

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin 54911
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April 28, 1972

Project 2942

Dear Dr. Marteny:

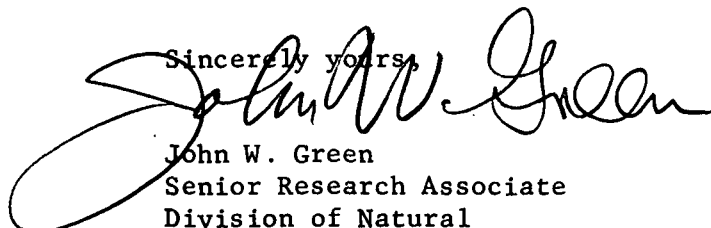
Enclosed is Progress Report Three for Project 2942. As we mentioned in an earlier letter, work on this project has been delayed by slow progress in the assembly of the high-speed flow reactor, and again we wish to apologize for the delay and any inconvenience it has caused you.

The reactor was constructed partly from equipment designed and made here in our shops and partly from equipment purchased from various suppliers. Many of the latter were not available as stock items, and so delivery from the suppliers would range from one to three months. This was vexing to us, of course, and made it difficult to schedule our work here.

The mechanical construction of the reactor is almost completed, as shown in the accompanying report, and now we can devote some time to testing the apparatus under pressurized conditions, and carrying out kinetic studies of alkaline degradation of sugars at higher temperatures.

We would appreciate any comments you have on the present work. The reactor has been designed, based on our experience with glass reactors operating under milder conditions, as described in earlier reports, and is an extrapolation into a region of higher temperature and pressure.

Sincerely yours,


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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INCREASED YIELDS IN ALKALINE PULPING. I.
A STUDY OF THE PEELING REACTION AT THE CONDITIONS
OF KRAFT PULPING

Project 2942

Report Three

A Progress Report

to

MEMBERS OF GROUP PROJECT 2942

April 26, 1972

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INCREASED YIELDS IN ALKALINE PULPING. I.
A STUDY OF THE PEELING REACTION AT THE CONDITIONS
OF KRAFT PULPING

SUMMARY

A flow reactor capable of operating under pressure at temperatures above 100°C. and at high-flow rates has been constructed. The driving system consists of hydraulic rams, connected to an oil pump operating at pressures up to 1000 p.s.i.

This hydraulic system will move the reaction and quenching syringes at flow rates up to 60 ml./sec.; their movements are monitored by linear potentiometers, connected to a high-speed oscillograph recorder.

The movements of the syringes (i.e., the hydraulic rams) are controlled by speed controls and by solenoid-actuated directional valves. The precision of movement of the rams is very good. The movement of the quenching syringe, relative to the movement of the two reaction syringes, is controlled by microswitches, so that exact quenching of the reaction solution can be done at high-flow rates.

INTRODUCTION

In earlier kinetic work on this project, with glass syringes moved by electrical stepper motors at temperatures below 100°C., the reaction solutions were driven through heating and reaction coils at relatively low speeds, up to 60 ml./min. The back pressure in the coils at such low rates is small, of the order of one-half atmosphere and the low torque of the stepper motor was adequate.

For short reaction times and faster flow rates, of the order of milliliters per second, rather than milliliters per minute, we find a much higher back pressure in our mixers and in our reaction coils. This increased pressure has a square factor, based on a modified Bernoulli equation:

$$(\text{flow rate})^2 = \text{driving pressure}$$

So, if we increase our flow rate by a factor of ten, the driving pressure needed is increased by a factor of one hundred. Thus, the back pressure on our system of coils and mixers, to give a flow rate of 20 ml./sec., is about 160 p.s.i. The stepper motors we have been using are effective up to a driving pressure of about 20 p.s.i. at the most.

We have decided to use a hydraulic system to drive our syringes at these higher speeds (Fig. 1). The advantages of such a system are: (1) driving pressures up to 1000 p.s.i.; (2) fast linear movements, up to 4 inches a second; (3) the hydraulic pistons driving the syringes can be operated in forward and reverse directions by use of solenoid-actuated switches; (4) the action of such switches requires only 15-20 milliseconds, according to the manufacturers; and (5) only the hydraulic pistons (rams) need be installed in the pressure chamber housing our syringes; these rams are about 15-inches long by 1.5-inches diameter and will fit easily into the chamber (52-inches long by 8-inches diameter).

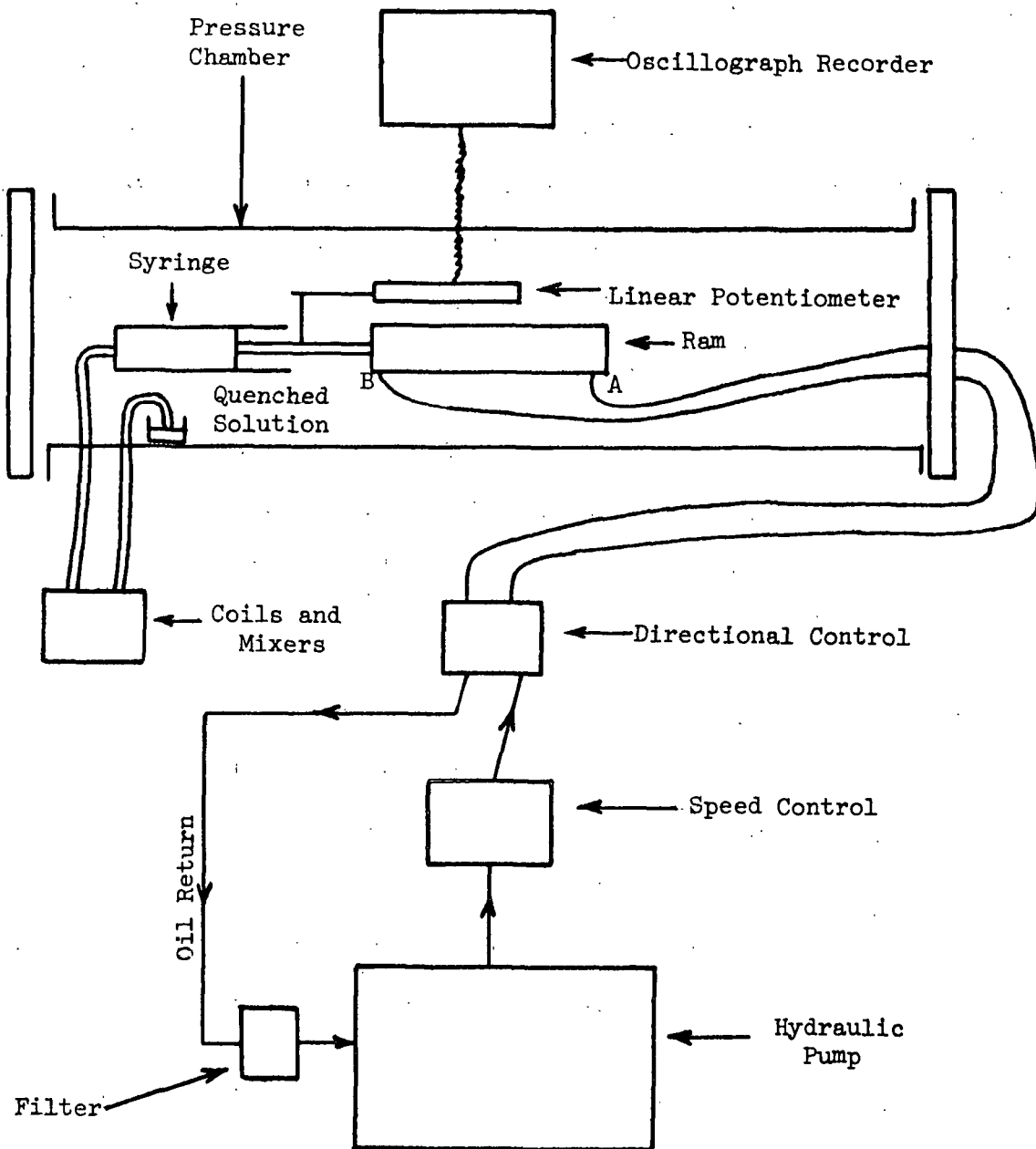


Figure 1, Outline of Hydraulic System and Pressure Chamber

Two other driving systems were considered and rejected: (1) Electrical stepper motors. Such motors, now used in our low-speed reactor, have low torque at higher driving speeds, and these speeds are limited. (2) High-speed electrical motors, connected to a magnetic clutch. A high torque and high speed is available here. However, both systems have to be converted to a linear drive and the motor has to be placed inside the pressure chamber. Also, special arrangements have to be provided to give a reverse direction to the linear drive. Both systems can be started and stopped rapidly, but a flexible coupling is needed for the stepper motor to overcome high-initial loads.

Finally, a pneumatic system was considered briefly. It was rejected, as it cannot provide an intermittent starting and stopping action, or a reverse linear movement. Also, its action is not very reproducible. It does have the advantage of a linear drive.

The hydraulic system will operate up to a pressure of 1000 p.s.i. Our system of coils and mixers, operating at a flow rate of 20 ml./sec., is about 160 p.s.i., so with our hydraulic system we can easily handle such back pressures, and even go to higher flow rates. The linear movement of our syringe pistons is rapid, of the order of 4 inches a second, and the movement is followed by two linear potentiometers and recorded on an oscillograph recorder.

