CHAPTER 2

CLEAN LIQUID AND GASEOUS FUELS FROM ORGANIC SOLID WASTES

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INTRODUCTION

The United States has begun to consume far greater amounts of gas and oil than can be produced domestically; it has also begun to produce far greater quantities of organic solid wastes than can be consumed by landfills and other conventional methods of disposal. This chapter deals with some efforts now being made to help alleviate these two critical problems simultaneously: the so-called energy crisis and pollution due to solid wastes. Simply put, organic solid wastes would be transformed to convenient forms of clean energy.

A rather large book could be written on all the present and planned efforts to solve the growing problems of solid wastes,[1-4] and a veritable flood of articles have appeared on the energy crisis.[5-10] This chapter, however, will confine itself to three methods for obtaining energy from organic solid wastes; although we shall emphasize the first process discussed, all three are important and may have different application. The processes are (1) the conversion of wastes to low-sulfur fuel oil by treatment with carbon monoxide (or synthesis gas) and water, (2) the conversion of these wastes to pipeline gas by hydrogasification, and (3) the pyrolysis of organic wastes to yield gas, char, and oil--conversion of wastes by these three processes was pioneered at the Pittsburgh Energy Research Center (PERC) of the Bureau of Mines, U.S. Department of the Interior.

The processes listed above certainly meet today's requirements of relevancy; in fact, the Bureau has been besieged by students (high school to graduate school), by industry, and by state, federal, and foreign government agencies, all desiring to learn about these novel approaches to today's headline problems. There is a strong feeling that these examples of synergetic recycling are but among the first of many similar solutions to apparent confrontations between use of our resources, an increasing rate of growth and the needs of the environment.

ENERGY AND SOLID WASTE PROBLEMS

The Energy Crisis

Both the energy and the solid waste problems are so well publicized that only the bare facts need be given here. First, let us discuss the energy crisis.

We are moving in a tide of significant and historic changes--a major realignment of the energy resources of the United States, if not the entire world. The outlines of the direction of this change and its causes are coming slowly into focus and are still disputed in some circles but the force of this change is not to be denied, regardless of your viewpoint.

The troublesome features of our energy situation did not simply emerge full-blown in the last few years. They have been a long time in the making--the result of adverse trends that are increasingly leading to a less tenable supply posture with the passage of time. We have long been using our cheapest, most accessible, and most convenient energy supplies; in recent years, it has become increasingly more difficult and costly to maintain an adequate reserve base in the major fuels. As the reserve base narrows for the crucial hydrocarbon fuels, our dependence on foreign sources grows.

The nation's requirements for energy will probably double between now and 1985. In this period, we shall have to rely upon oil, gas, coal and nuclear power for at least 95% of our needs. But our indigenous resources will not be developed fast enough to meet our growing requirements. Capital inputs will also have to double, with an annual average of about $30 billion, compared to present outlays of about $16 billion for the energy industry.

Energy costs are bound to rise; new indigenous supplies will come at higher prices. At present, the cost per million Btu of energy produced in the United States is about 35 cents for coal at the minemouth, 50 to 60 cents for new contracts for natural gas at the wellhead, and 90 cents for low-sulfur fuel oil at major ports (currently selling at $5.50 per barrel). These prices are rising now and could easily be twice as high in the near future. But these increases can be absorbed into our economy without serious disruptive effects. Fortunately, we are in a favorable position with respect to basic energy costs and will probably continue to be so even with the increases suggested above. Our most urgent problem is really one of adequacy and continuity of supplies of clean energy--not one of energy costs.

While our medium-term problems--through about 1985--are acute, our long-term energy position is reasonably sound. With proper technological developments, we can depend on fossil fuels and nuclear energy to supply our energy for many generations to come, perhaps for several hundred years. And long before our fossil fuels are exhausted, new energy sources, such as the breeder reactor, nuclear fusion, solar power or even geothermal energy, will be supplying a good part of our energy needs.

Energy and the Environment

Coincident with the growing shortage of clean-burning domestic fossil fuels, we have begun to make environmental demands. We want adequate clean energy, obtained from sources that do not endanger our workers or foul our air and waters. We may have overreacted in some cases to environmental considerations but we must find satisfactory solutions to pollution as well as energy problems. In any case, our energy supply has been made less available because of ecological factors--we cannot burn much of our eastern coal because of its high sulfur content, oil and gas from the North Slope of Alaska are just coming into sight after long delays, offshore drilling has been held up, and nuclear plant siting has been delayed.

We need practical trade-offs in the ecological area. Some ecological impairment is inevitably involved in the production and consumption of energy. We must aim for as clean an environment as possible, but we cannot achieve all our environmental goals overnight and still provide all the energy the public requires. Sincere, pragmatic, graduated approaches to our ecological goals are needed.

We should conserve our energy as much as possible. There are a number of schemes for reducing waste in the consumption of energy through the development of more efficient conversion systems. For example, in the President's third energy statement on June 30, 1973,[10] federal agencies were asked to reduce their energy consumption 7%; the private sector was also asked to conserve fuel by lowering driving and airline flight speeds and raising thermostat settings of air conditioners. These leads should be vigorously pursued. We should insist on the consumption of energy in an efficient way and on making certain that energy is used for socially desirable ends.

Before we move to the discussion of organic solid wastes, we would like to decry the use of the word "alternatives" in describing ways of solving our short-term energy problems. We shall have to use all our options, and in using every one of them, we shall probably still have an energy shortage in 1985. Organic solid wastes, rather than a thorn in our side, are actually one of our energy options.

Pollution from Organic Wastes

Our view of solid wastes tends to depend on our background, where we live and what we do to make a living. To the city dweller, solid wastes means that rapidly accumulating mass of smelly "garbage" that annoys him terribly if a pickup is missed (and is a calamity if the collectors go on strike); occasionally he is miffed by an abandoned old car, but not too often. To the farmer, solid wastes refer to the corn cobs, rice hulls, walnut shells and other agricultural material remaining after the crops are harvested. To the cattle raiser and dairy farmer, the term solid wastes means the mountains of cattle manure that plague him and the nearby towns and pollute the surrounding waters; to the pharmaceutical industry, it means fermentation residues; to the lumberman, the remains of harvested trees are a nuisance; and to the sanitary engineer, sewage sludge disposal is a very serious problem. There are industrial wastes of all kinds--from mines, mills and smelters, and from the manufacture of plastics, lead batteries, electronic equipment gadgetry, plating sludges, etc.

It is obvious that large quantities of solid organic wastes are generated each year. But how much is generated and what is the energy potential of these wastes? The Bureau of Mines asked Dr. L. L. Anderson of the University of Utah, while working temporarily with the Division of Coal in Washington, D.C., to determine our annual production of organic wastes in an effort to furnish reliable figures for estimating their potential conversion to oil or gas. This was no easy job for there were no accepted definitions for many of the wastes. The term "manure," for instance, varied tremendously in water and in ash content, depending on whom you were talking to. Anderson, after an enormous amount of work, came up with what is now considered the definitive estimation of our organic solid wastes; the report,[11] if it errs, is too conservative in estimating the quantity of wastes and their available energy potential. This summary, for the first time, itemized and evaluated in detail the quantities and sources of moisture- and ash-free organic material contained in urban refuse, manure, agricultural wastes, industrial wastes and sewage solids. In addition, estimates were presented for amounts of organic wastes collected or concentrated. The main categories of solid wastes sources are listed in Table 2.1; the amounts have been adjusted upward slightly to update the original conservative estimates.

Table 2.1

Fuel Potential of U.S. Wastes; Estimated for 1974

Type of Waste	*Wastes Generated*[a] *10^6 tons/yr.*	*Wastes Collected*[a] *10^6 tons/yr.*
Agricultural and food	412	25
Manure	210	30
Urban	160	80
Logging and manufacturing	70	7
Industrial	50	7
Municipal sewage solids	18	2
Miscellaneous	80	10
Total wastes	1000	161
Fuel potential		
As residual fuel, 10^6 bbl/yr	2300	370
As high Btu gas, 10^{12} cu ft/yr	10	1.6

[a] Moisture- and ash-free (maf) organic solids.

In terms of their pollution risk, organic wastes vary greatly; some are especially bad. A particularly pressing problem arises wherever there are large feedlots for cattle. The trend has been to utilize mass production and feedlots handling 50,000 to 100,000 head and more are becoming popular (Figure 2.1). The accumulation of cattle manure from 100,000 cattle is equivalent to the waste disposal in a city of well over one million people. Typically, this quantity of manure cannot be field-spread or otherwise disposed of in an efficient and economical manner. The manure is stacked and has become a source of pollution within the watershed area (Figure 2.2). The effects range from fly breeding and strong odors to rather complex biological interactions which pollute streams and kill fish. Stream pollution due to bacteria and nitrogen compounds in runoff from cattle manure is an especially devastating problem.

The domestic, municipal and commercial components of urban refuse amount to 3.5, 1.2, and 2.3 pounds per capita per day, respectively. Thus, the total amount of urban waste in 1971 is estimated at 260 million tons, of which at least half is dry organic material.[11] At present, approximately 90% of this refuse is disposed of in landfills, while most of the remainder is burned in municipal incinerators. The quantity of refuse per capita is expected to increase in the future and landfilling and incineration are now being attacked as methods of disposal since pollution of either ground water or air results, and available space for landfills is running out.

Conversion of urban refuse to oil or gas for fuel would appear to be an ideal method of disposal. The energy source represented by this waste is also constantly renewable. Plants convert energy received from the sun into organic materials which then are a form of potential energy. Animals eat plants or eat plant-eating animals as their source of energy and body materials. Thus, the organic portions of plants and animals represent chemical potential energy which has come from the sun. We must learn how to make the best use of this "waste" (wastes are really just misplaced resources) as an energy source.

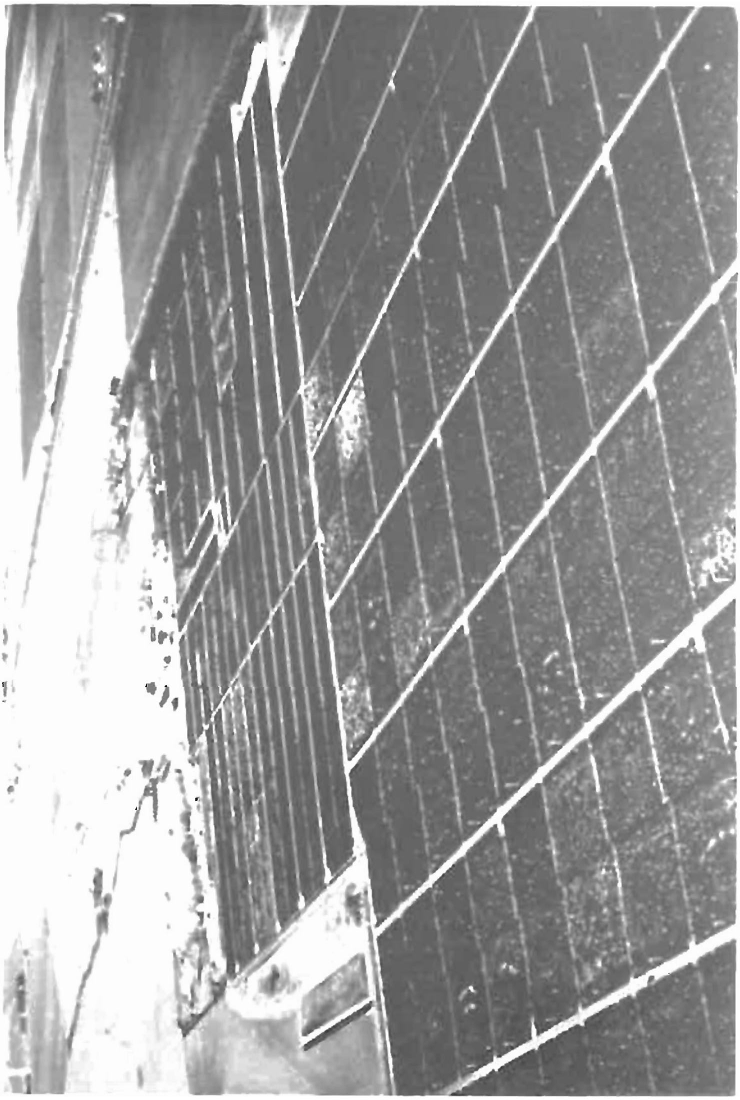


Figure 2.1. Photo of large cattle feedlot in Greely, Colorado.

