

PILOT-PLANT PREPARATION OF HYDROXYETHYLATED FLOURS¹

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ABSTRACT

Reaction of ethylene oxide with various cereal flours was accomplished in a simple reactor that prepared 10-lb. batches of hydroxyethyl flours for evaluation studies. One satisfactory method for integrating 2.5% of sodium hydroxide catalyst into the reaction mixture was, first, to prepare a catalyst from 50% sodium hydroxide solution and a small portion of the flour, and then to dry and grind this catalyst before adding it to the bulk of the flour. The reaction rate was increased by using active catalysts which were specially prepared, or by aging the reaction mixture. The reaction of flour with ethylene oxide was exothermic, and the rate also depended upon batch size, temperature, and mol ratio of reactants. Larger batches lost less heat, thus allowing a higher reaction temperature and reaction rate. Reaction rate was decreased by lower ratio of ethylene oxide to flour.

At present, specialty products are available on the market which are produced by subjecting commercial starches to oxidation, esterification, or etherification (1). Recently, the etherification reaction with ethylene oxide has been applied to commercially available grain flours by Rankin, Mehlretter, and Senti (3) to produce materials of improved properties. Because the hydroxyethyl flours were required for use tests, a reactor was designed in which up to 15 lb. per batch could be made. The problems that arose are pointed out, and the means used to solve them are discussed.

Equipment and General Procedure

The reaction vessel consisted of a stainless-steel cylinder with a cone at one end and a flanged cover at the other. The vessel was equipped with a wooden tire near the conical end, and the tire and flange were covered with rubber sheeting, as shown in Fig. 1. The assembly was placed on a large ball-mill drive roll to provide agitation. The reactor rotated at 45 r.p.m. Ethylene oxide gas was introduced intermittently through stainless-steel valves, fittings, and tubing connecting the ethylene oxide cylinder to the cone of the reaction vessel. The pressure gage shown had a range of 15 p.s.i.g. to 30-in. vacuum, and its fitting and Bourdon tube were constructed of stainless steel. The drive motor for the rolls was explosion-proof, and all equipment was grounded.

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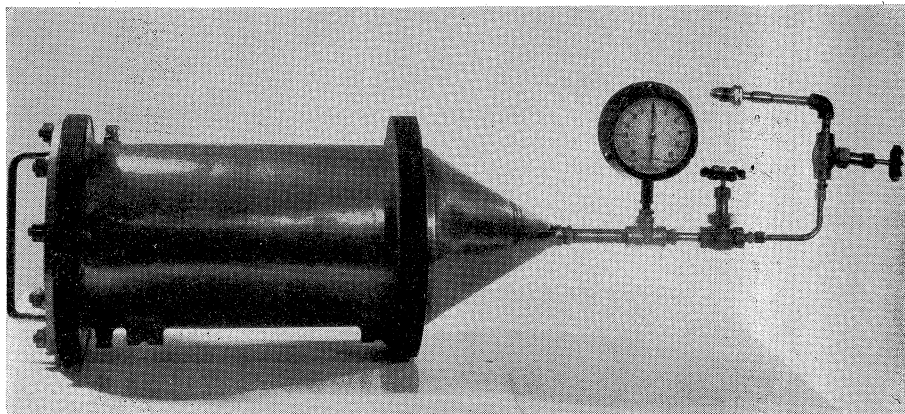


Fig. 1. Reactor used in preparing hydroxyethylated flours.

After the solid reaction mixture was introduced into the vessel through the flanged end, the cover was secured and the vessel was put on the rolls and evacuated. The rolls were started, and the solids were allowed to mix under vacuum for about 15 minutes. The rolls were stopped, nitrogen was introduced to 15 p.s.i.g., and mixing was resumed. The process of mixing under vacuum and then under nitrogen was repeated at least once.

Next, nitrogen was removed to 10 in. of mercury vacuum, leaving about 10 p.s.i.a. in the vessel. Ethylene oxide gas was introduced to bring the pressure to 15 p.s.i.g. or about 30 p.s.i.a.; pressure was periodically increased to that level by adding ethylene oxide at intervals depending on the rate of fall. For most runs, after three additions in the first ten minutes of operation, further increments were added at 20-minute intervals unless excessive heating was observed. To obtain sufficient gas pressure from the ethylene oxide cylinder to give 15 p.s.i.g. in the reaction vessel, it was necessary to heat the cylinder with water at about 140°F. (60°C.). Under these conditions, some ethylene oxide condensed in the connecting tubing, and care was taken during and after disconnection to avoid personal contact as far as possible with the liquid or vapors. The reaction was carried out in a special room equipped with explosion-proof electrical fixtures, including three high-capacity fans to maintain good ventilation.

