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ABSTRACT

A laboratory-scale, batch operated gasifier was used to evaluate the heating value, process and cooling water requirements, and water pollution potential of gasification of carbonaceous shales. These potentially valuable fossil fuels are found over large areas of Southern and Eastern Utah and vary widely in quality depending on the amount of intermixed inorganic material. The results indicate that a synthesis gas, consisting primarily of hydrogen and carbon monoxide, can be produced from carbonaceous shales. The total heating values of the synthesis gas from the carbon shales examined ranged from 4 to 62 percent of that of coal.

The process water requirements per unit of heating value obtained for gasification of the carbonaceous shales tended to be 5 to 15 percent higher than that for coal. Cooling water requirements were similarly higher due to the greater quantity of ash quenching water needed for the shales.

The quantity of phenols, ammonia-N, and total organic carbon produced from the gasification of coal was significantly greater than for either of the shales, when compared on a mass basis. Differences in process condensate constituents, such as mutagenicity and trace elements, were also determined for the coal and shale samples.

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INTRODUCTION AND OBJECTIVES

Introduction

The energy crisis in the world and the United States in particular lends a note of urgency to the search for new energy sources. A possible energy source which is not now being considered is the vast deposits of lignaceous shales in the areas adjacent to coal deposits now considered as waste.

Coal has long been gasified as a source of commercial fuel gas. Can the same processes being used to produce gas from coal be utilized to produce gas from the lignite shales and other forms of carbon bearing materials? If this can be accomplished, what quantities of water will be required? What quality of fuel gas or gases can be obtained? What about pollutants?

The thrust of the present investigation is to shed light, in a preliminary way, on the above questions.

Objectives

The specific objectives of the present research are directed at answering the following questions:

1. Can carbon sources other than coal be gasified by the coal processes?

2. If so, how do these gases compare to the gases from Utah coal?

3. What are the water requirements for the production of steam to process these materials?

4. What percentage of the waters condensed from steam in (3) can be reused?

5. How much ammonia-nitrogen, phenol, and organic carbons relative to Utah coal is produced?

6. What is the fate of selected trace elements in the carbon sources compared to coal, during gasification?

Background

Coal gas was an important fuel source in the United States prior to the early 1900s, when natural gas replaced the use of coal gas in most applications (Tetra Tech, Inc. 1976). Recently, interest in the gasification of coal has been renewed by the increasing demand and decreasing supplies of natural gas and oil. An intensive program has been undertaken by both the public and private sectors to develop processes producing clean liquid and gaseous fuel from coal (Tetra Tech, Inc. 1976).

Classification of Carbon Sources

Common coals have mass percentage compositions ranging from 65 to 95 percent carbon (lignite having the least amount of carbon and anthracite the most); 2 to 7 percent hydrogen; up to 25 percent oxygen, 10 percent sulfur, 1 to 2 percent nitrogen; and up to 50 percent ash (with < 15 percent most typical) (Smoot 1979). Figure 1 indicates the different coals with their associated heating values based on the proximate analysis. The proximate analysis determines the ash, moisture, sulfur, fixed carbon, and volatile percentages.

One difference between carbonaceous shales and coal is in the quantity of carbon and ash (Moore 1968). Carbonaceous shales have up to 40 percent carbon and 95 percent ash.

Coal and Carbonaceous Shale Characterization

The proximate and ultimate analysis is the industry standard for the determination of the rank (lignite to anthracite) and characteristics (friability, caking, etc.) of coal. These characteristics and properties are important for determination of the most appropriate fuel conversion method, characterizing the products, and determining the process water requirements (Probstein and Gold 1978). The amount of moisture in the coal sample does not change the quantity of steam required because the moisture is usually driven off in a countercurrent gasifier and will not enter into the reaction with coal. The amount of moisture is important in determining the amount of process condensate that needs to be treated and potentially recycled.

Figure 1 and Table 1 show various properties of selected ranks of coal. The heating values shown in Table 1 were computed using the Dulong Formula for higher heating value (HHV):

$$Q_{HHV} \text{ (Btu/lb)} = 145.4 * C + 620 \left(H - \frac{O}{8}\right) \qquad \cdots \qquad (1)$$

where C, H, and O are the percentages by weight of carbon, hydrogen, and oxygen, respectively. The small heating value contributed by sulfur is neglected, but the heat released by the condensation of steam during combustion is included. The heat released by the condensing steam is usually not recoverable and, therefore, a lower heating value (LHV) is normally used:

$$Q_{LHV} \text{ (Btu/lb)} = Q_{HHV} - 92.7 \text{ H} \qquad \cdots \qquad (2)$$

Sulfur in coal is usually in the pyritic form or organic form, and

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comprises between 0.3 to 8 percent by weight. Eastern coals usually have higher sulfur content; however, most eastern coals have sulfur in the easier to remove pyritic form. The western coals, usually low sulfur coals, contain sulfur in an organic form chemically linked to the coal. Sulfur in pyritic form can be removed by physical processes; whereas, the organic sulfur-removal requires more difficult chemical processes.

The carbon in coal consists of two types which behave much differently in the coal conversion processes (Probstein and Gold 1978). The carbon associated with the volatile fraction is highly reactive at temperatures of 760 to 930°F. The residual or char fraction is less volatile and temperatures above 1090°F are usually needed for efficient conversion. The highly volatile coals have an agglomerating characteristic that usually causes loading problems into the reactor (Smoot 1979). For this reason highly volatile coals are not usually considered for conversion.

There is little literature pertaining to the characterization of carbonaceous shale; however, the same
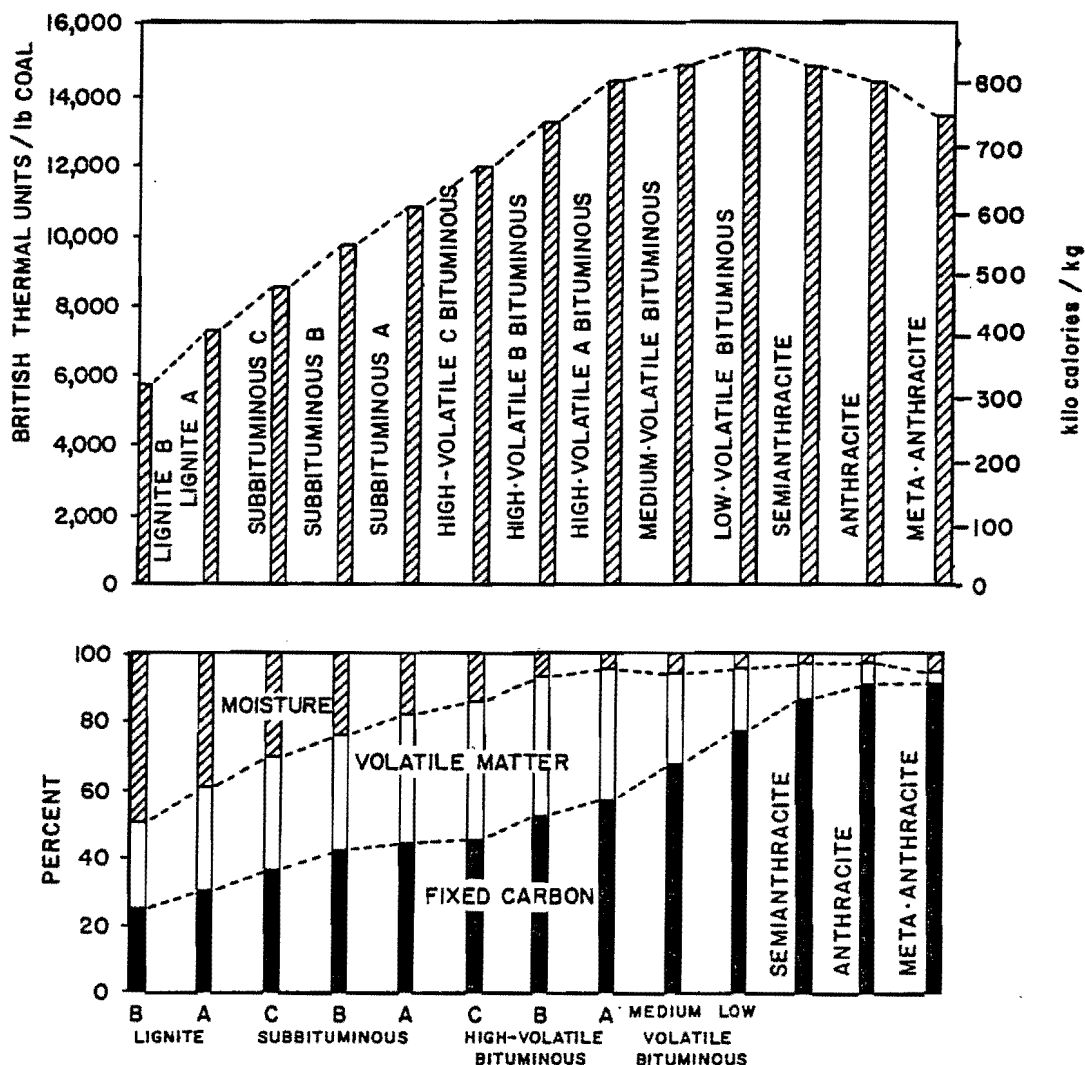
Figure 1. Heat content and proximate analyses of ash-free coals of different rank (Probstein and Gold 1978).

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Table 1. Ultimate analyses in weight percent of representative coals of the United States (after Probstein and Gold 1978).

Component	Fort Union		Powder River		Four Corners		Illinois		Appalachia	
	Lignite	Dry	Subbituminous	Dry	Subbituminous	Dry	C Bituminous	Dry	Bituminous	Dry
Moisture	36.2		30.4		12.4		16.1		2.3	
Carbon	39.9	62.5	45.8	65.8	47.5	54.2	60.1	71.6	73.6	75.3
Hydrogen	2.8		3.4		3.6		4.1		4.9	
Nitrogen	0.6		0.6		0.9		1.1		1.4	
Sulfur	0.9		0.7		0.7		2.9		2.8	
Oxygen	11.0		11.3		9.3		8.3		5.3	
Ash	8.6		7.8		25.6		7.4		9.7	
Total	100		100		100		100		100	
Higher Heating Value (Btu/lb)	6,720	10,533	7,920	11,379	8,440	9,635	10,700	12,753	13,400	13,715
(Kcal/kg)	3,730		4,400		4,690		5,940		7,440	

procedures used for coal are applicable. The most significant difference is the amount of ash or inorganic mineral matter.

Gasification Fundamentals

The gasification of coal can be accomplished by many different methods resulting in a variety of product gases. The various methods for producing low, medium, high Btu gas (900-2230, 2231-4450, and 4451-8900 Kcal/m^3 respectively) and liquid fuels are shown in Figure 2 (Probstein and Gold 1978). When air is used as the oxygen supply, a low heating value gas is produced because of the high concentration of atmospheric nitrogen. The nitrogen in the product gas can be eliminated by supplying pure oxygen to the reactor (Probstein et al. 1978). Another method of producing a medium heating value gas is by using a hydrogen-steam mixture which has the added benefit of producing more methane (Probstein and Gold 1978; Tetra Tech, Inc. 1976).

The conversion of coal into gaseous products requires several stages. The initial stage is pyrolysis where coal is converted into CO, CO_2, and CH_4 (Probstein and Gold 1978). The complex gasification chemistry that follows pyrolysis has been presented by Probstein and Gold (1978) as:
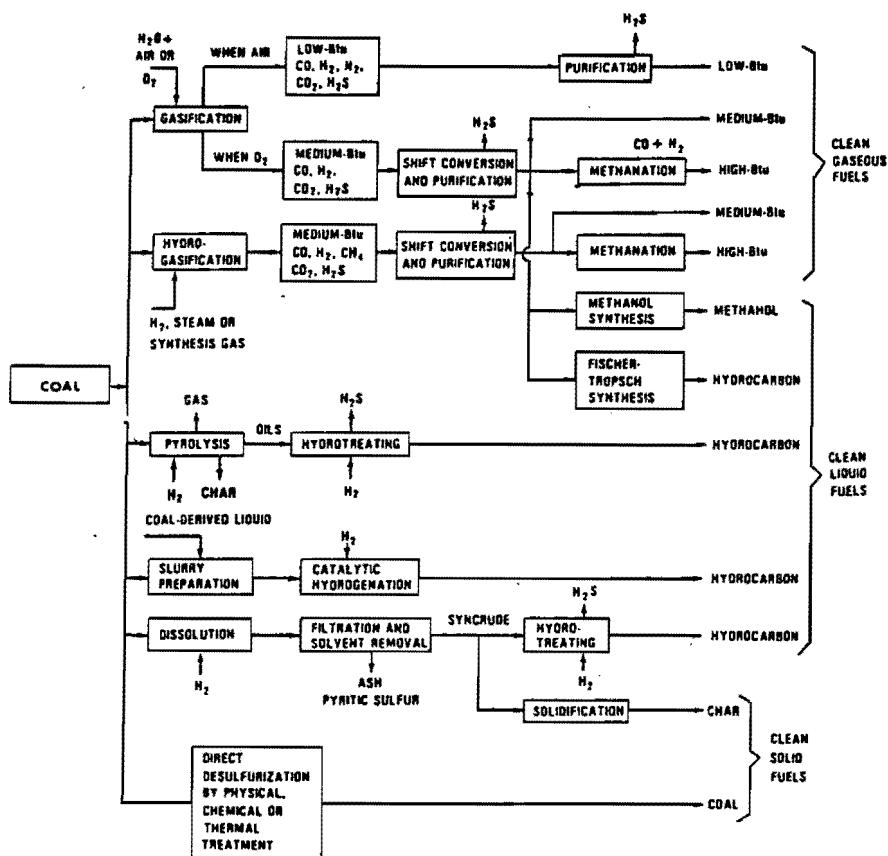
Figure 2. Methods of producing clean synthetic gaseous, liquid, and solid fuels (Probstein and Gold 1978).

