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# The Disposal of Cattle Feedlot Wastes by Pyrolysis

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# THE DISPOSAL OF CATTLE FEEDLOT WASTES BY PYROLYSIS

by

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## ABSTRACT

Steer manure was obtained from a source that was generally free from extraneous mineral contaminants. This material was dried at 100°C and pulverized. Three types of laboratory scale pyrolysis reactors were used in a study of reaction conditions and of the characteristics of the materials that were produced.

Replicate batch pyrolyses were carried out in stainless steel vessels equipped with devices to scrub the exhaust in an ice-cooled trap and a solid carbon dioxide-cooled trap. There was also provision to sample the noncondensable gases. These pyrolyses were carried out with carefully controlled heating regimen and at atmospheric and low pressures. Optimum operating conditions were established by the criteria of maximizing yield of liquid organic products and minimizing the yield of carbonaceous solid residue. Low pressure and a maximum temperature of 400°-500°C were optimum.

A rotating glass device was used to prepare larger batches of pyrolysate. These runs, however, were not quantitative as it was not possible to completely remove condensables from the exhaust stream. Materials from these runs and the runs described above were used for one scheme of qualitative analysis of the organics.

A third pyrolysis study was carried out in a long iron tube that was progressively heated to 500°C along its length while the heated contents were swept with a slow stream of helium. Multiple condensate traps and scrubbers were used to collect condensate from the exhaust stream. This setup approximated a continuous run. The material from this run was analyzed by a classical organic separation scheme.

The yields of the long tube run were, based on dry weight:

| | |
|---|---|
| Char | 35.7% |
| Ash | 9.2 |
| Carbonaceous residue | 26.5 (by difference) |
| Low-boiling organics | 7.3 |
| Tarry volatile organics | 14.2 |
| Reaction water | 16.7 |
| Noncondensable gases | 26.1 (by difference) |

Under comparable conditions, other runs had yielded a noncondensable mixture of 8.6% $H_2$, 10.9% $N_2$, 16.0% CO, 38.9% $CO_2$, 12.9% $CH_4$, 0.3% $C_2H_4$, and 1.8% $C_2H_6$. The yield of this combustable mixture is equivalent to 2 - 3 million Btu/ton of dry manure.

The liquid pyrolysates contained a wide variety of alcohols, aldehydes, ketones, acids, amines and phenols as well as polyfunctional compounds. This complex mixture of organic compounds is valued at 1 to 2¢/lb based on the current prices for crude petroleum and coal tar obtained from coking operations.

Economic analysis of a proposed pyrolysis unit for a 40,000-head beef cattle feedlot shows the cost of pyrolysis with benefit of sale of pyrolysis products to be $5.60/ton of 80% moisture manure. This would place a liability of $25.30 on each market beef in addition to usual manure handling costs but less the cost of field disposal. Break-even pyrolysis economics will be achieved only if the pyrolysis product has a value of 8¢/lb.

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## SECTION I

## CONCLUSIONS

The vast quantity of manure produced as a by-product of the cattle feeding industry is both an economic burden on the industry and a potential environmental hazard to air, water and land quality. An attractive solution to these problems is the development of processes that would use the manure either as a fuel, or a source of basic raw materials for the chemical industry. Pyrolysis is possibly such a process.

Laboratory scale pyrolyses were conducted to determine the optimum pyrolysis conditions and the characteristic of the materials that were produced. The criterion for optimization was the yield of liquid organic compounds which were produced as water-soluble and water-insoluble oils and tars. Maximum yields were obtained with pyrolysis temperatures of 400°-500°C and low pressures. The liquid pyrolysate contains a wide variety of alcohols, aldehydes, ketones, acids, amines and phenols as well as polyfunctional compounds. Within the scope of the study, it was possible to completely characterize only a few of these compounds. In view of the complexity of this mixture, and the attendant cost of separation into components, its value must be placed at no more than 1 - 2¢/lb, the current price range of crude petroleum and coke oven tars.

Under optimum conditions the pyrolysis of unadulterated manure produced a char that contained about one-third ash. This char was difficult to burn in the open air. It had some properties as an adsorbent.

The pyrolysis produced a combustible gas with a fuel content of 300 - 400 Btu/ft$^3$ that contained $H_2$, $CH_4$, CO, $CO_2$, and $N_2$ with traces of $C_2H_4$ and $C_2H_6$. Approximately 2 - 3 million Btu/ton of dry manure, 20-30% of the fuel value of the dry raw manure, was recovered in the gas mixture.

Differential thermal analysis indicated that a portion of the reaction would proceed exothermically at 250°-300°C. The exothermic reaction yielded a mixture of gases and condensibles that could not be completely separated.

The pyrolysis process applied to cattle feedlot wastes is uneconomical in relation to simple incineration, as the cost of equipment to separate potentially valuable materials from the exhaust stream is not offset by the market value of these materials. The fuel oil that would be used to fire a predryer is probably more valuable than the pyrolysate. If materials isolated from the pyrolysate are merely used as fuels, the pyrolysis process becomes in essence a multistage incinerator with no particular advantage over simple burning.

Economic pyrolysis might be feasible if the fresh manure were allowed to dry in an arid climate. In such a case, however, the whole premise of rapid manure disposal to prevent the accumulation of an environmental hazard is defeated.

## SECTION II

## RECOMMENDATIONS

The results of this study do not encourage the immediate development of a pilot or large scale program to pyrolyze cattle wastes as a means of disposal.

Additional research can be done in anticipation of some of the possible trends in our economy. A long-term, low-level study could more fully characterize the exact nature of the pyrolysis products. This would permit more exact design of the pyrolysate separation units. Such a research program might well be conducted at a university where a by-product would be well-trained environmental scientists.

One economic trend that might bring pyrolysis into favor would be a steep rise in the price of feed grains. This would bring rough fodder back in use as a main dietary energy source, causing production of a bulkier, drier manure. Also, as oil and other fossil sources of carbon become scarce, manure pyrolysate may become competitive with crude petroleum and coal tar.

The pyrolysis process has its own environmental liabilities. Pyrolyzing manure has a distinct odor, somewhat like popular barbecue sauces. Some of the low boiling fractions on standing developed a particularly objectionable smell. If pyrolysis is to be developed into a usable process, devices for complete scrubbing of exhausts will need to be developed.

Coal tar, soot, and fumes of broiling meat are all reported to carry cancer producing agents. There is sound rationale in suspecting that the manure pyrolysates would also be carcinogenic. Adequate research should be conducted on this subject before an environmental hazard to aquatic wildlife is traded off for a real hazard to humans.

## SECTION III

## INTRODUCTION

The cattle feeding industry is experiencing two trends: growth in numbers of cattle fed and marketed annually; and growth in the size of the individual operations. Feedlots with 50,000 head are no longer unique. Since each animal produces from 40 to 60 lb. of manure daily, handling and disposal of the manure is a major operating task for the industry. With the competition of chemical fertilizers, the value of manure in most areas is below handling costs. On the other hand, there is a potential hazard to the environment, especially the natural watershed, from large quantities of impounded manure. The BOD load, high ammonia content, and suspended solids of manure have been responsible for specific fish kills and general degradation of aqueous bodies. Any economically attractive alternative to piling or concentrated field spreading should be investigated.

Pyrolysis, a common chemical process, is, in concept, an attractive solution for manure disposal. The dry animal manure produced in the USA is equal in mass to coal or oil production. Thus, manure could rival the fossil fuels as a source of carbonaceous material. A 60,000-head cattle feedlot produces daily, on a dry weight basis, some 300 tons of dry organic material of fairly uniform composition. Preliminary qualitative studies of manure pyrolysates indicated the presence of many common commercial organic chemicals.

Pyrolysis is thermal decomposition that can be achieved by heating in an inert atmosphere or by partial combustion. The process equipment must include a burner or heat sources, a pyrolysis chamber and a system for separating the condensable pyrolysate. A good benchmark for estimation of capital and operating costs of such a process would be incineration of municipal refuse. The pyrolysis process would thus require equipment at least as expensive as incineration and the process could be economically attractive in relation to incineration if there were a market for the products of the process.

Based on the above background, a program was conducted to determine if it is economically feasible to pyrolyze feedlot wastes as a method of volume reduction, stabilization and production of marketable by-products.

Preliminary to any cost analysis of the pyrolysis process was an iterative analysis of the process in terms of (1) type of product,

(2) yield of product, and (3) reaction conditions for producing this product. The assumption was made that the most valuable products would be liquid organics that contained either oxygen or nitrogen, that is, the alcohols, ketones, acids, and amines that might be used as either special solvents or synthesis intermediates.

Process parameters were first approximately established by small scale instrumental methods analyses. The thermodynamic character of manure pyrolysis was established by Differential Thermal Analysis (DTA). Weight loss in relation to time and temperature was established by Thermogravimetric Analysis (TGA).

Next, replicate small scale pyrolyses were made using samples containing approximately 30 g of dry manure. The condensable portion of the pyrolysate was collected in two sequential traps cooled to 0°C and -78°C. The mixture of tarry distillate and aqueous liquor that collected in the 0°C trap was extracted with chloroform. The chloroform extract and the aqueous layer were evaporated separately to yield two fractions plus the low boilers that condensed out in the -78°C trap.

The range of optimum conditions was established by use of Evolutionary Operation (EVOP). The techniques of EVOP are given in Appendix A. A maximum yield of the three fractions described above was sought, as well as minimization of the residue of carbonaceous material that remained in the pyrolysis vessel. Principal parameters studied were temperature, pressure and mineral content of the manure.

At this point, the need for a more definitive analysis of the liquid pyrolysis product was apparent. The pyrolysate was partially characterized by two versions of a standard qualitative analysis scheme. A wide variety of compounds were isolated. It was concluded that the pyrolysate was of low value by virtue of its complexity and the attendant cost of separation. Further, the pyrolysate contained no single unique or high valued compound that could be gleaned from the mixture to offset process costs.

The remainder of this report discusses the chemistry of the pyrolysis reaction, details of the experimental studies, and presents an economic analysis of a tentative process. Infrared spectra of isolated pyrolysis fractions are included as Appendices B and C. Waste production by cattle is discussed in Appendix D.

SECTION IV

## A LITERATURE REVIEW OF PYROLYSIS OF NATURAL PRODUCTS

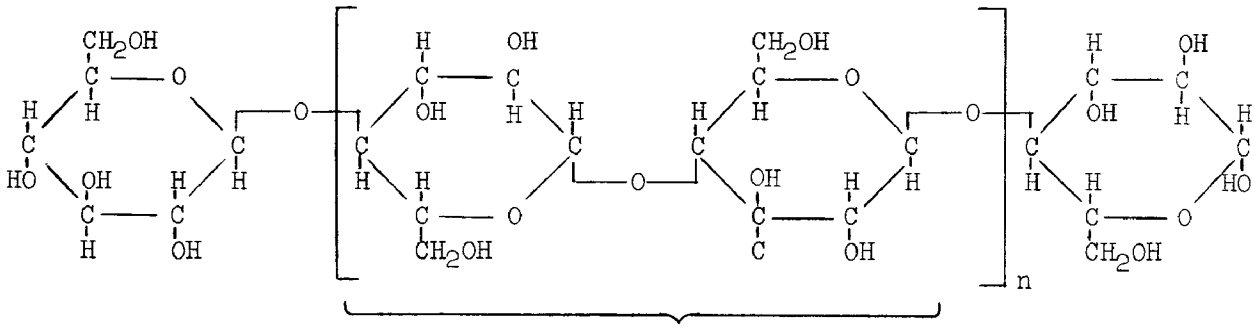
A preliminary literature survey disclosed no studies concerning the pyrolysis of cattle manure. The following is a review of literature related to such a pyrolysis study. The review covers the chemistry and composition of the manure; the pyrolysis of the polysaccharides--cellulose and hemicellulose--and of lignin; the pyrolysis of wood and possible relations to manure pyrolysis; the systems for analysis of cellulose pyrolysis products, and the application of these systems to manure pyrolysis products.

Cattle manure is largely a mixture of polysaccharides and long chain aromatic polymers usually found in the cell walls of plants.

Grub[1/] describes cattle manure as a combination of undigested food, unabsorbed digestive juices, cells and mucous from the digestive tract, and waste minerals. Fresh manure contains 80-85% water. Dry matter consists largely of undigested cellulose, hemicellulose, lignin, and lignoprotein complexes.

Cellulose is a homopolysaccharide containing glucose units linked together by 1-4-β-glucosidic bonds. The sugar formed by two glucose units is cellobiose.

Cellulose

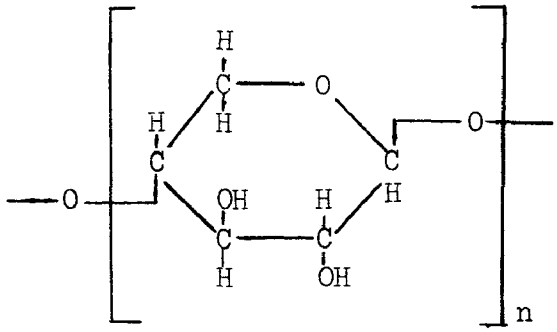



Cellobiose

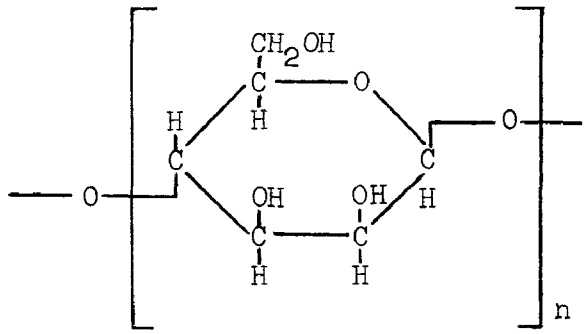
Hemicelluloses include heteropolysaccharides and uronic acids.

Hemicelluloses

Pentosans $(C_5H_8O_4)_n$

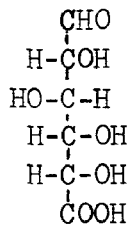


Hexosans $(C_6H_{10}O_5)_n$

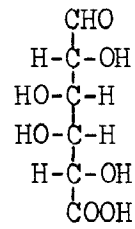


Pentosans include xylan and araban, while the hexosans may be mannan, glucan, galactan and others.

Uronic Acids

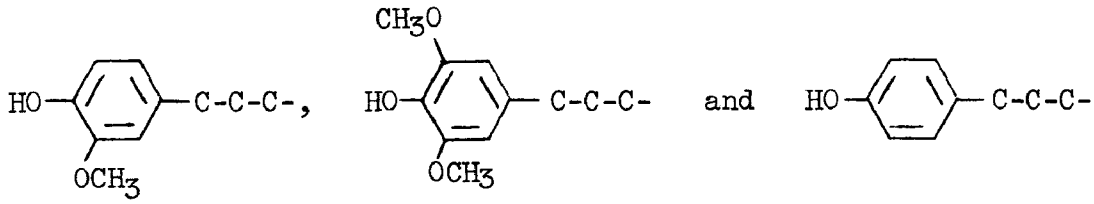


D-Glucuronic Acid



D-Galacturonic Acid

Although Pigman[2] suggests that the composition and genesis of lignin is unsettled, Nikitin[3] believes that lignin is composed of polymers containing the following units:



Ligno-protein complexes are highly stable humus-like compounds which are produced in the digestive tract of the ruminant by the reaction of lignin with bacterial protein. Grub[1] believes these compounds may comprise up to 25% of the total dry weight of the feces.

## Pyrolysis of Cellulose

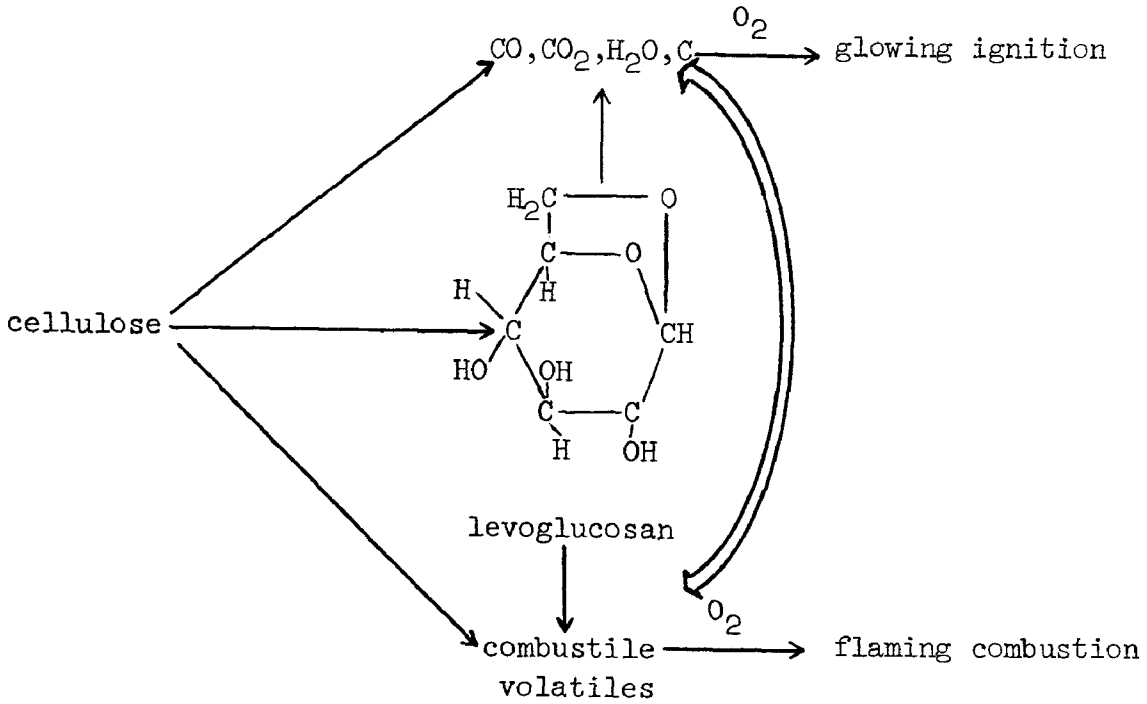
When dry cellulose is heated slowly to 120°C in the presence of air, water, vacuum or in various liquids, the molecule begins to depolymerize and changes occur in viscosity, α-cellulose content, strength, solubility in alkali, and copper number.[4,5] An aqueous distillate begins to form at 200°C, and tar and gases at 230-240°C. The reaction becomes exothermic at 270°C and extensive decomposition results with formation of solid, gaseous, and liquid products. Between 270-350°C the rate of production of gases is greatest, while above 350°C the rate of production of gas is constant until it is complete at 470°C.

The char resembles natural coal. Heuser[4] states that Bergius' experiments showed natural anthracite could be formed from plants rich in cellulose and poor in lignin. He also cites the conflicting opinion of Fisher, who believed that in the natural process the cellulose would be entirely destroyed by bacteria before the coalification could be completed. Contrary to both these arguments, Heuser himself believed the exposure of the mixture of cellulose, lignin and their biological decomposition products to heat produced a natural coal.

The aqueous distillate from cellulose pyrolysis contains small amounts of acetic and formic acids, acetone, methyl ethyl ketone and other ketones, while the tar is chiefly composed of phenols and undecomposed levoglucosan. The gases include CO, $CO_2$, hydrocarbons and $H_2$.

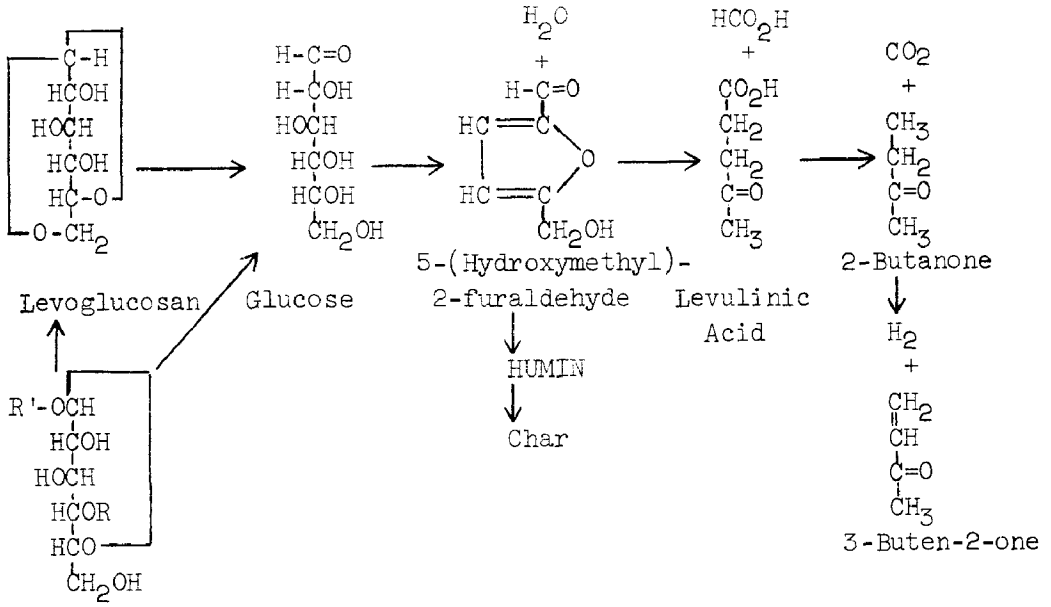
The nature of these pyrolysis products depends on the temperature and duration of heating, the presence of impurities and the surrounding atmosphere during pyrolysis. Coppick[5] observed that the amount of the flammable tarry compounds increased with an increase of the final pyrolysis temperature. Heuser[4] points out that cellulose loses much more of its tensile strength and α-cellulose at lower temperatures and longer periods of heating than at higher temperatures and shorter heating times.

Studies on the effect of impurities on cellulose pyrolysis have led to a mechanism involving the intermediate, levoglucosan. Shafizadeh[6] suggests that at high temperatures the following reactions take place:

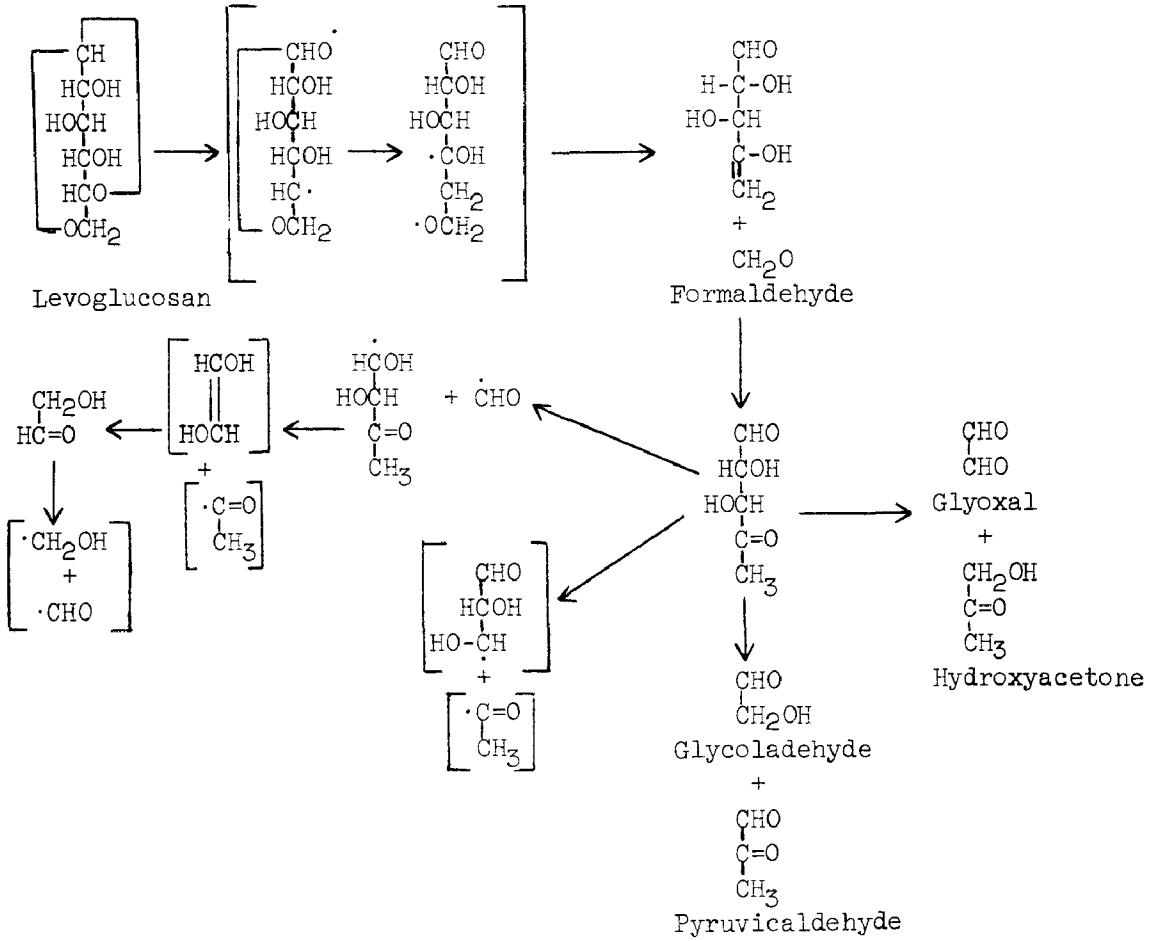



He cites the works of Martin, and Glassner and Pierce to prove that these secondary reactions occurred from the thermal degradation of the levoglucosan. Martin proved that flash pyrolysis produced a large percentage of levoglucosan. Under longer duration heating, the amount of levoglucosan decreased due to formation of secondary products. Glassner and Pierce compared cellulose pyrolysis and levoglucosan pyrolysis at isothermal conditions between 170-360 °C. The secondary products from these pyrolyses were essentially the same.

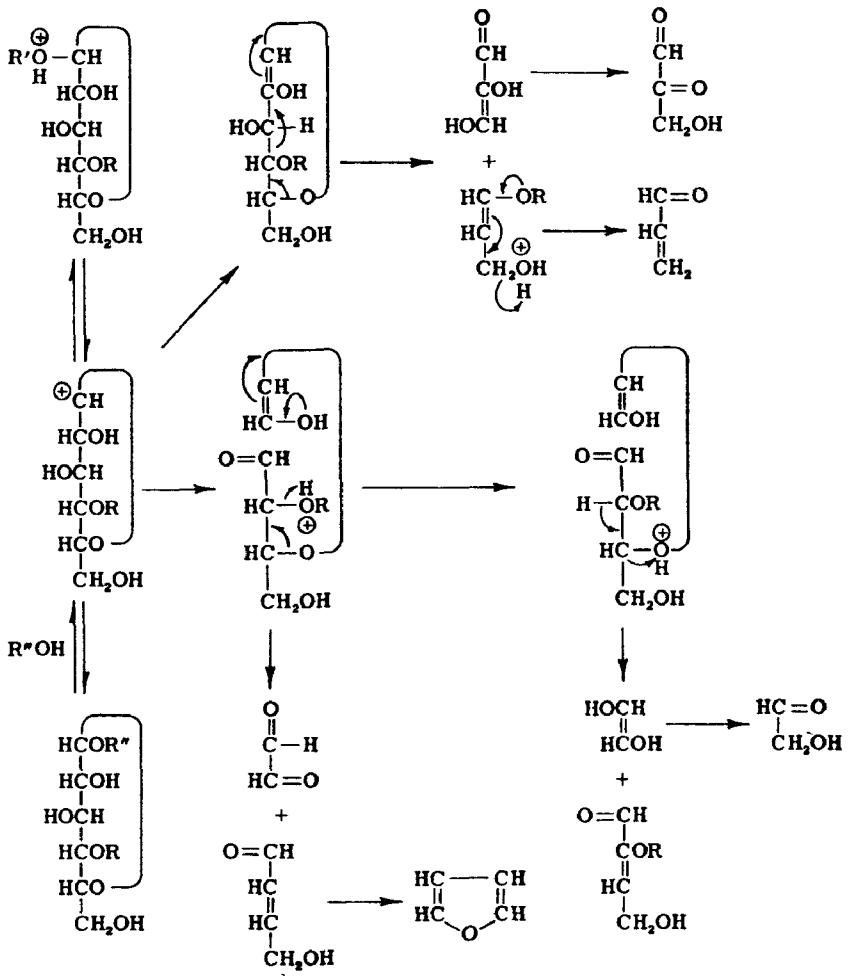
Shafizadeh cites several mechanisms for the secondary reactions. The secondary products could be formed in a way similar to the acid-catalyzed degradation of D-glucose residues:




Levoglucosan could also degrade through free radical formation and molecular rearrangement:



Shafizadeh cites another possible route for this degradation proposed by Byrne, Gardiner, and Holmes that would proceed through a carbonium ion intermediate:



Nikitin[3] suggests that polysaccharides hydrolyze at low temperatures and isomerize, decompose, condense and polymerize with increased heating. However, Shafizadeh believes that the pyrolysis of cellulose involves oxidation, hydrolysis, degradation, and decomposition at low temperatures, while thermal degradation occurs with an increase in temperature and duration of heating.

Some impurities in cellulose act as flame retardants by inhibiting the formation of levoglucosan and increasing the production of char, water

and gas. Several workers have used impurities such as water-soluble salts,[7,8] and organophosphorous compounds[9] as flame retardants.

Several pyrolysis experiments have been performed on cellulose in vacuum: Vann,[10] Madorsky,[11] Golova,* Pakhomov,* and Epshtein.* The vacuum prevents decomposition of levoglucosan by minimizing the secondary decomposition reactions of this tar. The vacuum removes as formed such oxidizing agents as CO, $CO_2$, $H_2O$, and $O_2$. Schwenker and Beck[13] have proposed that the same products are obtained in either nitrogen, air, or helium atmosphere. They suggested, therefore, that most secondary products were produced by a nonoxidative process.

## Pyrolysis of Hemicellulose and Lignin

Not many generalizations can be made concerning pyrolysis of lignin or hemicellulose since, as Shafizadeh[6] explains, few experiments on such pyrolyses are reported. One reason for the lack of research may be the difficulty in separating these two constituents from one another in wood. Nikitin[3] states that it is not possible to completely extract either lignin or carbohydrate from wood without contamination of the other. He has, however, noted (from the temperature curves in the data of Heuser, Skioldebrand, and Hägglund* and also from Heuser and Bretz*) that acidified lignin from spruce exothermally decomposes at a higher temperature range (350-450°C) than the cellulose. The pyrolysis of this lignin yielded more carbon and tar and less aqueous distillate than cellulose pyrolysis. Mishin* observed that hemicellulose must begin to decompose around 250°C, below the decomposition point of cellulose which is 270°C.

