Technical Report Documentation Page

1. Report No. FHWA/RD-80/031	2. Government Accession No. -	3. Recipient's Catalog No. PB82-259631
4. Title and Subtitle Highway Binder Materials from Cellulosic and Related wastes.		5. Report Date December 1980
		6. Performing Organization Code -
7. Author(s) Walter A. Butte, Edward M. Kohn, Edward G. Scheibel		8. Performing Organization Report No. -
9. Performing Organization Name and Address SUNTECH, Inc. P. O. Box 1135 Marcus Hook, PA 19061		10. Work Unit No. (TRAIS) FCP No. 34G1-103
		11. Contract or Grant No. DOT-FH-11-9131
12. Sponsoring Agency Name and Address Offices of Research and Development Federal Highway Administration U. S. Department of Transportation Washington, D.C. 20590		13. Type of Report and Period Covered Final Report
		14. Sponsoring Agency Code MTC/0004

15. Supplementary Notes

FHWA Contract Manager: Edward Harrigan (HRS-23)

16. Abstract

The abundance of cellulosic-based wastes was reviewed by section of the country and type which includes: wood wastes, municipal wastes and manures. Of the most promising waste conversion processes now under consideration, pyrolysis, liquefaction, and hydrolysis were selected for preliminary laboratory screening. Model wastes for this study included several pyrolysis oils, paper, sawdust and dried cow manure. Distillate oils produced during wood waste pyrolysis (WPO) served best as precursors of products that approximated bitumens and highly viscous fluids.

In the statistically designed study of process parameters which followed, the best conditions were identified for distilling and hydrogenating the crude WPO for conversion to a usable product (hydrogenate). This hydrogenate, because of its high oxygen content, could be added to conventional asphalt only in amounts up to ca. 15 weight percent concentration with little or no observed property change.

In combination with sulfur, the ternary system - AC/hydrogenate/S:29/29/42 had a penetration value comparable to that of AC/S:65/35.

A 909 metric ton/day waste processing facility could be cost effective in producing 72.7 metric tons per day of pyrolysis product equivalent to 318 metric tons or more of blended binder. This assumes that waste is available at no cost and that coproduct oil and char are credited at equivalent heating values.

17. Key Words Sulfur, asphalt, aggregates characterizations, fatigue, creep, compliance, solid wastes, municipal wastes, cellulosic wastes, pyrolysis, pyrolysis oil, hydrogenation, liquefaction.	18. Distribution Statement No restriction. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 165	22. Price

Form DOT F 1700.7 (8-72)

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CHAPTER I

INTRODUCTION AND SUMMARY

Background

Cellulosic wastes represent a vast potential source of oil, tar, pitch and chemical intermediates. Some technology already exists that is applicable to the conversion of cellulose to hydrocarbon products. This technology has not been widely developed or exploited in the past because competitive products were more economically derived from coal or petroleum. However, this situation has changed markedly in recent years because of dwindling supply and increasing cost of petroleum coupled with increased generation and higher disposal costs of cellulosic wastes.

Cellulose is the most abundant renewable form of organic carbon. An estimated 90.9 - 182 x 10^9 metric tons of carbon is fixed annually by the photosynthesis of atmospheric carbon dioxide into cellulose and related vegetable material. Most of this is so dilute in the environment that it is not readily available to man, but a small percentage is concentrated as a waste product of man's domestic agricultural and industrial activities. While the percentage is small, the quantities are enormous -- amounting to over 0.91 x 10^9 annual metric tons in the U.S. alone.

There are strong environmental and economic incentives for converting cellulosic wastes to useful products. Large quantities are presently accumulated at or transported to specific locations where they can create serious pollution and health hazards. These wastes are usually disposed of by incineration or land-filling, but increasingly stringent environmental controls tend to preclude disposal by these historical methods or make them unduly expensive.

Decreasing supply and escalating cost of petroleum provides additional incentive for converting these wastes to useful materials. These factors enhance the position of cellulose as a possible source of fuel, chemicals, road binder and other important products that are largely derived from petroleum today. Development of cellulose based products would free petroleum for other uses and reduce our dependency upon foreign petroleum sources.

Purpose

The primary purpose of this investigation is to develop and evaluate processes for converting cellulosic and related wastes into road binder materials and to evaluate the performance of such materials alone and in mixtures with typical paving aggregates. The process would preferably utilize those wastes that are readily available in abundance and that pose ever increasing disposal problems. Production of a binder from these wastes would not only help alleviate environmental problems but would also reduce dependence of highway building materials upon limited and costly petroleum sources.

Scope

Although extensive literature exists on the conversion of cellulosic waste to petroleum substitutes, the emphasis is almost entirely upon alternate fuel production. Relatively little information in recent times deals with the generation of other materials, such as asphaltic binders, that are commonly derived from petroleum. This study seeks to partially fill that void by assessing the potential for generating a road binder from cellulosic wastes. It includes consideration of waste availability, process feasibility and product performance. Insofar as possible, it is based on literature results but also includes extensive experimental studies needed to complete the evaluation. Other ways of using cellulosic wastes in highway construction, e.g. as fillers, aggregates and mulches, are not considered.

A determination was made of the supply, availability and geographic distribution of cellulosic waste materials based largely upon relevant literature sources. The data generated was analyzed and tabulated according to type of waste and geographic location, placing emphasis on the identification of large concentrations of specific waste materials.

Three candidate processes, viz. pyrolysis, liquefaction and hydrolysis, were evaluated for conversion of cellulosic waste to binder material. This evaluation was based on a combination of literature reports and laboratory studies. The evaluation was based on considerations such as process conditions, yield of useful products, properties of the products and conversion costs. Since the initial products were generally unsuitable for direct use as a binder material, secondary procedures were investigated to adjust properties to specifications. These procedures included distillation, extraction, air-blowing, and hydrotreating. Additionally, the effect of blending with petroleum asphalts was investigated.

Based on the results of preliminary evaluations described above, a more detailed evaluation and analysis of the pyrolysis process was conducted. Important process parameters were identified and their effect upon rate, yield and critical performance properties of the product was evaluated experimentally. A process flow sheet was developed for a hypothetical 72.7 metric ton per day binder plant. An assessment was made of manufacturing costs including estimates of capital investment, operating expenses and disposal and by-product costs or credits.

Sufficient binder material was prepared for additional testing and evaluation. This included characterization alone and in admixture with petroleum asphalt. A portion was formulated in conventional highway construction-type mixes, employing three aggregate types. The mixtures were evaluated to determine critical performance properties and thermaloxidative stability. Selected samples were also subjected to dynamic testing in order to evaluate field performance and long-term durability of the binders.

Conclusions

Principal conclusions based on the results of evaluations carried out in this study are as follows:

1. An estimated 74 x 10^9 kg. per year of cellulosic waste is available for processing. This waste consists of wood manufacturing residue, animal manure and municipal solid waste. All three forms are available in large quantity at numerous locations throughout the country. Disposal of these wastes is often problematic at present and they could be available at low or negative cost in many instances.

2. Pyrolysis is the preferred method for converting cellulosic waste to substitute binder material. Hydrolysis does not produce products suitable for use in flexible paving. Liquefaction produces a high yield of bitumen but the product is thermally unstable and process costs are relatively unattractive.

3. Pyrolysis products are not suitable for direct use in highway binder applications. Rheological properties do not meet accepted performance criteria and cannot be readily adjusted with usual processing procedures. Furthermore, compatability with conventional petroleum asphalt is extremely poor.

4. Hydrogenation of wood pyrolysis products improves its compatibility with petroleum asphalt. This procedure alters the chemical composition allowing stable admixture of up to about 25 percent in petroleum asphalt.

5. A pyrolysis-hydrogenation procedure could be cost effective in a 909 metric ton-per-day waste processing facility. This assumes that waste is available at no cost and that coproduct oil and char would be credited at equivalent heating values. The facility would produce 72.7 metric tons per day pyrolysis product equivalent to 318 metric tons or more of blended binder.

6. Hydrogenated pyrolysis-oil is suitable for use as an extender of asphalt in paving applications. Paving mixtures containing 88:12 asphalt:pyrolysis oil meet Marshall Stability requirements for wearing and binder courses with granitic or limestone aggregates. Stability of sand and gravel mixtures is marginal to poor, according to the PennDot standards.

7. The durability of a wearing surface mixture containing hydrogenated pyrolysis-oil was not significantly different from that containing only the reference AC. Dynamic testing showed that hydrogenate could be added to AC in amounts up to 12 weight percent without altering mixture performance significantly in both fatigue life and incremental creep tests.

Recommendations for Future Work

1. Laboratory studies have shown that hydrogenated pyrolysis oil derived from wood waste is useful as an extender for asphalt binder in a common paving mixture. In accordance with the current need to utilize waste materials more efficiently and to identify the ways to replace heavy residue hydrocarbon, either partially or completely, it is recommended that additional converted waste residue be prepared and blended with asphalt for road testing as a wearing surface mixture.

2. Preliminary results indicate that sulfur is more compatible with asphalt-pyrolysis oil blends than with asphalt alone. Further studies are needed to confirm this result, to determine optimum compositions and to evaluate the performance characteristics of these ternary blends. It is expected that a flexible binder could be formulated that contains only about 30-40% petroleum asphalt admixed with approximately equal amounts of pyrolysis oil and sulfur.

3. The penetration value of asphalt-pyrolysis oil mixtures is much greater than expected based on additive properties. This suggests possible advantages in use of pyrolysis oil for rejuvenating and recycling aged asphalt. Further studies would include preparation of blends and measurement of critical physical properties.

4. Application of neat pyrolysis oil as a road binder is precluded by high volatility and low viscosity at elevated temperature. Both properties could be adjusted by suitable chemical modification that increases the average molecular weight. Methods deserving further study include condensation with crosslinking agents such as formaldehyde.

5. Although liquefaction currently appears less advanced than pyrolysis for production of petroleum substitutes, developments in progress may enhance its position. In that case, it would be desirable to find means of stabilizing the liquefaction product against deterioration that makes it unacceptable in binder applications. In this connection, additives or caustic treatment may be beneficial.

6. Oils derived by pyrolysis or liquefaction of coal represent another potential source of road binder that does not depend on petroleum. With the development of coal technology for production of fuel substitutes, residual fractions can be expected that could be utilized in this application. It would be useful to examine these fractions alone or in combination with asphalt, sulfur and/or waste pyrolysis oil to determine if they are possible replacements for petroleum asphalt.

CHAPTER II

LITERATURE REVIEW

General Background

Practically all organic waste materials are of vegetable origin and consist chiefly of cellulose and lignin. These substances represent a vast potential source of oils, tars, pitches, and various chemical intermediates, and technology has long existed for converting wood and other plant residues into more useful products.[1-4] However, this technology has not been widely exploited because competitive products were usually more economically derived from petroleum.

Today's energy and environmental problems have changed the relative values of petroleum, coal and cellulosic materials significantly. The need for new energy sources has stimulated the development of more efficient processes for converting coal and cellulosic wastes into gaseous and liquid fuels.[5-10] Much of this emerging technology may also be applicable to the production of bituminous materials, but this apspect has been largely neglected to date.

Cellulose and lignin are complex, high molecular weight substances that must be severely degraded in order to convert them into more tractable materials. Processes under development to accomplish this involve three basic reactions: pyrolysis; hydrogenolysis and hydrolysis. Literature on the application of these reactions to the degradation of cellulose and lignin is far too voluminous to review here. The following discussion summarizes the current state of technology only insofar as it applies to the processing of organic wastes that may be useful for the production of bituminous materials.

Pyrolysis of Cellulosic Waste

Pyrolysis (destructive distillation) has been used on a large scale for many years in the petroluem and coal processing industries. The process requires heating of the feed material to a high temperature in the absence of air. Volatile matter is distilled, leaving behind carbon and inert material. The volatiles may be burned to fuel the process, or the gases may be cooled to condense oils and tars. Alternatively, the gases may be purified for use as gaseous fuel.

The large scale application of pyrolysis to solid waste disposal is a relatively recent development. Several processes developed in the past several years have been reviewed.[11-12] Among the more highly developed are the Garett Pyrolysis Process designed to produce an oil and Union Carbide's Oxygen Refuse Converter System that produces fuel gas. Other pyrolysis processes such as Monsanto-Landgard and Torrax Processes are intended primarily to serve as low-pollution waste disposal systems but can also be used to generate fuel gas. Several other processes are in advanced development stages at West Virginia University, U.S. Bureau of Mines and Battelle Institute.

To date, much of the experience in waste pyrolysis has been gained in the processing of urban refuse.[13-14] Since this material is over two-thirds ligno-cellulosic in nature, i.e., paper, garbage, grass, leaves and wood, similar results can be anticipated from processing of related ligno-cellulosic materials such as wood waste, crop residues and animal manure. Depending upon feed composition and pyrolysis

TABLE 1

YIELD OF PYROLYSIS PRODUCTS PER 100 LB. REFUSE

Temp., °F	Gases (lb.)	Pyroligneous Acids & Tars (lb.)[a]	Char (lb.)
900	12.3	61.1	24.7
1200	18.6	18.6	59.2
1500	23.7	59.7	17.2
1700	24.4	58.7	17.7

[a] Includes 70-80 pct. water.

$°C = (F-32) \times \frac{5}{9}$ kg. = 2.20 lb.

temperature, various amounts of gas, char and tar acids are produced. Typical results obtained on batch pyrolysis of urban refuse appear in Table 1.

The Bureau of Mines has examined the pyrolysis of several organic waste materials in a modified coal-pyrolysis pilot plant.[15] Similar data on the pyrolysis of wood wastes and cotton gin wastes has been obtained at Georgia Tech's Experimental Station in a 45.5 metric ton/day demonstration unit.[16] Compositional analysis of some typical waste materials and the yields of products obtained on pyrolysis are shown in Table 2.

TABLE 2

ANALYSIS AND PYROLYSIS YIELDS OF SOME DRIED WASTE MATERIALS

Composition	Municipal Refuse	Cattle Manure	Rice Hulls	Paper Mill Sludge
Carbon, wt. pct.	27.2	41.2	38.5	30.9
Hydrogen, wt. pct.	8.2	5.7	5.7	7.0
Nitrogen, wt. pct.	0.7	2.3	0.5	0.5
Oxygen, wt. pct.	56.8	33.3	39.8	51.2
Sulfur, wt. pct.	0.1	0.3	0.0	0.2
Ash, wt. pct.	7.0	17.2	15.2	10.2
Moisture, wt. pct.	4.9	3.6	7.6	23.2
Pyrolysis Temp., °F	900	900	200-700	900
Product Yield, wt. pct.				
Char	31.3	36.3	40.0	24.2
Gas	45.3	38.5	20.6	30.8
Tar, Oil	6.9	4.4	5.1	0.5
Aq. Liquor	14.6	15.6	32.4	36.3

Available information on the liquid fractions obtained from pyrolysis is limited mainly to its compositional analysis and heating value. The liquid fraction can be separated into a tar, a heavy oil, and a liquid containing aromatic hydrocarbons, aldehydes, ketones, and acids, but it seems unlikely that further separation and marketing of individual organic components would be economically attractive.[14] This fraction may be useful as a wood preservative or insecticide [17] or as a highway binder material.[18]

Hydrogenation and Liquefaction

As with pyrolysis, the hydrogenation of solid organic wastes is an extension of coal conversion technology to produce gaseous and liquid fuels. Much of the recent work dealing with gas production (gasification) from coal[6] and solid wastes [19] is not directly applicable to this discussion. Technology for the production of liquid products from coal, often called liquefaction, involves direct [20] or indirect [21] methods of hydrogenation.

The hydrogenation procedure has been widely investigated in an attempt to convert lignocellulosic materials into commercially valuable products. These studies have been reviewed. [2,22] A catalytic hydrogenation procedure for converting lignin into phenolic products has been developed in Japan [23] and the U.S. [24] Over 55 percent of the lignin is converted into a remarkably simple mixture of distillable phenolic products.

Extensive work on the indirect hydrogenation of organic wastes to liquid products has been carried out by the Bureau of Mines.[25] High yields of heavy liquid products are obtained from many types of cellulose waste by treating them with carbon monoxide and water at elevated temperature and pressure in the presence of alkali. This reaction, long known in connection with the liquefaction of low-rank coals, [26] is applicable to ligno-cellulosic materials under milder reaction conditions.

In contrast to pyrolysis, an indirect hydrogenation process provides mainly liquid product with relatively little solid or gaseous by-products. [27] It also has advantages over direct hydrogenation insofar as no costly catalysts are employed, lower temperature and pressures can be used, and the carbon monoxide consumed may be generated (as synthesis gas) from the organic wastes.

The reaction has been conducted in both batch and continuous equipment and the influence of reaction variables such as temperature, pressure and residence time on the yield and nature of the products has been investigated. [28] Cellulosic wastes can be processed at 250-350°C, 1500-3500 psi (10.4×10^6 - 24.2×10^6 Newtons/m^2) with a residence time of 0.5 to 2 hours. Under these conditions, liquid products have been obtained from cellulosic wastes including urban waste, wood waste, cattle manure, and sewage sludge as shown in Table 3. It has been suggested that with process improvements a 58 percent yield of liquid products is attainable, based on the dry, organic content of the feed.

The properties of the liquid product depends upon the reaction conditions. At high temperature and pressure a black viscous oil is obtained; about 55 percent is distillable under vacuum. At lower temperature, e.g., 250°C, the primary product is a bitumen-like solid that flows at 100°C.

Considerable pioneering work on liquefaction processes involving both direct and indirect hydrogenation has been carried out over the past decade. These studies establish the important role of catalysts in achieving high yields. [29] Techniques have been developed for the evaluation of performance of various coals in liquefaction studies that are equally applicable to solid wastes. [30] Low pressure, catalytic procedures have been identified that permit process simplifications. [31]

Hydrolysis of Cellulose and Lignin

Ligno-cellulosic wastes of native origin, such as crop and wood residues, contain from 15-25 percent hemicullulose, 20-30 percent lignin and about 50 percent cellulose. [32] In paper manufacture, hemicellulose and lignin are separated from the cellulose by dissolution in alkali. Extensive degradation of the ligno-cellulosic material occurs, resulting in the formation of a complex heterogeneous mixture that is extremely difficult to process.

In recent years alternate solvents have been identified that extract the lignin and hemicellulose without extensive modification. One of the more powerful and least expensive of these is aqueous dimethylsulfoxide.[33] This solvent produces cellulose pulp and a spent liquor from which lignin can be recovered in 90 percent yield by precipitation with water. Carbohydrates derived from hemicellulose are left in solution.

The carbohydrate fraction of hemicellulose is rich in xylose, which is the precursor of furfural in present commercial practice. [34] Furfural is produced in a single-step operation. The raw material is treated with dilute acid to hydrolyze the pentosans and the resulting furfural is removed by steam distillation. Corncobs are the primary source of furfural, but bagasse, cottonseed hulls, oat hulls, and rice hulls are also used commercially. Yields obtained from typical crop residues are shown in Table 4. In addition, the possibility of producing furfural from wood has been studied.

TABLE 3

LIQUEFACTION OF CELLULOSIC WASTES WITH CO/H_2O

Waste Material	Urban Refuse	Pine Waste	Cattle Manure	Sewage Sludge
Conversion, wt. pct.	87	81	90	86
Liquid Product, wt. pct.	37	35	40	24

TABLE 4

POTENTIAL YIELDS OF FURFURAL FROM CROP RESIDUES

Raw Material	Yield, Percent	Raw Material	Yield, Percent
Oat hulls	22	Bagasse	17
Corncobs	22	Oak tanbark	13
Cottonseed bran	20	Rice hulls	12
Cornstalks	16	Flax shives	14
Buckwheat hulls	17	Peanut hulls	12

The technological aspects of wood-based furfural have been evaluated in some detail and no major engineering problems were encountered during pilot plant operation.

Furfural is widely used to form fusible resins that are cured by heating in the presence of catalysts. Furfural resins make excellent binders. They are usually combined with phenols in this application. Furfuryl alcohol is also a highly useful resin precursor that is extensively used in binders, mortars and adhesive formulations. It is easily produced from furfural by hydrogenation at nominal pressures and continuous processes are available. Furfuryl alcohol resins can be designed to cure rapidly at installation temperature to form binders with excellent chemical and mechanical resistance. They are commonly employed as resin mortars in the manufacture of pipes, ducts and reaction vessels and as gap-filling adhesive in industrial construction requiring chemical resistance.

Although highway binders based on furfural and furfuryl alcohol, so called furane resins, have received limited attention in the U.S., their use in the Soviet Union has been publicized.[37,38] Several percent, used in combination with tars and aggregate, reportedly produce exceptionally strong, durable road surfacing materials. Properties of similar compositions[39] are shown in Table 5 illustrating the high strength and oil resistance imparted to conventional road binder materials by the addition of furane resins.

Process Economics

Cost analysis have been reported for pyrolysis and hydrogenation processes dealing with coal and solid organic wastes.[12,28] Because of the lack of large scale operating experience, uncertain capital requirements and possible variations in feed, caution must be used in applying this information. Furthermore, it is difficult to make valid comparisons because of differences in scale and the various accounting techniques and cost correlations that have been employed.

The cost of processing depends not only upon the process used but also upon the nature of the waste material used. In cases where preliminary separation, drying or shredding is required, these operations may contribute substantially to the overall cost. If metal, glass or ceramic is separated, the value or cost of disposal of these materials must also be considered.

Estimated operating cost for waste pyrolysis plants range from \$5.50 to \$11.50 per metric ton, depending on how the fuel credits are handled. The Landguard pyrolysis system for processing 909 metric ton/day solid waste (Baltimore, Maryland) is projected to cost \$9.93/metric ton. Plant cost is \$15.4 million. Garrett has estimated \$5.50/metric ton operating cost for a 1,818 metric ton/day pyrolysis unit with a capital cost of \$12.4 million. Net costs (1973) were estimated to be \$10.18/metric ton at 227.3 metric tons/day and \$4.27/metric ton at 1,818 metric tons/day.

A hydrogenation plant converting wood waste, urban waste or cattle manure would cost \$10.43/metric ton to operate, according to Bureau of Mines estimates. With current values assigned to the low-sulfur oil produced, this operating cost could be almost completely offset by-product credits. Additional credit for waste disposal that runs into several dollars per metric ton in many areas may make this process a profitable operation.

Compared to indirect hydrogenation, pyrolysis has the advantage of operating at normal pressures. Therefore, construction and operating costs are relatively low. However, three products are produced and this may create problems of storage and disposal. With indirect hydrogenation a single product can be produced, thereby simplifying product handling, but cost factors associated with high pressure equipment and process gas purity are still uncertain. A method of modeling the economic performance of liquefaction processes has been reported.[40]

Estimates are also available on the cost of converting crop and wood wastes to both furfural and mixed phenolic products.[24,36] Although in the past these processes have been of limited economic interest, recent changes in raw material and product values warrant their reconsideration. The possible utilization of a larger portion of the ligno-cellulosic wastes and economics of scale may make these processes more competitive.

TABLE 5

PROPERTIES OF BITUMEN-AGGREGATE MIXTURES
MODIFIED WITH FURANE RESIN

Coal Tar, pct.	25	20	12.5	5
Filler & Aggregate, pct.	75	75	75.0	75
Furane Resin, pct.	0	5	12.5	20
Compressive Strength, psi.				
As cured	None	378	2126.0	8152
Aged in benzene	None	320	1634.0	9554

1 Newton/m^2 = 14.45 x 10^{-5} psi.

CHAPTER III

AVAILABILITY OF CELLULOSIC WASTE MATERIALS

Summary

An estimated 630 x 10^9 kgs. (moisture, ash-free basis, maf) of cellulosic waste is generated annually in the U.S. as a result of agricultural, manufacturing and domestic activities (Table 6). Most of this amount is widely dispersed and unavailable but an estimated 74 x 10^9 kgs. (maf) occurs in a concentrated form that presently poses a serious disposal problem. Animal manure, wood industry residue and municipal solid waste make up the bulk of the readily available material. All three of these wastes are available in large quantities at numerous locations throughout the country.

Of the 273 x 10^9 kgs. of animal manure (maf) generated annually, 25.5 x 10^9 kgs. is concentrated in large commercial animal feedlots located in 24 states. Commercial cattle feeding is growing rapidly and the trend is toward larger feedlots so cellulosic waste from this source is likely to increase substantially in the future.

Wood and paper industries generate an estimated 78.6 x 10^9 kgs. of cellulosic byproduct of which about 40 x 10^9 kgs. is not presently utilized. High concentrations are located at sawmills in major logging areas of 23 states across the country. This material consists of bark as well as fine and coarse residues produced in lumber

TABLE 6

SUPPLY AND AVAILABILITY OF MAJOR
CELLULOSIC WASTE MATERIALS

Waste Type	10^9 Pound/yr., (maf) Generated	Available[a]	Location of Available Waste
Agricultural:			
Crop Residues	476	b	major cattle feedlot areas in 24 states
Animal Manure	600	56	
Forestry Residue	>40	b	
Manufacturing:			
Food Processing	b	b	Major sawmill areas in 23 states
Wood & Paper Industry	88[c]	44	
Urban Refuse:			
Municipal Solid Waste	156	63	50 ranking SMSA's thruout the U.S.
Manufacturing Plant Trash	25	b	
TOTAL	1,385	163	

a. Only localized quantities of 500 x 10^6 pounds or greater that presently present a disposal problem were considered to be available.

b. Amounts are negligible for purposes of this study but some portion might be utilized in conjunction with other wastes.

c. Not including about 85 x 10^9 pounds already used for fuel, pulp and manufactured products.

1 kg. = 2.20 pounds

manufacture. Particularly large concentrations are generated in the South and Pacific Coast regions.

Municipal solid waste is the largest and currently the most problematic cellulosic waste stream. Some 142 x 10^6 metric tons (maf), largely paper, is collected in metropolitan areas of which 57.3 x 10^6 metric tons is readily available in large volume within the 50 most populated districts of the U.S. It is mixed with scrap metal & glass but there is already a developing trend toward removing the latter materials for recycling. This trend coupled with projected increases in amounts generated will enhance future availability of the cellulosic portion for resource recovery.

Methodology

This assessment of waste supply is based on numerous reviews appearing in recent years as well as reports of surveys and studies conducted by the federal government. Most recent detailed and comprehensive information on this subject is available from EPA, Office of Solid Waste Management Programs, (OSWMP), which lists 463 OSWMP publications and several hundred NTIS reports on solid-waste-related studies through 1975 (SW-58.25). Seven types of cellulosic waste materials are identified that are generated in sufficient quantity to satisfy the overall objectives of the program. These were analyzed in greater detail to evaluate their availability and concentration on a geographic basis.

Cellulosic wastes commonly occur in combination with water and inorganic materials. Published accounts of quantities may or may not include these materials leading to wide variations in the amount of waste reported. Since this study is concerned only with the cellulosic and associated organic portion of the waste, quantities are reported on a moisture, ash-free basis (maf). This method leads to much lower values than often encountered in the literature but the values are more realistic in terms of utilization of the cellulosic fraction and can be applied directly in comparisons of various waste types.

Reliable measurements of quantities by waste type and specific location are not readily available. Methods have been developed and utilized in various EPA sponsored projects that can be used in estimating. These methods employing available statistical data and average waste generation rates were used in the present study. In the case of one major waste, viz. wood manufacturing waste, the best method available is based on a stream flow approach that combines waste generated from a large variety of manufacturing industries. Regional statistics on wood waste and timber production are published by the Forest Service. This source was used as the data base since it more accurately reflects highly concentrated material of a uniform nature. Statistical sources and methods employed in the evaluation are described in greater detail in connection with the discussion of individual waste types below.

In assessing the total amount of waste readily available for processing, only quantities greater than 227 x 10^6 kgs. were considered. This selection was made on the basis that sufficient material would be needed to support a plant of at least 455-909 metric ton/day for economical operation. Projected economics of waste utilization plants in Baltimore, St. Louis, San Diego and Franklin, Ohio emphasize economics of scale for cost-effectiveness. All indicate that a throughput of at least 455 metric ton/day is required.

It should be emphasized that the average waste generation rates used to estimate regional concentrations provide only approximate values. Depending on local conditions such as disposal codes, manufacturing practices and general life-style, small differences from the norm are expected and in some special instances, very large deviations may be encountered. Such local variations would not alter the general conclusions reached in this study.

Agricultural and Forestry Wastes

Crop Residues. The USDA reports[41] over 273 x 10^9 kgs. of major field crops harvested in 1973. Based on production figures and estimated waste coeffecients[42] reported for individual crops, almost 227 x 10^9 kgs. of dry, cellulosic waste is produced annually in the cultivation of these crops (Table 7). About three-fourths of this cellulosic waste occurs as field residue from grain corn, wheat and sugarcane production. Currently, this residue is burned or plowed and the trend is to plow under most of the field residue even though the soil beneficiation effect may be marginal. This practice also carries the risk of pesticide build-up and pest infestation but unless cost incentives are provided for collection, these wastes are not likely to be available in high concentration.

A significant portion of sugarcane residue, bagasse, is collected and utilized in fueling cane extraction plants. This use is likely to increase in the future as alternate fuels rise in cost. Bagasse is also used in manufacture of short fiber pulp for paper. Bagasse pulp capacity is currently 235,000 metric tons.[43]

Animal Manure, An estimated 2.09 x 10^9 metric tons of animal manure is generated annually in the U.S.[42,44] Most of this waste is widely dispersed and does not represent a problem. A significant fraction, however, is generated by animals raised in confinement with attendant pollution and disposal problems.[45,46] The

TABLE 7

MAJOR CROP RESIDUES GENERATED IN THE U.S. (1973)

Crop	Production, 10^9 lb.	Dry Waste Coeff. [a]	10^9 lb. Residue/yr. (mf)
Corn (grain)	31.6	5.63	178
Corn (silage)	225	0.010	2.2
Wheat	102.3	0.472	48.3
Oats	21.3	0.960	20.4
Barley	20.2	0.820	16.6
Rye	1.47	1.21	1.8
Rice	9.28	0.602	5.6
Cotton [b]	16.5	1.19	19.6
Soybeans	92.8	0.488	41.6
Peanuts	3.47	0.579	2.0
Potatoes	29.9	0.058	1.7
Sugarcane	51.6	2.62	135
Sugarbeets	49.0	0.074	3.6
TOTAL CROP			476.4

a. Waste coefficient = weight dry residual/weight production for cultivated crops. Moisture content estimated as 60 pct.

b. Includes seed and linter production.

Sources: Agricultural Statistics, 1975, Table 612; Problem and Opportunities in Management of Combustible Solid Wastes, International Research and Technology Corporation.

1 kg. = 2.20 lb.

cattle feeding industry is by far the largest source of concentrated animal waste but dairying and hog feeding operations also constitute significant sources. Except for poultry manure, the nutrient level in animal wastes is too low and unbalanced for economical use as a fertilizer on a large scale but this is the only practical method of disposal currently available. Furthermore, special precautions must be taken with field disposal to prevent groundwater contamination and adverse affects upon crop production.

Statistical data on statewide animal populations and the number of beef cattle on feed is reported by USDA. Estimates of average waste rates and their composition are relatively uniform [44, 45,47] although the range may vary depending on factors such as animal weight, confinement conditions and type of feed. Average values used in determining the quantity of cellulosic waste (moisture-and ash-free, maf) are shown in Appendix A. Data on feedlot size and distribution were taken from a USDA report.[48]

Almost one-third of the U.S. beef cattle production is processed through large commercial feedlots and the proportion is rising steadily. There is some seasonal fluctuation in the population of feedlots but the number used, in the third quarter of the year, is fairly representative of the average. The amount of waste generated in feedlots was estimated by multiplying appropriate regional data by the average waste factor. Quantities generated in leading cattle feeding states are listed on a moisture-free (mf.) and moisture-and ash-free (maf) basis.

Data on dairy cows and hogs was used to estimate the amount of waste generated from these sources in leading dairying and hog producing states.

TABLE 8

WASTE GENERATED BY CONFINED ANIMALS (1974)

State	10^9 lb./yr. (maf) Milk Cows	Fed Beef	Hogs	Total
Ariz.	0.05	1.43	0.05	1.53
Calif.	0.61	2.88	0.04	3.53
Colo.	0.06	2.01	0.09	2.16
Ga.	0.10	0.18	1.59	1.87
Idaho	0.11	0.55	0.04	0.70
Ill.	0.20	1.23	2.13	3.56
Ind.	0.17	0.59	1.41	2.17
Iowa	0.31	3.96	4.40	8.67
Kansas	0.11	2.46	0.57	3.14
Ky.	0.23	0.12	0.36	0.71
Mich.	0.32	0.51	0.23	1.06
Minn.	0.68	1.10	1.21	1.99
Mo.	0.24	0.51	1.28	2.03
Nebr.	0.12	3.36	1.00	4.48
N.Y.	0.68	0.42	0.03	1.13
N. Mex.	0.02	0.57	0.02	0.61
N.C.	0.12	0.15	0.62	0.89
Ohio	0.31	0.55	0.64	1.50
Okla.	0.10	0.69	0.10	0.89
Pa.	0.51	0.17	0.21	0.99
S. Dak.	0.13	0.93	0.56	1.62
Tex.	0.26	5.33	0.31	5.90
Wash.	0.14	0.53	0.02	0.69
Wis.	1.35	0.36	0.46	2.17
		TOTAL		55.68

1 kg. = 2.20 lb.

Numbers of animals and quantity of waste generated are listed by state in Appendix A. These sources are smaller and more dispersed than beef cattle feedlots but in many areas they would provide significant supplementary amounts of cellulosic waste.

The total amount of cellulosic waste generated by cattle and hogs raised in confinement is shown in Table 8. Quantities greater than 227 x 10^6 kg. per year are available in 24 states in every region of the country. Much more than 45.0 x 10^7 kgs. is generated annually in nearly all the states listed. Particularly high concentrations occur in the southwest and in the corn-belt states.

Although the area of a state constitutes an unduly large collection district, most animal feeding operations are concentrated in relatively small regions of the state that would form a natural collection district. This is particularly true of beef cattle feedlots as can be seen from USDA data showing the areas of the states in which cattle feeding is concentrated. Individual feedlots in these regions are very large. An estimated 90 percent of the commercial lots have a capacity of ten-thousand head or more. Several hundred lots have a capacity of over thirty-thousand head.[49] Particularly large lots, some with an average one-hundred-thousand head or more are located in California, Colorado and the Texas Panhandle.[50] The trend is toward even greater concentration. According to recent projections, almost 30 x 10^6 head will be marketed from feedlots with an aggregate area of 229.6 square kilometers.[47] This amounts to an average population of one head per 17.6 square meters and a corresponding annual manure accumulation of over 0.34 metric tons per square meter of feed-lot.

Forestry Waste. In 1970, an estimated 45.3 x 10^6 cubic meters of logging residues plus large volumes of cull material was left in the woods unutilized.[51] Although the percentage of residue that is used is increasing, the quantity of unused material is projected to grow in future years because of increased logging activity.[42] Based on current generation rates, up to 28.2 and 40.9 x 10^9 kgs. will be generated in 1980 and 1990, respectively.

For the most part, forestry waste is widely dispersed in relatively inaccessible areas. It consists of vegatation and foliage in addition to limbs, much of which is bulky and would have to be chipped on-site at an average cost of $11 to $13/metric ton. Coupled with transportation costs, the economics of utilizing these residues are highly unfavorable at present. In some special instances, useable material is generated in fire prevention activities. In this connection, some 1,230 square kilometers of forest slash from timber harvest was chipped or burned in 1971.[52] Public concern over environmental impacts of logging residues may supplement economic pressure to remove residues from the forests in the future.

Manufacturing Wastes

Food Processing. Although a large amount of residual is produced in food processing, almost none of it is presently discarded.[42] With a few minor exceptions, e.g., tomato processing waste, food processing residues are entirely utilized in prepared animal feeds. In 1973, 30.9 x 10^6 metric tons of by-product feed was produced including 14.7 x 10^6 metric tons of oilseed cake and meal, 2.27 x 10^6 metric tons of protein from meat, fish and milk processing and 9.0 x 10^6 metric tons of grain mill residue and dried beet pulp that was formulated into commercial animal feeds.[41] An unreported quantity of wet beet-pulp was also channeled into this use.

Wood Manufacturing. In 1970, an estimated 16.4 x 10^7 cubic meters of residue accumulated at U.S. sawmills. About 9.6 x 10^7 cubic meters was used for fuel, pulp and particleboard. The remainder was burned or dumped.[51] Enactment of state laws controlling disposal is stimulating closer utilization of wood residue. Increasing production counters this trend so the amount of unused wood manufacturing residue is not likely to decline sharply in the near future and one projection[52] shows an increase in industrial wood waste. Lumber production increased 11.2 percent from 1970 to 1973, declined to the 1970 level in 1974 and is rising again in parallel with renewed construction activity.

Large quantities of unused wood waste are generated in every region of the U.S. Particularly high concentrations are found in the logging areas of the South and West. The quantities vary depending upon species, mill practices, utilization and local burning regulations. Most recent comprehensive statistics on volumes generated at saw mills according to region, species, type of residue and uses has been reported by the Forest Service. This information on 10.8 x 10^7 cubic meters of wood residue and an estimated 5.7 x 10^7 cubic meters of bark is summarized in Appendix A.

Residues other than bark consist of slabs, sawdust, veneer cores resulting from the manufacture of lumber, plywood, pulp and other wood products. Green wood may have a moisture content of from 30 to 60 percent and a density of about one. Oven dry density is commonly in the range of 0.40 to 0.72 gms./c.c. It contains a few tenths percent inorganic material and for practical purposes can be considered pure carbohydrate consisting of sugars, cellulose and lignin. Bark contains different proportions of these components but is otherwise essentially equivalent to heartwood.[53,54]

An estimate of the volume of unused wood and bark residue generated by principal wood manufacturing states and areas was obtained by allocating regional data according to statistics on sawtimber removals. The corresponding weight of moisture-and ash-free ligno-cellulosic waste was computed assuming an average content of 0.40 gms./c.c. Based on annual sawtimber removals in the U.S. of 19.1 x 10^9 board meters, the corresponding quantity of unused, dry cellulosic waste is estimated at 22.6 x 10^9 kgs., (Appendix A). Concentrations greater than 227 x 10^6 kgs. totalling to 20.1 x 10^9 kgs. are generated in 23 states located in six regions of the U.S. Most of these states generate concentrations in excess of 45.4 x 10^7 kgs. annually. Especially large quantities, greater than 227 x 10^7 kgs., are located in California, Oregon, and Washington.

Although most states comprise an unduly large collection area, sawmills are concentrated in districts of the state adjacent to productive timberlands covering a small fraction of the total area. These areas contain many smaller units but mills with annual capacities greater than 6.1 x 10^6 board meter are not uncommon particularly in the South and West regions. Average capacities and waste rates as well as principal locations of wood industries within the main wood manufacturing states is shown in Table 9.

TABLE 9

UNUSED WOOD RESIDUE AT SAW MILLS IN MAJOR LUMBER MANUFACTURING STATES

State	Number of Mills[a]	Unused Residue (maf)		Principal Locations Office of Business Economics of the Dept. of Commerce[b]
		Statewide, 10^9 pounds	Average/mill, 10^6 pounds	
South Atlantic				
N.C.	705	1.78	2.5	High Point
S.C.	225	1.32	5.9	Charleston
Va.	584	0.99	1.7	Roanoke
Fla.	96	1.00	10.4	Jacksonville
Ga.	415	2.53	6.1	Augusta
South Central				
Ala.	319	2.06	6.5	Birmingham
Miss.	233	1.96	8.4	Greenville
Tenn.	421	0.59	1.4	Knoxville
Ark.	284	1.81	6.4	Little Rock
La.	150	2.15	14.3	Shreveport
Tex.	192	1.31	6.8	Tyler, Texarkana
West				
Ore.	340	6.17	18.1	Portland, Eugene
Wash.	255	5.64	22.1	Seattle, Everett
Cal.	302	6.04	20.0	Redding, Eureka
Id.	118	2.00	17.0	Boise City
Mont.	116	1.72	14.8	

a. Source: Census of Manufacturers, 1972

b. Selected from reference 2, Table 119, Industrial Process Waste, locales are designated by the Office of Business Economics of the Department of Commerce.

1 kg. = 2.20 pounds

Geographical distribution and output of the wood manufacturing industry has not changed much in the last decade and except for overall growth, major changes are not foreseen in the near future. In recent years, the trend toward increased utilization of residues has been counteracted somewhat by the general softness in markets for major wood products. It is estimated that about 22.7 x 10^6 metric tons of wood residue and 66.4 x 10^6 metric tons of bark is generated in the Pacific Coast states.

Unusually large volumes are also available in the southern-pine areas where wood-chips are often in long supply.[55]

An additional 28.3 x 10^5 cubic meters of unused wood residue is generated by the veneer, plywood and other primary wood product manufacturers. These operations are usually smaller and more widely dispersed than lumber sawmills but much of this material would also be available in major wood-industry locations. The same is true of the estimated 10.2 x 10^9 kgs.[42] of residuals generated by pulp, paper and allied industries. However, pulp and paper industry wastes are highly variable depending upon the nature of the process. They often contain major amounts of chemical sludge that may complicate their processing. Availability of a suitable waste stream for use in combination with primary woodwastes would have to be determined on an individual basis.

Refuse

Municipal Solid Waste. The category of municipal solid waste (MSW) as defined for the purpose of this study corresponds to the Environmental Protection Agency's definition of the "post-consumer" portion of the municipal solid waste stream. It includes household refuse as well as similar materials collected from commercial and governmental office buildings, wholesale and retail establishments and other general business and service sectors of the local economy. Based on statistics thru 1973,[56] an estimated 123 x 10^6 metric tons of this material is disposed of annually by municipalities. Well over one-half of this waste stream is organic material of cellulosic nature, e.g., paper, food waste and yard waste. The average composition based on nationwide generation statistics is shown in Appendix A.

Detailed analysis of measurements of the weight and composition of MSW based on extensive surveys of solid waste practices in typical municipalities have been published.[57] The measured values are more conservative than most widely published estimates since they account for the moisture content of the refuse output. On a dry basis, the annual generation rate is estimated at 497 kg. per capita and the concentration of organics, principally cellulosics, is 289 kg. per capita or 58.2 percent of the total waste stream. Similar values are derived from EPA data by assuming a realistic moisture content of 60 percent in the food and yard waste categories.

Per capita generation rates were used to tabulate the cellulosic waste generated in the Standard Metropolitan Statistical Areas. (Table 10). Such areas represent natural collection districts in which large volumes of refuse are readily available. There are 243 statistical areas located throughout the U.S. for which census figures are available.[58,59] It is established that the twenty most populated areas generate from 4.5 to 27 x 10^8 kgs. of dry cellulosic waste annually. The next 30 generate an average of 30.4 x 10^7 kgs./year. These fifty areas of high population density account for 57.4 x 10^9 metric tons, 70 percent of the total MSW stream. Aside from geographical effects on the amount and peak-appearance of garden waste that introduces approximately 8 percent variation in average waste load, refuse from large municipalities is much the same the country over.[60]

MSW is growing on both a total volume and per-capita basis. The organic content is also on the increase particularly because of increased use of paper and plastic in packaging. Currently, almost 90 percent of MSW is disposed of by landfilling but this method is becoming increasingly impractical and expensive. EPA has mounted a major program to develop technology for recovery of resources from MSW. Several projects are in final stages and it is expected that by 1985, about 10 percent of the waste will be processed by resource recovery plants.[57,61]

The more advanced processes under development involve a preliminary classification method for separating metal, glass and other inorganics from raw refuse.[62-70] Several demonstration and commercial projects are operating or are in various stages of completion.[71] A highly concentrated cellulosic fraction essentially free of inorganics is produced in such operations. Larger installations are located in St. Louis (7,273 metric tons/day) and San Diego (182 metric tons/day). Many others have been announced or are under construction in SMSA's throughout the U.S..

Manufacturing Plant Trash. Some 11.35 x 10^9 kgs. of non-process trash consisting mainly of wood and paper is discarded annually at manufacturing plants.[42] It is commonly disposed of in the same manner as MSW. Since manufacturing plants are located in or near urban areas, much of this material is available in MSW collection regions.

TABLE 10

MUNICIPAL SOLID WASTE GENERATED IN MAJOR METROPOLITAN AREAS OF THE U.S.

Rank/SMSA		Population[a]		MSW Generated, 10^9 lb./yr.	
		10^6	Thousands/sq. mi.	Total	Cellulosic (maf)
1.	New York	9.81	7.04	10.7	6.37
2.	Chicago	7.05	1.88	7.72	4.49
3.	Los Angeles-Long Beach	6.95	1.70	7.61	4.43
4.	Philadelphia	4.82	1.35	5.28	3.07
5.	Detroit	4.45	1.14	4.87	2.84
6.	Boston	3.42	1.92	3.74	2.18
7.	San Francisco	3.12	1.27	3.42	1.99
8.	Washington, D.C.	3.04	1.07	3.33	1.94
9.	Nassau-Suffolk	2.61	2.16	2.86	1.66
10.	Dallas-Fort Worth	2.44	0.20	2.67	1.55
11.	St. Louis	2.38	0.49	2.61	1.52
12.	Pittsburgh	2.37	0.78	2.60	1.51
13.	Houston	2.13	1.15	2.33	1.36
14.	Baltimore	2.12	0.94	2.32	1.35
15.	Newark	2.01	2.04	2.20	1.28
16.	Cleveland	2.00	1.32	2.19	1.27
17.	Minneapolis	1.99	0.43	2.18	1.27
18.	Atlanta	1.73	0.40	1.89	1.10
19.	Anaheim	1.58	2.04	1.73	1.00
20.	San Diego	1.47	0.34	1.61	0.94
1-20	Total	67.5		73.9	43.0
21-50	Average	1.05		1.15	0.67
	Total	31.6		34.6	20.1
51-243	Average	0.23		0.25	0.14
	Total	43.8		48.0	27.9
1-243	GRAND TOTAL	142.9		156.5	91.0

a. Sources: Statistical Abstracts of the United States, 1974; A Guide to Consumer Markets 1975/1976, The Conference Board, 1975.

1 kg. = 2.20 lb.

Population: 386/square kilometer = one thousand/square mile

CHAPTER IV

EVALUATION OF LIQUEFACTION AND HYDROLYSIS PROCESSES

Liquefaction of Cellulosic Waste

Based on observations of Fisher that low rank coal can be hydrogenated with carbon monoxide and water, the U.S. Bureau of Mines has studied the conversion of cellulosic materials to oil. A pilot plant has been erected in Albany, Oregon to evaluate the production of low-sulfur fuel oil from agricultural and forestry waste.

Most of the past studies have been carried out at high reaction severities in an effort to produce a liquid burning fuel. This generally entails temperatures of 350-400°C and pressures up to 4000 psi (27.7 x 10^6 Newtons/m^2) in the presence of alkaline catalyst. The process has been successfully applied to a variety of wastes including sawdust, bovine manure and urban refuse.

Under relatively mild reaction conditions, a bitumen-like semisolid is reportedly formed from cellulosic wastes. This product, though not desirable as a fuel oil substitute, may be useful as an asphalt substitute or extender. Since samples of this product were not available and its properties have not been fully evaluated, a preliminary study was undertaken to evaluate its production and characteristics.