Combustion ($\frac{1}{2} \leq n \leq 1$):

$$C + nO_2 \rightarrow (2 - 2n)CO \qquad \Delta H = - (2 - 2n)\ 26.4$$
$$+ (2n - 1)CO_2 \qquad\qquad - (2n - 1)\ 94.0 \qquad \cdots\cdots (3)$$

Carbon-steam or gasification reaction:

$$C + H_2O \text{ (steam)} \qquad \Delta H = + 31.4$$
$$\rightarrow CO + H_2 \qquad\qquad \cdots\cdots (4)$$

Carbon-hydrogen or hydrogenation reaction:

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -17.9$$
$$\cdots\cdots (5)$$

Water-gas shift reaction:

$$CO + H_2O \text{ (steam)} \rightleftharpoons H_2 \qquad \Delta H = - 9.8$$
$$+ CO_2 \qquad\qquad \cdots\cdots (6)$$

Methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -49.3$$
$$\cdots\cdots (7)$$
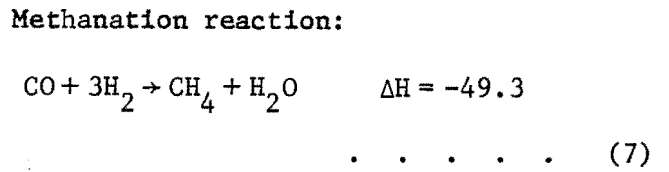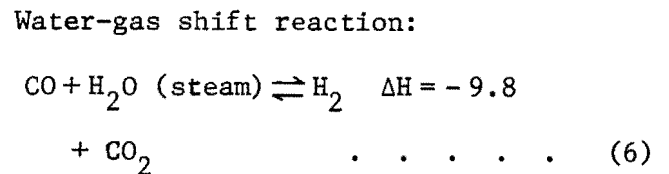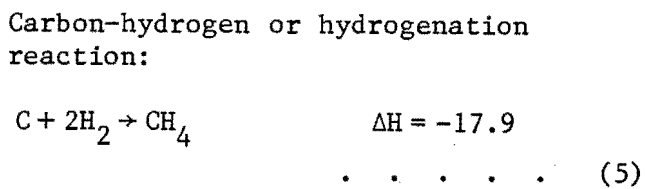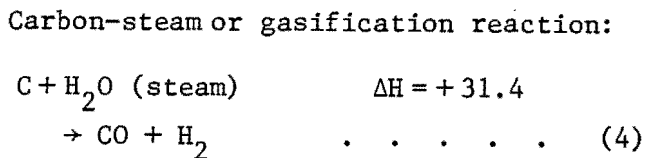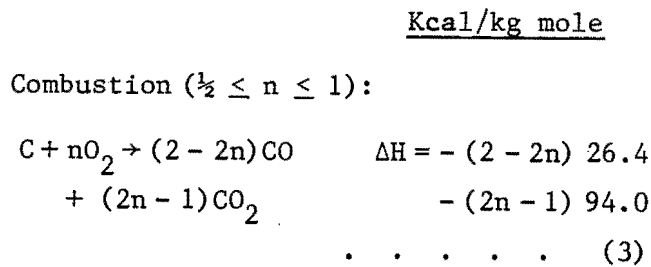
A variation on these equations was presented by Case et al. (1978):

		500 °K	1000 °K	1500 °K	
$O_2 + C \rightarrow CO_2$	$\Delta G^o =$	-94.4	-94.6	-94.7	
	$K =$	2.1×10^{41}	4.7×10^{20}	6.2×10^{13}	(8)
$CO_2 + C \rightarrow 2CO$	$\Delta G^o =$	$+9.9$	-1.5	-15.3	
	$K =$	5×10^{-5}	2.12	164	(9)
$H_2O + C \rightarrow H_2 + CO$	$\Delta G^o =$	$+15.1$	-1.9	-18.9	
	$K =$	3×10^{-7}	2.59	545	(10)
$2H_2 + C \rightarrow CH_4$	$\Delta G^o =$	-7.1	$+4.4$	$+17.9$	
	$K =$	1212	0.11	0.0026	(11)
$NH_3 \rightarrow \frac{1}{2}N_2 + 3/2\ H_2$	$\Delta G^o =$	-1.1	-14.8	-28.9	
	$K =$	3.16	1717	16258	(12)
$NH_3 + C \rightarrow HCN + H_2$	$\Delta G^o =$	$+23.9$	-1.7	-14.6	
	$K =$	5.3×10^{-11}	2.35	134	(13)
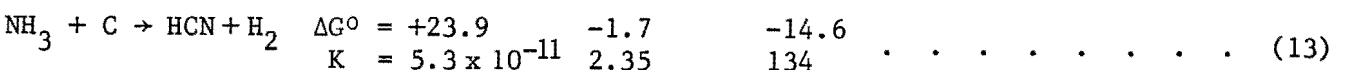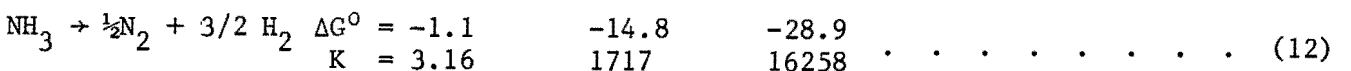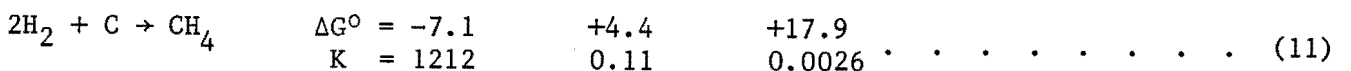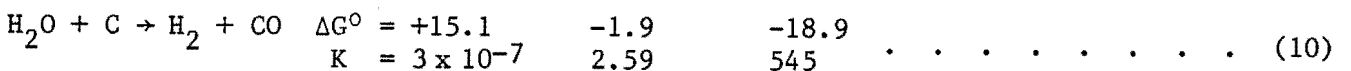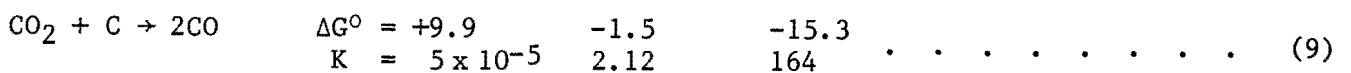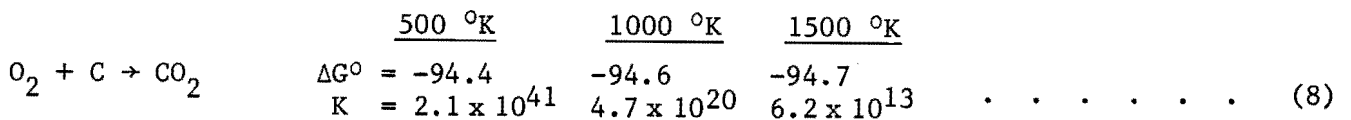
These contain some of the same equations presented by Probstein and Gold (1978); however, Equations 8, 12, and 13 are different. The work by Case et al. (1978) also describes the variations in the rate constants (K) associated with increases in temperature (degrees Kelvin, °K). The free energy of forma- tion has units of Kcal/kg-mole. The thermodynamic equilibrium constants presented by Case et al. (1978) indicate that an increase in temperature in- creases the production of CO, H_2, and HCN. Higher temperatures reduce the quantity of CO_2 produced (Probstein and Gold 1978) based on Equation 3.

Various processes have been developed to take advantage of the different equations presented above. Many of the processes involve a multi-stage reactor which produces a low or medium heating value gaseous product which must be upgraded to produce a high quality pipeline gas (Probstein and Gold 1978; Tetra Tech, Inc. 1976). The quality of the gas steam is a function of the gasifier type (Case et al. 1978).

Process Descriptions

Many different processes are being developed for commercialized production of synthetic fuels, both liquid and gaseous. The gasifiers have been classified into one of four process categories, entrained flow, fixed bed, fluidized bed, and molten medium (Dravo Corp. 1976).

1. The entrained flow gasifiers utilize pulverized coal which is injected through nozzles into a gasifier burner with steam and oxygen or air (Dravo Corp. 1976).

2. The fixed-bed gasifiers utilize coal nuggets (1 to 4 cm) which fall from the top of the gasifier onto grates. The grates are agitated to allow ash to fall into an ash hopper for removal.

3. Fluidized-bed gasifiers also use pulverized coal. The bed of coal and ash is fluidized by an upflow of gas which allows equilibrium to be achieved more rapidly.

4. Molten-medium gasifiers use coal with a maximum size of 0.5 cm; however, the coal is usually pulverized. The pulverized coal is fed into a molten medium, which acts as the heat source.

The Lurgi process is a commercially proven high pressure (24 to 30 atmospheres) process which utilizes crushed coal screened to 0.32 cm to 3.8 cm (Dravo Corp. 1976). The gasifier is a water-walled, fixed-bed unit with several distinct zones. Coal drying and volatilization occur at the top of the unit, and gasification begins in a lower zone where temperatures are at 620°C to 760°C. A lower gasification zone where the coal is in residence for an hour has temperatures between 760°C to 870°C. Char that is left over (14 percent of the original carbon content) is introduced to a combustion zone to supply the heat for endothermic reactions.

The Koppers-Totzek (K-T) process is a commercially proven, low pressure (0.6 atmosphere), high temperature (1920°C) entrained flow process (Tetra Tech, Inc. 1976). The carbon is oxidized by two high temperature burners. The high temperatures instantaneously gasify the coal and convert 96 percent of the carbon. The advantages associated with the K-T process are that only gaseous products are formed, and the process can accept any type of coal.

The Synthane process, being developed by the Pittsburgh Energy Research Center, produces a high-Btu pipeline gas, tars, and char (Dravo Corp. 1976). The gasifier unit is a vertical, high pressure (70 atmospheres) fluidized-bed reactor. The fluidized bed operates at temperatures of 760°C to 980°C. Part of the carbon reacts to become CO and CH_4 and other gaseous fuels which are subsequently converted to methane in the methanator. Approximately 30 percent of the carbon in the feedstock is released as char and tars. Part of the char can be used to produce steam for utility operations; the rest can be sold.

The Hygas process also utilizes a fluidized bed gasifier. The pulverized coal is fed into the Hygas reactor as a slurry with recycled light oil (Probstein and Gold 1978). The first phase of the reactor dries the coal, using the sensible heat of the existing product gas, in a pressure of 80 atmospheres. The second section (first stage hydrogasification) allows the coal

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to react with hot gases (925°C to 980°C) from the countercurrent flow in a temperature of 675°C. In the first stage, hydrogasification, 20 percent of the coal is converted to methane, endothermically. The coal left over falls into the zone where the second stage hydrogasification occurs. The second stage hydrogasification produces methane from the exothermic reaction of the hydrogen with char. Also produced are CO and H_2 by endothermic reactions of steam with char. The remaining char falls into a fluidized bed where a hydrogen rich gas is produced by the reactions of char with steam and oxygen.

Water Requirements

Coal conversion processes consume water (Bostwick et al. 1979; Probstein and Gold 1978). The degree of pretreatment required before process uses depends on the chemical characteristics of the water such as pH, biochemical oxygen demand (BOD), hardness, alkalinity, silica content, total dissolved solids (TDS), and salt species (e.g., Ca^{++}, Mg^{++}, Na^+, Cl^-, $SO_4^=$). The high temperatures associated with conversion of coal to synthetic fuels, however, preclude the need for high quality water for steam generation.

The following figures demonstrate how water consumption for a standard 250 $\times 10^6$ ft^3/day (7 $\times 10^6$ m^3/day) coal gasification plant varies with different processes and different coals. Figure 3 indicates the water consumed by a standard-size synthetic fuel plant for the 15 combinations of three processes and five coals. Figure 4 indicates the process water and Figure 5 the cooling water requirements for five coals.
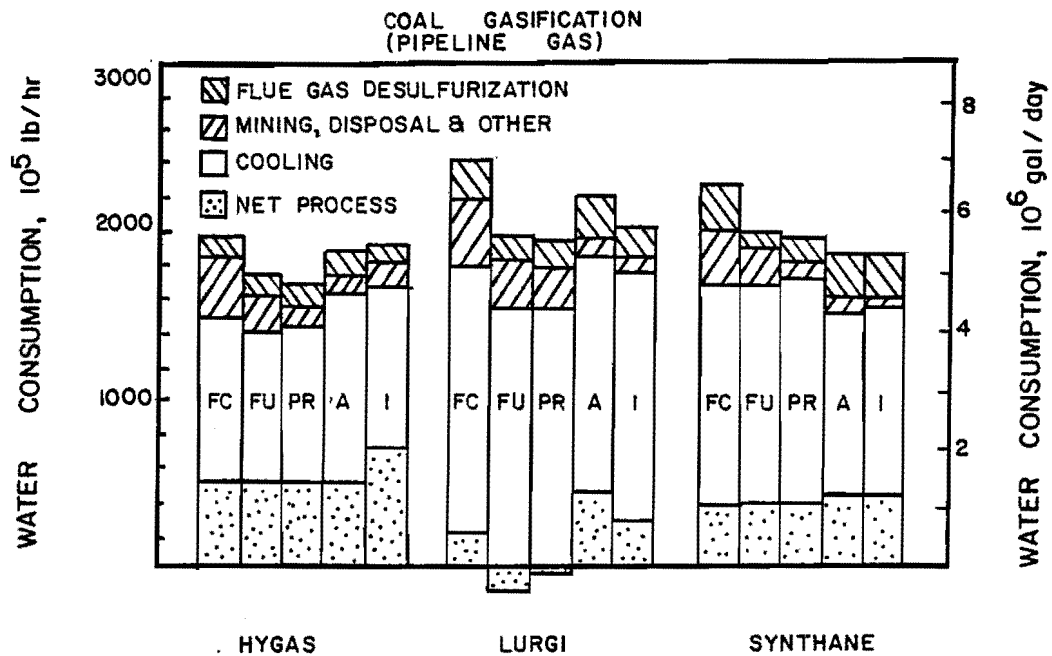
Figure 3. Net water consumption for standard-size coal gasification plants utilizing 18,000 metric tons of coal per day (FC, Four Corners region; FU, Fort Union region; PR, Powder River region; A, Appalachian Basin; I, Illinois Basin) (Probstein and Gold 1978).