## Pyrolysis of Wood

Nikitin[3] provides a comprehensive review of wood pyrolysis. Wood begins to decompose considerably above 150°C. He cites the work of Violett* that shows the weight loss due to volatilization increases by 60.9% between 160°C and 270°C. Nikitin concluded from data of Klason* that the exothermal decomposition of wood begins at about 270-280°C. Large amounts of CO and $CO_2$, acetic acid and liquid distillate are produced, followed by production of light and heavy tars. By further heating to 380-400°C, heavy tars, plus $CO_2$, CO and hydrocarbon gases, were formed. The residue was carbon with adsorbed impurities.

---

* References cited by Nikitin.

The final pyrolysis products from charring depend on the type of wood, the final reaction temperature and duration of the heating. Klason* heated various woods to 400°C for 8 hr and obtained 32-38% carbon, 45-50% liquid, and 15-20% gas (including loss). Water accounted for 21-23% of the liquid distillate. Between 250-350°C more volatile products were liberated than in the final range of 350-450°C. As the heating duration increased, the yield of tars decreased and the yield of carbon increased.

The various constituents of wood are believed to decompose sequentially. Above 150°C and up to 270°C hemicellulose is almost completely decomposed, while cellulose decomposition is initiated and a small amount of lignin is lost. A large amount of gas is produced along with the aqueous distillate and tars. At 270-280°C, the cellulose decomposition becomes exothermic with some decomposition of lignin to produce the liquids, hydrocarbon gases, and tars. From 380°C to completion at 470°C, the lignin decomposes completely to light and heavy tars and hydrocarbon gases.

Charcoal from wood pyrolysis is not pure carbon, but contains volatile products. Bergstrom* reports that the amount of volatile products is a function of the final pyrolysis temperature. As this temperature was increased from 300-500°C, methoxy group content in charcoal decreased from 5.7 to 0.2%. Long heating periods also lead to an increase in the carbon content of the charcoal.

Although the liquid distillate may contain 60 organic compounds, the predominant compounds are acetic acid, methanol, methyl acetate and acetone. The liquid fraction also contains "soluble" tars. These tars contain condensation products of phenols and aldehydes, soluble acids, alcohols, and ketones. The work of Wacek, Tichcheuko, and Bobrov* confirms the production of the soluble tars as the pyrolysis of carbohydrates and cleavage of sugars.

The "settled" tar is composed of water-insoluble volatile products, nonvolatile products, and some water-soluble volatile products. The most important components of this tar include phenol, pyrocatechol, pyrogallol and their homologs (10-20%). Hydroxy acids also make up 20% or more of the tars.

The gases are noncondensed vapors saturated with volatile compounds trapped as droplets. Yvon* showed that only water vapor, $CO_2$ and CO are eliminated up to 280°C; hydrocarbons begin to be produced at 280°C and reach a maximum production between 380°C and 500°C, while hydrogen appears between 700-900°C.

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* References cited by Nikitin.

With an increase of pressure, the yield of soluble tar decreases and settled tar yield remains fairly constant. In a stream of reducing hydrogen the amount of these soluble tars increases while the secondary reactions decrease. Superheated steam is also another deterrent to secondary reactions by providing more uniform heating and continuous removal of volatile products. Liquid hydrocarbons can also be used as the reaction meddium to avoid producing dilute aqueous solutions. Pyrolysis in these media also lowers the exothermal decomposition point, which reaches a maximum rate of heat liberation between 260-270°C. Above this temperature, wood will almost entirely dissolve by a mechanism of thermal dissolution. Continuous circulation ovens also produce effects on the pyrolysis of wood similar to those produced *in vacuo*.

## Analytical Systems for Pyrolysates

Systems for the analysis of pyrolysis products have been mostly developed through the study of cellulose pyrolysis. Swenker and Pascu[14] used paper and partition chromatography for identification of nonvolatile acids and levoglucosan. Madorsky and co-workers used mass and infrared spectroscopy to identify vacuum pyrolysis products from cellulose[11] as well as products from derivatized cellulose.[12] Lindsey[15] suggests the use of elution chromatography for the identification of pyrolysis products. Greenwood, Knox and Milne[16] suggested the use of gas chromatography to identify the unidentified trace components found by conventional, IR, and mass spectrometry. Schwenker and Beck[13] used pyrolysis gas chromatography and found 37 different volatiles in contrast to the 8 to 18 products found by other workers. Lincoln[17] employed flash pyrolysis in which the reactant was exposed to a very short and intense impulse of heat. Only the light absorbing cellulose was heated, while the transparent container stayed cool. Under these conditions, there was complete volatilization of the sample. Lincoln adapted his apparatus to feed directly to a gas chromatograph or to a mass spectrometer. With these techniques he found that cellulose did not decompose below 600°C as compared to decomposition at 300°C by slower heating. Martin and Ramstad[18] used coupled gas chromatographic columns, attached directly to the flash pyrolysis unit, to measure separately the high molecular weight products and the fixed gases.

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* References cited by Nikitin.

## SECTION V

## EXPERIMENTAL PROCEDURES

This section of the report describes the collection and handling of the raw material, contains a description of the pyrolysis and collection equipment used and an outline of the separation procedures and analytical techniques used to identify pyrolysis products.

### Raw Material

Manure from two sources was used for this study. Manure used in early studies was obtained through the courtesy of Mr. Don Elfson, Farm Manager for Reorganized Church of Jesus Christ of the Latter Day Saints (RLDS). Manure from this source was from three Holstein yearling steers being maintained on a whole corn plus protein supplement diet. Manure from the RLDS farm proved to be of variable nature and contained up to 40% ash, largely $SiO_2$. This material is designated Sample "A" throughout this report.

Four yearling steers were subsequently purchased by MRI and kept on a partially covered concrete pad. These animals were fed a finishing ration. Two composite batches of manure collected from these steers were used as pyrolysis samples. These batches are identified as Samples "B" and "D".

Samples were dried for 24 hr at 212°F. This reduced the moisture level to approximately 7%. The material was then passed through a Wiley Mill using a 3/32 screen. Finely divided material prepared in this manner was used for all pyrolysis studies. Table 1 shows the ash and moisture content of the various samples.

TABLE 1

MANURE SAMPLES USED FOR PYROLYSIS

| Sample | % Moisture | % Ash | Source |
|---|---|---|---|
| "A" | 10.8 | 40 | RLDS Farm |
| "B" | 6.3 | 8.65 | MRI Feedlot |
| "D" | 2.7 | 8.95 | MRI Feedlot |

## Pyrolysis and Collection Equipment

Pyrolysis is the process of thermal decomposition in an inert or controlled atmosphere. Three pyrolysis procedures were employed in this research program.

The first unit developed and constructed for pyrolysis of manure consisted of a furnace designed to accommodate six 75-ml pressure bombs. Each bomb was connected in series to two pyrolysate collecting traps: the first at 0°C (ice) and the second at -78°C (dry ice). The sample collection train also contained a gas collection bulb that enabled sampling and analysis of noncondensables. The total volume of noncondensables was measured with a wet test meter. Approximately 30 g of dried manure was pyrolyzed in each bomb per run. The pyrolyses were conducted under vacuum and at atmospheric pressure. The unit is shown in Figure 1.

A second pyrolysis device was constructed from a 1.5 in. diameter black iron pipe 3 ft long. This pyrolysis tube simulated a unit which could be operated continuously. It enabled the pyrolysis of 350-g batches of dry manure.

Helium was used to maintain a nonoxidizing atmosphere. Heating burners were lit sequentially at 15-min intervals. After lighting all burners, heating was continued for an additional 67 min. Air input to the burners was adjusted to produce a sooty yellow flame. A thermocouple attached to the surface of the tube read 500°C ± 25°C. A schematic of this unit is shown in Figure 2.

A rotary glass device was also used to prepare several batches of tarry condensate. It was not possible, however, to get quantitative recovery with this system.

## Separation and Analysis of Pyrolysate

Two extraction procedures were used to separate the pyrolysate into fractions having different solubility characteristics and into different types of compounds. Schematics of the two separation procedures are shown in Section VII as Figures 6 and 7.

Figure 6 shows the schematic of the separation procedure that was developed specifically for this complex mixture of materials. It was designed, partially through trial and error, to separate products collected from the bomb pyrolysis studies. Also shown on this schematic are the types and yields of compounds found in various fractions.

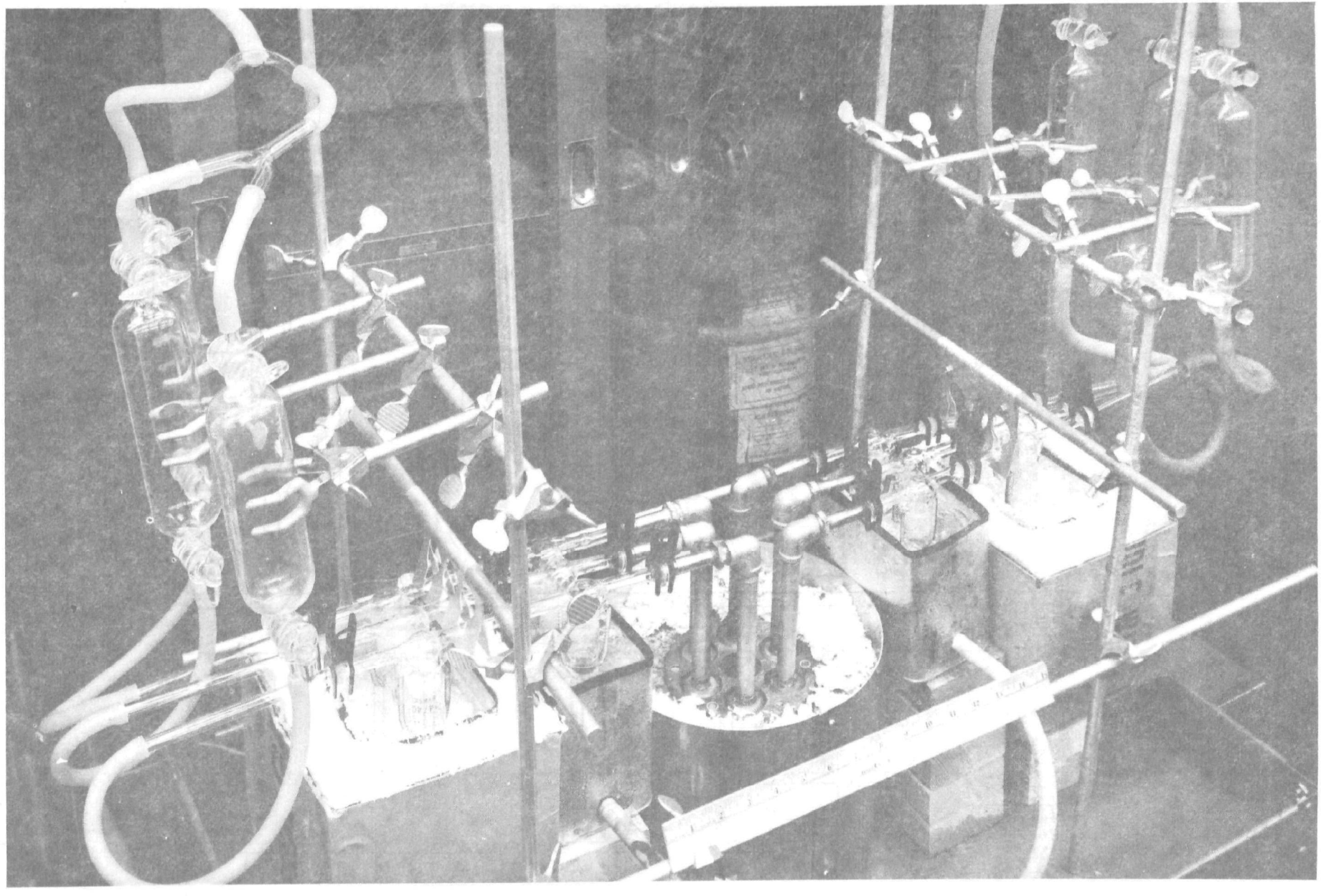


Figure 1 - Bomb Pyrolysis Unit

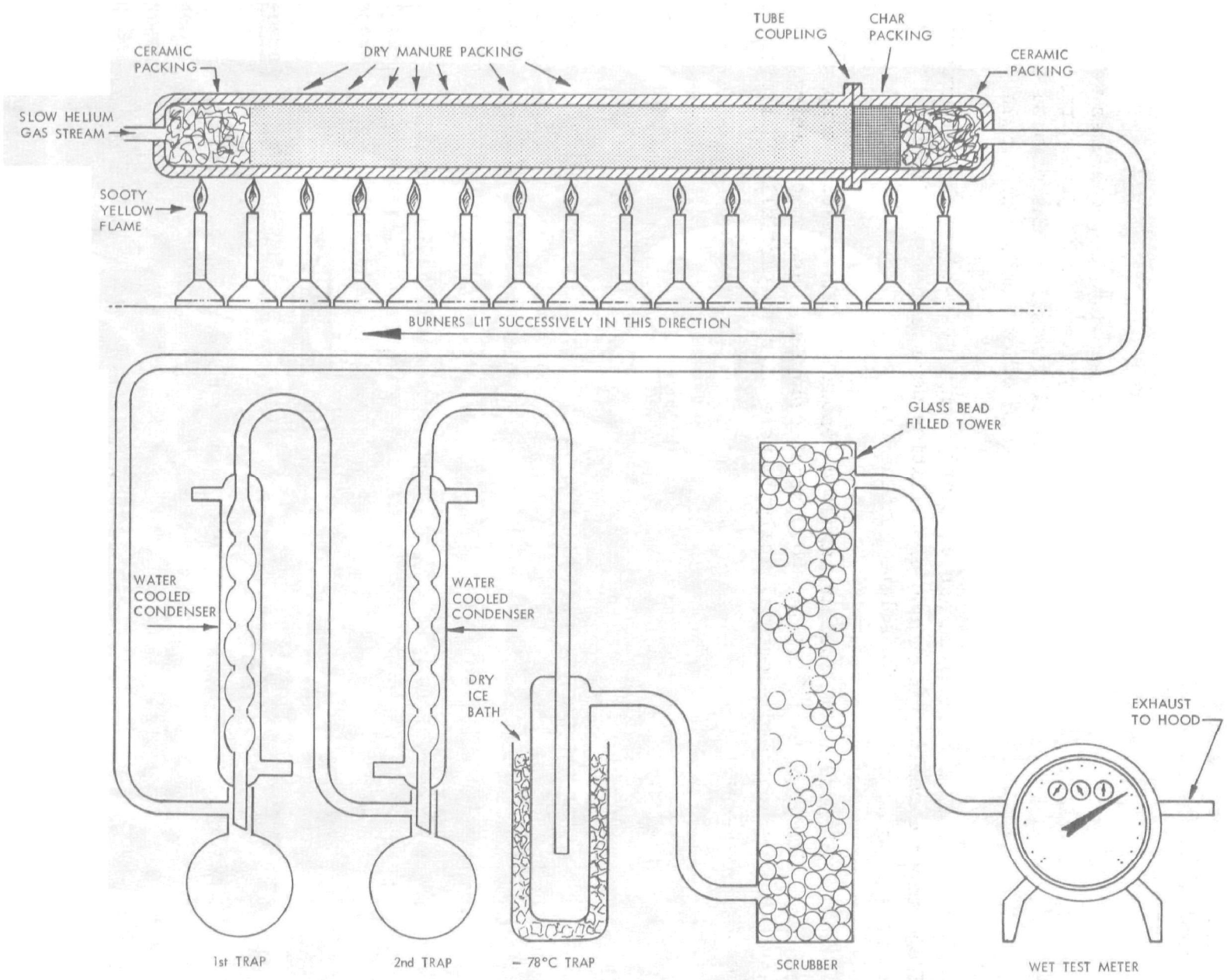



Figure 2 - Long Tube Pyrolysis

Figure 7 shows the schematic of the classical separation procedure taken from Cheronis and Entrikin's text "Semimicro Qualitative Organic Analysis."[19] This separation scheme was slightly modified for this separation task.

A variety of identification and other separation procedures were used in analysis of the components of the pyrolysate. These procedures were patterned after methods used in structural investigations of wood pulp, lignins, coal tar pitch, humic acids and other similar materials.

Vacuum sublimation, gas chromatography, thin-layer chromatography (TLC), paper chromatography, and distillation were used in addition to extraction to separate and isolate components.

Infrared (IR), nuclear magnetic resonance (NMR), electron spin resonance (ESR), and ultraviolet (UV) spectroscopies, mass spectrometry, gas chromatography and elemental analysis were used to partially characterize the tar fractions.

## SECTION VI

## QUANTITATIVE RESULTS OF PYROLYSIS EXPERIMENTS

Pyrolyses of bovine waste were conducted over a range of temperatures and at two pressures using the three pyrolysis units previously described. This section of the report contains a tabulation of the results of all pyrolyses conducted including yields for the various fractions of the distillate (tar, water, volatiles, noncondensables, and char).

Prior to initiating pyrolysis studies, preliminary investigations were conducted using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) to identify a temperature range for conducting the pyrolyses. Thermogravimetric analysis of Sample "A" was obtained using a Perkin Elmer TGS-1 instrument. Five-milligram samples of the manure were placed in a nickel sample cell. Five thermograms were obtained from samples maintained in a nitrogen atmosphere and one thermogram from a sample at $10^{-3}$ torr. Heating rates of 5°, 10°, 20° and 40°C/min were used.

Figure 3 shows percent weight loss as a function of temperature under a vacuum of $10^{-3}$ torr and at 1 atm. under nitrogen, both obtained using a heating rate of 5°C/min. Rapid weight loss began to occur in the temperature range of 200°-250°C for the sample maintained under a nitrogen atmosphere. A first derivative of this curve would show a maximum at about 300°C. Figure 4 shows weight loss at heating rates of 5°C/min and 40°C/min. The curves have essentially the same configuration; however, the curve obtained using the higher heating rate is displaced toward a higher temperature by 25°-30°C. This displacement may be attributed to inefficient heat transfer and hence to temperature lag in the sample.

The major difference observed was between the sample heated under vacuum and an identical sample heated under a nitrogen atmosphere. The temperature where rapid weight loss began to occur for the evacuated sample was at 350°-400°C, or approximately 150°C higher than for the sample under nitrogen. The maximum rate of weight loss occurred at approximately 450°C. The only obvious explanation for this difference is that some constituent of the manure, perhaps water, promotes degradation. If this constituent is removed under vacuum it is not available for hydrolytic decomposition of the manure.

Isothermal TGA studies were also conducted at two temperatures, 250°C and 325°C. The results of these studies are shown in Table 2.

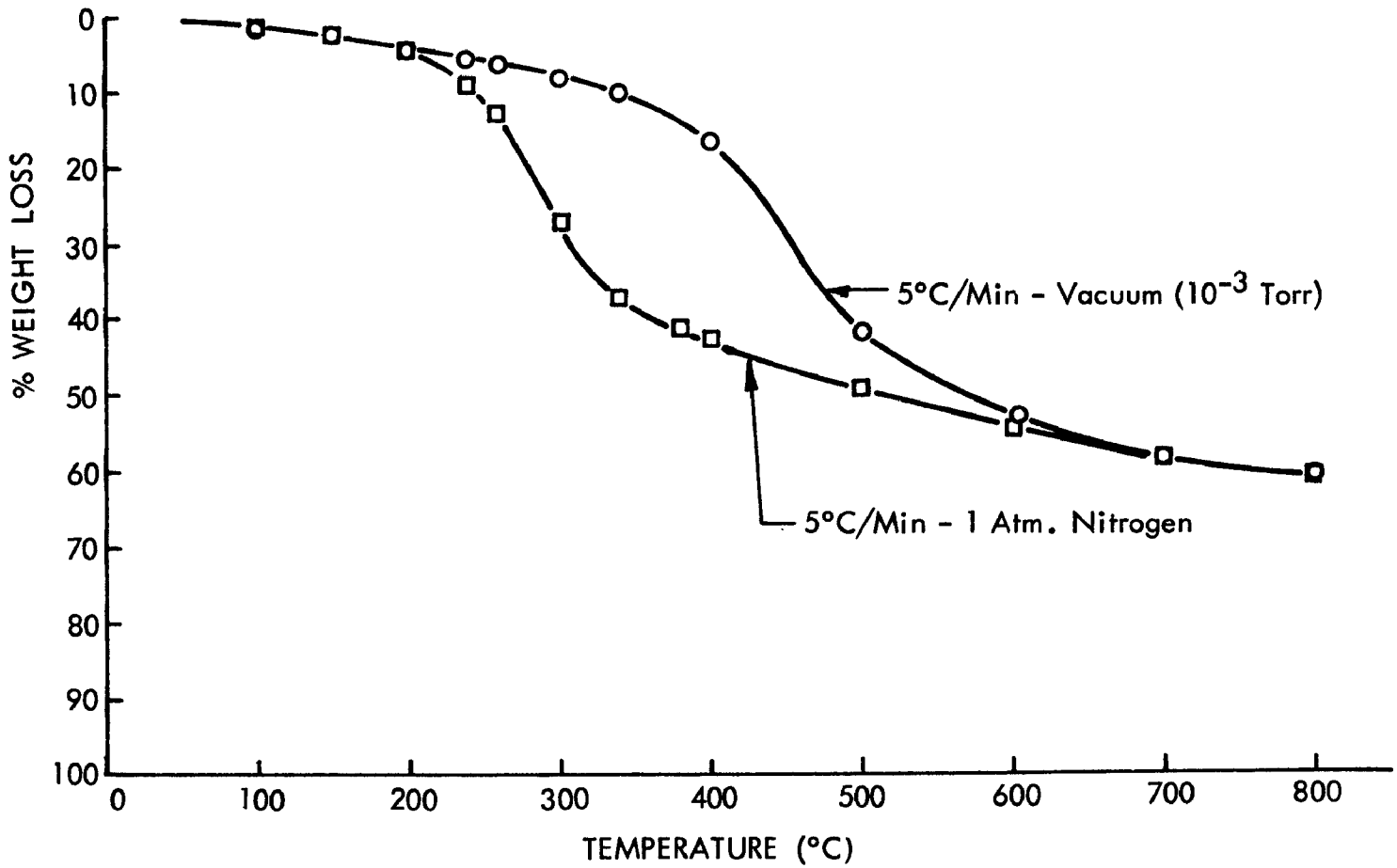



Figure 3 - Manure Weight Loss as a Function of Temperature

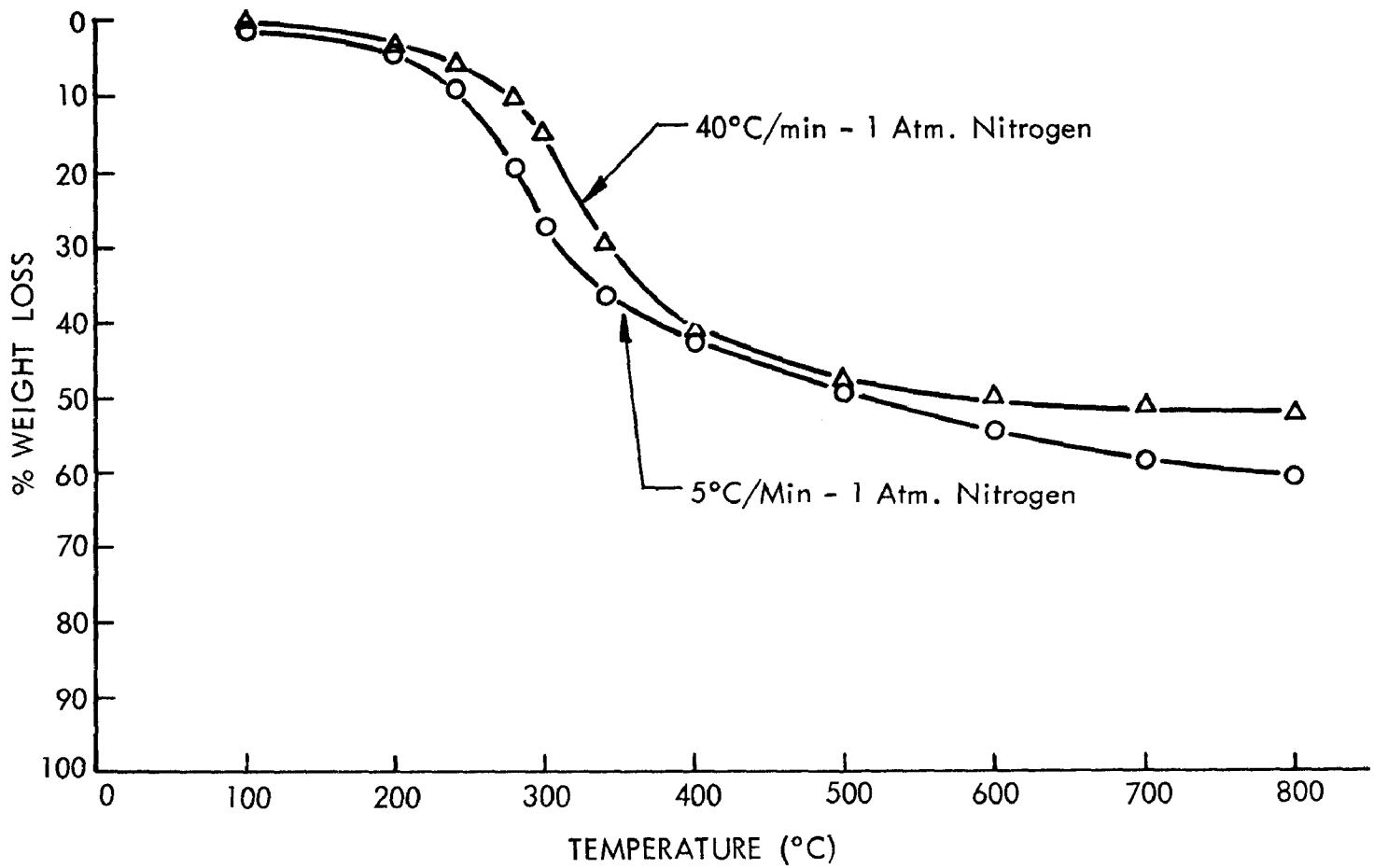



Figure 4 - Manure Weight Loss as a Function of Heating Rate

TABLE 2

ISOTHERMAL PYROLYSIS OF MANURE IN A NITROGEN ATMOSPHERE

| Temperature | Weight Loss[a] in Heating Period | |
|---|---|---|
| | 18 Min. | 90 Min. |
| 250°C | 18% | 29% |
| 325°C | 38% | 39% |

a/ A maximum of 59% of the sample could be volatilized by heating to constant weight at 600°C in air.

This study clearly demonstrated that a substantial portion of the volatiles was lost within 18 min. at 325°C.

Differential thermal analyses were conducted on this same sample of manure. A Du Pont 900 thermal analyzer was used for these measurements. Five thermal analyses were conducted over the temperature range 25°-800°C using heating rates of 5°, 15° and 30°C/min.

The general patterns of all the DTA curves were similar. Each demonstrated an endotherm, exotherm, endotherm, exotherm sequence. The temperature ranges were not completely uniform, even on curves repeated at the same heating rate. The lack of reproducibility was possibly due to variations in the samples. The change in the pattern from endothermic to exothermic is indicative of a multicomponent mixture in which the components pyrolyze or volatilize independently. The similar patterns exhibited at all heating rates seem to demonstrate that change of heating rate within this range does not change the reaction significantly. A typical tracing of the instrument readout is shown in Figure 5.

TGA and DTA studies showed clearly that little or no pyrolysis occurred below 200°C and that no advantage was realized by pyrolyzing at temperatures above 600°C. High temperatures could also be expected to cause second order reactions and a larger number of pyrolysis products.

The results of these experiments provided certain guidelines for process development. Slow heating is preferred to fast heating; 300°C seems a minimum temperature, and very high temperatures have no advantage. These guidelines agree with the results obtained by other workers who are investigating the pyrolysis of refuse,[20,21] tires,[22] etc.

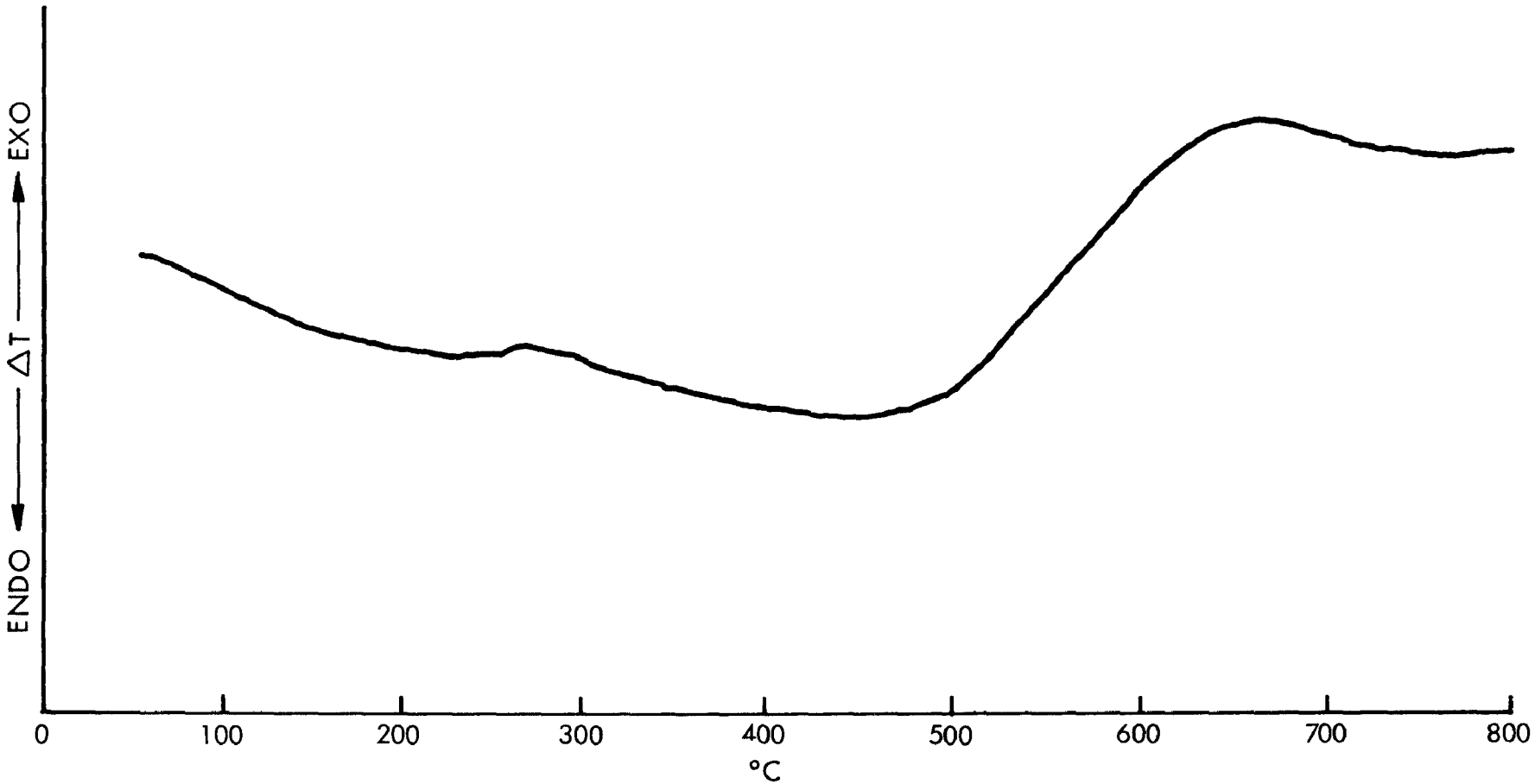



Figure 5 - Typical Readout from Thermal Differential Analysis

As a consequence of these studies, samples of manure pyrolyzed in the bomb apparatus were rapidly heated to 200°C (~ 10°C/min). The temperature program (heating rate, temperature, time) was then varied between 200°C and 600°C to determine what effect temperature and time had on the amounts of pyrolysate and char. Results from these experiments are shown in Table 3. Also contained in this table are the results of studies in which portland cement, sodium bisulfate monohydrate and sodium carbonate were added to the manure. These materials were evaluated as potential pyrolysis catalysts. They are inexpensive, readily available, and had been evaluated previously as catalysts for pyrolysis of other organic materials.[23]

Table 4 shows the composition of the noncondensable gases that were obtained from these batch pyrolyses.

