



CONVERSION OF WASTE GLASSES INTO SODIUM SILICATE SOLUTIONS

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ABSTRACT

In this study, hydrothermal and fusion methods used to prepare sodium silicate solution from waste glasses. Three different color of waste glasses (white, green and brown), the waste products of municipal and industry are rich in amorphous silica was used to produce sodium silicate solution. The best condition for sodium silicate solution production was reacted waste bottle glass reaction with 90 wt. % NaOH at 650°C for 60 min. The chemical compositions of liquid products were analyzed by standard TIS 433-1996 method. The results indicated that under favorable conditions, liquid sodium silicate with having Na₂O/SiO₂ molar ratio of about 1 : 5 can be produced by this method. The silicate solution contains 0.01-0.05 wt./v% of iron and 0.00-0.01 wt./v% of sulfate as impurity. The process established in the present study was found to have a potential applicability as a recycling process of waste glasses.

Key words: Sodium silicate, Water glass, Waste glasses.

INTRODUCTION

Recycling and valorization of by-products and waste materials coming from municipal and industrial processes has become a problem more and more urgent for the next future. In the light of environmental norms aiming at limiting the use of the dump, the development of new recycling techniques capable also of exploiting the wastes into new marketable products aquires an increasing importance. In Thailand (2010), there are approximately 1.71 million tons of waste glasses generated into sanitary landfills. The proportion of the utilization of recyclable waste glass in industrial sector had utilized 60% of the total waste (1.02 million tons). Approximately 40% of waste glass are generated, which organizations of manage waste to prevent the contaminate in the environmental.¹ Recycling glass form the municipal solid waste stream for use as a raw material in new glass product is limited due to high costs, impurities and mixed color. Although colored waste glasses with

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their low recycling rate have been dumped into landfills sites. For the above waste glasses, it is known that silicon dioxide (SiO_2) is the main component in the glasses, e.g., 60-80 mass % SiO_2 for the colored glass bottles, lamps and laboratory glass wares. Soluble sodium silicate (waterglass) is liquids containing dissolved glass which have some water like properties. They are widely used in industry as sealants, binders, deflocculants, emulsifiers and buffers. Their most common applications in Thailand are in the pulp and paper industry and the detergent industry, in which they improve the action of the detergent and lower the viscosity of liquid soaps etc. Sodium silicate is produced by direct fusion of precisely measured portions of pure silica sand (SiO_2) and soda ash (Na_2CO_3) in oil, gas or electrically fired furnaces at temperatures above 1000°C . Also, it's may be produced either by dissolving the alkali silicate lumps in water at elevated temperatures (and partly at elevated pressure) or for contain qualities also by hydrothermally dissolving a reactive silica source (mainly silica sand) in the respective alkali hydroxide solution. Various raw materials can be used in the manufacturing of sodium silicate solution as silica sources, such as quartz sand², oil shale ash³, rice hull ash⁴, cristobalite⁵, tridymite⁵, perlite⁴, clay⁷, and kimberlite tailing⁸. Bareness is reported in published or patented literature wherein waste bottle glass has been used as a source of silica for the preparation of sodium silicate. This work has as objection to produce sodium silicate solution using waste bottle glass as silica source. The detailing of the production process is presented.

EXPERIMENTAL

Materials and methods

The waste bottle glasses were supplied by Meuang district market (Lampang, Thailand). Waste bottle glasses were used as replacement silica with different colors (white, green and brown). They were milled to homogenize to less than $63\ \mu\text{m}$ (230 mesh). Due to economic reasons, no purification process was performed in order to increase silica content. Sodium hydroxide (purity 98%) from Sigma-Aldrich was used as received.