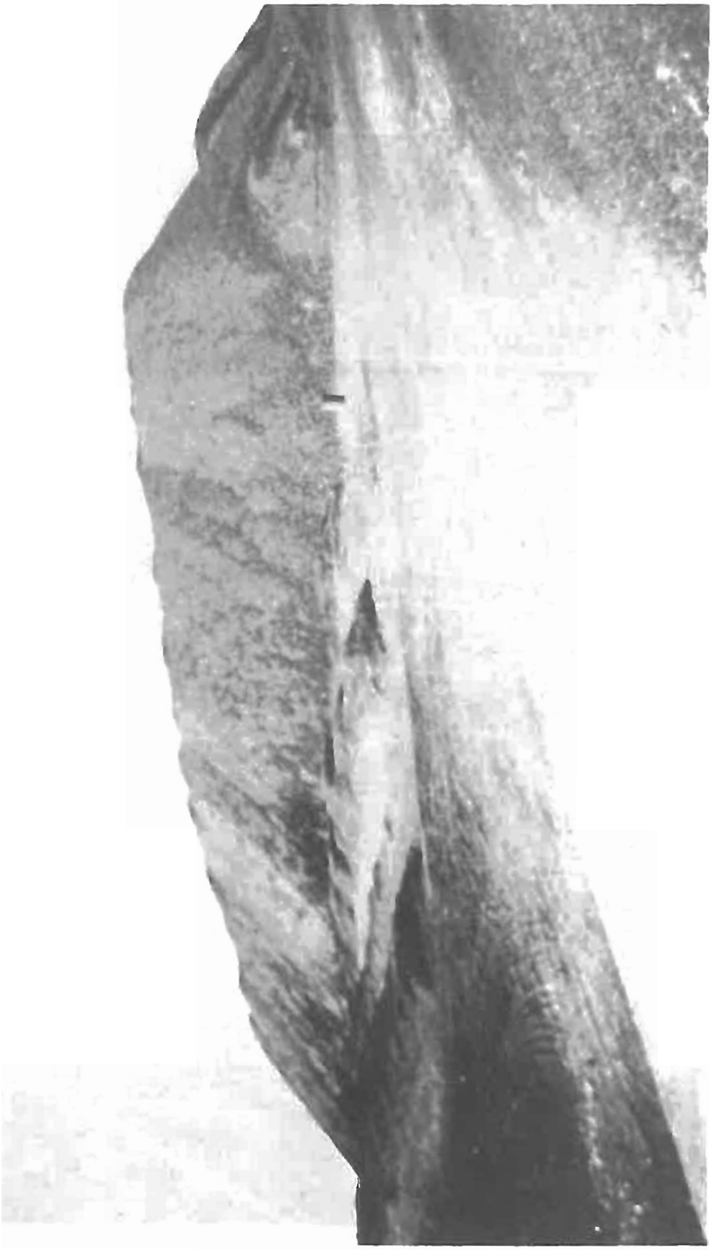


Figure 2.2. Photo of large manure stack in Artesia, California.

CLEAN, HIGH-ENERGY FUELS FROM WASTES

Early Work on Fuels from Organic Wastes

A worthwhile alternative to merely disposing of organic wastes, usually in a manner detrimental to the environment, is to capitalize on their fuel value, the chemical potential energy referred to earlier. The heat of combustion of organic wastes can vary from 3,000 to 7,000 Btu per pound for dried manure, to 6,000 to 8,000 Btu per pound for wood scraps. These values are below the heating value of coal, 11,000 to 15,000 Btu per pound, or fuel oil, 18,000 to 19,000 Btu per pound. Organic wastes contain mineral constituents and commonly a rather large amount of water. The mineral content of organic wastes has essentially no heating value and acts as a diluent. Moisture not only acts as a diluent but also has a high heat of vaporization which can consume large amounts of heat. If enough moisture is present, it can prevent the waste from sustaining its own combustion. Manure, for example, may contain as much as 80% moisture and cannot be burned until dried.[12] Fossil fuels have much higher heats of combustion than do dry organic wastes largely because of the lower oxygen content of the fossil fuels.

One advantage of organic wastes as a source of fuel energy is their relatively low sulfur content. However, these moist wastes do not combust completely nor easily and their combustion products may be polluting or corrosive.

In 1974, the generation of organic solid wastes in the United States, on a moisture- and ash-free basis, will approximate a billion tons per year. It is worth noting that, in the past, considerable research has gone into utilizing some of the large volume wastes, such as sawdust, bagasse, and lignin for end uses such as building materials, animal feed, fuel and chemicals.[13] The work of Berl,[14] which covered more than a decade, showed that treatment of cellulosic materials with sodium hydroxide solution at about 350°C under pressure resulted in a bitumen, a protoproduct for petroleum type materials. Berl calculated that if 4% of our arable land were planted in sugar cane, the potential yield could satisfy the 1940 demand for petroleum products; now it would take about three times as much land. Heinemann[15] also reported on the yields of oil products obtainable from sugar cane.

Our Approach

The Bureau of Mines, an agency of the U.S. Department of the Interior, has been looking into ways of converting organic wastes into energy-rich, clean-burning fuels. Cellulosic material, which makes up the bulk of organic wastes, is greatly improved as a fuel if it is treated in such a way that low-oxygen content product is obtained. Not only does this increase its fuel value but it also makes the fuel hydrophobic (that is, nonwetting) so that a water-free fuel is easily obtained. Three basic approaches have been used (1) a reaction which produces predominantly a low-sulfur heavy oil product resembling a fuel oil, (2) hydrogasification--conversion to pipeline gas, and (3) pyrolysis--a reaction at much higher temperature which produces predominantly a gaseous product. Work on all three approaches stemmed from our efforts to convert our most abundant fossil fuel resource, coal, into low sulfur liquid and gaseous fuels. A closed reactor/product recovery system is used in each process so that pollution is minimized (all power pollutes to some degree; so does just "living"). The conditions used in these three processes are summarized in Table 2.2.

Conversion of Wastes to Oil in Batch Reactors

Work on the conversion of organic wastes to oil at the Pittsburgh Energy Research Center of the Bureau of Mines is based on the observation of Fischer[16] that low rank coals could be hydrogenated with carbon monoxide and water. Indeed, this is a novel way to turn coal into low-sulfur liquid fuels and we are actively researching this process at present. Our work on this reaction showed that high yields of heavy oil could be obtained from lignite with carbon monoxide and water and that the reaction was also applicable to lignin and to all types of carbohydrates including cellulose.[17] Carbohydrates were actually converted to oil under milder conditions than those required for lignite. Inasmuch as solid organic wastes consist predominantly of carbohydrates, especially cellulose, reduction of these materials with carbon monoxide and water was applied to the solid wastes problem.[18] The fact that solid waste is converted into a liquid product is very important. Liquid fuels are more universally

Table 2.2

Distinguishing Characteristics of Waste to Fuel Processes

	Waste to Oil	*Hydro-gasification*	*Pyrolysis*
Fuel product distribution, typical			
Gas, %	0	>95 (high Btu)	50 (med. Btu)
Fuel oil, %	>95	0	20[a]
Char, %	< 5	< 5[b]	30
Conditions			
Temperature, °C	250-400	500-700	500-900
Temperature, °F	480-750	930-1290	930-1650
Pressure, kg/cm^2	100-300	70-180	1
Pressure, psi	1500-4500	1000-2700	15
Gas added[c]	$CO-H_2O$ or $CO-H_2-H_2O$	H_2	None

[a] Can be separated as tar and light oil.

[b] The char formed is consumed in a second gasifier to form synthesis gas which is then shifted to hydrogen to be used in the first gasifier.

[c] These gases can also be produced from solid wastes.

usable than solid fuels; also, on a Btu basis, they store better and they are cheaper to transport. The development and application of the reaction to a variety of wastes in a batch reactor (autoclave) is described first; this is followed by a discussion of the chemistry and mechanism of conversion of carbohydrates to oil. The extension of this work to conversion in larger continuous units is described in the section "Continuous Processing of Wastes to Oil" (page 63).

The initial experiments were conducted in one-liter or smaller stainless steel rocking autoclaves. The feedstock, water, and catalyst were charged to the cold autoclave, carbon monoxide or other gas was added at the desired cold startup pressure, and the autoclave was then brought to operating temperature.

The reaction time reported does not include the heating and cooling periods. These periods, where significant reaction may have occurred, are about one hour for runs at 250°C and about two hours for runs at 350°C and above. In later work, experiments were also conducted in stirred reactors in which the heating and cooling periods were much shorter.

There are advantages and disadvantages to studying reactions in batch pressure autoclaves. The advantages include low cost, easy handling and ready availability of the equipment. The disadvantages, however, are many and limiting: The reactants are slowly heated to the desired temperature (the reaction usually starts before this point), the main products remain in contact with the reactants and byproducts for long periods of time, the pressure usually changes as the reaction proceeds because gases are taken up or evolved, the whole mixture must be cooled to room temperature before the products are removed, and the quantity processed per batch is small. Most of these disadvantages do not occur when the reaction is conducted in a continuous unit. In general, batch experiments carried out in autoclaves furnish good clues as to what will happen in a continuous reactor but new problems, often associated with the continuous feeding of reactants, may arise. In the present case, the results of batch autoclave studies were very helpful in predicting conditions needed in subsequent continuous unit investigations.

Autoclave reaction products were flushed from the stainless steel vessel with solvent and the oil was extracted in a Soxhlet unit. Acetone was used as an extractant for oil produced at 300°C or less, and benzene was used for runs carried out above 300°C. The oil, or bitumen, was recovered by distilling off the solvent. The percent conversion is determined by subtracting the percent of insoluble residue, remaining about solvent extraction, from 100. All calculations are based on moisture- and ash-free (maf) organic materials.

The first application of the liquefaction of solid organic wastes to oil was conducted on urban refuse obtained from the Fairfield Aerobic Mulch Corporation near Altoona, Pennsylvania. This material was free of metal and glass and was shredded. Because of the 30% moisture content of this refuse, it was not necessary to add additional water when it was charged to the autoclave. The early experiments utilized rather severe conditions that had proven successful with lignite and pure cellulose. The alkali salts already present in this urban refuse had sufficient catalytic activity so that no addition of catalyst was necessary.

Table 2.3 gives the results obtained with carbon monoxide as reducing agent compared with hydrogen reduction at operating pressures near 4500 psig.

Table 2.3

Conversion of Urban Refuse to Oil
(20 min at 380°C, 4200 psig operating pressure)

Reaction in the presence of	*CO*	*H_2*
Conversion, % maf refuse	94	80
Product distribution, wt %		
Oil	41[a]	18
Residue	6	20
Water	31[b]	45
CO_2	20[b]	15
Other	2	2

[a] Composition: C, 78.4; H, 10.5; N, 2.9; O, 8.3; S, 0.05%.

[b] Estimated.

The high oil yield and low residue obtained with carbon monoxide show its advantages over the use of hydrogen. A specific hydrogenation catalyst, such as cobalt molybdate, would be needed for hydrogen to be more effective and, even then, temperatures above 380°C would be required. Thus, one advantage of the reaction with carbon monoxide is that no costly catalyst is required to obtain high conversion and good oil yields.

The carbon monoxide does not have to be pure. In fact, synthesis gas, a mixture of carbon monoxide and hydrogen, behaves in a similar, although slightly less reactive, manner. Synthesis gas is much cheaper to produce than is carbon monoxide and it can be made readily from organic wastes. A conversion plant would probably be operated using synthesis gas rather than carbon monoxide alone. Some water and carbon monoxide are consumed in the water-gas shift reaction and the carbon dioxide formed by this reaction can only be estimated. It is apparent from the product distribution, however, that less dehydration and more decarboxylation of cellulose occurred in the presence of carbon monoxide than in the presence of hydrogen. This shift in the extent of the dehydration and decarboxylation reaction removes more of the oxygen in the original carbohydrate as carbon dioxide rather than water and therefore yields a liquefied, more hydrogen-rich product. Typically, solid fuels like coal and char have high molecular weight and a hydrogen to carbon molar ratio of $\leqq$ 0.8 H/C, whereas liquid petroleum fuels have, in general, a lower molecular weight and a much higher H/C ratio, about 1.5. Our product from the reaction of organic waste with carbon monoxide is liquid because it has been partially depolymerized and its hydrogen to carbon ratio is close to that found in petroleum (moreover it has retained little oxygen from the cellulosic structure). The maximum oil yield from waste would be about 60 weight percent based on ash-free, dry organic material since 60 to 90% of oxygen is removed and a portion of carbon is too. Our objective is to maximize the conversion of waste into liquid product, regardless of the oxygen content and resultant Btu/lb heating value of the product.

