COMPARATIVE SYNTHESIS OF SODIUM SILICATE FROM RICE HUSK AND KAOLIN

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ABSTRACT

Sodium silicate in powdered form was successfully synthesized from both rice husk ash and Kankara kaolinite clay. The impure nature of both monomer and NaOH used does not seems to hinder the depolymerization reaction viz-a-viz product formation. The crystallinity of sodium silicate produced tends to increase with reaction time, temperature, and Na_2O/SiO_2 ratio. About 93% crystallinity for as-synthesized sodium silicate was obtained using Na_2O/SiO_2 molar ratio of 0.9, reaction time and temperature of 75mins and 100°C, respectively. The starting material and product formed were characterized using XRF, XRD and SEM analysis. The result proved that the sodium silicate produced can serve as an excellent replacement to its commercial counterpart.

Keywords: *Kankara kaolin, deploymerization, rice husk ash, sodium silicate*

Introduction

Sodium silicate is a critical raw material for many consumer chemical processes as well as monomer for many consumer and commercial products including corrosion inhibitor, anti-scaling agent, viscosity adjustor and zeolites, just to mention but few. Sodium silicate is commonly prepared via reaction in liquid phase or in solid phase, using alkaline and quartz as raw materials [1,2]. In liquid phase, mixture of caustic soda, quartz sand and steam is feed into a reactor and allowed to react following equation (1).

$$nSiO_2 + 2NaOH \rightarrow Na_2O.nSiO_2 + H_2O \; . (1)$$

The solid phase involves reaction between either sodium sulphate or sodium carbonate and quartz at very high temperature (between 900^0C and 600^0C) in molten state to form sodium silicate as depicted by equations (2) and (3).

$$Na_2CO_3 + \; SiO_2 \rightarrow Na_2O\,(SiO_2) + CO_2. (2).$$

$$2Na_2SO_4 + C + \; 2SiO_2 \rightarrow 2Na_2O\,(SiO_2) + 2SO_2 + CO_2. (3).$$

This process of manufacturing sodium silicate, depicted in equations 2 and 3, is considered expensive due to the high energy required at the calcination stage (above 1000^0C), in addition to considerable air pollution by emission of dust, nitrogen and sulphur oxides [3,4]. Although this calcination process is widely used in industrial scale, there is another process based on the reaction of amorphous silica (am-SiO_2) with NaOH [5].

Kalapathy *et al.,* [6] in 2000 reported the successful production of flexible sodium silicate films from rice husk ash. Cha and Park in 2001 [7] also reported successful synthesis of sodium silicate from clay from Sancheong-Hadong, Korea via alkaline leaching at 25-100^0C under atmospheric pressure. Ayegba *et. al*., [8] in 2015 reported successful production of silica gel from clay, they claimed that the yield of production depends on the reaction time and alkaline concentration.

In 2000, Icenhower and Dove [9] established the fact that the dissolution of amorphous silica (am-SiO_2) is a function of the temperature and the concentration of simple electrolyte solutions. The solubility of am-SiO_2 is relatively low at pH 7, with reported values ranging between 100 and 130 ppm at 25^0C. However, the solubility increases dramatically above pH 9. The number of silicate anions present rises as Si concentration is increased, pH is decreased and/or temperature is decreased. [10-13].

Silicon dioxide (SiO_2), also known as silica, is prevalent within diverse marine and terrestrial environments and comprise a significant fraction of the Earth's crust. It is the oxygen bridge bonds between silicon atoms that give SiO_2 many of its unique properties. The bond angle Si-O-Si is nominally about 145 degrees, but can vary from about 100 to 170 degrees with very little change in bond energy. It's this structure that gives silica its stability and rigidity toward depolymerisation, a major setback in energy minimization in sodium silicate production. [14,15].