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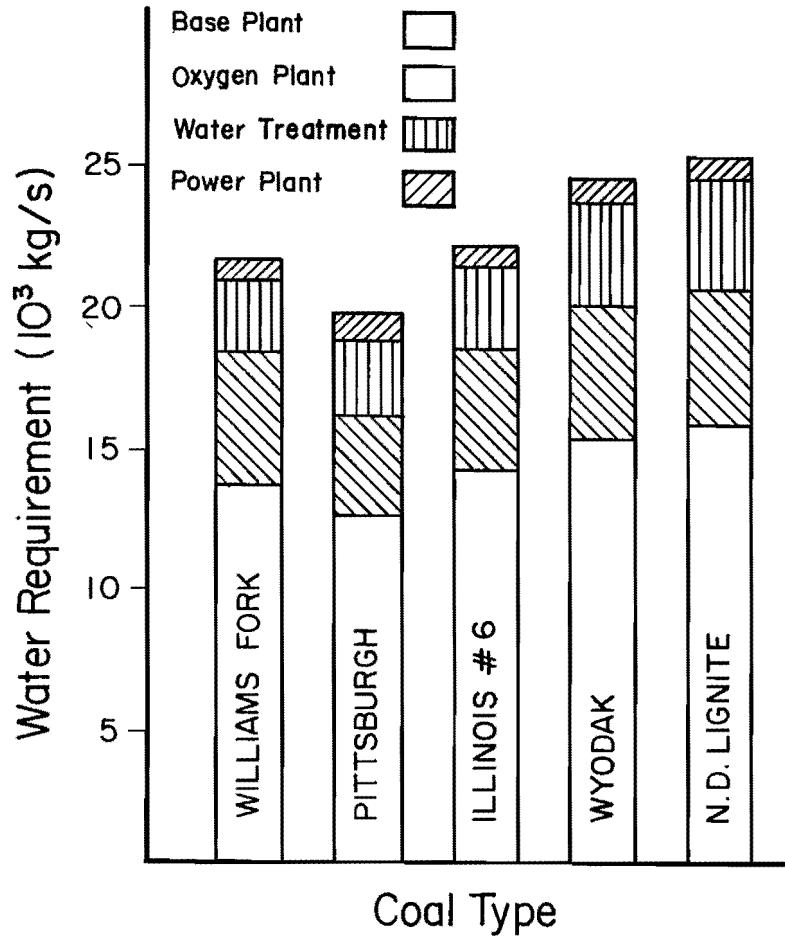
Figure 4. Process water requirements, Synthane plant, 250 million std. cu. ft/day (Chiang et al. 1978).
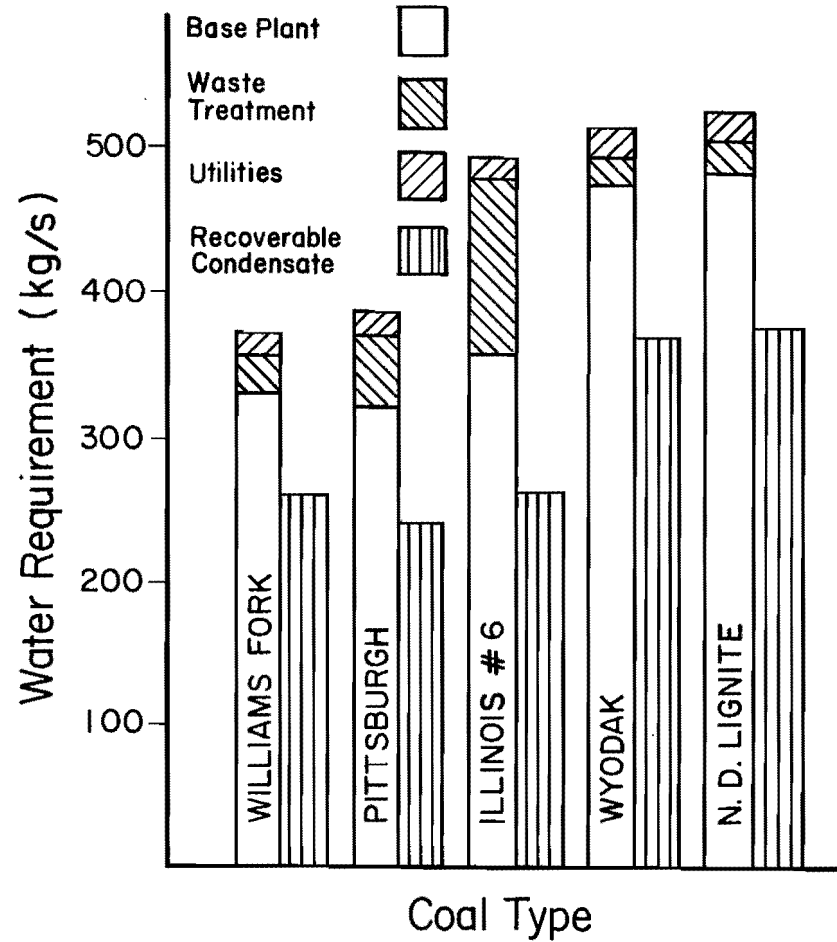
Figure 5. Required cooling water circulation, Synthane plant, 250 million std. cu. ft/day (Chiang et al. 1978).

The amount of water needed to quench the ash output from a coal conversion facility increases with the amount of ash produced (Probstein and Gold 1978). The ash content in the coal exits from the reactor either as bottom ash or fly ash. The division between fly ash and bottom ash in the waste stream depends on the coal conversion process; the Hygas process produces only 12 percent by weight fly ash, and the Synthane process generates 80 percent by weight fly ash.

The bottom ash and slag are usually sluiced to settling ponds or dewatering bins. The net consumption of water includes the water evaporated to quench the ash and also the occluded water in the settled ash sludge (Probstein and Gold 1978). The water required to cool the ash from a temperature of 1070°C to 65°C is between 30 and 60 percent of the weight of ash. The water consumed by the occlusion in the settled ash can be estimated as 50 to 100 percent by weight of the bottom ash quantity.

Alternatively, the fly ash can be handled dry; however, disposal of dry fly ash requires water consumption of between 10 and 20 percent by weight of fly ash for dust control (Probstein and Gold 1978). The quantity of water consumed in the ash handling system will be a function of the amount and type of ash generated by the coal gasification process.

Where gasification facilities require direct combustion of coal to produce power, the sulfur oxides produced must be treated. Flue gas desulfurization uses water in removing sulfur oxides (Probstein and Gold 1978, Chiang et al. 1978). Some common processes involve wet limestone, or hydrated lime, or a combination of the two (Probstein and Gold 1978). The largest single factor determining the flue gas water requirement is the moisture content of the fuel. The other major factor is the sulfur content of the coal. Table 2 shows the quantity of

Table 2. Weight of solids and water of hydration per unit weight of sulfur in lime and limestone sludges, and for crystalline forms of calcium sulfite and sulfate (Probstein and Gold 1978).

Crystal or Process	kg Solid/kg Sulfur	kg Water/kg Sulfur
$CaSO_3 \cdot \frac{1}{2}H_2O$	4.0	0.28
$CaSO_4 \cdot 2H_2O$	5.4	1.13
Lime	5.2	0.38
Limestone	6.6	0.38

scrubber sludge makeup water required for flue gas desulfurization. The quantity of coal fed to the utility boilers varies according to the process utilized; for example, a Hygas unit needs about 2270 metric tons/day of subbituminous coal whereas 3640 metric tons/day are needed for the Synthane process. The water requirements are less if a gas with low or medium heating value for power generation is the objective.

Wastewater Characteristics

The composition of the coal and the type of coal gasification process used affect the effluent wastewater characteristics (Probstein and Gold 1978; Jahnig and Bertrand 1977; Page 1978). The major contaminants found in the process condensate are sulfur, nitrogen, organic compounds, and trace elements (Luthy et al. 1977; Page 1978; Probstein and Gold 1978).

Total consumption of the influent water is possible in the coal gasification process through complete recycling (Case et al. 1978; Probstein and Gold 1978). In designing such a system, the quality of water needed for each of the processes must be considered, and these needs determine the degree of treatment needed before each process. The treat-

ment requirements in turn affect the quantity of wastewater effluent that can be economically recycled.

For analyzing the effects of water quality on the system and of the system on the quality of any effluent waters, it is convenient to recognize three broad groups of contaminants that affect the quality of a water: physical, chemical, and biological. The biological contaminants may lead to biological and algae buildup on the heat exchange surfaces (Porcella 1980).

Physical contaminants that affect the process water stream are solid and liquid suspended matter in the form of ash or char particulates, tars, or oils (Forney et al. 1974). The tar, oils, and particulates entrained in the synthesis gas are highly dependent on the coal type and gasifier operating parameters (Page 1978).

The chemical contaminants are more numerous and difficult to remove (Probstein and Gold 1978) and may be organic or inorganic (Luthy et al. 1977; Milios 1975; Page 1978; Probstein and Gold 1978). The inorganic contaminants most abundant in the coal gasification wastewater are soluble gases, acids and bases, hardness, heavy metals, and soluble salts. The organic contaminants, found chiefly in the foul process condensate are creosols, fatty organic acids, and large quantities of phenols (Jahnig and Bertrand 1977).

The evaporation associated with cooling concentrates the constituents in the makeup water (Jahnig and Bertrand 1977). The chief problem associated with cooling tower effluents is the high concentration of soluble salts, a violation of water quality standards, which may prevent the direct discharge into receiving streams. The gasifier process condensate and the flue gas desulfurization effluent generate other major contaminants (Jahnig and Bertrand 1977; Luthy et al. 1977). The qualities of the foul process condensate and the

flue gas desulfurization effluents (indirectly) are linked to the contaminants present in the off-gas synthesized from the coal (Probstein and Gold 1978).

The foul process condensate quality has been found to be a function of the type of gasifier utilized, defined by the operating variables, and the type of the coal used (Massey et al. 1977). Massey found that with an increase in temperature the product gas became cleaner. The Koppers-Totzek process of coal gasification, which is a high temperature process, produced relatively clean process condensate (Farnsworth et al. 1974, Massey et al. 1977). The Synthane and Lurgi gasifiers, which are relatively low temperature gasifiers, produced highly contaminated effluents.

Process variables that have been found to affect the effluent quality are gas residence time, heatup rate of the coal, and the degree of gas and solid intermixing (Massey et al. 1977). The product gas was not found to be significantly affected by the increased reaction temperature, coal heatup rate, and gas residence time in a Synthane gasifier (alternately varied); however, there were reduced concentrations of chemical oxygen demand (COD), total organic carbon (TOC), and tar production. An increased gas residence time with the other variables held constant showed a decrease in phenol production with only a moderate change in the COD, TOC, and tar parameters.

The process condensate quality characteristics can be estimated from the type of gasifier and the type of coal used (Probstein and Gold 1978). Table 3 presents typical concentrations of various contaminants associated with several processes that have been assessed by Luthy et al. (1977), Massey et al. (1977), Farnsworth et al. (1974), and Forney et al. (1974).

The composition of the coal as determined by the ultimate analysis,

Table 3. Typical condensate quality from various processes (Luthy 1977, Massey 1976, Farnsworth 1975, Forney et al. 1974).

Process	pH	TOC (mg/l)	Phenol (mg/l)	Ammonia-N (mg/l)	Thiocyanate (mg/l)
Synthane ($\simeq 980^{o}$C)					
w/Illinois #6 C Bituminous	8.6	4,300	2,600	8,100	152
w/N. Dakota Lignite	9.2	11,000	6,600	7,200	22
Hygas ($\simeq 980^{o}$C)					
w/Illinois #6 C Bituminous	–	700	270	8,700	260
w/Montana Lignite	–	3,900	1,200	3,400	380
Koppers-Totzek ($\simeq 1900^{o}$C)	8.9	25	–	122	–
CO_2-Acceptor (1020°C)	–	20	2.0	1,220	2.0
Lurgi (1370°C)					
Illinois #6 C Bituminous	–	3,000	2,200	3,100	70
Fine Montana Sub-Bituminous Coal	–	4,500	6,200	2,600	84

has an important effect on the aqueous and gaseous effluents from the gasifier (Malte and Rees 1979). The pollutants resulting from combustion may be a very important consideration because the coal burned in the utility boilers may account for up to 20 percent of the coal used for gasification. The inorganics and trace elements found in coal vary in patterns that cannot be estimated from information on the rank of the coal.

Chlorine and the alkali metals

The volatilization and subsequent condensation of sodium chloride and potassium salts on furnace surfaces during combustion processes have been studied by Halstead and Raaske (1969). The effect of chloride and the alkali metals on coal combustion pollutants is to decrease SO_x and HCl emissions, and to increase corrosion due to NaCl condensation. Combustion with excess oxygen in a pulverized-coal fired plant causes Na_2SO_4 rather than NaCl. The result is that less SO_2 is emitted and less corrosion is apparent due to the decreased amount of NaCl in the process stream. The gas-phase sodium chloride will react with water, under high temperature conditions, to produce sodium hydroxide and hydrochloric acid. The gasifier reaction mechanisms have not been studied at this time; however, chlorine in the coal will yield chlorides in the process condensate (Probstein and Gold 1978).

Gasification of fuel-nitrogen

Gasification of coal has the advantage of converting the fuel-nitrogen primarily into gas phase ammonia which is more easily removed from the product stream than are coal combustion products (Malte and Rees 1979). The mechanism releasing nitrogen from the coal and the forms that the nitrogen takes depend on the type of fuel-nitrogen in the coal, the process parameters such as gas residence time,

particle residence time, temperature, and pressure. Nitrogen oxides could form early in the combustion zone and then subsequently react to form ammonia, cyanide, thiocyanate, gaseous nitrogen, or other compounds.

Fleming (1976) proposed an ammonia forming reaction of nitrogen bound in the char with the reduced atmosphere of the gasification zone

$$2'N' + 3H_2 = 2NH_3. \quad . \quad . \quad . \quad (14)$$
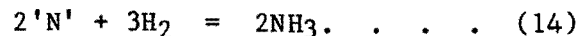
where 'N' represents the fuel-bound nitrogen. Subsequent reactions involving ammonia nitrogen may form hydrogen cyanide, cyanide, or atmospheric nitrogen (Malte and Rees 1977). The molecular nitrogen usually results from the high temperature decomposition of ammonia. Equations 12 and 13 show the ammonia destruction mechanisms as a function of temperature.

Gasification of fuel-sulfur

The sulfur content of coal in the United States ranges from 0.3 to 8 percent (Averitt 1975). Sulfur-containing compounds are found in tars, char, ash and product gas (Magee et al. 1974; Forney et al. 1974; McMichael et al. 1977). Most of the fuel-sulfur appears in the gas phase. In the Synthane process, 71 percent of the fuel-sulfur is gasified, the Koppers-Totzek gasifier decomposes 90 percent of the fuel-sulfur into gaseous compounds.

The extent of desulfurization is a function of the hydrogen concentration (Maa et al. 1975). It has been theorized that hydrogen attacks the binding sites, resulting in the synthesis of H_2S gas (Yergey et al. 1974). The gaseous species found in the product gas are H_2S, carbonyl sulfide (COS), and SO_2. The concentrations of H_2S and COS found in the product gas depend on the amounts of H_2 and CO present in the gasifier. The thermodynamics of the reactions involving H_2, CO and fuel-

sulfur indicate that 96 percent of the gaseous sulfur species will be of the H_2S form and 4 percent of the COS form (Malte and Rees 1979). In the Koppers-Totzek entrained-flow gasifier, 93 percent of the fuel-sulfur becomes H_2S, 6 percent COS, and 1 percent becomes SO_2 (Becker and Murthy 1976). The combustion of coal for the utility boilers will produce substantial amounts of SO_2 (Jahnig and Bertrand 1977). About 20 percent of the total coal is used in the utility boilers, and SO_2 is the primary gaseous pollutant from the fuel-sulfur degeneration.

Phenols and polynuclear aromatics

The major organic carbon contaminants found in the process condensate are polynuclear aromatic hydrocarbons and phenolic compounds (Klein and Barker 1978; Probstein and Gold 1978). The quantity of output will depend on the process conditions in the gasifier. High temperature processes typically produce fewer phenols.

The polynuclear aromatic hydrocarbons (PNA's) produced in coal conversion processes appear in the heavy tar fractions (Klein and Barker 1978). Many of the larger ringed PNA compounds are suspected of being highly carcinogenic and mutagenic. PNA's are not removed sufficiently by conventional wastewater treatment processes. Any PNA's produced have to be segregated and recycled to prevent their discharge to the environment.

The production of phenolic effluents during gasification processing is largely determined by gasification process conditions and quench system operation. The quantity of phenolic compounds produced is extremely variable with even similar processes and coals. However, some processes such as the CO_2 accepter and Koppers-Totzek gasification processes produce significantly less phenolic compounds than most of the low-temperature processes (Probstein and Gold 1978).

Phenols produced in the gasifier are formed during the devolatilization stage of the coal processing. They exit in the raw product gas and are subsequently removed from the gas stream in the quenching operations (Fillo and Massey 1979). The phenols are also highly susceptible to thermal and catalytic decomposition.

There are two basic options for removing the phenolic compounds from the process condensate: the first one is by biological or some other type of destruction process which may include separation and thermal destruction; the other option is to separate the phenols for use as a commercial byproduct (Fillo and Massey 1979). If the phenols are to be separated for commercial sale, gasifier conditions may be altered to enhance phenolic compound production without adversely affecting the primary gaseous products from the gasifier. Efficient biological oxidation of the phenolic compounds will depend on the types of phenolic compounds generated, ammonia concentrations, fatty acid, cyanide, and thiocyanate concentrations (Jahnig and Bertrand 1977). Ammonia interferes with the biological oxidation of phenols, and vice versa. Thiocyanates are difficult to destroy and interfere with the oxidation of the phenolic compounds. Steam volatile phenols can be removed completely whereas other phenols and fatty acids will be removed to between 5 and 10 percent of their original concentration.