The reaction was continued until slightly more than the theoretical amount of ethylene oxide had been added. When the pressure indicated that the proper amount had been absorbed, the remainder was removed by evacuating the vessel with a water jet, followed by nitrogen sweeping in the same manner described for preparing the solid

reaction mixture before introducing ethylene oxide.

The solids were weighed before and after the reaction, giving a check of the extent of substitution. From the volume of the vessel, the weight of solid reaction mixture, and the gas law, a factor was obtained to convert total pressure drop during reaction to extent of substitution. Neither method agreed perfectly with the chemical analyses of the final product. In most runs, 7.3 lb. of dry flour yielded 9 to 11 lb. of finished product with a moisture content of about 10%.

Materials and Methods

Screen analyses were carried out by shaking 200 g. of product in a screen set consisting either of 12-, 16-, 30-, and 60-mesh or of 30-, 60-, 100-, and 140-mesh, for 15 minutes. The ethylene oxide substitution was determined essentially by the Lortz modification of Morgan's method (2). Moisture determinations were obtained with the Brabender Moisture Tester² although the Karl Fischer or vacuum-oven method gave equal results.

The solid reaction mixture was prepared by adding 2.5% sodium hydroxide equivalent to it. Several methods of doing this were tried, and these are discussed in the next section. The following procedure evolved as the method of choice: to 300 g. of flour in a sigma-blade mixer were added 140 cc. of 50% sodium hydroxide solution over a period of at least 10 minutes. The moist granular mixture was then heated at 140°F. for at least 1 hour in a forced-draft oven. After cooling, the mixture was ground in a Mikro-pulverizer using a 0.020-in. screen. The larger material on the first grind was reground until less than 5% was retained on a 60-mesh screen. An amount of material passing a 60-mesh screen was then used as the catalyst.

The sodium hydroxide content of the catalyst was estimated by adding about 150 ml. of water to a flask containing about 0.25 g. of catalyst accurately weighed. The mixture was titrated with 0.10*N* hydrochloric acid to both a phenolphthalein and then a methyl red end point. The difference was taken as an indication of carbonates, and it was sometimes appreciable.

Results and Discussion

Several lots, grades, and types of wheat flour, two types of corn flour, and a commercially available grain sorghum flour were used in these limited experiments. Any differences among them during hydroxyethylation appear to be minor. Because the flours are currently

² The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

being evaluated, a complete description of their properties is not given.

In early experiments, several methods of incorporating the sodium hydroxide catalyst into the flour were tried. In one, sodium hydroxide was ground in an attrition mill mounted in a dry-air box, the powder was added to 2 lb. of flour, and the mixture reground. In another experiment, the sodium hydroxide was ground in a mortar and pestle, screened through 140-mesh screen, and added to the flour. Despite all precautions, appreciable quantities of large, pink, jellylike particles were found in the final product. The minimum amount was about 0.5% over a 16-mesh screen. These particles were analyzed and found to contain about double the sodium hydroxide and moisture concentrations of the remaining product, and about one-fourth of the protein content.

Because it was most difficult to mix dry sodium hydroxide and flour into a relatively homogeneous system without particle formation, methods of preparing a better catalyst and of reducing particle size were investigated. The biggest problem encountered was overheating, followed by browning and plasticizing in the materials. Soda ash can be used to prepare a high-sodium mixture very successfully, but the rate of reaction of the mixture of dry soda ash, flour, and ethylene oxide in one run was very slow. Finally, it was found that considerable 50% sodium hydroxide could be added to flour without appreciably developing plasticity in the flour, but that at a certain stage of the addition, granulation occurred with a consequent swelling of the mass.

