

PRODUCTION OF BINDERS FROM CELLULOSIC WASTES

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FROM CELLULOSIC AND MAN-MADE
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IN ARKANSAS

by

G. David Jimerson
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FINAL REPORT
HIGHWAY RESEARCH PROJECT 37

conducted for
The Arkansas Highway and Transportation Department
in cooperation with
The U.S. Department of Transportation
Federal Highway Administration

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Arkansas State Highway Department or the Federal Highway Administration.

Staffing of this project was consistent with The Affirmative Action Program of Arkansas State University.

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ABSTRACT

Several cellulosic and man-made polymeric substances were treated by pyrolysis. The object was to examine them as potential sources of asphalt substitutes or extenders and as potential sources for filler materials. From the initial studies a technique, which we call, "Inverted" pyrolysis seemed to be the most promising.

Two major designs for the "Inverted" pyrolysis systems were developed and scaled up to accomodate approximately 100 gallon batch charges. The first design produced a higher percentage of binder, based on initial sawdust input, but required an external heat source and the removal of the "char" residue. The second design, even though producing a lower percentage yield, supplied its own energy by combustion of the char and produced only small amounts of ash. The second design is believed to be the more practical of the two since sufficient "excess" energy appears to be produced that with proper engineering the entire system could be energy self-supporting with the exception of normal electrical controls and flow devices.

Due to the use of the second, energy saving, system the production of filler materials was dropped from the project objectives. About 20 gallons of the final binder material were produced. The binder was used for chemical and physical testing as well as investigating the improvement of its quality through blending with other substances and by further chemical and physical processes.

GAINS, FINDINGS AND CONCLUSIONS

A binder has been produced from sawdust, which could be substituted for asphalt in low wear areas. The early, energy intensive nature of the process has been completely removed and the process design is essentially self-sufficient with respect to energy.

Conservative estimates suggest that binder, at a rate of 5% by weight, could be produced from sawdust with not more than 5%, by volume, residual matter (ash) remaining. Thus the elimination of waste sawdust is a coincidental gain in the process. The yield translates into 1000 tons/mo. of binder since, as determined by a previous work, 20,000 tons/mo. of sawdust are available for processing in Arkansas.

Changes in the final treatments of the binder by chemical and physical processes were not successful in improving its quality. Further, no treatment which resulted in a product that had binding properties eliminated, or even substantially reduced, the objectionable odor of burning wood.

Studies involving blends of the binder with asphalts and sulfur indicated that such mixtures might have specific applications in maintenance work but that precautions would have to be observed if objects containing this binder are in direct contact with those cemented with asphalt.

A possible self-binding pot-hole aggregate was produced using blends of asphalt and sulfur as well as the synthetic binder and sulfur.

Some of the chemical components of the binder and its decomposition products have been separated and identified. The by-products of the process were not studied.

IMPLEMENTATION STATEMENT

The implementation of the process developed in this work is feasible and should be ultimately energy extensive. The practicality of the use of the binder will hinge to a large extent on economic and political conditions. The increasing cost of petroleum products and our dependence on imported oil make the use of such processes even more attractive (and perhaps necessary) than was true when this work was started.

The material produced in these studies is of lower quality than asphalt cement of comparable penetration grade and would not be suited for major heavy-use projects. It could, however, be used in temporary maintenance work and on low usage projects. The binder is similar to asphalt in many aspects, and can be produced with a desired penetration grade. It should be possible to use the binder in hot-mix plants and employ conventional construction procedures. In addition, the material should be suitable for use as a cutback binder. The major drawback to at least limited use of the binder is its objectionable odor which seems to persist.

Certainly, further work should be done in this field of research. It would seem reasonable that larger scaled research efforts toward use of a trichloroethylene-soluble binder produced from wood products could be carried out by or near a charcoal manufacturer or similar industry.

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INTRODUCTION

This project originated from a previous research project contracted by the Arkansas State Highway Department and The Federal Highway Administration, Project HRC-34 (1).

In the course of Project HRC-34, a survey of wastes in non-urban areas of Arkansas, the wastes were divided into nine categories. A list of the monthly production of each type was:

<u>Waste Type</u>	<u>Amount in tons/month</u>	<u>Weight % of Total</u>
Minerals	31,214	44.4
Wood	19,735	28.1
Agricultural	11,353	16.2
Liquids	6,000	8.6
Metals	1,049	1.5
Paper	687	0.9
Polymeric	46	0.1
Leather and Cloth	41	0.1
Glass and Fiber Glass	27	0.1

Minerals and glass wastes held the potential for some direct use application in highway construction and maintenance. Metals were being sold for scrap-metal prices and for economic reasons merited no further study. After removing these three categories from the above list, about 55% of the wastes remained. Assuming that half of the liquids would be unfit for use because of large volumes of water or poisonous chemical content, 50% of the wastes would require other than minor processing before they were suitable for use in highways.

Sixteen states were currently using waste materials in highway construction. Another eleven states were involved in research efforts which they hoped would lead to use of wastes in their construction work. Almost all of the presently used materials and those under study were considered from the standpoint of potential aggregates. No work appeared to be aimed

in the direction of using the "non-obvious" materials such as sawdust, cotton gin waste, and scrap paper, except in token amounts for mulch and erosion deterrents.

The long-term accepted method for disposal of these materials, burning at the site of production, had recently come under attack. In fact, new pollution control legislation had all but eliminated this method. While these wastes were used in the manufacture of such materials as pressed board, cardboard or recycled paper, large amounts of these wastes were piling up and creating tremendous storage problems due to the lack of an approved method of disposal. Because of the large scale operation of the highway building industry, use of these wastes could be the solution to reduced construction and maintenance costs as well as the waste disposal situation.

Destructive distillation of tires has been found to produce heavy oils (2). The molecular weight of these oils depends upon the distillation conditions. Tires have also been converted into hydrogen and acetylene gases for fuels. This conversion was accomplished by means of laser pyrolysis. Various types of pyrolysis and distillation have been used to convert other materials such as wood, paper, plastics, used oil, cloth, agricultural wastes and sewage into fuel gases and other useful products (3,4,5,6,7,8).

A preliminary study at Arkansas State University (9) has shown that under the proper conditions, pyrolysis of sawdust and agricultural wastes can produce tars in appreciable amounts. According to a German patent the residual carbon can be mixed with these tars as a filler.

From recent studies in the United States (11), a process for producing a fuel oil by the pyrolysis of cellulosic agricultural wastes had been

developed. In this context, as well as throughout this work, pyrolysis refers to any destructive distillation where less than complete combustion occurred. Thus, this project was initiated because it was believed that pyrolysis could be used to produce binders and fillers from most of the remaining unused wastes (50% as previously stated).

OBJECTIVE AND SCOPE

The main objective of this work has been to produce, from cellulosic wastes, predominantly sawdust, a binder that would serve as a substitute for asphalt. Several changes in the scope of the study have occurred during the course of the project.

In Phase A of the study, the objective was to conduct a bench scale study which would allow the investigators to:

1. Recommend a process for converting waste materials into binders and fillers suitable for use in highway construction and maintenance.
2. Derive the external parameters which would make the overall process applicable to mixtures of many different waste materials, thereby avoiding costly separation procedures prior to processing.

As a result of the Phase A studies, the scope was reduced to include only cellulosic wastes and ultimately sawdust from a single source. Phase A work led to the design of Processor I which was built to fulfill the objectives of Phase B. Phase B objectives were to:

1. Demonstrate the functionality of inverted pyrolysis in the production of binders from cellulosic wastes.
2. Permit road testing of the binder.
3. Critique the apparatus design and suggest any required modification prior to implementation.

Phase B work yielded far less binder than anticipated, based on the lab scale tests, thus road testing was not possible. This was due primarily to the length of time required to process each batch of sawdust.

Processor I was judged to be too energy intensive to be feasible for implementation. The char produced by Processor I was to have been investigated as a potential filler. When Processor II was designed and tested in the lab, no char was produced and therefore the filler studies were dropped from the scope of the project.

Processor II was constructed and operated in Phase C in order to:

1. Produce as much binder as possible.
2. Road test the binder.

Processor II was not energy intensive, however, and the per batch yield of binder was reduced significantly so that only 18-20 gallons of binder were available for testing.

Consultation with the Research Division of the Arkansas Highway Department resulted in a decision to cancel the planned road test in the fall of 1977 so that sufficient binder would be available for lab testing and study. This decision fortuitously avoided almost certain failure of the road test due to the severity of the winter.

Although the object of the project had become the production of a binder that matched, as nearly as possible, the physical characteristics of Asphalt Cements, test results on the binder produced from sawdust indicated that it was not, in its state of development, compatible with asphalt. In fact, tests conducted by the AHTD Materials & Tests Division indicated that the binder was too weak and oxidized too easily to be readily suited to highway construction applications.

Even though it should have been possible to eventually match the properties of the substitute binder to those of petroleum based asphalt, the course of study was altered. Rather than continue the effort to make the HRC-37 binder match asphalt in all of the usual tested properties, studies were conducted in an attempt to develop useful and needed materials from the available supply of binder. Possible uses of the binder in cold-mix patching materials, crack or joint fillers, seal coats and other similar applications on low volume roads seemed to be more easily and rapidly implemented than the original objective of a total asphalt substitute.

In the final phase of this project, the investigation of possible treatments of the binder prepared in HRC-37 were broken into 3 classes:

1. Those that will extract or remove some component that may be causing an undesirable feature. (Example is excessive water solubility).
2. The addition of other substances to change the overall physical properties of the binder.
3. The addition of other substances to produce an immediately usable product.

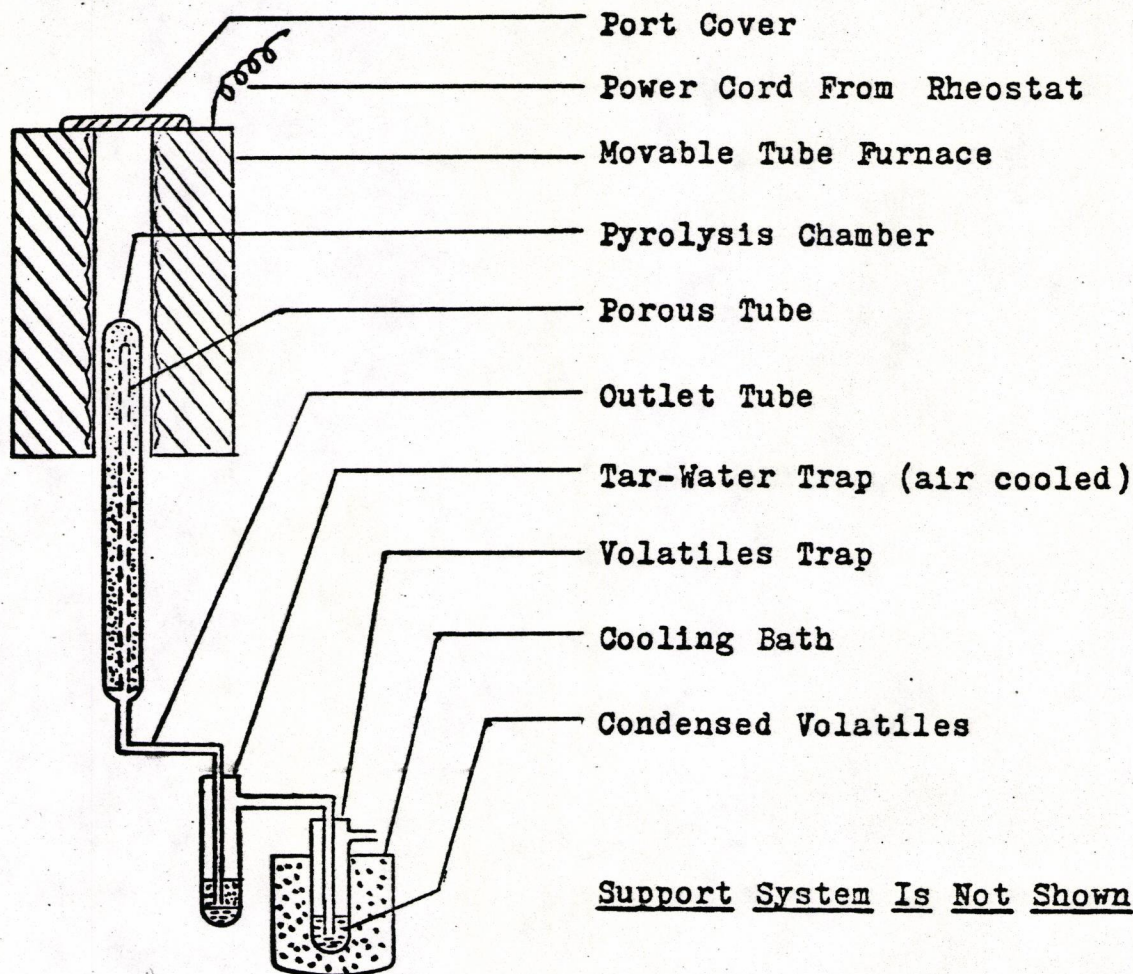
PHASE A STUDIES

Phase A studies were conducted from July 1, 1973 to August 15, 1974. Laboratory scale pyrolysis of a variety of cellulosic and man-made polymeric waste were conducted during this phase.

Project HRC-34 revealed an abundance of sawdust and other waste from which it was suspected that a binder would be produced by pyrolysis (1,9). It was immediately found that prolonged heating of the binder, during pyrolysis, resulted in rapid carbonization of the product. Carbonization appeared to take place even at the lowest pyrolyzing temperature and thus, in its production, it was essential that the material be removed from the reaction vessel as soon as possible after formation. This presented more of a problem than one might expect. The binder had to be removed from both the raw material and the solid residue on which it was absorbed. Heating to temperatures sufficiently high to vaporize the binder, thus allowing easy removal from the reaction vessel, caused decomposition of the desired material.

The approach adopted was to continually remove the products from the bottom of the reaction vessel as they were formed instead of distilling them through the top of the apparatus. While this overcame the first problem, it did not remove a second obstacle. The decomposition reaction became exothermic when temperatures somewhat greater than 250°C were employed. Once this point was reached, carbonization and the formation of unwanted products proceeded rapidly. Thus lower temperatures had to be used if the process was to be successful.