Nigeria is richly blessed with kaolin amounting to about two (2) billion metric tons deposit scattered all round the country [16]. The clay of kaolinite nature contains both alumina, silica and other associated impurities depending on source location. For effective removal of alumina from clay, calcination is a critical step for kaolin activation and enhanced digestibility of alumina, followed by acid leaching for longer contact time of reaction. At the same time, Nigeria is also a high consumer of rice products, Obassi and Ajoku [17] reported an annual national paddy rice production of 3.32 million tons amounting to about 664, 000 tons of rice husk generated per year. The disposal of rice hulls is a substantial problem for rice growers, since the hulls are not suitable for use as fertilizers and until now have to be disposed of either by open burning or burying. When burnt in an uncontrolled manner, the ash which is essentially silica is converted into crystalline forms and becomes less reactive [18].

Accordingly, we sought to make use of the silica resulting from acid-treated kaolin and rice husk ash for sodium silicate production, while comparing the quantity and quality of the as-synthesized products from both sources.

Materials and Methodology

Materials

The rice husk was obtained from a local market in Zaria, Kaduna State, kaolin from Kankara village, Katsina State. The NaOH and H_2SO_4 were of laboratory grade, obtained from local vendors. The distill water used was prepared in our laboratory (Department of Chemical Engineering, ABU, Zaria).

Methodology

Rice husk pre-treatment

Rice husk was soaked for 4 days in tap water to remove stones and dirt and then dried under atmospheric condition. The rice husk was then soaked in 10 w/w % sulfuric acid, boiled at 85^0C for 1 hour, then allowed to steep for 24 hours in the acid solution [19]. The acid treated rice husk was thoroughly washed, until neutrality and then dried at 100^oC for seven (7) hours, in an oven.

Charring and Calcination of the Husk

The pre-treated rice husk was charred in the open furnace for two hours at 200^oC. The rice husk was charred to ensure it does not smoke during calcination in the furnace. The charred rice husk, black in colour was transferred to the muffled furnace where it was calcined at 500 ^{0}C for 6 hours [19]. The rice husk ash (RHA), white in colour was then ball milled for 4 hours to obtain fine particles size below 53µm.

Beneficiation of Kankara Kaolin

Raw Kankara kaolin was soaked in tap water in a plastic bucket and the slurry was allowed to stand for three (3) days. During the three days, it was periodically stirred and fresh water added after decanting the supernatant water every 12 hours. This was done to get rid of soluble impurities in the clay mineral and grits amongst others. The slurry was sieved to get rid of coarse particles with a 53 µm mesh sieve. The fine suspension thus obtained was allowed to settle and the supernatant water decanted. The sediment was dried at atmospheric condition, followed by oven drying at 100^oC for 12 hours. The product from this stage was hereafter referred to as Beneficiated Kaolin.

Calcination and Dealumination Process

The dry beneficiated kaolin powder was placed in crucibles after grinding and calcined in a muffled furnace at 750^0C for 6 hours to obtain metakaolin - a more reactive phase of kaolin [16]. 20 g of metakaolin was measured into a conical flask and 20 cm^3 of distilled water was added to it. 16.8$cm^3$of 98 w/w% sulfuric acid (3 folds stoichiometric requirement) was measured and then added to the metakaolin slurry in the conical flask and the reaction was left for about 35 minutes on a heating mantle, after which additional distilled water was then added to quench the reaction. This time ensured complete dealumination of metakaolin. The reaction mixture was then filtered through the sinter glass filter, after washing to neutrality.

Synthesis of Sodium Silicate

32.5 cm^3 of water was poured into a beaker containing 1.3g of NaOH to make 1M NaOH solution. The dealuminated kaolin and rice husk were placed in a beaker containing 1M NaOH solution and left to age for 14 hours at 35^0C. The resulting slurry was made to react at 100^0C for 90 mins. After which the reaction was quenched with distilled water and washed to neutrality. This was later dried atmospherically and in oven, set at 140^0C for 24 hours.

