Effects of silica on chemical recovery in the direct causticization of wheat straw black liquor

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ABSTRACT: Straw black liquor is relatively difficult to recover using the Tomlinson process because of the presence of silica in inorganic components. Gasification with direct causticization might serve as a promising alternative; however, the interaction between silica and direct causticization agents needs to be evaluated. In this work, desilication was achieved using a laboratory-scale membrane electrolysis cell adopted from the chlor-alkali industry. Then raw and desilicated straw black liquors were carried out through direct causticization with titanium dioxide (TiO_2) and recycled sodium tri-titanate ($Na_2O{\cdot}3TiO_2$) at 850°C using a tube furnace. The results show that these two agents exhibit different silica transfer mechanisms. When using TiO_2, approximately 80% of the silica is retained in the solid residue after hydrolysis because of chemical interactions. Almost all of the silica transfers to the hydrolysis-derived white liquor when using $Na_2O{\cdot}3TiO_2$. This means that the process of treating straw black liquor by direct causticization might need additional lime causticization to improve the efficiency of sodium recovery. This observation also indicates that silica will not consume the direct causticization agent $Na_2O{\cdot}3TiO_2$ after the initial step using TiO_2. The sodium hydroxide (NaOH) yield was 60% when using raw black liquor as the feed to the $Na_2O{\cdot}3TiO_2$ recycling tests and 80% when using desilicated straw black liquor. Considering the NaOH recovered in the electrolysis cell, the total NaOH yields exceed 85% of total titratable alkali. No detectable deterioration of the direct causticization agents was found within the limited number of recycles tested. A greater number of cycles need to be tested at a larger scale to evaluate the feasibility of applying a direct causticization process to straw black liquor.

Application: This work provides some understanding of the interaction between the direct causticization agents TiO_2 and recycled $Na_2O{\cdot}3TiO_2$ and the silica present in straw black liquor. The findings will assist in designing a better chemical recovery process for straw black liquor.

Black liquor is the spent liquor produced from the digestion of wood or nonwood fiber materials in the soda or kraft pulping process. These days, wood kraft black liquor is usually concentrated to a high solid content (e.g., 65%) for combustion using a Tomlinson recovery boiler. This type of recovery boiler has served the pulp and paper industry for nearly 80 years, treating black liquor to recycle the digestion chemicals and produce pressurized steam; however, nonwood (e.g., wheat straw, bamboo, bagasse) black liquor is relatively difficult to recover because of the presence of silica in the inorganic components. The silicates in straw black liquor make it difficult to concentrate above a solids content of 50%, and the white mud is usually not suitable for reuse because of impurities. The heating value of these solids is also lower than that of wood black liquor solids (BLS). Auxiliary fuel must usually be added to the recovery boiler to maintain stability when treating straw black liquor.

Despite these obstacles, the nonwood pulping process plays an important role in the virgin pulp markets of countries such as China, India, Egypt, and Turkey that are poor in wood resources. According to the China Paper Association, China produced 7.55 million metric tons of nonwood pulp (wheat and rice straw pulp comprising 3.36 million metric tons) in 2014, which accounted for more than 40% of virgin chemical pulp production (alkali pulping process and kraft pulping process) [1]. Because not every nonwood pulp mill is equipped with a recovery boiler, researchers have sought alternatives to conventional combustion to enable full use to be made of straw black liquor lignin or silica [2-6]. In some Chinese pulp mills, black liquor is dried to produce alkali lignin, which can be used as an additive in the production of many materials, including cement, ceramics, and coal water slurry.

To date, however, no single process has been able to completely replace recovery boilers, especially when considering aspects of the associated energy and chemical balances and the large capacity requirement. To improve recovery of straw black liquor, a desilication process using carbonation has been pursued since the early 1980s [7]. The basic principle of the desilication process is selective precipitation of silica by lowering the pH of the black liquor. The major challenge is the efficient separation of the resulting silica sludge.

Gasification is an important technique that could be used for straw black liquor. This approach has been extensively pursued for nearly 40 years by many companies and institutions [8,9], most of which were concerned with wood kraft black liquor and how to improve the thermodynamic efficiency, safety, and economics of the process. Some experiments have studied pyrolysis or gasification of straw black liquor [10-12]. In Sweden, Chemrec has run a 20 tons dry solids/day high temperature gasification demonstration project [13,14]. Low temperature gasification technology was demonstrated in North America in the early 2000s [15]. Similar to the outputs of a conventional recovery boiler, black liquor gasification can recover chemicals and energy. Furthermore, the gasifier capacity might be more applicable to straw or other nonwood pulp mills, because such mills have relatively small capacities, usually less than 100,000 air-dried tons of pulp per year.

The potential for commercialization of black liquor gasification technology currently seems promising, and technical issues such as materials corrosion [16] are being addressed. The advantages of black liquor gasification may be further increased when it is combined with direct causticization [17,18], because the gasifier would be able to run at higher temperatures without generating a smelt and the solid titanate products release sodium hydroxide (NaOH) directly when hydrolyzed so the conventional lime cycle could be replaced. The reactions involved in direct causticization are as follows [17,19]:

$$Na_2CO_3 + 3TiO_2 \rightarrow Na_2O{\cdot}3TiO_2 + CO_2 \quad (1)$$

$$7Na_2CO_3 + 5(Na_2O{\cdot}3TiO_2) \rightarrow 3(4Na_2O{\cdot}5TiO_2) + 7CO_2 \quad (2)$$

$$3(4Na_2O{\cdot}5TiO_2) + 7H_2O \rightarrow 14NaOH + 5(Na_2O{\cdot}3TiO_2) \quad (3)$$

The rate of direct causticization at about 850°C is high enough for the reaction to be completed within the materials residence time of some types of gasifiers, such as fluidized beds or entrained-flow reactors [19-23]. The hydrolysis behavior of sodium penta-titanate ($4Na_2O{\cdot}5TiO_2$) and the leaching properties of sodium tri-titanate ($Na_2O{\cdot}3TiO_2$) have been investigated [24,25]. The energy performance of black liquor gasification with direct causticization has been compared with that of black liquor gasification using lime causticization [26]. The reactivity of the recycled titanates as direct causticization agents appears to be maintained for several leaching cycles [27]. There are still some unresolved aspects of the direct causticization process [18]. It is also not yet clear whether direct causticization is suitable for the processing of straw black liquor in light of possible interactions between silica and the direct causticization agents. Nonprocess elements [28], especially silica, might transfer to the recycled $Na_2O{\cdot}3TiO_2$, either chemically or physically, so the mass of the direct causticization agents would increase with each cycle. Such a situation would overload recovery boilers or gasifiers or substantially increase the titanium dioxide (TiO_2) makeup requirement.