Experimental production of sodium silicate solution by hydrothermal method

Hydrothermal treatment of waste bottle glasses with sodium hydroxide solutions was carried out in a closed stainless steel vessel by volume of 125 mL. The following variables in this work had been performed: NaOH/SiO_2 molar ratio (1, 2, 3 and 4), $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio (11, 15, 19 and 23), reaction time (varying of 20 to 100 min) and reaction temperature (110, 130, 150, 170 and 190°C). The conversion silica to silicate, expressed in weight percentage, was determined by mass balance as described by Foletto et al.⁹

Experimental production of sodium silicate solution by alkaline fusion method

Before melting the waste bottle glasses by alkaline fusion method, the condition alkali was clarified. Samples of sodium silicate [(100-x) SiO₂.xNaOH (x = 50, 60, 70, 80 and 90 mas%)] were prepared by melting the crushed waste glass, which the particle sizes were within 63 μm, and reagent grade NaOH. After mixing the waste glass and NaOH in nickel crucible with a capacity of 200 mL, a batch (10 g) was melted in the nickel crucible in an electric furnace at 450, 500, 550, 600 and 650°C. The melting times were 20, 40, 60, 80 and 100 min, respectively. The melts of sodium silicate were then naturally cooled, and these samples were dissolved in deionized water (600 mL) in a beaker (a capacity of 100 mL). Thus, sodium silicate solution was obtained.

Quantitative chemical analysis of waste bottle glasses were carried out by X-ray fluorescence (XRF, Oxford, Model ED2000). X-ray diffraction patterns were performed on an Bruker D5005, using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) beam with an acceleration voltage of 35 kV and current of 35 mA. The diffraction angle (2θ) was scanned from 5° to 80°. The obtained sodium silicate was analyzed by standard wet chemical and spectroscopic methods. The Na₂O content of the silicate solution was measured by titration with HCl and the SiO₂ content by precipitation, iron content by photometric of ferrous iron with 1,10-phenanthroline and sulfate content by gravimetric procedure given by TIS 433-1996 (Thai Industrial Standard Institute).

RESULTS AND DISCUSSION

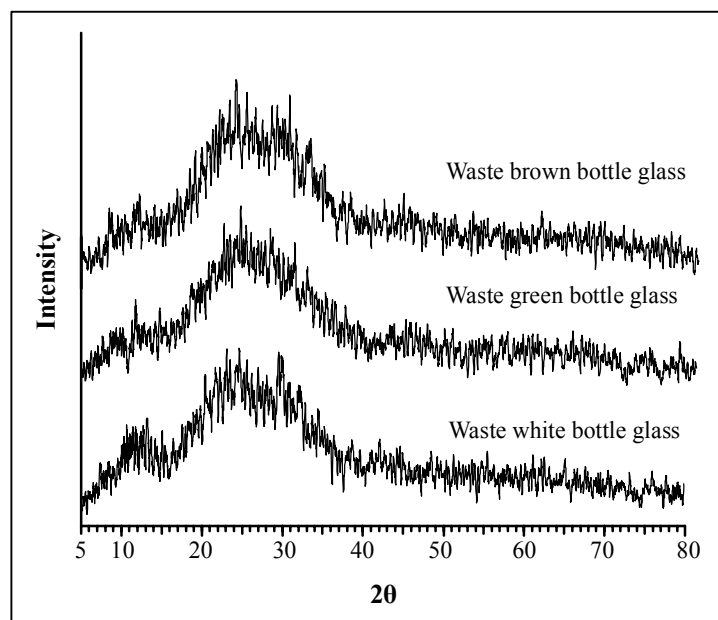
The chemical compositions of waste bottle glasses in the form of stable oxides are shown in Table 1. The major component was SiO₂ content with 75.54, 71.80 and 79.46 wt.% for waste white, green and brown bottle glasses, respectively, which silica is sufficient to use as a source of silica for produce sodium silicate solution.