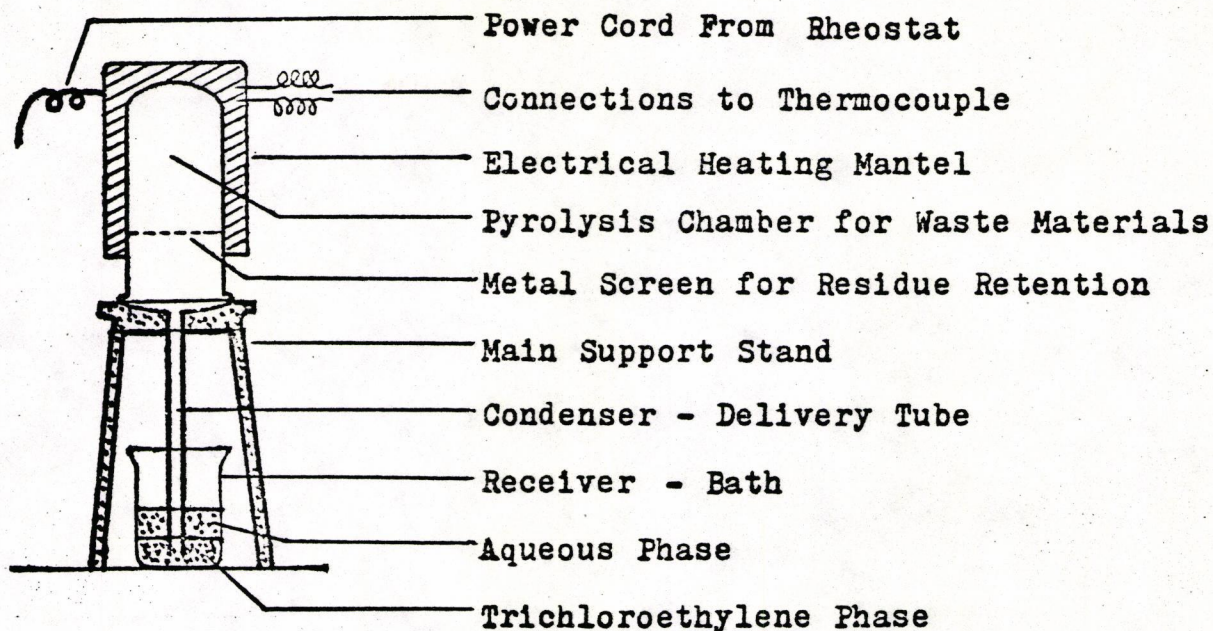
Two systems which overcame these problems were assembled as shown in Figures 1 and 2. Both systems permit easy removal of the products and do so by forcing them, inward and down, away from the heated zone.

FIGURE 1

Fixed Tube - Movable Heater - Center Core Pyrolysis Unit

OPERATION:

- (1) The pyrolysis chamber is filled with the waste material.
- (2) The furnace is adjusted to the desired temperature and the port cover is closed.
- (3) The furnace is lowered at a rate of about 3 inches per hour.
- (4) The pyrolysis products move downward and thus away from the heated area.
- (5) The more volatile materials pass through the system and are condensed in the cooled trap while the less volatile ones are collected in the first trap.

FIGURE 2**Fixed Cylinder - Fixed Heater Pyrolysis Unit****OPERATION:**

- (1) The pyrolysis chamber is filled with the waste material.
- (2) The Rheostat is adjusted to give a selected final temperature.
- (3) As the mantel heats the waste materials, the pyrolysis products are driven inwards and down to the outlet.
- (4) Trichloroethylene soluble products are collected in the lower phase in the receiver while the water soluble products are concentrated in the aqueous phase.

MODIFICATION:

The unit can be used with a water-cooled or air-cooled condenser rather than the bath type collection. This is accomplished by removing the condenser - delivery tube and replacing it with an adapter that permits connection to a condenser system.

The process was called "Inverted Pyrolysis."

To further ease the escape of the products, a "gatherer" was inserted into the middle of the pyrolysis chamber of the apparatus shown in Figure 2. This consisted of a section of pipe with slotted walls, plugged top, and open bottom. The "gatherer" reduced the processing time thereby indicating that it was effectively increasing the rate of escape of the products.

The distillates were passed through trichloroethylene where the desired product and other compounds of low polarity were dissolved. The more polar compounds were collected in the upper layer (water) or escaped into the air. The gaseous discharge was noted to burn with a blue flame.

Initial pyrolysis was carried out on red oak, pine, cyprus, tupelo (gum), newspaper, ditto paper, rice hulls, soybean cleanings, asphaltic roofing wastes, cardboard, rubber tires, thermosetting plastic and thermoplastic. The trichloroethylene was stripped with a roto-evaporator and reused, and the product stored for future processing or study.

Yields of the desired product were difficult to measure. Estimated yields for all sawdusts used were in the range of 10-15% by weight. Materials that produced binders are listed in Table II on the following page.

TABLE II

YIELDS OF RESIDUE AND BINDER FROM VARIOUS WASTES USED

Based on a 100 gram sample of nondried material

MATERIAL	MASS OF RESIDUE IN GRAMS	TOTAL HEAT VALUE (calories) Available for Pyrolysis	MAXIMUM YIELD OF BINDER IN GRAMS
Sawdust (average of all types used)	23.9	1.32×10^5	16
Wheat Straw	34.6	1.72×10^5	29
Rice Hulls	45.4*	1.17×10^5	17
Soybean Cleanings	34.0	1.96×10^5	29
Paper (mixture of types)	34.2	2.31×10^5	22
Cardboard	30.2	1.84×10^5	13

* The residue from rice hulls contains about 50% by weight silica

The Heat Value Available for Pyrolysis, given in the above table, has been corrected for the heat required to drive off the moisture that was present in the materials when they were obtained as well as the heat required to vaporize the water that was formed during the pyrolysis process. In other words, that amount of heat was available for the energy required in the pyrolysis unit.

Several series of studies were conducted on the final product obtained from the organic phase produced in wood pyrolysis. It was found that the softening points and the penetration grades could be varied. If one plots the log of the penetration against the softening point an almost linear relationship exists. For penetration grade of 60-70 the softening point was approximately 45°C.

A different binder was produced from the water layer. No attempts were made to perfect or test its properties since it would not dissolve in trichloroethylene and appeared to be of lower quality.

The results of the work, up to that time, lead to the conclusion that sawdust, which was available at more than 20,000 tons/mo., could be pyrolyzed to produce binder for more than 300 miles of road per year in Arkansas. This assumed a 10% yield and 6% binder in the surfacing material. It was suggested that this would be feasible if the heat value of the solid residue was recovered and used in the processing.

The expected yields and energy balance, extrapolated from the lab studies, for a fifty gallon unit are shown in the following table.

TABLE III

ESTIMATED YIELDS AND ENERGY BALANCE FOR A FIFTY GALLON UNIT

MATERIAL	MAXIMUM WEIGHTS IN KILOGRAMS			HEATS IN MILLION BTU'S		
	<u>CHARGE</u>	<u>BINDER</u> ¹	<u>RESIDUE</u>	<u>USED</u> ²	<u>AVAILABLE</u> ³	<u>DEFICIT</u> ⁴
Sawdust	77	12	18	760	498	262
Wheat Straw	25	7	9	760	202	558
Rice Hulls	32	5	15	760	173	587
Soybean Cleanings	35	10	12	760	297	463
Paper	82	18	28	760	820	-60
Cardboard	32	4	10	760	272	488

1. Maximum yield of material, i.e. charge minus residue and water formed.
2. Calculated from laboratory electrical values assuming eight hours of processing to be average.
3. Heat available from residue if burned.
4. Note that sawdust had the least energy deficit of those wastes which are available in large quantities.

It was predicted that with a 50 gallon batch processor up to 5,000 pounds of sawdust could be processed during a one month period of operation and that 450 to 800 pounds of binder could be produced. Although the production during later phases of this project did not approach this estimate, it was still believed to be the theoretical maximum output for the proposed design. Sawdust was the only material suggested for large scale processing due to its local availability and the mounting disposal problem.

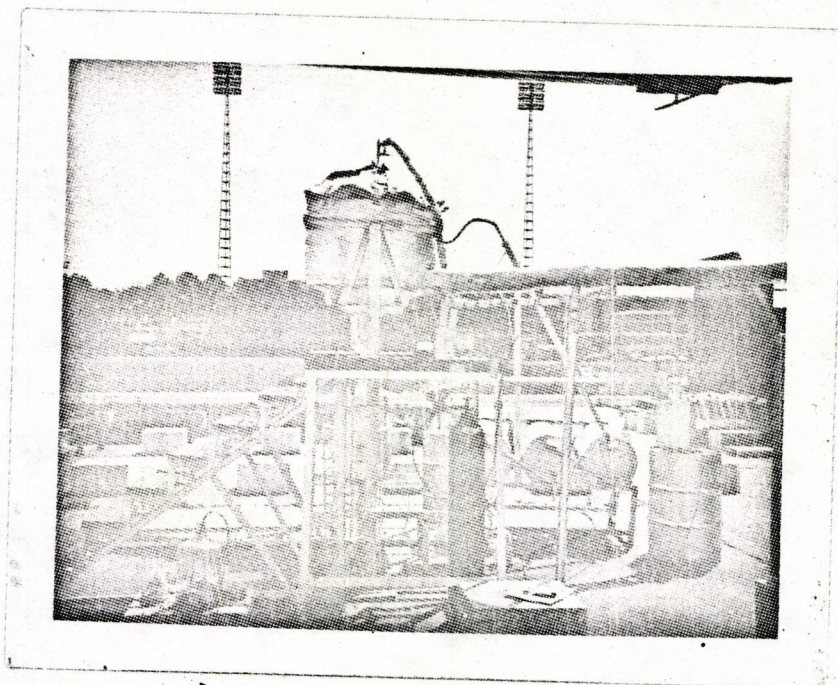
The results obtained in Phase A led to the design of Processor I, which would handle 50 or more gallons of sawdust per batch. It was also designed to burn the carbon residue in order to reduce the energy input needed for pyrolysis and thus make the processor less energy intensive. Due to time and financial limitations, the residue burner was eliminated from the energy system shown in Figure 3.

PHASE B STUDIES

Phase B studies spanned the period from August 15, 1974 through March 31, 1976, most of the work being conducted during the summer months.

Processor I, shown in the accompanying photographs, was built from the designs shown in Figures 3, 4, and 5. The events of the summer of 1975 are summarized as follows.

Several weeks were required to complete the construction of Processor I. A 120 gallon water treatment tank from a swimming pool was obtained at a local junk yard. This tank was cut, a flange was milled, gaskets were prepared, the heat exchanger pipe was shaped and fitted through the side, a downspout was attached, a top cover plate was fitted, platforms and steps were built, a cradle was formed for the tank and the tank was mounted on the cradle. The processor and cradle were supported on 4 X 4 steel posts that were guyed by the platforms.

PROCESSOR I

Photographs of the Converter System

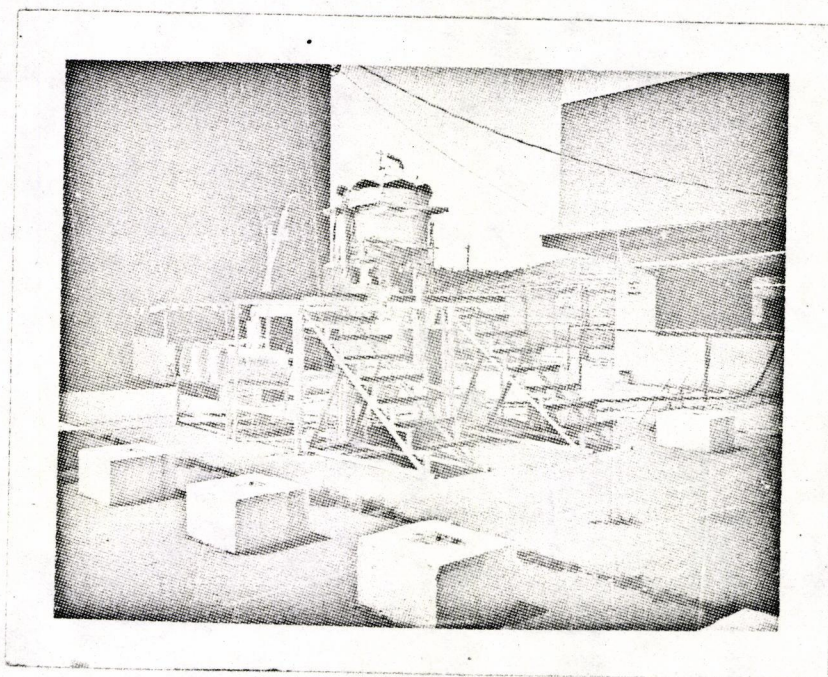
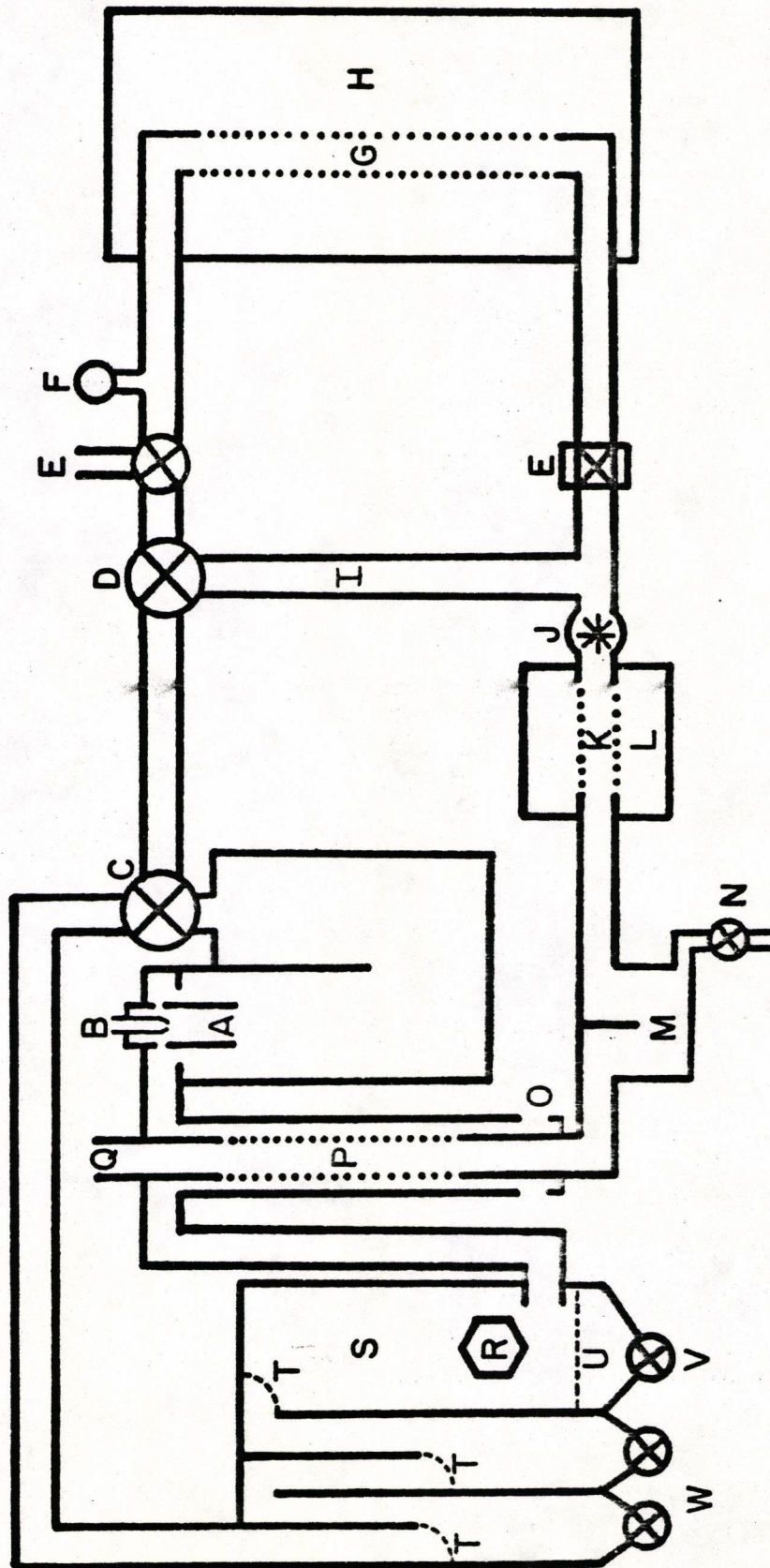