Trace elements

Coals vary widely in trace element content. Many of the trace elements found in coal are extremely toxic. The trace elements found in the waste streams from a gasifier vary according to the characteristics of the coal, the operating conditions of the gasifier, and the methods used for quenching the gas stream and ash (Jahnig and Bertrand 1977, Anderson et al. 1979). Volatile metals are carried in the gas

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stream and have to be separated out of the gas (Probstein and Gold 1978). The metals not carried in the gas stream are found in one of the ash streams, and proper care is needed to prevent leaching of the metals from the solid waste into the environment.

Some trace elements have appreciable volatility under the reducing conditions of a coal gasifier (Jahnig and Bertrand 1977). Some of these may be reduced to metal in the presence of carbon. Of particular concern are mercury, cadmium, selenium and zinc, whose boiling points are lower than the 900°C which is a typical gasification temperature. The halides are also volatile in the range of temperatures found in a gasifier.

Hydrogen and carbon monoxide present in the gasifier can react with the metals to take on different forms. Hydrogen combines with elements such as arsenic, selenium, and some others to form hydrides, whereas carbon monoxide reacts with iron, nickel, and cobalt to form volatile carbonyls (Jahnig and Bertrand 1977). Compounds of alkali metals have a significant vapor pressure at the temperatures encountered in a gasifier.

An estimate of the quantity of trace elements for one coal, along with the percent volatility, is presented in Table 4. The amount of trace elements is extremely variable from within and among different ranks of coal. From the data shown in Table 4 the quantity of the different trace elements entering the gas stream is strongly dependent on both the quantity and volatility of the trace elements. The volatility is a function of the operating conditions within the gasifier, but the values shown in Table 4 are generally typical of gasifier conditions (Attari et al. 1973).

Anderson et al. (1979) analyzed the transformations that arsenic-, selenium-, boron-, lead- and mercury-

containing compounds undertake during gasification. The compounds may deposit or be removed in the quenching, sulfur removal, CO_2 removal, or the catalytic water-gas shift methanation phase.

Arsenic concentrations found in U.S. coal range from 0.5 to 93 ppm, with an average of 14 ppm (Anderson et al. 1979). Arsenopyrite is the major form of arsenic found in coal (Duck and Himus 1951). The decomposition of arsenopyrite into pyrrhotite and metallic arsenic begins to proceed under gasification temperatures of 550°C and proceeds rapidly at temperatures of greater than 750°C (Anderson et al. 1979). Hygas process data indicate that arsenic is not lost until the coal

Table 4. Estimated volatility of trace elements (Jahnig and Bertrand 1977).

Typical Coal Parts/Million		% Volatile[a]	kg/day[b]
Cl.....	1,500.....	90+.....	14,700
Hg.....	0.3.....	90+.....	3
Se.....	1.7.....	74	14
As.....	9.6.....	65	68
Pb.....	5.9.....	63	40
Cd.....	0.8.....	62	5
Sb.....	0.2.....	33	1
V	33.....	30	108
Ni.....	12.....	24	31
Be.....	0.9.....	18	2
Zn.....	44..... e.g.	10	48
B	165..... e.g.	10	180
F	85..... e.g.	10	94
Cr.....	15.....	nil	nil

[a]Volatility based mainly on gasification experiments (14) but chlorine taken from combustion tests, while zinc, boron, and fluorine taken at 10 percent for illustration in absence of data.

[b]Estimated amount volatile for 10,900 metric tons/day of coal to gasification.

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reaches the steam-oxygen gasification stage, where temperatures range from 900°C to 1010°C (Attari et al. 1976).

After volatilization, the stable forms of arsenic compounds are As_4, AsH_3(arsine), and As_2 (Anderson et al. 1979). Table 5 indicates the form and distribution of some trace elements in the raw product gas from the Lurgi, Hygas, and Koppers-Totzek processes. The values shown in the table indicate that at high temperatures and low pressures the form of elemental arsenic with negligible amounts of arsine is favored.

The arsenic compounds in the raw product gas are removed in part or whole in the gas quenching, sulfur removal, CO_2 removal, and methanation systems (Anderson et al. 1979). The elemental sulfur, which will exist as suspended solids, is removed by the gas quenching system. The arsenic in arsine form has very low solubility in water, and less than 1.0 percent of the arsine is removed by the gas quenching operation. The removal of arsine in the sulfur removal system depends on the solvent system used to remove the sulfur stream. Physical solvent systems should remove the arsine, whereas chemical solvents remove negligible amounts. The residual arsine in the product gas stream is generally removed in the CO_2 removal process. Exceptions are the Lurgi and Hygas processes using chemical solvents. There, the arsine separated from the product gas is vented with the CO_2; concentrations of arsine in the vented gas for the Lurgi and Hygas processes range from 33 to 212 $\mu g/m^3$. Arsine that passes through the CO_2 removal system is catalytically changed to elemental arsenic and removed in the gas quench system following the methanation process.

Selenium concentrations found in U.S. coals range from 0.45 to 7.7 ppm, with an average of 2.25 ppm (Anderson et al. 1979). The primary form of selenium found in the coal is seleno-

Table 5. Form and distribution of select trace elements in raw gasifier product gas (Anderson et al. 1979).

Process	Lurgi	HYGAS	Koppers-Totzek
Operating Pressure, atm	20	80	2
	g-mol/g-mol raw product gas		
AsH_3	1.71×10^{-7}	2.79×10^{-7}	2.47×10^{-15}
As_4	1.56×10^{-7}	1.71×10^{-7}	9.56×10^{-12}
As_2	3.20×10^{-9}	1.77×10^{-9}	1.20×10^{-6}
H_2Se	1.36×10^{-7}	1.13×10^{-7}	3.68×10^{-7}
$B(OH)_3$	4.88×10^{-5}	2.43×10^{-5}	7.92×10^{-5}
PbS	8.13×10^{-14}	2.05×10^{-14}	7.62×10^{-7}
$PbCl_2$	1.11×10^{-11}	2.46×10^{-11}	1.30×10^{-12}
PbO	2.81×10^{-25}	7.65×10^{-26}	2.31×10^{-9}
Pb	6.94×10^{-16}	1.42×10^{-16}	1.67×10^{-6}
Hg	8.55×10^{-9}	1.03×10^{-8}	1.28×10^{-8}

pyrite. Approximately 70 percent of the selenium is volatilized from the coal during gasification, although some processes volatilize as little as 30 percent (Jahnig and Bertrand 1977; Anderson et al. 1979).

The mechanism for volatilization of selenium from coal has been postulated as decomposition of $2FeSeS \rightarrow 2FeS + Se_2(g)$ (Anderson et al. 1979) followed by further reactions that produce H_2Se, a thermodynamically preferred form, from H_2 and Se_2. The temperatures within gasifiers are high enough so that the selenium present in the raw product gas is almost exclusively H_2Se.

Hydrogen selenide removal in the quench system is expected to be negligible (Anderson et al. 1979). The predicted concentrations of hydrogen selenide in the process condensate is less than 0.07 ppm, based on the solubility of H_2Se in water. Hydrogen selenide would rather be expected to be removed in the sulfur removal system, either using the physical or chemical solvent systems. Residual H_2Se in the product gas is removed in the CO_2 removal processes and vented with the CO_2 gas to the environment.

The boron content of U.S. coals ranges between 2 and 224 ppm, with an average of 67 ppm (Anderson et al. 1979). Boron is found in coals in a chelated form, and between 50 and 100 percent of the boron is expected to be volatilized during coal gasification. The Koppers-Totzek process is expected to volatilize all of the boron, whereas the Hygas and Lurgi processes are expected to volatilize about half of the boron.

The chelated boron in the gasification environment produces BH_3, especially at high temperatures and with hydrogen present in the gasifier (Anderson et al. 1979). The thermodynamically preferred form of boron is $B(OH)_3$. Equilibrium is assured at all

gasification temperatures within a gasifier with production of $B(OH)_3$, and the boron exits in this form in the product gas stream. The $B(OH)_3$ in the gas stream is removed in the gas quench system.

The average lead concentration found in U.S. coals is 39 ppm, and is believed to generally exist initially in the form of PbS (Anderson et al. 1979). The volatility of the lead in the coal depends on the vapor pressures of the various lead compounds at various temperatures found in the gasifier. The high-temperature Koppers-Totzek Process (1950°C) is expected to volatilize all of the lead in the coal and produce lead compounds in the product gas.

The vapor pressures of the PbS, $PbCl_2$, PbO, and Pb found in the product gas are low enough at the temperatures in the quenching system that the compounds will be solidified. The quenching system should thus remove the lead compounds (Anderson et al. 1979).

The concentration of mercury found in coal ranges from 0.02 to 1.6 ppm, with an average concentration of 0.2 ppm (Anderson et al. 1979). The temperatures within a gasifier will volatilize the mercury. The thermodynamically preferred form of mercury in the product gas is Hg(g).

The removal of mercury from the product gas stream is negligible in the quenching system and the chemical-type solvent sulfur removal process (Anderson et al. 1979). Mercury removal in the physical solvent sulfur removal process depends on the solubility of mercury and the temperature of the solvent. Temperatures of -43°C and 7°C, typical of the Lurgi-Rectisol and Selexol processes, respectively, will condense 56 and 99 percent of the Hg, respectively. The CO_2 removal system removes approximately 25 percent of the Hg in the H_2S-free gas stream.

The research objectives were accomplished in four integrated phases: 1) survey of existing carbon-shale deposits; 2) sample acquisition and characterization; 3) experimental gasification of subsamples; and 4) pollutant analysis. The results are reported in the next chapter.

Phase I: Survey of Existing Carbon-Shale Deposits

Surface deposits of carbonaceous shales in Utah were located on Utah Geological and Mineralogical Survey Maps of the Surface Geology in Utah. The geological literature was searched for references on the relationship between coal and carbon-shales. A better understanding of this relationship helps in assessing the extent of carbon-shale deposits in Utah.

Phase II: Sample Acquisition and Characterization

Samples used

The shale samples used in the analyses came from Summit and Carbon Counties of Utah. The coal was a commercial Utah coal and the sludge came from an oxidation ditch of the Hyrum City sewage treatment plant. Approximately 12 percent of the area of Utah is underlain by carbon shales.

Analysis of samples used

The samples selected were sent to Commercial Testing and Engineering Co., 16775 East 51st Ave., Denver, Colo., for ASTM characterization by proximate and ultimate analyses. From the carbon shale samples analyzed,

two were picked (based on Btu values per pound) for experimental gasification. A municipal sludge was also used for experimental gasification. The gasification of coal was used for reference or control.

Phase III: Experimental Gasification

The objective of the gasification study was to compare the gas outputs and wastewater qualities from the various materials sampled. For this comparison, it was necessary to select a gasification system, and select standard values for the operating variables so that all the carbon sources tested would be treated equally. The standard values should represent near optimal performance, maximum production of fuel gas, so that the test would be made under operating conditions close to what would be expected commercially.

The choice of a gasification system is shown in Figure 6. System optimization involved selected values for 1) the duration of the test run, 2) the operating temperature, 3) oxygen input, and 4) the quantity of water injected to produce steam. Once optimum values were selected for these operating variables, runs were replicated to verify gas output and to generate sufficient wastewater to run the analyses indicated in Table 6.

As determined by process optimization, the environmental conditions were at a temperature of $1070°C$ and a subsample reaction time of 30 minutes. The quantities of oxygen and water injected into the experimental gasifier were varied for each sample. Oxygen was varied from 0.2 to 1.5 gram O_2 per

gram sample, and water was varied between 0 and 2 grams water added per gram of sample.

The quantity of oxygen was varied by increasing the oxygen pressure (5 to 40 atm) to the injection tube area (see Figure 6). The amount of water injected into the reactor for producing the steam used in gas production was varied from 0 to 3 milliliters per gram of subsample; however, no increase in fuel gas production was achieved by using more than 1.2 milliliters of water per gram of subsample.

The initial gasification experiments indicated that higher temperatures produced more and higher heating value fuel gas. However, the Inconel 600 reaction tube used in the gasification experiments could not accept temperatures above 1080°C, due to metal oxidation and pressure-temperature stress failure. A temperature of 1070°C was used as the reaction temperature for all samples.

The reaction time was selected to insure maximum conversion of the samples into gaseous products and ash. A pressure gage and gas output were used to determine the amount of time needed to completely convert the subsamples into gaseous products. The pressure gage indicated an increase in the internal pressure of the reaction tube, thus the increase in gaseous products. The quantity of gas produced during the reaction was also used to insure that an increase in time would not affect the amount of gas output substantially. The standardized time used for all samples and the subsample runs was 30 minutes which insured complete or nearly complete conversion of the subsamples into gaseous products and ash.

The experimental procedure for gasifying the subsamples was as follows: (Circled numbers refer to Figure 6 schematic.)

1. Subsamples of each sample (coal, two shales and sludge) were weighed to 1.000 gram each.

2. A subsample was placed into the injection tube, ①. Several subsamples were run consecutively to minimize cross contamination.

3. Oxygen was supplied to the injection tube at a specific pressure ②.

4. The straight-through injection valve ③ was then opened momentarily to blow the sample into the reaction tube ④.

5. A specific volume of water was injected ⑦ into the reactor tube to produce steam for the reaction.

6. After 30 minutes the bleeder valve ⑥ was opened to allow gaseous products and waste steam to flow into a cold trap ⑤ with dilution water.

7. The gas was collected into a 9 liter bottle ⑧ containing 2.5 percent HCl to minimize gas solubility. The volume of liquid was measured after the hydrostatic head was adjusted to zero to determine the quantity of gas produced in the reactor.

The first subsample of a sample run was wasted to reduce contamination from the previous run and from air. Periodically the system was flushed with oxygen, heated at the gasification temperature for 4 hours to oxidize any residual, cooled, and internally cleaned by dismantling the apparatus and rinsing with deionized water.

Phase IV: Pollutant Analysis

After the 1 gram subsample had been in the reaction chamber for 30 minutes, the product gases were bled through a cold trap containing various amounts of dilution water to trap the different pollutant constituents. A summary of the tests performed on the gas, wastewater and samples is shown in Table 7.

Table 6. Procedures for analysis performed at the Utah Water Research Laboratory.

