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Ruthenium ion catalytic oxidation depolymerization of lignite under ultra-low dosage of RuCl₃ catalyst and separation of the organic products with inorganic salts

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Depolymerization of lignite into valuable chemicals *via* ruthenium ion catalytic oxidation (RICO) is a potential route for the non-energy utilization of lignite. However, the high cost of the Ru catalyst during depolymerization and the high content of inorganic salts in the product solution limit the development of this route. In this work, RICO depolymerization of lignite was conducted under an ultra-low dosage of RuCl₃ catalyst to decrease the usage of the catalyst during the RICO process. Different approaches were attempted to fulfill the separation of benzene polycarboxylic acids (BPCAs) products with the inorganic salts derived from the oxidant NaIO₄, including butanone extraction and desalting *via* crystallization under different temperatures. The results show that lignite can be efficiently depolymerized under the mass ratio of RuCl₃/lignite as low as 1/1000 by prolonging the reaction time without decreasing the depolymerization degree and BPCAs yields compared to the commonly used mass ratio of 1/10. Butanone can extract *ca.* 91% of the total BPCAs in the product solution, and the inorganic salts content (mainly NaIO₃) in the extraction solution was as low as 0.19 mg mL^{-1}. A new strategy of first acidification of depolymerization aqueous solution by HCl and then extraction by butanone is proved to be efficient for the separation of BPCAs with inorganic salts. Salting out *via* crystallization under lower temperature can remove *ca.* half content of the salts, and the efficiency is inferior to butanone extraction. The low usage of RuCl₃ can efficiently decrease the catalyst cost of the RICO process, and butanone extraction can fulfill the enrichment of BPCAs and the separation of BPCAs with inorganic salts. This work is meaningful for the potential application of RCIO depolymerization of lignite for the production of valuable chemicals.

Introduction

Coal is an important fossil resource and has played significant roles in the development of the Chinese industrial economy.[1] Lignite accounts for about 41.2% of China's coal reserves,[2] and its characteristics of high moisture and volatile matter make it unable to be widely used in traditional utilization modes such as combustion, pyrolysis, gasification, and liquefaction like middle–high rank coal.[3–8] With the continuous consumption of high rank coal, the utilization of low rank coal with high H/C ratio and high oxygen-containing functional groups becomes more and more important.[9] Therefore, how to use the low rank coal more efficiently and cleanly has become an important issue.

The typical representative of low-rank coal is lignite, which is abundant in aromatic ring structures, making lignite potential as raw materials for the production of high value-added benzene polycarboxylic acids (BPCAs).[9] Thermal extraction by organic solvent and oxidative depolymerization are typical procedures for the transformation of lignite into valuable chemicals. Extraction of lignite with organic solvent CS₂ shows that lignite is also rich in aliphatic hydrocarbon structure, which also provides the possibility of its degradation into small molecular fatty acids.[10] There are many oxidation methods for the preparation of carboxyl chemicals by oxidation depolymerization, such as alkali-oxygen oxidation,[11] sodium hypochlorite oxidation,[13,14] nitric acid oxidation,[15] catalytic O₂ oxidation,[16] H₂O₂ oxidation,[17,18] ruthenium ion catalytic oxidation,[22–25] *etc.* Alkali-oxygen oxidation method can obtain various small molecular fatty acids and BPCAs.[12] However, the reaction conditions are relatively harsh, requiring high temperature, high pressure, and a large amount of acid and alkali, which is difficult to recover and unfriendly to the environment. In the

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sodium hypochlorite oxidation process, besides the water-soluble fatty acids and a large number of BPCAs, many chlorinated products are also produced, and the depolymerization of lignite is not complete.[29] Liu *et al.*[19] investigated that the pretreatment of Shengli lignite with H_2O_2 before sodium hypochlorite oxidation could significantly improve the yield of fatty acids and BPCAs, and the generation of chloro-substituted alkanoic acids was inhibited. However, the price of the oxidant was high and limited the application of this route. For nitric acid oxidation, the strongly oxidative and corrosive nitric acid is used, which limit its large scale application. For catalytic O_2 oxidation, Yang *et al.*[20,21] proposed the oxidation method using $NaVO_3$, $Fe_2(SO_4)_3$, and $FeCl_3$ as co-catalyst and O_2 as oxidant. Although the reaction avoids the use of a large number of inorganic acids and bases, the reaction conditions are not mild, still under high temperature and high pressure, and the carbon yield is low. For ruthenium ion catalytic oxidation (RICO), the reaction conditions are relatively mild typically under 35 °C. Lv *et al.*[26] studied the aromatic species structure of Huolinguole lignite by RICO, and found that the soluble species mainly consist of alkanedioic acids while BPCAs mainly contain carboxylic acids with less than four carboxylic groups. Due to the mild reaction condition and high efficiency in the depolymerization, RICO exhibits high potential for the application in the depolymerization of lignite.

However, the high cost of the precious ruthenium catalyst limits the development and application of RICO. In our previous study, the efficient recycling procedure of the homogeneous ruthenium catalyst using CCl_4 extraction was established.[27] It was proved that the ruthenium catalyst could be reused for at least 5 times with no obvious decrease of the BPCAs yields. The dosage of the ruthenium catalyst in the reported work is often high, with mass ratio of $RuCl_3$/lignite as high as 1 : 10, which makes it impossible to be adopted in real application. Together with the reuse of the ruthenium catalyst, decreasing the usage of the ruthenium catalyst is another route to cut the cost of the catalyst in RICO. Besides the high cost of the catalyst, another bottleneck for RICO is that the high usage of the oxidant $NaIO_4$ leads to the formation of large amount of $NaIO_3$, which causes troubles in the separation of the target products and the formation of salt-containing wastewater. Therefore, studies concerning RICO under low-dosage of the ruthenium catalyst and the separation of inorganic salt from organic products are highly desired.