FIGURE 3



ENERGY SYSTEM SCHEMATIC

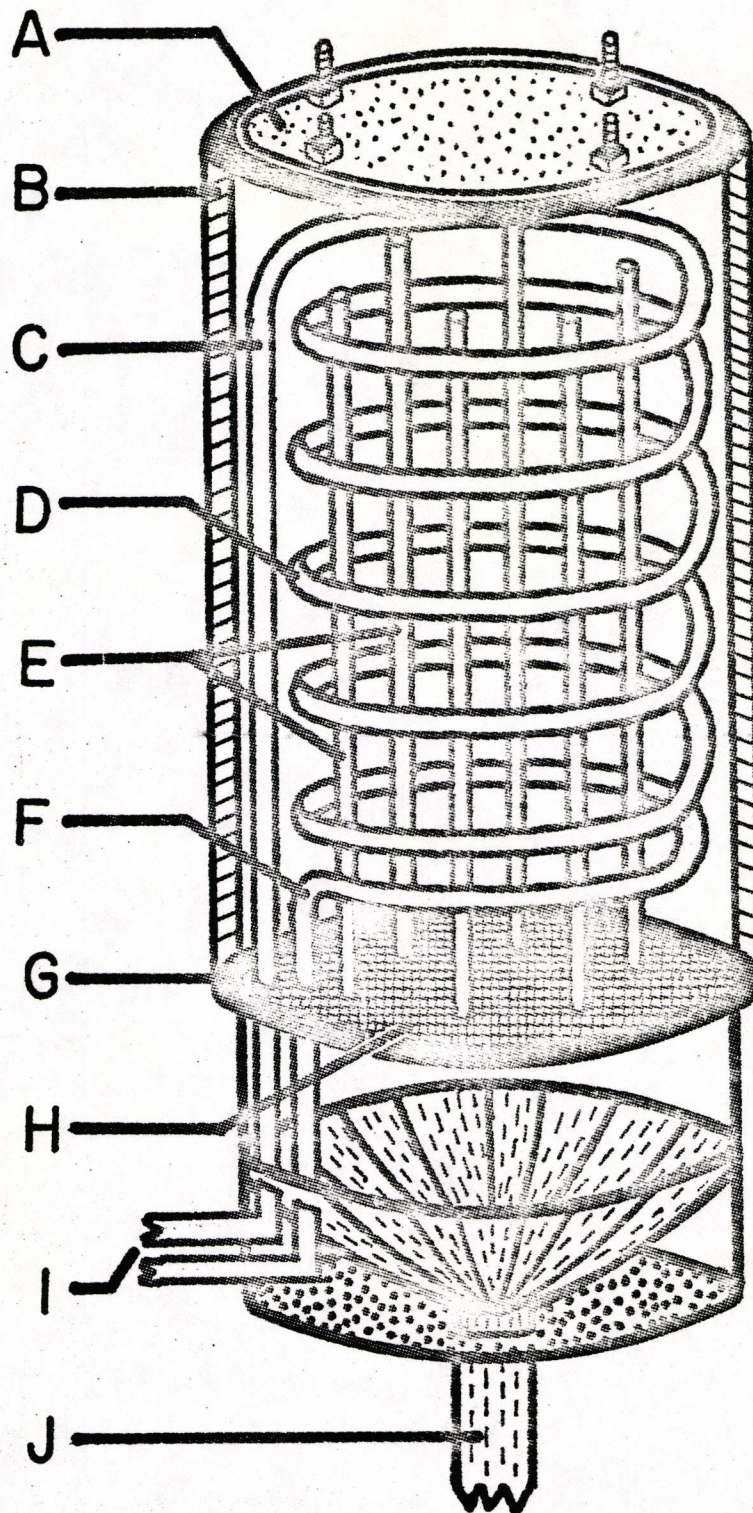
FIGURE 3 (Legend)KEY to the ENERGY SYSTEM SCHEMATIC

<u>ITEM</u>	<u>DESCRIPTION and/or FUNCTION</u>
A	<u>GAS BURNER</u> - Initial heating source for each run and for supplemental heating when the "waste" fuel is exhausted
B	<u>GAS SUPPLY</u>
C	<u>VALVE SYSTEM</u> - to permit the use of either the gas burner and/or the waste carbon burner
D	<u>VALVE, SHUNT</u> - permits the total or partial by-pass of the pyrolysis unit
E	<u>VALVE SYSTEM</u> - permits pressure testing of the heat exchanger within the pyrolysis unit
F	<u>PRESSURE GAGE</u>
G	<u>HEAT EXCHANGER</u>
H	<u>PYROLYSIS UNIT</u>
I	<u>SHUNT DUCT</u>
J	<u>FAN</u> - draws hot air through the pyrolysis unit and forces the air through the remainder of the energy system
K	<u>HEAT EXCHANGER</u>
L	<u>SAWDUST DRIER</u> - uses residual heat content of the air to pre-dry the next charge unit for the pyrolysis system
M	<u>BAFFLE</u>
N	<u>TRAP</u> - removes condensed materials from the hot air system
O	<u>FRESH AIR INLET</u> - air inlet for both burner systems
P	<u>HEAT EXCHANGER</u> - uses any residual heat content of the hot air system to pre-heat the fresh air that enters the burner systems
Q	<u>EXHAUST STACK</u>
R	<u>PORT</u> - for the placement of the waste carbon from the pyrolysis unit into the waste burner
S	<u>COMBUSTION CHAMBER</u>

See the separate diagram for details

(Legend cont'd)

- T SCREENS - prevent the passage of small carbon particles into the hot air system
- U GRID - supports the waste carbon during combustion
- V PORT, CLEAN OUT - for the removal of any noncombustible materials
- W PORTS, CLEAN OUT - for the removal of small carbon particles that are removed from the hot air system by the screens "T"

FIGURE 4

PYROLYSIS UNIT

FIGURE 4 (Legend)
KEY to the PYROLYSIS UNIT

<u>ITEM</u>	<u>DESCRIPTION and/or FUNCTION</u>
A	<u>COVER PLATE</u> - permits access to the pyrolysis chamber for filling with sawdust and removing the charcoal residue
B	<u>INSULATION LAYER</u> - covers only the pyrolysis chamber
C	<u>HOT AIR INLET</u> - hot air from the "Energy System" passes to the top of the pyrolysis chamber and then through the heat exchanger coils - hottest zone will originate at the top of the unit and gradually expand downward
D	<u>HEAT EXCHANGER COILS</u>
E	<u>GATHERER TUBES</u> - sealed on top end - open end extends below the grid, "H", - permits the vaporized pyrolysis products to escape from the pyrolysis chamber without passing through the sawdust at the lower levels - the tubes have a series of spiraling slits that run from the top to the level of the grid
F	<u>HOT AIR RETURN</u> - returns air with residual heat content to the energy system
G	<u>FLANGE</u> - permits the removal of the pyrolysis chamber casing for inspection and/or repairs of the heat exchanger coils and the gatherer tubes
H	<u>GRID</u> - holds the sawdust in the pyrolysis chamber - supports the gatherer tubes - permits escape of vapors and liquids from the pyrolysis chamber
I	<u>UNION JOINTS</u> - permit rapid connection or disconnection of the pyrolysis unit and the energy system
J	<u>PRODUCT OUTLET</u> - pyrolysis products pass into the receiver system

FIGURE 5

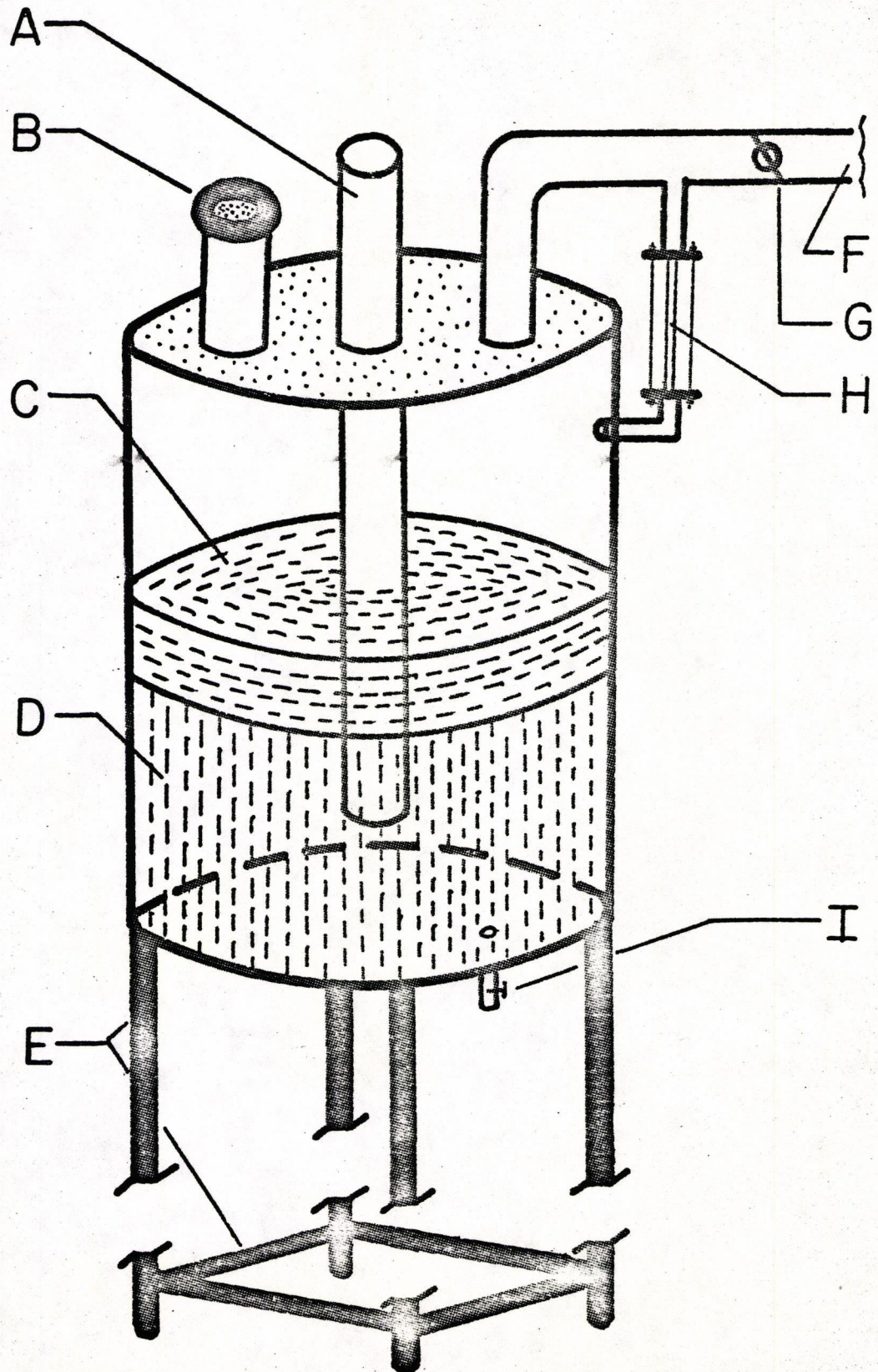
PRODUCT RECEIVER UNIT

FIGURE 5 (Legend)KEY to the PRODUCT RECEIVER UNIT

<u>ITEM</u>	<u>DESCRIPTION and/or FUNCTION</u>
A	<u>INLET TUBE</u> - conducts pyrolysis products from the pyrolysis unit into the product receiver unit
B	<u>CAP</u> - permits the addition of water and/or trichloroethylene to the unit
C	<u>WATER LAYER</u> - absorbs the water soluble pyrolysis products that were not absorbed by the trichloroethylene layer
D	<u>TRICHLOROETHYLENE LAYER</u> - absorbs the pyrolysis products that are soluble in trichloroethylene
E	<u>SUPPORT STAND</u>
F	<u>OUTLET</u> - all unabsorbed species and carry-over material is conducted to the necessary traps
G	<u>FLAPPER VALVE</u> - to maintain positive pressure within the receiver unit
H	<u>SIGHT TUBE</u> - allows visual inspection for a dangerously high liquid level
I	<u>OUTLET VALVE</u> - for removal of products for final processing

An old 30 gallon hot water heater was used to construct the main receiver which was mounted on a stand made of welded half inch pipe. A series of 5 gallon traps was constructed but was later discarded and replaced since it was too small for the volume of products that was liberated.

A heat source was constructed from an old central furnace. It was lined with ceramic-wool insulation and connected to the processor by a two inch insulated steel heat pipe. The hot exhaust gases from the gas burners were to serve as the heat supply within the processor unit.

The heat pipe from the processor was connected to the heat exchanger from the old central furnace. The heat exchanger was located in a box which was to be filled with sawdust, in an attempt to pre-dry the sawdust. The reason for discarding the furnace was apparent as several pin holes in the heat exchanger made it unusable for this purpose. The final point on the heat line was a vacuum consisting of a shop vacuum motor mounted on a 55 gallon drum.

The processor was insulated with full thick fiberglass insulation which had aluminum backing and was sealed around the top to prevent water damage with a concoction of portland cement and asbestos heat pipe insulation. This arrangement was quite adequate for its purpose.

The initial run was started about six weeks behind schedule. For this run an attempt was made to load the processor by a vacuum system, but the available vacuum was insufficient and future runs were loaded by hand. The usual volume of sawdust added was 100-120 gallons depending on the effectiveness of the packing. The first run was marred by small leaks in the sawdust drying system which caused smoke to be emitted from the vacuum exhaust and a fire to occur in the drying box. The processor was shut down and the drying system removed.

