



Analysis of hazardous organic residues from sodium hydrosulfite industry and utilization as raw materials in a novel solid lubricant production

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ABSTRACT

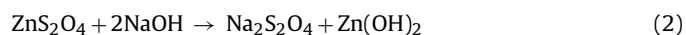
The hazardous organic residual wastes produced by the sodium hydrosulfite industry are demonstrated to be convertible into a novel solid lubricant. Identification and isolation of the organic residues are achieved by Fourier transform infrared (FTIR) spectroscopy, gas chromatography–mass spectrometry (GC–MS), and nuclear magnetic resonance (NMR). FTIR and GC–MS provide important information about the residues and the two main components obtained by column chromatography are further analyzed by NMR. The main organic residues are found to be thiodiglycol and 2,2'-dithiodiethanol which have potential applications in petroleum drilling because of their S–S and/or C–S functional groups. The lubricity of the organic residues is subsequently studied and the influence of different adsorbents on the lubricity is investigated and discussed. This homemade lubricant is observed to have good lubricity and by increasing the concentration of the commercial solid lubricant M, the lubricity diminishes. The process is expected to not only have commercial impact but also help to reduce environmental pollution.

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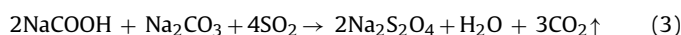
1. Introduction

Sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), also known as sodium dithionite or hyposulfite, is widely used in the textile, pulp and paper industry as a bleaching agent [1,2] and also dye materials and in biochemical processes as a reducing agent [3]. Sodium hydrosulfite is the common commercial name for products containing sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, as the effective ingredient. China is by far the largest producer of the dry product producing 30% of the world's capacity. There are main two conventional approaches to produce sodium hydrosulfite.

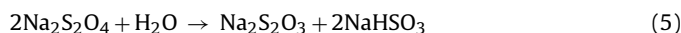
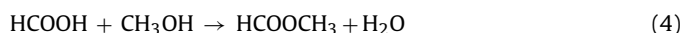
(i) Sodium hydrosulfite is prepared by the reaction of sodium bisulfite with zinc by the following reaction:



(ii) A second approach is based on sodium formate. The main stoichiometry of the reaction is:



Sodium formate approach is the popular method with the following side reactions:



Residues from sodium hydrosulfite manufacturing contain various inorganic and organic compounds. It is estimated that over 10,000 t of residues are produced annually in China. According to European Waste Catalogue (EWC), the organic residual waste is absolute hazardous (07 07 08*). Therefore proper treatment and recycling of the byproducts is important to environmental protection and public health. Landfilling has been the main disposal method [4,5] and these residues can contaminate soil and ground water. Alternatively, the residues can be incinerated but it leads to acid rain because the organic residues contain organic sulfur compounds. In China, some factories discharge the residues only after dilution and sometimes no pretreatment is conducted thereby posing serious environmental threats. Hence, it is important to develop methods to recycle and utilize the industrial waste but there have only been limited studies up to now along this direction. The

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concentrations of byproducts such as SHES ($\text{HO}_2\text{C}_2\text{H}_4\text{SO}_3\text{Na}$), SHET ($\text{HO}_2\text{C}_2\text{H}_4\text{S}_2\text{O}_3\text{Na}$), SF (HCOONa), and inorganic anions (Cl^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$) in the waste have been determined by ion chromatography [6]. Although the organic residues are separated from the solid residues by heating determination of these organic residues has not been reported to the best of our knowledge.

How to deal with the residues is a thorny problem and the safe disposal is critical for public health. A more effective approach to waste management is Cleaner production (CP), a strategy for addressing the generation of pollution as well as efficient use of resources at stages of the production process [7,8]. CP is most commonly understood as positive economic benefits arising from efficient use of materials and energy [9]. Research [10] indicated that cleaner production practices could generate promising results in reducing pollution at low costs.

The organic components in the residues have potential applications such as additives in lubricants and detergents [11–14]. Solid lubricants have inherent lubricating properties while exhibiting firm bonded to the surface of the substrate [15,16]. Graphite and molybdenum disulfide (MoS_2) are the predominant solid lubricants [17–19] whereas other solid materials including plastic microspheres and glass microspheres have been employed in drilling fluids. The organic residual byproducts produced from sodium hydrosulfite industry are a good additive to solid lubricants used in petroleum drilling. In this work, the organic residues produced as waste by the sodium hydrosulfite industry are characterized by FTIR, GC–MS, and NMR and the materials are used to improve the lubricity of solid lubricants.