In this work, the RICO depolymerization efficiency of lignite under ultra-low dosage of the ruthenium catalyst was studied. The depolymerization degree and BPCAs yields were analyzed under different dosage of the ruthenium catalyst. After depolymerization, the separation of organic products with the inorganic salt was studied using different routes, including salting out[28] under different temperatures and butanone extraction. The results showed that lignite could be efficiently depolymerized even under ultra-low dosage of the ruthenium catalyst with the mass ratio of $RuCl_3$/lignite 1/1000 compared to the commonly used 1/10, with depolymerization degree and total BPCAs yields up to 87% and 8.9%, respectively. Among the studied separation routes, butanone extraction is the most efficient in both removing the inorganic salt and enriching the BPCAs products. This work provides basic data for promoting the development of RICO depolymerization of lignite for the production of valuable organic acids.

Material and methods

Materials

Raw Shengli lignite (RSL), from Inner Mongolia Shengli Coal-field in China. Ruthenium(III) chloride ($RuCl_3$, AR, 99.5%), sodium periodate ($NaIO_4$, AR, 99.5%), sodium iodate ($NaIO_3$, AR, 99.5%), acetonitrile (CH_3CN, AR, 99.5%), carbon tetra-chloride (CCl_4, AR, 99.5%) were purchased from Innochem. Butanone was distilled before use. The distillation procedure is as followings: The purchased butanone is placed in a round-bottom flask and heated at 100 °C in an oil bath connected to a distillation device, and the system is sealed to prevent butanone volatilization out of the system. Other solvents (except butanone) used in the experiments are analytical grade reagents and directly used as received without further treatment.

RICO depolymerization reaction

As shown in Fig. 1, RSL (5 g), $RuCl_3$ (0.5 g, 0.05 g, 0.005 g), $NaIO_4$ (100 g), and $CCl_4 : CH_3CN : H_2O$ with volume ratio of 2 : 2 : 3 (total volume, 700 mL) were put into a 1000 mL spherical flask. The mixture was allowed to react with magnetic stirring under the temperature (35 °C) and different reaction time (0–139 h). After the reaction, the reaction mixture was filtered to obtain filter cake and filtrate, and the filtrate was separated by phase separation to obtain organic phase and aqueous phase. The target small molecules such as BPCAs exist in the aqueous phase. The filter cake is washed with distilled water until it is clear. The purpose is to remove the sodium iodate salt and sodium periodate salt as well as humic acid. The residual solid phase is then placed in a 105 °C air drying oven for
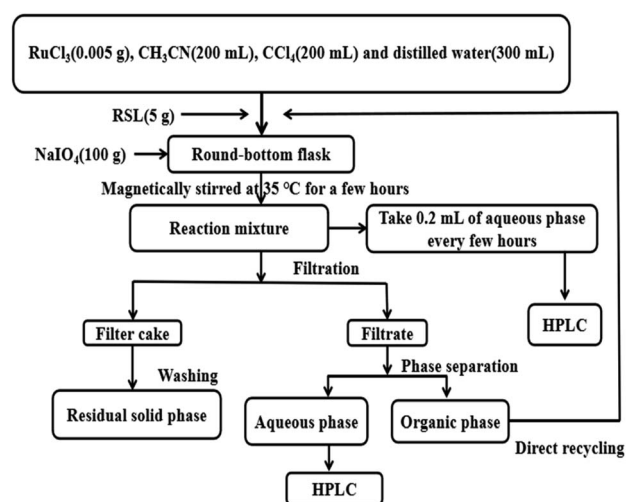

Fig. 1 Procedure of the RICO reaction, subsequent sample treatment, and the recycling of the Ru-containing solvent.

approximately 12 h. The mass ratio of RuCl₃ to lignite was varied, *i.e.* 1 : 100 and 1 : 1000, respectively.

$$\text{Depolymerization degree of lignite} = \left(1 - \frac{\text{the mass of residual solid}}{\text{the initial mass of lignite}}\right) \times 100\%$$

$$\text{Yields(BPCAs)} = \frac{\text{Mass of BPCAs}}{\text{Mass of organic matter in lignite}} \times 100\%$$

where the mass of organic matter in lignite = mass of lignite-mass of ash-mass of moisture.

Separation of BPCAs with inorganic acids

Butanone extraction was adopted to separate BPCAs from the mixture and fulfill the separation of organic products with the inorganic salt. The aqueous phase was extracted three times with equal volume of butanone. After extraction, butanone was removed *via* rotary evaporation under reduced pressure and 40 °C. Then the obtained depolymerized product powder was dried in a drying oven at 105 °C to prevent the presence of residual butanone. Finally, the depolymerized product powder was diluted with distilled water to the same volume as the water after depolymerization. The extraction phase was analyzed by HPLC to calculate the contents of BPCAs. The extracted phase was subjected to ICP-MS to determine the content of sodium ions.