The product was a black, viscous, high-boiling oil; about 55% was distillable under vacuum. Mass, infrared, and ultraviolet spectrometric examination of the product oil showed it to be largely paraffinic or naphthenic. Oxygen was present as ether linkages, carbonyl groups and hydroxyl groups. A small amount of fatty and amino acids were also present; mass spectrometric data indicated the presence of palmitic and stearic acids in the ratio normally found in animal fat. Nuclear magnetic resonance showed that most of the hydrogen in the oil was part of methyl or methylene groups, a large proportion being alpha or beta to a carbonyl group or to an unsaturated carbon atom. Hydrogen on unsaturated carbon atoms was low, about 4%, with about 60% of this unsaturation being aromatic and 40% olefinic. (Most of this aromatic material probably came from polystyrene; work with pure carbohydrates gave very small amounts of aromatic material.) Three percent of the hydrogen was part of -OH groups. No aldehydic hydrogen was found. The fractionation and elemental composition of an oil obtained from urban refuse is shown in Table 2.4. Nitrogen and sulfur are distributed over a wide boiling range. The oxygen content decreases with boiling point, whereas the carbon content increases. The ratio of hydrogen to carbon is higher

Table 2.4

Composition of Oil From Urban Refuse
(Vacuum distillation[a] of oil formed at 380°C and 5000 psig)

Material	*Boiling range, °C*[b]	*Composition,*[c] *wt %*					
		C	*H*	*N*	*S*	*O*	*H/C mole ratio*
Original	-	79.8	10.4	3.0	0.05	6.8	1.56
0-5% cut	175-240	74.3	10.8	3.0	0.11	12.1	1.73
15-20% cut	365-420	78.5	10.3	3.2	0.04	8.0	1.57
34-40% cut	468-480	78.3	11.5	1.6	0.05	8.6	1.75
50-55% cut	510-550	82.7	11.7	1.7	0.03	3.9	1.68
Bottoms	Over 550	84.4	9.9	2.5	0.04	3.1	1.40

[a] Distilled by Houdry Process and Chemical Co., Marcus Hook, Pa.

[b] Temperature corrected to atmospheric pressure.

[c] Analysis by Huffman Laboratories, Inc., Wheatridge, Colorado.

than that in coal or the original waste material and is close to the H/C ratio in petroleum residuum.

The fate of polymers commonly found in urban refuse would be important in a waste to oil process. The small amount of polyethylene present in these urban waste samples melted and partially depolymerized; this oil usually separated from the carbohydrate-derived oil, forming a thin upper layer. Polystyrene apparently depolymerized extensively but its fragments were soluble in the product oil. Furthermore, the addition of several percent of polyvinyl chloride to the refuse did not alter the course of the oil-forming reaction. Urban refuse appears to be sufficiently alkaline to absorb the hydrochloric acid liberated by small amounts of polyvinyl chloride in the refuse. Since hydrochloric acid is very corrosive, this is an important point.

Factors Important in Waste to Oil Conversion

Temperature

The conversion of carbohydrates to oil was investigated over the range 250° to 400°C. Below 250°C the reaction is too slow to be of practical value. There appears to be no advantage to operating above 400°C with carbon monoxide. It would be best to operate at the lowest possible temperature to avoid high steam partial pressures and thereby reduce the operating pressure and capital costs of a proposed plant.

Yields at high conversions do not change appreciably in the 250-400°C range but significant changes in the oxygen content and in the viscosity of the product do occur. The oxygen content of the product increases to about 20% when the reaction is conducted at 250°C and the heating value of the oil is reduced to about 14,400 Btu/lb compared to low oxygen content product having up to 16,000 Btu/lb. The product formed at 250°C is a soft, bitumen-like solid at room temperature, but becomes readily pourable as its temperature is raised to near 100°C. The oil formed at 380°C is a free-flowing liquid with a viscosity of 650 centistokes at 50°C and 102 centistokes at 88°C.

Mechanism

Soon after beginning research on converting solid wastes to oil, it became apparent that high capital costs would be a serious obstacle to the commercial success of this process. Therefore an investigation of catalysts for the reaction and a study of the fundamentals of the reaction were undertaken to find mild conditions at which wastes would rapidly be converted to oil.

Many forms of solid organic wastes can be processed at 250°C and an operating pressure near 1500 psig if sufficient water to maintain an aqueous phase is present. But the reaction is very slow without the addition of an alkaline catalyst, such as sodium carbonate. At higher temperatures, above 325°C, the usual low to moderate alkaline content of most wastes is adequate to maintain a reasonable reaction rate.

The reducing action of carbon monoxide in the presence of sodium carbonate and water was more effective than hydrogen on vicinal glycols (-COH-COH-) and on carbonyl compounds. In the presence of carbon monoxide, ethylene glycol gave an 18% yield of ethanol in 15 minutes at 380°C, whereas hydrogen at the same conditions gave a 12% yield. Both experiments also gave a large number of unidentified compounds. Ethanol was stable to further reduction by carbon monoxide.

The difference in behavior between carbon monoxide and hydrogen upon carbonyl compounds at 250°C was especially striking. Using benzaldehyde as a model compound, sodium carbonate as the catalyst, and an initial carbon monoxide pressure of 1500 psig, a 91% conversion of benzaldehyde to benzyl alcohol was obtained in one hour. When hydrogen was used, the yield was only 6%.

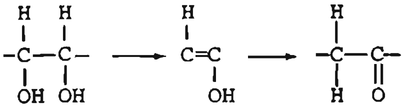
A mechanism for the conversion of carbohydrates to oil consistent with the observed data, consists of the following steps:

1. Reaction of sodium carbonate and water with carbon monoxide to yield sodium formate:

$$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCO_2Na + CO_2$$

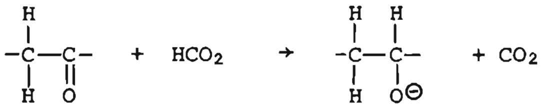
The reaction of alkalies with carbon monoxide is well known.[19,20] In the presence of sodium hydroxide, carbon monoxide reacts to produce sodium formate readily at 160°C. Using sodium carbonate, the reaction proceeds at significant rates at 240-250°C, and rapidly above 275°C.

2. Dehydration of vicinal hydroxyl groups in carbohydrates to an enol, followed by isomerization to a ketone; this is a well-known reaction of 1,2-glycols:

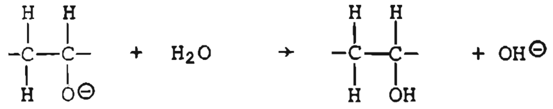


$$-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}- \longrightarrow \overset{H}{C}{=}\underset{OH}{C} \longrightarrow -\underset{H}{\overset{H}{C}}-\underset{\overset{\|}{O}}{C}-$$

3. Reduction of the newly formed carbonyl group to the corresponding alcohol with formate ion and water:



$$-\mathrm{CH_2}-\mathrm{C}(=\mathrm{O})- + \mathrm{HCO_2} \rightarrow -\mathrm{CH_2}-\mathrm{CH}(\mathrm{O}^{\ominus})- + \mathrm{CO_2}$$



$$-\mathrm{CH_2}-\mathrm{CH}(\mathrm{O}^{\ominus})- + \mathrm{H_2O} \rightarrow -\mathrm{CH_2}-\mathrm{CH}(\mathrm{OH})- + \mathrm{OH}^{\ominus}$$

The hydrogen on the formate ion resembles an aldehydic hydrogen and is known to be a strong reducing agent. This is similar to the Cannizzaro reaction where the aldehydic hydrogen of one molecule of benzaldehyde reduces another molecule to benzyl alcohol, the original molecule being oxidized to benzoic acid.

4. The hydroxyl ion, or its equivalent as sodium carbonate, liberated during the reaction of the carbohydrate-derived anion with water, then reacts with additional carbon monoxide to regenerate the formate ion. This is similar to and another way of writing step 1:

$$\mathrm{OH}^{\ominus} + \mathrm{CO} \rightarrow \mathrm{HCO_2}^{\ominus}$$

Experimental evidence was obtained showing that formates reduce carbonyl compounds but at relatively low efficiency. Given a stoichiometric amount of formate needed to reduce a carbonyl compound, at the temperature used, much of the formate decomposes to hydrogen and carbon dioxide before it can reduce the carbonyl compound. The advantage of carbon monoxide is that it keeps generating formate ion in adequate concentration to reduce the carbonyl groups as they are being formed by dehydration of the carbohydrate. There are, of course, many side reactions and the final product is a complex mixture of compounds.

The addition of an alkaline catalyst, such as sodium carbonate or bicarbonate, is essential if high conversions are to be realized at low reaction temperatures. Table 2.5 gives the results obtained with three typical wastes which can be processed at 250°C. In general, the more readily hydrolyzable forms of cellulose, especially those containing pentosan units, can be readily converted to an oil or bitumen at 250°C. Organic wastes containing considerable high

Table 2.5

Wastes to Oil Conversion at Mild Conditions (500 psig initial CO pressure, 1500 psig operating pressure, 1 hr at 250°C)

	Urban refuse	*Pine needles and twigs*	*Sewage sludge*
Waste material, g	50	50	300
Water, ml	200	200	None[a]
$NaHCO_3$ catalyst, g	10	10	None[a]
Conversion,[b] wt %	87	81	86
Oil yield,[c] wt %	37	35.5	24.5
Product composition, wt %			
Carbon	70.5	72.2	77.0
Hydrogen	9.8	8.7	10.7
Nitrogen	1.9	1.05	2.80
Sulfur	0.11	0.10	0.64
Oxygen	18.7	18.0	8.8

[a] The sludge contained 87% water and enough alkaline mineral matter to catalyze the reaction.

[b] 100 less the percent unreacted organic residue (maf).

[c] Based on dry, organic matter charged.

molecular weight crystalline cellulose and/or lignin require higher temperatures, 300 to 350°C, unless an organic solvent is also present.

Pressure

The pressure in the system is largely a function of the steam pressure, the reducing gas (carbon monoxide or synthesis gas) pressure, and the pressure of the carbon dioxide evolved in the reaction. Part of this carbon dioxide results from oxidation of the carbon monoxide used in the process but a substantial portion comes from rearrangements and disruption of carbonydrate-type molecules. Other volatile decomposition products have only a minor influence on the pressure.

In general, as the carbon monoxide partial pressure is increased, the extent of conversion, the yield of oil, and the product quality all improve. This is a result of an increased rate of reaction of the carbon monoxide (via the catalyst) with the reactive materials in the system undergoing conversion to oil. As the pressure increases, however, the efficiency of utilization of carbon monoxide decreases and more is wasted by thermal decomposition of formate ion than is used to convert the carbohydrates to oil. Mechanistically, this means that the formate, resulting from the reaction of the carbon monoxide and sodium carbonate catalyst, is present in higher concentrations at higher pressures than can be adequately used for converting wastes and thus a larger percentage of formate molecules decompose to hydrogen and carbon dioxide (the water-gas shift reaction) in place of being utilized in oil formation. The formate intermediate in the water-gas reaction has been identified in other catalytic systems.[21]

Although improved results are obtained at higher pressures, the high consumption of carbon monoxide and possible high capital costs in a continuous commercial process argue for a compromise. Accordingly, pressures near 2500 psi were investigated and found to give adequate product quality with low but relatively efficient carbon monoxide consumption.

The pressure is greatly influenced by the operating temperature because of the necessity of water being present. The vapor pressure of water at 250°C is 577 psi; it increases rapidly with temperature to 3200 psig at 374°C (the critical temperature of water). Above 300°C, over half of the total pressure may be due to steam. Therefore, despite decreased viscosity and oxygen content of oil product obtained at 375-400°C, an effort has been made to reduce the temperature to the 300-350°C area. Current work is achieving success in this temperature range.