The system will be coupled to a flow reactor composed of heating coils, jet mixers, and reaction coils, made of stainless steel, and heated in an oil bath at temperatures above 100°C. The syringes will be operated in a pressure chamber with a nitrogen atmosphere. Both the flow reactor and the pressure chamber were described in Progress Report Two.

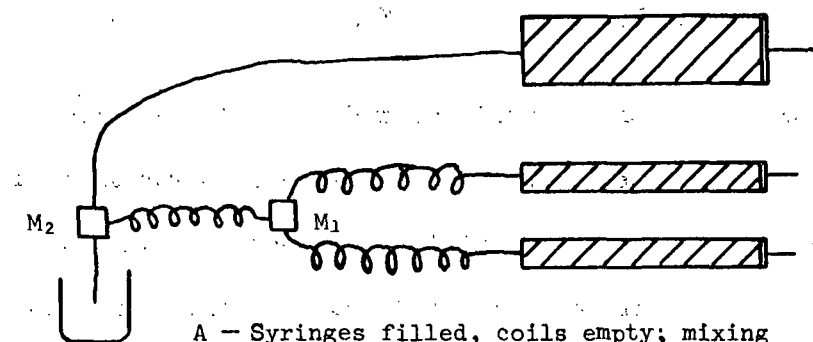
SEQUENCE OF FLOW OF SOLUTIONS THROUGH THE REACTOR

Before the operation of the syringes and hydraulic system is described, a description is given below of the desired flow of liquids through the reactor. The four stages, shown in Fig. 2 are: (A) filling the heating coils; (B) thermal equilibration of the liquid in these coils, (C) pushing the mixed solutions through the reaction coil, and (D) quenching the reaction solution by addition of acid. The timing of the last two stages is very important and the controls of the hydraulic system are designed to facilitate this.

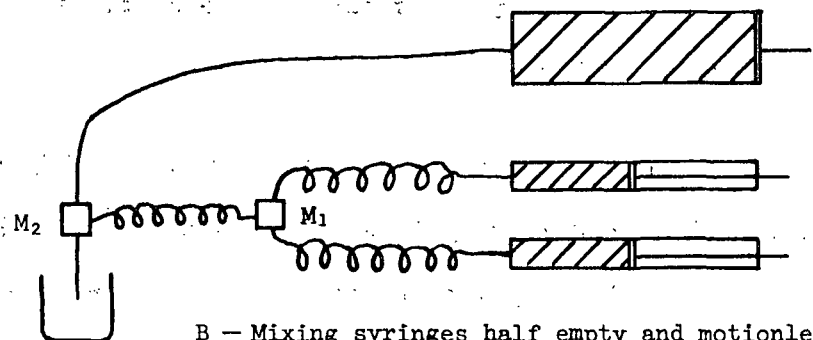
Initially the three syringes are filled with liquid by fully retracting their respective pistons. The two mixing syringes hold 20 ml. each of alkali and carbohydrate solution. The quenching syringe holds 100 ml. of boric acid. Care must be taken to remove all air from the syringes so that a reproducible liquid flow is maintained in subsequent operations.

In Stage A the pistons of the two mixing syringes are advanced one-half stroke, so that 10 ml. of each solution is forced into the heating coils. The volume of these coils is such that the liquid does not quite reach the mixer M_1 . In the hydraulic system there is a microswitch control which stops the two syringes at this half-way point.

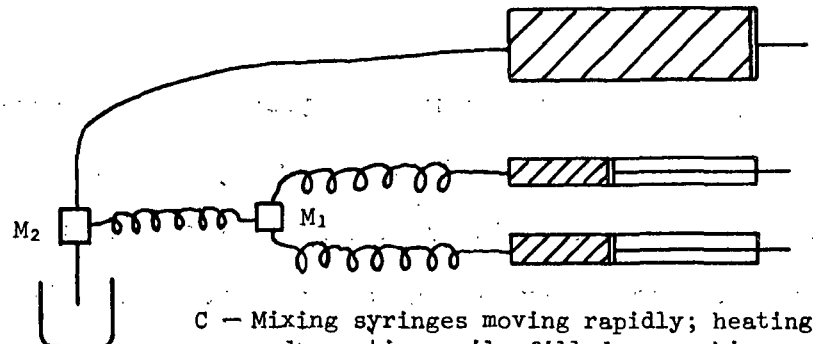
The two syringes are held motionless for thermal equilibration (Stage B) of the liquid in the two heating coils. This time interval will range from several seconds up to two minutes, depending on the temperature of the oil bath surrounding the coils. This delayed stage is needed as the rapid flow of solution through the coils during the reaction stage will be very short, probably too short for cold solution coming from the syringes to reach the reaction temperature. (See Progress Report Two, pages 48-54.)



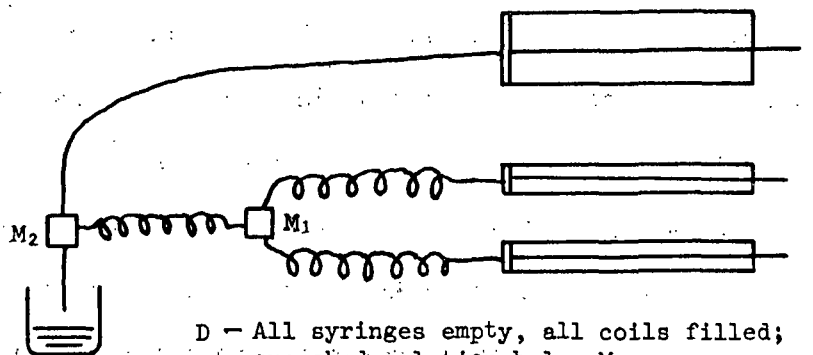
A - Syringes filled, coils empty; mixing syringes are just starting to empty at a low rate



B - Mixing syringes half empty and motionless; heating coils filled; no syringe movement during thermal equilibration



C - Mixing syringes moving rapidly; heating and reaction coils filled; quenching syringe just starting



D - All syringes empty, all coils filled; quenched solution below M2

Figure 2. Operation of Reactor

In the reaction Stage C the two mixing syringes are started up again, at a rapid rate, and the heated solution in the heating coils is pushed rapidly through mixer M_1 and into the reaction coil. When the reaction solution just reaches the second mixer, M_2 , the large syringe is started, so that the acid solution and the alkaline reaction solution reach M_2 simultaneously and the reaction is quenched. This timing is done by relating the mechanical movement of the two smaller syringes to the flow of liquid through the reaction coil. At the appropriate stage of linear travel, a microswitch connected to the piston rods of the smaller syringes will start the movement of the large syringe. The interval when this switch is turned on is shown in Stage C in Fig. 2, and depends on the volume of the reaction coil.

Finally, in Stage D, all three syringes are empty. Ideally, the two small syringes should empty in the same time interval as that required to empty the large syringe. This means that we are dealing with a liquid flow of $(20 - x$ ml.) from the two small syringes in the same time as a liquid flow of 100 ml. from the large syringe. Here x is the volume of the reaction coil (1 to 5 ml.).

In summation, we start with 20 ml. in each small syringe and 100 ml. in the larger syringe, a total of 140 ml. If the two heating coils are 10 ml. each, and we use a reaction coil of 5 ml. volume, the total volume of solution left in the reactor at Stage D is 25 ml. Thus, we have pushed 15 ml. of reaction solution through the reactor and quenched it with 100 ml. of solution. So our quenched solution emerging from the reactor is 115 ml. total volume. (The volume of the two mixers is very small, probably of the order of 1 ml.)

This is an ideal description of the reactor operation, and limitations will be discussed later. At present it serves to make more intelligible the design and operation of the controls operating the hydraulic system described below.

DESCRIPTION OF THE APPARATUS

ASSEMBLY OF MIXING AND QUENCHING SYRINGES

The three syringes are mounted on a piece of channel iron. The two mixing syringes, with a common connection to a hydraulic ram, are mounted on one side; as shown in Fig. 3. The quenching syringe is mounted on the other side of the channel iron, as shown in Fig. 4.

The mixing syringes are made of stainless steel tubing (0.459-inch I.D.), and have a 20-ml. volume for 7.5-inch stroke. The hydraulic ram is 1-inch in diameter and has a 3.14-cu.in. cylinder volume for a 4-inch stroke. The rod of the ram is connected by a cross bar to both syringes and to a linear potentiometer. A "travel bar" is also connected to this same cross bar and serves to actuate two microswitches (MS-1 and MS-2).

The quenching syringe (Fig. 4) is also made of stainless steel (1.01-inch I.D.) and has a 100-ml. volume for a 7.5-inch stroke. The arrangement is much simpler, with a connection to a 1.5-inch hydraulic ram (14.13-cu.in. cylinder volume for a 7.5-inch stroke). There is also a linear potentiometer connected to the cross bar but no travel bar.