2. Experimental details

2.1. Materials

Residues of sodium hydrosulfite were obtained from Shangdong Shuangqiao Chemical Industry Co., Ltd., China. All the chemicals such as hexane, ethyl acetate, acetone, ethanol and methanol were analytical grade and obtained from Beijing Chemical Plant, China. A homemade column chromatograph with a length and width of 40 cm and 3 mm, respectively, packed with silica gel (ZCX.H, 200–300 mesh size, Branch of Qingdao Haiyang Chemical Plant, China) was used in the study. Standard HSGF254 HPTLC plates (100 mm × 25 mm) were purchased from Yantai Chemical Industry Research Institute, China.

2.2. Methods

The organic residues were obtained by heating the sodium hydrosulfite residues at 100 °C for 2 h. Afterwards, stratification of the solution occurred and the top layer (organic layer) was decanted (Fig. 2(A)). FTIR was conducted on the residues on a Perkin-Elmer SP100 FTIR spectrometer operated in the ATR (attenuated total reflectance) mode, and 32 scans were collected at a resolution of 4 cm^{-1} .

A GC–MS Thermo Finnigan equipped with an electrospray soft ionization mass spectrometry system (SHIMADZU GC/MS-QP5050A) was used to identify the organic compositions. 0.4 μL of the sample was injected into the GC–MS operated from 50 to 250 °C at a ramping rate of 20 °C $\cdot\text{min}^{-1}$ and then held for 15 min. A DB-5MS capillary column with an inner diameter of 0.25 mm and length of 60 m was adopted in the separation system. Helium was the carrier gas and introduced at a flow rate of 1.24 $\text{mL}\cdot\text{min}^{-1}$. The eluent used in the column chromatography experiments was a hexane/acetone/ethanol (80/20/0.2, v/v/v) mixture which was determined by previous thin-layer chromatography experiments. The materials obtained by column chromatography were dried at

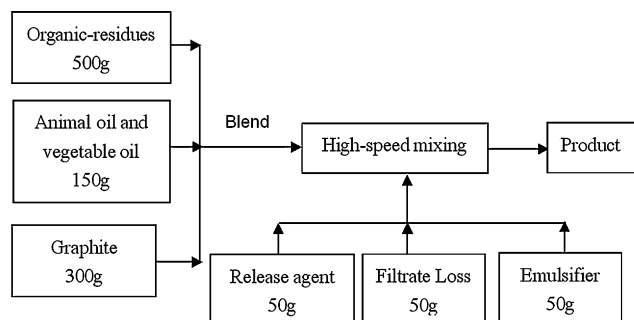


Fig. 1. Schematic diagram illustrating the preparation of the solid lubricant, Slube.

50 °C for 24 h in a vacuum oven to a constant weight. Nuclear magnetic resonance spectra (^1H NMR, 400 MHz) were acquired on a Bruker-400 spectrometer with the 1 mm TXI microliter probe using chloroform- d (CDCl_3) as the solvent. The measurements were carried out without spinning at 25 °C. The lubricity was determined by the NF-1 differential sticking tester. The pressure difference was 3.5 MPa and filtration time was 30 min. The friction coefficient was determined using an extreme pressure lubrication tester.

2.3. Production process of solid lubricant Slube

The preparation process of the solid lubricant is presented in Fig. 1 which illustrates the production of 1 kg of product. The reagents including organic residues, graphite, animal oil, and vegetable oil are proportionately added to the reactor and stirred for 20 min. Afterwards, the release agent, filtrate loss, and emulsifier are added to the mixture and mixed at a high speed for 30 min to obtain the product. The nomenclature of this solid lubricant containing the organic residues is designated as Slube here. It should be noted that very little byproducts are produced from this process which is environmentally green.

3. Results and discussion

3.1. Elemental analysis

According to elemental analysis, inorganic salts constitute as much as 45.14% and the sulfur content is relatively high reaching 17.51%. Hence, incineration of the waste will definitely produce sulfur containing gases and environmental hazards. Fig. 2(B) shows the ATR-IR spectra of the organic residues showing a prominent $-\text{OH}$ stretching band at 3366 cm^{-1} . The absorption peaks at 2933, 2882, 1407, 1383, and 1352 cm^{-1} can be assigned to the vibrational modes of CH_2 and/or CH_3 . An intense C–S stretching mode can be observed at 1027 cm^{-1} confirming the presence of carbon–sulfur compounds.

