

Sugar-Derived Causticization Additives for the Bayer Process

Amit Desai, Jun Su An, and LoongYi Tan

Abstract

Bauxite digestion in the Bayer process results in a buildup of sodium carbonate in the caustic liquor, which reduces the efficiency of alumina production. This effect is mitigated by lime causticisation, during which carbonate is removed, preferably as calcium carbonate. The extent and efficiency of causticisation in Bayer liquors are limited by the formation of tricalcium aluminate (TCA) and aluminocarbonates, which also reduce overall plant productivity due to the consequent loss of alumina from the liquor. We demonstrate that TCA formation can be minimized or eliminated by using sugar-derived molecules, specifically gluconic acid, a mixture of gluconic and glucaric acids, and sodium gluconate. This reduction in TCA formation improves the efficiency of causticisation by three to four times as determined by the rate constants for carbonate consumption or by the relative increase of C/S ratio. This in turn reduces alumina and caustic losses in the causticiser, with the potential to improve the plant liquor C/S and hence the overall productivity of the Bayer circuit.

Keywords

Bayer process • Causticization • Organic acids and salts • Tricalcium aluminate inhibition

Introduction

Bayer process liquors are inevitably contaminated with carbonate, which arises from base-catalyzed oxidation of organic compounds and dissolution of inorganic carbonate from the bauxite, and absorption of CO_2 from the air [1, 2]. The carbonate content of Bayer liquor is conventionally expressed as the caustic to soda ratio, C/S , where $C = [\text{NaOH}]$ in units of g/L of Na_2CO_3 and $S = C + [\text{Na}_2\text{CO}_3]$ in the same units. $C/S = 1$ for pure NaOH.

Lime causticisation is used to limit the carbonate content of the liquor and thus maintain its productivity. Improvements in the causticization process therefore lead to better liquor productivity, and hence higher alumina production, as well as lower lime consumption. The C/S of the main liquor stream in Bayer refineries is generally in the range of 0.80–0.95, depending on carbonate inputs and the efficiency of the causticisation process. The desired solid product of causticisation (calcium carbonate) is rarely formed directly in Bayer liquors, but mostly via aluminocarbonate intermediates, with tricalcium aluminate (TCA) as the undesired byproduct. TCA formation not only reduces causticisation and increases lime usage but also results in alumina loss that directly reduces the overall alumina yield of the Bayer plant. The relative proportions of calcium carbonate and TCA depend on a range of equilibrium and kinetic factors [3, 4]. Approaches to limiting TCA formation include causticising at high temperature (e.g., at 145 °C) in a single stage [5] or multiple stages [6], or at normal temperatures (<105 °C) using chemical additives such as phosphate [7] or gluconate [8] as ‘TCA inhibitors’.

In this paper, we describe preliminary results on sugar-derived molecules as TCA inhibitors or causticization additives. The inhibitors tested are gluconic acid, a mixture of gluconic and glucaric acid, and sodium gluconate. These molecules were produced by oxidizing sugars using Solugen’s proprietary, carbon-negative chemenzymatic process.

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Materials and Methods

Materials

Laboratory-grade hydrated lime and sodium aluminate, and analytical-grade sodium hydroxide were purchased from Chem-Supply, Australia. Analytical-grade sodium sulfate, sodium carbonate, aluminium hydroxide, and silica were purchased from Sigma-Aldrich. A 50 wt% aqueous solution of gluconic acid, sodium gluconate in powder form, and 45 wt% aqueous solution of a proprietary mixture of gluconic and glucaric acid ('Gluconic-Glucaric Mix') were supplied by Solugen Inc.

Preparation of Synthetic Bayer Green Liquor (SBGL)

Synthetic Bayer Green Liquor was used to mimic the liquor during the causticization process in a production setting. Sodium hydroxide, aluminium hydroxide, sodium carbonate, silica, sodium sulfate, and quick lime were dissolved in deionized (DI) water at 70 °C in a stainless-steel vessel with stirring using an OLS Aqua Pro Shaking Water Bath. In accordance with the American Bayer industry convention, **A** is the concentration of Al_2O_3 in g/L, **C** (caustic) is the concentration of $\text{NaOH} + \text{NaAlO}_2$ in units of g/L Na_2CO_3 equivalent, and **S** (soda) = $\text{C} + \text{Na}_2\text{CO}_3$ (g/L). The concentrations of the ingredients were adjusted to achieve the composition shown in Table 1. Batches of SBGL were prepared prior to each experimental run and used immediately to avoid auto-precipitation of alumina.