It was obvious after the initial trial that the original trap system was inadequate. It was replaced with a new trap system which consisted of a 15 gallon air trap, three 30 gallon liquid scrubber traps and a water cooled reflux column having a length of six feet. This system was not completely adequate for trapping the gaseous materials, therefore, a final water trap was added. The final trap was made of glass and served as an indicator of the rate of reaction within the tank by its rate of bubbling.

The processor was not emptied following the trap system modifications and the run was restarted. This run continued for another 29 hours, during which gaseous emissions did not stop. The processor tank was allowed to cool and was then opened in order to inspect residue. Uniform heating had not been obtained and many pockets of unreacted sawdust remained. It was decided that the effect of better packing of the sawdust would be investigated before the system was modified further.

The second run proved to be no more productive since the packing of the sawdust caused the heat pipe to shift and as a result opened a crack in a coupling, causing smoke to be issued from the vacuum exhaust due to pyrolysis products entering the heat system. The system was again shut down and overhauled by adding 20 feet of heat exchange pipe to the 30 feet already present and by brazing copper fins onto the pipe to increase the heat transfer to the sawdust. In addition, the gasket material used to form the seal for the 36 inch diameter flange of the processor was a problem of long duration. Several materials were used, the most satisfactory being formed by boiling castor oil, adding asbestos fibers and forming the mixture into ribbons (12).

The next six runs, of approximately 30 hours each, were more productive, with the last four producing almost a gallon of the refined material per 50 gallon batch of sawdust.

Certainly, additional heating time would have increased the yield as much as two-fold, but runs of 60 consecutive hours were not possible.

In the course of the successful runs, an inert gas was tested as a heat transfer medium but had only limited success. Other suggestions which were not feasible at the time were a fluidized bed approach and a tamper mechanism to maintain uniform packing, thus improving the thermal transfer as the process progressed.

In summary 8, attempts involving 218 hours of actual running time were performed. This running time, corresponding to at least 24 runs of the process as originally anticipated, was in excess of the scheduled processing time. It was obvious that an improved heat transfer system would shorten the process and increase the yield.

From Processor I, the product which was to yield a binder was collected in the organic layer (trichloroethylene) of the receiver. The density of the solvent was such that most of the solid residues were floated to the water interface. By carefully removing the organic layer from the bottom of the receiver, the solid residue was excluded. This eliminated a subsequent processing problem encountered in earlier studies (9). It was necessary to transport the separated organic layer to the laboratory where vacuum distillation and recovery of the solvent was carried out. The recovered trichloroethylene which contained any process derived oils which were carried over under the conditions of the vacuum distillation was returned to the processor site and reused.

Some solvent was lost in this procedure but exact amounts were not measured. Some of the contributing factors to this loss are its solubility in water, its absorption on the carbon residue and its easy evaporation. The loss of solvent presented another obvious expense to the process.

The binder was finished by cooking down. Several laboratory methods of determining when to terminate the process in order to obtain a desired penetration grade were tried during the period. While methods for this determination exist, none were available to the investigators which were rapid enough to avoid over cooking of the binder. The procedure that was chosen for the final processing was an open pot cook down using a subjective determination of the termination point. This determination was done by pouring a small sample into the dimple of a spot plate adjacent to a sample of asphalt having the desired penetration grade and comparing them by touch, after cooling, to approximate the penetration.

The results of solubility tests made during this period are given in Table IV. These tests were performed to show the dissimilar nature of the HRC-37 pyrolysis product and that produced by a method known as the Georgia Tech Process (11). As indicated, solubilities were significantly different, which led to the conclusion that the local product was more likely to produce a binder which could be used by conventional asphalt paving methods and equipment.

An evaluation of the first eight (8) pyrolysis runs and laboratory studies showed that less than five (5) gallons of binder had been produced; the time per run and, more importantly, the energy required caused serious consideration of drastic changes in the process; lab tests of another method yielded binder which appeared to be the same as that being produced in Processor I while at the same time reducing the required energy input and residue removal problems. It was concluded that the existing pyrolysis unit should be abandoned and Processor II constructed and tested.

TABLE IV

SOLUBILITY PROPERTIES OF "BINDER" MATERIALS

Solvent System *	HRC-37 Steady Boil Product	Asphalt -60/70	Georgia Tech Product
Pure Trichloroethylene (TCE)	Sol - some fine particles remained	Sol	Floats on top slight color in TEC (insol)
TCE & Water	Insol in water, Sol in TCE & no material between	Insol in water Sol in TCE	Slight Sol in water, insol in TCE, most in a layer between
Water	Insol - settled to the bottom	Insol - settled to the bottom	Very-slightly sol, settled to bottom
Benzene	Sol	Sol	Very-slightly sol, settled to bottom
Carbon Disulfide	Sol - some fine particles remained	Sol	Very-slightly sol, floats on top
Naptha Solvent	Slight Sol - most settled to bottom	Slight Sol most settled to bottom	Very-slightly sol, settled to bottom
Carbon Tetrachloride	Sol.- some fine particles remained	Sol	Very-slightly sol, floats on top
Xylene	Sol - some fine particles remained	Sol	Very-slightly sol, settled to bottom
Acetone	Sol - some fine particles remained	Very-slightly sol, settled to bottom	Sol - more particles left than HRC-37 material
1.0 Molar Potassium Hydroxide Solution	Slightly sol, most material adhered to glass tube or was suspended as a solid	Insol - Floats on top	Sol - some fine partles remained on bottom

* Pure solvents = 10 ml of indicated solvent

Solvent Pairs = 5 ml of each solvent listed

Approximately 3 ml of the indicated binder material were placed in the solvent system, shaken vigorously several times over a 2 hr. period, left standing for one week and then observed for solubility behavior.

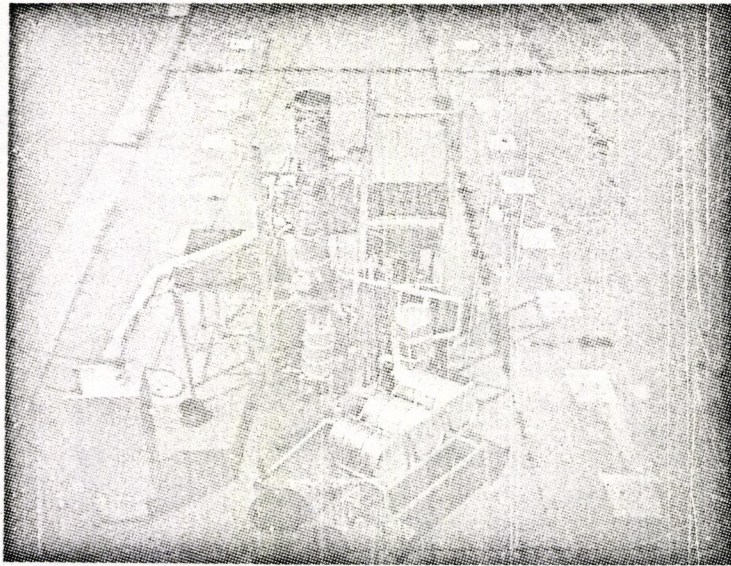
PHASE C STUDIES

Phase C studies were conducted in various periods from April 1, 1976 to June 30, 1978, during which Processor II (photo) was built and operated.

Processor II was constructed according to the diagram shown in Figure 6. It was built on the same platform and used as much of the original trap system as possible. The smoker stack was approximately the size of two, high form, 30 gallon water heaters, placed end to end on top of a low form, 30 gallon, water heater. Two inch pipe and valves were used except where smaller 3/4 inch pipe is indicated. The traps were 30 and 55 gallon drums as indicated by the relative size in the diagram.

Processing was drastically changed in this configuration since no outside heat source was required. The sawdust was loaded in the smoker stack by hand with light packing. The top was ignited, as evenly as possible, and the vacuum motor started. The heat and exhaust fumes, from the burning sawdust were drawn, down, through the sawdust. Fresh air was drawn in from the top to support combustion. By this method the combustion and pyrolysis products moved ahead of the hot zone and were out of the smoker before they decomposed. The binder under study was a part of the recovered products.

The products, due to the design of Processor II, could not be simultaneously collected and extracted as in Processor I since trichloroethylene was too volatile and toxic to be introduced into the gas train. Therefore, a mist extraction chamber and several water filled traps were used. The products were separated from the water and solid residue by a separate, manual extraction with trichloroethylene. The extract was transported to the laboratory and treated in the same manner as described in the Phase B studies.

PROCESSOR II

Photographs of the Converter System

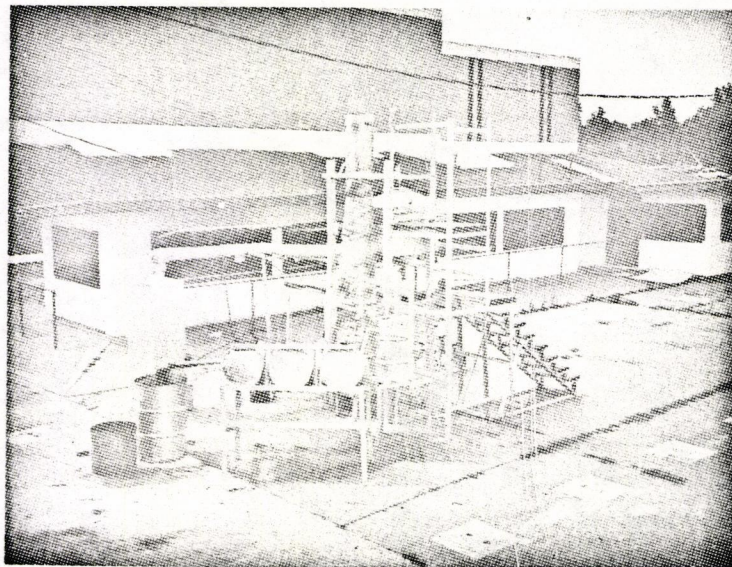


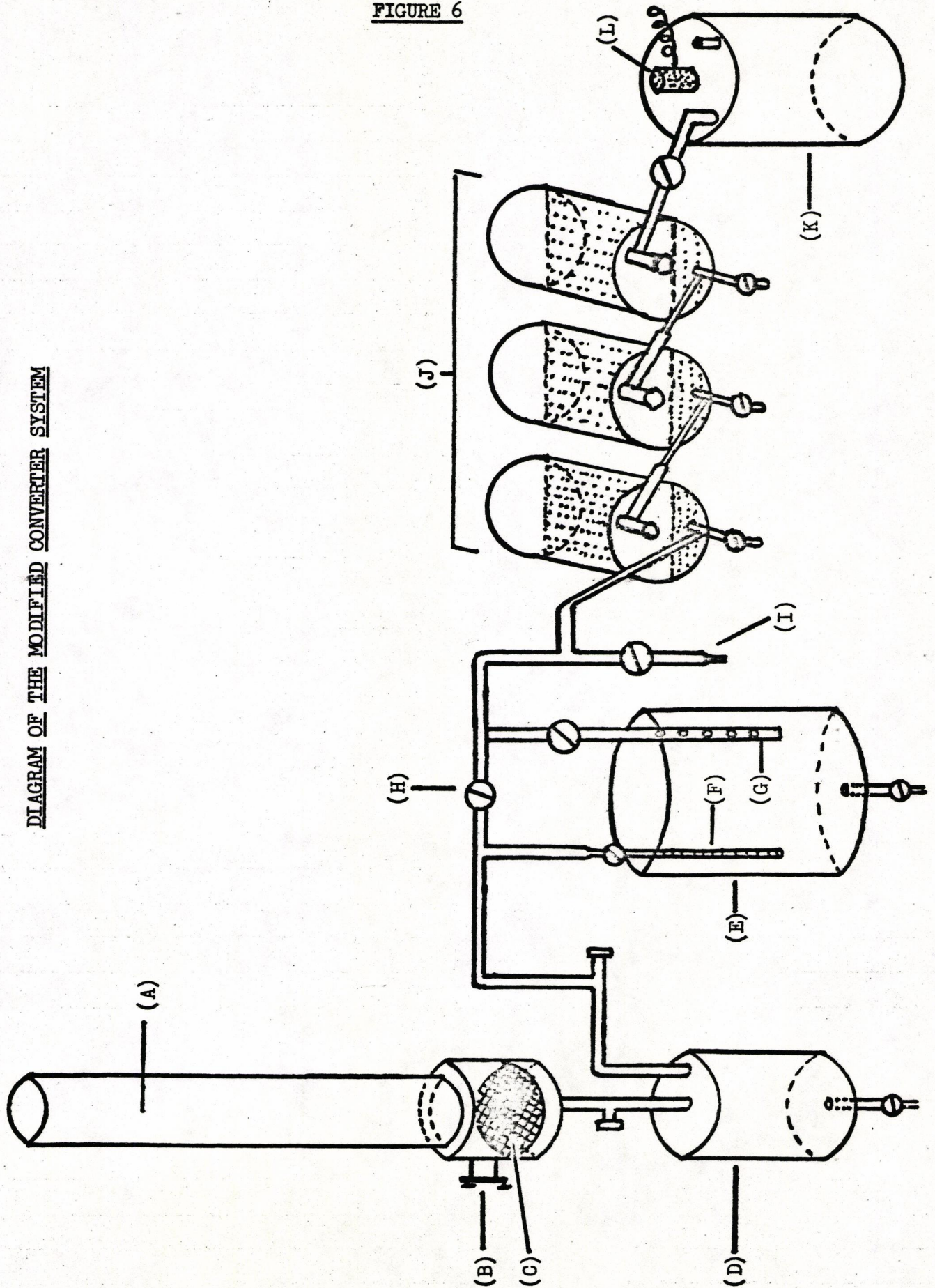
FIGURE 6

FIGURE 6 (Legend)KEY TO THE MODIFIED CONVERTER DIAGRAM

- (A) SMOKER TUBE
Sawdust is loaded in this tube and ignited at the top. The sawdust is then burned from the top to the bottom by use of a vacuum.
- (B) CLEAN OUT PORT
- (C) SUPPORT SCREEN
- (D) ASH TRAP
- (E) MIST EXTRACTION CHAMBER
Materials being carried through the system as small droplets are removed at this point.
- (F) VAPOR FLOW CONSTRICTION TUBE
This tube has many small slits which produce a reduced pressure inside this chamber compared to the pressure inside the lines up to this point. As the hot gases enter the chamber they are cooled slightly and further condensation takes place.
- (G) VAPOR EXIT TUBE
This tube has several large diameter holes which face the wall of the chamber. Vapors are thus forced to pass against the wall of the chamber and are thereby further cooled.
- (H) SHUNT
- (I) MONITORING DRAIN
This outlet makes it possible to sample the materials reaching this point in the system.
- (J) VAPOR SCRUBBING TRAIN
- (K) FINAL TRAP and MAIN VACUUM CHAMBER
- (L) VACUUM MOTOR

Early runs with Processor II were much shorter than with Processor I. In fact, on the first day of operation two runs were made in one eight hour period. This turned out to be an error since the majority of the useful product was only slightly ahead of the hot zone and did not reach the receiver in the first run. It was apparently decomposed during the second run. As a result of trying various procedures, it was found that approximately 6 hours per run was optimum. It was also necessary to completely burn all residue until only cool ash remained, before refilling the smoker stack. This permitted only one run per day with this design.

