Non-catalytic steam hydrolysis of fats and oils
by Richard Charles Archuleta

A thesis submitted in partial fulfillment of the requirement's for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:

The hydrolysis of fats or oils with water produces fatty acids and glycerol. Currently, the countercurrent, continuous, high pressure, high temperature, liquid phase Colgate-Emery process, which uses a catalyst to promote the reaction, is the state-of-the-art method of fat hydrolysis. Non-catalytic steam hydrolysis is a possible alternative. Significant degrees of hydrolysis may be achieved by continuously sparging superheated steam through high temperature fat at atmospheric pressure.

A "bench-scale" hydrolyzer was designed and constructed to investigate the feasibility of steam hydrolysis and was tested with soybean oil and beef tallow. Each of the five stages in the 316 Stainless Steel, 1.77 inch inside diameter, 18-3/4 feet high hydrolyzer included a riser, a downcomer, and a steam dispersion plate similar to a distillation column. Investigations of the degree of hydrolysis were conducted at various temperatures and fat/steam feed ratios. The compositions of the overhead and bottoms products as well as stage liquid samples were analyzed.

Soybean oil was not a good feed source because its highly unsaturated fatty acids polymerized at high temperatures. The degrees of hydrolysis achieved using tallow were 15% at 280°C and 35% at 300°C at a tallow-to-steam feed ratio of 4.2. At a feed ratio of 9.2, the degree of hydrolysis was 21% at 300°C. Decomposition of glycerol was strongly evident at 325°C but not at lower temperatures. Over 95% fatty acids were present in the readily separated organic portion of the overhead product.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The hydrolysis of fats or oils with water produces fatty acids and glycerol. Currently, the countercurrent, continuous, high pressure, high temperature, liquid phase Colgate-Emery process, which uses a catalyst to promote the reaction, is the state-of-the-art method of fat hydrolysis. Non-catalytic steam hydrolysis is a possible alternative. Significant degrees of hydrolysis may be achieved by continuously sparging superheated steam through high temperature fat at atmospheric pressure.

A "bench-scale" hydrolyzer was designed and constructed to investigate the feasibility of steam hydrolysis and was tested with soybean oil and beef tallow. Each of the five stages in the 316 Stainless Steel, 1.77 inch inside diameter, 18-3/4 feet high hydrolyzer included a riser, a downcomer, and a steam dispersion plate similar to a distillation column. Investigations of the degree of hydrolysis were conducted at various temperatures and fat/steam feed ratios. The compositions of the overhead and bottoms products as well as stage liquid samples were analyzed.

Soybean oil was not a good feed source because its highly unsaturated fatty acids polymerized at high temperatures. The degrees of hydrolysis achieved using tallow were 15% at 280°C and 35% at 300°C at a tallow-to-steam feed ratio of 4.2. At a feed ratio of 9.2, the degree of hydrolysis was 21% at 300°C. Decomposition of glycerol was strongly evident at 325°C but not at lower temperatures. Over 95% fatty acids were present in the readily separated organic portion of the overhead product.

CHAPTER 1

INTRODUCTION

Industrial Uses for Fat and Oil Hydrolysis Products

The hydrolysis of fats and oils produces several important industrial chemicals. These products include fatty acids, monoglycerides, diglycerides, and glycerols. Depending on the type of fat or oil feed and the conditions of the reaction itself, a wide array of product possibilities can be achieved.

According to 1990 statistics, the United States alone consumed over a billion pounds of fatty acids [1]. The primary sources for fatty acids were animal fats, coconut oil, and vegetable oils [2]. It has been also estimated that over 185 million pounds of mono- and di- glycerides were produced [3]. Finally, approximately 310 million pounds of glycerol were produced in 1990 by hydrolysis of fats and oils [4].

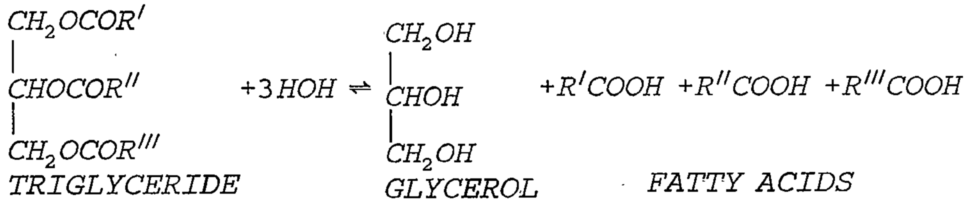
Fatty acids are manufactured for several uses. Products in which purified fatty acids are used in large quantities include soaps, synthetic surface-active agents, plasticizers, polymers, lubricating greases, and many rubber applications. The largest consumption of fatty acids is in the areas of soaps and surfactants [5].

Monoglycerides and diglycerides are specialty chemicals because performance rather than price is the main factor for purchasing decisions. Applications are limited mostly to the food industry. However, monoglycerides and diglycerides are also used in cosmetics, surfactants, and protective coatings [6].

Glycerol products are encountered in many areas. Glycerols are used in solvents, plasticizers, emollients, sweeteners, cosmetics, liquid soaps, liqueurs, copying inks, and antifreeze for automobiles to name a few [7]. Glycerol produced from hydrolysis is not the only source of glycerol for the market, but it contributes significantly.

The Chemistry of Fat and Oil Hydrolysis

The hydrolysis of fat and oil triglycerides to free fatty acids and glycerol requires conditions which promote triglyceride and water miscibility. The reaction is not simple because it proceeds in stages and is reversible. The general chemical reaction formula for fat and oil hydrolysis is:

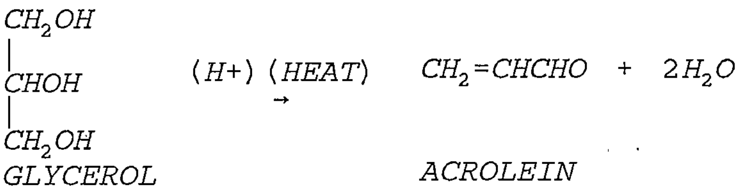


$$\underset{\text{TRIGLYCERIDE}}{\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOR'' \\ | \\ CH_2OCOR''' \end{array}} + 3HOH \rightleftharpoons \underset{\text{GLYCEROL}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \underset{\text{FATTY ACIDS}}{+ R'COOH + R''COOH + R'''COOH}$$

where R', R'', and R''' are straight chain compounds containing from three to eighteen carbons. Only acids containing an even number of carbons are present in substantial amounts. Acids may be saturated or partially unsaturated depending on the fat. The proportions of the various acids vary from fat to fat; each fat has its characteristic composition, which does not differ very much from sample to sample.

Hydrolysis products must be removed from the area of reaction to ensure a forward rate of reaction. A high degree of hydrolysis is ensured in the standard industrial process by using a large excess of water and withdrawing the aqueous glycerol-rich phase and replacing it with fresh water. High temperatures also accelerate hydrolysis [8]. If hydrolysis does not completely remove the fatty acids from a triglyceride molecule, the resulting product is either a monoglyceride (one remaining fatty acid esterified on glycerol) or a diglyceride (two remaining fatty acids esterified on glycerol).

At high temperatures, there is a side reaction that results in the decomposition of glycerol into acrolein. The most sensitive indication of acrolein is its lachrymatory odor. The dehydration of glycerol to yield acrolein involves acid-catalyzed dehydration and keto-enol tautomerization [9]. The chemical reaction for decomposition is:



$$\begin{array}{lcl} CH_2OH & & \\ | & & \\ CHOH & (H+)\,(HEAT)\ \rightarrow & CH_2{=}CHCHO \ + \ 2H_2O \\ | & & \\ CH_2OH & & \\ \text{GLYCEROL} & & \text{ACROLEIN} \end{array}$$

The acid catalyst is provided by fatty acids from the reaction.

CHAPTER 2

CURRENT INDUSTRIAL HYDROLYSIS TECHNOLOGY

The Colgate-Emery Process

Current industrial fat hydrolysis utilizes primarily the Colgate-Emery process which was developed in the 1940's. There has been little change in the technology and the process is widely used today. This continuous high temperature fat splitting process employs a countercurrent reaction in a pressure tower with internal heat exchange resulting in efficiencies of 98%. Using high temperatures and pressures permits relatively short reaction times. Countercurrent fat and water flow produces high degrees of hydrolysis without the use of a catalyst, but plant capacity can be increased by adding a small amount of catalyst to the reaction. However, catalysts promote decomposition of glycerol into acrolein which is undesirable [10].

The well insulated reactor tower is approximately 20-48 inches in diameter, 60-80 feet high, made of solid 316 stainless steel to withstand operating pressures of over 700 psi. Fat is introduced by means of a sparge ring about 3 feet from the bottom, with a high pressure feed pump. Water is introduced near the top of the column at a ratio of 40-50% of the weight of the fat which is about 21 moles of water feed per mole of fat feed. As the ascending fat nears the reaction temperature of approximately 260°C, hydrolysis proceeds rapidly. The approximate residence time of both the fat and water phases through the process is 2 to 3 hours. Temperature independence of the point of equilibrium is an indication of a zero heat of reaction in the Colgate-Emery process [11].

Reaction Kinetics of Hydrolyzing Fats and Oils

There is a generally accepted mechanism for fat hydrolysis. The hydrolysis of fats and oils to fatty acids is sequential from the tri- to the di- to the monoglyceride and finally to the glycerol. It has been observed that in the initial stages of the reaction, an oil/water emulsion forms and the reaction proceeds slowly. That is, initially, the reaction takes place at the interface of the organic and aqueous phases. As the reaction continues, the emulsion breaks down and the reaction rate increases significantly. At this point, the fatty acid content in the oil increases causing the solubility of water in the organic phase to increase. The reaction becomes more homogenous in the organic phase. Finally, as the degree of hydrolysis increases further, the net reaction rate begins to decrease because the reesterification reactions begin to occur at significant rates. In the Colgate-Emery process, the hydrolysis forward reaction is driven nearly to completion by preferential extraction of the glycerol from the organic phase into the water phase [12].

The solubility of water in fats and oils is almost non-existent at room temperature and very low at higher temperatures. However, it is difficult to determine the solubility of water in fats at high temperatures because of the effects of hydrolysis. The solubility of water in fatty acids is much higher than in mono-, di-, or triglycerides. This helps to explain the stages of the hydrolysis mechanism at higher degrees of reaction.

CHAPTER 3

THE FEASIBILITY OF STEAM HYDROLYSIS

Steam Hydrolysis of Fats and Oils

The Colgate-Emery process is limited since it requires a reaction time of 2-3 hours. There is a significant cost of energy required to recover glycerol from the reaction products. To decrease the reaction time and the amount of energy required to separate and purify the products, Kenneth Lunde has investigated the possibility of steam hydrolysis in contrast to water hydrolysis [13].

The steam hydrolysis of fats and oils involves the contact of superheated steam at a pressure of approximately one atmosphere with a fat or oil feed. Glycerol is removed almost entirely from the reaction mixture by vaporization rather than by extraction from the liquid organic phase to liquid water. There is not a need for a catalyst to increase the rate of reaction.

For an industrial steam hydrolysis process the fat or oil feed would initially be deaerated and then heated to reaction temperature. The feed would then be pumped into the top of the reaction column. Steam at a temperature equivalent to the entering fat feed supply would be sparged into the base of the column. The reactor operates essentially adiabatically since there is insignificant heat of reaction. The mechanism of the reaction and the solubility of water in the organic phase is similar to high pressure, high temperature water hydrolysis. As steam ascends through the hydrolyzer and liquid fat or oil descends, the reaction proceeds, and glycerol is stripped away from the reaction by the ascending vapor, driving the reaction forward. Almost complete hydrolysis should occur.

Steam ascending through the column would strip glycerol from the system resulting in a shorter glycerol residence time for steam hydrolysis over the Colgate-Emery process. Because the density of steam is much less than the density of liquid water, a faster volumetric flow rate of vapor can be provided in steam hydrolysis over the Colgate-Emery process assuming that the same relative mass feed rates of fat and water are utilized.

A high reaction temperature may be necessary for a non-catalyzed steam hydrolysis reaction, but less decomposition of products should occur in the reaction vessel due to the shorter residence time of the glycerol in the reactor and the absence of a catalyst which promotes the glycerol decomposition reaction. Because the product streams should show little decomposition, less processing and energy may be necessary to purify the products.