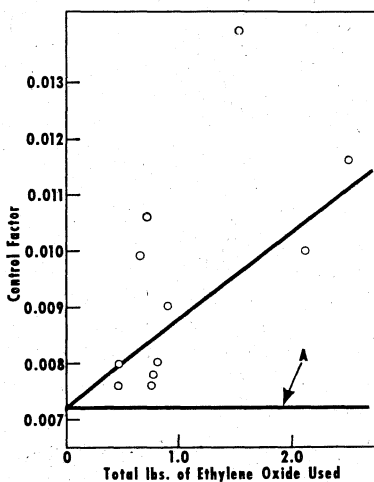


Fig. 2. Relation of control factor, the pounds of ethylene oxide actually used for each p.s.i.g. drop in pressure in the reactor, to the total amount used for the batch. *A* is the relation computed from the reactor volume.

Some ammonia is liberated near the end of the addition, and heat is liberated. The finished mixture is a mass of relatively soft aggregates, 80% of which pass a 30-mesh screen. This material, when fresh, could be readily ground in a "pug" mill, but attrition or hammer mills cause it to plasticize.

The next series of experiments was run using catalyst ground in a pug mill to pass a 30-mesh screen. The results are shown in Figs. 2 and 3. The horizontal line in Fig. 2 is the computed factor for converting total drop in pressure to weight of ethylene oxide introduced into the reactor; whereas the diagonal line represents actual results using a standard operating procedure in which a 9-p.s.i.g. increase in reactor pressure was accomplished in a fixed time (about 10 seconds). Deviation of the control line from its predicted horizontal position is a matter of relative rates of addition and reaction. As will be shown, the reaction rate increases for extended runs, so that the net effect is to increase the control factor as higher amounts of total ethylene oxide are used. Once this curve is established, substitutions can be carried out to within 0.5% of the desired values.

Figure 3 indicates the swelling of the catalyst particles. Since all the catalyst passed a 30-mesh screen, the presence of particles over 30-mesh can probably be interpreted as particle-size growth in the catalyst.

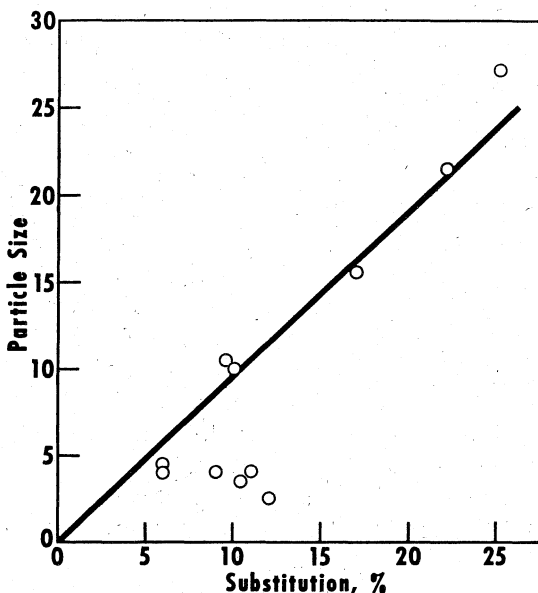


Fig. 3. Particle size, as weight percent of particles in the hydroxyethylated flours retained on a 30-mesh screen, increased with percentage ethylene oxide substitution.

These large particles appear as translucent, insoluble spheres in pastes made in the usual way, and in some applications these particles would not be permissible. The cluster of low points probably represents a finer catalyst owing to the slower addition of 50% sodium hydroxide to the flour. One of these points is for a run made with preground solid sodium hydroxide.

During the experiments, it was noticed that the catalyst particles became harder on air-drying and that the catalyst lost moisture with little gain in carbonate. The dried catalyst was readily ground in a hammer mill to pass a 60-mesh screen. When this catalyst is used immediately, the reaction rate is reduced to about half, but when it is mixed with the flour and the mixture is allowed to age for over 2 days, the reaction proceeds as usual. In any case, there are no particles in the product larger than 30-mesh, and pastes made from hydroxyethylated flours seem to be greatly improved.

To avoid long aging times the catalysts were prepared by oven-drying the fresh material, although some yellowing occurred and the dried material was somewhat softer than the air-dried catalyst. If a vacuum cleaner bag was used as a receiver to prevent moisture condensation on the ground product, the oven-dry catalyst could be ground in a hammer mill. It performed well in two runs. In a third run when the catalyst was dried for an intermediate time, subjected to the maximum grinding action (i. e., two repasses of about 30% of the first grind), and stored in a covered glass jar for 1 day before use, it produced a lower rate of reaction. Typical examples using various methods of making the catalyst for 12%-ethylene oxide-substituted flours are presented in Table I.

