Behavior of Glycerin in the Presence of Alkali at High Temperatures

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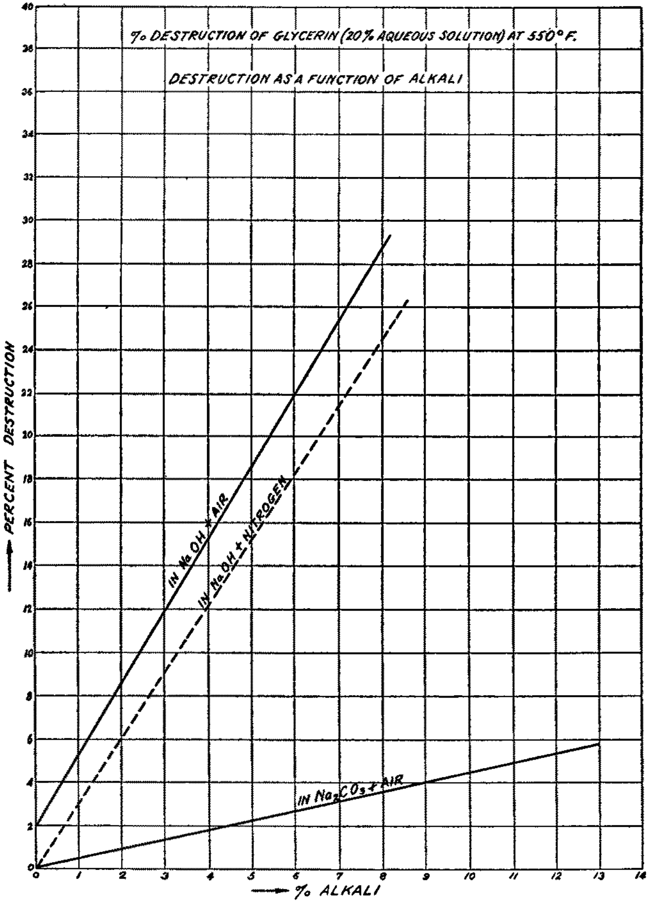
The advent of high-speed, high-temperature processes of making soap with the simultaneous recovery of glycerin created a void in the data applicable to these systems. The temperatures were so much higher and other conditions, particularly the time factor, so different from the conventional method of manufacturing soap that a special investigation was thought necessary for the proper evaluation of the variables involved.

There is little information available in the literature on the subject of the behavior of glycerin at high temperatures, particularly its thermal destruction in the presence of alkali. General statements to the effect that oxygen and alkali help destroy glycerin at high temperature are found. In the International Critical Tables (Volume 2, Page 151), it is reported that at one atmosphere pressure of oxygen a temperature of 774° F. is necessary to ignite glycerin, and at thirty-three atmospheres of oxygen, ignition takes place at 401° F.

In this study attention was focused on glycerin. The effect of alkali, temperature and time of heating on its destruction under pressure was investigated. The method used consisted of placing a given volume of solution or mixture of water, glycerin and alkali of known composition in a nickel bomb, which was a section of nickel pipe five inches long and one and one-half inches in diameter, closed on one end and fitted with threaded plug and gasket on the other. The bomb, put into an oil bath maintained at a specified temperature, was withdrawn at given intervals. While in the bath, the contents of the bomb were agitated by shaking. The bomb, allowed to cool in the air upon withdrawal from the bath, was weighed before and after immersion to determine whether or not there was any leakage during the experiment. In none of the runs reported was there any loss of charge. In those experiments where no soap was used, the charge was 25 c.c. of 25% glycerin to which 5 c.c. of aqueous alkali solution of the desired concentration were added. The bomb was sealed, shaken and placed in the oil bath maintained at a temperature 5° F. higher than the one recorded on the graphs. After the run, the contents were removed and analyzed for glycerin, using the dichromate method.

The destruction of glycerin at 550° F. as a function of per cent and nature of alkali was studied. The bomb, containing glycerin and alkali of known concentration, was immersed in the oil bath, kept at 555° F. Results are given and summarized in Figure I. The destruction is a linear function of the per cent alkali. In the presence of 1% sodium hydroxide, 5.5% of glycerin was destroyed; in the presence of 2% sodium hydroxide, the destruction was 8.5%. In the presence of nitrogen, the destruction was somewhat lower than in air. The difference in destruction between sodium hydroxide and sodium carbonate is very striking, as is shown in the following table:

FIG. I.