The liquefaction process concept consists of heating cellulosic waste and water to about 250°C. In order to minimize dehydration of cellulose and consequent formation of char, an alkaline catalyst is employed that promotes loss of oxygen as carbon dioxide rather than water. An idealized equation for the process is:

$$(C_6H_{10}O_5)_n \rightarrow (C_4H_8)_n + 2nCO_2 + nH_2O$$

where $(C_6H_{10}O_5)_n$ is cellulose and (C_4H_8) represents a high molecular weight unsaturated hydrocarbon of unspecified structure.

The actual reaction mechanism is much more complex than the above equation suggests. For example, there is evidence that carbon monoxide produced in situ is the deoxygenating agent either directly or via the formation of hydrogen, formate ion or both. Thus, addition of either carbon monoxide or formate has a beneficial effect upon conversion rate and oil yield. Cellulose may undergo a shift reaction with water to produce carbon monoxide and hydrogen under the reaction conditions so that stoichiometric addition of supplementary carbon monoxide is not necessary. In theory, the following equations apply to a self-sustaining process:

$$5\ C_6H_{10}O_5 + 5\ H_2O \rightarrow 30\ CO + 30\ H_2$$

Shift:

$$30\ H_2 + 30\ CO_2 \rightarrow 30\ CO + 30\ H_2O$$

Liquefaction:

$$12\ C_6H_{10}O_5 + 60\ CO \rightarrow 12\ C_6H_{10} + 30\ CO_2$$

Overall:

$$17\ C_6H_{10}O_5 \rightarrow 12\ C_6H_{10} + 30\ CO_2 + 25\ H_2O$$

The theoretical yield of oil is 35.7 wt. percent based on this ideal reaction stoichiometry but actual yield may be higher if the oxygen is not completely removed from the cellulosic. Actual yields are commonly on the order of 40-50 weight percent of the cellulose charged.

Experimental Procedure

Batch liquefaction experiments were carried out on wood, paper and bovine manure. Fine hardwood waste consisting of wood and bark was obtained from a local sawmill. The paper was commercial paper pulp sheet and dry bovine manure was obtained from a commercial source. All materials were dried in a forced air oven at 100°C to constant weight.

Liquefaction was conducted in a 2 liter stirred, stainless-steel autoclave fitted with cooling coils. The cellulosic feed, water, catalyst and carbon monoxide were charged to the cold autoclave which was heated rapidly to the specified reaction temperature. The mixture was stirred at 600 rpm at reaction temperature for 40-120 min. depending upon the rate of pressure rise. It was then rapidly cooled with circulating water and excess gas was vented. Gas samples were taken during venting and analyzed by mass spectrometry.

Water was decanted from the reactor and the reaction product was recovered by flushing the reactor with acetone. The acetone extract was filtered and stripped in a flash evaporator at 80°C and 40 mm. mercury. Conversion and yield were calculated based upon the weights of acetone insoluble residue and acetone soluble product recovered after evaporation i.e.

$$\text{Percent Conversion} = \frac{C_f - C_i}{C_f} \times 100$$

$$\text{Percent Yield} = \frac{C_s}{C_f} \times 100$$

Where C_f = weight of dry cellulosic feed
C_i = weight of acetone insoluble residue
C_s = weight of acetone soluble product

Process Variables

Reaction parameters evaluated in the study included temperature, time, catalyst, reducing gas, solvent and cellulosic waste source. The effect of these parameters upon conversion, yield, pressure, product composition was determined.

Base line experiments conducted with three waste types under various reaction conditions are listed in Table 11. Results in this table show the influence of sodium carbonate catalyst and carbon monoxide upon the course of reaction.

It can be readily seen that the catalyst has a large effect upon conversion and yield. In the case of wood waste, conversion increases from 58-65 percent to 96 percent on addition of 10 weight percent sodium carbonate and yield increases from 6 to 45-46 percent.

The influence of added carbon monoxide is less apparent. Conversion and yield is not substantially influenced but added carbon monoxide does have a beneficial effect upon the properties of the wood derived product. Its main effect is to reduce oxygen content of the product with attendant improved thermal stability of the product. Stability of products formed in the absence of CO was so poor that it was not possible to make viscosity measurements at elevated temperature.

TABLE 11

EFFECT OF MAIN VARIABLES IN LIQUEFACTION OF CELLULOSIC WASTES

Experiment Number	509	514	510	513	521	512	515	528
Charge:								
Waste	Wood	Wood	Wood	Wood	Wood	Paper	Paper	Manure
wt., g.	243	250	250	250	250	250	250	250
Water, g.	800	800	800	800	800	800	800	800
Na_2CO_3, g.	-	-	25	25	25	25	25	25
CO, psig.	-	400	500	-	200	400	-	200
Pressure, Max. psig.	1000	1290	1620	1225	1575	1625	1175	1030
Products								
Soluble, g.	15.7	29.5	111.0	115.4	84.3	58.6	53.3	13.9
Residue, g.	83.7	105.9	9.5	10.6	15.8	15.6	14.8	162.5
Conversion, pct.	65	58	96	96	94	94	94	35
Yield, pct.	6	12	44	46	34	23	21	6
Gas Composition, mole pct.								
Hydrogen	-	-	1.2	1.5	3.8	1.7	1.3	2.3
Carbon Monoxide	-	66.7	49.1	14.7	10.2	38.4	18.6	88.1
Carbon Dioxide	-	32.9	49.7	83.2	85.5	59.9	79.8	9.1

Newton/m^2 = 14.45 x 10^{-5} [psig. + 14.7 psi.]

Carbon monoxide had less effect upon the liquefaction of paper except to improve the hydrocarbon solubility of the products. In the case of manure liquefaction, conversion and yield were relatively poor even in the presence of carbon monoxide. Overall, the results suggest that lignin, present in wood and manure but essentially absent from paper, undergoes liquefaction less readily and leads to products that are not thermally stable. Also, the results indicate that more severe reaction conditions would be needed to liquefy manure efficiently.

It should be noted that in agreement with the proposed reaction mechanism, substantial amounts of carbon monoxide are generated during liquefaction. In the absence of carbon monoxide the gas pressure starts to build rapidly at 225-250°C signalling the onset of reaction and levels out after about 80 min. indicating approach to completion. The off-gas is mostly carbon dioxide admixed with 15-20 percent carbon monoxide and 1-2 percent hydrogen.

In the presence of added carbon monoxide, the reaction is considerably accelerated so that an equivalent pressure rise occurs in about half the time. These reactions were necessarily terminated because of pressure limitations of the equipment. Nevertheless, conversions and yields were at least equivalent to those obtained after longer times with carbon monoxide initially absent. Buildup of reaction pressure due to water vapor, thermal expansion and gas evolution increases similarly as a function of conversion regardless of the waste source, catalyst and carbon monoxide concentration. Pressure-time and pressure-temperature relationships for typical experiments are found in Figures 1-4. A slight pressure rise occurs in the liquefaction of wood waste even at 100°C. This probably stems from the facile hydrolysis or decarboxylation of a component such as lignin or hemi-cellulose.

Several exploratory experiments were carried out to determine if liquefaction could be enhanced

TABLE 12

EFFECT OF ADDED HYDROGEN DONORS UPON THE LIQUEFACTION PROCESS

Experiment Number	501	507	508	511	533	530
Charge:						
Waste	Wood	Wood	Wood	Wood	Wood	Manure
Wt., g.	248	252	250	250	250	250
Water, g.	146	298	400	800	800	100
Na_2CO_3, g.	12	30	-	25	25	12.5
CO, psig.	200	200	200	400	200^a	200
Cobalt Catalyst	-	-	-	12.5	10	-
Solvent	Cresol	Tetralin	Anthracene	-	-	Cresol
vol., ml.	450	300	Oil,400	-	-	450
Pressure, Max. psig.	1325	1435	1475	1625	1610	1010
Products:						
Soluble, g.	180.5	28.0	200	96.9	96.6	95.2
Residue, g.	-	87.0	-	22.3	18.3	154
Conversion, pct.	-	65	-	91	93	38
Yield, pct.	$(73)^b$	$(21)^c$	$(150)^b$	39	38	48
Gas Composition, mole pct.						
Hydrogen	4.4	-	1.0	2.0	37.1	1.3
Carbon Monoxide	56.7	20.7	38.1	42.6	5.6	57.6
Carbon Dioxide	36.6	79.3	60.9	55.1	55.4	41.1

a. Hydrogen used in place of carbon monoxide
b. Contains residual solvent.
c. Includes light oil dissolved in tetralin.

Newton/m^2 = 14.45 x 10^{-5} [psig. + 14.7 psi.]

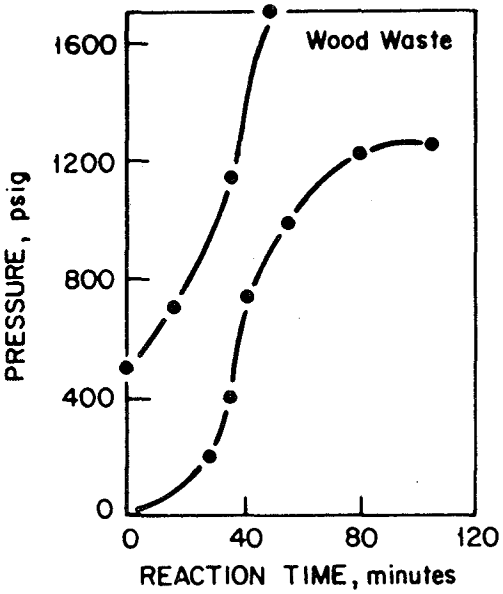


Fig. 1 Reaction Pressure During Liquefaction

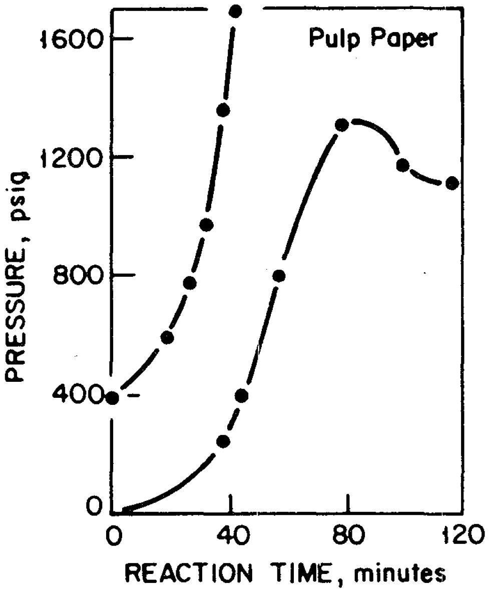


Fig. 2 Reaction Pressure During Liquefaction

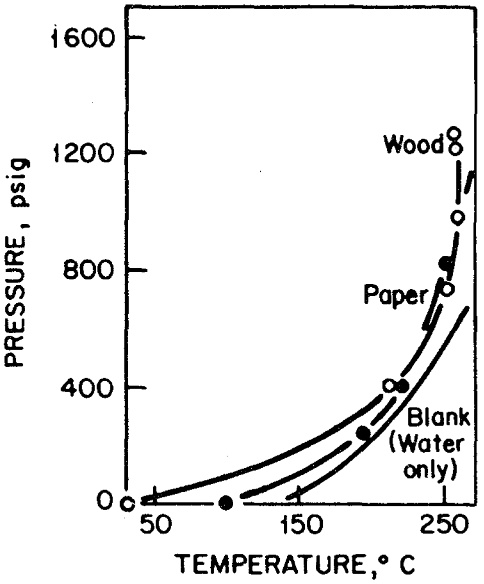


Fig. 3 Liquefaction with Water

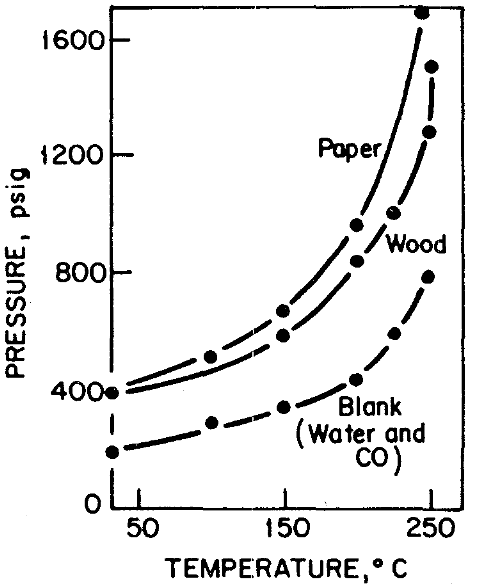


Fig. 4 Liquefaction with Water and CO

Newton/m^2 = 14.45 × 10^{-5} (psig + 14.7 psi) by certain hydrogen transfer solvents or with catalytic hydrogenation. The solvents including tetralin, anthracene oil and cresol gave mixed results as shown in Table 12. While tetralin was not at all effective, anthracene oil promotes the liquefaction of wood waste even in the absence of sodium carbonate catalyst. However, the solvent is partially incorporated into the product and could not be completely recovered by the usual distillation procedure. Similarly, cresol enhanced the liquefaction of wood and manure but the yield of liquefaction product is unrealistically high also indicating that the solvent is partially incorporated into the product.

The effect of hydrogen on liquefaction is also seen in Table 12. Liquefaction of wood-waste was not substantially altered by addition of cobalt molybdate catalyst to the reaction charge either with or without additional hydrogen. It seems likely that higher pressure hydrogen is necessary for a significant effect upon the course of reaction.

As discussed in the next section, compatibility of liquefaction products with asphalt is poor. An attempt was made to correct this deficiency by using petroleum vacuum residua as the reaction vehicle. As noted above, solvents of this type may be incorporated into the liquefaction product. Conditions and results are shown in Table 13.

An apparently homogeneous product was formed from wood waste at a charge ratio of 2.5:1, wood: resid. At higher ratio, the product from the reactor separated into two phases. Paper also formed a homogenous product at a ratio of 1.5 parts paper to 1.0 part resid.

Two additional liquefaction procedures employing chemical reducing agents were evaluated in an attempt to reduce operating severity:

1. It has been suggested that sodium formate

TABLE 13

LIQUEFACTION OF CELLULOSIC WASTE IN PRESENCE OF PETROLEUM VACUUM RESIDUE

Experiment Number	564	571	584	560
Charge:				
Waste	Wood	Wood	Wood	Paper
wt., g.	250	740	250	150
Water, g.	800	800	800	800
Na_2CO_3,g.	25	25	25	25
Pet. Residue, g.	100	150	70	100
Pressure, Max. psig.	1210	1040	1230	925
Product, g.[a]	170	512	172	122
Yield, pct.	28	49	41	15
Gas Composition, Mole pct.				
Hydrogen	0.8	-	-	1.3
Carbon Monoxide	15.1	-	-	24.3
Carbon Dioxide	80.3	-	-	71.5

a. Total toluene soluble material

b. (Wt. Product - Wt. Petroleum Residue)/Wt. Waste

Newton/m^2 = 14.45 x 10^{-5} [psig. + 14.7 psi.]

is formed during the liquefaction of cellulosics with CO and base.[72] The formate serves to reduce carbonyl-containing pyrolyzate intermediates to alcohols and is regenerated. Excess sodium formate was used in the standard liquefaction procedure in the absence of CO. No bitumen product was generated following 8 hours at 250°C in a 2 liter stirred autoclave to which was charged 150 gm each of the paper and sodium formate in addition to 500 gms of water. A gas sample taken following the run showed the presence of 60 percent CO_2, 32 percent H_2 and about 5 percent CO.

2. Wood Waste liquefaction was conducted in the usual way at 250°C using 250 gms of dry sawdust, 800 mls water and 152 g. of sodium sulfide. No bitumen-like product formed in any significant amount. In another experiment, 32 gms of sulfur was used in place of Na_2S in addition to 25 gms of Na_2CO_3. A small amount of bitumen-like product was recovered having a strong ordor of sulfur but conversion was poor. Only 13 percent of the initial charge was recovered as product, far below average. Off-gas from the reaction consisted largely of CO_2 (approximately 90 percent) with H_2S (approximately 7 percent) making up most of the remainder.

Product Characteristics

The products of liquefaction are high-viscosity, semi-solid bitumens that superficially resemble elastic asphalts. Properties of typical products are shown in Table 14. Although the rheological properties are somewhat deficient, it appears possible that these properties could be adjusted by application of usual procedure such as distillation, air-blowing and/or blending.

TABLE 14

ANALYSIS AND PROPERTIES OF WASTE LIQUEFACTION PRODUCTS

Experiment Number	510	511	513	521	564	512	515	560
Source	Wood	Wood	Wood	Wood	Wood/ Vacuum Residua	Paper	Paper	Paper Vacuum Residua
Softening pt., °C	95	73	64	88	47	45	44	46
Penetration, 0.1 mm (25°C)	79	56	200+	200+	136	76	183	103
Viscosity, poise (135°C.)	10.2	44	a	a	5.5	27.0	23.0	2.4
Penetration, (after viscosity)	2	5	20	5	-	85	78	-
Solubility, wt. pct.								
Methanol	71	66	78	74	15	90	92	-
Hexane	18	14	8	7	-	12	6	-
Ultimate Analysis:								
Carbon, pct.	74.6	70.7	70.2	71.8	80.5	72.4	72.7	85.6
Hydrogen, pct.	6.3	6.4	6.3	6.8	9.1	6.8	6.7	11.3
Oxygen, pct.	17.3	22.6	23.2	21.2	8.6	20.7	21.0	3.1
Nitrogen, pct.	0.3	0.3	0.3	0.2	-	0.1	0.1	0.7

a. Extreme instability prevented measurement

However, in other properties such as thermal stability and solubility characteristics, the products are very different than asphalt. In most cases, the differences are so great as to preclude characterization using standard asphalt test procedures. Thus, for example, viscosity at elevated temperature could not be determined in many instances because of rapid changes ocurring upon heating to test temperature.

In general, the viscosity of the products increased markedly during the course of measurement at 135°C. This was particularly true of liquefaction products produced from wood waste in the absence of carbon-monoxide. However, products produced with carbon-monoxide or from pulp paper behaved similarly. Because of these difficulties viscosity measurements were made with a Brookfield Rotating Disc./Viscometer in an open cup. Measurements were taken over a period of several hours until a stable value was reached and recorded. Initial values were ordinarily on the order of several poise but increased one or more orders of magnitude in some instances.

The change in viscosity on heating is also apparent from a comparison of room temperature penetration values measured before and after viscosity testing. Penetration values dropped as much as 95 percent in the case of wood liquefaction products. It was also noted that on storage, the liquefaction products, especially those derived from wood and manure, developed a hard crust. In view of the high viscosity of these products, phase separation seems unlikely and it may be presumed that the change is caused by oxidation or polymerization on exposure to air.

Attempts were made to characterize products in terms of oil, asphaltene and resin content as is common practice with asphaltic materials. However, the solubility properties encountered did not provide useful results. In general, the liquefaction products are highly soluble in methanol and acetone but very sparingly soluble in hydrocarbons.

The unexpected solubility characteristics and thermal reactivity of liquefaction products is probably related to their high oxygen content. The presence of lignin in the waste feed, i.e. wood and manure, appears to be particularly detrimental and suggests that phenolic residues derived from lignin may be responsible for the thermal instability. However, the hydrocarbon solubility is poor even with products derived from paper indicating that species such as alcohols, ketones and acids are formed from the cellulose and that these are equally undesirable.

An unsuccessful attempt was made to improve the hydrocarbon solubility of the paper liquefaction product by subjecting it to catalytic hydrogeneration. Paper was liquefied using the procedure previously outlined and the product was hydrogenated at 300°C and 500 psig. (3.46 x 10^6 Newtons/m^2) initial hydrogen pressure. The

TABLE 15

HYDRO-PROCESSING AND CHARACTERIZATION OF PAPER LIQUEFACTION PRODUCTS

Experiment	551A	551B	554
Charge	Paper	[a]	Residue
wt. g.	450	61.2	42.8
Procedure	Liquefaction	Hydrogenation	Hydrogenation
Conditions			
Temp., °C	250	300	300
Pressure, psig.	1600	500	2000
Conversion, wt. pct.	89.1	-	-
Yield, g.	91.0[a]	31.0[b]	5.0[b]
wt. pct.	20.2	51.0	11.7
Product Inspection			
Penetration (25°C), 0.1 mm	78	60	
Viscosity, cp. (135°C)	2700	200	
Softening pt., °C	45	48	oil
Ultimate Analysis:			
Carbon, pct.	72.1	78.8	85.5
Hydrogen, pct.	7.1	9.1	10.3
Oxygen, pct.	20.0	12.3	1.4
Nitrogen, pct.	0.1	-	-
Blend with Petroleum Asphalt (85 Pen)			
Penetration, 25°C	not	45	-
Softening pt., °C	miscible	51	-

a. Acetone soluble material.

b. Benzene soluble material.

Newton/m^2 = 14.45 x 10^{-5} [psig. + 14.7 psi.]

hydrogenation product was separated into benzene soluble and insoluble fractions. A further attempt to hydrogenate the benzene insoluble fraction without solvent was unsuccessful but hydrogenation of this fraction in cyclohexane produced a small additional amount of hydrocarbon soluble material. However, the bulk was essentially unchanged. Details are shown in Table 15.

The benzene soluble fraction represents 51 wt. percent of the charge to hydrogenation corresponding to 10 wt. percent overall yield based on paper (maf). The physical properties of this fraction are acceptable as shown in Table 15. However, the penetration value of a 75 percent blend with petroleum asphalt indicates that the materials are still not completely compatible. Apparently, some oil is extracted by the petroleum asphalt which forms a light phase, and the residual liquefaction product forms a denser, harder phase., Further inspection confirmed the presence of the two phases.

Products formed by liquefaction of wood waste in the presence of petroleum residua were also poorly miscible as shown by data in Table 16. This was determined by allowing the mixture to equilibrate in a 7/16 x 3" teflon vertical tube for 16 hrs. at 110°C. On cooling, the contents were removed and penetration was determined at regular intervals of depth.

TABLE 16

PENETRATION OF LIQUEFACTION PRODUCT - PETROLEUM ASPHALT BLENDS

Experiment Number	564	365	560	508
Asphalt, pct.	59	100	82	0
Penetration, 0.1 mm				
at depth = Top	>110	54	68	100
.2	>110	50	66	85
.4	>110	51	67	97
.6	2-3	48	72	100
.8	2-3	62	81	100
Bottom	2-3	67	82	58

The wood derived product consisting of 41:59 liquefaction product: petroleum asphalt separated into roughly equal volumes of soft, light and hard, dense material. Mixtures containing more liquefaction product were so poor in appearance that no further effort was made to characterize them. The product obtained from liquefaction of paper in the presence of asphalt resisted separation as did material produced by liquefaction of wood waste in anthracene oil.

Additional results that demonstrate the contrast between solubility properties of wood liquefaction products and petroleum residua are plotted in Figure 5 as a function of solubility parameter. The wide disparity of solubility properties supports a conclusion that the liquefaction products would not form homogeneous blends with petroleum residua except in very limited concentrations.

Process Design and Economics

This preliminary evaluation considers the technical and economic feasibility of a facility for converting 909 metric tons per-day wood waste to specification road binder. Feed preparation, liquefaction and product between fractionation are included in the evaluation.

Analysis of the liquefaction section is based upon reports of investigations at the Pittsburgh Energy Research Center of the Bureau of Mines culminating in the design and construction of a liquefaction pilot plant.[73] This pilot plant is designed to convert agricultural wastes to fuel oil. Operating conditions are in the range of 2000-4000 psi (13.8 - 27.7 x 10^6 Newtons/m^2) and 250 to 400°C. With sodium carbonate catalyst and carbon monoxide reducing agent, oil yields are in the range of 40-50 percent and char yield is less than 5 percent. There is no recoverable gas yield.

The conditions selected in the present design are 1500 psi (10.4 x 10^6 Newtons/m^2) and 250°C, since experimental studies showed that bitumen-like products are formed more readily at these parameters. Also, a continuous reaction system with a total residence time of one hour has been assumed based on laboratory results. Where mechanical problems, such as controlling the flow of solids into the high pressure reactor have been noted, it is assumed that these problems can be resolved at a reasonable cost.

Figure 6 shows the process flowsheet for a cellulosic waste liquefaction plant based essentially on the Bureau of Mines pilot plant. This pilot plant was constructed to provide three different methods for introducing the feed into the high pressure reaction system. In the pre-

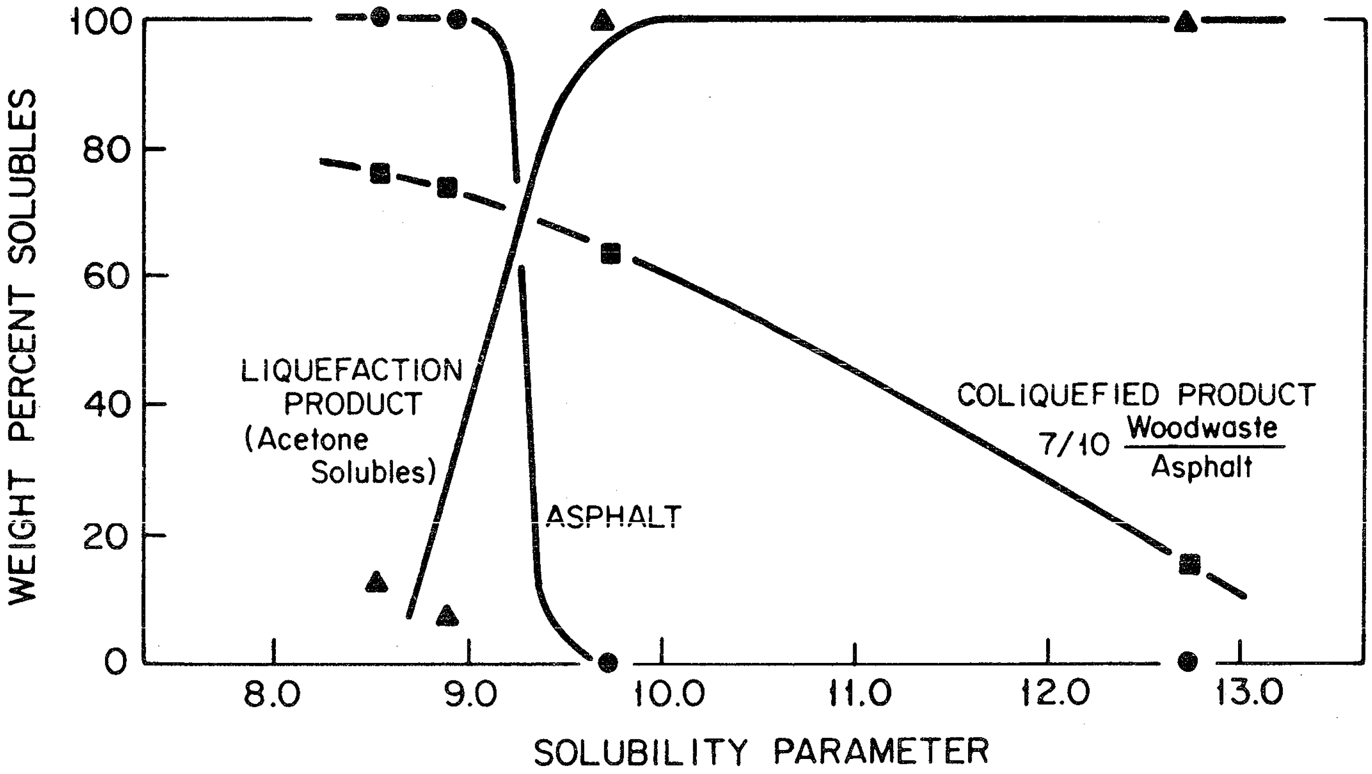
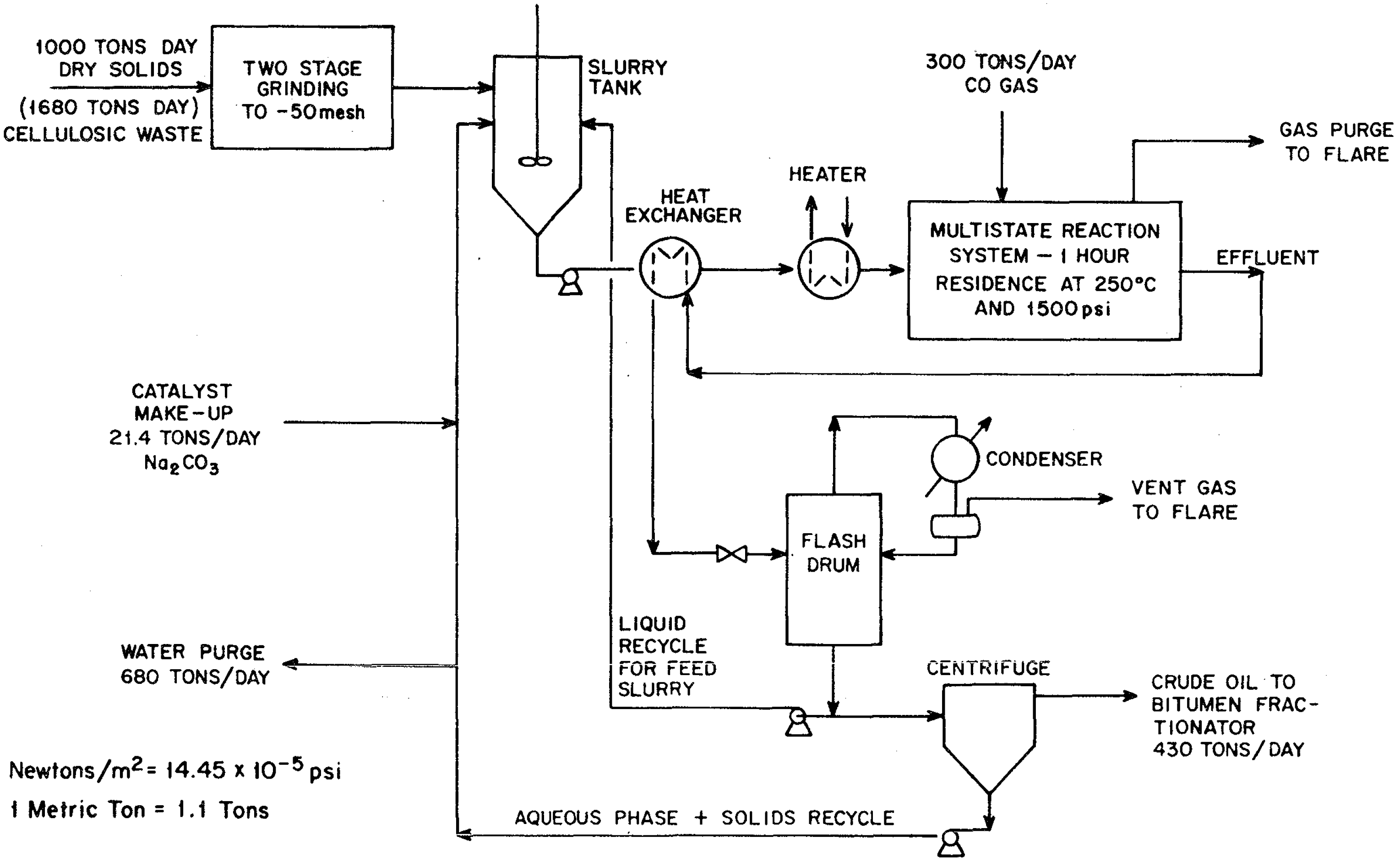


Fig. 5 Solubility Character of Liquefaction Products

Figure 6

PROCESS FLOWSHEET FOR LIQUEFACTION OF CELLULOSIC WASTE



Newtons/m^2 = 14.45 x 10^{-5} psi

1 Metric Ton = 1.1 Tons

sent design, the preferred method of adding the solid as a slurry with recycle liquid has been assumed to be acceptable since this will require the minimum investment. A multistage centrifugal pumping system such as anticipated in this design would probably not be practical on the small scale of the existing pilot plant and there is little doubt that the pilot plant will encounter problems in feeding the reactors that may not arise in a larger scale plant.

After preheating by exchange against the reactor effluent and finally in a hot oil heater or direct fired furnace to 250°C, the feed slurry enters a multistage reaction system. Mechanical design and structural considerations dictate a multiplicity of reactors. Ten units, 6 ft. (1.83m) in diameter and 16 ft. (4.88 m) deep are required for a one hour residence time. The wall thickness will be 6" (15.24 cm) to withstand the pressure and the weight of each unit including support skirt and agitator will be about 54.55 metric tons. The reactor charge pump will require 887.6 metric HP and this might be broken down into three centrigugal pumps in series each with 296.1 metric HP drives. However, the most practical approach would be with two or three feed lines each with 148 metric or 98.7 metric HP pumps respectively. This would reduce the cost of the spares that would be required for the plant and also permit partial throughput when pump failure occurs.

After the reactor effluent has been partially cooled by exchange against the feed, it is flashed to eliminate dissolved gases. The flash vapors are then cooled to 35°C to remove the volatile components of the solvent which are returned to the flash drum. Noncondensible gases are passed to flare. In this flowsheet, it has been assumed that no appreciable phase separation in the liquid occurs during the 20-minute miximum residence in the flash drum. If it should occur, the aqueous phase could be recycled directly to the slurry tank with the recycle solvent or some of this phase could be purged directly, thus reducing the load on the centrifuge and the amount of the water purge from the recycle slurry.

Since the two-phase liquid stream will also contain some undissolved solids, the centrifuge considered in this estimate was the DeLaval "self opening" unit which permits separate removal of the solids in addition to the two-liquid phases. This will be essential if pilot plant operation discloses that recycle of the undissolved solid does not result in complete solution. About three of the largest units would be required to handle the volume of normal solvents. Because of the small density difference and high viscosity of the oil phase, four to six units will probably be required and six have been included in the estimate.

The water purge will remove some of the soda ash catalyst and this must be made up with fresh catalyst solution prepared by dissolving soda ash in water in a mixing tank. The feed slurry system consists of two separate tanks in parallel and operated intermittently. The catalyst solution tank was made the same size to provide reserve storage as well as solution capability.

Since the published information on feed preparation and product fractionation sections was not sufficiently detailed, evaluation of these sections is based on design information developed for the analogous sections in a pyrolysis process. Therefore, additional discussion of these two sections are found in the following chapter on pyrolysis which may be consulted for details. In order to provide a valid comparison of these two processes, costs for feed preparation and fractionation were prorated directly from the pyrolysis process. Adjustments in the estimate made to account for differences in scale and complexity of the liquefaction process are pointed out below.

Table 17 summarizes the cost breakdown for the different steps in the liquefaction process. Cost of the fractionator and vacuum flash drum, not shown in Figure 6, is considerably higher than in a pyrolysis process because the yield of bitumen is more than three times as great in the liquefaction process. The liquefaction process is more complex requiring the design of a multiplicity of high pressure units and interconnecting piping. For this reason, design costs are 20 percent over those for the pyrolysis plant. The liquefaction plant will also require more site development costs, particularly due to the weight of the reactors, and the same ratio has been applied to this cost.

Since the amount of feed is the same for both plants, the receiving and feed storage costs will be identical. The feed preparation in the liquefaction plant consists of the grinding to -50 mesh and mixing with the catalyst and recycle solvent in the slurry tank to produce a mixture of not more than 30 percent solids. The catalyst solution tank is also included in this section. Installation costs have been estimated at the same ratio to equipment cost as in the pyrolysis case.

The liquefaction and catalyst recycle section consists of the reaction system, the charge pumps, slurry, the CO compressor, the flash drum, centrifugal separators, and recycle transfer pumps. It should be noted that about half of the cost in this section results from the reaction system and charging equipment. Doubling the operating pressure would essentially double the costs of these items and this must be recognized in the selection of the optimum liquefaction pressure. The installation costs for this section have been based on the same ratio used for the corresponding section for the pyrolysis estimate.

The bitumen fractionation section must also be larger to handle the increased crude oil feed

TABLE 17

BREAKDOWN OF CAPITAL COST ESTIMATE FOR 1000 TON PER DAY
CELLULOSIC WASTE LIQUEFACTION PLANT WITH BITUMEN FRACTIONATION

ITEM	SUB - COST	COST
Design		$1,147,000
Site development costs		2,333,000
Construction		13,869,000
Receiving and feed storage		
Equipment	$569,000	
Installation	845,000	
Feed preparation		
Equipment	965,000	
Installation	932,000	
Liquefaction and catalyst recycle		
Equipment	3,330,000	
Installation	5,217,000	
Bitumen fractionation		
Equipment	131,000	
Installation	204,000	
General and utility		
Equipment	505,000	
Installation	1,171,000	
Inflation, overhead and contractors' profit		3,931,000
TOTAL		$21,280,000

1 metric ton = 1.1 ton

and the installation costs have also increased by the same ratio.

General and utility costs have been estimated 20 percent over those of the pyrolysis plant, primarily due to pollution control equipment that may be required for disposal of the aqueous phase from the centrifuge. This will contain suspended solids in addition to the sodium carbonate catalyst and dissolved organic compounds, particularly acids and alcohols. Filtration, pH adjustment, extraction and steam stripping will probably be required. If another catalyst, such as potassium carbonate, is found to increase the rates of the liquefaction reactions, it would also be necessary to evaporate the water to recover the catalyst. A more effective catalyst will reduce the volume and pressure required for the liquefaction reactors which contribute more than half the cost to this part of the plant which, in turn, represents more than 60 percent of the total construction costs. Catalyst research and development provides the most effective means for reducing the plant investment and operating costs for the liquefaction process.

TABLE 18

ESTIMATED COST OF PRODUCTION

Binder via Liquefaction of Cellulosic Waste

Basis: 1977$ Capital Cost: $21.28 million

Capacity - 1000 ton waste/day
Operating Factor - 1.00
Production Rate - 260 ton/day bitumen
170 ton/day fuel oil

Chemicals:	Annual Cost, $ Thousands	$/ton
Carbon Monoxide	10,950	
Soda Ash	477	
Total Chemicals	11,427	120.41
Operating Costs:		
Utilities	1,930	
Labor	266	
Maintenance	1,111	
Residue Disposal	136	
Total Operating Costs	3,443	36.28
Overhead Expenses:		
Rents	120	
Capital Amortization	2,191	
Total Overhead Expense	2,311	24.35
Byproduct Credits:		
Fuel Oil	(1,911)	(20.14)
Net Cost of Bitumen	14,793	160.90
Cost of Hydrofinishing	1,423	15.00
Net Cost of Binder	16,216	175.90

1 metric ton = 1.1 ton

Table 18 summarizes the annual costs for the liquefaction plant. The carbon monoxide consumed in the liquefaction process represents the largest cost of the process. It is normally produced at the plant site and in the past the most economic process has been the increasing cost of natural gas, CO can now be more economically produced by the reaction of a mixture of CO_2 and O_2 with coke. The production cost of the CO formed by this process is about $.11/kg. and the additional investment in the CO plant would be about $7.5 million. The production cost includes amortization but does not include profit on the manufacture of the CO.

The soda ash loss is based on the catalyst concentration in the aqueous phase and the quantity of water which must be purged from the system. It is doubtful whether the recovery of the soda ash from the 3 percent solution in water would be economically justified based on a delivered price of $67.1 per metric ton for this material. One method for reducing the purge and the resulting catalyst loss would be by drying the feed to a slightly charred condition before making up the slurry, but this increases the processing cost as well as the investment and would only be justified if it also improved the liquefaction process.

Electric power and other utilities in Table 18 have been determined from a preliminary process design of the plant. Labor costs have been assumed identical to those of a pyrolysis plant. Maintenance costs have been prorated from that estimate based on the total investment cost. Land rent cost and the residual transfer and disposal cost have been increased by 20 percent over those of the estimate for the pyrolysis process. The residual transfer cost in the present case would be small because all the products are liquid but the disposal cost of the waste water would be considerably greater to make the combined cost higher than in the pyrolysis process.

The yield of high boiling asphaltic fraction from the crude bitumen has been assumed identical to that of the pyrolysis process, i.e., 60 percent so that the liquefaction plant will produce 236.4 metric tons per day of residual fraction and 154.5 metric tons of light solvent which will be equivalent to 1000 BPD (159×10^3 l/D). This compares with 72.7 metric tons per day of bitumen and 320 BPD (50.9×10^3 l/D) of solvent from the pyrolysis process as discussed in Chapter V. If the combined value of the bitumen and solvent is taken equivalent to $5.00/barrel ($5.00/159 l.) the value of the annual production from the liquefaction plant becomes $4.8 million. Thus a disposal charge of $37.4/metric ton of wood waste would have to be levied to allow this process to break even.

The major reason for this high disposal charge is the cost of the CO consumed in the liquefaction process. The cost of CO can be decreased by recovering it from the exhaust gas of a basic oxygen furnace.[74,75] Almost all the CO required for the present liquefaction plant could be recovered from a single 181.8 metric ton/day steel converter. The cost of the collection system would be about $1.6 million and the CO could be produced at a total operating and investment cost of 2 cents/kg. This would reduce the total manufacturing cost of the liquefaction process by $8.0 million to $9.2 million per year. It would require that the liquefaction plant be erected adjacent to a steel mill using the basic oxygen process. However, even with this reduction in production cost, the liquefaction plant would still have to charge a disposal fee of $13.2 per metric ton of dry waste to break even.

The present economic study has been based on a 43 percent yield of oil from the dry solids. The maximum yield based on the carbon and oxygen content of the charge is about 60 percent. If this could be attained, the total annual value of the products from the liquefaction process would be $6.68 million and it thus appears that even under the most favorable circumstances, the liquefaction plant will operate at a deficit of about $2.5 million and have to charge about $7.50 per metric ton for the disposal service to break even. Thus, on the basis of present technology, it is doubtful that the liquefaction process can provide an economical source of binder material.

Hydrolysis

Hydrolysis of cellulosic wastes that contain pentosans results in formation of furfural. Furfural and its main derivative, furfuryl alcohol, form furan resins used in foundry binders, construction cements and mortars. They are also added to high-melting pitch to improve its plasticity for use as binder. Resin-aggregate mixtures have been used in the Soviet Union and are proposed for use in road and subway construction.

Process Description

Furfural is conventionally produced by mixing a cellulosic waste material with dilute sulfuric acid. The pentosans (complex carbohydrates) present are hydrolyzed to pentoses, such as xylose, which are dehydrated to furfural. The furfural is continuously removed by steam distillation and purified by fractionation.

Typical conditions in the hydrolyzer are 100-120°C., 2-5 percent sulfuric acid and 5-25 wt. percent solids. Depending on flow rate and acid strength, 90-95 percent of the pentosans are converted to xylose and furfural. Conditions are controlled to prevent hydrolysis of high molecular weight polysaccharides. The hydrolysate contains approximately 15 percent xylose, 2 percent furfural and 4 percent sulfuric acid. The furfural is removed by feeding the hot solution to a vacuum column and a water-furfural azeotrope is removed from which furfural is recovered by further fractionation. The xylose solution can be treated further at elevated temperature to produce additional furfural that is recycled to the recovery section.

Preferred raw materials are corn cobs since they contain 30 percent pentosans and yield up to 20 percent furfural. Other sources and potential yields are shown in Table 19. Municipal wastes that are primarily paper and manure wastes do not contain pentosans and therefore are not useful for furfural production. Wood chips can be used and provide about 8 percent yield based on the dry weight of raw material.

Economics

Domestic production of furfural is about 45.5×10^6 kgs. or about 50 percent of capacity. Tank car prices are in the range of 88 cents to $1.10

TABLE 19

ANNUAL CROP PRODUCTION OF FURFURAL-PRECURSORS

Crop	Average Prod'n	Precursor (tons)	Potential Furfural (tons)
Sugar cane	25 x 10^6 tons	1.25 x 10^6 Bagasse	0.25 x 10^6
Cotton Seed	-	1.2 x 10^6 Hulls	0.24 x 10^6
Oats	620 x 10^6 bushels	1 x 10^6 Hulls (1)	0.1 x 10^6
Rice	3 x 10^6 tons	0.3 x 10^6 Hulls (2)	0.03 x 10^6
Corn (3)	6 x 10^8 bushels	30 x 10^6 Corncobs	6 x 10^6

(1) basis: 32 lbs./bushel

(1,2) basis: hull weight at 10% of production

(3) Re: Corn Refiners' Association, 1977 predicted Production

basis: 1 bushel of corn = 10 pounds of corncobs.

1 metric ton = 1.1 ton

1 kg. = 2.20 pounds

per kg. This relatively high price results from its method of manufacture requiring large amounts of energy to evaporate a large quantity of water. The cost of new facilities is high because of special alloys required to withstand the highly corrosive acid conditions. Therefore, there is little likelihood that the cost of furfural would drop substantially as a result of expanded production.

The cost of furan resins is directly related to the cost of furfural since they typically contain up to 85 percent furfural. On this basis, a binder formulation would have a minimum cost of about $1.05 per liter and is obviously far too expensive for highway use.

Even if it were blended with asphalt at the 10-20 percent level, the cost of the mixture would be two to three times that of the contained asphalt.

Properties

The properties of furfural-based resins, such as melting point and curing time, can be varied by adjusting the composition. Typically, the products are formulated to a melting point of 50-100°C. Acid catalysts will promote curing at room temperature over a period of minutes to several hours depending upon acid concentration.

Uncured resins are usually liquids with viscosities of 50 to 15,000 cPs. and are stable for long periods of time. On curing a highly cross-linked network structure develops to give a hard brittle solid with a compressive strength of 5,000-10,000 psi. (34.6 - 69.2 x 10^6 Newtons/m^2). Because of their low ductility, the resins above are not suitable for flexible paving applications.

In combination with asphalt, desirable properties could result. However, the polar nature of the resin and its high oxygen content precludes the formation of uniform blends. A resin blended with asphalt by vigorously mixing at 100°C. separated into two distinct phases on standing less than one hour at that temperature or after several hours at room temperature.

Assessment

Development of hydrolysis of cellulosic wastes to produce a furfural-based binder is not attractive for several reasons:

1. The process is not applicable to cellulosic wastes such as manure or municipal solid wastes.

2. Production costs are relatively high for highway application.

3. Cured products lack the ductility required for flexible paving and are not miscible with conventional asphalt binders.

CHAPTER V

PYROLYSIS

Pyrolysis, the destructive distillation of lignocellulosic materials, produces char, condensible organics, non-condensible gas and water. Potential applications in production of liquid burning fuels from biomass has stimulated operation of several pyrolysis pilot plants in recent years. Technology under development includes partial oxidation as well as direct pyrolysis. Various feedstocks have been investigated such as wood-waste, municipal solid waste and agricultural residues. Discussions of the process variants and their current development status

TABLE 20

TBP* DISTILLATION ANALYSIS

Sample: Wood Pyrolysis Oil
Sample Size: 1000 mls.