Sample	Analysis	Method
Carbonaceous Shales and Coal	Proximate and Ultimate Analysis	ASTM D3172-73[a] ASTM D3176-74
Synthesis Gas		Gas Chromatography (Similar to 511 B)[b]
	Hydrogen (H_2)	Molecular Sieve-5A Column
	Carbon Monoxide (CO)	Molecular Sieve-5A Column
	Methane (CH_4)	Porapak "R" Column
	Carbon Dioxide (CO_2)	Porapak "R" Column
		Matheson Toxic Gas Detector[c] (Model 8014-Kitagawa)
	Sulfur Dioxide (SO_2)	#103 C Detector Tube[c]
	Hydrogen Sulfide (H_2S)	#120 C Detector Tube[c]
	Nitrogen Oxides (NO_x)	#174 Detector Tube[c]
Condensed Process Stream after Reaction	Trace Metals (Hg,Cd,Pb,As,Cr, Se,Zn,Sr)	Metals by Atomic Absorption Spectrophotometry (Part 300)[b]
	Ammonia Nitrogen	Phenate (No. 418 C)[b]
	Phenols	Chloroform Extraction (No. 510 C)[b]
	Nitrites	Autoanalyzer (No. 605)[b]
	Nitrites and Nitrates	Autoanalyzer (No. 605)[b]
	Total Organic Carbon	Combustion-Infrared (No. 505)[b]
	Mutagenicity	Ames Test[d]
Carbonaceous Shales	Trace Metals	ASTM D 3684-78[a]
Coal	Trace Metals	ASTM D 3684-78
Carbon Shale Ash	Trace Metals	ASTM D 3682-78
Coal Ash		ASTM D 3682-78

[a]American Society for Testing Materials, 1978 Annual Book of ASTM Standards, Part 26, 906 p.

[b]Standard Methods, 14th ed., 1193 p. 1975.

[c]Matheson Catalog 50, 1978.

[d]Ames, McMann, and Yamasaki, Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammalian-Microsome Mutagenicity Test, Mutation Research, 31, p. 347-364, Elsevier Scientific Publishing Company, Amsterdam, 1975.
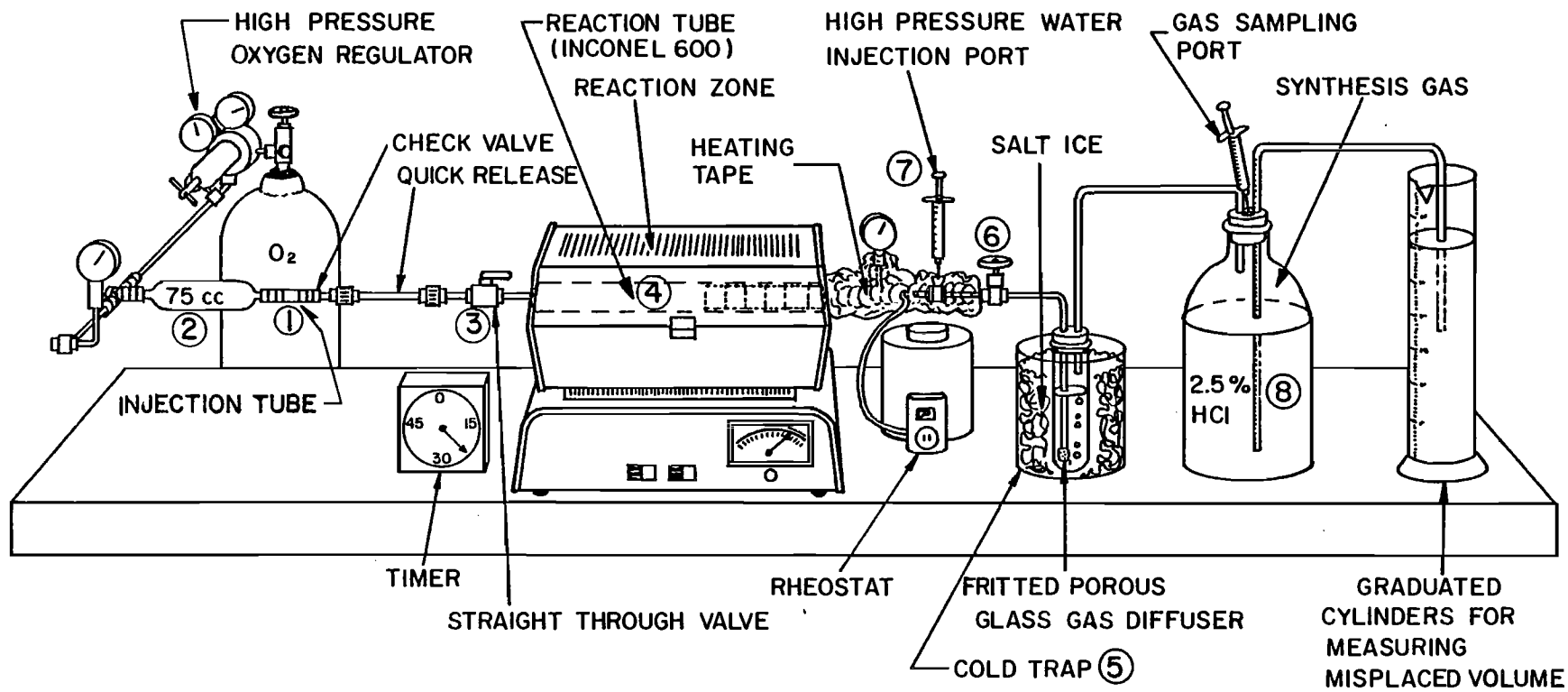
Figure 6. Schematic of batch operated carbon gasification unit.

Table 7. Proximate and ultimate analyses of samples.

	Proximate Dry Basis		Ultimate Dry Basis	
Bituminous Coal 5.19% Moisture				
% Ash	7.51	% Carbon	72.87	
% Volatile	46.19	% Hydrogen	5.49	
% Fixed Carbon	46.30	% Nitrogen	1.34	
Kcal/kg	7214	% Chlorine	0.08	
% Sulfur	0.60	% Sulfur	0.60	
		% Ash	7.51	
		% Oxygen (diff.)	12.11	
Shale #1 6.16% Moisture				
% Ash	34.25	% Carbon	52.78	
% Volatile	19.75	% Hydrogen	2.15	
% Fixed Carbon	46.00	% Nitrogen	1.33	
Kcal/kg	4520	% Chlorine	0.02	
% Sulfur	0.64	% Sulfur	0.64	
		% Ash	34.25	
		% Oxygen (diff.)	8.83	
Shale #6 3.49% Moisture				
% Ash	54.35	% Carbon	30.69	
% Volatile	22.82	% Hydrogen	2.23	
% Fixed Carbon	22.83	% Nitrogen	0.77	
Kcal/kg	2660	% Chlorine	0.03	
% Sulfur	0.35	% Sulfur	0.35	
		% Ash	54.35	
		% Oxygen (diff.)	11.58	
Sludge 9.90% Moisture				
		% Carbon	18.2	
		% Nitrogen	5.50–6.36	
		% Phosphorus (P_2O_5)	3.33	

Operational Problems

Several problems arose with the design and operation of the laboratory scale gasifier. The initial months in the experimental gasification phase of the project were spent debugging the experimental apparatus. Most of the problems occurred as a result of the temperature and pressure stresses.

Temperatures of over 1000°C and pressures of 30 atmospheres precluded the use of stainless steel in the reactor. Inconel 600 was tried even though no data were available on allowable stresses at temperatures over 870°C. The first Inconel 600 tube used failed at a temperature of 1125°C (with an internal pressure of 30 atmospheres). Oxidation of the metal also occurred at 1125°C. Afterwards, the operating temperature was reduced to 1070°C. Some creeping still occurred after 100 runs, but amounts were within acceptable limits.

The coal and low grade carbon sources were pulverized and aspirated into the gasifier with oxygen. Several problems arose when loading the apparatus. If the pulverized samples were smaller than the #200 sieve, back explosions occurred and damaged the pressure gages, valves, and quick release fittings. Samples coarser than the #120 sieve were used in the gasifier to prevent explosions. The high temperatures and pressures degraded the stainless steel valves and fittings, requiring periodic maintenance and replacement to prevent gas from leaking from the reactor.

Steam was produced by injecting water through a special double septum valve. The septums degraded rapidly as a result of the high temperatures. When more than 1.5 cc of water was injected, the pressures caused by the steam made the injection difficult and increased the vaporization temperature. The reaction tube and all fittings between the inlet and outlet valve had to be heated to prevent steam condensation.

RESULTS AND DISCUSSION

Location, Acquisition, and Characterization of Potential Carbon-Shale Deposits in Utah

While carbonaceous shales are known to be widespread in Southern and Eastern Utah, no one had ever systematically mapped the deposits. The first phase of this study used geologic mapping of the state to identify coal bearing, marine and non-marine sandstone, and shale formations, and from this information the potential shale deposit areas shaded in Figure 7. This mapping was followed by extensive field exploration to locate deposits.

Samples of the located deposits were then acquired and examined for the purpose of characterizing the range of carbonaceous shales indigenous to Utah. The samples were collected from the overburden of abandoned coal mines or from road cuts. The counties where the carbon-shale samples were taken were Summit, Carbon, Duchesne, and Emery. The samples were chosen to represent a broad range of heating values.

The reference coal and the carbon-shale samples were characterized using ASTM procedures for proximate and ultimate analyses, performed by an independent testing laboratory in Denver, Colorado.[1] The results are shown in Table 8.

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[1]Commercial Testing and Engineering Co., 10775 East 51st Ave., Denver, Colorado.

The moisture values for the various samples varied within the range expected in surface deposits with seasonal changes. The important differences among the samples are in the percentages of ash and carbon. The shales essentially have between 30 and 60 percent dry ash, whereas the coal sample has approximately 7.5 percent dry ash. The greater ash content in the shales can be explained by the geologic formation of the shale deposits in marine environments, where inorganic materials are continually deposited, or in areas where inorganic material was deposited by some other method. Primarily because of its lower ash content, the carbon content of the coal was substantially greater than that of any of the shales tested. Another cause of this difference is that the coal was formed from peat which is a much more concentrated carbon deposit than are the sorts of carbon deposits found in a marine environment where greater varieties of sediments are introduced.

The sulfur content of the coal and all of the shale samples are typical of western coals. Sulfur content is extremely important because it determines the amount of gaseous sulfur given off during burning.

The nitrogen content in the samples varied between 0.74 to 1.34 (dry) percent with very little difference between the coal and #1 shale. The nitrogen content in coal is usually of the organic pyridine, pyrrole, quinoline, and amine types (Smoot 1979). In low-temperature gasification processes, the nitrogen usually exits the gasifier as ammonia and cyanide.

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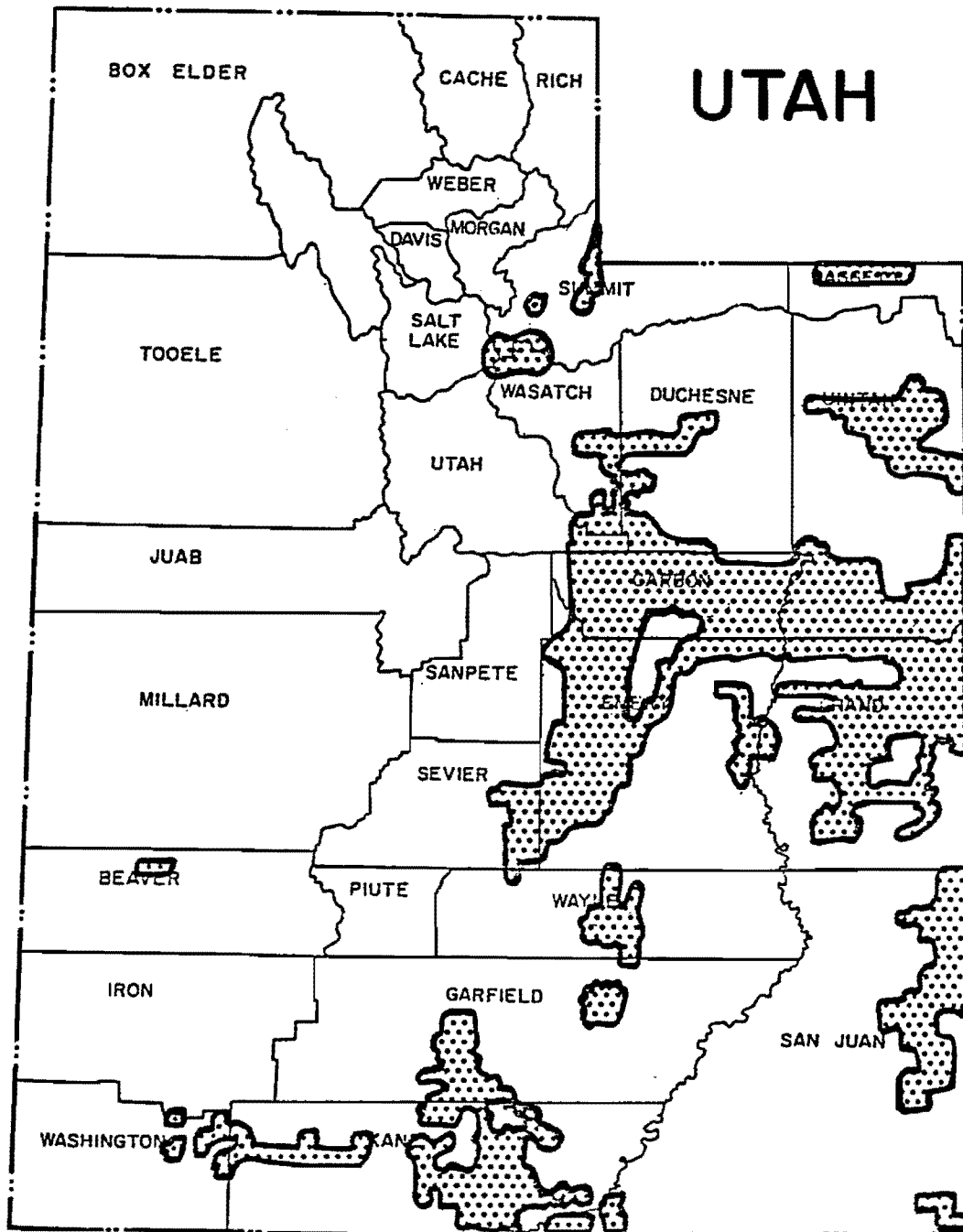
Figure 7. Existing probable lignite shale deposits in Utah.

Table 8. Water and oxygen used in the experimental gasifier compared with typical steam and oxygen requirements of other gasifiers.

Sample Type	Oxygen Input Mass/Mass Sample	Water Input Mass/Mass Sample
High Volatile Bituminous Coal[a]	0.91	1.2
#1 Carbon Shale[a]	0.82	1.2
#6 Carbon Shale[a]	0.74	0.7
Municipal Sludge[a]	0.33	0.5
Utah Bituminous Coal (Medium Btu-Gasifier)[b]	0.61-1.03	0.41-0.89
Williams Fork Coal (Synthane Gasifier)[c]	–	0.52
Illinois No. 6 Coal (Synthane Gasifier)[c]	–	1.15

[a]Samples used in experimental gasification.

[b]Coal used in process design study by Coates (1976). The values reported are a range of oxygen and steam conditions used in study.

[c]Estimated process water requirement in a Synthane gasifier (Chiang et al. 1978).

The concentration of chloride in a sample is important because of the corrosive effects of condensed NaCl. The chloride concentration in the coal was four times that of #1 shale.

The type of carbon found in the samples is important because of the way the carbon reacts in a gasifier. The carbon associated with the volatile fraction is highly reactive at temperatures between 760°C and 925°C (Probstein and Gold 1978). The fixed carbon or residual char is less reactive, requiring temperatures above 1090°C for conversion. The coal and #1 shale samples have virtually the same concentration of fixed carbon.

