CELLULOSE NANOCRYSTAL STABILIZED PICKERING EMULSIONS

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DEDICATION

I would like to dedicate this thesis to my belated grandfather, Jhanka Prasad Adhikari, who taught me to value time, hard work and patience.

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Abstract

The use of *Pickering Emulsions* in place of conventional surfactants has opened new doors in fields like pharmacy, cosmetology, and oil and gas industry. Pickering emulsions using *Cellulose Nanocrystals* (CNCs) are generally stable to heating in a wide range of temperatures and show great stability against salt and pH changes. The management of water resources in the United States has been a challenge. The injection of water in aging oil fields and unconventional tight-gas, shale-gas, and coal bed-fields often generate substantial amounts contaminated wastewater. This research project is expected to help future efforts in promoting oil biodegradation in emulsified mixtures. Here, we are correlating viscosity of aqueous phases of 0.4, 0.8, and 1 wt.% CNC in *American Petroleum Institute* (API) brine (2 wt.% $CaCl_2$ and 8 wt.% NaCl) and *Synthetic Seawater* (SSW**)** to explain the high stability of a Pickering emulsion stabilized by CNCs. Emulsion stability was assessed through creaming front analysis and optical microscopy measurements. The most stable emulsions over six months had aqueous phases with high viscosity; lower viscosities were found for emulsions that broke at room temperature. Highly viscous interfacial films retard the rate of oil-film drainage during the coalescence of the water droplets by providing a mechanical barrier to coalescence, which can lead to a reduction in the rate of emulsion breakdown.

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List of Abbreviations

CNCs	Cellulose Nano Crystals
API	American Petroleum Institute
SSW	Synthetic Sea Water
Wt. %	Weight Percentage
LED	Light Emitting Diode
O/W	Oil in Water
W/O	Water in Oil
NaCl	Sodium Chloride
$CaCl_2$	Calcium Chloride
$MgCl_2$	Magnesium Chloride
cP	Centipoise
B.E.V.I.S.	Brookfield Engineering Viscometer Instruction Set

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Introduction

An emulsion is a mixture of two or more liquids that are normally immiscible, i.e. insoluble or partially soluble. Solid-stabilized emulsions were described by Pickering and Ramsden in early 20th Century [1]. However, this concept (solid-stabilized emulsions or Pickering emulsions) has been lately identified to be used in the fields of cosmetics, pharmaceutics, food industry to minimize the use of the conventional use of surfactants. In 1907, Pickering observed that colloidal particles situated at the oil-water (O/W) interface can also stabilize emulsions of oil and water. [2] Some of the potential applications of Pickering emulsions include underground sequestration of CO_2, oil bioremediation, low energy separations, and energy generation as well. In addition, Pickering emulsions have ultra-high stability, low toxicity, and environmental responsive character, and can be used for drug delivery or making the functional material.

Previous studies have shown that CNCs efficiently stabilize O/W interfaces due to the amphiphilic surface nature, which originates from the hydrophobic face and hydrophilic edge of the cellulose chains. [3] The main objective of this project is to study the viscosity of the aqueous phase and correlate it with the stability of an emulsion. The initial hypothesis was that an increase in viscosity improves the stability of an emulsion and series of experimental works were performed to work on the very hypothesis.

Background Research

Colloidal science has been a very hot research topic for last 16 years and many applications-based types of research have been going on in various parts of the world. It has been known that the emulsions can be stabilized by small molecular emulsifiers and some macromolecules. [4] The use of the Pickering emulsions in place of the conventional surfactants have been increasing due to the following advantages:

i. Solid particles reduce the possibility of coalescence, bringing higher stability to emulsions
ii. Many solid particles can endow as-prepared materials characteristics such as conductivity, responsiveness, porosity etc.
iii. Solid particles like CNCs have lower toxicity.

Figure 1: Left: AFM image of CNC, Right: 1 wt. % CNC suspension in DI water. [5]

The characteristics of the Pickering emulsions highly depend on the properties of the solid particles and it is significant to choose the right kind of the nanoparticles to use for a specific character and application. Before I joined Dr. Ureña-Benavides and his team, before they did some preliminary research on nanocrystals ability to stabilize emulsions. CNCs are generally stable to heating in a wide range owing to their structural stability and emulsions formed shows great stability against salt and pH changes. [6]

This research project uses the suspended CNC that is manufactured in the Nano-Material Pilot Plant at the University of Maine. An alpine pulp is hydrolyzed with sulfuric acid to produce 9.8 % wt of cellulose nanocrystal slurry.