Besides butanone extraction, crystallization under low temperatures was also attempted to fulfill the removal of the inorganic salt. As shown in Fig. 2, before crystallization, certain volume of the depolymerized aqueous solution was taken and condensed to different volume by rotary evaporator to improve the concentration of inorganic salts, and partial inorganic salts were crystallized and removed. Then the solution was stored under different temperatures, *i.e.* room temperature, 4 °C and −7 °C for 2–3 h. The precipitate was removed by centrifugation. The precipitated salts were dried, weighed, and characterized by XRD. The precipitated salts were also solubilized in water and

analyzed by HPLC and TOC to test the residue of BPCAs and the total organic carbon.

$$\text{Desalination efficiency (\%)} = \left(\frac{\text{The mass of precipitated salt}}{\text{The mass of salt in the aqueous phase of depolymerization}}\right) \times 100\%$$

$$\text{The loss ratio of BPCAs (\%)} = \frac{\text{The mass of BPCAs in the precipitated salt}}{\text{The mass of BPCAs in the aqueous phase of depolymerization}} \times 100\%$$

Analysis and characterization method

The BPCAs in the depolymerized product was determined by HPLC(SHIMADZU LC-20AT).[30] A binary gradient elution procedure was used for HPLC analysis. The mobile phase was acetonitrile and 0.1% (volume fraction) phosphoric acid aqueous solution, and the stationary phase was C18 bonded to silica gel (Shim-pack GIST C18, 5 mm). The BPCAs were quantified using a UV detector at 235 nm. The cylinder temperature was 45 °C, and the flow rate of the mobile phase was 0.8 mL min⁻¹. The gradient elution procedure was as follows: at the beginning, the volume ratio of acetonitrile to aqueous solution was 5 : 95, the ratio linearly increased to 15 : 85 over 10 min and then remained unchanged for 20 min, and finally, the ratio was decreased to 5 : 95 over 2 min. The structures of typical BPCAs obtained from RICO reaction of lignite are shown in Scheme 1. The salts precipitated by the crystallization method were analyzed by XRD. XRD was performed on a Japan-Science SmartLab-9 kW diffractometer with a scanning range of 5–90° at a rate of 10° min⁻¹. The total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC) in the depolymerization solution and salt precipitated by crystallization were analyzed on Total Organic Carbon Analyzer (SHIMADZU TOC-L VCPN).
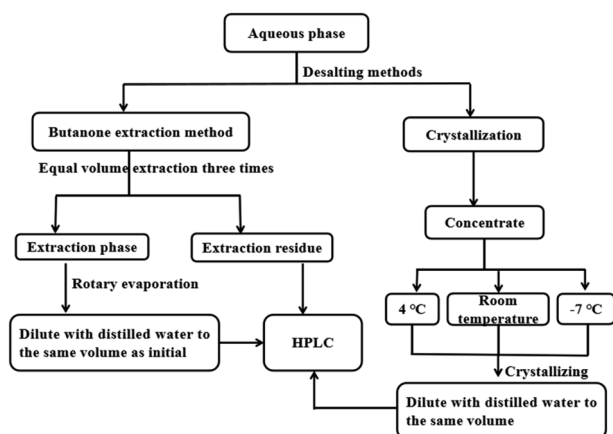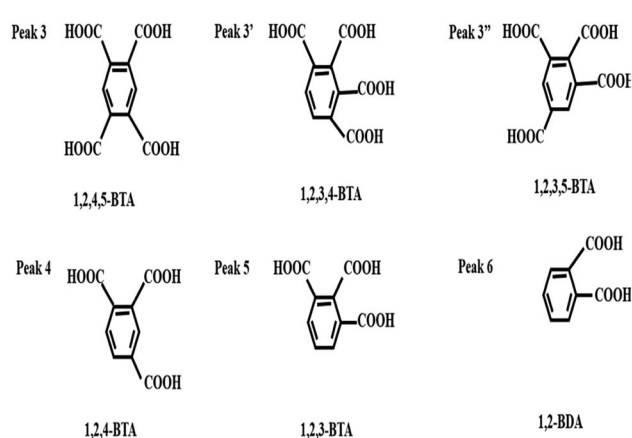

Fig. 2 Different procedures of removing inorganic salts in the depolymerized solution.

Scheme 1 The typical structures of BPCAs obtained from the depolymerized products *via* RICO of lignite.

Results and discussion

Comparison of the raw and demineralized lignite

The RICO depolymerization efficiency of raw lignite and demineralized lignite were compared. The content of inherent minerals in lignite was analyzed in our previous work.[27] For comparison, the raw lignite was demineralized before depolymerization according to our previous report to check the effect of minerals on the depolymerization and subsequent separation.[31] The results were shown in Fig. 3. The differences in the yields of several typical BPCA products were not obvious for the raw and demineralized lignite (Fig. 3a). This result indicates that the inherent minerals in lignite have no significant effect on the yields of BPCAs during RICO depolymerization of lignite. Butanone extraction experiment shows that the extraction yields of different BPCAs have no obvious difference for the raw and demineralized lignite (Fig. 3b). These results show that the inherent minerals have no obvious effects on the depolymerization. Besides, the demineralization of the lignite requires a large amount of hydrochloric acid, leading to the formation of a large amount of wastewater containing acid and organic matter. Therefore, the raw lignite was directly used in the following studies.

Depolymerization of lignite under different RuCl$_3$ dosage

In order to decrease the usage of RuCl$_3$ and study the dosage of RuCl$_3$ on the depolymerization efficiency of lignite *via* RICO process, the mass ratio of RuCl$_3$ to lignite was decreased from the commonly used $1:10$ to $1:100$ and $1:1000$, respectively. The reaction time was prolonged under low RuCl$_3$ dosage. Different from the common reports, the initial amount of lignite is scaled up ten times, which can increase the amount of BPCAs in the depolymerized products because large amount of the depolymerized products was required in the following separation. The results were shown in Fig. 4. The depolymerization degree increased to around 90% in a short reaction time,
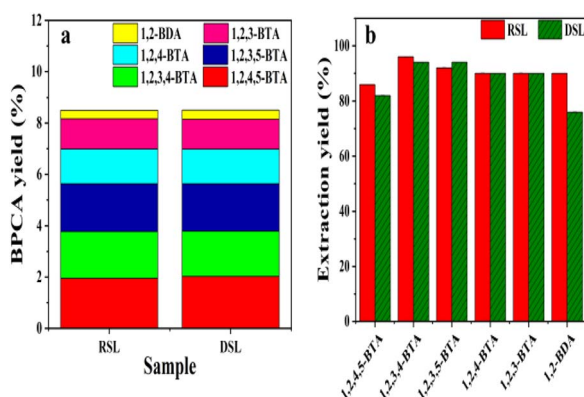