X-ray diffraction (XRD) patterns of all waste bottle glasses are shown in Fig. 1. The waste bottle glasses diffractogram indicated the presence of silica in the amorphous form due to the predominant one broad peak entered at 25°. The broadening of the X-ray peaks occurs when the crystallite or grain size of the material is very small (< 0.1 μm). Peak broadening increases with decreasing crystallite size. Another researcher recommended a crystallite silica is the most stable form while amorphous silica is the most soluble.¹⁰⁻¹² Therefore, due to its high percentage in the silica (amorphous form), waste bottle glasses were considered as a new economically viable raw materials to produce sodium silicate solution.

Table 1: Chemical compositions of waste bottle glasses

Chemical compositions (wt. %)	Waste bottle glasses		
	White	Green	Brown
SiO ₂	75.54	71.80	79.46
Al ₂ O ₃	0.60	1.55	0.91
Fe ₂ O ₃	3.90	4.50	5.28
CaO	3.92	3.45	2.09
MgO	1.80	2.10	0.85
Na ₂ O	3.86	4.57	1.39
K ₂ O	5.06	3.14	3.95
P ₂ O ₅	2.34	1.36	1.86
TiO ₂	0.51	0.51	0.58
MnO	0.00	0.00	0.00
LOI*	1.54	2.67	0.82

*Loss on ignition

**Fig.1: X-ray diffraction patterns of waste bottle glasses**

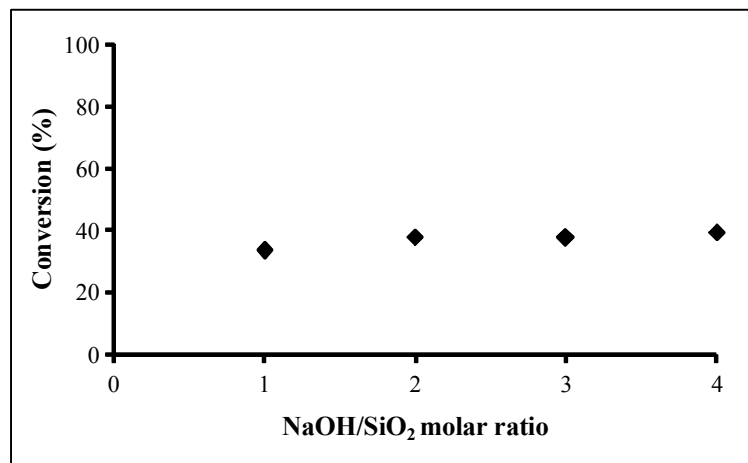


Fig. 2: Silica conversion as function of NaOH/SiO₂ molar ratio (using WGBG as silica source under hydrothermal conditions: 150°C for 60 min, H₂O/SiO₂ molar ratio = 23)

Fig. 2 presents the effect of NaOH/SiO₂ molar ratios on silica from waste green bottle glass (WGBG) conversion into soluble silicate by employed H₂O/SiO₂ molar ratio = 23. It is observed that the increasing of NaOH/SiO₂ molar ratio from 2 to 4 are not significant different the values of the conversion. Fig. 3 presents the conversion results as a function of H₂O/SiO₂ molar ratio. From Fig. 2 and 3, both of NaOH/SiO₂ and H₂O/SiO₂ molar ratios increase with little inducing the increasing of silica conversion.