This work evaluates TiO_2 and recycled $Na_2O{\cdot}3TiO_2$ as direct causticization agents with respect to their possible interaction with silica. Raw and desilicated straw black liquors are used to compare the sodium recovery efficiency. These results further advance understanding of the technical feasibility of applying direct causticization to straw black liquor.

EXPERIMENTAL

Silica removal from straw black liquor by electrolysis

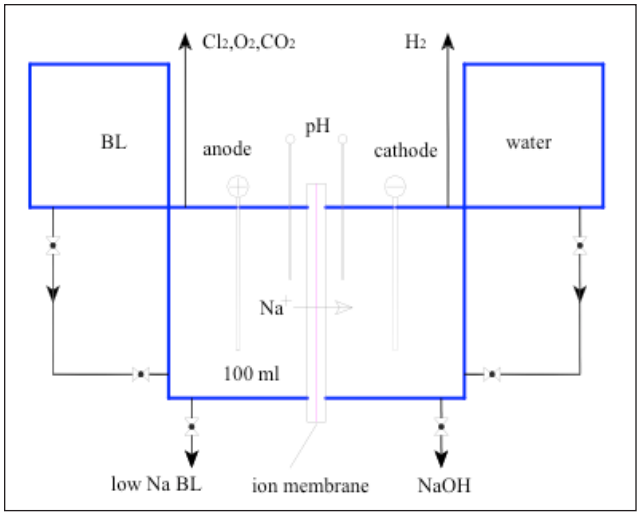
Silica removal was carried out by lowering the pH value of black liquor, an approach that has been used by many researchers [7]. In previous studies, silica removal (desilication) was usually performed by carbonation to control the pH, followed by precipitation and separation operations. Boiler flue gas can serve as a carbon dioxide (CO_2) source that is very accessible in a pulp mill. Foaming problems are usually encountered in the desilication reactor when using carbonation. Based on a technique adapted from the chlor-alkali industry, this work used electrolysis [29,30] as the desilication method. The ionic membrane based chlor-alkali process is an industrial process for the production of high purity NaOH by electrolysis of a sodium chloride solution, which yields hydrogen and chlorine as byproducts. The process has been applied to wood black liquor to reduce the organic load to the recovery boilers and to convert a portion of the sodium salts to caustic soda [30,31]. This method has also been used to obtain lignin from straw black liquor without the assistance of a membrane [29]. Equations (4)-(6) show the principle of ionic membrane electrolysis. The ease with which electrons are lost from the anode follows the order: $S^{2-} > I^- > Br^- > Cl^- > OH^-$ > oxyacid radicals. The pH of the black liquor is gradually lowered during the electrolysis process.

$$\text{Anode:}\quad 2Cl- - 2e \rightarrow Cl_2\uparrow \quad (4)$$

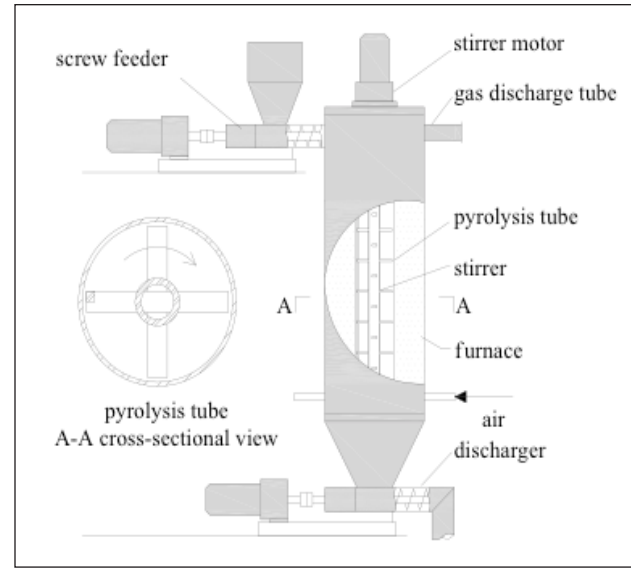
$$4OH- - 4e - 4Na+ \rightarrow 2H_2O + O_2\uparrow \quad (5)$$

$$\text{Cathode:}\quad 4H^+ + 4OH^- + 4e + 4Na^+ \rightarrow 4NaOH + 2H_2\uparrow \quad (6)$$

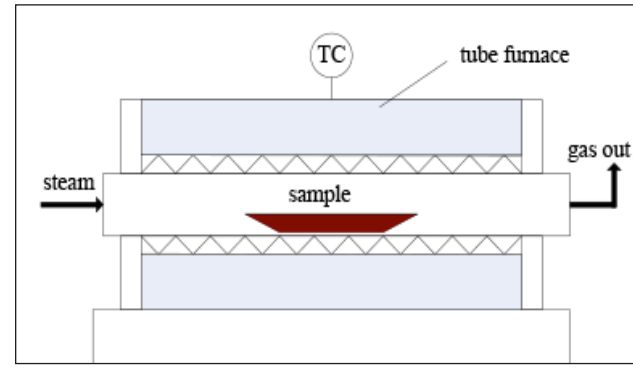
Figure 1 shows the experimental apparatus in which the electrolysis operations were carried out. The cell had a volume of about 100 mL. The direct current voltage was set to 16 volts in all of the runs. The final pH values of the electrolysis were set to 9.0 and 8.0 to derive low-sodium and silica black liquor samples for use in direct causticization, and the precipitation of lignin was expected to be as low as possible. Electrolysis runs were carried out separately on sodium carbonate (Na_2CO_3) and sodium silicate (Na_2SiO_3) as model compounds representing black liquor inorganics. We found that both salts were able to produce NaOH and hydrogen in the cathode cell, similar to the use of sodium chloride in the chlor-alkali process. Electrolysis runs using weak black liquor (solid content



1. Diagram of black liquor electrolysis reactor.



2. Stirrer-type black liquor pyrolysis setup.



3. Tube furnace used for direct causticization reactions.

below 20%) were ended when the pH reached the designated value. The low-sodium black liquor was filtered to separate the precipitated silica.

