# Taguchi Optimization of Carboxymethylation Process and Effect Reaction Efficiency on Swelling Capacity

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**ABSTRACT---- *The aim of this research paper was to ascertain the optimum conditions required to economical synthesis carboxymethylated starch using experimental design technique by Taguchi for Larger-is-better and smaller-is better of reaction efficiency (RE). Orthogonal Array method was utilized in the design of the experiment which consisted of eighteen (18) runs based on three (3) independent Factors which are; Sodium hydroxide (NaOH) with three concentration levels (1, 1.5, and 2.0M), Sodium monochloroacetate (SMCA) with three concentration levels (1, 1.5, and 2.0M) and Reaction Time (T) with two (2) levels (2 and 4 hours) respectively and the response is reaction efficiency (R.E). The result obtained from the experiment was interpreted using the Taguchi method of larger-is-better and smaller-is-better was apply to estimate the Response for Signal-to-Noise Ratios. The analysis showed that for larger-is-better, the optimal condition to obtain high reaction efficiency (R.E.) of 9.97%, will require NaOH at 2.0 M, SMCA at 1.0 M, at reaction period of, while for smaller-is-better, the optimal condition to obtain low reaction efficiency (RE) of 1.93 %, will required the concentration of NaOH (aq) and SMCA (aq) to be 1.5 M and 1.5 M with a reaction period (T) of 4 hours respectively. The result was also study the influence of variable SMCA (aq) and NaOH (aq) concentrations on swelling capacity (SC) at reaction time of 2 hours. The result shows that 2M NaOH is the optimum concentration for carboxymethyl starch (CMS) synthesis. .Significant difference was ascertained using Tukey method, and at 95% Confidence level.***

**Keywords**--- Taguchi methods, Optimization, Carboxymethyl starch (CMS), Reaction efficiency (R.E), Swelling Capacity (SC).
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## 1. INTRODUCTION

Carboxymethylation of polysaccharides is an environmental friendly process to convert native polysaccharides into more versatile useful green products. Starch and cellulose are the two major biomaterials that are utilized in making commercially available carboxymethyl products known as carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC) via chemical modification. The chemical modification has become the most convenient route to changing the chemical nature and physical properties of native polysaccharides in order to improve on the inherent undesirable properties[1] (Kavlani *et al.,* 2012). CMS is produced by Williamson's ether synthesis in a two-step reaction, where the mechanism is a double nucleophilic substitution reaction; the first step which is alkalization of starch utilizing an aqueous solution of sodium hydroxide to an intermediate product called sodium glycolate, the second step is etherification process that involves the sodium glycolate and sodium monochloroacetate reacting to give starch carboxymethylate. Degree of substitution indicates the mean amount of carboxymethyl group per Anhydrous Glucose Unit (AGU). The AGU is monomer unit of starch has three hydroxyl groups, the degree of displacement hydroxyl group by the carboxymethyl group is the measure of DS, and the maximum obtainable DS is three (3). The Carboxymethyl starch is versatile product that has found application in various industries from pharmaceuticals, petroleum, paper, cosmetics, pastries, food e.t.c. due to its ability to improve clarity, swelling capacity, absorption capacity, among others that are too numerous to mention.[2], [3], [4], [5], [6], [7].

Study by Tatongjai and Lumdubwong [8] indicates that CMS gel and film has significantly enhanced transparency, and storage stability. In cold water, the solubility of CMS is significantly enhanced with increases in value of substitution (DS), and the most of physicochemical characters are remarkable altered such as: water absorption which is described by hydration capacity and swelling capacity, adhesiveness and film forming properties are improved simultaneously [9].

Carboxymethylated starch derivatives exhibited reduced temperature of gelatinization, characteristic change in rheology and pH stability [10], [11] when compared to native starch.

In research industries, the essence of optimization is to decrease experimental time, and numbers runs, select optimal conditions to maximize profit, thereby cutting production cost, reduce waste of chemicals, raw materials, ultimately reducing product and service rejection rate, with an overall enhanced customer satisfaction.