Fig. 3 The BPCA yield (a) and extraction yield of each BPCA (b) in the RICO of the raw lignite (RSL) and demineralized lignite (DSL). Reaction conditions: lignite sample 0.4 g, CCl$_4$ 20 mL, CH$_3$CN 20 mL, H$_2$O 30 mL, RuCl$_3$/lignite mass ratio 1/10.0, NaIO$_4$/lignite mass ratio 20.0/1, 35 °C, 6 h (a); RICO depolymerized aqueous phase (30 mL), constant volume of butanone (30 mL), extract for 1 h each time, three times (b).

indicating the high efficiency of RICO in the depolymerization of lignite (Fig. 4a). The total yields of BPCAs came to 9.0% when the initial amount of demineralized Shengli lignite (DSL) was 0.4 mg. The yields of BPCAs can also reach more than 8% after the initial amount of RSL was amplified to 5.0 g (Fig. 4b). The total content of BPCAs changed little after 15 hours, and the highest yields of BPCAs occurred at the reaction time of 27 hours. When the mass ratio of RuCl$_3$/lignite decreased to $1:100$, both the depolymerization degree and the total yields of BPCAs increased gradually (Fig. 4c and d). Compared to the mass ratio of RuCl$_3$/lignite $1:10$, the increase of depolymerization degree and the total yield of BPCAs became slower, but similar level could be achieved by prolonging the reaction time. The depolymerization yield can reach to 89% at reaction time of 24 h, and the total yield of BPCAs comes to 8.8% at the reaction time of 56 h. Further decreasing the mass ratio of RuCl$_3$/lignite to $1:1000$, with the extension of time, the depolymerization degree can also reach to nearly 87% at the reaction time of 120 h, and the total yield of BPCAs gradually increased until 115 hours to the maximum 8.9%. Another interesting phenomenon is that the increasing of the depolymerization degree is fast, while the increasing of the BPCAs yields is relatively slow. This is due to that lignite was first converted to humic acid macromolecules and then BPCAs during RICO reaction.[34] Lignite was first converted to humic acid macromolecules together with small amount of BPCAs, and this step was fast, leading to the fast increasing of the depolymerization degree. Humic acid macromolecules were further converted into BPCAs, but this step was slow, leading to the slow increasing of the BPCAs yields. In the Fig. 4a, c and e, the amount of catalyst RuCl$_3$ has a great influence on the depolymerization degree of lignite. When other conditions are the same, the less the catalyst amount, the lower the depolymerization degree, and only by extending the reaction time can we achieve similar depolymerization levels. In the Fig. 4b, d and f, the yield of BPCAs under the condition of different dosage of RuCl$_3$ and different time was studied. With the increasing of reaction time, the yield of BPCAs gradually increased and reached the maximum at a certain time. Subsequently, the acid yields tended to decrease, which is because the further increase of time may lead to the excessive oxidation of BPCAs, and the yields of BPCAs will decrease.[32] These results show that decreasing the mass ratio of RuCl$_3$/lignite has no obvious influence on the final depolymerization effect of lignite, only requiring a longer reaction time. Therefore, decreasing the mass ratio of RuCl$_3$/lignite is an efficient and potential approach to cut the catalyst cost of RICO depolymerization of lignite.

Comparison of desalting methods for the depolymerized supernatants

In the depolymerized supernatants, large amount of NaIO$_3$ exists due to the reduction of NaIO$_4$ as oxidant for RuCl$_3$ during RICO reaction, and the residual NaIO$_4$ also exists in the product solution. How to fulfill the removal of these inorganic salts and the separation of inorganic and organic components is a critical issue for the separation of target products. In this work,
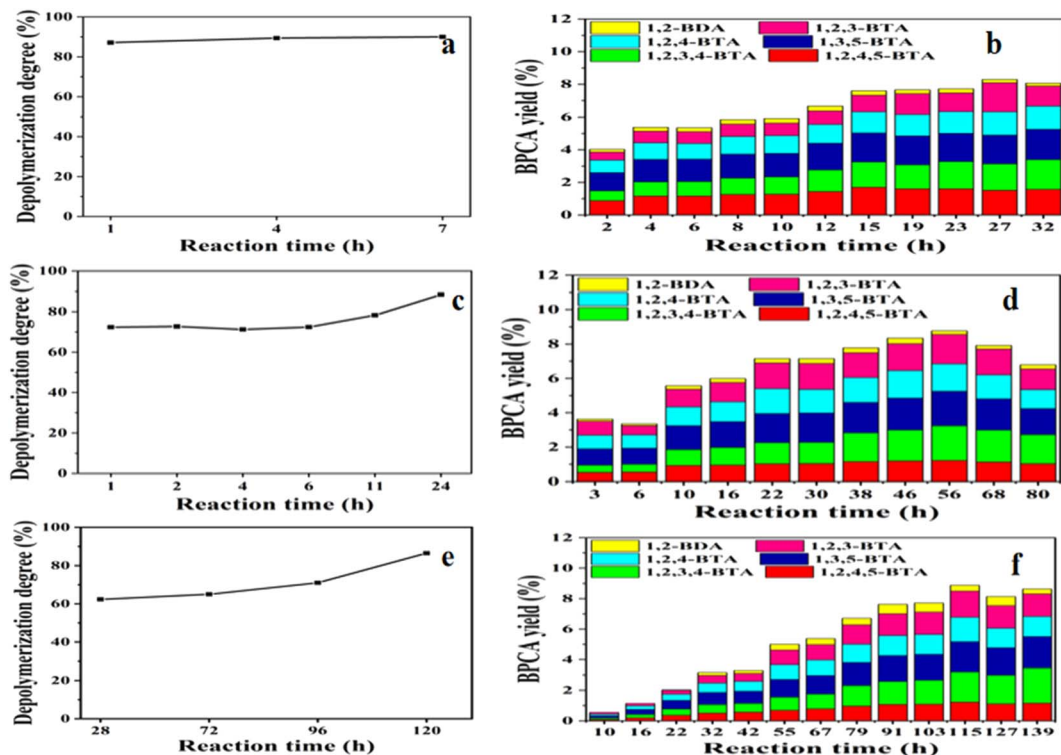
Fig. 4 Effect of the reaction time on the depolymerization degree of lignite (a, c and e) and BPCA yields (b, d and f) under different dosage of RuCl$_3$. Reaction conditions: RSL 5 g, CCl$_4$ 200 mL, CH$_3$CN 200 mL, H$_2$O 300 mL, NaIO$_4$/lignite mass ratio 20.0/1, 35 °C, (a and b) RuCl$_3$/lignite mass ratio 1/10, (c and d) RuCl$_3$/lignite mass ratio 1/100, (e and f) RuCl$_3$/lignite mass ratio 1/1000.