Samples used for gasification were the coal sample (#8), and shale samples #1 and #6. A sludge sample acquired from a municipal treatment plant oxidation ditch was also gasified.

Experimental Gasification

The initial gasification experimentation was to choose a set of optimum conditions that could be used to compare the results from the sample gasifications. The parameters varied were temperature, oxygen input, and water input.

Temperature was varied from 650°C to 1200°C. The heating value of the fuel gas increased with temperature in part because increases of carbon monoxide (CO) were observed. The upper limit to the temperature which could be used was determined by the furnace materials. Temperatures above 1120°C caused oxidation of the Inconel 600 metal pipe used as the reaction chamber. A temperature of 1070°C was used for maximum conversion of the samples into gaseous fuels without stress failure and oxidation of the reaction tube.

Oxygen was the next parameter varied to maximize gas production (5 to 40 atmospheres). Originally helium gas was used to increase the pressure within the reactor to enhance methane production. However, the allowable reactor stress prevented increasing pressures beyond those created by the oxygen and carbon steam reactions (50 atmospheres). The fuel gas produced

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was qualitatively and quantitatively compared at various quantities of oxygen input.

The amount of water used to optimize the production of gaseous fuels was varied (from 0 to 2 ml/gram of coal). After the optimum quantity of water was determined at a specific input of oxygen, the oxygen was varied to determine if better results could be obtained. The quantity and fuel value of the product gas was not improved perceptibly. The time used for assuring complete conversion of the sample into gaseous products was determined by monitoring a pressure gage and measuring the time required until no further pressure increases occurred within the reactor. The measured time was 20 minutes, but the selected time was increased to 30 minutes to assure maximum conversion of the carbon in the samples.

The optimum oxygen and water inputs vary according to the type of process used for gasification, the gaseous products desired, and the carbon source used. The data in Table 8 compare the quantities of water and oxygen used for the samples gasified with the water and oxygen used in a typical medium-Btu gasifier and Synthane gasifier.

The amount of oxygen used in the experimental gasifier for the coal and two shales correlates well with the values reported by Coates (1976). Gasification of the municipal sludge required substantially less oxygen. The gas output from the gasification of the municipal sludge, however, was only 661 cc per gram of sludge, compared to 1071 cc for the #6 shale, 2154 cc for the #1 shale, and 2500 cc for the coal. Table 9 presents a summary of the gasification results from coal, sludge, #1 shale, and #6 shale.

The total heating values for the gas produced from the gasification of the high-volatile Utah bituminous coal increased with water input. The maximum output of gas (corrected to standard pressure and a temperature of 23°C) was produced with a water input of 1.2 grams per gram of coal. The differences between the total heating values for coal in Table 9 are significant to the $\leq$ 1 percent level. The composition of the synthetic gas produced from the gasification of coal is shown in Figure 8. The concentration of hydrogen increased significantly at the $\leq$ 5 percent level, whereas the concentration of carbon monoxide (CO) decreased significantly with the increased addition of water. The increased concentrations of hydrogen (H_2) must result from hydrogen producing reactions within the reactor that do not produce CO as the carbon-steam reaction (Equation 4). The water-gas shift reaction (Equation 6) will produce H_2 at the expense of CO; however, the quantity of CO_2 will increase. The data in Table 10 show a substantial increase in the volume of CO_2 with an increase in water input. The increase of CO_2 gas is approximately equal to the difference between the CO and H_2 gas output.

The quantity of hydrogen produced with no water input in each of the samples gasified could be explained by either the initial moisture in the samples or by the degradation of hydrogen within the samples. The proximate and ultimate analyses, Table 7, show that coal has the greatest amount of hydrogen with 5.49 percent, the #1 and #6 shales have 2.02 and 2.15 percent, respectively. The greatest percent moisture was found in the #1 shale (6.16), with coal having 5.19 percent and #6 shale having 3.49 percent moisture. On the basis of moisture content and percentage hydrogen in the samples, the percentage of hydrogen appears to have the most effect on the quantity of H_2 gas produced without any water input. The coal produced 400 cc of H_2 gas whereas #1 and #6 shales produced 210 and 180 cc, respectively. If the initial moisture content has a substantial effect on the amount of H_2 gas, the #6 shale would have produced sub-

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Table 9. Summary of the experimental gasification results of #8 coal, #1 shale, #6 shale, and sludge.

Sample	Dry Heating Value of Sample		Water	Gas Volume[c] Produced	Higher Heating Value of Gas Produced[c]		Total Heating Value of Gas Produced[c]	
	Kcal/kg	Btu/lb[a]	mass/mass sample	cc/gram sample	$Kcal/m^3$	Btu/scf	Kcal/kg sample	Btu/lb sample[b]
High Volatile Utah Bituminous Coal	7210	13,000 99.1%	0.052	1180	2700	300	3185	5,733
			0.752	1990	2880	320	5731	10,316
			1.252	2502	2860	320	7157	12,883
#1 Carbonaceous Shale	4520	8130 122.6%	0.064	920	2220	250	2042	3,676
			0.764	1720	2530	285	4352	7,834
			1.264	2154	2570	290	5536	9,965
#6 Carbonaceous Shale	2660	4790 77.2%	0.035	736	2080	230	1531	2,756
			0.735	988	2080	230	2055	3,699
			1.235	1123	1830	205	2055	3,699
Municipal Sludge	--	--	0.785	660	1100	123	726	1,307

[a]Estimated from the proximate and ultimate analysis results.

[b]Estimated from quantity and composition of fuel gas produced.

[c]Gas volumes are standardized to 760 mn Hg and 23°C, and represent a mean of three replicates.
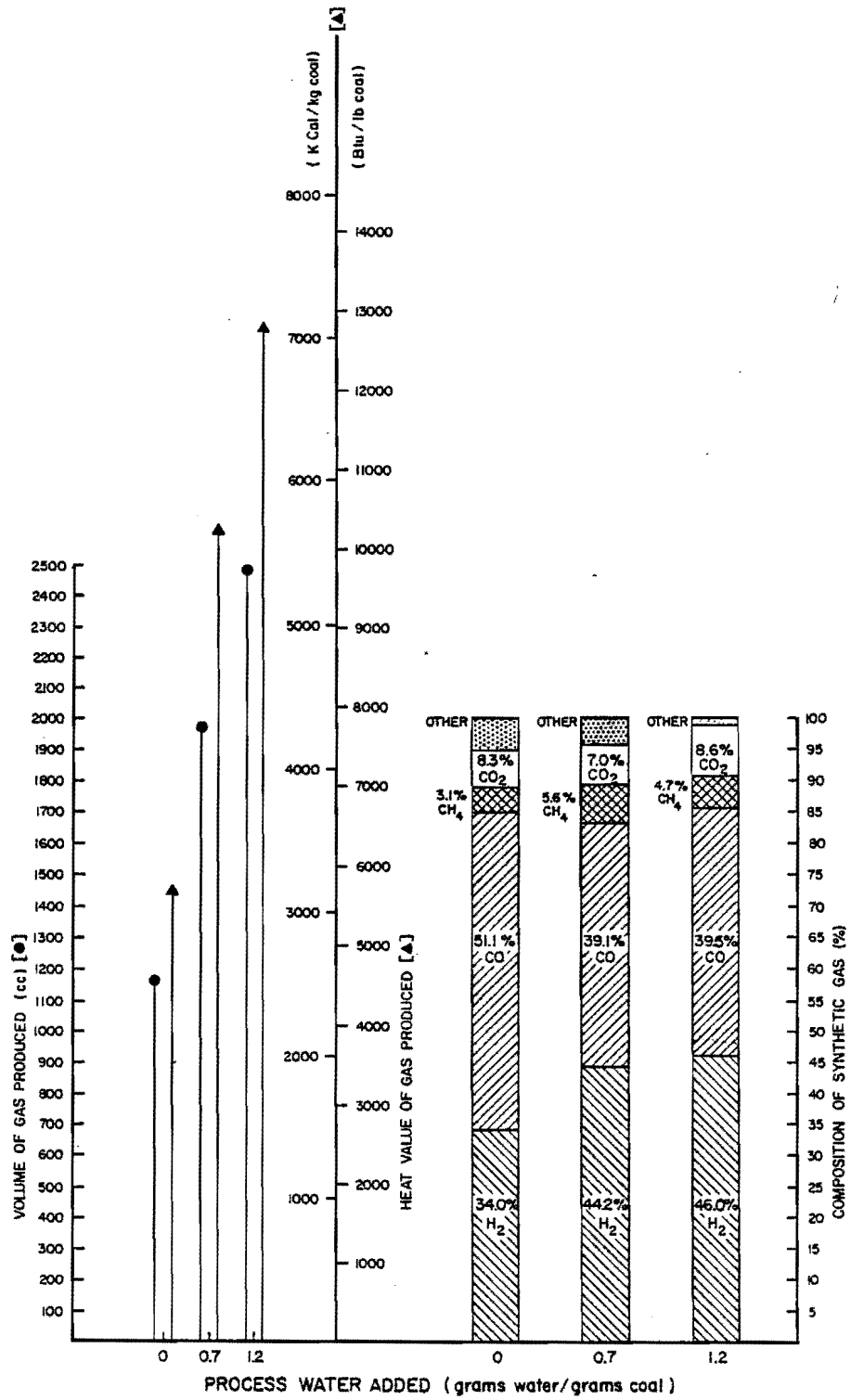
Figure 8. The composition, heating value, and volume of fuel gas produced from the experimental gasification of the high-volatile bituminous coal.

Table 10. The quantities of gases[a] produced during experimental gasification.

Sample	Water Input (mass/mass sample)	CO (cc/gram sample)	H_2 (cc/gram sample)	CO_2 (cc/gram sample)	CH_4 (cc/gram sample)	Percent of Fuel-Carbon in Gas
High-Volatile Bituminous Coal	0	603	401	98	37	58
	0.7	778	880	140	111	80
	1.2	987	1150	215	118	94
#1 Shale	0	460	211	202	15	68
	0.7	731	724	120	22	89
	1.2	818	967	301	49	100
#6 Shale	0	326	181	189	10	81
	0.7	342	391	214	14	88
	1.2	310	381	331	9	100
Sludge	21.5	139	111	412	2	
	22.5	86	95	508	29	

[a]Standardized to 23°C and 760 mn Hg.

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stantially more hydrogen gas than the #1 shale.

The total heating value of the gas produced increased with the increase in water input. Table 9 indicates that at a water input of 1.2 grams per gram of shale, the total heating value of the gas produced from #1 shale was 5540 Kcal/kg (9980 Btu/lb), an increase of 1190 Kcal/kg from the 4350 Kcal/kg obtained using 0.7 gram water per gram of sample. The increase in the total heating value results from a net increase in production of CO and H_2. The differences in the total heating value of the gas produced with increases in water input are significant to the $\leq$ 1 percent level.

The data in Table 9 show that the difference between the quantity of CO and H_2 is nearly the same as the increase in CO_2 from a water input of 0.7 gram per gram of sample to 1.2 grams of water per gram of sample. Increasing quantities of CO_2 and H_2 suggest that an increase in water input makes the water-gas shift reaction more important. The composition, quantity, and total heating value of the synthesis gas produced from the shales are shown in Figures 9 and 10.

The results from the gasification of #6 shale are shown in Table 9. The total heating value of the gas produced increased as water inputs increased from 0.0 to 0.7 gram of water per gram of sample. By further increasing water inputs from 0.7 to 1.2 gram of water per gram of sample, the heating value decreased slightly from a high of 2210 Kcal/kg shale at 0.7, although the difference was significant only at the 20 percent level. The increase in the heating value of the gas produced resulted from increases in the quantity of hydrogen. There were no substantial increases in the quantity of CO_2 at the 0.7 gram of water input level to account for the increases in the quantity of hydrogen. The CO produced from the gasification of #6 shale with no water input

may have resulted from the pyrolysis and incomplete combustion of the sample; Equations 1 and 2 indicate the mechanisms for pyrolysis and combustion.

The selected water content for the coal and #1 shale was 1.2 grams of water per gram of sample. The selected water content for the #6 shale was 0.7 gram of water per gram of sample. The results from the gasification of the municipal sludge showed that the best results, relative to other water inputs, were obtained when 0.5 gram of water was used for a gram of sample gasified. Increasing the water input only increased the concentration of carbon dioxide in the product gas and thus decreased the total heating value of the fuel gas produced from the sludge. Decreasing the mass of water input with the sludge decreased the quantity of hydrogen output. The differences between the total heating values at the optimum conditions are significant at the $\leq$ 1 percent level. The percent of carbon found in the gas stream increased with the addition of water. Table 10 shows that the percent of carbon in the coal accounted for in the gas increased from 58 to 94 percent as water input increased from 0.0 to 1.2 grams of water per gram of coal. The same effect occurred with the gasification of #1 shale when the water was increased from 0.0 to 1.2 grams per gram; the percent of carbon found in the gas increased from 68 to 100 percent. The percent of carbon found in the gas stream resulting from the gasification of #6 shale increased from 81 to 100 percent with the increase of water. Greater percentages of carbon found in the gas stream were observed for the shales than the coal at coinciding water inputs. Graphical presentations of the results from the gasification of the coal and shale samples are shown in Figures 8, 9, and 10, for water inputs of 0.0, 0.7, and 1.2 grams.

The total heating values for the gas produced from the gasification of

the samples may not reflect actual values in a commercial gasifier. The tube furnace provided the thermal energy necessary for the endothermic reactions such as the carbon-steam reaction. A self-sustaining reactor may burn some of the fuel generated to provide energy for the ensuing reactions. A high-Btu gasifier typically uses about 20 percent of the coal for utility power generation. This would be equivalent to 600 Kcal (2380 Btu). A low-Btu gasifier would require substantially less sample material, and a medium-Btu gasifer uses an intermediate amount. A typical low-Btu gasifier converts up to 80 percent of the heating value of a 7000 Kcal/kg coal to fuel gas energy when integrated directly with a power plant.