Optimization can be defined as a process of ascertaining those values of controllable factors referred to as independent variable that results to the most desired responses also known to as dependent variable. A vivid image of all suitable approach must be put in perspective, when an optimization studies is to be embarked on.

Most experiment are designed using one-factor at time method (OFAC) which is usually cumbersome, confusing, ambiguous, and non-predictable responses are obtainable because it doesn't follow any statistical model in its design. Experimental Designs (D.O.E) are utilized to plan overall experimental processes and create experiments for different phases of the process used to fit a model to a data, analyze the factor effects, and ascertain the direction of the process under evaluation. In essences the importance of experimental designs is to plan, create, analyze and interpret designs to obtained optimum condition, and the major known designs are Factorial, Response Surface, Mixture, and Taguchi [12]. Numerous researchers have employed the Taguchi technique because it is an efficient route to the designing of superb experimental systems. Also it gives an easy, efficient and step wise approach to improve quality, affordability and enhance processes and product design ([13]. This technique is consistent method for designing excellent reliable process and suitable conditions over variable factors. This design is utilized in decreasing the counts of experimental runs by applying orthogonal arrays.

Khuri *et al.,* [14], described that Taguchi methods has two types independent factors in experiments,
  i.   Control factors: easy to control and
  ii.  Noise factors: Not easy to control.
These Noise factors that are not easy-to-control cause fluctuation in the outcome of experimental or production process. The main intention of parameter design is to ascertain the settings of the control factors for which the process response is robust to the divergence in the system induced by the noise factors. To accomplish this purpose, the application of crossed arrays by crossing an orthogonal array of control variables (inner array) with an orthogonal array of noise variables (outer array) was put forward by Taguchi. He pinpointed that every experiment has three unique aims which are given as follows:
**1.** The smaller, the better: This is applied when the goal is to minimize the response
**2.** The larger, the better: This is applied when the aim is to maximize the response
For each of the various aim, Taguchi defined performance criteria referred to as signal-to-noise (S/N) ratios which considered both the process average and the variance.

## 2.  MATERIALS AND METHODS

### 4.1 Taguchi Experimental Design
The experimental design was performed by applying Taguchi Orthogonal Array (1 2 3) with columns of L18 ($2^1$ $3^7$) was applied in this design of experiment as shown in Table 1. The experimental design has 18 runs with 3 factors, which are; Time with 2 levels (2 and 4 hours), NaOH $_{(aq)}$ with 3 levels (1, 1.5, and 2 $mol/dm^3$) and SMCA with 3 levels (1, 1.5, and 2 $mol/dm^3$) as shown in table 1 below.
The exact optimal condition for obtaining CMS with upper (larger-is-better) and lower (small-is better) level of DS will be ascertained by Taguchi technique as stated earlier, using Statistical software (Minitab17). The signal-to-noise (S/N) ratio will be analyzed for every factor level combination. For each of the two different goals, Taguchi defined the S/N ratios as follows: Equation (1) and (2) below are the mathematical expressions for the larger-is-better, and smaller-is-better S/N ratio applying base 10 log respectively:

$$S/N = -10 \times \log_{10}\left[\text{sum}\ (1/Y^2)/n\right] \text{-----------------------------------}(1)$$

$$S/N = -10 \times \log_{10}\left[\text{sum}\ (Y^2)/n\right] \text{--------------------------------------}(2)$$

Where $\bar{Y}$ is the response mean and $S^2$ is the sample variance, Y is responses for the given factor level combination and n = number of responses in the factor level combination.

**Table 1:** The Experimental Design of Independent Variables using Taguchi Methods

| Sample | Time (Hr) | SMCA (mol/dm$^3$) | NaOH (mol/dm$^3$) |
|--------|-----------|-------------------|-------------------|
| C1 | 2 | 1 | 1 |
| C2 | 2 | 1 | 1.5 |
| C3 | 2 | 1 | 2 |
| C4 | 2 | 1.5 | 1 |
| C5 | 2 | 1.5 | 1.5 |
| C6 | 2 | 1.5 | 2 |
| C7 | 2 | 2 | 1 |
| C8 | 2 | 2 | 1.5 |
| C9 | 2 | 2 | 2 |
| C10 | 4 | 1 | 1 |
| C11 | 4 | 1 | 1.5 |
| C12 | 4 | 1 | 2 |
| C13 | 4 | 1.5 | 1 |
| C14 | 4 | 1.5 | 1.5 |
| C15 | 4 | 1.5 | 2 |
| C16 | 4 | 2 | 1 |
| C17 | 4 | 2 | 1.5 |
| C18 | 4 | 2 | 2 |