The function of the two microswitches is to control the movement of the two syringes relative to the mixing and quenching operations. The first switch (MS-1 in Fig. 3) is positioned so that it will stop the movement of the 1-inch ram exactly half-way through the 7.5-inch stroke. This "half-stroke" movement will

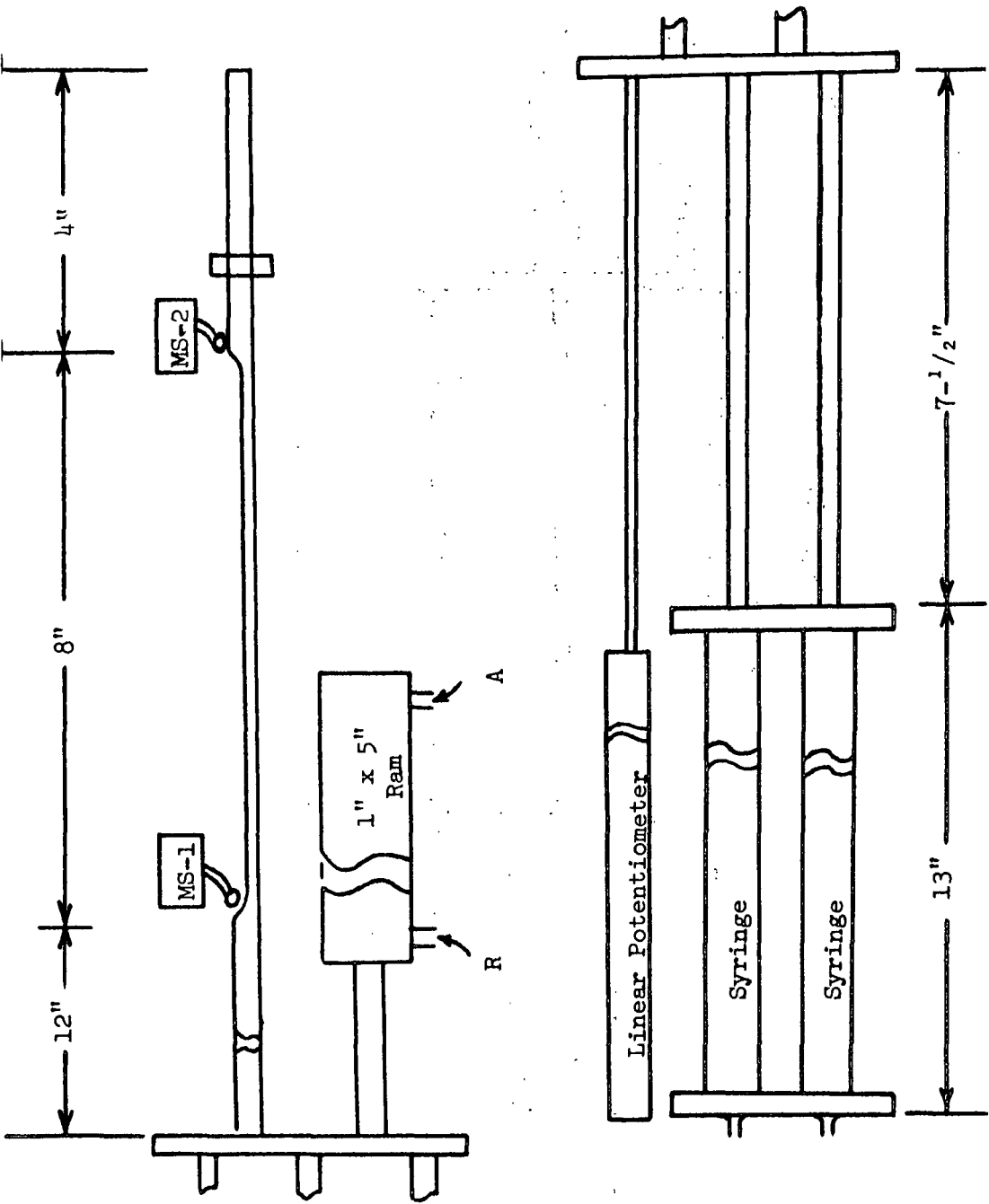


Figure 3. Arrangement of Mixing Syringes and Hydraulic Ram

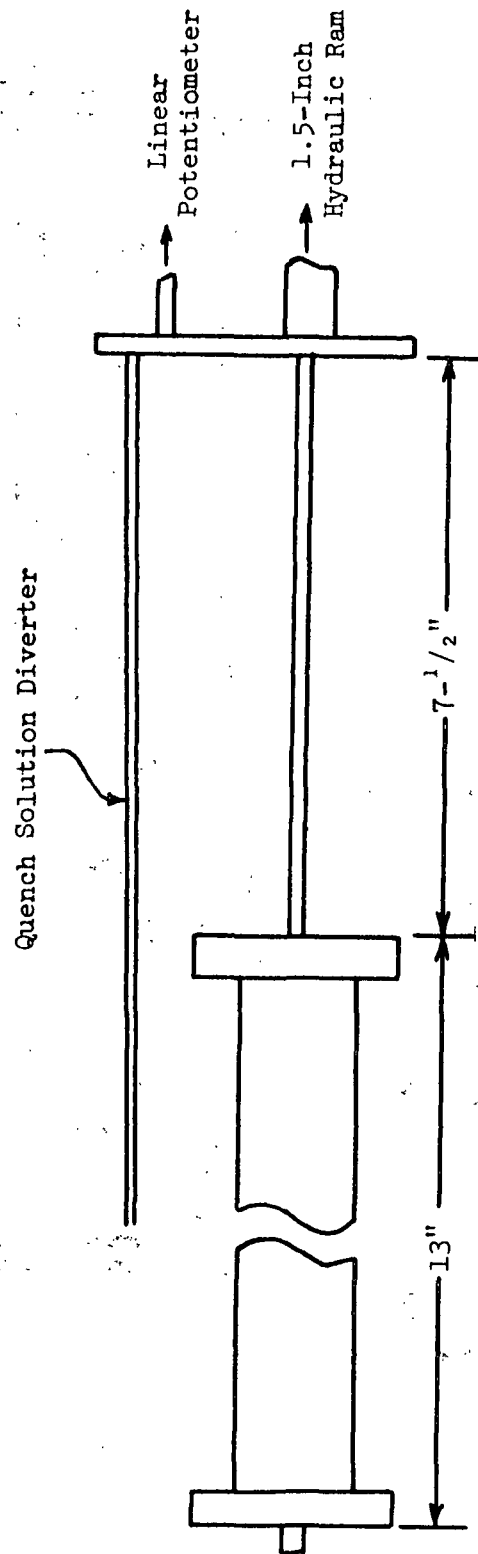


Figure 4. Arrangement of Quenching Syringe

allow the driving of 10 ml. of solution from each of the mixing syringes into the heating coils just short of the first mixer (Stage A, Fig. 2). The second "half-stroke" will then drive this heated solution into the reaction coils (Stage C, Fig. 2).

The second switch (MS-2, Fig. 3) controls the start of the 100-ml. syringe relative to the movement of the first syringe. The position of this switch can be adjusted so that the quenching syringe will be started when the reaction solution just reaches the second mixer. This position will depend on the volume of the reaction coil and will be independent of the rate of movement of the two mixing syringes. This is Stage C in Fig. 2. The speed of the quenching syringe has to be adjusted relative to the speed of the two mixing syringes so that they all finish their movements at the same time.

HYDRAULIC SYSTEM FOR DRIVING SYRINGES

This system consists essentially of a hydraulic pump, operating to 1000 p.s.i. maximum pressure and 346 cu.in./min. maximum flow, and two rams, described earlier. The three units are connected by two directional controls to allow advance and retract movement of the rams, and two flow controls. This arrangement is shown in Fig. 5. The details of the hydraulic controls, operated by solenoids, are shown in Fig. 6. There are two switches, S1 and S3, operating these controls, and they are mounted on the panel of a switchboard. Each switch has four positions. Three of them (retract, stop, and advance) are similar in nature.

Switch S1 operates the mixing ram and the mixing syringes. The normal operation of the switch in the several positions is as follows:

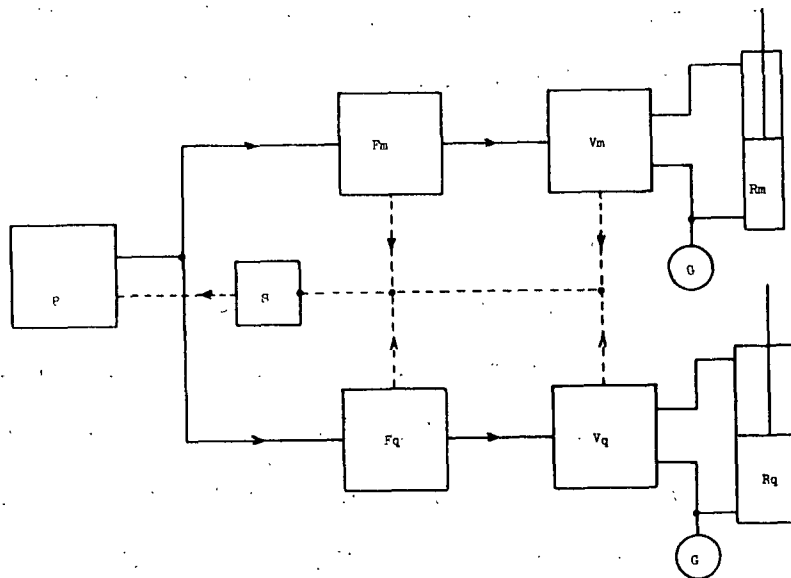


Figure 5. Hydraulic System. Notations for Hydraulic System:

