CHAPTER VII
CONCLUSIONS
CHAPTER VII
CONCLUSIONS

Heterogenous oxidation of starch using sodium hypochlorite is affected by impurities present in starch, the speed of stirring, particle size of the starch, pH of the medium, ionic strength of the medium, type and nature of inorganic salts and/or buffer components, temperature of the reaction and concentration of the reactants. Therefore, maize starch used in the kinetic runs was purified by extractive methods to remove lipids and inorganic salts and sieved to pass through 200 mesh (B.S. sieve) screen but not through 240 mesh in order to maintain constant particle size. The reactions were conducted at constant rate of stirring, mostly with a constant starch to liquor ratio. The effect of the rest of the parameters which affect the rate have been studied in greater detail.

The rate of oxidation at initial 10.0 pH, has been studied for the unbuffered system. The rate of reaction changes with the time of reaction, as pH also drops from 10.0 to 4.0. The unbuffered system gives three slopes, when 'ln Co/C' versus 't' is plotted, the initial and the third slopes are almost the same but much lower than the middle one. The middle rate is quite similar to that of the system buffered at 7.0 pH. The middle rate is invariably observed between 6.1 to 7.9 pH, whereas above and below this pH range, rate appears to remain constant. All the three rates are significantly affected by the presence of sodium
chloride and above 0.5 M sodium chloride, there is no perceptible change in the rate.

In heterogenous oxidation of starch at 10.0 pH about 7.5 percent soluble fraction oozes out, which affects the rate of reaction considerably.

At 10.0 pH the concentration of buffer and the nature of the buffering agents affect the rate considerably.

Heterogenous hypochlorite oxidation of starch buffered at various pH but in the absence of catalyst, obeys first order kinetics. This is also observed by Lewin et al. 202-204 Thus, a plot of \( \ln \frac{C_0}{C} \) versus 't' is linear at any oxidant concentration, at any pH between 4.0 to 10.5 and at any temperature in the range of 27° to 47°.

The rate constants determined from the first order plots do not remain constant, but vary considerably with change in chlorine concentration, pH and the oxidate concentration.

At 10.0 pH (buffered), the rate constant decreases as the chlorine concentration is increased from 28 m.moles per litre to 112 m.moles per litre, and then, it remains almost constant upto about 170 m.moles per litre. Above this chlorine concentration, the starch granules get disrupted and soluble reaction products, formed, interfere. Therefore, the reaction kinetics do not follow a simple trend. The decrease in reaction rate with initial increase in chlorine concentration is though abnormal, can probably be attributed to the more rapid rate of chemisorption of the oxidant on the oxidate surface.
At 10.0 pH (buffered) the rate constant increases with increasing concentration of starch at a given (170 m.moles per litre) chlorine concentration. A plot of the rate constants versus the starch concentrations is a linear one which passes through origin. This suggests that the rate of reaction is directly proportional to the starch concentration. In fact, when the data are recalculated using equation for the second order, the rate constant values are almost the same for any starch concentration. This signifies that the rate of reaction is also first order with respect to starch concentration and the overall oxidation reaction is second order.

The first order and the second order rate constants, decrease with increasing hydroxide ion concentration (alkalinity) and with increasing hydrogen ion concentration. The highest rate is observed at 7.0 pH. Similar behaviour is also observed by Lewin, Theander and others for starch and other carbohydrates.

Increase in temperature, increases the rate of reaction at all pH levels. The increase is approximately 2-3 fold for every 10° rise in temperature.

Energy of activation, derived from Arrhenius plots shows considerable variation with change in initial oxidant concentration and pH. The energy at 5.5 and 7.0 pH is lower than that at all other pH levels.
The energy of activation of the uncatalyzed reaction at 7.0 pH is higher than that at 5.5 pH, though the rate of reaction shows a reverse trend. Thus, it appears that the factors other than energy of activation also play an important part in deciding the overall rate of reaction.