### 4.2 Extraction of Starch

Starch isolate was obtained from mango seed kernel employing the technique described in [15], [16], [17], and [18] with some modification in the method where necessary. Starch was extract using hot water extraction method. 100.00 g of powdered mango seed kernel was soaked in a 1000 cm$^3$ beaker containing 200 cm$^3$ of deionized water in a thermostatic water bath (WBH 6/FL, Genlab Thermal Eng., UK) at a constant temperature of 40$^0$C for about 24 hours. One portion of the suspended powdered mango seed kernel and three portions of deionized water were homogenized for 3 minutes at moderate and fast speed. The resultant slurry was filtered with a double layer of muslin cloth and then centrifuged (TDL-4, Ningbo Hinotel Tech, China) at 5000 rpm for 20 minutes. The supernatant was poured out and removed while the deposit re-suspended in surplus 0.02% NaOH $_{(aq)}$ to eliminate any left-over proteins and phenolic compounds. After standing for 4 hours the supernatant was poured out and removed. The process was replicated about 6-8 times till the supernatant became colourless. Final white sediment was suspended in deionized water and before been filtered through 0.045 mm sieve, neutralized with deionized water to pH 7.0, and finally filtered on Buchner funnel. The filtered cake was dried in an electric oven (Nuve Oven/FN-055) at 70$^o$C for 12 hour, and the resulting dry starch was grounded to fine powdered particles with electric blender (Binatone blender), weighed and stored in an air-tight container for future utilization.

### 4.3 Synthesis of Carboxymethyl Starch

Organic slurry technique of modification was applied as stated by Lawal *et al.,* [11]. The unmodified starch isolate derived from the mango kernel (10.0 g) was suspended in 2-propanol (200 cm$^3$) placed in a beaker. 20cm$^3$ of various concentrations (1.0M, 1.5M or 2.0M) of sodium hydroxide was introduced. The mixture was homogenized at a regulated temperature (30°C) for 10 minutes. 80cm$^3$ of various concentrations (1.0M, 1.5M or 2.0M) of Sodium monochloroacetate was introduced and homogenized continuously up to the stipulated period in the experimental design (2 or 4 hours) in shaker–water bath (Uniscope/DKZ-2, Hanna, Italy). The pH (Jenway 3510 pH meter) of the mixture was attuned to about 5.0 by introducing glacial acetic acid at 50% concentration. The synthesized carboxymethyl starch was filtered, and washed with 80 % aqueous ethanol until the pH of the residue was neutral (7.0) and dried in an oven (Nuve Oven/FN-055) at 50°C for 6 hours. Fine particles of the dried carboxymethyl starch were obtained by passed it through a 100-mesh sieve. This process was replicated 18 times with variable concentration of SMCA $_{(aq)}$, NaOH $_{(aq)}$, and reaction time and the products of the synthesis were labeled C1 to C18.

### 4.4 Determination of the Reaction Efficiency (RE)

The degree of substitution (DS) was determined with flame atomic absorption spectrometry (Corning 400, Ciba-Corning, USA) with respect to the level of sodium in the CMS as described by Lawal *et al.*[19]. The sample (50.00 mg) was dissolved in undiluted nitric acid (4 cm$^3$) in a glass vessel and heated with a hot plate. The digested sample was filled-up to 100 cm$^3$ mark with deionized water before analysis with the spectrometer. The flame composition was air–acetylene while the wavelength of sodium was 589.0 nm. The degree of substitution was determined as follows:

$$DS = \frac{162\%Na}{(2300-80\%Na)} \text{---------------------------(i)}$$

%Na of the unmodified starch was predetermined by flame atomic absorption spectrometry and it was corrected in the CMS derivative.

$$R.E = \frac{DS}{DSt} x \ 100\% - - - - - - - - - - - (ii)$$

Since DS of 3 is the maximum any starch carboxymethylated can attain, the Reaction efficiency (R.E) becomes the percentage comparison between the Degree of Substitution(DS) usually obtained from the synthesis, and the theoretical degree of substitution (DSt = 3), which is show the maximum degree to which the carboxymethyl group can replace hydroxyl group on the starch molecule.