Temp.,°F	Wt.,Gms.	Vol. Mls.	Sp. Gr. 60/60°F	Wt. Pct.	Vol. Pct.
230		1		0.1	0.1
433		50		5.5	5.6
452		100		11.1	11.2
470		150		16.7	16.8
406		200		22.2	22.4
506		225		25.0	25.2
522		250		27.8	28.0
589		275		30.6	30.8
615		300		33.4	33.7
662		350		38.9	30.3
704		375		93.1	42.5
719		400		44.5	44.9
737		425		47.3	47.7
746		465		51.8	52.2
746	485.9		1.0664	51.8	52.2
746+	451.9		1.0850	48.1	47.7
TOTAL	937.9		1.0752		
CHARGE	945.9		1.0741	100.0	100.0
LOSS	8.0				

Proximate Analysis:

	wt., g.	wt. pct.
water	29.0	12.1
distillate oil	485.9	45.6
residual oil	451.9	42.3
Total	1,066.8	100.0

gms./ml. = 0.999 [sp. gr. 60/60°F]

$°C = [F - 32] \times \frac{5}{9}$

*True Boiling Point

have been reported. This information provided the starting point of this evaluation.

The composition of oil obtained by batch pyrolysis can be markedly different from that formed in continuous processing because of differences in the operating characteristics of these procedures. Pyrolysis oils used in this evaluation were obtained from continuous pilot plant operations that would best approximate the properties of large scale pyrolysis plant products.

Wood pyrolysis oil (WPO) was produced in a nominal 1.8 metric ton/hr. plug flow pyrolysis unit[76] operating on pine waste including bark residues. The oil was collected with an air-cooled condenser and distilled at atmospheric pressure. A second type of pyrolysis oil was produced from municipal solid waste (MPO) by flash pyrolysis of the shredded organic fraction in the Garret pilot plant at LaVerne, California.[77]

Characteristics of Pyrolysis Oils

The wood pyrolysis product is a fluid oil that leaves a hard pitch-like residue upon distillation. Results of distillation analysis are shown in Table 20. At the end point, the distillate contained 12.1 wt. percent water and 45.6 wt. percent oil based on total charge. The residue, 42.3 wt. percent, has a specific gravity

TABLE 21

DISTILLATION OF PYROLYSIS OILS AND PROPERTIES
OF THE RESIDUAL PRODUCT

Source Code	MPO	MPO	WPO	WPO
Charge, g.	466.0	565.5	455.8	562.0
Pressure, mm.	atm.	0.2	2.5	atm.
Pot Temp., °C	190	90	260	240
Head Temp. °C	100	no reflux	no reflux	130
Distillate, g.	118.8	159.4	76.7	157.7
pct.	25.5	28.2	16.8	28.1
Residue, g.	321.5	395.9	370.6	391.7
pct.	69.0	70.0	81.3	69.7
Recovery, pct.	94.5	98.2	98.1	97.8
Residue:				
Analysis:				
Carbon, pct.		59.0	71.1	68.4
Hydrogen, pct.		7.1	7.0	7.2
Oxygen, pct.		29.0	21.5	22.5
Nitrogen, pct.		1.3	0.2	0.1
Penetration, 25°C, 0.1 mm.		15	0	200+ [a]
Softening Point, R&B,* °C		63	78	46

[a] Penetration, 18 after air blowing 1 hr. at 180°C

*Ring and Ball

similar to that of the whole oil, i.e., approximately 1.07.

Atmospheric distillation (Table 21) of the oil gave 69.7 wt. percent of a soft residue (200 + penetration) with a softening point of 46°C containing 22.5 wt. percent oxygen. This material was air blown for one hour at 180°C to give a product with a penetration value of 18. Vacuum distillation of the atmospheric bottoms removed additional oil leaving a hard pitch-like solid with a softening point of 78°C. This material also contains a high concentration of oxygen.

On the other hand, attempts to reduce MPO by atmospheric distillation were not as successful. About 20 wt. percent water was evolved followed by severe decomposition as the temperature was raised. Additional water was released during decomposition and a hard coke-like residue resulted.

The evolution of water during decomposition suggests that controlled distillation at reduced pressure could reduce the oxygen content of the oil without coking. This procedure gave far better results. After removal of 28 wt. percent combined water and oil, the residue had a penetration value of 15 and softened at 63°C. However, the oxygen content remained high.

A light oil, 10 wt. percent, separated from the vacuum distillate. Nuclear Magnetic Resonance and Vapor Phase Chromatography analysis, (Figures 7 and 8) , both indicate that the oil is a complex mixture of highly paraffinic materials with a CH_3/CH_2 ratio of about 0.5 and some aromatic character. It is not representative of the residue which is highly oxygenated and has a carbon-hydrogen ratio of 1.2 indicative of a highly condensed structure.

Other samples of wood pyrolysis oil distillation residues produced by topping to different levels were examined. Results are shown in Table 22. As expected, the softening point and viscosity of the residue increases as additional oil is removed overhead. The residue, after steam stripping, is a hard solid softening at 63-68°C with a penetration of 1-2. At 135°C, its viscosity is in the range of 1450-1700 cPs.

All of the above residues contain from 19-27 percent oxygen compared to less than 1 percent for typical petroleum residua. The oxygen content decreases with removal of distillate oil indicating that the lower molecular weight pyrolysis fractions are the most highly oxygenated. Carbon/hydrogen atom ratios range from about 0.7 to about 0.8 compared to petroleum asphalt that typically has a carbon/hydrogen ratio of ca. 0.7.

Melt blending of WPO with petroleum asphalt at compositions of 25,50 and 75 percent gave mixtures that appeared to be homogeneous. However, penetration measurements revealed the presence of two separate phases: an upper layer with penetration value essentially the same as the petroleum asphalt and a lower layer with a value proportional to the WPO content having a penetration of nearly zero. It is concluded that the highly oxygenated pyrolysis oils are not very miscible with petroleum asphalt. This was verified in later studies.

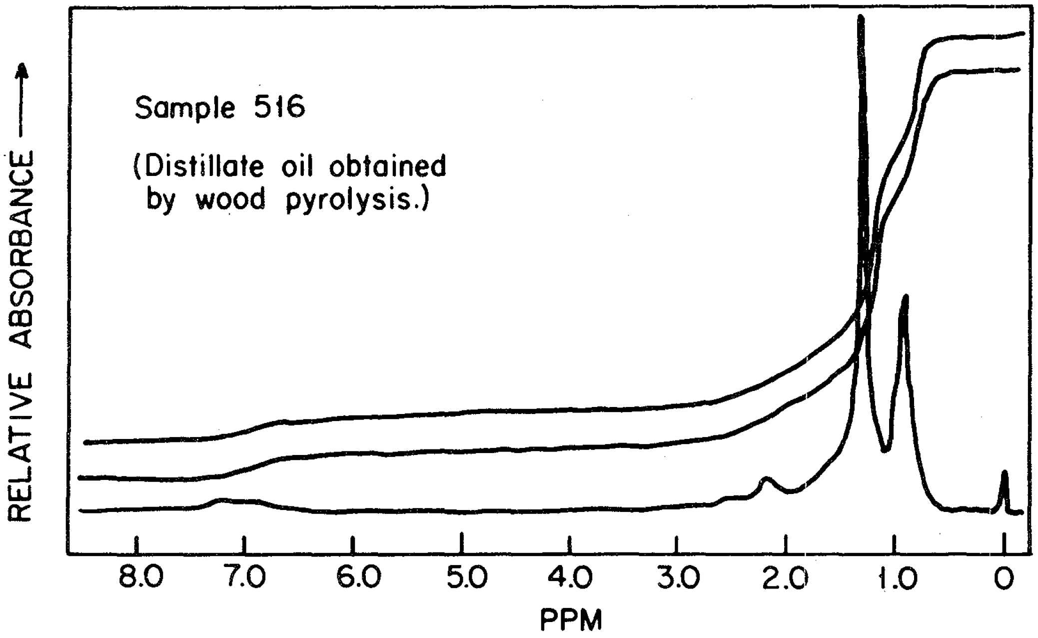
It is apparent from above that the temperature-viscosity characteristics of pyrolysis oils

TABLE 22

PROPERTIES OF WOOD PYROLYSIS OIL DISTILLATION RESIDUE

WPO CODE	END-POINT TEMP., °F	PENETRATION	S.P. (R&B),°C	VISCOSITY, cPs. (135°C)	ANALYSIS, PCT.		
					C	H	O
A	225	> 400	n.a.	< 30	58.3	6.6	27.0
B	332	> 400	n.a.	< 30	68.8	8.5	22.1
C	388	275	38	< 30	65.5	7.1	23.1
D	Steam-Stripped	1	68	1700	68.6	7.1	21.9
E	Steam-Stripped	1	67	1600	68.5	7.3	19.0
F	Steam-Stripped	2	64	1450	68.8	7.1	21.2

$°C = (F-32)\ x\ \frac{5}{9}$



Spectrum Amplitude: 1.0 Integral Amplitude: 3.6
Spinning rate (RPS): 38

Fig. 7 Nuclear Magnetic Resonance Spectrum of Distillate Oil.

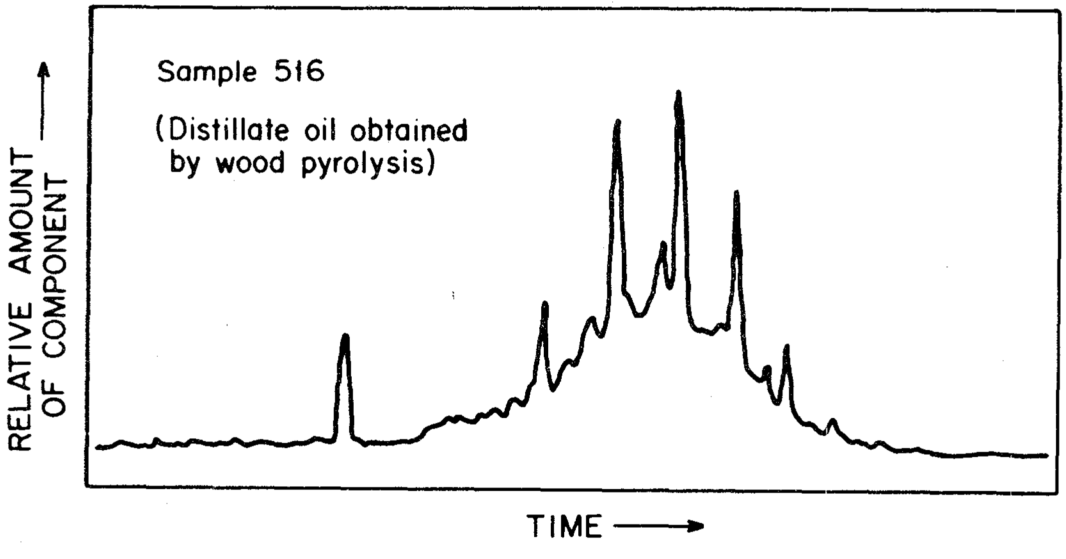


Fig. 8 VPC Analysis of Distillate Oil

make them unsuited for direct use as flexible binder. Adjustment of the viscosity and softening point to a useful range is accompanied by a severe drop in penetration. Moreover, the oils are not compatible with petroleum products precluding the possible use of blends to achieve useful properties.

Hydrogenation of Wood Pyrolysis Oil

In an attempt to modify the properties of pyrolysis oil, it was hydrogenated at elevated temperature in the presence of Cobalt/Kieselguhr Catalyst (Table 23). This procedure is effective in removing a significant amount of oxygen as water. Relatively little hydrogen is consumed but the rheological properties and solubility characteristics are markedly improved.

Hydrotreating WPO-D at 2000 psi. (13.84×10^6 Newtons/m^2) and 300°C reduced the oxygen content from 19.7 to 14.3 wt. percent without significantly altering the H:C ratio. The hydrotreated product has a penetration of 86 compared to the original value of 1. Solubility in hexane increased from 1.4 percent to 39.5 percent and the softening temperature dropped from 78 to 43°C. The viscosity at elevated temperature was significantly reduced.

Laboratory scale hydrogenations were conducted in a stirred stainless-steel autoclave which was then sealed and pressured with hydrogen. The autoclave was heated to operating temperature in

TABLE 23

HYDROTREATING OF WOOD PYROLYSIS OIL

Charge, g.	150	500
Catalyst, [a] g.	15	30
Pressure, psig.	2000	1000
Temp., °C	300	250
Pressure Drop, psig.	1300	-
Product Recovery, g.:		
Oil	102.8	474
Water	3.9	26
Total	106.4	500
Product Inspection:		
Penetration, 25°C, 0.1 mm	86	200+
Softening Point, °C	43	43
Viscosity, 135°C, poise	6.5	-
Solubility, pct.		
Methanol	82.5	-
Hexane	39.5	-
Benzene	-	63.0
Ultimate Analysis:		
Carbon, pct.	77.1	73.1
Hydrogen, pct.	8.1	8.2
Oxygen, pct.	14.3	18.7
Nitrogen, pct.	0.1	0.1

[a] Girdler, G-61RS, supported cobalt catalyst

Newton/m^2 = 14.45×10^{-5} [psig. + 14.7 psi.]

an electric heater over a period of about one-half hour. It was held at temperature for an additional one-half to one hour until the pressure stopped dropping. The reactor was rapidly cooled in cold water, vented and the contents removed.

The hydrogenate was diluted with two volumes of toluene and filtered to remove the residual catalyst. Solvent was recovered from the product by evaporation in a rotary evaporator at about 30 mm. and 90°C.

Similar changes resulted in a larger scale experiment conducted under milder operating conditions of temperature and pressure i.e. 250°C and 1000 psi. (6.92×10^6 Newton/m^2). In this case, the product water, 5.2 percent by weight of charge, readily separated from the reaction mass and was decanted. The hydrotreated oil, a soft, adherent solid, contains 18.7 percent oxygen and is largely soluble in benzene. As shown later, atmospheric topping further reduces the oxygen content indicating the formation of other low molecular weight oxygenated coproducts.

Hydrotreating is effective in transforming hard pitch-like pyrolysis products into materials resembling elastic asphalts. The procedure is very efficient with less than 1 wt. percent hydrogen consumed based on pressure drop and yield of water. Efficient utilization of hydrogen is an important aspect since the formation of large amounts of dry gas at the expense of hydrogen is obviously undesirable from an economic standpoint.

The change in solubility as a result of hydrotreating is shown in Figure 9.

Adjustment of Properties of Hydrogenated Oil

Screening studies were carried out to evaluate secondary processing for adjustment of properties of the hydrogenated oils. These procedures include distillation, extraction, air-blowing and blending.

Vacuum distillation (Table 24) is effective for adjustment of penetration and viscosity. Removal of 10 percent distillate oil lowered the penetration from 300+ to 6 and increased viscosity to 175 Cp. Oxygen content of the residue was 15.2 percent.

Extraction with four volumes of hexane gave 78 percent by weight of insolubles. The effect on the properties of the insoluble residue was directionally the same as that of distillation.

Air-blowing tests (Table 25) were conducted at

TABLE 24

DISTILLATION AND EXTRACTION OF HYDROGENATED WOOD PYROLYSIS OIL

	Distillation	Extraction	
Procedure:	546	548	Charge
Conditions:			
Temp., °C.	165	50	–
P, mm Hg.	0.7	1 atm	–
Hexane Solvent, ml.	-	250	–
Charge, g.	61.5	69.0	–
Product, g.	55.1	53.2	–
Byproduct, g.	4.6	12	–
Mat. Bal., wt. pct.	90	77	–
Yield, wt. pct.			
Product Inspection:			
Softening Point, °C	55	52	43
Penetration (25°C), 0.1 mm	6	20	300+
Viscosity, (135°C) cp.	975	900	175
Oxygen, wt. pct.	15.2	17.0	18.7

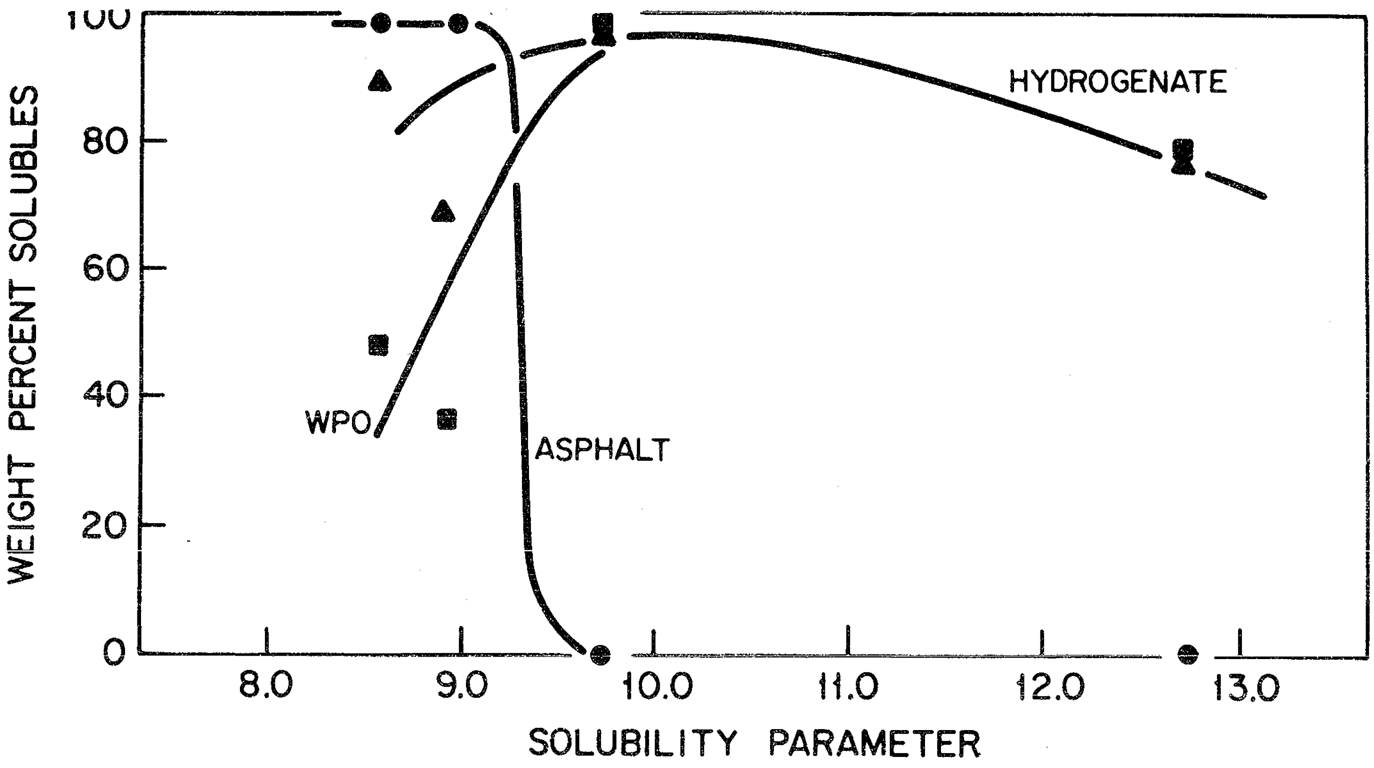


Fig. 9 Solubility Character of WPO and Hydrogenate

TABLE 25

BLOWING OF HYDROGENATED WOOD PYROLYSIS OIL AND PROPERTIES OF PRODUCTS

Conditions: Temperature, 200°C
Air rate, 1.0 vol./vol. min.

Procedures:	Refluxed		No Reflux
Time, min.	60	120	60
Charge, g.	60.5	60.5	36.6
Product, g.	60.0	59.5	34.6
Yield, wt. pct.	99	98	95
Product Inspection:			
Softening Point, °C	43	44	44
Penetration (25°C) 0.1 mm.	300+	110	53
Viscosity (135°C), cp.	175	-	50

200°C with passage of 1 volume air per volume oil per minute both at total reflux and without reflux provisions. Although needle penetration dropped significantly as a result, softening point was not substantially altered. This procedure had an adverse effect upon viscosity which dropped under 100 cPs. (135°C).

Blends of the hydrogenated oil with asphalt (Venezuelan Crude, 85 Penetration) were evaluated. Results of viscosity and penetration measurements are plotted in Figure 10. In the range of 50-100 percent petroleum asphalt content, the properties of the blends vary in a regular manner suggesting that it is miscible with the pyrolysis oil. At lower asphalt levels, the viscosity is essentially that of the pyrolysis oil.

Based on the comparisons shown in Table 26, a combination of distillation and blending appears to offer the best possibility for adjusting the product to specification i.e. distillation to reduce the penetration and blending to increase the viscosity. Air-blowing offers no advantage because it further reduces viscosity. Extraction has the same effect as distillation but is less efficient.

Effect of Hydrotreating

None of the pyrolytic oil bottoms had initial physical properties resembling those of asphalt. Preliminary studies summarized in Table 26 demonstrated that hydrogenation of bottoms, followed

TABLE 26

SUMMARY OF PROPERTIES OF WOOD PYROLYSIS PRODUCTS

Preparative Procedure	Softening Point, °C	Penetration 0.1 mm (25°C)	Viscosity cp. (135°C)
Pyrolysis	78	1	165
Hydrogenation	43	300+	175
a. Vacuum Distillation	55	6	975
b. Extraction	52	20	900
c. Blowing	-	53	50
d. Blending	43	300	200

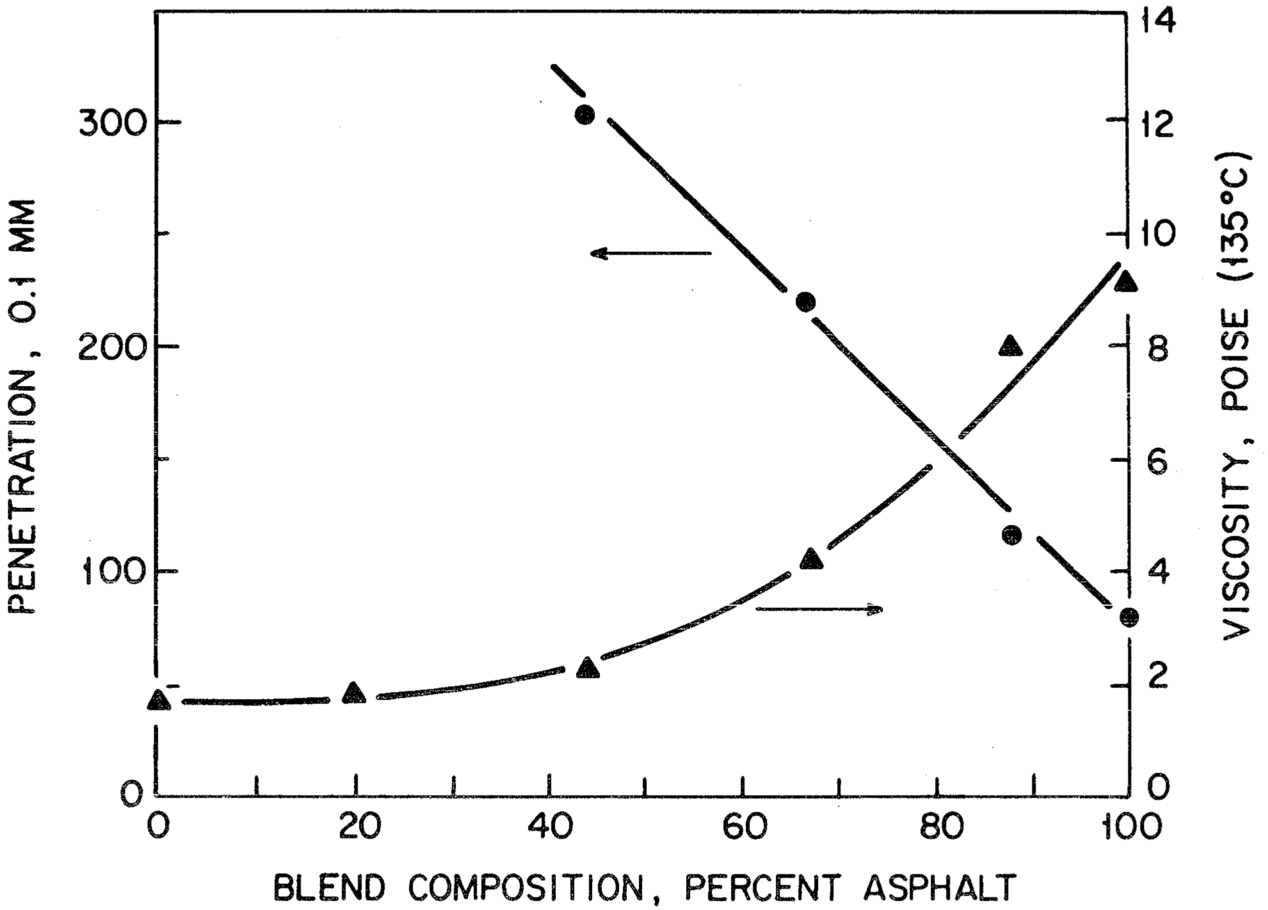


Fig. 10 Blending Correlation for Hydrogenated Wood Pyrolysis Oil and Asphalt

separately by distillation or by extraction, changed properties in the direction of asphalt, i.e., the Ring and Ball softening point was reduced and pen was increased. Depending on extractant, components could be isolated from hydrogenated products which did not show asphalt like properties. The part of the hydrogenated product prepared from WPO-F which was insoluble in toluene but was acetone soluble, was found to be a brown solid which remained largely unchanged by heating in air up to 180°C.

The compositions of three hydrogenated pyrolysis oil bottoms are reported in Table 27. The chief result of hydrogenation appears to be the reduction in oxygen down to levels which range between 60-70 percent of that in the feed. Gas analysis showed that little carbon converted to gaseous product and that the C/H atom ratios were barely changed. This suggests that during hydrogenation, dehydration and hydrogenolysis of carbon-oxygen linkages occurs, viz;

$$ROH + H_2 \longrightarrow RH + H_2O$$

Infra-red curves of WPO-A before and after hydrogenation (Figures 11a and 11b, respectively) bear out that these changes occur during hydrogenation. A peak reversal in the 2.8-3.5 micron region indicates that -OH drops relative to -CH-. A second peak reversal occuring in the 6.5-7.0 region means that -C=C- drops relative to -C-C. Nuclear Magnetic Resource curves before and after hydrogenation, (Figures 12a and 12b, respectively), show that olefinic groups in the 5.0-5.6 ppm region disappear.

Spectral changes were not as dramatic following the hydrogenation of WPO-B and E. The results of hydrogenating WPO-F are reported in Table 28 and include the compositions of various fractions. Before hydrogenation, WPO-F shows large differences in oxygen contents between fractions which are soluble and insoluble in ethanol and also in trichloroethylene. The toluene soluble fraction following hydrogenation contains even less oxygen.

Effect of Hydrogenation on Solubility Character

In the range of solubility parameter values[78] between 8 and 13 very large differences are observed between the solubilities (ASTM 2042) of asphalt and those of WPO and its hydrogenate. The solubility of asphalt (see Figure 9) drops precipitously to zero somewhere between toluene, 8.9, and acetone, 9.7, remaining zero for greater solubility parameter values. On the other hand, WPO-E shows nearly reverse behavior, becoming more insoluble as the solubility parameter decreases apparently due to its relatively high oxygen content. The hydrocarbon solubility of WPO-B is improved somewhat by hydrogenation. Figure 9 shows the solubility of hydrogenated WPO-F to increase in the region where asphalt is also soluble. Thus, one can expect hydrogenation of pyrolysis oil followed by toluene extraction to improve compatibility with asphalt.

Optimization of Hydrogenation

The best candidate feed stock of all types reviewed experimentally proved to be the pyrolysis product of waste pine and bark. To one degree or another, hydrogenation of it produced viscous liquids which on further treatment furnished products meeting basic highway binder properties. The method of Plackett and Burman[79] was applied to identify which variables were process controlling and to what degree. Their approach enables a study to be made with a relatively small number of experiments even though the number of variables for screening is relatively large.

TABLE 27

EFFECT OF HYDROGENATION AND WORK-UP PROCEDURE ON COMPOSITION

OF PYROLYSIS WASTE BOTTOMS

WPO	Work-Up Procedure	C, pct.	H, pct.	O, pct.	C/H/O Atom Ratio
A as-received	--	58.3	6.6	27.0	6/8.25/2.1
A hydrogenate	Filter to remove catalyst	72.1	7.8	16.3	6/7.8/1
E as-received	--	68.5	7.3	19.0	6/7.7/1.25
E hydrogenate	Extraction with acetone	77.2	12.9	13.5	6/11.4/0.8
F as-received	--	68.8	7.1	21.2	6/7.4/1.39
F hydrogenate	Extraction with toluene	74.5	8.3	14.7	6/8.05/0.89

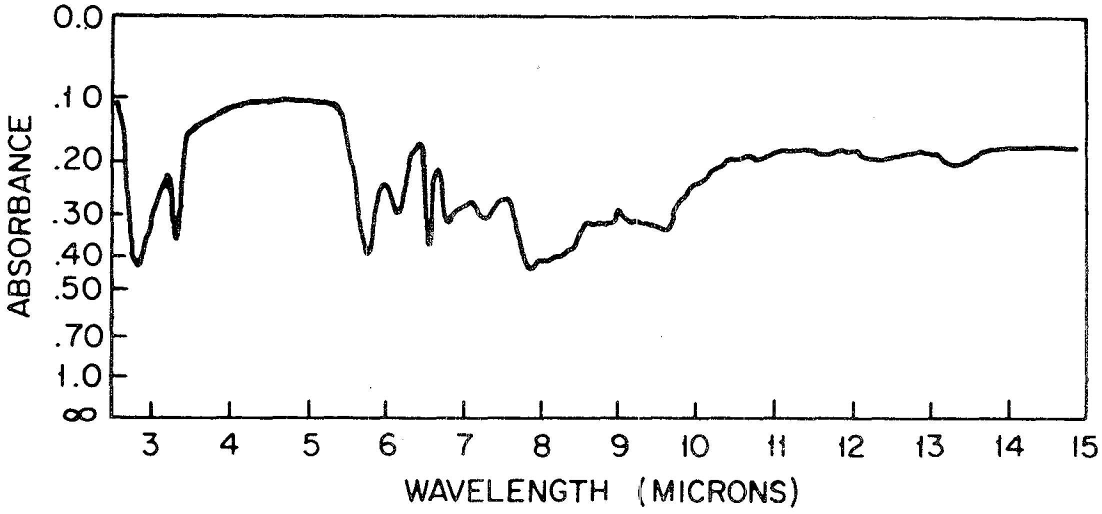


Fig. 11a Infra-Red Scan of WPO-A (as received)

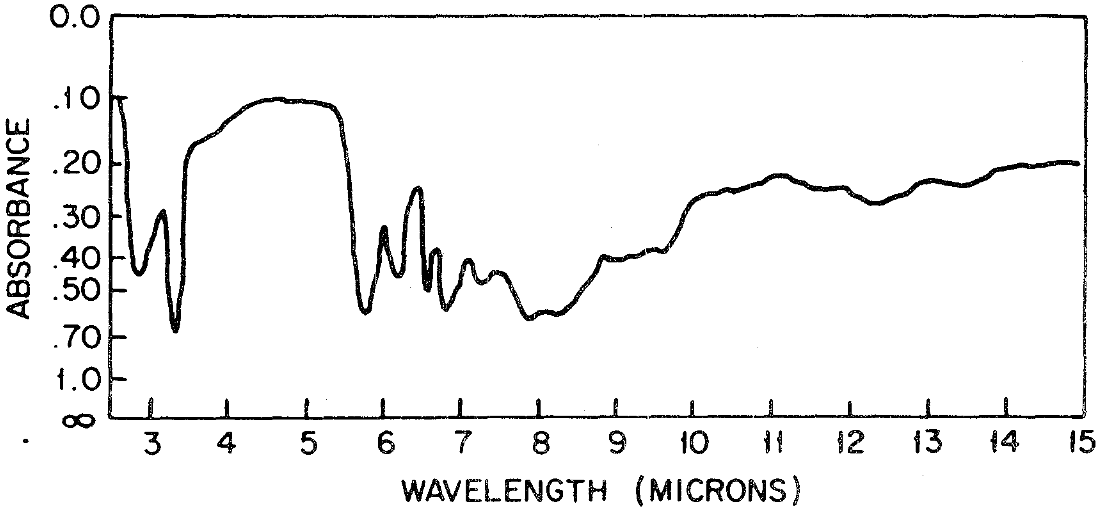


Fig. 11b Infra-Red Scan of WPO-A After Hydrogenation

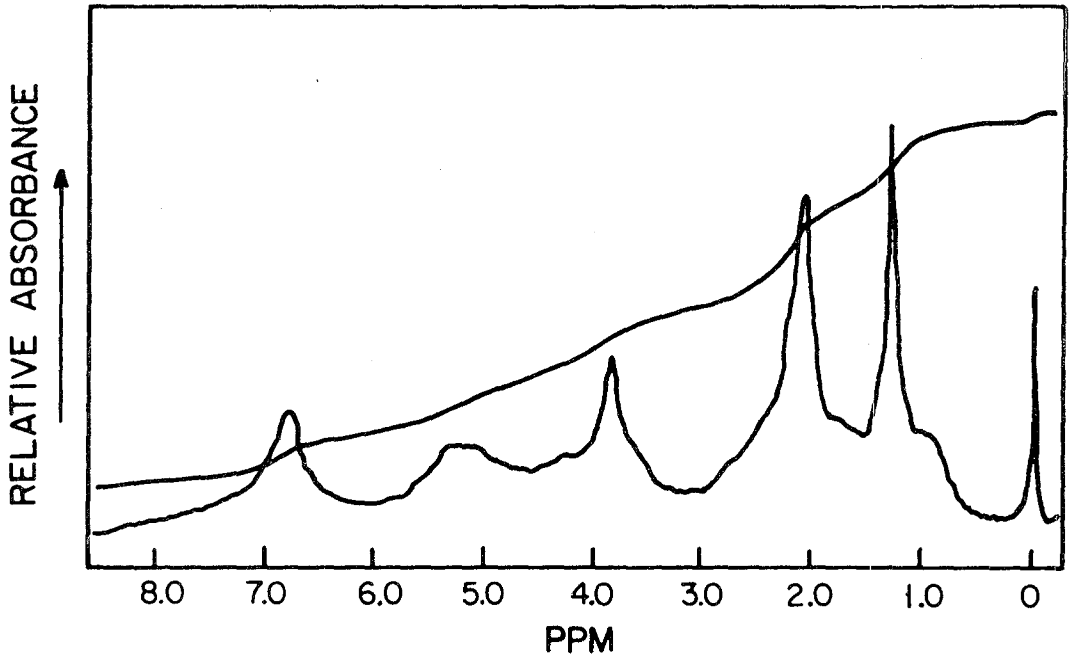


Fig. 12a Nuclear Magnetic Resonance of WPO-A (as received)

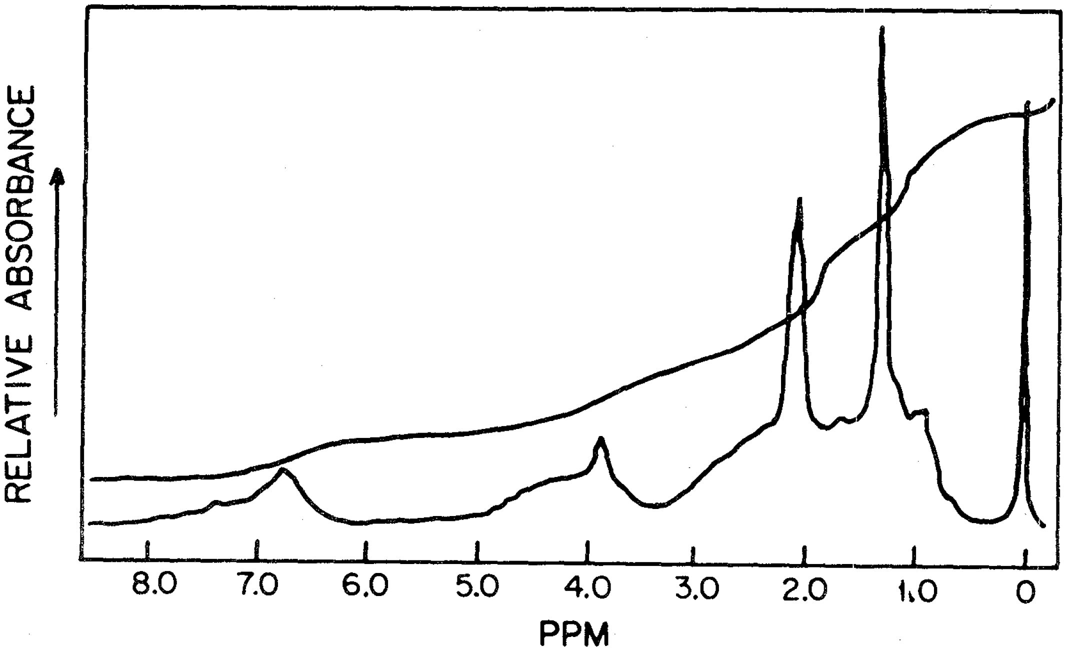


Fig. 12b Nuclear Magnetic Resonance of WPO-A After Hydrogenation

TABLE 28

THE COMPOSITION OF VARIOUS SOLUBLE AND INSOLUBLE PYROLYTIC OIL FRACTIONS

WPO	Solvent	ASTM* Solubility, pct.	C, pct.		H, pct.		O, pct.	
			Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
F as-received	Ethanol	74.4	68.3	69.2	7.4	6.4	13.8	16.2
	Acetone	99.5	68.7	-	7.2	-	18.3	-
	Trichloroethylene	46.7	74.0	64.1	8.5	6.2	14.5	18.8
	Toulene	47.2	73.6	67.5	8.8	6.5	14.0	19.3
F Hydrogenate (no extraction)	Ethanol	77.5	72.1	-	8.2	-	11.6	-
	Acetone	95.9	72.6	-	7.9	-	10.1	-
	Ethylene Trichloride	89.7	74.2	-	8.4	-	8.8	-
	Toluene	68.7	74.6	-	8.7	-	9.2	-

*Re: ASTM D-2042

The method involves the use of a partial factorial design and furnishes only estimates of main effects, i.e. the change in a response paralleling the increase in a variable from its low level value to its high level value. Because the method involves fewer experiments than a full factorial design, it will not estimate interactions between variables, i.e. the change in main effects due to an increase in another variable from its low to high level value.

The experimental design requires two or three more experiments to be run than the number of variables to be tested for significance. In these studies, five process variables were tested for significance in eight experiments. The extra runs provide an estimate of overall experimental error. For a process variable to be significant, its main effect has to exceed this error by a factor of at least t, a statistical parameter taken from the Student t table.

Process Variables

Figure 13 shows schematically the basic steps involved in converting wood pyrolysis oil to hydrogenated product and the various material transformations which occur throughout the process. The finished product, (5), has been distilled in step D to reach a desirable pen.

Table 29 lists the process variables chosen for screening and their low and high experimental levels. The values used in each experiment are stipulated by the design. Bottoms WPO-B and WPO-E, (Table 22) represented products where there either was minimal topping or significant topping respectively during step A.

The seven independent variables listed horizontally in Table 30 include the two "dummy" variables. Experimental conditions are based on the Hi or Lo values of the process variables. The Hi or Lo values of both "dummy" variables are used only in calculating experimental error.

Experimental Procedure

Eight experiments were run in random order. The conditions of each experiment were based on the experimental design shown in Table 30. The experimental procedure was as follows:

All hydrogenations were run in a stirred two-liter Parr Autoclave containing a 500 gm charge of Pyrolysis Oil Bottoms along with a 30 gm charge of Girdler catalyst G-61RS, Cobalt on Kieselguhr. The system was flushed first with hydrogen and then partially charged. Additional hydrogen was added after reaching the running temperature and whenever pressure fell by more than 100 psi. (6.92×10^5 Newtons/m^2) below the nominal running pressure. Following the run, product was filtered to remove catalyst. Gases

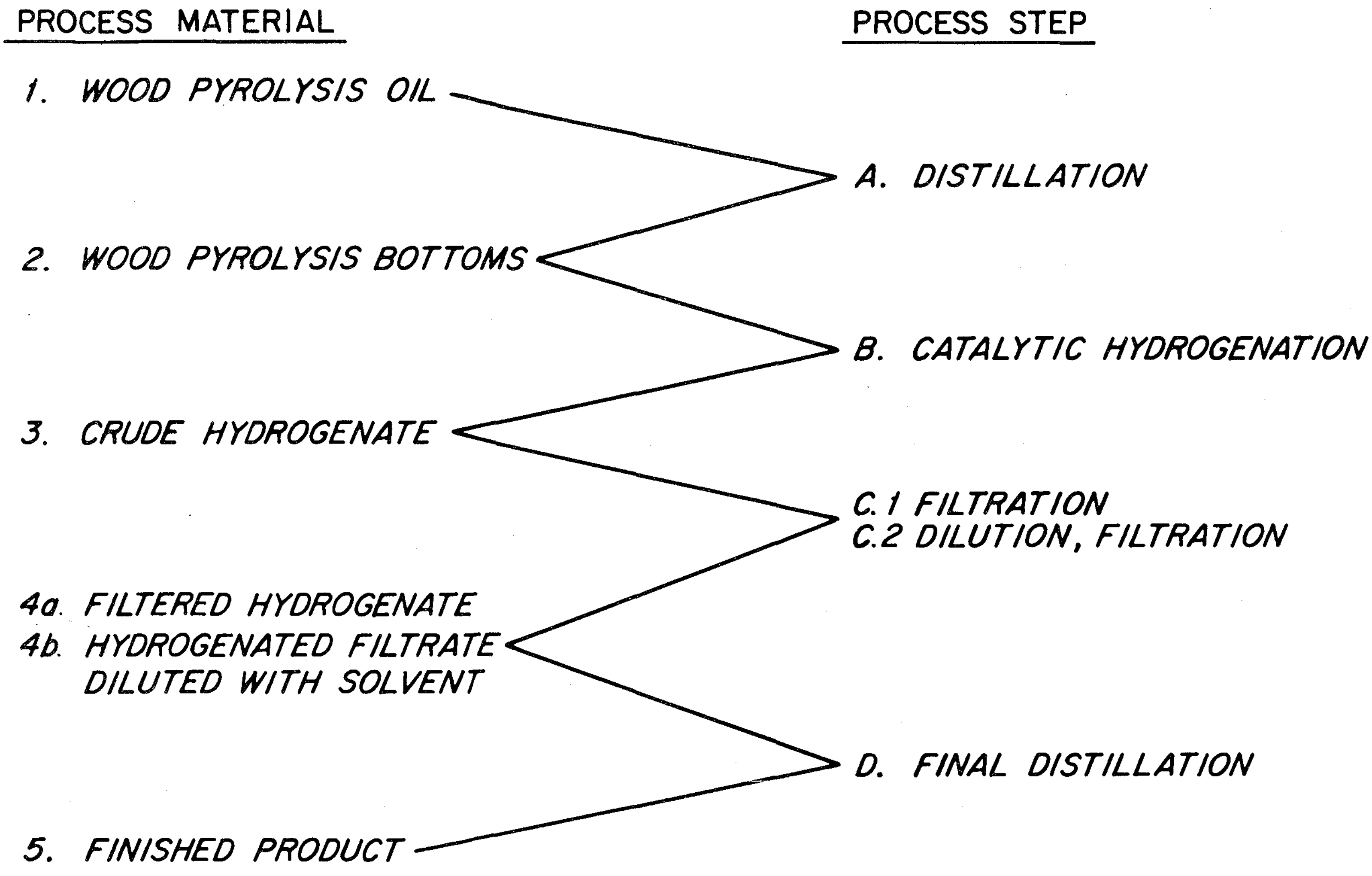


Fig. 13 Conversion of Wood Pyrolysis Oil to Hydrogenated Product

TABLE 29

SUMMARY OF VARIABLES STUDIED FOR SIGNIFICANCE

VARIABLE NO.	VARIABLE	STEP*	- (LOW)	+ (HIGH)
1	Amount of Overhead taken in preparing WPO Feed Stock	A	Light Topping (WPO-B)	Heavy Topping (WPO-E)
2	Hydrogen, psi.	B	750	1,250
3	Dummy	-	-	-
4	Reaction Temp., °C	B	225	275
5	Contact Time, Hrs.	B	1.0	2.0
6	Dummy	-	-	-
7	Volume Deasphalting **Solvent, mls.**	C	0.0 (C1)*	700 mls. Toluene (C2)*

*Refer to Figure 13.

Newtons/m^2 = 14.45 x 10^{-5} psi.

were bled off through dry ice traps before taking a gas sample. The product was filtered either hot without solvent or diluted at room temperature with 700 mls. of toluene, stirred and then filtered to remove insolubles. Finally, each product was vacuum distilled to pen in the range between 65-100.

Responses and Effects

Each measured property, e.g., yield, density, softening point, etc. is referred to as a response. For eight experiments, the main effect of a specific process variable on a response is defined as:

$$\frac{\left(\begin{array}{c}\text{Sum of all responses}\\ \text{for Variable High}\end{array}\right) - \left(\begin{array}{c}\text{Sum of all responses}\\ \text{for Variable Low}\end{array}\right)}{4}$$

The root mean square of the main effects of all dummy variables represents experimental error. The student t statistic for two degrees of freedom at a 95% significance level is 4.303. For a variable to be significant at this level, its effect must be greater than the experimental error multiplied by this factor.

Results

The results of the eight experiments are summarized in Table 31. The yield is based upon product recovered after vacuum distillation to reach pen in the specified pen range. The details of each run are reported in Appendix B. Details of the Plackett-Burman analysis calculated with the help of a computer program is also reported in Appendix B. When products were too hard or too viscous, and measurements became difficult, response values were assigned on a reasonable basis to permit the mathematical analysis to be carried out. For the Ring and Ball softening temperature, when necessary, the value of 100°C was assigned. In those cases where viscosity could not be measured easily at 135°C and 140°F (60°C) values of 300 cPs and 100,000 cPs respectively were assigned.

Significant effects and directions, are summarized in Table 32. Note: a positive effect means that the response increases as the variable increases. Accordingly, yield is favored by a low viscosity WPO charge stock, longer periods of hydrogenation, and the use of solvent. These same conditions lower the softening point and viscosity of the product, however.

Ductility and thin film oxidation studies are summarized in Table 33. The Plackett-Burman Analysis for ductility (Appendix B) shows that charge stock is significant with WPO-B yielding product having best ductility. However, no ductility exceeds 100 before thin film oxidation (TFO). Following TFO, all samples behaved poorly and displayed considerable weight loss, reduced pen and total loss of ductility. On the other hand, a sample of Sun-Tulsa 85-100 reference AC had a ductility of 150+ following this test.

Two of the three hydrogenation variables examined for effects - temperature and pressure - were not found to be significant in any of the responses studied except in hydrogen consumption

TABLE 30

SUMMARY OF EXPERIMENTAL CONDITIONS

EXPERIMENT	RUN NO.	INDEPENDENT VARIABLES						
		PYROLYSIS BOTTOMS (1)	HYDROGEN PRESSURE Psi (2)	(DUMMY) (3)	TEMPERATURE °C (4)	TIME (HRS.) (5)	(DUMMY) (6)	EXTRACTION (7)
663	1	WPO-E	1250	Hi	225	2	Lo	None
624	2	WPO-E	1250	Lo	275	1	Lo	Extract with Toluene
629	3	WPO-E	750	Hi	225	1	Hi	"
627	4	WPO-B	1250	Lo	225	2	Hi	"
618	5	WPO-E	750	Lo	275	2	Hi	None
623	6	WPO-B	750	Hi	275	2	Lo	Extract with Toluene
631	7	WPO-B	1250	Hi	275	1	Hi	None
625	8	WPO-B	750	Lo	225	1	Lo	None

Newtons/m^2 = 14.45 x 10^{-5} psi.