Participation of hydroxyl groups in the oxidation reaction has been ascertained by studying the rates of oxidation of partially acetylated starches at 37° and 8.5 pH. As the degree of acetylation increases, the rate decreases. Studies on various other modified starches have also been conducted. The rate of reaction is less with hydroxyethyl starch, periodate-chlorous acid oxidized starch, periodate oxidized and borohydride reduced starch, and the soda starch as compared to unmodified starch. In the case of dialdehyde-starch the rate is more. Starch hydrolysed mildly with dilute hydrochloric acid shows lower rate of reaction than the unmodified starch. This is though seemingly inconsistent, can be attributed to the increase in ordered region of starch on mild hydrolysis.

The rates of oxidation of modified starches at other two temperatures also follow the same trends as observed at 37°. Energy of activation, however, does not correlate with observed rate, because, dialdehyde starch which shows highest rate of reaction, shows the highest energy of activation, whereas, acetylated starch showing low rate shows the least. All the modified starches show lower energy of activation than the unmodified starch.
The rates of oxidation of starch using potassium hypochlorite are higher than that using sodium hypochlorite at pH levels 4.0 to 10.0, in buffered systems.

Properties of starch oxidized at various pH levels and with different chlorine concentrations have been investigated in detail. Carboxyl and carbonyl contents, ferricyanide number and alkali-labile value have been determined. $\beta$-Amylolysis of the oxidized starch and intrinsic viscosity of the acetylated oxidized starches have been measured for certain selected samples.

Carboxyl contents, ferricyanide number and alkali-labile values are highest at 4.0 pH and all the properties show decreasing trend with increasing pH up to 10.0. The carboxyl contents are high for acidic systems than for the basic systems. Intrinsic viscosity is the least at 4.0 pH and increases with increasing pH. $\beta$-Amylolysis values do not show any trend, but are lower for oxidized products, than the unmodified one. Increase in the oxidant concentration shows increase in the carboxyl content, carbonyl content, ferricyanide number and alkali-labile value. The intrinsic viscosity of the acetylated oxidized starches decreases with increased oxidant concentration. $\beta$-Amylolysis does not show any significant trend but for its decreased values.

Hypochlorite auto-oxidation in the presence of a number of catalysts but in the absence of starch has been investigated at various pH levels, temperature and chlorine concentrations. Chlorate formation under such conditions but in the absence of
added catalysts was found to be negligible. Autodecomposition in the absence of any added electrolyte is negligible at 10.0 pH and 8.5 pH, but it is observed at 7.0, 5.5 and 4.0 pH. The rate of autodecomposition increases with increasing temperature and it is highest at 47° and 7.0 pH. Autodecomposition is observed at 10.0 and 8.5 pH in the presence of salts of cobalt and nickel and it is very high at pH 4.0, 5.5 and 7.0 in the case of these two salts. Silver catalyst does not show autodecomposition on alkaline side, but the autodecomposition in presence of silver increases with increasing acidity of the medium. Presence of other salts does not essentially alter the rate of autodecomposition at all pH levels. The rates of autodecomposition do not change with change in chlorine concentration at 10.0 pH. Increase in concentration of the catalysts, particularly salts of cobalt and nickel, leads to increase in autodecomposition of hypochlorite.

Rate of heterogenous oxidation of starch at initial 10.0 pH in unbuffered system has been studied for various catalysts. The rate of reaction for the salts of cobalt, nickel and silver does not change with time though the pH decreases. In other systems, the rate changes with time of reaction, as the pH also drops. Silver salts catalyzed reaction shows maximum fall in pH, which has been attributed to greater depolymerization (chlorinolysis). This is further supported by oxygen balance which is higher for silver salt catalyzed oxy-starch, than for uncatalyzed oxy-starch. The oxygen balance of the oxy-starches prepared in the presence of copper and magnesium salts is also higher. However, in these
two cases the rate of reaction is the same as that of uncatalyzed reaction. In case of cobalt and nickel salts catalyzed reactions, the drop in pH was minimum. This has been attributed to greater catalytic autodecomposition of hypochlorite and is supported by the lower oxygen balance of these oxy-starches than that of uncatalyzed oxy-starch.