Yields were hard to establish due to the distribution of product in the traps, but have been estimated to average $\frac{1}{2}$ gallon of finished binder per 100 gallons of sawdust. Many of the runs during this period yielded less than $\frac{1}{2}$ gallon of binder. The important factors contributing to this reduced yield are: the presence of more than one hot zone, losses in the trapping system, material failure of the smoker stack and lack of uniformity in the sawdust packing step.

The smoker had a hot zone at the bottom as well as the top when the bottom layer of char and ash was not completely burned or extinguished prior to reloading. The combustion products from the upper hot zone supported combustion in the lower hot zone and decomposed most of the useful product. Likewise, the shape of the sides of the smoker and the non-uniformity of the packing caused channeling of the upper hot zone whereby it overtook and decomposed portions of the useful product front before it reached the receiver.

In order to improve the uniformity of packing, the sawdust was screened by hand to eliminate the larger pieces of bark and chips. This improved the burning uniformity, but from brief studies it was indicated that more control of the flow rate was a better solution to this problem.

The flow studies were conducted in an all glass system in the laboratory after Processor II was shut down and production had stopped.

The brief lab study produced another interesting possibility for improving the design. It indicated that a filter packed with sawdust, substituted for the vapor extractor, would trap the products of several runs. Subsequent extraction of the product with trichloroethylene or simple burning the filter in place of the smoker stack would recover the product. This possibility, while not implemented in this project on a large scale, remains an intriguing possibility both for the reduction of the size and/or the number of water traps required and for the localization of the desired product within the gas train.

During processing with Processor II, the product was found to be present in the vapor extractor, all water traps, and the vacuum barrel. Its location was not completely predictable and none of the attempts to determine its behavior in order to achieve its collection at one point were successful. The desire to produce as much binder as possible during Phase C did not allow for major construction changes in the trapping system. The product was simply collected from all points and combined.

Early supplies of sawdust were dumped on the "red dog" track by mistake. In moving the sawdust, significant amounts of the sand from the track were picked up. The result was a steady plugging and subsequent failure of the screen at the bottom of the smoker stack by glassy clinkers. This problem, once recognized, was eliminated by discarding the contaminated sawdust. Once this was done, no clinkers developed.

Material failures of the smoker stack were a significant problem. The heat generated by the burning sawdust was sufficient to deform the smoker stack, causing the yield to be reduced by channeling and actual reduction

in capacity (it melted down). Again, the subsequent in-glass studies showed that melt-down could be eliminated by jacketing the smoker stack and extracting the heat with a heat exchange medium, thus limiting the temperature. This could also provide a source of heat for the subsequent processing required to recover the solvent and finish the binder.

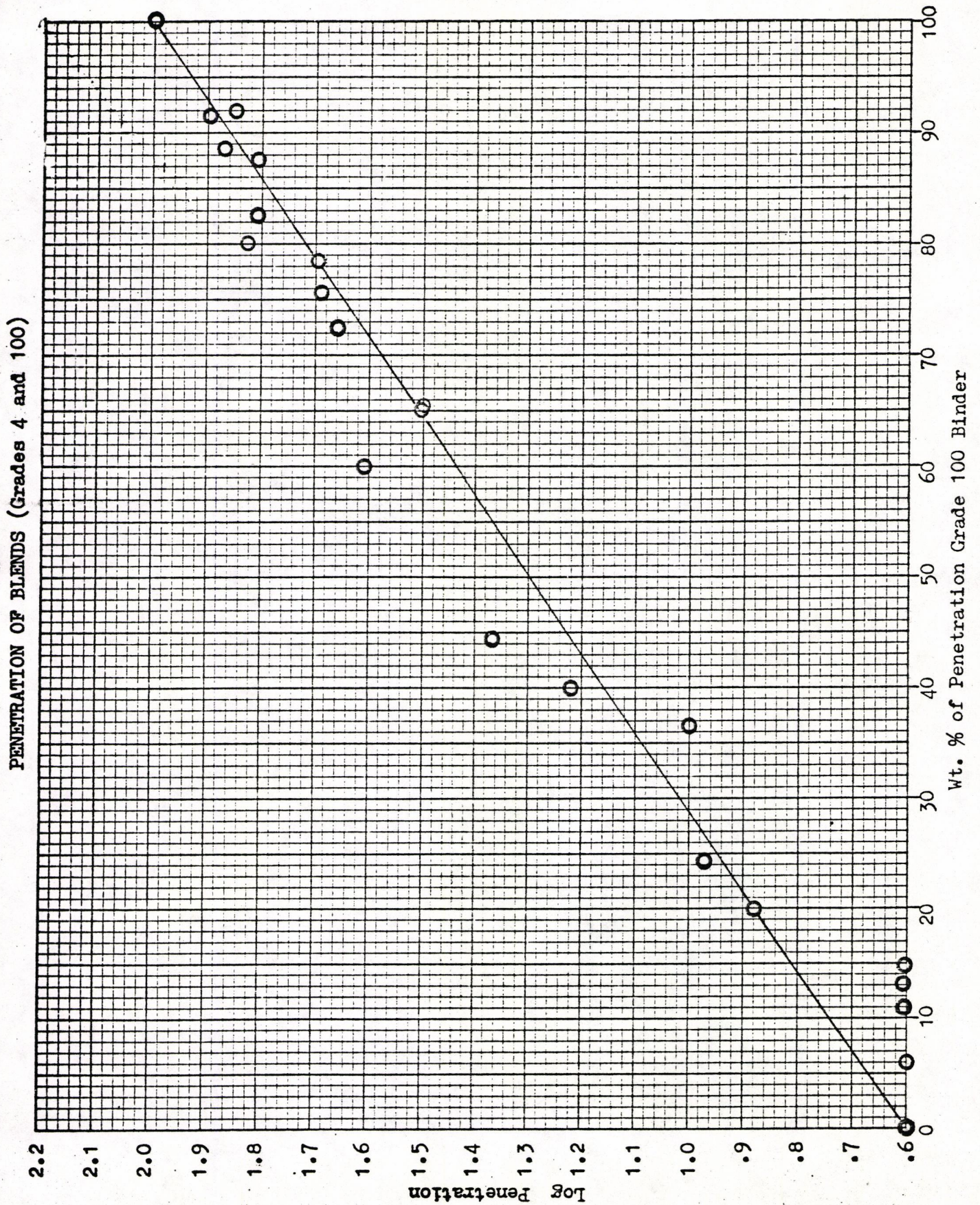
One other material failure was the development of leaks in the smoker stack. When these existed, the yield was reduced, primarily by the increased tendency of the fire to channel toward the additional air supplied by the leak.

Phase C involved in excess of 60 attempts and 400 hours of operating Processor II. When the binder had been finished, the yield from this phase was about 15 gallons. Consideration of the factors described herein leaves the opinion that this method, with adequate processor design, would be feasible to operate and would be energy extensive.

During this phase of the work, laboratory studies were conducted on blends of different penetration grade binders and binders with asphalt. The study of blends involving different penetration grade binders indicated that a desired penetration grade could be obtained by blending individual binders which had penetrations that bracketed the desired value. This was shown when the log of the penetration grade of the blend was plotted against the weight percentage composition of the mixture. This plot gave a reasonably straight line with intercepts at the penetration values of the two binders used in the blend.

An example from this work is shown in Figure 7 where blends of binders with penetration grades of 4 and 100 were studied. A variety of penetration grades were investigated to a lesser extent and the results seemed consistent with this example. In order to further confirm this finding, several predetermined penetration grades were successfully prepared through blending.

FIGURE 7



Thus, a desired penetration grade binder could be produced by blending products from several runs and it, therefore, became unnecessary to fix the end point of the final cook down step.

The studies involving blends of asphalt and binders initially showed penetration values much larger than either of the components. When the same samples were looked at some months later, the penetration was down in the range originally expected. Insufficient mixing may have caused this result.

Other work showed that the penetration grade of the binder material was unchanged after nine cycles of heating to 302°F (150°C) and maintaining this temperature for five minutes, followed by slow cooling. This indicated that normal processing through a hot mix plant should cause no changes in the penetration properties of the binder.

July 1, 1977 was the date of the last operation of Processor II. The demolition of the old stadium, where it was located, required that the utilities be disconnected and no further runs could be made at that location.

During the summer, the Division of Research and Planning of the Arkansas Highway Department was given a sample for testing in their lab. The results of these tests are shown in Figure 8. From these tests it was obvious that the binder produced was not strong enough and that it oxidized too easily.

Some of the weaknesses were likely due to the binder's density being greater than asphalt, so that equivalent mixes should contain more HRC-37 binder, by weight, than would be required if asphalt were used.

No effort had been made to remove water soluble components from the binder. When the sample was soaked in water during the standard test procedures these components may have leached out, further weakening the test sample.

ARKANSAS STATE HIGHWAY DEPARTMENT

DIVISION OF MATERIALS AND TESTS
LITTLE ROCK, ARK.

2-3-77

REPORT OF TESTS ON BINDER FROM WOOD RESIDUE
HRC-37

Laboratory No. A-541
XFlash Point - 345°F D92
XFire Point - 350°F
✓Penetration, 77°F - 85 DS
✓Ductility, 77°F - 52 D113
✓Solubility in Trichloroethylene - 93.1%
Solubility in Acetone - 99.7%
{Kinematic Viscosity at 275°F - 29 centistokes D2170
{Absolute Viscosity at 140°F - 178 poises D2171
XSpecific Gravity at 60°F - 1.13 D70
XThin Film Oven Loss - 16.8% D1754

Note: Residue tests were impossible to obtain after the thin film oven test due to the material becoming hard and crystalized.

Comparison of Mixes

Binder Content	Experimental Mix		Control Mix	
	Stability	Flow	Stability	Flow
5.0%	345	8	1163	10
5.5%	342	8	1240	12
6.0%	438	9	1245	14

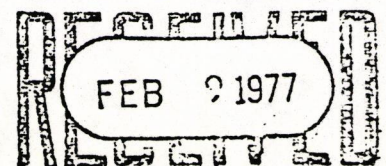
Aggregate for above mixes was a blend of fine sand and crushed syenite from Granite Mountain Quarries. The gradation for all specimens was as follows:

Sieve Size	3/4"	1/2"	3/8"	No.4	No.10	No.40	No.80	No.200
Percent retained	0	4	11	37	57	76	89	92

Note: When heated to 125°F and above, the material produces fumes and an objectionable odor. The binder for the control mix was an AC 20 from MacMillan Petroleum Corp., Norphlet, Arkansas.

cc: S. Teague, Research Section

RESEARCH SEC. - P & R DIV.
ARK. STATE HIGHWAY DEPT.



LITTLE ROCK, ARK.

During the remainder of the period, the final processing of all batches was completed and all binder (18-20 gallons) obtained during the project (except a small sample of each batch) was combined into one kettle in preparation for the construction of a test patch.

In the fall, when all things were considered, all parties agreed not to risk the entire batch in a single test patch but rather to save the binder for studies designed to improve its quality, to investigate its combination with asphalt for possible use as an extender, and to develop blends with other materials to produce products that should be immediately useful.

PHASE D STUDIES

PROCEDURES, TEST RESULTS, AND DISCUSSION

TEST PROCEDURES

The samples resulting from the various treatments of ASUphalt in the following studies were tested by some or all of the following methods:

Penetration @ 25°C (D-5), Softening Point (D-36), Specific Gravity @ 25°C (D-70), Flash Point & Fire Point (D-92), Thin Film Oven Test (D-1754), Solubility of Bitumens Material (Soxhlet Method). Some additional solubilities were measured by ASTM Method D-2042.

In most cases the sample size was too small to include all tests. Most Thin Film Oven test results represent only one sample, however, when multiple samples were run, the precision was excellent, and taken to justify the inclusion of data from a single run.

The Bitumen content, (i.e. material soluble in CS_2) was obtained by Soxhlet extraction of each sample for 24 hours. This was done to avoid the hazards of openly handling carbon disulfide. ASUphalt was tested by ASTM D-2042 and showed the same solubility as that obtained by the Soxhlet method.

Blends of ASUphalt

The earlier studies that were conducted using blends of asphalt and the experimental binder, as well as, those made using only ASUphalt of various penetration grades (Phase C Studies) suggested that blending methods might be useful in producing improved properties of the binder and/or other materials of limited specific use. The substances that were selected for investigations as blending agents were asphalt cement (60-70 penetration grade), sulfur, cured rubber, semi-cured rubber and polyethylene (a thermoplastic). The attempted blends and the resulting materials are described in the following sections and are separated according to the blending agent used.

Sulfur Blends:

Sulfur was chosen as a blending agent because of the well documented studies of sulfur-asphalt mixes and the techniques that have been reported. Asphalt was used in analogous studies of sulfur blends in order to compare and contrast the effects of sulfur addition to the individual binders. Mixtures of ASUphalt-Sulfur and Asphalt-Sulfur were made simultaneously using the same procedures and conditions. Penetration tests' results and a summarized treatment process for each series of blended samples are shown in Tables V and VI.

In the case of ASUphalt-Sulfur blends it was observed that at temperatures required to maintain the mixtures in the molten state hydrogen sulfide gas appeared to be evolved. This was interpreted to indicate that the sulfur was not only a physically blended agent but that it at least partially reacted with the binder. It was expected that some oxidation by the sulfur would be observed based upon the previously noted "air" oxidations. These reactions were vigorous and resulted in frothing of the mixes if elevated temperatures were maintained. No evolution of gas was observed under the same conditions in the case of Asphalt-Sulfur blends. It was, therefore, concluded that the

TABLE V
PENETRATION GRADES OF BLENDS OF SULFUR WITH ASPHALT

XS	100	95	90	80	70	60	50	40	30	25	20	10	5	0	DELTA
DATE PREPARED															
7-28-78							41			50		53			61
7-31-78							19			7		25		53	60
8-3-78							14			10		40		60	60
6-29-79		1	2	20	33	41	51	66	70		42	53	63	54	58
7-28-78	SOLID SULFUR ON TOP OF BINDER IN PENETRATION CANS HEATED AND STIRRED IN CANS WITH GLASS ROD.														
7-31-78	SOLID SULFUR ON TOP OF BINDER IN BEAKER HEATED, MIXED WITH GLASS ROD AND TRANSFERRED TO PENETRATION CANS.														
8-3-78	BINDER POURED ONTO MOLTEN SULFUR AT = 176 C IN BEAKER AND MIXED WITH GLASS ROD.														
6-29-79	SOLID SULFUR PLACED ON TOP OF BINDER IN LIQUID STATE, HEATED AND BLENDED WITH ELECTRIC MIXER. SEVERAL CANS OF EACH BLEND WERE COLLECTED.														