Table 1 Target composition of SBGL

Components	A	C	A/C	S	SiO_2	Na_2SO_4
Conc. (g/L)	75	115	0.65	140	1	6

Table 2 Data for causticization of SBGL with and without sodium gluconate using 40% excess lime, 95 °C

Additive	Time (min)	A	C	S	C/S
Blank	0	74.6	117	141.8	0.83
	30	70.3	127.2	145.6	0.87
	60	70.4	128.3	146.9	0.87
	180	69.0	125.7	146.6	0.86
Sodium gluconate	0	75.7	118	142.1	0.83
	30	73.3	135.3	145.2	0.93
	60	72.8	138.3	145.7	0.95
	180	70.7	130.6	146.5	0.89

Procedure to Evaluate Causticization Additives

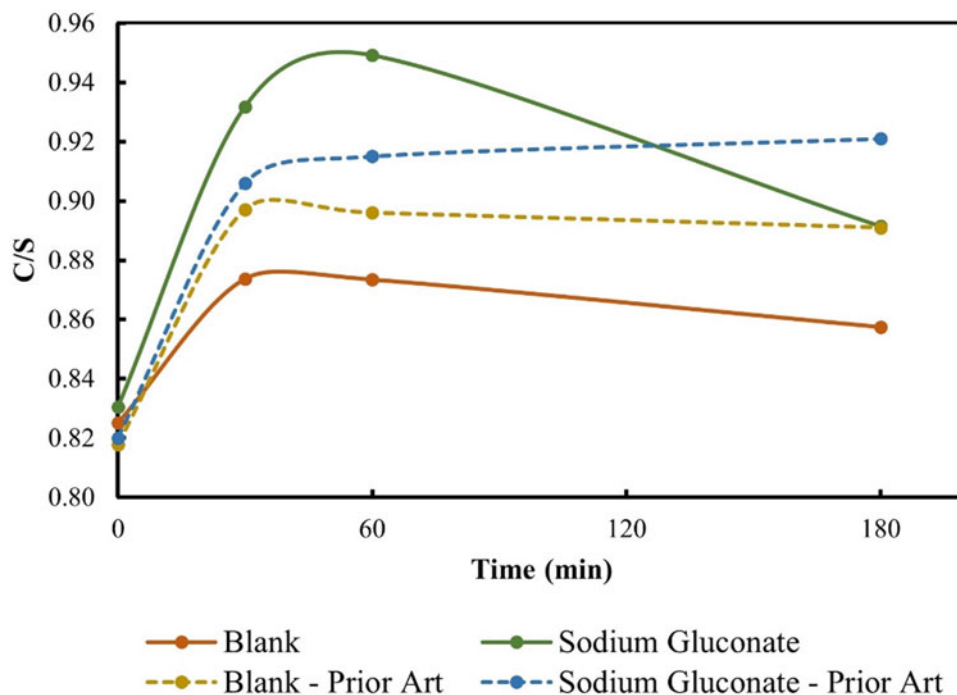
SBGL (0.5 L) was heated to 95 °C with agitation. The causticization additive was dosed at a molar concentration of 4.58 mM (equivalent to 1 g/L sodium gluconate, as per prior art [3, 5]). Reaction was initiated ($t = 0$) by adding a 140% stoichiometric lime charge, and the reaction mixture was continuously agitated in a shaking water bath at 95 °C in separate bottles according to the number of samples required. After the desired reaction time, the appropriate sample was filtered (through a 0.45 μm Acrodisc®) and analyzed for **A**, **C**, and **S** using the Bayer Liquor Analysis by Infra-red (BLAIR) system [9, 10]. At the end of the pre-determined reaction time, the bulk slurry was filtered and the filtrate was analyzed for **A**, **C**, and **S**.

Results and Discussion

The results of an initial test on the effect of gluconate on causticisation are shown in Table 2.

C/S ratio as a function of time is plotted in Fig. 1 along with comparative values for a similar test in a plant liquor from the literature [3]. The current test shows a significantly greater initial enhancement by gluconate, followed by a decline which is not evident in the presence of gluconate in the previous work. These differences are probably due to differences in testing protocols and/or differences between the specific plant liquor and our SBGL. Such drops in **C/S** ratio have been attributed to a change in reaction mechanism favoring the formation of tricalcium aluminate (TCA) over calcium alumino-carbonate or carbonate solids [3]. Our

Fig. 1 C/S ratio as a function of time along with comparison to prior art [3], 40% excess lime, temperature 95 °C



results indicate that the greatest benefits of reagent addition will be evident in the first 60 min of reaction, so the effects of the different additives were evaluated in that period with more frequent sampling.

