KINETICS OF PROCESSING ASPHALTIC RESIDUES

By

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I. INTRODUCTION

In 1951 13,000,000 short tons of petroleum asphalt were produced in the United States at a value of 216 million dollars (19). Of this total 70 per cent was used for paving, 24 per cent for roofing and waterproofing and 6 per cent for specialty products as rubber, molding compounds and paints. These materials are processed by a variety of methods, one of the most important of which is by subjecting a residual stock to air at elevated temperatures. The processing of asphaltic residua obtained from the distillation of petroleum oils with oxygen containing gases at elevated temperatures is known as air blowing and has been practiced commercially for over sixty years (7).

According to the present practice the asphalt residuum is blown at about 450 to 575 °F. at a rate of 30 to 50 cubic feet of air per minute, per ton of asphalt, for a period of 5 to 12 hours in a suitable reactor vessel (1). Air blowing the residuum is carried out in either a batch or continuous operation. In a batch operation the asphalt is contacted with air by either blowing or sucking the air through the asphalt charge. In continuous blowing the stock is moved through one or more vessels in series each having a reaction zone. The finished asphalt is removed continuously and part of it can be recycled with fresh feed. The asphalt is reacted until the desired product consistency is obtained.

Asphalts as a class are non-aqueous colloidal systems of very high viscosity, which may have the character of either a sol or gel.

They consist principally of hydrocarbons and hydrocarbon derivatives and may contain groups of saturated aliphatics, naphthenics or cyclo-paraffins, aliphatics with olefinic double bonds and aromatics (16).

Exact knowledge of the chemical composition of asphalts is not known but there has been recognition of distinct constituent groups as asphaltous acids and anhydrides, asphaltenes, asphaltic resins, petroleum resins, petroleum oils, carbenes, carboids and inorganic material.

The resulting reaction of oxygen with asphalt residuum is generally called an oxidation process. Actually this term oxidation is a misnomer, because the reaction has been characterized as essentially: (a) the removal of a small amount of hydrogen to form water followed by condensation and polymerization of the hydrocarbons (13), (b) the addition of oxygen which forms unstable compounds from which water is eliminated leaving unsaturated compounds which polymerize (18), or (c) slow polymerization of the oils and resins to asphaltenes (9).

Air blowing of asphalts changes the physical properties of the residuum which results in increased hardness, gravity, softening point and lower ductility. The extent of these changes depend on the original asphalt and the processing and conditions to which it is subjected. The chemical and polymerization reactions which cause these effects are very complex and very little is known about the mechanism, stoichiometry or kinetics of the reaction. It is known that the air blowing process is an exothermic reaction (6) and that among the water and carbon dioxide that are eliminated are also oxygenated hydrocarbons, oil vapor and

mechanically entrained oil. In the work reported by Thurston and Knowles (18) on one asphalt, 68 per cent of the weight of the oxygen that was used reacted to form water and 14 per cent formed carbon dioxide. The remaining unaccounted for oxygen apparently formed other oxygenated compounds. Katz (13) found that oxygen and nitrogen are present in the products in very small amounts at Ring and Ball softening points up to 200 °F. and only to an extent of approximately 2 per cent in very high melting samples. Similar results (9) were also obtained for a different residuum where the oxygen content and the change in quantities of oils, resins and asphaltenes were determined for the air blowing process.

The literature on the air blowing of asphalt is very limited outside of the references given by Abraham (1) on patents. A series of articles by Holland (11) and more recently a staff article by Hoiberg (10) constitute about the only detailed discussions on the asphalt blowing process from a manufacturer's view point. Blakely, et al. (5) have reported the effect of agitation on air blowing Venezuelan and Mexican asphalts on a pilot plant scale.

Because of the complex nature of the reactants and reaction mechanism for the air blowing process, the degree of reaction is generally described by some physical property of the residuum. The rate of change of this property in turn is a function of several process variables as the type of asphalt residuum, volume of the reactor, feed gas flow rate, temperature, degree of agitation and oxygen content in the feed gas. There is no suitable pilot plant or laboratory data presently available to correlate and relate the preceeding process variables for design

considerations of commercial asphalt blowing units. Therefore, it is the object of this investigation to present principles that may serve as the basis for design and operation of commercial asphalt blowing equipment. These principles include: (a) kinetic equations and evaluation of reaction rate constants, (b) reaction mechanism including kinetic order and oxygen utilization, (c) scale up procedures from pilot plant equipment to industrial processing equipment.

II. THEORY

A. The Asphalt Blowing Reaction

The gross chemical reaction for the asphalt blowing process might be described as follows:

$$A_r + O_2 + \text{inerts} \longrightarrow A_{ox} + L_x + CO_2 + H_2O + O_2 + \text{inerts} + \Delta H$$

where

A_r = the asphalt charge stock

A_{ox} = the composite air blown asphalt product not removed from the reacting zone

L_x = the composite condensed product removed overhead minus CO_2, H_2O and other fixed gases

ΔH = the heat of reaction

To arrive at this gross reaction, the actual mechanism could consist of a series of progressive reactions described in the following diagram:

$$A_r + O_2 \longrightarrow A_{o_1} + O_2 \longrightarrow A_{o_2} + O_2 \longrightarrow A_{o_x} + \Sigma CO_2 + \Sigma H_2O + \ldots$$
$$\searrow L_1 \qquad \searrow L_2 \qquad \searrow L_3 \longrightarrow L_x$$

Each step of this progressive reaction probably yields oxygenated compounds of unknown and complex composition, some of which remain in the blown asphalt and some appear as overhead products as designated by L. The residual material is dehydrogenated and decarbonized as shown by the appearance of H_2O and CO_2. Polymerization also occurs to produce a product with an increase in viscosity as evidenced by the increase in Ring and Ball softening point. No information is available on the exact chemical reactions occuring either as the above gross reaction

or as the progressive reaction. It is necessary, therefore, to study the degree of chemical reaction in terms of a change in a physical property of the system as suggested by Frost and Pearson (8). For this study the physical property is determined as the Ring and Ball softening point by the A. S. T. M. method D 36-26 (4) to evaluate the gross reaction from A_r to A_{ox}.

B. Heterogeneous Reactions

Gas-liquid reactions may be typified as a gas-absorption operation in which a chemical reaction occurs. The actual reaction may occur at the interface separating the gas and liquid phase or in either the gas or liquid films adjacent to the interface. In either case, a problem of mass transfer of reacting materials from one phase to another phase or to the interface is involved. The net rate of reaction is then determined by the rate of chemical reaction itself and by the rates of mass transfer of reacting materials (12).

Rates of gas absorption accompanied by chemical reaction in the liquid have been calculated kinetically for certain simple cases, for example, the absorption of carbon dioxide with ethanolamine. No estimates have been made for cases involving second order chemical kinetics. The differential equations involving transient accumulations, diffusions and reaction are known, but the mathematical solutions are too involved for practical solutions. Perry and Pigford (15) used a digital computer to calculate the solutions of a number of theoretical second order cases. The results were represented as the ratio of the local mass transfer

coefficient with reaction to the mass transfer without reaction. These results were found to depend on the rate and chemical equilibrium constants, the ratio of reactants and the time exposure of the liquid surface. Sherwood and Pigford (17) present a more general treatment for the process of simultaneous absorption and chemical reaction.

The process of blowing asphalt residuum can be classified as a heterogeneous and exothermic reaction of a liquid phase and a gas phase. It is a flow system where the active agent in the gaseous phase (oxygen) reacts with the liquid asphalt to form asphalt products of increasing consistency. A consideration of the physical system in the asphalt blowing process leads to a concept of two possible controlling mechanisms or a combination of both. As the feed gas is exposed to the liquid asphalt, the chemical reaction may occur at the interface of the gas-liquid or in the gas or liquid films adjacent to the interface. If the chemical reaction takes place very rapidly at the gas-liquid interface, it then becomes necessary to replace the oxygen used from the film with fresh oxygen for the process to continue. This fresh oxygen must diffuse from inside a gas bubble, through the gas film to the interface where the reaction is occurring. When this diffusion rate is slow compared to the chemical reaction rate, the diffusion resistance will control the gross rate of reaction. Conversely, if the chemical reaction rate at the interface is slow relative to diffusion, then the chemical reaction is the controlling rate. The effect on the gross reaction rate for a combination of the diffusion and chemical reaction mechanism might be expressed as

$$\text{gross reaction rate} = \frac{\text{driving potential}}{\text{diffusion resistance} + \text{chemical resistance}}$$

Considering the possible progressive type of reaction and physical system involved, it is conceivable that the diffusion resistance might control for some of the steps while the chemical resistance might control for other steps.

The gross reaction rate is the degree of chemical reaction with time and is measured as the change of Ring and Ball softening point with reaction time. The driving potential for the gross reaction is assumed to be a combination diffusion and chemical reaction driving force. The driving force for the diffusion mechanism is the difference of partial pressure of the oxygen in the gas bubble and at the gas-liquid interface. The driving force for the chemical reaction is the concentration of reacting materials. Assuming the driving potential to be a combination of diffusion and chemical reaction, the resistance for the gross reaction rate will also be a function of these two mechanisms.

A general rate equation might be derived to relate the processing variables in terms of a gross reaction rate. This equation is

$$dR/dt = kP^{p}S^{s}R^{r} \qquad (1)$$

where

dR/dt = the gross reaction rate measured as Ring and Ball softening point

The diffusion driving force is $P^{p}S^{s}$ which is the oxygen concentration and space gas velocity for the feed gas. The asphalt concentration term is related to the instantaneous value of softening point, R, at any time, t. The value, k, is a pseudo reaction velocity constant and is a function of the gross reaction rate resistance. The value of k also includes

a factor that accounts for a decrease in driving potential as the reaction proceeds. The data for this investigation was evaluated in terms of this proposed rate equation.

III. MATERIALS

The asphaltic residues used in this investigation were supplied through the courtesy of The Texas Company. The samples represent four different types of asphalts having substantially different properties. The properties of the residues used in this study are tabulated in Table 1.

TABLE 1

PROPERTIES OF ASPHALTIC RESIDUES

Sample	TA-1023-2	TA-1024	TA-1025	TA-1026
Identification	Gulf Coast Naphthenic	East Texas	East Central Texas	South Texas Heavy
Density @ 60 °F.	0.9670	1.0215	1.0203	0.9908
Viscosity, Saybolt Fural Seconds, 210 °F.	106	....	....	85
Ring and Ball Softening Point, °F.	70*	100	98	73*
Penetration, 77 °F.	....	227	283	....

*Estimated by extrapolating values of Ring and Ball versus reaction time curves to zero time.

IV. APPARATUS

The asphalt blowing unit was designed and constructed to blow asphalt in either a continuous or a batch operation. The asphalt apparatus consists of an asphalt storage tank, asphalt reactor, electrical precipitator, flow panel board, temperature panel board and a continuous gas analysis unit. A picture of the unit is shown in Figure 1 and a flow diagram in Figure 21. Complete piping and wiring diagrams are shown in Figures 22 and 23.

A. Processing Equipment

1. Asphalt storage tank. The asphalt storage tank is a heated tank used to store and preheat the asphalt reactor feed. Circulation is maintained in the storage tank by pumping the asphalt through a closed piping system.

The storage tank shell was fabricated from a piece of 12 inch steel pipe and fitted with ring flanges on both ends. A flanged dished bottom with a centered 3/4 inch outlet drain was bolted to the lower shell flange. A round 1/4 inch transite cover was fastened to the top shell flange.

The tank is heated with eight 500 watt electrical strip heaters bolted to the outside shell. They are alternated one long and one short. The dished bottom is heated with a 1,000 watt ring heater. The heaters are wired in parallel and connected to a three-heat snap switch. High heat position on the switch utilizes the long, short and bottom heaters. Medium heat uses only the short and bottom heaters. Low heat turns on

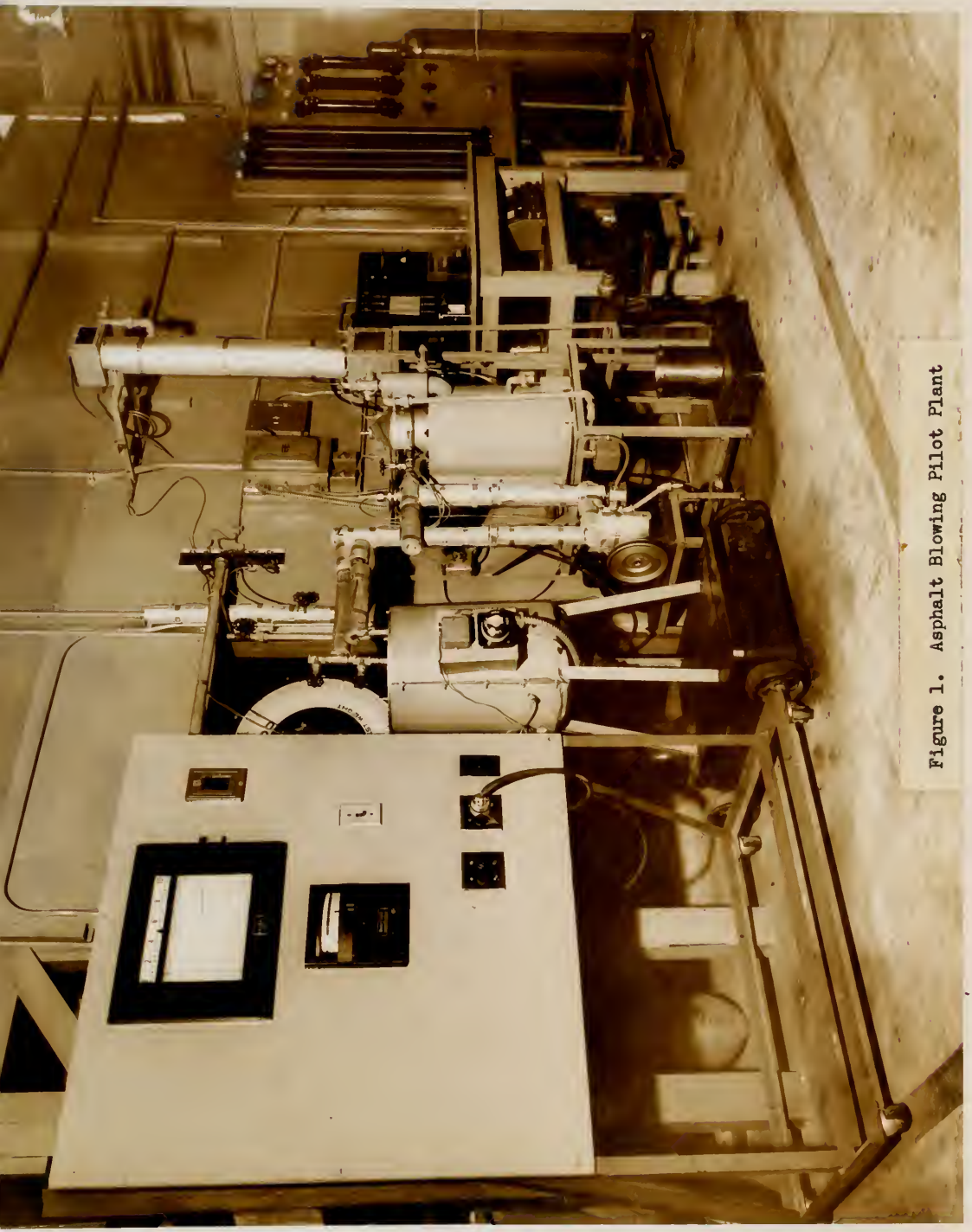

Figure 1. Asphalt Blowing Pilot Plant

only the bottom heater. The heaters were selected and arranged in this manner to permit changing the heated length of the storage tank as determined by the height of the liquid asphalt in the tank. A General Electric Thermostat is used to control the temperature of the asphalt in the tank and directly controls the electrical line load to the heaters. Thermostat and thermocouple protection tubes were made from steel pipe and welded in the side of the reactor shell. The tank was insulated on the side and bottom surfaces with block magnesia insulation and then covered with a sheet metal protective cover. The entire assembly was mounted on four angle iron legs. It was then placed on a Toledo platform scale. The scale is used to measure mass feed rates of the asphalt to the reactor.

The hot asphalt in the storage tank is circulated and transferred to the asphalt reactor with a Viking pump. This is a positive displacement gear type pump which is mounted on the floor below and to the side of the asphalt storage tank. Asphalt is pumped from the storage tank with a free suspension suction pipe that is inserted into the storage tank through the transite cover and extends close to the bottom. The recirculation return pipe is also freely suspended and discharges asphalt near the top of the tank. An auxiliary three-heat immersion heater, thermostat control and thermocouple are placed in the recirculation line to indicate and prevent any appreciable temperature drop in the asphalt while it is being recirculated and adjusted to the reactor asphalt temperature. The recirculation piping is steam traced with 1/4 inch copper tubing and the asphalt recirculation lines are preheated to prevent any asphalt freeze-up during initial recirculation. Drain valves are suitably located to

completely drain the recirculation lines. A detail of the asphalt storage tank is shown in Figure 24.

2. Asphalt reactor. The asphalt reactor is a heated and agitated tank which permits blowing reacting gas through the hot asphalt. It is possible to blow the asphalt as a batch operation with no fresh asphalt feed or as a continuous operation where fresh asphalt feed is pumped in and asphalt product continuously removed. The reacting asphalt occupies only 60 per cent of the total reactor volume. The remaining 40 per cent is used as a vapor space for entrainment separation.

The asphalt reactor was made from a piece of 8 inch steel pipe that was flanged on both top and bottom. The bottom is fitted with a dished plate with a 3/4 inch center drain pipe. The top 1/4 inch steel plate cover is used to support the agitator assembly, thermocouple protection tubes, asphalt feed line and entrainment baffle plate. The reactor has welded pipe fittings for the reactor gas feed, converter gas product and reacted asphalt product.

The reactor is heated with five 500 watt strip heaters equally spaced and bolted to the outside surface of the reactor pipe. The lengths of the heaters were selected so that they would provide heat directly to the height of the reactor pipe that would be filled with liquid asphalt. This prevents localized heating in the vapor section and reduces the amount of coke formed on the reactor walls. The temperature of the reacting asphalt is controlled with a Minneapolis-Honeywell-Brown Pyr-O-Vane proportional temperature controller.

The agitator assembly for the asphalt reactor is a laboratory model Turbo Mixer Agitator. The combination used for this investigation was a hooded ring cover and aerator impeller. The hooded ring is supported from the top cover of the reactor by two guide rods. The impeller is located 4 inches from the bottom of the reactor and is fastened to a shaft that extends through the top cover and packing gland into the agitator head and pulley assembly. The agitator pulley is a four step cone pulley and is matched with a similar pulley on the 3/4 horsepower 1750 r.p.m. agitator drive motor. This pulley arrangement permits variable agitator speeds with a V-belt drive. The minimum agitator speed is 700 r.p.m. and the next speed is 1300 r.p.m..

Thermocouple protection tubes were made from 1/8 inch steel pipe and were threaded into welded couplings on the top reactor cover plate. There are three thermocouple tubes; one for the Minneapolis-Honeywell-Brown reactor temperature controller and two for the Bristol temperature recorder. The last two were fabricated with a differential height of 1 inch so that they could be used to indicate asphalt liquid level in the reactor. The long thermocouple indicates the liquid temperature while the short thermocouple indicates the vapor temperature. Since the gas temperature is several degrees lower than the liquid temperature, a differential reading between the two thermocouples indicates that the liquid level is between these two thermocouple positions.

The asphalt feed line extends through the top of the reactor cover and through the edge of the agitator hood ring. The feed line was reduced to 1/4 inch nominal pipe inside the reactor to prevent any excessive

asphalt feed holdup. The bottom of the asphalt feed line is flush with the bottom of the agitator hood ring. Thus the asphalt is fed directly into the side of the rotating aerator impeller. A needle valve on the asphalt storage recirculation line controls the asphalt feed to the reactor and a thermocouple measures the asphalt feed temperature.

Reactor feed gas is introduced beneath and into the aerator impeller through a T-tube sparger. The feed gas line comes into the reactor in a 3/8 inch pipe directly above the bottom reactor flange. This pipe extends into the reactor and then branches into a horizontal "T" directly under the impeller. Two 1/8 inch vertical pipe tips are located on the end of this "T" at a distance of 1/2 the radius of the aerator impeller. The feed gas line to the reactor is piped as an inverted "U" stand pipe to prevent any asphalt from flowing through the distributor tips back into the air feed line.

The reacted gas or converter gas is removed from the reactor through a 1-1/2 inch pipe located directly beneath the top reactor flange. The exit gases from the reactor first pass over an entrainment separator baffle plate that is fitted below the converter gas outlet. This baffle plate prevents swirling of the hot asphalt by agitation into the converter gas outlet pipe. The baffle plate is fastened to the bottom side of the top reactor cover. After leaving the reactor, the converter gases pass through a short heat exchanger before entering the electrical precipitator. This heat exchanger or cooler is used to help break any foam that may form in the reactor and flow up into the converter gas discharge pipe. The cooler is a 3 inch steel pipe that is welded around the 1-1/2 inch converter gas

outlet pipe. The annular area between the pipes is fitted with 1/2 inch pipe fittings for inlet and outlet cooling water. A thermocouple at the top of the converter gas cooler measures the exit reactor converter gas temperature.

During a batch or continuous run the reactor asphalt product or asphalt samples are removed from the reactor through the 3/8 inch pipe reactor side drain. This drain is located beneath the converter gas outlet line and has a quick-opening valve.

The reactor shell is insulated with asbestos insulation and enclosed in a protective sheet metal cover. The top and bottom of the reactor are not insulated. These surfaces were purposely left uncovered so that the exothermic heat of reaction of the reacting asphalts would be dissipated. Closer temperature control can be obtained when this heat is dissipated and the temperature controller and reactor heaters are used to maintain the desired temperature.