Analysis of wheat straw black liquor

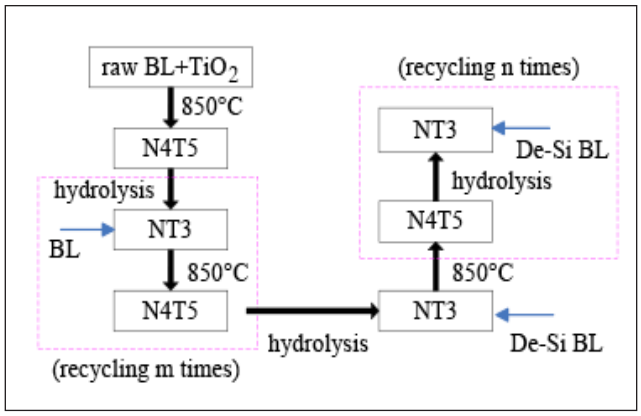
Industrial soda wheat straw black liquor was used in this study. It was converted to solid powder form by spray drying at the pulp mill. Two separate elemental analyzers were used to determine carbon, hydrogen, sulfur, nitrogen, and oxygen contents. Chlorine content was determined by ion chromatography using a Metrohm 761 Compact IC (Herisau, Switzerland) according to TAPPI Standard Test Method T 699 "Analysis of pulping liquors by suppressed ion chromatography," after oxidizing the black liquor solution to transparency with nitric acid. The volatiles content was analyzed under a nitrogen atmosphere and devolatilized at 850°C for 15 min. The char from volatiles analysis was calcined at the same temperature to a melting state and then cooled down to determine the ash content.

The insoluble residues present in the weak black liquor and green liquor were determined by filtration (TAPPI Standard Test Method T 692 "Suspended solids in green liquor"). The residues, together with the quantitative filter paper on which the residues were filtered, were calcined at 850°C and weighed after cooling. The filtered black liquor was then concentrated to a solid content above 50% and calcined using a tube furnace at 850°C in a ceramic crucible. The obtained smelt was dissolved in water and the filtration and calcination procedure was repeated to determine the green liquor dreg content (mainly insoluble silicates). The filtered green liquor was titrated potentiometrically with 1 mol/L hydrogen chloride (HCl) to pH 5 to release all CO_2 from the carbonates and condense the silica to polysilicic acids. The filtration and calcination procedure was repeated to the polysilicic acid precipitate to determine the silicon dioxide (SiO_2) (cristobalite) content.

The sodium oxide (Na_2O) content (no distinction is made between potassium carbonate [K_2CO_3] and Na_2CO_3) was calculated based on the HCl titrant volume and SiO_2 mass. Determination of the SiO_2 content in the filtered green liquor was also conducted using the ISO 6382:2009 Standard Method "General method for determination of silicon content — Reduced molybdosilicate spectrophotometric method," in which the yellow molybdosilicate complex is reduced to the blue complex and measured spectrophotometrically at a wavelength of 800 nm.

Direct causticization recycling of raw and desilicated straw black liquor

The black liquor solids were gasified with air to devolatilize most of the organics at around 800°C in a stirrer-type fixed bed reactor (**Fig. 2**). The reactor tube was 150 mm in diameter and 1400 mm in height. The stirrer pulverized the swollen heated black liquor solids and prevented the materials from agglomerating in the bed so that the black liquor char was discharged in the form of a powder. The char was mixed with TiO_2 (rutile) or $Na_2O{\cdot}3TiO_2$ to carry out direct causticization at 850°C using the tube furnace shown in **Fig. 3**. **Figure 4** shows a flow diagram of the direct causticization experimental process. The amount of TiO_2 or



4. Flow diagram of direct causticization recycling (BL = black liquor, N45T = $4Na_2O{\cdot}5TiO_2$; NT3 = $Na_2O{\cdot}3TiO_2$; and De-Si = desilicated).

$Na_2O{\cdot}3TiO_2$ used was calculated according to the total titratable alkali, rather than the Na_2CO_3 content. Steam was selected as the gasification agent and the reaction time was set to 15 min to complete the conversion of the organics and the decarbonization of Na_2CO_3. The residue was then withdrawn, hydrolyzed with boiling water for 10 min, and the filtrate divided into three parts to separately analyze the contents of total alkali (NaOH, Na_2CO_3, and Na_2SiO_3), NaOH, and SiO_2. The solid-phase product was analyzed by X-ray diffraction (XRD) using a PANalytical (Eindhoven, Netherlands) X'Pert Pro MPD diffractometer and then returned to the process to undergo the next cycle. After several cycles, the feed material was changed to desilicated black liquor char to continue the recycling process.

RESULTS AND DISCUSSION

Characterization of raw and desilicated straw black liquors

Table I provides the analyses of the raw and desilicated black liquors. Differences compared with samples used in previous work [32] arise because of the different batches of black liquor. **Table II** shows the main components of the black liquor ash. In the spectrophotometric analysis procedure, the blue silicate complex exhibited an intense absorption peak at 800 nm (**Fig. 5a**) and a good linear relationship between SiO_2 concentration and absorbance (Fig. 5b).