### 4.5 Determination of Swelling Capacity

Okhamafe *et al.,*[20] technique was adopted. 1g of CMS was measured into a calibrated centrifuging tube and tapped for 500 times consecutively and the volume occupied by the CMS was measured to be $V_{500}$. The distilled water was added to the CMS in the tube, sealed, and agitated vigorously before centrifuging at 5000 rpm for 20 minutes. The water on top of the CMS after centrifuging was discarded and the new volume occupied by the hydrated CMS was measured to $V_2$. The swelling capacity was calculated using the mathematical equation below (iii).

$$Swelling \ capacity \ \% \ (S) = (V_2 - V_{500})/ \ V_{500} --------------------(iii)$$

Where S is the % swelling capacity, $V_2$ is the volume of the hydration or swollen material and $V_{500}$ is the tapped volume of the material prior to hydration.

## 3. RESULTS

**Table 2:** The Independent Variables, and Response variable (R.E) and Swelling capacity (SC)

| Sample | Time (Hr) | SMCA (mol/dm³) | NaOH (mol/dm³) | RE (%) | SC (v/v) |
|--------|-----------|----------------|----------------|--------|----------|
| C1 | 2 | 1 | 1 | 6.1±0.173 | 144±0.02 |
| C2 | 2 | 1 | 1.5 | 8.6±0.063 | 54±0.03 |
| C3 | 2 | 1 | 2 | 9.97±0.078 | 46±0.004 |
| *C3 | 2 | 1 | 2.5 | NA | 45±0.032 |
| C4 | 2 | 1.5 | 1 | 5.2±0.245 | 216±0.04 |
| C5 | 2 | 1.5 | 1.5 | 6.7±0.114 | 159±0.018 |
| C6 | 2 | 1.5 | 2 | 8.6±1.172 | 94±0.072 |
| *C6 | 2 | 1.5 | 2.5 | NA | 85.7±0.002 |
| C7 | 2 | 2 | 1 | 4.63±0.066 | 273±0.16 |
| C8 | 2 | 2 | 1.5 | 5.73±0.049 | 288±0.03 |
| C9 | 2 | 2 | 2 | 10.3±0.092 | 322±0.59 |
| *C9 | 2 | 2 | 2.5 | NA | 334±0.004 |
| *C10 | 2 | 2.5 | 1 | NA | 336±0.102 |
| **C11** | 2 | 2.5 | 1.5 | NA | 135±1.04 |
| **C12** | 2 | 2.5 | 2 | NA | 115±0.011 |
| **C13** | 2 | 2.5 | 2.5 | NA | 113±0.224 |
| C10 | 4 | 1 | 1 | 5.47±0..069 | NA |
| C11 | 4 | 1 | 1.5 | 7.13±0.584 | NA |
| C12 | 4 | 1 | 2 | 8.6±0.399 | NA |
| C13 | 4 | 1.5 | 1 | 3.3±0.130 | NA |
| C14 | 4 | 1.5 | 1.5 | 1.93±0.062 | NA |
| C15 | 4 | 1.5 | 2 | 1.3±0.035 | NA |
| C16 | 4 | 2 | 1 | 4.77±0.175 | NA |
| C17 | 4 | 2 | 1.5 | 2.7±0.057 | NA |
| C18 | 4 | 2 | 2 | 5.73±0.632 | NA |

**R.E** = Reaction efficiency, **SMCA**= sodium monochloroacetate, **SC** = Swelling Capacity, **NA**= Not ascertained or measured, **\*C=** levels of the factors not given by Taguchi design.