The resulting sodium silicate from both rice husk ash and kaolinite clay were compared with commercial one using XRD, to establish the desirable source of silica for further investigation. Kaolinite clay was chosen for further considerations while investigating the effects of alkalinity, reaction times and temperatures.

Calculated amount of NaOH was mixed with the dealuminated sample to obtain Na_2O/SiO_2 molar ratio ranging between 0.7 and 0.9. The resulting mixture was homogenized left to age for 4hrs at 35^0C, prior to reaction at 90^0C and 60mins. At this stage, the best Na_2O/SiO_2 molar ratio was established, while the other factors, namely, reaction time (45-75mins) and temperature (70-100^0C) were determined following OVAT method of experimentation. The water quantity used was kept constant for all the experimentation.

Result and Discussion

Treatment of RHA and Kankara Kaolin

The compositional analysis of the raw kaolin depicted in the second column of Table 1 indicated significant amount of oxides of potassium, iron, titanium and magnesium which are considered to be impurities. The silica/alumina ratio of kaolin was calculated as 2.29, which is an indication of the crystallinity state and purity level of the kaolin.

Beneficiation process shifted silica/alumina ratio towards 2, by reducing the free silica, which was removed through dissolution or floatation. The silica to alumina ratio of beneficiated kaolin calculated from data obtained from Table 1 gave a value of 2.11 and comparing with silica to alumina ratio of raw Kankara clay indicates a decrease in the silica to alumina ratio. The alumina content was noticed to increase proportionally to the removal of impurities. Impurities such as potassium oxide and iron oxide were observed to reduce owing to beneficiation

Table 1 showed that inorganic content of the rice husk has a high amount of silica (95.1%) and a few impurities which can be attributed to the nature of soil, the rice was cultivated on. The silica content was observed to increase tremendously with treatment. Dealuminated samples was observed to have 91.7% silica (as shown in Table 1) pointing to removal of alumina-enrichment in term of silica. The increase in other oxides were blamed on the water used for quenching and washing. The silica content of dealuminated Kaolin was 91.7%, which is also high when compared to the rice husk ash, the sodium silicate synthesized is compared on this premise.

Figure 1(a) showed that the clay possess all the necessary characteristic peaks attributed to kaolinite material. Upon heating, these peaks were observed to disappear leading to formation of semi-amorphous metakaolin, as depicted in Figure 1(b).

Table 1: compositional analysis of samples

Oxides	**Percentage Composition (weight %)**				
	Raw Kankara Kaolin	Ben. Kaolin	Deal. Kaolin	Raw Rice Husk	Rice Husk Ash
SiO_2	58.300	53.1	91.7	48.8	95.1
Al_2O_3	43.2	42.750	*ND	5.0	*ND
Na_2O	0.120	0.074	*ND	0.16	*ND
SO_3	0.189	0.185	0.68	8.75	0.05
Fe_2O_3	3.160	1.320	0.212	3.23	0.162
CaO	0.150	0.113	0.441	3.23	0.287
K_2O	1.260	0.981	1.87	10.2	0.092
ZnO	0.176	0.175	0.313	0.10	0.01
PbO	0.043	0.042	ND	1.30	0.99
MnO	0.09	0.019	0.01	0.679	0.044
Si/Al (mol %)	2.29	2.11			