In the electrolysis process, sodium ions contained in the black liquor pass through the membrane, driven by the voltage gradient, and accumulate in the cathode cell, leaving low-sodium black liquor in the anode cell. The total titratable alkali in the black liquor when the electrolysis was ended at pH 8.0 had decreased to about 5.6 mol/kg black liquor solids, compared with 7.8 mol/kg black liquor solids for the raw black liquor. Approximately 60% to 80% of the silica was removed from the raw black liquor in all runs. Most silica precipitated at the bottom of the anode cell, although a thin layer of silica deposited on the anode surface when the pH initially decreased.

The lower heating value (LHV) of the black liquor solids increased after electrolysis because of the decreased sodium and silica contents. More lignin would precipitate if too low a final pH value (e.g., pH 8.0) was adopted. A final pH value of 10.3 is generally appropriate to achieve relatively high silica removal efficiency and low lignin precipitation [33]. For recovery boiler operations, mills prefer to process black liquors

Material	Elemental Analysis, wt %						Ash, wt %	LHV, MJ/kg
	C	H	N	S	O	Cl		
Raw BLS	31.84	4.95	0.31	0.85	36.67	0.44	40.10	11.25
BLS-DeSi pH 9.0	30.41	3.79	0.66	0.61	32.74	0	31.8	13.36
BLS-DeSi pH 8.0	32.64	3.95	0.78	0.65	30.38	0	31.6	11.47

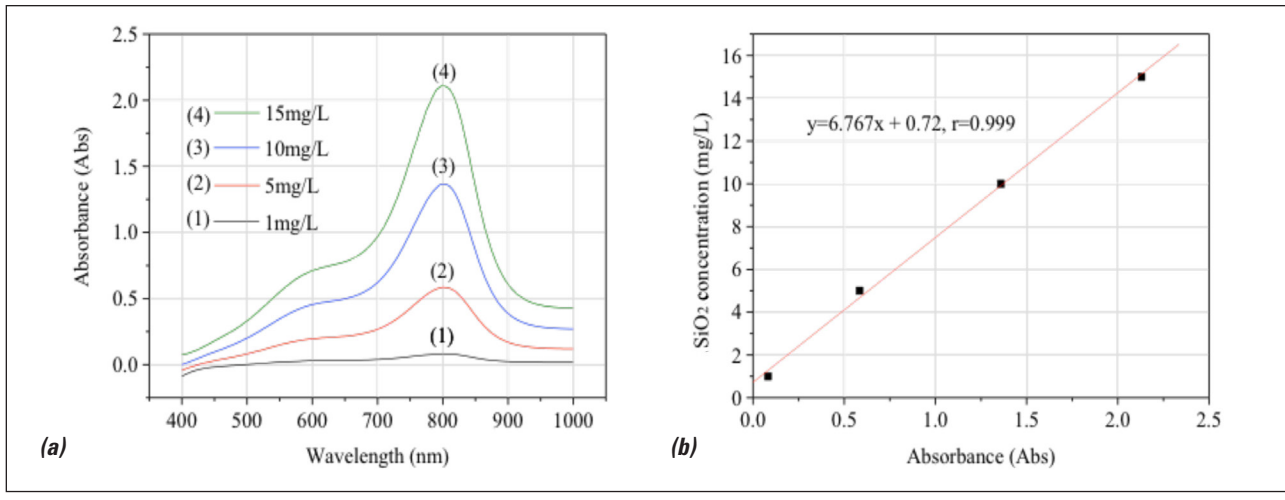
BLS = black liquor solids; BLS-DeSi = desilicated black liquor solids; C = carbon; H = hydrogen; N = nitrogen; S = sulfur; O = oxygen; Cl = chlorine; LHV = lower heating value; MJ = megajoule.

I. Analysis of raw and desilicated black liquor (dry basis).

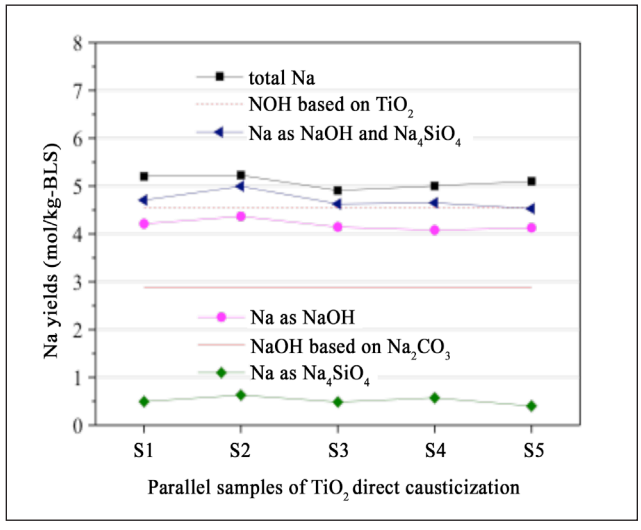
Material	Main Inorganics in Black Liquor Solids, wt %				Total Titratable Alkali, mol/kg BLS
	Black liquor residue	Green liquor dreg	Na_2CO_3	Na_4SiO_4	
Raw BLS	2.11	0.65	26.1	12.1	7.82
BLS-DeSi pH 9.0	0	2.27	27.78	5.29	6.39
BLS-DeSi pH 8.0	0	2.92	24.68	4.39	5.61

BLS = black liquor solids; BLS-DeSi = desilicated black liquor solids; Na_2CO_3 = sodium carbonate; Na_4SiO_4 = sodium orthosilicate.

II. Main inorganic components of straw black liquor ash (dry basis).



5. (a) Absorbance as a function of wavelength for the blue silica complex, and (b) standard calibration curve used to determine silicon dioxide (SiO_2) content.



6. Sodium (Na) recovery from raw straw black liquor in the direct causticization process using titanium dioxide (TiO_2).

with LVH as high as possible. To obtain silica and lignin materials as in previous studies [3-5], we could expect a lower operational final pH. The gasification or combustion characteristics [34] of desilicated straw black liquor need further study. In this work, desilicated straw black liquor was used to investigate the effects of silica on direct causticization agents.