Previous Experimental Results on Steam Hydrolysis

Preliminary work has been performed on the feasibility of steam hydrolysis. Kenneth Lunde has investigated the possibility of catalyzed steam hydrolysis [13]. Some important conclusions were reported that affect the design of the experimental steam hydrolyzer.

Some reactions are limited by chemical kinetics at low temperatures, but with elevated temperatures the rate constant is sufficiently large that the reaction rate is limited by mass transfer. The "Carad" experiments by Lunde were performed to ascertain whether this is the case in the hydrolysis of fats and oils [13]. An investigation was made to increase the solubility of water into the organic phase by use of superheated steam at relatively low pressures in the presence of a catalyst. Tallow at 200-280°C was 16% hydrolyzed at only 10-30 second residence time through a specially designed parallel flow pipe reactor using a zinc oxide catalyst. A second pass of the oil phase through the system resulted in 70% hydrolysis. The experiments indicated that even at high temperatures, the reaction rate is limited by chemical kinetics. It was also concluded that catalysts accelerate the decomposition of glycerol, tallow, and the fatty acids of tallow. This decomposition limits the operating temperature and, therefore, the reaction rate [13].

Research Objectives

1. Investigate feed rate and temperature operating parameters for a bench-scale hydrolyzer.

2. Analyze stage and overall product samples for the extent of hydrolysis and determine if decomposition of the products is apparent.

3. Gain initial insight into the commercial feasibility for the non-catalyzed steam hydrolysis of fats.

CHAPTER 4

THE BENCH SCALE HYDROLYZER

Background

To investigate the feasibility of non-catalytic steam hydrolysis, a bench scale reactor has been designed and constructed. The five tray hydrolyzer reactor is approximately 18 feet long and approximately 1-1/2 inch diameter. A steam source is provided from a boiler, and a tallow feed supply is used.

Investigation of various fat to steam feed ratios is desired to understand the feasibility of the process. Further, there is a need to analyze the content of overhead and bottoms products to understand the extent of the reaction. Finally, by adjusting the temperature of the reaction, the extent of the reaction can be determined for various temperature ranges. The presence of decomposition can also be determined by sensing for an acrolein odor.

The bench-scale hydrolyzer allows several variables to be tested. A range of temperatures, fat feed rates, steam feed rates, and fat/steam feed rate ratios can be tested and a range of outputs observed. These observations can be used to establish the feasibility of an industrial sized process. Investigations of various grades of stainless steel to determine an appropriate hydrolyzer construction material is important. Fatty acids are corrosive which can lead to poor initial color of fatty acids or poor stability during further processing [14].

The bench scale hydrolyzer was constructed in Ryon Lab 2 at Montana State University. The hydrolyzer was constructed during the Spring and Summer of 1990 with minor design modifications made later. At the current time, investigation of its operation continues.

There are five main components which comprise the design of the hydrolyzer. These are a steam source, a fat or oil feed source, the reactor itself, a bottoms collection system, and a system to condense and collect overhead vapor products as liquids. A heating and temperature control system is necessary for the entire process. The discussion which follows describes the components of equipment which are included in the overall system diagramed in Figure 1.

The Steam Feed System

The steam feed system is illustrated in Figure 2. The system includes a steam boiler, a calibrated fine metering needle valve, a steam superheater, and a nitrogen purge supply. This section provides a calibrated superheated steam feed or nitrogen purge supply to the hydrolyzer.

The boiler is a 316 Stainless Steel (SS) tank with 3/16 inch thick walls which is 45 inches high with a diameter of 8

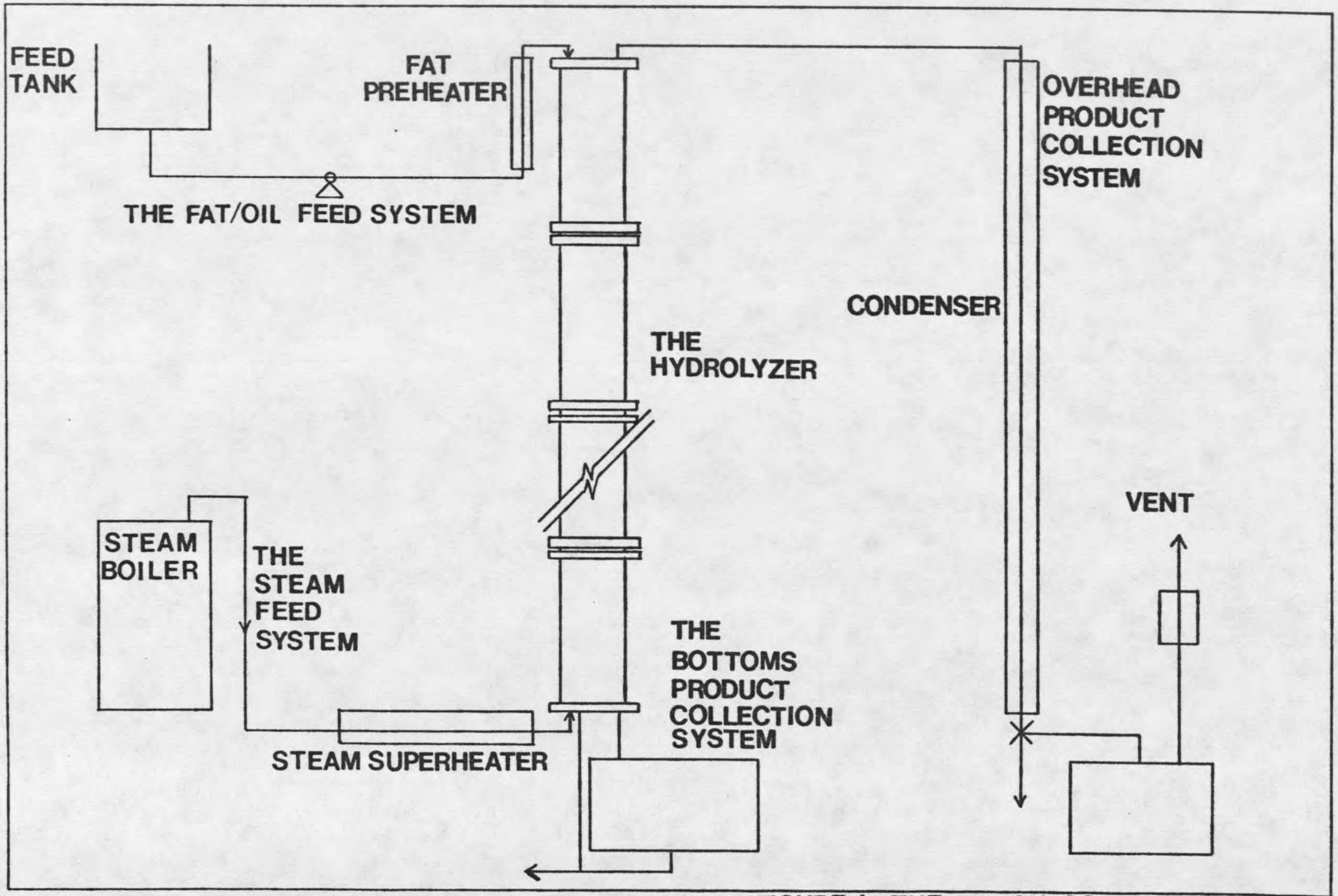


FIGURE 1. THE BENCH SCALE HYDROLYZER

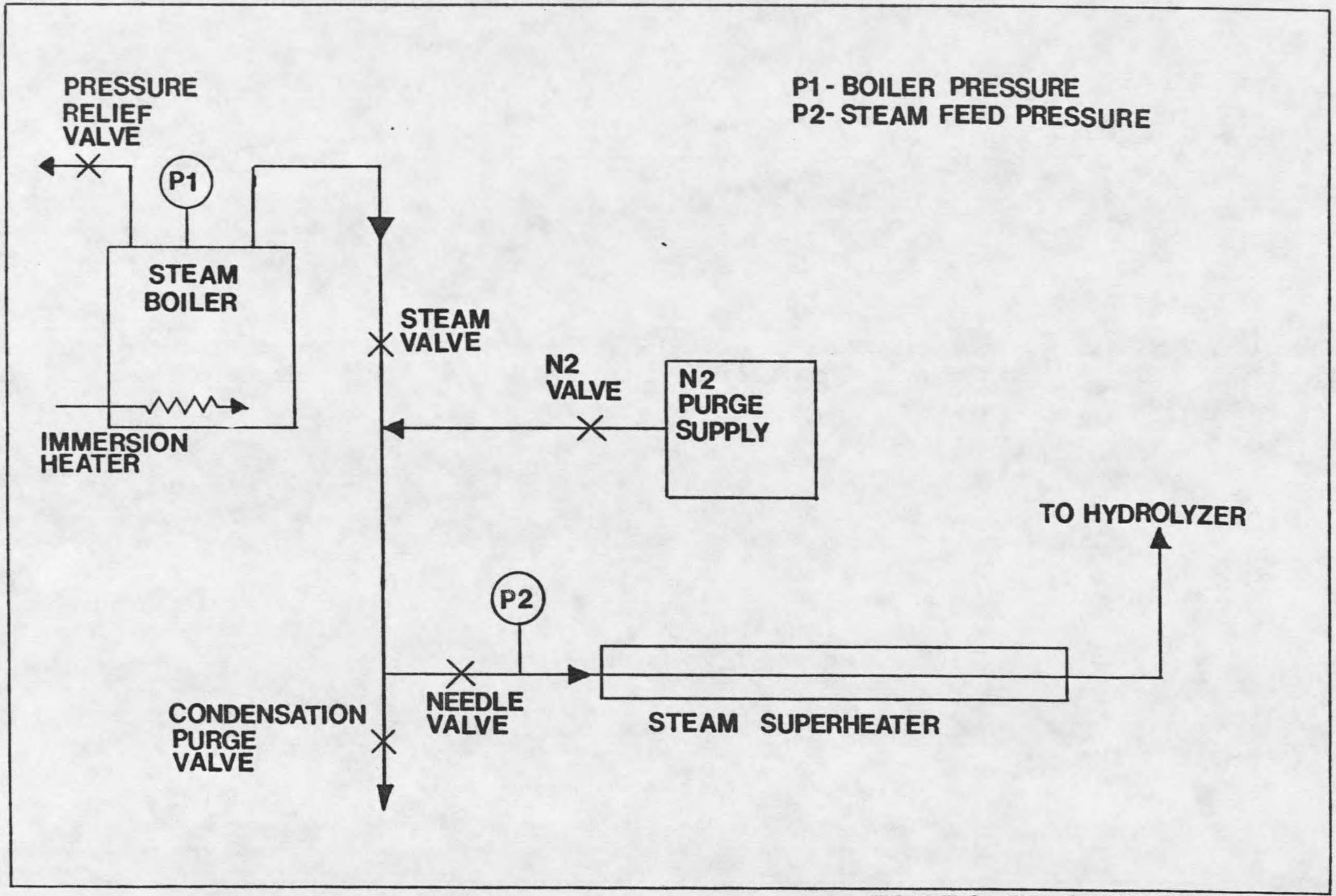


FIGURE 2. THE STEAM FEED SYSTEM

inches. By partially filling the vertical tank with distilled water and applying thermal energy to bring the temperature of the boiler to 130°C, a 30 psig steam source is made available. The boiler is equipped with a pressure relief valve which is set for safe operation of the unit.

Thermal energy is supplied using a 240 volt Chromalox Screwplug Immersion heater located 3-1/2 inches up from the bottom of the boiler. The water temperature is monitored by two thermocouples located in a thermocouple well located 8 inches up from the bottom of the boiler. Energy supply to the heater is controlled by an on-off temperature controller attached to one of the thermocouples. Steam pressure is monitored by a Bourdon gauge at the top of the boiler.

Steam occupies the top space in the boiler. Steam exits the boiler through a shut off valve. Condensation in the steam is purged to the outside atmosphere through a shut off valve in an open branch of a union tee ahead of a metering valve. The steam then flows through the fine metering valve.

A purge gas supply for the reaction system can be provided upstream of the needle valve from a cylinder of high pressure nitrogen. The nitrogen is used to purge process lines and the reactor. As will be discussed later, it was also used for determining a stable fluid flow operating range for the reactor.