*ND-Not detected

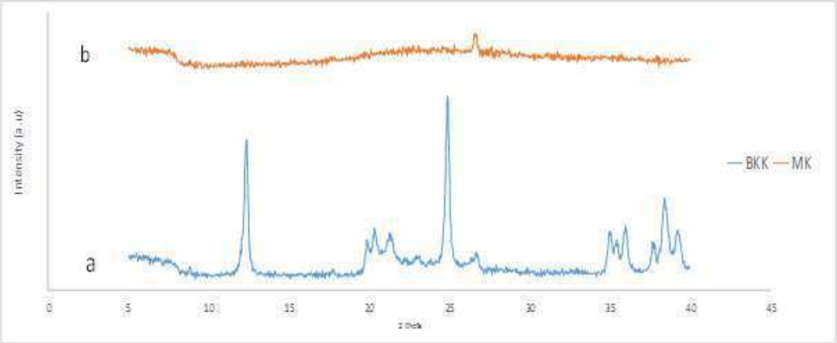

Fig. 1: XRD analysis Kankara kaolin

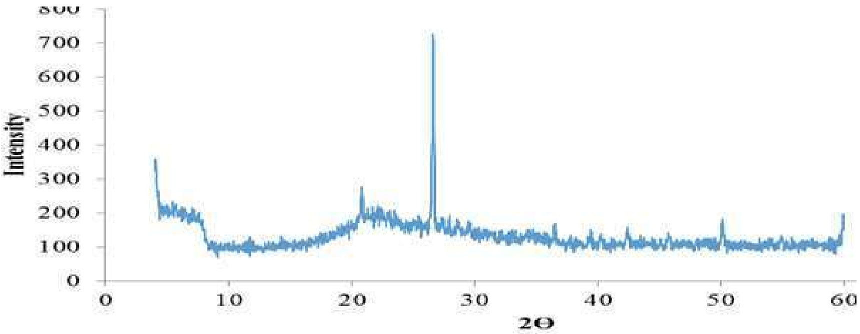

Fig 2: XRD analysis for RHA calcined at 500°C

Figure 2 shows the diffratogram for riche husk ash. The peaks at 2Θ of around 26 show the formation of silica [20] which when compared with that of the husk (diffratograph not shown) tends to be sharper. The appearance of this peak suggest the effect of thermal treatment of the rich husk, which also corroborate the findings from XRF and SEM.

Figure 3a depicts the SEM for raw Kankara kaolin showing aside the silica-alumina card-like pattern, the rod-like halloysite material and dark spot responsible for accommodating both water molecules and cellulosic materials.

Beneficiation was able to handle some of the water soluble impurities as well as the free uncombined phases, as shown in figure 3b.