The results of large-scale (350-g) pyrolyses are presented in Table 3 as experiments 11 to 15.

TABLE 3

RESULTS OF PYROLYSIS EXPERIMENTS

| Experiment No. | Sample | Sample Wt. (g.) | Dry Wt. (g.) | Temperature Program | Pyrolysis Procedure | Pyrolysis Pressure (Atm.) | Pyrolysis Products (g.) Water | Water Soluble | Volatiles[b] | Tar | Non-condensible[c] | Char | % Yield[d] Tar |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | "A"[a] | 50 | 44.6 | 25°C ⟶ 200°C in 45 Min. | Bomb | < 0.1 | 9.3 | 2.5 | 0.2 | 7.5 | 3.5 | 27.0 | 16.8 |
| | | 50 | 44.6 | Hold at 200°C for 165 Min. | Bomb | < 0.1 | 8.1 | 2.2 | 0.2 | 7.6 | 5.9 | 26.0 | 17.0 |
| | | 50 | 44.6 | 200°C ⟶ 500°C in 65 Min. | Bomb | < 0.1 | 10.3 | 2.4 | 0.3 | 7.1 | 3.9 | 26.0 | 15.9 |
| | | 50 | 44.6 | Hold at 500°C for 95 Min. | Bomb | 1.0 | 8.9 | 1.3 | 0.5 | 3.9 | 8.4 | 27.0 | 8.7 |
| | | 50 | 44.6 | | Bomb | 1.0 | 8.9 | 1.6 | 0.6 | 2.9 | 8.5 | 27.5 | 6.5 |
| | | 50 | 44.6 | | Bomb | 1.0 | 9.0 | 1.8 | 0.6 | 3.2 | 9.0 | 26.5 | 7.2 |
| 2 | "A" | 51 | 45.5 | 25°C ⟶ 200°C Fast<br>200°C - 30 Min.<br>200°C ⟶ 350°C at 1°/Min<br>350°C ⟶ 500°C Fast | Bomb | 1.0 | 8.5 | 1.2 | - | 5.3 | 12.0 | 24.0 | 11.7 |
| 3 | "A" | 50 | 44.6 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | 8.8 | 0.7 | - | 3.7 | 8.4 | 28.4 | 8.3 |
| | | 50 | 44.6 | 200°C ⟶ 400°C at 5°/Min | Bomb | < 0.1 | 9.9 | 1.0 | - | 3.2 | 9.7 | 26.5 | 7.2 |
| | | 50 | 44.6 | 400°C - 140 Min. | Bomb | < 0.1 | 10.1 | 0.5 | - | 3.1 | 9.4 | 26.9 | 7.0 |
| | | 50 | 44.6 | | Bomb | 1.0 | 9.9 | 1.5 | - | 3.2 | 6.5 | 28.9 | 7.2 |
| | | 50 | 44.6 | | Bomb | 1.0 | 10.2 | 1.3 | - | 3.5 | 6.5 | 28.5 | 7.9 |
| | | 50 | 44.6 | | Bomb | 1.0 | 9.7 | 0.8 | - | 2.4 | 8.4 | 28.7 | 5.4 |
| 4 | "A" | 50 | 44.6 | 25°C ⟶ 200°C Fast<br>200°C ⟶ 300°C at 1°/Min<br>300°C - 120 Min. | Bomb | 1.0 | 9.7 | 0.2 | - | 0.5 | 3.3 | 36.3 | 1.1 |
| 5 | "A" | 50 | 44.6 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | 10.3 | 0.5 | 0.5 | 5.3 | 10.4 | 23.7 | 11.9 |
| | | 50 | 44.6 | 200°C ⟶ 600°C at 5°/Min | Bomb | < 0.1 | 10.2 | 0.7 | 0.5 | 3.9 | 10.7 | 24.0 | 8.8 |
| | | 50 | 44.6 | 600°C - 100 Min. | Bomb | < 0.1 | 9.5 | 0.5 | 0.4 | 5.1 | 10.2 | 24.3 | 11.4 |
| | | 50 | 44.6 | | Bomb | 1.0 | 10.2 | 0.3 | 0.5 | 1.8 | 11.0 | 26.2 | 4.0 |
| | | 50 | 44.6 | | Bomb | 1.0 | 10.2 | 0.3 | 0.8 | 1.2 | 11.3 | 26.3 | 2.7 |
| | | 50 | 44.6 | | Bomb | 1.0 | 10.2 | 0.3 | 0.9 | 1.1 | 10.3 | 27.2 | 2.5 |
| 6 | "B"[e] | 20 | 18.7 | 25°C ⟶ 300°C Fast<br>300°C - 180 Min.<br>300°C ⟶ 500°C Fast<br>500°C - 75 Min. | Bomb | 1.0 | 5.8 | 0.2 | 0.2 | 1.2 | 6.6 | 6.0 | 6.4 |
| 7 | "B" | 33 | 30.9 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | 10.8 | 0.4 | 0.2 | 1.5 | 8.8 | 11.3 | 4.9 |
| | | 33 | 30.9 | 200°C ⟶ 500°C at 5°/Min | Bomb | < 0.1 | 8.9 | 0.4 | 0.2 | 2.1 | 11.2 | 10.2 | 6.8 |
| | | 33 | 30.9 | 500°C - 120 Min. | Bomb | < 0.1 | 9.3 | 0.6 | 0.2 | 2.5 | 10.2 | 10.2 | 8.1 |
| | | 33 | 30.9 | | Bomb | 1.0 | 9.1 | 0.3 | 0.4 | 1.8 | 9.8 | 11.6 | 5.8 |
| | | 33 | 30.9 | | Bomb | 1.0 | 8.5 | 0.3 | 0.4 | 1.2 | 11.1 | 11.5 | 3.9 |
| | | 33 | 30.9 | | Bomb | 1.0 | 8.9 | 0.3 | 0.4 | 0.9 | 11.3 | 11.2 | 2.9 |

TABLE 3 (Continued)

| Experiment No. | Sample | Sample Wt. (g.) | Dry Wt. (g.) | Temperature Program | Pyrolysis Procedure | Pyrolysis Pressure (atm.) | Pyrolysis Products (g.) Water | Water Soluble | Volatiles[b] | Tar | Non-condensible[c] | Char | % Yield[d] Tar |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | "B" | 33.0 | 30.9 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | 8.7 | 0.5 | - | 2.2 | 8.7 | 12.9 | 7.1 |
| | | 33.0 | 30.9 | 200°C ⟶ 400°C at 5°/Min | Bomb | < 0.1 | 8.5 | 0.5 | - | 2.2 | 8.6 | 13.2 | 7.1 |
| | | 33.0 | 30.9 | 400°C - 140 Min. | Bomb | < 0.1 | 8.2 | - | - | 2.2 | 9.6 | 13.0 | 7.1 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 8.0 | 0.3 | 0.3 | 0.8 | 10.0 | 13.6 | 2.6 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 8.9 | 0.4 | 0.2 | 1.0 | 9.4 | 13.1 | 3.2 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 7.8 | 0.2 | 0.2 | 0.7 | 10.6 | 13.5 | 2.3 |
| 9 | "B" | 33.0 | 30.9 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | - | - | - | - | - | 10.2 | - |
| | | 33.0 | 30.9 | 200°C ⟶ 600°C at 5°/Min | Bomb | < 0.1 | 9.9 | 0.6 | - | 3.2 | 9.3 | 10.0 | 10.3 |
| | | 33.0 | 30.9 | 600°C - 100 Min. | Bomb | < 0.1 | 9.4 | 0.6 | - | 3.3 | 10.1 | 9.6 | 10.7 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 9.8 | 0.3 | 0.6 | 0.8 | 10.6 | 10.9 | 2.6 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 9.6 | 0.3 | 0.6 | 1.0 | 10.7 | 10.8 | 3.2 |
| | | 33.0 | 30.9 | | Bomb | 1.0 | 8.8 | 0.2 | 0.6 | 1.2 | 11.8 | 10.4 | 3.9 |
| 10 | "B" | 33.0 | 30.9 | | Bomb | 1.0 | 8.3 | 0.6 | - | 3.3 | 11.6 | 9.2 | 10.7 |
| 11 | "B" | 33.0 | 30.9 | Yellow Flame (~ 500°C) 120 Min. | Rotovac | 1.0 | 8.3 | 0.3 | - | 1.8 | 9.9 | 12.7 | 5.8 |
| 12 | "D"[f] | 150.0 | 145.9 | Yellow Flame (~ 500°C) 120 Min. | Rotovac | 1.0 | 34.8 | 6.2 | - | 8.1 | 33.9 | 67.0 | 5.6 |
| 13 | "D" | 150.0 | 145.9 | Yellow Flame (~ 500°C) 120 Min. | Rotovac | 1.0 | 35.4 | 2.6 | 0.6 | 8.2 | 37.9 | 65.3 | 5.6 |
| 14 | "B" | 398.5 | 373.5 | Yellow Flame (~ 500°C) 120 Min. | Rotovac | 1.0 | - | - | - | 17.6 | - | 165.0 | 4.9 |
| 15 | "D" | 331.0 | 321.8 | ~ 500°C - 277 Min. | Tube[g] | 1.0 | 62.3 | - | 23.5 | 45.9 | 84.3 | 115.0 | 14.3 |
| 16 | "B"/Portland Cement 80/20 | 30.0 | 22.5 | ~ 500°C | Bomb | 1.0 | 6.4 | 0.2 | - | 1.7 | 8.7 | 13.0 | 5.2 |
| 17 | "B"/$NaHSO_4 \cdot H_2O$ 90/10 | 33.0 | 27.9 | 25°C ⟶ 300°C at 10°/Min, 300°C - 60 Min. 300°C ⟶ 450°C at 10°/Min, 450°C - 120 Min. 450°C ⟶ 500°C at 10°/Min, 500°C - 150 Min. | Bomb | 1.0 | 10.0 | 1.0 | - | 2.2 | 10.8 | 10.0 | 7.9 |
| 18 | "B"/$NaHSO_4 \cdot H_2O$ 33/3 | 36.0 | 30.9 | 25°C ⟶ 200°C at 10°/Min | Bomb | < 0.1 | 10.4 | 0.2 | - | 0.9 | 8.4 | 16.1 | 2.9 |
| | | 36.0 | 30.9 | 200°C ⟶ 400°C at 5°/Min | Bomb | < 0.1 | 10.6 | 0.3 | 0.3 | 1.1 | 8.3 | 15.4 | 3.6 |
| | | 36.0 | 30.9 | 400°C - 140 Min. | Bomb | < 0.1 | 9.5 | 0.6 | 0.3 | 2.8 | 8.6 | 14.1 | 9.0 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 10.3 | 0.3 | - | 1.5 | 8.6 | 15.3 | 4.6 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 10.2 | 0.3 | - | 0.9 | 8.9 | 15.7 | 2.9 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 10.5 | 0.4 | - | 1.3 | 8.7 | 15.1 | 4.2 |

TABLE 3 (Concluded)

| Experiment No. | Sample | Sample Wt. (g.) | Dry Wt. (g.) | Temperature Program | Pyrolysis Procedure | Pyrolysis Pressure (atm.) | Pyrolysis Products (g.) Water | Water Soluble | Volatiles[b] | Tar | Non-condensible[c] | Char | % Yield[d] Tar |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 5.0 | 4.3 | 25°C → 200°C at 10°/Min | Bomb | < 0.1 | 0.2 | 0.3 | - | 0.15 | 2.7 | 1.9 | 3.5 |
| | | 10.0 | 8.6 | 200°C → 400°C at 5°/Min | Bomb | < 0.1 | 0.8 | 0.2 | - | 0.3 | 5.4 | 3.3 | 3.5 |
| | | 15.0 | 12.9 | 400°C - 140 Min | Bomb | < 0.1 | - | - | - | - | - | - | - |
| | | 20.0 | 17.2 | | Bomb | < 0.1 | 3.0 | 0.4 | - | 0.7 | 9.1 | 6.8 | 4.1 |
| | | 25.0 | 21.5 | | Bomb | < 0.1 | 5.5 | 0.7 | - | 1.1 | 8.3 | 9.4 | 5.1 |
| | | 30.0 | 26.8 | | Bomb | < 0.1 | 6.7 | 0.9 | - | 1.6 | 9.6 | 11.2 | 6.0 |
| 20 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 36.0 | 30.9 | 25°C → 200°C at 10°/Min | Bomb | < 0.1 | 9.7 | 1.1 | 0.3 | 1.7 | 12.2 | 11.0 | 5.5 |
| | | 36.0 | 30.9 | 200°C → 500°C at 5°/Min | Bomb | < 0.1 | 9.4 | 1.0 | 0.3 | 1.85 | 12.4 | 11.0 | 6.0 |
| | | 36.0 | 30.9 | 500°C - 120 Min. | Bomb | < 0.1 | 9.3 | 1.0 | 0.3 | 1.85 | 12.2 | 11.3 | 6.0 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 11.9 | 0.6 | - | 1.25 | 7.9 | 14.3 | 4.1 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 11.6 | 0.5 | - | 1.5 | 8.2 | 14.2 | 4.9 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 10.7 | 0.4 | - | 1.3 | 9.2 | 14.4 | 4.2 |
| 21 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 36.0 | 30.9 | 25°C → 200°C at 10°/Min | Bomb | < 0.1 | 9.4 | 1.1 | - | 2.25 | 12.1 | 11.1 | 7.3 |
| | | 36.0 | 30.9 | 200°C → 600°C at 5°/Min | Bomb | < 0.1 | 9.3 | 1.2 | - | 2.5 | 11.8 | 11.2 | 8.1 |
| | | 36.0 | 30.9 | 600°C - 100 Min. | Bomb | < 0.1 | 9.7 | 0.9 | - | 2.3 | 12.0 | 11.1 | 7.5 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 9.9 | 0.6 | - | 1.75 | 11.0 | 12.7 | 5.7 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 11.6 | 1.1 | - | 1.9 | 9.5 | 11.9 | 6.2 |
| | | 36.0 | 30.9 | | Bomb | 1.0 | 10.1 | 1.3 | - | 1.8 | 9.9 | 12.9 | 5.8 |
| 22 | "B"/$Na_2CO_3$ 99/1 | 30.0 | 27.8 | 25°C → 200°C at 10°/Min | Bomb | 1.0 | 8.6 | 0.2 | - | 1.0 | 9.3 | 10.9 | 3.6 |
| | | 30.0 | 27.8 | 200°C → 500°C at 5°/Min | Bomb | 1.0 | 8.9 | 0.2 | - | 0.75 | 8.7 | 11.4 | 2.7 |
| | | 30.0 | 27.8 | 500°C - 120 Min. | Bomb | 1.0 | 9.2 | 0.3 | - | 0.9 | 8.6 | 11.0 | 3.2 |

a/ All "A" samples contained 10.8% moisture and 40% ash.
b/ Water insoluble volatiles, condensed at -78°C.
c/ Calculated by difference.
d/ Calculation base on dry weight of sample.
e/ All "B" samples contained 6.3% moisture and 8.65% ash.
f/ All "D" samples contained 2.7% moisture and 8.95% ash.
g/ Pyrolysis run under helium atmosphere.

TABLE 4

COMPOSITION OF NONCONDENSIBLES

| Experiment No. | Sample | Dry Wt. (g.) | Temperature Program | Pyrolysis Pressure (atm.) | Pyrolysis Procedure | Composition (volume %) $H_2$ | $N_2$ | $O_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | "B" | 92.7 | 25°C ⟶ 200°C at 10°/Min | < 0.1 | Bomb | - | 40.2 | 12.2 | 12.6 | 24.9 | 6.0 | - | 0.4 |
| | | 92.7 | 200°C ⟶ 500°C at 5°/Min<br>500°C - 120 Min. | 1.0 | Bomb | 8.6 | 10.9 | - | 16.0 | 38.9 | 12.9 | 0.3 | 1.8 |
| 8 | "B" | 92.7 | 25°C ⟶ 200°C at 10°/Min | < 0.1 | Bomb | - | 43.8 | 10.8 | 17.0 | 32.4 | 3.7 | - | - |
| | | 92.7 | 200°C ⟶ 400°C at 5°/Min<br>400°C - 140 Min. | 1.0 | Bomb | - | 14.0 | - | 23.6 | 49.6 | 3.2 | - | 0.4 |
| 9 | "B" | 92.7 | 25°C ⟶ 200°C at 10°/Min | < 0.1 | Bomb | 17.0 | 23.8 | 7.6 | 14.2 | 27.3 | 8.8 | 0.3 | 0.8 |
| | | 92.7 | 200°C ⟶ 600°C at 5°/Min<br>600°C - 100 Min. | 1.0 | Bomb | 16.4 | 7.0 | - | 16.7 | 37.2 | 15.5 | 0.4 | 1.7 |
| 19 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 86.0 | 25°C ⟶ 200°C at 10°/Min<br>200°C ⟶ 400°C at 5°/Min<br>400°C - 140 Min. | < 0.1 | Bomb | - | 27.1 | 17.5 | - | 43.0 | 3.0 | - | - |
| 20 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 88.5 | 25°C ⟶ 200°C at 10°/Min | < 0.1 | Bomb | 3.6 | 19.2 | - | 26.4 | 38.8 | 9.2 | 0.6 | 1.4 |
| | | | 200°C ⟶ 500°C at 5°/Min<br>500°C - 120 Min. | 1.0 | Bomb | 2.2 | 27.9 | - | 19.8 | 34.8 | 11.0 | 0.6 | 2.1 |
| 21 | "B"/$NaHSO_4 \cdot H_2O$ 11/1 | 88.5 | 25°C ⟶ 200°C at 10°/Min | < 0.1 | Bomb | 12.0 | 15.8 | - | 28.3 | 31.2 | 13.2 | 0.8 | 1.6 |
| | | | 200°C ⟶ 600°C at 5°/Min | 1.0 | Bomb | 6.5 | 19.4 | - | 21.6 | 34.0 | 15.4 | 0.5 | 1.9 |

## SECTION VII

## SEPARATION AND CHARACTERIZATION OF ORGANIC COMPOUNDS PRODUCED BY PYROLYSIS

Prior to proceeding with detailed fractionation and separation, the tar from the pyrolysis had been extracted with water and then with chloroform. The combination of water and chloroform dissolved all of the pyrolysate. These solvents were used to primarily remove the tar from the condenser traps and to clean the lines between the pyrolysis cell and the traps. These two extracts were then evaporated to dryness at 100°C. The resultant residues were designated as "Tar H," an $H_2O$-soluble material; and "Tar C," the $CHCl_3$-soluble material. The water-soluble fraction amounted to 25 - 30% of the pyrolysate condensables, excluding water.

### Preliminary Separation and Analysis

Samples of Tar C and Tar H were subjected to a variety of separation procedures that had previously been used in structural investigations of wood pulp lignins, coal tar pitch, humic acids and similar materials.

Vacuum sublimation, thin-layer chromatography (TLC), paper chromatography, and extraction (liquid-liquid and Soxhlet) experiments were performed in order to isolate major constitutents from either the water or chloroform-soluble tars. Infrared (IR), nuclear magnetic resonance (NMR), electron spin resonance (ESR), and ultraviolet (UV) spectroscopies, and elemental analysis were used to characterize the tar fractions.

### Procedures and Results

a. Vacuum sublimation: Samples of Tar C and Tar H (0.5 g) were placed in a standard vacuum sublimation apparatus and evacuated (~ 0.1 torr) for 30-60 min at room temperature. The temperature was then raised to 180°C by means of an oil bath.

A trace of yellow oil condensed on the cold finger from the chloroform-soluble material (Tar C) at 80°-100°C. A majority of the sample remained (~ 98%) as residue under these conditions. The infrared spectra of the residue before and after loss of the oil were essentially the same. Both tars lost water and entrapped gases that were not condensed

on the cold finger. Thus, vacuum sublimation resulted only in the isolation of a minor component of the chloroform-soluble tar, and was useful for removal of entrapped gases and water prior to other analyses.

b. Thin-layer chromatography: Silica Gel G chromatographic plates and a chloroform-ethyl acetate-formic acid solvent mixture (50-40-10) were used in an attempt to separate the $H_2O$-soluble material. The plates were sprayed with Fast Blue Salt B-NaOH (Reagent 61). This system has been used to separate various phenolic carboxylic acid mixtures (e.g., pyrolgallol, gallic acid, etc.).[24]

The entire sample moved with the solvent front and no separation of components of the water-soluble tar fraction was observed by this method.

c. Paper chromatography: Whatman No. 54 paper was used as the support. The solvent system consisted of butanol-water-ethyl alcohol (50-40-10). This system had been used by others in an attempt to separate levoglucosan and organic acid components.[25]

As with TLC, the entire sample migrated with the solvent front.

d. Extraction studies: Each tar fraction was extracted with solvents. The results of these experiments are given in Table 5.

With one exception, the solvent extraction experiments resulted only in partitioning or dissolution of the entire sample. The one exception was hexane extraction of the chloroform-soluble tar. Approximately 10% of this tar was insoluble in hexane. No difference was observed between the UV spectra of the two fractions.

e. Infrared analyses: Infrared analyses were made on thin films of both tars deposited from chloroform and other solvents used in extractions. Spectra of the water-soluble tars were also obtained from KBr pellets. Infrared spectra of the dried water-soluble and chloroform-soluble fractions revealed several significant structural differences. The most significant were: (1) greater O-H and/or N-H content of the water-soluble fraction as indicated by the stronger bands present at 3 and 6 μ, (2) the absence of a strong C=O absorption in the chloroform-soluble sample; and (3) the absorption, at 7.3 μ, of the chloroform-soluble material indicating $CH_2$ chains of length greater than four carbons. The ratio of O-H to C-H absorption indicates that the water-soluble material may contain hydroxyquinone; the C=O absorption is of course typical of carboxylic acid type structures; and the pH of a saturated solution of the

TABLE 5

EXTRACTION OF CHLOROFORM- AND WATER-SOLUBLE PYROLYSATES

| Tar | Solvent | Result |
|---|---|---|
| Chloroform-soluble pyrolysate | Benzene | 50 mg. solid dissolved in 5 ml. |
| | Ethyl acetate | 50 mg. solid dissolved in 5 ml. |
| | Carbon tetrachloride | 50 mg. solid dissolved in 5 ml. |
| | 70% sulfuric acid | 50 mg. solid dissolved in 5 ml. (test for lignin neg.) |
| | Hexane | 50 mg. in 5 ml. was 80-90% soluble. Subjected extract and $CHCl_3$ solution of residue to UV analysis. Attempted to separate hydrocarbons from aromatic carbonyl (observed in IR), but residue showed no UV maxima at 280 mμ. |
| Water-soluble pyrolysate | Methanol | 50 mg. solid dissolved in 5 ml. |
| | Ethanol | 50 mg. solid dissolved in 5 ml. |
| | DMSO | 50 mg. solid dissolved in 5 ml. |
| | Benzene | Insoluble. |
| | Hexane (Soxhlet) | Somewhat soluble but infrared of extract and residue indicated partitioning rather than separation. |

$H_2O$-soluble material was 5, consistent with carboxylic acid structures. The IR spectra of water-soluble tars show a close similarity to those of sodium salts of humic acids.[26]

f. Nuclear magnetic resonance analyses: The NMR spectra of the chloroform-soluble fraction were obtained from carbon tetrachloride solutions. A singlet was observed at a $\tau$ value of 8.7 and a second peak with an intensity of less than 10% of the first occurred at 9.1. The peak at 8.7 $\tau$ is characteristic of methylene groups; the lesser peak at 9.1 $\tau$ indicates the possible presence of a few methyl groups.

The spectra of the water-soluble tar were obtained in $D_2O$ and acetone. The sample was run in a nondeuterated solvent because no proton resonance was observed in $D_2O$. It was thought that the absence of resonance may have been due to exchange of the OH and NH protons with $D_2O$. Resonance was also not observed in the nondeuterated solvent; this could be due to unpaired electron broadening of the resonance or a shifting of the resonance to $\tau$ values greater than 10 if the protons are positioned above the plane of a polyaromatic ring system.

The conclusions drawn from the IR spectra complement the results of the NMR experiments. The water-soluble material showed no proton resonance in deuterated and nondeuterated solvents, indicating a highly substituted structure similar to that proposed by Flaig[26] for the humic acid formed from lignin. The chloroform-soluble fractions showed sharp resonance at 8.7 $\tau$ with no splitting. The spectrum of this fraction indicated that the majority of protons were in long chain $CH_2$ groups.

g. Electron spin resonance analyses: Humic acid and related model compounds have been shown to have a stable free-radical content. For this reason, electron spin resonance spectra of both fractions were obtained. Both samples gave a single line spectrum at "g" values near 2.0. The intensity of the signal was approximately $10^{17}$ spins/g of the water-soluble material. A spin density of $10^{18}$ spins/g was observed in EPR studies of soil humic acids.[25] These results indicate the similarity of this pyrolysate to soil humic acids.

h. Ultraviolet analyses: Ultraviolet analyses of the tar samples on the Beckman DK showed the water-soluble material to have an absorption maximum at 281 m$\mu$. The chloroform-soluble material showed no UV absorption maxima above 240 m$\mu$. The quinone moiety has an absorption maximum at 280 m$\mu$.

i. Elemental analyses: Elemental analyses were performed on a standard F&M C, H, & N Analyzer. Table 6 shows the results of

elemental analysis of the dried tar samples and also literature values for humic acids extracted from straw.[26]

TABLE 6

ELEMENTAL ANALYSES - PYROLYSATE FRACTIONS

| | C | H | N | O (by difference) |
|---|---|---|---|---|
| $CHCl_3$-soluble | 77.7% | 9.8% | 4.8% | 7.7% |
| $H_2O$-soluble | 53.4 | 5.9 | 6.6 | 34.0 |
| Straw humic acid | 53.7 | 5.2 | 3.4 | 37.6 |

Again, these results showed the similarity of the straw humic acid to water-soluble tar fractions; the reduced oxygen and nitrogen content of the chloroform-soluble material is also evident. The latter result indicates that the chloroform-soluble tar is a high-temperature product from which some $H_2O$, $NH_3$, and $CO_2$ have been eliminated. This conclusion is supported by infrared spectra reported in the literature[27] for chars of cellulose and coal produced at various temperatures. The spectrum of a cellulose char produced at 190°C was similar to the spectrum of the uncharred material, but the intense C=O band from the cellulose and 190°C char was absent in char produced at 250°C. Corresponding decreases in the O-H stretching and bending frequencies were also observed. The amount of water-soluble and chloroform-soluble materials produced from the manure might similarly be controlled by the control of pyrolysis temperature.

## Characterization of Pyrolysates by Classical Methods of Separation

The general characteristics of pyrolysates were defined by the above-discussed preliminary studies. Further characterization was undertaken through classical methods of fractionation and analysis. Of primary interest in this investigation was the possible existence of economically significant concentrations of useful, or potentially useful, chemical compounds.

Two separation procedures were employed. Scheme I is depicted in Figure 6; Scheme II in Figure 7 (p. 40). These methods require a substantial quantity of starting material. Several samples of Tar C and Tar H produced in bomb pyrolysis were combined to furnish a large sample for fractionation. A large sample of pyrolysate produced in the hot tube pyrolysis unit was also subjected to fractionation.

