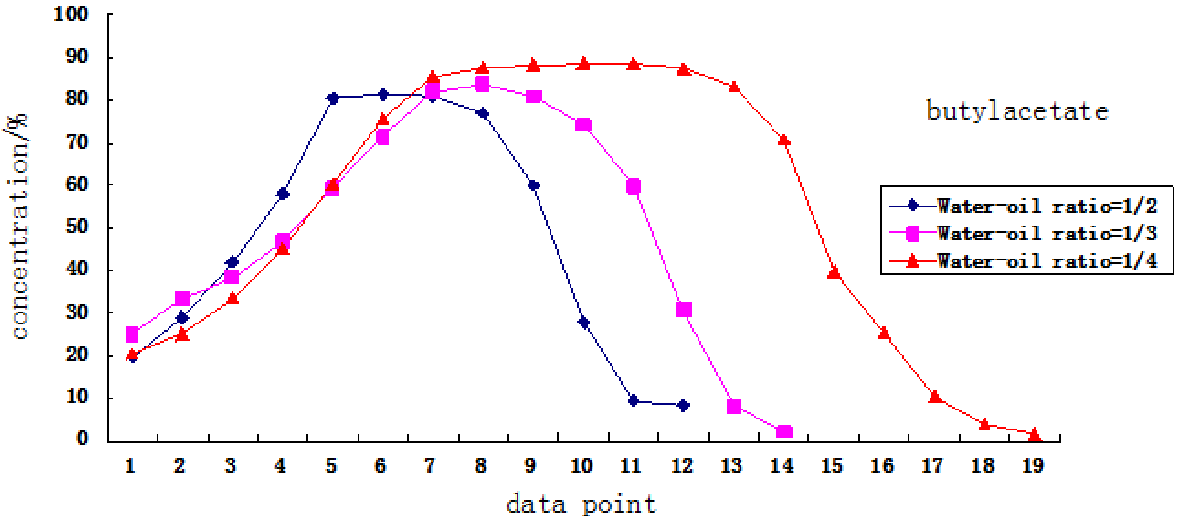

Fig. 7 Butyl acetate concentrations at different sampling time points during the heterogeneous batch distillation process

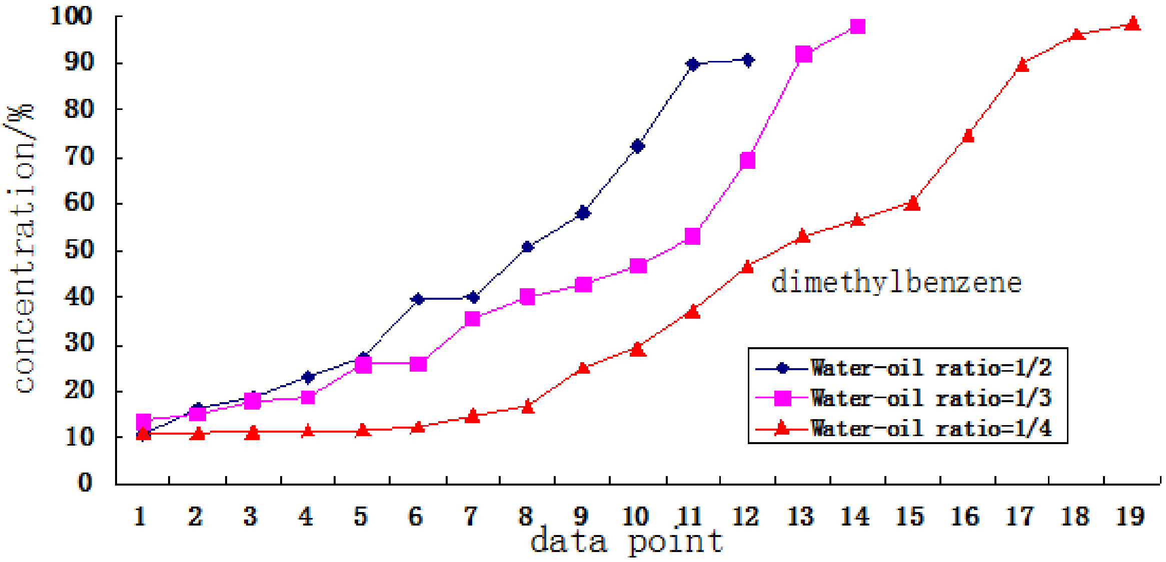

Fig. 8 Dimethylbenzene concentrations at different sampling time points during the heterogeneous batch distillation process

Figures 7 and 8 show the butyl acetate and dimethylbenzene concentrations, respectively, in the distillate at different sampling time points in the heterogeneous batch distillation process using different oil–water ratios (and R = 4). It can be seen that the butyl acetate and dimethylbenzene concentrations changed, following similar trends to the trends found in the simple batch distillation process.