IN ALL CASES THE SAMPLES WERE MELTED AND STIRRED WITH A ROD PRIOR TO PENETRATION DETERMINATION.

TABLE VI

PENETRATION GRADES OF BLENDS OF SULFUR WITH ASPHALT

XS	100	95	90	80	70	60	50	40	30	25	20	10	5	0	DELTA
DATE PREPARED															
7-28-78						NA				120		102			61
7-31-78						100				110		101		78	60
8-3-78						112				106		111		76	60
6-29-79	0	7	45	80	82	60	64	111	55		101	95	91	73	58

7-28-78 SOLID SULFUR ON TOP OF BINDER IN PENETRATION CANS HEATED AND STIRRED IN CANS WITH GLASS ROD.

7-31-78 SOLID SULFUR ON TOP OF BINDER IN BEAKER HEATED, MIXED WITH GLASS ROD AND TRANSFERRED TO PENETRATION CANS.

8-3-78 BINDER POURED ONTO MOLTEN SULFUR AT = 176 C IN BEAKER AND MIXED WITH GLASS ROD.

6-29-79 SOLID SULFUR PLACED ON TOP OF BINDER IN LIQUID STATE, HEATED AND BLENDED WITH ELECTRIC MIXER. SEVERAL CANS OF EACH BLEND WERE COLLECTED.

IN ALL CASES THE SAMPLES WERE MELTED AND STIRRED WITH A ROD PRIOR TO PENETRATION DETERMINATION.

two systems should not be expected to show analogous trends.

The collected data showed that the addition of sulfur to asphalt would result in an increased penetration value. The observed trend could result from the physical blocking of the intermolecular forces between the molecular units of asphalt by the sulfur molecules. The addition of sulfur to ASUphalt generally resulted in reduced penetration values as would result if sulfur oxidation of the binder's molecules occurred and would be very marked if cross-linking or bridge formation resulted. Other samples showed only small and incidental changes as if the presence of the added sulfur had little or no effect. It was determined later that sulfur tends to separate from ASUphalt upon slow cooling of the blends and crystalizes into a solid from which the ASUphalt can be washed with solvents.

It was concluded that the evolution of H_2S gas and the increased brittleness of blends containing ASUphalt and sulfur would make them both impractical and potentially hazardous.

A potentially useful sulfur-asphalt product was produced in the course of these studies. The investigators choose not to pursue its development because of the scope and objectives of this project. It was decided to report the following findings and ideas in the hopes that others, who are investigating the potential uses of sulfur, may find a successful application.

At temperatures between $160^{\circ}C(320^{\circ}F)$ and $200^{\circ}C(392^{\circ}F)$ liquid sulfur changes from a yellow, transparent, and mobile liquid into a brown viscous fluid containing high molecular weight polymeric sulfur molecules instead of the S_8 rings normally present in the crystalline solid at room temperature. Upon slow cooling the equilibrium between rings and chains will

shift to the ring form and the characteristic light yellow color of solid sulfur returns as it forms crystals. If the polymeric form of sulfur is quickly cooled, such as by pouring into ice water, it will solidify before the equilibrium reaction back to rings can take place and a hard, amorphous or plastic solid is formed. On the surface of the amorphous solid there appears to be a slow shift of the equilibrium in favor of the S_8 species and the solid will slowly become coated with light yellow powdered sulfur.

The procedures followed in the formation of blends containing sulfur would have followed the path of $S_8 \xrightarrow{180^\circ C} S_8 + \text{polymers}$. Slow cooling would have allowed the separation of most of the sulfur into S_8 units in a crystalline structure which would have excluded the liquid binder. In an attempt to "trap" the blend in a homogeneous mixture before separation could take place, several hot ($180^\circ C$, $356^\circ F$) blends of sulfur-asphalt and sulfur-ASUphalt were rapidly cooled by pouring the mixture into ice water. The result was a solid, pelletized material that had various degrees of tackiness depending upon the percent asphalt or ASUphalt used. In all cases an aggregate type product was formed. With sulfur contents of about 80-90%, there was no tendency for the lumps to stick together and they could be broken with a hammer into smaller pieces. In the range of 50% sulfur and either 50% 60-70 penetration asphalt cement or 50% ASUphalt, the materials produced did have adhesive surfaces and could be compacted together under pressure. In all cases the solids could be easily stuck together by passing a bunsen burner flame over their surfaces. With continued heating it was possible to completely melt the solids as was expected. After two years only slight surface decomposition has resulted. These materials seemed to hold promise as synthetic aggregate, conventional

patching materials or an easily handled, hot-mix binder and patch material.

Blends with Polyethylene:

Thermoplastics can be softened or even melted, molded and cooled to produce new objects. This process can be repeated several times without decomposition of the polymers due to thermal degradation. Thermosetting plastics cannot be melted without chemical breakdown. Thus, attempts were made to produce blends of ASUpfalt and thermoplastic polyethylene. Polyethylene was chosen because of its availability as a waste material at several manufacturing concerns in Arkansas. It was hoped that the addition of small amounts of polymer molecules might produce a more useful binder due to increased flexibility and strength.

Several attempts were made to prepare mixes using polyethylene from various sources and having different physical forms. In all cases the results were nil. The temperatures required to melt the polyethylene caused rapid decomposition of the binder. In the trials at lower temperatures the polymer softened but formed mats on the surface of the liquified binder and no mixing could be accomplished. Thus, this line of studies was discontinued.

Asphalt Blends:

Several series of asphalt containing blends have been prepared and studied during the course of this project. They were made from asphalt that was obtained from more than one source and ASUphalt that was of various ages and had been subjected to different heat-cooling cycles. In addition, the blends were prepared by several investigators and the tests were run by various persons. The observed trends did not appear to be operator or source dependent.

Early in the project it was reported that test results seemed to change with aging of the blended samples. In order to varify or disprove the effect of age a set of blends were prepared in July, 1978. These samples were periodically checked throughout the remainder of the project. Significant changes in the penetration values and the softening points of the blends were not detected.

The results of the penetration tests on two series of blends are shown in Table VII. Graphs of the values given for the two series are are shown separately in Figures 8 & 9 and combined in Figure 10. The early studies of ASUphalt-Asphalt blends had been confined to the composition range of zero to fifty percent asphalt (i.e. the range of 50 to 100 on the graphs). As can be seen from the data the use of ASUphalt as an extender of asphalt would have to be carefully controled since the addition of small amounts of either material to the other causes large changes in the physical properties. Additionally, in the range of thirty to seventy percent ASUphalt the blends exhibit very low cohesive natures. While it may be possible to use blends of these two materials for specific purposes their use in the construction of materials that would be in contact with

TABLE VII

PENETRATION GRADES OF BLENDS OF ASPHALT WITH ASPHALT

ASPHALT	100	95	90	80	70	60	50	40	30	20	10	5	0	DELTA
FIRST BLEND (OPERATOR ONE)	49	38	23	49	85	+	+	245	214	177	130	95	76	45
			(43)	**	**	**	220	245						
SECOND BLEND (OPERATOR TWO)	54	38	50	108	124	+	+	226	180	138	110	80	61	
		**	**	**	**	227	260	226						

+ = HIT BOTTOM AT OR BEFORE 5 SECONDS
 ** = EVIDENCE OF SECOND LAYER HAVING LOWER PENETRATION VALUE
 () = RETESTED BY OTHER OPERATOR
 FIRST BLEND WAS WITH ASPHALT #157
 SECOND BLEND WAS WITH ASPHALT #158
 BOTH BLENDS WERE PREPARED BY MIXING WHILE WARM WITH AN ELECTRIC MIXER.
 DELTA WAS A CONTROL SAMPLE OF ASPHALT AND INDICATES THE VARIANCE BETWEEN OPERATORS.

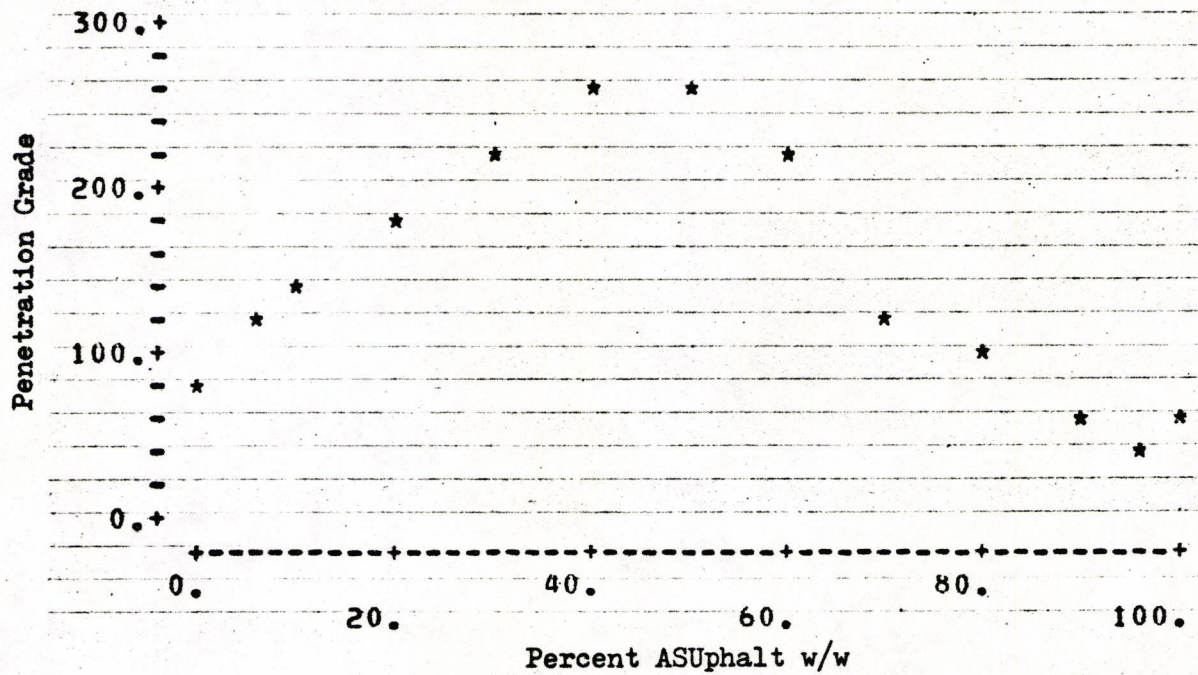
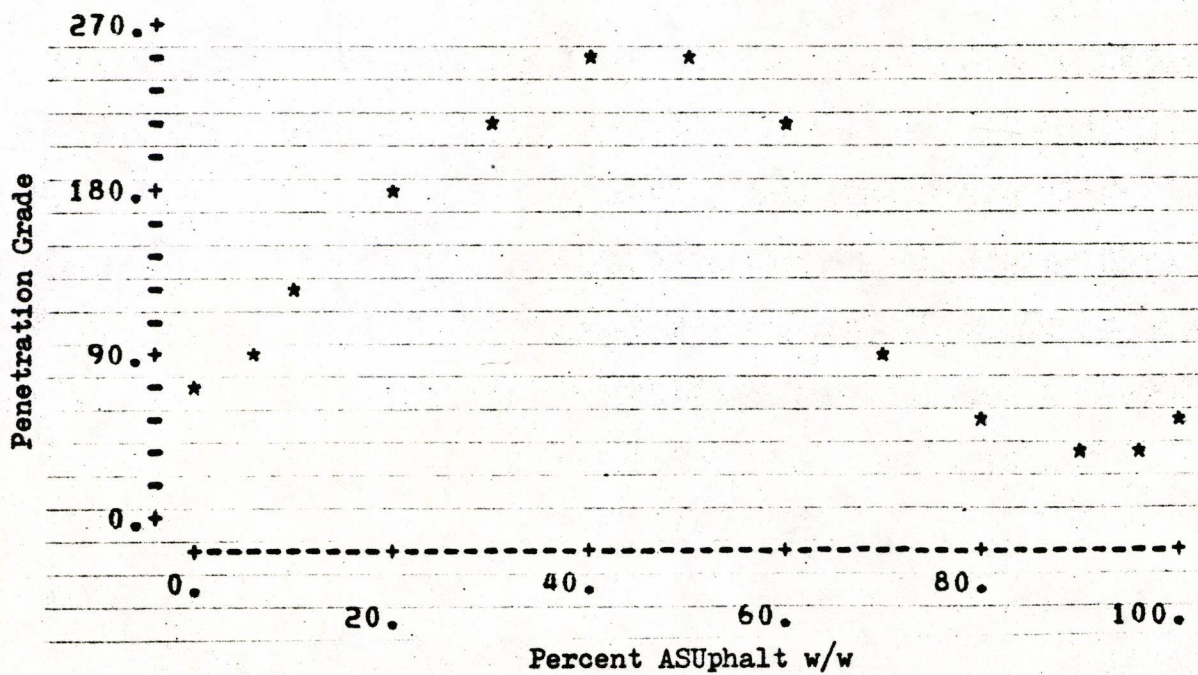
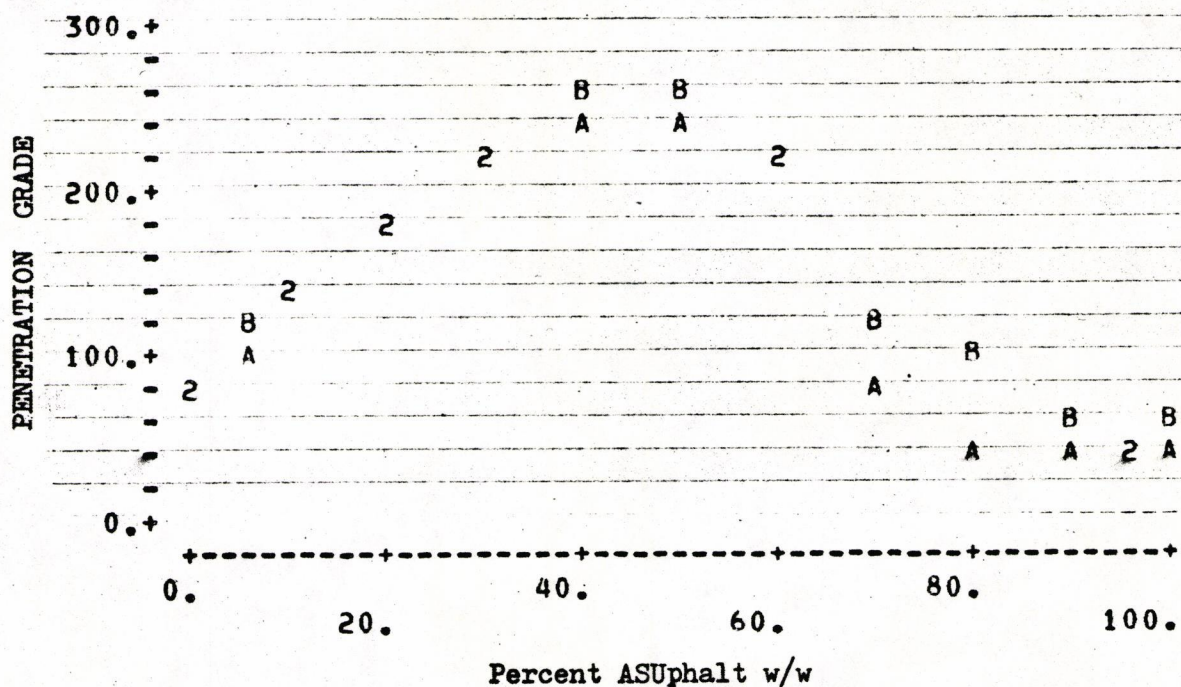
FIGURE 8PENETRATION GRADES OF ASPHALT BLENDED WITH ASUPHALT (Series 1)FIGURE 9PENETRATION GRADES OF ASPHALT BLENDED WITH ASUPHALT (Series 2)

FIGURE 10PENETRATION GRADES OF ASPHALT BLENDED WITH ASUPHALT (Series 1&2)Legend

- A = Values from Series 1
- B = Values from Series 2
- 2 = Values from both Series 1 and 2 are equal within the precision of the plot

those that contain either binder in its pure form would certainly result in unpredictable changes at the surface of contact.