Experimental

Preparation of API Brine Solution

A standard API brine solution contains 8 wt% NaCl and 2 wt% $CaCl_2$. By specifying the desired volume of the solution, using the appropriate mass of both salts by the desired percentage, API brine solution is prepared in the laboratory. The pH of the solution is also reported.

Preparation of Synthetic Sea Water

We purchased SSW from Sigma Aldrich. A known volume of the synthetic seawater (SSW) in a beaker was taken and then a mineral oil is added in a beaker to act as a heat sink. We reduce the volume of the SSW to half at 95 °C, which gives us SSW of 200 % by volume.

Preparation of Aqueous Solution

An aqueous solution contains a mixture of CNC and API/SSW. Various concentrations of the aqueous solution are prepared that undergoes the viscosity measurement in the lab. We prepared 5 different sets of an aqueous solution with the different concentration of CNC and API/SSW, which has been tabulated below:

0.4 % CNC + 100 % API Brine
1 % CNC + 100 % API Brine
1% CNC + 100 % SSW

Table 1: Various Concentration of the aqueous solution

An equal volume of the CNC and API/SSW is mixed and then used for measurement of the viscosity. As mentioned above in the background research, our research lab buys CNC from The University of Maine processing facility that has a standard concentration of 9.8 wt % of CNC. We use the dilution equation and get the concentration of CNC at desired wt % for a desired volume of the solution. A sample calculation is presented in *Appendix A.1* that explains how we dilute the concentration of the CNC and API brine into desired concentration from the known concentration.

For example, 2 .0 mL of 0.4 % CNC was mixed with 2.0 mL of 100 % API Brine and the mixture was put in the centrifuging tube and 50 μL was taken for measurement.

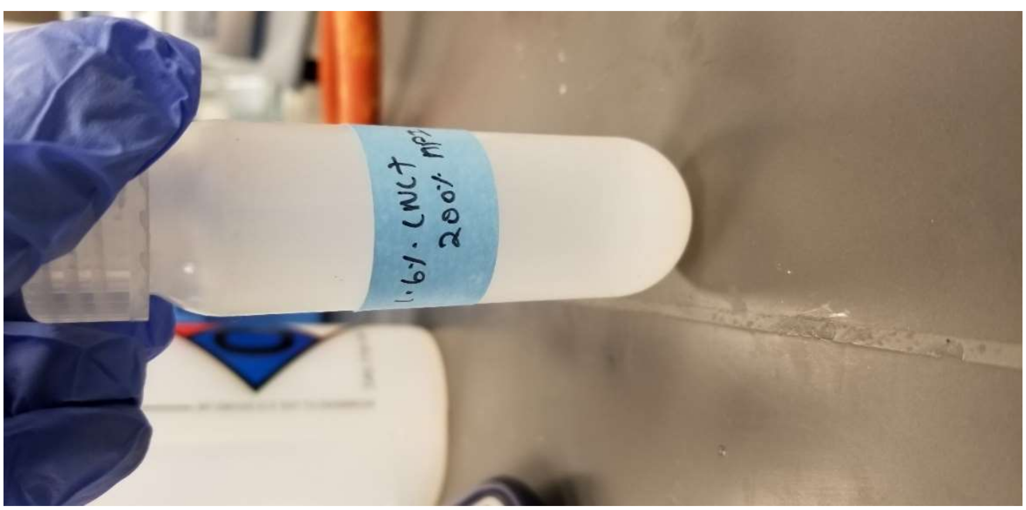

Figure 2: 1.6 % CNC + 200 % API Brine

Preparation of Emulsion

In general, an emulsion is a fine dispersion of minute droplets of one liquid in another liquid in which it is not soluble. In this project, we are using two different kinds of liquids with CNC as an emulsifier with Crude oil to observe properties.