The reactor and agitator drive motor are arranged on a special stand. The length of the asphalt piping from the asphalt storage tank is as short as possible to reduce the amount of asphalt in the recirculation lines. Details of the asphalt reactor are shown in Figure 25.

3. Electrical precipitator. The purpose of the electrical or Cottrell electrostatic precipitator is to remove the mechanically entrained mist and smoke from the reactor converter gases.

The precipitator unit was fabricated from a piece of 3 inch steel pipe and welded to inlet and outlet gas chambers. A round 1/8 inch steel rod is used as a high voltage electrode with a steel ball welded

to the bottom of the electrode. The entire assembly is supported by a high voltage insulator bushing and the insulator bushing is mounted on a 1/4 inch Bakelite plate which serves as the top of the outlet gas chamber. A baffle plate is placed over the inlet feed gas line in the bottom gas chamber to prevent the gas from impinging directly on the high voltage electrode. A drain on the bottom gas chamber permits removal of the condensed and precipitated smoke and fog products.

Access panels on the front of the gas chambers are provided to allow alignment of the high voltage electrode and cleaning of the precipitator. The panels are covered with Lucite plastic windows and it is possible to observe the smoke content of the converter gas entering and leaving the precipitator.

The precipitator pipe shell is wrapped with 1/4 inch copper tubing on a 2 inch coil spacing. Cooling water passes through the tubing. As a result water condenses out of the converter gas as it cools in the precipitator. The condensed water is collected through the bottom drain together with the precipitated oils. The cooled converter gases from the precipitator pass through another heat exchanger to lower the temperature of the gases below room temperature and to prevent any condensation from occurring in the gas rotameters. The electrical precipitator after-cooler is a coil of 1/4 inch copper tubing placed inside a piece of 3 inch steel pipe 12 inches in length. The converter gases pass across the water cooled copper coil and the condensed water is removed from a bottom drain on the cooler. Both the electrical precipitator and after-cooler are insulated with air cell asbestos pipe insulation.

The laboratory model high tension rectifier used to obtain the

high voltages necessary for the electrical precipitator is a Carpco Engineering Company Model RL High Voltage Rectifier. This rectifier unit permits variable direct current output voltages from 0 to 40,000 volts. The current output is variable from 0.1 to 15.0 milliamperes. Figure 26 is a detail of the electrical precipitator and Figure 2 is a picture of the storage tank, reactor and electrical precipitator.

4. Flow panel board. All the instruments necessary to control and meter the gas flows in the asphalt blowing process are grouped together on the gas flow panel board.

Three rotameters measure the air feed, oxygen feed and converter gas flow rates. The air feed and converter gas rotameters are standard Schutte and Koerting 3F tubes with millimeter scales. The rotameters are calibrated with specially made aluminum floats for the gas flow rates required in this study. The oxygen feed rotameter is a standard Schutte and Koerting 1R tube and stainless steel float. Gas flow control for the metered feed gases is obtained by using bronze needle valves. Gas pressures in the asphalt reacting system are measured by using panel mounted, well type manometers. The feed gas manometers measure the pressure drop across the gas rotameters. These indicated pressures are also the reactor gas pressures. The feed gas manometer indicates the pressure of the reactor feed gas; the converter gas manometer measures the pressure of the gas in the reactor vapor space or back pressure in the reactor. For constant feed gas flow rates the feed gas pressure changes with any change in the reactor asphalt liquid level height. Therefore, during continuous operation this feed gas manometer is used to control the asphalt product rate and to

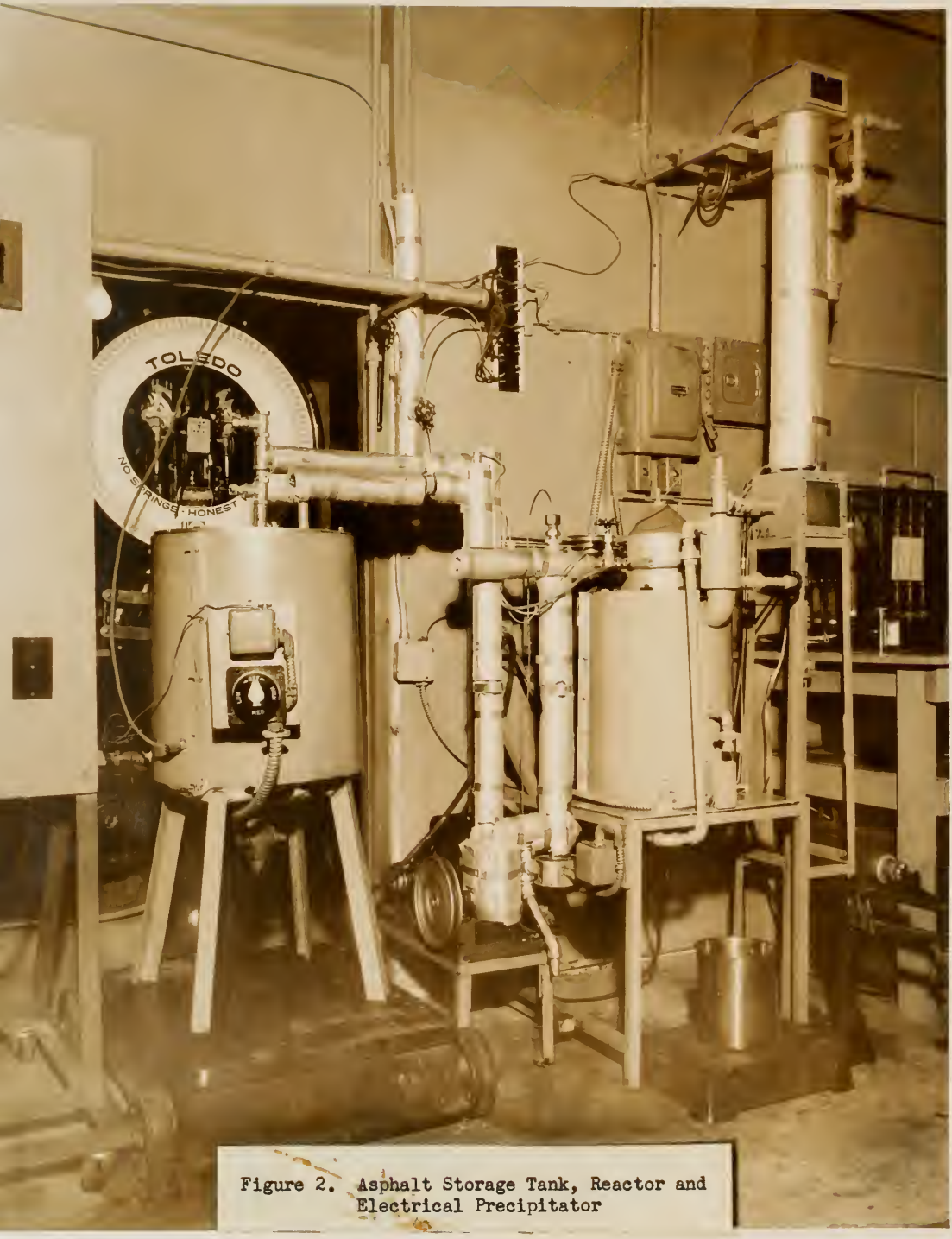

Figure 2. Asphalt Storage Tank, Reactor and Electrical Precipitator

maintain a constant asphalt reactor liquid level height. The converter gas back pressure is controlled by the depth of immersion of the converter gas stand pipe in a tank of water. A slight back pressure is required to allow for pressure drop of the sample gas through the gas analysis unit. The magnitude of this back pressure is about 5 inches of water.

The back pressure regulator that is used is a small tank mounted on tripod legs and provided with an overflow line to a drain. A constant water liquid level is maintained in the tank by running the cooling water used in the copper coil heat exchangers into the back pressure tank and letting the water drain out through the overflow pipe. To prevent excessive bubbling in the back pressure tank for high converter gas rates a by-pass needle valve is piped into the exit converter gas line so that only a small portion of the converter gas passes through the dip leg.

The inlet air feed line is fitted with a pressure reducing valve and sediment separator. The air then passes through a Tel-Tale silica gel dryer before it is metered to the reactor. The dryer column is a piece of 3 inch by 36 inch Pyrex glass pipe.

The entire assembly of rotameters, manometers, control valves and dryers are mounted on a movable panel board. A picture of the panel board is shown in Figure 3.

5. Temperature panel board. The asphalt blowing temperature recorder and temperature controller are located on the temperature panel board.

Chromel-alumel thermocouples are used to measure all process stream temperatures in the asphalt blowing system. The thermocouples

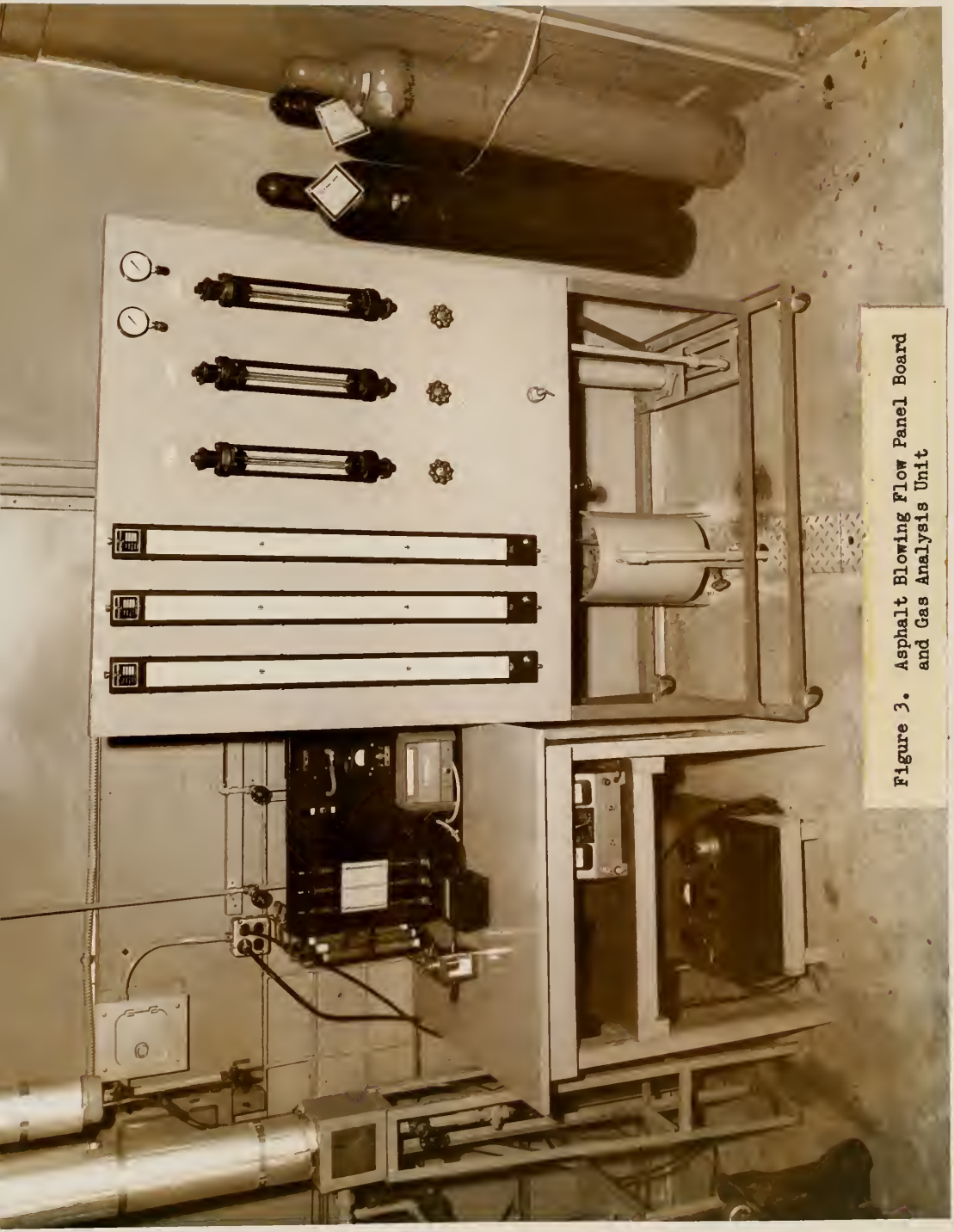

Figure 3. Asphalt Blowing Flow Panel Board and Gas Analysis Unit

are mounted in protection tubes and these units are incorporated in the process piping. Temperatures are recorded with a Bristol Dynamaster 12 point Pyrometer using 10 points as indicated on the diagram in Figure 22.

The temperature controller that is used for the asphalt reactor is a Minneapolis-Honeywell-Brown Pulse Pyr-O-Vane Controller. This is a time-proportioning-indicating type controller that eliminates any temperature cycling or "hunting" effects. The wiring on the temperature controller is such that the controlled output goes through both 110 volt and 220 volt outlets. The 220 volt outlet is used in this investigation to control the reactor heaters. Two other outlets for continuous 110 and 220 volts are also provided on the panel board.

The temperature recorder, controller, outlets and circuit breakers are mounted on a movable panel similar to the gas flow panel board. A picture of the temperature panel board is shown in Figure 1.

6. Piping. The majority of the equipment piping is 1/2 inch steel pipe. Larger 3/4 inch pipe is used for the converter gas lines, the asphalt drains on the asphalt storage tank and the asphalt reactor. Gas cock valves are used for the asphalt piping while globe and needle valves are used for the asphalt blowing gas piping. All hot asphalt lines are insulated with air cell asbestos insulation. A piping diagram is shown in Figure 22.

B. Analysis Equipment

1. Gas analysis unit. The gas analysis unit provides a continuous volume analysis of oxygen and carbon dioxide of either the asphalt blowing feed gas or converter gas. Dew points of these gases may also be determined.

The analysis cells for the gas train are as follows: (a) Beckman Oxygen Analyzer - Model C, 0-100 per cent Oxygen; (b) Gow-Mac Thermal Conductivity Cell for Carbon Dioxide; (c) Pittsburgh Electrodryer Dew Point Apparatus. The Beckman analyzer gives volume percentage oxygen as a direct reading while the output of the thermal conductivity cell is measured in millivolts.

In the gas analysis train the continuous gas sample for the oxygen and carbon dioxide analysis cells is first dried by passing the gas through a tube of Tel-Tale silica gel. Then the total flow rate is measured with a rotameter. The sample gas is now divided into two streams and the flow rate for each stream is determined with two additional rotameters. One gas stream is for the oxygen analyzer and the other stream is for the carbon dioxide analysis cell. Constant gas flow rates are maintained to the analysis cells to prevent the introduction of an analysis error because of the effect of a change in gas velocity in the analysis cells. The feed gas line and converter gas line have separate sample lines and dryer tubes. After the sample gas passes through the dryer tube it flows into a common header and then to the rotameter measuring the total gas flow. With the two sample lines it is possible to select either the feed gas or the converter gas for analysis. Only one gas can be analyzed at any particular time.

A constant 6 volt direct current source for the thermal conductivity cell is provided with a small Mallory power supply. The thermal conductivity cell output is measured with a Weston direct current millivoltmeter. The Electrodryer dew point apparatus is a rectangular metal box fitted with a removable polished hollow cylinder cup which screws into the top of the box. A window in the front of the box is used for observing the surface of the cylinder. The hollow cylinder is filled with a liquid so that the temperature of the cylinder may be lowered by cooling the liquid. The dew point of a sample gas is obtained by impinging the gas on the liquid cooled cylinder and recording the liquid temperature at the first appearance of fog or mist on the polished surface of the cylinder. The hollow cylinder may be cooled with a mixture of acetone and dry ice for extremely low dew points or water and ice for higher dew points. Dew point temperatures are measured with an alcohol thermometer and dew points can be made on either the asphalt feed gas or the converter gas. A flow diagram and picture of the analysis unit may be seen in Figures 21 and 3.

2. Gas analysis calibration. The thermal conductivity cell and oxygen analyzer are calibrated for a ternary system of dry gases; oxygen, nitrogen and carbon dioxide. The range of the calibration is 0-40 per cent carbon dioxide in a residual gas of nitrogen and oxygen, 0-100 per cent oxygen.

The instruments were calibrated by measuring the thermal conductivity cell output and reading the Beckman oxygen analyzer for known mixtures of the ternary gas system. The individual gases were metered from

gas cylinders using a pressure reducing valve and rotameter for each gas stream. After the flow rate for each gas stream was determined, the individual gases were mixed together to form the gas sample for the instrument calibration. The analysis of this sample gas was determined with the use of an Orsat analyzer that determines the concentration of carbon dioxide. The concentration of oxygen was determined through the use of the Beckman oxygen analyzer and the concentration of nitrogen was calculated by subtracting the oxygen and carbon dioxide concentration from 100. The sample gas flow rates for the analysis instruments were maintained at about 900 cc./minute for the thermal conductivity cell and 125 cc./minute for the oxygen analyzer. Excess sample gas was exhausted to the atmosphere. The output of the thermal conductivity cell was measured as millivolts and the reference point for this unit was zero millivolts for dry air.

Table 2 is a tabulation of the calibration data for the oxygen analyzer and thermal conductivity cell. Figure 4 is a plot of the ternary calibration data as a function of thermal conductivity cell millivolt readings and oxygen concentration with parameters of volume per cent carbon dioxide.

TABLE 2

CALIBRATION DATA FOR GAS ANALYSIS INSTRUMENTS

Run No.	Gas Concentration Volume %			Thermal Conductivity Cell Millivolts	Beckman Oxygen Analyzer %
	O_2*	CO_2	N_2		
1	20.9	....	79.1	0.0	20.9
2	40.7	....	59.3	-11.7	40.7
3	61.0	....	39.0	-20.6	61.0
4	81.4	21.0	18.6	-28.0	81.4
5	90.0	....	10.0	-30.7	90.0
6	100.0	....	....	-34.0	100.0
7	69.8	....	30.2	-24.2	69.8
8	49.9	....	50.1	-16.0	49.9
9	30.5	....	69.5	- 6.3	30.5
10	9.9	....	90.1	2.8	9.9
11	10.0	10.6	79.4	23.9	10.0
12	10.0	15.0	75.0	33.2	10.0
13	10.1	27.5	62.4	59.2	10.1
14	10.0	34.2	55.8	74.2	10.0
15	9.9	40.6	49.5	88.5	9.9
16	10.1	6.0	83.9	15.1	10.1
17	19.9	....	80.1	- 1.6	19.9
18	20.9	....	79.1	0.3	20.9
19	20.9	....	79.1	0.0	20.9
20	20.1	....	79.9	- 1.9	20.1
21	19.9	10.0	70.1	17.8	19.9
22	20.0	17.1	62.9	31.8	20.0
23	20.0	36.9	43.1	72.8	20.0
24	20.0	47.1	32.9	93.0	20.0
25	20.0	26.8	53.2	51.1	20.0
26	20.0	4.8	75.2	6.4	20.0
27	....	....	100.0	7.1	....
28	30.0	....	70.0	- 6.3	30.0
29	30.0	9.1	60.9	9.8	30.0
30	30.0	25.5	44.5	44.3	30.0
31	30.0	37.2	32.8	69.8	30.0
32	30.0	47.0	23.0	88.6	30.0
33	30.0	30.8	39.2	55.8	30.0
34	30.0	15.1	54.9	23.0	30.0
35	....	....	100.0	7.2	....
36	....	....	100.0	7.1	....
37	....	42.8	57.2	97.0	....
38	40.0	12.9	47.1	13.5	40.0

TABLE 2--Continued

Run No.	Gas Concentration Volume %			Thermal Conductivity Cell Millivolts	Beckman Oxygen Analyzer %
	O_2*	CO_2	N_2		
39	39.9	....	60.1	-11.8	39.9
40	40.0	26.1	33.9	41.0	40.0
41	40.0	35.8	24.2	61.8	40.0
42	40.0	46.7	13.3	85.2	40.0
43	40.0	17.2	42.8	23.0	40.0
44	40.0	6.1	53.9	0.6	40.0
45	50.0	....	50.0	-16.2	50.0
46	50.0	18.1	31.9	20.2	50.0
47	50.0	28.0	22.0	41.7	50.0
48	50.0	49.7	0.3	89.0	50.0
49	50.0	39.5	10.5	66.2	50.0
50	50.0	7.6	42.4	- 1.3	50.0
51	60.0	....	40.0	-19.8	60.0
52	60.0	12.8	27.2	5.2	60.0
53	60.0	20.2	19.8	21.0	60.0
54	60.0	31.4	8.6	44.2	60.0
55	10.0	41.0	44.0	86.5	10.0
56	....	....	100.0	7.0	....
57	70.1	....	100.0	-24.0	70.1
58	70.0	8.1	21.9	- 7.4	70.0
59	70.0	15.0	15.0	5.8	70.0
60	70.1	20.9	9.0	18.0	70.1
61	80.1	....	19.9	-28.0	80.1
62	80.0	10.7	9.3	- 6.1	80.0
63	30.0	....	70.0	- 6.2	30.0
64	30.0	14.1	55.9	21.0	30.0
65	30.0	31.1	38.9	56.7	30.0
66	30.1	41.4	28.5	77.7	30.1
67	10.1	45.0	44.9	93.8	10.1
68	10.0	30.4	69.6	64.3	10.0
69	20.9	....	79.1	....	20.9
70	....	....	100.0	....	0.0
71	100.0	....	....	....	100.5

*Beckman oxygen analysis for runs 1-68.