The calibrated Nupro fine metering needle valve controls the flow rate of the steam to the reactor. A thermocouple attached at the needle valve monitors its temperature. The pressure of the steam supply to the reactor is measured by a Bourdon gauge downstream of the needle valve which indicates the pressure drop across the column to the atmosphere at the exit of the overhead condenser.

Calibration of the steam flow rate was performed by adjusting the needle valve to each of a series of settings and allowing the steam to pass through the reactor to the overhead condenser. Steam condensate was collected in a graduated cylinder at the exit of the overhead condensate line. Steam condensate collections were made for at least 30 minutes. The resulting calibration for the steam feed rate is shown in Figure 3 for steam feed rates from 0.5 g/min to 4.9 g/min.

Before the steam enters the reactor, it is superheated to the reaction temperature in a 10 foot long 3/4 inch, Schedule 80 316 SS pipe. The pipe is wrapped with two 400 watt heating tapes in series. The upstream tape increases the steam temperature to near the operating temperature. The steam exit temperature downstream of this tape is manually controlled by a variac in the electric supply to this tape. The power supply to the downstream heating tape is regulated by an on-off temperature controller which establishes the final steam temperature. Thermocouples attached to the pipe at the end of each heating tape monitor the steam temperatures at those locations. A third thermocouple is attached to the end of the

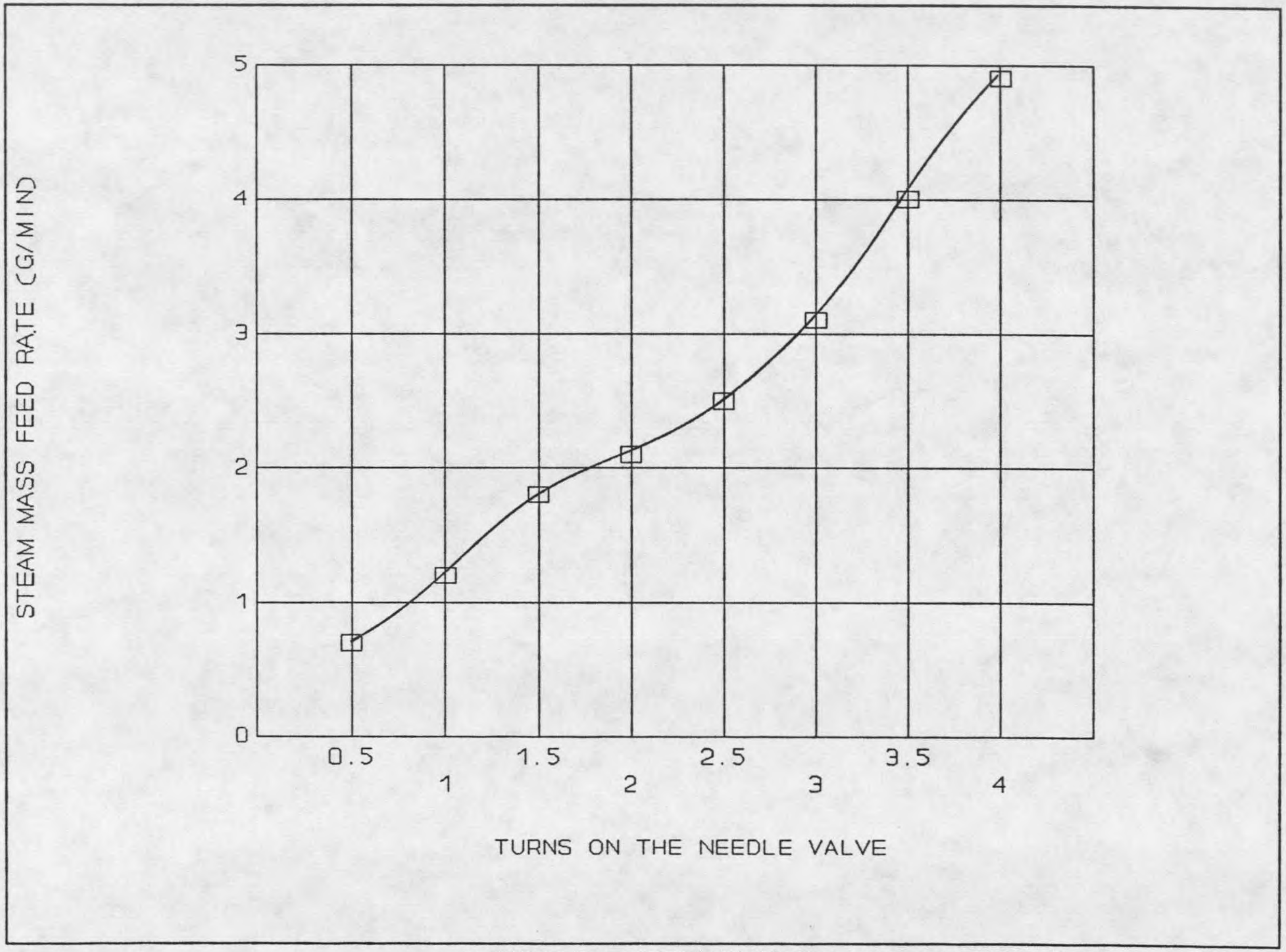


FIGURE 3. NEEDLE VALVE CALIBRATION OF STEAM FEED

downstream heating tape to provide the signal to the steam supply temperature controller.

The Fat/Oil Feed System

The fat/oil feed system is designed to supply any of several different preheated fat and oil materials to the hydrolyzer. As illustrated in Figure 4, the fat/oil feed system consists of a heated feed tank, a calibrated metering pump, and a fat preheater.

Since beef tallow, the typical feed material, has a softening point higher than room temperature, it is necessary to melt the feed. The tallow is melted in a 15 inch long, 12.5 inch diameter 316 SS feed tank that is open at the top. The outside of the tank is wrapped with heating tape and is temperature controlled. Two thermocouples are attached to the side of the tank near the bottom. One monitors the tank temperature, and the other provides a signal for the temperature controller. The fat feed tank is approximately three feet off the ground to provide a head for the feed pump. Tallow exits the tank through a 1/4 inch 316 SS tube connected to the center of the bottom of the tank. The tube intake is raised one inch above the bottom of the tank to avoid allowing water that may be present in the feed to flow into the system. The tube to the feed pump is wrapped with heat tracing cable to prevent fat from hardening in the feed line.

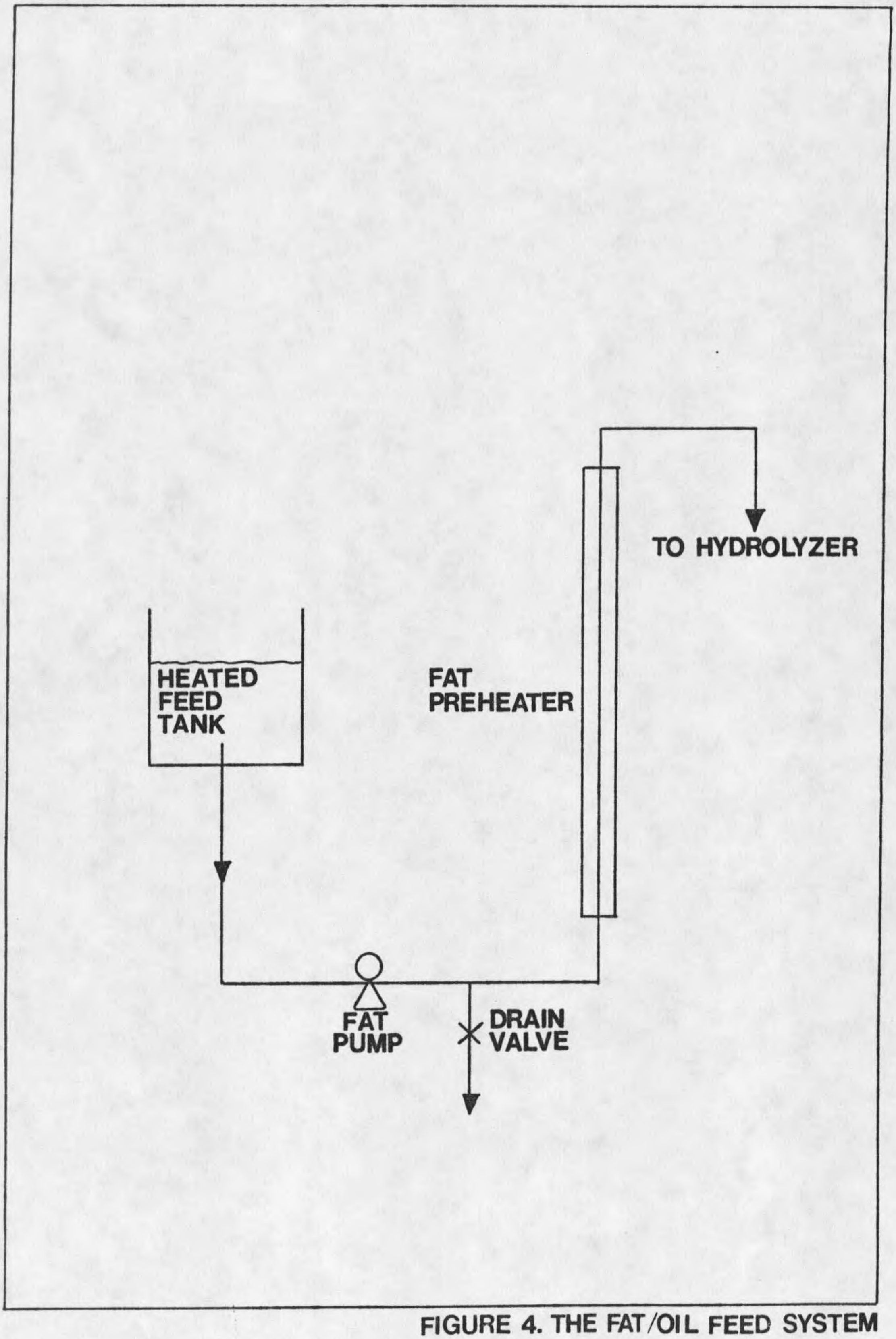


FIGURE 4. THE FAT/OIL FEED SYSTEM

A Simplex Milroyal Type B controlled volume, positive displacement reciprocating pump with a 5/16 inch plunger was used to feed the tallow from the supply tank to the top of the reactor. The pump was calibrated for a range of fat feed rates by turning a control knob which adjusted the plunger stroke and by collecting the feed for at least five minutes in a 400-ml preweighed beaker. By weighing the beaker contents, the mass flow rate of the feed could be determined for each pump setting. The results of the tallow feed calibration are reported in Figure 5 for fat feed rates from 5 grams/min to 90 grams/min.

Heat tracing cable is wrapped around the plunger area of the pump to prevent tallow from hardening within the pump. The tallow is pumped through 1/4 inch 316 SS tubing of approximately 10 feet in length to the fat preheater. A drain valve is used for purging the feed line when the process is shut down. A thermocouple is located midway along this tubing to monitor its temperature to ensure the tallow is above its hardening temperature.