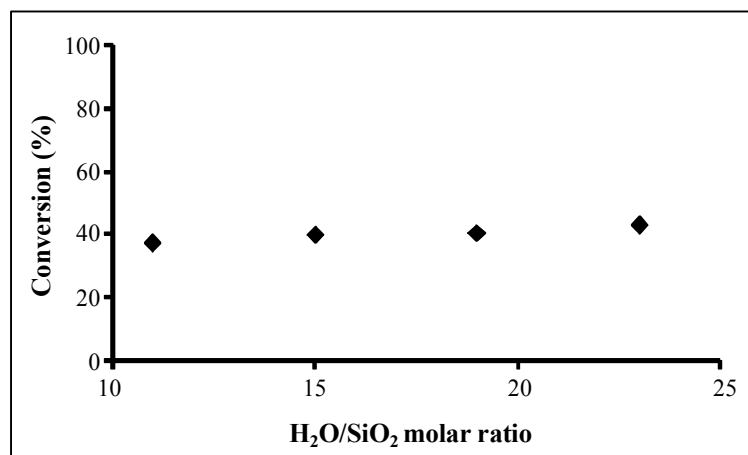


Fig. 3: Silica conversion as function of H₂O/SiO₂ molar ratio (using WGBG as silica source under hydrothermal conditions: 150°C for 60 min, NaOH/SiO₂ molar ratio = 4)

With this, for the following assays a $\text{NaOH}/\text{SiO}_2 = 4$ and $\text{H}_2\text{O}/\text{SiO}_2 = 23$ molar ratios were used as conditions in Fig. 4 with presents the effect of reaction time and temperature on silica conversion. It is observed that the conversion increases up to 72.07% at 190°C for 60 min, the optimized hydrothermal conditions. We also used the other method, the alkaline fusion, to converse the waste bottle glasses as Fig. 5 and 6. Fig. 5 shows the effects of NaOH concentration on preparation of soluble sodium silicate at 550°C for 60 min, indicate the concentration of NaOH increases as well as the silica conversion increase.

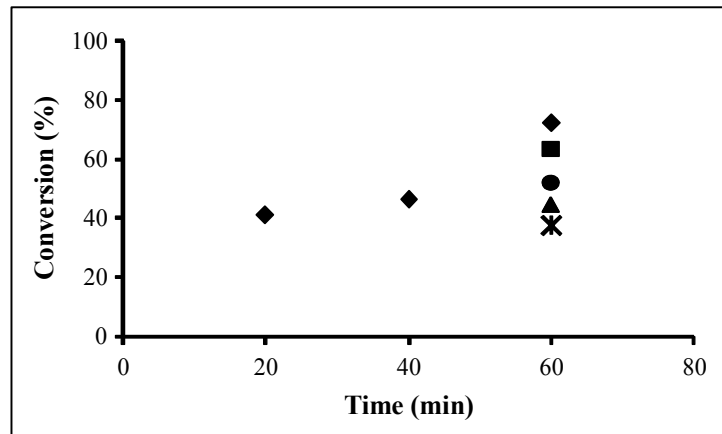


Fig. 4: Silica conversion as function of reaction time for different temperature (♦) : 190°C, (■) : 170°C, (●) : 150°C, (▲) : 130°C, (*) : 110°C (using WGBG as a silica source under hydrothermal conditions: $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio = 23, NaOH/SiO_2 molar ratio = 4)

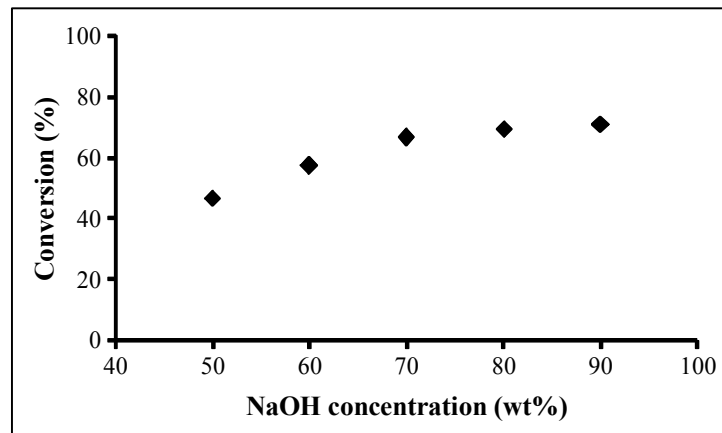


Fig. 5: Silica conversion as function of NaOH concentration (wt. %) at 550°C for 60 min (using WGBG as silica source under alkaline fusion conditions)