butanone extraction and desalting under different temperatures are used and compared to remove the inorganic salt and recycle the BPCAs products. As shown in Fig. 5, NaIO$_3$ and NaIO$_4$ indeed exist in the depolymerization solution with a total sodium concentration as high as 12.5 mg mL^{-1} (Table 1).

The separation of BPCAs with the inorganic salt NaIO$_3$ and NaIO$_4$ is a critical step for the production of BPCAs from lignite

by RICO. Therefore, how to separate BPCAs from the inorganic salts was studied. In the depolymerized solution (mother solution), there are high concentration of NaIO$_3$ and NaIO$_4$, which makes the signal intensity of BPCAs in HPLC profiles rather weak (Fig. 5a1). After extraction, no obvious NaIO$_4$ was detected in the residual solution, but it was detected in the extraction phase (Fig. 5a2 and a3). This result shows that NaIO$_4$ can be extracted by butanone together with BPCAs, which brings difficulties in the separation of BPCAs. The results also show that butanone can extract BPCAs efficiently (Fig. 5b1–b3). The total extraction yield of BPCAs can reach 91% after 3 subsequent extraction with equal volume butanone (Fig. 1b). The sodium residue in butanone phase was 0.19 mg mL^{-1} by ICP analysis (Table 1). In order to study the distribution behavior of NaIO$_3$ and NaIO$_4$ in the butanone and aqueous phase, the simulated
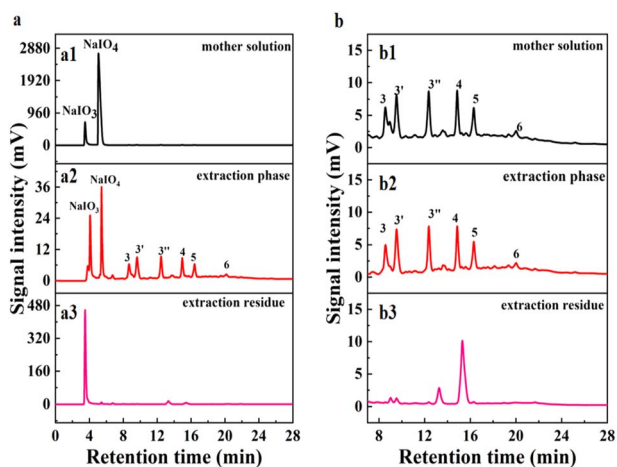

Fig. 5 HPLC profile of the depolymerized products from RSL. Profiles (b) are the enlarged view of the corresponding profiles (a) with retention time from 7 to 28 minutes. Separation conditions: extract the supernatant three times with an equal volume of butanone reagent.

Table 1 Sodium content in desalting methods[a]

Method of removing salt	Sodium content after desalting (mg mL^{-1})	Desalination efficiency (%)
Mother solution	12.5 mg mL^{-1}	
Room temperature	8.5 mg mL^{-1}	32.0
4 °C	5.9 mg mL^{-1}	52.8
−7 °C	5.8 mg mL^{-1}	53.6
Butanone extraction	0.19 mg mL^{-1}	98.5