In our project,

Pickering Emulsions = Solid Emulsifier +Aqueous solution + Oil

Where,

Aqueous solution = SSW or API

Oil = Crude Oil

Solid Emulsifier = CNC

One has to be very careful in the preparation of the emulsion as various literature and even my personal experience says that the order of mixing is important to make a specific type of emulsions. There are basically two types of emulsions as oil-in-water (O/W) and water-in-oil (W/O). A solution is said to be O/W emulsion if the dispersed phase is an organic material and the continuous phase is water or an aqueous solution. Similarly, a solution is said to be W/O if the dispersed phase is water or an aqueous solution and the continuous phase is an organic liquid (in our scenario crude oil).

In our project, various concentrations of the CNC and aqueous solution has been mixed to form an emulsion with crude oil, that undergoes the viscosity measurement to further study the stability of the emulsions. For example:

1 % wt CNC + 100 % API Brine Solution of equal volume is mixed with the specific volume of crude oil to form solutions.

We have two control samples of 10 mL of Aqueous Solution, 0 mL of Crude oil and then conversely 10 mL of crude oil with 0 mL of aqueous solution as another control sample. Eight different combinations of samples with different volume ratio as illustrated in Figurer 3 was prepared.

Figure 3: Sample of O/W emulsion after time 0.

Let's briefly talk about this Figure. This is a sample of O/W emulsion and the photo has been taken right after the sample was prepared as time 0. From left to right, there are various ratios of an aqueous solution (100 % API +1 % CNC) with the crude oil by volume. The first one on the left, whitish solution contains 10 mL of the aqueous solution of (100 % API +1 % CNC), which is 100 % by volume. The one next to it has 5 mL of the aqueous solution and 5 mL of crude oil, i.e. 50 % each by volume. Then, respectively the aqueous solution is: 75 %, 80 %, 90 %, 95 % by volume from left to the right until it reaches another control sample of 100 % crude oil.

Viscosity measurement using Viscometer

A Cone and Plate Viscometer that provides high accuracy viscosity measurement of Non-Newtonian fluids like an aqueous solution of Brine and CNC is used in our experiment.

This viscometer is designed to provide stringent testing conditions to allow measurement as viscosity changes according to the shear stress that is applied. It has cone and plate geometry provide the precision necessary for the development of complete rheological data. The system is accurate to within ± 1.0 % of full range and a spring torque of 673.7 dyne-cm. The stationary plate forms the bottom of a sample which can be removed, filled with 0.5 mL of sample fluid while using spindle C-40. It also has got an electronic gap setting for faster set-up time and minimizing the possibility of gap adjustment errors that exist in older viscometers. A bright LED lights up when it touches the plate and a simple turn of the micrometer adjusts the required gap. [7]

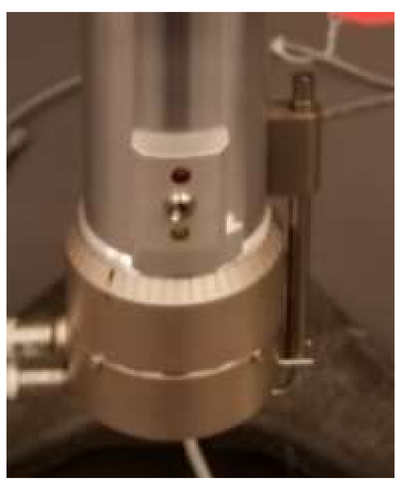

Figure 4: Cone and Plate with electronic gap setting function

We used the spindle C40, which has a geometric angle of 0.8 degrees and radius of 2.4 cm. It measures a fluid with a minimum viscosity of 15 Centipoise (cP) and a maximum of 100,000 cP. We used trial and error to find the spindle that suits our measurement. While calibrating the standard oil with different viscosities, spindle C40 came out to be more accurate and we decided to use it.

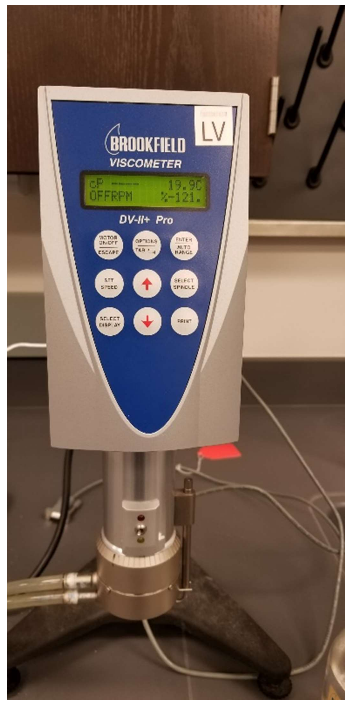

Figure 5: Brookfield Viscometer LV DV-II PRO

We used B.E.V.I.S. (Brookfield Engineering Viscometer Instruction Set), a scripting language that allows for the creation of the programs to control the programmable DV-II+ Pro Viscometer. We used this software to study the rheological properties of aqueous phases, which can be seen in the figure 11 presented in the Results and Discussions section.