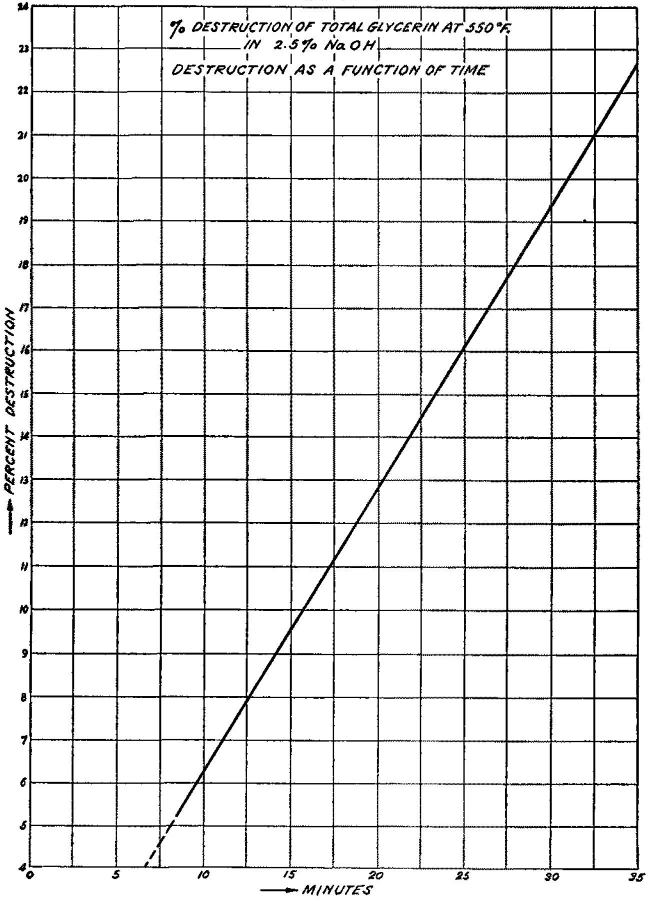


Alkali		% Glycerin Destroyed
1%	Sodium Hydroxide	5.5%
	Sodium Carbonate	0.5%
2.5%	Sodium Hydroxide	10.0%
	Sodium Carbonate	1.1%
5.0%	Sodium Hydroxide	18.5%
	Sodium Carbonate	2.0%

So, it may be asserted that sodium carbonate destroys approximately one-tenth of the glycerin that sodium hydroxide does, at equal per cent concentrations of alkali. It is thus possible to use sodium carbonate in excess without appreciable destruction of glycerin in rapid high temperature soap-making processes.

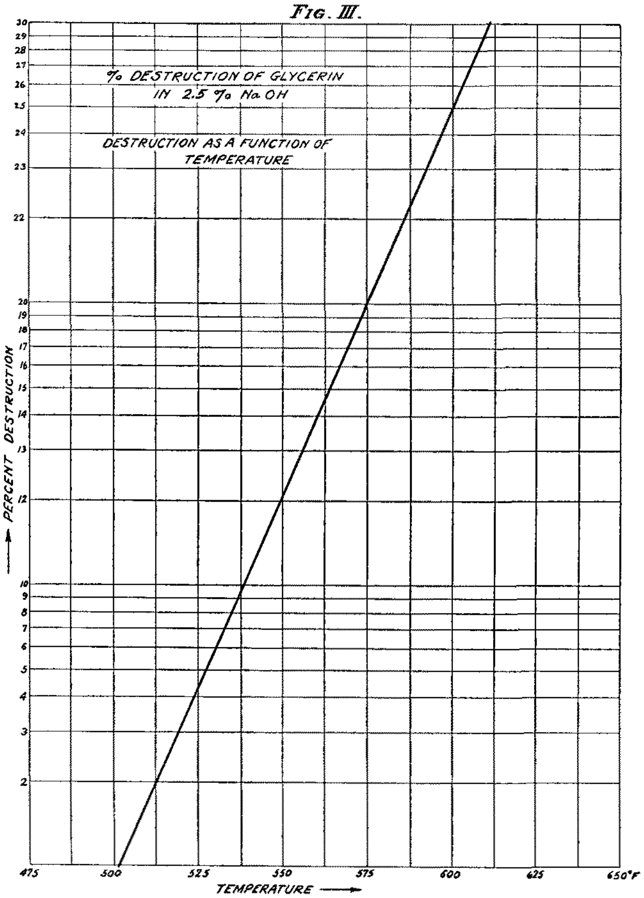
The extent of destruction of glycerin in the presence of 2.5% sodium hydroxide was then studied. The results are shown in Figure II. In the operation of a high temperature soap unit, the saponifying sodium hydroxide solution is often 25%. For every pound of tallow, there are approximately 0.1 lb. glycerin, and 0.4 lb. water from the alkali solution. Or, in terms of glycerin water, a 20% solution of glycerin is produced. This concentration was therefore chosen. The period of fifteen minutes is an upper limit for the contact time of the reactants under pressure, and the temperature 550° F. is a common operating temperature for high temperature soap-making processes. A rationale for the choice of our system was thus established. In Figure II the destruction of glycerin at 550° F. in 2.5% NaOH is plotted against time. There was 6.0% destruction when the bomb was immersed for nine minutes, while for fifteen minutes 9.5% was destroyed. The destruction is a straight line function of time.

FIG. II.



Finally, the destruction of glycerin in the presence of 2.5% NaOH as a function of temperature was determined. Results are given in Figure III. There is no appreciable destruction until beyond 500° F., after which destruction increases noticeably. In the neighborhood of 550° F., the destruction doubles every 25° F. rise in temperature.

FIG. III.



The extent of destruction of glycerin by alkali is independent of the soap present. For example, a mixture of 50% soap, 40% water and 10% glycerin gave less than 1% destruction at 550° F., whereas the same charge containing 2½% sodium hydroxide, at 550° F., gave 10% destruction, as if soap were not present.

The results in the nickel bomb may be summarized:

1. At 550° F., there is about 4% destruction (for a seven minute period) per percent NaOH in system.
2. The destruction is proportional to the time.
3. The rate of destruction is about doubled per 25° F. rise in temperature in the presence of alkali.
4. Destruction takes place in oxygen, that is air, at 550° F.; there is less destruction in absence of oxygen, that is, in the presence of nitrogen.
5. Soda ash has relatively little effect on the destruction of glycerin.
6. With small excess of sodium hydroxide, the destruction of glycerin at 550° F. under pressure is small for small intervals.

There appears to be a relationship between pH and destruction, but just what it is, is difficult to formulate on the basis of the data.