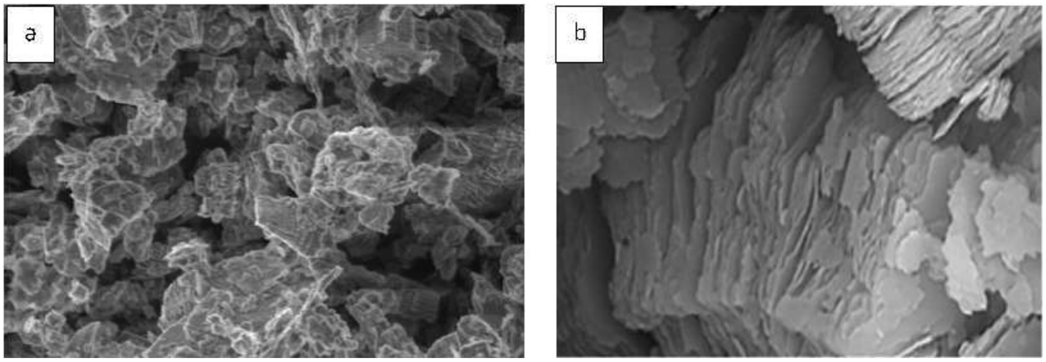

Figure 3. SEM images for (a) Raw Kaolin (b) Beneficiated Kaolin

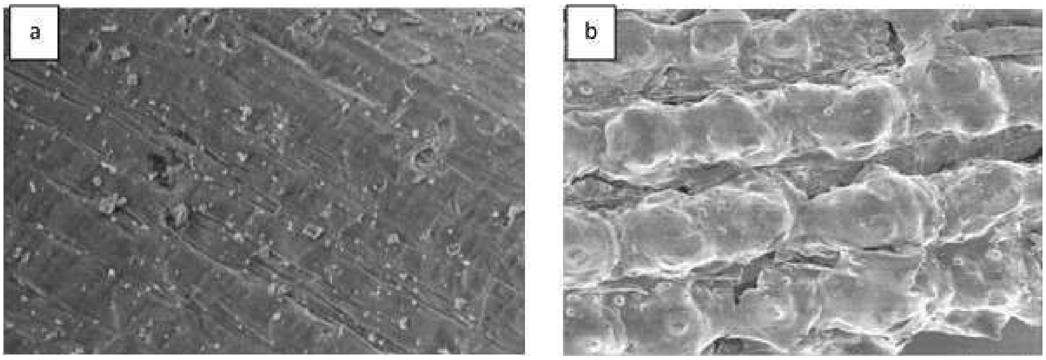

Figure 4. SEM images for (a) Raw Rice Husk (b) Rice Husk Ash

The SEM image in figure 4a shows that the surface structure of the raw rice husk was intact and smooth, while that of the husk (figure 4b) appeared to be exposed and uneven with cracks. This distruption might have been caused by the effect of acid treatment followed by calcination, thereby rendering the rice husk ash more amorphous.

Synthesis of Sodium Silicate

The diffractograms in figures 5a and b are similar for silica from both rice husk ash and Kankara kaolin respectively, providing a ground for comparison of products formed from the two sources. The diffractograms indicate the presence of silica in predominantly amorphous form. The broad peak observed around 2Θ value of 26^0C in both cases is characteristic of opaline silica. The intensity of the peak at 26^0C is somewhat the same, but there are more peaks in the XRD for rice husk than in Kaolin, indicating that the silica from Kankara kaolin is slightly more amorphous and therefore expected to be more reactive.

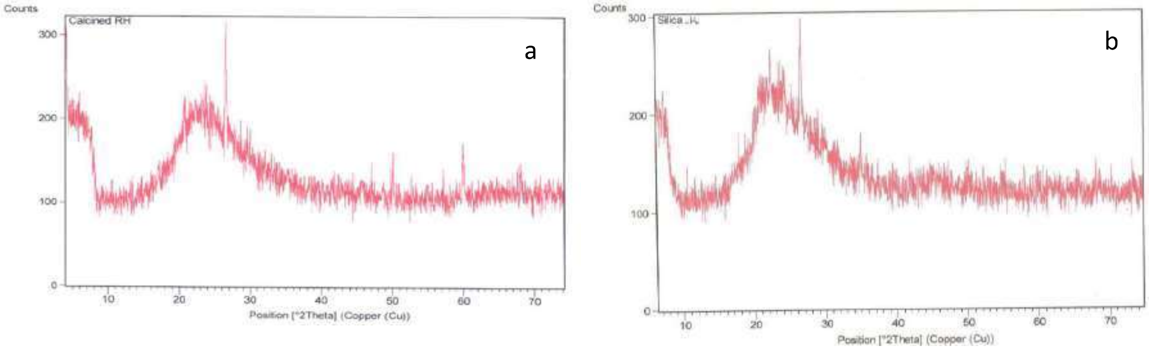

Figure 5: XRD patterns for silica from (a) rice husk ash and (b) Kankara kaolin

The prominent peaks used to identify sodium silicate are at about 2θ position of 16.8^o, 25.0^o and 29.3^o. The XRD patterns for as-synthesized sodium silicate from rice husk and Kankara kaolin in figure 6 gave all the characteristic sodium silicate' peak when compared with diffractogram of commercial sodium silicate, indicating its purity viz-a-viz crystallinity. Figure 7 shows some bumps (scattered pattern) in the XRD pattern of sodium silicate from RHA and commercial sodium silicate which might suggest an amount of amorphousity. The aforementioned statement reveals that sodium silicate from kaolin might be more crystalline than that from RHA. Consequently, Sodium silicate from kaolin was therefore used for the characterization.