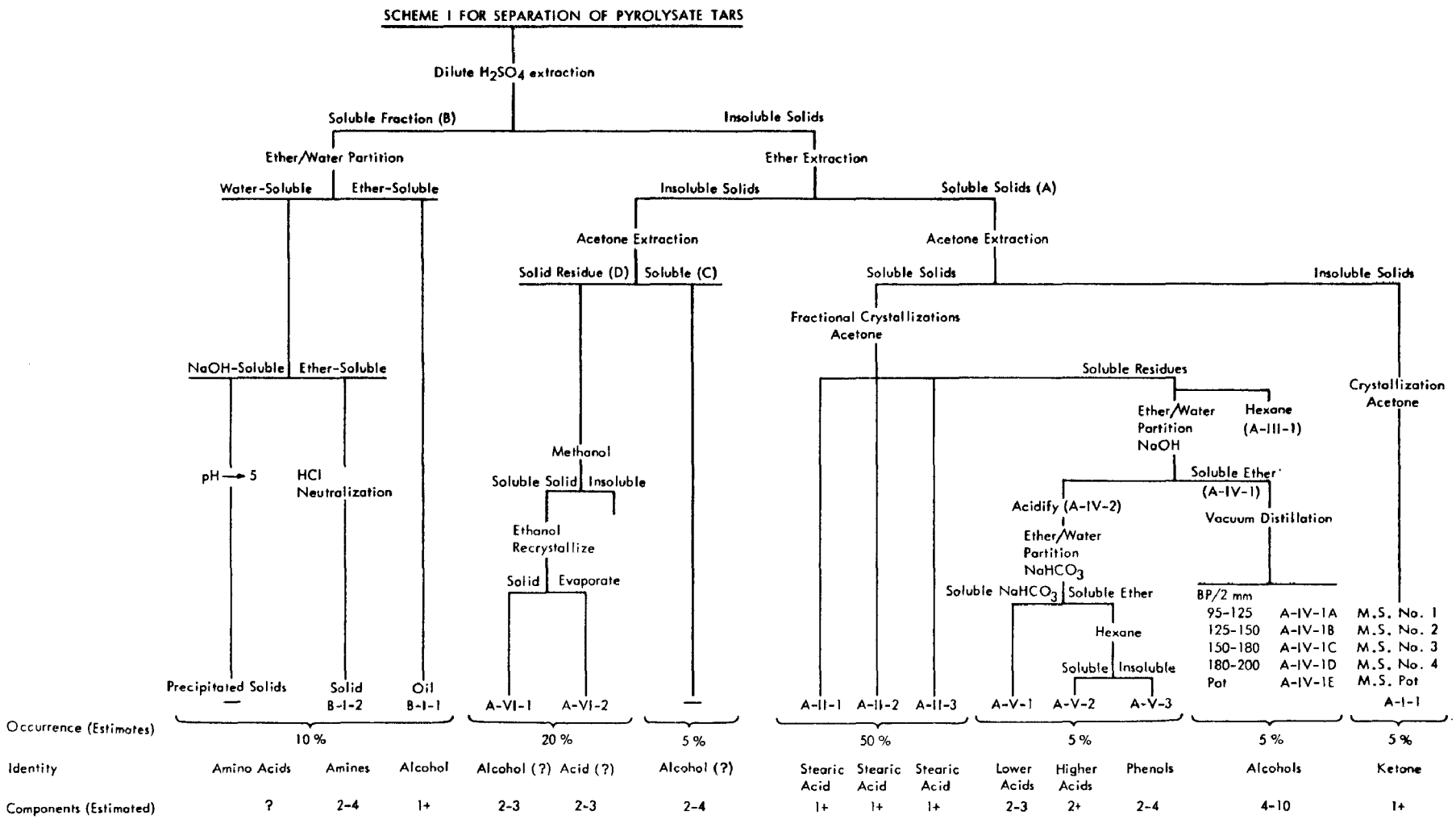



Figure 6 - Extraction Procedure Used for Bomb Pyrolysate

Separation by Scheme I

A composite sample of Tar C and Tar H was subjected to the procedure shown in Figure 6.

The primary separation step involved extracting the mixture twice with warm dilute $H_2SO_4$ (pH ~ 1). This separated water-soluble material and amine sulfates from the main product which remained as an unctuous black mass. The solubles are designated as Fraction "B".

The remaining material was then extracted three times with ether to dissolve the major portion of the organic materials. This fraction is designated as Fraction "A". A pasty black mass remained.

Two acetone extractions resolved this latter fraction into a soluble Fraction "C" and a friable, powdery black mass, Fraction "D".

The Fractions "A", "B", "C", and "D" were further resolved into component products as outlined in Figure 6.

Ether extractives (A): Solids obtained by evaporating Fraction "A" dissolved partially in cold acetone.

a. Two successive recrystallizations of the acetone-insoluble material from cold acetone yielded a fairly pure product. The IR spectrum (A-I-1) suggests that it was an aliphatic ketone.

b. The cold acetone extract was slowly evaporated. Successive crystal crops give solids which through further recrystallization from acetone provided fairly pure materials: A-II-1, A-II-2, A-II-3. These fractions, which constituted approximately 50% of the pyrolysate, were found to be largely stearic acid although minor differences in the IR absorbance bands indicate them to be incompletely separated from other components.

c. The combined acetone raffinates from these recrystallization experiments when concentrated yielded a fourth crop consisting primarily of stearic acid.

d. A portion of the acetone raffinate, after removal of the solvent, dissolved incompletely in n-hexane. Heating to dissolve the mixture followed by cooling gave a very minor amount of crystalline material. The IR spectrum (A-III-1) suggests stearic acid, although some difference in specific absorbances was noted.

e. The major portion of the combined acetone raffinates, after evaporation of solvent, was further resolved in acid and neutral fractions by partitioning between ether and aqueous alkali. At this stage in the separation scheme the soaps of the residual fatty acids do not interfere greatly with separation of the ether and aqueous layers.

Evaporation of the ether layer gave an appreciable quantity of a liquid product whose IR spectrum (A-IV-1) indicates a keto-alcohol This material was separated by vacuum distillation (~ 2 mm. Hg) into five major fractions. Cuts were taken arbitrarily according to the following schedule.

| Fraction | Temperature | IR |
|---|---|---|
| 1 | 95°-120° | A-IV-IA |
| 2 | 120°-150° | A-IV-1B |
| 3 | 150°-180° | A-IV-1C |
| 4 | 180°-200° | A-IV-1D |
| Pot | > 200° | A-IV-1E |

Infrared analyses of each fraction indicated them to be primarily alcohols; however, a strong carbonyl absorption appeared in all fractions.

The fractions were subjected to mass-spectrometric analysis. Numerous molecular species were evident in each of the spectrograms, but the differences of molecular weight suggested by the different boiling ranges were quite evident. The analysis of the pot fraction indicated materials of mass ~ 400. This finding suggests the possible presence of steroids in the pyrolysate. The inherent stability of the steroid nucleus to chemical attack and the generation of steroids in the animals' digestive processes make it seem highly probable that these materials could be obtained from pyrolysis of manure.

f. The basic aqueous layer was acidified and extracted with ether. The ether layer gave an appreciable quantity of semi-solid upon evaporation. This solid dissolved in warm acetone and gave a semi-solid precipitate when cooled. The IR spectrum corresponded fairly closely with that for oleic acid. However, a second recrystallization from acetone gave a solid whose IR pattern corresponded to that for stearic acid. The raffinate upon evaporation of the solvent again yielded an IR spectrum (A-IV-2) suggestive of that for oleic acid.

g. The balance of the base soluble fraction from the acetone raffinate was then resolved into a carboxylic acid and phenolic

fraction by partitioning between $NaHCO_3$ solution and ether. This procedure gave an appreciable quantity of $NaHCO_3$-insoluble acids, material A-V-1, after acidification. The $NaHCO_3$-insoluble acids contained in the ether layer after evaporation of the solvent were further separated into two fractions by hexane extraction. The hexane-soluble fraction (A-V-2) was recovered as a semi-solid whose IR absorption spectrum resembles that of oleic acid. The IR spectrum of the hexane-insoluble fraction (A-V-3) closely resembles that of a substituted phenol.

Aqueous acid extractives (B):

a. The dilute acid extract of the pyrolysis products contained a very small quantity of ether extractable liquid material whose IR spectrum (B-I-1) after solvent removal indicated the presence of alcoholic hydroxy groups.

b. Ether extraction of the aqueous phase when it had been strongly alkalinized with sodium hydroxide gave a small quantity of amines recoverable from the ether solvent as hydrochloride salts. These products were judged to contain lower aliphatic amines because the dried salts were appreciably soluble in methanol. However, treatment with acetone dissolved part of the HCl-salt mixture. After removal of the acetone this portion gave an IR spectrum (B-I-2) corresponding roughly to that of an amine-HCl salt.

Ether-insoluble, acetone solubles (C): Evaporation of the acetone extracts from the ether-insoluble residue gave a small quantity of black solid material. This material was soluble in methanol. It was also partially soluble in ethanol indicating the presence of several materials. No clean-cut separations have been obtained. IR spectra obtained from samples of the material are very indistinct although a strong hydroxyl or amine absorption is observed.

The small quantity of recovered materials in this fraction did not warrant further study.

Ether-insoluble, acetone-insoluble solid residue (D): The relatively large quantity of black material remaining after the successive ether and acetone extractions prompted a further investigation of its composition. It was found to be almost completely dissolved by multiple extraction with methanol. Stepwise evaporative concentration of the methanol extracts allowed the recovery of small quantities of black solids from each succeeding concentrate until the entire concentrate gelled on cooling. The gel was warmed, further methanol evaporated, and recooled. Two layers now formed, which permitted removal of the residual solvent layer.

The bulk of the black solids, combined with the precipitates from each previous methanol concentration step, was then dissolved in hot ethanol. On cooling the solution gelled but on standing produced a crystalline solid (A-IV-1) that was recovered by filtration. Attempted recrystallization of this from solution in hot ethanol resulted in a gelled mixture that could not be filtered.

The ethanolic mother liquor on evaporation gave a solid material (A-IV-2).

Infrared spectra of the two materials suggest that A-IV-1 is primarily an alcohol and that the solid residue A-IV-2 is primarily a carboxylic acid. The evidence obtained in this investigation suggests that the pyrolysis products were largely functional derivatives of long chain aliphatic compounds, small amounts of steroidal or benzene nuclei, and a small quantity of lower aliphatic amines. Very little evidence was obtained to indicate the presence of significant quantities of products that were derived from the pyranose structure present in cellulosic components of dried manure.

These findings, therefore, suggest that the conditions employed resulted in a combination of distillation, thermal decomposition and accompanying interaction of reactive materials in the vapor phase developed within the heated reaction chamber.

Infrared spectra of the various fractions obtained using Scheme I are contained in Appendix A.

### Characterization, by Scheme II, of Products of Pyrolysis in Iron Tube

A pyrolysis experiment was conducted by filling a 4 ft long, 2 in. diameter iron pipe with manure. Additionally, the exhaust end of the tube was filled with a 2-in. layer of char from previous pyrolyses, and a 3-in. layer of ceramic packing. The char and the packing were preheated and then the tube was progressively heated along its length with a sooty yellow flame (500°C). The char was added to improve the opportunity for secondary reaction. The ceramic packing was put in to prevent flow-over of unreacted manure.

The exhaust from the pyrolyzer tube was passed through two water-cooled condensers, then through a solid carbon dioxide-cooled condenser, through a scrubber tower and finally through a wet test meter. Throughout the experiment, a slow stream of helium was passed through the apparatus. This setup is shown in Figure 2.

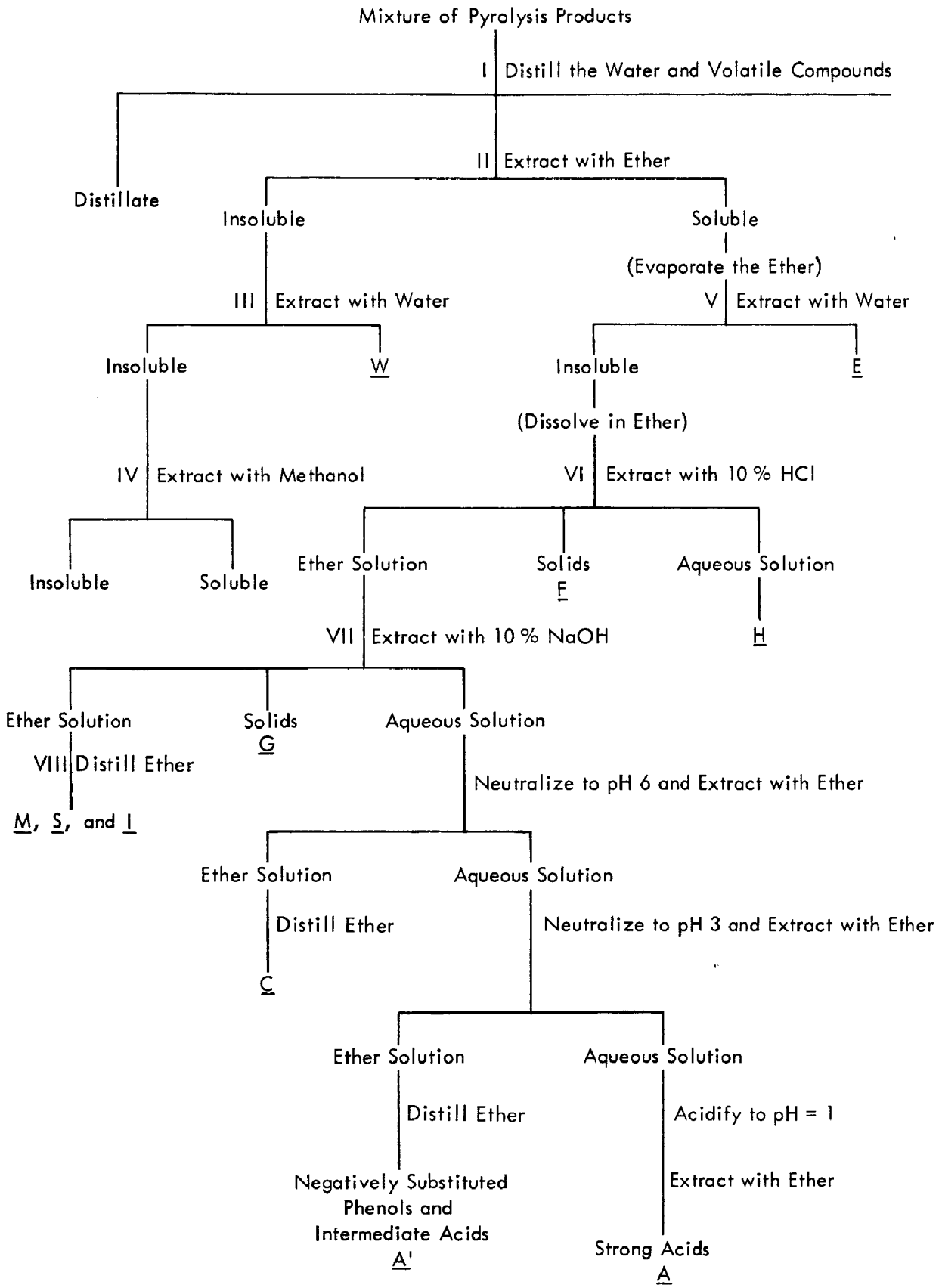



Figure 7 - Scheme II for Separation of Condensable Pyrolysis Products

The tube was charged with 331 g of manure "D" (2.7% moisture, 8.95% ash) and 3 hr were taken to bring the entire length to maximum temperature. The mass balance for the study was as follows:

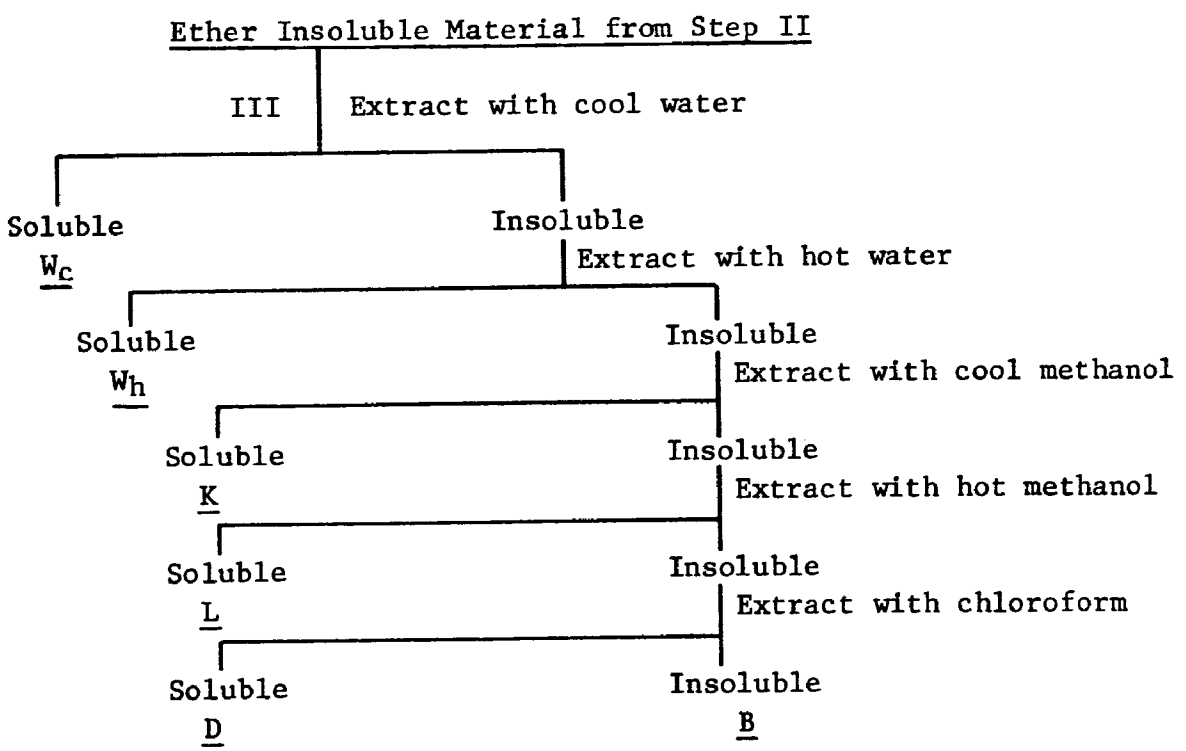
| | |
|---|---|
| Tube loading | |
| Dry manure | 331 g |
| Char plug | 25 g |
| | 356 g |
| Char recovered | 140 g |
| Char plug | 25 g |
| New char produced | 115 g |
| Manure charge | 331 g |
| New char | 115 g |
| Loss on pyrolysis | 216 g |
| Net gas generated | 2.576 $ft^3$ |
| Net gas generated | 72.942 liters |
| Assume density of 1.2 g/liter | 87.53 g |
| Contents of first trap | |
| Water | 62.3 g |
| Organics boiling below 100°C | 8.6 g |
| Organics boiling above 100°C | 45.9 g |
| Total | 116.8 g |
| Contents of second trap | 7.1 g |
| Contents of -78°C condenser | 7.6 g |
| Total condensate | 131.5 g |
| Total of char, gas and condensate | 334 g |
| Error in mass balance | 1% |

The mixture of water and organics from the first trap was separated according to the classical scheme for separation of organic mixtures with further separation of the fractions by selective solubility. The scheme used is shown in Figure 7. It has been designated as Scheme II.

The initial step (I) was to distill the contents of the first trap so that the pot temperature did not exceed 115°C. In this manner, the low boilers and the water were separated from the main bulk of the pyrolysate.

The distillate from Step I (70.9 g.) was redistilled in an attempt to identify the organic components; 1.3 g of material boiled at less than 100°C. No sharp boiling points were observed, and gas chromatographic separation of this fraction indicated the presence of at least 10 different compounds, none in high enough concentration to warrant further separation. Water (62.3 g.) was then distilled out leaving 7.3 g. of liquid residue boiling at greater than 100°C. This residue was later shown by GC to contain at least 14 different compounds; again, none was of high enough concentration to warrant further separation.

The residue from Step I was extracted with ether (Step II). The ether-insoluble material was then extracted as follows:



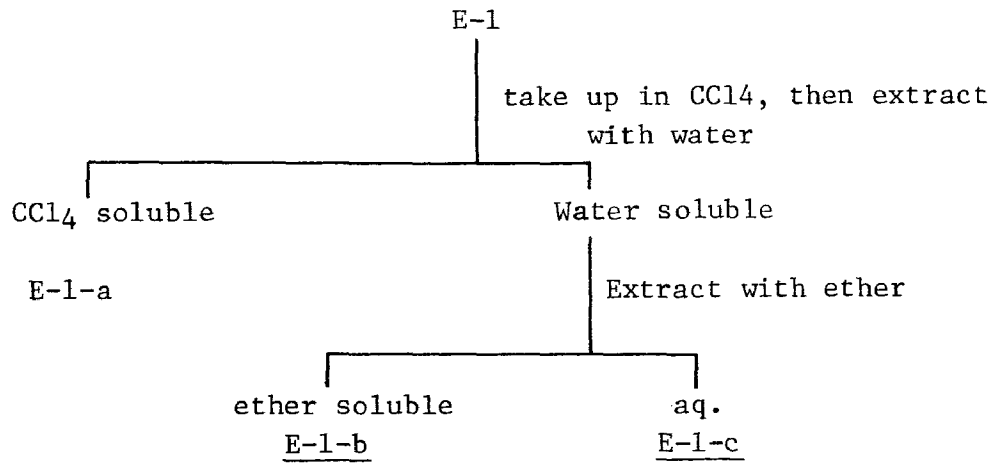
The ether-insoluble, cool water-soluble material is designated "$W_c$." The Molisch test for carbohydrates on this portion was essentially negative, as was the test for amine salts.

$W_c$ was distilled at atmospheric pressure and yielded fractions boiling at 68°, 70°, 73°, 80°, 80°-120°, and 145°C. The nitrochromic acid test for -OH was positive for all but the last distillate fraction. It was negative for the fraction boiling at 145°C, and for the pot residue. The ferric hydroxamate test for $-CO_2H$ was positive for the residue and the fraction boiling at 80°-120°C; it is probable that it would have also been positive for the higher boiling fraction. The fraction boiling at 68°C appeared from its IR spectrum to be mostly methanol. The IR spectra of the fraction boiling at 145°C and of the residue showed strong absorptions indicative of a carboxylic acid. The UV spectrum of the $W_c$ material taken prior to distillation indicated the presence of an aromatic structure. Maximum absorbance in ethanol occurred around 230 mμ, with a lesser peak at 276.5 mμ. Benzoic acid in water gives a primary peak at 230 mμ ($\epsilon$ max. 11,600) and a secondary peak at 273 mμ ($\epsilon$ max. 970). The specific class tests together with the IR and UV spectra indicated that a component of $W_c$ was an aromatic carboxylic acid.

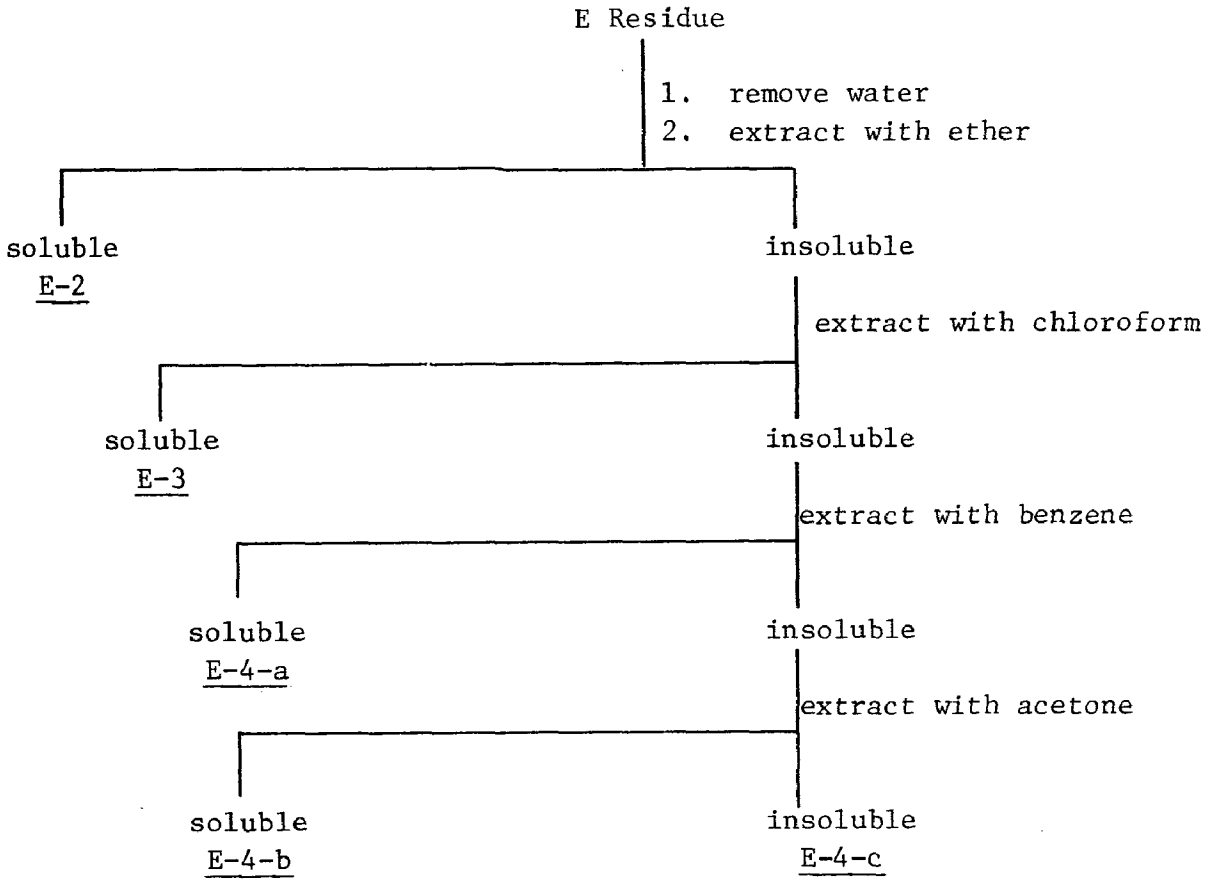
The residue from Step III was then extracted with hot water. The soluble material was designated "$W_h$." The IR spectrum of $W_h$ was nearly identical with that of $W_c$, indicating little, if any, separation.

The material which was insoluble in ether and in water was extracted with cool methanol, followed by extraction with hot methanol, yielding fractions "K" and "L", respectively. The residue from this latter extraction was extracted with chloroform, yielding "D", which is soluble in chloroform; and "B", which is not. The ferric hydroxamate test for -COOH and the nitrochromic acid test for -OH are negative for each of the above fractions. The IR spectra for K and for L indicate strong methylene absorption (2925, 2870 and 1460 $cm^{-1}$) and strong absorption indicative of a primary amine (1690, 1600 $cm^{-1}$).

The ether solution from Step II was evaporated to remove the ether, then extracted with water (Step V). The soluble material was designated "E." The aqueous mixture has a pH of 4.5; it was neutralized to pH 7, then steam-distilled until the distillate was colorless. The distillate was extracted with ether; the ether was then removed to yield fraction "E-1." The test on this fraction for -COOH was negative; tests for -OH and -CHO or =CO were positive. The UV spectrum indicated the presence of an aromatic structure (major peak at or near 215 mμ, secondary peak at 266.6 mμ). The material E-1 was then further separated by the following scheme:



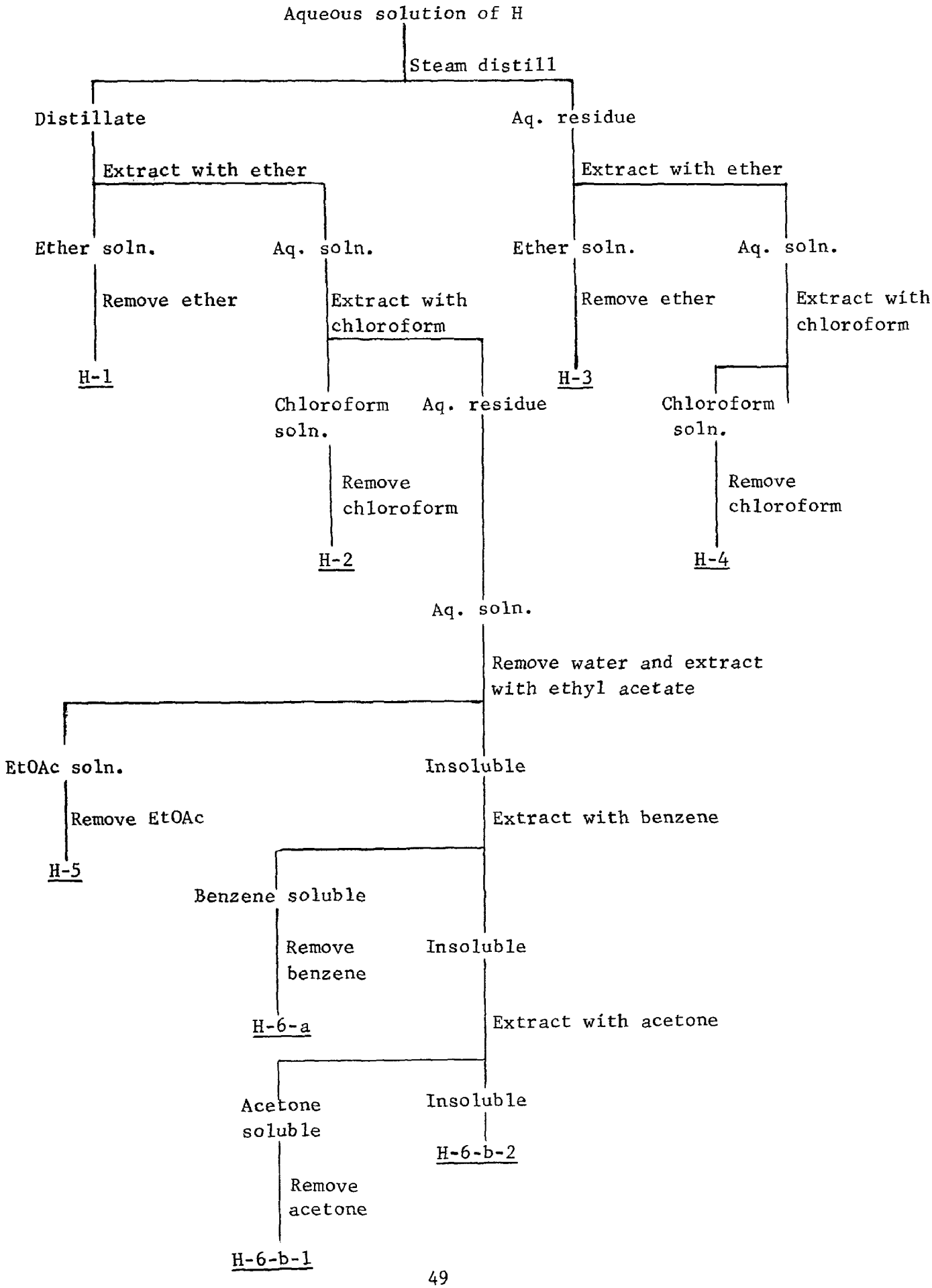

The portion of E remaining after steam distillation was separated as follows:



The test for -COOH indicated that it was absent in E-2 and E-3 but present in E-4-c. The test for -CHO and =CO was positive for E-2 and negative for E-3 and E-4-a. The test for -OH was marginally positive for E-2 and E-4-a and negative for E-3, E-4-b and E-4-c. The IR spectra for E-2, E-3, and E-4-a were quite similar, and indicate the presence of an aromatic amide or an alcohol.