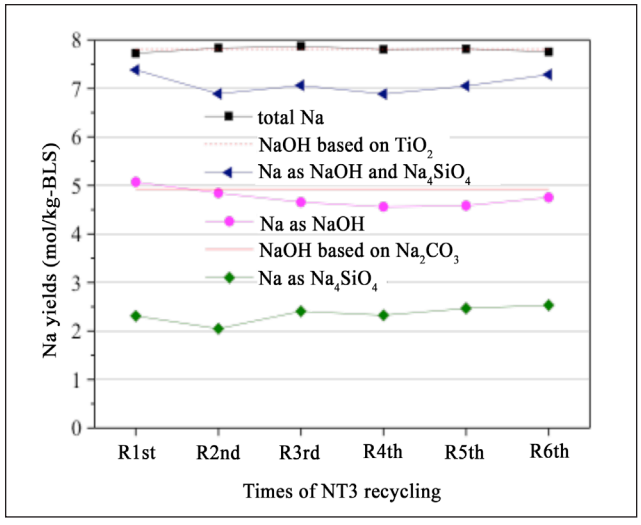
Sodium recovery from raw straw black liquor in direct causticization process

Figure 6 shows sodium recovery from raw straw black liquor in the direct causticization process using TiO_2. Five batches of black liquor char and TiO_2 mixtures were completely gasified and causticized in the tube furnace. The derived solid residue was hydrolyzed to white liquor and $Na_2O{\cdot}3TiO_2$. Theoretically, the NaOH content of the white liquor should be in accordance with Eqs. (1)-(3), shown as the red solid line in Fig. 6. The products of the direct causticization reaction depend on the mole ratio of the reactants (Na_2CO_3 and TiO_2). The hydrolysis of $Na_2O{\cdot}3TiO_2$ to sodium hexatitanate ($Na_2O{\cdot}6TiO_2$) can be neglected at high NaOH concentrations. Considering the mole ratio of TiO_2 to Na_2CO_3, the actual NaOH content obtained should not be higher than the theoretical value based on Na_2CO_3. However, the measured value of NaOH was nearly 50% higher than that calculated based on Na_2CO_3 and much closer to that calculated based on TiO_2. The sodium orthosilicate (Na_4SiO_4) content in the white liquor was much lower than it would be if all silica in the black liquor had transferred to the white liquor; in fact, nearly 80% of silica deported to the hydrolysis-derived solid phase.

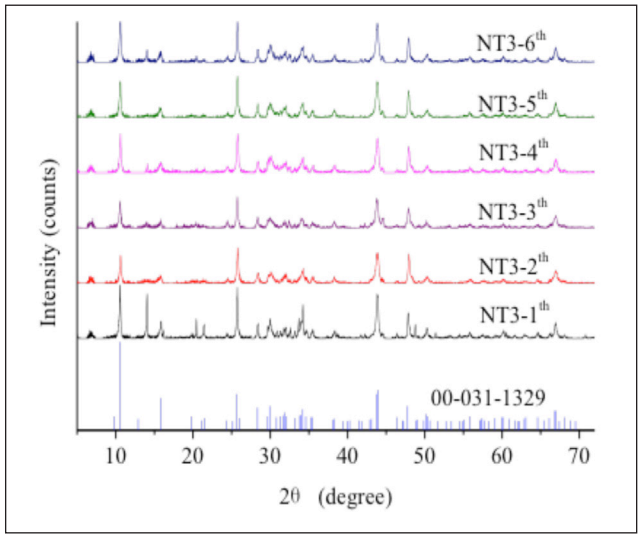
The previous analysis hints that the sodium silicates might react with TiO_2 in a manner similar to the direct causticization of Na_2CO_3 shown in Eqs. (1) and (2), and the products can be hydrolyzed to release NaOH. This inference is further investigated in the following discussion.

The hydrolyzed solid products were used as the starting material for testing $Na_2O{\cdot}3TiO_2$ as a reagent in direct causticization recycling tests. Six cycles were conducted using black liquor char derived from raw black liquor. On measuring the mass of the solid products produced in each cycle, no obvious increase was detected. That is, the accumulation of inorganics (nonprocess elements [35]) in $Na_2O{\cdot}3TiO_2$ can be neglected for a limited number of recycles. This implies that the direct causticization process can potentially be applied to straw black liquor, which generally has a higher content of nonprocess elements than wood black liquor.

Figure 7 shows the sodium recovery from raw straw black liquor using $Na_2O{\cdot}3TiO_2$. The yields of NaOH are relatively stable, which means that the reactivity of $Na_2O{\cdot}3TiO_2$ did not deteriorate as the number of recycles increased (within the limited number of runs carried out). XRD analysis of recycled $Na_2O{\cdot}3TiO_2$ supports the same conclusion (**Fig. 8**). The XRD patterns also showed that $Na_2O{\cdot}3TiO_2$ was the major phase in the hydrolyzed solid products of each cycle and that no significant amounts of $Na_2O{\cdot}6TiO_2$ were identified.



7. Sodium (Na) recovery from raw straw black liquor in the direct causticization recycling process using NT3.



8. X-ray diffraction patterns of solid products produced from raw straw black liquor by direct causticization using NT3.

In contrast with the use of TiO_2, when the direct causticization agent changes to $Na_2O{\cdot}3TiO_2$, the NaOH yields (NaOH ratio in total titratable alkali) are close to the calculated value based on Na_2CO_3 and almost all of the silica deports to the hydrolyzed liquid phase (Fig. 7). This means that a reaction similar to that occurring between silicates and $Na_2O{\cdot}3TiO_2$ might not occur when TiO_2 is used as the direct causticization agent. This characteristic has two effects on the sodium recovery from straw black liquor: 1) the silica will not consume $Na_2O{\cdot}3TiO_2$ or accumulate in the hydrolyzed solid products, and 2) lime causticization will still be needed to increase the efficiency of sodium recovery.