TABLE 31

SUMMARY OF EXPERIMENTAL DESIGN STUDY

EXPERIMENT	RUN NO.	PYROLYSIS BOTTOMS	PRESSURE PSI	TEMP. °C	TIME (HRS.)	TOLUENE EXTRACTION	AVE. PEN. at 25°C	% YIELD OF PRODUCT	RING AND BALL, °C	VIS, CPS		DENSITY
										135°C	60°C	
633	1	WPO-E	1250	225	2	No	Ca. 1	0	>100	Cannot Determ.		1.21
624	2	WPO-E	1250	275	1	Yes	90	52.4	43,43	50	15,000	1.12
629	3	WPO-E	750	225	1	Yes	67	44.2	45,45	30	10,000	1.18
627	4	WPO-B	1250	225	2	Yes	77	47.4	43,43	30	12,500	1.12
618	5	WPO-E	750	275	2	No	Ca. 1	0	>100	Cannot Determ.		1.09
623	6	WPO-B	750	275	2	Yes	85	52.4	48,48	40	28,500	1.13
631	7	WPO-B	1250	275	1	No	85	66.0	45,45	70	27,500	1.16
625	8	WPO-B	750	225	1	No	74	63.4	48,49	110	42,500	1.17

°C = (F - 32) x $\frac{5}{9}$

Newton/m^2 = 14.45 x 10^{-5} psi.

TABLE 31 (Continued)

SUMMARY OF EXPERIMENTAL DESIGN STUDY

EXPERIMENT	RUN NO.	PERCENT SOLUBLES				ATOM PERCENT			H/C ATOM RATIO
		TOLUENE	TRICHLORO-ETHYLENE	ACETONE	ETHANOL	CARBON	HYDROGEN	OXYGEN	
633	1	41.3	44.0	53.3	46.6	71.44	7.49	17.73	1.26
624	2	90.5	97.5	-	-	75.25	8.37	15.66	1.33
629	3	94.2	96.4	-	-	74.02	8.57	16.28	1.39
627	4	91.8	94.2	99.7	96.4	73.46	8.70	18.46	1.42
618	5	35.4	34.6	43.7	16.4	77.46	7.68	12.36	1.19
623	6	88.8	92.0	98.7	94.7	76.44	8.36	15.79	1.31
631	7	79.3	80.1	99.5	87.2	72.56	8.18	17.69	1.35
625	8	66.9	72.9	94.9	87.4	71.30	7.79	20.81	1.31

TABLE 32

ANALYSIS OF RESPONSES

Response	Remarks
Per Cent Yield of Product	Made poorer both by the use of WPO-E and longer reaction times. Extraction with toluene improves yield.
Softening Point and Viscosity	These responses increase with the use of WPO-E and with longer reaction time. They are reduced by extraction.
Product Solubility	Extraction with toluene increases this response. Increasing the time of reaction reduces it. Products made with WPO-E are found to be less soluble in ethylene trichloride.
Elemental Composition and Density	There are no significant effects observed.

where all variables were found to be significant.

No process variable had a significant effect upon the elemental composition of the product including the oxygen content of diluted products. Nevertheless, we continued to dilute to facilitate handling during work-up of the preproduct.

Density is another response which was found to be insensitive to all five process variables. In general, the densities of all hydrogenates are greater than that of petroleum-derived asphalt by about ten percent.

Experimental Models

Normally, continuous variables are used in con-

TABLE 33

DUCTILITY AND THIN FILM OXIDATION RESULTS

EXP'T.	EXP'T. NO.	CHARGE	TOLUENE EXTRACTION	INITIAL PEN. 77°F	DUCTILITY	PROPERTIES AFTER TFO		
						WEIGHT LOSS,[a] Gms.	PEN. 77°F	DUCTILITY
663	1	WPO-E	No	ca. 1	0	-	-	-
624	2	WPO-E	Yes	94	26	7.2969	7	0
629	3	WPO-E	Yes	68	35	-	-	-
627	4	WPO-B	Yes	64	40	5.1716	14	0
618	5	WPO-E	No	ca. 1	0	-	-	-
623	6	WPO-B	Yes	73	44	6.2558	7	0
631	7	WPO-B	No	53	60	-	-	-
625	8	WPO-B	No	57	50	10.5106	3	0
85-100AC	-	-	-	73	150+	0.012 gain	54	150+

[a] Sample Size: 50 gms.

$°C = (F - 32) \times \frac{5}{9}$

structing model equations. Factors in these equations are based on the magnitudes of significant effects obtained by the Plackett-Burman analysis. Of the five screened variables, three are continuous. They include:

- the temperature of hydrogenation
- the time of hydrogenation
- the pressure of hydrogenation

As defined, the two remaining variables appear to be discontinuous, i.e.:

- the WPO feed stock
- the use of toluene or its absence during the filtering step

The latter two variables become continuous, however, on the following basis:

(a) the two batches of pyrolysis oil bottoms evaluated differed in the final temperatures reached during their manufacture. This temperature was 332°F (166.7°C) for WPO-B and 390°F (198.9°C) for WPO-E.

(b) Seven hundred mls. of toluene were used in diluting hydrogenate. Undiluted hydrogenate however, can be viewed as the product of processing by 0 mls. of toluene.

The standard procedure was used to generate model equations where response was related linearly to significant variables.

The following relationships were developed from the Plackett-Burman analysis:

- Percent yield of product = $286.15 - 0.572B + 0.024V - 31.55T$ (1)
- Percent TCE solubles = $192.68 - 0.288B + 0.053V - 20.53T$ (2)
- Softening Temperature (°C) = $-128.65 + 0.446B - 0.041V + 27.37T$ (3)
- Viscosity Cps (135°C) = $-628.04 + 1.854B - 0.225V + 102.5T$ (4)

Where:

B - represents the final distillation temperature in °F $[^\circ C = (F - 32) \times \frac{5}{9}]$ reached in the production of the Pyrolysis Bottoms,

V - represents the volume of toluene in mls. used in processing the hydrogenate, and

T - represents the time of hydrogenation in hours.

The remaining two variables, temperature and pressure of reaction, were not found to be significant.

Both equations (1) and (2) above show similar

TABLE 34

COMPARISON OF OBSERVED AND CALCULATED RESPONSES

	MODEL EQUATIONS							
	(1) Yield, pct.		(2) TCE Sol., pct.		(3) SP, Deg. C		(4) Vis @ 135°C.	
Exp't.	Obs'd	Calc'd	Obs'd	Calc'd	Obs'd	Calc'd	Obs'd	Calc'd
1	0.0	0.03	44.0	39.3	100*	100	300*	300
2	52.4	48.3	97.5	96.9	43	44	50	40
3	44.2	48.3	96.4	96.9	45	44	30	40
4	47.4	50.0	94.2	93.1	43	45.5	30	35
5	0.0	0.03	34.6	39.3	100*	100	300*	300
6	52.4	50.0	92.0	93.1	48	45.5	40	35
7	66.0	64.7	80.1	76.5	45	46.8	70	90
8	63.4	64.7	72.9	76.5	48.5	46.8	110	90

*Assigned Values

dependence upon the same three process variables. As a result, adjusting these parameters to increase the yield will also have the effect of maintaining solubility at high levels. Note that high percent solubles should assure good miscibility between product and asphalt. To achieve this, both T and B need to remain low while V should be held high. This means that hydrogenation charge stock ought to be WPO-B or another Bottoms of Pyrolysis Oil whose final distillation temperature is even less than that of WPO-B. Keeping V high implies the need to use more toluene than that used in the above experiments (700 ml per 500 gm of charge). Finially, the time of reaction needs to be kept low which, in terms of the range of reaction times studied, means reaction times of one hour or less.

Equation (3), the softening point, and equation (4), viscosity at 135°C, both depend upon the same three variables as above, but in exactly the opposite way. In order to increase the values of these two properties it would be necessary to hydrogenate for longer times, i.e., for two or more hours using a feed like WPO-E or one produced by an even higher final distillation temperature and to bypass the solvent extraction step. Whether this is desirable is uncertain because two products prepared at or near these conditions were found to be extremely brittle at room temperature, i.e. their ductility was very poor. This is discussed further below.

Comparisons made in Table 34 show good agreement between observed responses and those calculated using these equations to indicate that these models can be used with confidence within the range studied.

Appendix B summarizes all of the hydrogenation experiments conducted in the statistical study. For the most part, the error in failing to account for the overall mass balance is at worst ca. 5 percent. Most of the source of this error is ascribed to removal of hydrogenated volatiles while removing toluene from extracted products prior to vacuum stripping. In the one case where more mass was recovered than was charged, the difference is attributed to incomplete removal of toluene from the insoluble fraction.

The quantity of hydrogen consumed was calculated on the basis of the difference between the total amount of hydrogen charged and that recovered based on mass spectral analysis of the sample removed from the reactor at completion of the reaction. The ratio of the quantities in grams of penned product to consumed hydrogen is reported below for each of the eight runs:

Run No.	Grams of Penned Product/ Grams of Consumed Hydrogen
1	0.0
2	57.0
3	116.0
4	57.2
5	0.0
6	67.5
7	56.6
8	104.6

The Plackett-Burman analysis of this data, see Table 74, shows that all process variables play a role in hydrogen consumption. Only extraction of the product with toluene, however, has the effect of keeping down consumption. But part of the reason for this apparent influence is the poor results observed with the unextracted hydrogenate of WPO-E. The remaining process variables all appear to have comparable effects upon increasing hydrogen consumption except for reaction time which appears to be twice as effective in raising hydrogen consumption. Conditions favoring reduced hydrogen uptake include: the use of WPO-B for feed, lower pressure levels, lower reaction temperature, and shorter reaction times.

Additional hydrogenates were prepared based on the outcome of the statistical study. The purpose was to seek improvements in efficiency and to test for the accuracy of models.

Of the two WPO feed stocks evaluated, Sample B was judged to be considerably better. Accordingly, further hydrogenation studies were carried out only with this material. The results of these experiments are reported in Table 35.

(1) Since pressures in the low (750 psi, 5.19 x 10^6 Newtons/m^2) to high (1,250 psi, 8.65 x 10^6 Newtons/m^2) range did not show significant effects, a lower pressure of 500 psi (3.46 x 10^6 Newtons/m^2) was evaluated in Experiment No. 640. The reduced yield of 36 percent indicated that the benefit of hydrogenating at pressures below 750 psi (5.19 x 10^6 Newtonw/m^2) is uncertain to unsatisfactory.

(2) Experiments No. 640 and 643 were hydrogenations of WPO-B run under conditions selected from high/low values shown in Table 30 except that time of hydrogenation and extraction, were chosen to complete the corners of the square experimental design shown in Figure 14. For comparison, results of appropriate experiments made with WPO-B are also included.

The experimental model represented by Equation (1) predicts that yield decreases by 32 percent when reaction time is increased from one to two hours. It turns out however, that increasing the time of hydrogenation from one hour to two hours, produced little or no change in yield. The inaccuracy of the model is due in part to two of the eight experiments both made with WPO-E under conditions of zero solvent treat where hydrogenation lasted two hours. Although product was obtained here, since it was pitch-like in character, the yield of useful product was arbitrarily assigned the value of zero. This led to

	EXTRACTION	
TIME	NONE (−)	700 ml TOLUENE (+)
2 HRS (+)	SAMPLE No. 643 69 PERCENT	SAMPLE No. 627 (Run No. 4) 47.4 PERCENT SAMPLE No. 623 (Run No. 6) 52.4 PERCENT
1 HRS (−)	SAMPLE No. 631 (Run No. 7) 66.0 PERCENT SAMPLE No. 625 (Run No. 8) 63.4 PERCENT	SAMPLE No. 640 55.3 PERCENT

Fig. 14 Time/Extraction Study of WPO-B Hydrogenate. (Yield is shown)

TABLE 35

SUMMARY OF SUPPLEMENTARY RUNS MADE WITH WPO-B

Exp't.	Yield, Pct.	Pen.	Softening Temp. °C	Viscosity, cps.[b]		Density	C pct.	H pct.	O pct.
				140°F	135°C				
640	55.5	96	49	15,000	40	1.13	73.06	8.38	14.89
643[a]	69	97	41	18,500	45	1.17	70.33	8.24	16.62
646	36	74	49	18,250	35	1.12	74.92	8.25	12.81
85-100AC	-	70	50	380,000[c]	720	0.99	87.41	11.14	0.68

ALL HYDROGENATES ARE EXTRACTED WITH TOLUENE BEFORE VAC TOPPING TO PEN. EXCEPT WHERE INDICATED.

(a) Hydrogenate was not extracted.

(b) Using Brookfield Viscometer

(c) Viscosity measured at 0.6 RPM.

$°C = (°F - 32) \times \frac{5}{9}$

an inference which was biased strongly against longer reaction times. In the case where WPO-B was hydrogenated and then diluted with toluene (the right hand side of Figure 14), longer reaction time reduced the overall yield only slightly, if at all. However, yield of product through dilution but prior to vacuum finishing shows somewhat more dependence on time of hydrogenation. Compare 71.2 percent yield of prepenned product in Experiment 640 (1 hr.) with 64.5 pct. and 66.5 pct. for that in Experiments 627 and 623 respectively, (both 2 hrs.). This result suggests that the solubility of hydrogenate in toluene decreases somewhat with increasing reaction time, meaning that thermal effects can occur slowly during hydrogenation to reduce the solubility of hydrogenate in toluene, possibly by a cross-linking mechanism.

The influence of extraction on the vacuum finishing step was examined. Distillation of hydrogenates prepared from WPO-B are plotted in Figure 15. In the finishing step, hydrogenate is vacuum distilled to a pen value in the range of 65-100. The amount of volatiles removed from toluene-extracted hydrogenate is roughly twice that removed from unextracted hydrogenates. It should be noted that when toluene is used for extraction, all of it is removed by vacuum stripping at a temperature which is much lower than the final distillation temperature.

Results indicate the following:

1. As vacuum finishing nears completion, i.e., where the pen ranges between 65-250, all products show approximately the same rate of pen decline with percent of distillate removed. This rate ranges between 20 and 30 pen units reduction per each percent of overhead removed.

2. The chief difference between diluted and undiluted hydrogenate is that the former requires removal of about twice as much overhead to reach the desired final pen range. This reduces yield, but may be necessary because preliminary dilution with toluene prior to vacuum stripping improves the product's solubility character.

Results of distilling hydrogenate at 3 mm show that the undiluted product reaches a desirable pen at 83°C some 35°C in temperature below that required for the diluted hydrogenate, i.e. undiluted product contains more volatiles. This translates to equivalent 1 atm. topping temperatures of 455°F (235°C) and 555°F (290.6°C) respectively, based on standard conversion factors and contrasts with the usual end point topping temperature of >1000°F (537.8°C) at 1 atm. (10.2 x 10^4 Newtons/m^2) for asphalt. Since the undiluted product is penned satisfactorily, even though it contains more volatiles, it also must contain a component which hardens it and which is apparently removed by the dilution step.

The very high weight losses observed during TFO of hydrogenates, see Table 33, reflect the relatively large amounts of volatiles remaining after vacuum finishing. The apparent greater volatility of penned hydrogenate as compared with AC may lead to flash point problems. Hydrogenate topped to 443°F (228.3°C) at 1 atm. (10.2 x 10^4 Newton/m^2) equivalent, and a pen of

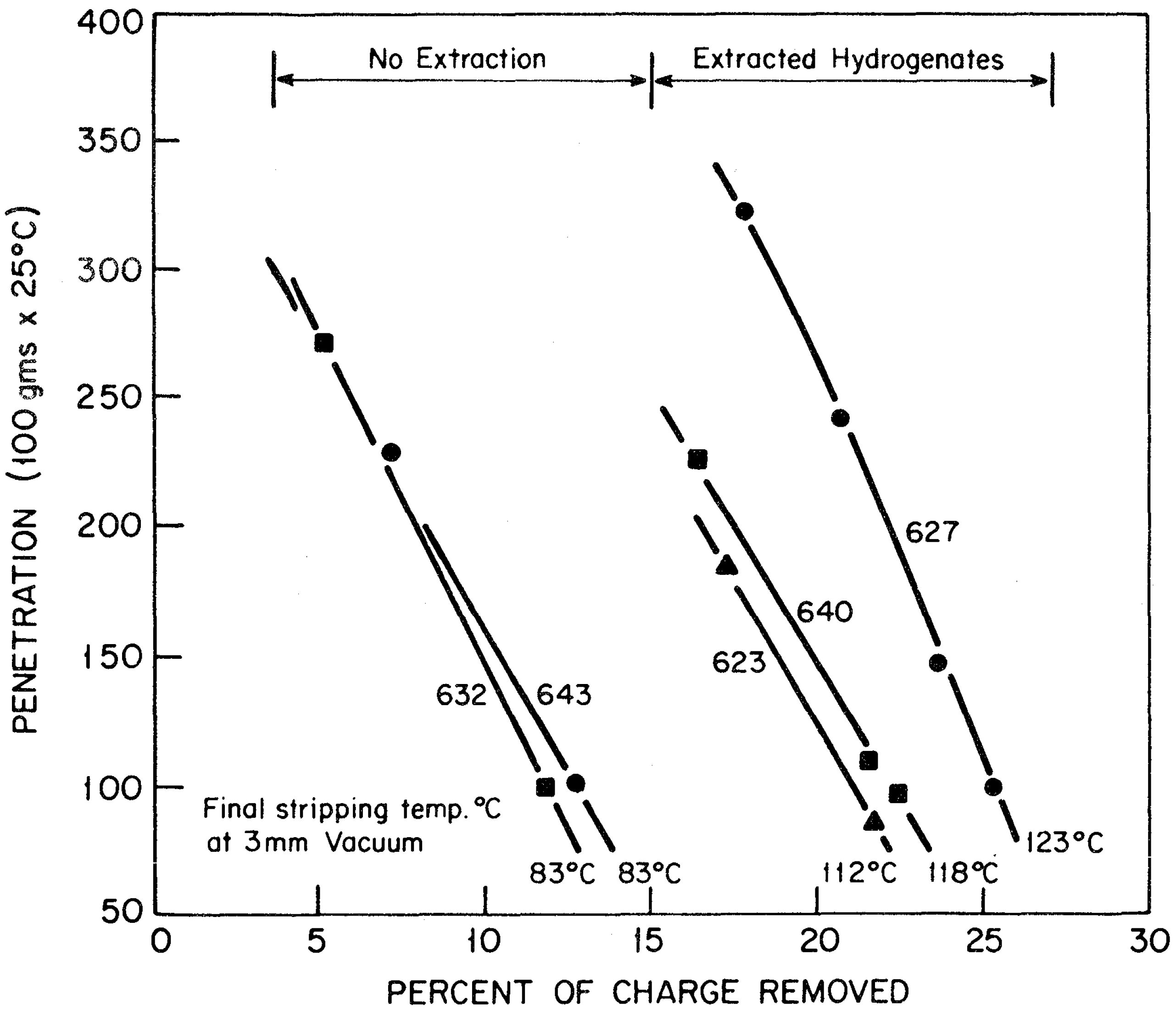


Fig. 15 Effect of Vac Topping on the Penetration of WPO-B Hydrogenate

70, had a flash point of 195°F (90.6°C).

Further Process and Product Modifications

The hydrogenation of wood pyrolysis oil yields products having properties which do not match the relatively wide range of AC specifications. This is due primarily to the more rapid reduction in viscosity with an increase in temperature as compared to asphalt. However, there are several ways of improving working properties of the product.

Viscosity - Temperature Characteristics

In the vicinity of 25°C, flow-related properties of hydrogenate and 85-100AC are reasonably similar but at elevated temperatures, the viscosity is considerably lower. For example, hydrogenate prepared from WPO-B, Experiments 623 and 627 have pens at 25°C ranging between 77 and 85 and Ring and Ball Softening Points of 43°C and 48°C. The pen and softening point of AC are respectively 73 and 50°C. At temperatures between 140°F (60°C) and 135°C however, the viscosity is some 10 to 15 times less than that of AC (Figure 16). This suggests that paving mixtures based solely on hydrogenate would exhibit poor Marshall Stability.

In an effort to raise the viscosity of hydrogenate at 135°C, other hydrogenate prepared from WPO-E was added. The use of this second hydrogenate, which is barely mobile at 135°C, did not produce satisfactory results. Although the viscosity at this temperature nearly doubled at the 25 wt. percent level, (Figure 17) it remained some five times less than that of typical asphalt cements while the 25°C pen dropped to a value of 30.

Final Distillation

Vacuum distillation and extraction are both effective in adjusting the penetration and the viscosity of the hydrogenate. Examples follow:

1. Hydrogenation of WPO-A, initially quite fluid, furnished product which could be filtered easily to remove the hydrogenation catalyst. Final product could be tailored to a desired pen based on the amount of hydrogenate distilled, viz:

Percent Hydrogenate Distilled	Pen (25°C, 150 gm.)
2.6	> 400
11.3	120
18.9	25

The distillate removed by vacuum topping typically is chemically unstable, i.e., at room temperature it changes color slowly from water-white to a purple characteristic of quinone structures. This suggests that higher mole wt. phenols are also present in the finished residue.

2. Figure 15 illustrates that the 25°C pen of hydrogenate decreases as volatiles are removed by distillation. As a class, toluene-diluted hydrogenates require the removal of more volatiles than undiluted hydrogenates to reach acceptable pen values.

Blending Studies

As discussed earlier, hydrogenation adjusts the solubility character of WPO towards that of asphalt. However, crucial differences remain, as are shown in Figure 9, which are attributable to the product's oxygen content. Thus, the miscibility limit observed in a 50 wt. percent blend of extracted hydrogenate and AC-20 was not surprising.

In this study, samples of both of the blend's components and the blend itself were allowed to settle for 23 hrs. at 110°C in sealed vertical teflon tubes 7/16" I.D. (1.1 cm.). Following this treatment, each 3" (7.62 cm.) long specimen was divided into four sections of equal length cut perpendicular to the direction of settle. Each section was then analyzed for its percent C, H, and O. The large difference in percent oxygen between both neat components was used to detect separation.

When fresh, the compositions of both of the neat components and that of the untreated blend were found to be:

	C pct.	H pct.	O pct.
Hydrogenate	75.3	8.4	14.6
AC-20	85.4	10.6	0.6
50 wt. percent blend	81.4	10.0	5.4

Compositional analysis of both neat components following settle showed that virtually no stratification had occurred, viz.

Section	Hydrogenate			AC-20		
	C pct.	H pct.	O pct.	C pct.	H pct.	O pct.
Top	75.2	8.4	16.3	86.1	10.5	1.0
Upper Middle	75.6	8.4	16.0	86.1	10.9	0.7
Lower Middle	75.8	8.4	15.3	86.3	10.6	1.2
Bottom	76.2	8.5	14.1	85.6	10.6	1.2

However, the oxygen content of the blend after settle showed that approximately one-quarter of the hydrogenate had separated neat, indicating that compatability is limited between the hydrogenate and AC, to a value less than about

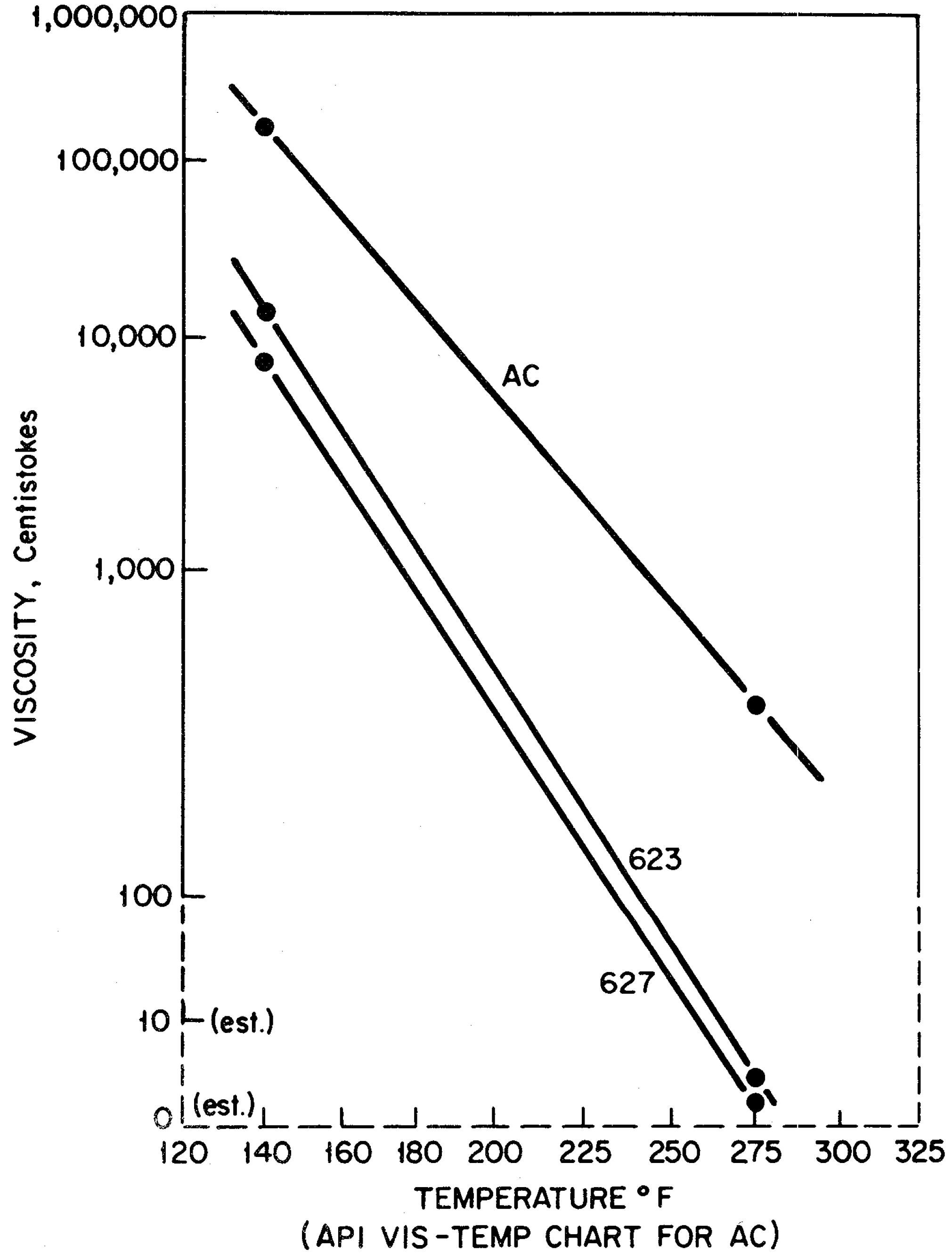


Fig. 16 Viscosity-Temperature Character of Experimental Asphalts and Standard.

°C = (F-32) x 5/9

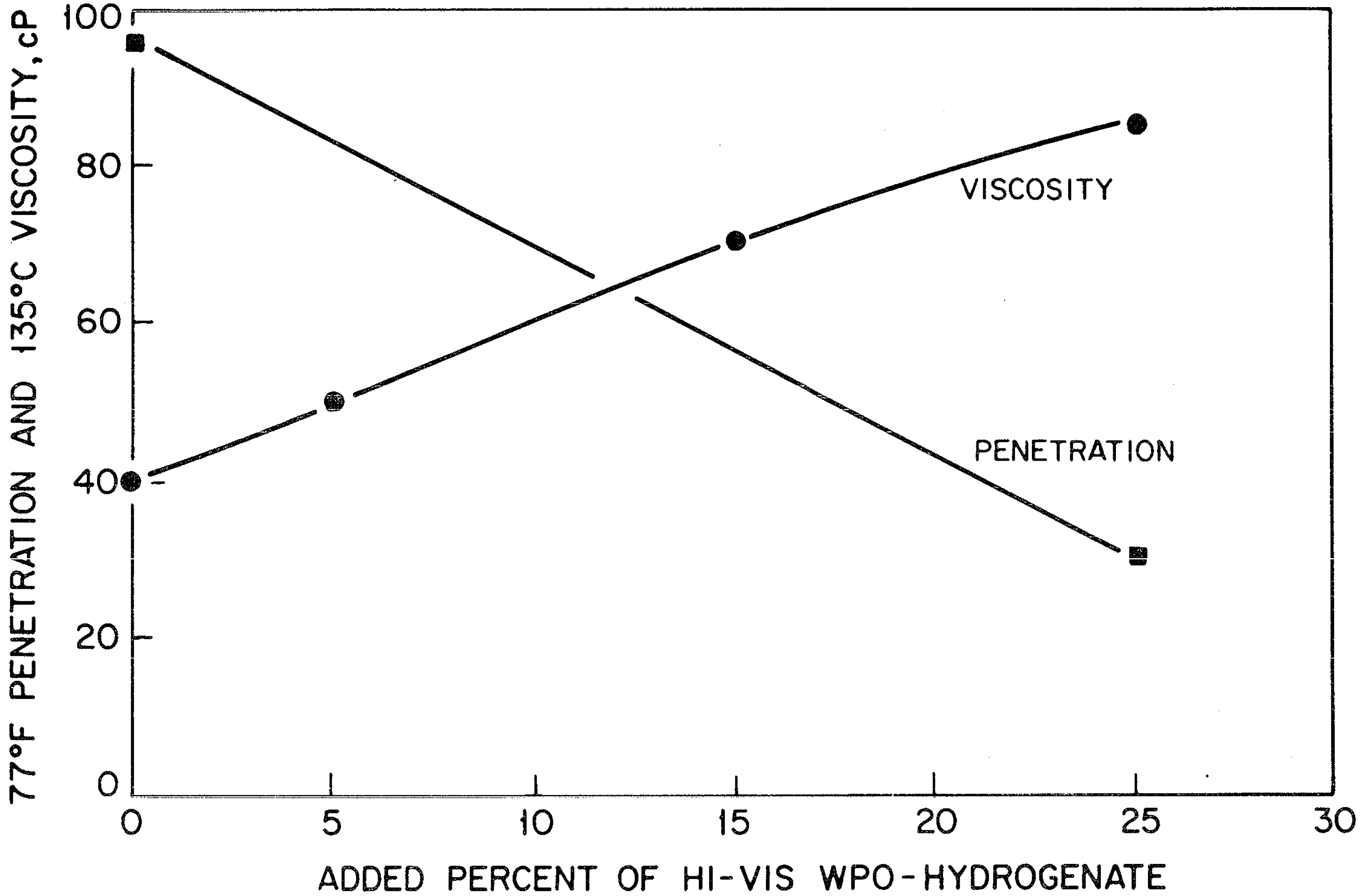


Fig. 17 Effect of Adding Hi-Vis Hydrogenate

°C = (F-32) x 5/9

TABLE 36

AC/HYDROGENATE SEPARATION STUDIES

SECTION	(1) 85-100AC			(2) WPO-B HYDROGENATE			(3) 93/7 AC/HYDROGENATE			(4) 88/12 AC/HYDROGENATE		
	C,pct.	H,pct.	O,pct.	C,pct.	H,pct.	O,pct.	C,pct.	H,pct.	O,pct.	C,pct.	H,pct.	O,pct
Top	87.85	11.45	0.37	75.35	7.68	12.23	87.22	11.43	1.24	87.10	11.25	0.93
Upper Middle	87.39	11.68	0.37	76.14	8.93	12.56	87.09	11.30	1.63	86.39	11.11	1.22
Lower Middle	87.78	11.73	0.49	76.49	8.98	12.68	86.91	11.53	0.62	86.61	11.37	0.89
Bottom	87.80	11.79	0.41	76.50	8.97	13.67	87.15	11.26	0.94	86.89	11.34	1.36
Ave.	87.71	11.66	0.41	76.12	8.64	12.78	87.09	11.45	1.11	86.75	11.27	1.10
S.D.*	0.21	0.15	0.06	0.54	0.64	0.89	0.13	0.15	0.43	0.31	0.12	0.23

* Standard Deviation

30 percent, viz.

Section	C pct.	H pct.	O pct.
Top	81.3	10.8	4.8
Upper Middle	82.3	10.4	4.9
Lower Middle	83.3	10.2	5.4
Bottom	77.1	8.2	14.3

The incompatibility of the 50 percent blend was confirmed in a second set of similar studies which emphasized the AC-rich end of the range since blends rich in hydrogenate were found to be poor in TFO performance.

Results are summarized in Table 36 following settle at 110°C for 24 hours. Both neat components, columns 1 and 2, showed essentially no separation on standing. The anlysis averaged over the four sections of each sample, was then taken to be a good estimate of the composition of each component. These values are:

	C pct.	H pct.	O pct.
85-100 AC	87.71	11.66	0.41
WPO-Hydrogenate	76.12	8.64	12.78

AC blends containing up to 12 percent of hydrogenate are reported in columns (3) and (4). Results show a reasonable similarity among the compositions of all four sections of each sample indicating that little or no stratification or seperation had occurred in test.

Softening Effect of Hydrogenate

While hydrogenate and AC separately exhibit comparable penetration values, both below 100, blends of hydrogenate and AC may exhibit pens which are sometimes considerably greater than this value. The softening of AC by hydrogenate is shown in Figure 18, where the penetration of blends are plotted against the concentration of hydrogenate up to 50 wt. percent. Penetration is reduced following TFO but softening effects are still apparent even at higher hydrogenate concentrations, despite any immiscibility effects that might also arise.

To overcome the softening action of hydrogenate and to determine if greater quantities of hydrogenate could be blended with AC, hydrogenate was distilled further to unusually low pen values. Figure 19 shows the pen of blends made with AC and samples of WPO-B hydrogenate at two low pen levels. The lower curve shows the behavior of asphalt blends containing hydrogenate of initial pen equal to 3 made by removing 15.4 percent more weight from a charge of typical penned hydrogenate by further distillation. The upper curve is similar except that only 14 percent by weight of charge was removed.

The properties of three blends were also studied which contain AC and hydrogenate of low initial pen. These samples are shown plotted on the lower curve in Figure 19. The hydrogenate concentration and pen of these formulations are respectively; 20 percent/66; 27 percent/92; 34 percent/100. Following settle tests in tubes held vertically for 24 hours at 110°C, horizontal penetrometer scans of the two blends of lowest concentration showed no significant settle. The third sample, however, showed clear

TABLE 37

PENETRATION OF AC AND HYDROGENATE

HYDROGENATE CONCENTRATION	PEN OF THE FRESH BLEND	PEN FOLLOWING SETTLE, CMS. FROM BOTTOM				
		0	1.5	3.0	4.5	6.0
20 pct.	66	51	66	71	73	69
27 pct.	92	73	77	80	84	99
34 pct.	100	5*	92	94	98	101

*Sediment Thickness 0.5 cm.

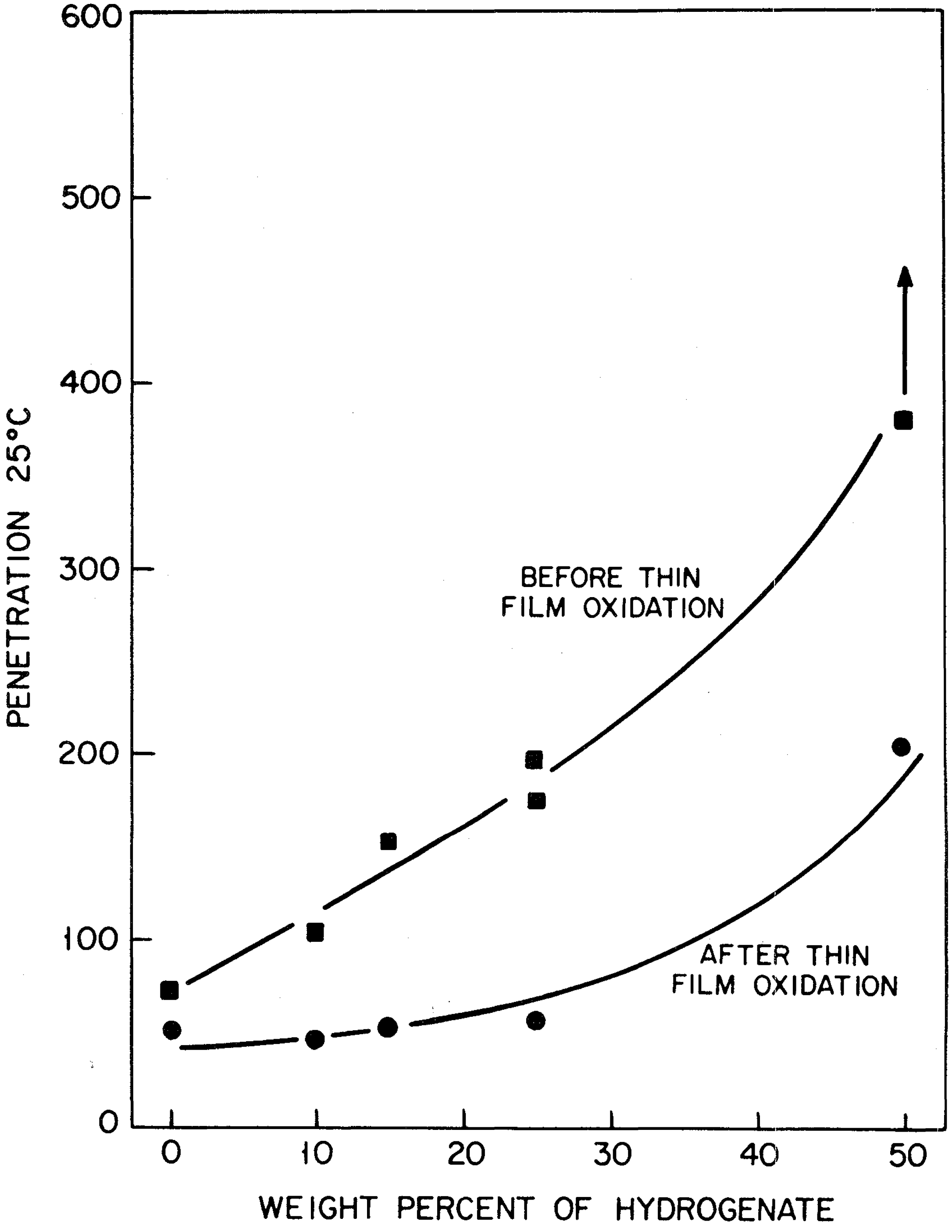


Fig 18 Softening of AC by Hydrogenate

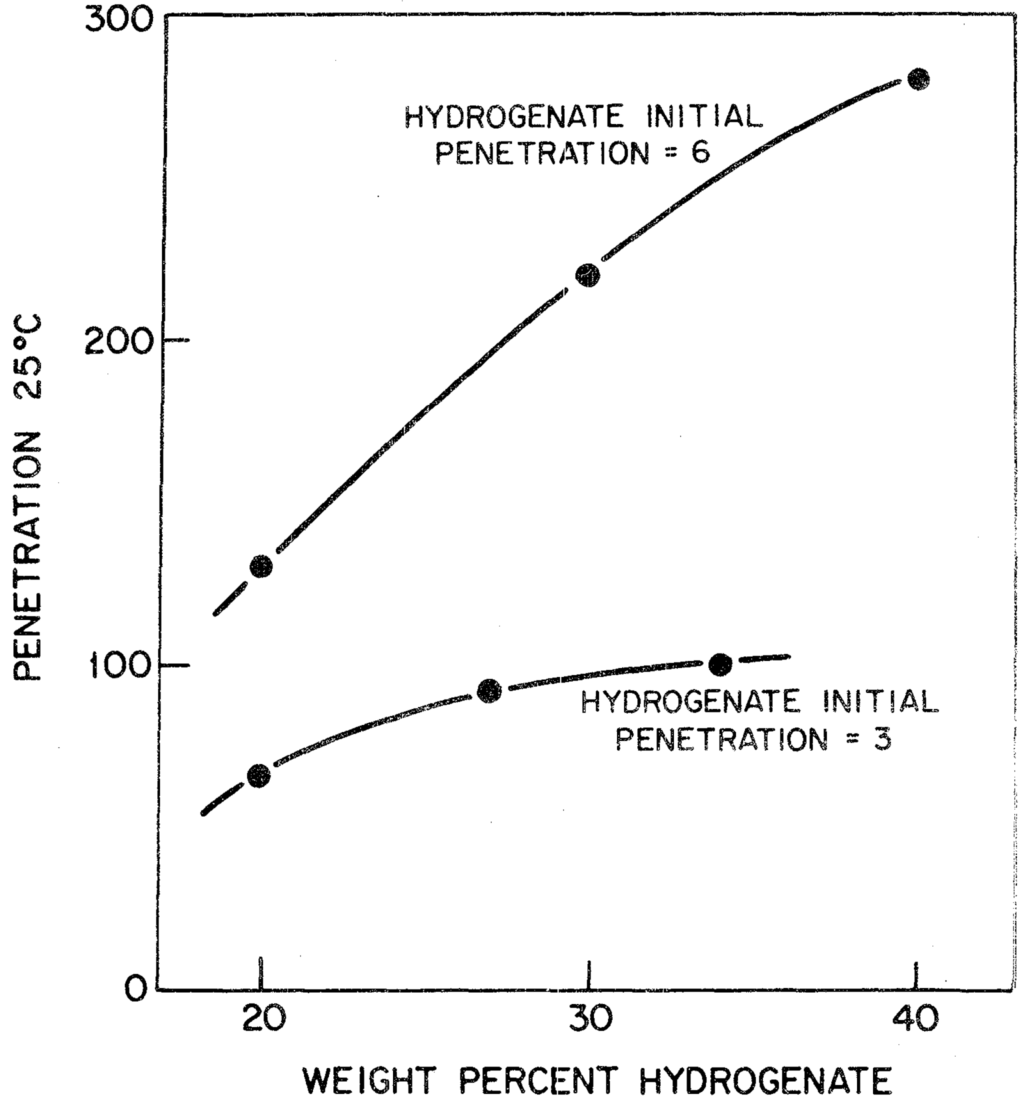


Fig. 19 Penetration of AC-Hydrogenated Pitch Blends

evidence of settle judged by the presence of a low pen layer at the bottom of the settle tube. Results are reported in Table 37 for settle samples of length each about 7 cm. Samples were permitted to settle in teflon tubes, 1.1 cm. I.D. Following cooling, sections of tubing were removed lengthwise enabling pens to be measured perpendicular to the direction of settle.

In the case of the 20 percent and 27 percent blends, no low-pen layer was observed at the bottom of the settle tube. However, a gradual decrease in pen was noted which proceeded in a uniform manner from the tube's top to its bottom. At the top, the observed pens were similar to those of the blends measured before settle. However, in the case of the 34 percent blend, where a clearly defined layer of low pen was observed, the supernatant did not show as large a gradient as that shown by the other two samples. Although no low-pen layer was present at the bottom of the 20 percent and 27 percent settle samples, the presence of a pen gradient suggests that some stratification of layers had occurred.

Properties of AC/Hydrogenate/s Blends

Efforts by others to extend AC with sulfur have been reported.[80] The softening of AC by hydrogenate appeared to be a basis for determining whether increased sulfur levels could be realized in binder blends without dropping pen seriously. Accordingly, the ternary system AC/Hydrogenate/Sulfur was investigated. All blends studied were prepared by stirring at high rates for one half hour at 140°C in a 500 ml. flask under a N_2 blanket. Product was usually prepared in 150 gm. batches.

Figure 20 represents the initial pen of each blend plotted in Triangular coordinates. When this plot is viewed with sulfur held at the apex, movement horizontally across lines of constant sulfur concentration away from pure AC on the left towards hydrogenate on the right shows pen decreasing in the middle portion reflecting the softening action of hydrogenate upon AC. Moving far enough over to reach pure hydrogenate returns the pen back to low values. These results indicate that blends of AC and hydrogenate will accept more sulfur than either pure component within the range of acceptable pen values.

These results, interpreted in another way, are illustrated in Figure 21. Here a response surface represented by contour lines of constant pen is overlaid upon an XY plot of percent of hydrogenate in the AC blend vs. the wt. percent of sulfur. Note that as the amount of hydrogenate increases (i.e. increasing Y values), lines of constant pen move to the right to indicate that blended binders accept more sulfur at constant pen than does neat AC. No more than 35 wt. percent of sulfur can be added to neat AC before its pen drops below a value of 100. In a blend of 50/50 AC/Hydrogenate, however, as much as 42 wt. percent of sulfur can be added before the pen falls below this value. On the basis of pen, a blend of 65/35 AC/Sulfur is equivalent to a mixed binder blend of 29/29/42 AC/Hydrogenate/Sulfur. Thus, by adding hydrogenate to sulfur-extended AC, the AC requirement can be reduced appreciably.

The aging character of AC/Hydrogenate/Sulfur blends are summarized in Table 38. The initial pens and softening temperatures of these blends and their pen values following aging at room temperature for up to two months are reported.

Results indicate that the pen is more stable in blends which are AC-rich, i.e. where the blends contain low levels of hydrogenate. However, the stability of neat AC containing 33.3 percent sulfur, is not good.

The sulfur level can also influence stability. For example, note formulations of initial pen greater than 100. These are Experiments 696-2, 8, 9, 11, 689 and 693. When AC/Hydrogenate is ca. 1/1, stability is poor at 38.7 percent of sulfur (696-2), but improves as the sulfur level drops to 33.3% (689). When AC/Hydrogenate is ca. 2/1, stability is good, viz. formulations 696-8 and 11. When AC/Hydrogenate is ca. 1/2, stability is poor even at the low sulfur level of 25 percent, 696-9.

Sulfur-Settling Results

The method of sectional analysis was used to estimate the stability of several sulfur-extended asphalts. These included blends of: AC/S, Hydrogenate/S, and the ternary system of AC/Hydrogenate/S. In these studies the wt. percent of sulfur contained in each section was determined by the standard LECO (ASTM D-1522) analysis. The resulting concentration profile was used to characterize the settle character of sulfur following static heat treat of samples at 100°C for either 16 hours or 24 hours. All blends were prepared by vigorous mixing for one half hour at 140°C under N_2 blanket followed by cooling to 110°C while mixing before transferring each sample into the settle tube.

Figure 22 shows the concentration in a 75/25 AC/S blend following settling for 16 hours at 110°C. Referring to the base line located at 25 wt. percent indicates that significant sulfur settled out of the upper layers to enrich lower layers. Somewhat similar settle behavior is noted for the 50/50 Hydrogenate/S blends shown in Figure 23, particularly for the top section which lost most of its sulfur. Assuming that sulfur remains dispersed, settling becomes limited in lower sections because of the increased viscosity. The failure to report the higher sulfur concentrations expected in these regions can be due in part to the analytical procedure.