Results and Discussions

Various concentration of the CNC with API Brine/ SSW with different volumes of crude oil were mixed to form O/W emulsions. Initially, an emulsion with 1 wt% CNC with 100% API Brine with various volumes of crude oil at different time intervals was prepared.

Figure 6: 1% CNC + 100% API O/W emulsion after an hour

Figure 7: 1% CNC + 100% API O/W emulsion after an hour

The volumes of an aqueous phase and crude oil are labeled on top of each vial. The first part denotes the aqueous phase while the second part denotes the volume of crude oil. For example, 9.50/0.5 means 9.5 mL of an aqueous phase and 0.5 mL of crude oil. If we look at the comparative Figure of the emulsions of an hour and after 32 hours, we can see the phase separation. The clear part at the bottom is the continuous phase of brine solution. An emulsion with 9.5 mL of aqueous solution with 0.5 mL of crude oil tends to separate the phase in the Figure above.

An image analysis software (Image-J) was used to measure droplet size and creaming analysis to study the stability of emulsions through an optical microscope.

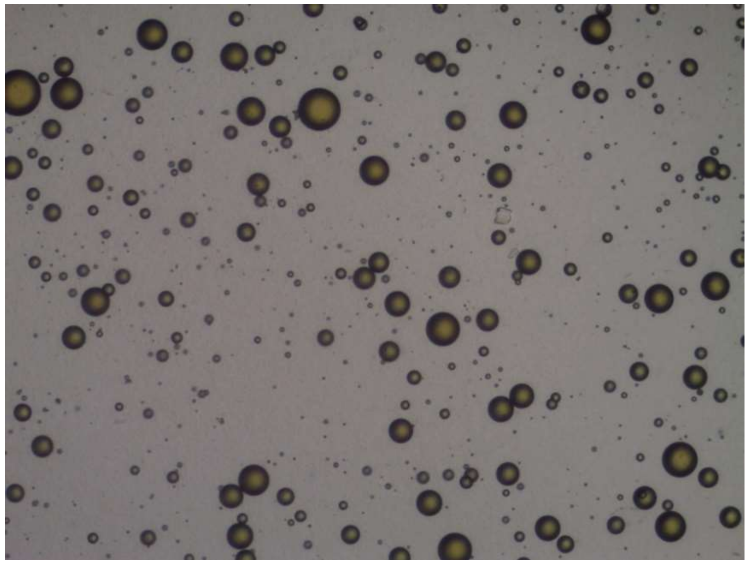

Figure 8: Droplets of 1 % CNC + 100 % API Brine at time zero. Courtesy of Omayma Azzam.

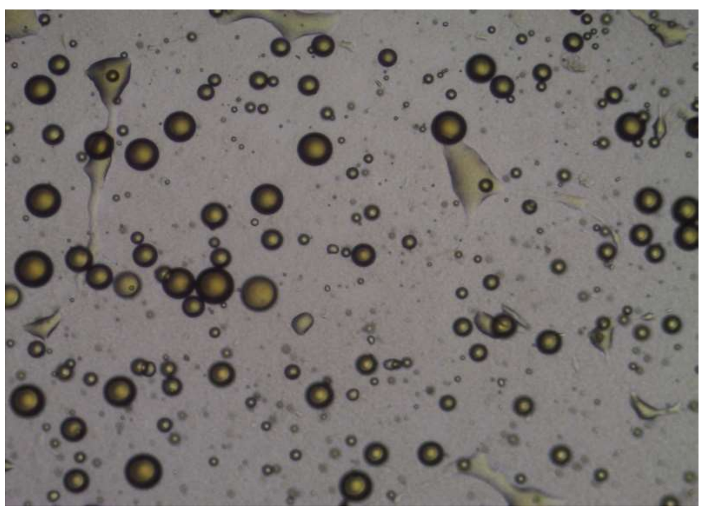

Figure 9: Droplets of 1 % CNC + 100 % API Brine after a week. Courtesy of Omayma Azzam.