3.2. Chemical structural analysis

Gas chromatography/mass spectrometry (GC–MS) is used to isolate and determine the organic molecules. The chromatogram of the residues is depicted in Fig. 3(A). Good separation and peak profiles are accomplished in 12 min and three components can be isolated from the residues. The three peaks labeled #1, #2, and #3 which are 25.2%, 55.6%, 16.4%, respectively add up to 97.2% (Table 1). Fig. 3(B)–(D) shows the partial mass spectra of the three constituents. The main molecular ions in the three components have m/z values of 122, 154, and 104, respectively, suggesting that #1 is thiodiglycol, #2 is 2,2'-dithiodiethanol, and #3 is 1,4-thioxane. Thiodiglycol is a viscous, clear to pale-yellow liquid used as a

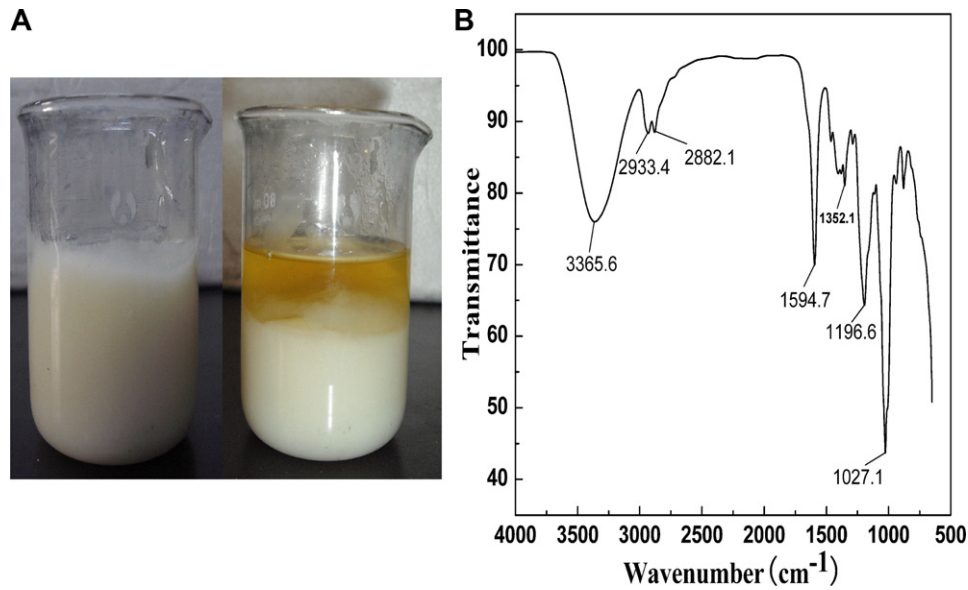


Fig. 2. (A) Comparison between the organic residues before and after heating and (B) FTIR spectra acquired from the organic residues.

Table 1
GC–MS results obtained from the organic residues.

Peak	Retention time (min)	Assignments	Molecular ion	Content (%)
#1	5.5	Thiodiglycol	122	25.2
#2	7.2	2,2'-Dithiodiethanol	154	55.6
#3	10.4	1,4-Thioxane	104	16.4

solvent in many applications and as an antioxidant, it is an additive in lubricants. 2,2'-Dithiodiethanol is a clear to yellow liquid.

Although these results are encouraging, complete separation of the organic residues is important. Thiodiglycol, 2,2'-dithiodiethanol, and 1,4-thioxane have similar structures, and the polarity is close. Hence, it is difficult to separate the components absolutely. In our column chromatography experiments, two components are obtained and they are further identified by ^1H NMR and the results are in agreement with those from GC–MS. As