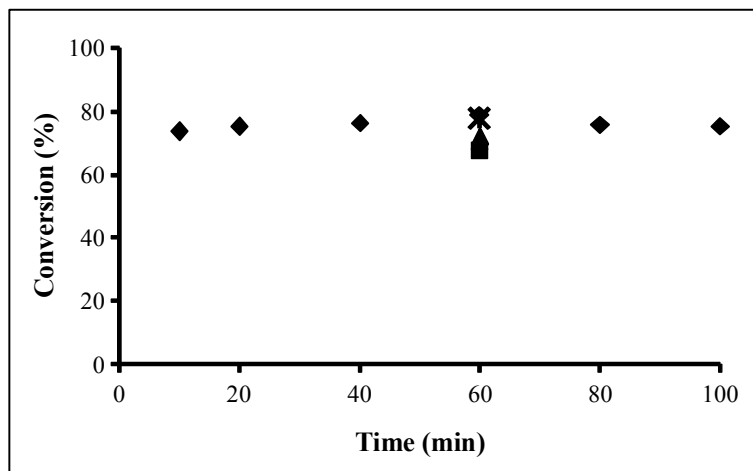


Fig. 6: Silica conversion as function of reaction time for different temperature (♦): 650°C, (■): 600°C, (●): 550°C, (▲): 500°C, (*): 450°C (using WGBG as a silica source under alkaline conditions: 90 wt. % NaOH)

Fig. 6 presents the influence of reaction temperature and time on silica conversion. It is observed that the conversion increases with the temperature rise, reaching 78.91% at 650°C for 60 min, are optimized.

Table 2: Chemical compositions of soluble sodium silicate for the two types of method: hydrothermal and fusion

Production method	Molar ratio of Na ₂ O : SiO ₂	Iron (wt./v %)	Sulfate (wt./v %)
Hydrothermal			
WWBG ^a	1 : 7.74	0.05	0.01
WGBG ^b	1 : 6.88	0.03	0.01
WBBG ^c	1 : 5.72	0.02	0.01
Fusion			
WWBG ^a	1 : 4.89	0.01	0.00
WGBG ^b	1 : 5.16	0.03	0.00
WBBG ^c	1 : 4.64	0.01	0.01

^aWaste white bottle glass, ^bWaste green bottle glass, ^cWaste brown bottle glass

To compare two methods for silica conversion as show in Table 2, the molar ratio of $\text{Na}_2\text{O} : \text{SiO}_2$, iron and sulfate obtained from hydrothermal and fusion method at various starting waste bottle glasses. All hydrothermal was at 190°C for 60 min with NaOH/SiO_2 and $\text{H}_2\text{O}/\text{SiO}_2$ molar ratios of 4 and 23, respectively. Other, we used the optimized condition (the composition (wt. %); $\text{NaOH} : \text{waste bottle glass} = 90 : 10$, melting temperature and time at 650°C for 60 min). It was found that for all waste colored bottle glasses, hydrothermal method give more molar ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ than fusion method. Generally, a high $\text{Na}_2\text{O}/\text{SiO}_2$ value is preferable because the system needs lower equivalent of $\text{Na}_2\text{O}/\text{SiO}_2$, we get the maximum percent silica conversion (soluble silica)¹³. From this result, it is expected that the soluble sodium silicate converted from waste colored bottle glasses by NaOH fusion. Also, we observed that soluble sodium silicate prepared contain relatively small amounts of iron and sulfate, which may be considered advantageous because iron and sulfate are undersirable for use in detergent industry.

CONCLUSION

In this study, waste bottle glasses, a municipal and industrial waste, was used as raw material to produce a sodium silicate solution. We demonstrated that by alkaline fusion treatment of raw waste glass with NaOH , soluble sodium silicates of optimized compositions can be produced. For example, alkaline fusion treatment of waste glass at 650°C with NaOH and waste glass ratio of 90 wt. % for 60 min gives liquid sodium silicate composition, which is commercially an important product.

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