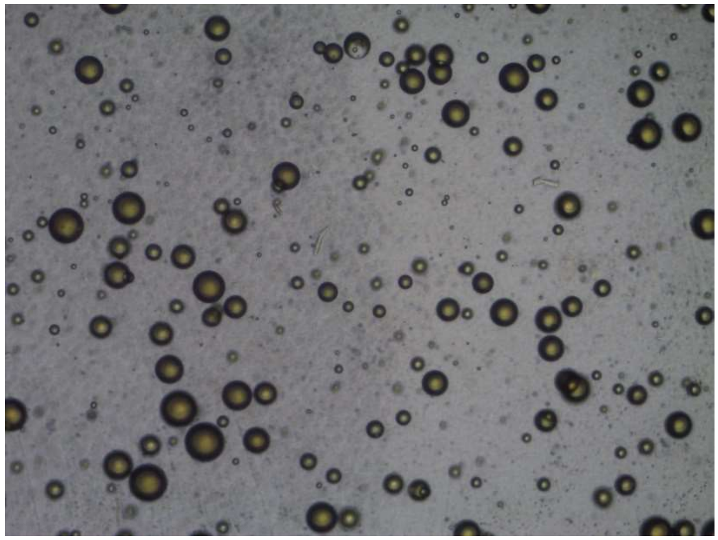

Figure 10: Droplets of 1 % CNC + 100 % API Brine after a month. Courtesy of Omayma Azzam.

Viscosity Measurement

We decided to study the rheological properties of the aqueous phase to correlate the stability of the emulsions.

A sample was prepared as explained in the experimental section and we ran it three times for two different trials using different shear rate. The table from the experiment has been attached in *Appendix A2* for all different concentration as mentioned in Table 1. We varied the shear rate to plot it against shear rate in log-log scale.