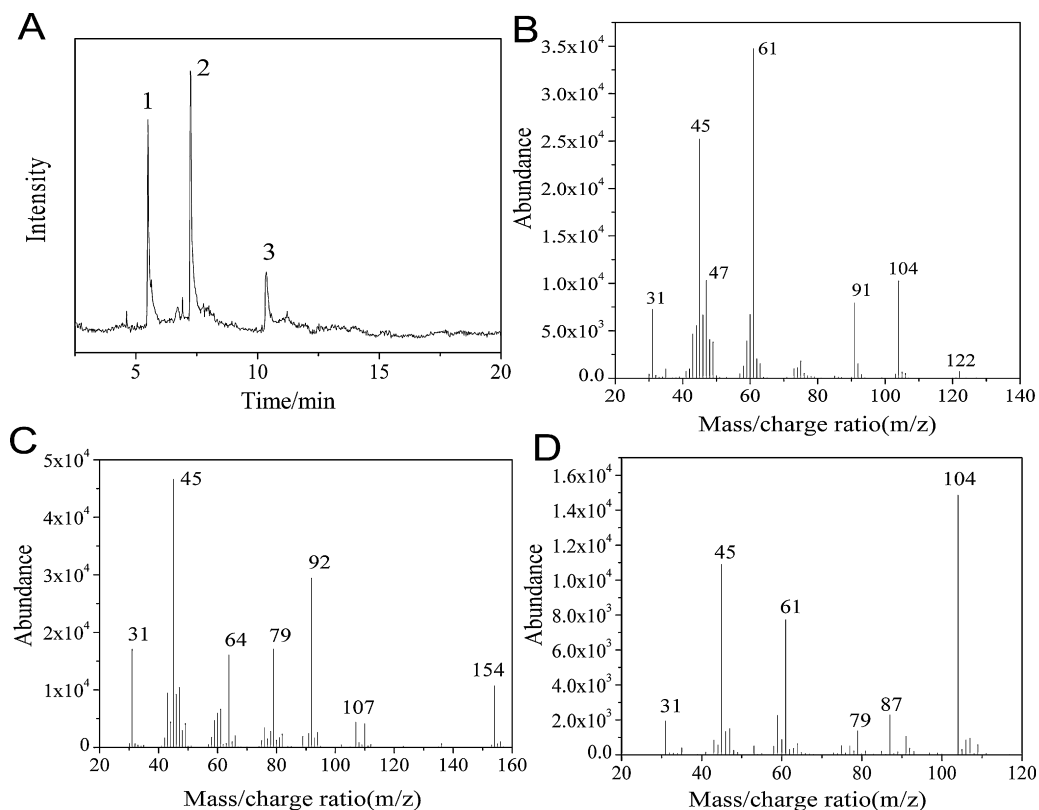


Fig. 3. (A) Chromatogram of the organic residues (80 μg residues injected into 0.4 μL acetone) and mass spectra of the three components (peaks 1–3 in the chromatogram) at different retention times from the organic residues at different retention times of (B) 5.5 min (thiodiglycol), (C) 7.2 min (2,2'-dithiodiethanol), and (D) 10.4 min (1,4-thioxane).

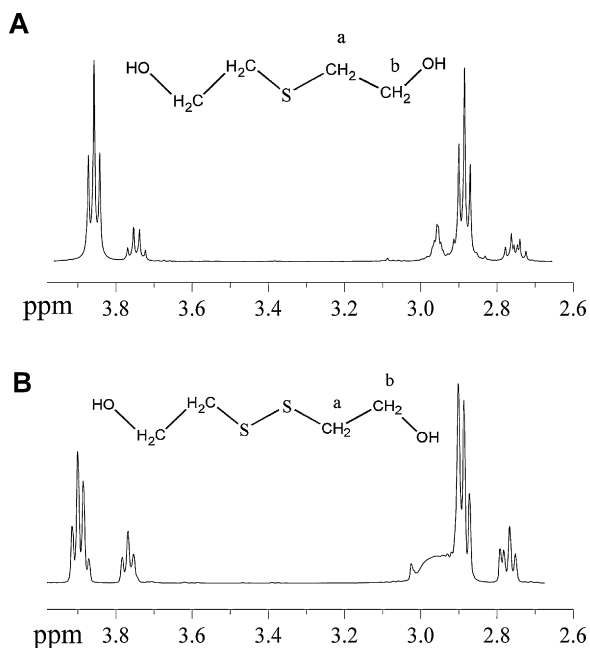


Fig. 4. Proton nuclear magnetic resonance spectrum acquired from (A) #1 and (B) #2 in CDCl_3 (64 scans).

shown in Fig. 4(A), the resonances at 2.870–2.900 ppm (s, 4H) and 3.842–3.872 ppm (s, 4H) can be attributed to protons a and b, respectively. Hence, compounds #1 is indeed thiodiglycol, also known as dihydroxyethyl sulfide. In Fig. 4(B), the resonances at 2.749–2.778 ppm (s, 4H) and 3.761–3.790 ppm (s, 4H) arise from protons a and b, respectively and #2 is identified to be 2,2'-dithiodiethanol.

According to our results, the organic residues produced by the sodium hydrosulfite industry consist of mainly three components, thiodiglycol, 2,2'-dithiodiethanol, and 1,4-thioxane. 1,4-Thioxane does not play a major role in the study because of the tiny amount. Hence, we focus on the other two constituents, thiodiglycol and 2,2'-dithiodiethanol, and study its lubricating characteristics.