**Taguchi Analysis: %RE versus Time (Hr), SMCA, NaOH**

The result for the Taguchi analysis for the larger-is-better and smaller-is-better are shown in Figure 2 and 3 below.
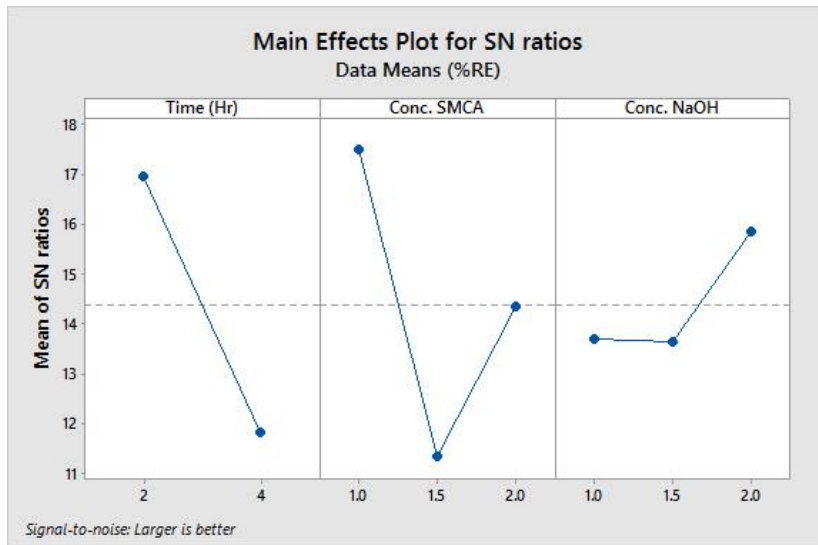


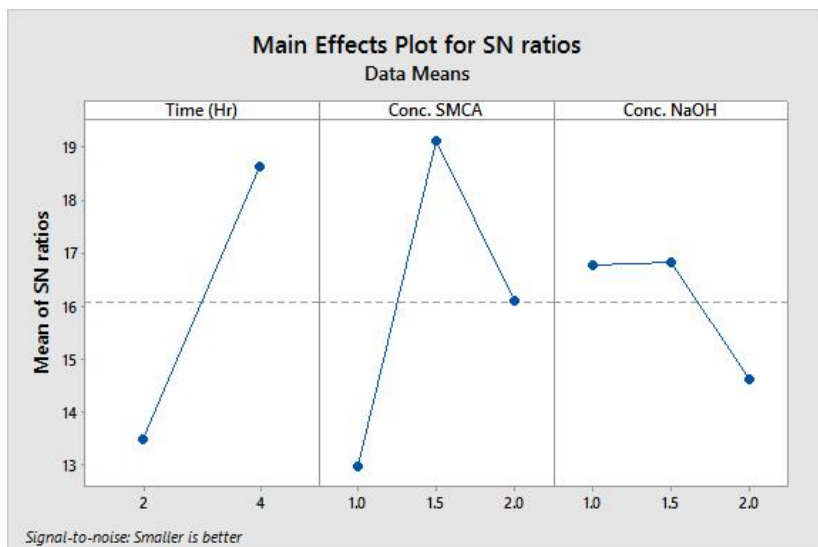**Figure 1: Main Effects Plot for Signal to Noise ratios for Larger-is better**