- Fm Flow control valve for mix ram; 1-120 CIPM
- Fq Flow control valve for quench ram; 1-231 CIPM
- G Pressure gage in ram advance line; 1000 p.s.i.
- P Pump; 1000 p.s.i., 346 CIPM
- Rm Mix ram; 1-in. diameter, 8-in. stroke
- Rq Quench ram; 1-1/2-in. diameter, 8-in. stroke
- S Cartridge filter
- Vm Directional control valve for mix ram;
solenoid actuated, spring centered.
- Vq Directional control valve for quench ram;
solenoid actuated, spring centered

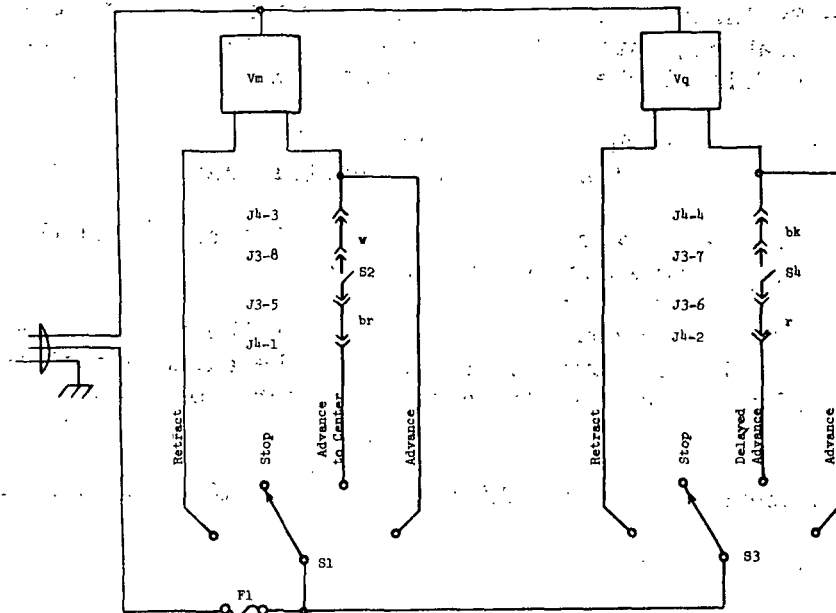


Figure 6. Hydraulic Controls. Notations for Hydraulic Controls:

- F1 Fuse, 1 A, Slo-Blo
- J3 Pressure seal fitting, Conax Type PL-18-A12
- J4 Jones Type 304
- S1 Mix ram manual control switch
- S2 Microswitch operated by mix ram. Closed until ram advances to center (= MS-1 in Fig. 3)
- S3 Quench ram manual control switch
- S4 Microswitch operated by mix ram. Closes at adjustable advance past center (= MS-2 in Fig. 3)
- Vm Directional control valve for mix ram; solenoid actuated, spring centered
- Vq Directional control valve for quench ram; solenoid actuated, spring centered

Advance - Syringes are completely empty

Retract - Syringes, attached to tubing immersed in appropriate beakers, are filled with desired solution. This is a full stroke and each syringe contains 20 ml. solution

Advance to center - The ram advances one "half-stroke" and 10 ml. of solution is expelled from each syringe

Advance - The ram advances the second "half-stroke" and the remaining solution is expelled

Note - A full stroke can be effected, after the retract position, by turning the switch directly to the advance position, and bypassing the "advance to center" position

Switch S3 operates the quenching ram and the 100-ml. quenching syringe.

The normal operation is as follows:

Advance - Syringe is completely empty

Retract - Syringe, connected to appropriate beaker, is filled with 100-ml. solution

Delayed advance - Syringe does not move until microswitch MS-2 on the mixing ram (see Fig. 3) is activated. Then the quenching ram will move a full stroke and the 100-ml. syringe is completely emptied

Advance - This bypasses the microswitch MS-2 and empties the syringe

The above operations are given for the complete movements. Actually the syringes can be moved either forward or backward a certain amount by turning the switches to retract and then stop, or to advance and then stop. Normally the rams are operated to either fully advanced or to fully retracted positions, or to the half-way position for the mixing ram. These positions are reproducible and their precision will be described later.

RECORDING SYSTEM FOR SYRINGE MOVEMENTS

As shown in Fig. 3 and 4, there are two linear potentiometers connected to the two mixing syringes and to the quenching syringe. These monitor the movements of the two syringes and the extent of these movements and the rate of these movements are recorded on an oscillograph. The latter instrument has dual channels, with two differential amplifier circuits so that movements of both syringes can be shown simultaneously. The electrical circuits are shown in Fig. 7. A recording from the oscillograph is shown in Fig. 8.

The oscillograph is a high-speed recorder, operating at paper speeds of 0.1 to 80 in./sec., and with timing lines on a photographic paper at 1, 10, or 100 lines/sec. The paper used is Kodak Linagraph and the recording traces are made by two 35-watt xenon lamps. A xenon flash lamp exposes for the timing lines. The traces on the paper are made visible by a short exposure to daylight and can be made permanent by treatment with photographic developers and fixers.

The traces in Fig. 8 show (a) T_H , the first half-stroke of the mixing syringes to fill the heating coils, (b) T_{EQ} , a time interval to allow thermal equilibration, (c) T_K , the second half-stroke of the mixing syringes to mix the two solutions and drive them through the reaction coil, and (d) T_Q , the movement of the quenching syringe to mix acid with the reaction solution at the second mixer.

The time of the second half-stroke of the mixing syringe, the reaction stroke, is very important, as it determines the flow rate of solution through the reaction coil and hence the time of reaction. This flow rate is a function of the time of this stroke and the volume of liquid driven from the syringe. (The precision of this volume is discussed below.)

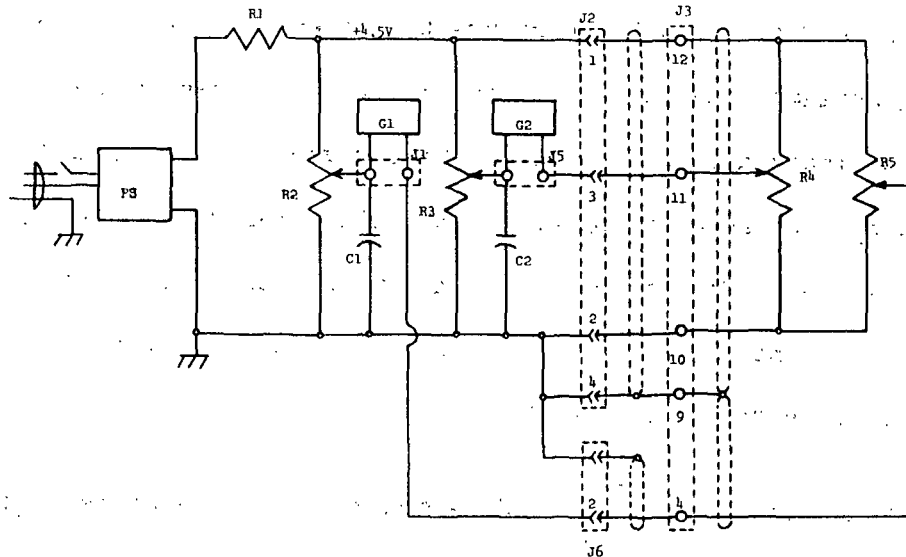


Figure 7. Ram Position Recorder. Notations for Ram Position Recorder:

- C1, C2 33 UF, 20V, tantalum
- G1, G2 Galvanometers of Century Type GPO 460; oscillograph, with two Model 563D differential amplifiers
- J1, J5 Binding posts
- J2 Jones Type 304
- J3 Pressure seal fitting, Conax Type PL-18-A12
- J6 Jones Type 302
- PS Power supply, Power Mate Type MD15LL
- R1 4.32K
- R2, R3 5K, 10-turn, zero control potentiometers, panel mounted
- R4 Linear motion potentiometer attached to MIX ram. 10-1/2-Inch stroke, 25K, conductive plastic. Computer Instruments Model 111
- R5 Linear motion potentiometer attached to QUENCH ram. 10-Inch stroke, 10K, conductive plastic. New England Instrument Company Model 114L