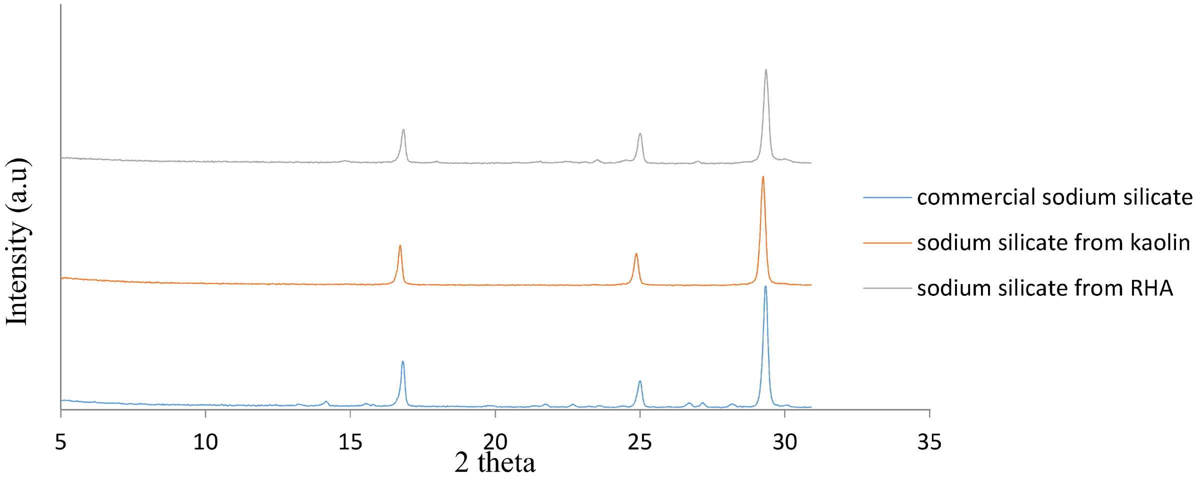

Fig.7. XRD of sodium silicate from commercial, kaolin and rice husk ash

The rate of conversion of inherent silica in both RHA and kaolin was compared from a preliminary investigation. The result obtained is depicted in Figure 8. In line with the observations made from XRD for the silica and sodium silicate, kaolin tends to have a higher conversion.

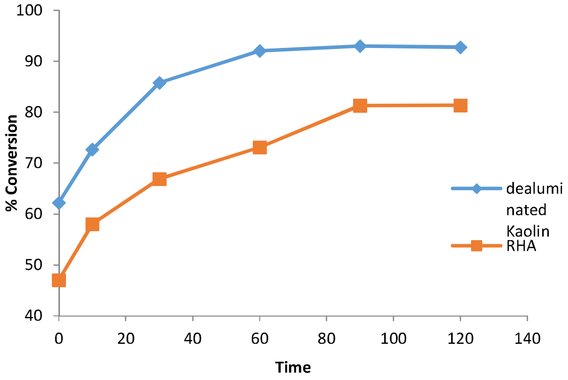

Figure 8: Silica conversion as a fuction of time

Effect of NaOH concentration

The absence of quartz peak in the diffractographs of synthesized sodium silicates with Na_2O-SiO_2 of 0.7 (S0.7), Na_2O-SiO_2 of 0.8 (S0.8) Na_2O-SiO_2 of 0.9 (S0.9) indicate that all the quartz was attacked and destroyed by sodium hydroxide solution, as shown in Figure 9.

The peaks in sample S0.7 is a little broad when compared to others, this suggest that it is due to insufficient NaOH in the sample needed to complete the reaction. Note that RSS denotes the commercial sodium silicate. The crystallinity was observed to increase as the NaOH concentration in the sample increases as shown in Figure 10, which can be used to ascertain the extent of silica depolymerization.