The concentration profile of sulfur in a blend of 50/25/25 AC/Hydrogenate/S following heat treat at 110°C for 24 hours is shown in Figure

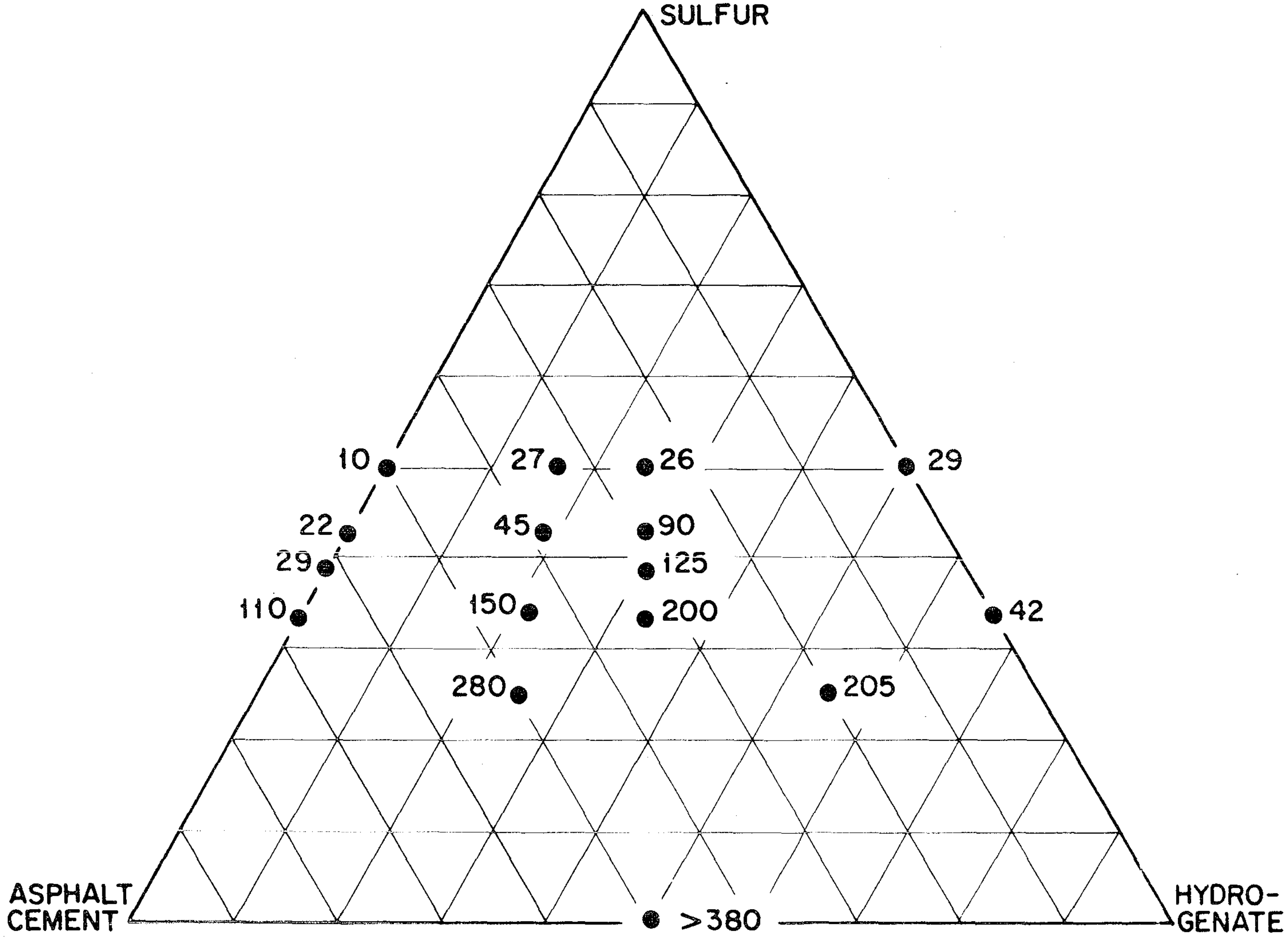
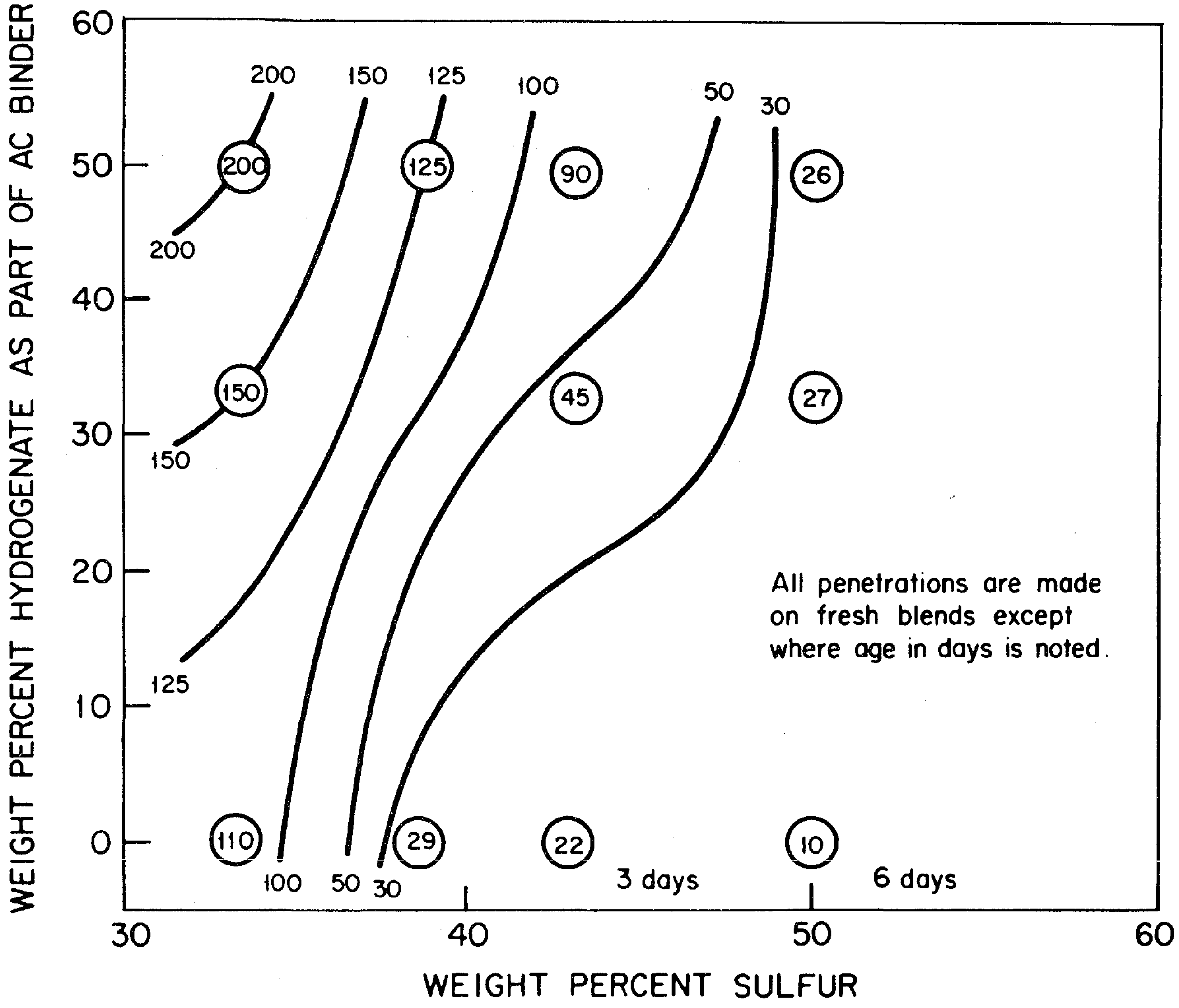


Fig. 20 Penetration of AC/Hydrogenate/Sulfur



All penetrations are made on fresh blends except where age in days is noted.

Fig. 21 Penetration Response Surface for AC/Hydrogenate/Sulfur

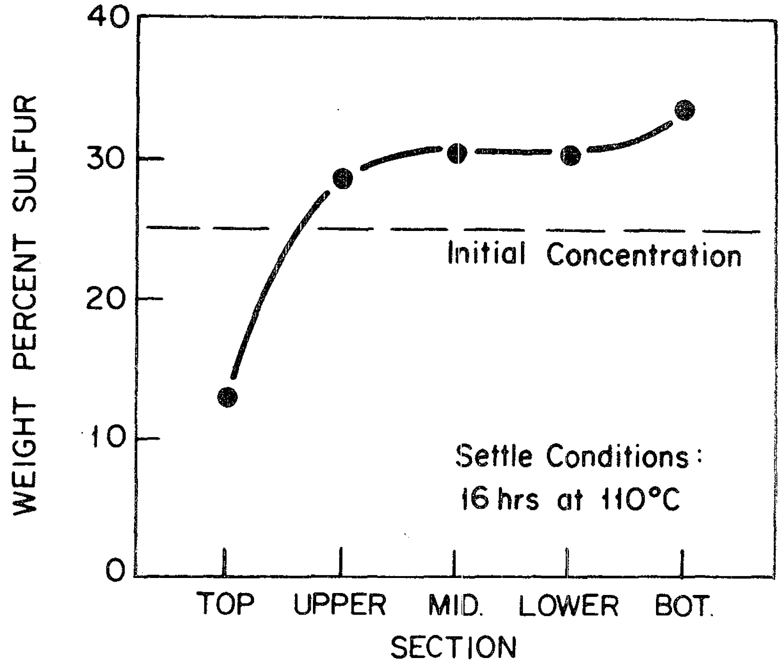


Fig. 22 - Sedimentation Profile of AC/Sulfur 75/25

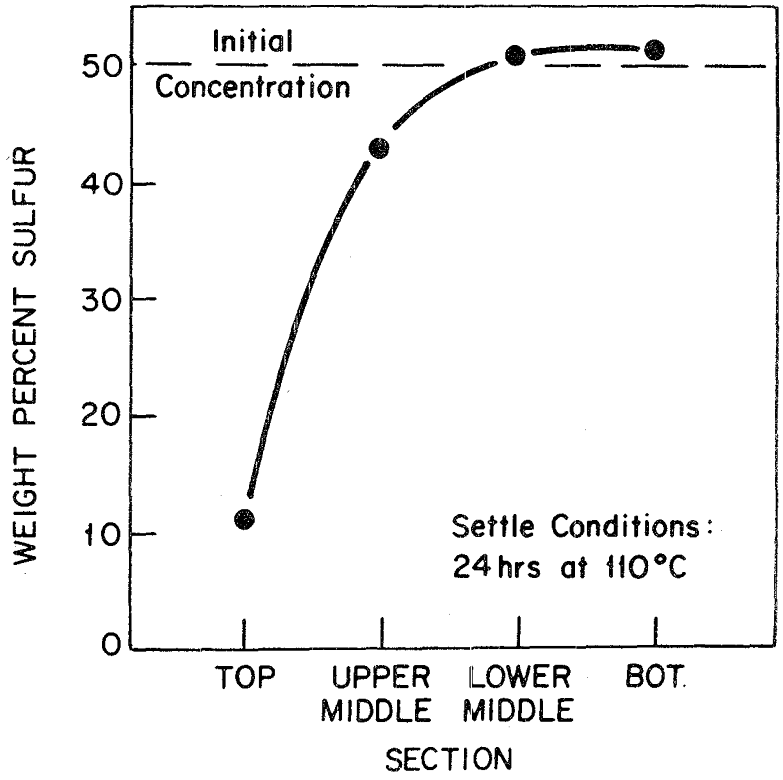


Fig. 23 - Sedimentation Profile of Hydrogenate/Sulfur 50/50

°C = (F-32) x 5/9

TABLE 38

AGING OF AC/HYDROGENATE/SULFUR BLENDS

EXPERIMENT:	COMPOSITION PERCENT			INITIAL SOFTENING POINT, °C	PEN - 25°C			
	AC	HYDRO-GENATE	SULFUR		INITIAL	5 DAYS	14 DAYS	56 DAYS
696-1	61.3	0	38.7	72	29	26	28	24
696-2	30.7	30.7	38.7	47	125	50	43	72,85
696-3	33.5	16.5	50	82	27	-	19	22
696-4	38.3	18.7	43.0	42	45	-	24	37
696-6	0	66.7	33.3	50	42	-	28	47
696-8	44.7	22	33.3	41	150	-	125	142
696-9	20	55	25	50	205	-	40	42,52
696-10	0	50	50	49	29	-	28	36
696-11	50	25	25	38	280	-	158	155,16
687	50	0	50	86 (6D)*	- 10 (6D); 23 (29D); 34 (73D)			
688	25	25	50	82 (6D)	- 26 (6D); 33 (29D); 20 (73D)			
689	33.3	33.3	33.3	47 (6D)	200; 145 (6D); 140 (29D); 144 (73D)			
690	28.5	28.5	43.0	69 (3D)	90; 45 (3D); 90 (27D); 90 (70D)			
691	57.0	0	43.0	65 (3D)	45; 22 (3D); 28 (27D); 25 (70D)			
693	66.7	0	33.3	49	110; 55 (16D); 45 (23D); 30 (68D)			

*D denotes aging time in days.

24. This blend contains equal weights of AC and 50/50 Hydrogenate/S. Thus, we can compare the stability of neat AC and a blend of AC/Hydrogenate 2/1 where both contain 25 percent dispersed sulfur.

In such a comparison, sulfur appears to be somewhat more stable in the blend of 50/25 AC/Hydrogenate than in neat AC despite the eight hour longer settle time. This conclusion is based on finding less sulfur after settle in the lower sections of the blend than in the AC. The matter is somewhat complicated, however, by the fact that the blend's 33 percent concentration of hydrogenate exceeds the observed saturation concentration of 25 percent hydrogenate when neat. On the credit side, however, the mixed binder is known to have a lower viscosity. Therefore, there is reason to infer that hydrogenate can improve the suspension of sulfur in AC.

Process Description

Based on the above, a process for the conversion of cellulosic waste to highway binder would include:

1. pyrolysis of cellulosic waste to oil and char.

2. fractionation to remove light oil from the pyrolysis liquid.

3. hydrogenation of the distillation residual to adjust properties.

Both plug-flow[16] and flash pyrolysis reactors[81, 82] have been tested on pilot plant scale with satisfactory results. The flash pyrolysis concept is used in the present evaluation except that the oil recovery system has been modified to include separation of the pyrolysis oil into light and heavy fractions. Wood-waste is assumed as the primary feed but this could be supplemented with other agricultural wastes and with the cellulosic fraction of municipal wastes. This permits simplification of the feed preparation section compared with the published design information for processing of whole municipal solid waste.

As in the references above, the pyrolysis reactor is a vertical, stainless steel tube (Figure 25). Finely divided organic waste and hot char is carried into the reactor by recycled product gas. Reactor temperature is regulated at about 500°C. in order to obtain the maximum yield that can be obtained from mixed wood waste based on dry charge weight. Higher operating temperature and use of less volatile cellulosic waste would increase gas formation at the expense of oil yield.

Pyrolysis vapors are separated from the char in a cyclone separation. Part of the hot char is conveyed to a char heater where it is combusted with air and recycled to the pyrolysis reactor. Excess char is removed from the system and quenched with water.

The pyrolysis reaction is generally carried out at such a high temperature that the heat in the effluent gas is more than adequate to fractionate the condensible portion into asphalt-type bottoms and one or more fuel oil fractions. Figure 26 shows a process flowsheet for recovering the pyrolysis oil as a vacuum resid and a light and heavy oil fraction. The oil fractions may ultimately be combined as a fuel oil but their removal as separate streams from the fractionator will facilitate the stripping of light ends from the final binder product and thus provide maximum yield of highest quality residuum.

The pyrolysis gas is fed into a fractionating column containing 14 trays where it is successively quenched in three stages by recycling cooled liquid to the column over four-stage sections. The bottom two trays provide contact between the gas and liquid phases to condense out the bulk of the asphaltic compounds and the bottoms pass to a vacuum flash drum where the light ends are stripped out at 70 mm. Hg., simultaneously cooling the liquid about 50°F (10°C). Conditions at the bottom of the fractionator and in the flash drum are typical of petroleum asphalt processes and it is not known at this time whether they will have to be modified for the pyrolysis oil fractionation.

For purposes of the present process design, the light and heavy oils have been arbitrarily selected to have boiling points of 360°F (182.2°C) and 520°F (271.1°C) respectively. By distributing the duties of the three intercoolers on the fractionator differently, it will be possible to obtain different specifications but the total duty must remain the same. Consequently, the equipment will not be affected by the specifications ultimately established for the light and heavy oil fractions unless more than two oil fractions are desired.

The total intercooler duty has been selected to keep the off-gas from the fractionator above the water dew point. In the conventional pyrolysis process, the gas is cooled below this dew point because the oil must contain at least 10 percent water to have a sufficiently low viscosity to be handled in fuel oil burners. In the present process, the asphaltic compounds have been removed from the oil fractions and it would be preferable to separate the more or less anhydrous oils so their net heating values will not be decreased by evaporation of the dissolved water.

The heavy oil will be essentially anhydrous and for this reason might be kept separate from the light oil which will contain a small amount of water. Since the partial pressure of water in the gas stream at 340°F (171.1°C) at the eleventh tray of the column is only 4 percent of the vapor pressure of pure water, the liquid phase in equilibrium with it will theoretically have a water concentration equal to 4 percent of

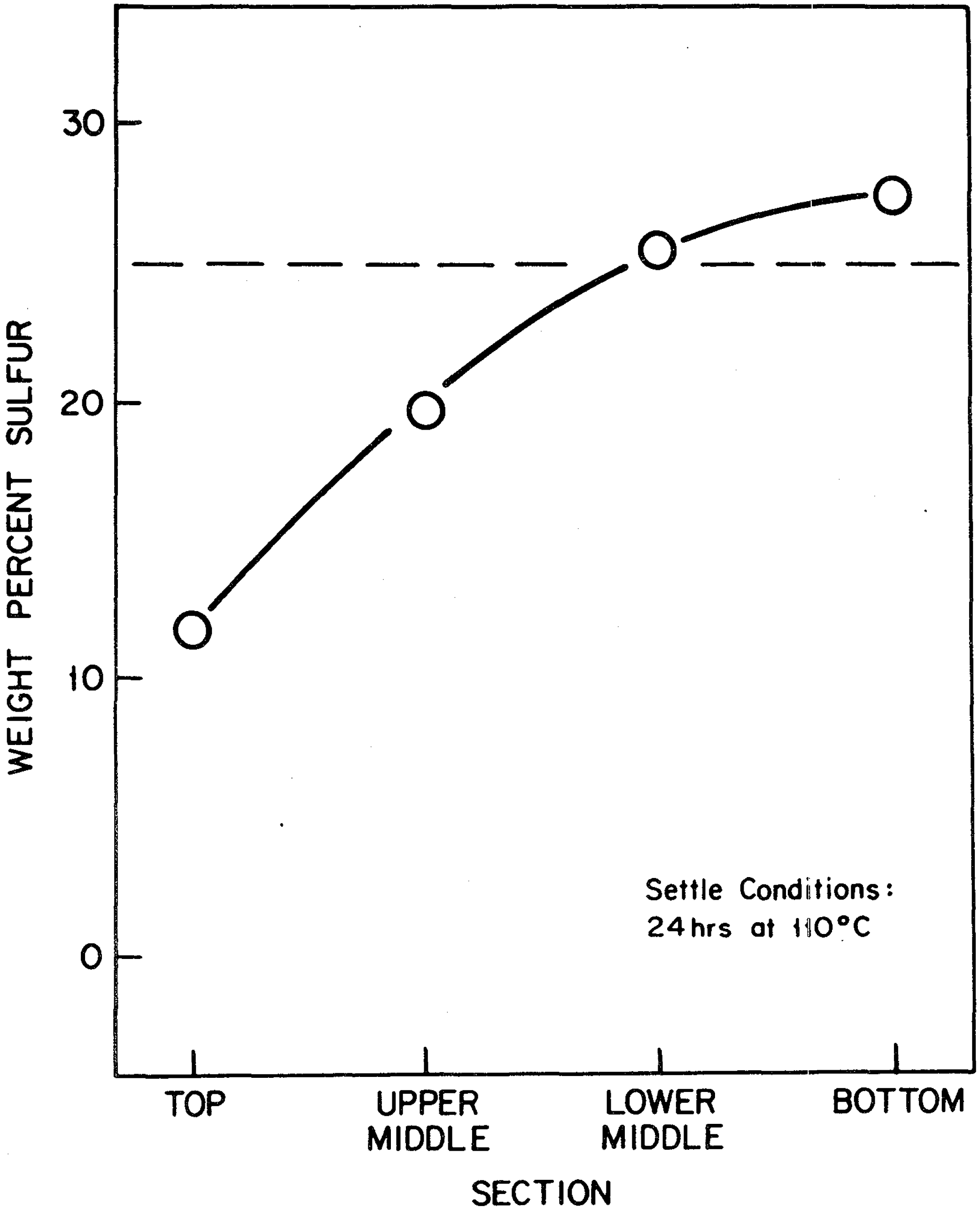


Fig. 24 Sedimentation Profile of AC/Hydrogenate/ Sulfur 50/25/25

Figure 25

PYROLYSIS SYSTEM

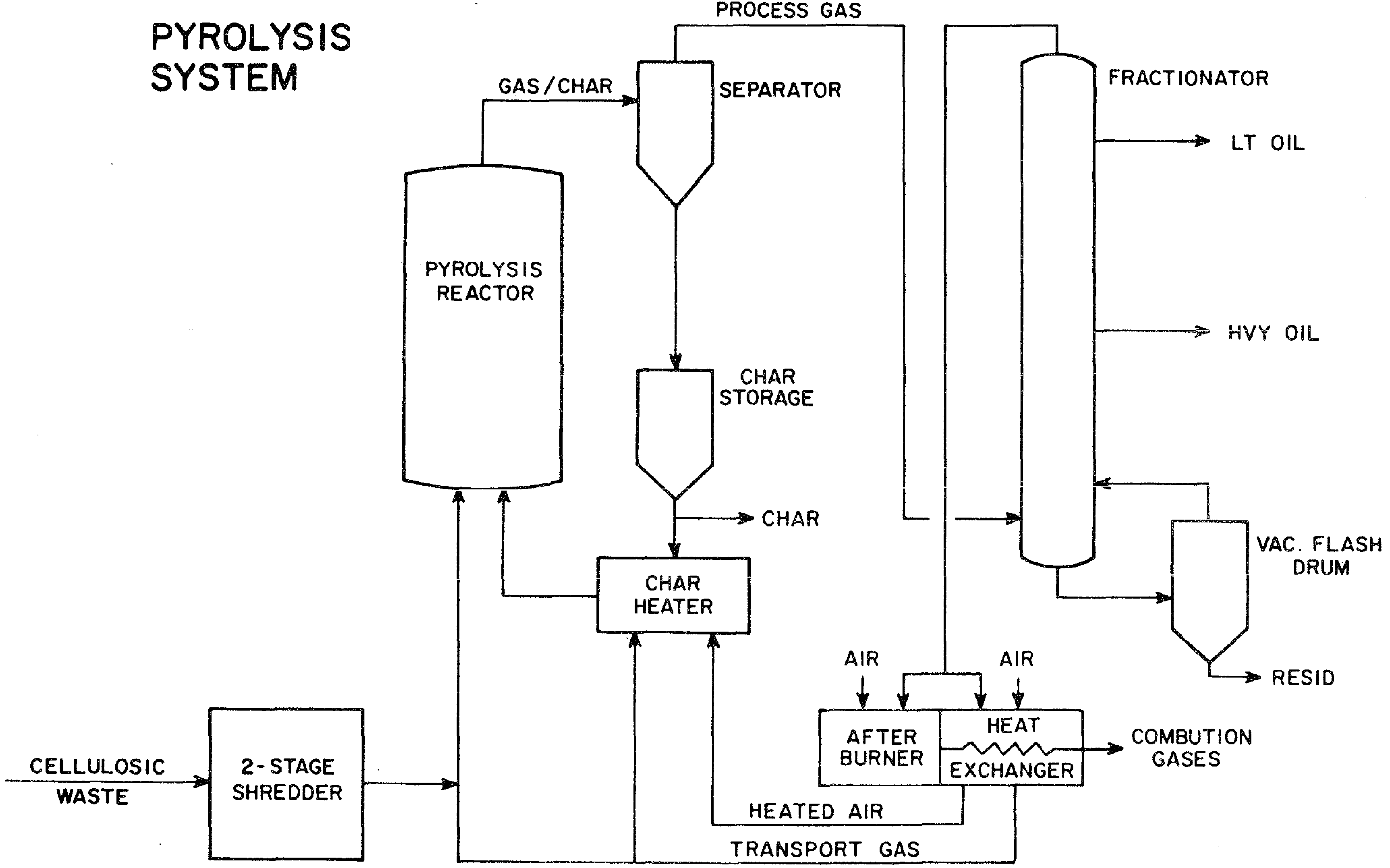
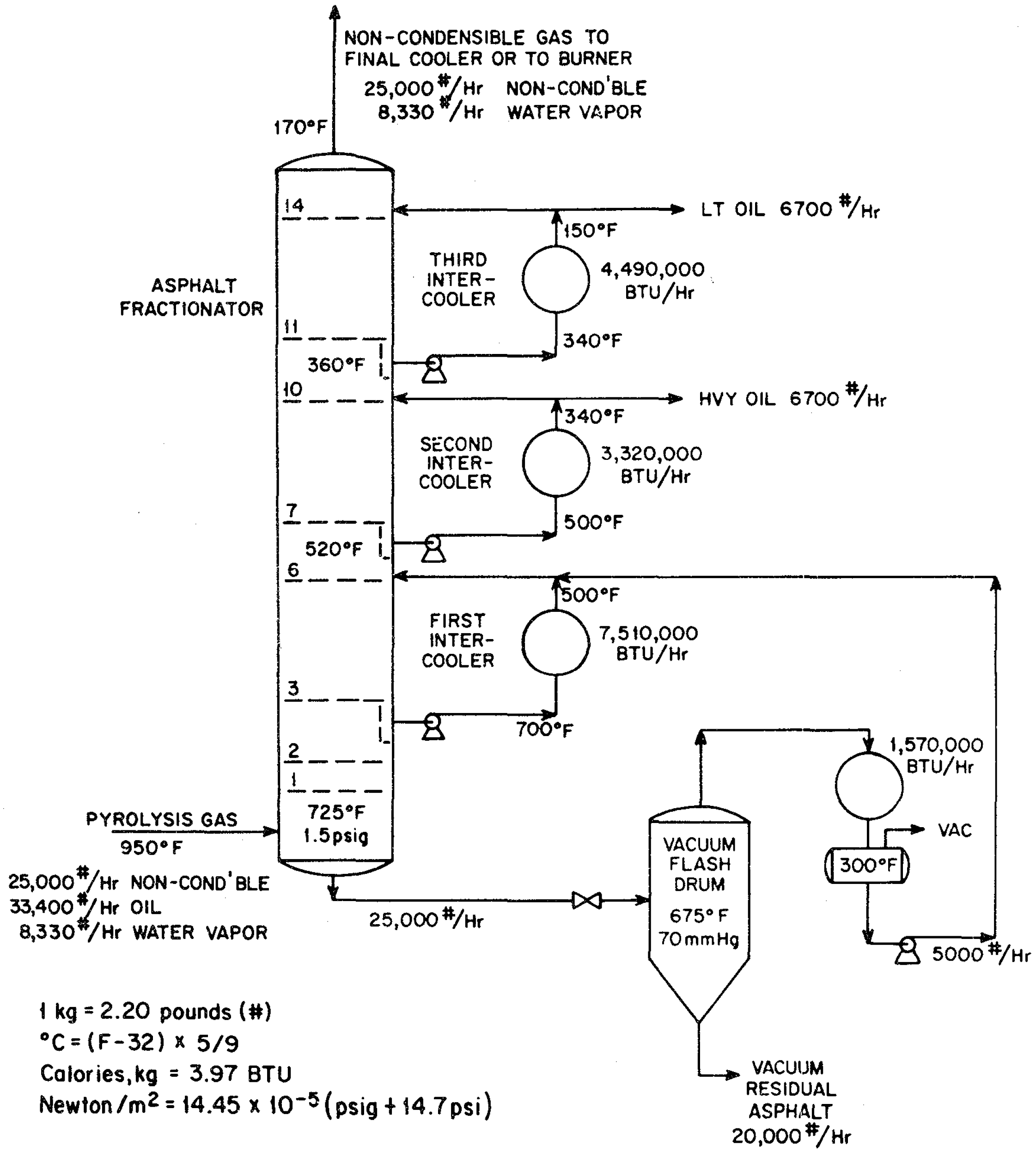


Figure 26

ASPHALT RECOVERY FROM PYROLYSIS OF MUNICIPAL SOLID WASTE



1 kg = 2.20 pounds (#)
°C = (F-32) x 5/9
Calories, kg = 3.97 BTU
Newton/m^2 = 14.45 x 10^{-5} (psig + 14.7psi)

the saturation concentration. Deviations from ideality over the concentration range will alter this fraction slightly but the actual water concentration on a mole basis will be significantly less than 4 percent. In view of the molecular weight ratio, the water concentration in the light oil from the fractionator will probably be less than 5 percent by weight. Thus both oil fractions from this process will probably be more desirable than the original pyrolysis oil containing 10 percent. However, due to the removal of the binder fraction, quantities will be less.

Part of the uncondensed pyrolysis gas is used to transport waste and char into the pyrolysis reactor. Remaining gas containing pyrolysis water is passed directly to the gas burner for waste heat recovery because further cooling will produce an aqueous phase requiring disposal. One might consider the possibility of recovering the acetone, methanol and other organic compounds from the gas stream by cooling with a water quench. However, quantities will probably be too small to make this economically feasible.

The composition of the gas from the pyrolysis reaction will vary depending upon the materials charged to the reactor. The present process design has been based on the publication by K. Pober and H. Bauer[83]. Compositions of the different products from solid waste pyrolysis have been used and the binder yield from the pyrolysis oil was assumed to be the same as found for the pyrolysis oil from wood waste, i.e., 60 percent by weight.

Average molecular weights of the different oil fractions were also estimated from a molecular weight distribution curve for pyrolytic oil from bark. The average molecular weights of the light oil, heavy oil and asphalt recycle from the vacuum flash drum were taken as 180, 300, and 700 respectively and all liquid phases were assumed to have a specific heat of 0.5 and vapor phases specific heats were taken as 0.3. These values were selected because corresponding values for oxygenated compounds are usually larger and hydrocarbons are usually smaller than these average values. Latent heats of vaporization at the normal boiling points were taken as 170 BTU/lb. (93.9 Cal.,kg./kg.) for the same reason and the boiling points of the light oil, heavy oil and asphalt recycle were selected as 340°F (171.1°C), 500°F (260°C), and 700°F (371.1°C) respectively. Appendix C shows the enthalpy curves for these fractions which were used for the present process calculations.

The specific heat of the gas was evaluated at an average temperature of 270°C and this value was assumed constant to evaluate the enthalpy curve for the non-condensible gas. In the course of the thermodynamic studies on the gas, liquid, and solid streams from the pyrolysis reaction, the heat of combustion were calculated for comparison with the values given by Pober and Bauer. The gross heating value for the gas based on condensing all the water to liquid was 372 BTU/lb. (205.5 Cal.,kg./kg.) which compares with their reported range of 350-500 BTU/lb. (193.4 - 276.2 Cal.,kg./kg.). Other publications give heating values of different pyrolysis gases in the range of 350 - 400 BTU/lb. (193.4 - 221.0 Cal.,kg./kg.) so the composition of the gas used in these calculations may be considered typical of all pyrolysis processes.

The gross heating value of the char was calculated as 8800 BTU/lb. (4,862 Cal.,kg./kg.) compared to the reported value of 9000 BTU/lb. (4,972.4 Cal.,kg./kg.), however, this was based on the assumption that all the oxygen was combined with the metals in the ash. If the oxygen is combined with the carbon and hydrogen at an enthalpy level approximately equal to that of water, the gross heating value of the char would be about 7800 BTU/lb. (4,309.4 Cal.,kg./kg.).

The gross heating value of the oil based on the same assumption, that all the oxygen content was at the same enthalpy level as the oxygen in water, the calculated value of 10,200 BTU/lb. (5,635.4 Cal.kg./kg.) compared favorably with the value of 10,500 BTU/lb. (5,801.1 Cal.,kg./kg.) reported by Pober and Bauer.

The material balance for the fractionator and heat balances are given in Appendix C.

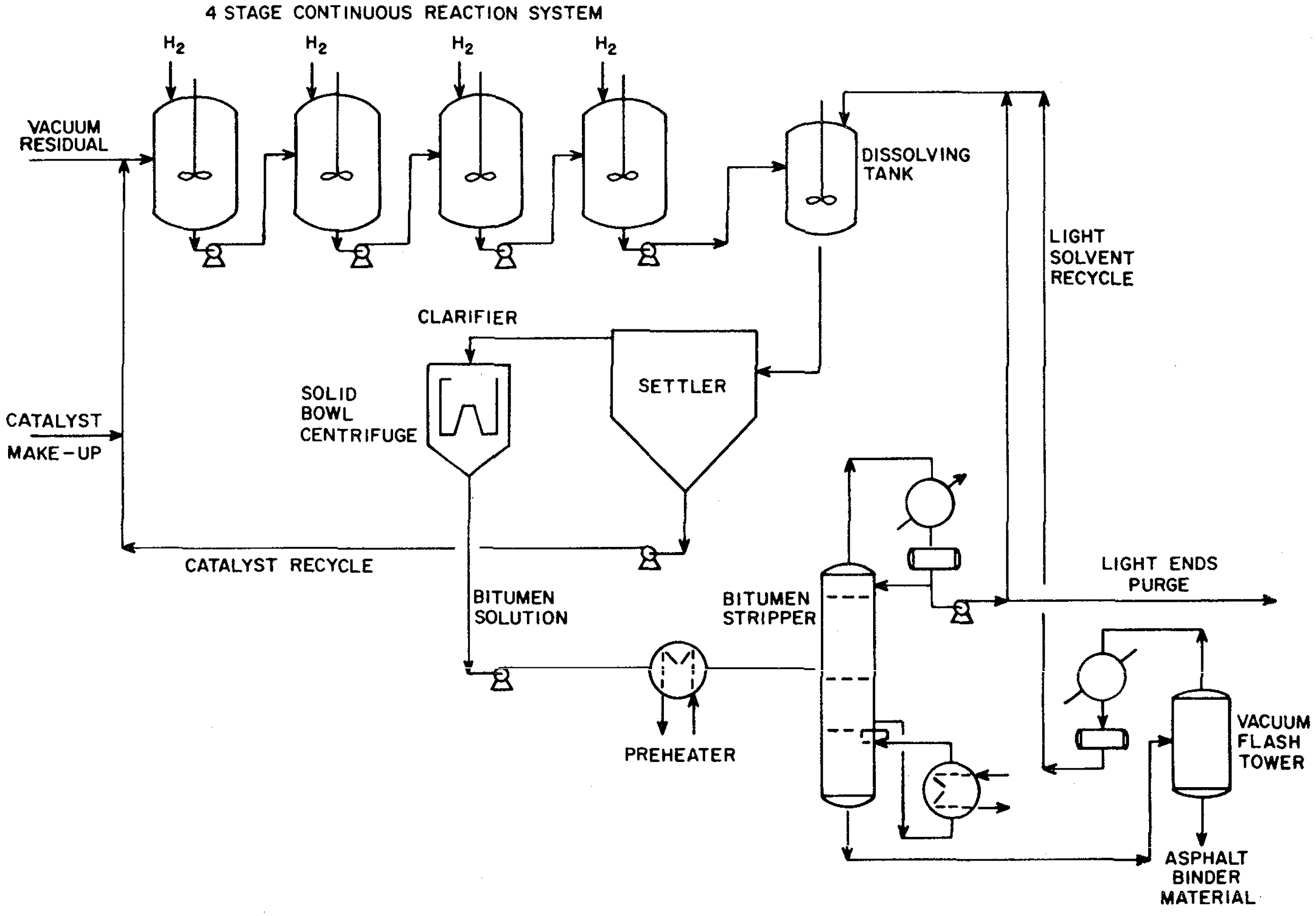
The temperature distribution in the fractionator cannot be based on rigorous bubble point calculations because of the lack of adequate knowledge of the exact composition of pyrolysis oil. The variation with the different charge stock also makes it irrelevant to attempt a precise design. Consequently, a reasonable temperature pattern was selected and the relative intercooler duties necessary to maintain this temperature variation have been calculated.

The fractionator will also alter the distribution of oxygenated compounds in the light and heavy oil fractions, and there is a chance that one or both of these fractions will be more compatible with ordinary fuel oil. By maintaining a higher temperature for the off-gas from this absorber to prevent condensation of the water, a larger portion of the more volatile oxygenated compounds such as alcohols and acids will remain in the vapor phase and be burned in the gas. This should reduce corrosion as well as increase the miscibility of the oil fractions with a hydrocarbon oil. Thus additional subtle advantages may be realized by fractionation of pyrolysis oils to produce binder.

A conceptual process flow sheet for the hydrogenation of the distillation bottoms is shown in Figure 27. The heavy oil is hydrogenated in a four stage continuous reaction system at 800 psi. (5.54×10^6 Newtonw/m^2) and 250°C. The hydrogenate, diluted with light solvent oil from a downstream stripping column, is led to a settling tank from which a catalyst slurry is withdrawn and combined with fresh feed entering the hydrogenation reaction system. Hydrogenated oil

Figure 27

ASPHALT BINDER PROCESS – HYDROGENATION STEP



solution from the settler is centrifuged to remove residual catalyst fines. It is pumped to the stripping still and then to the vacuum flash tower where volatiles and light recycle oil are removed.

Process Economics

The following economic analysis is based on a facility producing 80 ton/day (72.7 metric tons/day) binder by pyrolysis of 1000 ton/day (909.1 metric tons/day) cellulosic waste, distillation and hydrogenation of the pyrolysis oil. Investment costs of the pyrolysis section are based on economics for a 200 ton/day (181.8 metric tons/day) municipal solid-waste demonstration plant disclosing total cost for each process step[70]. These totals have been adjusted to the present case using best engineering judgment for the equipment required in each step and then scaled to the required capacity by the .6 power and finally adjusted by the engineering cost index from the average 1974 index of 165.4 to the mid-77 index of 203. The combined cost factor for the original values becomes:

$$\left[\frac{1000}{104}\right]^{0.6} \times \frac{203}{165.4} = 4.77$$

TABLE 39

BREAKDOWN OF CAPITAL COSTS ESTIMATED FOR 1000 TON PER DAY
CELLULOSIC WASTE PYROLYSIS PLANT WITH BITUMEN FRACTIONATION

Item	SUB-COST	July 1977 Estimated Cost
Design		$ 956,000
Site development costs		1,944,000
Construction		9,002,000
Receiving and feed storage		
Equipment	569,000	
Installation	845,000	
Organic feed preparation		
Equipment	1,512,000	
Installation	1,461,000	
Pyrolysis and fuel recovery		
Equipment	1,172,000	
Installation	1,836,000	
Bitumen fractionation		
Equipment	82,000	
Installation	128,000	
General and utility		
Equipment	421,000	
Installation	976,000	
Inflation, overhead and contractors' profit		2,697,000
Total		$14,599,000

1 metric ton = 1.1 tons

Installation costs for larger equipment will normally be a smaller fraction of the total installed cost but this was ignored in the present evaluation and the same factor was applied to both the equipment and installation costs.

Table 39 summarizes the capital costs for a pyrolysis plant to process 1000 tons per day (909.1 metric tons/day) of cellulosic waste on a dry basis. The design cost should be independent of the size of the plant and has thus been increased by the cost index ratio only. The actual area required by the organic feed preparation, including the drying, and the pyrolysis and fuel recovery steps will probably be about half that required for the total plant but the site development costs will be greater. Thus, the cost for the present plant will be about 60 percent of the cost obtained by increasing the published cost by the combined size and cost index factor.

The construction cost breakdown has also been considered in detail to arrive at the total cost. The receiving and preparation step previously estimated included the feed storage and drying step which would be required in the present plant. Other phases of the feed preparation section, such as the shredder to reduce the waste to pass a 3" (7.62 cm.) screen, the air classifier, the metal and glass separating system and other screening equipment, will be required. Thus, the installed cost of this step has been taken as 20 percent of the adjusted value in the previous estimate.

The organic feed preparation includes grinding particles which pass through a 3" (7.62 cm.) screen down to a size where 80 weight percent of the feed passes through 14 mesh and intermediate storage and transfer equipment. This will all be required in the present plant, and it might thus be noted that the cellulosic waste for this plant has been assumed to be less than 3" (7.62 cm.) in size, although with relatively soft agricultural or wood wastes, size will not be a significant factor. The cost of this equipment has been estimated from the above size and cost index factor.

The pyrolysis and fuel recovery equipment cost has been estimated using the size and cost index factor and the cost of the heat exchanger equipment ($40,000) has been deducted since this is included in the bitumen fractionation section discussed later.

Metal and glass recovery equipment are not required, although magnetic seprators would be used in the organic feed preparation step primarily to protect the grinding equipment from tramp iron. Product storage, spare parts and

TABLE 40

SUMMARY OF ANNUAL COSTS OF 1000 TON PER DAY
CELLULOSIC WASTE PYROLYSIS PLANT WITH BITUMEN FRACTIONATION

Item	Cost
Operating Costs	
Electric Power	$ 902,000
Other Utilities	460,000
Labor	266,000
Maintenance	762,000
Land Rent	82,000
Residual Transfer and Disposal	91,000
Total Operating Costs	$2,563,000
Capital Costs	
Ammortization of $14,599,000 15 Years at 6 pct.	1,503,000
Total Annual Cost	$4,066,000

1 Metric ton = 1.1 ton

other general and utility costs have been estimated at 50 percent of the scaled-up and updated costs of the MSW plant.

Inflation, overhead and contractor's profit in the present plant has been based on the same fraction of the total design, site development and construction costs as in the previous estimate.

Public financing at 6 percent for 15 years has been assumed in the annual cost summary in Table 40. The total capital cost in the previous estimate amounted to 3.98 times the equipment cost and, in the new estimate for the larger plant, the ratio is 3.89. This ratio normally decreases more with the size of the plant but, in this case, there is very little change because the installation costs were estimated at the same ratio. This is a conservative approach and the actual capital cost may be slightly less.

The total electric power required had been estimated at 135 x 200, or 27,000 KWH per day (9.72 x 10^{10} Joules/Day). A 1,000 HP (987 Metric HP) shredder would be operated only eight hours and thus consumes about 6,000 KWH per day (2.16 x 10^{10} Joules/Day). This is 22.2 percent of the total power and gives a size reduction to less than 3" (7.62 cm.). The major portion of the power is required for the size reduction to 14 mesh and will be several times the initial shredding requirement. Allowing a small amount for the air classification and metals removal, the power requirement for the organic waste treatment was estimated at 60 percent of the amount given in the previous estimate which processed 104 tons (94.6 metric tons) per day of dry organic feed. This value was prorated up to 1000 (909.1 metric tons) tons per day and the power costs were increased by the engineering cost index ratio. Power costs in the present estimate are 1.6 cents per KWH (3.6 x 10^6 Joules).

Other utilities are heat and cooling water and these would all be consumed in the pyrolysis step. The total amount is, therefore, included as scaled-up on the basis of the total organic feed and the engineering cost index.

An appreciable amount of labor in a municipal-waste pyrolysis plant would be devoted to solids handling, particularly for the glass and metals recovery. On the other hand, the feed preparation, i.e., grinding, etc., would be continuous and most of the products from the pyrolysis and asphalt fractionation are liquid, requiring minimum labor for operation and transfer. It has been assumed that only half of the labor in the previous estimate is concerned with these steps and the operating labor would be independent of plant size. However, the feed and char handling is greater in the larger plant so the labor requirements of the wood-waste pyrolysis plant will amount to 60 percent of the labor of the municipal-waste pyrolysis plant. The labor cost was also increased by the engineering cost index.

Maintenance costs will vary proportional to the cost of the equipment, i.e., the .6 power of the

TABLE 41

SUMMARY OF COST ESTIMATE

Item	Cost
Vessels	
Fractionator	$ 35,000
Flash Drum	5,000
Heat Exchangers (Air Cooled)	
Vacuum Flash Condenser	5,000
First Intercooler	10,000
Second Intercooler	9,000
Third Intercooler	20,000
Pumps	
Four Required @ $2,000 Each	8,000
Total Equipment Cost	$ 82,000
Total Installed Cost	$400,000

capacity, and this has also been increased by the engineering cost index. It has been assumed that half the maintenance cost in an MSW plant is due to the organic feed preparation and pyrolysis steps. These same factors were applied to the land rent and the residual transfer and disposal items.

The cost estimate for the complete fractionation unit is summarized in Table 41. The investment cost will be about $400,000. Recovery of pyrolysis oil from the vapor without fractionation would utilize a single-stage quench involving essentially the same total heat exchange surface, a quench tower of the same diameter as the fractionator but less height and probably two pumps, one for recirculation and one for pyrolysis oil transfer. The cost of a single heat exchanger with the same total surface could be .5 and .6 times that of the multiple units in the fractionation plant and this same ratio would probably apply to the total investment, making the incremental cost of the fractionation plant about $200,000.

Applying the same cost-accounting procedures used by R. A. Lowe[84] for evaluating the economics of the St. Louis municipal solid-waste recovery plant, the incremental cost of fractionating binder from a pyrolysis plant would amount to $.32 per ton ($.352 per metric ton) with public financing, and $.50 per ton ($.55 per metric ton) with private financing. This represents the capital cost above and is based on the assumption that

TABLE 42

BITUMEN HYDROGENATION -

EQUIPMENT COST FOR PROCESSING RESID FROM 1000 TON/DAY PYROLYSIS PLANT

Reaction System	
4 - 300 Gal. Reactors - 800 psig.	$ 70,000
Catalyst Recycle System	
Resid Dissolving Tank	5,000
Settling Vessel	10,000
Disc Centrifuge, 12" diameter, 15 gpm liquid feed	25,000
Finishing Step	
Bitumen Stripping Column - 24 in. diameter, 12 trays	10,000
Vacuum Flash Tower - 10 in dia.	2,000
Heat Exchange Equipment:	
Preheater, 400 sq. ft.	10,000
Condenser, 300 sq. ft.	8,000
Reboiler, 400 sq. ft.	10,000
Vacuum Flash Condenser, 500 sq. ft.	2,000
Total Equipment Cost	$152,000
Total Installed Cost	$912,000

1 metric ton = 1.1 ton

Newton/m^2 = 14.45 x 10^{-5} [psig. + 14.7 psi.]

1 liter = 0.264 gallons

1 liter/sec. = 15.85 gpm.

1 cm. = 0.394 inch

1 m^2 = 10.76 sq. ft.

the fractionation column could be adequately automated so that it could be run with no additional operators. An additional operator would add more than twice the above costs to the asphalt processing charge and would be far less economical in a smaller plant such as the 100-200 ton/day (90.9 - 181.8 metric tons/day). Capital costs on this latter scale of operation would be more than $1.00/ton ($1.10/metric ton) of binder produced.