[a] Conditions: the volume was condensed from 40 mL to 8 mL. Storing time under different temperature: 3 h.
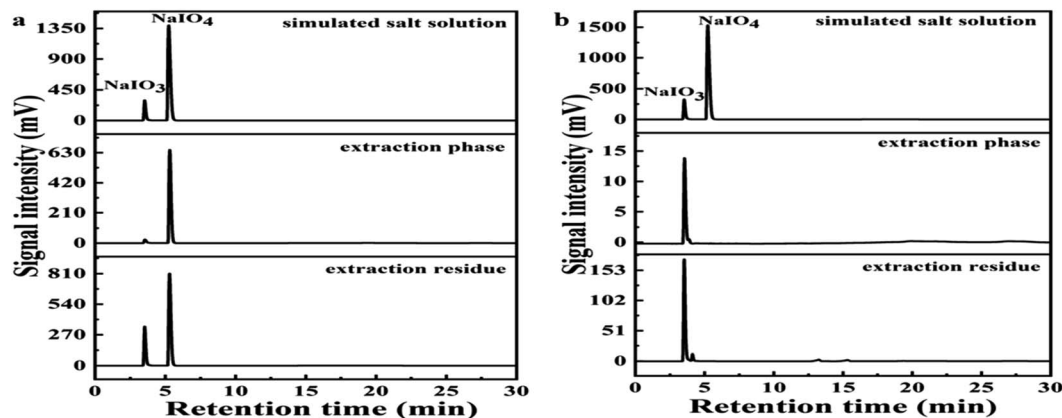
Fig. 6 HPLC profile of the simulated salt solution of sodium iodate and sodium periodate (a) and the simulated salt solution of sodium iodate and sodium periodate acidified by HPLC (b). Reaction conditions: extract the solution three times with an equal volume of butanone reagent. Conditions for the acidification of the simulated solution: the simulated solution of sodium iodate and sodium periodate with a molar ratio of 1 : 1; pH < 1.5; extract the simulated solution three times with an equal volume of butanone.

solution of sodium iodate and sodium periodate with a molar ratio of 1 : 1 was prepared and extracted by butanone (Fig. 6a). It can be seen that butanone can indeed extract $NaIO_4$ in the aqueous solution, while the extraction of $NaIO_3$ was much less. Next, the simulated solution of sodium iodate and sodium periodate was acidified with 1 mol L^{-1} HCl solution to pH 1.5 (consistent with the conditions before butanone extraction of depolymerization supernatant). The acidified simulated salt solution was extracted three times with the same volume of butanone, the results was shown in Fig. 6b. It was found that no $NaIO_4$ existed in both extraction phase and extraction residue, indicating $NaIO_4$ was converted into $NaIO_3$ under the presence of HCl. XRD analysis of the inorganic salts was conducted to prove the transformation of $NaIO_4$ to $NaIO_3$ (Fig. 7). After acidification, typical diffraction peaks of $NaIO_3$ appear, indicating $NaIO_4$ can be converted to $NaIO_3$ by the addition of HCl. However, the diffraction peak of $NaIO_4$ still exists, which may be due to that the amount of HCl was not enough to convert $NaIO_4$. The peak for $NaIO_3$ in the extraction phase is very weak, which

further proved that butanone cannot extract $NaIO_3$ from aqueous solution. These results give an efficient route for the separation of BPCAs from the aqueous solution containing inorganic salts. The depolymerization solution can be first acidified using HCl solution to convert the residual $NaIO_4$ into $NaIO_3$, and then butanone extraction can be used to extraction BPCAs from the solution. This route can fulfill the separation of BPCAs with the inorganic salts. Based on our previous report,[33] the first two peaks in the HPLC diagram are the peak of benzene hexacarboxylic acid and benzene pentacarboxylic acid. These results provides an efficient route for the separation of BPCAs with the inorganic salts after RICO depolymerization of lignite.

Besides butanone extraction, the desalting at different temperatures were attempted and compared to butanone extraction. The temperatures attempted for desalting are set at room temperature, 4 °C and −7 °C, respectively. The
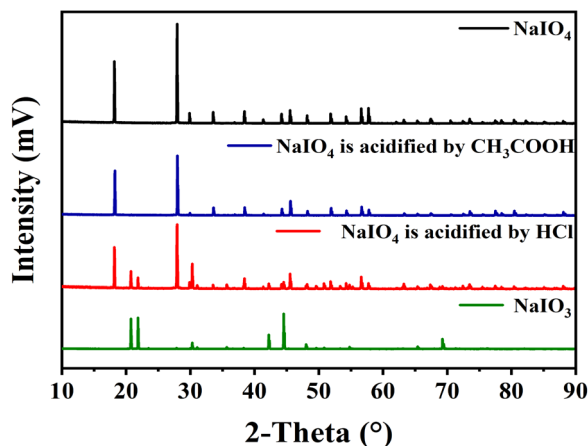

Fig. 7 A comparison diagram of XRD patterns of $NaIO_4$ after acidification by HCl or CH_3COOH.
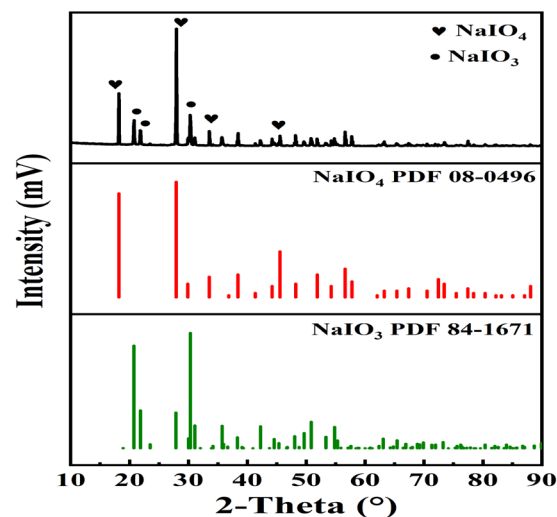