Mechanism of silica transformation during direct causticization

To analyze the transformation of silica during direct causticization using TiO_2, we assumed that the silicate reactions given in Eqs. (7)-(14) occur under the same conditions as for Na_2CO_3 direct causticization. **Table III** lists the thermochemical data for Gibbs free energy, G, where the values for $4Na_2O{\cdot}5TiO_2$ and $Na_2O{\cdot}6TiO_2$ are derived by linear regression using the data for $Na_2O{\cdot}TiO_2$, $Na_2O{\cdot}2TiO_2$, and $Na_2O{\cdot}3TiO_2$ from [36] and verified by [37].

Substances	G (kJ/mol), 1100 K	G (kJ/mol), 1200 K
Na_2SiO_3	–1772.990	–1803.967
$Na4SiO_4$	–2448.819	–2496.649
TiO_2 (rutile)	–1041.550	–1055.784
SiO_2	–993.498	–1006.262
$Na_2O{\bullet}TiO_2$	–1776.534	–1808.916
$Na_2O{\bullet}2TiO_2$	–2852.778	–2896.934
$Na_2O{\bullet}3TiO_2$	–3897.781	–3956.492
$Na_2O{\bullet}6TiO_2$*	–7084.858	–7182.599
$4Na_2O{\bullet}5TiO_2$*	–8187.587	–8328.425
* calculated value		

III. Thermochemical data for substances used in spontaneity calculations.

$$4Na_2SiO_3 + 5TiO_2 \rightarrow 4Na_2O{\cdot}5TiO_2 + 4SiO_2 \quad (7)$$

$$7Na_2SiO_3 + 5Na_2O{\cdot}3TiO_2 \rightarrow 3(4Na_2O{\cdot}5TiO_2) + 7SiO_2 \quad (8)$$

$$Na_2SiO_3 + 3TiO_2 \rightarrow Na2O{\cdot}3TiO_2 + SiO_2 \quad (9)$$

$$Na_2SiO_3 + 6TiO_2 \rightarrow Na2O{\cdot}6TiO_2 + SiO_2 \quad (10)$$

$$2Na4SiO_4 + 5TiO_2 \rightarrow 4Na2O{\cdot}5TiO_2 + 2SiO_2 \quad (11)$$

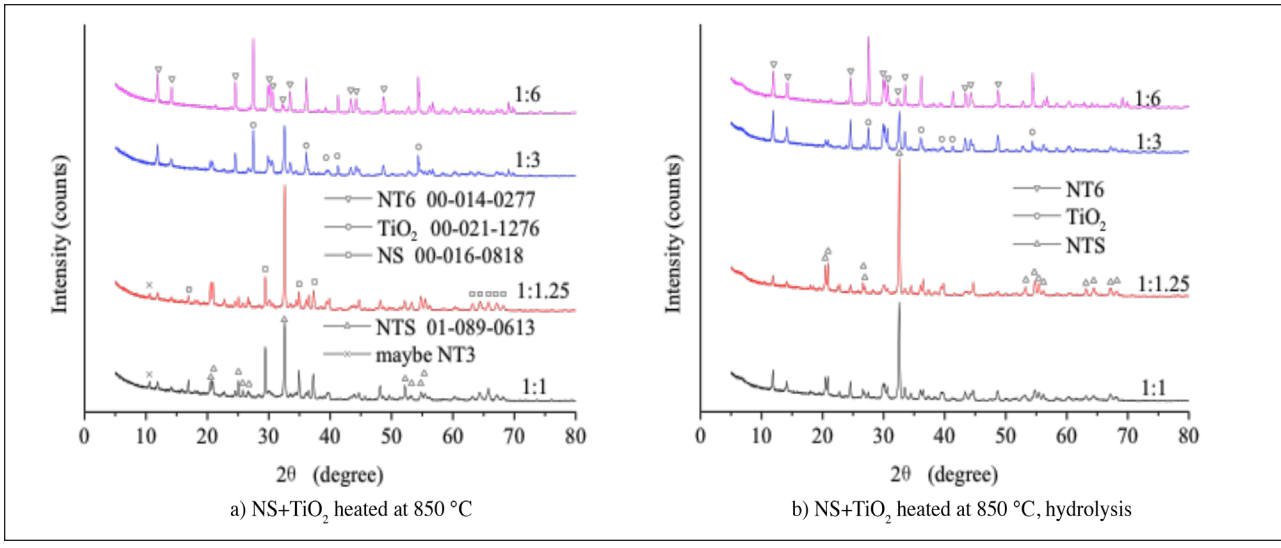
$$3.5Na4SiO_4 + 5Na_2O{\cdot}3TiO_2 \rightarrow 3(4Na_2O{\cdot}5TiO_2) + 3.5SiO_2 \quad (12)$$

$$Na4SiO_4 + 6TiO_2 \rightarrow 2(Na_2O{\cdot}3TiO_2) + SiO_2 \quad (13)$$

$$Na4SiO_4 + 12TiO_2 \rightarrow 2(Na_2O{\cdot}6TiO_2) + SiO_2 \quad (14)$$

The calculation showed that, within the temperature range of direct causticization, reactions (Eqs. [7] and [8]) do not proceed spontaneously, the reaction in Eq. (9) might be spontaneous, and the reactions in Eqs. (10)-(14) are spontaneous. To confirm this inference, Na_2SiO_3 was selected as a model compound for straw black liquor silicates, and the mole ratios of TiO_2 and Na_2SiO_3 were set at 1, 1.25, 3, and 6. Mixtures of these different mole ratios were heated at 850°C for 15 min and the solid products were hydrolyzed after sampling. **Figure 9** shows the XRD analyses of two solid products.