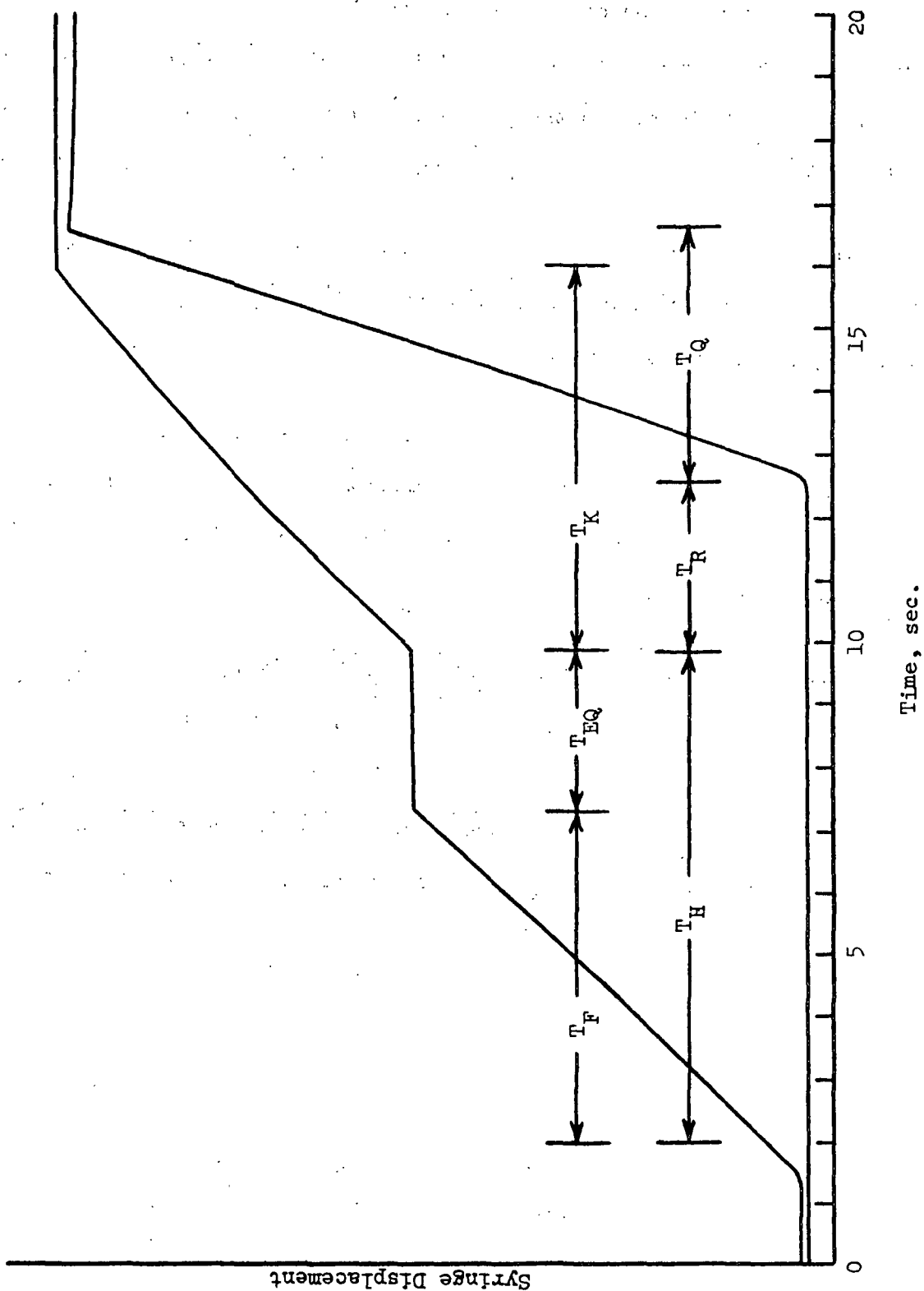


Figure 8. Photographic Recording of Syringe Movements

The initiation of the stroke of the quenching syringe is determined mechanically by the position of the microswitch MS-2 (Fig. 3). This position is set for the time (T_R) when the first portion of the reaction solution reaches the second mixer, and is dependent only on the volume of the reaction coil. It is independent of the flow rate and so can be set by visual observation at very low-flow rates.

The end of the movement of the quenching syringe is dependent on the relative rates of the reaction and quenching strokes, and they are adjusted so that the quenching stroke continues for a short time after the reaction stroke is finished.

Ideally, the flow of quenching solution should bracket the flow of reaction solution, so as to insure that all of the latter solution is quenched when it reaches the second mixer.

The slope of the first half-stroke of the mixing syringes and the following time interval are of secondary importance. The combined time for the two intervals should be sufficient for thermal equilibration of the two reactant solutions. More careful control of these factors may be necessary if an appreciable thermal decomposition of the carbohydrate solutions before reaction is observed.

OPERATION OF THE APPARATUS

FILLING OF SYRINGES

The angle iron assembly with the three syringes and two rams is placed in the 8-inch pressure chamber. An end view of the cylinder and assembly is shown in Fig. 9. Short lengths of 1/8-inch O.D. stainless steel tubing lead from the syringes to valve systems, fastened through the chamber wall with bulkhead fittings. Only one such connection and set of valves are shown in Fig. 7 for clarity.

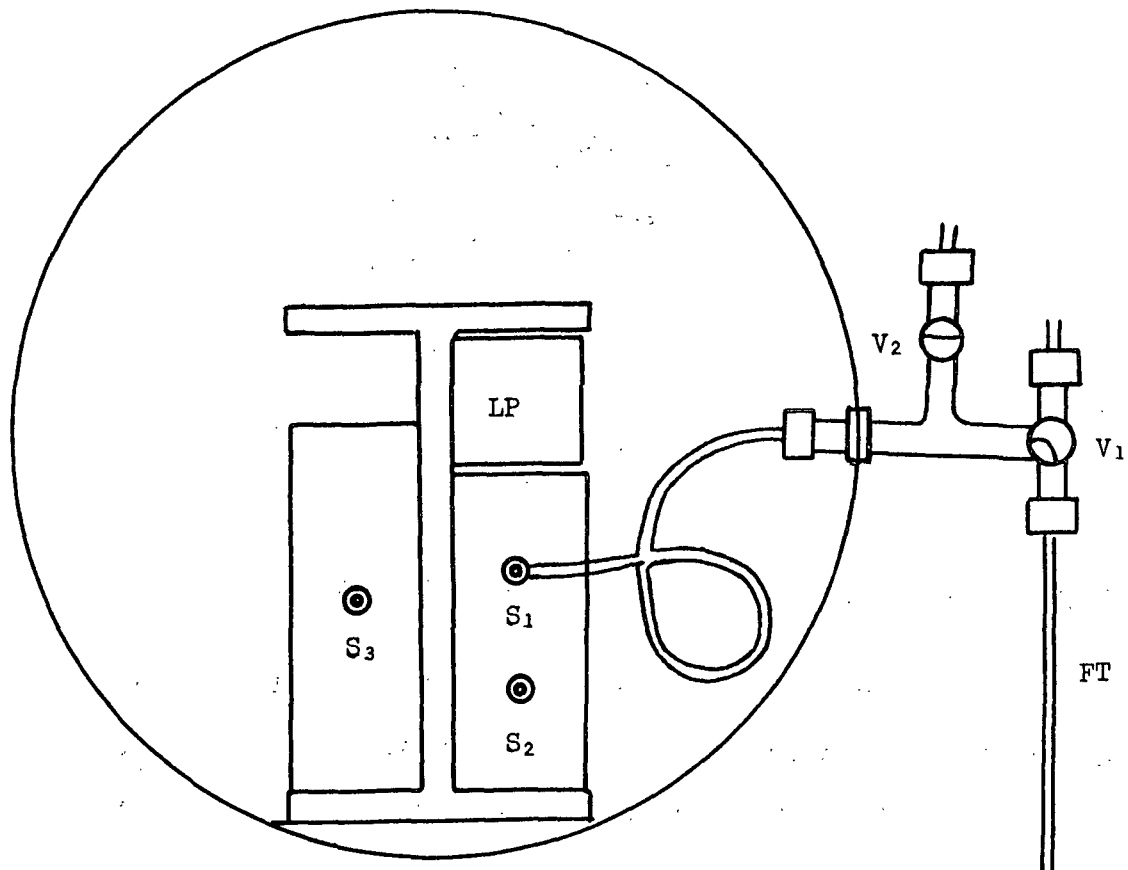


Figure 9. End View of Syringes in Pressure Chamber (S_1 and S_2 are 20-ml. Syringe Ports, S_3 that for the 100-ml. Syringe; LP is the Linear Potentiometer and FT is a Feed Tube)

The various connections to the tubing are made with Swagelok tube fittings. Those at the syringe are male connectors, with 1/4-inch pipe thread fittings (see Fig. 10). The bulkhead unions have a male Swagelok thread at one end and a 1/4-inch pipe thread at the external end. This external end is connected by a 1/4-inch pipe thread tee to a two-way ball valve, V_2 , and to a three-way ball valve, V_1 . The first valve serves as a filling port or as an air vent; valve V_1 is usually connected to the various stainless steel coils of the flow reactor. In Fig. 9, valve V_1 is connected to a short length of tubing, FT; this tube was used to fill the syringes with water and check the precision of their movements.

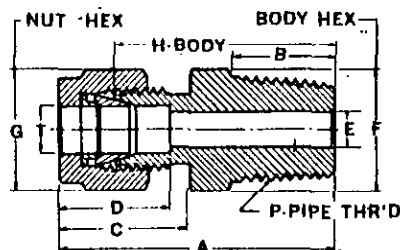


Figure 10. Swagelok Male Connector
 $T = 0.125$ in., $E = 0.094$ in.

VOLUMES DELIVERED BY MIXING SYRINGES AND THEIR PRECISION

It is necessary to know the exact volumes of liquid delivered during the two half-strokes. The first volume is necessary so that the heating coils are filled just short of the first mixer. The second volume is necessary so that the flow rate through the reaction coil can be calculated; the time of delivery of this volume is determined on the oscillograph recorder.