Synthesis Gas vs. Carbon Monoxide

Large quantities of carbon monoxide would be needed for a waste to oil process. Carbon monoxide consumptions can range from as high as 50 weight percent of waste converted at high temperature, 380°C, to less than 10 weight percent at 300°C. These quantities of carbon monoxide consumed will represent a very significant portion of the process cost. Since the first step in the oxy-gasification of wastes produces a crude synthesis gas, a mixture of CO and H_2 from which carbon monoxide must then be recovered, the substitution of synthesis gas for carbon monoxide would be more economic in practice.

A 1:1 synthesis gas was used under a variety of conditions with little loss of waste conversion. An oil yield loss of 2 to 4 weight percent of maf waste was observed when synthesis gas was substituted for carbon monoxide. This small loss is justified since the cost of purifying the synthesis gas to a carbon monoxide-rich gas would be avoided.

Continuous Processing of Wastes to Oil

In the process for the continuous production of low-sulfur fuel oil from various organic wastes via reaction with carbon monoxide and steam, a number of process operations are involved. The organic material being processed (manure, wood chips, urban waste, etc.) is dried to a moisture content of 30 weight percent or less. Since water is required for the waste to oil process via the steam-carbon monoxide reaction and possibly for hydrolytic cleavage, the needs of these reactions can be conveniently supplied by adjusting the moisture content of the waste. The mode in which the organic waste material is to be conveyed into the reactor also dictates the degree of drying. Thus, a waste material containing 30 weight percent moisture could be pumped into a reactor in an oil slurry but assuredly would pack in a lock-hopper if dry feeding were attempted.

The dried waste is then reduced to approximately -60 mesh (0.25 mm and smaller) and made into a slurry containing as much as 30 weight percent solids. Although both aqueous and oil slurries have been used, oil slurries are favored as being more stable, permitting the transport of a larger concentration of waste material and having a wider range of operability. The loss of aqueous phase at temperatures above 374°C, the critical temperature of water, imposes a restrictive limitation on the use of aqueous slurries. At or above this temperature, charring of the organic material occurs with no significant attendant oil formation, accompanied by eventual flow stoppage. Therefore, the presence of some liquid phase, either aqueous or nonaqueous, in the reactor appears to be a requisite of operability.

The tendency for the separation of solids from the vehicle is always present to some degree, regardless of the concentration of solids and the nature of the vehicle. Ideally, process derived oil is used as the slurry vehicle; however, for startup operation, a coal tar product, anthracene oil, is used. This slurry is then pumped into a stirred reactor maintained at 2000-4000 psi pressure and 300-350°C. Efficient contact of the gas and liquid phases, essential for high conversion of the waste, is achieved by a high speed turbine type agitator in the reactor. The residence time in the reactor is generally of the order of 0.5-1.0 hr. The material in the reactor section overflows into a high-pressure receiver from which the product is removed. A schematic drawing of such a plant is shown in Figure 2.3. The product is separated from water, the unreacted solids and ash are removed by centrifugation or filtration, and the product oil and vehicle recovered.

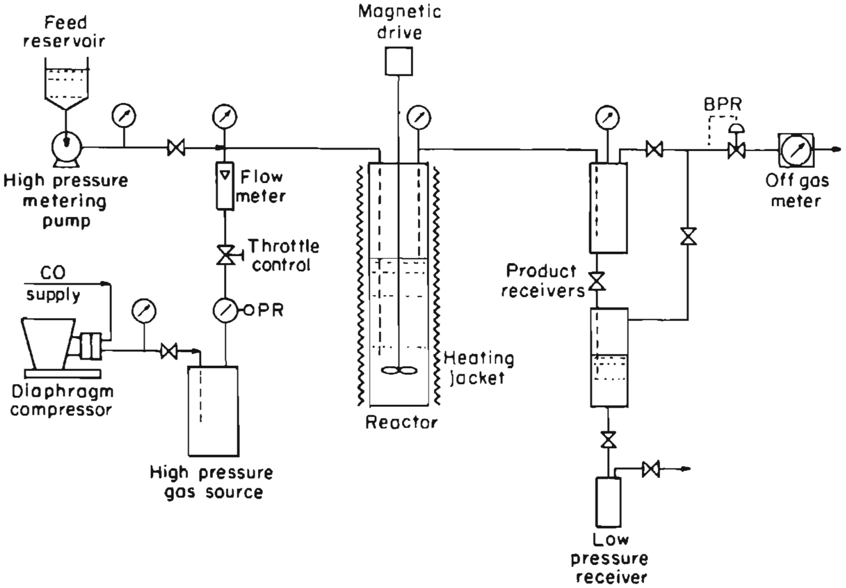


Figure 2.3. Continuous unit for converting solid waste to oil with carbon monoxide and water.

Perhaps the areas of greatest operational difficulty in the bench scale plant involves the pumping of the waste slurry. Organic waste materials are generally of cellulosic origin, although lignin and synthetic polymeric compounds are also present to some degree. These waste products are fibrous in nature and tend to collect at the check valves in the pumps and at the line restrictions and fittings. The severity of these problems appears to be in inverse proportion to the size of the unit and has led to the scaleup of a 1 lb/hr unit to one of 20 lb/hr capacity. Development work on pump design resulted in improved operability. The various methods attempted for feeding slurries of organic waste materials were as follows: (1) a valveless progressing-cavity pump installed in a pressurized feed hopper, (2) a commercial high-pressure plunger pump, (3) the same pump with modified ball-check valves, and (4) a Bureau of Mines designed plunger pump with pneumatically operated ball valves in place of the conventional ball-check valves. Moderate pumping success was achieved with the modified commercial pump and the Bureau of Mines designed pump. It is doubtful, however, because of the low bulk density of dried organic refuse, that slurries containing greater than 30 weight percent solids can be pumped (even in a commercial installation). Indeed, this concentration cannot be attained in some cases because of the lack of flow exhibited by the waste-oil mixture. Solids feeding systems which will permit the introduction of dry waste directly into a high-pressure reactor containing the vehicle oil are being considered for the waste to oil processes and are currently in the initial development stage. Such a feed system should permit greater throughput per unit volume of reactor space.

Initial work on the continuous conversion of waste to oil was performed with a model compound. Sucrose was selected because it is a water soluble carbohydrate and produces an oil similar to that formed by the cellulosic constituents of organic wastes. Solutions of sucrose could be pumped much more easily than aqueous slurries of fibrous wastes. A positive displacement plunger pump was used to feed 85 to 340 ml/hr of 30% aqueous solution of sucrose containing 5% sodium carbonate as catalyst into a reactor for on-stream periods of 5 to 20 hr.

The effect of temperature on continuous processing is demonstrated for sucrose solutions in Figure 2.4. The reaction is very temperature sensitive with a maximum rate at about 350°C. The yield of oil drops

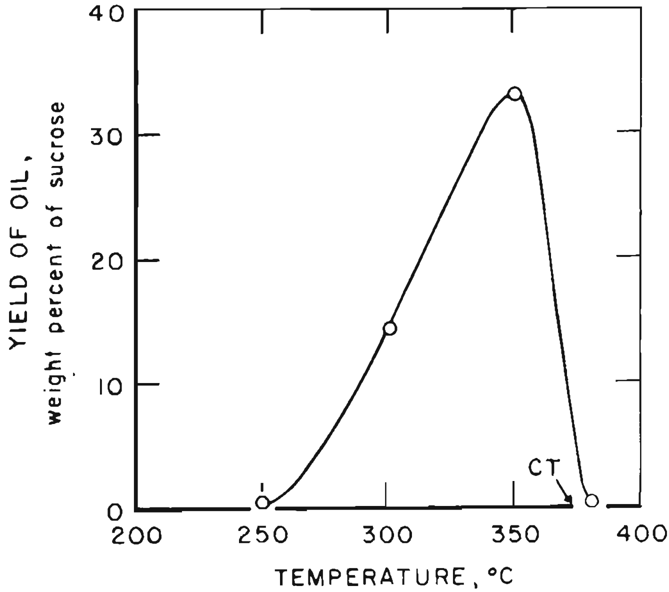


Figure 2.4. Effect of temperature on yield of oil produced from sucrose in the continuous unit at 4000 psig, 1 hr residence time. 2 scf CO/100 g sucrose solution (30%).

off drastically above 350°C because the system becomes inoperable as temperatures approach the critical temperature of water. At this or higher temperatures, the water is essentially all in the gas phase and thus there is no vehicle left to convey the feed or oil and solid-residue products out of the reactor, causing it to plug. Product oil cokes and solidifies upon excessive residence time above 350°C. For long runs, 315°C is preferred to reduce vehicle evaporation, to permit lower pressure operation and to conserve energy.

As seen in Figure 2.5, there is a positive effect of increasing pressure, but the effect is not large between 2000 to 4000 psig. It would probably not be worth the expense to use higher pressure equipment. The low dependence on pressure indicates that availability of carbon monoxide is not the rate-controlling step for the oil-producing reaction in this stirred reactor. Also, increasing the catalyst concentration from 5 to 15% did not markedly influence

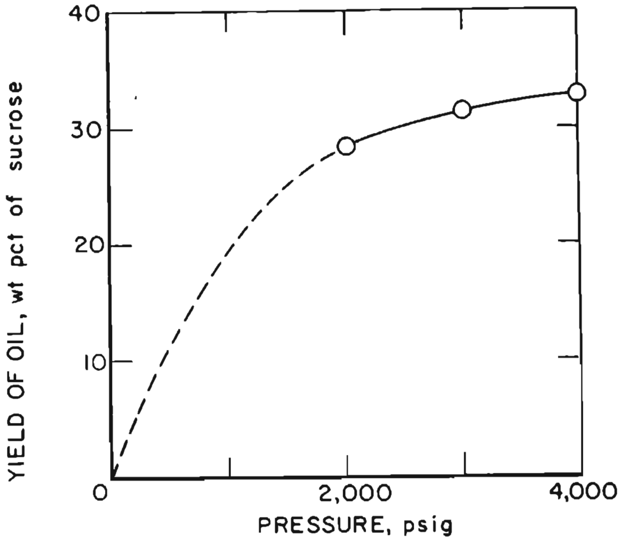


Figure 2.5. Effect of pressure on oil yield (350°C).

conversion to oil. It is not yet clear what the rate-controlling step is.

The effect of residence time is shown in Figure 2.6. It is seen that additional conversion to oil

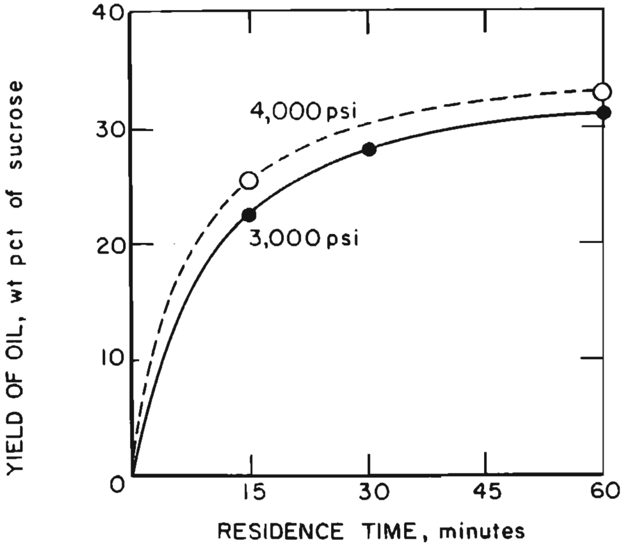


Figure 2.6. Effect of residence time on oil yield (350°C).

is slow beyond a 30-minute residence time. The residual organic material, still water-soluble even after a 60-minute residence time, contained organic acids. The separated aqueous phase was therefore reprocessed for an additional one hour residence time; about 5% more oil could thus be obtained, raising the oil yield from 33 to 38%. The water-soluble acidic byproducts are apparently fairly resistant to reduction in this system.

Guided by the results of the sucrose runs, a slurry of urban refuse from Altoona, Pennsylvania, was fed to the unit, under the conditions shown in Table 2.6; the yield and product oil characterization are also shown in this figure. The oil yield was not as high as expected from data obtained in the sucrose runs. This may have been due to erratic pumping of refuse on such a small scale. This pumping problem is not anticipated in large-scale operation.