The low-temperature pyrolysis process, such as developed by the Georgia Tech Engineering Experiment Station, results in a gas stream of 550-600°F (287.8 - 315.6°C) and this may not be adequate for flashing off sufficient volatile material in the flash drum. In that case, it would probably be necessary to provide a small furnace to preheat the bottoms from the asphalt fractionator to above 700°F (371.1°C) before injecting it into the vacuum flash drum. This would increase the incremental cost of the asphalt recovery unit but presumably the saving in the initial pyrolysis step due to the lower operating temperature would cover this additional cost.

Table 42 shows projected cost of the bitumen hydrogenation equipment including four pressure reactors, the catalyst recovery units and finishing distillation equipment. Total equipment costs are projected at $152,000.

The total installed cost for the pyrolysis plant was in the range of 3.8 to 4.0 times the equipment cost. For a hydrogenation unit of the present size, this ratio will be about 6, making the installed cost of the hydrogenation plant $912,000. If subsequent development work indicates that the hydrogenation can be carried out equally well in a trickle-bed reactor, the cost of the first two sections of this plant would be reduced to about $40,000 to $60,000, depending upon the residence-time required and the total investment might be reduced to about $600,000.

Table 43 summarizes the annual operating and amortization costs for this hydrogenation step. Hydrogen consumption is based on laboratory data of 1 percent by weight of charge and the delivered cost of the small quantities required is $.40/lb. ($.88/kg.). Catalyst loss has also been taken as 1 percent of the charge per batch. This

TABLE 43

SUMMARY OF ANNUAL COSTS FOR HYDROGENATION OF BITUMEN RESIDUE FROM 1000 TON PER DAY PYROLYSIS PLANT

Item	Cost
Operating Costs	
Chemicals	
H_2	$ 228,000
Catalyst	340,000
Electric Power	2,000
Other Utilities	35,000
Labor	100,000
Maintenance	50,000
Land Rent	10,000
Residual Transfer and Disposal	10,000
Total Operating Cost	$ 775,000
Capital Cost	
Amortization of $900,000 15 years at 6 pct.	93,000
Total Annual Cost	$868,000

1 metric ton = 1.1 ton

may be reasonable for the multi-stage agitated reactor system shown, which duplicates current laboratory work. It is the largest single expense and would probably be reduced in a trickle-bed reactor, and provides additional incentive for future work on this approach to the hydrogenation reaction.

Power has been charged at 1.6 cents/KWH (4.44 x 10^{-7} cents/Joule) as in the previous estimates. Other utilities include heat at $1.0/MM BTU ($1.0/2.52 x 10^5 Cal.,kg.) and cooling at 20 percent of the heat cost. Labor corresponds to one man per shift. Other items have been prorated based on the capital investment. Capital costs have also been taken on the same basis as in the previous estimates. Also, consistent with the previous estimates, the operating costs have been calculated on the basis of 100 percent stream factor.

It is interesting to analyze these costs to determine the minimum operating cost if the hydrogenation were carried on a larger scale at a central location. The hydrogen cost amounts to $8.00/ton ($7.27/metric ton) and in a larger plant, which might justify its own hydrogen plant, this cost might be reduced to $5.00/ton ($4.55/metric ton). The catalyst cost on the basis of 1 percent loss per cycle amounts to about $12.00/ton ($10.91/metric ton) and, if sufficient life could be realized in a trickle-bed reactor, this might be reduced to a tenth of this value. Labor, rent, maintenance and amortization would also be reduced in a larger plant but power and utilities would not be affected.

The total net annual cost (Table 44) for a 1000-ton/day (909.1 metric ton/day), dry cellulosic-waste pyrolysis plant with fractionation and hydrogenation is $3,255,000 and, on the basis of a 100 percent stream factor, this amounts to $8.92 per ton ($8.11 per metric ton) of dry charge and $111.47 per ton ($101.34 per metric ton) of binder produced.

The cellulosic waste charged to the pyrolysis plant is assumed to contain about 32 percent water and it may vary to 55 percent, depending upon weather conditions and particle size. A yield of 13-14 percent oil on a dry basis may be expected and about 60 percent of this oil is recovered as bitumen. Thus, the yield of bitumen from the 1000 ton/day (909.1 metric ton/day) plant should average about 80 tons (72.7 metric tons) per day of bitumen. The char yield will be about 300 tons (272.7 metric tons) per day based on 30 percent yield from the dry weight of charge. Thus, the economics of a pyrolysis plant is more sensitive to obtaining a high price for the char than to upgrading the bitumen to asphalt binder material. A char value of $20/ton ($18.2/metric ton) will be equivalent to $6.00 per ton $5.46 per metric ton) of dry cellulosic waste charged to the pyrolysis plant, and this is over half the processing cost.

Char production rates would vary with the feed and its moisture content. Additional heat required to vaporize water could be obtained by combusting hot char and preheated air. The low sulfur content of the char makes it an ideal fuel with a heating value of about 9,000 BTU/lb. (4,972.4 Cal.,kg./kg.)[85]. The present estimate assumes that an average 50 percent of the char would be sold at $20/ton ($18.2/metric ton). Appendix C shows the relation between volume of char sales and net production cost of binder.

Light ends from the fractionation would amount to about 52 tons (47.3 metric tons) per day, or about 320 BPD (0.589 l/sec.) based on a projected heating value of 10,500 BTU/lb. (5,801.1 Cal.,kg./kg.), it is conservatively valued at $5/bbl. ($0.032/l). Although the volumetric heating value of this oil is only 60-70 percent of No. 6, its low sulfur content would be attractive for installations that lack stack gas-treating facilities.

These economics assume operation of the plant as a waste-disposal facility with feed available at no cost. This is justified in some circumstance since a dumping fee could be charged for disposal of nuisance wastes offsetting the cost of other wastes purchased at alternate value. The sensitivity of binder production costs to the value of the cellulosic-waste feed is shown in Appendix C.

TABLE 44

ESTIMATED COST OF PRODUCTION OF HIGHWAY BINDER via PYROLYSIS OF CELLULOSIC WASTE

Basis:

Capacity - 1000 ton waste/day
Operating Factor - 1.00
Production Rate -
80 ton/day binder
52 ton/day fuel oil
150 ton/day char

Capital Cost:

Pyrolysis/
Fractionation - $14,599,999
Hydrogenation - 912,000
Total Capital - $15,511,000

Chemicals	Annual Cost (Credit), $M	$/ton Binder
Hydrogen	228	
Catalyst	340	
Total Chemicals	568	19.45
Operating Costs		
Electric Power	904	
Other Utilities	495	
Labor	366	
Maintenance	812	
Residue Disposal	101	
Total Operating Costs	2,678	91.71
Overhead Expense		
Rents	92	
Capital Amortization	1,597	
Total Overhead Expense	1,689	57.84
Byproduct Credits		
Fuel Oil	(585)	
Char	(1,095)	
Total Byproduct Credit	(1,680)	(57.53)
Net Cost of Production	3,255	111.47

1 metric ton = 1.1 ton

CHAPTER VI

BINDER FORMULATION AND TESTING

Production of Test Samples

Charge Stock Preparation

Feed for the scaled-up hydrogenation of WPO was made by distilling virgin pyrolysis oil stock. Distillation studies showed that removal of 15 percent volume to weight gave a residue whose viscosity at 140°F (60°C) resembled that of the earlier sample labeled WPO-B. It was this sample which appeared to be best in the process study. Two distillations were made in large batch, Experiments 629 and 631. Results are shown in Figure 28. Although both runs finished reasonably similar to WPO-B in viscosity, each contained ca. 2/3 the amount of oxygen found present in WPOB-B. This lowered oxygen level apparently improved the solubility in toluene and Trichloroethylene compared with that of unmodified WPO-B. Properties of product prepared in Experiments 629 and 631 are shown in Table 45.

Preliminary Studies

Before preparing a pilot-plant batch of hydrogenated WPO, several small-scale hydrogenations were conducted in a 2 liter stirred autoclave in the usual manner described previously. Run conditions were 225°C x 750 psi. (5.19×10^6 Newton/m^2). Results of these studies are reported in Table 46. The properties of a sample of hydrogenate are summarized in Table 47. This sample was prepared by combining equal portions of the three products described in Table 46. Hydrogen uptake during the runs which lasted for two hours is shown in Figure 29.

The yields of hydrogenate following extraction by toluene and that following vacuum distillation to specified penetration were both greater that those yields for WPO-B. This is attributed mostly to the lower initial oxygen content. The lower oxygen content can result because this WPO sample was collected at a take-off point in the process where oxygen-rich volatiles were not as likely to be present.

Procedure

Hydrogenation was carried out in a 5 gallon (18.93 liter) reactor. The run procedure was similar to the one used earlier in hydrogenation runs conducted in a 2 liter stirred autoclave. The heat-up time of the large batch, however, was somewhat longer, as was the running time due to continued hydrogen uptake.

The autoclave was charged with 9,419 gm. of WPO and 576 gm. of Girdler catalyst 61-RS (reduced and stabilized Cobalt on Kieselguhr). The system was flushed several times with hydrogen before charging with several hundred psi. of hydrogen at room temperature. Additional hydrogen was added when reaching the reaction temperature, 225°C. Hydrogen was also added whenever pressure dropped by as much as 100 psi. (6.92×10^5 Newtons/m^2) below the nominal running pressure of 750 psi. (5.19×10^6 Newton/m^2). Figure 30 shows a plot of the uptake of hydrogen vs. reaction time which continued for five hours.

TABLE 45

PYROLYSIS OIL RESIDUE - PREPARATION AND PROPERTIES

Exp. Number	Charge (gms.)	$\frac{\text{Vol. Overhead}}{\text{Wt. Charge}} \times 100$	Final Topping Temp. °F	140°F Vis. of Residue, (CPS.)	C, pct.	H, pct.	O, pct.	ASTM Solubility			
								Acetone	Toluene	Ethanol	Trichloroethylene
629	19,550	15.8	330	1500	75.6	8.43	16.3	99%	90.1%	98%	99.7%
631	19,000	13.9	329	1600	75.5	8.2	14.9				
WPO-B	-	-	332	1180	68.8	8.5	22.9	98.2	ca. 0	-	ca. 0

$°C = (°F - 32) \times \frac{5}{9}$

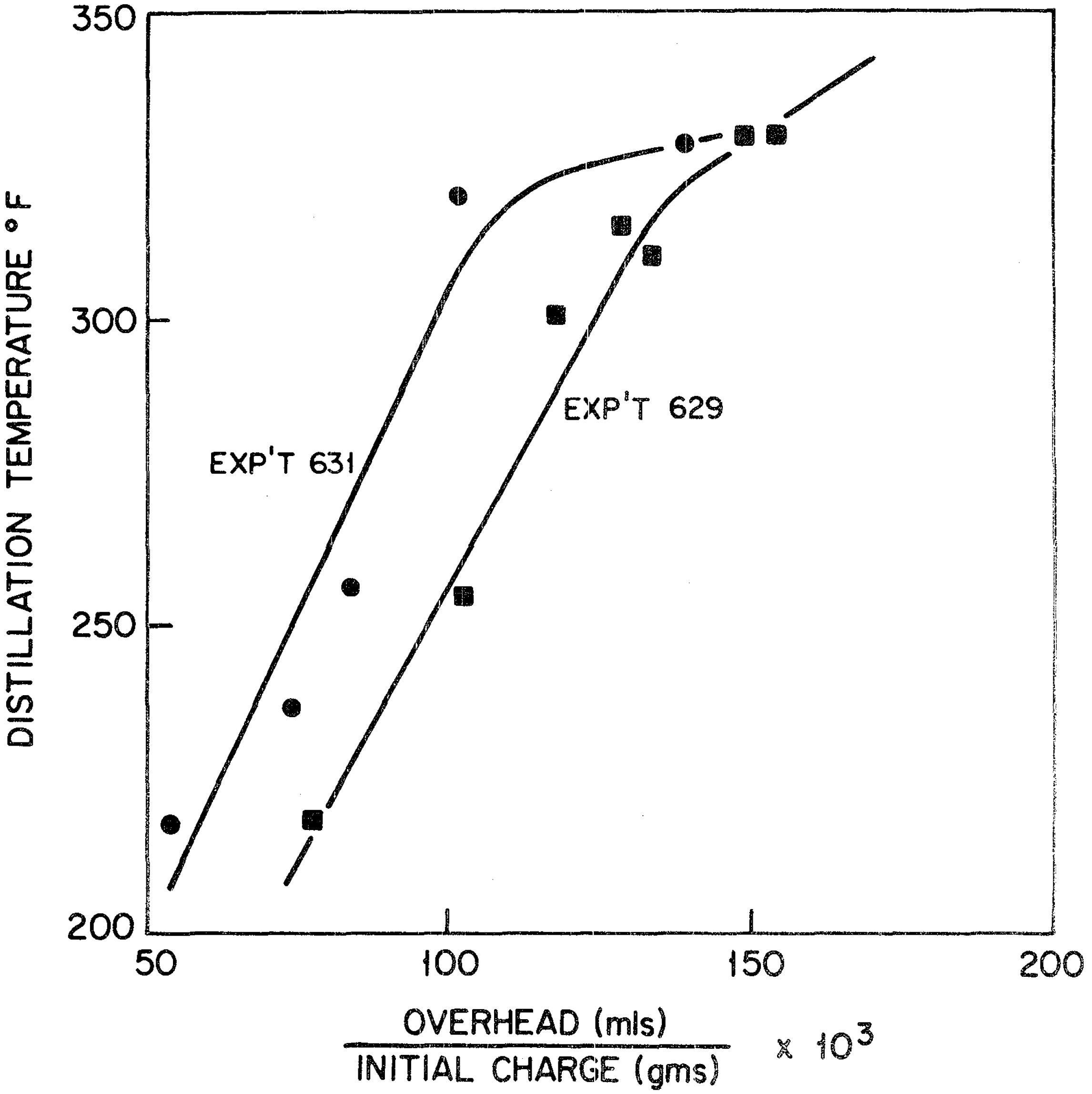


Fig. 28 Distillation of Pyrolysis Oil

°C = (F-32) x 5/9

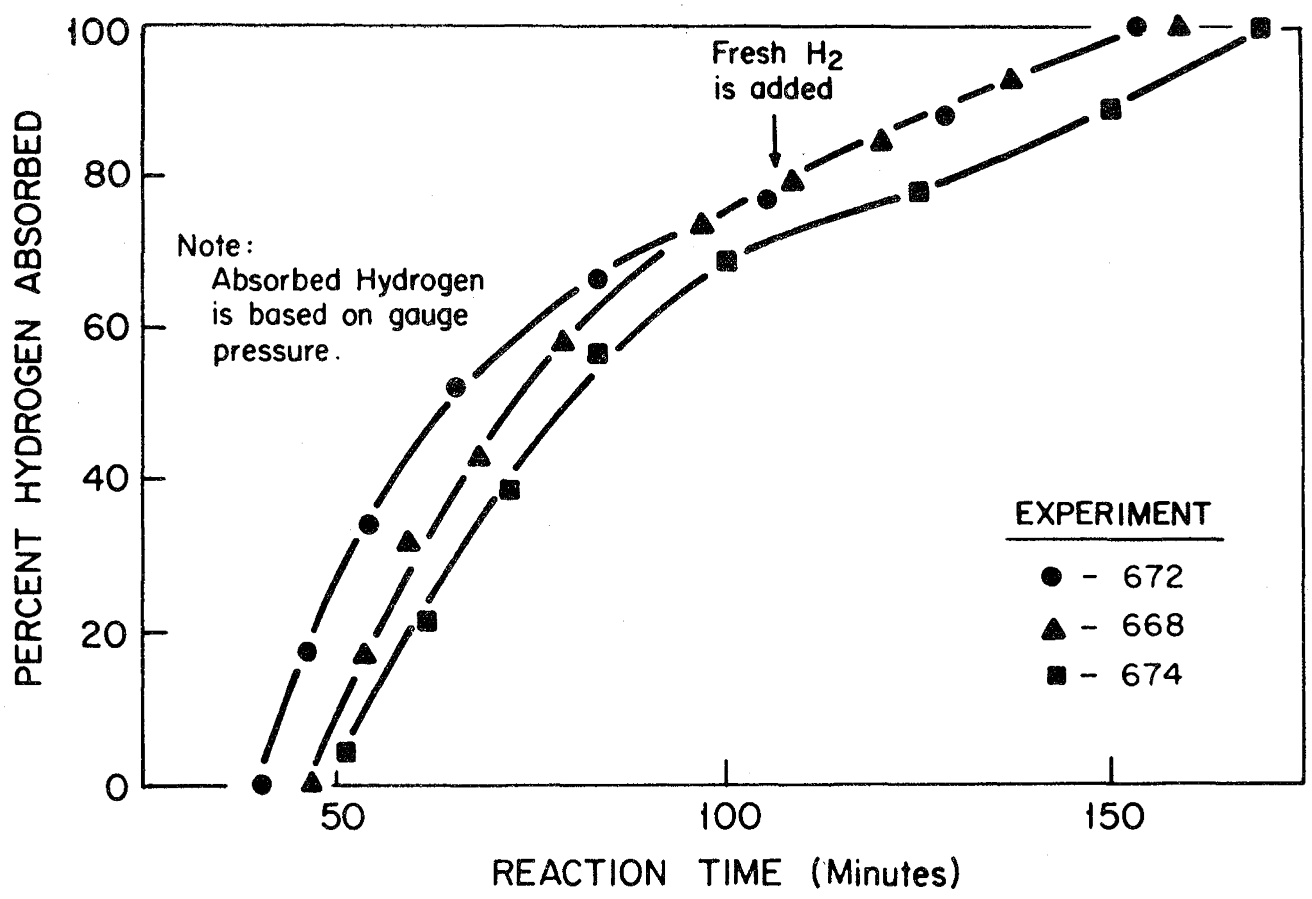
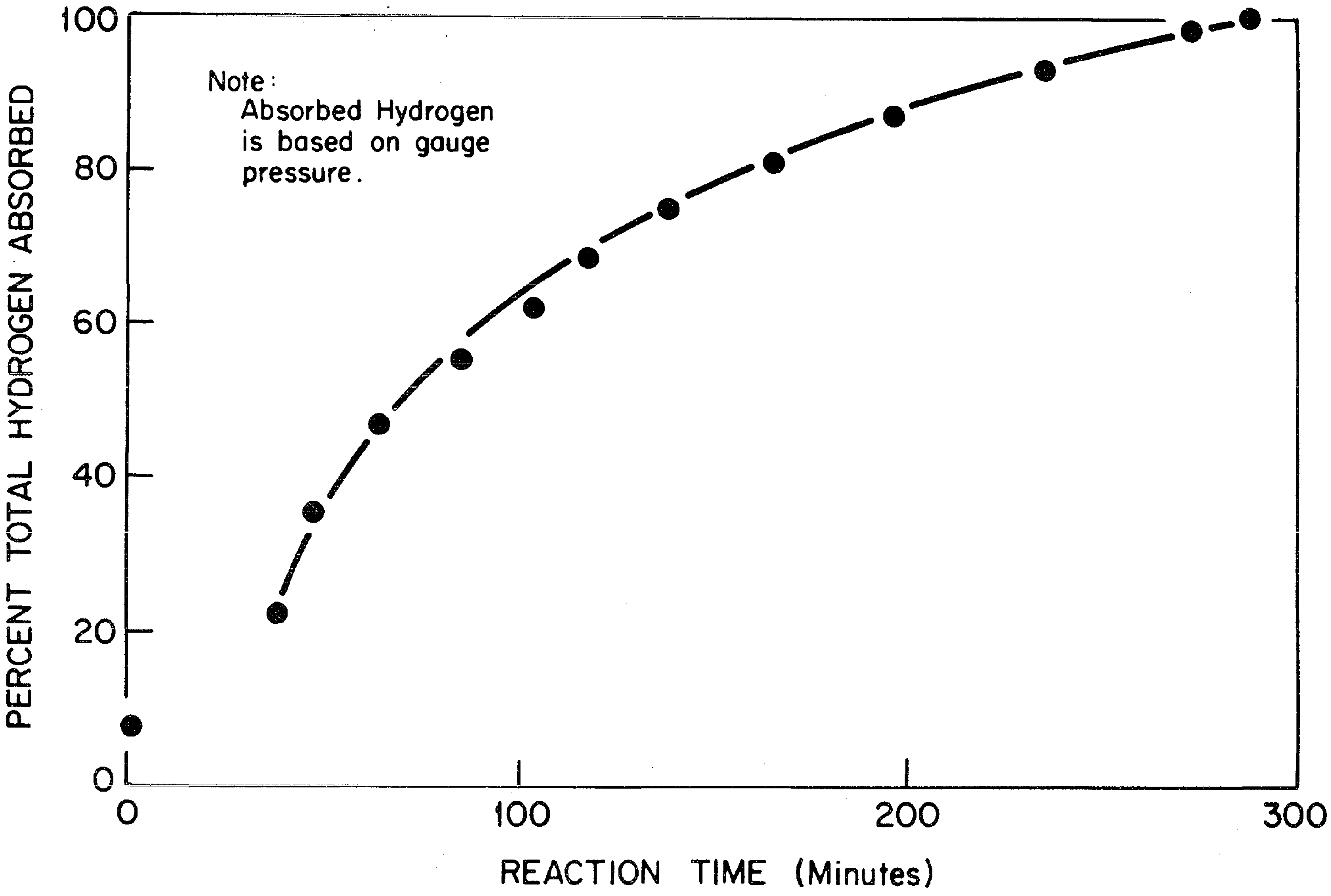


Fig. 29 Laboratory Hydrogenation of Pyrolysis Oil



Note:
Absorbed Hydrogen is based on gauge pressure.

Fig. 30 Hydrogenation of Pyrolysis Oil in 5-Gallon Reactor

TABLE 46

SUMMARY OF SCALE-UP STUDIES [a]

Experiment	Product Yield, pct. (Toluene Solubles)	Yield of Vacuum-Topped Product, pct.	Final Topping Temperature °F (1 atm.)	25°C Penetration
669 [b]	86.5	78.0	530	65
673 [b]	93.3	79.2	553	65
675	89.9	81.2	518	66

[a] Run conditions: 2 hours x 225°C x 750 psi.

[b] Replace most of the charged hydrogen with fresh charge after one hour.

°F 1 atm. psi.

$°C = (F-32) \times \frac{5}{9}$

$\text{Newton/m}^2 = 14.45 \times 10^{-5}$ psi.

$1.02 \times 10^5\ \text{Newton/m}^2 = 1$ atm.

TABLE 47

PROPERTIES OF HYDROGENATE (LABORATORY SCALE)

Ring and Ball Softening Temp.		48°C
Penetration @ 25°C		75
Viscosity at 60°C		9,400 cPs.
Viscosity at 135°C		30 cPs.
Density		1.08
ASTM Solubility -	Acetone	100 pct.
	Toluene	99 pct.
	Ethanol	90.7 pct.
	Trichloroethylene	99.9 pct.
C, pct.		76.5
H, pct.		8.8
O, pct.		17.1 (14.7)[a]

[a] Corrected to sum analysis to 100 percent

The hydrogenated product was stripped of toluene following extraction and then vacuum distilled at 119°C x 0.4 mm. [equivalent to 622°F (327.8°C) at 1 atmosphere (1.02×10^5 Newton/m^2)]. Overall yield of product topped to pen was 77 percent. Properties of the hydrogenated product are shown in Table 48.

Characterization of Binders

Preparation of Test Binders

Three binders were submitted to Valley Forge Laboratories for Marshall Stability testing. They included the reference sample, Sun-Tulsa 85-100 AC and two experimental blends containing hydrogenate at concentrations of seven and twelve wt. percent. The blends contained hydrogenate prepared in the five gallon (18.93 liter) autoclave. All blends were prepared by stirring in glass under an inert gas blanket for 1/2 hour at 110°C.

The concentrations were selected to provide broad coverage over the range up to ca. 15 percent hydrogenate; blend concentration was limited because of softening effects on AC and viscosity reduction. Softening occurred even though both neat components exhibit pens between 70-75. Also, there was a noticeable percent weight loss following TFO in blends containing more than 15 weight percent of hydrogenate.

Chemical and Physical Properties

The initial properties of all test binders are summarized in Table 49. Also included are the properties of these same binders following TFO at 162°C x 5 hours. The chief properties to change following TFO, which are readily attributable to the presence of hydrogenate, are: reduced ductility and pen and a heightened viscosity increase. The API-Vis/Temp. plot, (Figure 31), shows more similarity among binders following TFO than before TFO.

Using the ratio Vf/Vi to represent the relative viscosity increase following TFO, (Table 50), binder containing 12 percent of hydrogenate shows the greatest increase at both viscosity-testing temperatures.

Matrecon Inc. characterized the reference Sun-Tulsa asphalt twice, first in April 1978 (Sample M-25) and again in August 1979 (Sample M-26) when three experimental hydrogenate blends were also evaluated. These three binders are referred to as M-27, M-28 and M-29. Hydrogenate concentration in M-27 and M-28 was seven and twelve percent respectively; Sample M-29 contained 25 percent of hydrogenate whose initial pen was below 5 to avoid excessive softening of the asphalt.

TABLE 48

PROPERTIES OF HYDROGENATE (PILOT PLANT)

Softening Temperature, °C	49-51
Penetration at 25°C	64-82
Viscosity at 60°C	6,300 cPs.
Viscosity at 135°C	25 cPs.
Density	1.10
ASTM Solubility:	
Acetone -	99.7 pct.
Toluene -	93.6 pct.
Ethanol -	94.9 pct.
Trichloroethylene -	99.9 pct.
C, pct.	77.6
H, pct.	9.2
O, pct.	13.0

$°C = (F-32) \times \frac{5}{9}$

TABLE 49

PROPERTIES OF TEST BINDERS -
INITIAL AND AFTER THIN FILM OXIDATION

	106-A		106-B		106-C	
	Sun-Tulsa 85-100 AC		7 pct. Hydrogenate		12 pct. Hydrogenate	
	Initial	After TFO	Initial	After TFO	Initial	After TFO
Weight Loss, grams (ca. 50 gm. charge)	-	+0.05	-	0.36	-	0.72
Pen 25°C	70	52	90-97	35	122-126	37
Density	-	0.996	-	1.002	-	1.005
Softening Temp. °C	50	51	48	55	46	52
C, pct.	87.4	87.7	84.5	86.5	83.6	87.1
H, pct.	11.1	11.5	11.4	11.3	11.1	11.4
O, pct.	0.68	0.77	2.9	1.4	4.1	1.47
Viscosity :						
140°F Poise	1772	3647	819	4551	543	3882
275°F KV	407	514	271	466	223	408
Solubility:						
Toluene	-	ca. 100%	-	99.8	-	99.2
Trichloroethylene	-	99.7	-	99.8	-	99.4
Ductility	150+	150+	150+	80	150+	21

$°C = [°F - 32] \times \frac{5}{9}$

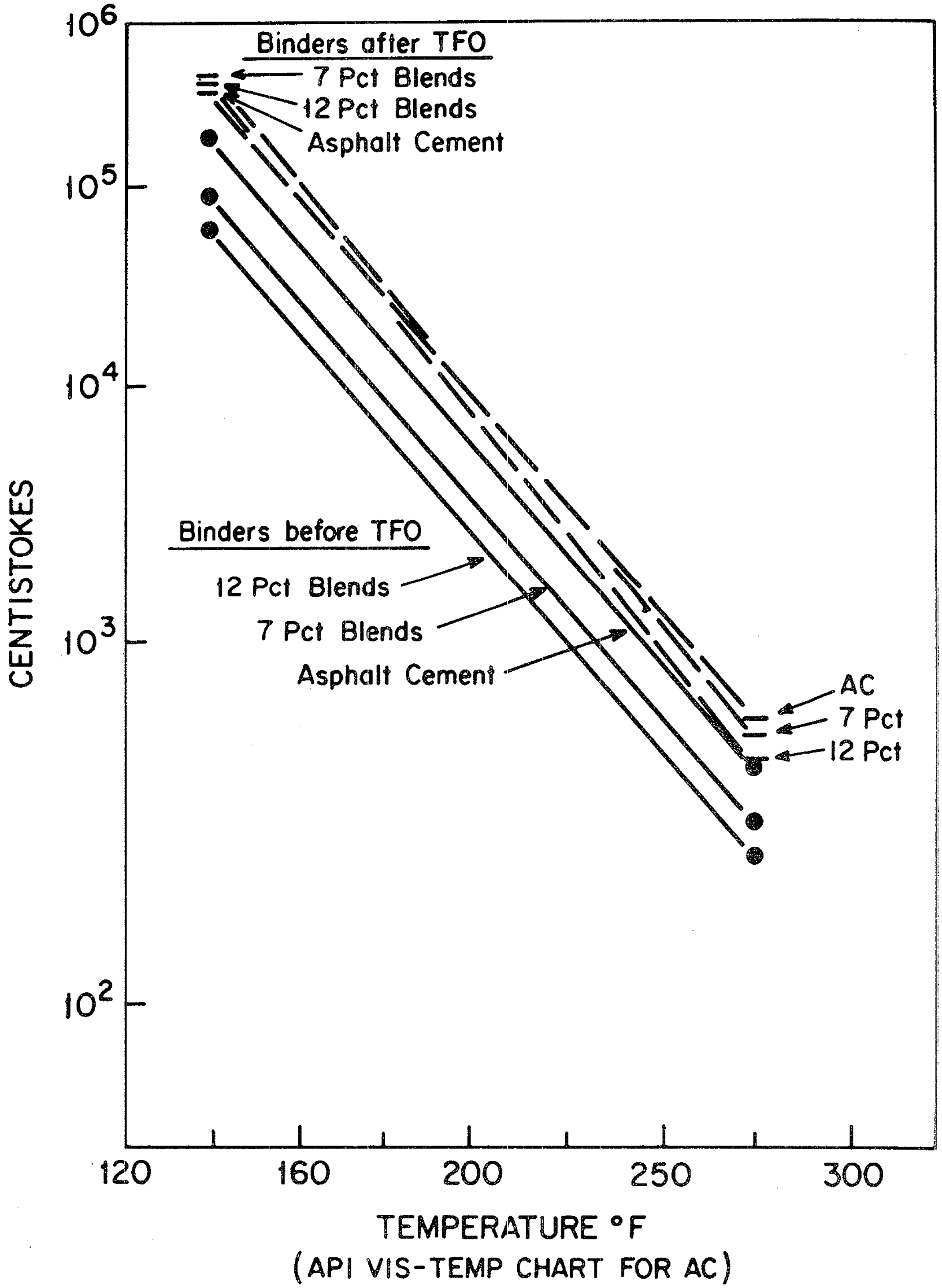


Fig. 31 The Vis-Temp Character of Test Binders Before and After Thin Film Oxidation

°C = (F-32) × 5/9

TABLE 50

EFFECT OF THIN FILM OXIDATION ON VISCOSITY

Binder	$\frac{\text{Vis., After TFO}}{\text{Vis., Before TFO}}$ 140°F	275°F
Seven Percent Hydrogenate	5.56	1.72
Twelve Percent Hydrogenate	7.15	1.83
Reference AC	2.06	1.26

$°C = (°F - 32) \times \frac{5}{9}$

All Matrecon testing results are included in Appendix D. A summary of important results are reported in Table 51.

The incorporation of hydrogenate in AC reduced the binder's net paraffinic character based on the gradual increase in the N/P ratio with increased hydrogenate content. Also, as was reported earlier, hydrogenate softens asphalt, as judged by decreased penetration values at 25°C and reduced viscosities at 60°C.

Because the hydrogenate used in formulation M-29 was more pitch-like than that used in M-27 and M-28, its binder properties are sometimes influenced in unexpected directions. For example, the percent weight reduction of M-29 in TFO is not as great because more overhead was removed during the finishing process.

A comparison of all data in Appendix D reported for the two reference asphalts, M-25 and M-26 shows two distinct differences between them. They include for M-26, the shelf-aged sample, a slightly greater refractive index of the paraffinic fraction and reduced mole weight of the asphaltene fraction. Since the latter is a number average mole weight, it is sensitive to the presence of any low mole weight material which may have formed during aging. The differences observed between M-25 and M-26 in pellet abrasion are not important at the observed abrasion levels.

Despite the differences reported between M-25 and M-26, Matrecon found that M-26, (represent-

TABLE 51

SUMMARY OF MATRECON TEST RESULTS ON REFERENCE AC AND BLENDS

Property	M-25	M-26	M-27	M-28	M-29
Hydrogenate, pct.	0	0	7	12	25
$\frac{\text{Nitrogen Bases}}{\text{Paraffins}}$ (N/P)	1.02	1.02	1.22	1.41	1.81
Vis. 60°C (P)	1833	1885	860	694	504
Pen 25°C	80	82	109	125	129
Weight Change in Thin Film Oven Test, pct.	+0.04	+0.01	-0.73	-1.26	-0.76

ing the AC used in all experimental blends), matched two other Data Bank Asphalts in finger print parameters and a greater number of asphalts in Behavior parameters. The addition of hydrogenate to the reference asphalt reduced the incidence of this type of property match. The seven percent blend matched some asphalts in only the Behavior parameters while the twelve percent blend did not match any of the asphalts listed in the Data Bank. This is very nearly the case for M-29 which contained 25 percent of the pitch-like hydrogenate. Its properties matched several Data Bank Asphalts in Behavior Parameters only.

Toxicity Study

The caffeine number CN [86] represents a measurement aimed at assessing a compound's carcinogenicity based upon the UV character of its aqueous caffeine extract. It is sensitive, however, to the presence of excessive quantities of oxygen. The CN of common petroleum fractions range up to slightly more than 1.0 reported for Catalytic Clarified Oil. However, fluid cat-cracking resdiuum has a CN value of 1.57. By contrast, the CN for coal tar is 15.5.

The CN of several samples of pyrolysis oil were measured at different stages of treatment. Results are shown below in Table 52.

The rather high CN value observed for the sample of as-received pyrolysis oil may be due to the presence of volatile water-soluble oxygenated compounds. The CN of the charge stock to hydrogenation is roughly mid-way in value between the values of petroleum products and coal tar. This value is reduced upon hydrogenation. The CN of the 10 percent blend of hydrogenate in AC exceeds the usual CN values of petroleum-based products.

Mixture Performance Evaluation

Marshall Stability

The Marshall stability and flow values of the three binders were measured by Valley Forge Labs (VFL) according to ASTM-D-1599. All Marshall testing was conducted on specimens preheated to 140°F (60°C). Specific gravity measurements were made on compacted laboratory test specimens according to ASTM Procedure C-127.

The test program involved three paving mixtures which included: a wearing surface mix, a binder course, and a bituminous concrete base course. The aggregates chosen for this program included:

(1) A granitic gneiss from General Crushed Stone, Glen Mills, Pa.

(2) A limestone from McCoy Quarry, Bridgeport, Pa.

(3) Sand and gravel from Warner Company, Morrisville, Pa.

The gradations used in each of the three paving mixtures are reported in detail in Appendix D. Nearly all test values are located at the midpoint of the range specified by PennDot ID-2A requirements for the wearing surface and binder course. In the case of the base course aggregate, the size distribution favored larger sizes within PennDot's BCBC spec. The Appendix also includes percent air-voids calculated for those mixtures whose stabilities exceeded PennDot requirements. According to VFL, air voids should be between 3-5 percent to be considered acceptable.

Usually, five asphalt contents at one-half percent increments are recommended for test in the Marshall mix design method. In the interest of efficiency, however, only three asphalt contents were tested. But in the course of testing, the practice of limiting binder to three contents sometimes complicated efforts to locate Marshall stability maxima.

For each paving mixture, the ranges of asphalt contents selected were determined by a series of preliminary Marshall tests serving to identify the approximate percent range of asphalt con-

TABLE 52

THE CAFFEINE NUMBER OF PYROLYSIS OIL PRODUCTS

Sample History	Caffeine Number
Pyrolysis Oil - as received	23.7
Pyrolysis Oil Following atmospheric distillation	9.83
Hydrogenate distilled to pen	7.08
10 percent blend of hydrogenate in AC 85-100	3.20
AC 85-100	0.144

TABLE 53

COMPARISON OF MARSHALL TEST RESULTS FOR WEARING SURFACE MIXTURES

Description of Mix	Asphalt Content[1] (Percent)	Granitic Gneiss		Limestone		Sand and Gravel	
		Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)
Control	5.0	1,622	7	1,367	11	792	8
	5.4	1,130	7	1,069	12	758	7
	5.8	1,409	12	N.T.	N.T.	1,032	8
7 Percent Blend	5.0	1,707	9	1,486	12	1,000	10
	5.4	2,006	10	1,172	13	1,112	10
	5.8	1,844	7	699	12	776	6
12 Percent Blend	5.0	1,951	7	1,245	11	1,150	11
	5.4	1,342	7	1,162	14	624	9
	5.8	1,513	7	1,000	17	701	6

NOTE: Marshall stability of at least 1200 pounds and Marshall flow between 6 and 16 for wearing surface mixtures as required by PennDOT Form 408 specifications.

[1] Expressed as percent by weight of aggregate in mix.

[2] Represents average of three specimens tested at each asphalt content.

N.T. indicates no test performed at that asphalt content.

1 kg. = 2.20 pounds

1 cm. = 0.394 inches

TABLE 54

COMPARISON OF MARSHALL TEST RESULTS FOR BINDER COURSE MIXTURES

Description of Mix	Asphalt Content[1] (Percent)	Granitic Gneiss		Limestone		Sand and Gravel	
		Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)
Control	4.2	572	13	1,496	13	507	12
	4.5	750	13	1,127	13	N.T.	N.T.
	4.8	870	9	1,003	18	Failed in bath	
	5.0	N.T.	N.T.	726	16	N.T.	N.T.
	5.4	N.T.	N.T.	780	33	N.T.	N.T.
7 Percent Blend	4.2	515	13	988	11	134	12
	4.5	454	13	1,111	10	N.T.	N.T.
	4.8	344	14	1,157	12	357	12
	5.0	N.T.	N.T.	726	16	N.T.	N.T.
12 Percent Blend	4.2	N.T.	N.T.	1,090	9	523	11
	4.5	537	10	1,051	11	N.T.	N.T.
	4.8	746	9	975	14	591	10

NOTE: Marshall stability of at least 1000 pounds and Marshall flow between 6 and 16 for binder course mixtures as required by PennDOT Form 408 specifications.

[1] Expressed as percent by weight of aggregate in mix.

[2] Represents average of three specimens tested at each asphalt content.

N.T. indicates no test performed at that asphalt content.

1 kg. = 2.20 pounds
1 cm = 0.394 inches

TABLE 55

COMPARISON OF MARSHALL TEST RESULTS
FOR BASE COURSE MIXTURES

Description	Asphalt Content[1] (Percent)	Granitic Gneiss		Limestone		Sand and Gravel	
		Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)	Marshall Stability[2] (Pounds)	Marshall Flow[2] (.01 Inch)
Control	3.2	N.T.	N.T.	540	12	N.T.	N.T.
	3.4	780	9	635	12	627	14
	3.6	N.T.	N.T.	575	14	N.T.	N.T.
7 Percent Blend	3.2	627	9	593	9	N.T.	N.T.
	3.4	672	11	609	13	344	11
	3.6	N.T.	N.T.	493	12	N.T.	N.T.
12 Percent Blend	3.2	758*	11*	412	10	Failed in bath	
	3.4	N.T.	N.T.	659	13	N.T.	N.T.
	3.6	602*	15*	387	11	Failed in bath	

NOTE: Marshall stability of at least 700 pounds and Marshall flow between 6 and 16 for bituminous concrete base course mixtures as required by PennDOT Form 408 specifications. For aggregate-bituminous base course mixtures, Marshall stability of at least 500 pounds and Marshall flow between 6 and 16 is required.

[1] Expressed as percent by weight of aggregate in mix.

[2] Represents average of three specimens tested at each asphalt content.

N.T. indicates no test performed at that asphalt content.

*Average based on only two Marshall plugs tested.

1 kg. = 2.20 pounds

1 cm. = 0.394 inches

TABLE 56

SUMMARY OF DYNAMIC TEST PROCEDURES

TEST	SAMPLE SIZE	DESCRIPTION OF TEST
1. Static Indirect Tensile Test.	Molded Specimens: 4" Diameter X 2" Thick	• Samples are compressed along their diameter. Tensile failure occurs perpendicular to diameter. (See Figure 44).
2. Fatigue Life and Resilient Modulus.	Molded Specimens: 4" Diameter X 2" Thick	• Apply load for 0.1 sec./relieve for 0.9 sec., T = 70°F. • Pre-condition for 1,000 cycles at test load of 15 psi, 22.5 psi or 30 psi; Compute resilient modulus. • Resume repetitive loading and measure no. cycles to failure.
3. Permanent Deformation.	Test Specimen: 4" Diameter X 6" Height Cored From Molded Sample: 8" Diameter X 6" Height	• Sample loaded axially at 22.5 psi, T = 40°F, 70°F, 100°F. (See Figure 45). • Apply load for 0.1 sec., relieve for 0.4 sec. • Measure compressive strain over the sample's half; compute modulus.
4. Incremental Creep Strain Test.	Test Specimen: 4" Diameter X 6" Height Cored From Molded Sample: 8" Diameter X 6" Height	• Pre-condition for 1,000 cycles at 22.5 psi and 70°F (apply load for 0.1 sec., relieve for 0.4 sec.). Measure strain and modulus at 70°F. (Sample loaded axially). • Match duration of 22.5 psi load and rest period then measure modulus. This is done after 1, 10, 100, and 1,000 sec.

$°C = (°F - 32) \times \frac{5}{9}$

$\text{Newton/m}^2 = 14.45 \times 10^{-5}$ psi sidered to be adequate for proper blending and particle coating. Following preliminary testing, it was decided that optimum asphalt contents for the three paving mixtures would probably fall within the following ranges:

Wearing Surface -
5.0 to 5.8 weight percent of asphalt

Binder course -
4.2 to 4.8 weight percent of asphalt

Base Course -
3.2 to 3.6 weight percent of asphalt

In the case of binder course testing, some additional measurements were made at higher percents of asphalt.

The results of Marshall stability measurements made on the three test binders are summarized in Tables 53, 54, and 55 for wearing, binder, and base course paving mixtures respectively.

PennDot criteria for wearing mixtures specifies that Marshall stability should be at least 1200 lb. (545.5 kg) and that flow should be between 6 and 16 hundredths inches (1.52×10^{-1} and 4.06×10^{-1} cms.). Results of Marshall stabilities for wearing surface mixtures show that requirements are met easily by the Granitic aggregate but are barely met by limestone at low binder content. Sand and gravel do not meet these requirements at the binder levels tested. For the limestone mixtures, the data show that stability maxima were not bracketed as intended, and suggest that maxima are probably located at binder levels less than those tested where reduced flow would also be expected. Where Marshall stabilities exceed the 1200 lb. (545.5 kg.) load requirement, there does not appear to be a significant difference between binders. Therefore, at least 12 percent of hydrogenate can effectively replace AC in wearing mixtures.

In the case of binder course mixtures which are reported in Table 54, only Limestone aggregate exceeded PennDot's 408 spec of 1000 lb. (454 kgs) minimum Marshall load and flow of between 6 and 16 hundredthes inches (1.52×10^{-1} and 4.06×10^{-1} cms.). No large property differences are observed between AC and the two experimental binders at 4.5 weight percent binder and above. There is an exception at 4.2 weight percent where the reference binder appears to be much better.

Finally, the test results of base course mixtures, shown in Table 55, indicate that stabilities are similar for granitic gneiss and limestone mixtures at all binder levels tested. In all of these cases, stabilities ranged from slightly less to considerably below PennDot's 700 lb. (318 kg.) load requirement for bituminous concrete base course mixtures. It should be noted that the aggregate mixture was used on the coarse side. It is believed that the presence of additional fines would raise stabilities which are near 700 lb. (318 kg.) to greater values.

Dynamic Testing

Review of all Marshall data, led to the selection of a wearing mixture containing granitic gneiss at the 5 percent binder level for further dynamic testing at Austin Test Labs.

Table 56 summarizes all tests conducted by Austin

TABLE 57

INDIRECT TENSILE STRENGTHS OF WEARING SURFACE MIXTURES*

Hydrogenate in Binder, wt. pct.	Indirect Tensile Strength** psi
0	87
	95
7	87
	87
12	73
	73

*Contains Five weight percent of binder.

**Indirect Tensile Strength = $0.153 \frac{P}{h}$. P is the applied load at failure in pounds and h is the initial height in inches (See Figure 44).

1 kg. = 2.20 pounds

1 cm. = 0.394 inches

Test Laboratory on the paving mixture. Generally, binder properties either were not effected by the addition of hydrogenate to AC or dropped slightly as a result of this addition.

The tensile strength decreased slightly with an increase in hydrogenate content as shown in Figure 32 and Table 57. The fatigue results are shown in Figure 33. Only the composition containing 12 percent hydrogenate declined in the expected linear manner. At the highest loading, the samples containing hydrogenate performed somewhat poorer than AC.

The scatter in resilient modulus, shown in Table 58, makes it difficult to judge a clear-cut effect due to hydrogenate. However, no significant deficiencies are apparent due to the presence of the hydrogenate.

Permanent deformation results are shown in Figures 34, 35, and 36 for 40°F (4.4°C), 70°F, (21.1°C), 100°F (37.8°C) respectively. At 70°F, with all data grouped in a tight band, there was essentially no effect produced by adding hydrogenate to AC. At 100°F, the slight in-increase in strain at greater number of loading cycles may reflect the tendency of hydrogenate to soften AC. At 40°F accumulated strain increases with the number of cycles as expected. But any significant property increase or decrease due to the addition of hydrogenate is not clearly evident.

Figure 37 summarizes the incremental creep strain tests. Results are consistent with those of other tests, i.e., the incorporation of hydrogenate did not produce either a significant benefit or reduction in the properties of the reference AC.