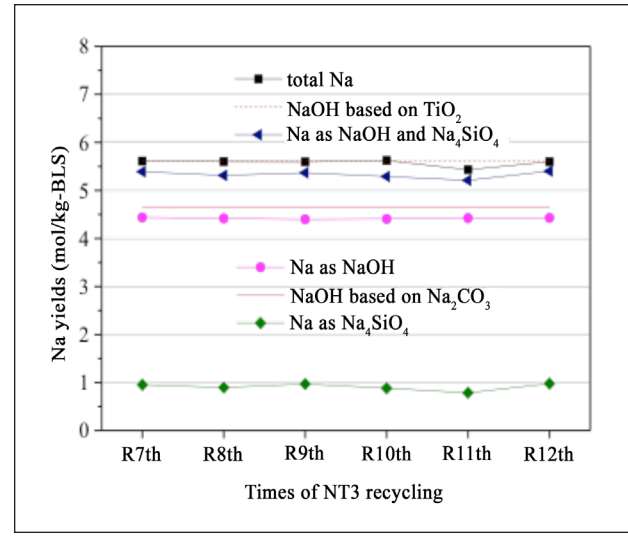
As indicated by Eqs. (7)-(10), these data confirm that $Na_2O{\cdot}6TiO_2$ formed during the heating process in three of the sodium titanates. Furthermore, according to the titration data, little NaOH was detected, the NaOH yields decreased gradually as the mole ratios increased, and almost no NaOH was



9. X-ray diffraction patterns showing the presence of a silicon–titanium–sodium ternary compound.

generated in the liquid phase at a mole ratio of 6. We therefore conclude that a small quantity of $Na_2O{\cdot}3TiO_2$ might be present in the heated solid products when the mole ratios are less than or equal to 3 and that the $Na_2O{\cdot}3TiO_2$ also might be slightly hydrolyzed at very low hydroxide concentrations in solution [26]. The correlation between the experimental results and the assumptions further confirms the spontaneity of reactions that occur during the direct causticization of straw black liquor (Eqs. [11]-[14]).

The previous analysis can also explain the mechanism of silica combining with the hydrolyzed solid products and the increasing NaOH yield. A strong diffraction peak at about 32.6°, attributed to $Na_2O{\cdot}TiO_2{\cdot}SiO_2$ (NTS), is observed in the XRD patterns shown in Fig. 9. According to literature [38], NTS is a congruent ternary compound with a melting point of about 965°C. There is no evidence in this study or in literature indicating that it is easily hydrolyzed. The formation of NTS should therefore be considered an important factor that leads to the combining of silica and TiO_2.



10. Sodium (Na) recovery from desilicated straw black liquor (pH 8.0) by direct causticization.

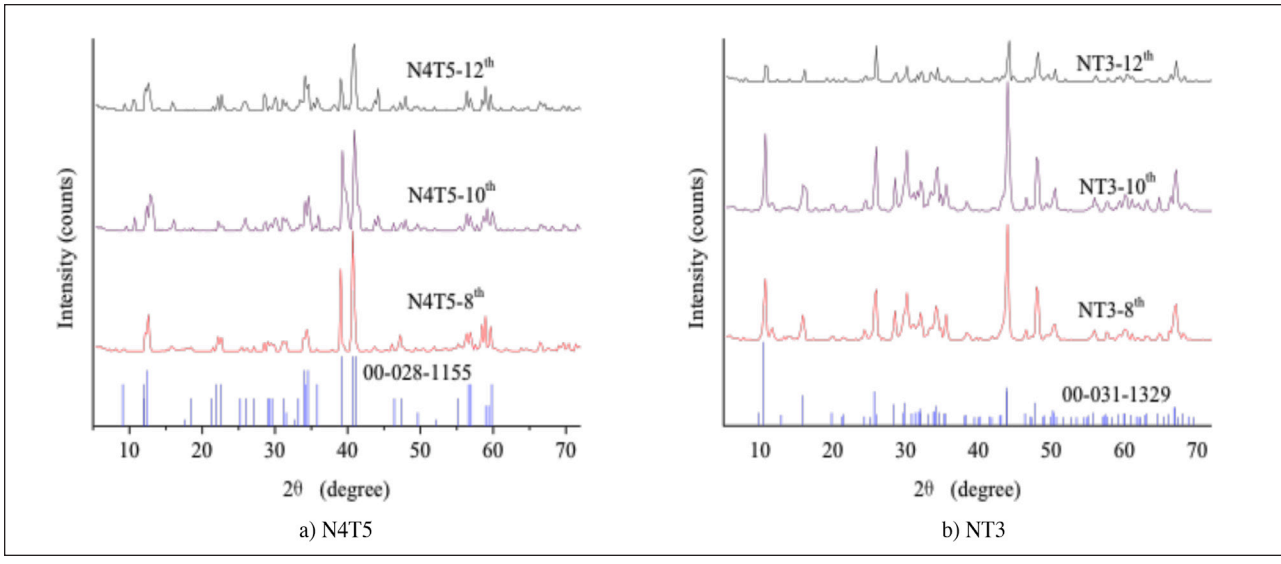
Sodium recovery from desilicated straw black liquor in direct causticization process using recycled $Na_2O{\cdot}3TiO_2$

As discussed previously, silica present in straw black liquor transfers to the white liquor during direct causticization with $Na_2O{\cdot}3TiO_2$, so conventional lime causticization might still be needed to remove silica and recover as much NaOH as possible. This means that the silica problem will not be completely overcome by applying direct causticization technology to straw black liquor. To further understand the effects of silica on direct causticization agents and to improve the sodium recovery efficiency, the feed material was changed to desilicated straw black liquor at a final pH of 8.0 on the seventh recycle. **Figure 10** shows the results for the recovery of sodium from desilicated straw black liquor using recycled $Na_2O{\cdot}3TiO_2$.

The NaOH yields increased from 60% to 80% on changing from raw to desilicated black liquor (Fig. 7). Considering the NaOH recovered in the cathode cell, the total NaOH yields exceed 85% of total titratable alkali. The presence of sodium silicates and the conversion limits of Na_2CO_3 to $4Na_2O{\cdot}5TiO_2$ are the two major factors that affect the total NaOH yield. In all recycling runs, the conversion of Na_2CO_3 reached 95%; so, improving the total NaOH yield is highly dependent on the silica removal efficiency.