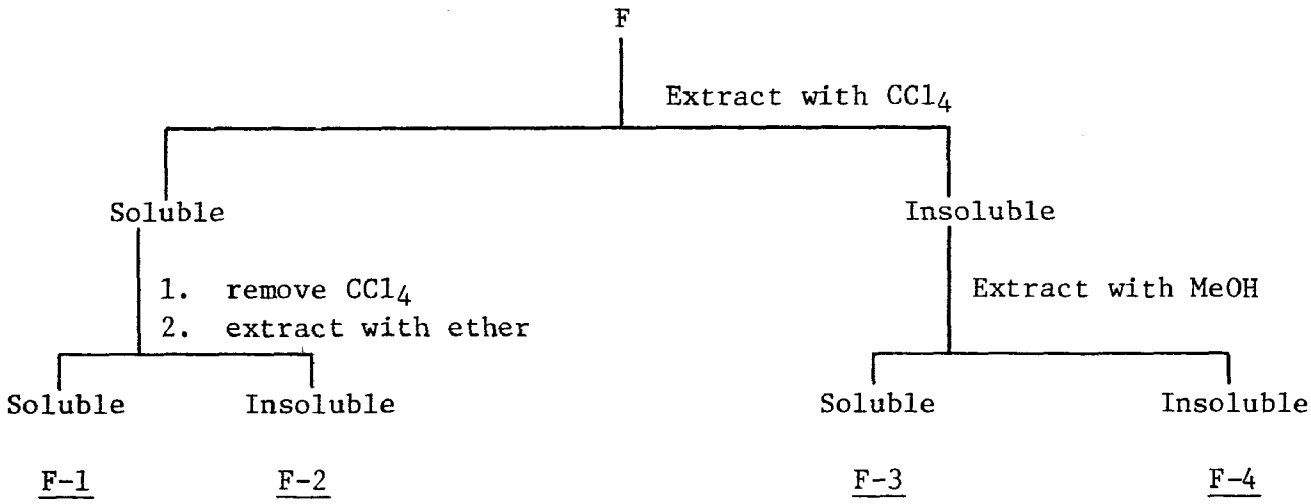
The IR spectrum of E-4-c suggested a salt of a carboxylic acid. Elemental analysis of this material gave the following: C - 37.61%, H - 4.19%, N - 0.5%. The values for sodium adipate most nearly approximate the observed values for C and H: $C_{calcd.}$ 37.9%, $C_{obs.}$ 37.61%; $H_{calcd.}$ 4.2%, $H_{obs.}$ 4.19%. The extracted material decomposed around 340°C. The melting point or decomposition temperature of sodium adipate has not been recorded in the literature. Dibasic acid salts will, in general, decompose rather than melt; this, together with the class tests, the IR spectrum and the elemental analysis, strongly suggest sodium adipate.

The water-insoluble material from Step V was dissolved in ether and extracted with 10% HCl. A solid formed during the extraction was filtered off and set aside. The acidified aqueous portion was designated "H." Separation of H proceeded as follows:


Aqueous solution of H
Steam distill
Distillate
Aq. residue
Extract with ether
Extract with ether
Ether soln.
Aq. soln.
Ether soln.
Aq. soln.
Remove ether
Extract with chloroform
Remove ether
Extract with chloroform
H-1
H-3
Chloroform soln.
Aq. residue
Chloroform soln.
Remove chloroform
Remove chloroform
H-2
H-4
Aq. soln.
Remove water and extract with ethyl acetate
EtOAc soln.
Insoluble
Remove EtOAc
Extract with benzene
H-5
Benzene soluble
Remove benzene
Insoluble
H-6-a
Extract with acetone
Acetone soluble
Insoluble
H-6-b-2
Remove acetone
H-6-b-1

The H group of compounds primarily contained amines or amino acids. Tests for -COOH were negative. The UV spectrum of H-4 showed no aromaticity. The IR spectra of several of the H group showed relatively strong absorptions in the ranges 3300-2200 $cm^{-1}$, and 2100-1800 $cm^{-1}$, which are indicative of an amine hydrochloride.

The solid which formed during extraction (Step VI) was designated "F." It was separated as follows:




The IR spectra for the F group indicate a carboxyl salt rather than an amine salt; however, the tests for -COOH were negative. No further work was done with this fraction.

The ether solution from Step VI was extracted with 10% NaOH (Step VII). A solid that separated during the extraction was designated "G." The ether solution should have contained groups M, S, and I.

The aqueous solution from Step VII was acidified to pH 6, then extracted with ether. The ether extract contained compounds of Group C. The aqueous solution was further acidified to pH 3, then extracted with ether to get compounds of Group A'. The aqueous solution was finally acidified to pH 1 and extracted with ether to get compounds of Group A.

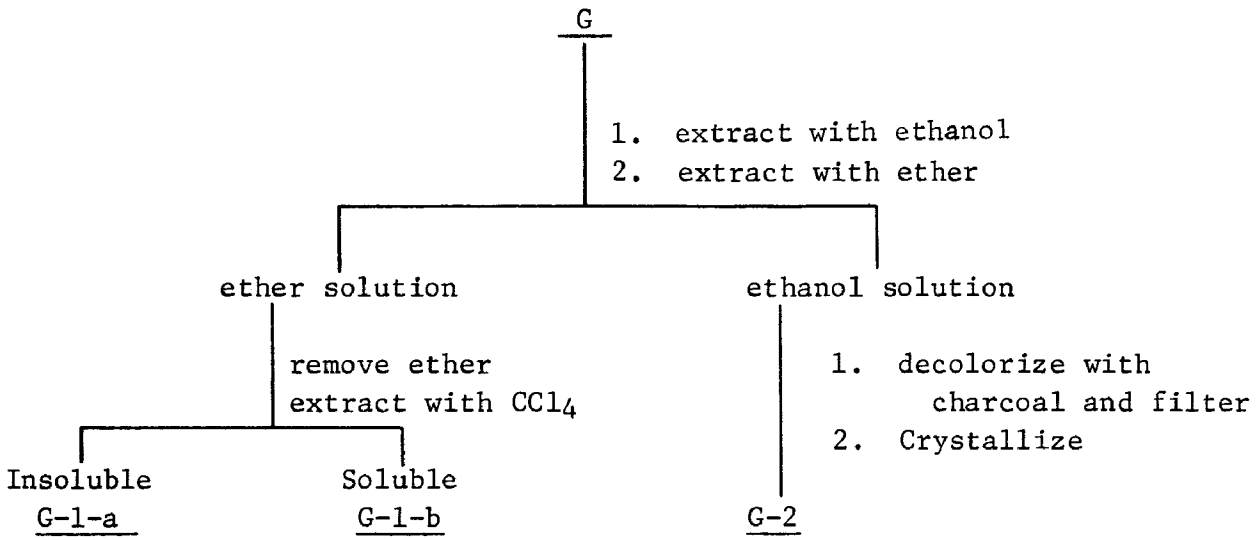
The fractions A, A' and C were quite small and were analyzed only by infrared. The spectrum of A indicated that it was largely comprised of silicone lubricant, a probable contaminant. The IR spectrum of A' indicated the presence of one or more carboxylic acids. The spectrum of C suggested one or more aromatic amino acids, not necessarily an $\alpha$-amino acid of natural origin.

The ether solution containing M, S and I from Step VII was distilled to remove the ether, then extracted with absolute ethanol to

remove a substituent, later identified as silicone lubricant. The total mass, M-S-I, gave a positive test for -CHO or =CO, a negative test for -OH and -COOH. The IR spectrum indicated both a ketone and a secondary amide; however, the ferric hydroxamate test for $-CONH_2$ was negative.

The mixture M-S-I incompletely dissolved in concentrated sulfuric acid, indicating the presence of hydrocarbons which could have been both saturated acyclic and cyclic. The mixture dissolved incompletely in 85% phosphoric acid indicating the presence of hydrocarbons having more than 8 carbon atoms per molecule. The UV spectrum indicated an absence of aromatic compounds in this mixture.

The solid G was separated as follows:




The fraction G-2 consisted mostly of the sodium salt of stearic acid as shown by IR spectra. The IR spectrum of G-1-a also indicated the presence of another organic acid salt.

The IR spectrum of G-1-b was very similar to the spectrum M-S-I. It is probable that a portion of the group of M-S-I was occluded in solid G.

The mass balance of the above fractionation by Scheme II is as follows:

| | |
|---|---|
| Total organic material | 45.9 g |
| Material insoluble in ether | 10.7 g |
| $W_c$ - soluble in cold water<br>$W_h$ - soluble in hot water<br>K + L - soluble in methanol<br>D - soluble in chloroform<br>B - insoluble in organic solvents | |
| Material soluble in ether, soluble in water - E | 6.9 g |
| Material soluble in ether, insoluble in water, soluble in 10% hydrochloric acid - H | 4.0 g |
| Material soluble in ether, insoluble in water and dilute acid, soluble in 10% sodium hydroxide - C, A + A' | 1.2 g |
| Material soluble in ether, insoluble in water, acid or base - M-S-I | 7.9 g |
| Solid G - Sodium salts of long chain fatty acids | 13.4 g |
| Solid F - Amine salts | 1.8 g |
| Total | 45.9 g |

Infrared spectra of the significant fractionated products separated by this scheme are shown in Appendix B.

The condensate of the second water-cooled trap was a mixture of water and organic compounds. It was felt that the quantity of the organics was too small to justify separation and fractionation.

The condensate in the dry-ice trap was a mixture of materials, including carbon dioxide, acetaldehyde, propionaldehyde, iso-butyraldehyde, n-butyraldehyde, and other uncharacterized compounds as determined by gas chromatography.

## Discussion

The types of pyrolysis products recoverable from the combined tars are representative of compounds that could be obtained from full scale commercial thermal decomposition of cattle manure. Since the samples of tars used in the initial test and Scheme I separation were composites of products obtained in several pyrolytic experiments which had been evaporated to apparent dryness both by heating and subsequent air-drying, some of the low-boiling fractions originally present in the condensates must have been lost.

Although some preliminary estimates of the quantitative proportions of type components in the products have been made, the number of ingredients in the composite tar sample and the varied techniques involved in their separation and classification precluded the derivation of highly quantitative measures of their abundance. Clearly, a large number of compounds are present in the pyrolysate. It must be recognized that the relative proportions of the components could vary with both the source of the manure and the reaction conditions for conducting its pyrolysis. These variations, however, are not expected to be large.

Stearic acid was the only significant fraction of the pyrolysate recovered in pure enough form to enable positive identification. The small quantities available and the presence of more than one component in each major fraction were limiting factors. In most instances, several compounds endowed with the same general functionality were present in each fraction. Further separation into pure components was not warranted in this phase of the program.

## SECTION VIII

## ECONOMIC CONSIDERATIONS

The economic evaluation of a potential process cannot be made independently of alternative approaches. Thus, pyrolysis as a method of manure stabilization and disposal must be viewed in relation to alternate processes to accomplish this end. The simplest approach to manure management is to establish a stocking rate sufficiently low that the manure is stabilized in the feedlot. In such a case, the only processing costs would be provision for runoff retention and runoff disposal.

One may progress from this low level of sophistication up through a variety of physical, chemical, and biological processes, that have been designed to stabilize similar wastes. The sophisticated processes hopefully would produce a greater degree of environmental protection at no greater fraction of operating cost than for the simplest case cited above.

There is, however, insufficient information available to construct a very accurate table of cost/benefit ratios. A rather subjective list of approaches to manure disposal is presented in increasing order of both technical sophistication and, hopefully, higher degree of environmental protection:

1. On-lot stabilization of manure.
2. Lot scraping and field disposal of manure.
3. Partial stabilization of solid waste to abate odor. This assumes a system of manure collection as well.
4. Complete biological stabilization of all waste by (a) wet biological treatment such as activated sludge, (b) "dry" biological treatment such as composting, or (c) heat drying to the point where no further biological activity can occur.
5. Incineration.
6. Pyrolysis.
7. Wet oxidation of a manure slurry by Zimmerman process.

In actual practice, any one of these approaches could be the best one. The choice can be made intelligently only after a thorough engineering study of the particular site, the surrounding environment and prevailing economic conditions. (Any consideration of environmental management on feedlots must recognize the problem of runoff. Runoff is more simply managed by containment, followed by subsequent evaporation or use as irrigation water. Other systems for disposal of runoff include partial or complete stabilization without or with simultaneous treatment of solid waste.)

A preliminary cost analysis of pyrolysis can be made on the basis of literature values and the data obtained in the experimental portion of this study. The pyrolysis process itself is depicted in Figure 8, which gives both the energy and material balances of the processes. The value most susceptible to criticism is the 400 Btu/lb pyrolysis energy, but if this were to vary by 100%, it would still have little effect on the overall analysis.

The process itself must consist of (1) drying, (2) thermal decomposition of manure, (3) separation of decomposition products, and (4) combustion of a portion of the pyrolysis products (char, gases, or liquids) with auxiliary fuel.

The estimated cost/ton of pyrolyzing manure (80% moisture) in a feedlot of 40,000 head capacity is $5.60. Cost/market animal is $25. Details of the estimate are presented below. Particularly worthy of note is the fact that fuel oil costs (2.26/ton) are more than the value of recoverable tars and oils (1.29/ton). This comparison makes it quite clear that pyrolysis cannot pay its way, and that a useful fuel--oil, gas, or coal--must be sacrificed to yield a product of presently questionable commercial value.

## ECONOMIC EVALUATION OF PYROLYZER FOR MANURE FROM A 40,000-HEAD BEEF CATTLE FEEDLOT

Assumptions:

1. Manure production - 50 lb/day/head; 80% moisture, 2% ash.
2. 65% thermal efficiency on predryer and pyrolyzer.
3. 1,135 Btu/lb for moisture removal.
4. 400 Btu/lb pyrolysis activation energy.
5. Capital costs - dryer $2,000/ton*
   pyrolyzer $10,000/ton**
   separator $30,000/ton***
6. Amortization - 10 years.
7. Delivered fuel oil at $40/ton; 13,000 Btu/lb.
8. Lot occupancy - 360 days = 2 x 180-day cycle.

---

* Prevailing cost for similar equipment.

** Low estimate based on 1971 costs of municipal refuse incinerators.

*** Estimated as 1/5 the cost of petroleum refinery costs reported in "Hydrocarbon Processing" February 1971, and adjusted by 6/10 factor.

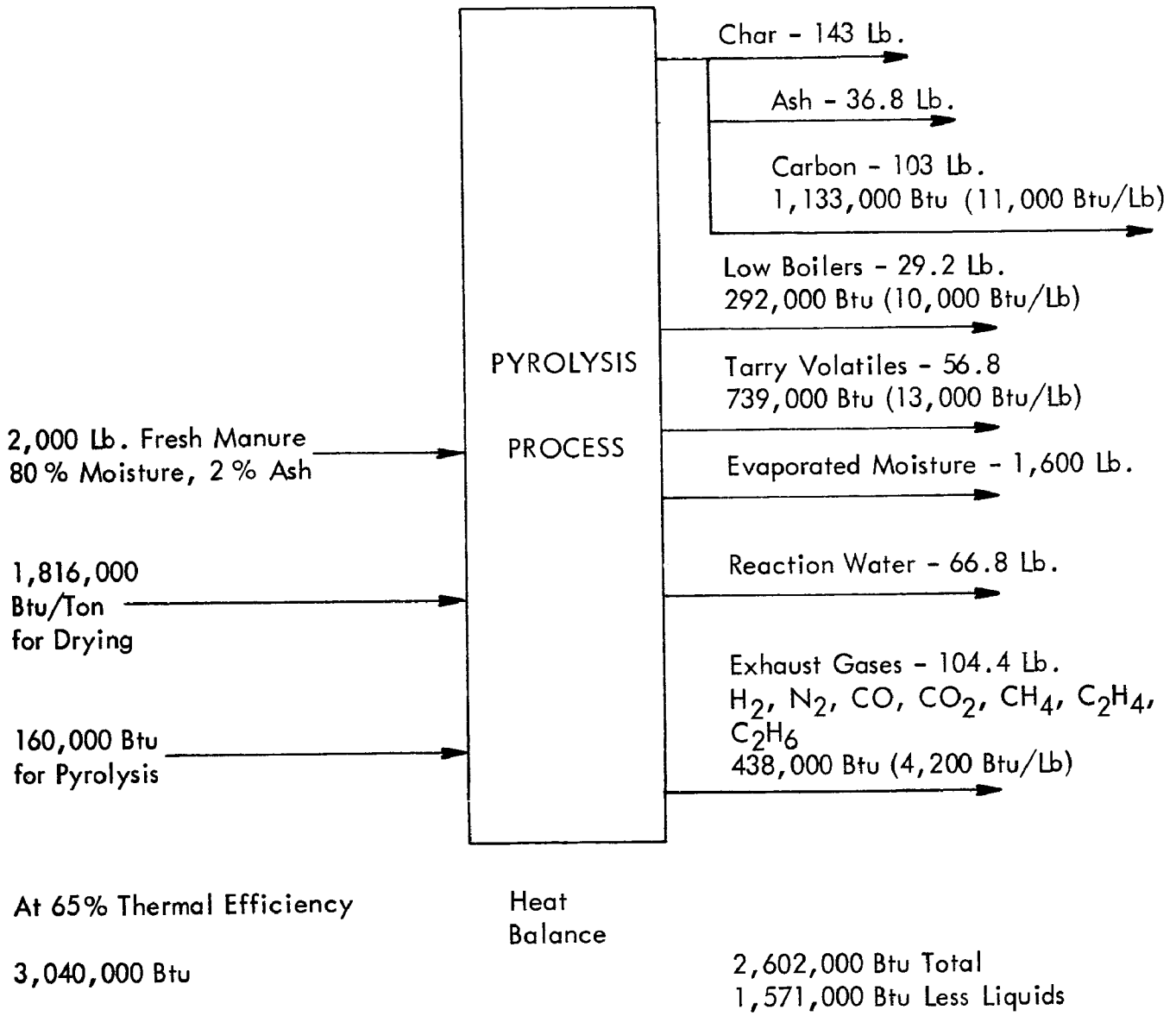



Figure 8 - Material and Energy Balance in Pyrolysis Processing of Cattle Feedlot Wastes

## BALANCE SHEET

Capital costs

| | | | |
|---|---|---|---|
| Dryer | $2,000 x 1,000 | = | $ 2,000,000 |
| Pyrolyzer | $10,000 x 200 | = | 2,000,000 |
| Recovery unit | $30,000 x 50 | = | 1,500,000 |
| Total capital cost | | | $ 5,500,000 |

Operating costs

| | |
|---|---|
| Depreciation at 10% | $ 550,000 |
| Capital charges at 6% | 330,000 |
| Taxes and insurance at 5% | 275,000 |
| Maintenance at 4% | 220,000 |
| Labor (18 men: 4/shift plus 5 relief plus 1 supervisor at $5/hr) | 180,000 |
| Fuel at $40/ton | 812,000 |
| Miscellaneous at 2% | 110,000 |
| Total | $ 2,477,000 |
| Credit for pyrolysate at 1.5¢/lb | 464,000 |
| | $ 2,013,000 |

| | | |
|---|---|---|
| Cost per ton manure at 80% moisture | = | $ 5.60 |
| Cost per market steer | = | $ 25.30 |

SECTION IX

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SECTION X

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APPENDIX A

# EVOLUTIONARY OPERATION APPLIED TO EXPERIMENTAL MANURE PYROLYSES

## I. Introduction

The experimental manure pyrolyses on this program have been performed using a set of experimental conditions, and a relatively new experimental design system called Evolutionary Operation.[1/] The objective of this system is to determine optimum process conditions for manure pyrolysis using a minimum number of experiments.

Evolutionary Operation (EVOP) is an experimental method using factorial design for experimental conditions. It differs from standard factorial design experiments, which tend to be large and complicated, in that it limits the number of experimental conditions being investigated at any one time. Using EVOP, many experimental conditions may be investigated, but only a certain number at any one time. The advantages of this method of operation are that less experimental measurements are needed to find an optimum set of conditions; the freedom to add new experimental conditions is not restricted, and the results of one run may be used to indicate a set of conditions nearer the optimum, for the next run.

In the terminology of EVOP, an experimental test is called a phase. A phase consists of sets of four or eight experimental runs of predetermined combinations of two levels of experimental conditions. A cycle is a replicate test on the same phase. In the factorial design terminology, the phase design is either $2^2$ or $2^3$ factorial design.

## II. Pyrolysis Conditions

The experimental test conditions for manure pyrolyses were made up of combinations of pyrolysis temperatures and pressures, and two kinds of manure. The first manure (manure A) was a farm lot sample from cattle fed on corn and alfalfa. The second manure (manure B) was a concrete pad sample from cattle fed on cracked corn with a diet supplement. The combinations of these experimental factors, with their phase numbers, are given in Table A-1. Three cycles of each phase were run.

1/ "Evolutionary Operation" G.E.P. Box and N.R. Draper, John Wiley and Sons. New York, 1969.

TABLE A-1

PYROLYSIS CONDITIONS

| Phase | Temperature Levels (°C) | Pressure Levels (atm) | Manure Component(s) (A or B) | Factorial Design |
|---|---|---|---|---|
| 1 | 400/500 | 0/1 | A | $2^2$ |
| 2 | 500/600 | 0/1 | A | $2^2$ |
| 3 | 400/500 | 0/1 | B | $2^2$ |
| 4 | 500/600 | 0/1 | B | $2^2$ |
| 5 | 400/500 | 0/1 | A/B | $2^3$ |
| 6 | 500/600 | 0/1 | A/B | $2^3$ |

## III. Experimental Goals

The experimental results are expressed as percentages of the weight of volatile[2/] material charged to the reactor. Pyrolysis components were determined as:

PCT.(DIC) - The weight percent of material condensed in the dry ice trap,

PCT.(TAR-H) - The weight percent of distillable tar, soluble in water,

PCT.(TAR-C) - The weight percent of distillable tar, soluble in chloroform, and

PCT.(CHAR) - The weight percent of residue remaining in the reactor, minus the determined percentage of ash in the original manure.

The experimental goals were to adjust conditions to maximize PCT.(TAR-H) and PCT.(TAR-C) and minimize PCT.(CHAR).

## IV. Experimental Results

The experimental results were analyzed using a computer program written for use in a time-shared computer. The program name is EVOP, and it is written in the Extended Basic Language for use on United Computer Services' GE-265 computer system.

2/ Volatiles = loss on ignition at 600°C.

Computer outputs of the experimental results are shown in Figures A-1 to A-6. Each figure represents a phase of experimentation shown in Table A-1. In the figures, the following items may be noted reading down the page (the reference is Figure A-1):

| | |
|---|---|
| Phase: | Number. |
| Factors: | High and low level experimental conditions. |
| Results: | Kind of data. |
| Latest Results: | Factorial analysis of the experimental data (converted to percentage) at Cycle 3. |
| Latest Average: | First, the factorial analysis of experimental data averaged over three cycles; second, the averages, once three cycles, of the experimental data at each level (H or L) of temperature (T) and pressure (P). |
| Standard Error: | The estimated standard deviation of the experimental results, often three cycles. |
| 2S.E. Limits: | The estimated limit for real means and effects in the factorial analysis. Means and effects larger than the 2S.E. Limit may be counted as real at approximately the 90% confidence level. |

## V. Interpretation of Results

The interpretation of factorial analysis results depends on the various averages of combinations of factor levels. With reference to Figure 1 ($2^2$ design), the Mean is the average around the cycle of all four experimental readings for each percentage. T, the temperature effect, is the average change in percentage, going from low to high temperature, for each percentage. P, the pressure effect, is the average change in percentage, going from low to high pressure, for each percentage. TP, the interaction effect, measures the curvature of the percentage response to changing conditions. If the square, bounded by $T_LP_L$, $T_HP_L$, $T_LP_H$, and $T_HP_H$ is considered to be a planar surface, the TP interaction introduces a curvature which can show the contours of the response surface for each kind of percentage measured experimentally. Such a contour map of the experimental area points out clearly the ways to adjust experimental conditions to approach optimum yields.

The general run of the results is as follows:

- At Phase 1, high temperature decreases char and increases tar, with similar effects for low pressure. Therefore, Phase 2 was run at a higher set of temperature conditions (500 and 600°C).

FACTORIAL ANALYSIS

PHASE: 1

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 500 | 400 |
| PRESSURE: | 1 | 0 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAR-H) | PCT.(TAR-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 2.82 | 4.60 | 12.58 | 23.43 |
| T | 1.05 | 4.80 | 6.85 | -5.15 |
| P | -1.45 | -.50 | -6.45 | 3.85 |
| TP | -1.05 | -1.50 | -4.15 | -2.15 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAR-H) | PCT.(TAR-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 2.48 | 4.88 | 14.07 | 24.49 |
| T | .63 | 3.32 | 6.90 | -4.28 |
| P | -.70 | -.55 | -6.87 | 3.62 |
| TP | -.30 | -2.12 | -5.90 | -1.18 |

DESIGN

| T P | PCT.(DIC) | PCT.(TAR-H) | PCT.(TAR-C) | PCT.(CHAR) |
|---|---|---|---|---|
| L L | 2.37 | 2.43 | 11.10 | 24.23 |
| H L | 3.30 | 7.87 | 23.90 | 21.13 |
| L H | 1.97 | 4.00 | 10.13 | 29.03 |
| H H | 2.30 | 5.20 | 11.13 | 23.57 |
| STD. ERROR: | .64 | .81 | 1.39 | 2.55 |
| 2S.E.LIMIT: | .74 | .94 | 1.61 | 2.95 |

Figure A-1 - Phase 1

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FACTORIAL ANALYSIS

PHASE: 2

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 600 | 500 |
| PRESSURE: | 1 | 0 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 3.05 | 4.15 | 13.15 | 20.00 |
| T | -.60 | -5.70 | -5.70 | -1.70 |
| P | -.20 | -1.50 | -12.00 | 5.70 |
| TP | 2.30 | .50 | -1.40 | 4.00 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 2.66 | 3.97 | 13.86 | 19.97 |
| T | -.28 | -5.13 | -7.32 | -4.75 |
| P | .05 | -1.83 | -12.08 | 5.52 |
| TP | 1.05 | .83 | .68 | 3.08 |

| DESIGN T P | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| L L | 3.30 | 7.87 | 23.90 | 21.13 |
| H L | 1.97 | 1.90 | 15.90 | 13.30 |
| L H | 2.30 | 5.20 | 11.13 | 23.57 |
| H H | 3.07 | .90 | 4.50 | 21.90 |
| STD. ERROR: | 1.28 | .46 | 2.54 | 2.08 |
| 2S.E.LIMIT: | 1.48 | .53 | 2.93 | 2.40 |

Figure A-2 - Phase 2

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FACTORIAL ANALYSIS

PHASE: 3

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 500 | 400 |
| PRESSURE: | 1 | 0 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 6.71 | 1.34 | 5.18 | 31.15 |
| T | -3.81 | .30 | .93 | -8.44 |
| P | -11.42 | -1.16 | -5.26 | 2.48 |
| TP | 4.47 | -.03 | -.20 | .83 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 6.54 | 1.30 | 5.24 | 31.59 |
| T | -1.71 | -.06 | .55 | -7.34 |
| P | -10.98 | -.76 | -3.54 | 2.04 |
| TP | 2.26 | .09 | 1.03 | .83 |

| DESIGN T P | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| L L | 14.02 | 1.75 | 7.25 | 34.66 |
| H L | 10.04 | 1.60 | 6.77 | 26.49 |
| L H | .77 | .91 | 2.68 | 35.87 |
| H H | 1.32 | .94 | 4.26 | 29.36 |
| STD. ERROR: | 2.46 | .24 | .48 | .65 |
| 2S.E.LIMIT: | 2.84 | .28 | .56 | .75 |

Figure A-3 - Phase 3

EVOP 010:56 TUES. 08/25/70

FACTORIAL ANALYSIS

PHASE: 4

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 600 | 500 |
| PRESSURE: | 1 | 0 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAP) |
|---|---|---|---|---|
| MEAN | 6.37 | 1.42 | 6.56 | 25.77 |
| T | 3.15 | -.15 | 1.84 | -2.32 |
| P | -9.44 | -1.31 | -6.11 | 2.98 |
| TP | -2.48 | -.12 | -.65 | -.33 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAP) |
|---|---|---|---|---|
| MEAN | 6.84 | 1.35 | 6.29 | 26.79 |
| T | 2.32 | .17 | 1.56 | -2.26 |
| P | -10.38 | -.91 | -4.92 | 2.70 |
| TP | -1.66 | -.25 | -2.41 | -.17 |

| DESIGN T P | PCT.(DIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAP) |
|---|---|---|---|---|
| L L | 10.04 | 1.60 | 6.77 | 26.49 |
| H L | 14.02 | 2.02 | 10.73 | 24.39 |
| L H | 1.32 | .94 | 4.25 | 29.36 |
| H H | 1.99 | .86 | 3.40 | 26.93 |
| STD. ERROR: | 1.77 | .41 | 1.31 | 1.36 |
| 2S.E.LIMIT: | 2.05 | .47 | 1.51 | 1.57 |

Figure A-4 - Phase 4

FACTORIAL ANALYSIS

PHASE: 5

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 500 | 400 |
| PRESSURE: | 1 | 0 |
| MANTLE: | 2 | 1 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(LIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 4.77 | 2.97 | 8.88 | 27.29 |
| T | -1.38 | 2.55 | 3.89 | -6.80 |
| P | -6.44 | -.83 | -5.86 | 3.17 |
| TP | 1.71 | -.77 | -2.17 | -.66 |
| M | 3.88 | -3.26 | -7.39 | 7.73 |
| TM | -2.43 | -2.25 | -2.96 | -1.65 |
| PM | -4.99 | -.33 | .59 | -.68 |
| TPM | 2.76 | .73 | 1.98 | 1.49 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(LIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 4.51 | 3.69 | 9.65 | 28.04 |
| T | -.54 | 1.63 | 3.72 | -5.81 |
| P | -5.84 | -.65 | -5.20 | 2.83 |
| TP | .98 | -1.01 | -2.43 | -.18 |
| M | 4.06 | -3.58 | -8.83 | 7.16 |
| TM | -1.17 | -1.69 | -3.18 | -1.53 |
| PM | -5.14 | -.10 | 1.66 | -.79 |
| TPM | 1.28 | 1.11 | 3.47 | 1.01 |

| LEVEL T P M | PCT.(LIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| L L L | 2.37 | 2.43 | 11.10 | 24.23 |
| H L L | 3.30 | 7.87 | 23.90 | 21.13 |
| L H L | 1.97 | 4.00 | 10.13 | 29.63 |
| H H L | 2.30 | 5.20 | 11.13 | 23.57 |
| L L H | 14.02 | 1.75 | 7.25 | 34.66 |
| H L H | 10.04 | 1.66 | 6.77 | 26.49 |
| L H H | .77 | .91 | 2.68 | 35.37 |
| H H H | 1.32 | .94 | 4.26 | 29.36 |
| STD. ERROR: | 1.10 | .83 | 1.48 | 2.56 |
| 2S.E.LIMIT: | .89 | .68 | 1.21 | 2.09 |

Figure A-5 - Phase 5

PAGE

FACTORIAL ANALYSIS

PHASE: 6

FACTORS:

| | HI LEVEL | LO LEVEL |
|---|---|---|
| TEMPERATURE: | 600 | 500 |
| PRESSURE: | 1 | 0 |
| MANURE: | 2 | 1 |

RESULTS:

VOLATILES:

LATEST RESULT:

CYCLE: 3

| EFFECT | PCT.(LIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 4.71 | 2.78 | 9.86 | 22.89 |
| T | 1.27 | -2.92 | -1.93 | -2.01 |
| P | -4.82 | -1.40 | -9.05 | 4.34 |
| TP | -.69 | .19 | -1.02 | 1.83 |
| M | 3.32 | -2.73 | -6.59 | 5.77 |
| TM | 1.87 | 2.78 | 3.77 | -.31 |
| PM | -4.62 | .10 | 2.95 | -1.36 |
| TPM | -2.39 | -.31 | .38 | -2.17 |

LATEST AVERAGE:

CYCLE: 3

| EFFECT | PCT.(LIC) | PCT.(TAP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| MEAN | 4.75 | 2.66 | 10.07 | 23.38 |
| T | 1.62 | -2.48 | -2.88 | -3.51 |
| P | -5.16 | -1.37 | -8.50 | 4.11 |
| TP | -.30 | .29 | -.86 | 1.46 |
| M | 4.18 | -2.61 | -7.57 | 6.82 |
| TM | 1.30 | 2.65 | 4.46 | 1.24 |
| PM | -5.21 | .46 | 3.58 | -1.41 |
| TPM | -1.35 | -.54 | -1.54 | -1.62 |

| DESIGN T P M | PCT.(LIC) | PCT.(AP-H) | PCT.(TAP-C) | PCT.(CHAR) |
|---|---|---|---|---|
| L L L | 3.30 | 7.87 | 23.90 | 21.13 |
| H L L | 1.97 | 1.90 | 15.90 | 13.30 |
| L H L | 2.30 | 5.20 | 11.13 | 23.57 |
| H H L | 3.07 | .90 | 4.50 | 21.90 |
| L L H | 10.04 | 1.00 | 6.77 | 26.49 |
| H L H | 14.62 | 2.62 | 10.73 | 24.39 |
| L H H | 1.32 | .94 | 4.25 | 29.36 |
| H H H | 1.99 | .86 | 3.40 | 26.93 |
| STD. ERROR: | 1.28 | .48 | 2.54 | 2.08 |
| 95.% LIMIT: | 1.65 | .39 | 2.07 | 1.70 |

Figure A-6 - Phase 6

• At Phase 2, high temperature decreases char slightly, but decreases tar greatly. Low pressure is still advantageous. Optimum run conditions have been located near 500°C, and Phase 3 was run using different manure.