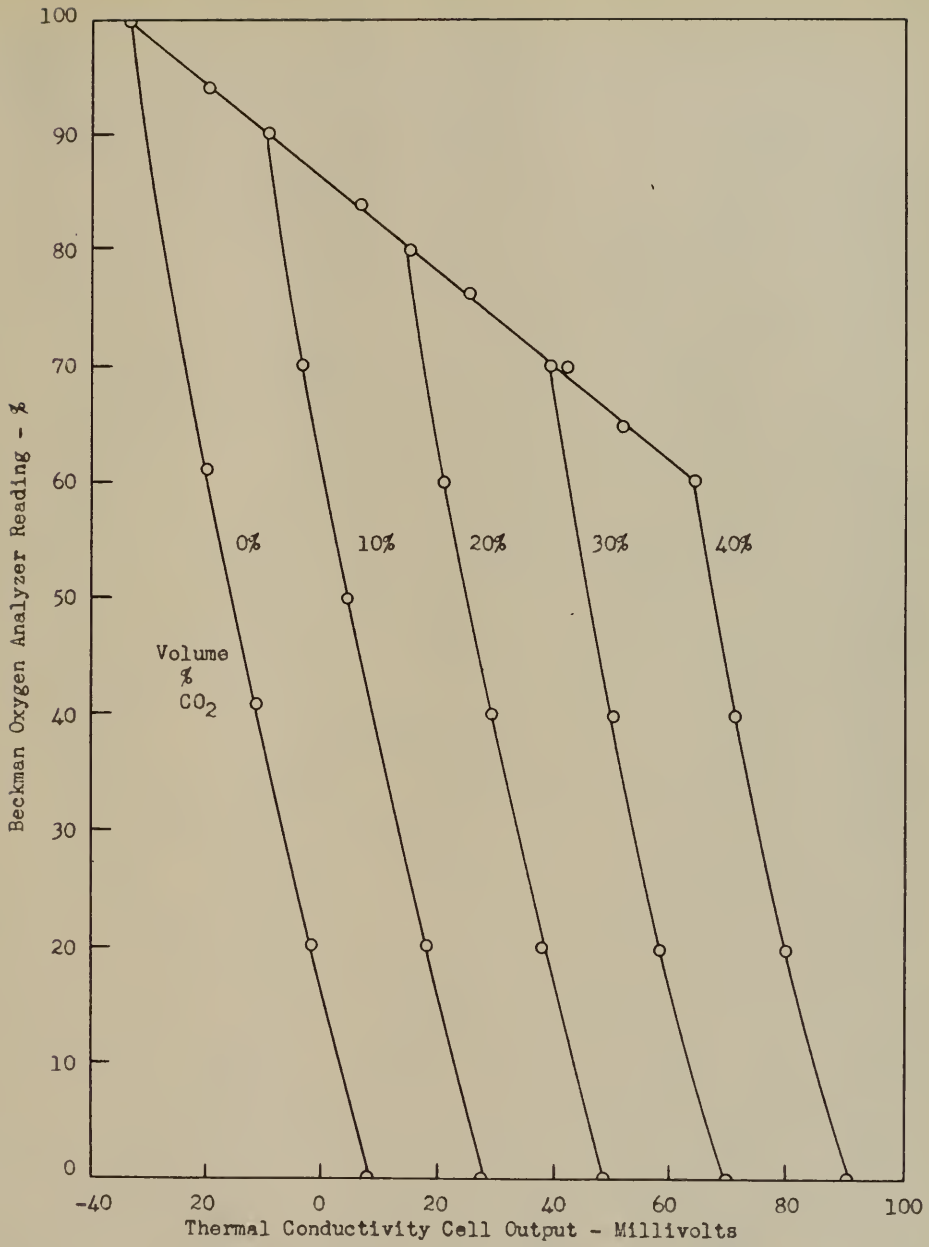

Figure 4. Thermal Conductivity Cell Calibration Curve for Ternary System of Oxygen, Nitrogen and Carbon Dioxide

V. PROCEDURES

The following is an outline of the conditions and procedures that are used to operate the asphalt blowing equipment. The method is applicable to either continuous or batch operation, with the exception that during the continuous operation a constant asphalt feed is fed to the reactor and a product is continuously removed.

The five variables under consideration in this investigation are temperature, feed gas space velocity, feed gas oxygen concentration, agitator speed and continuous or batch operation. The effect of these variables were determined by making runs at essentially atmospheric pressure and fixing all but one variable. A total of 39 runs was made under the following conditions to determine the overall effect of the variables on each other. The extent to which the conditions were changed for any of the materials under consideration is shown in Table 3.

TABLE 3

ASPHALT PROCESSING CONDITIONS

Material	TA-1023-2	TA-1024	TA-1025	TA-1026
Temperature ^{o}F.	450-550	500	500	500
Air Space Velocity CFMT	25-200	25-100	25-100	25-100
Oxygen Concentration Per Cent	21-50	21-50	21-50	21-50
Agitator R.P.M.	700-1300*	700	700	700

*25CFM, 21% and 50% oxygen, 500 ^{o}F. only.

A. Operating Procedure

The operating procedure for the asphalt blowing apparatus is composed of the following steps: (a) heating a charge of asphalt in the reactor, (b) blowing with a feed gas, (c) measuring the gas flow rates, (d) recording the gas analysis, (e) taking asphalt product samples.

The first step in the start of the asphalt blowing unit is to heat a charge of residuum to a temperature of 475-500 °F. in the asphalt storage tank. To charge the storage tank, the asphalt suction and recirculation return lines are removed and the transite cover taken off. After the storage tank is charged with asphalt, the cover and pipes are replaced and the asphalt storage heaters turned on by turning the three-heat switch to the high position. While the asphalt charge is being warmed in the tank, the asphalt circulation line is preheated by turning on the steam to the copper tubing trace line. When the temperature of the asphalt in the storage tank has reached 225-250 °F., it may be recirculated with the pump to provide some degree of agitation in the storage tank. The recirculation procedure is to open the asphalt suction line valve, close the recirculation line bottom drain valve, close the reactor feed valve, open the recirculation valve to the asphalt storage tank, close the vent valve above the asphalt suction line valve, and turn on the pump. The pump is a gear type pump and there is a sufficient residuum seal so that it will pull a small vacuum on the asphalt suction line until the asphalt flow is started from the storage tank. Once the recirculation asphalt flow is started, the steam may be turned off to the steam trace line and the auxiliary heater in the recirculation line turned on. This heater

must not be turned on unless there is a flow of asphalt in the recirculation line. Heating and recirculation of the asphalt is continued until the temperature of the asphalt is 475-500 °F.

A charge of asphalt is transferred to the reactor by first closing the reactor drain valves, closing the air feed valve, reading a gross weight on the Toledo scales, and then pumping the asphalt to the reactor by opening the reactor feed valve and closing the recirculation valve to the storage tank. The last few pounds of asphalt charged to the reactor may be controlled with more precision by opening the recirculation valve to the storage tank and throttling the asphalt reactor feed valve. When the desired charge has been transferred to the reactor, the reactor feed valve is closed and a final reading as net weight is taken from the Toledo scales. The difference in the weight readings of the scale is the mass of asphalt charged to the reactor. If a continuous run is made, the asphalt in the storage tank is continually recirculated at the desired reactor temperature. If a batch run is made, the recirculation is discontinued and the asphalt lines drained. The lines are drained by turning off the recirculation heater, opening the vent valve, allowing the pump to run several minutes, opening the recirculation line bottom drain valve and shutting off the pump. An asphalt feed run sample may be taken from the draining residuum.

Immediately after the charge of asphalt has been pumped to the reactor the reactor temperature controller and agitator are turned on. The reactor is continuously heated and agitated until the desired operating temperature is obtained. To pre-cool the condensers cooling water may be circulated through the reactor cooler, electrical precipitator coil

and water condenser. While the reactor asphalt charge is being heated, the analysis instruments are turned on and the calibration point checked with dry air. The instruments are calibrated for a specified flow rate of gas: the oxygen analyzer flow rate is 125 cc. per minute and the thermal conductivity cell flow rate is 800-900 cc. per minute. The zero point for the oxygen analyzer is a 21 per cent oxygen scale reading for dry air. The zero point for the thermal conductivity cell is a zero millivolt reading on the Weston Millivoltmeter for dry air. The electrical input to the thermal conductivity cell is always maintained at 6 volts d. c. and 138 milliamperes using a Mallory power supply. The thermal conductivity cell zero adjustment and current control are located on the panel mounted remote control unit. The knob marked "C" is for current adjustment and the one marked "A" is for millivoltmeter indicator adjustment. The instruments are permitted to operate with a continuous dry air sample until a constant zero reading is obtained on the thermal conductivity cell and the oxygen analyzer is up to operating temperature. Care should be taken when opening the rotameter feed valve on the panel board for the air gas sample, because the air feed valve to the reactor is closed and the feed gas manometer can be blown readily with a sudden surge of air.

When the gas analysis instruments have been zeroed and the temperature of the reactor charge is up to the conditions desired, the actual blowing operation may be started. The valving on the panel board is checked to insure the flow of two separate gas streams and also to eliminate the possibility of any closed valves. The power source for the electrostatic precipitator is turned on and the voltages adjusted to 29,000-31,000 volts

d. c.. The gas feed valve to the reactor is then opened and the flow rate of feed gas to the reactor is started and adjusted to the desired rate at the flow panel board. For a batch operation the time that the gas flow is started to the reactor is considered zero time for the run. The drain valves on the precipitator and water condenser are closed and the valving is changed on the gas analysis unit so that a continuous sample of converter gas may be taken. Gas flow rates are continuously checked and adjusted to maintain the desired flow rate. The needle valve on the converter gas discharge back pressure line is adjusted to give a slight gas flow through the back pressure dip tube. This back pressure of 5 to 6 inches of water provides a driving force for the gas sample to the gas analysis unit. At frequent intervals flow rate, gas analysis and instrument readings are recorded. For some of these readings asphalt reactor samples and precipitator samples are taken. The reactor asphalt samples are taken from the side drain allowing a small flush to flow from the reactor (2-3 ounces) to remove the previous product. The weight of sample and flush is recorded so that a material balance can be obtained and the residence weight of asphalt in the reactor at the sample time can be calculated. Precipitator and water samples are taken by closing the top drain valves and opening the bottom valves. The sample is in the stand pipe between the valves. Two valves are provided so that it is possible to take the samples without lowering the pressure in the reactor. Often the volume of the sample collected is larger than the volume of the standpipe, and it will be necessary to repeat the sampling procedure until the complete sample is obtained. To obtain an exact sample at a specified

time, this procedure is followed prior to the sample time so that when the top valve is closed at the sample time no part of the sample is omitted. The run is continued in this manner until the asphalt charge in the reactor is at the desired consistency. For batch runs the final product consistency is approximately 200 °F. Ring and Ball. This point must be estimated from the consistency of the reactor asphalt samples. Often when the asphalt in the reactor is approaching 200 °F. Ring and Ball the side asphalt sample line plugs with the hard asphalt. In this case the asphalt samples may either be taken from the bottom reactor drain valve or by heating the side reactor valve with a small gas torch and melting the solidified asphalt. When the asphalt is at or above 200 °F. Ring and Ball, final readings and samples are taken and the reactor contents drained into a previously tared 5 gallon steel bucket. The agitator and the reactor temperature controller are turned off. The reactor feed gas is allowed to flow for a few minutes to clear the air feed line of any asphalt.

The reactor feed gas is shut off and the power source to the electrical precipitator is also turned off. The feed gas valve to the reactor is closed and clean air is again turned on to the analysis instruments to sweep them of any residual converter gas and also to check the calibration zero point. The analysis instruments and air flow are turned off and the asphalt drain bucket weighed to obtain the final weight of asphalt for a material balance. This ends the operating part of a batch run.

The conditions and procedure for making a continuous run are similar to a batch run. In effect they are a combination of both a batch and continuous operation. The reactor is charged, heated and blown as a batch

operation to a predetermined Ring and Ball consistency as estimated from an analysis of a previous batch run. When the desired consistency is obtained, the reactor charge is blown as a continuous operation by simultaneously introducing fresh asphalt feed and removing asphalt product at a similar, constant rate. The feed rates are determined by the equivalent residence time that the fresh asphalt must remain in the reactor to be blown to the desired Ring and Ball consistency. The continuous run is continued in this manner until a constant converter gas analysis is obtained for fixed gas flow rates and asphalt feed rates. The continuous run may then be discontinued and the reactor charge again blown as a batch operation to a new asphalt product consistency. A continuous run may be repeated again with decreased asphalt feed flow rates. The run is terminated in the same manner as a batch run.

During continuous or batch runs an indication of the asphalt liquid level in the reactor may be obtained by observing the manometer pressure reading for the inlet reactor feed gas. This is particularly useful for continuous runs when the asphalt feed and product flow rates are being adjusted. Best results are obtained for controlling a continuous asphalt feed to the reactor when the feed valve to the reactor is opened slightly and the recirculation valve to the storage tank carefully throttled. A great deal of caution must be used to prevent closing the recirculation line valve, because the displacement pump would be damaged.

For fortified oxygen runs additional amounts of pure oxygen is metered into the asphalt reactor gas to increase the oxygen feed gas concentration. A pressure reducing valve on the oxygen cylinder reduces the

pressure to a low value and the flow rate of the gas is then metered with the oxygen rotameter. The composition of the feed gas is checked several times during a run by closing the converter gas sample line and opening the feed gas sample line to the analysis unit. The composition of the feed gas is indicated when consistent readings are obtained from the analysis unit.

As a run progresses the mass of the asphalt charge in the reactor decreases due to losses by blowing and from sampling. To maintain a constant gas to asphalt ratio for the particular run conditions, the reactor feed gas flow rate is continuously adjusted for the estimated asphalt mass in the reactor. Dew points of the converter gas are obtained with the dew point apparatus at the gas analysis unit during batch runs and at the panel board converter rotameter during continuous runs. The converter rotameter is used to prevent any change in reactor gas pressure during a continuous run. A drop in the reactor gas pressure generally results in an increased asphalt feed flow rate. The double valve sampling device on the electrical precipitator and water condenser was developed to eliminate this pressure drop while sampling. All equipment drain valves are left open when the equipment is not in operation.

B. Analytical Procedures

In this study the extent of reaction in the asphalt reactor charge was determined by the converter gas analysis and the change in physical properties of the asphalt product. The asphalt properties that were measured were softening point and penetration while the volume per cent oxygen, carbon dioxide and water were determined for the converter gas. The electrical

precipitator and water condenser products were separated into an oil and aqueous sample. Acid numbers were determined for these fractions.

The softening point of the asphalt product and feed samples were run by the A. S. T. M. Ring and Ball method, designation D 36-26 (4). The standard method was followed and a quadruple holder unit was used to permit attachment of four brass rings. A water bath was used for materials having softening points below 176 °F. and a glycerin bath for the higher softening point asphalts. A small air agitator was used to provide agitation when using the more viscous glycerin. The values of Ring and Ball are reported as temperature degrees Fahrenheit. Asphalt penetration values were measured with a standard penetration apparatus and needle according to the A. S. T. M. procedure designation D 5-25 (3). The load time and temperature for the penetration tests were 100 gm., 5 seconds and 77 °F. (25 °C.) respectively.

The oil and water mixtures from the electrical precipitator and condenser were separated into two samples, one aqueous and one oil, by centrifuging and decantation. The volume of each water sample was measured and likewise the weight of the oil sample was determined. The acid numbers for the electrical precipitator and condenser products were evaluated for the purpose of completing an oxygen material balance for the asphalt blowing products. The aqueous fraction of the sample was titrated with 0.1N sodium hydroxide using phenolphthalein for an end point indicator. The acid number for the oil fraction of the sample was obtained by a color indicator titration following the A. S. T. M. procedure D 663-46T (2). A standard 0.1N sodium hydroxide solution was used instead of the suggested potassium hydroxide solution.

The gas composition of the converter gases was measured with the gas analysis unit instruments. The Beckman oxygen analyzer gave a direct, continuous reading in volume per cent oxygen. The thermal conductivity cell ternary calibration plot was used to obtain the carbon dioxide content in the converter gases. The conductivity cell millivolt output and the oxygen analysis were the only parameters required to estimate directly the precentage of carbon dioxide gas. The partial pressure of water vapor in the exit converter gas was determined from the dew point analysis. The volume per cent of water in the converter gas is equal to the partial pressure of the water divided by the total pressure. The total pressure was assumed to be equal to one atmosphere at all times. Since the oxygen and carbon dioxide analysis was made using a dried converter gas, it was necessary to correct the indicated analysis of those gases for the effect of water vapor.

As the concentration of carbon dioxide in the converter gas was very small, no corrections were made for the oxygen analyzer analysis. Orsat analyses for percentage oxygen and carbon dioxide in the converter gas were measured at intervals to check the operation of the gas analysis unit. The Orsat gas analyzer was used to obtain the original thermal conductivity cell calibration and ternary plot for gaseous mixtures of oxygen, nitrogen and carbon dioxide.

VI. CALCULATIONS

The experimental data for the batch and continuous runs were analyzed for: (a) kinetics, development of rate equations and evaluation of reaction rate constants: (b) reaction mechanism, kinetic order, oxygen balance and utilization, and reaction products; (c) scale up, comparison of batch and continuous data and practical application. A tabulation of the calculated results for all experimental runs is included in the Appendix.

A. Kinetics

The general rate equation for the reaction rate of the processed asphalts was assumed to be related to various physical process variables in the form of the expression

$$dR/dt = kP^{p}S^{s}R^{r} \qquad (1)$$

where

dR/dt = rate of change of softening point or gross asphalt blowing reaction rate

R = asphalt Ring and Ball softening point, $^{o}F.$

S = process gas space velocity, $(ft.^{3})/(min.)(ton\ asphalt)$ at ($70\ ^{o}F.$, 1 atm.)

P = original process gas oxygen concentration, vol. %

t = process reaction time, hours

p, s, r = exponents on the process variables

k = paeudo reaction velocity constant

This form of the rate equation suggests that the rate of reaction is a function of the space gas velocity and the feed gas oxygen concentration. Temperature is another variable but is included in the pseudo

reaction velocity constant, k. The values of the exponents, p, r, and s, indicate the reaction order for the process variables. The degree of variation of the pseudo reaction velocity constant, k, with temperature will indicate certain conclusions regarding the rate controlling mechanism. The resulting equation with all constants evaluated, can be used for scale up and design considerations for larger commercial processing units.

The exponents and constants in the general rate equation may be evaluated by putting the equation in the logarithmic form as

$$\ln(dR/dt) = \ln(kP^{p}S^{s}R^{r}) \tag{2}$$

or

$$\ln(dR/dt) = \ln(kP^{p}S^{s}) + r\ln R \tag{3}$$

If the logarithm of the reaction rate (dR/dt) is plotted on the ordinate against the logarithm of asphalt consistency (R) on the abscissa, and the plot results in a straight line, the slope of the line is the exponent, r, and the intercept is $\ln(kP^{p}S^{s})$. Each batch run may be plotted as a line to give a measured value of slope and an intercept value at $\ln R = 0$. For this general treatment of the data to be of any value, the value of the slope for all runs must be the same. However, the intercept values will not be constant because the intercept is a function of k, S and P.

The values of the remaining exponents p, s, and constant, k, may be obtained from the intercept data as

$$I_a = \ln(kP^{p}S^{s}) \tag{4}$$

and

$$I_a = \ln(kP^p) + s\ln S \tag{5}$$

where

I_a = intercept of $\ln(dR/dt)$ versus $\ln R$ plot at $\ln R = 0$

The intercept, I_a, is now plotted as the ordinate value and lnS on the abscissa. The resulting curves should be plotted as straight lines with parameters of oxygen concentration. The slopes of this plot should again be constant and will be the value of the exponent, s. The intercept will be equal to the $\ln(k,P^p)$ at the value of $\ln S = 0$.

The intercept equation from this second logarithm plot may now be written as

$$I_b = \ln(kP^p) \tag{6}$$

or

$$I_b = \ln k + p\ln P \tag{7}$$

where

I_b = intercept of the I_a versus lnS plot at $\ln S = 0$.

The intercept values for this equation are again plotted on the ordinate against abscissa values of lnP. The resulting curve for this plot should be a straight line with a slope value of p and an intercept value of lnk at $\ln P = 0$. The value of k is then

$$I_c = \ln k \tag{8}$$

$$k = e^{I_c} \tag{9}$$

where

I_c = intercept of the I_b versus lnP plot at lnP = 0.

e = base of natural logarithms

The pseudo reaction velocity constant, k, will be a specific value for any given temperature. In the preceding analysis only the data at one given temperature are evaluated together to derive the desired values of exponents and constants.

This procedure is repeated for treatment of data at different temperatures. The resulting values of the exponents, p, r, and s, should be constant and independent of the temperature if a general reaction rate expression is to be developed. The only variable constant is k, the pseudo reaction velocity constant, which is a function of the reaction temperature.

B. Reaction Mechanism

The reaction mechanism for the asphalt blowing reaction can be described by the order of the process variables in the general reaction rate equation, by the variation of the reaction velocity constant with temperature, and by the oxygen utilization and oxygen balance for the reacting asphalts.

The order of reaction for the previously described rate equation (Equation 1) is the sum of all the exponents, p, r, and s, on the process variables, P, R, and S. The order with respect to each variable is the value of the exponent for that variable. The exponents are usually simple positive integers, but they may be fractional or even negative, depending upon the complexity of the reaction.

For a true chemical reaction rate the specific reaction rate constant, k', is a function of the processing temperature and is related to the temperature by the Arrhenius equation

$$k' = Ae^{-E/RT} \tag{10}$$

or

$$\ln k' = -E/RT + \ln A \tag{11}$$

where

k' = specific reaction velocity constant

E = the molal energy of activation

A = proportionality factor characteristic of the system and termed the frequency factor

R = gas constant

T = absolute temperature

If the lnk' is linear with 1/T the molal energy of activation can be evaluated by plotting the lnk' against reciprocal absolute temperature, 1/T. It is usually found that this plot is nearly linear with a negative slope, and the value of the slope is equal to -E/R. High values of the activation energy, E, is typical of reactions where the chemical reaction step is the rate controlling mechanism. Low values of the activation energy, E, indicate a reaction where the rate of diffusion is the controlling mechanism. A pseudo molal energy of activation for the asphalt blowing process can be evaluated if k from Equation 9 is substituted for k in Equation 11. This pseudo energy of activation can be used to derive certain conclusions regarding the rate controlling mechanism.