Table 2.6

Oil From Municipal Garbage (Altoona, Pennsylvania)
[Produced in continuous bench-scale unit (1 lb/hr)]

Feed = pumped garbage slurry, 85% water
Gas = carbon monoxide
Temperature = 350°C
Pressure = 4000 psig (CO + steam)
Residence time = 2 hr
Oil yield = 23% of dry garbage

Oil properties:

Viscosity = about 200 centipoise at 150°F
C = 79%, H = 11%, O = 9.5%
Approx. formula = $(C_{11}H_{15}O)_n$
Heating value = 15,000 Btu/lb

It should be mentioned that these initial oil yields (23% from garbage and up to 38% from sucrose) were fairly good because, as mentioned earlier, the ultimate theoretical yield from these materials is about 60%. Up to half of these carbohydrate materials is oxygen, so that when most of the oxygen is removed as water and/or carbon dioxide, the resultant oil yield cannot exceed this 60% figure.

The production of fuel oil from cattle manure was also accomplished in the one lb/hr continuous unit. The content of water and mineral matter in cattle manure varies considerably, depending upon the collection facilities at the source. Aged field manure may contain as much as 45 weight percent ash on a moisture-free basis; fresh manure, on the other hand, may contain as much as 85 weight percent water. Excrement collected in concrete stalls would generally contain less than 10% mineral matter. Obviously, a source of low-ash manure is preferred for continuous processing since the ash solid becomes wetted with oil and reduces the amount of easily recovered product oil. Ash is also an inert mass burden on the system.

For our purposes, manure containing 8.3 weight percent ash was secured from the Department of Agriculture station in Beltsville, Maryland. This material was dried to 5.9 weight percent moisture content, pulverized to -60 mesh, and then made into a slurry containing 20 weight percent manure and 80 weight percent anthracene oil fraction. Operation at 3000 psig and 350°C for an on-stream period of 80 hours gave an average conversion of 90%. These results are summarized in Table 2.7. Since unit operability was the principal concern at this time, only a single pass through the reactor was made. Consequently, the content of manure-derived oil in the liquid product was small and no attempt was made to recover this material from the vehicle oil. Operation under similar conditions in a batch autoclave indicated an oil yield of approximately 40% of the maf manure could be attained.

A larger continuous unit (20 lb/hr) of similar design was built to improve the chances of smoother passage of fibrous waste slurries through the larger pump, pipes and valves. Again, anthracene oil was used to slurry the feed wastes instead of water. This permitted an increase in the waste feed concentration to 30% as opposed to the 15% limit for flowable aqueous slurries. With a special forced-closure-valved pump, we have managed to continuously process enough 30% oil slurries of manure and wood waste in this 20 lb/hr unit to show that oil yields of about 50% could be obtained continuously at 4000 psi and 350°C. However, pumping such wastes will continue to be a problem in small equipment unless more work is done to develop a dependable way of feeding concentrated solid wastes into pressurized reactors. In commercial plants, of course, dilute slurries cannot be processed economically because the effective reactor throughput would be too low and oil collection difficult.

Table 2.7

Conversion of Cattle Manure to Oil

Feed: Cattle manure .... 20 wt %
Anthracene oil ... 80 wt %
Pressure: 3000 psig
Temperature: 350°C
CO rate: 4 scfh

Composition of various materials (wt %)

	Manure	*Anthracene oil*	*Liquid product[a] (dry)*
C	44.7	92.4	91.1
H	6.4	5.7	6.1
N	3.0	1.1	1.4
S	0.4	0.5	0.5
O	31.3	0.3	0.9
H_2O	5.9		
Ash	8.3		

Exit gas (vol %)

H_2	8.7
CO	79.3
CO_2	11.7
CH_4	0.2
C_2H_6	0.1

---

[a] Single pass product in anthracene oil.

Preliminary Economic Study

An economic evaluation of a conceptual commercial plant for converting 50% wood wastes and 50% urban waste into oil by reaction with synthesis gas and water was made by a chemical construction company. A summary of the results appears in Table 2.8. These

Table 2.8

Summarized Economics for Conversion of Urban and Wood Wastes[a]

Urban wastes	1500 tpd
Wood wastes	1500 tpd
Total wastes utilized	3000 tpd
Waste to oil production	2082 tpd
Waste for synthesis gas and heat	918 tpd
Oil production rate	3618 bbl/day
Operating costs	$9.48/ton waste

Assumed value of oil *$/bbl*	*Break-even disposal charge* *$/ton of wastes*
4.00	4.66
5.00	3.45
5.50[b]	2.85
6.00	2.24
7.00	1.04
8.00	-0.17
9.00	-1.37
10.00[c]	-2.58

[a] Total wastes contain 52.41% dry organics, 3.59% ash and 44.00% water.

[b] Spot prices for No. 6 fuel oil are currently at this level in New York (max. 0.3% S) and Chicago (max. 1.0% S).[22]

[c] James E. Akins, U.S. Ambassador to Saudi Arabia, predicted that oil will be priced at $10/bbl by 1980.[23]

estimates would also apply to processing low-ash manure. This evaluation was made at this time chiefly to point out areas for process improvement. An earlier evaluation was helpful in locating expensive steps and equipment and we have been able to reduce costs by several process improvements. Such changes include reduction in process temperature and pressure, reduction of carbon monoxide consumption from 50 lb to 7 lb per 100 lb of moisture- and ash-free waste, and increased oil yield to 58% instead of 40%. At the realistic price of \$5.50/bbl for low-sulfur oil produced,[22] the \$2.85 per ton disposal charge is less than that charged today for waste disposal in various cities. We expect this estimated disposal charge to drop even more due to future process improvements. The disposal charge is greatly affected by the value of low-sulfur oil which has already exceeded \$5.50 per barrel in New York and is rising rapidly.[23] Also, improvement in the extraction step to recover absorbed oil from residual ash could save a considerable amount in plant cost.

For manure disposal, the \$2.85 per ton predicted disposal charge translates to \$5.70 per head of cattle per year. Compared to the selling price of a beef carcass this charge appears tolerable. This charge will undoubtedly be lowered by further process improvements and by economics achieveable in larger plants and by the rapidly rising price of low-sulfur fuel oil. With present conditions in the Mideast affecting the price and availability of petroleum products, waste conversion to oil may be a necessary and even profitable operation with no disposal charge at all.

A fuel oil production plant would consume manure in large quantities and should be attractive to feedlot operators because it would mean (1) an increase in the number of steers per feedlot, (2) elimination of ground water contamination by runoff, and (3) reduction in the odor problem. The cattle feedlot of the future may be similar to a high-rise tower, with cattle being raised in the upper stories. All wastes would be collected by gravity and processed to oil (or to gas, see below) in the lower part of the building.

CONVERSION OF WASTES TO GASEOUS FUEL

Hydrogasification

Another approach the Bureau is developing to dispose of solid wastes in an environmentally acceptable fashion is hydrogasification. In addition to disposal, this approach would alleviate our growing shortage of pipeline gas by producing a substitute natural gas (SNG).[24]

Hydrogasification is simply the reaction of the organic portion of the solid waste with hydrogen at high temperature to produce methane directly. This process utilizes much the same technology developed during our extensive work on the Hydrane Process,[25] the conversion of coal to methane.

We investigated the conversion of both animal manure[26] and a "typical" municipal solid waste[24] in laboratory batch reactors. In the case of the manure, we also conducted some continuous experiments to provide data for a process design and feasibility study.[27] The experimental studies indicated that solid wastes could indeed be converted to methane and at conditions considerably milder than those required for coal conversion. For example, these tests indicate that pipeline quality gas (heating value > 900 Btu/scf) can be prepared directly from either municipal solid wastes or cattle manure at transmission pipeline pressure (approximately 69 atm) and 550°C. Examples of observed gas compositions from the hydrogasification of a typical municipal solid waste (MSW), as defined by HEW, and a cattle manure are shown in Table 2.9.

Table 2.9

Composition of Raw Product Gas[a] from the Hydrogasification of Solid Wastes

	Municipal solid waste	*Cow manure*
Hydrogen, vol %	32.8	19.7
Methane, vol %	52.6	61.3
Ethane, vol %	11.2	17.8
Carbon monoxide, vol %	3.4	1.2
	100.0	100.0

[a] On a carbon dioxide- and water-free basis.

Thus, we can produce a gas from municipal solid waste that can be methanated to convert the carbon monoxide to additional methane so that the product can be substituted for natural gas. The raw gas from the hydrogasification of cow manure is ready for the pipeline after simply shifting the carbon monoxide in the presence of water to carbon dioxide and hydrogen and scrubbing out the carbon dioxide.

Preliminary economic studies[28] indicate that the most important variables affecting the cost of disposing of solid waste by hydrogasification are the amount of solid waste available, its composition, and the price of supplementary pipeline gas in the area. Some of the results of this economic study are given in Table 2.10, showing how pipeline gas cost and the population served by the plant influence the cost of waste disposal.

This table shows that for larger municipalities, solid wastes can have an asset value and still allow the production of pipeline gas at lower prices than SNG from naphtha feed stocks or improved LNG. A more detailed process and economic study[27] based on the above reference and experimental data with cattle manure indicates that, at least for larger plants, cattle manure would be a cheaper source of SNG than would coal or naphtha.

Thus, there are many potential advantages in converting solid wastes to pipeline gas. Among the most important of these are:

1. The large urban areas generating the most solid wastes and in which the waste disposal problem is most extreme also have the highest pipeline gas requirements.
2. There is a shortage of pipeline gas and an abundance of solid wastes. In fact, solid wastes may represent one of our largest most easily recoverable resources which is also replenishable.
3. The organic fraction of solid wastes has the chemical composition to be a good feed material for a pipeline-gas plant and may also be considered to have a negative price. Wastes are hydrogasified at milder conditions than coal.
4. The high value of pipeline gas, its short supply, and the low value of the solid waste feed stock justifies the capital investment to build a conversion plant.
5. Converting solid wastes to pipeline gas will solve two important environmental problems by converting solid wastes to a sterile residue (ash) greatly reduced in volume and by providing clean burning gas which will alleviate air pollution problems.

The main disadvantage of hydrogasification is the expensive, high pressure equipment required. However, all processes which generate pipeline gas similarly require expensive equipment. This is a process which benefits from economics of increasing plant size and

Table 2.10

Effect of Pipeline Gas Price[a] and Population on Average Solid Waste Disposal Cost[b] in $/ton[28]

Metropolitan area	*1966 metropolitan population, millions*	*Using MSW and sewage sludge*			*Using MSW, industrial solid wastes, and sewage sludge*[c]		
		Gas price, $/M cu ft			*Gas price, $/M cu ft*		
		0.40	*0.50*	*0.70*	*0.40*	*0.50*	*0.70*
Fresno, Calif.	0.409	5.42	4.71	3.21	3.78	3.03	1.53
Akron, Ohio	0.652	4.35	3.60	2.10	3.20	2.45	0.95
Denver, Colo.	1.083	3.10	2.35	0.85	1.90	1.15	-0.35
Pittsburgh, Pa.	2.376	1.74	0.99	-0.51	0.82	0.07	-1.43
Detroit, Mich.	4.06	0.98	0.23	-1.27	0.91	-0.56	-2.06
Chicago, Ill.	6.73	0.36	-0.39	-1.89	-0.29	-1.04	-2.54
New York, N.Y.	11.41	-0.16	-0.91	-2.41	-0.72	-1.47	-2.97

[a] Includes all taxes and 7.5% profit on undepreciated investment.

[b] Does not include collection costs, (-) indicates waste value rather than disposal cost.

[c] Including industrial solid wastes and sewage sludge with municipal solid wastes benefits economics due to increasing plant size.

is, therefore, unlikely to be used for small scale operation (Table 2.10). The same comments apply to the high pressure waste to oil process.

Pyrolysis

Pyrolysis (destructive distillation) converts organic wastes to char, tar and oils, and gas. The char has fuel value, is sterile and may be useful as landfill, soil conditioner or filter medium. The liquids have fuel value and may also have chemical value. The medium Btu gas (400-600 Btu/scf) can provide more than enough energy needed to "run" the process. As shown earlier in Table 2.1, the annual production of dry organic animal manure is about 200 million tons, of which about 90% is cattle manure. Based on our pyrolysis experiments, the yield of tar and oils from manure alone, if all were processed, is 58 million barrels or 7% of the domestic residual fuel oil used in 1971. The pyrolysis gas potential from manure is equivalent to about 1.4 trillion cubic feet of methane or 6% of the United States consumption of gas in 1971.