The precision of the 20-ml. syringes, moving from one end to the other, and in the half-stroke position, was found to be very good. This depended on the

movement of the ram, from one end of the cylinder to the other, and on the exclusion of air from the system. This was determined by filling the syringe, the valve system and the filling tube FT, then removing the beaker, wiping any drop of liquid carefully from the end of FT, and catching the liquid forced out by syringe movement into a weighing bottle. Data are shown in Table I, for the two syringes, and for various flow rates, and for the two half-strokes.

TABLE I
PRECISION OF DELIVERY OF LIQUIDS FROM 20-ML. SYRINGES

Flow Control Setting ^a	Half-Stroke of Ram	Syringe A	Syringe B
0.200	First	10.466	10.466
		10.466	10.464
		10.463	10.471
0.300	Second	10.386	10.392
		10.395	10.390
		10.379	10.401
0.200	First	10.471	10.471
		10.460	10.463
		10.471	10.471
0.200	Second	10.377	10.375
		10.388	10.368
		10.365	10.378
0.200	First	10.477	10.469
		10.477	10.475
		10.457	10.459
0.100	Second	10.380	10.376
		10.374	10.366
		10.391	10.387

^aThe flow controls are micrometer distances, and correspond approximately to 5, 4, 3.3, and 1.2 ml./sec. for 0.300, 0.200, and 0.100 settings.

Note: In each case the ram was retracted fully at 0.200 flow rating to fill the syringes, and a time delay of 30 sec. allowed. A time interval of 60 sec. was observed between the first and second half-strokes. All values given are grams weighed, equivalent to ml. volume.

The operating procedure is as follows: A 12-inch length of 1/8-inch O.D. stainless steel tubing, FT, is connected to valve V₁, as shown in Fig. 9, and the lower end placed in a beaker of water (well below the liquid level). The ram is retracted and advanced fully several times to suck water into the syringes and to remove air. This is best done at a flow setting of 0.200 inch on the flow control. Some air is often entrapped in the tee below valve V₂ and this is removed as follows: (a) retract fully to fill the syringe via tube FT; (b) close valve V₁ (turn half-way between up and down); (c) open valve V₂; (d) advance the ram at a slow rate so that a little water and the air issues above V₂; and (e) close V₂ and open V₁ to the down position. Repeated advances and retractions should now give no air bubbles in the filling beaker of water.

Several errors were found and their occurrence carefully avoided. The first of course is air, just mentioned. Secondly, when the syringe is retracted, 30 seconds is allowed to elapse before the beaker is removed from the filling tube, to allow complete suction of liquid into the syringe. This assumes that the piston movement on retraction is faster than liquid flow into the syringe. Thirdly, there was a tendency for the syringe to creep when in the half-stroke position. This was due to a slight leak in the directional valve, and this was corrected by replacement of the spool in the valve by a different style. The Grimstad Company had suggested a check valve also, but this was not needed. With the new spool there was no pressure development at the end of the half-stroke, whereas with the old spool pressure slowly rose within 30 seconds to 500 p.s.i. on both sides of the ram.*

*This equal pressure on both sides of the ram piston was offset by the greater force exerted on the piston face away from the shaft; this face has a greater area than the other face, and so the ram tended to move slowly toward the shaft side, or in the advance direction.

VOLUME OF TUBING AND OF MIXERS

The volume of a given length of tubing, coiled or straight, or of a mixer, can be measured readily by determining the difference in weight of liquid expressed from a syringe via a full or an empty tube. This is done by filling the syringe, valve system and the tube FT shown in Fig. 9, carefully removing the beaker, and advancing the syringe so that all the liquid emitted from the lower end of FT is caught and weighed. Then the system is again filled, and the tube FT carefully disconnected from V_1 and dried, then reconnected. The syringe is again advanced and the second volume weighed. This volume is less than the first volume by the volume of the empty tube FT. The "break" in the liquid line at the Swagelok connection, is apparently rather clean, where the end of the 1/8-inch O.D. tubing is connected to the male connector, with a 3/32-inch opening. (See Fig. 10.) There is no tendency for liquid to drain out of the vertical 3/32-inch opening, with the syringe and the ram in a stationary position.

Data for volumes of various tubings and coils are given in Table II. Also, the volume of the two jet mixers, connected by a minimum length of tubing, is given. This volume of about 0.75 ml. seems rather large, but it includes connecting Swagelok fittings, and can be regarded to a certain extent as (a) part of either the heating coils; (b) part of the reaction coil; and (c) part of the quench system, beyond M_2 . Ideally, the housings around the jet mixers should be very small, but this is very difficult to attain.

Volumes given in Tables II and III are in ml. and are equivalent to grams of water weighed.

TABLE II

PRECISION OF MEASUREMENT OF VOLUMES OF TUBING

Tubing Measured	Syringe Delivery	Syringe Plus Tubing	Net Volume of Tubing
12 x 1/8-Inch O.D.	10.467	9.627	0.840
	10.452	9.645	0.807
Similar tubing	10.444	9.578	0.866
	10.445	9.593	0.852
Two jet mixers, connected by 1 x 1/8-inch tube	10.459 ^a	9.670	0.789
	10.459	9.706	0.753
	10.459	9.712	0.747
5-Ml. heating coil	10.459	5.270	5.189
	10.469	5.276	5.183
12.5-Foot length of 1/8-O.D. tubing	20.648 ^b	7.344	13.304
	20.849	7.258	13.591
Kenics mixer	10.416	9.437	0.979
	10.412	9.451	0.961

^aThis value of 10.459 is an averaged value derived from the first two figures in this column.

^bThese values are for the full stroke of a 20-ml. syringe.

EFFECT OF COILING ON INTERNAL VOLUME OF TUBING

In the preparation of heating coils, a definite volume is desired, so that the liquid from the first half-stroke of the 20-ml. syringes will just about fill it, but not reach the first mixer. Therefore, it was decided to cut a piece of tubing to a certain length, and then coil it. It was felt that the coiling might reduce the internal volume a small amount, so the volumes of two pieces of tubing were measured before and after coiling, to determine this decrease. To our surprise, an increase (see Table III) was observed instead. The experiment was repeated and again an increase of about 3% was obtained.

TABLE III

INCREASE IN VOLUME OF TUBING AFTER COILING

Tubing Used	Volume of Straight Tubing	Volume of Coiled Tubing	Net Change, %
62 In. x 1/8-in. O.D.	5.559	5.758	
	5.567	5.733	+3.3
60.5 In. x 1/8-in. O.D.	5.518	5.684	+3.0
	5.516	5.686	
60.5-In. coil straightened	5.573		+1
	5.572		
60.5-In. coil recoiled		5.696	+3 again
		5.674	

The tubing, 1/8-inch O.D. and with an I.D. of 0.085 inch, has a wall thickness of about 0.020 inch. The tubing is coiled by hand on a mandrel; the mandrel is simply a piece of galvanized pipe, 1-inch O.D., with a slot in one end to hold one end of the tubing during coiling. Apparently, the inner wall of the coil does not compress appreciably, being restricted by the mandrel, but the outer wall of the coil does stretch a definite amount. Also, the circular cross section of the tubing apparently does not change.

One of the coils was straightened, and the internal volume of the tubing decreased, almost to the original volume, so that the outer wall of the coil compressed appreciably. Here there is no mandrel to restrict such compression. When this straightened tubing was recoiled, the original increase in volume was obtained.

EVALUATION OF THE APPARATUS

SPEED OF THE HYDRAULIC SYSTEM

The hydraulic pump has a pumping speed of 346 cu.in./min. and this flow is directed into moving the two rams. These rams have certain internal cylinder volumes and the rate of movement of the rams is determined by these volumes and the pumping speed of oil against the rams. Two flow controls are connected between the pump and the rams and they divide, for maximum flow control rate, the flow of the oil into roughly 1/3- and 2/3-portions, as shown in Table IV*.

TABLE IV

FLOW CONTROL CHARACTERISTICS OF THE HYDRAULIC SYSTEM

	Flow Control A (120 cu.in./min.)		Flow Control B (231 cu.in./min.)	
	3/4-Inch Ram	1-Inch Ram	1-Inch Ram	1.5-Inch Ram
Internal volume of ram, cu.in.	3.53	6.28	6.28	14.13
Time for 8-in. stroke, in seconds	1.77	3.14	1.63	3.67
Volume of syringe con- nected to ram, ml.	20	20	100	100
Rate of flow from syringe, ml./sec.	11	6	60	27
Rate of flow from two syringes into re- action coil, ml./sec.	22	12		
Reaction time for 5-ml. reaction coil, sec.	0.23	0.42		
Reaction time for 1-ml. reaction coil, sec.	0.05	0.08		
Reaction time for 0.2-ml. reaction coil, sec.	0.01	0.016		

*These flow controls have micrometer settings, and allow regulation of oil flow from 1 to 100% of the maximum rate.