Implications for straw pulp mills

The theoretical white mud ($CaCO_3$) production is 1.25 tons per ton NaOH in the lime cycle, but actual output typically exceeds 2 tons per ton NaOH in a straw pulp mill chemical recovery process, which amounts to about 0.6 tons white mud per ton of dry straw black liquor. The presence of silica prevents white mud produced from straw black liquor from being



11. X-ray diffraction patterns showing the presence of a silicon–titanium–sodium ternary compound.

recovered using a rotary kiln, such as is done in wood pulp mills. Treating straw black liquor as solid waste incurs considerable disposal fees for the pulp mill. Researchers have therefore explored ways to make full use of straw black liquor white mud, such as by making paper-filling calcium carbonate or using it as a sulfur absorbent [39].

Substituting the lime cycle with a titanate cycle would avoid the disposal of white mud, provided that silica could be removed effectively. The price of TiO_2 is some five times that of calcium oxide, so the possibility of changing of the reactivity during the recycling process is particularly noteworthy. In this study, after changing the feed material to desilicated black liquor, the direct causticization reactions went well and no detectable deterioration of the direct causticization agents were found, according to the XRD patterns (**Fig. 11**) and titration data. A greater number of recycles in a larger-scale test unit need to be carried out to further evaluate the feasibility of applying direct causticization to straw black liquor.

CONCLUSIONS

This preliminary study evaluated TiO_2 and recycled $Na_2O{\cdot}3TiO_2$ as direct causticization agents for recovering sodium from wheat straw black liquor, which is rich in silica compared with wood black liquor. The study has shown that there are differences in the mechanism of silica transfer between these two agents.

1) When using TiO_2, most of the silica is retained in the solid residue after hydrolysis, which can be attributed to the reactions between sodium silicates and TiO_2, similar to those that occur during direct causticization with Na_2CO_3. The formation of $Na_2O{\cdot}TiO_2{\cdot}SiO_2$ also accounts for the deportment of silica to the hydrolyzed solid products.

2) When using $Na_2O{\cdot}3TiO_2$ as the direct causticization agent, however, nearly all of the silica transfers to the hydrolyzed liquid phase. This characteristic means that the silica in straw black liquor will not consume considerable amounts of $Na_2O{\cdot}3TiO_2$, but further causticization with lime might be necessary to improve the sodium recovery efficiency.

Adopting practice from the chlor-alkali industry, straw black liquor was treated by ionic-membrane electrolysis to recover NaOH and hydrogen at the cathode, and leaving low-sodium black liquor and precipitated silica at the anode. This desilicated, low-sodium straw black liquor was subjected to direct causticization recycling using $Na_2O{\cdot}3TiO_2$. The NaOH yields increased to about 80% from 60% when compared with use of raw straw black liquor. Considering the NaOH recovered in the electrolysis cell, the total NaOH yields exceed 85% of total titratable alkali. The results show the technical feasibility of applying the direct causticization process to straw black liquor, provided that silica can be removed effectively. **TJ**

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Nonwood fibers still play an important role in the virgin pulp markets of countries such as China, India, and Egypt that are poor in wood resources. However, silica is present in such materials, and straw pulp mills usually encounter problems from silica that dissolves from those into the black liquor. If the black liquor is concentrated in a multiple-effect evaporator, some of the silica deposits onto the heating surfaces, gradually decreasing capacity. The chemical recovery efficiency is not so high as wood kraft black liquor because of some sodium silicates, and the white mud is not proper for recycle using a rotary kiln.

Direct causticization technology has been pursued for nearly 30 years by the pulp and paper industry. However, it is not yet clear whether direct causticization is suitable for the processing of straw black liquor. Silica might transfer to the recycled sodium tri-titanate ($Na_2O{\cdot}3TiO_2$), either chemically or physically, so the mass of the direct causticization agents would increase with each cycle. Such a situation would overload recovery boilers or gasifiers or substantially increase the titanium dioxide (TiO_2) makeup requirement. This work evaluates TiO_2 and recycled $Na_2O{\cdot}3TiO_2$ as direct causticization agents with respect to their possible interaction with silica.

Dahlquist et al. [18] summarized some of the still-unresolved problems related to the direct causticization process, including the following:

- How did different types of black liquor respond?
- Would it be possible to add all TiO_2 in a reasonable way, so as not to destroy the energy balance?
- Would the TiO_2 react with the sodium carbonate (Na_2CO_3)?

Nohlgren et al. [22] carried out repeated direct causticization recycling using wood kraft black liquor.

This work selected silica-containing straw black liquor (silica removed or not) as a material to conduct direct causticization recycling. Electrolysis was used for silica removal instead of acid precipitation. The findings would expand the knowledge on direct causticization process, especially the interaction between TiO_2 and nonprocess elements.

The results of the research show that the silica present in straw black liquor will not consume considerable $Na_2O{\cdot}3TiO_2$, but further causticization with lime might still be needed to improve the sodium recovery efficiency. We are pursuing practical and economic methods, such as electrolysis, to remove silica from straw black liquor.

This study provided several interesting findings. In the direct causticization process, there are some mechanism differences between TiO_2 (the initial direct causticization agent) and $Na_2O{\cdot}3TiO_2$ (the recycling direct causticization agent):

1. When using TiO_2, most of the silica is retained in the solid residue after hydrolysis, which can be attributed to the reactions between sodium silicates and TiO_2, with $Na_2O{\cdot}TiO_2{\cdot}SiO_2$ as a major product.
2. When using $Na_2O{\cdot}3TiO_2$ as the direct causticization agent, however, nearly all of the silica transfers to the hydrolyzed liquid phase. This characteristic means that the silica present in straw black liquor will not consume considerable causticization agent in the industrial scale.

Straw pulp mills that have surplus black liquor load might test to dispose this part of the black liquor using a direct causticization process.

As a next step, we are planning to find ways for silica removal from straw black liquor, and to construct a small scale setup for black liquor gasification experiment.

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