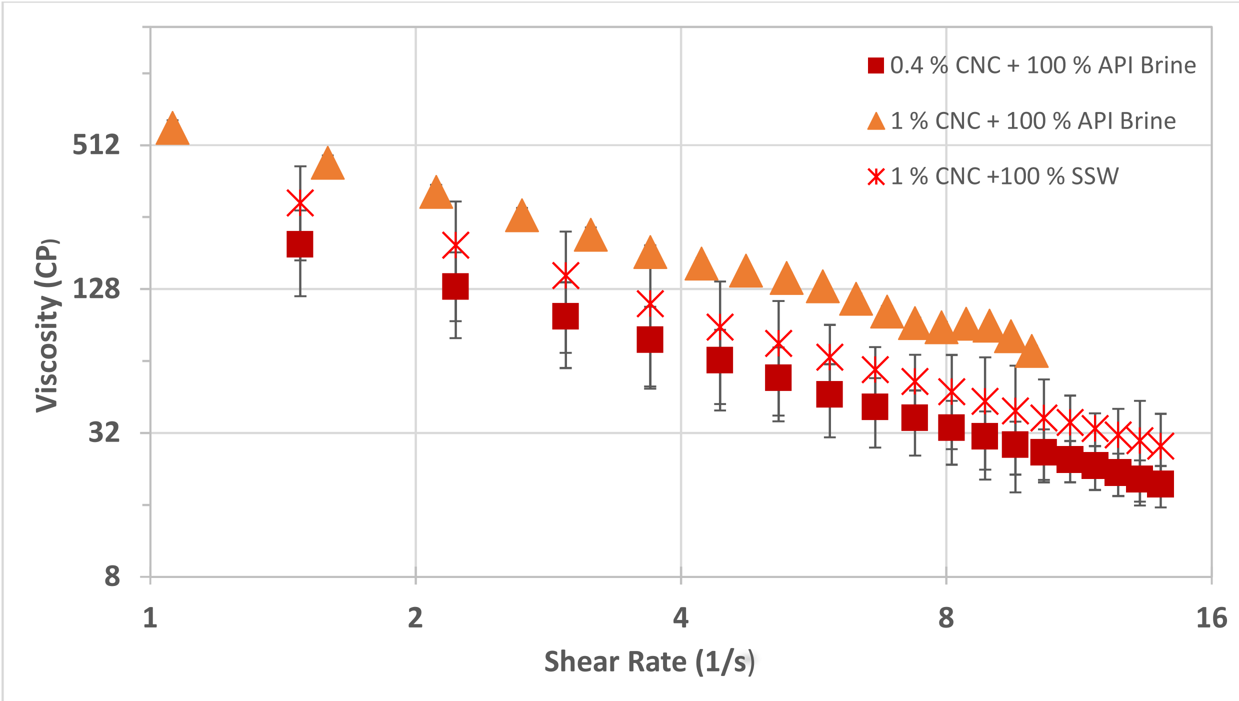

Figure 11: Log-Log scale plot of Viscosity Vs Shear Rate

When we look at the plots of various conc. of CNC with API Brine and SSW, it suggests that higher the viscosity of the aqueous solution, more stable it becomes and looking at different brine, it concludes that API brine with CNC has more stability than the SSW as it was found to be more viscous, which agrees with our hypothesis of the project.

Conclusion

My project with Dr. UB involved studying about the emulsions and their stability. I used the rheological property to study the viscosity of the aqueous phase and correlating with the stability of the emulsions. Our data suggest that the initial hypothesis was correct. Viscosity correlates with the stability of emulsions. Higher the viscosity, the more stable becomes. Comparing the aqueous solution with SSW and API, our data indicate that API becomes more stable than SSW. It is because API brine has higher ionic strength than that of SSW, which has been explained by perturbation theory. Cellulose Nanocrystals have some negative sulfate ions and when we make a CNC in a DI water, it has abundant negative charges. We all know that negative charges repel each other. Both the brines have cat ions that come closer and form a skeleton inside the perturbation that makes it viscous. Hence, API brine having higher ionic strength than SSW forms a viscous solution, which is likely explained by the figure 11.

Future Work

Future steps would be using the brine with different ionic strength and compare the stabilities and viscosities with it. Like we can use the NaCl solution with an ionic strength of 1.9 and 0.61, which has the same ionic strength of SSW and API brine. With these data points, we would be able to draw a broader conclusion. I have only measured the viscosities of the aqueous phase, but we could also measure the viscosity of the emulsions and simultaneously study the effect of asphaltenes in an emulsion.

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Appendices

Appendix 1

Using the Molarity equation,

$$M_1 \cdot v_1 = M_2 \cdot v_2$$

Here, M_1 is the concentration of the CNC that we bought from University of Maine, and v_1 is the volume of CNC in mL, M_2 is the required concentration that we are looking, from which we can calculate the v_2. This v_2 will be the volume of DI water that we will add into the CNC solution we initially had.

Appendix 2

Here is the attachment of the average values of the viscosity that were calculated using three trials in two samples using different shear rate.

Average Viscosity (cP)	**Shear Rate (1/s)**
387.72	0.75
196.48	1.48
130.99	2.22
98.24	2.96
78.49	3.69
64.34	4.43
54.35	5.16
46.36	5.90
41.02	6.64
36.96	7.37
33.59	8.11
30.91	8.85
28.55	9.58
26.51	10.32
24.76	11.05
23.30	11.79
21.83	12.53
20.54	13.26
19.46	14.00

Table 1: 0.4 % CNC + 100 % API Brine

Average Viscosity (cP)	**Shear Rate (1/s)**
604.32	1.06
432.28	1.59
325.74	2.11
260.13	2.64
215.87	3.16
182.53	3.69
163.28	4.22
152.76	4.74
142.42	5.27
131.21	5.79
116.57	6.32
103.02	6.85
92.01	7.37
88.53	7.90
91.53	8.42
89.86	8.95
81.07	9.47
70.51	10.00

Table 2: 1 % CNC + 100 % API Brine

Average Viscosity (cP)	**Shear Rate (1/s)**
293.55	1.48
195.70	2.22
146.00	2.96
111.20	3.69
88.73	4.43
75.96	5.16
66.43	5.90
58.85	6.64
52.56	7.37
47.62	8.11
43.38	8.85
39.59	9.58
36.98	10.32
35.47	11.05
33.44	11.79
31.37	12.53
29.73	13.26
28.16	14.00

Table 3: 1 % CNC + 100 % SSW