Oxygen utilization for the asphalt blowing process is determined by the disappearance of gaseous oxygen from the process gas streams. An oxygen balance for the process is an accounting and comparison of the oxygen in the feed gas against the oxygen in the reacted products. This balance includes the accounting of oxygen in the converter gas and precipitator products as oxygen (O_2), carbon dioxide (CO_2), water vapor (H_2O_g), water (H_2O_l) and acids. The mass weight of oxygen is calculated for specified time intervals by using an average gas concentration over the time interval used. Cumulative oxygen results are used and reduced to a basis per one pound of asphalt reacted.

The values for the oxygen balance for the gaseous products are calculated from the general equation

$$(G)(C)(\Delta t)(f) = \text{lbs. oxygen} \qquad (12)$$

where

G = gas flow rate, CFM, 70 °F., 1 atmosphere

C = gas concentration, volume per cent

Δt = time interval, hours

d = gas density, lbs./ft.^{3}

f = conversion factor, lbs. oxygen/lbs. gas

Table 4 is a listing of some of the gas properties that were used in this equation. The conversion factor, f, is the equivalent weight of oxygen, O_2, per unit weight of carbon dioxide, air and water.

TABLE 4

GAS PROPERTIES

Gas	Density, ρ_d Lb./Ft.^{3} 70 °F., 1 Atm.	Conversion Factor, f Lbs. O_2/Lb. Gas
O_2	0.0892	1.0
CO_2	0.1235	0.728
H_2O (g)	0.0501	0.888
Air	0.0808	0.231
N_2	0.0780	.....

The amount of oxygen in the condensed liquid water from the precipitator was determined by the relation

$$0.001956(v) = \text{lbs. oxygen} \qquad (13)$$

where

v = the volume of water, cc.

The oil and aqueous precipitated samples were titrated for acid determination by assuming that the acid was formic acid. The equivalent amount of oxygen as acid was then calculated by the relationship

$$7.05 \times 10^{-5}(V)(B)(N) = \text{lbs. oxygen} \qquad (14)$$

where

V = volume of water or weight of oil sample, cc. and gms. respectively

B = volume of sodium hydroxide per cc. of water or per gm. or oil, cc.

N = normality of the sodium hydroxide

The feed and converter gas flow rates were obtained from the gas rotameter data. Since the metered gas temperatures and pressures were essentially 70 °F. and 1 atmosphere, no rotameter correction factors were used. The amount of oxygen in the feed gases was very easily calculated from the rotameter data because the concentration of oxygen was either 21 per cent for air or 100 per cent for pure oxygen. The gas concentrations in the converter gas were those values that were recorded from the gas analysis unit and corrected from a dry basis to a wet gas basis by the following relationship

$$Pp.(CO_2, N_2, O_2) = D(760-Pp.\ H_2O_g) \qquad (15)$$

where

D = concentration of gas on dry basis, volume per cent

Pp. H_2O_g = partial pressure of the water vapor in the converter gas as determined from the dew point

Pp.(CO_2, N_2, O_2) = partial pressure of the converter gases on a wet gas basis

The partial pressure of the various gases on a dry basis was calculated from the gas analysis data by the expression

$$Pp.\ gas = 760D \qquad (16)$$

The gas concentration, C, is determined from the partial pressure of the converter gas on a wet basis by the relation

$$C = Pp.(CO_2, N_2, O_2)/760 \qquad (17)$$

A constant pressure of 1 atmosphere or 760 mm. Hg. was assumed for all calculations. For the feed gas oxygen balance the weight of oxygen as O_2 and equivalent weight of O_2 as air was added for each time

interval to give the total pounds of oxygen feed. For the converter gas oxygen balance the weight of oxygen as O_2 and the equivalent weights of O_2 as CO_2, H_2O and acids were added for each time interval to give the pounds of oxygen in the converter gas. The amount of oxygen used or the oxygen utilization was the difference between the oxygen in the feed gas and the oxygen as pure O_2 in the converter gas. The difference between the total oxygen feed and the sum of the oxygen and equivalent oxygen in the converter gas is the oxygen loss or unaccountable oxygen. The amount of oxygen calculated in the previous equations was based on the total asphalt charge in the reactor. This charge decreased during the course of a batch reaction and did not remain constant, because of sampling, entrainment and reaction losses. The amount of asphalt in the reactor at any time during the reaction was determined by a material balance. The calculated values of oxygen for any time interval were reduced to a basis of one pound of asphalt by dividing the mass of oxygen by the average weight of the asphalt reactor charge for the same time interval. The results were plotted as a cumulative plot of pounds of oxygen per pound of asphalt versus elapsed reacting time.

C. Scale Up

All batch runs were analyzed and calculated by the preceding reaction rate and oxygen balance methods. Continuous runs were also evaluated by these methods and compared to the batch run results. The two types of operation can be compared only at a similar asphalt residence time, using a differential treatment for continuous operation and an integral treatment for batch operation.

For continuous runs there was a continuous asphalt feed and simultaneous removal of asphalt product. As the mass of the asphalt charge in the reactor was kept constant, the asphalt residence time in the reactor was equal to the mass of the asphalt charge divided by the asphalt feed rate, that is

$$t_c = M_a/F_a \tag{18}$$

where

t_c = asphalt residence time, hours

M_a = mass asphalt in the reactor, pounds

F_a = feed rate of fresh asphalt, pounds per hour

The asphalt residence time, t_c, for continuous operation is equivalent to the elapsed reacting time, t, for batch operation. The differential analysis for continuous operation requires only a material balance around the reactor while the integral evaluation requires determining areas under curves plotted from the initial to the final reaction time, t.

The batch and continuous runs were compared for product consistencies and oxygen utilization at equivalent residence times. In a subsequent section practical application of the developed rate equation is illustrated by a sample calculation for the design of a commercial reactor vessel. The calculated results using the developed rate equation are compared with the actual commercial reactor data.

VII. RESULTS AND DISCUSSION

The majority of the batch and continuous runs were made by using the Gulf Coast Asphalt, TA-1023-2. A total of thirty runs were made for this residuum. The process conditions that were studied included temperature, feed gas space velocity (flow rate), feed gas oxygen concentration and agitator speed. Nine additional runs using the East Texas TA-1024, East Central Texas TA-1025 and the South Texas Heavy TA-1026 residua were made for purposes of comparison with the TA-1023-2 Gulf Coast material. These four types of materials represent four different types of asphalt.

The analysis of the data was made according to: (a) kinetics, (b) reaction mechanism, and (c) scale up.

A. Kinetics

The general rate equation relating the process variables to the reaction rate was evaluated to describe the reaction rate of the processed asphalts. This equation

$$dR/dt = kP^{p}S^{s}R^{r} \qquad (1)$$

was put in the logarithmic form and the exponents and reaction rate constants were evaluated as outlined in the calculation procedures.

Reaction rate data is obtained by plotting a curve of Ring and Ball softening point against reaction time. The slope at any point on the resulting curve is the reaction rate dR/dt when R is plotted on the abscissa and t on the ordinate. A typical set of batch runs are plotted in this manner and shown in Figure 5. Each curve in Figure 5 indicates a batch

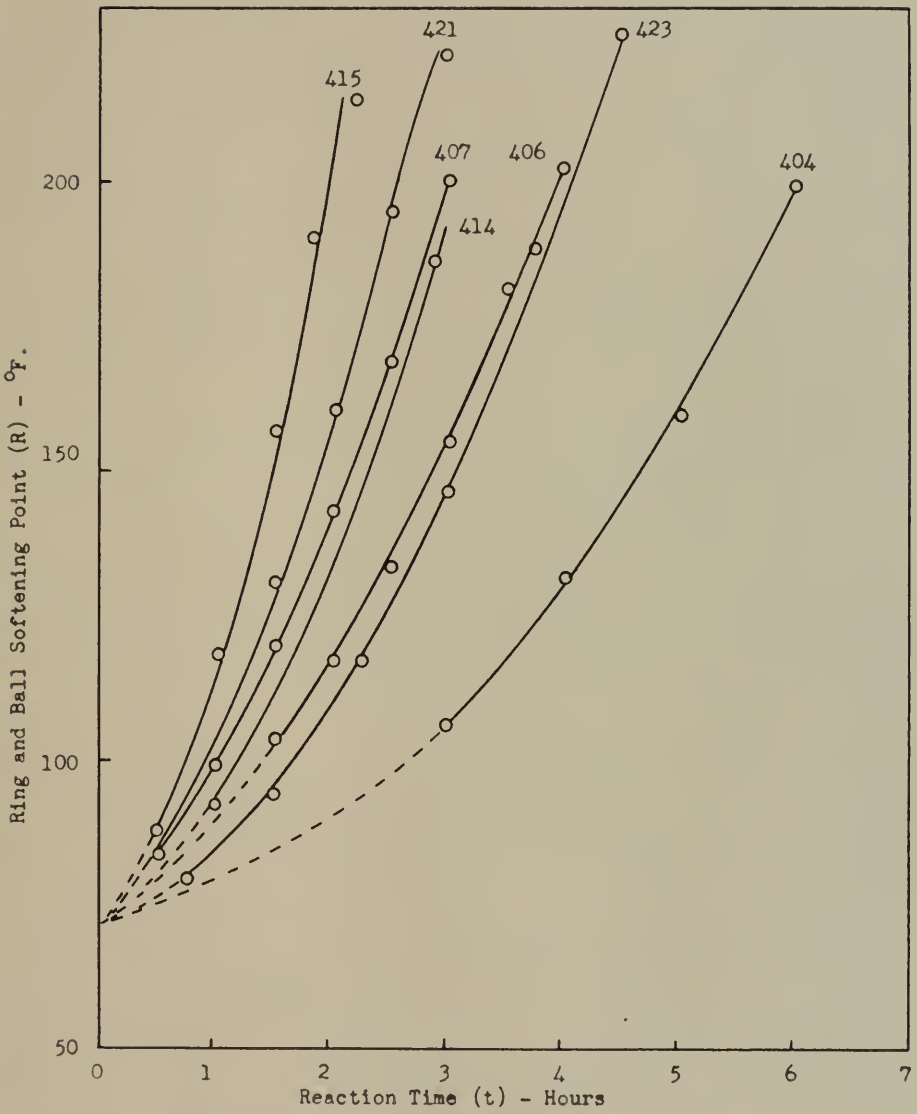

Figure 5. Softening Point and Reaction Time Relation for Batch Runs Using Gulf Coast Asphalt TA-1023-2

run for given process conditions of space gas velocity, oxygen concentration, agitation rate and reaction temperature.

Each curve shown in Figure 5 is the result of one batch run. The reproducibility of the data for the batch runs was checked by making duplicate runs for similar process conditions. Figure 6 is a comparison of two batch runs for the Gulf Coast asphalt, TA-1023-2, which were processed under similar conditions of temperature, feed gas space velocity, oxygen concentration and agitation rate. The results for the two batch runs shown in Figure 6 check within the limits of experimental error for Ring and Ball analysis. Table 5 is a tabulation of the results when the two batch runs in Figure 6 are compared.

TABLE 5

REPRODUCIBILITY OF BATCH RUN DATA

Run No.	Reaction Time, t Hours	Softening Point °F.	Oxygen Utilization Lb. O_2/Lb. Asphalt	Unaccountable Oxygen Lb. O_2/Lb. Asphalt
406	2.1	120	0.040	0.011
	3.1	160	0.056	0.020
	4.0	200	0.068	0.019
442	2.2	120	0.035	0.017
	3.2	160	0.060	0.023
	4.0	200	0.070	0.021

From Figure 5 the slopes of the batch run curves at various values of R are plotted in the logarithmic Equation 3

$$\ln(dR/dt) = \ln(kP^{p}S^{s}) + r\ln R \qquad (3)$$

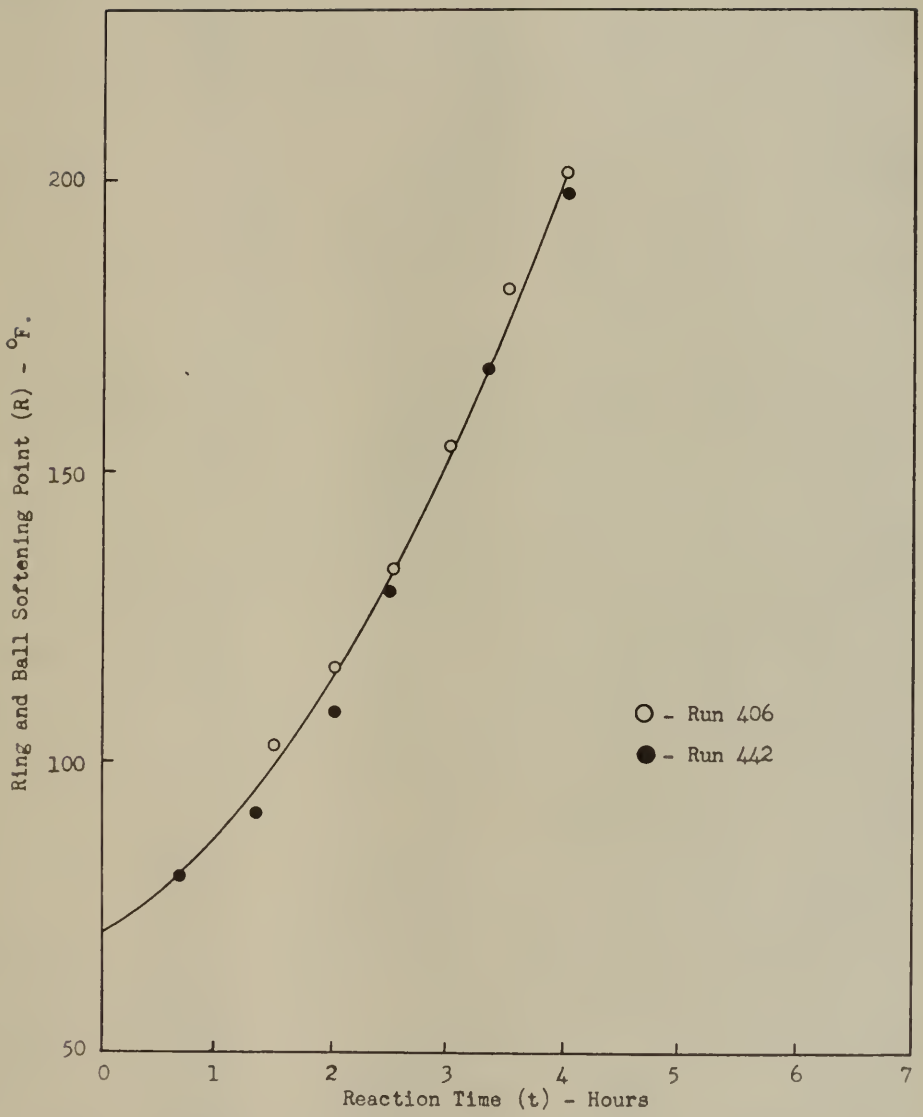

Figure 6. Reproducibility of Batch Run Data, Gulf Coast Asphalt TA-1023-2

as the ln(dR/dt) against the lnR. The resulting straight line plots are those given in Figure 7. In all the batch runs the asphalt was reacted to consistencies of 190-220 °F. Ring and Ball. The limits of the curves in Figure 7 are product consistencies of 200 °F. Ring and Ball which were selected as the upper limits for the processing analysis of this investigation. The average of the slopes of the curves was equal to one and each curve was adjusted to this value to give a corrected intercept value at lnR = 0. A tabulation of the original slopes and the intercept values based on a common slope of one are listed in Table 6 for the runs shown in Figure 7.

TABLE 6

SLOPE AND INTERCEPT VALUES FROM FIGURE 7

GULF COAST ASPHALT TA-1023-2

TEMPERATURE = 500 °F.

AGITATOR SPEED = 700 R.P.M.

Run No.	S CFMT	P % O_2	Slopes	Intercepts (Slope = 1.0, lnR = 0)
404	25	21	1.16	-1.60
406	100	21	0.91	-1.28
407	200	21	0.60	-1.06
414	25	50	1.28	-0.91
415	100	50	0.95	-0.64
421	100	35	1.01	-0.81
423	25	35	1.10	-1.16

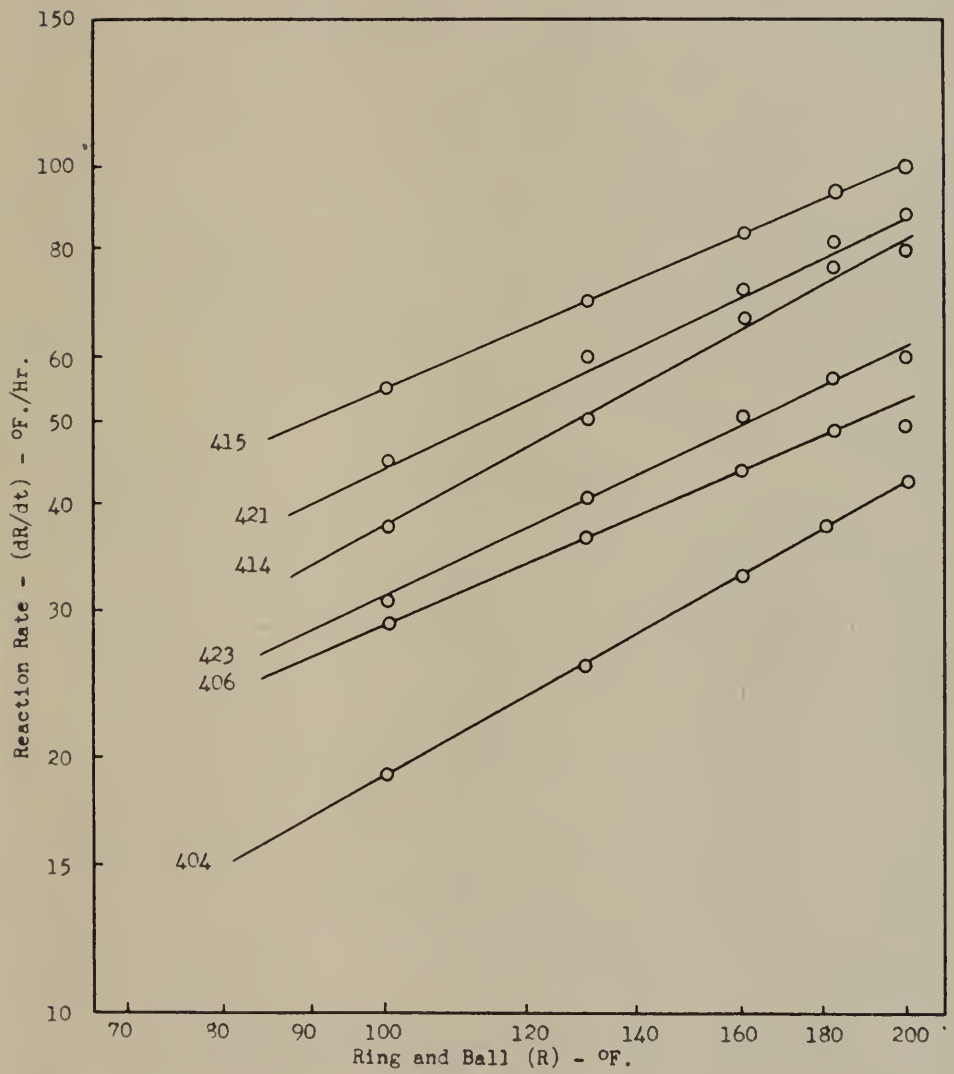

Figure 7. Reaction Rate and Product Consistency for Batch Runs, Gulf Coast Asphalt TA-1023-2

The experimental values of the slopes show an average variation of 15.6 per cent with a maximum of 40 per cent for run 407. The use of a common slope of one is believed valid for this analysis. As will be shown later, the average observed data are within 7.2 per cent of predicted values by the procedure used. The slope variations found do not show trends for space gas velocity and oxygen concentration. Since all the slopes have approximately the same value, this provides the basis for the use of a common slope. The selection of a common slope greatly simplifies the correlation of the data. The important point is to recognize the limitations of the relations presented for design application. The intercept values from Table 6 were plotted against lnS according to Equation 5,

$$I_a = \ln(kP^p) + s\ln S \qquad (5)$$

This data gave a family of straight lines with a constant slope value of s equal to 0.23. The parameter for this set of curves is the value of oxygen concentration, P. The curves are plotted in Figure 8 and the intercept values at lnS = 0 are tabulated in Table 7.