The present assembly has a 1-inch ram connected to the 20-ml. syringes and to the slower flow control (A), and a 1.5-inch ram connected to the 100-ml. syringe and to control B. Thus, it can be seen that the maximum liquid flow rate from the two types of syringes will be about 6 and 27 ml./sec. Since the quenching syringe should be operated at 10 times the rate of the mixing syringes, the maximum flow rate practical for the 20-ml. syringes will be 2.7 ml./sec. This would then provide a maximum rate of about 5.4 ml./sec. in the reaction coil, supplied by the two 20-ml. syringes.

As long as we are using boric acid to quench the alkaline reaction solution, we are restricted to a 10:1 ratio of flow rate for the quenching and mixing syringes. This is because the boric acid solution is dilute (0.5M) compared to the alkali; higher concentrations of boric acid cannot be obtained because of its limited solubility in water. Therefore, with the 10:1 ratio, the flow rate of the quenching syringe is the limiting factor in the rate of reaction studied in the flow reactor. We can increase the quench rate to 60 ml./sec. by use of a 1-inch ram, and then use a flow rate of 6 ml./sec. for the mixing syringes. This would give a flow rate of 12 ml./sec. in the reaction coil. With a 1-ml. reaction coil and this flow rate, our dwell time would be about 0.1 sec. With a 0.1-ml. reaction coil (this is equivalent to a 1.1-inch length of tubing of 0.085-inch I.D.) the dwell time can be decreased to 0.01 sec.

If still faster flow rates are needed, quenching of the alkaline solution can be done with a more concentrated acid solution, such as aqueous acetic acid. If we quench the 2N sodium hydroxide reaction solution with 2N acetic acid, the flow rate of the 100-ml. syringe need be only twice that of each of the smaller syringes. This means we can match easily the 27 ml./sec. of the large syringe and 1.5-inch ram against the 11 ml./sec. of the small syringes and a 3/4-inch ram.

There are three disadvantages to the use of acetic acid as a quenching agent. First, the final pH of the quenched solution will be slightly acid, due to buffering. Secondly, this quenched solution will be fairly warm, as only one volume of cold acid will be used per volume of hot reaction solution, in contrast to the "thermal quenching" involved in the use of 5 volumes of boric acid. So there may be a possibility of acid hydrolysis. Finally, the chemistry of the work-up of the quenched samples will have to be altered, to remove the excess acetic acid from the system.

BACK PRESSURE OF SYSTEM OF COILS AND MIXERS

This work was done as a preliminary experiment before the hydraulic system was selected to drive the flow reactor at a faster rate, and to aid in design of syringes.

In the relatively slow reactions studied so far, the flow rates from syringes have been of the order of several milliliters per minute. If we translate a rate of 10 ml./min. into linear flow in a coil of 0.085-inch inside diameter, this will amount to 10.75×10 inches per minute or about 9 feet per minute, a relatively slow rate. Any back pressure in the system of heating and reaction coils will be very small. A little more back pressure will be contributed by the mixers, which have jets of 0.02-inch I.D. The smaller cross section of these jets is a more serious restriction to flow, even though they are of short length, than the long lengths (up to 5 feet) of the coils of larger (0.085-inch) diameter.

When the flow rate is increased to a region of 10-40-ml. seconds through a system of coils and mixers, we find that a considerable back pressure develops. This back pressure was determined by connecting a series of coils and mixers to a supply of water in a pressure chamber, and determining the flow rate

at various pressures. Thus, we found out (see Table V, Item E) that a pressure of 160 p.s.i. was needed to drive water through a system of two heating coils, two mixers, and a reaction coil at a flow rate of 20 ml./sec. It can also be seen that doubling the pressure (Items C/A or D/B) increases the flow rate by a factor of about 1.4, equivalent to the square root of 2. This conforms to a simplification of the Bernoulli equation, $(\text{pressure})^2 = \text{flow rate}$.

TABLE V

FLOW RATE OF WATER AT VARIOUS PRESSURES

Item	System of Coils and Mixers	Pressure Applied, p.s.i.	Resultant Flow Rate, ml./sec.
A	2 Heating coils 1 Mixer 1 6-Inch tube	80	26
B	2 Heating coils 2 Mixers 2 6-Inch tubes	80	17.5
(Net effect of one mixer, A-B, is 8.5 ml./sec. or about 33% reduction)			
C	2 Heating coils 1 Mixer 1 6-Inch tube	160	37
D	2 Heating coils 2 Mixers 2 6-Inch tubes	160	25.5

(Net effect of one mixer, C-D, is 11.5 ml./sec. or about 31% reduction)

E	2 Heating coils 2 Mixers 1 6-Inch tube 1 Reactor coil (60-inches long)	160	20
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(Net effect of reaction coil, D-E, is 5.5 ml./sec. or about 22%)

(Effect of doubling pressure on rate: C/A is $37/26 = 1.42$

D/B = $25.5/17.5 = 1.45$)

Also the comparison of flow through systems with one mixer and with two mixers (A-B or C-D) shows that the jets in the mixers reduce the flow rate by a factor of about 30%. In contrast, the net effect of a long reaction coil, 5 feet in length but 0.085-inch I.D. is much less than the small jets in the mixer. So a narrow constriction, such as the mixer jets, is far more effective in restricting flow than a long tubing of larger cross section.

DRIVING PRESSURE NEEDED AT THE SYRINGE PLUNGERS

In the preceding section the back pressures were "balanced" by that in the pressure chamber, exerted on the trough of water. Thus, these pressures, read on a gage, were in pounds per square inch. However, when liquid is forced from a syringe into a coil, there is a hydraulic effect. The smaller the cross section of the syringe plunger, the greater this effect, in relation to the force actually applied to the plunger. Conversely, however, the smaller this cross section, the faster the plunger has to be moved linearly to provide a given flow rate (Table VI).

TABLE VI

DATA FOR SYRINGES OF VARYING CROSS SECTION

Cross section, in. ²	0.166	0.317	0.89
Cross section, cm. ²	1.07	1.95	5.17
Inside diameter, in.	0.459	0.635	1.010
Wall thickness (commercial stainless tubing), in.	0.083	0.120	0.120
Barrel length for 20-ml. volume, cm.	18.72	9.78	19.3(100 ml.)
Barrel length for 20-ml. volume, in.	7.4	3.85	7.6(100 ml.)
Hydraulic factor	0.166	0.317	0.89
Safety factor for pressure (working pressure = factor x allowable stress value)	0.296	0.276	0.265
Listed pressure limit in p.s.i., from Swagelok manual	7,162	5,175	4,968

Our flow reactor consists of two syringes pushing alkali and sugar into a reaction coil, and a third syringe adding acid to quench the reaction. To simplify this presentation, only the first two syringes will be considered initially: In the study of back pressures, water was forced from two valves through two mixers; however, only one entrance port to the second mixer was used, and the second entrance port capped.

The mixing syringes are of stainless steel tubing, of 0.0459-inch I.D. The cross section of such a syringe, or of the plunger, is 0.166 square inch, so the actual pressure applied to the plunger, to overcome the back pressure in the system, will be modified by this hydraulic factor. To obtain a flow rate of 20 ml./sec. in the reaction coil, each syringe will be driven at a rate of 10 ml./sec. The actual driving pressure at the two plungers, to overcome the back pressure of 160 p.s.i., will be

$$2 \times 0.166 \times 160 = 53 \text{ p.s.i.}$$

This 53 p.s.i. will then be the force to be applied at both syringes to overcome the back pressure in the 3 coils and the two mixers.

Such 20-ml. syringes, of 0.166 sq. in. cross section, will have a barrel length of 7.4 inches. A rate of 10 ml./sec. then translates into a linear movement of the plunger at $(7.4/2)$ inches/sec. or about 4 inches a second. A syringe of larger cross section would have a larger hydraulic factor, but also would require a slower movement of the plunger (see Table VI).

DRIVING PRESSURE FOR THREE SYRINGES

In our "slow reactor" system we have used a large syringe filled with dilute boric acid solution to quench our alkaline reaction system. Solutions A

and B (4N NaOH and sugar solution) are operated at a certain flow rate, R; the resultant flow rate in the reaction coil, from these two syringes, of sugar in 2N NaOH, is 2R. The flow rate of the boric acid, 0.5M concentration, is 10R. This tenfold flow rate gives a pH of about 10 to the quenched solution and also the addition of a large volume of cold acid to the hot alkaline solution provides a certain amount of "thermal quenching," a reduction in reaction rate through a lowering of temperature.

The addition of this dilute boric acid solution at a flow rate of 100 ml./sec. will create a large amount of back pressure. If we use the Bernoulli relation, $(\text{pressure})^2 = \text{flow rate}$, then increasing the flow rate for one mixer and two heating coils (Item C in Table V) from 37 to 100 ml., a factor of about 3, will mean an increase of 9 in the back pressure, from 160 to about 1500 p.s.i. However, we will not be using heating coils, but connecting Syringe C directly to the second mixer. So, based on the factor of 22% for a reaction coil (equivalent in dimensions to a heating coil) this back pressure should be less than 1000 p.s.i. The hydraulic factor, 0.89, will not be very helpful here. The actual driving pressure needed for the large syringe will have to be determined empirically after the hydraulic system is installed. (This was found to be about 200 p.s.i.)

LIMITATIONS OF THE FLOW REACTOR

Several factors limit the accuracy of the reactor and attempts are being made to anticipate them, or to make corrections for them.