3.3. Utilization in solid lubricant for petroleum drilling fluid

In this section, the organic residues are reused in a homemade solid lubricant for petroleum drilling fluid field. Transportation and utilization of organic residues are not easy tasks due to their high viscosity. Therefore, graphite which can enhance the lubricity is utilized in our experiments to adsorb the organic residues. In addition, asphalt which is environmentally friendly and boasts good performance and low price is chosen as the release agent to prevent the organic residues from agglomerating. Other additives such as fluid loss reducers and emulsifier are also added to enhance the lubricating properties. The adhesion coefficient of the product is determined by the following relationship:

$$K_f = M \times 0.845 \times 10^{-2} \quad (6)$$

where M is the torque. The adhesion coefficient is obtained by:

$$\Delta K_f (\%) = \frac{K_f - K_{f1}}{K_f} \times 100 \quad (7)$$

where K_f and K_{f1} are the adhesion coefficients of the paste before and after the organic residue is, respectively. The reduction in the friction coefficient is calculated using the following expression:

$$\Delta f (\%) = \frac{f_0 - f_1}{f_0} \times 100 \quad (8)$$

Table 2
Influence of adsorbents on the lubricity.

Sample ID	Adsorbent ^a	ΔK_f (%)	Δf (%)	Total lubrication index ^b
1	FG + EG	48.98	35.71	99.38
2	100 mesh 99%FG + EG	48.98	27.55	91.22
3	+100 mesh 85%FG + EG	63.27	27.55	109.80
4	–100 mesh 85%FG + EG	59.18	29.85	106.78

^a FG, flake graphite; EG, expanded graphite.

^b Total lubrication index = $1.3 \times \Delta K_f + \Delta f$ (a empirical formula).

Table 3
Lubricity of homemade Slube compared to those of commercial lubricant M.

Lubricant	ΔK_f (%)	Δf (%)	Total lubrication index
Slube	57.14	55.41	129.69
M	28.57	65.18	102.32
Slube:M = 1:1	57.14	69.50	143.78
Slube:M = 1:2	44.90	63.51	121.88

where f_0 and f_1 are the friction coefficients before and after the organic residues are added, respectively.

As aforementioned, the organic residues consist of mainly thiodiglycol and 2,2'-dithiodiethanol. When the organic residues are used as lubricant additives, these molecules decompose via S–S bond cleavage to form thiolate species on the surface [20]. Hence, the lubricating properties are enhanced when the content of the organic-residue is increased. However, it should be noted that sulfur oxidizes the iron substrate to form pyrrhotite (Fe_{1-x}S) film [21].

Table 2 shows the lubricity of samples with different adsorbents. The ΔK_f determined from #3 graphite (100 mesh 85%FG + EG) is 63.27% which is a piece of excellent result. The Δf of #1 graphite (FG + EG) is 35.71% which is also a good result. However, taking all factors into account, #3 graphite (+100 mesh 85%FG + EG) is chosen as the adsorbent in our experiment due to a total lubrication index of 109.8. Some commercial solid lubricants have good Δf but the ΔK_f is not desirable. Our homemade solid lubricant Slube has excellent ΔK_f and the commercial solid lubricants and Slube have complementary performance. For comparison, we study the lubricity of one commercial solid lubricant M. As shown in Table 3, ΔK_f is 28.57% and Δf is 65.18% for M. As the content of M is increased from 1:1 to 1:2, ΔK_f diminishes from 57.14% to 44.90% representing a 21.4% reduction and Δf decreases from 69.50% to 63.51% reflecting a 8.6% reduction. Our data reveal that our homemade solid lubricant Slube has better lubricity than some commercial lubricants.

As previously stated, hazardous organic residues from sodium hydrosulfite production is analyzed and utilized in petroleum drilling. Actually, a pilot experiment of Slube is implemented in Shangdong Shuangqiao Chemical Industry Co., Ltd., China. By being able to optimize its own process and to make better use of hazardous organic residues, the company dramatically improved its environmental performance, shifting from a position of passive pollution control to a position of proactive pollution prevention and CP. In doing so, the financial benefits of the changes resulted in decreased materials, energy and waste disposal costs.

4. Conclusion

The organic residues produced as byproducts by the sodium hydrosulfite industry are analyzed by FTIR, GC–MS, column chromatography, and NMR. FTIR reveals bands corresponding to C–S stretching at 1027.1 cm^{-1} and GC–MS shows three main components in the residues, namely thiodiglycol, 2,2'-dithiodiethanol, and 1,4-thioxane. The NMR results confirm the compound identification. Different adsorbents make a difference to the lubricity. The

best lubricity improvement is achieved from sample #3 (+100 mesh 85%FG + EG) with a total lubrication index of 109.8. Furthermore, this homemade solid lubricant Slube containing organic residue shows good lubricity than some commercial solid lubricants. Our study indicates that the organic residues produced by the sodium hydrosulfite industry can be processed and reused as lubricants in petroleum drilling fluid field.

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