The intercept values from Table 7 were next plotted against the lnP as indicated in Equation 7

$$I_b = \ln k + p\ln P \qquad (7)$$

to evaluate the remaining rate equation constants, p and k. The slope of this straight line plot was equal to the exponent, p, and the value was 0.83. The value of the intercept, lnk, was evaluated at lnP = 0 and the value of k was equal to 0.0064. Figure 9 is a plot of the intercept

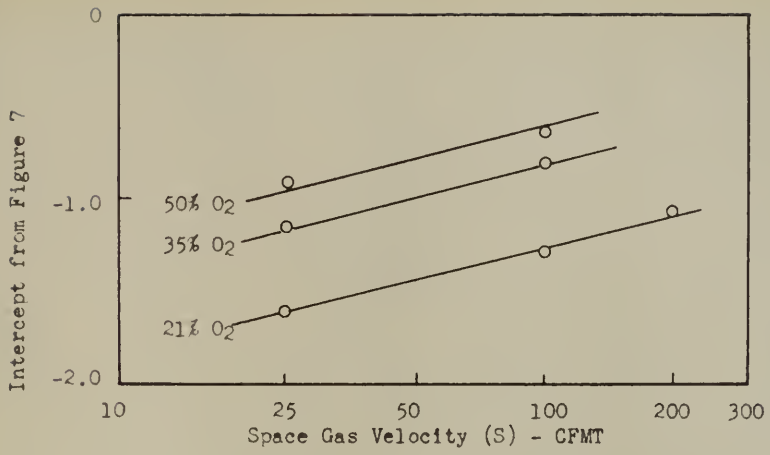

Figure 8. Evaluation of Rate Equation Exponent, s

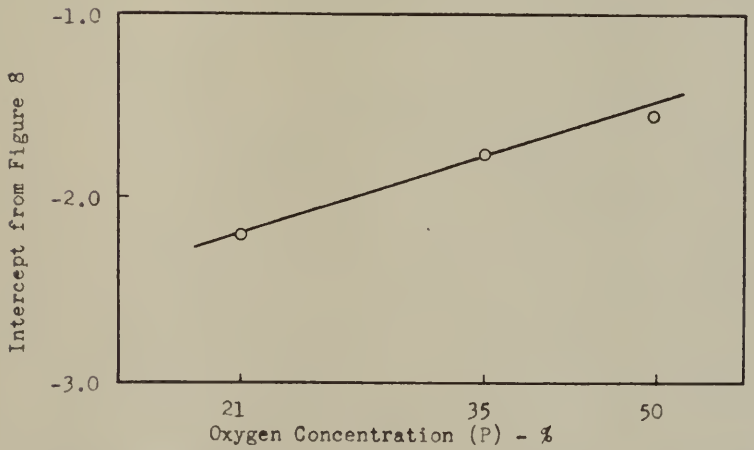

Figure 9. Evaluation of Rate Equation Exponent, p, and Pseudo Reaction Velocity Constant, k

data in Table 7 versus lnP The remaining batch runs for different temperatures and asphalts were analyzed and evaluated by this same procedure. The data for all the runs was plotted according to Figures 7, 8 and 9 and the values of the exponents, p, r, and s, were determined.

TABLE 7

SLOPE AND INTERCEPT VALUES FROM FIGURE 8

GULF COAST ASPHALT TA-1023-2

TEMPERATURE = 500 °F.

AGITATOR SPEED = 700 R.P.M.

P % O_2	Slope	Intercept lnS = 0
21	0.23	-2.66
35	0.23	-2.23
50	0.23	-1.73

The values of the exponent constants that best fit the data for the four different processed residues are

$$r = 1.0$$

$$s = 0.2$$

$$p = 0.9$$

The corresponding values for the pseudo reaction velocity constant, k, are tabulated in Table 8 for one asphalt at three different temperatures and the other three asphalts at 500 °F.

TABLE 8

PSEUDO REACTION VELOCITY CONSTANTS

AGITATOR SPEED = 700 R.P.M.

Temp. °F.	Pseudo Reaction Velocity Constant, k			
	TA-1023-2	TA-1024	TA-1025	TA-1026
450	0.0045	.....	.....	.....
500	0.0061	0.0090	0.0070	0.0056
550	0.0081	.....	.....	.....

The pseudo energy of activation, E, was determined by plotting the lnk versus the reciprocal of the absolute temperature 1/T and measuring the slope of the resulting straight line. According to Equation 11

$$\ln k = -E/RT + \ln A \qquad (11)$$

the negative slope of the plot is equal to -E/R. The value of E determined from the slope of the curve in Figure 10 was 5800 calories per gm. mole.

The effect of agitation was evaluated by changing the agitator speed from 700 r.p.m. to 1300 r.p.m. and making batch runs at similar process conditions. An increase in the value of the pseudo reaction velocity constant is the only variation to be expected for batch runs with a higher degree of agitation. It was determined that the batch runs using a higher agitator speed followed the same general rate equation and the values of the reaction velocity constant varied as shown in Table 9.

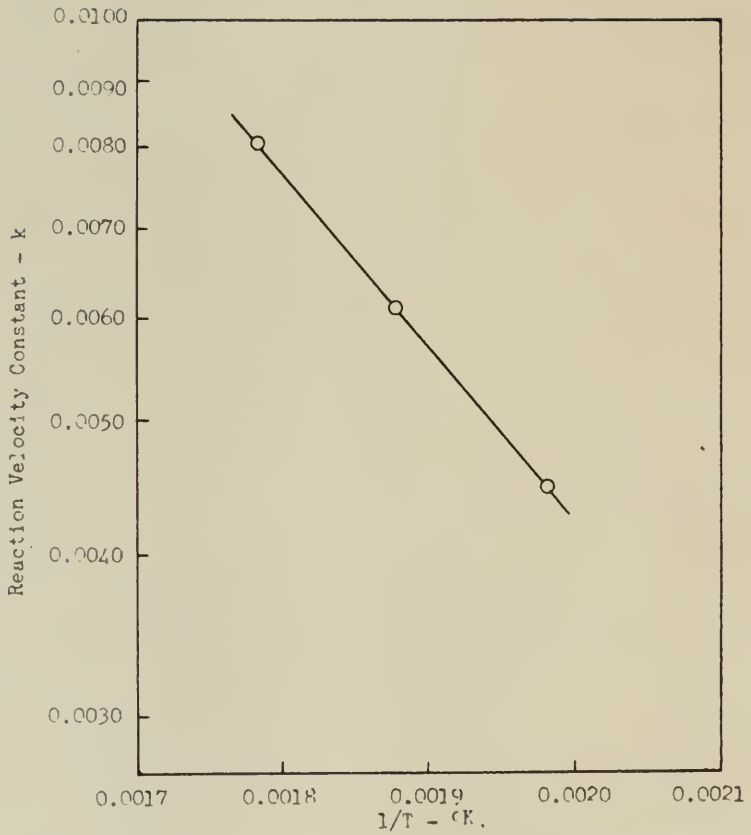

Figure 10. Variation of Pseudo Reaction Velocity Constant, k, with Temperature for Gulf Coast Asphalt TA-1023-2.

TABLE 9

VARIATION OF THE PSEUDO REACTION VELOCITY CONSTANT WITH AGITATION

TEMPERATURE = 500 °F.

ASPHALT TA-1023-2

Agitator Speed R.P.M.	k
700	0.0061
1300	0.0062

The small increase in the value of k for the increased agitator speed suggests that the degree of agitation that was used in this investigation was above the maximum agitation threshold. When this threshold value is obtained, the degree of agitation is no longer a process variable. The rate of reaction will then depend upon other process variables.

The rate equation that was developed for the asphalt blowing process was checked by substituting process conditions and reaction times to calculate final asphalt consistencies. The calculated values were checked against the experimentally determined values for the batch runs. The agreement of the developed equation was checked for all batch runs using the equation

$$dR/dt = kS^{0.2}P^{0.9}R \qquad (19)$$

or in the integrated form

$$\ln R_1/R_o = ktS^{0.2}P^{0.9} \qquad (20)$$

The values of k and R_o that were used for the different process conditions and asphalts were taken from Tables 8 and 1 respectively. The average percentage variation of the calculated consistencies based on the experimental values are tabulated in Table 10.

TABLE 10

PERCENTAGE ERROR FOR REACTION RATE EQUATION

EQUATION $\ln(R_1/R_o) = kt^{S^{0.2}P^{0.9}}$

Temp. °F.	Per Cent Error for Asphalt			
	TA-1023-2	TA-1024	TA-1025	TA-1026
450	4.1	...	...	...
500	7.1	3.4	3.6	9.5
550	15.1	...	...	...

For all batch runs the overall percentage variation for agreement to the developed rate equation was 7.2 per cent.

B. Reaction Mechanism

The order of the reaction for the asphalt blowing process is the sum of the exponents on the process variables and is approximately a pseudo second order reaction. The order with respect to each variable is the value of the exponent for that particular variable. The developed rate equation suggests that the mechanism is 0.2 order with space gas velocity, 0.9 order with oxygen concentration and first order with Ring and Ball consistency. These are all pseudo order values based on physical variables.

The evaluated constant, E, the pseudo molal energy of activation, was 5800 calories/gm. mole. This is a rather low value for the activation energy and indicates a reaction mechanism with diffusion controlling. The reaction rate for this mechanism depends on the rate at which the active reacting gaseous agent (oxygen) is transferred to the liquid asphalt interface. Process conditions that would increase this mass transfer of oxygen would be increased agitation, increased gas space velocity and increased oxygen concentration in the feed gas.

The oxygen utilization for the four different types of residua was a function of the asphalt product consistency and was independent of the processing conditions. The pounds of oxygen utilized per pound of asphalt processed was plotted against the change in Ring and Ball consistency of the asphalt. This average curve for the Gulf Coast residuum is shown in Figure 11. Curves for the other three residua are indicated in Figures 12, 13 and 14. Table 11 is a tabulation of the average values of oxygen utilization for specific changes in asphalt product consistency.

The oxygen utilization data indicates that the change in consistency, or the degree of reaction of the asphalt, is a stoichiometric relationship with the amount of oxygen that is used. The four residua that were used required different amounts of oxygen for a given change in asphalt consistency. The South Texas Heavy Asphalt TA-1026 utilized the most oxygen for a given change in product consistency while the East Texas Asphalt TA-1024 required the least oxygen for a similar change.

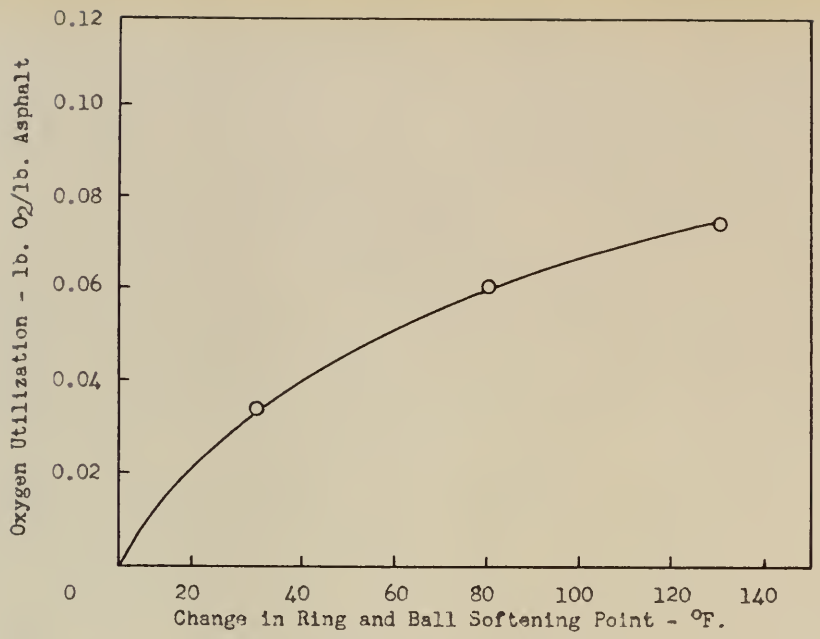

Figure 11. Oxygen Utilization and Product Consistency for Gulf Coast Asphalt TA-1023-2

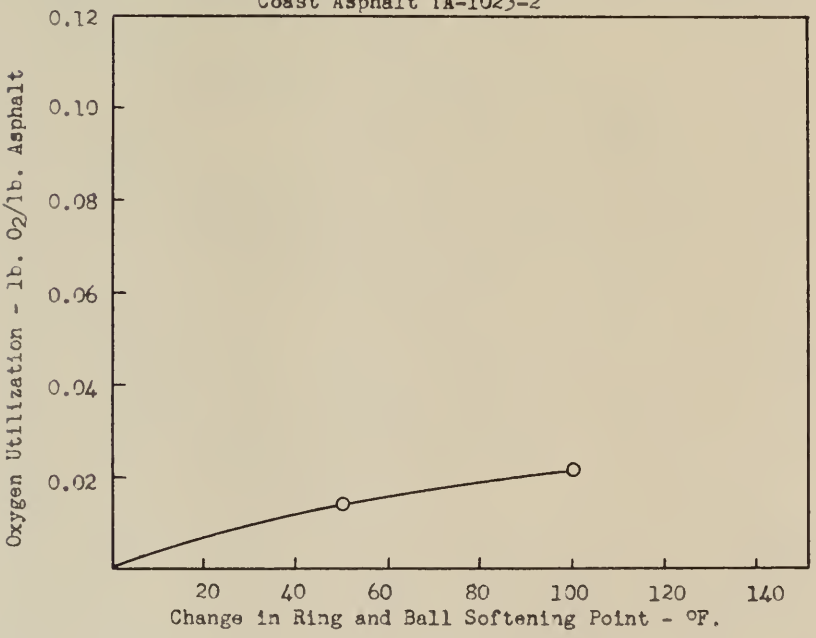

Figure 12. Oxygen Utilization and Product Consistency for East Texas Asphalt TA-1024

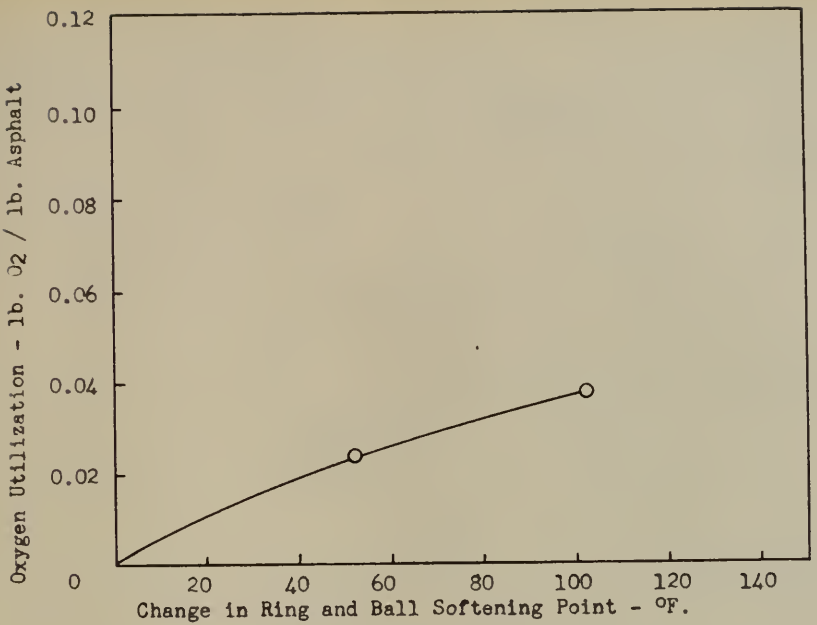

Figure 13. Oxygen Utilization and Product Consistency for East Central Texas Asphalt TA-1025

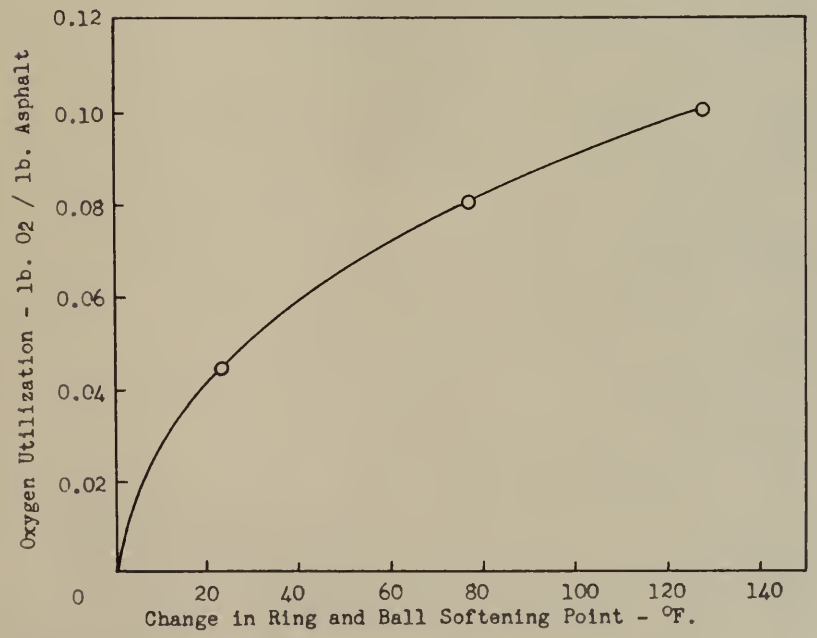

Figure 14. Oxygen Utilization and Product Consistency for South Texas Heavy Asphalt TA-1026

The data also indicate that as the reaction proceeds in the four different residua, less oxygen is required for a given change in product consistency.

TABLE 11

OXYGEN UTILIZATION FOR PROCESSED RESIDUA

Asphalt	Change in Ring and Ball Consistency* °F.	Oxygen Utilization** Lb. O_2/Lb. Asphalt
TA-1023-2	30	0.034
	80	0.061
	130	0.075
TA-1024	50	0.014
	100	0.025
TA-1025	52	0.023
	102	0.037
TA-1026	27	0.044
	77	0.079
	127	0.100

*Change in consistency from original residuum.
**Cumulative oxygen required for the given change in Ring and Ball consistency.

The reaction products from the air blowing process are the air blown asphalt and the converter gas containing water vapor, carbon dioxide, oxygen, nitrogen and an oil smoke and entrainment mist. A considerable portion of the water and essentially all the smoke and entrainment products were separated from the converter gas in the Cottrell electrical precipitator. The water and oil products that were condensed and precipitated in the Cottrell unit were called fume oil products.

When calculating an oxygen balance for batch and continuous runs, an unaccountable disappearance of oxygen occurred for each run.

The oxygen balance was made by comparing the amount of oxygen in the process feed gas to that calculated in the converter gas as oxygen, carbon dioxide, water vapor, liquid water and acids. The equivalent amount of oxygen as acids in the precipitator fume oil products was small and these values were not included in the calculation. The resulting oxygen balance, therefore, was based on the remaining converter gas constituents of oxygen, carbon dioxide, water vapor and liquid water. Nitrogen balances were calculated for all the runs on the feed and converter gas streams to make certain that the gas flow rates or analyses of the feed and converter gases were not responsible for the unaccountable oxygen loss. The average variation for the cumulative nitrogen balances on the feed and converter gas streams was ± 2.9 per cent by weight. This low variation for nitrogen balances indicates satisfactory flow rate measurements and analyses for the feed and convertor gas streams with no significant losses.

In Table 12 are listed the average cumulative unaccountable oxygen losses for batch runs where the final product consistency was 200 °F. Ring and Ball.

A comparison of the data in Table 11 and Table 12, for the total oxygen used to produce a 200 °F. Ring and Ball product, shows that between 0 and 55 per cent of the oxygen appears as an unaccountable loss. The unaccountable oxygen could have been absorbed in the liquid asphalt, reacted to form oxygenated compounds in the fume oil products, or appeared as oxygenated compounds in the converter gas stream. The previous investigation by Katz (13) proved that less than 1 per cent by weight of oxygen is absorbed in liquid asphalts at Ring and Ball consistencies of 200 °F.

or less. If it is assumed that 1 per cent of the oxygen was absorbed by the asphalt, 0.01 lb. O_2/lb. asphalt would be accounted for. This value is approximately 100 per cent of the average losses for the harder TA-1024 and TA-1025 asphalts and 25-35 per cent for the softer TA-1023-2 and TA-1026 asphalts.

TABLE 12

UNACCOUNTABLE OXYGEN LOSSES TO 200 °F.
RING AND BALL PRODUCT CONSISTENCIES

Asphalt	Total Oxygen Losses Lb. O_2/Lb. Asphalt		Average Oxygen Losses Lb. O_2/Lb. Asphalt
	Minimum	Maximum	Average
TA-1023-2	0.000	0.054	0.032
TA-1024	0.000	0.016	0.006
TA-1025	0.000	0.019	0.011
TA-1026	0.020	0.052	0.035

Considering the low variation for the cumulative nitrogen balances on the process gases, it is assumed that the remainder of the unaccountable oxygen reacted to form oxygenated products that could occur as vapors in the converter gas or as precipitated fume oil products. The appearance of oxygenated compounds in the fume oil products seems to be a more feasible explanation, because the Orsat analyzer indicated similar converter gas analysis as given by the gas analysis unit.

The appearance of water and carbon dioxide in the converter gas substantiate the dehydrogenation and decarbonization reactions. With

this mechanism, it is possible that the oxygenated materials in the fume oil are organic compounds such as aldehydes, ketones and ethers.

Typical cumulative curves of the oxygen balance for batch runs are plotted in Figures 15 and 16. Figure 15 shows the data for a low gas space velocity and low oxygen concentration run. Almost all the available oxygen is used for the reaction with the result of very little oxygen in the converter gas. Figure 16 is the plotted data for a high space gas velocity and high oxygen content run. Only a small fraction of the available oxygen is used for the reaction and the curves are close to each other. These curves may be used to determine the amount of oxygen used by the reacting asphalt to produce a specified degree of consistency. The data for Table 11 was obtained in this manner. The remaining batch runs gave similar plots depending on the processing conditions.

The fume oil products were collected for each batch and continuous run. At the end of a run, the various samples taken were separated into an aqueous and an oil fraction. The volume and weight of these samples were determined and then the samples were titrated for acid numbers.