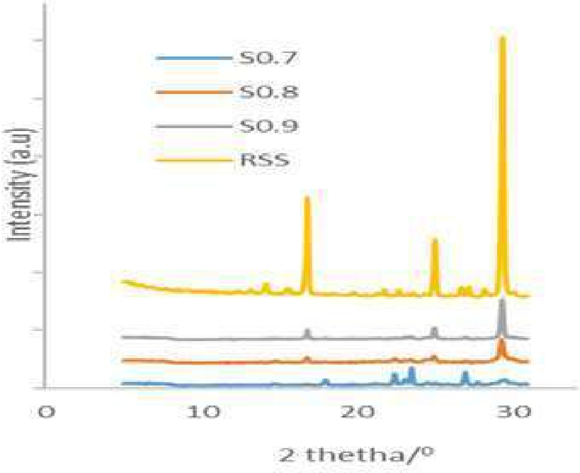

Figure 9: XRD for sodium silicate at various Na_2O/SiO_2 at 90^{0}C.

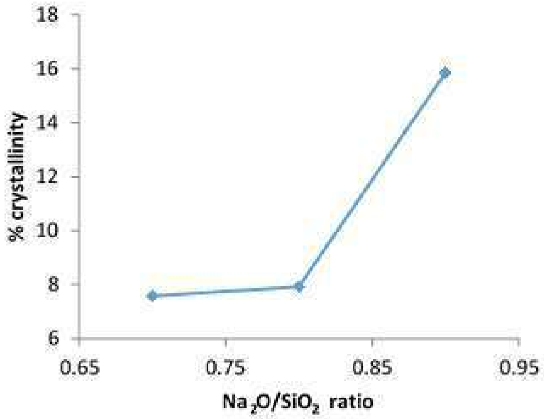

Figure 10. Crystallinity for sodium silicate at various Na_2O/SiO_2 at 90^{0}C.

Effect of reaction temperature

The XRD diffractograph shown in Figure 11, the sharp, clearly defined peaks indicates the crystalline structure. The XRD pattern for sample S70 (70^{0}C) does not exhibit the characteristic peaks attributed to sodium silicate. The peak at 22.82 indicates the presence of quarts, which might suggest that the temperature of 70^{0}C is inadequate for supplying the requisite heat of reaction for depolymerisation of quartz hence the failure in synthesis of sodium silicate at 70^{0}C. When the temperature was increased to 85^{0}C (sample S85) a drastic changed was observed in the diffractogram- peaks of sodium silicate began to emerge. Synthesis at 100^{0}C (S100) resulted in more crystalline sodium silicate. Comparing the XRD pattern for the various samples with that of commercial sodium silicate from Figure 11, it was evident that intensity of peaks increases with increased in temperature.

In the crystallinity curve (fig.12) it would be observed that, there is a sharp increase in the crystallinity with a small increase in temperature and gradual increase from 85^{0}C to 100^{0}C. This indicates that as the temperature of reaction between silica and sodium hydroxide increases, the solubility of the silicate also increases, thereby allowing for better crystallization of the targeted product.

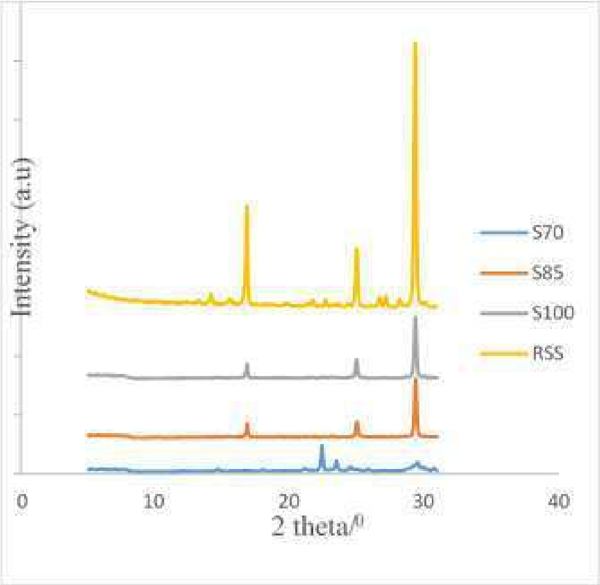

Figure 11. XRD of sodium silicate syntesized at different temperatures for 35 mins using Na_2O/SiO_2 of 0.85