Besides the observed effect of catalyst amount and condition on the rate of reaction, limited work has shown that pressure and batch-size control the rate also, apparently through a complex relationship with temperature. The pressure, of course, determines the concentration of ethylene oxide in the nitrogen-containing atmosphere and, therefore, the ratio of reactant to flour at constant batch-size. Reduction in batch-size at constant pressure increases the amount of ethylene oxide with respect to the flour but also increases the efficiency of heat exchange through the walls of the reaction vessel. The reaction is definitely exothermic, and the product becomes quite warm with extended reactions and active catalysts with an 8-lb. batch-size. The smaller batches react somewhat slower than larger ones. A typical course of an active reaction is presented in Fig. 4 when the usual procedure is followed. The slopes of the diagonal lines represent the rates of absorption of ethylene oxide by the flour; the height of the lines above the horizontal

TABLE I
COMPARISON OF SODIUM HYDROXIDE CATALYST PREPARATION METHODS

METHOD	PARTICLE SIZE ^a	FINAL RATE	PRODUCT PARTICLE SIZE
		<i>psig/minute at 15 psig</i>	<i>% over 60-mesh</i>
Ground dry by machine and mixed	26
Ground dry by hand, screened, and mixed	14.5
Mixed wet, pug ground	Coarse	0.2-0.5	15-30
Mixed wet, air dried, hammer-ground, aged	Fine	0.6	7.5
As above, not aged	Fine	0.2	7
As above, not aged hammer-ground, not aged	Fine	0.6	7

^a Coarse — 100% through 30-mesh. Fine — 100% through 60-mesh, about 65% through 140-mesh.

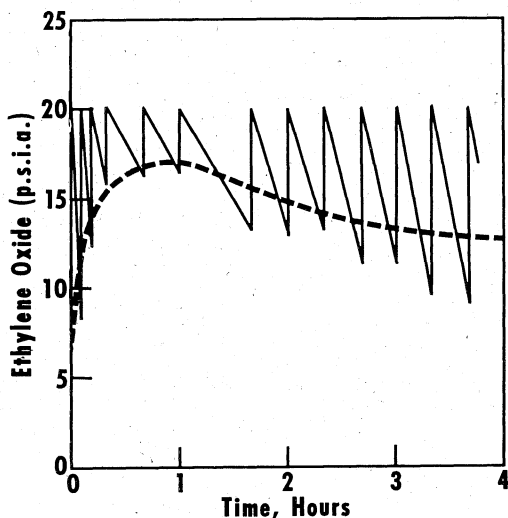


Fig. 4. Reaction rate at incremental adjustment to constant pressure. The pounds absolute pressure represent the weight of ethylene oxide present at any time in the reactor, which was refilled to 20 p.s.i.a. at about 20-minute intervals. The dotted line suggests the reaction with constant feed.

axis is an indication of driving force. The broken curve suggests the course that might be expected with a constant rate of ethylene oxide addition.

Although no attempt was made to analyze the degree of heterogeneity in the reaction product, there was one other indication, besides the swelling around the catalyst particles, that nonuniform reaction oc-

curs. In the "dead" spaces of the reactor (at the center of the two ends) occasionally the flour was found to be caked and, near the ethylene oxide inlet, to be somewhat pasty in character. The cake, if dry, was quite friable and could easily be blended back into the product.

Factors in Plant Design. The important consideration in the large-scale production of hydroxyethyl flours will be the control of the operation under safe conditions. The toxic and explosive properties of ethylene oxide are well known, and information on the precautions necessary in handling it is usually available from the distributor.

A practical reactor must be designed to bring together a solid and a gas and, probably more important, to remove heat from the solid without introducing surfaces to the gas which would be cold enough to cause condensation. Some provision may be necessary for heating the mixture at the start of the reaction.

Control of reaction by pressure drop is uncertain; an integration method such as continuous weight measurement of the ethylene oxide input would be preferred. Overheating, which would cause starch gelation, must be avoided, so that a good control is needed to adjust the feed rate of the gas by temperature change as well as by pressure limitation. Pressure control is necessary to avoid exceeding the explosive limits or condensation point of ethylene oxide gas in the vapor phase of the reaction.

Literature Cited

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