Heterogenous oxidation of starch buffered at various pH, in the presence of catalysts, obeys first order kinetics, i.e., the plot of $\ln \frac{C_0}{C}$ versus $t$ is linear at any oxidant concentration and any pH between 4.0 to 10.0 and at any temperature in the range of 27° to 47°. The salts of cobalt, nickel, copper, iron and silver show the catalytic effect either at one or more pH levels studied, whereas, the salts of magnesium, calcium, zinc, mercury, lead and aluminium and sodium sulphide do not show any catalytic effect in terms of the rate of reaction at any of the pH levels studied.

Rate constants determined from the first order plots do not remain constant, but vary considerably with chlorine concentration and pH. The rate of reaction is highest at 7.0 pH and decreases on increasing the acidity or alkalinity for all the catalytic systems except the system containing cobalt salt, which show the highest rate at 10.0 pH.

Silver salt catalyst has proved to be efficient even in the acidic pH. It is known that silver salt forms (AgCl$^{+}$) with unipositive silver and may suggest that this increases the stability of
chlorinium ion, which could be one of the expected species for the hypochlorite oxidation.

The salts of aluminium, lead and silver and sodium sulphide do not inhibit the rate of reaction at 10.0 pH suggesting that hydroxy and peroxy free radicals may be absent.

The energy of activation derived from the Arrhenius plots shows considerable variations with catalyst type, initial oxidant concentration and pH. This has been attributed to the Compensation\textsuperscript{270} or Theta\textsuperscript{271} effect, because frequency factor also increases with increase in the energy of activation.

The increase in rate of reaction with the corresponding increase in the catalysts concentration in the case of the salts of cobalt, nickel and copper at 10.0 pH suggests that, they are the solid catalyst\textsuperscript{264}.

Oxygen balance at various pH levels for the buffered systems suggests that in alkaline pH the soluble fraction oozes out from the starch and reacts with the oxidant at a faster rate in that pH range. This gives lower oxygen balance for oxy-starches prepared under alkaline pH than those prepared in the acidic pH range.

Carbonyl functions are higher in acidic pH than that in alkaline pH for all the systems.

Silver salt accelerates the chain depolymerization, because the intrinsic viscosity of acetate of oxy-starch prepared in the
presence of silver salt is considerably lower than that of
oxy-starch prepared in the absence or in the presence of any
other catalyst.

Studies on severe oxidation of starch show that the oxidation in
the presence of magnesium chloride gives yield of about 85 per
cent and the oxy-starch recovered possesses very high carboxyl
content. Though magnesium chloride does not accelerate the rate
of reaction, in its presence, the highly oxidized starches, which
are otherwise not possible using conventional oxidizing systems,
are produced.

The studies carried out here show that there are three distinct
types of effects of salts on the hypochlorite oxidation of starch
(i) salts act on the oxidant exclusively and accelerate the rate
of autodecomposition. The examples of the salts of this class
are cobalt and nickel, (ii) salts act on the substrate, starch
exclusively, and do not act on the oxidant. The examples of this
class are the salts of copper, iron, silver and magnesium, and
(iii) the salts which do not accelerate either oxidant or sub-
strate. The examples of this type of salts are calcium, zinc,
mercury, lead and aluminium and sodium sulphide.

Studies using \( \text{D}_2\text{O} \) as solvent suggest that the rate of oxidation
of maltose, methyl \( \alpha\text{-D}-\text{glucoside and amylopectin in H}_2\text{O} \) is more
than four fold than that in \( \text{D}_2\text{O} \). The ratio \( \frac{k_R}{k_D} \) is approxi-
mately the same for methyl \( \alpha\text{-D}-\text{glucopyranoside and amylopectin},
whereas it is higher for maltose. This higher ratio in the case
of maltose may be attributed to the free anomeric reducing groups.
It is assumed that there is an initial attack of chlorine molecule on the available hydroxyl groups of the substrate, forming the hypochlorite ester. This ester subsequently in a rate determining step removes proton from the carbon atom, liberating hydrochloric acid.

The results of the kinetic study suggest that the hypochlorite oxidation of starch shows negative catalysis in acidic and alkaline medium. The negative catalysis of rate inhibition under alkaline condition has been attributed to decreased interaction between negatively charged soda starch and $\mathrm{OCl}^-$ anion. The rate inhibition under acidic conditions can be attributed to the relatively decreased ease of removal of proton in acidic medium in the rate determining step.