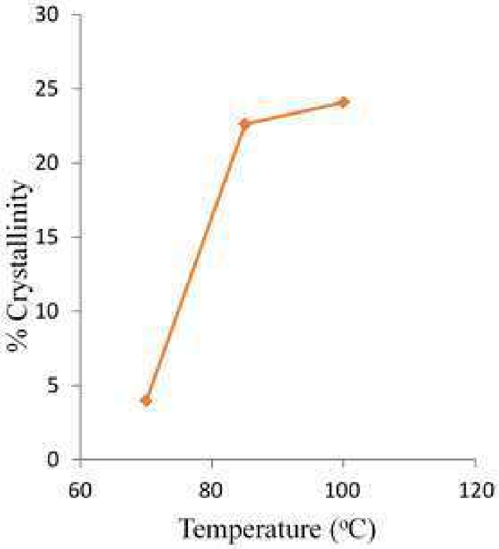

Figure 12. Crystallinity of Sodium Silicate with Reaction Temperature

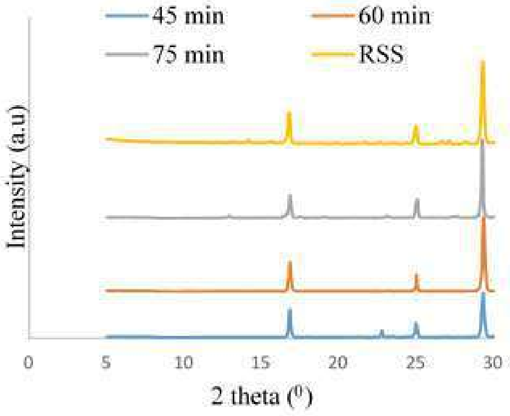

Figure 13: XRD of sodium silicate synthesized at various reaction times for***100^0 C and*** Na_2O/SiO_2 of 0.9

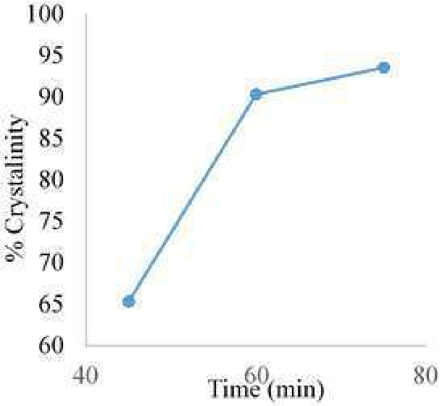

Figure 14: Crystallinity of Sodium Silicate with Reaction Time

Effect of time of reaction

Comparing the various XRD patterns of the samples with RSS which was for commercial sodium silicate, in Figure 13, it is conspicuous that sodium silicate was formed in all the three conditions. For sample subjected to reaction time of 45min, at 2θ position of 22.8 the peak was attributed to presence of quartz. This means that, the reaction time of 45 minutes was not sufficed for the quartz particles to dissolve in sodium hydroxide solution prior to chemical reaction. At 60 minutes, this peak was not present in the XRD graph, meaning 60 minutes was sufficient for the depolymerisation of quartz present in the silica. The crystallinity of the as-synthesized product tends to increase as the reaction time as depicted by Figure 14. This suggests that reaction contact time played a significant role in sodium silicate crystallization reaction.

Conclusions

Rice husk ash is a very good source of silicate with higher higher percentage composition of silica than it is present in Kankara Kaolin, but showed lower crystallinity when compared to sodium silicate obtained from Kankara Kaolin. Sodium silicate in solid form was successfully synthesized from both sources. The crystallinity for sodium silicate calculated from XRD based on the peaks from the commercial product tends to increase with increase in NaOH concentration, reaction time and temperature. Within the experimental range considered in this work, about 93% crystallinity was arrived at, when the Na2O/SiO2 ratio, reaction time and temperature were 0.9, 75mins and 100^0C, respectively.

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