The first is a "thermal pumping" caused by the lower density of water at higher temperatures. The increase in the volume of liquid in the heating coils at 170°C. will be about 11.5%, in comparison with the volume at room temperature.

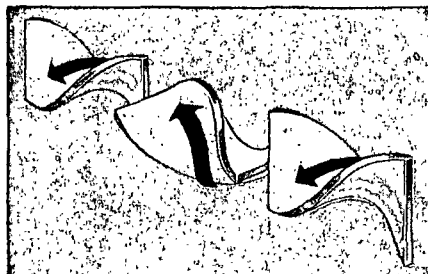
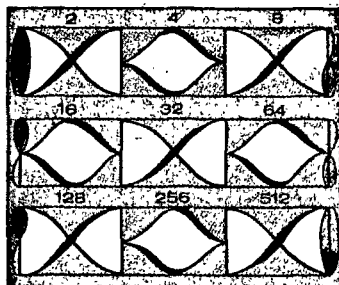
The operation of the flow reactor is based on pushing hot liquid out of the heating coils and through the reaction coil by displacing this hot liquid with cold liquid from the syringes. This cold liquid will start expanding as it moves into the heating coils, and therefore the rate of movement of the displaced liquid in the reaction coil will be greater than the rate of movement of liquid from the syringe. This increase will be accelerating during the reaction, so a spilling of the last part of the quenched sample should minimize the effect. A "diverter" rod has been connected to the 100-ml. syringe, which will mechanically misplace a funnel above the quenched solution during the last part of the syringe movement. This should divert the last part of the quenched solution into a separate receiver and provide a "cleaner" first portion. (See Fig. 4.)

A second factor is the problem of laminar and turbulent flow in the reaction coil. We do not know how serious wall effects, due to laminar flow, are, but have obtained a "static mixer" from the Kenics Corporation. This is a 5-inch length of 3/16-inch O.D. tubing, with internal elements to provide mixing and avoidance of laminar effects. The design of this tube is shown in Fig. 11. The performance of this tube, as a reaction coil, will be compared with an unpacked reaction coil of similar internal volume (0.96 ml.).

A third factor is the "dead time" of the apparatus. This is the extent of reaction, at a given temperature, for a reactor with a zero volume reaction coil. Essentially this means quenching the reaction solution immediately after mixing, and corresponds to zero reaction time. However, for very short reaction times and fast reaction rates, the volumes of the mixers and connections become important factors. As we go up in temperature to higher reaction rates, this dead time will become more appreciable, and will finally limit us in our studies.

how "STATIC MIXER" works

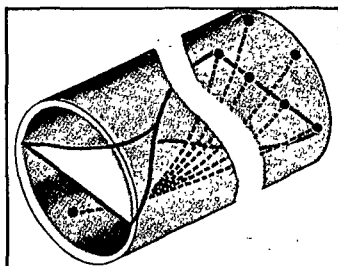
No parts of "STATIC MIXER" move. Components are mixed to any desired degree depending upon the selected number of bow-tie shaped blades or "Elements." Their configuration imparts four basic motions to the flowing material:



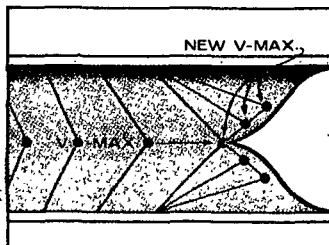
1. FLOW DIVISION — Each element divides material received from the preceding element. An exponential increase in division occurs — 2^n where "n" is the number of elements, i.e., 20 elements — one

million strata; 30 elements — one billion strata.

2. FLOW REVERSAL — The opposite twist of each succeeding element constantly reverses the circular direction of flow.



3. FLOW INVERSION — Material migrates from the center of the pipe to the outside walls and back — a full cycle occurs every ten elements.



4. BACK MIXING — This is obtained by a constant change in flow profile as the material moves through the pipe.

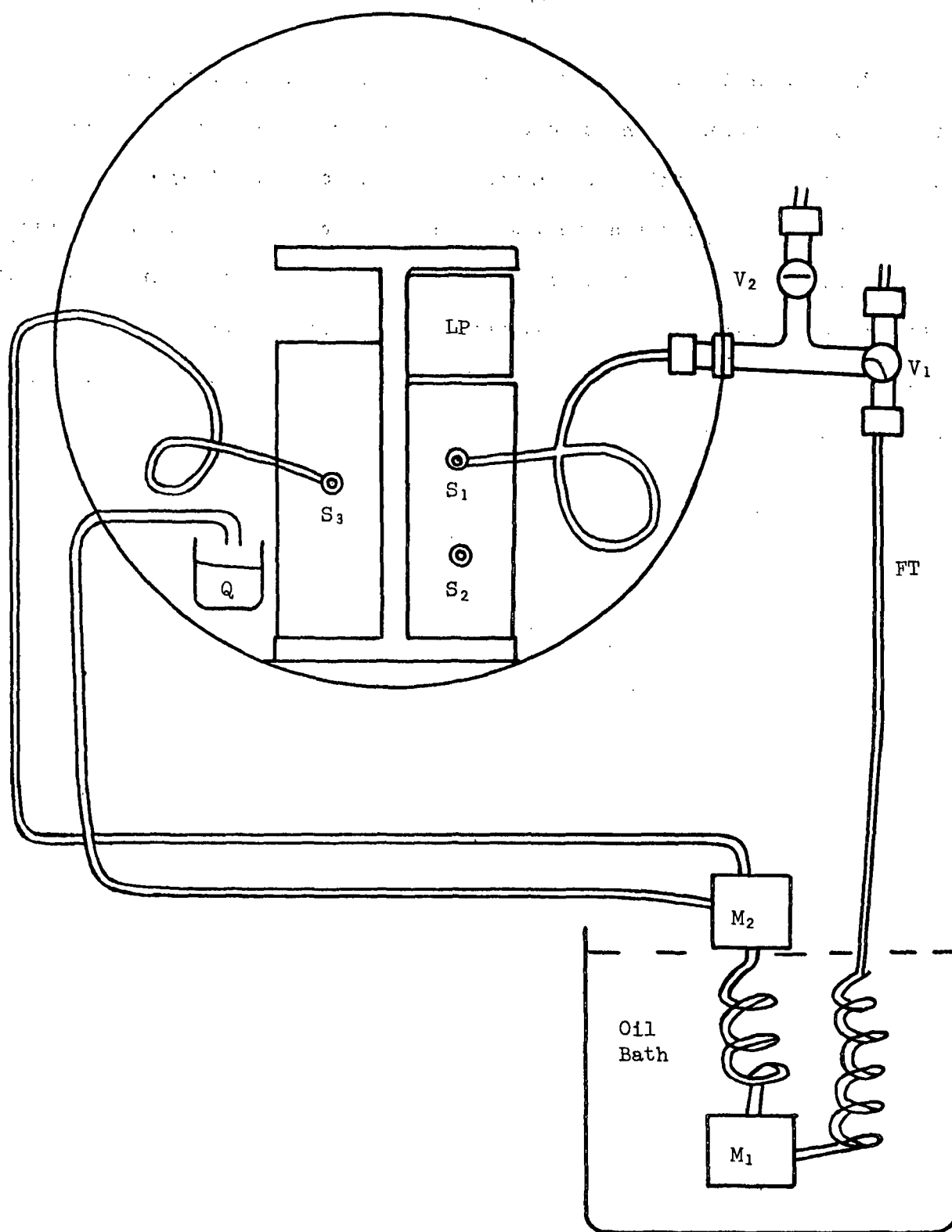
Velocity, pressure, and time have no influence upon degree of mix.

Figure 11. Details of Kenics Static Mixer

Thus, it can be seen in Table IV that we have to go to very small reaction coils, of the order of 0.1-ml. volume, for reaction times below 10 milliseconds. Here the dead time will become an appreciable factor. For a reaction coil of 1-ml. volume it will not be so important.

CONCLUSION

In Fig. 12 is given an end view of the pressure chamber, showing the connections of the three syringes to the flow reactor. The cold solutions are forced from the syringes into the reactor in the oil bath and then returned to the pressure chamber again, after quenching. Such an operation will be blind, with the syringes enclosed in the pressure chamber, containing a nitrogen atmosphere. The movements of the syringes will be followed by the recordings on the oscillograph. This will be the technique used to study the effect of alkali on carbohydrates at temperatures above 100°C.

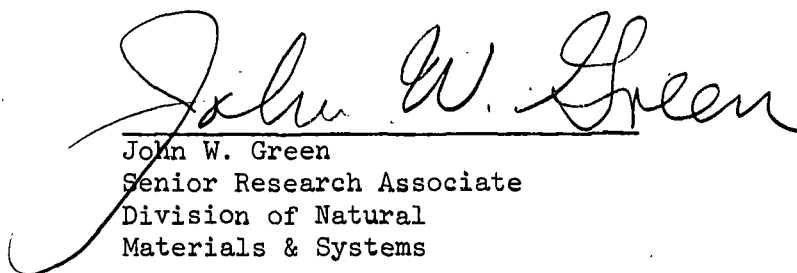


Note: Valve Connections to S_2 and S_3 are Omitted

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