The predominant gaseous sulfur compound found in the fuel gas stream was hydrogen sulfide. The concentration of hydrogen sulfide in the gas stream
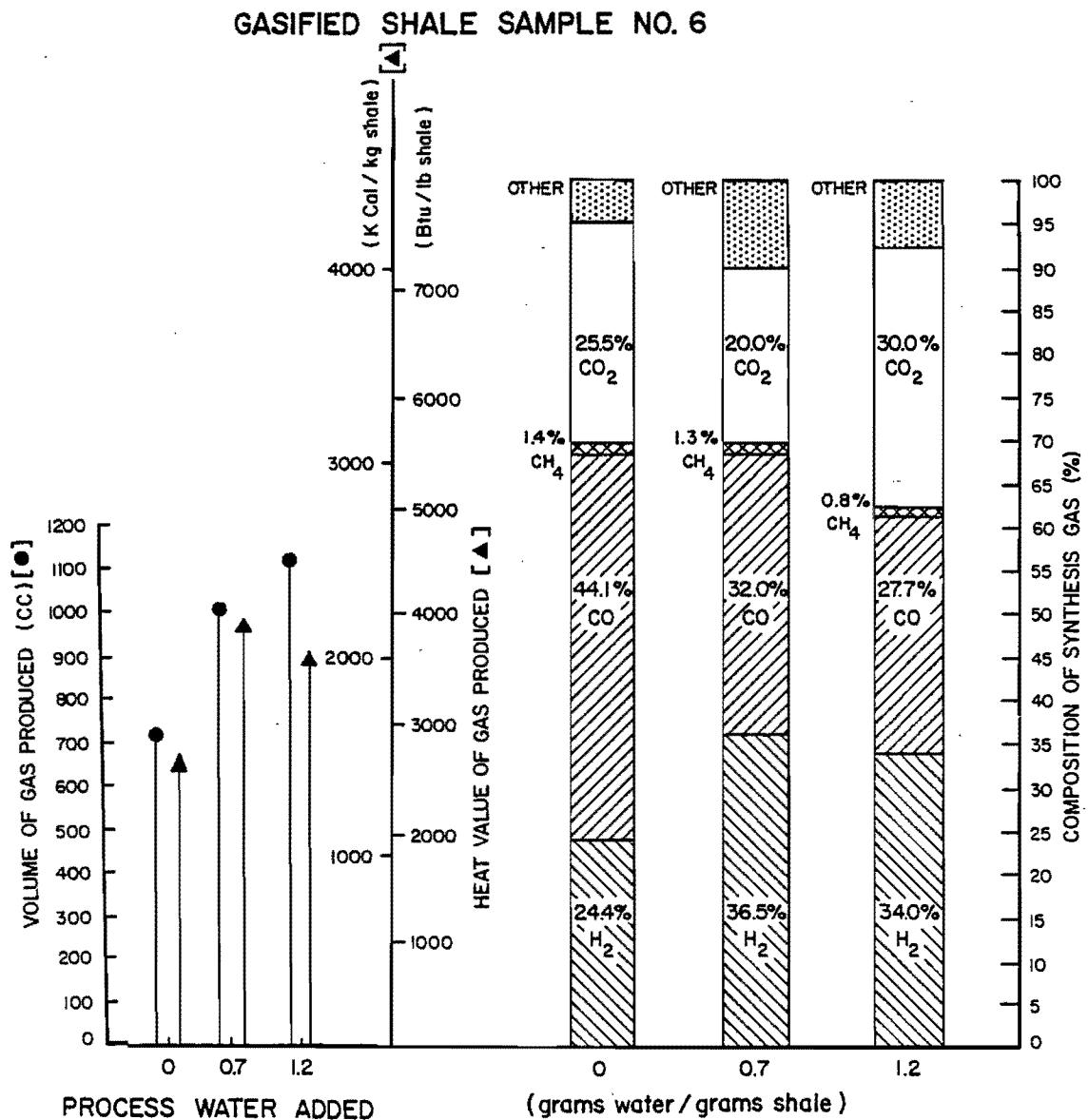
Figure 9. The composition, heating value, and volume of fuel gas produced from the experimental gasification of the #6 carbonaceous shale.

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GASIFIED SHALE SAMPLE NO. 1
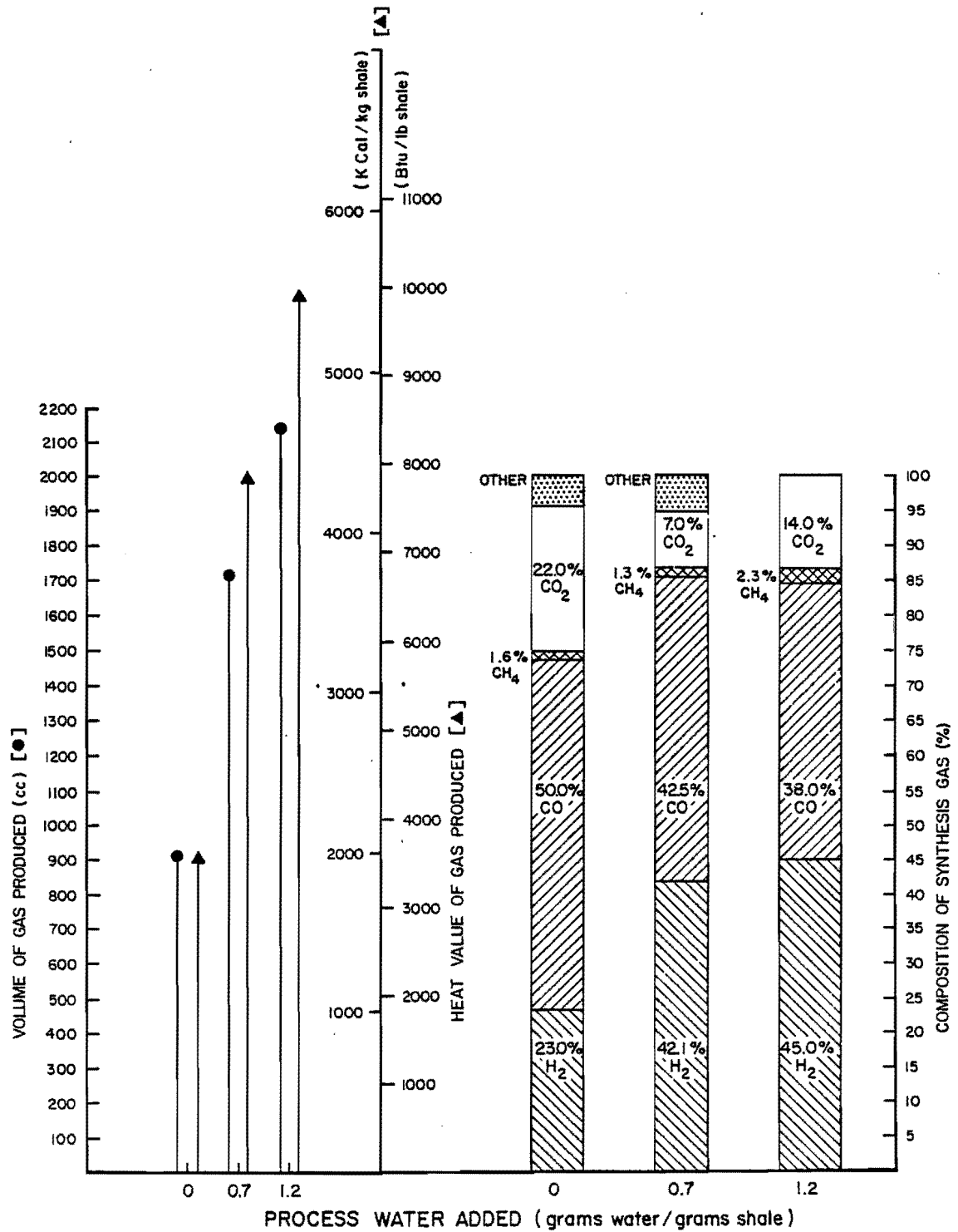
Figure 10. The composition, heating value, and volume of fuel gas produced from the experimental gasification of the #1 carbonaceous shale.

after quenching was found to be 750 ppm for the coal, 700 ppm for the #1 shale, and 450 ppm for the #6 shale. The differences in total mass output were significant among the samples at the $\leq$ 5 percent level. The hydrogen sulfide (H_2S) accounted for 25 percent of the fuel sulfur in the coal. The H_2S in the #1 shale and #6 shale accounted for 35 and 45 percent of the fuel sulfur in the samples respectively. The SO_2 concentrations were minimal at 3 ppm for both the #1 shale and coal, and 4 ppm for the #6 shale. The differences were insignificant at the $\leq$ 5 percent level.

The gasification of high quality carbon-shales appears to be as efficient as that of coal in conversion to medium-Btu gas. However, substantially more of the high quality shale, such as the #1 shale used in the experiment, will be needed to produce an equivalent amount of energy from the synthetic gas. If an equivalent amount of energy from the #1 shale is required to sustain gasification, then 30 percent more shale will be needed. A continuously fed experimental gasifier will be needed to ascertain the exact energy requirements to sustain the gasification of the #1 shale. The results from the experimental gasification indicate that it is plausible to obtain a fuel gas from the carbon-shale, however, the endothermic energy requirements to sustain gasification reactions can only be estimated. Based on previous estimates, the maximum cold gas efficiency that can be expected from the gasification of coal is 80 percent; of #1 shale is 70-75 percent; of #6 shale is 50 percent.

Summary

The first objective was to determine if the materials other than coal could be gasified. All of the materials tried gave some yield of gas so this question was answered. The second objective was to determine how these materials compared to a coal. The conditions used were temperature 1070°C with oxygen and water inputs as shown in

Table 8, where they are compared to the quantities used by other investigators. At 0.5 water #1 shale yields 69 percent of coal #8, shale #6 yields 44 percent, and sludge yields 15 percent, while at 3.0 water, shale #1 becomes 83 percent, shale #6 becomes 26 percent, and sludge drops to 8 percent.

The gasification is summarized in Table 9. It is of interest that the dry heating value of the material is not a good index of the heat available after gasification since this index ranged from 23 percent low to 23 percent high or just under 50 percent.

If the figures of Probstein and Gold (1978) are utilized to estimate total water consumed in terms of process water, coal #8 gives 9.75 billion Btu per acre foot of water with 1.2 ratio of water to sample; shale #1 gives 7.5 billion Btu per acre foot; shale #6 gives 2.79 billion Btu per acre foot; and sludge gives 2.37 billion Btu per acre foot of water consumed to answer objective No. 3. This is considering recycling of 38 percent of the process water to answer objective No. 4.

Water Requirements

The water requirements for the gasification of the carbon-shales were estimated from the experimentally determined difference between the high-volatile coal gasification water requirements and those of the shale. These estimates were then compared to values cited in the literature. The water requirements for production of fuel gas in an experimental gasifier depend on operating conditions within the experimental apparatus.

The hydrogen balances for both of the shales and the coal used as a basis for comparison are presented in Table 11. The hydrogen input accounts for the coal-hydrogen as determined by the ultimate analysis. Other inputs listed are the inherent moisture of the sample and the water input. Table 11 indicates

Table 11. Hydrogen balance in the experimental gasifier for a coal and two shales.

Parameter (Grams as H_2/gram of Sample)	Water Input (grams/gram sample)		
	0	0.7	1.2
Input			
Coal Hydrogen	0.0521	0.0521	0.0521
Coal Moisture	0.0058	0.0058	0.0058
Water	0	0.0778	0.1333
Total Input	0.0579	0.1357	0.1912
Output			
H_2 Gas	0.0327	0.0718	0.0939
CH_4 Gas	0.0060	0.0181	0.0200
Water Vapor (grams as H_2)	0.0192	0.0458	0.0800
(grams as H_2O)	0.17	0.41	0.72
Net Process Water Requirement (grams water/gram sample)	0	0.29	0.48
Input			
#1 Shale Hydrogen	0.0202	0.0202	0.0202
#1 Shale Moisture	0.0068	0.0068	0.0068
Water (grams as H_2)	0	0.0778	0.1333
Total	0.0270	0.1048	0.1603
Output			
H_2 Gas	0.0172	0.0591	0.0789
CH_4 Gas	0.0024	0.0036	0.0082
Water (grams as H_2)	0.0074	0.0421	0.00732
(grams as H_2O)	0.07	0.38	0.66
Net Process Water Requirement (grams water/gram sample)	0	0.32	0.54
Input			
#6 Shale Hydrogen	0.0215	0.0215	0.0215
#6 Shale Moisture	0.0039	0.0039	0.0039
Water	0	0.0778	0.1333
Total	0.0254	0.1032	0.1587
Output			
H_2 Gas	0.0148	0.0319	0.0311
CH_4 Gas	0.0016	0.0023	0.0015
Water (grams as H_2)	0.0090	0.0690	0.1261
(grams as H_2O)	0.0810	0.6216	1.13
Net Process Water Requirement (grams water/gram sample)	0	0.0784	0.0700

that larger water inputs increased the quality of the fuel but shows no significant difference between the water requirements for the coal and the #1 shale.

The table also indicates that the samples were supplied substantially more water input than was used. This additional requirement can be explained as an artifact of the system used for the gasification. A system having a more efficient water-carbon contact arrangement would use less process water than the gasifier used for this experiment.

The difference in the net process water requirements between the coal and the #1 shale is very little at both the 0.7 and 1.2 grams of water input. The difference between the shales, however, was substantial. The #6 shale used less than 0.08 gram of water per gram of sample whereas the #1 shale used 0.54 gram of water at the optimum production of fuel gas.

The process water requirements increase if the objective is to produce a high-Btu gas consisting of mostly methane. The increased water requirement for methanation is 1.33 grams of water per gram of coal (based on the hydrogen equivalent in the high Btu fuel gas), provided that there is 100 percent efficient use of the water. The additional water required for methanation is 1.09 grams of water per gram of #1 shale and 0.47 gram of water per gram of #6 shale.

These process water requirements are close to the optimal requirements for gasification of coal by various processes as shown on Table 8. The cooling water requirements for the shale, however, are greater than those for coal, due to the increased ash cooling requirements. The flue gas desulfurization requirements are slightly more for the #1 shale than for the coal because of the increased concentration of sulfur in the shale valve (0.60 versus 0.57 percent for #1 shale

and coal respectively) and the increased quantities to produce an equivalent amount of fuel gas energy. Table 12 summarizes the amounts of coal and shale needed to produce 7×10^6 m^3 of high heating value synthesis gas. The table also includes the various water requirements based on the needs of a Synthane gasifier and supporting plant facilities, using a similar coal (Chiang et al. 1978).

The quantity of coal or shale needed to produce 7×10^6 m^3 of high heating value synthesis gas varies according to the amount needed for the utility boilers and the amount of synthesis gas each sample will produce. For equivalent amount of fuel gas energy, the needed quantity of #6 shale is 82,700 metric tons versus 21,400 metric tons of #1 shale and 18,100 metric tons of coal. The much larger required amount of #6 shale is due to its low heating value and the low total heating value of the synthesis gas produced, 50 percent of the #6 shale would be used to sustain the boilers (assuming that a burn can be sustained).

The process water requirements were higher for the shales than for the coal due to the faster feed rate required to produce the equivalent fuel gas heating value. The process water flow rate for the #6 shale was estimated to be 277 kg/sec. The estimated water rate was based on a water input of 0.7 gram water per gram sample. If the gasifier could make more efficient use of the input process water, less would be required. Most of the water that is potentially recoverable from gasification of the #6 shale is lost due to evaporative cooling.

The larger cooling water estimates for the two shales (compared with the coal) result from the ash quenching requirements. The ash content of the #1 shale is 32.14 percent, requiring cooling water approximately equal to 0.45 times the ash quantity. The #6

Table 12. Total estimated water consumption of a Synthane plant producing 7.0 million cubic meters/day of synthesis gas.

Carbon Source	Quantity of Carbon Source Used[a] (metric tons/day)	Water Consumption Rate				
		Process[b] (kg/sec)	Net Boiler (kg/sec)	Cooling[c] (kg/sec)	Total	
					(kg/sec)	(kg H_2O/kg sample)
High Volatile[e] Bituminous Coal	18,100	147	6.5	670	844	4.03
#1 Carbon Shale	21,400	189	6.5	721	917	3.70
#6 Carbon Shale	82,700	277	6.5	891	1175	1.23

[a] Total coal or shale feed including the quantities needed for the gasifier and utility boiler.

[b] Net process water = total consumed process water - recovered condensate.

[c] Based on a recirculating evaporative cooling system.

[d] Total water consumption per total feed of carbon source including utility feed.

[e] The Utah coal is similar to the high volatile bituminous coal used in a study by Chiang et al. (1978).