**Figure 2: Main Effects Plot for Signal to Noise ratios for Smaller-is better**
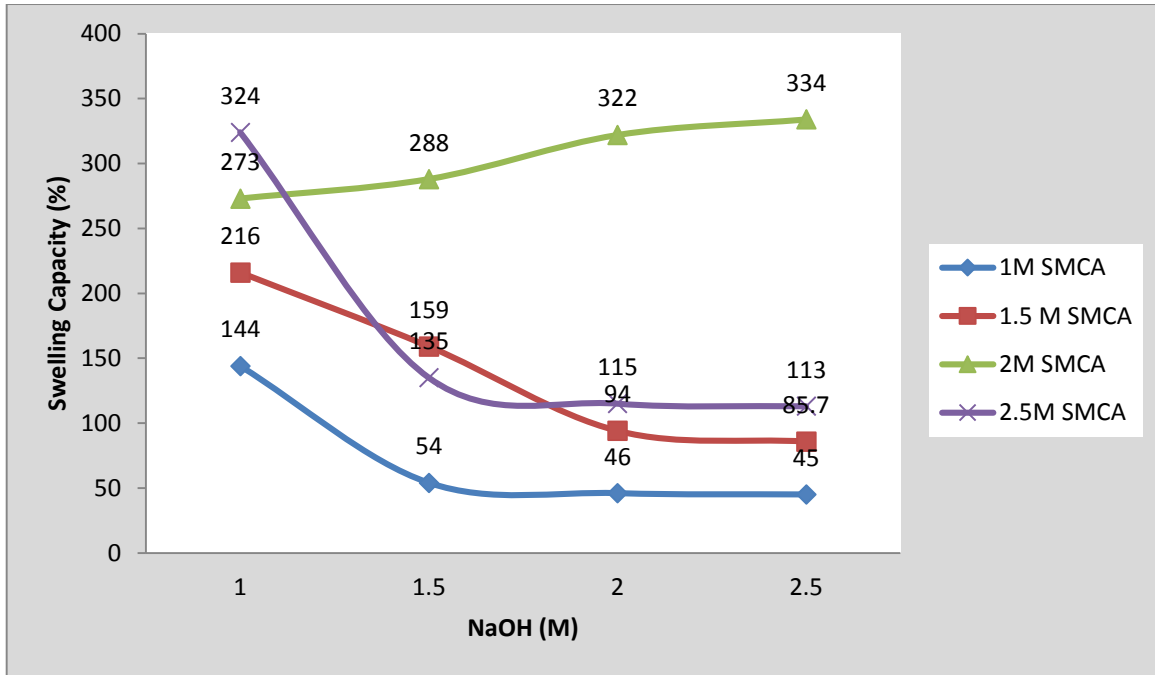
**Figure 3:** Effect of Variable concentration of NaOH (aq) on swelling capacity of Carboxymethyl starch
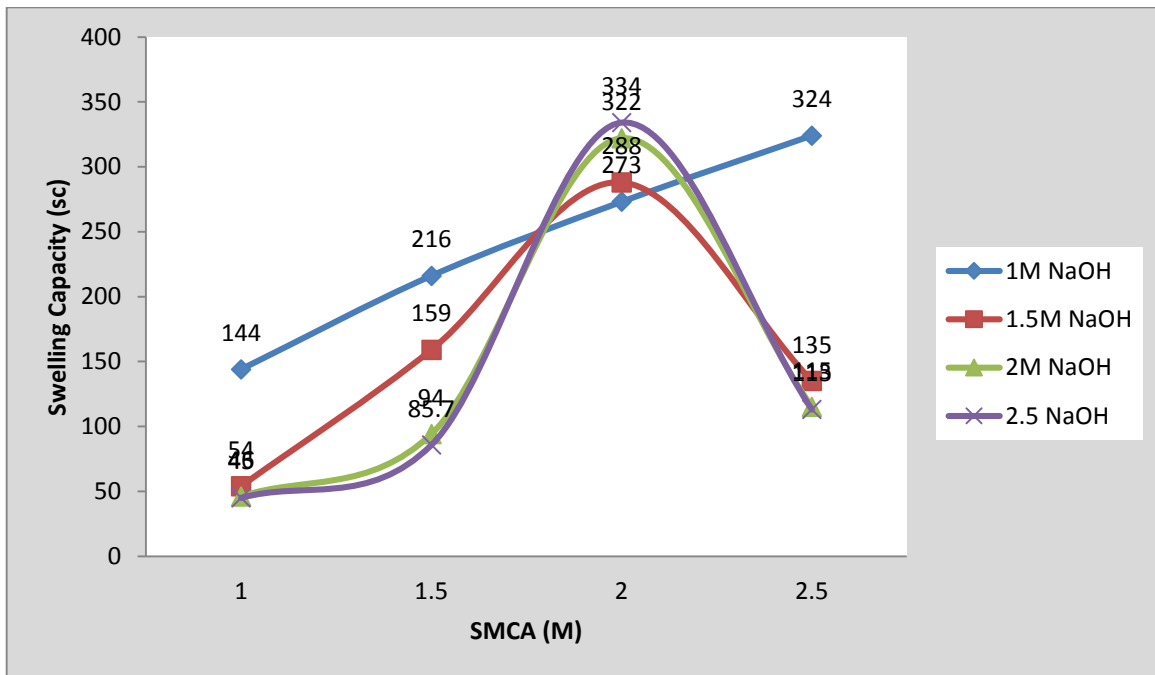