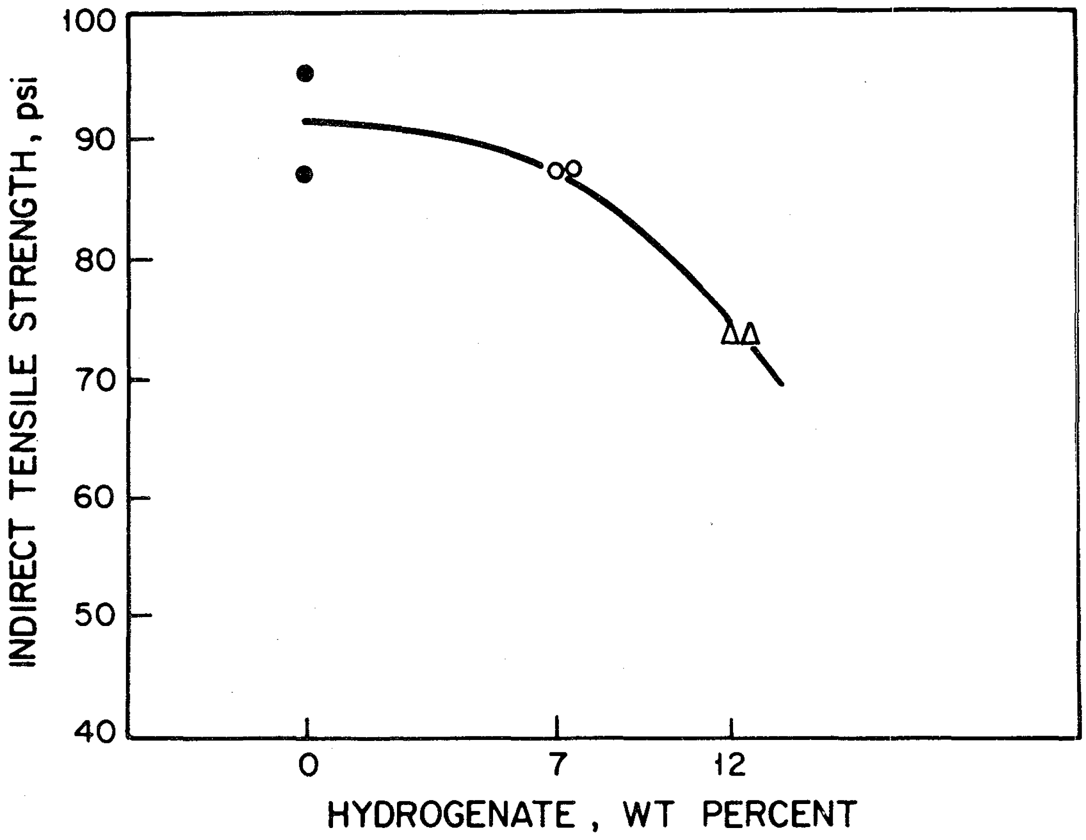


Fig. 32 Effect of Hydrogenate Content on Indirect Tensile Strength

Newton/m^2 = 14.45 x 10^{-5} psi

TABLE 58

WEARING SURFACE MIXTURES* - FATIGUE TEST RESULTS

Stress Level, psi	Hydrogenate in Binder, wt. pct.					
	0		7		12	
15.0	N_f = 536,620 E_r = 252,500	N_f = 585,200 E_r = 180,400	N_f = 547,464 E_r = 265,800	N_f > 585,600** E_r = 229,600	N_f = 432,260 E_r = 420,800**	N_f > 650,000** E_r = 265,800
22.5	N_f = 17,713 E_r = 270,500	N_f - 10,905 E_r = 445,000***	N_f = 90,213 E_r = 210,000	N_f = 100,903 E_r = 270,500	N_f = 6,823 E_r = 157,800	N_f = 7,512 E_r = 157,800
30.0	N_f = 12,243 E_r = 280,000	N_f = 14,700 E_r = 220,000	N_f = 5,240 E_r = 210,400	N_f = 7,085 E_r = 421,000***	N_f = 11,585 E_r = 250,000	N_f = 9,058 E_r = 315,600

*Contains five weight percent of binder.

**Did not fail.

***High Modulus values may be in error.

Newtons/m^2 = 14.45 x 10^{-5} psi.

LEGEND:

N_f = No. of Cycles to Failure

E_r = Resilient Modulus, psi.

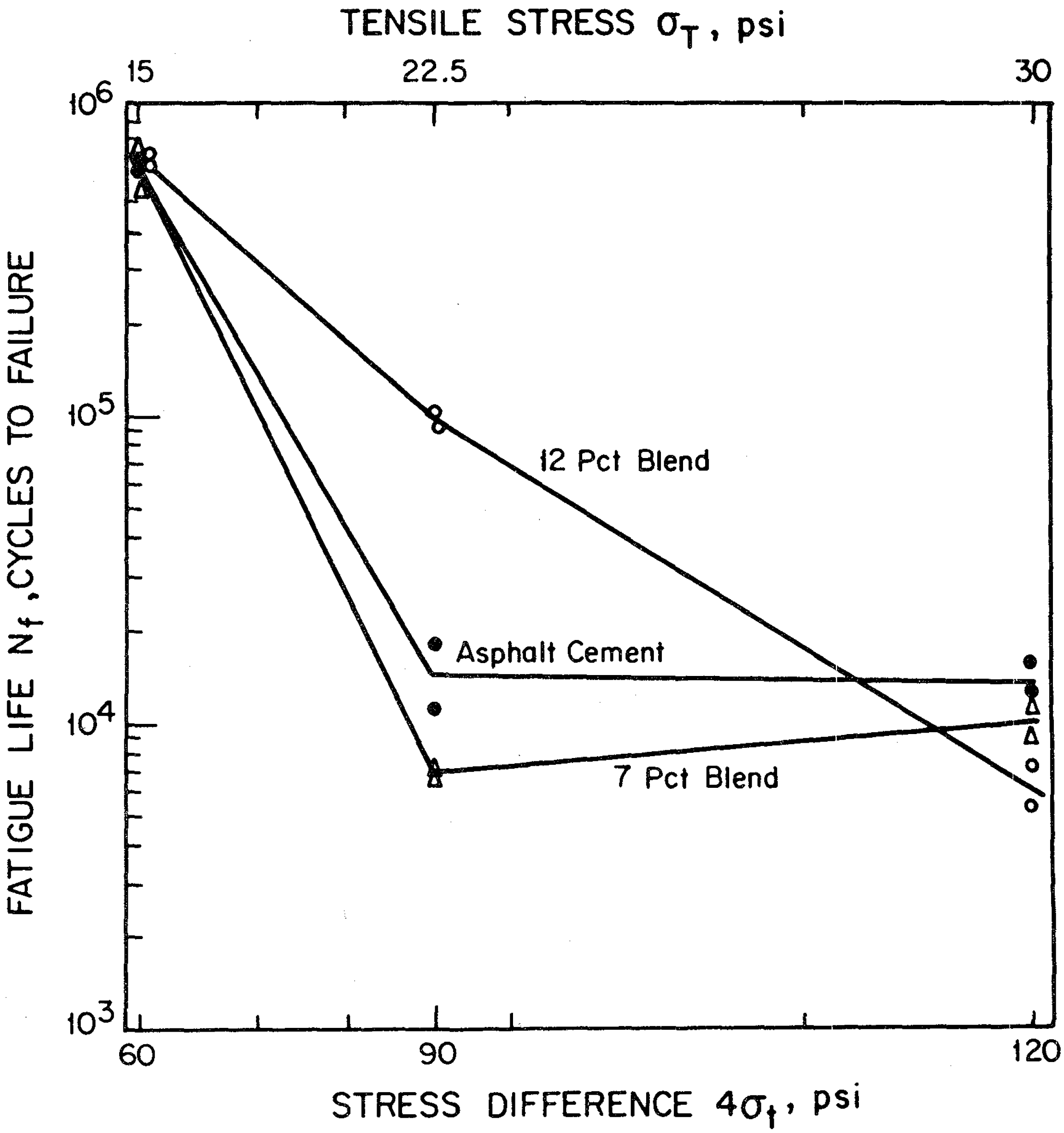


Fig. 33 Effect of Hydrogenate Content on Fatigue Life

Newton/m^2 = 14.45 x 10^{-5}psi

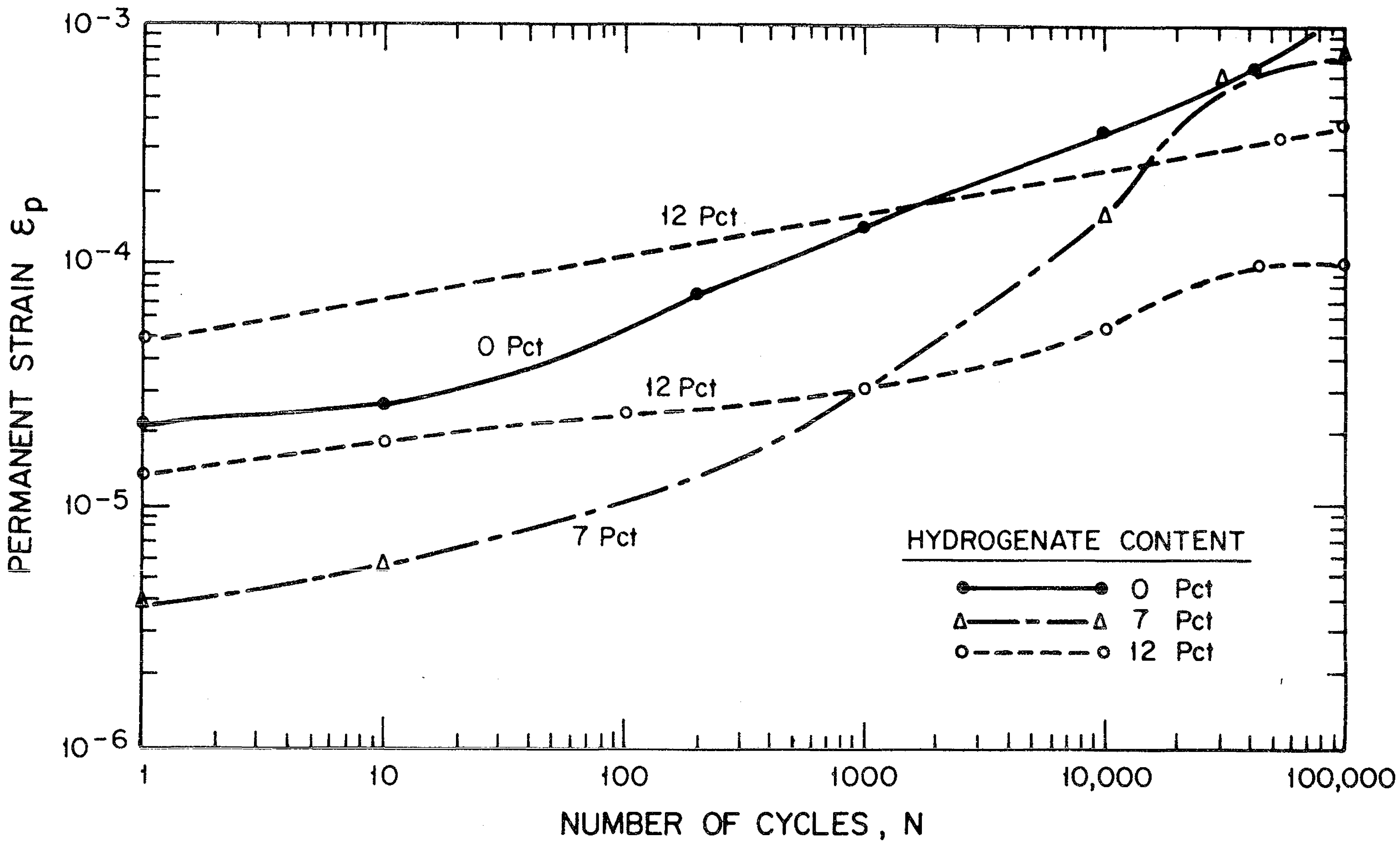


Fig. 34 Permanent Strain Results at 40°F

°C = (F-32) x 5/9

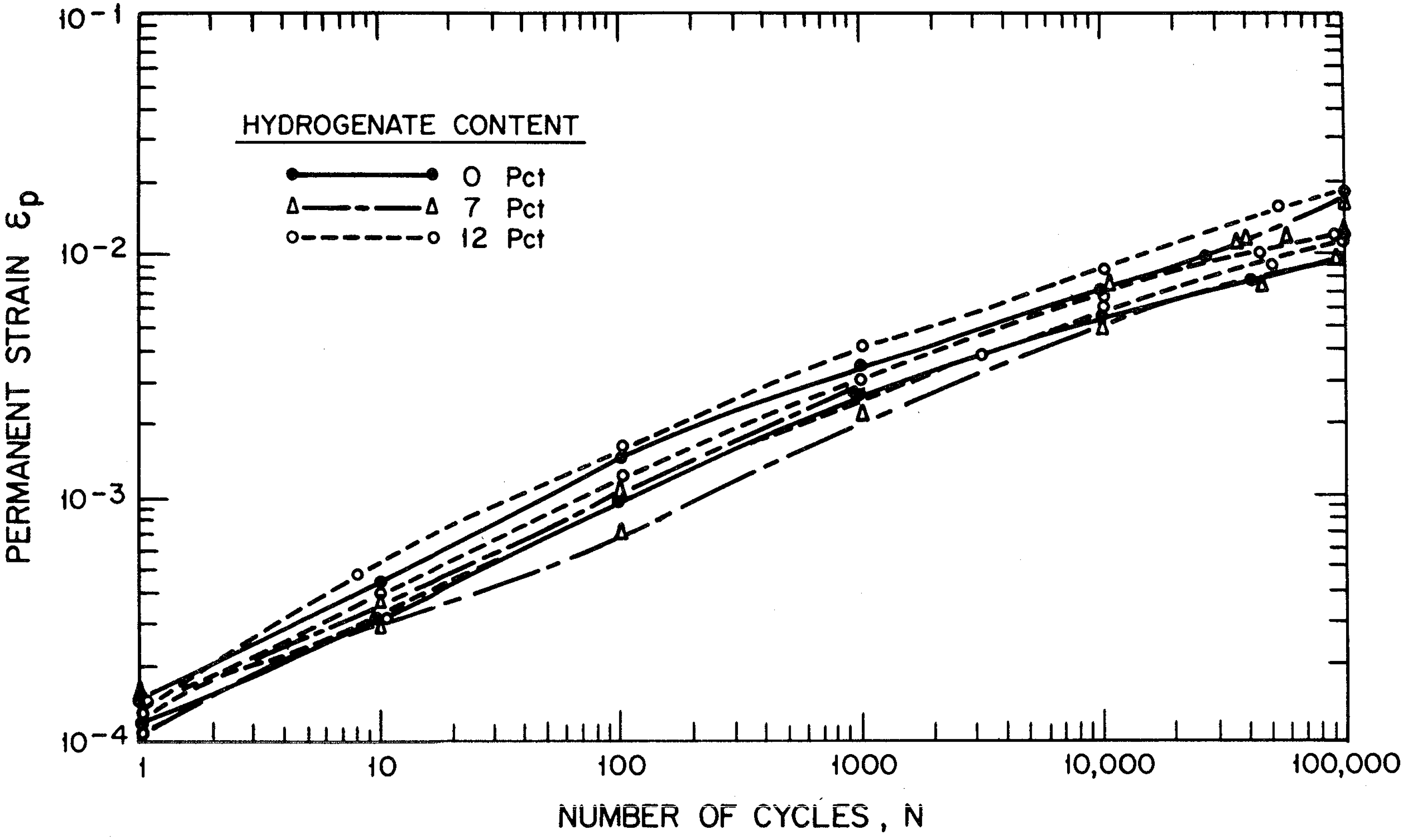


Fig. 35 Permanent Strain Results at 70°F

°C = (F−32) x 5/9

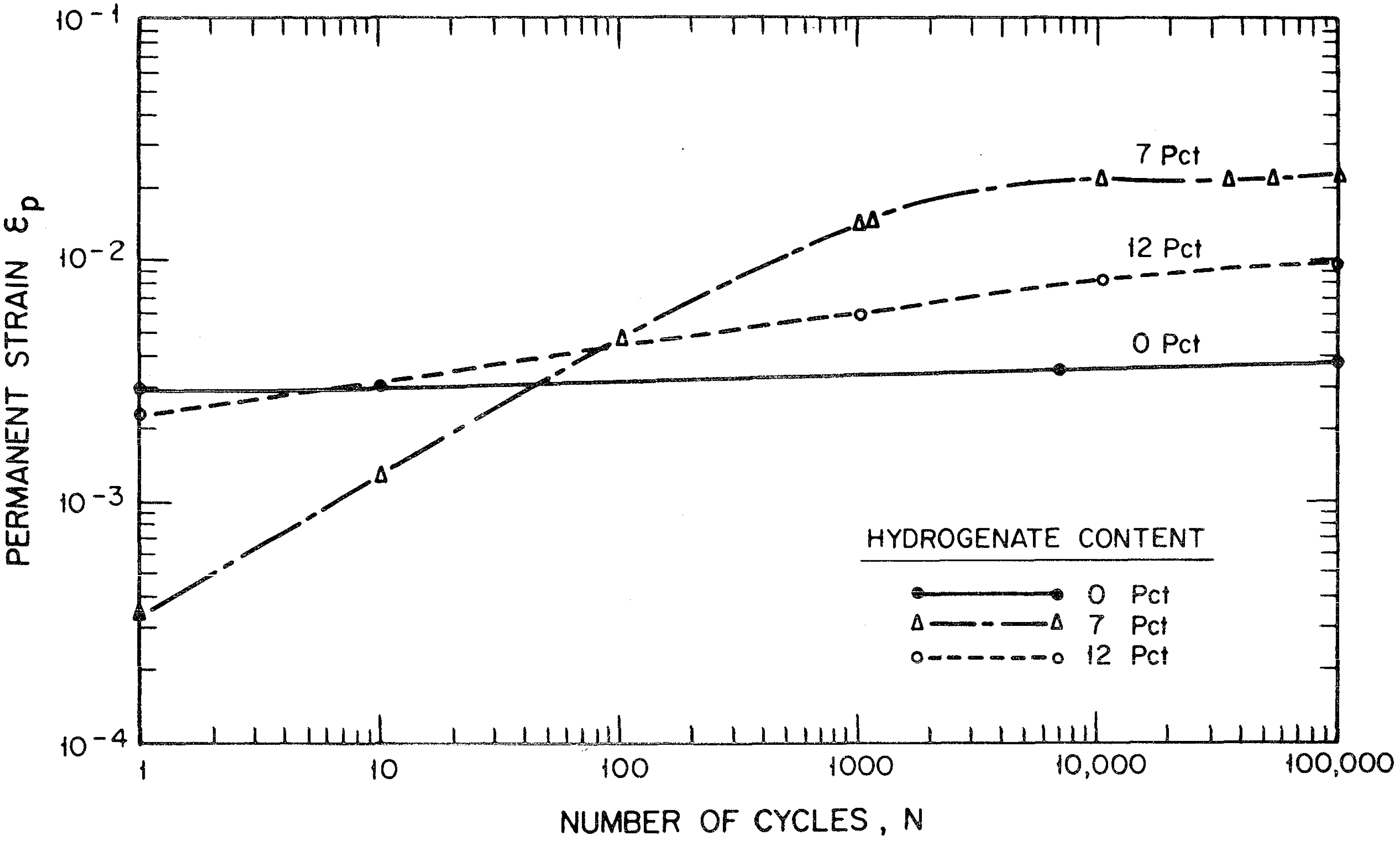


Fig. 36 Permanent Strain Results at 100°F

°C = (F-32) x 5/9

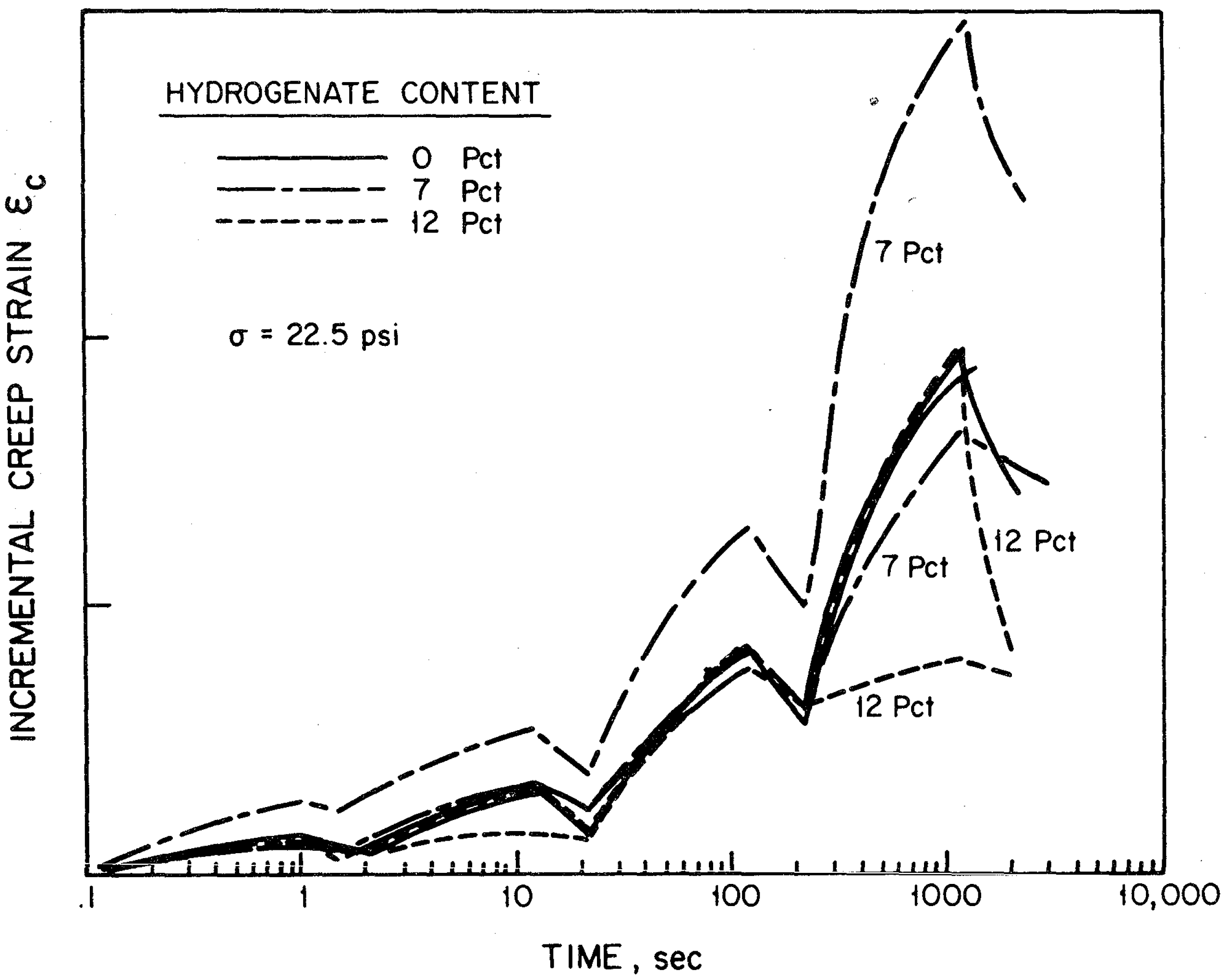


Fig. 37 Creep Test Results for the Three Test Mixtures

Newton/m^2 = 14.45 × 10^{-5} psi

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ABBREVIATIONS AND TERMINOLOGY

BCBC -

Bituminous Cement Base Course.

Hydrogenate -

The product after hydrogenating the heavy fraction of wood pyrolysis oil.

I.R. -

Infra Red Spectrum.

m.a.f. -

Moisture and ash free.

m.f. -

Moisture free.

MPO -

Municipal pyrolysis oil (the distillate produced during the pyrolysis of municipal wastes.

MSW -

Municipal solid waste.

MTD -

Mean temperature difference.

MW -

Molecular Weight.

NMR -

Nuclear Magnetic Resonance.

Pen -

Penetration (a measure of the relative stiffness of highway binder as determined by its resistance to needle penetration).

SCFM -

Standard cubic feet per minute.

SMSA -

Standard Metropolitan Statistical Area (designation of the U.S. Bureau of Census).

Solubility Parameter -

A measure of the solvent strength (related to polarity and other factors).

TBP -

True Boiling Point.

TCE -

Trichloroethylene (a solvent).

TFO -

Thin film oxidation.

USDA -

United Stated Department of Agriculture.

VMA -

Voids in mineral aggregate.

VPC -

Vapor phase chromatography.

Vacuum residua -

(Resid), the heavy ends remaining after vacuum distilling conventional petroleum charge stock.

WPO -

Wood pyrolysis oil (the distillate produced during the pyrolysis of wood wastes).

TABLE 59

WASTE GENERATION BY CATTLE AND HOGS (Dry Basis)

Item:	Cattle	Hogs
Daily Solid Waste, lb./animal	10.25	1.2
Organic Solid, lb./animal	8.20	0.91
Waste Rate, lb./animal-year:		
Moisture free (mf)	3,740	438
Moisture, ash free (maf)	2,990	328

Source: Based on L. L. Anderson, Energy Potential from Organic Wastes, NTIS, PB-211 429, July, 1972 and references cited therein.

1 kg. = 2.20 pounds

TABLE 60

WASTE GENERATED BY BEEF CATTLE ON FEED (1974)

State	Average Number,[a] Thousands	Wastes Generated, 10^9 lb/yr. (mf)	(maf)
Arizona	476	1.76	1.43
California	961	3.59	2.88
Colorado	672	2.51	2.01
Idaho	185	0.69	0.55
Illinois	410	1.53	1.23
Indiana	195	0.72	0.59
Iowa	1,320	4.93	3.96
Kansas	820	3.06	2.46
Michigan	170	0.63	0.51
Minnesota	365	1.36	1.10
Missouri	170	0.63	0.51
Montana	102	0.38	0.31
Nebraska	1,120	4.18	3.36
New Mexico	190	0.71	0.57
North Dakota	46	0.17	0.14
Ohio	185	0.69	0.55
Oklahoma	231	0.86	0.69
Oregon	49	0.18	0.15
Pennsylvania	57	0.21	0.17
South Dakota	310	1.16	0.93
Texas [b]	1,777	6.65	5.33
Washington	141	0.53	0.42
Wisconsin	95	0.36	0.29
Other	575	2.15	1.73
TOTAL	10,622	39.73	31.87

[a] Source: Agricultural Statistics 1975, Cattle and Calves: Number on feed, July 1, 1974.

[b] R. W. Douglas[31] lists 100 feedlots in the high plains region with a total population of about 2 million head. Four divisions each consisting of 13-19 lots are identified with capacities of 227, 270, 424 and 542 thousand head/division.

1 kg. = 2.20 pounds

TABLE 61

WASTE GENERATED BY MILK COWS (CONFINED, 25 pct.) (1974)

State	Number,[a] Thousands	Wastes Generated, 10^9 lb./yr. (mf)	(maf)
States (12) with > 225,000 (total: 7,559,000)			
California	810	0.76	0.61
Illinois	265	0.25	0.20
Iowa	410	0.38	0.31
Kentucky	302	0.28	0.23
Michigan	420	0.39	0.32
Minnesota	900	0.84	0.68
Missouri	316	0.30	0.24
New York	900	0.84	0.68
Ohio	412	0.38	0.31
Pennsylvania	678	0.64	0.51
Texas	350	0.33	0.26
Wisconsin	1,796	1.69	1.35
States (9) with 150,000-225,000 (total: 1,595,000)			
Florida	205	0.19	0.15
Indiana	224	0.21	0.17
Kansas	150	0.14	0.11
Nebraska	161	0.16	0.12
North Carolina	155	0.15	0.12
South Dakota	167	0.16	0.13
Vermont	189	0.18	0.14
Virginia	160	0.15	0.12
Washington	184	0.17	0.14
Other States (29)	2,132	1.99	1.60
TOTAL	11,286	10.58	8.50

[a] Source: Agricultural Statistics, 1975, Milk cows by state, 1974

1 kg. = 2.20 pounds

TABLE 62

WASTE GENERATED BY HOGS & PIGS (1974)

State	Number,[a] Millions	Wastes Generated, 10^9 lb./yr. (mf)	(maf)
Georgia	1.59	0.70	0.52
Illinois	6.50	2.85	2.13
Indiana	4.30	1.88	1.41
Iowa	13.40	5.87	4.40
Kansas	1.75	0.77	0.57
Minnesota	3.70	1.67	1.21
Missouri	3.90	1.71	1.28
Nebraska	3.05	1.34	1.00
North Carolina	1.89	0.83	0.62
Ohio	1.95	0.85	0.64
South Dakota	1.70	0.75	0.56
Other States (39)	11.33	4.96	3.71
	55.06	24.12	18.06

[a] Source: Agricultural Statistics, 1975.

1 kg. = 2.20 pounds

TABLE 63

RESIDUES AT PRIMARY WOOD PROCESSING PLANTS (1970)

Item:	Bark Residue, million cu. ft.	Wood Residue million cu. ft.
Used for pulp	-	1.77
Used for fuel [a]	0.54	0.73
Used for other products	0.08	0.31 [b]
Total Used	0.62	2.81
Unused		
Coarse	-	0.40
Fine	-	0.59
Bark	1.38	-
Total Unused	1.38	0.99

[a] Including material given away for domestic use.

[b] Mainly particle board.

Source: Adapted from the Outlook for Timber in the United States, USDA, Forest Service, FRR-20, October, 1973.

1 liter = 3.43×10^{-2} cubic feet

TABLE 64

UNUSED CELLULOSIC WOOD WASTE GENERATED BY REGIONS AND STATES

Region	Sawtimber, Removals, billion bd. ft.[a]		Unused Mill Waste (million cubic feet)		Unused Bark (million cubic feet)		Cellulosic Waste billion pounds (maf)	
Northeast	4.03		95.1		64.2		3.98	
Maine		1.30		30.7		20.7		1.29
Pennsylvania		0.72		17.0		11.5		0.71
West Virginia		0.66		15.6		10.5		0.65
Other (9 states)		1.35		31.8		21.5		1.33
Northcentral	4.92		76.9		78.4		3.88	
Michigan		0.86		13.4		13.7		0.67
Wisconsin		0.79		12.3		12.6		0.62
Kentucky		0.73		11.4		11.6		0.58
Other (10 states)		2.54		39.8		40.5		2.01
Southeast	8.77		167.2		140.0		7.62	
North Carolina		2.03		38.7		32.4		1.78
South Carolina		1.51		28.8		24.1		1.32
Virginia		1.19		22.7		19.0		0.99
Florida		1.15		21.9		18.3		1.00
Georgia		2.89		55.1		46.1		2.53
Southcentral	14.05		175.8		224.2		10.02	
Alabama		2.90		36.3		46.2		2.06
Mississippi		2.76		34.5		44.0		1.96
Tennessee		0.82		10.3		13.1		0.59
Arkansas		2.54		31.8		40.5		1.81
Louisiana		3.02		37.8		48.1		2.15
Texas		1.84		23.0		29.3		1.31
Other (Oklahoma)		0.19		2.4		3.0		0.14
Pacific Northwest	19.96		185.2		318.3		12.59	
Alaska		1.08		10.0		17.2		0.68
E. Oregon		2.10		19.5		33.5		1.33
W. Oregon		7.68		71.2		122.4		4.84
E. Washington		1.40		13.0		22.3		0.88
W. Washington		7.71		71.5		122.9		4.86
Pacific Southwest	5.65		152.0		90.0		6.05	
California		5.64		151.7		89.9		6.04
Other (Hawaii)		0.01		0.3		0.1		0.01
Northern Rocky Mtn.	4.20		93.0		67.0		3.99	
Idaho		2.11		46.7		33.6		2.00
Montana		1.81		40.1		28.8		1.72
Other (2 states)		0.28		6.2		4.5		0.27
Southern Rocky Mtn.	1.16		46.0		18.5		1.61	
TOTALS	62.74		991.2		1000.6		49.74	

[a] Source: The Outlook for Timber in the United States, U.S. Department of Agriculture, Forest Service, FRR-20, October, 1973

1 kg = 2.20 pounds

1 liter = 3.53 x 10^{-2} cubic feet

1 m^3 = 4.24 x 10^2 board-feet

TABLE 65

POST-CONSUMER NET SOLID MUNICIPAL WASTE[a] (1973)

Organic	Million Tons	Percentages
Paper	44.2	32.9
Wood	4.9	3.6
Food Waste	22.4	16.6
Yard Waste	25.0	18.6
Other[b]	10.5	7.8
Total Organic	107.0	79.5
Inorganic		
Glass	13.2	9.8
Metal	12.5	9.3
Other	1.9	1.4
Total Inorganic	27.6	20.5
Total Waste	134.6	100.0

[a] Based on Resource Recovery and Waste Reduction, U.S. EPA, 1975.

[b] Including plastic, rubber, leather and textile waste.

1 metric ton = 1.1 tons

TABLE 66

EXPERIMENT: 633

RUN NO. : 1

CONDITIONS: 1250 psi 225°C 2 hours No Extraction

MATERIAL CHARGED :

500 gms.	WPO-E
30 gms.	Catalyst
8.64 gms.	H_2
538.6 gms.	

RECOVERY:

GAS		SOLIDS	
H_2	5.7 gms.	Filtered Product	289.5 gms.
CH_4	0.5 gms.	Filter Plug	207 gms.
N + CO	1.4 gms.		496.5 gms.
CO_2	2.64gms.		
	10.24 gms.		

SUM RECOVERED MASS:

10.2 gms.
496.5 gms.
506.7 gms.

PERCENT MASS UNACCOUNTED:	6.3
PENNED PRODUCT RECOVERED	0 gms.
PERCENT YIELD CRUDE PRODUCT	57.9
PERCENT YIELD PENNED PRODUCT	0
gms. CRUDE PRODUCT/gms. H_2 CONSUMED:	96.5

1 Newton/m^2 = 14.45 x 10^{-5} psi.

TABLE 67

EXPERIMENT: 624

RUN NO. : 2

CONDITIONS: 1250 psi. 275°C 1 Hour Toluene Extraction

MATERIAL CHARGED :

500 gms.	WPO-E
30 gms.	Catalyst
9.5 gms.	H_2
539.5 gms.	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	4.9 gms.	H_2O	22 gms.	Toluene Solubles	278 gms.
CH_4	2.0 gms.	Oil	4.5 gms.	Toluene Insolubles	196 gms.
CO + N	1.49 gms.				
CO_2	6.02 gms.				
	14.4 gms.		26.5 gms.		474 gms.

SUM RECOVERED MASS:

14.4 gms.
26.5 gms.
474.0 gms.
514.9 gms.

PERCENT MASS UNACCOUNTED:	4.8	
PENNED PRODUCT RECOVERED:	262	gms.
PERCENT YIELD CRUDE PRODUCT	55.6	
PERCENT YIELD PENNED PRODUCT	52.4	
gms. PENNED PRODUCT/gms. H_2 CONSUMED:	57	

1 Newton/m^2 = 14.45×10^{-5} psi.

TABLE 68

EXPERIMENT: 629

RUN NO. : 3

CONDITIONS: 750 psi. 225°C 1 Hour Toluene Extraction

MATERIALS CHARGED :

500 gms.	WPO-E
30 gms.	Catalyst
5.16 gms.	H_2
535.2 gms.	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	3.28 gms.	H_2O	8.6 gms.	Toluene Solubles	236.5 gms.
CH_4	0.39 gms.			Toluene Insolubles*	308 gms.
N + CO	1.38 gms.				
CO_2	1.94 gms.				
	6.99 gms.		8.6 gms.		544.5 gms.

SUM RECOVERED MASS:

6.99 gms.
8.6 gms.
544.5 gms.
560.09 gms.

PERCENT MASS UNACCOUNTED	4.7
PENNED PRODUCT RECOVERED	221 gms.
PERCENT YIELD CRUDE PRODUCT	47.3
PERCENT YIELD PENNED PRODUCT	44.2
gms. PENNED PRODUCT/gms. H_2 CONSUMED	116

*Not entirely free of toluene

1 Newton/m^2 = 14.45 x 10^{-5} psi.

TABLE 69

EXPERIMENT: 627

RUN NO. : 4

CONDITIONS: 1250 psi. 225°C 2 Hours Toluene Extraction

MATERIAL CHARGED :

496.0	gms.	WPO-B
30.0	gms.	Catalyst
9.28	gms.	H_2
535.28	gms.	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	5.17 gms.	H_2O	34 gms.	Toluene Solubles	320 gms.
CH_4	2.08 gms.	Oil	7 gms.	Toluene Insolubles	143 gms.
N+CO	1.62 gms.				
CO_2	10.5 gms.				
	19.4 gms.		41 gms.		463 gms.

SUM RECOVERED MASS:

19.4	gms.
41.0	gms.
463.0	gms.
523.4	gms.

PERCENT MASS UNACCOUNTED:	2.3
PENNED PRODUCT RECOVERED:	235.1 gms.
PERCENT YIELD CRUDE PRODUCT:	64.5
PERCENT YIELD PENNED PRODUCT:	47.4
gms. PENNED PRODUCT/gms. H_2 CONSUMED	57.2

1 Newton/m^2 = 14.45×10^{-5} psi.

TABLE 70

EXPERIMENT: 617

RUN NO. : 5

CONDITIONS: 750 psi. 275°C 2 Hours NO Extraction

MATERIAL CHARGED :	500 gms.	WOP-E
	30 gms.	Catalyst
	6.7 gms.	H_2
	539.7	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	0.5 gms.	H_2O	36 gms.	Filtered Product	300 gms.
CH_4	2.9 gms.	Oil	6 gms.		
N+CO	3.9 gms.			Filter Plug	136 gms.
CO_2	49.3 gms.				
	56.6 gms.		42 gms.		436 gms.

SUM RECOVERED MASS:	56.6 gms.
	42.0 gms.
	436.0 gms.
	534.0 gms.

PERCENT MASS UNACCOUNTED:	1.1
PENNED PRODUCT RECOVERED	0 gms.
PERCENT YIELD CRUDE PRODUCT	60
PERCENT YIELD PENNED PRODUCT	0
gms. CRUDE PRODUCT/gms. H_2 CONSUMED	48.4

1 Newton/m^2 = 14.45×10^{-5} psi.

TABLE 71

EXPERIMENT: 622

RUN NO: 6

CONDITIONS: 750 psi. 275°C 2 Hours Toluene Extraction

MATERIAL CHARGED :

496 gms. WPO-B
30 gms. Catalyst
6.85 gms. H_2
532.9 gms.

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	3.0 gms.	H_2O	50 gms.	Toluene Solubles	330 gms.
CH_4	2.43 gms.	Oil	14 gms.	Toluene Insolubles	85 gms.
N+CO	-				
CO_2	22.8 gms.				
	28.23 gms.		64 gms.		415 gms.

SUM RECOVERED MASS:

28.23 gms.
64.0 gms.
415.0 gms.
507.23 gms.

PERCENT MASS UNACCOUNTED:	5.1
PENNED PRODUCT RECOVERED	259.9 gms.
PERCENT YIELD CRUDE PRODUCT	66.5
PERCENT YIELD PENNED PRODUCT	52.4
gms. PENNED PRODUCT/gms. H_2 CONSUMED	67.5

1 Newton/m^2 = 14.45 x 10^{-5} psi.

TABLE 72

EXPERIMENT:	631			
RUN NO. :	7			
CONDITIONS:	1250 psi.	275°C	1 Hour	NO EXTRACTION

MATERIAL CHARGED :

500 gms.	WPO-B
30 gms.	Catalyst
9.96 gms.	H_2
539.96 gms.	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	4.13 gms.			Filtered Product	377 gms.
CH_4	2.15 gms.	H_2O	43 gms.	Filter Plug	64.5 gms.
N+CO	1.40 gms.	Oil	11.5 gms.		
CO_2	14.8 gms.				
	22.5 gms.		54.5 gms.		441.5 gms.

SUM RECOVERED MASS:

22.5 gms.
54.5 gms.
441.5 gms.

518.5 gms.

PERCENT MASS UNACCOUNTED:	4.2
PENNED PRODUCT RECOVERED:	330 gms.
PERCENT YIELD CRUDE PRODUCT:	75.4
PERCENT YIELD PENNED PRODUCT	66.0
gms. PENNED PRODUCT/gms. H_2 CONSUMED:	56.6

1 Newton/m^2 = 14.45×10^{-5} psi.

TABLE 73

EXPERIMENT: 625

RUN NO. : 8

CONDITIONS: 750 psi. 225°C 1 Hour No Extraction

MATERIALS CHARGED :

503	gms.	WPO-B
30	gms.	Catalyst
6	gms.	H_2
539	gms.	

RECOVERY:

GAS		TRAP		SOLIDS	
H_2	2.95 gms.	H_2O	13.0 gms.	Filtered Product	367 gms.
CH_4	1.01 gms.	Oil	3.0 gms.		
N+CO	1.42 gms.			Insolubles	126.5 gms.
CO_2	9.23 gms.				
	14.61 gms.		16.0 gms.		493.5 gms.

SUM RECOVERED MASS:

14.61	gms.
16.0	gms.
493.5	gms.
524.1	gms.

PERCENT MASS UNACCOUNTED:	2.9
PENNED PRODUCT RECOVERED:	319 gms.
PERCENT YIELD CRUDE PRODUCT:	73
PERCENT YIELD PENNED PRODUCT:	63.4
gms. PENNED PRODUCT/gms. H_2 CONSUMED:	104.6

1 Newton/m^2 = 14.45×10^{-5} psi.

TABLE 74

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON HYDROGEN CONSUMPTION

```
   ENTER RESPONSE-
=  H2 CONSUMPTION

    ENTER DATA ACCORDING TO RUN NUMBER
= 0,57,116,57.2,0,67.5,56.6,104.6




    PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

    RESPONSE-H2 CONSUMPTION

EFFECTS GREATER THAN  16.21  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                IS FACTOR
           FACTOR              EFFECT           SIGNIFICANT?
           ******              ******           ************

           WPO                 -28.23               YES

           PRESSURE            -29.33               YES

           TEMPERATURE         -24.18               YES

           TIME                -52.38               YES

           EXTRACTION           34.12               YES


AVERAGE RESPONSE=    57.36

VARIANCE=    14.19

STANDARD ERROR=    3.77
```

TABLE 75

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON DUCILITY

```
   ENTER RESPONSE-
=  DUCTILITY

     ENTER DATA ACCORDING TO RUN NUMBER
= 0,26,35,40,0,44,60,50



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-DUCTILITY

EFFECTS GREATER THAN  20.89  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                IS FACTOR
             FACTOR               EFFECT        SIGNIFICANT?
             ******               ******        ************

             WPO                  -33.25            YES

             PRESSURE              -0.75             NO

             TEMPERATURE            1.25             NO

             TIME                 -21.75            YES

             EXTRACTION             8.75             NO


AVERAGE RESPONSE=    31.87

VARIANCE=    23.56

STANDARD ERROR=     4.85
```

TABLE 76

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT YIELD OF PENNED PRODUCT

```
   ENTER RESPONSE-
=  % PENNED PRODUCT

     ENTER DATA ACCORDING TO RUN NUMBER
= 0,52.4,44.2,47.4,0,52.4,66.0,63.4



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-% PENNED PRODUCT

EFFECTS GREATER THAN    8.08  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                   IS FACTOR
                FACTOR              EFFECT         SIGNIFICANT?
                ******              ******         ************

                WPO                 -33.15             YES

                PRESSURE              1.45              NO

                TEMPERATURE           3.95              NO

                TIME                -31.55             YES

                EXTRACTION           16.75             YES


AVERAGE RESPONSE=     40.72

VARIANCE=      3.52

STANDARD ERROR=      1.88
```

TABLE 77

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON RING AND BALL TEMPERATURE

```
   ENTER RESPONSE-
=  RING AND BALL

     ENTER DATA ACCORDING TO RUN NUMBER
= 100,43,45,43,100,48,45,48.5




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-RING AND BALL

EFFECTS GREATER THAN    5.62  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                IS FACTOR
             FACTOR               EFFECT        SIGNIFICANT?
             ******               ******        ************

             WPO                   25.87            YES

             PRESSURE             -2.62              NO

             TEMPERATURE          -0.12              NO

             TIME                  27.37            YES

             EXTRACTION           -28.62            YES


AVERAGE RESPONSE=    59.06

VARIANCE=      1.70

STANDARD ERROR=     1.31
```

TABLE 78

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON VISCOSITY AT 135°C

```
   ENTER RESPONSE-
=  VIS AT 135 DEG C

     ENTER DATA ACCORDING TO RUN NUMBER
= 300,50,30,30,300,40,70,110




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-VIS AT 135 DEG C

EFFECTS GREATER THAN  65.44  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                  IS FACTOR
             FACTOR                EFFECT         SIGNIFICANT?
             ******                ******         ************

             WPO                   107.50             YES

             PRESSURE               -7.50              NO

             TEMPERATURE            -2.50              NO

             TIME                  102.50             YES

             EXTRACTION           -157.50             YES


AVERAGE RESPONSE=   116.25

VARIANCE=   231.25

STANDARD ERROR=    15.21
```

TABLE 79

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON VISCOSITY AT 140°F

```
   ENTER RESPONSE-
=  VIS AT 140 DEG F

     ENTER DATA ACCORDING TO RUN NUMBER
= 100,15,10,12.5,100,28.5,27.5,42.5




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-VIS AT 140 DEG F

EFFECTS GREATER THAN  27.55  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                   IS FACTOR
             FACTOR                EFFECT          SIGNIFICANT?
             ******                ******          ***********

             WPO                    28.50              YES

             PRESSURE               -6.50               NO

             TEMPERATURE             1.50               NO

             TIME                   36.50              YES

             EXTRACTION            -51.00              YES


AVERAGE RESPONSE=    42.00

VARIANCE=    41.00

STANDARD ERROR=      6.40

   NOTE: THIS DATA IS CODED BY DIVIDING BY 1000. IN ORDER TO GET BACK
         TO THE ORIGINAL DATA AND TO OBTAIN  THE CORRECT VALUES FOR
         EFFECTS AND AVERAGE RESPONSE IT IS NECESSARY TO MULTIPLY
         BY 1000.
```

$°C = (°F - 32) \times \frac{5}{9}$

TABLE 80

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON DENSITY

```
   ENTER RESPONSE-
=  DENSITY

     ENTER DATA ACCORDING TO RUN NUMBER
= 1.21,1.12,1.18,1.12,1.09,1.13,1.16,1.17



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-DENSITY

EFFECTS GREATER THAN   0.15  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                    IS FACTOR
             FACTOR                EFFECT           SIGNIFICANT?
             ******                ******           ***********

             WPO                    0.00                NO

             PRESSURE               0.01                NO

             TEMPERATURE           -0.05                NO

             TIME                  -0.02                NO

             EXTRACTION            -0.02                NO


AVERAGE RESPONSE=      1.15

VARIANCE=      0.00

STANDARD ERROR=      0.03
```

TABLE 81

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT TOLUENE SOLUBLES

```
   ENTER RESPONSE-
=  % TOLUENE SOLUBLES

     ENTER DATA ACCORDING TO RUN NUMBER
= 41.3,90.5,94.2,91.8,35.4,88.8,79.3,66.9



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-% TOLUENE SOLUBLES

EFFECTS GREATER THAN  17.60  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                      IS FACTOR
             FACTOR                EFFECT             SIGNIFICANT?
             ******                ******             ************

             WPO                   -16.35                  NO

             PRESSURE                4.40                  NO

             TEMPERATURE            -0.05                  NO

             TIME                  -18.40                 YES

             EXTRACTION             35.60                 YES


AVERAGE RESPONSE=     73.52

VARIANCE=    16.73

STANDARD ERROR=     4.09
```

TABLE 82

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT SOLUBLES IN TRICHLOROETHYLENE

```
   ENTER RESPONSE-
=  % TCE  SOLUBLES

     ENTER DATA ACCORDING TO RUN NUMBER
= 44.0,97.5,96.4,94.2,34.6,92.0,80.1,72.9



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-% TCE  SOLUBLES

EFFECTS GREATER THAN  10.15  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                    IS FACTOR
             FACTOR              EFFECT             SIGNIFICANT?
             ******              ******             ************

             WPO                 -16.68                 YES

             PRESSURE              4.97                  NO

             TEMPERATURE          -0.83                  NO

             TIME                -20.53                 YES

             EXTRACTION           37.12                 YES


AVERAGE RESPONSE=    76.46

VARIANCE=     5.57

STANDARD ERROR=     2.36
```

TABLE 83

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT CARBON

```
   ENTER RESPONSE-
=  PERCENT CARBON

     ENTER DATA ACCORDING TO RUN NUMBER
= 71.44,75.25,74.02,73.46,77.46,76.44,72.56,71.3



     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-PERCENT CARBON

EFFECTS GREATER THAN   3.27  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                 IS FACTOR
             FACTOR             EFFECT           SIGNIFICANT?
             ******             ******           ************

             WPO                  1.10                NO

             PRESSURE            -1.63                NO

             TEMPERATURE          2.87                NO

             TIME                 1.42                NO

             EXTRACTION           1.60                NO


AVERAGE RESPONSE=     73.99

VARIANCE=      0.58

STANDARD ERROR=      0.76
```

TABLE 84

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT HYDROGEN

```
   ENTER RESPONSE-
=  % HYDROGEN

     ENTER DATA ACCORDING TO RUN NUMBER
= 7.49,8.37,8.57,8.70,7.68,8.36,8.18,7.79




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-% HYDROGEN

EFFECTS GREATER THAN   0.85  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                 IS FACTOR
             FACTOR              EFFECT          SIGNIFICANT?
             ******              ******          ************

             WPO                 -0.23                NO

             PRESSURE             0.03                NO

             TEMPERATURE          0.01                NO

             TIME                -0.17                NO

             EXTRACTION           0.71                NO


AVERAGE RESPONSE=      8.14

VARIANCE=      0.04

STANDARD ERROR=      0.20
```

TABLE 85

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON PERCENT OXYGEN

```
   ENTER RESPONSE-
=  PERCENT OXYGEN

     ENTER DATA ACCORDING TO RUN NUMBER
= 17.73,15.66,16.28,18.46,12.36,15.79,17.69,20.81




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-PERCENT OXYGEN

EFFECTS GREATER THAN    3.96  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                  IS FACTOR
               FACTOR                EFFECT      SIGNIFICANT?
               ******                ******      ***********

               WPO                    -2.68           NO

               PRESSURE                1.07           NO

               TEMPERATURE            -2.95           NO

               TIME                   -1.52           NO

               EXTRACTION             -0.60           NO


AVERAGE RESPONSE=     16.85

VARIANCE=      0.85

STANDARD ERROR=      0.92
```

TABLE 86

PLACKETT-BURMAN ANALYSIS OF PROCESS VARIABLES FOR SIGNIFICANT EFFECTS UPON H/C ATOM RATIO

```
   ENTER RESPONSE-
=  H/C ATOM RATIO

     ENTER DATA ACCORDING TO RUN NUMBER
= 1.26,1.33,1.39,1.42,1.19,1.31,1.35,1.31




     PLACKETT-BURMAN DESIGN FOR 8 EXPERIMENTS (*)
(*)-RE: CHEM ENG, 6/29/70, PP. 69-75

     RESPONSE-H/C ATOM RATIO

EFFECTS GREATER THAN   0.12  ARE SIGNIFICANT (+)
(+)-FOR 2 DEGREES OF FREEDOM AT THE 95% CONFIDENCE LEVEL

                                                  IS FACTOR
             FACTOR                EFFECT         SIGNIFICANT?
             ******                ******         ************

             WPO                   -0.06               NO

             PRESSURE               0.04               NO

             TEMPERATURE           -0.05               NO

             TIME                  -0.05               NO

             EXTRACTION             0.08               NO


AVERAGE RESPONSE=     1.32

VARIANCE=     0.00

STANDARD ERROR=     0.03
```

TABLE 87

OVERALL MATERIAL BALANCES FOR 1000 TON/DAY CELLULOSIC WASTE PYRCLYSIS PLANT

Non-Condensible Gas	Moles/hr.	M.W.	Lbs./hr.
H_2	97	2	194
CO	300	28	8,400
CO_2	300	44	13,266
CH_4	49	16	780
C_2H_4	24	28	680
C_2H_6	8	30	240
C_3	8	43	350
C_{4+}	16	57	920
H_2S	7	32	210
HCl	2	36.5	60
	811		25,000
Pyrolysis Oil	W pct.		Lbs./hr.
C	57		19,000
H	7.7		2,570
N	1.1		370
S	0.2		70
Cl	0.2		70
O	33.6		11,250
Ash	0.2		70
			33,400
Char			
C	48.8		8,130
H	3.3		550
N	1.1		180
S	0.4		70
Cl	0.3		50
O	12.8		2,130
Ash	33.3		5,560
			16,670

Asphalt (based on 60 percent of pyrolysis oil), 20,000 lbs./hr. - 700 molecular weight

Heavy Oil 6,700 lbs./hr. - 300 average molecular weight

Light Oil 6,700 lbs./hr. - 180 average molecular weight

1 metric ton = 1.1 ton

1 kg. = 2.20 lbs.