Comparative Effects of Solugen Additives

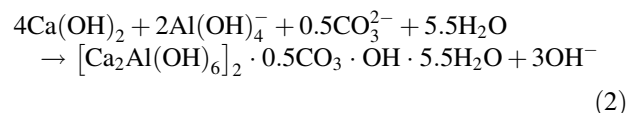
Experiments were conducted with 4.58 mM of gluconic acid, sodium gluconate, and gluconic-gluconic mix. Samples were collected at 0, 10, 20, 30, 40, and 60 min for the dosed solutions, with ‘Blank’ at 30 and 60 min. The results are shown in Table 3. The Causticisation Extent (CE) in the last column is the proportion of carbonate that is converted ($[S-C]$), expressed as a percentage. The performance of each additive is shown in Fig. 2 as a chart of CE versus time. The data in Table 3 and Fig. 2 confirm that the causticization additives are effective in increasing the C/S ratio, and consequently the consumption of carbonate. The total amount of caustic (C) increased by approximately 10% with use of causticization additive compared to ‘Blank’. As the theoretical yield of alumina extraction is proportional to the amount of caustic [1], the causticization additives can potentially increase the yield by almost 10%.

The curves in Fig. 2 indicate that the consumption of carbonate ($[S-C]$) follows a first-order reaction kinetic, i.e.,

$$\frac{d[S-C]}{dt} = -k[S-C] \quad (1)$$

Reaction rate constants, k , for the different experimental runs are listed in Table 4. The data in Table 4 indicate that the causticization additive leads to a faster rate of consumption of the carbonate, with gluconic acid being the most effective.

The reactions occurring during the causticization process have been described by Rosenberg et al. [3] and Roach [4]. From perspective of explaining the mechanism of causticization additives, the three important reactions are formation of calcium aluminate hemihydrate, hemihydrate to calcite conversion, and formation of tricalcium aluminate (TCA). The calcium hydroxide reacts with aluminium hydroxide ions and carbonate to form the hemihydrate version ($[Ca_2Al(OH)_6]_2 \cdot 0.5CO_3 \cdot 5.5H_2O$) of the calcium aluminate as follows (the hemihydrate converts to a more stable monohydrate version, but this conversion is not included to better elucidate the mechanism of causticization additives) [2]:



From the hemihydrate, two reactions can occur. The desirable reaction is with the carbonate to form calcium carbonate, thus increasing causticity of the liquor by removal of carbonate, as follows [3]:

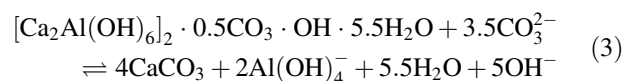


Table 3 Data for causticisation of SBGL with various additives. 40% excess lime, 95 °C

Additive	Time (min)	A	C	S	C/S	CE (%)
GOGA	0	80.2	123.7	147.4	0.839	0
	10	78.9	139.0	149.7	0.928	55
	20	77.8	139.2	149.8	0.929	55
	30	78.3	140.6	148.2	0.949	68
	40	78.4	143.1	149.9	0.955	71
	60	78.7	142.4	149.4	0.953	70
SG100	0	79.3	125.2	146.9	0.853	0
	10	76.2	136.6	149.7	0.912	40
	20	77.4	139.6	149.1	0.936	56
	30	77.6	139.7	148.5	0.941	59
	40	76.2	141.1	149.5	0.945	61
	60	77.0	141.7	149.4	0.948	65
GO50	0	75.8	119.2	143.5	0.831	0
	10	74.6	135.5	143.4	0.945	68
	20	74.6	138.0	144.4	0.956	74
	30	73.7	137.3	145.2	0.946	68
	40	73.8	139.0	143.5	0.968	82
	60	74.3	137.8	143.8	0.958	75
Blank	0	74.6	117	141.8	0.825	0
	30	70.3	127.2	145.6	0.874	26
	60	70.4	128.3	146.9	0.874	25

Fig. 2 Causticisation extent (CE) as a function of time for various causticization additives in relation to blank at 40% excess lime, 95 °C