**Figure 4:** Effect of Variable Concentration of SMCA (aq) on swelling capacity of Carboxymethyl starch
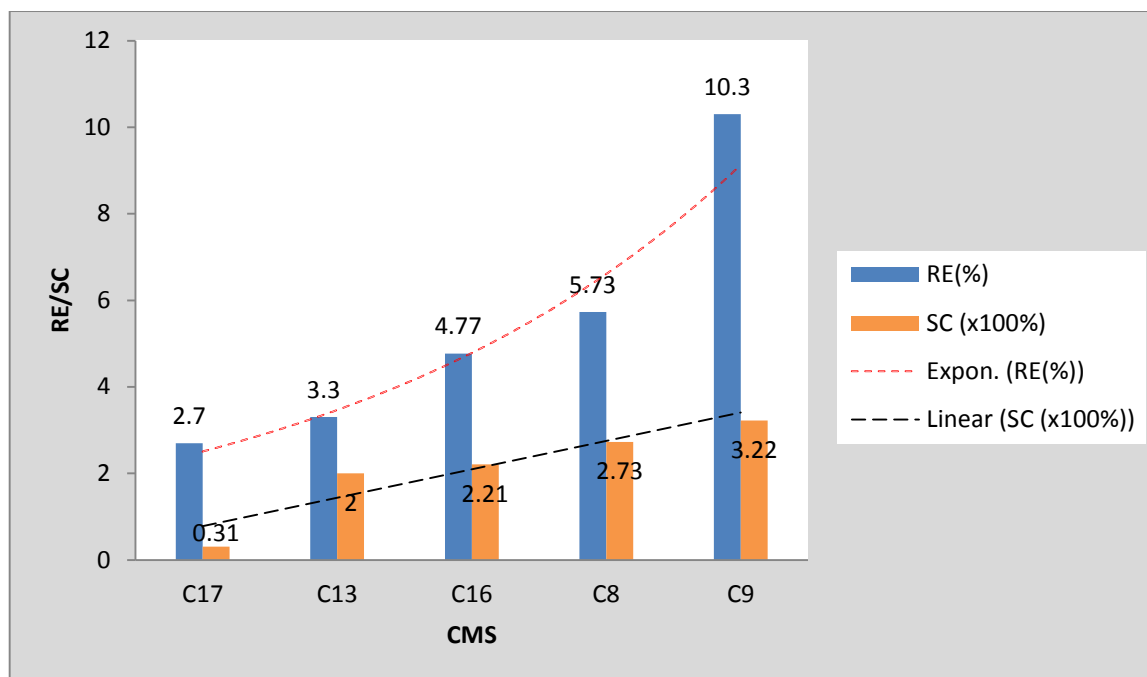
**Figure 5:** Effect of Reaction efficiency (RE) on Swelling Capacity (SC)

## 4. DISCUSSION

The optimization result from Main Effect plot for Signal to noise (S/N) ratios (Figure 1) and main effect plot for mean (Figure 2) using Taguchi method, has shown that the condition for optimum yield of carboxymethyl starch (C3) with reaction efficiency (R.E) of 9.97% was obtained for larger-is-better, at reaction time two (2) hours, when the concentration of Sodium monochloroacetate (SMCA) was 1.0M, and concentration sodium hydroxide (NaOH) was 2.0M. The ANOVA analysis of reaction efficiencies, indicate that C3 (9.97%) show no significant difference from C9 (10.27%) despite having a slight higher value. The exact amount of conc. SMCA 2.0M required to synthesis C9 will result to high cost, with significant reduction in production cost either in small or large scale.