Table 5 Dimethylbenzene and butyl acetate yields using different oil–water ratios in the heterogeneous batch distillation process

Oil–water ratio	2	3	4
Dimethylbenzene / Yield greater than 90%	18.7	15.48	15.21
Butyl acetate / Yield greater than 80%	51.07	40.28	34.04

As can be seen from Table 5, using a lower oil–water ratio (i.e., adding more water relative to the volume of oil) gave higher dimethylbenzene and butyl acetate recoveries.

2.3 More batch distillation tests

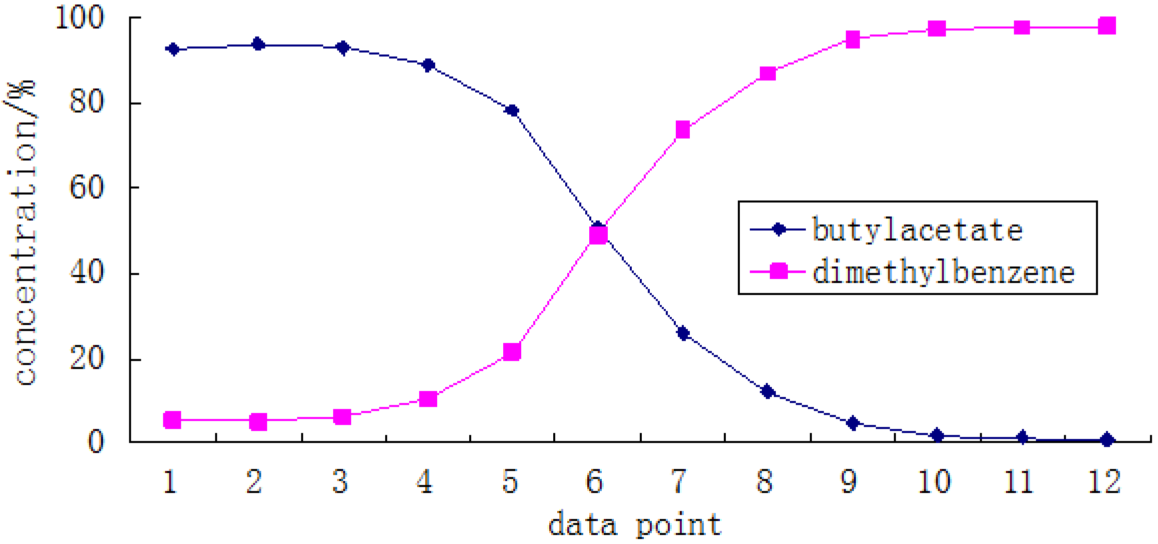

Fig. 9 The concentrations of butyl acetate and dimethylbenzene in a batch distillation process using a reflux ratio of 4 at different time points

Figure 9 shows the results of a distillation process using an R of 4. The raw material contained only butyl acetate and dimethylbenzene. Changing the temperature at the top of the cooling tower caused the concentrations of both solvents to change. The distillate contained a butyl acetate concentration of higher than 95% when the temperature at the top of the tower was 109.3–109.8 °C, and the dimethylbenzene concentration in the distillate began to increase and the butyl acetate concentration began to decrease when the temperature reached 110 °C. The dimethylbenzene concentration in the distillate was higher than 95% and the butyl acetate concentration was lower than 3% when the temperature at the top of the tower was higher than 119 °C.

CONCLUSION

The first experiment gave a butyl acetate concentration of 88.7–90.5% in the condensate and a yield of 97.3% when the temperature at the top of the cooling tower was 109–112 °C, and a dimethylbenzene concentration higher than 95% when the temperature at the top of the cooling tower was higher than 122 °C and the temperature at the bottom of the tower was higher than 144 °C. The highest butyl acetate and dimethylbenzene concentrations found in the condensate in the second experiment were 89% and 97%, respectively, when the oil to water ratio was 3:1 (by volume) and the reflux ratio was 4, and the temperatures at the top and bottom of the cooling tower were related to amount of water added to the system. The third experiment gave a butyl acetate concentration higher than 95% in the condensate and a yield of 95% when the temperature at the top of the cooling tower was 109.3–110.6 °C, and a dimethylbenzene concentration in the condensate higher than 95% and a yield of 74.2% when the temperature at the top of the tower was higher than 119 °C.

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