• At Phase 3, char is lower at high temperature, and low pressure is still advantageous. Therefore, Phase 4 was run at higher temperature conditions (500 and 600°C).

• At Phase 4, tars are increased at high temperature and char continues to decrease, indicating an optimum at even higher temperature conditions.

• Phase 5 is a recapitulation of results from Phase 1 and Phase 3 showing the effects of changing manure on experimental conditions in the range 400-500°C.

• Phase 6 is a recapitulation of results from Phase 2 and Phase 4 showing the results of changing manure experimental conditions in the range 500-600°C.

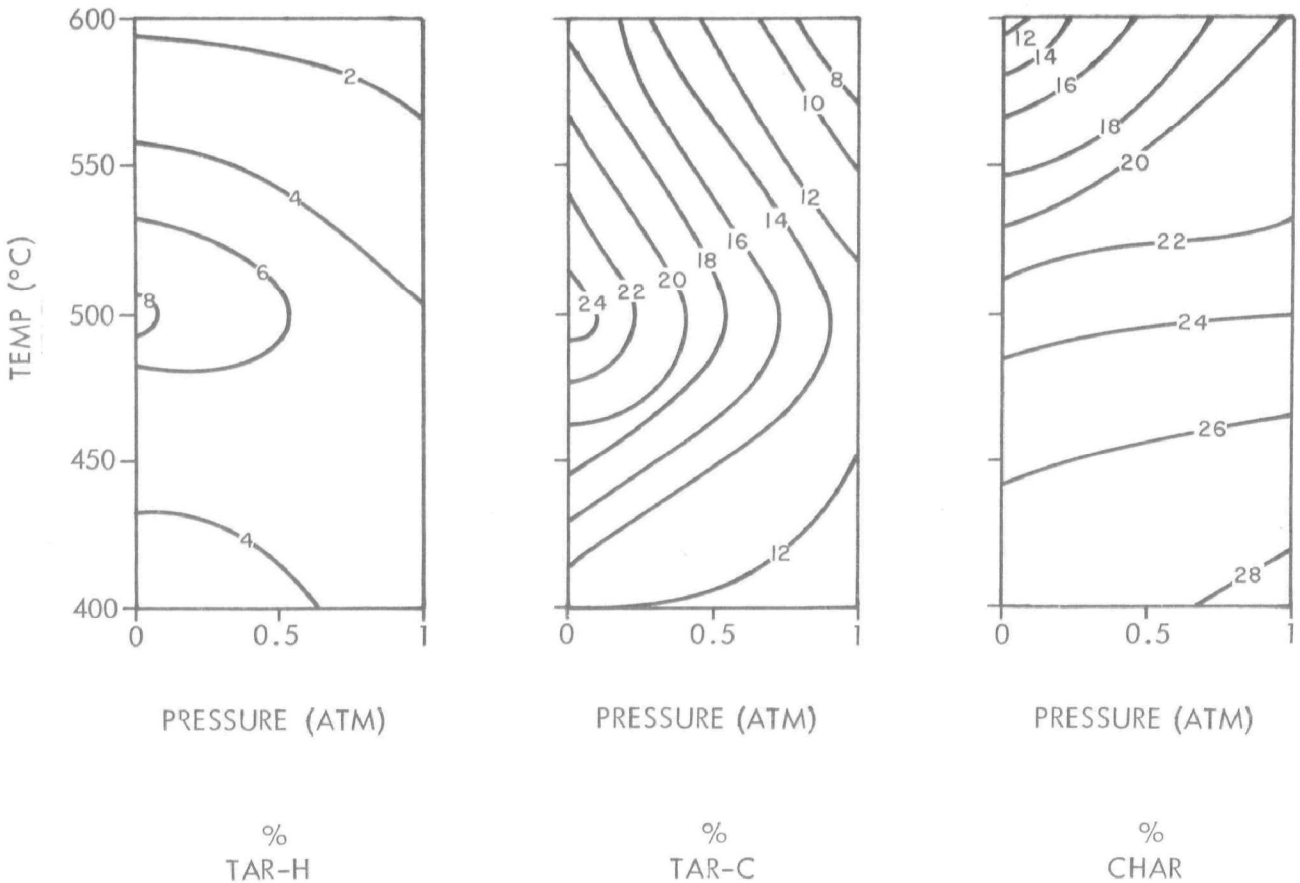
A comparison of the results of Phase 5 and Phase 6 against the goals of decreased char and increased tar shows clearly that the type of manure used is the overriding experimental factor in the pyrolyses.

Another view of the experimental process situation is shown in Figures A-7 and A-8, which give response contour surfaces for the experimental data. Percentages are shown on contour lines across the entire experimental region for manure A and manure B. The optimum regions for tar production using manure A can be easily seen in Figure A-7. For manure B, these optimums are absent except at the highest temperatures, where an optimal region is indicated. A rule that char decreases at high temperature can be made from both figures.

From an economic point of view, manure A would seem the most advantageous for processing because of the lower temperature optimums. Thus, we must isolate the characteristic of manure A that produces this effect. Vacuum conditions are not economically prohibitive.

Finally, sequential significance tests were made to compare experimental treatments of the two kinds of manure, and establish the validity of the indicated trends between them. After three cycles of experimental measurement, the validity of most of these trends is established at the 95% confidence level, and no more experimental runs to verify these trends are needed. The verified trends in going from manure A to manure B in Phase 1 and Phase 3 are shown in Table A-2.

MANURE "A"




% TAR-H

% TAR-C

% CHAR

Figure A-7 - Response Surfaces: Manure "A"

MANURE "B"

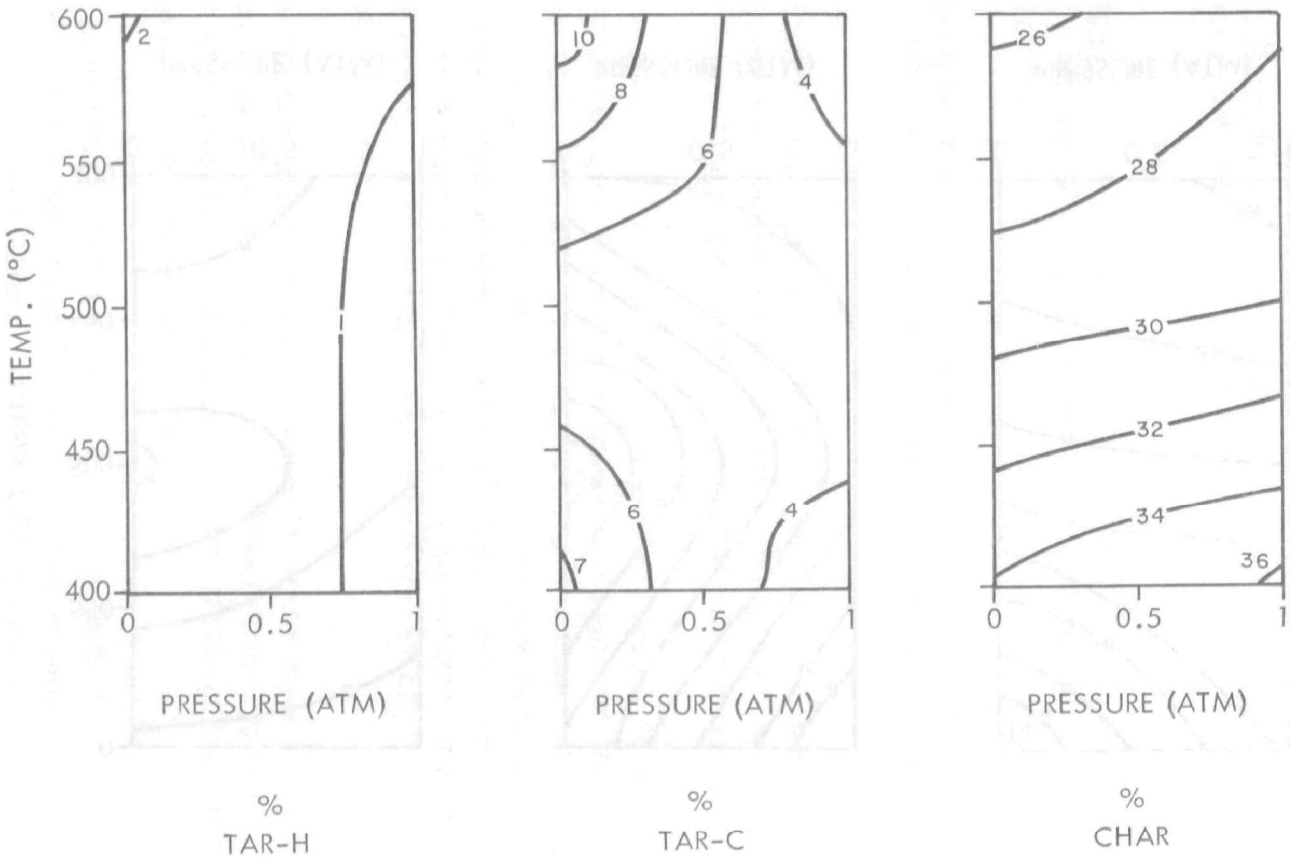



Figure A-8 - Response Surfaces: Manure "B"

TABLE A-2

VERIFIED TRENDS

Manure A to Manure B

| Design | PCT.(DIC) | PCT.(TAR-H) | PCT.(TAR-C) | PCT.(CHAR) |
|---|---|---|---|---|
| LL | Increase | - | Decrease | Increase |
| HL | Increase | Decrease | Decrease | Increase |
| LH | - | Decrease | Decrease | Increase |
| HH | - | Decrease | Decrease | Increase |
| **Effects** | | | | |
| Mean | Increase | Decrease | Decrease | Increase |
| T | Decrease | Decrease | Decrease | Decrease |
| P | Decrease | - | - | - |
| TP | Increase | Increase | Increase | - |

## VI. Conclusions

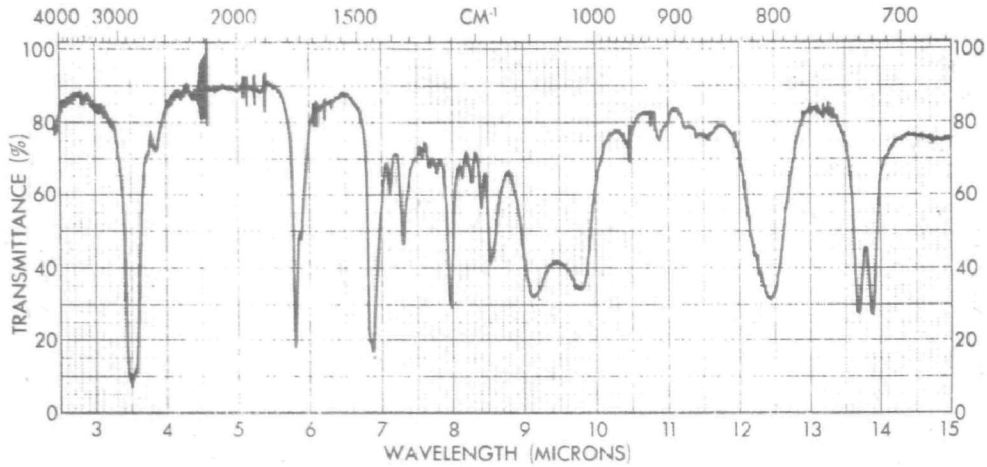
Factorial analysis on experimental measurements showed that the type of manure processed is the single most important factor in manure pyrolyses.

Of the experimental manures used, the feed lot manure sample showed more desirable process conditions than the concrete pad manure sample.

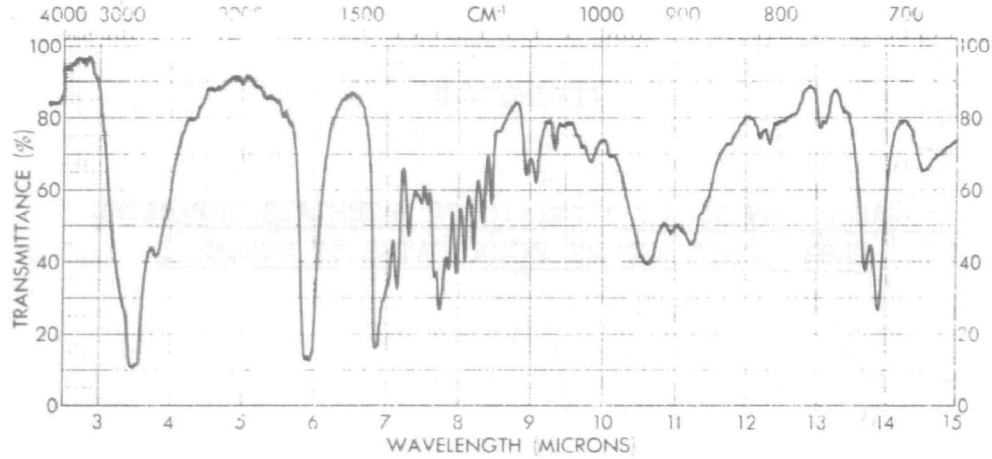
Three cycles (replicates) of each experimental run are sufficient to verify experimental trends.

# APPENDIX B

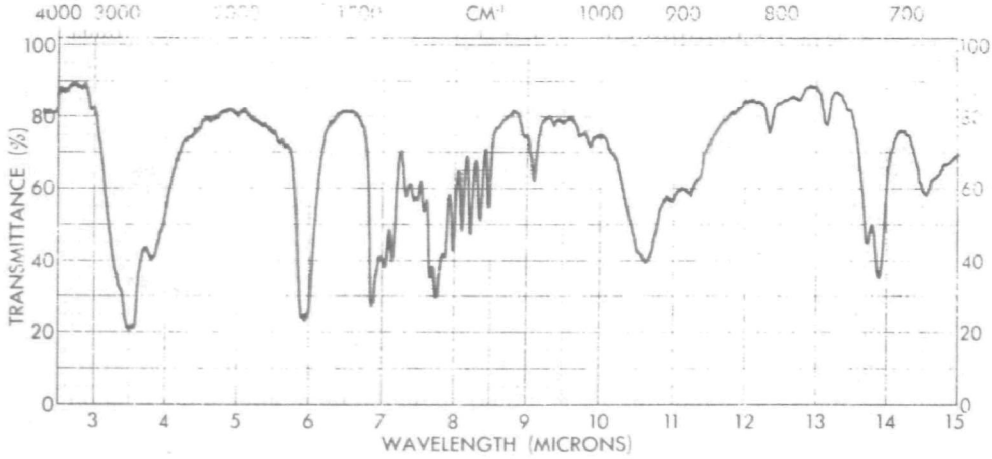
## INFRARED SPECTRA OF SIGNIFICANT MATERIALS SEPARATED FROM CATTLE MANURE PYROLYSATES BY SCHEME I