The 1/4 inch tube is connected to a thick walled 3/4 inch Schedule XX, 316 SS pipe which extends the remainder of the distance to the top of the reactor. There are two 400 watt heating tapes wrapped on this pipe. The upstream tape extends half way along the pipe and the second heat tape along the downstream portion of the pipe. The first tape is used to warm the tallow to a temperature near the reactor operating

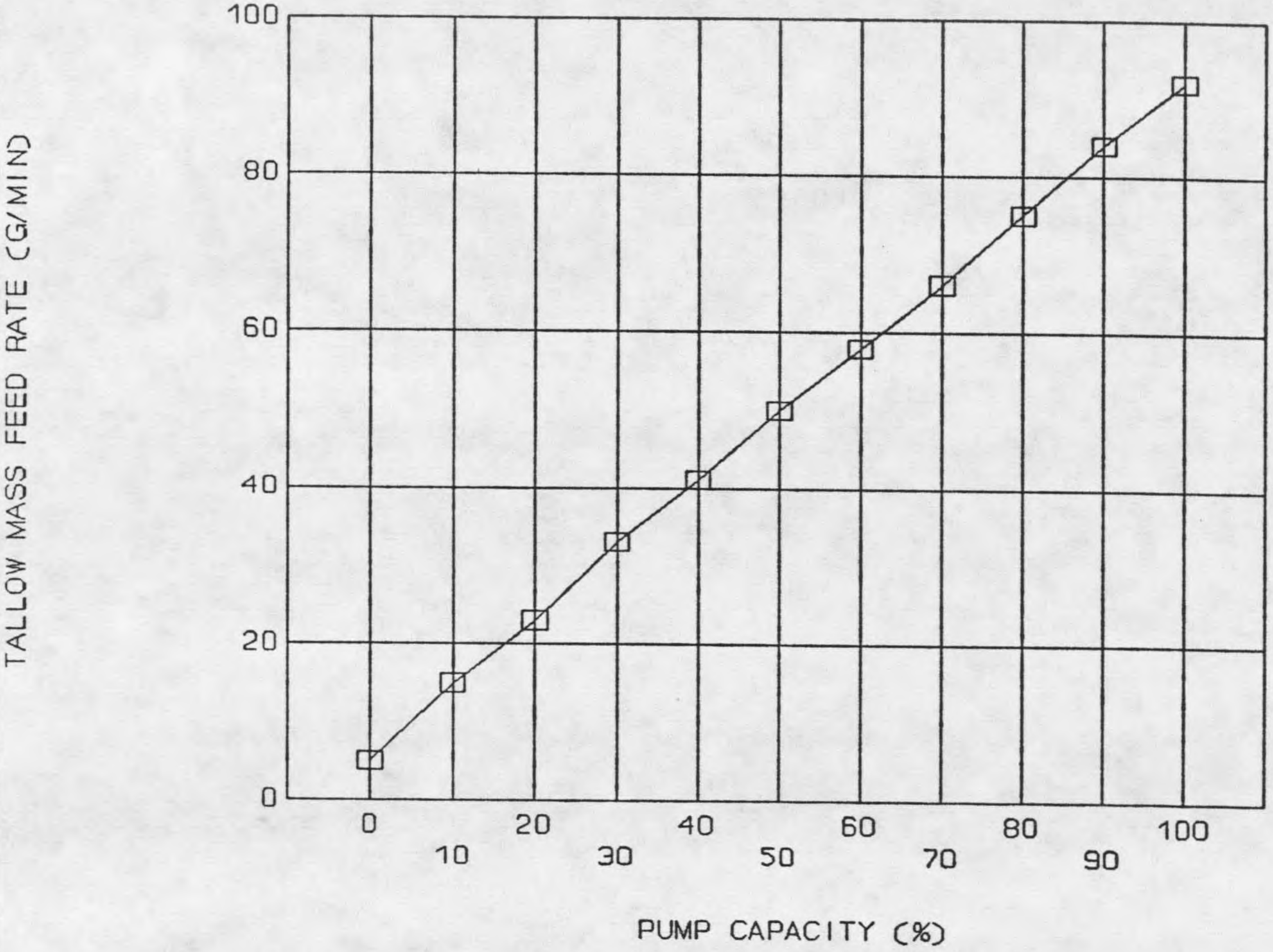


FIGURE 5. FEED PUMP CALIBRATION FOR TALLOW FEED

temperature. The energy supplied this heating tape is manually controlled by a variac. The energy supply to the second heating tape is temperature controlled. Two thermocouples connected to the pipe monitor the temperature of the feed, one midway down the pipe and the second at the end of the pipe near the entrance to the reactor. A third thermocouple is connected at the outlet of the pipe for temperature control of the downstream heating tape.

The Hydrolyzer

The five stage hydrolyzer is slightly over 18 feet in length. The reaction stages are numbered from the bottom to the top. The reactor is supported by a 5 inch girder which is welded to a building support girder. Steam enters at the bottom of the reactor through a riser. Tallow enters through the top of the reactor into the fifth stage. Vapor rises through the reactor and exits the top after which it is condensed and collected together with volatile reaction products. Liquid tallow and some liquid reaction products descend through the reactor to the first stage where they exit through a downcomer to a bottoms collection tank.

The reactor is wrapped with three heating tapes. Thermocouples are connected to each of the five stages of the reactor and are used to monitor their temperatures. A second set of three thermocouples are connected to the first, the third, and the fifth stage of the reactor for temperature control of the three heating tapes.

As illustrated in Figure 6, the design of each stage is similar to a distillation column stage. Each stage is equipped with a shell, a riser, a support plate, a riser cap, a downcomer, and a disperser plate. The shell of the reaction section is 1-1/2 inch, Schedule 5, 316 SS pipe. The riser is 1/2 inch, 20 gauge, 316 SS tubing which is 39 inches long. A 3-1/4 inch diameter, 12 gauge support plate at the bottom of each stage is used to support and center the riser. The riser cap is 1 inch, 20 gauge, 316 SS tubing, 40 inches in length. The downcomer is 1/4 inch, 22 gauge, 316 SS tubing, 84 inches in length. The disperser plate is 12 gauge and is 1-7/10 inch in diameter. There are ten 3/32 inch diameter holes through this plate for steam dispersion.

The steam and volatile reaction products ascend through the riser and down through the annulus of the riser cap. The riser cap is positioned around the riser and is supported by the disperser plate which is welded to the outer reactor shell wall. The base of the cap and disperser plate are set slightly above the riser support plate to allow vapor to flow out of the bottom of the riser cap and up through the disperser plate.

The downcomer for each stage extends from the top of the riser cap of that stage to just above the disperser plate for the stage below. The downcomer passes through a tight fitting

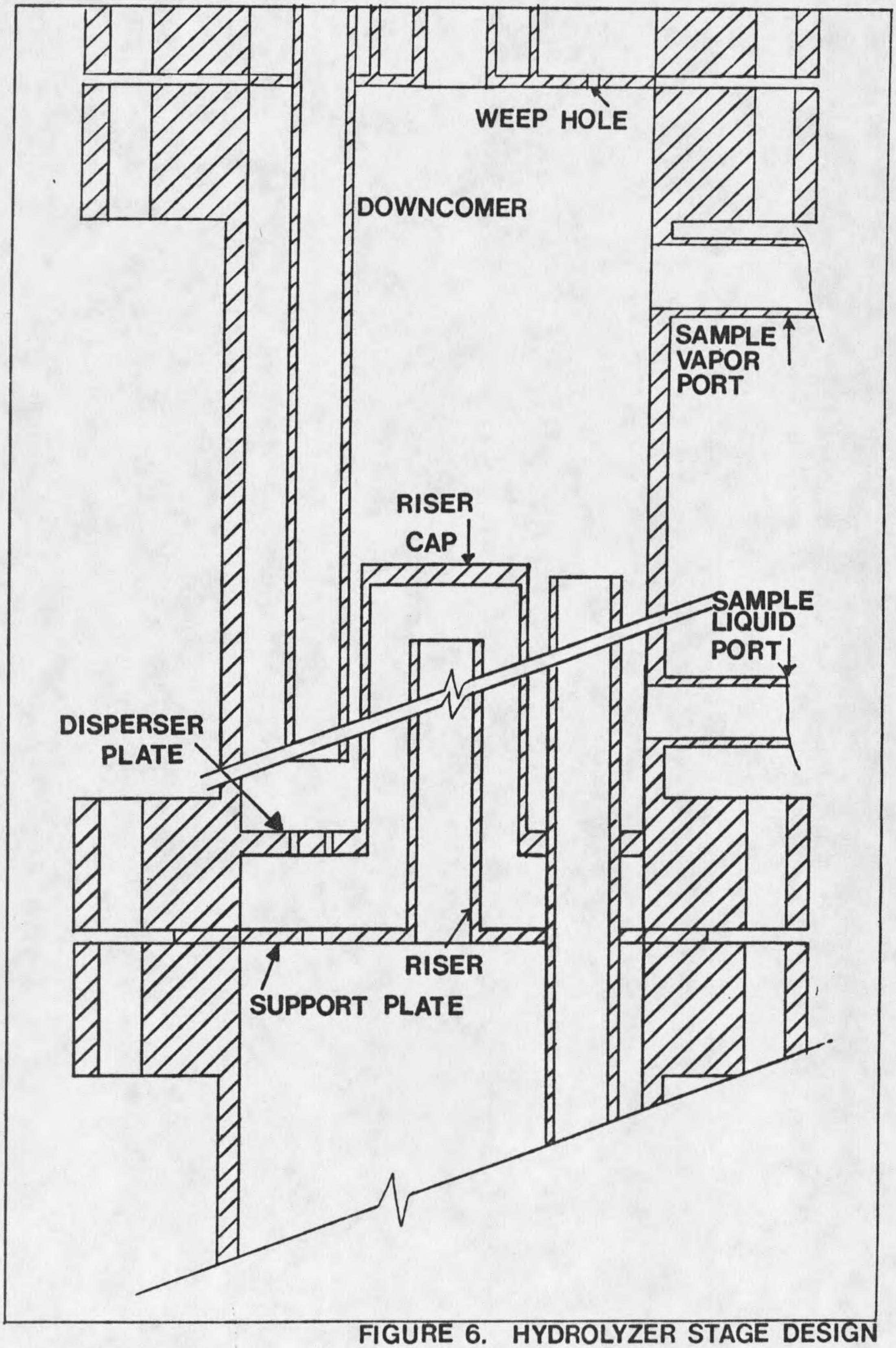


FIGURE 6. HYDROLYZER STAGE DESIGN

hole in both the disperser plate and is welded to the support plate. Liquid descending the column passes through the downcomers of each stage because the ascending vapor prevents the liquid from weeping through the disperser plate.

Figure 7 shows that the disperser plate has a hole in the center which is of equal outside diameter to the riser cap. The downcomer hole is located on the plate in the annulus between the riser cap hole and the outside wall of the reactor. The descending downcomer exits at a position opposite to the current stage downcomer. The ten dispersion holes for ascending vapor are located so that ascending vapor does not interfere with descending liquid from the downcomer from the stage above. The ten 3/32 inch diameter dispersion holes are located evenly 0.30 inches apart in the remaining space.

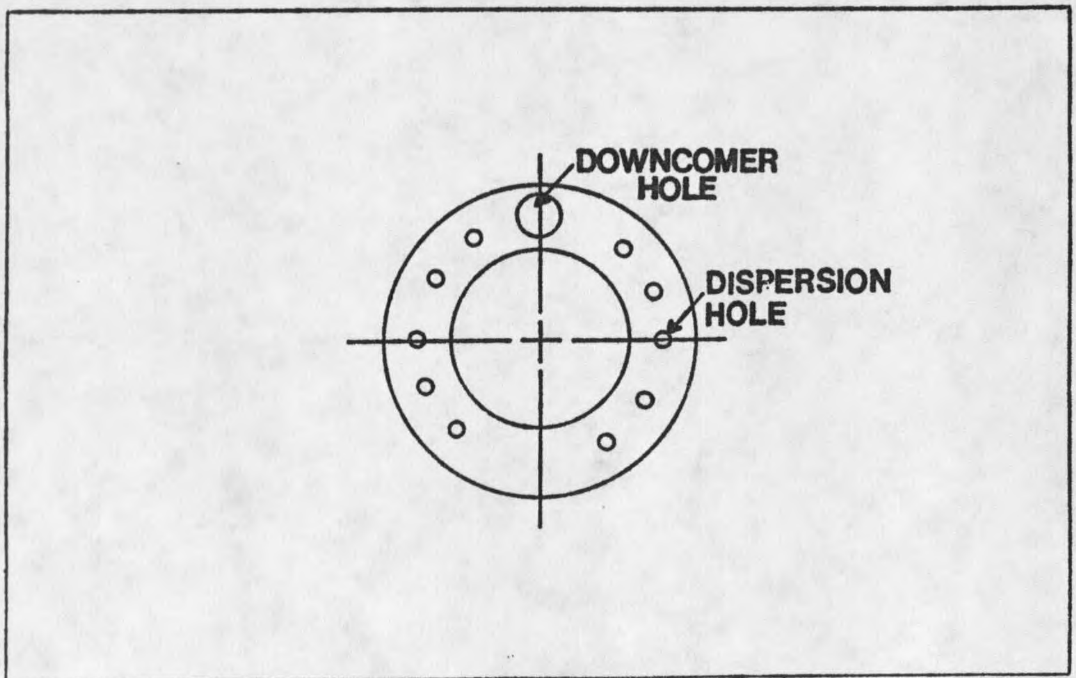


FIGURE 7. HYDROLYZER STAGE DISPERSER PLATE

The support plate serves as the base for each stage and as the top of the stage below. Stages are joined with 150 pound, 316 SS flanges. Gaskets are placed between flanges and the support plate to prevent leakage of reactor contents. Draining the column of liquid contents upon shut-down occurs through weep holes in the support plates down to the bottoms tank. The 3/32 inch diameter weep hole is located opposite of each support plate's downcomer weld location.