Pyrolysis has been used for many years to convert coal to coke for the iron-making industry. The coal-chemicals industry has been based on recovery of the distillation products from coking in slot ovens. The Bureau of Mines developed a pilot plant to pyrolyze coal and determine its suitability for coke making. The plant, with minor modifications, was adapted to pyrolysis of organic wastes. Figure 2.7 shows a sealed retort containing 85 pounds of waste being charged to the heated reactor on the left; the product condensation train is on the right. The process flow is shown in Figure 2.8. In operation, the temperature in the reactor is maintained at test conditions, char remains in the reactor, and the heated gases and vapors flow to the condensers where tars, oils, and aqueous products are removed. Tar fog and mists are removed from the gas by an electrostatic precipitator and ammonia, carbon dioxide, sulfides, and chlorides are scrubbed from the gas by acid and caustic solutions. Light oil is removed from a portion of the total product gas by a dry ice-acetone bath and the clean gas is stored in the holder shown. Excess gas is flared in our pilot plant but this gas, in a large-scale operation, could provide more than the needed process energy. Alternatively, the process heat could come from char, tar, oil and some gas; the

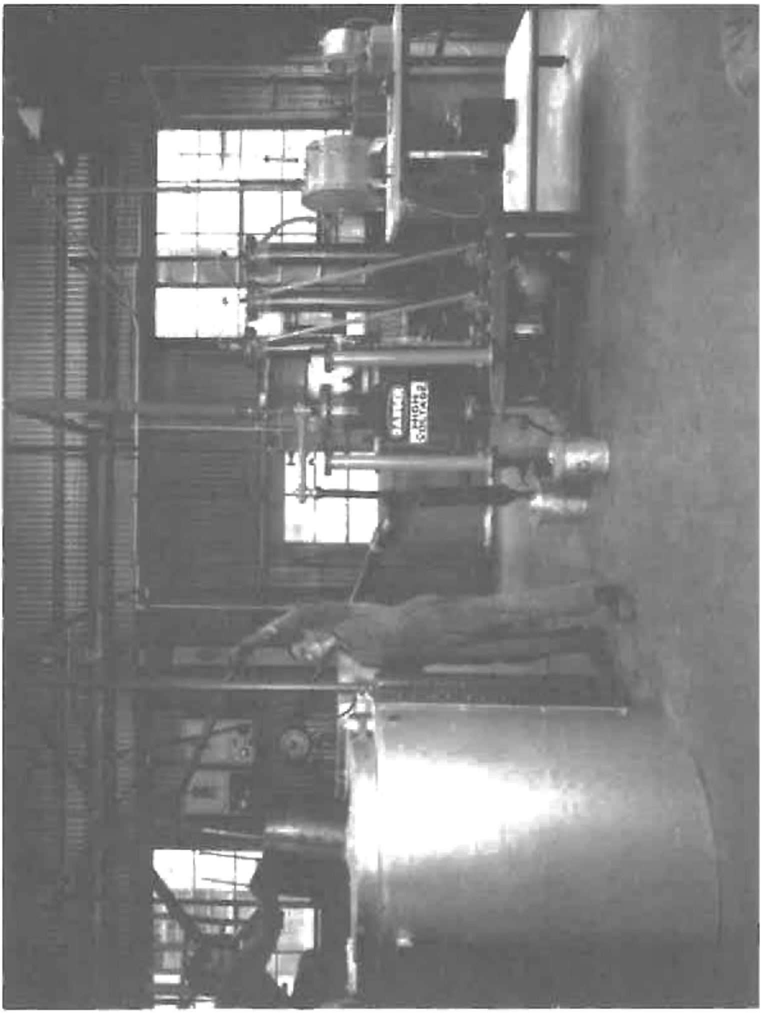


Figure 2.7. Pyrolysis pilot plant.

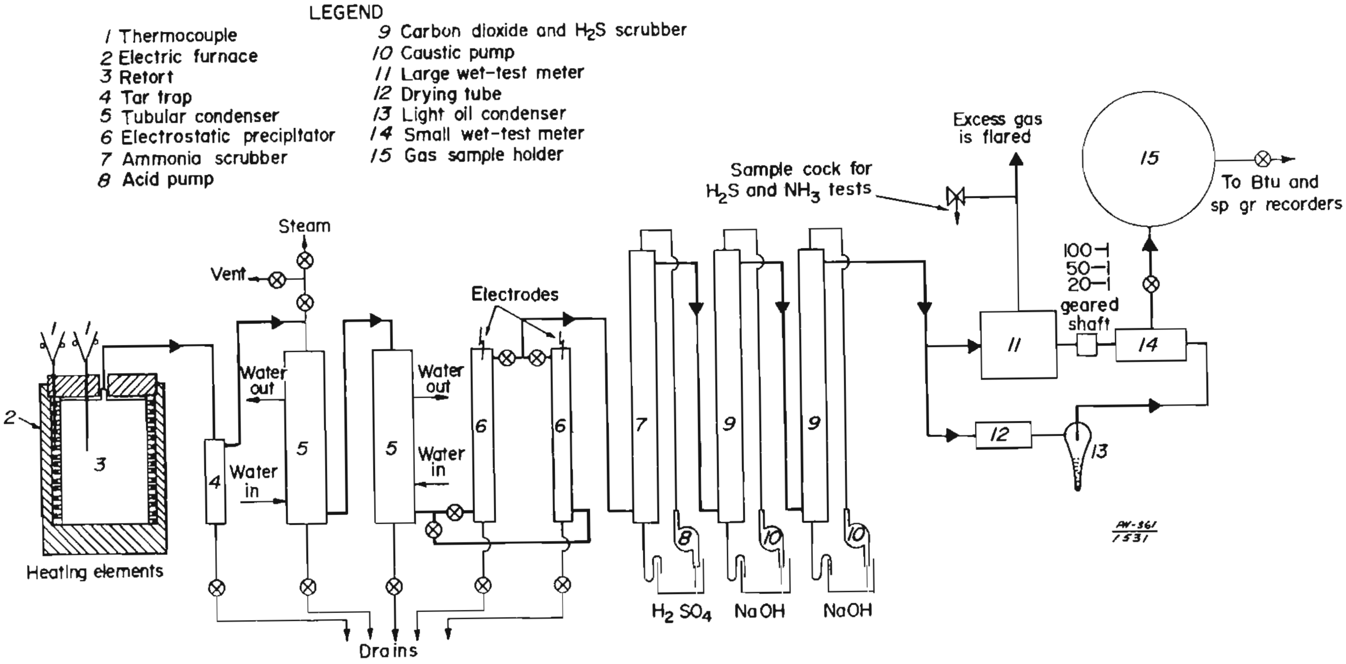


Figure 2.8. Process flow - pyrolysis pilot plant.

excess gas would be sold for industrial use. All of these reactions occur in a closed system in the absence of air at atmospheric pressure. The amount of oil and gas that can be produced by pyrolysis can be varied by simply changing the reaction temperature (high temperature yields more gas and less oils) or by changing the amount of moisture and the residence time.

Scrap Tires

The results of experiments on pyrolysis of scrap tires conducted by the Bureau of Mines in cooperation with the Firestone Tire and Rubber Company were reported.[29] About 180 million tires are discarded each year and they are a good example of a man-made composition that does not biodegrade. They also are difficult to incinerate without causing pollution. Experiments indicated that a ton of tires pyrolyzed at 500°C yielded 840 pounds of char residue (mostly carbon black-like material), 129 gallons of oil, and 1720 cubic feet of gas. If pyrolyzed at 900°C, the char yield is 1172 pounds; oil is 44.6 gallons; and gas is 12,630 cubic feet per ton. In 1971, the U.S. Rubber Manufacturers' Association[30] proposed a grid of ten tire pyrolysis plants placed strategically around the United States to convert some 60% of all scrap tires. The Firestone Company operated a continuous one ton per day pyrolysis pilot plant through 1972 and is evaluating the results of this work with scrap tires.

Municipal Refuse

In initial experiments using municipal (household) refuse, the waste was charged in the pyrolysis furnace as received, containing 40 to 50% moisture.[31] Later tests[32] indicated possible advantages of drying the wastes before pyrolysis, foremost being that less pyrolysis unit capacity would be needed, and the yield of products per unit of charge would be increased. The gas, for example, would contain more methane and less hydrogen. Energy is required for drying; however, there is an advantage, a ton of refuse dried to 7% moisture contains 1.63 times the amount of dry solids than a sample with 43% moisture. In all later experiments, the wastes were dried to less than 10% moisture at about 75°C and then pyrolyzed; see Tables 2.11-2.15.

Table 2.11

Analyses - Municipal, Agricultural, and Industrial Wastes

	Municipal refuse,[a]		*Sewage sludge, dried*	*Rice hulls, dried*	*Cattle manure, dried*	*Plastic battery cases*	*Paper mill sludge, dried*	*Raw sewage,*[b] *dried*
	Wet	*Dried*						
Ultimate analysis, as-received, percent:								
Hydrogen	8.2	7.2	2.1	5.7	5.7	12.2	7.0	6.8
Carbon	27.2	47.6	14.2	38.5	41.2	85.9	30.9	45.5
Nitrogen	0.7	2.0	1.1	0.5	2.3	0.0	0.5	2.4
Oxygen	56.8	35.7	10.5	39.8	33.3	0.2	51.2	25.8
Sulfur	0.1	0.3	0.7	0.0	0.3	0.1	0.2	0.5
Ash	7.0	7.2	71.4	15.5	17.2	1.6	10.2	19.0
Moisture	43.3	4.9	4.4	7.6	3.6	0.2	23.2	4.2
Btu per pound	4,827	8,890[c]	2,040	6,610	7,110	18,850	5,350	7,080

[a] Free of bulk glass and metals, obtained from the Fairfield Aerobic Mulch Plant, Altoona, Pennsylvania.

[b] Obtained from a Cleveland sewage treating plant.

[c] 940 Btu are consumed in the drying step to produce 1 lb of 4.9% moisture content waste; therefore, the net heating value of this waste is 7,950 Btu/lb or 15.9 million Btu/ton.

Table 2.12

Conversion of Wastes by Pyrolysis, Yields of Products

Pyrolysis, temperature, °C	*Municipal refuse* 900	*Sewage sludge* 900	*Rice hulls* 200-700	*Cattle manure* 900	*Plastic battery cases* 200-625	*Paper mill sludge* 900	*Raw sewage* 900
Yields, weight percent:							
Char	31.3	78.3	40.0	36.3	1.9	24.2	30.7
Gas	45.3	12.9	20.6	38.5	21.1	30.8	40.1
Tar and oil	6.9	0.6	5.1	4.4	78.9	0.5	8.6
Free ammonia	0.2	0.9	0.0	0.26	--	0.0	0.02
Liquor (aqueous)	14.6	5.8	32.4	15.6	--	36.3	15.7
Yields, per ton of wastes:							
Residue, lb	626	1,566	800	726	38	484	614
Gas, cu ft	18,470	5,594	5,872	13,940	4,438	12,399	15,713
Tar + oil, gal	16.2	1.5	11.8	13.2	169	1.1	20.1
Liquor (aqueous), gal	34.1	13.6	76.3	38.3	--	86.3	36.0
Ammonium sulfate, lb	37.5	72.7	8.4	65.8	--	6.9	34.4

Table 2.13

Composition of Residues from Pyrolysis of Wastes

Pyrolysis, temperature, °C	*Municipal refuse* 900	*Sewage sludge* 900	*Rice hulls* 200-700	*Cattle manure* 900	*Plastic battery cases* 200-625	*Paper mill sludge* 900	*Raw sewage* 900
Ultimate analysis, percent:							
Hydrogen	1.0	0.2	1.5	0.6	2.0	0.6	0.5
Carbon	55.4	9.5	55.4	48.5	57.4	61.1	33.7
Nitrogen	1.0	0.2	0.7	1.1	3.0	0.5	0.8
Oxygen	4.0	-	2.6	2.0	1.5	0.9	0.0
Sulfur	0.4	0.9	0.1	0.3	2.0	0.3	1.0
Ash	38.2	91.6	39.7	47.5	34.1	36.6	64.0
Btu per pound	8,200	1,420	8,720	7,140	7,300	9,020	5,130

Table 2.14

Composition of Gases from Pyrolysis of Wastes, volume percent

Pyrolysis, temperature °C	*Municipal refuse 900*	*Sewage sludge 900*	*Rice hulls 200-700*	*Cattle manure 900*	*Plastic battery cases 200-625*	*Paper mill sludge 900*	*Raw sewage 900*
Hydrogen	37.8	43.8	15.4	27.5	3.8	32.2	29.7
Carbon monoxide	23.0	25.0	34.2	18.0	2.6	34.4	21.1
Methane	24.4	18.2	31.0	22.7	19.6	18.0	24.9
Ethane	1.2	0.6	4.0	0.9	0.0	0.3	1.5
Ethylene	3.5	4.1	-	4.7	12.7	3.8	12.0
Carbon dioxide	9.1	6.7	12.1	24.5	-	9.7	7.1
Propane	-	0.6	0.9	0.2	1.5	0.5	0.4
Propylene	-	0.5	1.2	0.8	29.3	0.1	2.0
Other	1.0	0.5	1.2	1.7	13.5[a]	1.0	1.3
Btu per cu ft	545	505	613	450	1,871	370	529

[a] 8.1% Butene-1.