Table 13 shows the average amount of fume oil collected for the various asphalt residua used and processed at different conditions to a final product consistency of 200 ^{o}F. Ring and Ball softening point. The amount of fume oil products that was collected for these batch runs was independent of the process gas oxygen concentration but was dependent on the gas space velocity, reaction temperature and the type of asphalt processed. It may be noticed that for all the residua used, the percentage

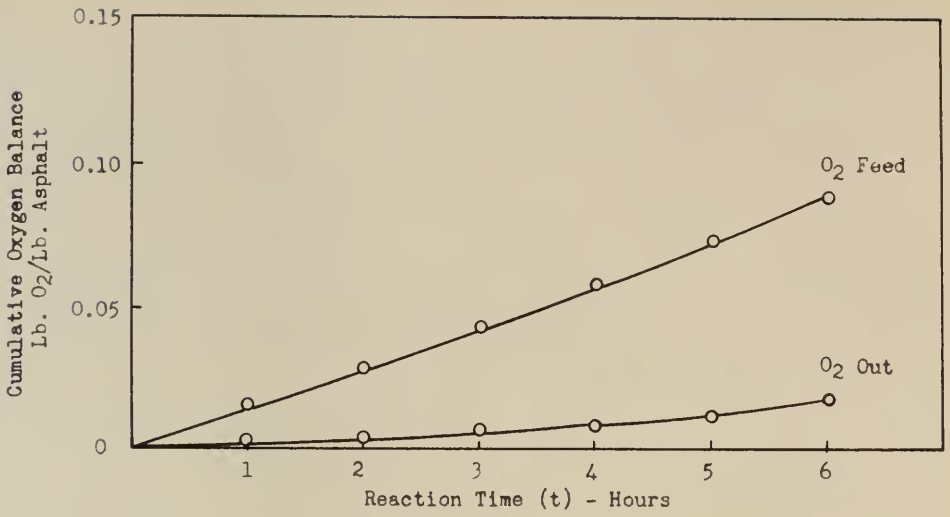

Figure 15. Cumulative Oxygen Balance for Low Space Gas Velocity and Low Oxygen Concentration, Gulf Coast Asphalt TA-1023-2

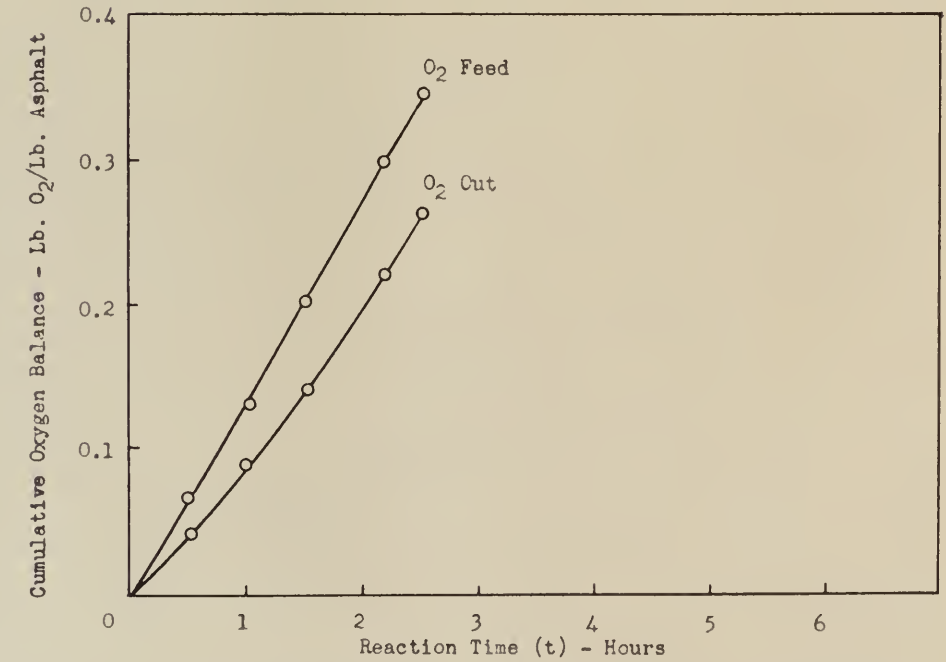

Figure 16. Cumulative Oxygen Balance for High Space Gas Velocity and High Oxygen Concentration, Gulf Coast Asphalt TA-1023-2

of the oil fraction increases with increasing reaction temperature and feed gas space velocity. The total amount of fume oil products collected for asphalts processed to 200 °F. Ring and Ball consistencies was not constant. The total amount of fume oil products per batch run was greatest for the South Texas Heavy Asphalt TA-1026 and smallest for the East Texas Asphalt TA-1024. The fraction of the fume oil products as oil was only 15 weight per cent for the East Texas Asphalt TA-1024 with a maximum of 50 weight per cent for the East Central Texas Asphalt TA-1025. The total weight of fume oil in Table 13 includes the weight of the precipitated oils and the sum of the weight of water as condensed water and water vapor in the converter gas.

The penetration values for the asphalt products were determined by the standard A. S. T. M. test D 5-25 (3) using a penetrometer. This penetration data for asphalts is generally used in conjunction with softening point data to determine the adaptability of bituminous materials for specific uses and for quality control. Figures 17, 18, 19 and 20 show the relationship between Ring and Ball softening point and penetration values for the asphalt residues used in this investigation. The relation of Ring and Ball softening point and penetration is almost identical for the four different residues.

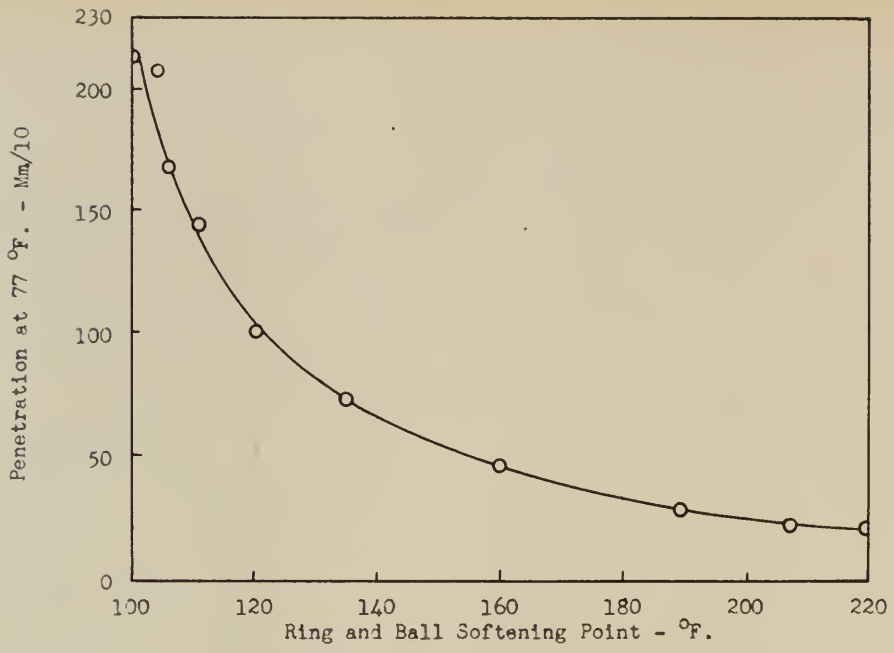

Figure 17. Properties of Asphalt Products, Gulf Coast TA-1023-2

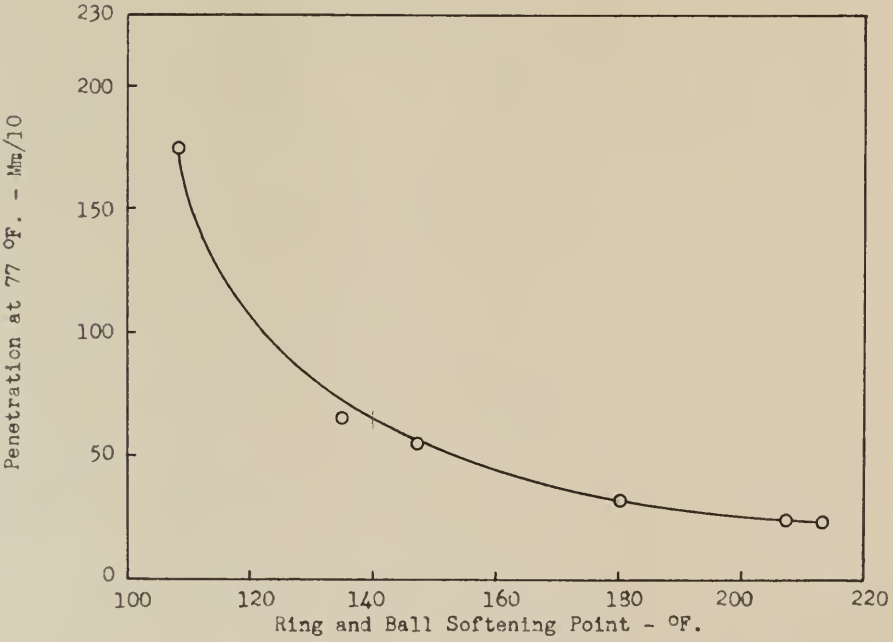

Figure 18. Properties of Asphalt Products , East Texas TA-1024

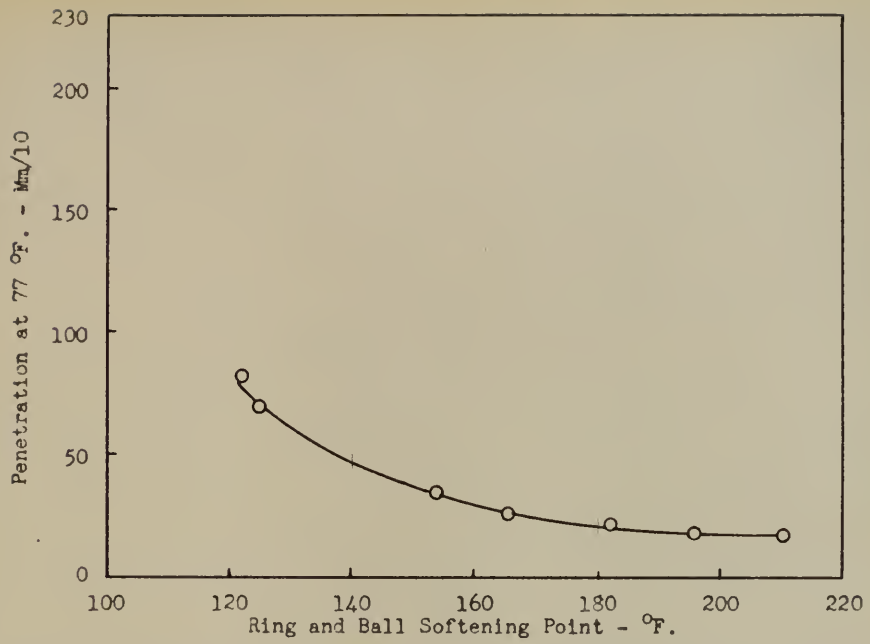

Figure 19. Properties of Asphalt Products, East Central Texas TA-1025

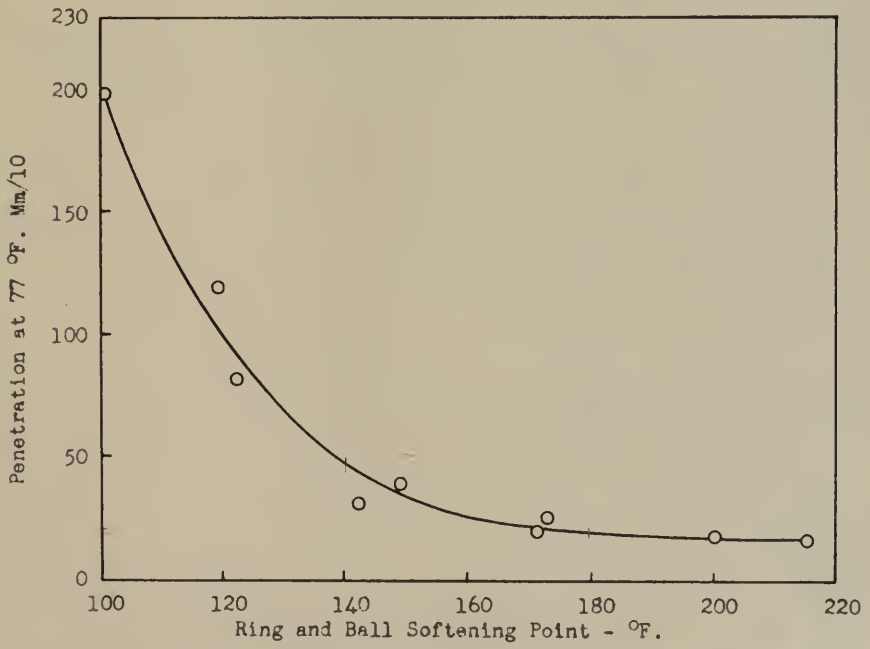

Figure 20. Properties of Asphalt Products, South Texas Heavy TA-1026

TABLE 13

FUME OIL REACTION PRODUCTS TO 200 °F.
RING AND BALL PRODUCT CONSISTENCIES

Asphalt	Temp. °F.	S CFMT	Total Wt.* Fume Oil, for Batch Runs, Gms.	Oil Wt. %	Water Wt. %
TA-1023-2	450	25	339	15	85
	450	100	470	17	83
	500	25	332	16	84
	500	100	457	25	75
	500	200	491	38	62
	550	25	467	27	73
	550	100	585	36	64
TA-1024	500	25	94	15	85
	500	100	403	15	85
TA-1025	500	25	241	50	50
	500	100	472	52	48
TA-1026	500	21	704	31	69
	500	100	1023	43	57

*Average value for batch runs independent of feed gas oxygen concentration.

C. Scale Up

The preceding analysis and development of the rate equation was based on batch run data. Several continuous runs were made at similar batch run processing conditions, to compare the batch or integral treatment against the continuous or differential treatment. The comparison was made by determining equivalent residence reaction time for the two types of operation and then comparing the asphalt product consistency and oxygen utilization. The reaction residence time used as the basis of comparison was calculated from the continuous operation data by

Equation 18

$$t_c = M_a/F_a \qquad (18)$$

This same value for reaction time was used for the batch operation data to estimate Ring and Ball softening points and oxygen utilization data from plots similar to Figures 5 and 15. Table 14 indicates the results for the batch and continuous runs where the processing conditions were the same for both types of operation. When the equivalent reaction times are equal for the two types of operation, the agreement of the oxygen utilization data is within 15 per cent and the product consistencies check within 10 per cent. These results indicate that the same product and oxygen consumption may be expected from either batch or continuous runs.

The practical application for the developed rate equation is paramount for the calculation of processing times and design capacities for commercial asphalt blowing equipment. A sample calculation to demonstrate the use of the rate equation is included to illustrate its usefulness.

Assume that it is required to determine the processing time and production capacity of an agitated reactor vessel 10 feet in diameter and 17 feet high. The depth of the asphalt charge is 12 feet. The reactor is agitated with a Turbo-Mixer agitator of the type used in the pilot plant experiments. The size of the agitator impeller is 42 inches. By selecting process conditions and substituting them in the developed rate equation, the processing time, process gas requirements and production capacity can be calculated for a product having a 100 °F. softening point rise.

TABLE 14

COMPARISON OF EXPERIMENTAL BATCH AND CONTINUOUS DATA

GULF COAST ASPHALT - TA-1023-2

TEMPERATURE = 500 °F.

AGITATOR SPEED = 700 R.P.M.

Continuous Runs	S CFMT	P % O_2	Residence Time, Hrs.	Product R, °F.	O_2 Used Lb. O_2/Lb. Asph.
411	25	21	3.1	110	0.0335
412	25	21	4.2	146	0.0498
413	25	21	4.65	170	0.0600
429	100	21	1.63	97	0.0317
430	100	21	2.48	124	0.0434
431	100	21	3.33	150	0.0500
408	200	21	1.28	95	0.0303
409	200	21	1.77	131	0.0318
410	200	21	2.54	161	0.0408
Batch Runs					
404	25	21	3.1	108	0.037
404	25	21	4.2	137	0.050
404	25	21	4.6	153	0.056
406	100	21	1.6	106	0.034
406	100	21	2.5	135	0.046
406	100	21	3.3	167	0.060
407	200	21	1.3	111	0.039
407	200	21	1.8	133	0.054
407	200	21	2.5	173	0.063

The residuum to be used in this sample calculation is the Gulf Coast Asphalt TA-1023-2.

The processing conditions are selected as follows:

Temperature = 500 °F.

Feed gas space velocity, S = 28CFMT

Feed gas oxygen concentration, P = 21

The reaction time necessary to change the product consistency by 100 °F. Ring and Ball can be calculated from the integrated form of the rate equation (Equation 20)

$$\ln R_1/R_o = ktP^{0.9}S^{0.2} \qquad (20)$$

For the Gulf Coast Asphalt processed at 500 °F., k = 0.0061 and R_o = 70. The remaining variables are substituted into Equation 20 and solved for the reaction time, t.

R_o = 70 °F.

R_1 = 100 + 70 = 170 °F.

k = 0.0061

S = 28CFMT

P = 21% O_2

$$\ln(170/70) = 0.0061(21)^{0.9}(28)^{0.2}t$$

t = 4.9 hours

The value of t is the reaction time necessary to change the product consistency from 70 °F. to 170 °F. Ring and Ball. This value is 4.9 hours for the process conditions chosen.

The process gas requirements are determined from the feed gas space velocity and the mass of reacting residuum. The mass of asphalt

charge per batch is

$$\text{Mass asphalt} = (\text{reactor volume})(\text{asphalt density})$$
$$= (\pi)(10)^2(12)(62.4)(0.967)/(4)(2000)$$
$$= 28.4 \text{ tons asphalt}$$

The corresponding feed gas flow rate is

$$\text{Gas feed rate} = (\text{mass asphalt})(\text{feed gas space velocity})$$
$$= 28.4(28)$$
$$= 795 \text{ ft.}^3 \text{ air/min.}$$

The calculated feed gas requirement for the reactor is 795 ft.^{3} air/min.

The daily production capacity for the reactor can be determined from the total cycle time required to process one batch. The operating cycle includes; time necessary to heat the charge to the reacting temperature, time necessary for the desired reaction, holding time for analysis and time to discharge to a product tank. If the sum of the time for all the operations except the reaction time is assumed to be 6 hours, the total cycle time is approximately 11 hours. The daily batch production would be 2.2 batches per day or 62 tons of Gulf Coast Asphalt having a final product consistency of 170 ^{o}F. Ring and Ball. A variation of the processing conditions would change the reaction time but would not appreciably affect the remaining cycle time.

When the feed gas space velocity and oxygen concentration is increased to 100 CFMT and 50 per cent respectively, the reaction time for the reactor is reduced to 1.7 hours. The total cycle time is now 7.7 hours and the daily production is increased to 89 tons of 170 ^{o}F. Ring and Ball asphalt. The production has been increased but at the

expense of a greater feed gas flow rate and oxygen concentration. An economic analysis must be considered to arrive at justified operating conditions.

The calculated results for the initial conditions selected for the design problem may be compared with actual refinery data as supplied by the Turbo-Mixer Corporation (14). The comparison is based on the same size reactor and similar operating conditions. The commercial data for refinery "A" lists a reaction time of 5.5 hours for increasing the softening point of an asphalt 100 ^{o}F. Ring and Ball. By assuming that this asphalt is similar to the Gulf Coast Asphalt TA-1023-2, the calculated reaction time of 4.9 hours may be compared with the 5.5 hours reaction time. The error is approximately 11 per cent. The agreement of these results verify the use of the general rate equation for design calculations of commercial asphalt blowing units.

VIII. CONCLUSIONS

From the results of the asphalt blowing process using four different kinds of residua, the following conclusions may be made concerning the kinetics of the asphalt blowing process within the limits of the conditions covered by this investigation:

1. The general rate equation for the reaction rate is

$$dR/dt = kP^{0.9}S^{0.2}R$$

where

dR/dt = gross asphalt reaction rate as rate of change of softening point

R = asphalt Ring and Ball softening point, °F.

S = process gas space velocity, $ft.^3/(min.)(ton\ asphalt)$ at (70 °F., 1 atm.)

P = original process gas concentration, volume %

k = pseudo reaction velocity constant

t = process reaction time, hours

2. The values of the pseudo reaction velocity constants are a function of the type of residua and the reacting temperatures. The corresponding values for the pseudo reaction velocity constants are:

Temp.	Pseudo Reaction Velocity Constant, k			
°F.	TA-1023-2	TA-1024	TA-1025	TA-1026
450	0.0045	.....	.....	.....
500	0.0061	0.0090	0.0070	0.0056
550	0.0081	.....	.....	.....

3. The reaction rate controlling step is a diffusion process based on the low pseudo molal energy of activation, E, of 5800 calories/gm. mole.

4. The gross asphalt blowing reaction may be considered a complex dehydrogenation, decarbonization and polymerization reaction. This is substantiated by the appearance of water and carbon dioxide in the converter gas and by the increased softening point for the asphalt products.

5. The asphalt blowing fume oil reaction products collected in the Cottrell precipitator contain a mixture of unknown oils and water. For asphalt residues reacted to 200 °F. Ring and Ball, the amount of fume oil products vary from 4-11 per cent of the weight of residue reacted.

6. The fraction of oil in the fume oil products was a minimum of 15 weight per cent for the East Texas Asphalt TA-1024 and a maximum of 50 weight per cent for the East Central Texas Asphalt TA-1025.

7. The change in asphalt consistency is related to the amount of oxygen used in the asphalt blowing reaction. The amount of oxygen used for a given change in product consistency was different for the four residua used. The East Texas Asphalt TA-1024 used a minimum amount of oxygen while the South Texas Heavy TA-1026 used the maximum amount of oxygen.

8. Of all the oxygen used in the asphalt blowing reaction, 0-55 per cent could not be accounted for in the converter gas and

fume oil products. It is assumed that the unaccountable oxygen reacted to form oxygenated products that could appear as vapors in the converter gas or as liquids in the fume oil products.

9. For the same residence reaction times, integral batch operation is equivalent to differential continuous operation.

10. The general rate equation may be used for the calculation and design of commercial asphalt blowing units.

IX. NOMENCLATURE

A = Arrhenius frequency factor

A_r = asphalt charge stock

A_{o_1}, A_{o_2} = intermediate asphalt products

A_{o_x} = composite air blown asphalt product not removed from the reacting zone

B = volume of sodium hydroxide per cc. of water or gm. of oil, cc.

C = gas concentration on a wet gas basis, volume per cent

D = concentration of gas on dry gas basis, volume per cent

d = gas density, lbs./ft.^{3}

E = molal energy of activation

e = base of natural logarithms

F_a = feed rate of fresh asphalt, lbs./hr.

f = conversion factor, lbs. oxygen/lbs. gas

G = gas flow rate, ft.^{3}/min. @ 70 ^oF. and 1 atm.