Fig. 8 XRD of the salt precipitated from the depolymerized supernatant after concentration by rotary evaporation and stored under 4 °C for 3 h.
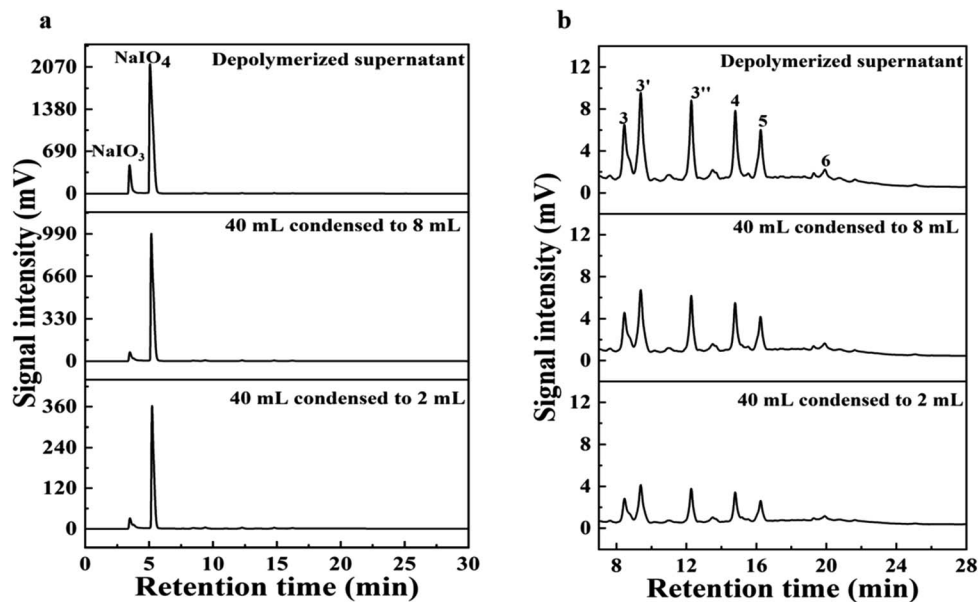
Fig. 9 The HPLC profiles of the depolymerization aqueous solution concentrated to different final volumes. Separation conditions: −7 °C, 1 h.

supernatant after concentration was stored under the above temperatures and white precipitate appeared after certain time. XRD analysis of the precipitate proves that the components of the precipitate are $NaIO_3$ and $NaIO_4$ (Fig. 8). $NaIO_4$ was provided excessively and the residual $NaIO_4$ was maintained in the solution after depolymerization, while $NaIO_3$ was derived from the reduction of $NaIO_4$ when oxidizing Ru^{3+} to RuO_4. In order to investigate the effect of concentration volume on the efficiency of salt removal and the loss of BPCAs. As shown in Fig. 9a, when the depolymerization solution was concentrated to a smaller

volume, the signal of the inorganic salts in the residual solution became weak, indicating higher efficiency of salt removal. However, a smaller concentrated volume also led to higher loss of BPCAs (Fig. 9b). Therefore, the volume of depolymerization supernatant was finally concentrated to around 1/5 of the original volume. The desalting efficiency under different temperatures with the prolonging of storing time is shown in Fig. 10. The desalting efficiency under −7 °C is better than that under room temperature and 4 °C. Before 80 min, the desalting efficiency under 4 °C is similar to that under room temperature,
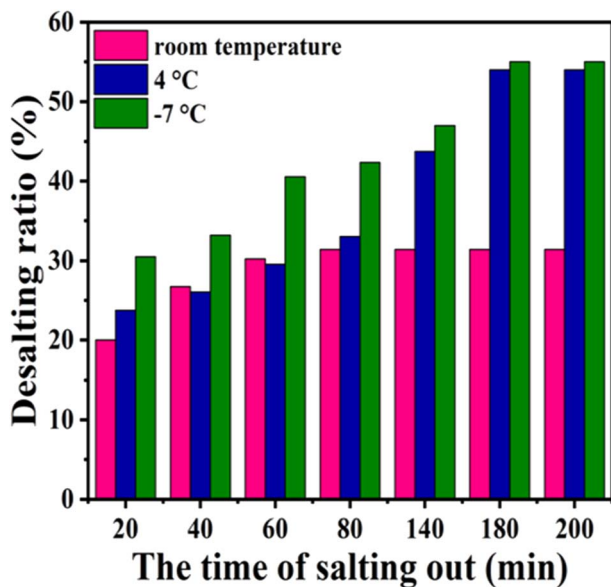

Fig. 10 The desalting efficiency *via* crystallization under different temperature conditions, the change of desalting ratio with time. Conditions: the volume was condensed from 40 mL to 8 mL.
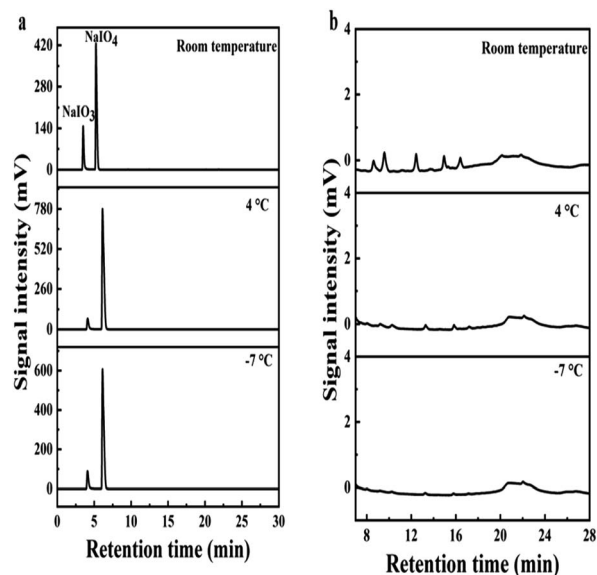

Fig. 11 The HPLC profile of salts precipitated at room temperature, 4 °C and −7 °C. (b) is an enlarged view of (a) with retention time from 7 to 28 minutes. The salt precipitated was dissolved in 100 mL distilled water.