Table 2.15

Composition of Light Oils from Pyrolysis of Wastes, volume percent

Pyrolysis temperature, °C	Municipal refuse 900	Sewage sludge 900	Rice hulls 200-700	Cattle manure 900	Plastic battery cases 200-625	Paper mill sludge 900	Raw sewage 900
Forecut	4.8	1.4	54.7	12.0	[a]	12.2	4.2
Benzene	85.5	79.2	19.3	43.4	-	78.6	84.0
Toluene	7.2	15.1	17.1	32.8	-	6.3	8.5
Ethylbenzene	0.3	0.4	0.4	0.7	-	0.4	0.2
Mixed xylenes	0.4	2.2	1.3	2.0	-	1.0	1.1
Unidentified	1.8	1.7	7.2	9.1	-	1.5	2.0

[a] Gas from plastic battery cases consisted of (in percent) ethane + ethylene 1.1; propylene 37.4, propane 4.3, isobutylene 1.3, butane 1.1, butene-1 31.1, pentenes 17.0, other (butenes, pentane) 4.3, unidentified 2.2.

Cattle Manure and Other Wastes

Table 2.11 shows analyses typical of the wastes pyrolyzed. The energy content of these wastes ranges from the very low amount, 4 million Btu per ton, for sewage sludge to 37.7 million Btu available in a ton of waste plastic battery cases.[33]

Table 2.12 shows the yields of the products from pyrolysis. The energy potential of pyrolyzed municipal refuse, cattle manure, and raw municipal sewage[33,34] is significant. By dry weight, 90-99% of these wastes can be converted to gas, char, and tar and oils. The char residue from a ton of such wastes (Table 2.13) contains 3.2 to 5.2 million Btu. Ash constituents concentrate in the residue, and a ton of the char residue contains from 10.3 to 16.4 million Btu compared to 24 million Btu in a ton of coal.

Table 2.14 indicates that the pyrolysis gas from a ton of these wastes can provide from 6.3 to 10.1 million Btu. The energy in the gas alone is more than sufficient to supply the heat for pyrolysis and drying. Excess gas can be used, in plant, for steam and electricity, or by other industrial gas users. The light oils, shown in Table 2.15 are primarily benzene, toluene, and xylene.

Table 2.16 shows the energy distribution in the pyrolysis products from typical wastes. Most of the energy potential of the raw wastes can be recovered as gas, char, tar and oil. Recoveries of 80 to 95% are typical for the wastes pyrolyzed, but pyrolysis and drying would consume a significant proportion of heat energy (see Table 2.17).

Larger-scale studies would provide data for scale-up to commercial plants. Areas for investigation should include the pollution aspects of the aqueous product, which contains up to 5% of water-soluble oxygenated products, the conditions required for optimum yield and quality of the gas, and the best type of reactor to be used. Studies should also include the effect of moisture, because of the possibility that the water-gas shift and steam-carbon or steam-hydrocarbon reactions will occur rapidly at high temperatures.

Cost of Pyrolysis

Data from experiments with dried municipal waste were used to estimate the cost of possible commercial pyrolysis plants. In making the cost estimate, the

Table 2.16

Energy Distribution - Pyrolysis of Wastes

		Energy in pyrolysis products, million Btu/ton of raw refuse[a]			
Materials pyrolyzed	Energy in raw refuse, million Btu/ton	Gas	Char	Tar and oil	Total[a]
Household refuse	17.8	7.1	5.9	2.3	15.3
Industrial refuse	9.1	6.1	1.7	0.6	8.4
Scrap tires	33.5	8.7	15.9	6.8	31.4
Battery cases - hard rubber	26.9	6.0	19.0	1.6	26.6
Waste bark and sulfite liquor	13.6	6.6	4.7	1.7	13.0
Battery cases - plastic	37.7	8.3	0.3	30.4	39.0
Rice hulls	13.2	3.6	7.0	1.6	12.2
Rice straw	12.2	4.0	5.9	1.5	11.4
Cattle manure	14.2	6.3	5.2	1.2	12.7
Paper mill sludge	10.7	4.6	4.4	0.2	9.2
Raw sewage	14.2	8.3	3.2	2.3	13.8

[a] Does not account for energy required for pyrolysis nor for heat of drying wastes.

Table 2.17

Estimated Costs for Pyrolysis of Municipal Refuse

Plant feed, tons per day of waste[a]	*Population served, thousands*	*Plant cost, millions of dollars*	*Operating cost after credit, dollars per ton of refuse*[b]
500	200	3.82	5.79
1,500	600	6.95	2.76
2,500	1,000	9.68	1.97

[a] Wet feed containing 43.5% moisture.

[b] Based on fuel value for char, tar and light oil, and market value of ammonium sulfate. Only 2% of the gas is credited; 79% of the total gas is used for pyrolysis, 8% for drying and 11% for steam raising.

waste was assumed to contain 43.5% moisture. In these plants, the yield of pyrolysis gas was estimated to be 45% by weight of the dried refuse and it was used to supply all process energy for drying, pyrolyzing, and generating steam. Fuel value for the excess gas and for the char, tar and light oil products were credited in making the estimates shown in Table 2.17. The estimates suggest that a plant to process the waste generated by a city of 600,000 people will cost about $7 million and have an operating cost of $2.76 per ton of waste fed to the plant. By contrast, the cost of incineration in Pittsburgh, Pennsylvania (now discontinued), was $13.40 per ton (late 1969-1970), and landfilling now costs about $6.80 per ton. Burning wastes along with coal is another disposal method being tested in St. Louis and Chicago but its economics are not yet available.

Commercial Pyrolysis Plants

Since about 1971, a number of companies have attempted to market pyrolysis systems for waste disposal. At this writing none have been built, but several are in the design stage and will be demonstrated at a few locations in the United States. Most of the plants are direct-fired systems that differ from pyrolysis in that oxygen is added. They make a dilute gas suitable for industrial use. Only two of the systems recover liquid products. A brief discussion of five systems, some of which are funded by EPA for demonstration purposes, follows.

In January 1972, Union Carbide Corporation announced development of an Oxygen Refuse Converter System by its Linde Division. It heats and partially oxidizes solid wastes to produce fuel gas and slag. The system uses a vertical furnace, adds oxygen, and attains temperatures high enough to slag all the inorganic materials. The process is akin to an oxygen-blown, slagging gas producer.[35] The City of Mt. Vernon, New York, has applied for a federal grant to erect a 150 ton per day demonstration plant.

The Koppers Company, Inc., is considering their Koppers-Totzek Process, commonly used for gasification of coal and lignite, for gasifying manure to produce a fuel gas. The gasification reaction of manure and oxygen requires very little steam and takes place at 8 psig and temperatures up to 1500°C. Due to the highly reactive carbon present in manure, carbon conversion of 99% is readily attainable and, in fact, it may be possible to use somewhat lower temperatures at this conversion level. Koppers Company has estimated that a plant processing 1000 tons per day of raw manure (8.7% H_2O) would require 463 tons per day of oxygen. The net raw gas produced, 20,000 scfm, has a heating value (dry) of 255 Btu/scf and contains 49.3% carbon monoxide, 18.0% carbon dioxide, 29.5% hydrogen, 2.4% nitrogen, and the remainder is hydrogen sulfide and carbonyl sulfide. The sulfur compounds and carbon dioxide can be removed before combustion.

The City of Baltimore, Maryland, has received a federal demonstration grant to erect Monsanto's Landguard pyrolysis system to process 310,000 tons per year of solid wastes (1000 tons per day). Total plant cost is $15.4 million and the projected operating cost is $9.03 per ton of waste processed. This includes credit taken for some electricity generated by extracting heat from the offgas in a waste heat boiler and for magnetic iron extracted from the residue.

The heart of the system is a direct-fired rotary kiln running oxygen deficient. The particulate laden kiln offgas is combusted in an after-burner before entering a waste heat boiler and gases from the boiler are scrubbed with water to minimize atmospheric pollution. No other products are recovered with the exception of magnetic iron.

The Garrett Process, developed by Garrett Research and Development Company, Inc., is a pyrolysis system that yields gas, oil and char. Some of the char product and all of the gas formed are used for process heat. The process, according to Garrett, takes place in a flash pyrolysis reactor and yields 1.1 barrels of oil (46 gallons from a ton of dry, inorganic-free municipal refuse). When a high yield of oil is desired, the pyrolysis temperature is 500°C. When the temperature is 750-770°C, Garrett claims 80% conversion of the dry organics to gas with a calorific value of 770 Btu/cu ft, 10% char and 10% liquids, mostly water. Garrett has estimated $5 per ton operating costs for a 2000 ton per day plant with a capital cost of $12.4 million. They claim $6 per ton net income from oil, metals, char and gases. The City of Portland, Oregon, has received a federal grant to build a 50 ton per day demonstration plant.

A $10 million waste-disposal plant, whose design is based largely on the Bureau's pyrolysis research, will be constructed by Rust Engineering Company for the Metropolitan Sewer Board serving Minneapolis, St. Paul, and nearby municipalities. This will be part of a complex for treating up to 290 million gallons of sewage sludge and 400 tons per day of refuse. Metals and activated carbon will be produced by the plant, and other possible products include fertilizer, ammonia, chemicals and gases.

SOLAR ENERGY VIA CONVERSION OF ORGANIC MATTER TO FUEL

Solar Efficiency of Plants

Carbohydrates are formed in green plants as the result of photosynthesis, which is the chemical combination or fixation of CO_2 and water by utilization of energy gained through the absorption of visible light.

$$xCO_2 + xH_2O \xrightarrow[\text{green plants}]{\text{light}} \underset{\substack{\text{carbo-}\\ \text{hydrates}}}{(CH_2O)_x} + xO_2$$

The importance of photochemical reduction can hardly be overemphasized; it is the very basis of our existence (food supply). It is the means by which carbon in its highest oxidation state (CO_2) is converted into a variety of substances having carbon in a lower state of oxidation. Photosynthesis makes carbon available for use by the plant, and the plant carries out a series of enzyme-catalyzed reactions which result in the synthesis of simple sugars, such as glucose ($C_6H_{12}O_6$), polymeric substances, such as the starches and cellulose, $(C_6H_{10}O_5)_n$ with $n > 1000$, and other organic substances, such as lignin.

It is important to realize that the fossil fuels had their origin via this same photosynthetic route, for they are the remains of organic materials, buried and converted to fossil fuels after millions of years. These fossil fuels are only a small fraction of the living material that was formed in the past. By special conditions and entrapment, coal, petroleum, gas, oil shale, and bituminous sands have been preserved. But most of the organic materials formed in the past have long since been converted by oxidation back to CO_2 and water.

Our supply of fossil fuels is, of course, fixed. But cellulose, the chief constituent of our organic solid wastes, continuously made by photosynthesis, is the most abundant renewable raw material in the world. Riley has estimated the total organic carbon production of the earth to be $146 \pm 87 \times 10^9$ tons per year.[36] Of course, much of this carbon is so dilute in the terrestrial environment that it cannot reasonably be considered as an energy source available to man.