Each stage is equipped with vapor and liquid sample ports through the outside shell of the reactor. Vapor ports are located just below the flange at the top of each stage. Liquid ports are at a location above the disperser plate. The ports are connected to 1/8 inch, 316 SS tubes. During operation, vapor and liquid samples of each stage can be drawn off for analysis.

This stage description is typical of all five stages with the exception of the first and fifth stage. The fifth stage does not have sample ports. The liquid at the base of this stage is the preheated tallow fed into the reactor from the feed tank. The vapor from this stage constitutes the overhead product. Therefore, there is no need for sample ports. The top of the fifth stage is designed to allow vapor to exit the reactor and for tallow feed to enter the reactor. The first stage does not have a complete downcomer. The downcomer in this stage passes out the bottom of the reactor to the base of the bottoms product collection tank. The weep hole in this stage is connected to a 1/4 inch stainless steel tube connected to the top of the bottoms product collection tank for pressure balancing. Liquid drained from the reactor passes through this tube into the bottoms tank upon shut down. The bottom of the first stage is designed for the steam from the boiler to enter into the reactor through the first stage riser.

The Bottoms Product Collection System

The bottoms product collection system is connected to the bottom of the hydrolyzer as shown in Figure 8. The system is equipped with a bottoms collection tank, a weep hole valve, a downcomer valve, a sample valve, and a bottoms tank valve. Liquid products flowing down the first stage downcomer are collected in the bottoms tank.

The bottoms tank is connected to the reactor by 1/4 inch, 316 SS tubing from the first stage downcomer and from the weep hole. The 316 SS tank is 15 inches in length and 12.5 inches in diameter. There is a 1/4 inch male fitting in the center of both ends of the tank that connect to the reactor. The downcomer from the first reactor stage connects to the bottom fitting of the tank. The weep hole valve is located in the weep hole to bottoms tank tube. A sample valve is connected to the open branch of a union tee in the downcomer line near the bottom of the tank. This valve is used to collect bottoms samples and to drain the bottoms tank. A downcomer valve is

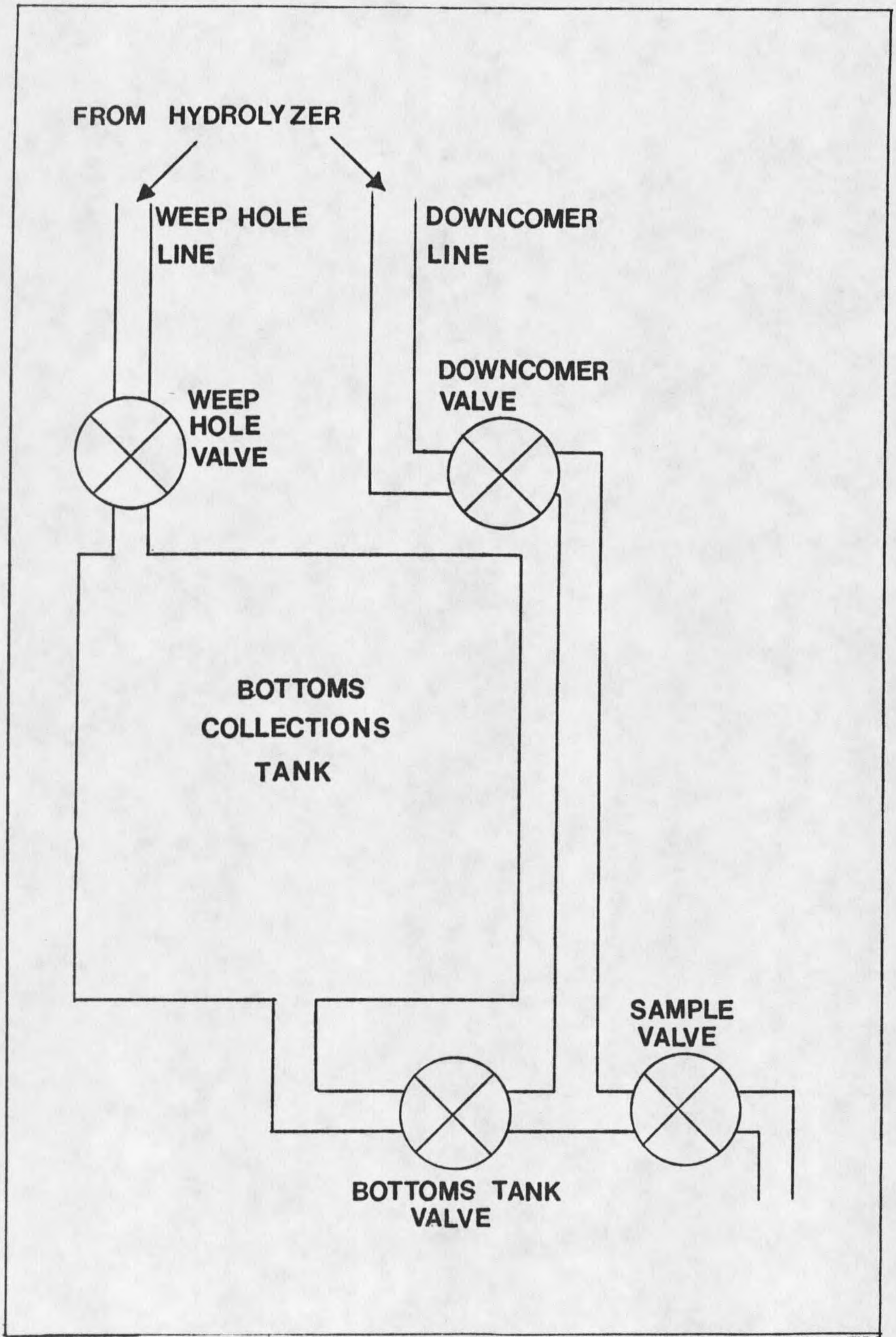


FIGURE 8. BOTTOMS PRODUCT COLLECTION SYSTEM

located in the downcomer line between the reactor and the sample valve tee, and a bottoms tank valve is between the sample valve and the bottoms tank connection.

The bottoms tank and the lines are wrapped with tracing tape to prevent the liquid product from hardening and are temperature controlled. Two thermocouples are attached to the bottom of the bottoms product tank. One is used to measure the temperature of the bottoms tank and the other is used for the input signal to the temperature controller for the tank. Two thermocouples are attached to the sample valve. One is used to measure the temperature of the downcomer line and the other for temperature control of the line.

The Overhead Product Collection System

The vapor from the fifth stage of the reactor is condensed and collected as overhead product. As illustrated in Figure 9, a 25 foot countercurrent double-pipe heat exchanger is used to condense the overhead product. Circulating heated oil from a heating-cooling oil bath is used to control the temperature of the heat exchanger. Overhead can be collected in an overhead collection tank or current overhead samples can be collected.

Hydrolyzer vapor products flow out of the reactor and condense on the inside walls of a 1/2 inch, 316 SS tube. Temperature controlled 10W motor oil flows through the annular space of a 3/4 inch diameter copper pipe jacket on the condenser tube. The condenser tube outlet is connected to a three-way valve. One exit of the tube connects to a 10 gallon, overhead collection, glass jug equipped with a ventilation filter. Unpleasant odors in the overhead from the reaction are filtered by ventilating uncondensed vapors through activated charcoal to the atmosphere. The other port of the three-way valve provides for the sampling of current overhead product.

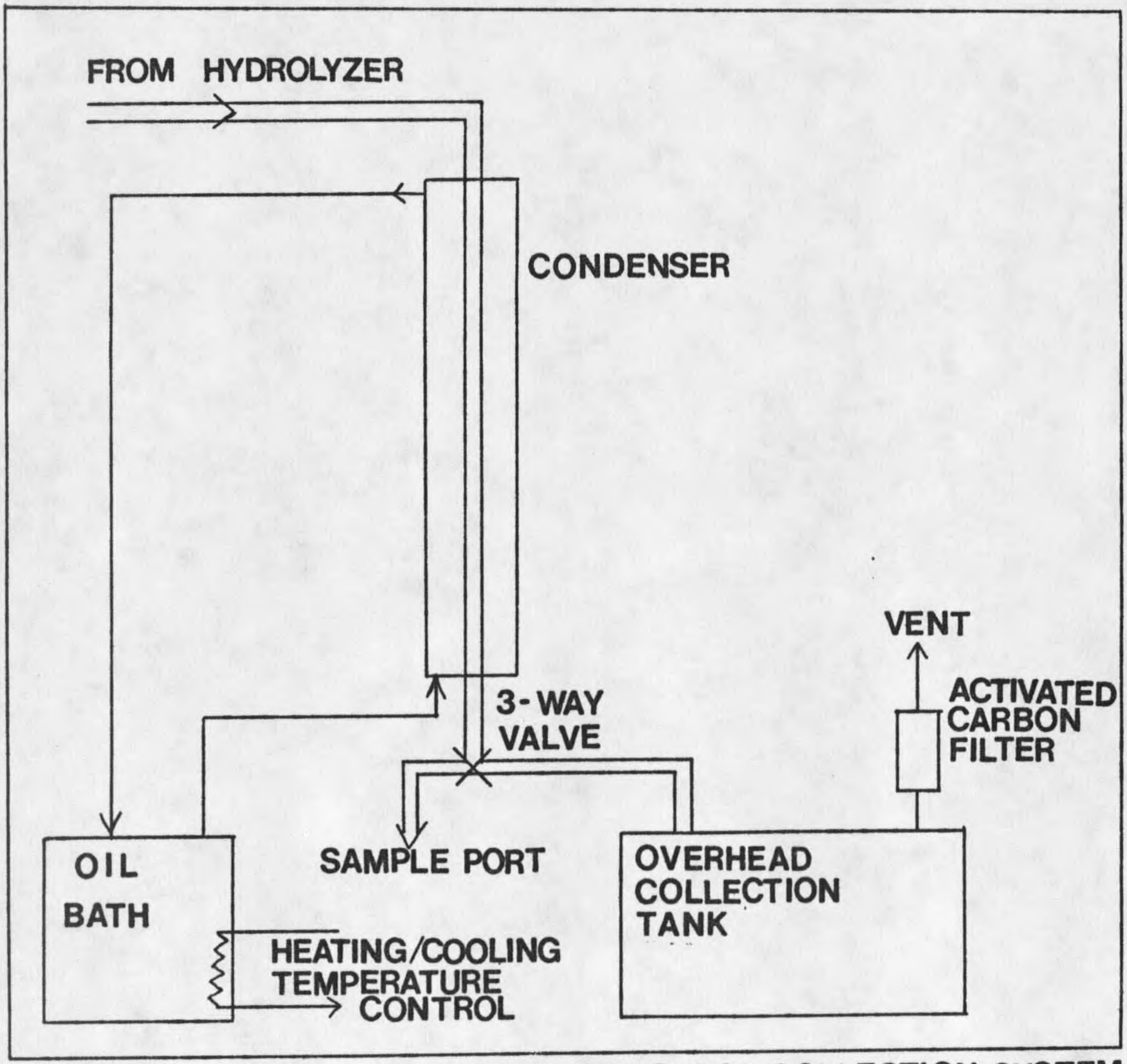


FIGURE 9. OVERHEAD PRODUCT COLLECTION SYSTEM

The condenser oil bath, normally operated at 50°C to prevent product solidification in the condenser, is equipped with a heating and cooling system. The oil is recirculated through the condenser annulus counter-current to the condensing product flow by a centrifugal pump. A thermocouple monitors the temperature of the return oil from the condenser.