Table 2 The residual amounts of BPCAs in the precipitated inorganic salts[a]

BPCA	The content of BPCAs in the precipitated salt (mg g^{-1})	The loss ratio of BPCAs (%)
1,2,4,5-BTA	0.014	0.5
1,2,3,4-BTA	0.007	0.3
1,2,3,5-BTA	0.004	0.2

[a] Conditions: 4 °C, 2.27 g salt was dissolved in 100 mL distilled water.

but further prolonging the storing time can promote the desalting efficiency, which is close to that under −7 °C. The residual salts after desalting and the desalting efficiency for different methods are summarized in Table 1. It can be seen that butanone extraction has the highest desalting efficiency. For the desalting *via* crystallization, the desalting efficiency under the temperature of 4 °C and −7 °C is similar. Considering the energy consumption, 4 °C seems to be the optimal temperature *via* crystallization.

In order to analyze the BPCAs loss during crystallization, the precipitate was solubilized in water and analyzed by HPLC. HPLC profiles shows that there are weak peaks of BPCAs besides the strong peaks of $NaIO_3$ and $NaIO_4$ (Fig. 11). The contents of BPCAs in the precipitate were given in Table 2. These results show that there are small amount loss of BPCAs during the desalting *via* crystallization, which may be due to that BPCAs were entrained into the precipitate salt crystals during the

Fig. 12 Comparison of the recycling ratios of BPCAs under different conditions. Separation conditions: RICO depolymerized aqueous phase (30 mL), constant volume of butanone (30 mL), extract for 1 h each time, three times; for the crystallization method, the volume was condensed from 30 mL to 6 mL, 3 h.

formation of the precipitate. The content of total organic carbon(TOC) in the precipitated salt (4 °C) is about 2.25 mg g^{-1}. This result indicates that the precipitated salt may contain other organic matter such as humic acid derived from lignite depolymerization besides the residual BPCAs. In our previous report,[34] it was also found that lignite was first converted to humic acid macromolecules together with small amount of BPCAs, and the humic acid macromolecules were further converted to BPCAs. Some humic acid macromolecules cannot be depolymerized by RICO and maintained in the solution.

The recycling ratios of BPCAs during butanone extraction and crystallization under different temperatures are compared (Fig. 12). It can be seen that butanone extraction has the highest recycling ratio of BPCAs, and the total recycling ratio can reach to 91%. The total recycling ratio of BPCAs for desalting by crystallization under 4 °C can reach to 73%. The desalting by crystallization under different temperatures has the slight loss of BPCAs in the precipitate. As discussed above, the desalting efficiency of butanone extraction is much higher than that of crystallization. Though it has high recycling ratios of BPCAs and high desalting ratio, butanone extraction suffers the use of organic solvent butanone. Comparatively, the desalting by crystallization can avoid the use of organic solvent butanone. Therefore, the two routes have their unique characteristics in future potential applications.

Conclusions

In summary, RICO depolymerization of lignite under a low dosage of $RuCl_3$ catalyst was conducted, and the separation of BPCAs products with the inorganic salts using different approaches were compared. The results show that the mass ratio of $RuCl_3$/lignite can be decreased to as low as 1/1000 without obvious decrease in depolymerization degree and BPCAs yields compared to the commonly used mass ratio of 1/10 just by prolonging the reaction time. Butanone extraction is an efficient way to enrich the BPCAs products with extraction ratio of total BPCAs as high as 91%. The residual $NaIO_4$ can be transformed to $NaIO_3$ under the presence of HCl. A new strategy of first acidification of depolymerization aqueous solution by HCl and then extraction by butanone is proved to be efficient for the separation of BPCAs with inorganic salts. Thus butanone extraction can also fulfill the separation of BPCAs with the inorganic salts. The shortcoming of butanone extraction is the use of organic solvent. Salting out *via* crystallization under lower temperature can remove *ca.* half content of the salts, and the efficiency is inferior to butanone extraction. The crystallization under low temperature can remove partial inorganic salts with slight loss of BPCAs in the salt precipitate. Besides, the concentration process of the depolymerization solution is required before crystallization to improve the desalting efficiency, indicating higher energy consumption during crystallization. Therefore, the two separation routes have their own advantages and disadvantages considering real application. From aspects of the recycling ratios of BPCAs and the desalting efficiency, butanone extraction is superior to the crystallization under low temperature. This work is meaningful to promote the
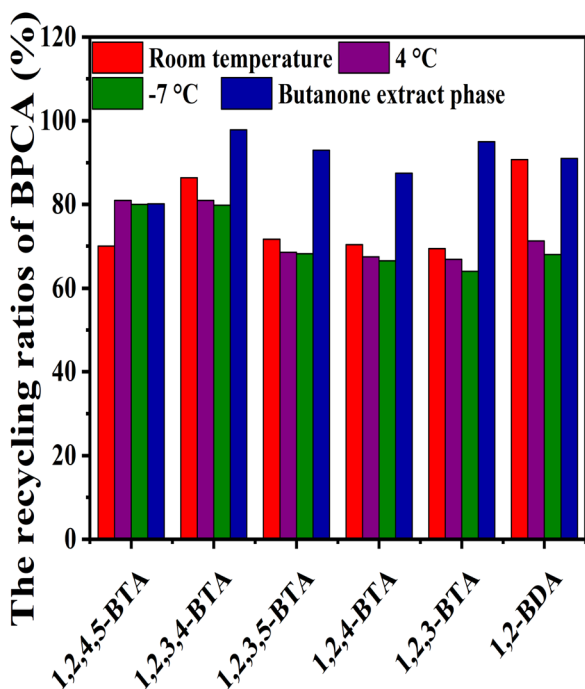
separation of the valuable BPCAs from the depolymerization production solution during the potential application of RCIO depolymerization of lignite.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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