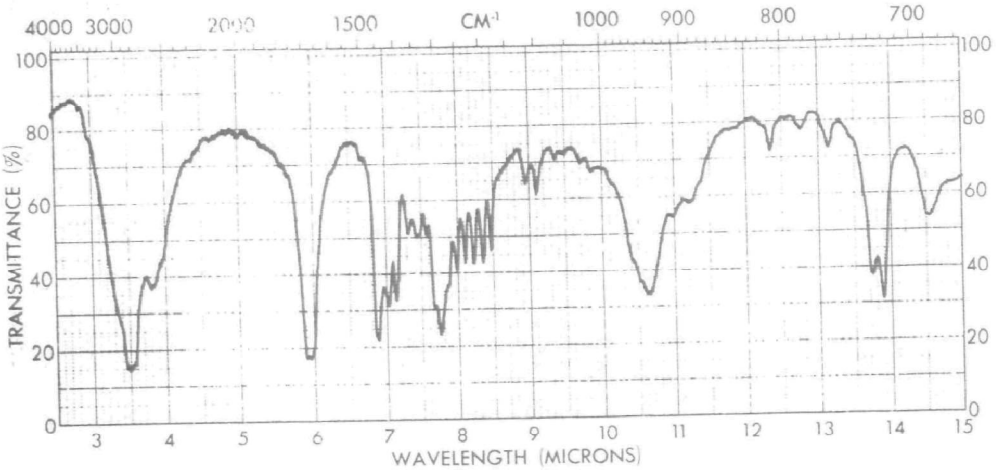

Material A-I-1



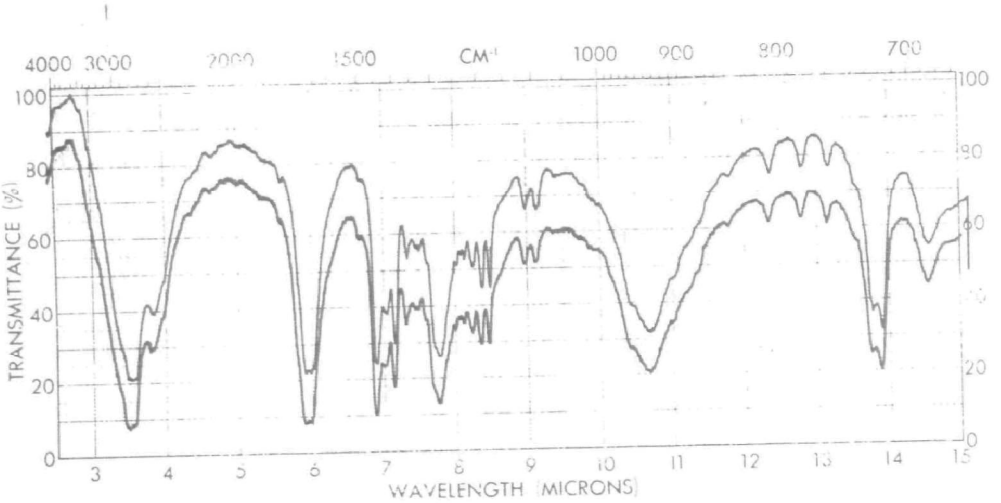

Material A-II-1



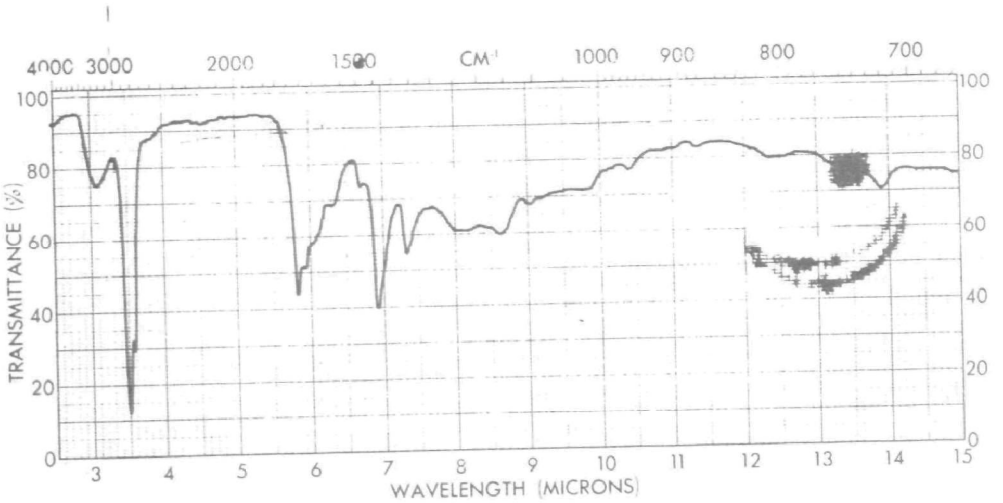

Material A-II-2



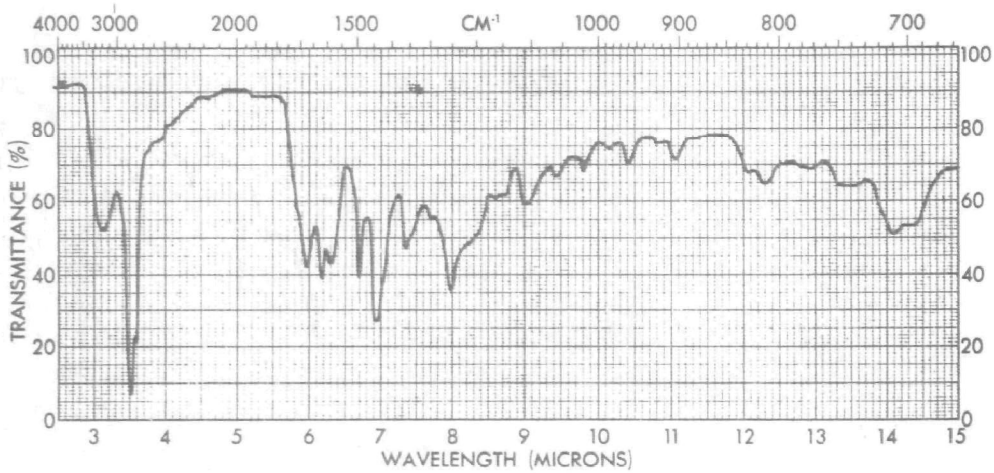

Material A-II-3



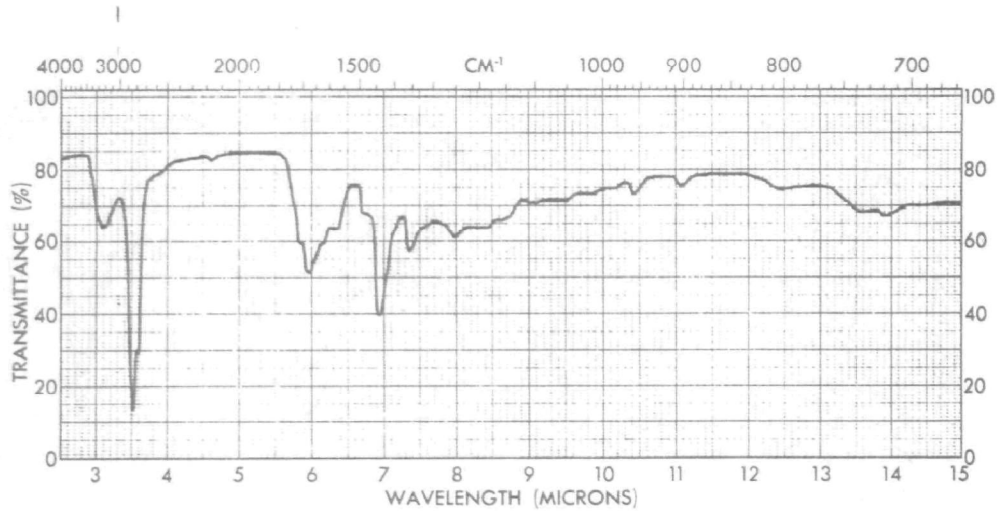

Material A-III-1



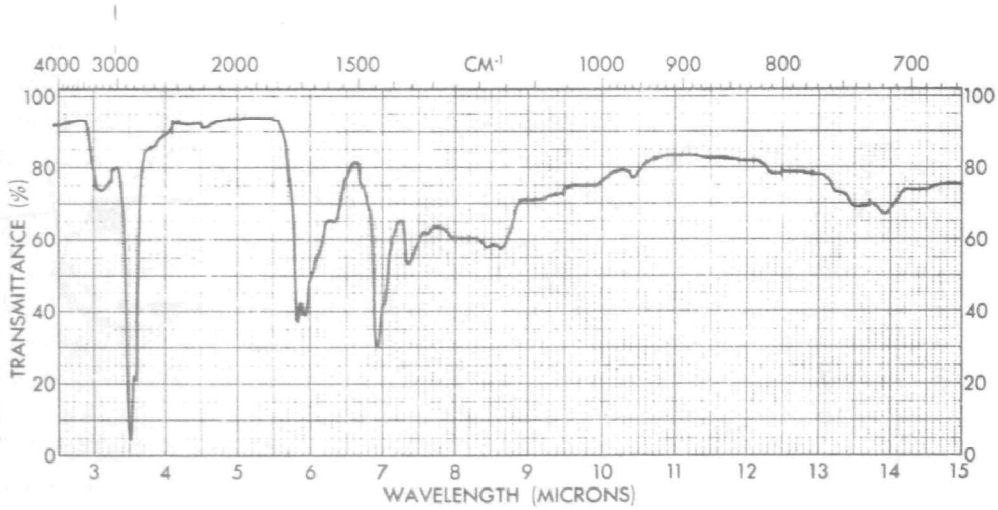

Material A-IV-1



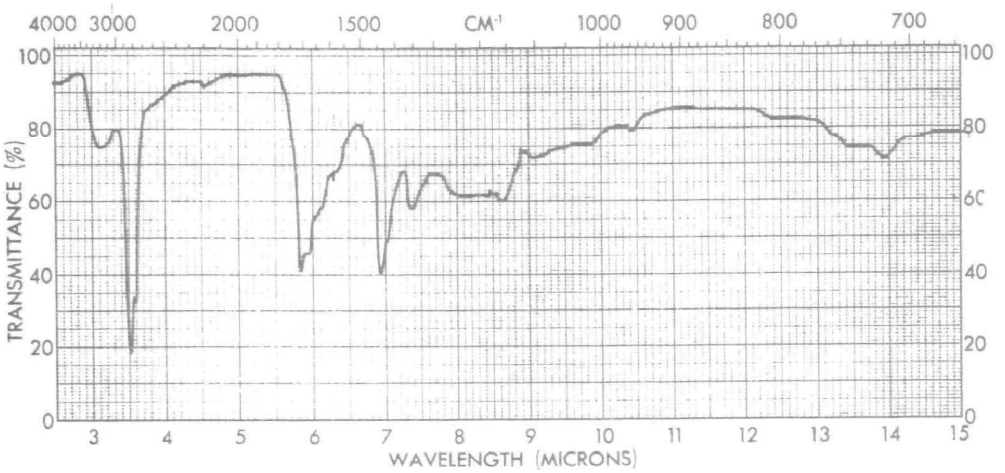

Material A-IV-1A



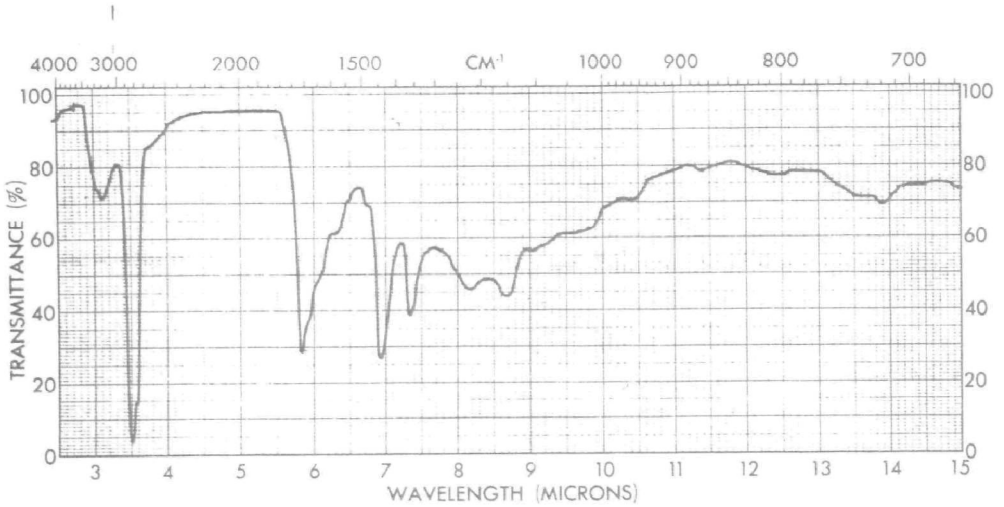

Material A-IV-1B



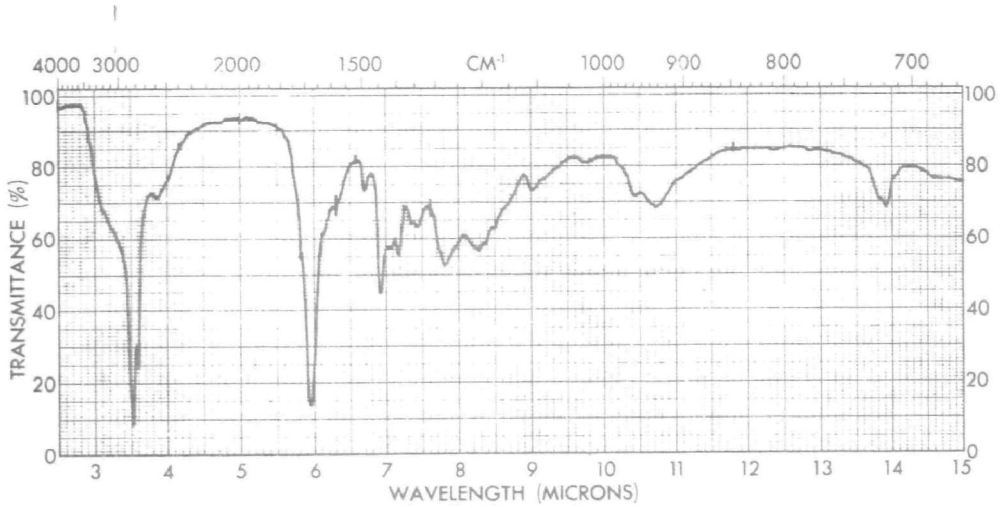

Material A-IV-1C



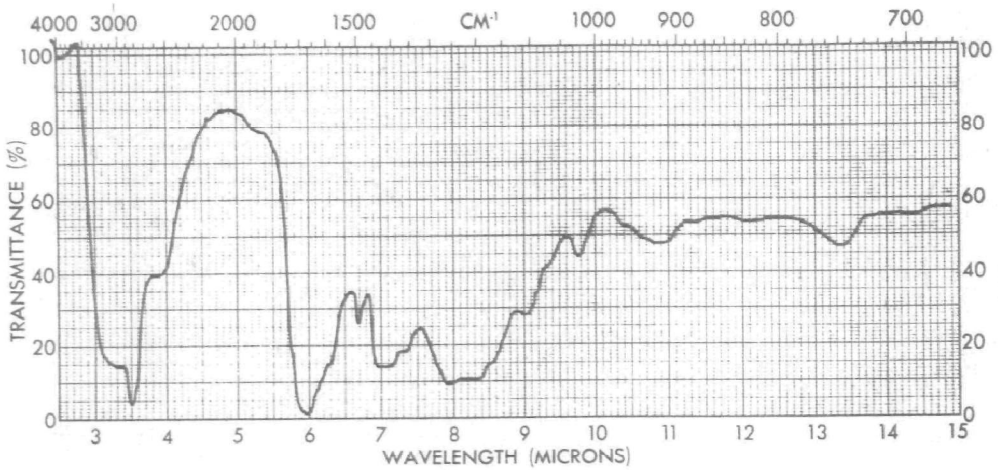

Material A-IV-1D



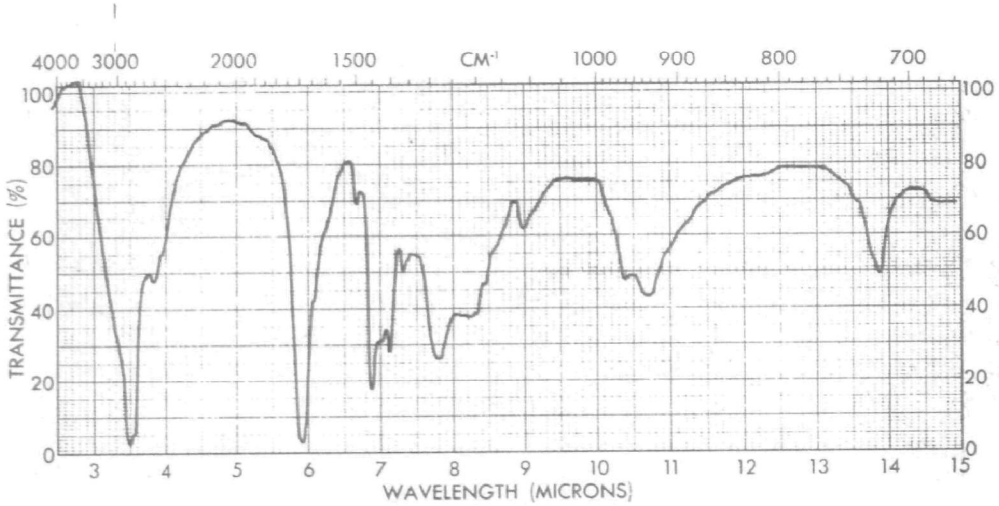

Material A-IV-1E



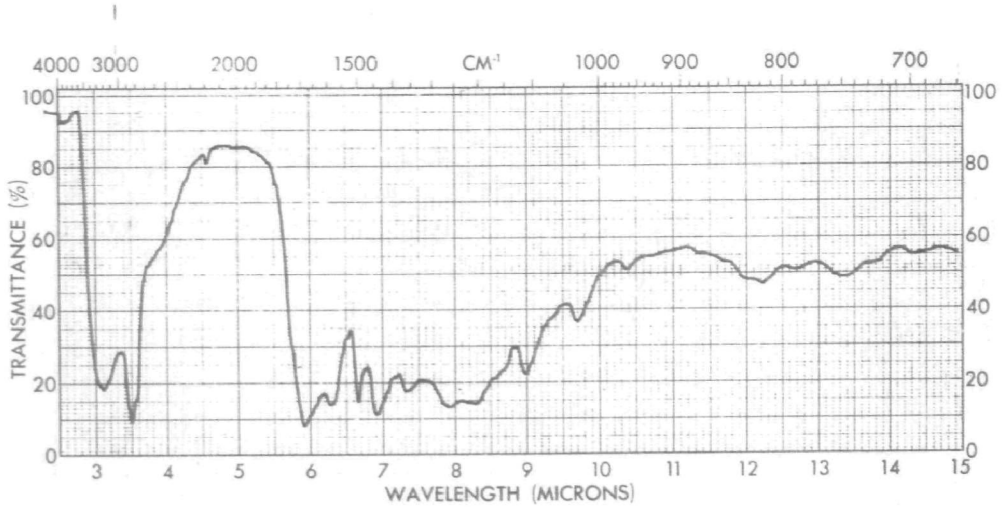

Material A-IV-2



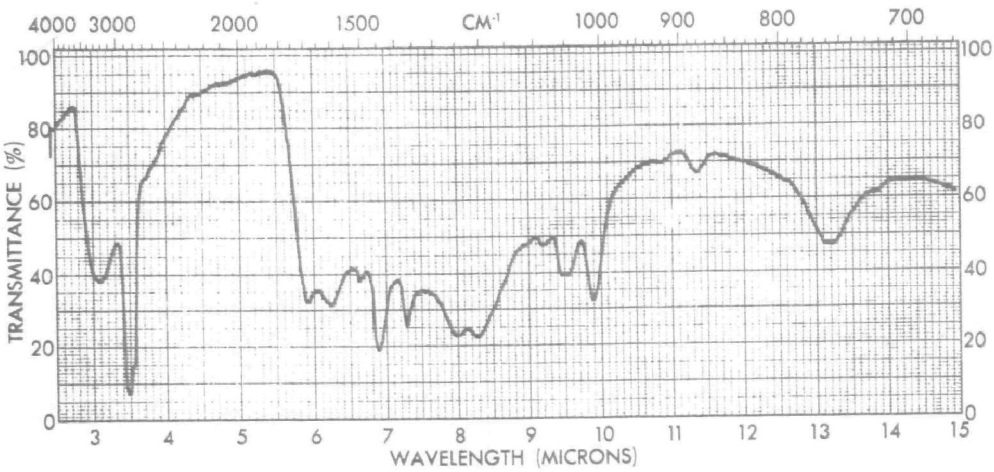

Material A-V-1



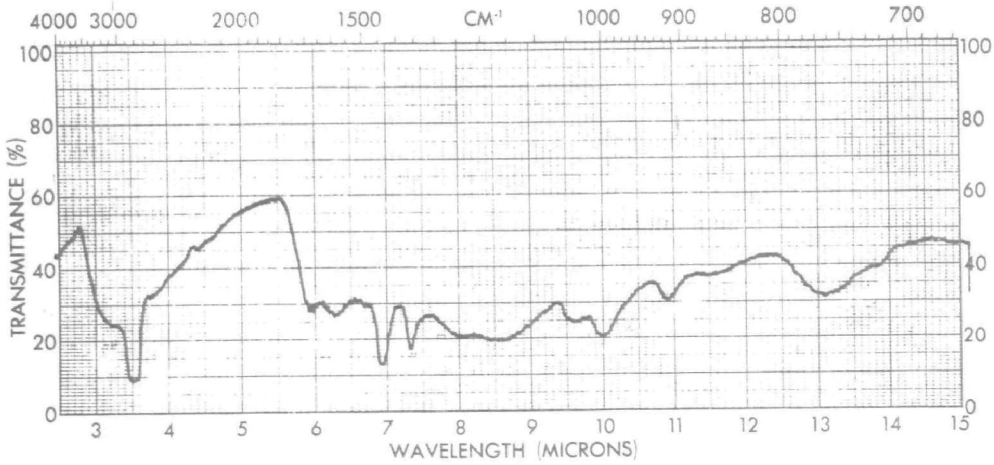

Material A-V-2



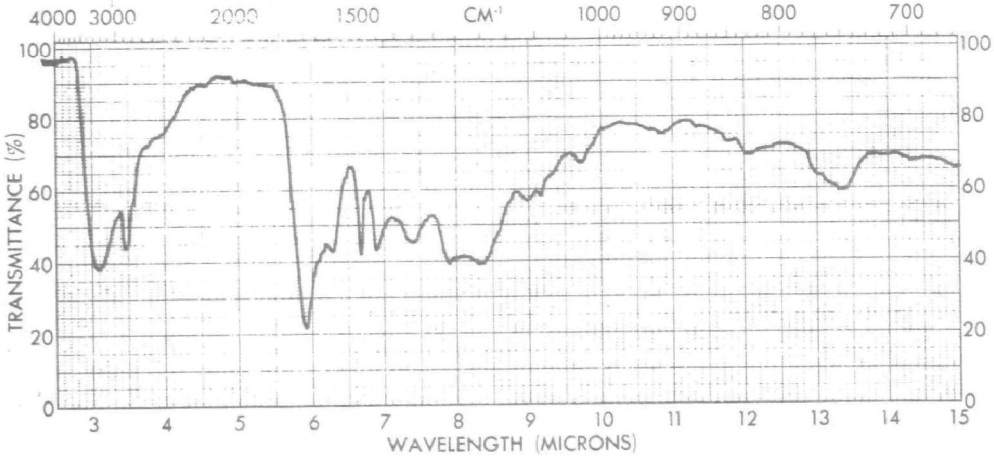

Material A-V-3




Material A-VI-1




Material A-VI-2

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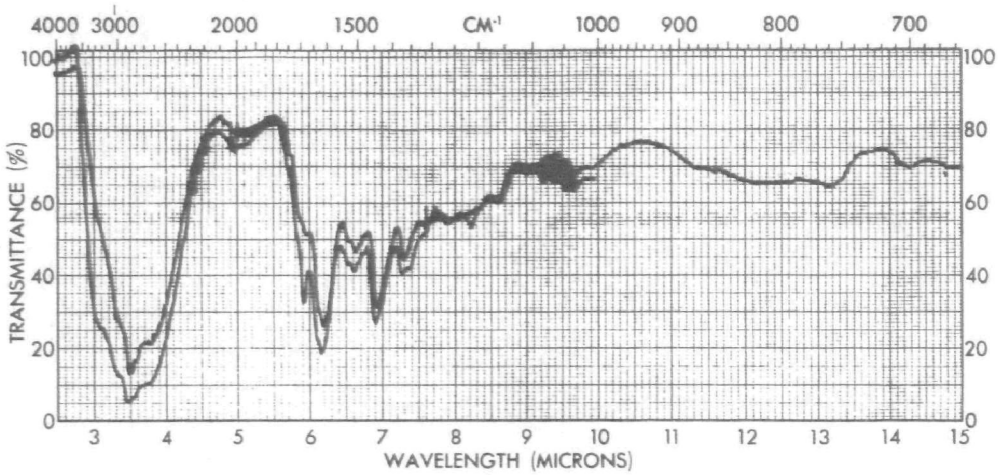
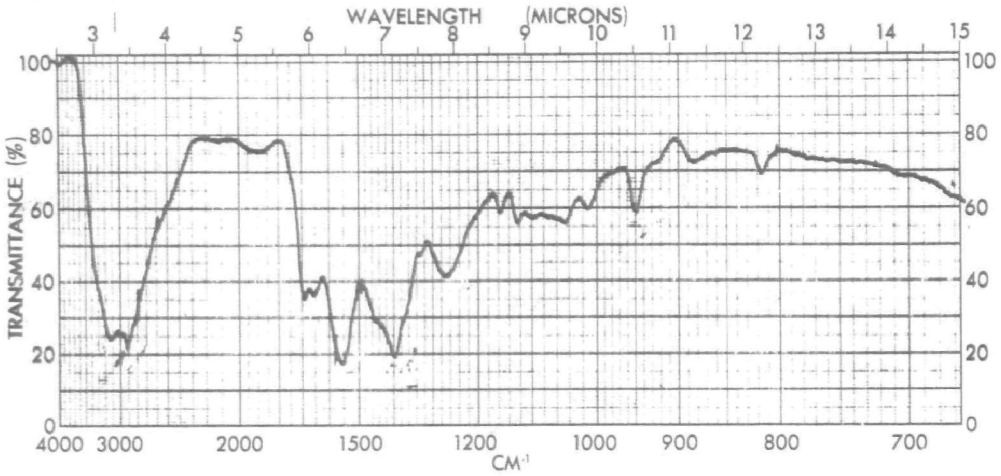


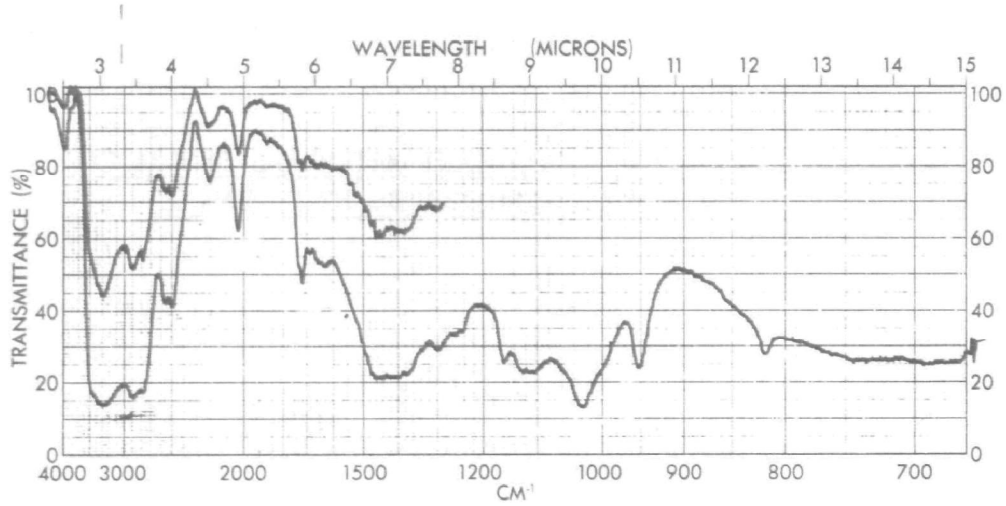

Material B-I-2

# APPENDIX C

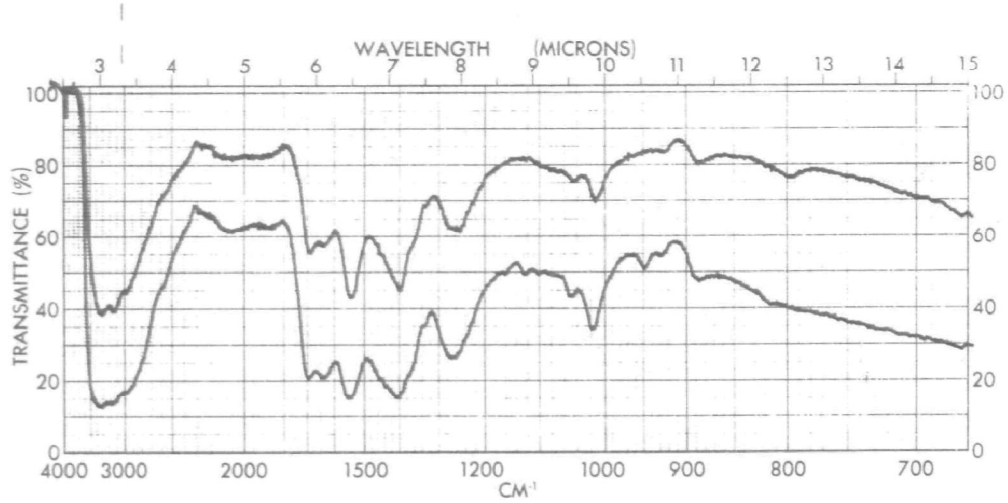
## INFRARED SPECTRA OF SIGNIFICANT MATERIALS SEPARATED FROM CATTLE MANURE PYROLYSATES BY SCHEME II



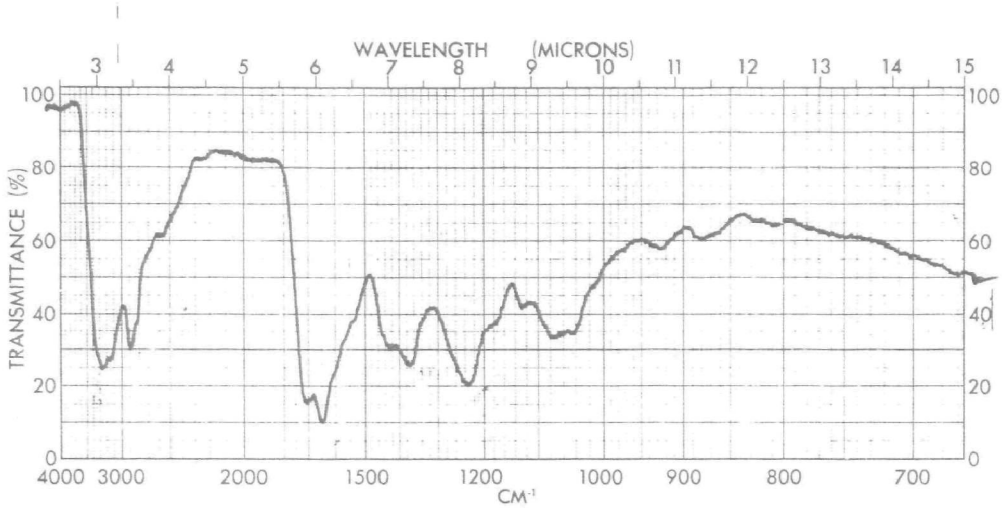

$W_c$



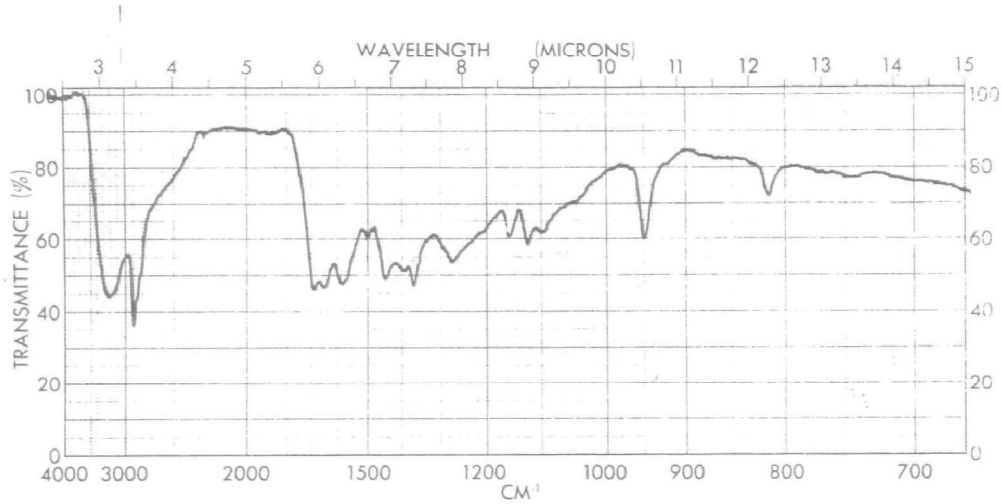

$W_c$ Distillate Fraction I, b.p. 68°C



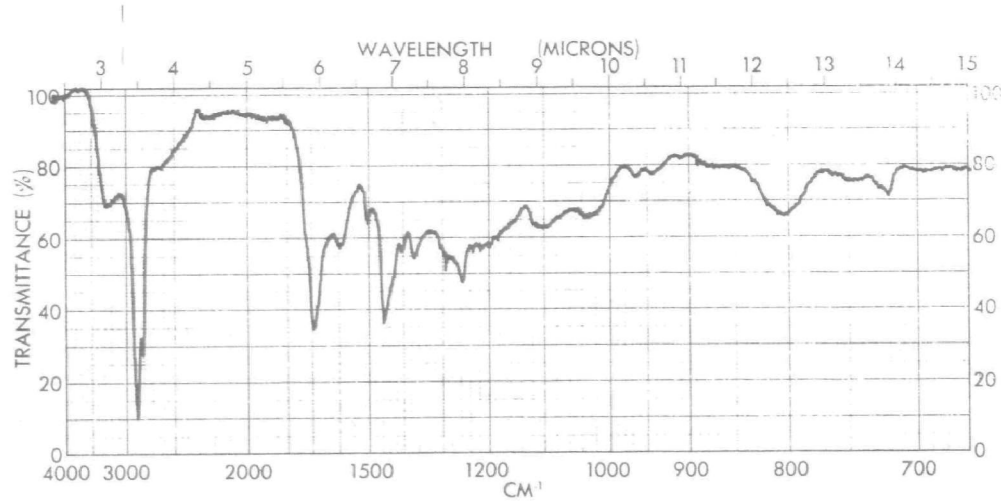

$W_c$ Distillate Fraction VI, b.p. 145°C



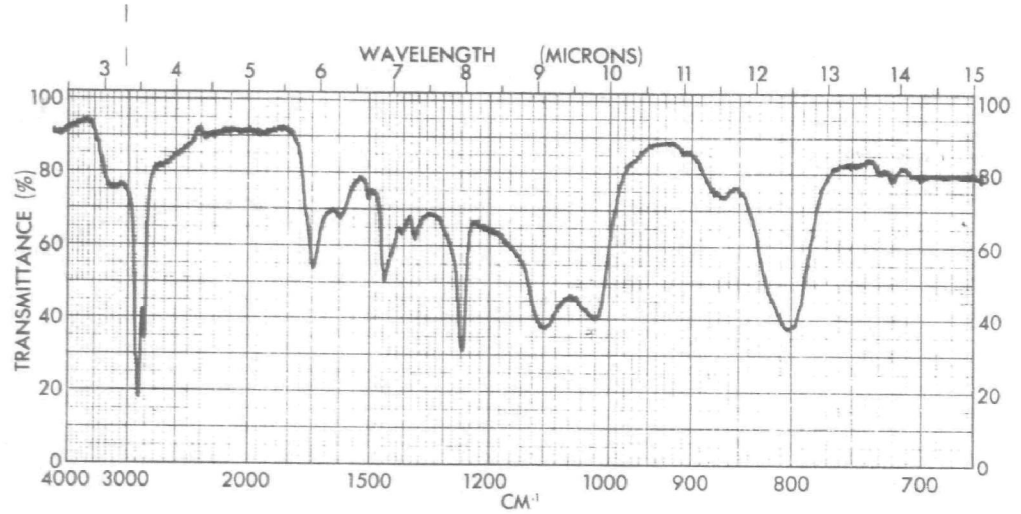

$W_c$ Residue After Distillation




$W_h$




K

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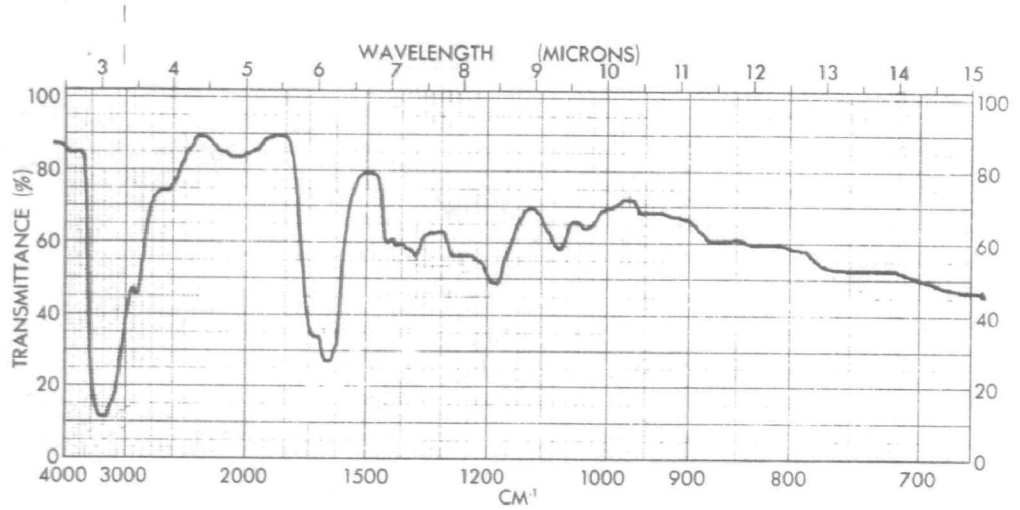
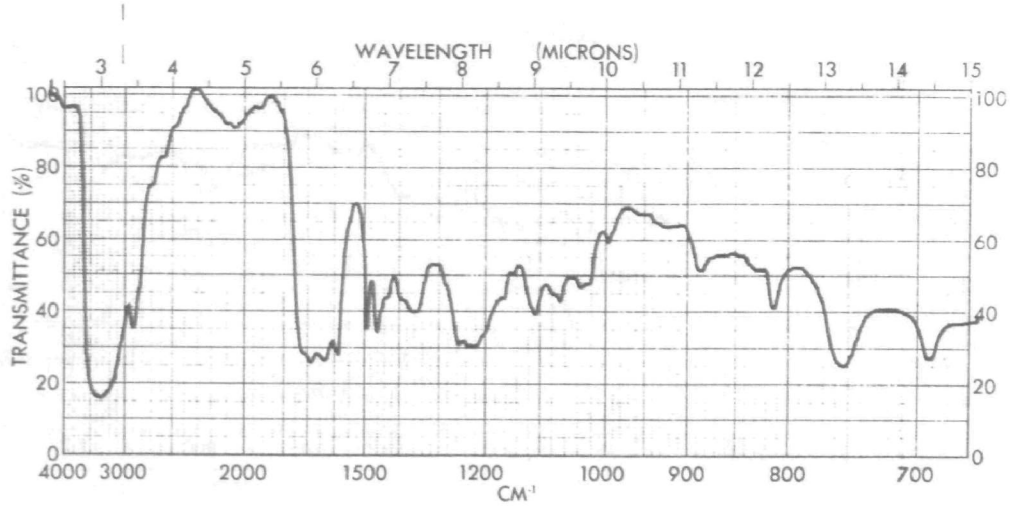
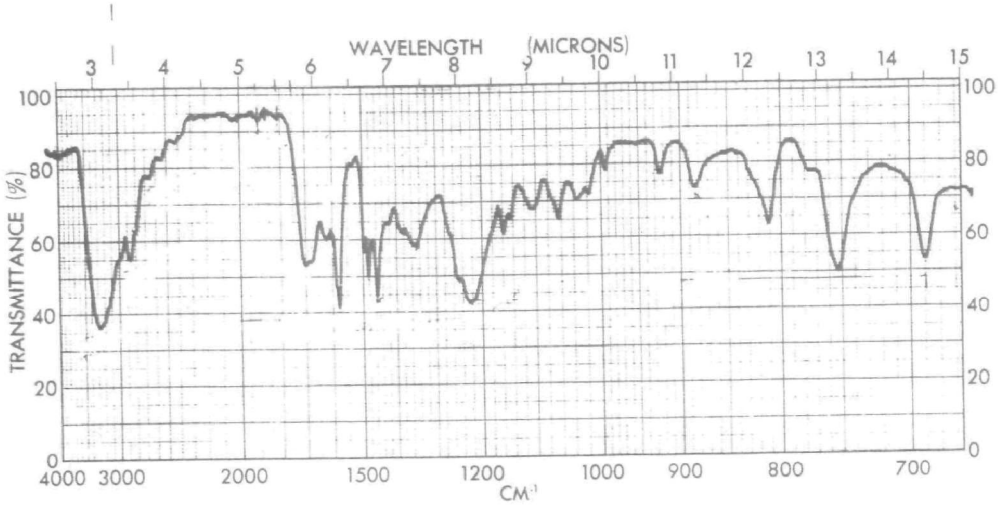