The oil bath may heat up during reactor operation and require cooling. Water flow through a 20 foot length of 1/8 inch copper tubing is used to cool the oil bath. A temperature controller is used to control an electric immersion heater and the water flow through the copper tube. There are two thermocouples placed in the oil. One monitors the temperature of the bath and the other is used for temperature control. An Omega SV100 Series, two-way normally open solenoid valve is positioned in a building cold water supply line. When the temperature of the oil is low, the solenoid shuts off the cooling water flow and turns on the heater in the oil bath. When the temperature of the bath is high, the solenoid opens up the cooling water flow and the bath heater is turned off.

The 1/8 inch lines for the vapor and liquid samples from the individual stages of the reactor are cooled by passing along the outside of the main condenser tube and exit through shut-off valves. The sample tubes are about four feet in length. The sample tubes extend from the reactor to the condenser where approximately three feet of the tubing is tied closely to the outside of the condenser and then extend to the shut-off valves.

Temperature Monitoring Thermocouples

Thermocouple readings are monitored using an Omega DP 701 model, Thermocouple Digital Thermometer. Each of the 17 monitored temperatures can be observed individually using an Omega Rotary Selector Switch. Each of these temperature monitoring thermocouples have been previously mentioned and are summarized in Table 1 in the order numbered on the rotary selector switch.

Temperature Control

Insulated, exposed junction chromel-alumel thermocouples are used for temperature measurement. All heating tapes and tracer lines discussed are Omegalux Flexible Heating Tapes. The on-off temperature controllers are Omega Series 6100 Temperature Controllers. Heating tape voltages are set by Powerstat voltage controller variacs. Fiberglass thermal insulation covers all areas of the process where heat loss to the atmosphere may inhibit temperature control.

Table 1. Thermocouple Numbering on the Selector Switch.

Selector Switch Number	Temperature Thermocouple Location
1	Stage One
2	Stage Two
3	Stage Three
4	Stage Four
5	Stage Five
6	Liquid Bottoms Tank
7	Middle Fat/Oil Feed Line
8	Final Fat/Oil Feed Line
9	Steam Boiler
10	Steam Feed Needle Valve
11	Middle Steam Feed Line
12	Final Steam Feed Line
13	Condenser Oil Bath
14	Returning Condenser Oil
15	Initial Fat/Oil Preheat Feed Line
16	Fat/Oil Feed Tank
17	Bottoms Tank Exit Port

CHAPTER 5

OPERATING THE HYDROLYZER

Investigations were conducted using an edible grade Wesson soybean oil for initial tests and a high grade bleached beef tallow provided by the Carolina By-Products Company for other tests. Tallow is a widely used hydrolysis reactant because of its properties and low cost. The proportional composition of the various fatty acids typically found in tallow are approximately 50% oleic acid, 27% palmitic acid, 14% stearic acid and 9% others.

Start-up Procedure

Operating the reactor required several preliminary start-up steps. A detailed procedure was followed to operate the hydrolyzer and collect samples of product streams as well as to shut down the system. Before operating the reactor, the steam boiler was partially filled with distilled water. The boiler immersion heater was then turned on and the boiler temperature set at 130°C. After the boiler temperature was achieved, steam and trapped air was bled out of the purge line. The boiler pressure gauge then read about 30 psig. The fat tank was filled with tallow and the tank was heated to about 50°C to melt the fat. All system heating was turned on.

Temperatures were set according to the desired operating temperature. Tracing line temperatures were about 50°C to ensure that the tallow would not harden. The overhead condenser was turned on and the oil bath temperature was set at about 50°C. The reactor was then purged with nitrogen to remove oxygen from the system.

The fat pump was set at about 90 grams per minute and tallow was pumped into the reactor to prime the system for operation. The weep hole valve to the bottoms collection system was closed. The bottoms sample valve and the downcomer valve was opened. An observation was made on the amount of time necessary for the fat to drain through the reactor and exit the bottoms sample valve. The bottoms sample valve and the downcomer valve were then closed. The reactor was allowed to fill completely, as noted by fat overflow into the condenser and out from the overhead product line.

The tallow feed rate was set to the desired valve setting according to the pump calibration flow curve. The desired steam rate was then established using the appropriate needle valve setting from its calibration curve, and the steam boiler valve was opened for steam flow. The weep hole valve, the downcomer valve, and the bottoms tank valve were opened. An initial slug of fat overflowed when the initial steam passed up through the reactor and the volume of this flow was noted to establish the reactor liquid priming volume.

The start-up was successful if overhead liquid slugging discontinued after a few minutes of steam flow. The overhead condenser was observed for 30 minutes to ensure that overhead slugging did not occur. If slugging did occur, the steam supply was discontinued and the reactor was primed again. If slugging did not occur, a preweighed 250-ml stock bottle was used to collect a 30 minute sample of overhead product.

Temperatures were monitored periodically to ensure that the reactor temperature was correct. After 30 minutes, the amount of overhead product collected was weighed, and the overhead product mass flow rate determined. If the overhead product flow was equal to the total feed rates of the steam and the tallow, the system had to be primed again. This latter step was not necessary when the reactor was operated in the liquid-vapor flow rate conditions established for stable operation in the tests discussed in Chapter 8.

Operating Procedure

If the overhead product flow rate was less than the sum of the fat and steam feed rates, sequential 30 minute overhead sample collections were continued using separate stock bottles to establish the overhead product flow rate. Between collections, 10 to 15 grams of overhead product was collected in preweighed sample vials. The weight fraction of the fatty acid content in the sample was analyzed. These tests were continued until a steady weight fraction of fatty acids was observed for the overhead product and the overhead flow rate was constant.

Between 30 minute collection periods, the bottoms product was sampled and analyzed for fatty acid content. To sample the bottoms, the bottoms tank valve was closed. Next, the bottoms sample valve was opened, and the bottom stage downcomer line was drained. The sample valve was then closed, and the downcomer was allowed to fill for about three minutes. After three minutes, the sample valve was opened and 10 to 15 grams of the bottoms product was collected in a preweighed sample vial. The bottoms sample was then analyzed for fatty acid content.

After the system reached steady state, preweighed sample vials were used to collect approximately 10 grams of liquid samples from the liquid sample ports from stages one through four. The sample collection rate did not exceed 3 cm^3 per minute.

Observations of decomposition by the acrid acrolein aroma were also noted during the procedure. A sample was taken of the original tallow feed for analysis of its contents. After these samples were collected, the system was shut-down or a new set of reactor operating conditions was established.

Shut-Down Procedure

To discontinue the operation of the hydrolyzer, the tallow and steam feeds were turned off. The temperature of the reactor was turned down to approximately 200°C and the reactor contents drained into the bottoms collection tank. The tank was then emptied through the bottoms sample valve. The fat feed line was purged through its drain valve.

After the reactor was drained, the temperature controllers, the condenser oil bath, and the recirculation pump were turned off. Nitrogen was purged through the system to clear any accumulated fat. The overhead collection tank was emptied.

CHAPTER 6

CHEMICAL ANALYSIS OF HYDROLYZER FEEDS AND PRODUCTS

Product Analysis

The overhead product contains glycerol, water, fatty acids, and perhaps some monoglycerides, diglycerides, and entrained fat. The vapor pressures of diglycerides, and tallow are low and they will probably not be significantly present in the overhead product stream. The overhead condensate is a white emulsion. Heating the overhead product emulsion to approximately 90°C results in its clean separation into aqueous and organic phases due to the poor solubility of water in fatty acids. The glycerol is highly soluble in water and will be primarily present in the separated aqueous phase.

The bottoms product will essentially be fatty acids if the reaction is complete. However, tallow, monoglycerides, diglycerides, glycerol, and a small amount of water may be present if conversion is incomplete.

Degree of Hydrolysis

The overall conversion in the process can be determined from chemical analysis and flow rates of feed and product streams. Assuming that the total steam and fat mass feed rates are equal to the sum of the overhead and bottoms mass flow rates, the degree of hydrolysis can be determined from:

$$\text{Degree of Hydrolysis} = \frac{X_O F_O + X_B F_B}{k F_F} \qquad (1)$$

F_F = Feed rate of fat (assumed to be free of fatty acids) in grams/minute

F_0 = Flow rate of overheads in grams/minute

F_B = $F_S + F_F - F_0$ = Flow rate of bottoms in grams/minute

F_S = Feed rate of steam in grams/minute

X_0 = Fatty acid weight fraction of overheads

X_B = Fatty acid weight fraction of bottoms

k = 0.9553, the maximum grams of fatty acids produced from one gram of fat.

The equation is defined as the total mass of fatty acids present in the product streams divided by the total potential mass of fatty acids that can be produced from the fat feed. This equation was utilized to estimate the extent of hydrolysis during experimental runs on the hydrolyzer.

The degree of hydrolysis can more accurately be established by analyzing the total number of free fatty acids of the product streams divided by the total possible fatty acids that could be produced from the fat feed:

$$\text{Degree of Hydrolysis} = \frac{F_O x_O (AV)_O + F_B (AV)_B - F_F (AV)_F}{F_F [(SV)_F - (AV)_F]} \qquad (2)$$

x_0 = Weight fraction of the overhead product organic phase

AV_0 = Acid value of the overhead product organic phase

AV_B = Acid value of the bottoms product

AV_F = Acid value of the fat feed

SV_F = Saponification value of the fat feed

In this relationship, the weight fraction of the organic phase in the overhead is determined and the acid value is measured for this phase. The acid value of the fat feed is determined for its small free fatty acid content.

These acid and saponification values are determined by the standard procedures outlined by the American Oil Chemists Society (A.O.C.S.) as described later in this chapter. Equation 2 was used after operating the hydrolyzer to accurately define the extent of the reaction from collected feed and product samples.

Acid Value Procedure

The acid value is determined using A.O.C.S. Official Method Te 1a-64 for industrial oils and derivatives [15]. The acid value is defined as the number of milligrams of potassium hydroxide necessary to neutralize fatty acids in one gram of sample. The method is used for determining the free fatty acid content of the overhead, bottoms, fat feed, and stage samples.

The procedure requires an accurately weighed test sample of approximately 5 grams which is placed into a 500-ml Erlenmeyer flask. An addition of 75 to 100-ml of boiling neutral ethyl alcohol places the fatty acids into solution.

A few drops of phenolphthalein indicator solution is added, and a titration using accurately standardized (A.O.C.S. Official Method H 12-52) 0.5 N sodium hydroxide solution is performed to the first pink color which persists for 30 seconds [15]. The acid value can be determined using the following expression.

$$Acid\ Value = \frac{ml.\ NaOH\ X\ Normality\ of\ NaOH\ X\ 56.10}{Weight\ of\ Sample}$$

Determining the weight fractions of fatty acids in feed and product samples were completed by using the same acid value procedure. The expression used to generate the fatty acid content is:

$$Wt.\ Fraction\ Fatty\ Acid = 0.136\ \left(\frac{ml.NaOH}{Weight\ of\ Sample}\right)$$

Saponification Value Procedure

The saponification value is determined using A.O.C.S. Official Method Tl 1a-64 for industrial oils and derivatives [15]. The saponification value is the number of milligrams of potassium hydroxide required to react completely with all the reactive groups in one gram of a sample. The method is used on the fat feed and reactor samples to determine the amount of free and potential fatty acids that can be produced per gram of sample.

The preweighed sample is placed in a 300-ml Erlenmeyer flask, and 50 ml. of alcoholic potassium hydroxide is added with a 50 ml. pipet. The alcoholic potassium hydroxide solution is prepared by dissolving approximately 27 grams of KOH and 95% ethyl alcohol in a 1-liter volumetric flask. The sample is boiled gently for about two hours using a condenser to avoid losses to the atmosphere. The flask is then cooled somewhat but not sufficiently to jell. A few drops of phenolphthalein solution are added to the sample and the blanks, and a titration using accurately standardized (A.O.C.S. Official Method H 14-52) 0.5 N hydrochloric acid is performed until the pink color has just disappeared [15]. The same procedure is followed for a test in which no fat is added to establish a blank titration volume. The saponification value can be determined using:

$$Sap.\ Value = \frac{56.10 \times N.\ of\ HCl \times (ml\ of\ blank - ml\ of\ sample)}{Weight\ of\ Sample}$$

CHAPTER 7

HYDROLYZER MATERIALS INVESTIGATION

Hot fatty acids are corrosive, and it is necessary to design hydrolysis reactors with a corrosion resistant alloy. A preliminary investigation of various alloys was conducted to determine a feasible construction material which is both corrosion resistant and inexpensive. The study was completed on 309 SS, 310 SS, 316 SS, 317 SS, and Carpenter 20 grades of alloy metals.