TABLE 88

THERMODYNAMIC PROPERTIES AND HEAT BALANCES

Average Specific Heat of Gas at Mean Temperatures of 270°C

	Moles/hr.	Cp, BTU/lb. Mole/°F	BTU/hr. °F
H_2	97	7.06	685
CO	300	7.25	2,175
CO_2	300	11.17	3,351
CH_4	49	12.80	529
C_2H_4	24	18.0	432
C_3H_6	8	21.3	178
C_3	8	20.0	160
C_{4+}	16	20.0	320
H_2S	7	8.6	50
HCl	2	7.1	14
	811		7,894

$$\text{Average Specific Heat} = \frac{7,894}{25,000} = .316 \text{ BTU/lb.}$$

Enthalpy data for light oil, heavy oil and asphalt vapors taken from Figure 40 based on specific heat of gas mixture of .3 BTU/Lb. and specific heat of liquid mixture of .5 BTU/Lb.

Overall Heat Balance (to determine total heat duty)

Heat In	Lb./hr.	Temp., °F	BTU/lb.	BTU/hr.
Feed				
Non-Cond. Gas	25,000	950	302	7,550,000
Air Vapors				
Light Oil	6,700	950	523	3,500,000
Heavy Oil	6,700	950	555	3,720,000
Asphalt	20,000	950	595	11,900,000
				26,670,000
Heat Out				
Non-Cond. Gas	25,000	170	54	1,350,000
Light Oil	6,700	150	76	510,000
Heavy Oil	6,700	340	170	1,140,000
Asphalt	20,000	675	339	6,780,000
Total Cooling Duty				16,890,000
				26,670,000

1 kg. 2.20 pounds

$°C = (°F - 32) \times \frac{5}{9}$

Calories, kg. = 3.97 BTU

THERMODYNAMIC PROPERTIES AND HEAT BALANCES

Heat Balance on Vacuum Flash Drum and Condenser (to calculate heat duty of vacuum condenser)

Heat In	Lb./hr.	Temp., °F	BTU/lb.	BTU/hr.
Liquid Feed	25,000	725	364	9,100,000
Heat Out				
Distillate	5,000	300	150	750,000
Vacuum Resid	20,000	675	339	6,780,000
Condenser Duty				1,570,000
				9,100,000

Heat Balance on Bottom Section of Asphalt Fractionator (to calculate bottom tray vapor rate)

Heat In				
Feed Stream				
Non-Cond. Gas	25,000	950	302	7,550,000
Oil Vapors	33,400	950		19,120,000
Bottom Tray Liquid	50,000	725	364	18,200,000
				44,870,000
Heat Out				
Vapor to Bottom Tray				
Non-Cond. Gas	25,000	725	230	5,750,000
Liquid Oil	6,700	725	455	3,050,000
Heavy Oil	6,700	725	487	3,200,000
Asphalt	45,000	725	528	23,770,000
Asphalt Bottoms	25,000	725	364	9,100,000
				44,870,000

1 kg. = 2.20 pounds

°C = (°F - 32) x $\frac{5}{9}$

Calories, kg. = 3.97 BTU

TABLE 88. Continued

THERMODYNAMIC PROPERTIES AND HEAT BALANCES

Heat Balance Around 6th Tray and Bottom of Column Including Vacuum Flash Drum (to determine duty of first intercooler)

Heat In	Lb./hr.	Temp., °F	BTU/lb.	BTU/hr.
Total Feed Streams	58,400	950		26,670,000
B-7 Liquid	6,700	500	250	1,670,000
				28,340,000
Heat Out				
B-6 Vapor				
Non-Cond. Gas	25,000	520	165	4,130,000
Light Oil	6,700	520	394	2,640,000
Heavy Oil	13,400	520	426	5,710,000
Asphalt Bottoms	20,000	675	339	6,780,000
Vacuum Flash Cond. Duty				1,570,000
First Intercooler Duty				7,510,000
				28,340,000

Heat Balance Around 10th Tray and Bottom of Column Including Vacuum Flash Drum (to determine duty of second intercooler)

Heat In				
Total Feed Streams	58,400	950		26,670,000
B-11 Liquid	6,700	340	170	1,140,000
				27,810,000
Heat Out				
B-10 Vapor				
Non-Cond. Gas	25,000	360	114	2,850,000
Light Oil	13,400	360	346	4,640,000
Heavy Oil Product	6,700	340	170	1,140,000
Asphalt Bottoms	20,000	675	339	6,780,000
Vacuum Flash Condenser Duty				1,570,000
First Intercooler Duty				7,510,000
Second Intercooler Duty				3,320,000
				27,810,000
Total Cooler Duty from Overall Heat Balance				16,890,000
Combined Duties of Vac. Flash Cond. and First and Second Intercoolers				12,400,000
Third Intercooler Duty (by difference)				4,490,000

1 kg. = 2.20 pounds

$°C = (°F - 32) \times \frac{5}{9}$

Calories, kg. = 3.97 BTU

TABLE 89

HEAT EXCHANGER DESIGNS - ALL AIR COOLED

1. Vacuum Flash Condenser - Total Duty 1,570,000 BTU/Hr.

Hot Side

Flow Rate 5000 lbs./hr asphalt vapor

Estimate Condensing Range 675 → 500°F

Condensing Duty 1,070,000 BTU/Hr.

Subcooling Range 500 - 300°C

Subcooling Duty 500,000 BTU/Hr.

Cool Side

Air in at 90°F - Out at 200°F

13000 SCFM Required

Subcooling Duty 90 → 125°F MTD 216°F

Condensing Duty 126 → 200°F MTD 475°F

Overall Average MTD = 344°F

Surface required based on overall U = 80 BTU/(hr.-ft.^{2}-°F) for inside surface of finned tube.

$$\frac{1,570,000}{80 \times 344} = 57 \text{ Sq. Ft.}$$

Estimate Cost at $80/Sq. Ft. = $5,000

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2. First Intercooler - Duty 7,510,000 BTU/Hr.

Hot Side - Light Asphalt Cut

In at 700°F - Out at 500°F

75,100 Lbs./Hr. 150 GPM

Cold Side

Air in at 90°F - Out at 200°F

63,000 SCFM Required

MTD = 455°F

Surface required based on overall U = 80 BTU/(hr.-ft.^{2}-°F) for inside surface of tube.

$$\frac{7,510,000}{80 \times 455} = 207 \text{ Sq. Ft.}$$

Estimate Cost at $50/Sq. Ft. = $10,000

$$°C = (°F - 32) \times \frac{5}{9}$$

Calories, kg. = 3.97 BTU

1 kg. = 2.20 pounds

1 liter/sec. = 15.85 GPM

1 m^2 = 10.76 Sq. Ft.

1 liter/sec. (15.56°C) = 2.12 SCFM

MTD = Mean Temperature Difference

HEAT EXCHANGER DESIGNS - ALL AIR COOLED

3. Second Intercooler - Duty 3,320,000 BTU/Hr.
Hot Side - Heavy Oil
In at 500°F - Out at 340°F
41,500 lbs./Hr. 85 GPM
Cold Side
Air in at 90°F - Out at 200°F
28,000 SCFM Required
MTD = 275°F
Surface required based on overall U = 80 BTU/(hr.-ft.^{2}-°F) for inside surface of tube.

$$\frac{3,320,000}{80 \times 275} = 150 \text{ Sq. Ft.}$$

Estimate Cost at $60/Sq. Ft. = $9,000

4. Third Intercooler - Duty 4,490,000 BTU/Hr.
Hot Side - Light Oil
In at 340 - Out at 150°F
47,500 Lbs/Hr.,(95 GPM)
Cold Side
Air in at 90°F - Out at 150°F
65000 SCFM Required
MTD = 112°F
Surface required based on overall U = 80 BTU/(hr.-ft.^{2}-°F) for inside surface of tube.

$$\frac{4,490,000}{80 \times 112} = 500 \text{ Sq. Ft.}$$

Estimate cost at $40/Sq. Ft. = $20,000

$°C = (°F - 32) \times \frac{5}{9}$

Calories, kg. = 3.97 BTU

1 kg. = 2.20 pounds

1 liter/sec. = 15.85 GPM

1 m^2 = 10.76 Sq. Ft.

1 liter/sec. (15.56°C) = 2.12 SCFM

MTD = Mean Temperature Difference

TABLE 90

VESSEL DESIGNS

ASPHALT FRACTIONATOR

Diameter controlled by bottom tray vapor rate

Bottom Tray Vapor

	Moles/hr.	M.W.	Lbs./hr.
Non-Condensable Gas	811	30.8	25,000
Light Oil	37	180	6,700
Heavy Oil	22	300	6,700
Asphalt	64	700	45,000
	934	90	83,400

Vapor Rate:

$$\frac{934 \text{ x } 360}{3,600} \text{ x } \frac{1,185}{492} \text{ x } \frac{14.7}{16.2} = 204 \text{ cubic feet/sec.}$$

$$\rho_L = \frac{83,400}{3,600 \text{ x } 204} = 0.114 \text{ lbs./ft.}^3 \qquad \rho_L = 50 \text{ lbs./ft.}^3$$

Allowable Velocity V for 30" Tray Spacing:

$$V = .30 \text{ x } \sqrt{\frac{50 - .114}{.114}} = 6.3 \text{ ft./sec.}$$

Use 7' Diameter Column (19 pct. excess capacity)

Cost of 7' diameter column containing 14 valve trays = $35,000

Vacuum Flash Drum

Vapor Rate:

$$\frac{5,000}{700} \text{ x } \frac{360}{3,600} \text{ x } \frac{760}{70} \text{ x } \frac{1,135}{492} = 17.8 \text{ cubic feet/sec.}$$

$$\rho_V = \frac{5,000}{3,600 \text{ x } 17.8} = .078 \text{ lbs./ft.}^3$$

$$\rho_L = 50 \text{ lbs./ft.}^3$$

Allowable Velocity V for Flash Drum:

$$V = .35 \text{ x } \sqrt{\frac{50 - 0.78}{.078}} = 8.8 \text{ ft./sec.}$$

Use 24" diameter vessel (55 pct. excess capacity) = $5,000

1 meter/sec = 3.28 ft/sec

1 kg. = 2.20 pound

$1 \frac{\text{gm.}}{\text{cc}} = 62.43 \text{ lbs/ft}^3$

$1 \text{ liter/sec} = 3.53 \text{ x } 10^{-2} \text{ ft}^3\text{/sec.}$

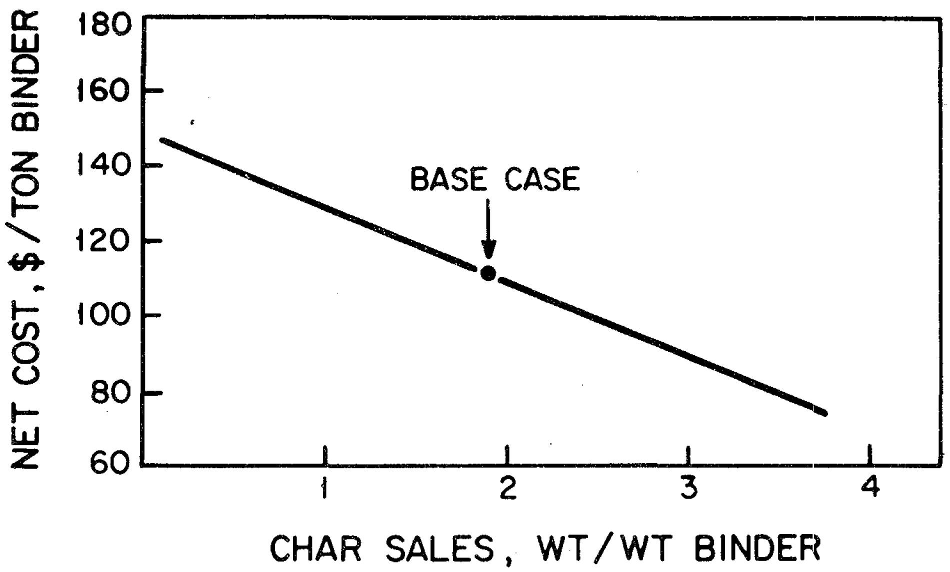


Fig. 38 Production Cost Sensitivity to Char Sales

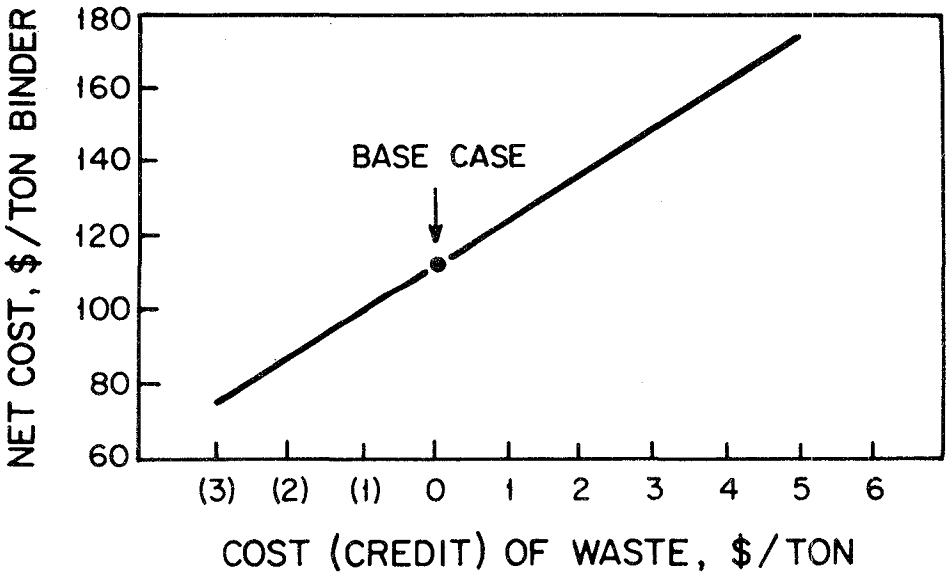


Fig. 39 Production Cost Sensitivity to Waste Cost

Metric Ton = 1.1 Ton

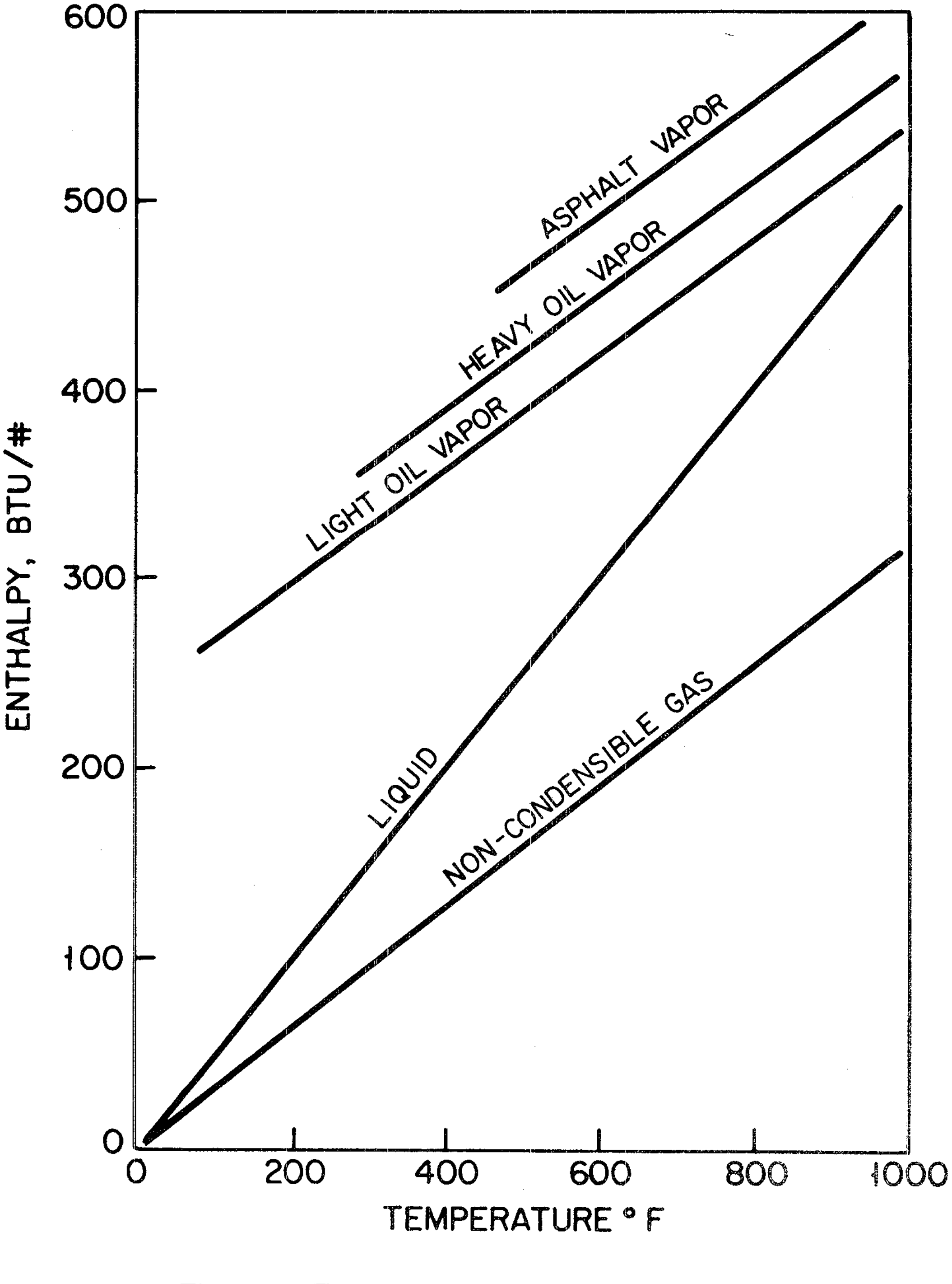


Fig. 40 Enthalpy Curves for Pyrolysis Oils

1 kg = 2.20 pounds (#)   Calories, kg = 3.97 BTU

°C = (F-32) x 5/9

TABLE 91

GRADATION OF BINDER COURSE MIXTURES USED IN LABORATORY TEST PROGRAM

(Percent Passing by Weight)

Sieve Size	Laboratory Test Mixes	PennDOT ID-2A Specification
1-1/2"	100	100
1"	95	90 - 100
1/2"	57.5	40 - 75
#4 (4.75mm)	40.5	20 - 47
#8 (2.36mm)	26	15 - 37
#16 (1.18mm)	20	10 - 30
#30 (600 microns)	14.5	5 - 24
#50 (300 microns)	11.5	4 - 17
#100 (150 microns)	6.5	3 - 10
#200 (75 microns)	4	2 - 6

TABLE 92

GRADATION OF BASE COURSE MIXTURES USED IN LABORATORY TEST PROGRAM

(Percent Passing by Weight)

Sieve Size	Laboratory Test Mixes	PennDOT BCBC Specification
2"		100
1-1/2"		95 - 100
1"	100	
3/4"	58	52 - 100
3/8"	37	36 - 70
#4 (4.75mm)	35	
#8 (2.36mm)	17	16 - 38
#16 (1.18mm)	7	
#30 (600 microns)		8 - 24
#50 (300 microns)		6 - 18
#100 (150 microns)		4 - 10
#200 (75 microns)	5	

1 cm = 0.394 inch

TABLE 93

MARSHALL TEST RESULTS
WEARING SURFACE MIXTURES

GRANITIC GNEISS

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)	Air Voids (Percent)	VMA (Percent)
Control	5.0	2.51	1622	7	4.67	16.12
	5.4	2.52	1130	7	3.38	16.11
	5.8	2.53	1409	12	2.35	16.09
7 pct. Blend	5.0	2.54	1707	9	3.16	15.12
	5.4	2.53	2006	10	2.95	15.78
	5.8	2.54	1844	7	1.93	15.76
12 pct. Blend	5.0	2.50	1951	7	4.69	16.46
	5.4	2.55	1342	7	2.19	15.11
	5.8	2.55	1513	7	1.54	15.43

LIMESTONE

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)	Air Voids (Percent)	VMA (Percent)
Control	5.0	2.57	1367	11	3.75	13.51
	5.4	2.55	1009	12	N.C.	N.C.
	5.8	N.T.	N.T.	N.T.	N.T.	N.T.
7 pct. Blend	5.0	2.55	1486	12	4.57	14.18
	5.4	2.53	1172	13	4.67	15.18
	5.8	2.46	699	12	N.C.	N.C.
12 pct. Blend	5.0	2.47	1245	11	7.56	16.88
	5.4	2.58	1162	14	2.83	13.50
	5.8	2.56	1000	17	N.C.	N.C.

*Expressed as percent by weight of aggregate in mix.

N.C. - Not computed because of unacceptable stability and/or flow values.

N.T. - Not Tested

NOTE: No voids computed for sand and gravel mixtures because none passed Marshall stability and flow requirements.

1 kg. = 2.20 lbs.

1 cm = 0.394 inch

TABLE 94

MARSHALL TEST RESULTS
BINDER COURSE MIXTURES

LIMESTONE

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)	Air Voids (Percent)	VMA (Percent)
Control	4.2	2.57	1496	13	5.05	12.85
	4.5	2.57	1127	13	4.60	13.10
	4.8	2.58	1003	18	3.77	13.01
	5.0		726	16	N.C.	N.C.
	5.4		780	33	N.C.	N.C.
7 pct. Blend	4.2		988	11		
	4.5	2.55	1111	10	5.31	13.77
	4.8	2.58	1157	12	3.73	13.01
	5.0		726	16	N.C.	N.C.
12 pct. Blend	4.2	2.55	1090	9	5.76	13.53
	4.5	2.57	1051	11	4.60	13.10
	4.8		975	14	N.C.	N.C.

*Expressed as percent by weight of aggregate in mix.

NOTE: No voids computed for granite gneiss or sand and gravel mixtures because none passed Marshall stability and flow requirements.

N.C. - Not computed because of unacceptable stability and/or flow values.

1 kg. = 2.20 lbs.

1 cm = 0.394 inch

TABLE 94 . Continued

MARSHALL TEST RESULTS
BINDER COURSE MIXTURES

GRANITIC GNEISS

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)
Control	4.2	2.50	572	13
	4.5	2.53	750	13
	4.8	2.53	870	9
7 pct. Blend	4.2	2.52	515	13
	4.5	2.54	454	13
	4.8	2.48	344	14
12 pct. Blend	4.2	N.T.	N.T.	N.T.
	4.5	2.50	537	10
	4.8	2.50	746	9

SAND AND GRAVEL

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)
Control	4.2	2.34	507	12
	4.5	N.T.	N.T.	N.T.
	4.8	2.30	Failed in Both	
7 pct. Blend	4.2	2.30	134	12
	4.5	N.T.	N.T.	N.T.
	4.8	2.32	357	12
12 pct. Blend	4.2	2.33	523	11
	4.5	N.T.	N.T.	N.T.
	4.8	2.35	591	10

*Expressed as percent by weight of aggregate in mix.

N.T. - Not Tested

1 kg. = 2.20 lbs.

1 cm = 0.394 inch

TABLE 95

MARSHALL TEST RESULTS
BASE COURSE MIXTURES

GRANITIC GNEISS

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)
Control	3.2	N.T.	N.T.	N.T.
	3.4	2.50	780	9
	3.6	N.T.	N.T.	N.T.
7 pct. Blend	3.2	2.47	627	9
	3.4	2.44	672	11
	3.6	N.T.	N.T.	N.T.
12 pct. Blend	3.2	2.48	758	11
	3.4	N.T.	N.T.	N.T.
	3.6	2.49	602	15

LIMESTONE

Description Of Mix	Asphalt Content*	Bulk Specific Gravity	Stability (Lbs.)	Flow (.01 in.)
Control	3.2	2.49	540	12
	3.4	2.47	635	12
	3.6	2.47	575	14
7 pct. Blend	3.2	2.50	593	9
	3.4	2.46	609	13
	3.6	2.46	493	12
12 pct. Blend	3.2	2.48	412	10
	3.4	2.52	659	13
	3.6	2.47	387	11

*Expressed as percent by weight of aggregate in mix.

N.T. - Not Tested

1 kg. = 2.20 lbs.

1 cm = 0.394 inch

TABLE 96

FINGERPRINTING DATA DETERMINED ON SUNTECH ASPHALT NO. 654-A

Composition, pct. of asphalt	
Fraction A (asphaltenes)	17.5
Fraction N (nitrogen bases)	18.9
Fraction A_1 (first acidaffins)	18.3
Fraction A_2 (second acidaffins)	28.1
Fraction P (Paraffins)	17.2
Wax	7.2
$(N+A_1)/(P+A_2)$	0.82
N/P	1.02
Refractive index of Fraction P (N_D^{25})	1.4799
Asphalt viscosity at 60°C, P	1833
Penetration at 25°C, 100g., 5 sec.	80
Maltenes viscosity at 25°C, P	11,150
at 60°C, P	76.1
at 135°C, cS	108.6
Molecular weight of Fraction A	5830
Weight change in Thin Film Oven Test, pct.	+0.04
Pellet abrasion loss, mg/revolution	
Unaged	0.037
Aged 7 days at 60°C	0.033
Average of unaged and aged	0.035

TABLE 97

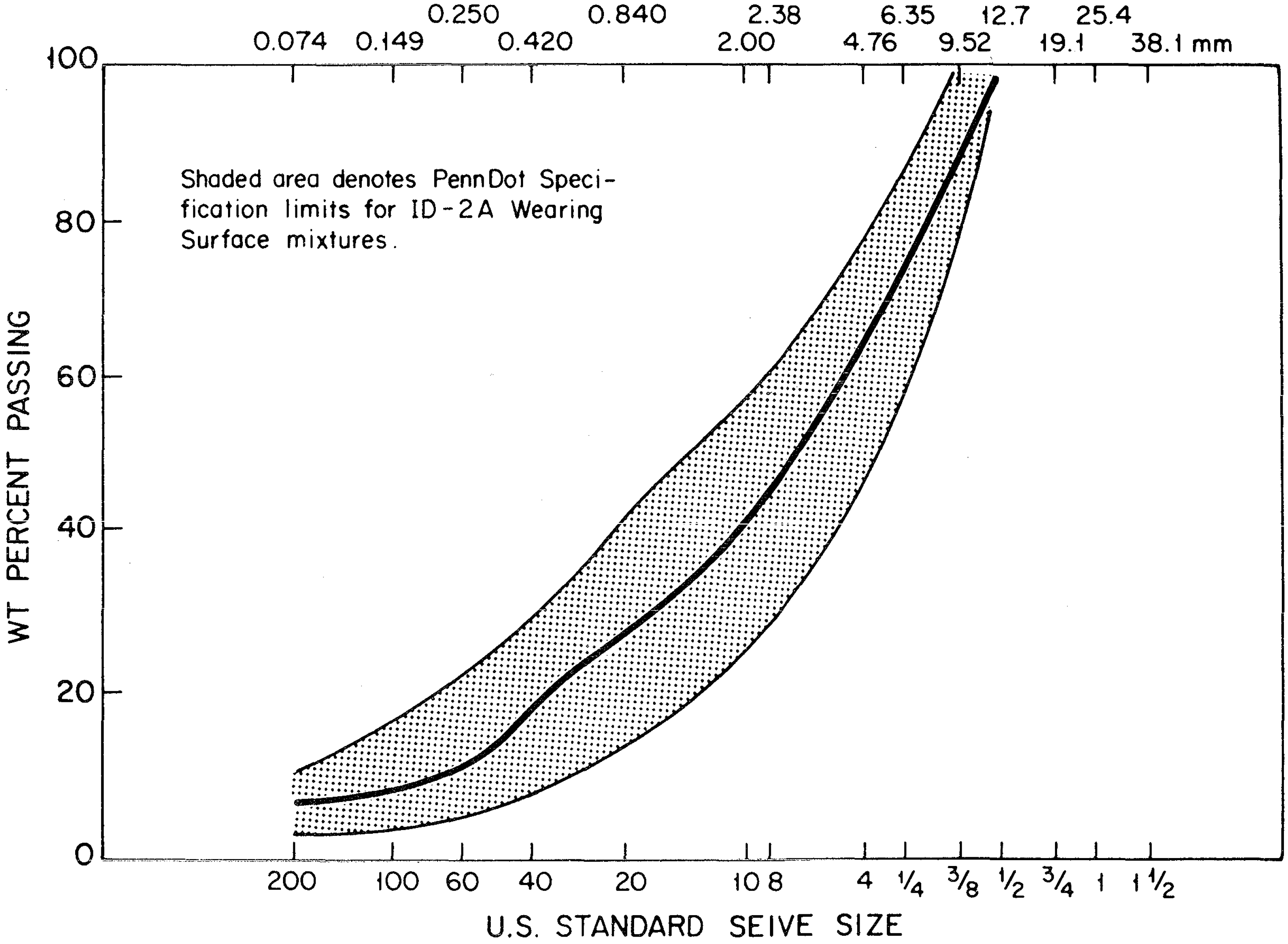
FINGERPRINTING DATA DETERMINED ON FOUR ASPHALTS FROM SUNTECH

Submitted June 7, 1979

Designation - Suntech	85-100 Fresh	7 pct. Blend	12 pct. Blend	7108-2
Asphalt Data Bank Card No.	M-26	M-27	M-28	M-29
Composition, pct of asphalt				
Fraction A (asphaltenes)	17.8	18.2	21.2*	22.8**
Fraction N (nitrogen bases)	14.7	18.0	18.7	22.5
Fraction A_1 (first acidaffins)	22.1	21.3	21.0	19.6
Fraction A_2 (second acidaffins)	31.0	27.8	25.8	22.7
Fraction P (paraffins)	14.4	14.7	13.3	12.4
Wax	9.7	9.8	14.8	8.5
$(N+A_1)/(P+A_2)$	0.81	0.92	1.02	1.20
N/P	1.02	1.22	1.41	1.81
Refractive index of Fraction P (N_D^{25})	1.4834	1.4827	1.4828	1.4832
Asphalt viscosity at 60°C, P	1885	860	694	504
Penetration at 25°C, 100g, 5 sec	82	109	125	129
Maltenes viscosity at 25°C, P	10,850	10,690	10,250	12,010
at 60°C, P	65.6	55.5	44.8	38.6
at 135°C, cS	89.5	77.4	66.8	59.5
Molecular weight of Fraction A	2780	1640	1503	1310
Weight change in Thin Film Oven Test, pct.	+0.01	-0.73	-1.26	-0.76
Pellet abrasion loss at 25°C, mg/revolution				
Unaged	0.004	0.008	0.005	0.007
Aged 7 days at 60°C	0.000	0.002	0.009	0.031
Average of unaged and aged	0.002	0.005	0.007	0.019

*includes 0.3% insoluble in benzene

**includes 0.7% insoluble in benzene



Shaded area denotes PennDot Specification limits for ID-2A Wearing Surface mixtures.

Fig. 41 Gradation of Wearing Surface Mix

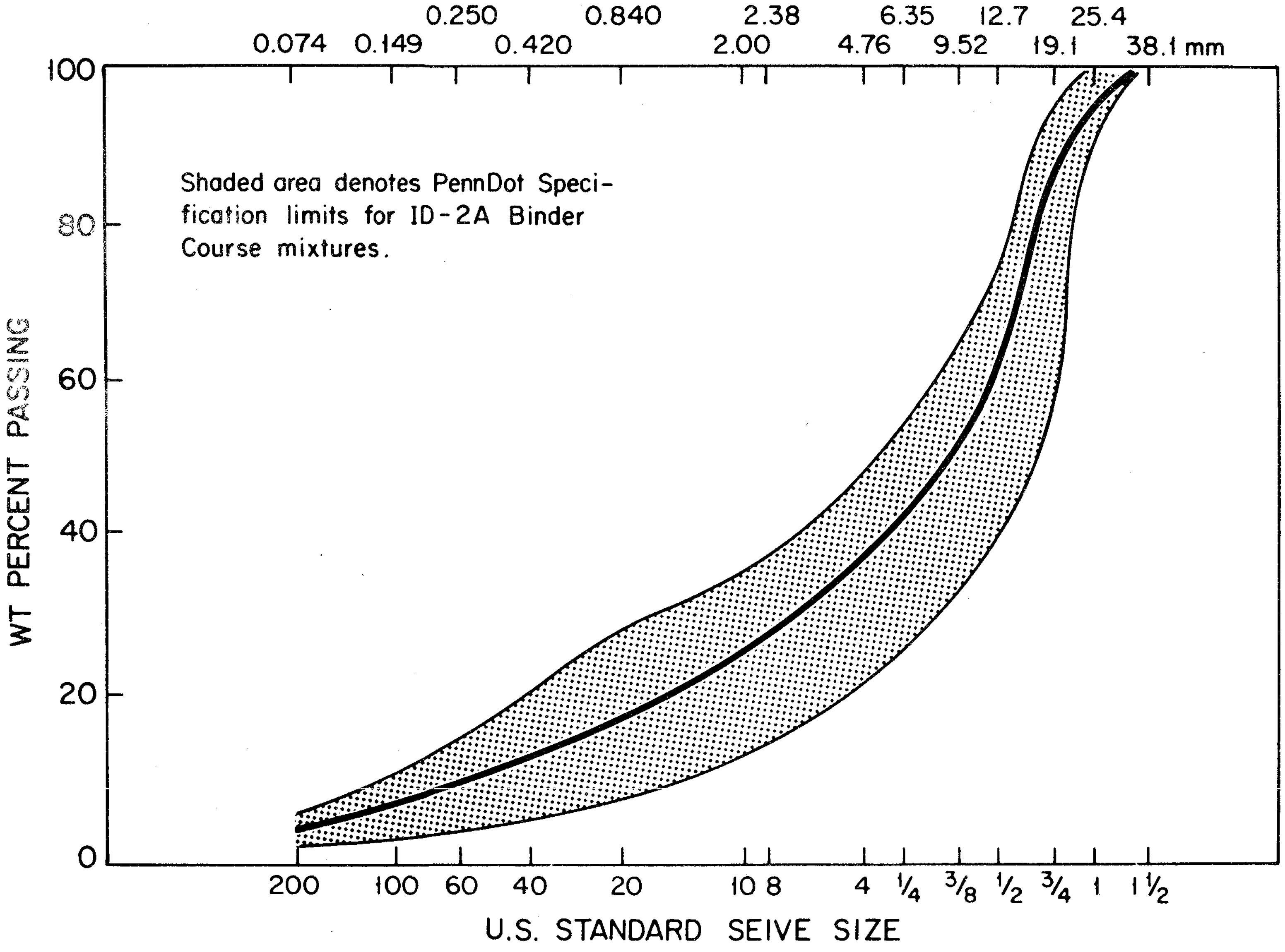
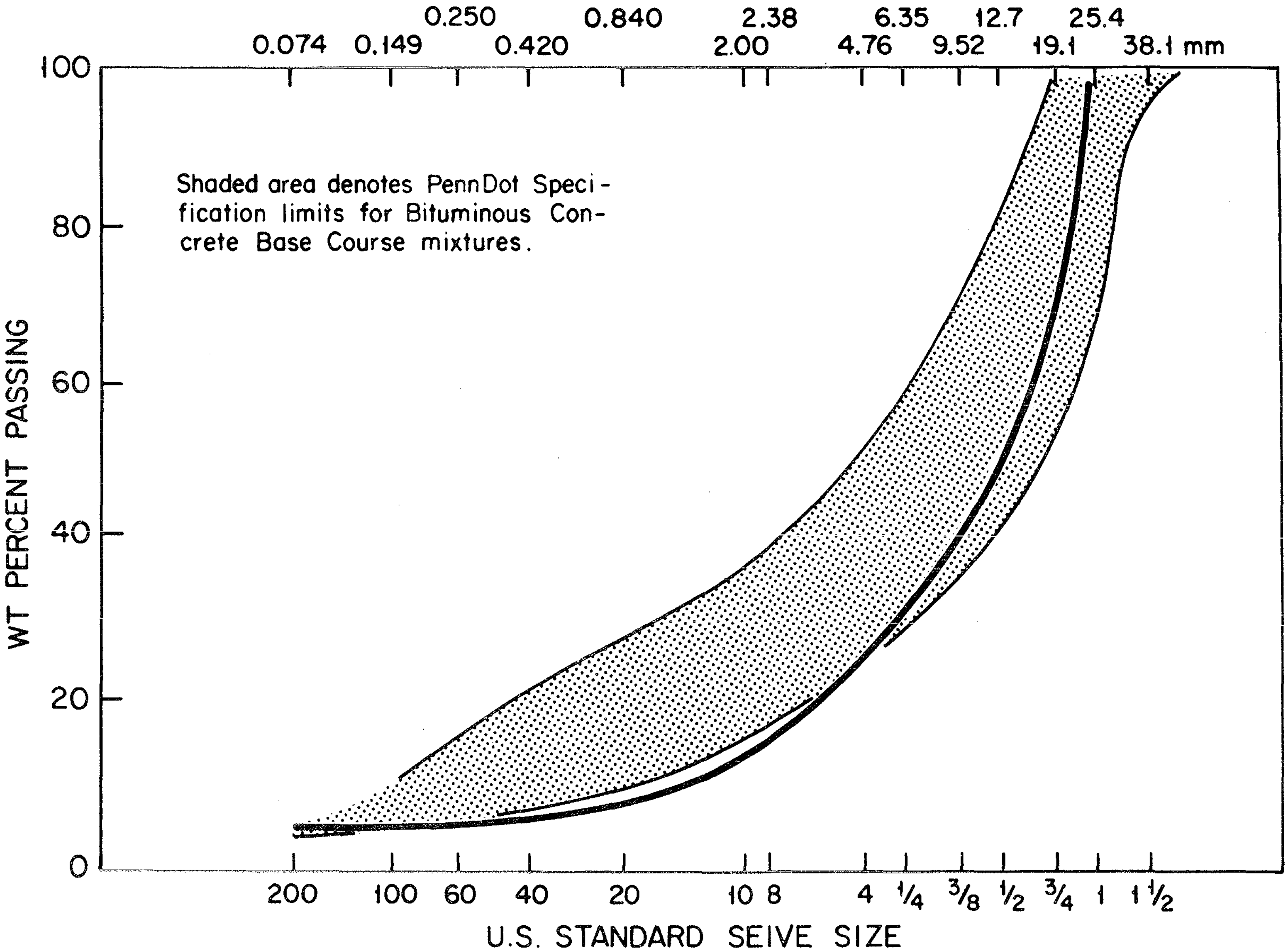


Fig. 42 Gradation of Binder Course Mix



Shaded area denotes PennDot Specification limits for Bituminous Concrete Base Course mixtures.

Fig. 43 Gradation of Base Course Mix

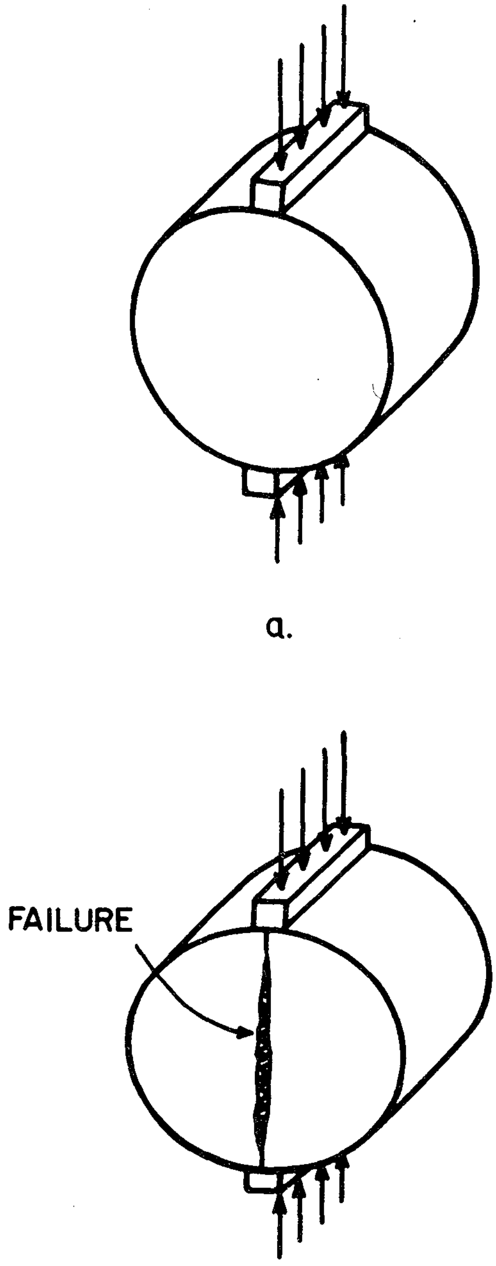


Fig. 44 Load Configuration Used in Measuring Indirect Tensile Failure

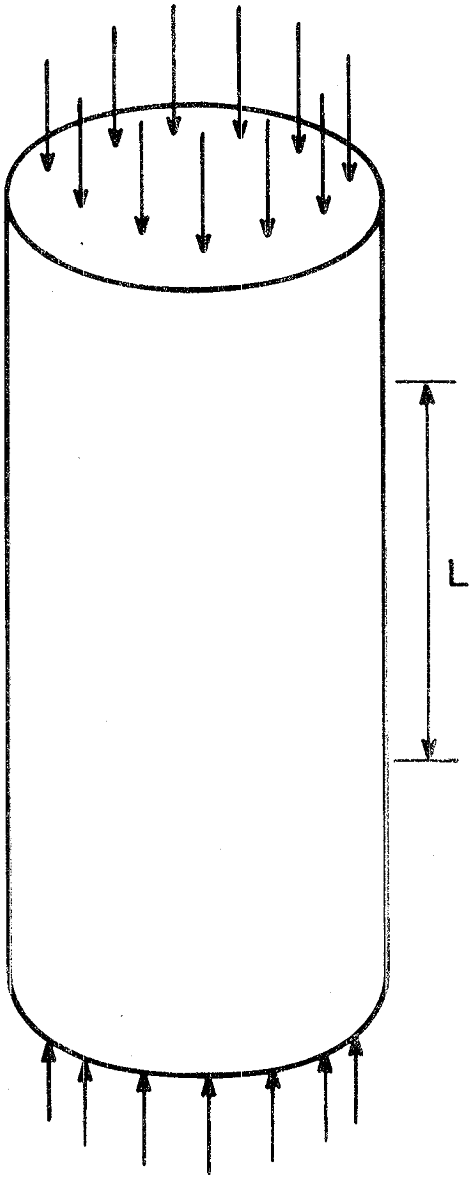


Fig. 45 Load Configuration Used in Measuring Permanent Deformation and Creep.

*U.S. GOVERNMENT PRINTING OFFICE: 1981-0-726-079/1272