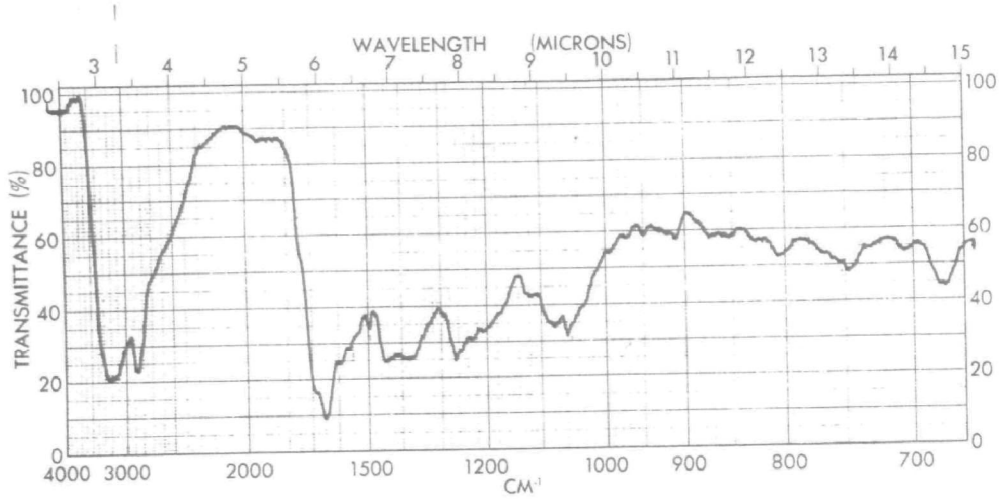

E-1-b GC Distillate Fraction III



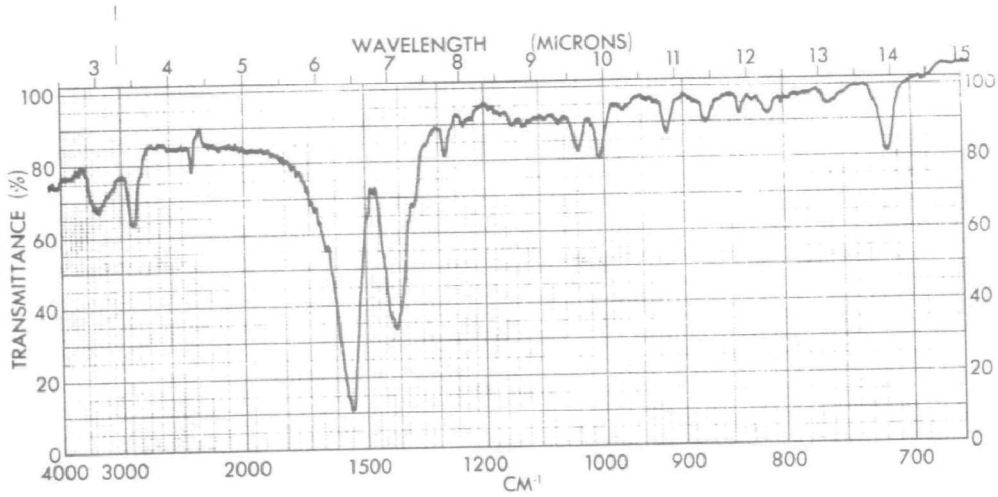

E-1-b GC Distillate Fraction IV



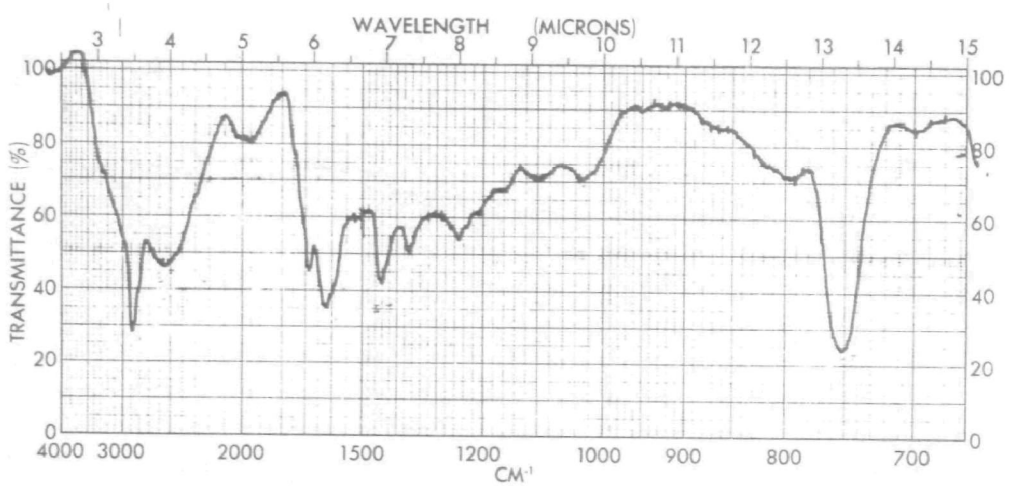

E-1-b GC Distillate Fraction V



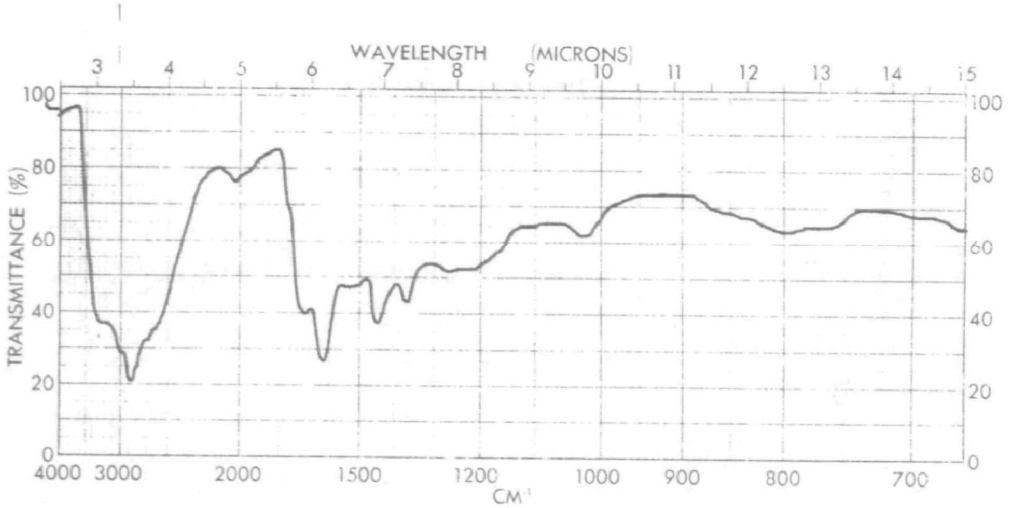

E-4-a



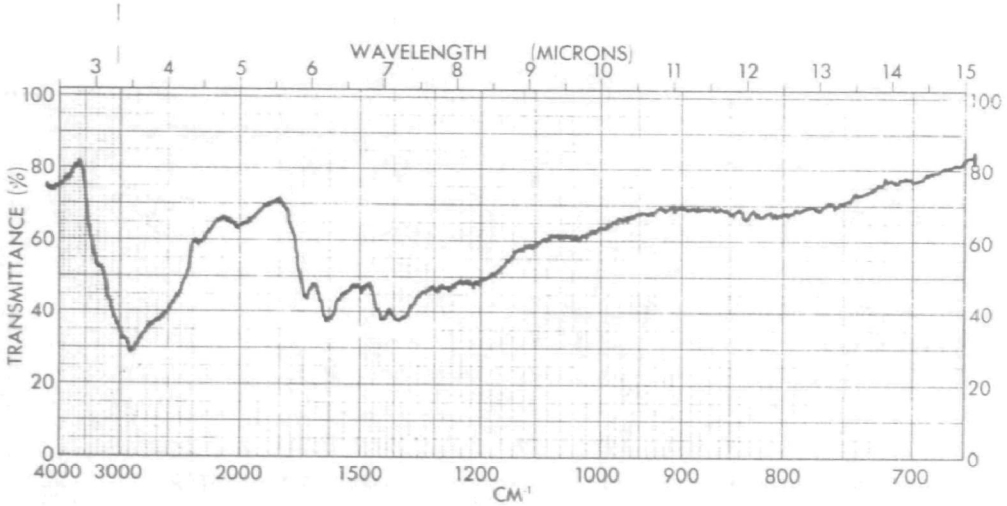

E-4-c


WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14 15
TRANSMITTANCE (%)
100 80 60 40 20 0
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

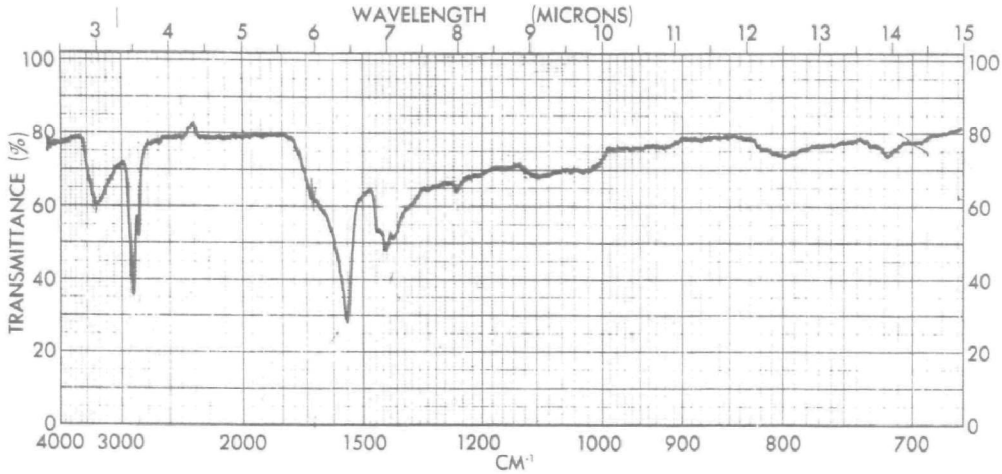
H-4


WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14 15
TRANSMITTANCE (%)
100 80 60 40 20 0
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

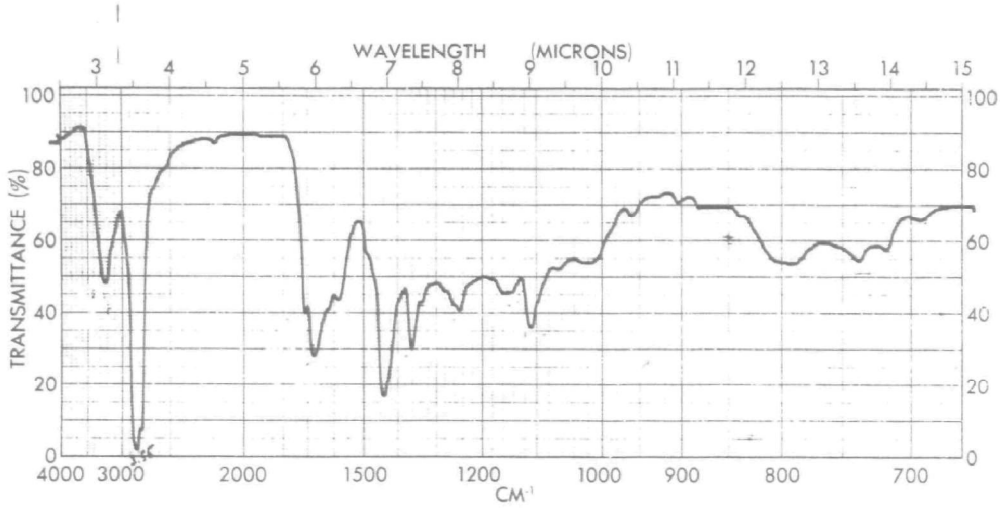
H-6-b-1


WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14 15
TRANSMITTANCE (%)
100 80 60 40 20 0
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

H-6-B-2


WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14 15
TRANSMITTANCE (%)
100 80 60 40 20 0
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

F


WAVELENGTH (MICRONS)
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TRANSMITTANCE (%)
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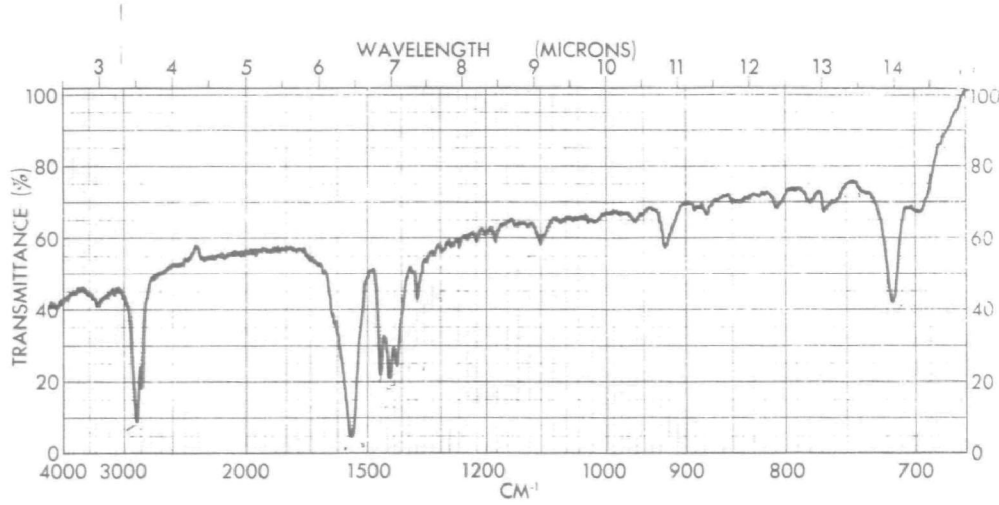
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

M-S-I


WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14
TRANSMITTANCE (%)
100 80 60 40 20 0
4000 3000 2000 1500 1200 1000 900 800 700
CM⁻¹

G-2

APPENDIX D

## WASTE PRODUCTION AS RELATED TO ANIMAL FEED*

General - This section deals primarily with feeds for beef cattle and the quantity and quality of the resultant waste. The basic approach used to estimate the waste characteristics can be extended to other animals using the concepts outlined and applicable data for specific animal species.

The type of feed consumed by an animal affects the quantity and characteristics of the waste that is produced. Fresh beef cattle manure will contain 80 to 85% moisture and will contain undigested feed from the digestive tract, unabsorbed digestive juices, residue of the digestive tract, and waste minerals. Lignin and hemicellulose are relatively stable materials that are not easily digestible by cattle and will exist in the waste. These materials are a large fraction of high roughage feeds and are in all rations to some extent.

It can be expected that the waste matter in beef cattle feedlots will be different from that of cattle on general farms or on pasture. Since the early 1960's, more efficient rations and feeding programs have helped maintain the economic position of the cattle feedlot operation. Increasingly large numbers of feeder cattle are fed high concentrate rations in the feedlots. High concentrate rations lend themselves to mechanical processing and handling. A concentrate:roughage ratio of 4:1 has been suggested as ideal with respect to rate of gain, feed efficiency, and carcass merit for commercial feeders. The large feedlot operator will prefer to feed a completely mixed feed.

A large quantity of cattle are still fed on farms and ranches that produce large quantities of harvested roughage or pasture. Because of the higher quantity of nondigestible matter in roughage, cattle on pasture or roughages will be expected to produce a higher quantity of waste per day than cattle fed a large quantity of concentrates.

Fattening cattle will consume daily an amount of dry feed equal to about 2.5 - 3.0% of their body weight. The type of roughage utilized in a feed ration will be a function of the operator's choice and relative feed costs.

Nutrition studies have established that the protein level in the feed ration will have a marked effect on the total digestibility of the

* Based on a report to the project by Dr. Raymond C. Loehr, Cornell University.

dry matter in ruminant rations. The addition of protein compounds to a ration having a low protein content will increase the breakdown of the carbohydrates and makes other nutrients more digestible. The feeding of 1 - 2 lb. of protein supplement apparently has no significant effect on the amount of grain and roughage consumed by an animal but can account for better digestibility of roughage.

Feed Rations - The ration fed beef cattle will vary from region to region, due to the costs of specific feed components, and will vary with the age of the animal. "Typical" feed rations rarely exist; however, examples can be noted to illustrate general composition:

AVERAGE RATIONS

| A | B |
|---|---|
| Ground corn | Corn silage |
| Corn silage | Soybean meal |
| Protein supplement | |

COMMERCIAL FEEDLOT HIGH ENERGY RATION

Ground alfalfa hay
Cottonseed hulls
Steam processed milo
Cottonseed pellets

Most of the large feedlot operations have installed their own feed processing operations, frequently automated and controlled by a skilled animal nutritionist. In addition to feed chopping and grinding, many feeds are pelleted or flaked prior to feeding.

Estimated Waste - The best approach to determine the waste produced by a given feed is to conduct nutritional trials and measure the quantity and quality of excreted wastes. While quite accurate, the process is time consuming and costly.

It is possible to estimate the quantity and quality of the waste if the nature and digestion coefficients for a feed are known. Such data have been obtained from nutritional studies over the years and have been compiled by Morrison[1/] and others. The data are available on the quantity of protein, fat (ethyl ether extract), fiber, nonfiber extract (NFE), and mineral matter in the feed. Other nutritional data of interest, such as

major mineral components, are also frequently available. The digestion coefficients for protein, fat, fiber, and NFE are listed by Morrison for certain feeds.

The digestion coefficients represent the percent of the feed component that is not in the waste matter. They represent the maximum utilization of a feed component by an animal. Some digestion coefficients, such as for protein, represent apparent digestibility because the waste contains metabolic as well as digested nitrogen. The digested or used portion is not determined directly in the case of any of the nutrients and the term coefficient of apparent digestibility frequently is used since the coefficients are determined by difference.

Digestion coefficients are not constants for a given feed or animal species and are influenced by factors such as the nature and relationships of the nutrients fed. Crude fiber tends to exert a protective influence against the digestibility of all nutrients. It is recognized that the digestibility of a mixture is not necessarily the average of the values for its constituents determined separately or indirectly. Each feed component may exert an influence on the digestibility of the other. In addition individual lots of a particular feed may differ from the average.

Even though these differences and variations are recognized, digestion coefficients can be used to estimate the quantity and quality of waste from a given feed. This has been done for selected feeds that may be components of beef cattle feed rations. The data on the composition of the wastes are presented in Table D-1. The data on the feed composition were obtained from Morrison.[1] Examples showing how the data were obtained are presented on page 93.

Assumptions implicit in the data noted in Table D-1 require clarification. It has been assumed that all of the mineral matter in the feed exists in the feces, i.e., the waste. The soluble minerals such as sodium, potassium, and urea are in the urine and may not be part of the feces depending upon how the wastes are held before collection and treatment or disposal. Depending upon the characteristics of the mineral content of the feed, up to about 50% of these minerals will be excreted with the urine and may not be part of the feces. Thus the data for mineral content of the waste as noted in Table D-1 may be on the high side. The actual mineral content of the wastes also will be a function of the quantity of dirt and inerts consumed by the animal in addition to that in the feed.

Urine from large beef cattle can be produced at a rate of 20 lb. per animal per day and contains about 6% dry matter. It is a major source of fluid in accumulated cattle wastes. Urine contains by-products of metabolism and serves as the major carrier of mineral wastes from the animal.

The data in Table D-1 are expressed as waste dry matter. While the waste may be defecated with 80-85% moisture content, the actual moisture content as well as chemical composition will be affected by the environmental conditions and the time the wastes lay in the feedlot prior to collection. Decomposition of organic matter and loss of nitrogenous matter will occur, especially during wet and warm weather.

The volatile content of the waste can be estimated by the sum of the protein, fat, fiber, and NFE percentages of the dry waste. The mineral content can be used as an estimate of the ash content. The composition of the fiber and NFE can be estimated as combinations of lignin, cellulose, and hemi-cellulose.

The estimated wastes for selected feeds (Table D-1) indicate that for dry roughages, green roughages, and silage, the waste matter is from 30 to 46% of the dry matter in the feed and that the mineral content of the waste is from 12 to 35% for these feeds as well as for concentrates. As expected the waste from the concentrates is a smaller portion of the dry matter in the feed, 11 to 35%.

This information may be useful in estimating the difference in the composition of wastes from cattle fed different feed rations. If this point is critical to a study, it is suggested that information be obtained regarding typical rations of the region as well as actual characteristics of wastes resulting from these feeds.

1. Morrison, F. B., Feeds and Feeding, 22nd Edition, Morrison Publishing Company, 1961.

2. Maynard, L. A., and Loosli, J. K., Animal Nutrition, 6th Edition, McGraw Hill, 1969.

3. Newmann, A. L., and Snapp, R. R., Beef Cattle, 6th Edition Wiley, 1969.

4. Wagnon, K. A., Albaugh, R., and Hart, G. H., Beef Cattle Production, Macmillan, 1960.

## TABLE D-1

POTENTIAL QUALITY AND QUANTITY OF WASTE FROM SELECTED FEEDS

| Feed | Total Dry Matter in Feed (%) | Waste Parameter | Protein | Fat | Fiber | NFE | Mineral Matter | Total | Dry Waste As Percent of Dry Matter in Feed |
|---|---|---|---|---|---|---|---|---|---|
| Dry Roughages | | | | | | | | | |
| Alfalfa Hay | 90.5 | Lb/100 Lb. Feed | 4.4 | 1.3 | 15.7 | 11.0 | 8.0 | 40.5 | 45 |
| | | % Of Total Waste | 10.4 | 3.2 | 38.9 | 27.0 | 19.7 | | |
| Brome Grass Hay | 88.8 | Lb/100 Lb. Feed | 5.1 | 1.3 | 11.6 | 14.4 | 8.2 | 40.8 | 46 |
| | | % Of Total Waste | 12.5 | 3.2 | 28.4 | 35.3 | 20.0 | | |
| Clover Hay, Red | 88.3 | Lb/100 Lb. Feed | 4.8 | 1.1 | 12.6 | 12.9 | 6.4 | 37.8 | 43 |
| | | % Of Total Waste | 12.6 | 2.9 | 33.3 | 34.2 | 17.0 | | |
| Corn Fodder, Well Eared, Very Dry | 91.1 | Lb/100 Lb. Feed | 4.0 | 0.6 | 8.4 | 14.7 | 6.4 | 34.1 | 37 |
| | | % Of Total Waste | 11.7 | 1.8 | 24.6 | 43.0 | 18.8 | | |
| Grass Hay, Mixed, Good Quality | 89.0 | Lb/100 Lb. Feed | 3.5 | 1.3 | 12.0 | 16.4 | 5.5 | 38.7 | 43 |
| | | % Of Total Waste | 9.1 | 3.4 | 31.0 | 42.4 | 14.2 | | |
| Milo Fodder | 88.5 | Lb/100 Lb. Feed | 5.0 | 1.3 | 8.5 | 18.4 | 6.9 | 40.0 | 45 |
| | | % Of Total Waste | 12.5 | 3.0 | 21.2 | 46.0 | 17.2 | | |
| Pasture Grass, and Clovers, Dry, Fertile Pasture | 90.0 | Lb/100 Lb. Feed | 5.3 | 1.2 | 4.1 | 7.7 | 7.7 | 26.0 | 29 |
| | | % Of Total Waste | 20.4 | 4.6 | 15.8 | 29.6 | 29.6 | | |
| Sorghum Fodder Dry, Sweet | 88.9 | Lb/100 Lb. Feed | 2.6 | 0.8 | 9.8 | 17.8 | 7.1 | 38.1 | 43 |
| | | % Of Total Waste | 6.8 | 2.1 | 25.7 | 46.7 | 18.6 | | |
| Timothy Hay | 89.0 | Lb/100 Lb. Feed | 3.5 | 1.2 | 13.0 | 18.4 | 5.0 | 41.1 | 46 |
| | | % Of Total Waste | 8.5 | 2.9 | 30.6 | 45.7 | 12.2 | | |
| Green Roughages | | | | | | | | | |
| Alfalfa Hay, Green | 24.4 | Lb/100 Lb. Feed | 1.1 | 0.6 | 3.5 | 2.6 | 2.2 | 10.0 | 41 |
| | | % Of Total Waste | 11.0 | 6.0 | 35.0 | 26.0 | 22.0 | | |
| Clover, Red | 24.5 | Lb/100 Lb. Feed | 1.2 | 0.3 | 2.8 | 2.3 | 2.1 | 8.7 | 36 |
| | | % Of Total Waste | 14.0 | 3.5 | 32.0 | 26.5 | 24.0 | | |
| Grasses, Mixed Pasture | 28.1 | Lb/100 Lb. Feed | 1.2 | 0.8 | 1.6 | 3.0 | 2.8 | 9.4 | 33 |
| | | % Of Total Waste | 12.8 | 8.5 | 17.0 | 32.0 | 29.7 | | |
| Pasture Grasses and Legumes, Mixed | 22.0 | Lb/100 Lb. Feed | 1.2 | 0.5 | 1.3 | 2.7 | 1.9 | 7.6 | 34 |
| | | % Of Total Waste | 15.8 | 6.6 | 17.1 | 35.6 | 25.0 | | |
| Sorghum Fodder Sweet | 24.9 | Lb/100 Lb. Feed | 0.7 | 0.3 | 2.7 | 3.5 | 1.4 | 8.6 | 35 |
| | | % Of Total Waste | 8.1 | 3.5 | 31.4 | 40.7 | 16.3 | | |

TABLE D-1 (Concluded)

| Feed | Total Dry Matter in Feed (%) | Waste Parameter | Protein | Fat | Fiber | NFE | Mineral Matter | Total | Dry Waste As Percei of Dry Matter in F |
|---|---|---|---|---|---|---|---|---|---|
| Silages | | | | | | | | | |
| Alfalfa, Not Wilted | 24.7 | Lb/100 Lb. Feed | 1.5 | 0.4 | 4.1 | 3.6 | 2.3 | 11.9 | 48 |
| | | % Of Total Waste | 12.6 | 3.4 | 34.5 | 30.3 | 19.3 | | |
| Atlas Sorghum | 29.7 | Lb/100 Lb. Feed | 1.1 | 0.4 | 3.1 | 4.8 | 2.3 | 11.7 | 39 |
| | | % Of Total Waste | 8.5 | 3.4 | 26.5 | 41.0 | 19.6 | | |
| Clover, Red Not Wilted | 29.5 | Lb/100 Lb. Feed | 1.3 | 0.4 | 4.2 | 4.3 | 2.5 | 12.7 | 43 |
| | | % Of Total Waste | 10.2 | 3.2 | 33.1 | 33.9 | 19.7 | | |
| Corn, Well Matured | 27.6 | Lb/100 Lb. Feed | 1.1 | 0.2 | 2.3 | 4.9 | 1.6 | 10.1 | 37 |
| | | % Of Total Waste | 11.0 | 2.0 | 23.0 | 49.0 | 16.0 | | |
| Concentrates | | | | | | | | | |
| Blood Meal | 91.6 | Lb/100 Lb. Feed | 23.8 | 1.2 | 0.7 | 0.7 | 5.7 | 32.1 | 35 |
| | | % Of Total Waste | 74.0 | 3.7 | 2.2 | 2.2 | 17.7 | | |
| Clover Seed, Red | 87.5 | Lb/100 Lb. Feed | 5.2 | 1.0 | 1.7 | 4.4 | 6.7 | 19.0 | 22 |
| | | % Of Total Waste | 27.4 | 5.2 | 9.0 | 23.1 | 35.2 | | |
| Corn, Grade No. 1 | 87.0 | Lb/100 Lb. Feed | 2.0 | 0.4 | 0.9 | 5.0 | 1.3 | 9.9 | 11 |
| | | % Of Total Waste | 20.0 | 4.0 | 9.0 | 50.0 | 13.0 | | |
| Corn Gluten Meal | 91.6 | Lb/100 Lb. Feed | 6.5 | 0.2 | 1.6 | 2.7 | 4.3 | 15.3 | 17 |
| | | % Of Total Waste | 42.5 | 1.3 | 10.5 | 17.7 | 28.1 | | |
| Cottonseed Meal Or Cake, 45% Protein Or More | 94.3 | Lb/100 Lb. Feed | 8.4 | 0.2 | 5.8 | 5.2 | 6.8 | 26.4 | 28 |
| | | % Of Total Waste | 31.8 | 0.8 | 22.0 | 19.7 | 25.8 | | |
| Linseed Meal | 91.1 | Lb/100 Lb. Feed | 4.6 | 0.4 | 3.6 | 6.6 | 5.7 | 20.9 | 23 |
| | | % Of Total Waste | 22.0 | 1.9 | 17.2 | 31.5 | 27.2 | | |
| Milo Grain | 89.0 | Lb/100 Lb. Feed | 2.4 | 0.7 | 1.0 | 6.4 | 2.1 | 12.6 | 14 |
| | | % Of Total Waste | 19.0 | 5.6 | 8.0 | 51.7 | 16.7 | | |
| Peanut Oil Meal, 45% Protein Grade | 94.0 | Lb/100 Lb. Feed | 3.9 | 0.5 | 2.7 | 3.9 | 5.4 | 16.4 | 17 |
| | | % Of Total Waste | 23.8 | 3.0 | 16.5 | 23.8 | 33.0 | | |

## EXAMPLES OF ESTIMATING WASTE CHARACTERISTICS FROM SPECIFIC FEEDS

Waste = Feed (1-Digestion Coefficient)

### Dry Roughage

Alfalfa hay, all analyses

| | Average Composition (%) | Digestion Coefficient | Waste | Component in Waste (%) |
|---|---|---|---|---|
| Protein | 15.3 | 71 | 4.4 | 10.9 |
| Fat | 1.9 | 30 | 1.3 | 3.2 |
| Fiber | 28.6 | 45 | 15.7 | 38.9 |
| NFE | 36.7 | 70 | 11.0 | 27.0 |
| Mineral | 8.0 | 0 | 8.0 | 19.7 |
| Total | 90.5 | | 40.5 | 100.0 |

Therefore, 100 lb. of this roughage as feed, would contain 90.5 lb. of total dry matter which would produce 40.5 lb. of dry waste matter, i.e., 45% of the dry matter intake.

### Concentrate

Milo Grain

| | Average Composition (%) | Digestion Coefficient | Waste | Component in Waste (%) |
|---|---|---|---|---|
| Protein | 10.9 | 78 | 2.4 | 19.0 |
| Fat | 3.0 | 78 | 0.7 | 5.6 |
| Fiber | 2.3 | 58 | 1.0 | 8.0 |
| NFE | 70.7 | 91 | 6.4 | 50.7 |
| Mineral | 2.1 | 0 | 2.1 | 16.7 |
| Total | 89.0 | | 12.6 | 100.0 |

Therefore, 100 lb. of this concentrate as feed, would contain 89.0 lb. of total dry matter which would produce 12.6 lb. of dry waste matter, i.e., 14% of the dry matter intake.

| 1 Accession Number | 2 Subject Field & Group | SELECTED WATER RESOURCES ABSTRACTS<br>INPUT TRANSACTION FORM |
|---|---|---|
| W | 05D | |

5 Organization

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6 Title

THE DISPOSAL OF CATTLE FEEDLOT WASTES BY PYROLYSIS

10 Author(s)

Dr. William Garner
Dr. Ivan C. Smith

16 Project Designation

Project No. 13040 EGH; Contract No. 14-12-850

21 Note

22 Citation

Environmental Protection Agency report number, EPA-R2-73-096, January 1973.

23 Descriptors (Starred First)

*Pyrolysis, *Qualitative Organic Separation, *Gas Condensation

25 Identifiers (Starred First)

*Pyrolysis, *Feedlot Waste, *Economic Analysis

27 Abstract

Beef cattle(steer) manure was obtained from a source that was free of soil contamination, and subsequently dried and pulverized. Replicate batch pyrolyses were carried out in stainless steel, glass, and iron tubes utilizing axial flow, at various levels of elevated temperature, and at atmospheric and lower pressures. Exhausts were carried by inert gas to traps and condensors. Qualitative separations and extractions were performed to determine the presence and quantity of various gasas, ash, tar, and organics. Many constituents were extracted, but in such small quantities that their value may not pay for the cost of pyrolizing. Larger scale pyrolyzing units should be tested to either confirm or disprove these findings.

| Abstractor | Institution |
|---|---|
| D. F. Anderson | Environmental Protection Agency, OR&M |