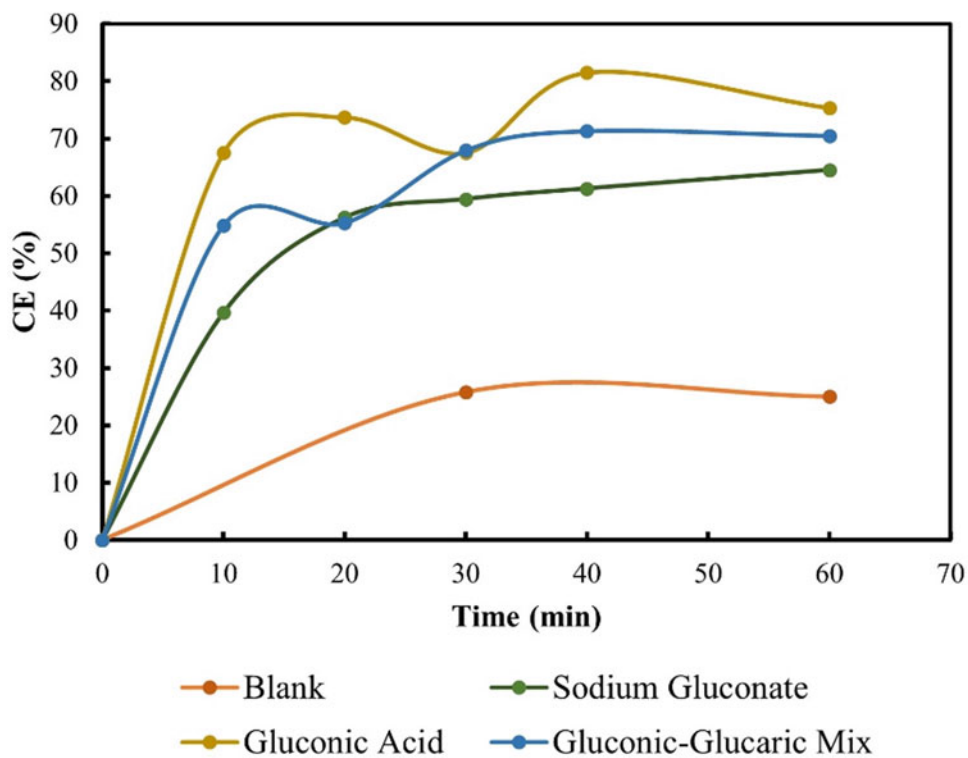
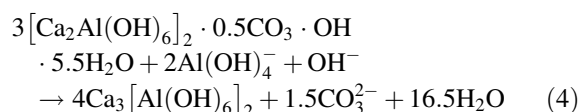


Table 4 Rate constants for consumption of carbonate based on data in Table 3

Additive	k (min^{-1})
Blank	0.48×10^{-2}
Sodium gluconate	1.55×10^{-2}
Gluconic acid	1.94×10^{-2}
Gluconic-gluconic mix	1.82×10^{-2}

The undesirable reaction is with the aluminate and hydroxyl species to form TCA and releasing carbonate back into the liquor [3]:



The formation of TCA ($\text{Ca}_3[\text{Al}(\text{OH})_6]_2$) is undesirable as it consumes caustic and aluminate from the liquor, creating caustic and alumina losses without removing carbonate. Reactions described in (3) and (4) are in competition, and for higher causticization efficiency it is desirable to promote (3) and/or inhibit (4). As gluconic acid, glucaric acid and their salts are good chelating agents for aluminium [11, 12], we hypothesize that they bind with the aluminate in reaction (4) and hence inhibit formation of TCA. It is important that this aluminate complexation is not so strong as to hamper the initial rapid formation of hemiacarbonate (reaction (2)). For this reason, strong aluminium chelants such as ethylenediaminetetraacetic acid (EDTA) or citric acid are likely not suitable causticisation promoters, whereas mild aluminium chelating agents such as gluconic acid, glucaric acid, and their salts function as excellent causticization additives. To better understand the mechanisms and further improve causticization efficiency through the use of additives, further investigations are needed to examine the effect of different concentrations of additives and lime, to analyze the compositions of the solid reaction products, and to verify performance in plant liquors. For instance, it has been shown that in synthetic Bayer liquor, gluconate can affect the crystallization rate by adsorbing on the alumina crystal and suppressing crystal growth [1].

Conclusions

Sugar-derived products (from Solugen) based on gluconic and glucaric acids have been shown to be effective additives in improving the causticisation of a synthetic Bayer process liquor. The use of these additives can improve the efficiency of causticisation, reducing alumina and caustic losses and

increasing the causticity achieved, as measured by the final C/S (caustic to soda) ratio in the causticiser, which has the potential to improve the plant liquor C/S and hence the overall productivity of the Bayer process (by almost 10%). The action of the inhibitors is explained in terms of their ability to bind with aluminate ions in solution to an extent sufficient to inhibit the undesirable formation of tricalcium aluminate (TCA) without detrimentally affecting reactions leading to the removal of carbonate from solution. Further work is needed to optimize the process, understand the mechanism, and evaluate their effectiveness in Bayer plant liquors.

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