ΔH = asphalt blowing heat of reaction

I_a = intercept of ln(dR/dt) versus lnR plot at lnR = 0

I_b = intercept of the I_a versus lnS plot at lnS = 0

I_c = intercept of the I_b versus lnP plot at lnP = 0

k = pseudo reaction velocity constant

k' = specific reaction velocity constant

L_1, L_2, L_3 = intermediate condensed reaction products

L_x = composite condensed reaction products

M_a = mass of asphalt in reactor, pounds

N = normality of sodium hydroxide

P = feed gas oxygen concentration, volume per cent

p = exponent for P

$Pp.$ = partial pressure, mm. Hg.

R = asphalt Ring and Ball softening point, °F.

R_o = Ring and Ball softening point for charge stock, °F.

R_1 = Ring and Ball softening point at any reaction time, °F.

r = exponent for R

S = feed gas space velocity, $ft.^3$/min. - ton asphalt at 70 °F. and 1 atm.

s = exponent for S

T = absolute temperature, °K

t = batch process reaction time, hours

Δt = time interval, hours

t_c = continuous process residence time, hours

V = volume of water or weight of oil, cc. or gms.

v = volume of water, cc.

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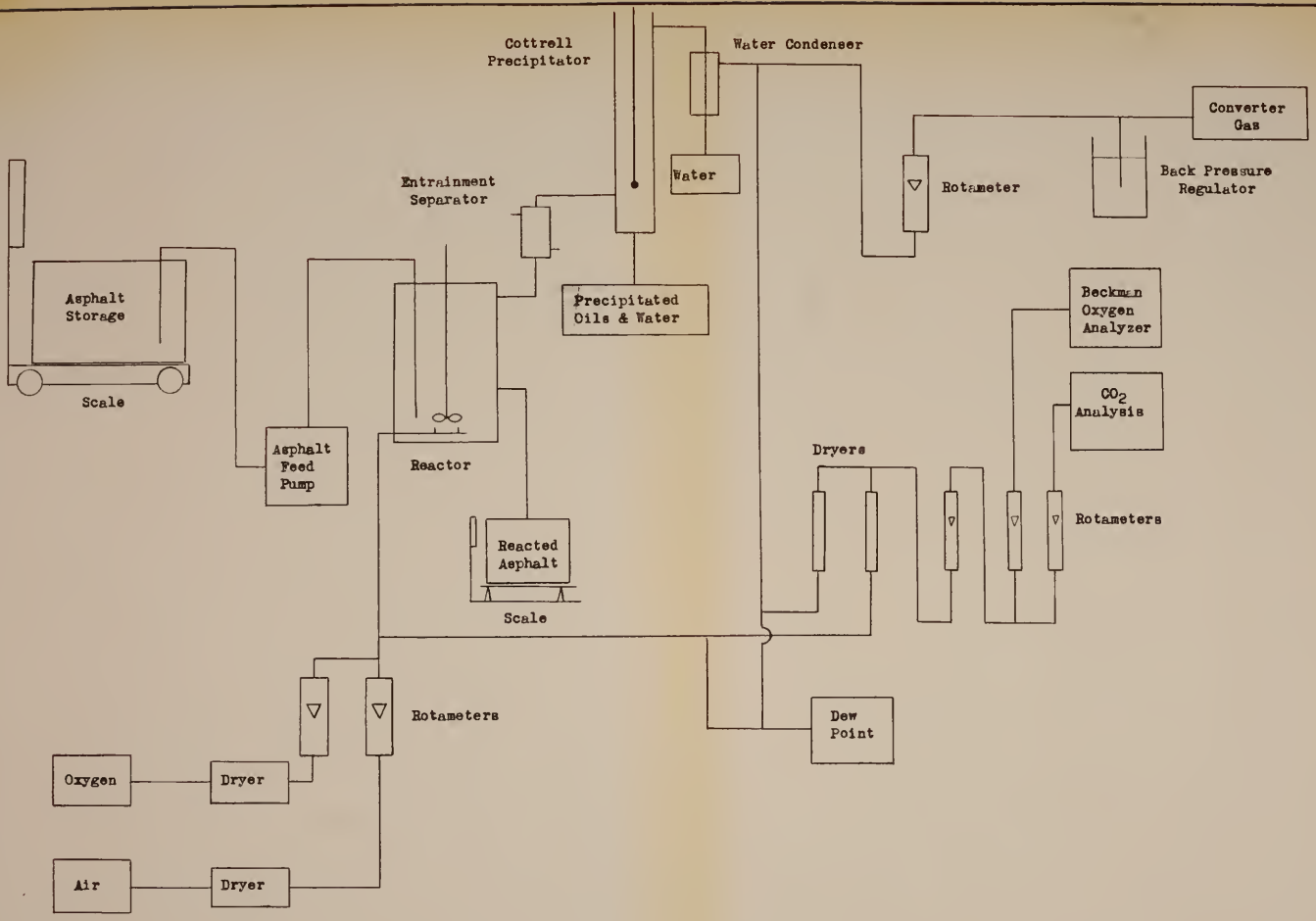
APPENDIX A

DRAWINGS

Figure 21



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DRAWING NUMBER 5203-1

Figure 22

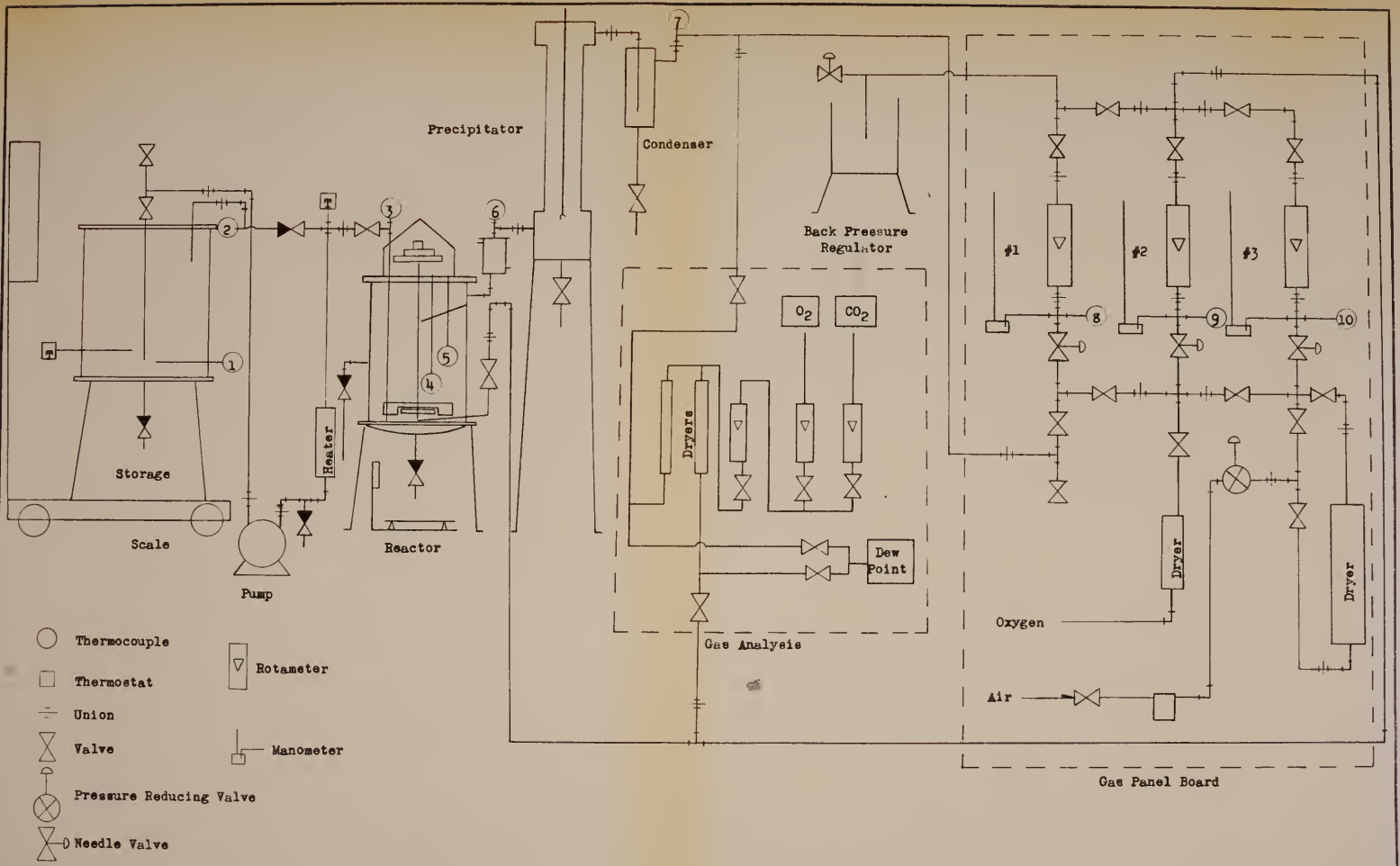

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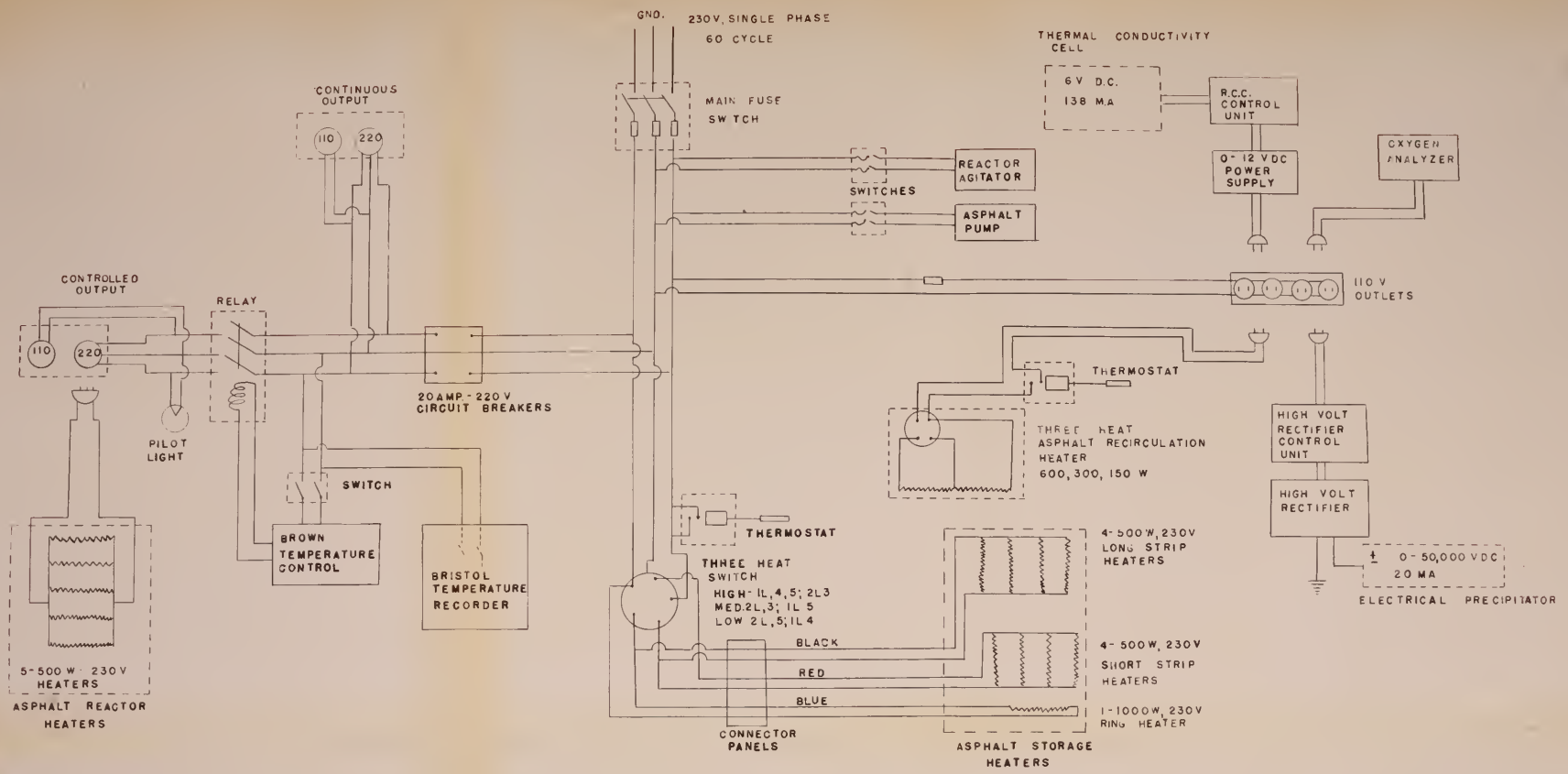
Figure 23



REVISION	DATE	MATERIAL

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL FRACTIONS

ASPHALT BLOWING WIRING DIAGRAM

DRAWN BY D. B.
CHECKED BY J. H.
DATE: 4-5-54
SCALE

ENGINEERING AND INDUSTRIAL EXPERIMENT STATION
UNIVERSITY OF FLORIDA
GAINESVILLE

DRAWING NUMBER
5302-3

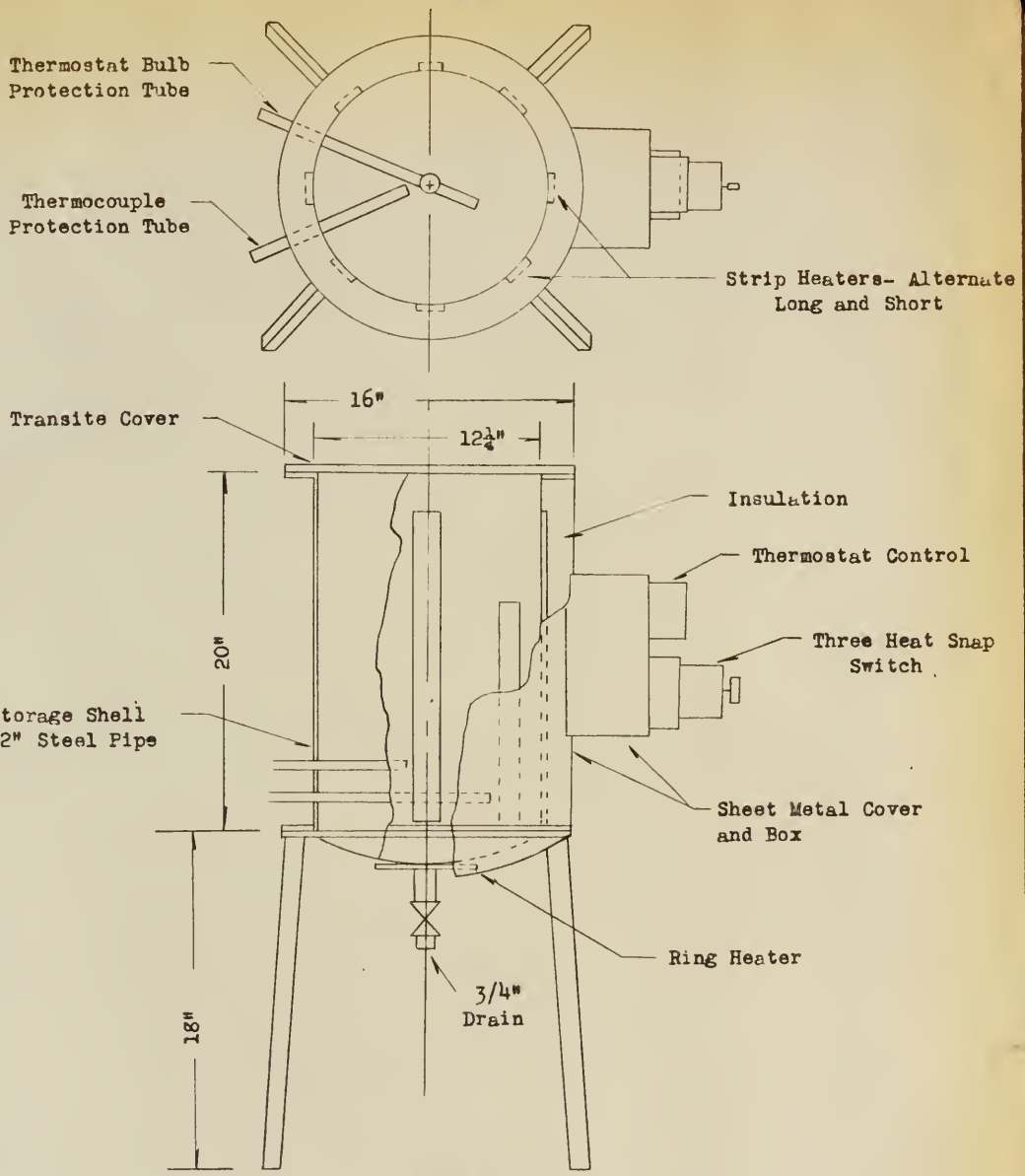


Figure 24

ASPHALT BLOWING STORAGE TANK

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REVISION	DATE	MATERIAL

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL FRACTIONS

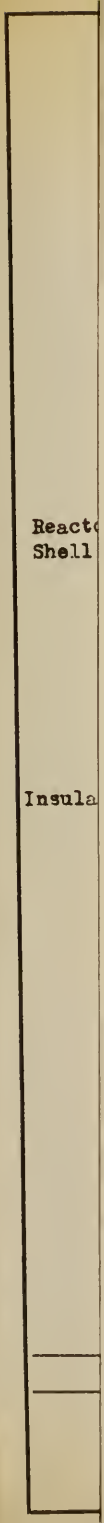
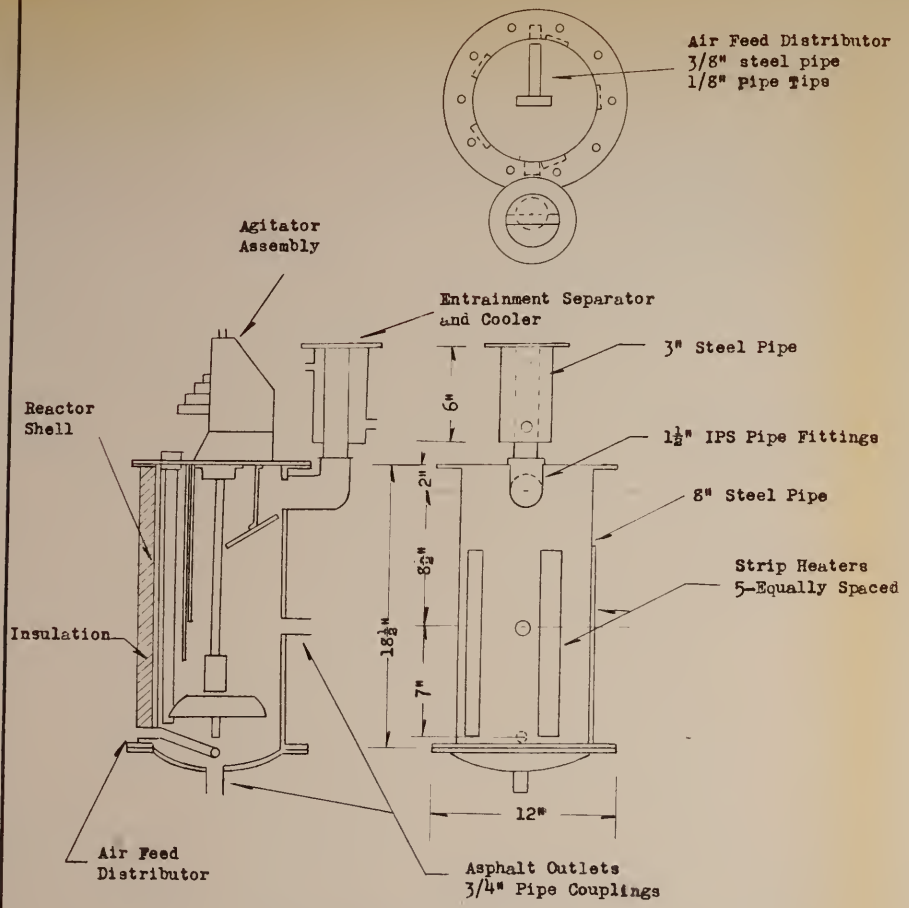
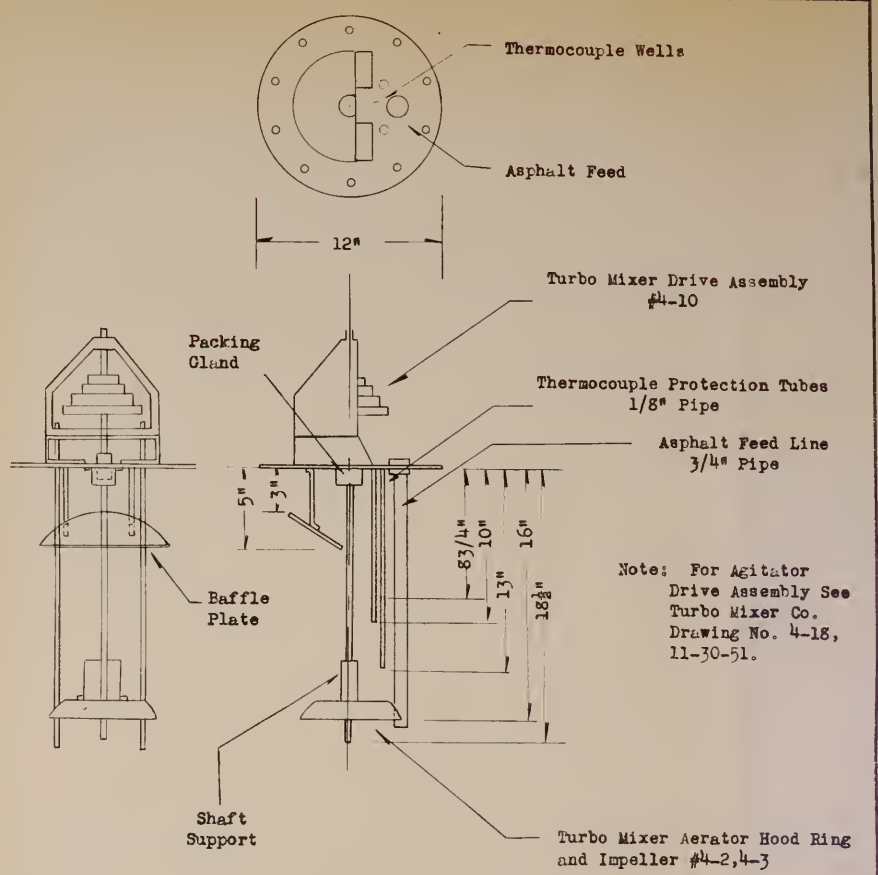