Green plants have as their distinguishing characteristic the ability to convert rarified CO_2 from the atmosphere into plant tissue. After we have harvested portions of the plant for our immediate use, we tend to think of the plant remains as waste. Because the conversion of organic wastes to clean energy fuels is technically now feasible, why not consider plants as an intermediate stage in the conversion of solar energy to fuel? From this point of view, it is but a short step to the concept of maximizing plant growth so that clean liquid or gaseous fuels can be continually generated in quantity. To a certain degree this can be visualized from our knowledge of existing crops. For instance, timber is grown in the Southeast for paper pulp but it could as readily be used for power generation.[37]

Most plants utilize less than 1% of incident sunlight for photosynthesis. In fact, slash pine converts but 0.24-0.30% of solar energy, corn 0.44-0.69% and, in general, agricultural crops range from 0.28 to 0.85%. Sugar cane appears to be exceptionally efficient and is capable of utilizing 1.2% of incident solar energy.[37] Plants only utilize light in the 0.4 to 0.7 μm region for photosynthesis; therefore, about half of the sun's energy falls outside of the usable range.[38] Estimates of the average total insolation energy received daily in the United States vary from 1300 Btu/ft^2 [37] to 1500 Btu/ft^2.[39]

Conventional agricultural crops have been selected because of their harvest of food or lumber and not because of their most efficient utilization of solar energy. As a fuel source, it is quite possible that rank-growing plants, unlike any present crops, would be more efficient. Those plants which yield the greatest dry weight per acre per year and which are woody but not succulent would be preferred. For example, some evidence has been reported that young forest plantations, after developing a complete canopy cover, are as efficient as any agricultural crops.[40]

Plantations of the solar energy crop would be located where land is relatively inexpensive and where biological needs of water, soil, weather and sunlight can be met. It is entirely possible that reclaimed, strip-mined areas could be terraced and planted with the crops. Dry desert areas, without irrigation water, or very hilly and rocky areas would not be suitable. Arable land would be needed in large acreage to ensure that a sufficient quantity of cellulose-lignin would be available to warrant construction of a fuel conversion plant. While the requirements for optimum yields of cellulose-lignin may be somewhat different than those for food crops, the land requirements probably would be similar. Therefore, the decision whether to devote land to food or fuel production would be based on economics and need.

Dual purpose crops could also be developed, of course. Corn is close to being such a crop because it has a moderately high solar efficiency and the weight of stalk, husk, and cob wastes is much greater than that of edible kernels.[41] Hybridization to produce even more robust plant growth, as well as high quality kernels, could provide two cash crops simultaneously, raw materials for canning and for generating clean fuels.

How should the production of cellulose-lignin be optimized? Szego and Kemp[37] have presented estimates of fuel prices for wood, assuming 0.4% solar efficiency and 5, 8, 11, or 14 year cycles between planting and harvesting the fuel crop, a crop having the characteristics of conifers grown in the South. The most favorable fuel prices were calculated using a current funding method (costs and profit funded currently) and showed a small benefit for longer growth cycles. These estimates are compared in Table 2.18 with estimates of fuel price based on deferred funding (costs paid from working capital and profit deferred until crop is sold) which favors shorter growth cycles.

Table 2.18

Estimated Fuel Price at 0.4% Solar Efficiency[37]

Growth cycle, years	*Fuel price, \$/10^6 Btu*	
	Current funding	*Deferred funding*
5	1.27	1.56
8	1.09	1.53
11	1.06	1.69
14	1.03	1.90

The most important conclusion to be drawn from the fuel plantation concept, however, is that forestry solar efficiencies must be improved by a factor of 2 or 3 to produce a wood fuel which could sell as low as \$0.70 per 10^6 Btu. This might be achieved through careful selection of species and hybridizing and by optimizing growth with improved forestry techniques, hormone growth stimulants and fertilization.

A very significant improvement in heating value would be attained by converting all harvested plant tissue to a high Btu, water-free fuel. The conversion to oil, for instance, increases the total available heating value compared to burning unconverted plants. This is true largely because of two factors: (1) field plants usually contain over 40 weight percent moisture and this detracts greatly from the available heating value, and (2) the low-oxygen content oil product is hydrophobic and, therefore, not only separates from water but has a much higher heating value per pound. Furthermore, the liquid fuel product can be more inexpensively stored or shipped than wood and its properties are reasonably close to that of residual fuel now used in many electric generation stations.

Energy Potential in Organic Wastes

Without waiting for the era of energy forests to dawn, there is potential at hand for an organic wastes to fuels industry. The nearly one billion tons per year of organic wastes represents an untapped fuel supply. Unfortunately, the largest portion of this material, agricultural waste, is dispersed and is not now collected. Large volume wastes which are collected would consist mainly of urban refuse and industrial wastes. Locations having large animal feedlots will, of course, rapidly accumulate manure which could easily be collected for a waste conversion plant. Sewage treating facilities occasionally must remove and dispose of the excess sewage sludge; this material would be available for conversion in large quantity a few times a year. Similarly, fermentation residues and slaughterhouse wastes (including paunch manure) are difficult to dispose of and could easily be accommodated by a large waste conversion plant. While such a plant would be built to handle a specific, large-scale waste material, it would also be able to convert these nuisance wastes. Actually, the elimination of odorous, polluting and pathogenic wastes with the simultaneous production of a sterile oil would, in many cases, be reason enough to consider such a process. However, the collection of all local organic wastes and the conversion of this to a high Btu fuel would represent an important addition to the locality's fuel supply. Table 2.1 lists the quantities of wastes estimated to be generated in the United States in 1974, the quantities of wastes which could be collected (or readily collectable) that year, and the amount of fuel oil in one case and gas in the other, which could be produced from the wastes.

The potential value of fuel from collected wastes alone is about $2 billion. While this is small compared to the nation's total fuel bill, its value will rise and it could be an important incremental addition to our fuel supply--besides we are getting rid of cluttering, maladorous, unwanted waste in a most desirable way.

Figure 2.9 illustrates the comparative heating value of the major fossil fuels needed to generate our electricity in 1971. Over half of this power

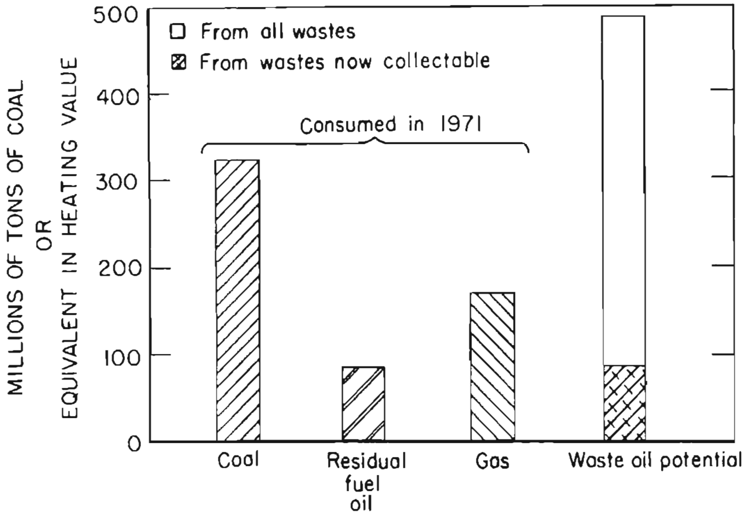


Figure 2.9. Fuel burned to generate electricity.

was generated from coal, our most abundant fuel (coal represents about 88% of our fuel resources). But large quantities of natural gas and residual fuels were also consumed. These are fuels in short supply whose continued use at these levels severely affects our domestic reserves or whose importation hurts our balance of payments position. The potential heating value of all organic wastes, if converted to oil, is much greater than the sum of gas and fuel oil burned to produce electricity.

In terms of importation of foreign fuel oil, conversion of wastes to oil would have a noticeable impact. Figure 2.10 shows how the U.S. demand for residual fuel oil has grown since 1965. But domestic oil production has remained about constant since 1968 and, therefore, our domestic fuel oil production has not increased with demand. Foreign fuel oil has been imported in ever-increasing quantity, which, in turn, means continually increasing imbalance of payments. While it may be impractical to consider the elimination of fuel oil imports by conversion of all wastes to fuel, certainly it is proper to point out that conversion of wastes, now collected, would greatly reduce the importation of fuel oil and reduce our balance of payments deficit. The electric utilities

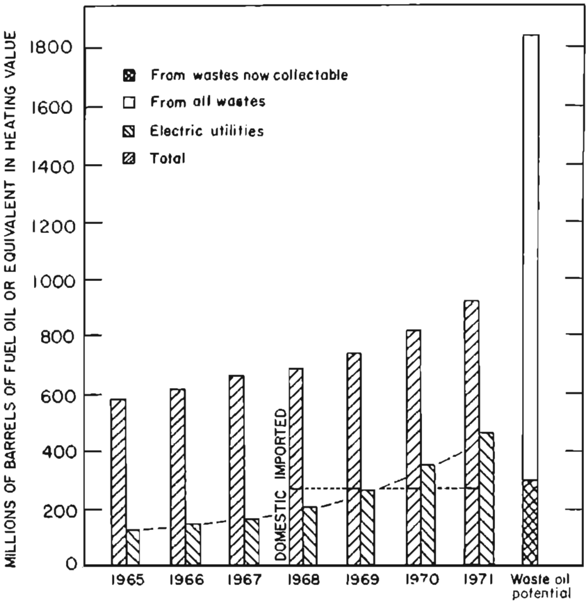


Figure 2.10. Residual fuel oil demand.

have, in recent years, rapidly increased their consumption of fuel oil and, since 1970, have used more than is domestically produced. Fuel oil from wastes could satisfy this demand without imports.

The potential for a wastes to fuel industry is at hand or nearly so. There is a shortage of low sulfur fuels required for a cleaner atmosphere in industrial areas; demand for fuel is increasing and its projection into the foreseeable future remains very strong; organic wastes are, at the least, expensive to dispose of and often a direct threat to the health of nearby populations; and organic wastes are convertible into replenishable, clean burning, high energy fuels. The only drawback to a wastes to fuel industry is in the area of relative cost of fossil fuels compared to synthetic fuels from wastes. Some fuel prices are changing so fast that present uneconomic differentials could disappear soon. For example, whereas fuel oil prices remained fairly constant at about $3.50/bbl for many years, recently, spot prices of low sulfur residual fuel oil have been much higher; No. 6 oil (max. 0.3% S) FOB New York is listed at $5.51/bbl and No. 6 oil (max 1% S) FOB

Chicago at $5.57/bbl.[22] Prices will undoubtedly rise to well over $8/bbl in the near future.[23] The desirability of utilizing wastes in this way may even obviate any economic disadvantage.

A preliminary evaluation of the Bureau of Mines waste to oil process by an outside engineering firm has concluded that a 3000 ton per day wood waste plant could produce 4000 bbl/day of fuel oil at a cost of $7/bbl. Similar processing of urban or industrial refuse, because these wastes contain significant amounts of ash, would produce about 3600 bbl/day at a cost of nearly $8/bbl. This, however, could be offset by a disposal charge. At a sales price of $8/bbl for low sulfur fuel from wastes, a city could then dispose of its collected garbage, sewage sludge, and industrial organic wastes at no disposal cost. Similarly, any improvement in processing which reduces costs, will help to make fuel oil from wastes competitive with petroleum fuel oil at today's prices.

Bureau cost estimates on conversion of organic wastes to high Btu gas fuel also suggest favorable economics. For instance, assuming a SNG price of $0.70/1000 cu ft, a city of 400,000 population would have a net disposal charge of about $1.55/ton for its combined urban, industrial and sewage sludge wastes. For populations over one million, the process appears to offer a net return and no disposal charge.[28]

All factors considered, it is unlikely that cities in the future can afford the extravagance of transporting their solid wastes 20 miles or more to a landfill. Nor will cattle feedlot operators prefer to pay for relocating their businesses to more remote areas in compliance with court orders based on pollution complaints. It is likely that the conversion of wastes to clean fuel energy will become a much needed and thriving industry. There are too many factors calling for this change and too few factors preventing its acceptance.

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ANN ARBOR SCIENCE
PUBLISHERS INC
P.O. BOX 1425 • ANN ARBOR, MICH. 48106

Third Printing, 1980

P.O. Box 1425, Ann Arbor, Michigan 48106

Library of Congress Catalog Card No. 72-96910
ISBN 0-250-40015-4

Printed in the United States of America