It should be noted that the blending of asphalt with the ASUphalt binder produced mixes that had the odor of ASUphalt. The reduction of the odor was one of the objectives of this project, however, blending techniques always resulted in mixes that smelled like burning wood.

Blends of ASUphalt with ASUphalt:

Please see 33 of this report.

Extraction Studies

It was thought that selective removal of some portion of the ASUphalt might improve its suitability for highway use. Two categories were defined in this work. The first was removal with various liquids (solvents), and the second was extraction with various gases. The objective of the study limited the processes for extraction to those which employed solvents which were common, relatively inexpensive, and to those methods which did not involve complex procedures. Both categories are described below.

Extraction with Liquids

After considering several possible methods, the following simple lab procedure was used for the extraction with the solvents Methanol, Water, Hexane, Acetone, Dioxane, and Trichloroethylene.

The general extraction procedure was to place approximately 500 grams of ASUphalt in a one liter, round bottom flask fitted through a standard taper joint to a refluxing condenser. To this flask, 250 ml of the solvent was added. In order to obtain adequate mixing, the flask was heated overnight with gentle refluxing of the mixture. At the end of this period, the sample was either filtered warm when most of the ASUphalt dissolved (Methanol, Acetone, Dioxane, TCE) or decanted and washed with cold solvent when ASUphalt was only slightly soluble (Water, Hexane). Finally, the product was "dried" in a rotary evaporator at about 70°C and 5 mm Hg.

The ammonia sample was extracted by a continuous procedure until no further changes in the pH of the extracted solution occurred. This procedure was excessively long, (3 weeks) and the resulting product was not obviously better than those obtained in the shorter process, so additional continuous extraction processes were not employed.

The results of testing the products obtained by these methods are shown in Table VIII.

The ASUphalt was relatively soluble in Methanol, Acetone, Dioxane, and Trichloroethylene (TCE). In all cases, it was visibly softer and had a lower softening point, higher penetration, and lower flash and fire points. Only the hexane and ammonia extracted samples had lower loss on heating. The lower flash points presented an increased hazard to handling and no further attempts at extractions were made.

The explanation of these changes in tested properties may be formed in any of three models. The first was simply that the solvents affinity for the ASUphalt was such that it was not totally removed from the sample by the rotary evaporation process. It was observed in other studies that when the ASUphalt was heated gently and subjected to high vacuum (.2 mm Hg) it outgassed extensively for long periods. This indicated that the affinity for oxygen was high. This affinity is known for many phenolic compounds with pyrogallol being the reagent for the quantitative analysis of oxygen in air. The more polar solvents would be expected to compete with the oxygen for the available sites and subsequently less easily removed at the temperatures and pressures used herein for solvent removal. The second possibility was that the solvents reacted chemically to break down the product to more volatile, smaller average molecular weight materials which would account for the test results. This was somewhat supported by gas chromatography studies but was not conclusive. The third possibility was that selective removal of small portions of the sample caused the changes. This was most probable with hexane and ammonia but no method of confirming this has been successful.

TABLE VIII
TEST RESULTS FOR ASPHALT EXTRACTED WITH VARIOUS LIQUIDS

SOLVENT	METHANOL	WATER	HEXANE	ACETONE	DIOXANE	AMMONIA	TCE	NONE
SPECIFIC GRAVITY @ 25 C	1.167	1.178	1.167	1.172	1.192	1.180		
SOFTENING POINT	33.8	42.5	40.5			44		
PENETRATION @ 25C	172	75	93			52		
FLASH POINT (C)	160	174	175	130	152	190	158	206
FIRE POINT (C)	175	194	185	130	152	200	185	220
*** THIN FILM OVEN TEST ***								
% LOSS ON HEATING	19	18	16	26	28	13	21	17

NOTES:

1. FILTERATE MATERIAL TESTED FOR METHANOL, ACETONE, DIOXANE, TCE
2. FILTERABLE MATERIAL TESTED FOR WATER, HEXANE
3. CONTINUOUS EXTRACTION PROCESS USED FOR AMMONIA
4. TCE IS TRICHLOROETHYLENE

Due to the general decrease in quality indicated by the test results, these procedures were judged to be unacceptable for the intended purpose and more time was directed to the other areas of the work.

The extractions with various pH water solutions were unsuccessful due to the formation of emulsions. This was consistent with the tentative identification of significant amounts of dicarboxylic acids in the ASUphalt by gas chromatography. When extraction was performed with deionized water, the final pH of the water was 4.0 which also indicated the presence of carboxylic acids.

Hydrochloric acid was liberated when carbon tetrachloride was used as the solvent in the normal procedure and was removed from the list of possible solvents due to the corrosive nature of the hydrochloric acid.

Extraction with Gases

ASUphalt samples of approximately 500 g were heated to various temperatures and Acetylene, Dry Nitrogen, Carbon Dioxide, Hydrogen, Natural Gas, and Air were bubbled through them in these studies. The time period for the gas passage was typically 24 hours with a flow rate of 15 ml/min. One of the 500 gram samples was subjected to steam distillation and has been included in Table IX with the results of the test performed on the samples resulting from gas extraction.

As shown in the test results, the trends of the softening point and penetration were similar for all gases used for extraction. Each increase in temperature resulted in a higher softening point and a smaller penetration. Only Natural Gas and Water reduced the flash point and then only at low temperature. This is probably due to the affinity of the Natural Gas for the ASUphalt, causing some gas to be held at the lower temperature in the one case, while in the other case, steam treatment

TABLE IX

TEST RESULTS FOR ASPHALT EXTRACTED WITH VARIOUS CASSES

*****ACETYLENE*****NITROGEN*****CO2*****									
TEMPERATURE (C)	90	130	180	240	140	230	140	220	
SPECIFIC GRAVITY @25 C	1.171	1.174	1.177	1.175	1.248	1.168	1.180	1.180	
SOFTENING POINT	50	43	46	51	44	51	47	53	
PENETRATION @25 C	52	37	32	18	26	9	24	12	
FLASH POINT			206	212	206	220	215	232	
FIRE POINT			220	220	220	240	225	245	
% SOLUBILITY IN CARBON DISULFIDE (BITUMENS)	77			74		75		74	
*****THIN FILM OVEN*****									
% LOSS ON HEATING	17	17	16	14	17	14	16	14	
PENETRATION OF RESIDUE @ 25 C	0	0	0	0	0	0	0	0	
SOFTENING POINT OF RESIDUE	75	75	75	80					

TABLE IX (Cont'd)

TEST RESULTS FOR ASPHALT EXTRACTED WITH VARIOUS GASES

GAS	HYDROGEN	NATURAL GAS	AIR	STEAM	NONE
TEMPERATURE (C)	140	140	140	230	
SPECIFIC GRAVITY @25 C	1.180	1.184	1.183	1.186	1.180
SOFTENING POINT	46	53	45	56	44
PENETRATION @25 C	18	8	36	10	47
FLASH POINT	210	220	193	214	206
FIRE POINT	220	248	200	232	225
% SOLUBILITY IN CARBON DISULFIDE (BITUMENS)	76	74	73	74	69
THIN FILM OVEN					
% LOSS ON HEATING	15	13	17	12	9
PENETRATION OF RESIDUE @ 25 C	0	0	0	0	0
SOFTENING POINT OF RESIDUE	74			76	74

probably hydrolyzed some esters to smaller, more volatile compounds.

Only in the case of Air at 230°C was the Bitumen content significantly changed. It is thought that the further oxidation to dicarboxylic acids accounts for this change. The accompanying change in loss on heating tends to confirm this judgment.

Steam treatments increased the loss on heating by either increasing the amount of volatile components as indicated by the decreased flash point and/or residual water content due to polar interaction with ASUphalt. Both of these possibilities seem likely.

All cases employed were superior to air extraction and indicated that the final processing of the ASUphalt would have produced more and better binder if a vacuum cookdown or a gas bubbler had been used for the final processing. Carbon dioxide appears to be most promising from this data.

Gas Chromatography Studies

The objective of this phase of the work was to identify as many of the chemical components of ASUphalt as possible. The method was chosen based on the equipment available and the suspected nature of components of the material. No effort was made to identify the low molecular weight components which were either present in the material or formed by thermal decomposition in the chromatography. In retrospect, this was a poor decision as more information on the lower weight products would have been helpful.

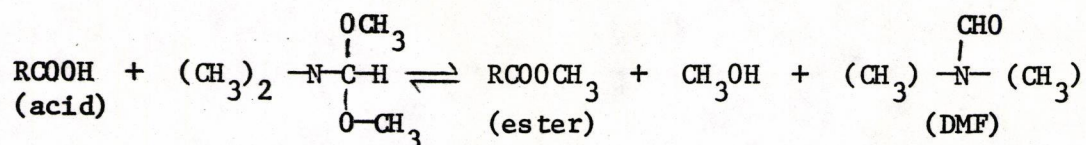
Early work, which was performed on a Gow-Mac 750, single column gas chromatograph equipped with a flame ionization detector, indicated

that more than 25 components were detectable when the ASUphalt was injected directly into the chromatograph. The certainty that the high temperature involved in these studies caused extensive decomposition left the actual identity of the components of the ASUphalt in question.

In order to avoid thermal decomposition and to render the higher molecular weight substances more volatile, derivatives were prepared and chromatographed. Methyl esters were formed to stabilize the organic acids present and silane derivatives were formed for the acids and phenols. These are common procedures for gas chromatographic analysis and no special techniques were used.

Esterification Procedure

The methyl esters were prepared from "Methyl-8" concentrate, supplied by the Pierce Chemical Corporation. It is a DMF-Dimethyl Acetal used in the esterification of carboxylic acids. The esterification reactions' by-products are dimethylformamide (DMF) and methanol.



Methyl-8 also reacts with water and alcohols, producing methanol and with certain diols epoxides are produced.

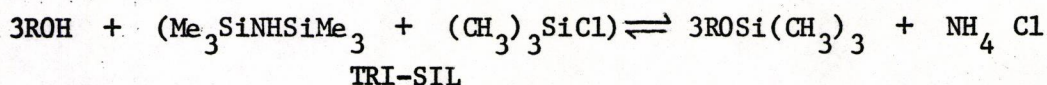
Two procedures were used to prepare the esters depending on the physical nature of the sample. For liquid samples, 30 μ l of the material was drawn into a syringe and injected into an air tight vial containing 300 μ l of "Methyl-8". The vial was then heated at 60°C for 15 minutes. During this time the solutions usually turned yellow. Aliquotes of this mixture were injected into the chromatograph.

When the sample was a solid or a viscous liquid, it was dissolved

in a solvent, usually methanol (benzene when not soluble in methanol) and filtered. A 300 μ l sample of this mixture was injected into a vial containing 300 μ l of "Methyl-8" and heated at 60°C for 15 minutes. Aliquots of this mixture were injected into the chromatograph.

Silylation Procedure

The silane derivatives were prepared using a mixture of 250 μ l DMF, 100 μ l of "TRI-SIL" concentrate (a mixture of hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS)) and 50 μ l of GSA (N,O-bis-(trimethylsilyl) - acetamide), all supplied by Pierce Chemical Corporation. A 100 μ l sample of material dissolved in a suitable solvent (DMF) was added to this mixture and vigorously shaken. Heat and a white precipitate (NH_4Cl) were generally produced.



The precipitate was allowed to settle and samples were carefully drawn from the supernatant liquid and injected into the chromatograph.

Instrumentation

All of the samples were analyzed with a Perkin-Elmer Model 3920B Gas Chromatograph equipped with dual flame ionization detectors. The column temperature was linearly programmed according to one of the four temperature programs given in Table X.

Two columns were used for the separations. For esters a six foot, 0.125 inch ID, stainless steel column packed with 10% Silar 10C on 100/120 mesh Gas Chrom Q with nitrogen flowing at 15 ml/minute was used. For silanes a six foot, 0.125 inch ID, stainless steel column packed with 5% SE 30 on 100/120 mesh WHP with nitrogen flowing at 10 ml/minute

was used. These columns were supplied by Alltech Associates, Inc.

Interpretation of Results

To confirm the esterification procedure, known carboxylic acids were carried through the procedures. The "retention time" obtained was compared with those of quant grade methyl esters obtained from the Polyscience Corporation. The peaks obtained from the carboxylic acid derivatives and from the corresponding methyl-esters compared well. Two peaks found in the "Methyl-8" alone were also present in the derivatives. They were at 0.6 and 8.1 minutes after injection. Injections of unreacted carboxylic acids eluted more rapidly than their corresponding ester and were poorly resolved.

Known methyl ester mixtures were then injected into the gas chromatograph under the same conditions and temperature program and a series of well resolved peaks was observed on the chromatogram. These peaks were identified by systematically adding to the ester mixture a small amount of a known pure ester, and noting which of the peaks was enlarged. The individual peaks were tentatively identified by this "spiking" technique when no splitting of the peaks due to the spiking was observed. Since a homologous series of methyl esters was used, a plot was made of the log of the "retention time" versus the number of carbons present in the compound and a straight line graph was obtained.