Metal alloy coupon samples approximately 1 inch in length and 1/2 inch wide and 1/16 inch thickness were weighed and placed in a 500-ml round bottom flask with approximately 250-ml of stearic acid. A few drops of water were added to the flask, and a one foot condenser tube was attached to the flask. The flask was equipped with a thermocouple well in which a thermocouple and a thermometer were placed. The thermocouple was connected to a temperature controller for a heating mantle on the flask. The mantle heated the contents of the flask to approximately 325°C. The contents were heated for three to six hour periods. Upon cooling the flask contents, the metal coupons were removed, cleaned thoroughly with warm acetone, and weighed. The difference between the starting weight and the final weight of the samples was interpreted to be caused by corrosion. Investigations were continued for oleic acid, tallow fatty acids, and soy bean fatty acids.

Results of the investigations are presented in Table 2 which indicates that 316 SS, 317 SS, and Carpenter 20 are adequate materials for design. Corrosion was significant on the 309 SS and 310 SS coupon samples. The 316 SS was found to be slightly more corrosion resistant than the 317 SS and the Carpenter 20. The 316 SS is also a cheaper design material than the other two alloys. Therefore, the material used for the bench scale hydrolyzer was 316 Stainless Steel.

Table 2: Corrosion Rates of Various Metal Alloys

Coupon Sample	Corrosion Rate (cm/hr)
309 SS	1.8×10^{-4}
310 SS	3.4×10^{-4}
316 SS	1.2×10^{-5}
317 SS	2.0×10^{-5}
Carpenter 20	6.2×10^{-5}

CHAPTER 8

DETERMINATION OF OPERATION PARAMETERS FOR TESTING

Soybean oil was used in preliminary studies of the reactor. The first attempt at operating the reactor with soybean oil resulted in a good overhead emulsion product. Failure to achieve stable operation of the reactor system prevented the determination of quantitative results.

Upon attempting a second run, it was noted that the overhead mass flow rate was nearly equal to the total of the oil and steam feed rates. There was little or no bottoms product observed. Most of the soybean oil from the initial run had been drained from the column, but some of it may have decomposed in the reactor. This decomposition was probably caused by polymerization of the highly unsaturated fatty acids typically present in soybean oil.

Beef tallow was used as the feed in subsequent reactor tests. Hot tallow was initially used as a solvent to clean the decomposed soybean oil from the reactor. It was again observed that the overhead mass product rate was equal to the total mass feed rate in each of a series of attempts to start-up the system.

An investigation was then made of the volumetric flow rate ranges for gas and liquid required for stable operation of the reactor system. High steam and fat flow rates caused overhead slugging of fat from the column probably due to downcomer flooding. To avoid these problems, an operating range in which flooding of the column does not occur was determined using nitrogen in place of steam and water in place of fat.

The stable operating range of the system determined for nitrogen and water flows is shown in Figure 10. The area above the curve is an indication of unstable liquid and gas flow rate conditions. The area below the curve is in the region of stable liquid and vapor flows. The curve indicates a maximum gas rate of approximately 9 liters per minute when the liquid flow rate is lower than about 10 cm^3 per minute. Liquid flow rates greater than 40 cm^3 per minute result in unstable operation. The liquid fat and steam flow rates attempted in the initial soybean oil and tallow tests were 38 cm^3 per minute and 7 liters per minute respectively. This is well in excess of the stable flow rate envelope in Figure 10.

The nitrogen-water flow curve was used to predict stable operating liquid and vapor flow rates for tallow and steam. Because nitrogen and water have different properties, extrapolating from the curve was conservative. A tallow feed of 10 cm^3/min or 9.3 g/min was chosen for the feed rate in subsequent tests. An excess of steam is required to completely react the fat and carry off the glycerol and fatty acid reaction products. Three moles of water are required to

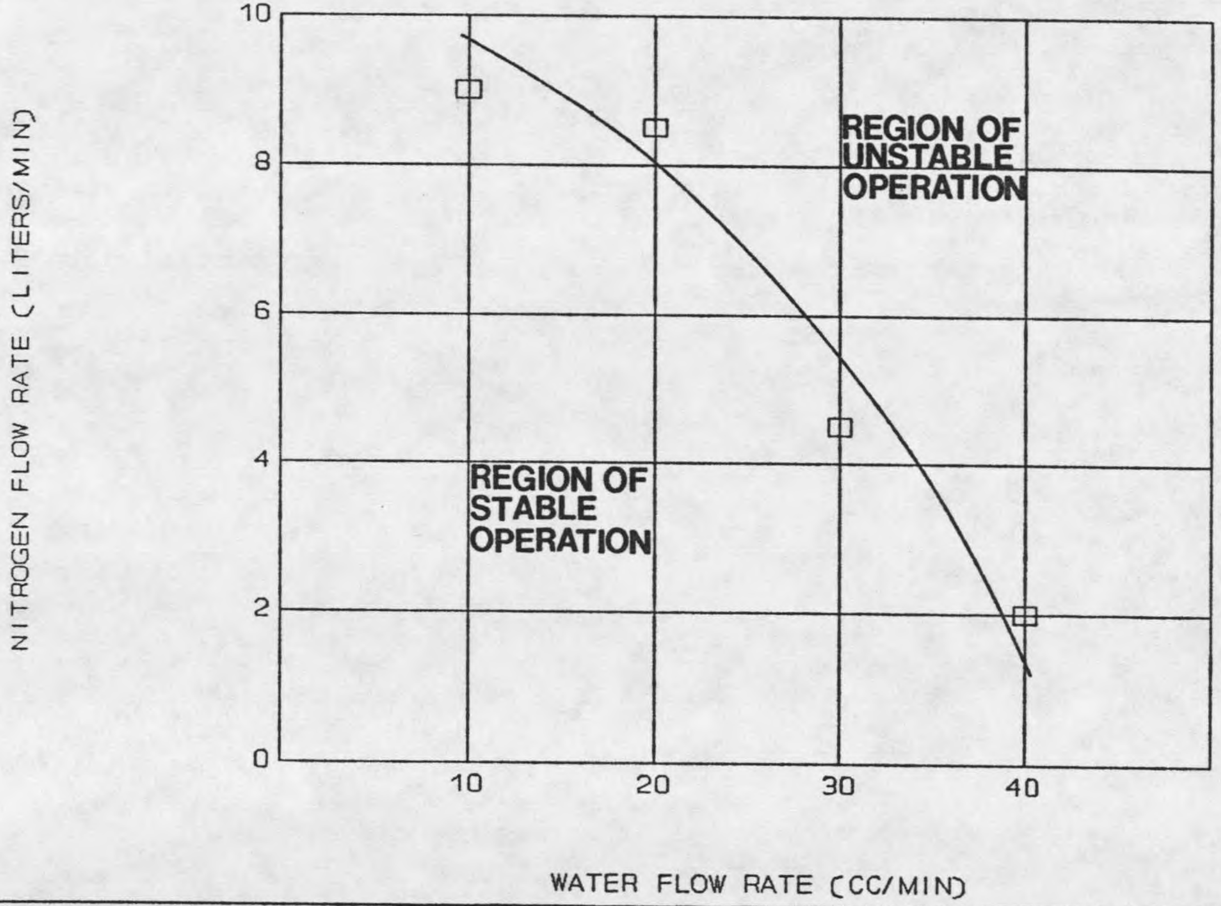


FIGURE 10. HYDROLYZER OPERATION RANGE FOR NITROGEN/WATER FEED

react with one mole of fat. To ensure a complete forward reaction, 2.1 g/min of steam feed was utilized as an initial test feed rate. This is about 3.5 times the amount of steam necessary to completely hydrolyze the 9.3 g/min of fat feed and is equivalent to a volumetric steam flow rate of 6 liters per minute at a reaction temperature of 300°C and a reactor pressure of about 12.3 psi (the approximate atmospheric pressure in Bozeman, Montana).

Five test runs were subsequently conducted. The conditions for the five investigations are summarized in Table 3. The temperatures evaluated in the initial three runs were 280°C, 300°C, and 325°C to gain an understanding of the effects of temperature on the degree of hydrolysis. These three runs were conducted in one continuous period of stable system operation over 24 hours. Decomposition of materials may affect the reaction system at higher temperatures. Therefore, a lower temperature was initially chosen to avoid excessive decomposition. The last two runs were conducted in a separate set of tests. The ability to reproduce results and the influence of the steam flow rate were the primary variables investigated in the latter two runs.

Table 3. Investigated Flow Tests for the Hydrolyzer

RUN NUMBER	TALLOW FEED RATE (G/MIN)	STEAM FEED RATE (G/MIN)	MASS RATIO (TALLOW/ STEAM)	TEMPERATURE (°C)
1	9.3	2.1	4.4	280
2	9.3	2.1	4.4	300
3	9.3	2.1	4.4	325
4	9.3	2.1	4.4	300
5	9.3	1.0	9.3	300

CHAPTER 9

RESULTS OF HYDROLYZER INVESTIGATION

The first run with tallow feed was conducted for approximately 250 minutes. A summary of the results is presented in Tables 4 and 5. Table 4 shows the results of the first run observations of flow rates, acid concentration values measured during the operating procedure, and the degree of hydrolysis estimated using Equation 1. Table 5 presents the results of applying Equation 2 to analyses conducted on column feed and product samples to determine more accurate conversions in the reactor. Table 5 required a measurement of the saponification value and the acid value of the tallow feed which were 198 and 1.5, respectively.

Table 4. Overall Degree of Hydrolysis for Run 1 Measured During Reactor Operation Using Equation 1.

RUN TIME MIN.	OVERHEAD FLOW RATE (F_0) (G/MIN)	BOTTOMS FLOW RATE (F_B) (G/MIN)	OVERHEAD FATTY ACID (X_0) (WT %)	BOTTOMS FATTY ACID (X_B) (WT %)	DEGREE OF HYDROLYSIS (%)
80	2.7	8.7	29	4	13
120	2.7	8.7	31	5	14
160	2.7	8.7	29	5	14
190	2.5	8.9	30	6	15
250	2.5	8.9	31	6	15

Table 5. Overall Degree of Hydrolysis for Run 1 from the Analysis of Collected Reactor Samples Using Equation 2.

RUN TIME MIN.	MEASURED OVERHEAD FLOW RATE (F_0) (G/MIN)	CALCULATED BOTTOMS FLOW RATE (F_B) (G/MIN)	ACID VALUE OF OVERHEAD $(AV)_O$	ACID VALUE OF BOTTOMS $(AV)_B$	ORGANIC IN OVERHEAD (x_0) (WT %)	DEGREE OF HYDROLYSIS (%)
140	2.7	8.7	193	9	36	14
220	2.5	8.9	174	10	30	12

The first column in Tables 4 and 5 defines the run time for which the degree of hydrolysis was established. The second column is the measured overhead product flow rate. The third column is the total bottoms product flow rate which is the difference between the total steam and fat feed rates to the hydrolyzer less the measured overhead product flow rate. The fourth column is the overhead fatty acid weight percent and the fifth column the bottoms product fatty acid content. The fourth column in Table 5 is the overhead acid value of the organic phase and the fifth column is the acid value of the bottoms product. The sixth column in Table 5 is the mass fraction of organics in the overhead product. The last column in the tables is the degree of hydrolysis achieved.

For the second run, the temperature of the system was increased from 280°C to 300°C. It took approximately two hours for the system to reach this operating temperature after which the run times noted were counted. The results of the second run are presented in Tables 6 and 7.

Table 6. Overall Degree of Hydrolysis for Run 2 Measured During Reactor Operation Using Equation 1.

RUN TIME MIN.	OVERHEAD FLOW RATE (F_0) (G/MIN)	BOTTOMS FLOW RATE (F_B) (G/MIN)	OVERHEAD FATTY ACID (X_0) (WT %)	BOTTOMS FATTY ACID (X_B) (WT %)	DEGREE OF HYDROLYSIS (%)
180	3.4	8.0	55	4	25
215	3.4	8.0	48	4	22
960	4.0	7.4	43	4	23
1005	4.0	7.4	47	3	24

Table 7. Overall Degree of Hydrolysis for Run 2 from the Analysis of Collected Reactor Samples Using Equation 2.