Figure 25



Reactor Assembly



Agitator Assembly

REVISION	DATE	MATERIAL	ASPHALT BLOWING REACTOR	
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DRAWING NUMBER 5203-5

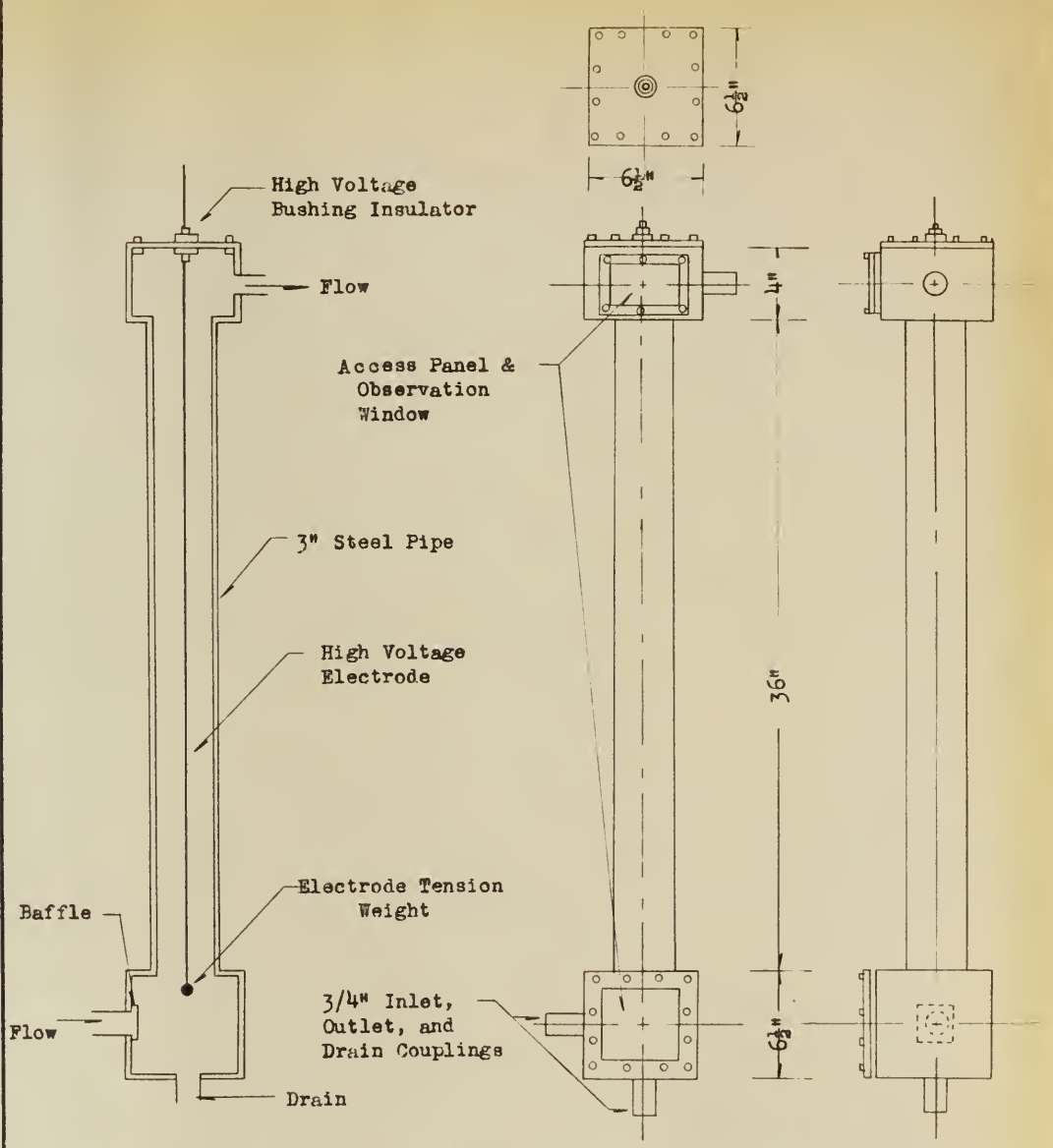

Figure 26

ASPHALT BLOWING ELECTRICAL PRECIPITATOR

DRAWN BY JB CHECKED BY: JH DATE: 3-27-54 SCALE:	ENGINEERING AND INDUSTRIAL EXPERIMENT STATION UNIVERSITY OF FLORIDA GAINESVILLE	DRAWING NUMBER 5203-6

REVISION	DATE	MATERIAL

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL FRACTIONS

APPENDIX B

EXPERIMENTAL DATA

TABLE 15

OPERATING CONDITIONS FOR ALL ASPHALT BLOWING RUNS

Run No.	Type Asphalt	Batch or Continuous B or C	Feed Gas Space Velocity CFMT	Feed Gas Oxygen %	Reactor Temperatures °F.	Agitator Speed R.P.M.	Asphalt Charge Lbs.
404	TA-1023-2	B	25	21	500	700	20.0
405	TA-1023-2	B	25	21	500	1300	20.0
406	TA-1023-2	B	100	21	500	700	20.0
407	TA-1023-2	B	200	21	500	700	20.0
408	TA-1023-2	C	200	21	500	700	20.0
409	TA-1023-2	C	200	21	500	700	....
410	TA-1023-2	C	200	21	500	700	....
411	TA-1023-2	C	25	21	500	700	20.0
412	TA-1023-2	C	25	21	500	700	....
413	TA-1023-2	C	25	21	500	700	....
414	TA-1023-2	B	25	50	500	700	20.0
415	TA-1023-2	B	100	50	500	700	20.0
416	TA-1023-2	B	25	50	500	1300	20.0
417	TA-1023-2	B	100	21	450	700	20.0

TABLE 15--Continued

Run No.	Type Asphalt	Batch or Continuous B or C	Feed Gas Space Velocity CFMT	Feed Gas Oxygen %	Reactor Temperatures °F.	Agitator Speed R.P.M.	Asphalt Charge Lbs.
418	TA-1023-2	B	25	50	450	700	20.0
419	TA-1023-2	B	100	50	450	700	20.0
420	TA-1023-2	B	100	21	550	700	20.0
421	TA-1023-2	B	100	35	500	700	20.0
422	TA-1023-2	B	100	50	550	700	20.5
423	TA-1023-2	B	25	35	500	700	20.0
424	TA-1023-2	B	25	21	450	700	20.1
425	TA-1023-2	B	25	21	550	700	20.2
426	TA-1023-2	B	25	50	550	700	20.0
427	TA-1023-2	B	100	21	500	700	12.0
428	TA-1023-2	C	100	21	500	700	20.0
429	TA-1023-2	C	100	21	500	700	20.0
430	TA-1023-2	C	100	21	500	700	....
431	TA-1023-2	C	100	21	500	700	....
432	TA-1026	B	25	21	500	700	20.0
433	TA-1026	B	100	21	500	700	20.0

TABLE 15--Continued

Run No.	Type Asphalt	Batch or Continuous B or C	Feed Gas Space Velocity CFMT	Feed Gas Oxygen %	Reactor Temperatures °F.	Agitator Speed R.P.M.	Asphalt Charge Lbs.
434	TA-1025	B	100	21	500	700	20.0
435	TA-1025	B	25	21	500	700	20.0
436	TA-1024	B	100	21	500	700	20.0
437	TA-1024	B	25	21	500	700	20.0
438	TA-1024	B	100	50	500	700	20.0
439	TA-1025	B	100	50	500	700	20.0
440	TA-1026	B	100	50	500	700	20.0
441	TA-1023-2	B	100	35	450	700	20.0
442	TA-1023-2	B	100	21	500	700	20.0

INTERNET ARCHIVE

Foldout too large for digitization

May be added at a later date

INTERNET ARCHIVE

Foldout too large for digitization

May be added at a later date

INTERNET ARCHIVE

Foldout too large for digitization

May be added at a later date

APPENDIX C

CALIBRATION CURVES

TABLE 17

AIR FEED ROTAMETER CALIBRATION DATA

SCHUTTE AND KOERTING 3F TUBE WITH MODIFIED ALUMINUM FLOAT NUMBER 2

Rotameter Scale Reading	Air Flow Rate CFM @ 70 °F. and 1 Atm.
0	0.107
5	0.142
10	0.175
15	0.206
20	0.241
25	0.270
30	0.298
59	0.505
90	0.735
120	0.964
149	1.187
180	1.443
210	1.672
242	1.952

TABLE 18

CONVERTER GAS ROTAMETER CALIBRATION DATA

SCHUTTE AND KOERTING 3F TUBE WITH MODIFIED ALUMINUM FLOAT NUMBER 1

Rotameter Scale Reading	Air Flow Rate CFM @ 70 °F. and 1 Atm.
1	0.135
7	0.180
15	0.232
20	0.272
25	0.308
30	0.350
59	0.575
90	0.830
118	1.065
149	1.324
181	1.595
209	1.848
242	2.130

TABLE 19

OXYGEN FEED ROTAMETER CALIBRATION DATA

SCHUTTE AND KOERTING 1R TUBE WITH
STAINLESS STEEL ROTOR

Rotameter Scale Reading	Air Flow Rate CFM @ 70 °F. and 1 Atm.
6	0.034
30	0.066
60	0.106
100	0.165
144	0.239
190	0.317
211	0.353
239	0.397

TABLE 20

GAS ANALYSIS ROTAMETER CALIBRATION DATA

FISHER AND PORTER TUBE NUMBER 01-N-15A WITH
PYREX AND STAINLESS STEEL FLOATS

Rotameter Scale Reading at Center of Floats		Air Flow Rate CFM @ 70 °F. and 1 Atm.
Pyrex	Stainless Steel	
11	4	0.0104
20	9.5	0.0213
28	14	0.0311
37	19.5	0.0452
39	20	0.0472
50	27	0.0635
60	35	0.0811
67	39	0.0922

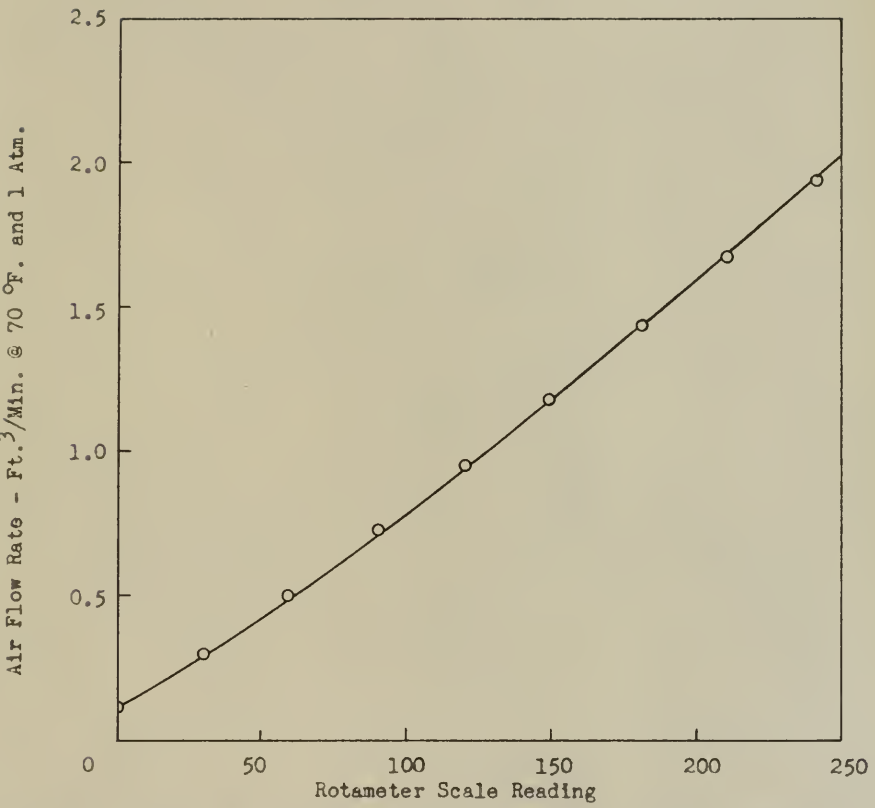

Figure 27. Air Feed Rotameter Calibration Curve, Schutte and Koerting 3F Tube and Number 2 Aluminum Float

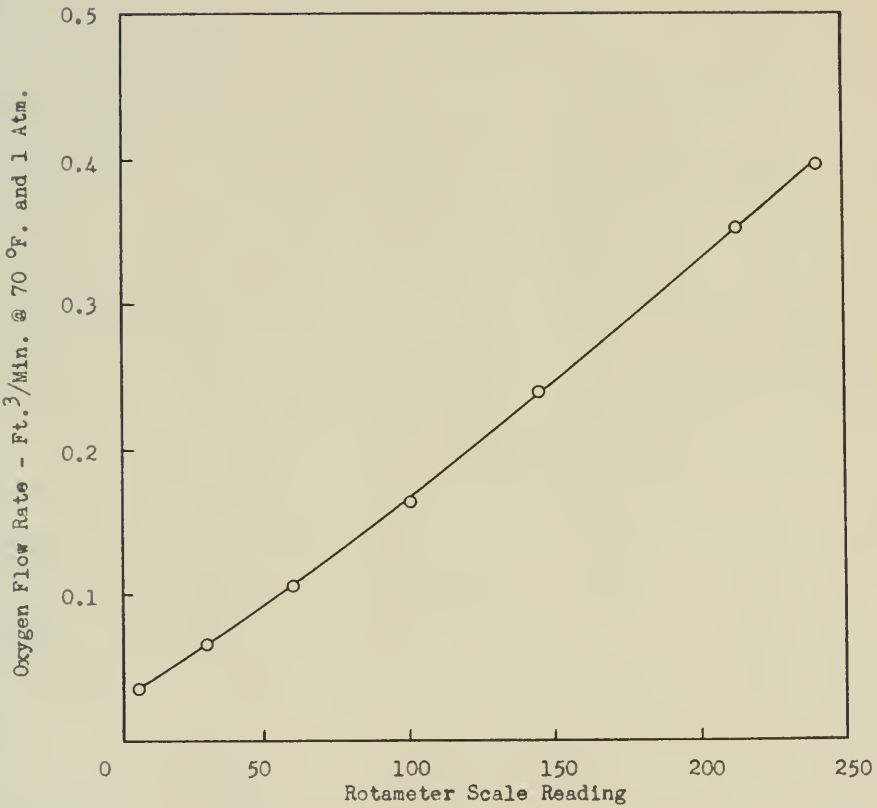

Figure 28. Oxygen Feed Rotameter Calibration Curve, Schutte and Koerting 1R Tube and Stainless Steel Float

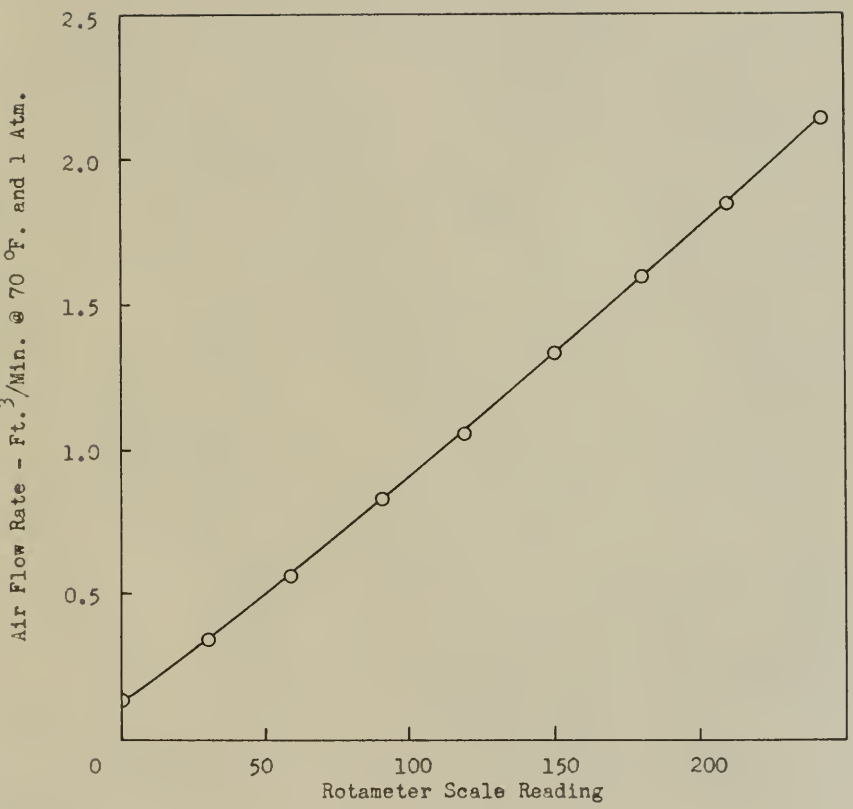

Figure 29. Converter Gas Rotameter Calibration Curve, Schutte and Koerting 3F Tube and Number 1 Aluminum Float

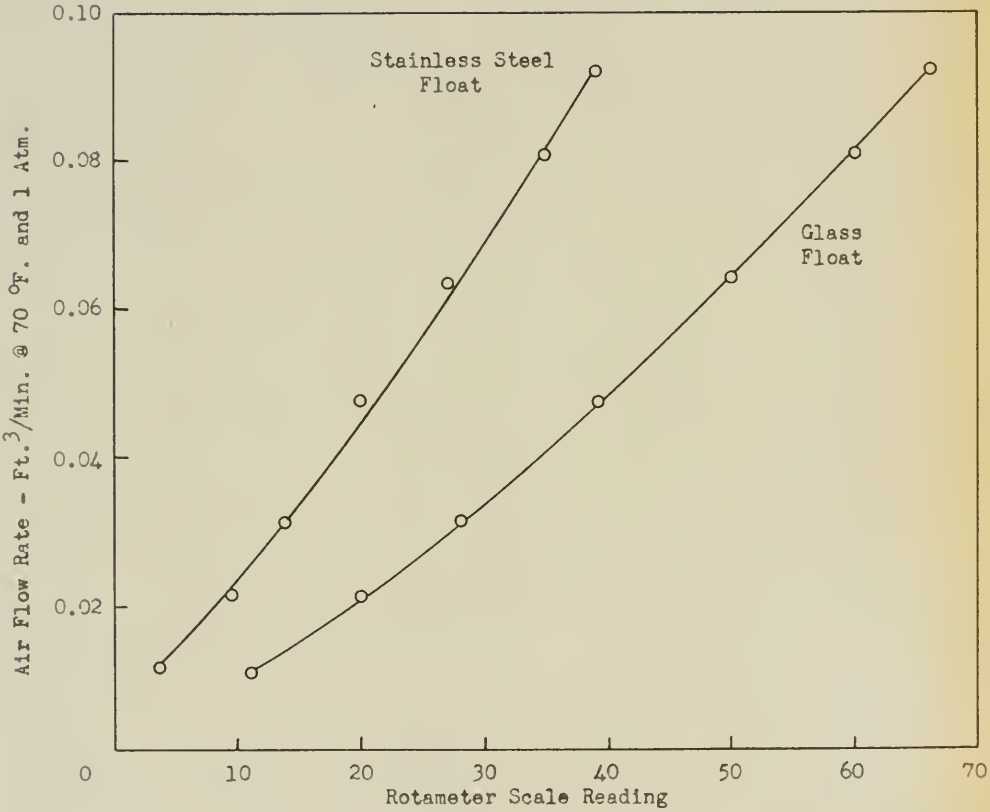

Figure 30. Gas Analysis Rotameter Calibration Curve, Fisher and Porter 01-N-15A Tube with Pyrex Glass and Stainless Steel Floats

XII. BIOGRAPHY OF AUTHOR

John Daniel Holmgren was born in Leadville, Colorado on March 20, 1927. Three months later he and his parents moved to Silverton, another small mining town high in the mountains of Southwestern Colorado. He graduated from the Silverton High School in June 1944, and entered the University of Colorado in October of that year. He graduated in June 1948 with a Bachelor of Science degree in Chemical Engineering. After graduation he accepted a position as Chemical Engineer with the General Electric Company in Richland, Washington and was assigned as research engineer to a pilot plant development group. During this time he studied various phases of atomic energy, such as, pile technology, chemical processing of uranium and plutonium, and radio-active waste disposal. In order to complete extension work on a Master's degree, he resigned his position with the General Electric Company and entered the University of Washington in September, 1950. He completed the work on his Master's degree in Chemical Engineering in September 1951 and transferred to the University of Florida to work towards a degree of Doctor of Philosophy. In June 1952 he received an appointment as Instructor at the University of Florida to work on a classified research project sponsored by the Department of Defense, and he is presently working on this project. He was married in June 1953. He is a member of the American Institute of Chemical Engineers, the American Chemical Society, Alpha Chi Sigma, and he is a Registered Professional Engineer in the State of Florida.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 7, 1954

Joseph Weil
Dean, College of Engineering

Dean, Graduate School

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