The optimum conditions for carboxymethylation for smaller-is-better, from the Figure 3 shows that time of 4 hours, SMCA at 1.5M, and NaOH of 1.5M, are the optimum conditions required to obtain a reaction efficiency of 1.93%. As shown in table 2.0, it indicates that C15 (1.3%) is lower, and shows significant difference in reaction efficiency with C13 (1.93%). It is more economical to synthesised C14 instead of C15 as described by smaller-is-better Taguchi model and this can be attributed to the higher concentration of NaOH (2.0M) required to synthesize C15, which will in industrial application results to increased production cost.

From Figure 3, the result shows that swelling capacity at 1M SMCA$_{(aq)}$ decreases as the concentration of the NaOH$_{(aq)}$ increases, similar with 2M SMCA$_{(aq)}$ the same decreasing effect was observed with increased NaOH$_{(aq)}$ concentration, but at a much higher swelling capacity. When swelling capacity was observed at 2M SMCA$_{(aq)}$ it shows a steady increasing effect, with increase in the concentration of NaOH$_{(aq)}$ even at a significantly higher swelling capacity compared to SMCA$_{(aq)}$ at 1, 1,5, 2.5M. for 2.5M SMCA$_{(aq)}$ the swelling capacity decreases with increase in NaOH concentration just as observed for 1M, and 1.5M SMCA$_{(aq)}$.

Figure 4 shows that at 1M NaOH$_{(aq)}$ the swelling capacity of the CMS increases significantly with increase in the concentration of SMCA$_{(aq)}$ from 1 to 2.5M. while at 1.5, 2, and 2.5M NaOH$_{(aq)}$ also shows an increase in the swelling capacity CMS with increase in SMCA$_{(aq)}$ concentration from 1 to 2M , which suddenly and significantly decrease when the concentration of SMCA$_{(aq)}$ was increased to 2.5M. This observation could be due to increase side reaction between NaOH$_{(aq)}$ at 1.5, 2, or 2.5M, and SMCA$_{(aq)}$ at 2.5M. the highest swelling capacity obtained was 334% which corresponded to the carboxymethylated mango starch synthesize with 2M SCMA$_{(aq)}$, and 2M NaOH$_{(aq)}$ (aq) per anhydrous glucose unit, which is approximately close to the optimum conditions predicted by Taguchi methods since C3 and C9 has no significant difference in reaction efficiency.

Swelling capacity is one of the most vital physicochemical properties of carboxymethylated polysaccharides, as the increase in carboxymethylation results to a significant alteration and enhancement the extent of the solubility and hydration capacity of the[20] thereby allowing the material to hold more water molecules within its modified matrices i.e. improved hydration capacity. This will in turn results to a significant measurable increase in the volume occupied by the carboxymethylated polysaccharides. Other studies has shown that increasing the degree of substitution results to increase in the swelling capacity, and hydration capacity due to increase in the solubility of the polysaccharide when compared to

the unmodified one [9]. The result observed is also in accordance with outcome obtained by Tatongjai and Lumdubwong [8], which indicated in CMS solubility in cold water, with increase in the DS which is directly related to R.E.

Therefore swelling capacity is a physicochemical property of polysaccharide that is directly dependent on degree of substitution i.e. reaction efficiency (RE),which is similar to what is observed in Figure 5 of this study, that the swelling capacity increases with respect to gain in the reaction efficiency.

## 5. CONCLUSION

The optimization of carboxymethylation process is very important, as it help ascertained optimally conditions for the synthesis of CMS, without extensive and unnecessary numbers of experimental run, cut wastage of reagents, reduced production time and ultimately cut production cost. The optimal conditions for the larger-is-better show that it is more profitable to produced M3 with R.E of 9.97% than C9 with R.E of 10.27%. Also we can conclude on the same premise for the Smaller-is-better that it's more economical or profitable to synthesized C14 with R.E 1.93%. It can be concluded that increase in the reaction efficiency has a direct effect on the swelling capacity of the carboxymethyl mango starch.

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