RUN TIME MIN.	MEASURED OVERHEAD FLOW RATE (F_0) (G/MIN)	CALCULATED BOTTOMS FLOW RATE (F_B) (G/MIN)	ACID VALUE OF OVERHEAD $(AV)_0$	ACID VALUE OF BOTTOMS $(AV)_B$	ORGANIC IN OVERHEAD (x_0) (WT %)	DEGREE OF HYDROLYSIS (%)
240	3.4	8.0	186	8	48	19
900	3.4	8.0	184	7	62	24
1080	4.0	7.3	184	7	51	23

The third run was initiated by increasing the temperature of the reactor from 300°C to 325°C. There is no analysis of the third run samples because after one hour of operation, large slugs of overhead were observed and extreme amounts of acrid decomposition products were noted.

The second set of runs (four and five) consisted of two separate flow test conditions at 300°C. The fourth run, which was the first of the second set, used a tallow feed rate of 9.3 g/min and a steam feed rate of 2.1 g/min at 300°C which is the same operating condition as the second run of the first set. The run lasted approximately two hours. The results of the fourth run are summarized in Tables 8 and 9.

Table 8. Overall Degree of Hydrolysis for Run 4 Measured During Reactor Operation Using Equation 1.

RUN TIME MIN.	OVERHEAD FLOW RATE (F_0) (G/MIN)	BOTTOMS FLOW RATE (F_B) (G/MIN)	OVERHEAD FATTY ACID (X_0) (WT %)	BOTTOMS FATTY ACID (X_B) (WT %)	DEGREE OF HYDROLYSIS (%)
40	3.6	7.8	50	4	24
70	4.9	6.5	57	5	35
100	4.7	6.7	59	4	35
130	4.8	6.6	57	4	34

Table 9. Overall Degree of Hydrolysis of Run 4 from the Analysis of Collected Reactor Samples Using Equation 2.

RUN TIME MIN.	MEASURED OVERHEAD FLOW RATE (F_0) (G/MIN)	CALCULATED BOTTOMS FLOW RATE (F_B) (G/MIN)	ACID VALUE OF OVERHEAD $(AV)_0$	ACID VALUE OF BOTTOMS $(AV)_B$	ORGANIC IN OVERHEAD (x_0) (WT %)	DEGREE OF HYDROLYSIS (%)
40	3.6	7.8	189		50	
70	4.9	6.5	194		60	
100	4.7	6.7	193		61	
130	4.8	6.6	192	7	62	33

The last run was performed using a tallow feed rate of 9.3 g/min and a steam flow rate at 1.0 g/min at 300°C which changes the tallow to steam mass feed ratio from 4.4 to 9.3. The run lasted two hours. The results are presented in Tables 10 and 11.

Table 10. Overall Degree of Hydrolysis of Run 5 Measured During Reactor Operation Using Equation 1.

RUN TIME MIN.	OVERHEAD FLOW RATE (F_0) (G/MIN)	BOTTOMS FLOW RATE (F_B) (G/MIN)	OVERHEAD FATTY ACID (X_0) (WT %)	BOTTOMS FATTY ACID (X_B) (WT %)	DEGREE OF HYDROLYSIS (%)
40	2.4	7.9	62	9	25
70	2.5	7.8	58	8	24
100	2.3	8.0	54	8	21
135	2.1	8.2	51	7	19

Table 11. Overall Degree of Hydrolysis of Run 5 from the Analysis of Collected Reactor Samples Using Equation 2.

RUN TIME MIN.	MEASURED OVERHEAD FLOW RATE (F_0) (G/MIN)	CALCULATED BOTTOMS FLOW RATE (F_B) (G/MIN)	ACID VALUE OF OVERHEAD $(AV)_0$	ACID VALUE OF BOTTOMS $(AV)_B$	ORGANIC IN OVERHEAD (x_0) (WT %)	DEGREE OF HYDROLYSIS (%)
40	2.4	7.9	181		67	
70	2.5	7.8	190		67	
100	2.3	8.0	190		59	
135	2.1	8.2	188	9	55	15

There are no results for the acid value of the bottoms product during early time periods for runs 4 and 5 due to the lack of bottoms product collections at those times.

The approximate residence time for the fat and steam in the reactor are shown in Table 12. The tallow feed rate was the same in every run resulting in the same residence time. The steam feed rate was the same for every run except the last.

The 4700 cm^3 liquid hold-up in the reactor was determined by the difference between the 5600 cm^3 of fat required to initially fill the reactor less the 900 cm^3 that initially purged during the start-up of steam flow. The 4400 cm^3 vapor hold-up in the reactor was determined by the difference between the 9100 cm^3 of total reactor volume less the 4700 cm^3 liquid fat hold-up volume in the reactor.

Table 12. Residence Time of the Tallow and Steam in the Reactor.

RUN	TALLOW FEED RATE (G/MIN)	RESIDENCE TIME FOR TALLOW (MIN)	STEAM FEED RATE (G/MIN)	RESIDENCE TIME FOR STEAM (SEC)
1	9.3	440	2.1	40
2	9.3	440	2.1	40
3	9.3	440	2.1	40
4	9.3	440	2.1	40
5	9.3	440	1.0	80

Decomposition was sensed primarily from the aroma of the overhead product stream. Decomposition was very apparent at the operating temperature of 325°C and less so at lower temperatures. The acrolein odor could not be detected in bottoms samples.

Liquid samples were taken from stages one through four at the end of the fourth and fifth runs. The degree of hydrolysis was calculated for each stage by dividing the samples acid value by its saponification value. The results are presented in Table 13. The samples retrieved from the fourth stage were observed to appear much like a condensed overhead vapor sample, and steam was noticed to exit the sample port along with the stage liquid product. Some decomposition products were apparent in the fourth stage sample.

Table 13. Degree of Hydrolysis for Stages One Through Four.

STAGE	RUN 4 (%)	RUN 5 (%)
1	3.2	4.6
2	4.7	7.9
3	6.8	6.4
4	83.8	63.3

CHAPTER 10

DISCUSSION

Steady State Analysis of the Hydrolyzer

As Table 12 illustrates, the residence time for tallow in the reactor was 440 minutes. Normally to achieve steady state operation of the hydrolyzer, operating time should exceed the residence time. Run 2 shown was conducted for 1080 minutes which exceeds the residence time of the fat in the reactor by about 2.5 times. The results for this run shown in Tables 6 and 7 indicate that the degree of hydrolysis averaged about 24% with little change over long periods of time. However, at the first sample time in Table 7, the degree of hydrolysis is calculated to be 19% which is significantly different than the other values. The basis for the difference between these degrees of hydrolysis for this run time is uncertain. The degree of hydrolysis after 1080 minutes is nearly the same as the degree of hydrolysis after 180 minutes for this run. This supports the validity for the degree of hydrolysis data observed for run times shorter than the tallow residence time for the other four runs.

Runs 2 and 4 were performed using the same operating conditions. The degree of hydrolysis data shown in Tables 6 through 9 indicate that the results for the second run are significantly different from those of the fourth run. The degree of hydrolysis for the fourth run is about 50% higher than for the second run, about 33% and 23% respectively. This indicates that further investigation of the hydrolyzer is necessary at these operating conditions to achieve consistent data.

Temperature Effects on the Rate of Reaction

Results of the first two runs shown in Tables 4 through 7 show that the impact of temperature on the reaction rate is significant. An increase from 280°C to 300°C caused the average degree of hydrolysis for each run to almost double from about 13% to about 23%. With the 20°C change in temperature, it is unlikely that there was any significant change in mass transfer that would significantly affect the rate of reaction. Therefore, it is probable that the reaction is rate limited and not mass transfer limited.

Steam Feed Effects on the Rate of Reaction

The premise for the fifth run was that by increasing the residence time of the steam in the reactor, a higher conversion would be attained since more fatty acid would remain in the liquid phase in the reactor promoting the solubility of water in the liquid phase. The results shown in Tables 10 and 11 indicate that although the acid content of the bottoms product increased to about 8% compared to those of other runs of about 4%, the degree of hydrolysis decreased to about 20% from higher values of about 33% determined at the previous higher steam feed rate tests.

In this run, the steam used was about 50% of the amount used in other runs. There was less excess water available to hydrolyze the tallow even though there was twice the residence time for steam in the reactor. Although there was a larger amount of bottoms fatty acid products than for other runs, any increase in the solubility of water resulting from this higher acid content was offset by other unexplained effects which decreased the net amount of hydrolysis. The steam feed for the fifth run was 1.7 times in excess of that needed for complete hydrolysis while it was 3.6 times in excess for the earlier runs.

Overhead and Bottoms Product Analysis

The separated organic layers produced from the overhead products were nearly pure fatty acids. In every run, the overhead organic layer content was between 94% and 96% fatty acids. At 280°C, the first run produced about 30% of organic phase in the overhead product. The second and fourth runs at 300°C produced about 55% and 60%, respectively, while the last run consisted of approximately 60% organic phase in the overhead product. The amount of fatty acids present in the bottoms product is small compared to those in the overhead. This indicates that the steam is stripping most of the fatty acids away from the reaction area and carrying them in the vapor flow to the overhead product collection system.

Stage Product Analysis

From Table 13, it is apparent that there is a large jump in the degree of hydrolysis from the third stage to the fourth stage. Stages one through three show a slight gradual increase in fatty acid content as the liquid flows down the reactor. The fourth stage is not typical of the other stages. Observations noted that the stage sample appeared to be similar to an overhead sample. Decomposition, which is typically observed in the vapor phase, was also sensed in the fourth stage samples. The fourth stage liquid sample port probably is blocked by vapor resulting in invalid sample collection.

Decomposition of the Reaction Products

At 325°C, a significant amount of decomposition was noted in the third run. The hydrolyzer system may have some hot spots which exceed 325°C because of distribution of the heating tapes on the reactor walls. These hot spots could promote decomposition in the system. Because decomposition was sensed in significant amounts, long term tests of the bench scale hydrolyzer were not feasible at 325°C. At other reaction temperatures, decomposition was sensed in small amounts and did not affect the operation of the hydrolyzer.

Commercial Feasibility of Steam Hydrolysis

The low degrees of hydrolysis determined using the test parameters so far investigated would indicate that steam hydrolysis is probably not feasible compared to the Colgate-Emery process. Better performance might be achieved with changes in the design and/or operating parameters. There is not enough current evidence to establish the feasibility of the concept of steam hydrolysis at the commercial level.

CHAPTER 11

SUMMARY AND CONCLUSIONS

The objective of this research was to develop evidence relating to the feasibility of steam hydrolysis using a bench scale reactor. Different temperatures and fat/steam feed rates were tested and overhead and bottoms products as well as stage liquid samples were analyzed to establish the degree of hydrolysis of the fat feed achieved. Decomposition of products was analyzed by sensing for acrolein aroma. The significant findings of these investigations are as follows:

1. A relatively pure fatty acid product was produced in the organic phase of the overhead product with little decomposition noted.

2. Little decomposition was sensed at operating temperatures of 280°C and 300°C, whereas significant amounts were present at 325°C.

3. Increasing the operating temperature from 280°C to 300°C doubled the degree of hydrolysis from about 23% to about 33% indicating that the reaction is not mass transfer limited.

4. Soybean oil was not a good feed source for the reactor because of its decomposition into polymerized materials at high temperatures.

5. Steam hydrolysis is not feasible at the commercial level using the operating parameters and the hydrolyzer design tested.

CHAPTER 12

RECOMMENDATIONS FOR FUTURE RESEARCH

Based on the results of this experimental work, the following recommendations are made:

1. Repeating identical operating conditions results in significant changes in the degree of hydrolysis indicating the need of further duplicate investigations of the operating parameters.

2. The fourth stage liquid produced significant amounts of fatty acids compared to the lower stages indicating a need to relocate this sample port or rebuild this reactor stage.

3. Glycerol, diglyceride, and monoglyceride analyses should be made on reactor product and stage samples to gain an improved understanding of the mechanism of the hydrolysis reaction.

4. Recycling bottoms products into the reactor feed might significantly increase the overall degree of hydrolysis and increase the amount of fatty acids produced in the overhead.

5. Testing other feed sources such as palm oil (a common feed source in current hydrolysis processing) would provide

additional information on future industrial uses of steam hydrolysis.

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