In a like manner, dimethyl esters, methyl esters of unsaturated carboxylic acids, aromatic methyl esters and phenols were examined. The "retention time" in each case was noted for comparison and identification of the samples under investigation.

Several known phenolic compounds were subjected to silylation to confirm the procedure and to provide standards of "retention time" for

comparison with the unknowns. These procedures were successful and were used to identify the components of the material being studied. It was found that in some cases better resolution could be obtained by separation of phenolic and acid components, prior to silylation and this was done.

Table X gives the complete list of standards used in this study. It also gives the relative retention times (RRT) for each column and temperature program.

While comparison of these retention times with the unknown and spiking procedures are not sufficient information for absolute identification, they represent the best information obtained in this work and the compounds found will be referred to as tentatively identified.

Results and Discussion:

ASUphalt:

A sample of ASUphalt collected from one of the open cookdowns was used as the typical sample and was identified as "Open #15". This sample was collected directly from the final processing and had not been subjected to additional heating or mixed with other batches.

Gas chromatographic results on the esterified mixture of this sample produced 20 peaks, with four esters being tentatively identified by spiking. The compounds identified were:

Dimethyl malonate
Dimethyl succinate
Methyl benzoate
Dimethyl terphthalate

Silane derivatives were not clearly chromatographed for this sample so separation was carried out with solvent extraction whereby carboxylic acids were partially separated from phenols. The carboxylic acid portion was thus more concentrated and revealed 11 peaks when the esterified

TABLE X

RELATIVE RETENTION TIMES [RRT] OF ALL COMPOUNDS			
COMPOUND	AS ESTER RRT [MIN]		AS SILANE RRT [MIN]
BENZENE	(2)	0.6	(4) 0.2
BUTADINOIC ACID, (1,4-)	(1)	2.9	(4) 10.9
CRESOL, (META)*	(2)	18.5	(4) 7.8
CRESOL, (ORTHO)			(4) 7.3
CRESOL, (P ARA)			(4) 8.0
DECANOIC ACID	(1)	2.8	
DECANOL, (1-)	(2)	7.1	
DIHYDROXYBENZOIC ACID, (3,4-)			(4) 27.7
DIMETHYL BUTA-1,4-DINOATE*	(2)	12.4	(4) 5.9
	(3)	16.9	
DIMETHYL CIS-2-BUTENOATE	(2)	14.3	
DIMETHYL ETHADINOATE	(2)	7.5	
DIMETHYL HEPTA-1,7-DINOATE*	(2)	20.0	(4) 13.2
	(3)	24.8	
DIMETHYL HEXA-1,6-DINOATE	(2)	17.8	(4) 10.2
DIMETHYL ISOPHTHALATE	(2)	24.6	
DIMETHYL OCTA-1,8-DINOATE	(2)	22.1	
DIMETHYL PENTA-1,5-DINOATE	(2)	15.1	(4) 7.3
DIMETHYL PHTHALATE*	(2)	28.9	
	(3)	33.7	
DIMETHYL PROPA-1,3-DINOATE*	(2)	10.1	
DIMETHYL TEREPHTHALATE*	(2)	23.6	(4) 17.4
	(3)	30.5	
DIMETHYL TRANS-2-BUTENOATE	(2)	9.8	
DIMETHYL-2,3-DIHYDROXY- 1,4-BUTADINOATE	(3)	18.9	
DIMETHYLDECA-1,10-DINOATE	(2)	26.5	
DIMETHYLFORMAMIDE	(3)	12.3	(4) 1.1
DIMETHYLNONA-1,9-DINOATE *	(3)	28.6	(4) 19.1
DITERTBUTYL-4-METHYLPHENOL, (2,6-)			(4) 18.3
DODECANOIC ACID	(1)	2.9	
DODECANOL, (1-)	(2)	8.3	
ETHYL 4-HYDROXYBENZOATE*			(3) 20.0
ETHYLPHENOL, (ORTHO)*	(2)	19.9	(4) 9.2
ETHYLPHENOL, (PARA)	(2)	21.0	(4) 10.3
HEPTANOIC ACID	(1)	2.2	(4) 8.7
HEXANOIC ACID	(1)	2.2	(4) 5.9
HYDROXYMETHYL-2,6-DITERBUTYLPHENOL			(3) 25.9
HYDROXYPHENOL, (ORTHO)*			(3) 13.1
METHANOL	(3)	1.7	
METHOXY-4-PROPENYLPHENOL, (2-)*			(3) 20.1
METHOXYL-4-HYDROXYL-BENZALDEHYDE, (2-)*			(3) 19.0
METHOXYPHENOL, (2-)*			(3) 10.2
METHYL CIS,CIS,CIS-9,12,	(2)	27.8	

TABLE X CONTINUED.

RELATIVE RETENTION TIMES [RRT] OF ALL COMPOUNDS				
COMPOUND	AS ESTER RRT [MIN]		AS SILANE RRT [MIN]	
15-OCTADECATRIENOATE				
OCTADECADIENOATE*				
METHYL CIS-9-OCTADECENOATE	(2)	22.4		
METHYL DECANOATE	(2)	6.5		
METHYL DODECANOATE	(3)	13.0		
METHYL HEPTANOATE*	(2)	3.6	(4)	4.8
	(3)	6.2		
METHYL HEXADECANOATE	(2)	21.1		
METHYL HEXANNOATE*	(3)	4.9		
	(2)	3.0	(4)	4.4
METHYL NONANOATE	(2)	5.4		
METHYL OCTADECANOATE*	(2)	23.8		
METHYL OCTANOATE	(2)	4.3		
METHYL SORBATE	(2)	8.5		
METHYL TETRADECANOATE	(2)	17.5		
METHYL-1-PHENYL-1-HYDROXYETHANOATE	(3)	27.5		
METHYL-4-HYDROXYBENZOATE*			(3)	17.9
OCTADECANOIC ACID	(1)	3.3		
PENTADINOIC ACID, (1,5-)	(1)	2.9	(4)	16.0
PENTANOIC ACID	(1)	2.1		
PHENOL*	(2)	17.7	(4)	2.2
PROPADINOIC ACID, (1,3-)	(1)	2.8		
SEDOHEPTULOSE ANHYDRIDE MONOHYDRIDE			(3)	30.6
TERTBUTYL-4-METHOXYPHENOL, (2-)*			(3)	19.9
TETRADECANOIC ACID	(1)	3.2		
TOLUENE	(2)	1.2	(4)	0.7
TRIMETHYL CITRATE	(3)	15.7		
TRIMETHYLPHENOL, (2,3,5-)*			(3)	2.9
XYLENE, (META)			(4)	3.2
XYLENE, (ORTHO)			(4)	3.1
XYLENE, (PARA)			(4)	3.4
=====				
TEMPERATURE PROGRAMS FOR GLC:				
CODE	RANGE	RATE	INITIAL	FINAL
NO.	OC	OC	TIME	TIME
(1)	90-260	4/MIN	1 MIN	8 MIN
(2)	90-260	4/MIN	0 MIN	8 MIN
(3)	60-260	4/MIN	0 MIN	8 MIN
(4)	60-200	4/MIN	0 MIN	4 MIN
SILAR 10C FLOW RATE OF 15 ML/MIN NITROGEN.				
SE 30 FLOW RATE OF 10 ML/MIN NITROGEN				
* = TENTATIVELY IDENTIFIED IN A SAMPLE				
EOF..				

mixture was chromatographed. Two additional esters were identified as:

Dimethyl pimelate
Dimethyl azelate

The phenolic fraction was silanized and the chromatograph revealed 15 peaks, three were tentatively identified as:

BHA
m-Cresol
Isoeugenol

A complete list of compounds were used as references for the ASUphalt chromatographs is given in Table XI.

Gas Extracted ASUphalt:

Various gas treatments were employed in this study. The resulting tar was analyzed for each by the procedures described. No new compounds were identified from these chromatograms.

When treated with Hydrogen none of the originally identified compounds were present. While oxygen and carbon dioxide treatment seemed to remove most of the compounds with longer retention times, little else was notable from these studies.

Liquid Extracted ASUphalt:

Several liquid extractions were carried out on ASUphalt and each product was analyzed by gas chromatography. When methanol was the solvent, additional esters were identified in the chromatographs. They were:

Methyl caproate
Methyl heptanoate
Pyrocatechol

Distillates of ASUphalt:

Several chromatographs were obtained for the derivatives of the heavy distillates obtained during ASUphalt production both from direct

TABLE XI

LIST OF COMPOUNDS CHECKED FOR IN ASUPHALT

STANDARDS ATTEMPTED	RRT	RESULT
=====		
SAMPLE: OPEN 15 TAR	INITIAL TEMP: 90 C	
METHYL CAPROATE	3.0 MIN.	NEGATIVE
METHYL HEPTANOATE	3.6 MIN.	NEGATIVE
METHYL DECANOATE	8.5 MIN.	NEGATIVE
METHYL LAURATE	14.0 MIN.	NEGATIVE
METHYL MYRISTATE	17.5 MIN.	NEGATIVE
METHYL STEARATE	23.8 MIN.	NEGATIVE
DIMETHYL MALONATE	10.1 MIN.	POSITIVE
DIMETHYL SUBERATE	22.1 MIN.	NEGATIVE
DIMETHYL SUCCINATE	12.6 MIN.	POSITIVE
DIMETHYL MALEATE	14.2 MIN.	NEGATIVE
METHYL LINOLENATE	27.8 MIN.	NEGATIVE
METHYL LINOLEATE	26.6 MIN.	NEGATIVE
METHYL BENZOATE	12.0 MIN.	POSITIVE
DIMETHYL ISOPHTHALATE	27.2 MIN.	NEGATIVE
DIMETHYL TEREPHTHALATE	26.3 MIN.	POSITIVE
=====		
SAMPLE: ACID EXTRACTION PRODUCT	INITIAL TEMP. 60 C	
METHYL HEPTANOATE	5.5 MIN.	NEGATIVE
DIMETHYL SEBACATE	25.3 MIN.	NEGATIVE
DIMETHYL PHTHALATE	34.6 MIN.	POSITIVE (?)
METHYL OLEATE	30.2 MIN.	NEGATIVE
DIMETHYL PIMELATE	20.2 MIN.	POSITIVE
DIMETHYL AZELATE	28.6 MIN.	POSITIVE
=====		
SAMPLE: PHENOLIC EXTRACTION PRODUCT	INITIAL TEMP. 60 C	
P-CRESOL	7.8 MIN.	NEGATIVE
SEDHEPTULOSE ANHYDRIDE	30.6 MIN.	NEGATIVE
O-ETHYLPHENOL	9.1 MIN.	NEGATIVE
GUAIACOL	10.2 MIN.	NEGATIVE
BHA	19.5 MIN.	POSITIVE
BHT	18.3 MIN.	NEGATIVE
M-CRESOL	7.8 MIN.	POSITIVE
ISOEUGENOL	20.1 MIN.	POSITIVE
VANILLIN	19.0 MIN.	NEGATIVE
=====		
EOF..		

processing and from the TCE solvent recovery distillation. A total of 13 compounds were identified by chromatography of the derivative mixtures of these distillates. The compounds identified along with those tried are given in Table XII.

Destructive Distillates of ASUpfalt:

Pyrolysis of ASUpfalt resulted in liquid distillates which were derivatized and chromatographed. Five compounds were tentatively identified in these samples. They are:

Dimethyl adipate
p-Ethyl phenol
Methyl paraben
Isoeugenol
BHA

Reference Materials:

A sample of Delta 2656 Asphalt was derivatized and chromatographed. The resulting chromatograph had 22 peaks. Dimethyl succinate and dimethyl terephthalate were the only substances tentatively identified in asphalt.

Samples of tall oil from crude to light fatty acids were analyzed. The chromatographs revealed from 17 to 27 peaks of which a few had similar retention times to those in ASUpfalt. None of the peaks were those identified in ASUpfalt, however. The presence of the C18 fatty acids was confirmed in all the tall oil samples and was conspicuously absent in ASUpfalt. This along with the difference in solubility was taken to indicate that ASUpfalt was significantly different from tall oil and no further work was done.

Pyrolytic oil produced by the Tech Air process was also derivatized and chromatographed. Several peaks similar to ASUpfalt were observed

TABLE XII

GLC STUDIES OF THE DISTILLATES OF ASPHALT

STANDARD ATTEMPTED	RRT	RESULT
METHYL PENTANOATE	3.6 MIN.	POSITIVE
METHYL OLEATE	29.8 MIN.	NEGATIVE
DIMETHYL PIMELATE	25.2 MIN.	POSITIVE
DIMETHYL PHTHALATE	33.5 MIN.	POSITIVE
DIMETHYL AZELATE	28.6 MIN.	POSITIVE
METHYL HEPTANOATE	6.8 MIN.	NEGATIVE
DIMETHYL SUCCINATE	16.8 MIN.	POSITIVE
METHYL CAPROATE	4.7 MIN.	NEGATIVE
4-HYDROXY-2,6-DITERTBUTYL PHENOL	25.9 MIN.	POSITIVE
ETHYL PARABEN	20.0 MIN.	POSITIVE
METHYL PARABEN	17.9 MIN.	POSITIVE
2,3,5-TRIMETHYLPHENOL	2.8 MIN.	POSITIVE
PYROCATECHOL	13.2 MIN.	POSITIVE
GUAIACOL	10.2 MIN.	NEGATIVE
M-CRESOL	7.6 MIN.	POSITIVE
O-ETHYLPHENOL	9.3 MIN.	POSITIVE
BHT	23.8 MIN.	NEGATIVE
VANILLIN	19.0 MIN.	POSITIVE
P-ETHYLPHENOL	10.3 MIN.	NEGATIVE
DIMETHYLTEREPHTHALATE	17.4 MIN.	NEGATIVE
P-CRESOL	8.0 MIN.	NEGATIVE
3,4-DIHYDROXYLBENZOIC ACID	27.7 MIN.	NEGATIVE
O-CRESOL	7.3 MIN.	NEGATIVE
HEPTANOIC ACID	8.7 MIN.	NEGATIVE
HEXANOIC ACID	5.9 MIN.	NEGATIVE

but none were identified. The solubility of the pyrolytic oil was known to be quite different from ASUphalt so no further work was performed.

Summary of GLC Studies:

The data summarized here while only partially conclusive represents over 400 hours of work in the lab. In all, 9 compounds were tentatively identified in ASUphalt as being either dicarboxylic acids, phenols, or both. Three additional compounds were found in the tar which had been extracted with methanol, two monocarboxylic acids and one phenol. Thirteen compounds were tentatively identified in the distillates and five in the pyrolysis products of ASUphalt.

From this information no definite conclusions about the chemistry of the production of ASUphalt can be drawn. It does provide a general knowledge of what is present and tends to indicate that the ASUphalt would be less stable than asphalt in use.