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shale had 52.45 percent ash, requiring considerably more ash-quenching water, especially considering the larger quantity of carbon-shale needed.

Since both processing and cooling water requirements are larger for the carbon shales, the total water requirements are significantly greater than for the coal. These estimated water requirements do not include mining and transport water needs. The greater mass of shale required would undoubtedly require more water than coal to mine, given the same site.

The local availability of water is one of the most important factors to consider in coal or carbon-shale gasification plant siting. In the source areas for these fossil fuels in the Upper Colorado River Basin, the water can be obtained by 1) purchase from prior agricultural users, 2) groundwater, particularly that associated with dewatering for mining or waters too brackish for agricultural use, or 3) new storage facilities developing additional waters that can be claimed under the Colorado River Compact. Farmers and ranchers are able to sell significant amounts of water without major losses in crop production, but some potential gasification sites could require nearly total shifts from agriculture and completely transform the local economy. Both economic and social costs need to be considered in selecting a water source for a given site, and the major message from this study is that gasification of high quality carbon shale requires about 10 percent more water for processing and cooling than does coal gasification. Because of the greater bulk of carbon shale required to produce gas of a given heating value, one can also predict that significantly more water will be required in its mining and transportation to a gasification plant than is required for coal.

Wastewater Characteristics

The difference in quality between the process condensate from the experimental gasifier and that from gasification processes being developed for commercial application was examined using coal as a common basis for making this comparison. The quality of the process condensate using coal in commercial gasifiers was presented in Table 3. The values for the TOC, phenol, and ammonia-nitrogen found in the process condensate from the experimental gasifier were in the lower ranges presented in Table 3. Table 13 summarizes the results and shows both the process condensate quality with the experimental gasifier and the range of values obtained from commercial gasifiers. The amount of process condensate was estimated from the amount of water vapor condensed from the experimental gasifier (see Table 11).

The mean values for each of the pollutants shown on Table 13 were significantly different at the 5 percent level among coal and the two carbon shales. The process condensate from the gasification of coal had significantly higher concentrations of TOC, phenols, and ammonia-nitrogen than did that from either of the shales. Higher concentrations would be expected from a commercial gasifier if there was more efficient use of the input process water.

The difference in process condensate quality was also determined between 0.7 and 1.2 grams of water per gram of sample. Figure 11 indicates the differences in the pollutant outputs per gram of sample gasified with 0.7 and 1.2 grams of water added per gram of sample. The pollutant output (TOC, phenols and ammonia-N) were also normalized to the production of 252 KKcal (1MBtu). These normalized outputs are shown in Figure 12.

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Table 13. Quality of experimental process condensate compared with the range of commercial process condensate quality.

Sample	Total Organic Carbon (mg/1)	Phenol (mg/1)	Ammonia-N (mg/1)	Nitrate-N (mg/1)	Nitrite-N (µg/1)
Coal @ 1.2 grams water / gram sample	$\bar{x}$ = 2600 s = 530 n = 4	$\bar{x}$ = 910 s = 68 n = 5	$\bar{x}$ = 4010 s = 350 n = 5	$\bar{x}$ = 2.82 s = 0.08 n = 4	$\bar{x}$ = 85.9 s = 8.8 n = 4
#1 Shale @ 1.2 grams water / gram sample	$\bar{x}$ = 1140 s = 200 n = 4	$\bar{x}$ = 70 s = 3 n = 5	$\bar{x}$ = 280 s = 11 n = 5	$\bar{x}$ = 6.56 s = 0.74 n = 4	$\bar{x}$ = 106.1 s = 40.2 n = 4
#6 Shale @ 0.7 grams water / gram sample	$\bar{x}$ = 800 s = 160 n = 4	$\bar{x}$ = 120 s = 20 n = 5	$\bar{x}$ = 770 s = 85 n = 5	$\bar{x}$ = 1.62 s = 0.34 n = 3	$\bar{x}$ = 32.5 s = 5.1 n = 3
Commercial Range[a]	20 - 11,000	0 - 6600	122 - 8100	--	--

[a] The range of values is from Table 6.

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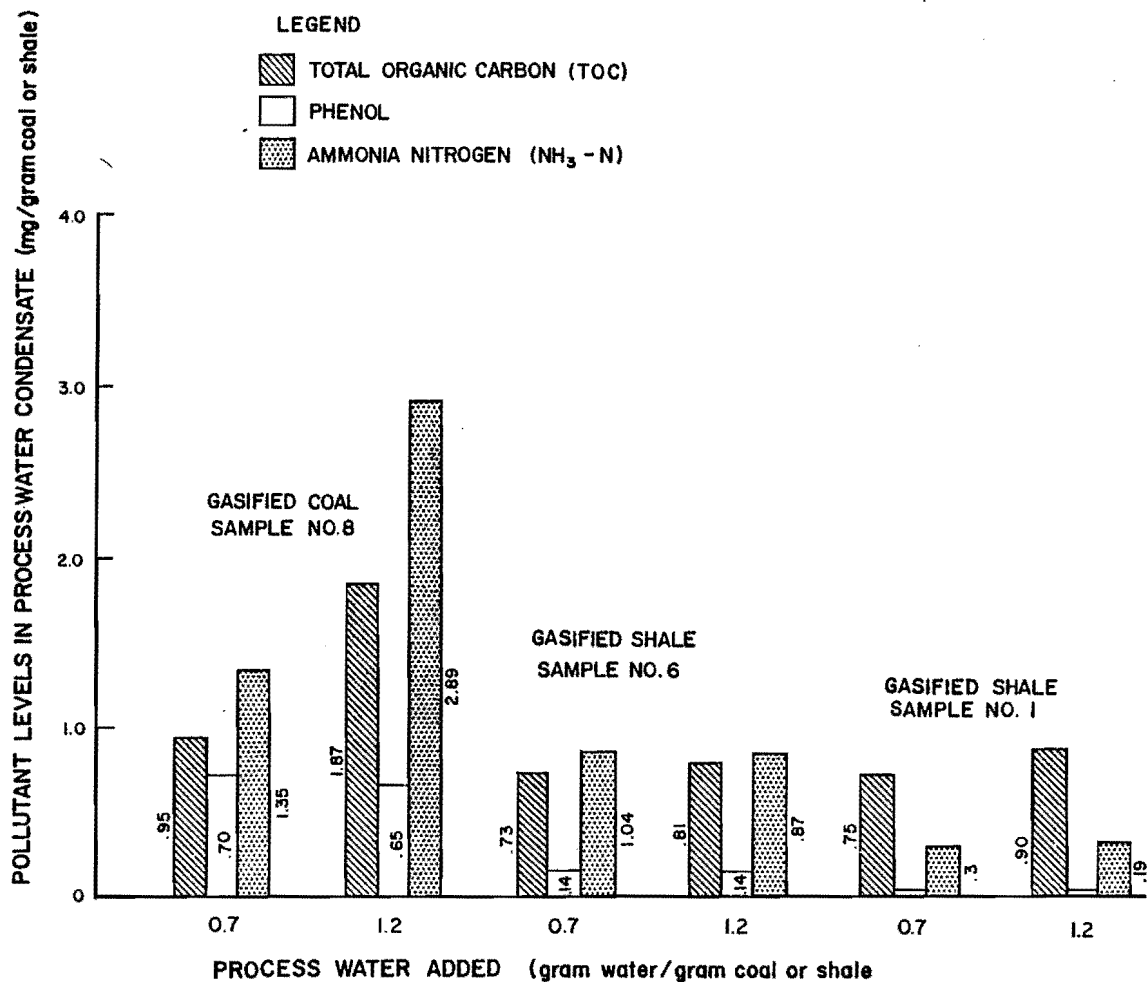
Figure 11. Pollutant levels in process water condensate after gasification of shales and coal--mass/unit mass of shale or coal.

When the pollutant outputs were normalized per unit weight of fuel, the quantity of phenolic compounds produced per gram of coal was significantly higher than that for either of the shales at the $\leq$ 1 percent level. The difference in phenolic output between the shales was significant at the $\leq$ 1 percent level. The output of phenols is slightly higher at the 0.7 gram of water input than at the 1.2 grams of water input for each of the samples gasified, although the difference was significant for only the #1 shale at the $\leq$ 5 percent level.

The difference that was detected may be explained by the destruction of phenolic compounds by reacting with the increased mole percentage of steam within the reactor. When the phenolic output was normalized to a unit heat value, the output from coal was significantly higher than that from either of the two shale samples. The #6 shale produced significantly ($\leq$ 1 percent) more phenolic compounds when gasified than did the #1 shale. Phenolic output varied significantly with water input for each sample except the #6 shale. The explanation for a significance level of $\leq$ 1 percent for the coal and #1 shale when normalizing phenolic output by heating value was the variation in heating values with water input. The difference in heating values for the

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fuel gas produced when the #6 shale was gasified using 0.7 and 1.2 grams of water per gram of shale was not significant at the $\leq$ 1 percent level, and congruently the phenolic output was not significant at the $\leq$ 1 percent level.

The ammonia-nitrogen output was at the lower range of values ($<$ 4100 mg/1), when compared to the typical concentrations of ammonia-nitrogen in commercial gasifiers in Table 13. The mechanism releasing nitrogen from the coal and the
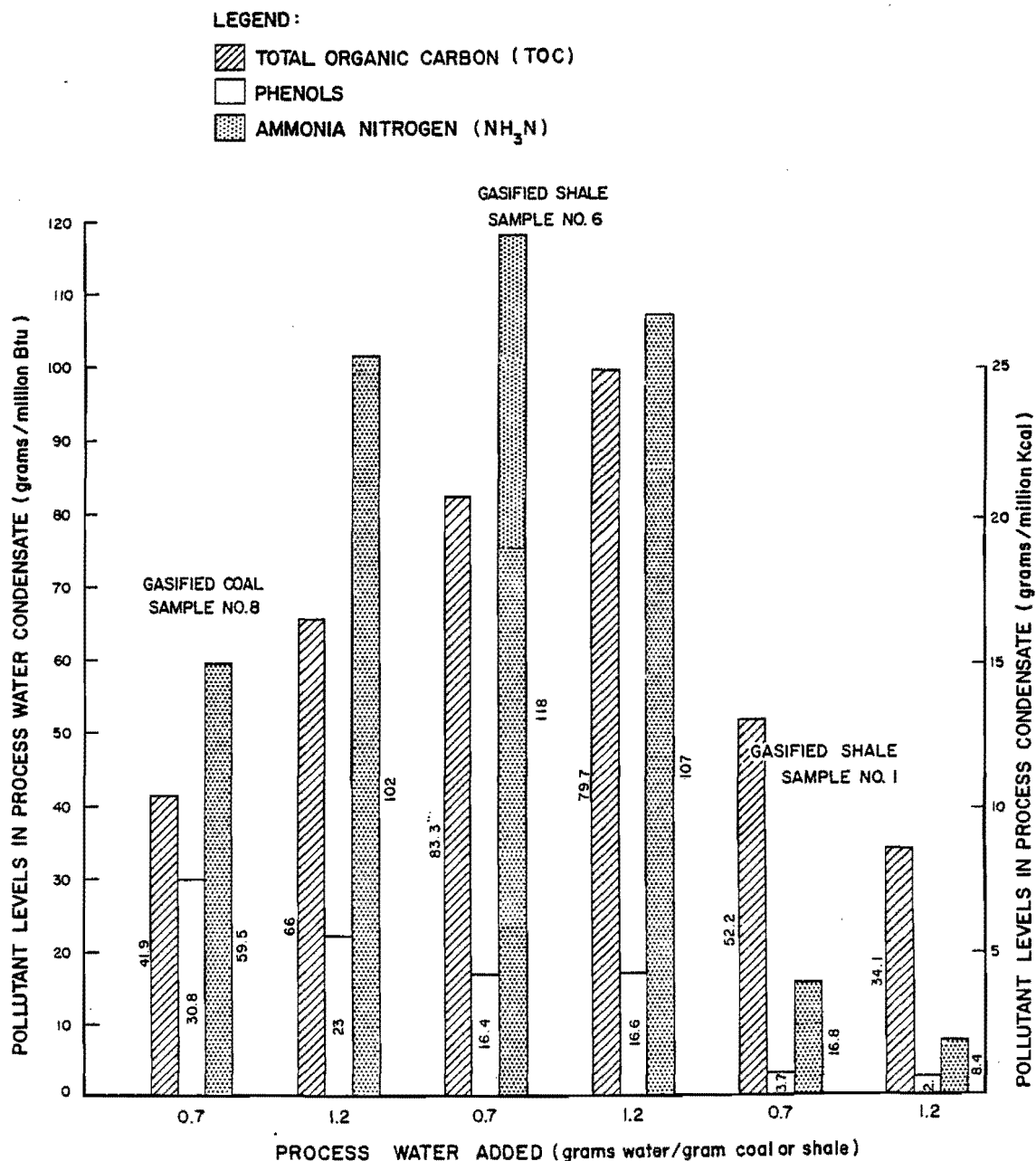
Figure 12. Pollutant levels in process water condensate after gasification of shales and coal--mass/unit heat value.

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forms that it will take after release from the gasification process depend on the type of fuel-nitrogen in the sample, gas residence time, particle residence time, temperature, and pressure (Malte and Rees 1979). In the experiment, the temperature and residence times were held constant for each of the samples gasified. The pressures varied, the highest was with coal, and pressures decreased with the quality of the fuel source.

The type of fuel-nitrogen would also affect the ammonia-nitrogen outputs for the samples. The percentages of fuel-nitrogen in coal and the #1 shale were nearly equal at 1.27 and 1.25 percent (dry), respectively, whereas the fuel-nitrogen in the #6 shale was 0.74 percent (dry). The concentration of ammonia-nitrogen in the process condensate (< 1 ml/run) was 4010 mg/l for coal, 280 mg/l for the #1 shale and 770 mg/l for the #6 shale. The difference in ammonia nitrogen concentrations cannot be explained by differences in the percentage of fuel-nitrogen, analyzed by the ultimate analysis. In fact, large differences in ammonia-nitrogen concentrations occurred between samples with relatively equal concentrations of fuel-nitrogen. One possible explanation would be that the fuel-nitrogen probably exists in different forms within the samples.

The amount of ammonia-nitrogen in the process condensate is less than that expected from a commercial gasifier because of the long sample residence time in the experimental gasifier. The residence time in commercial gasifiers depends on the size of the sample particles fed into the gasifier. The Lurgi system utilizes particles between 0.3 and 3.5 cm and requires a detention time of 1 hour (Probstein and Gold 1978). Entrained-flow gasifiers use pulverized coal that passes a #200 sieve and requires detention times of less than 1 minute. The experimental gasifier used sample sizes within a range of the

#30 and #120 sieves, with a detention time of at least 30 minutes.

Ammonia destruction mechanisms were presented as Equations 12 and 13. The equilibrium constants for the equations indicate that the reactions become spontaneous at temperatures above 1000°K. A potential explanation for the low production of ammonia-nitrogen is that reactions (12) and (13) cause a substantial decrease in the ammonia-nitrogen. The 30 minute residence time may have allowed the reactions to occur.

The output of ammonia normalized to unit mass is significantly different among the samples gasified. Gasification of coal produced 2.89 mg of NH_3-N per gram of coal when using 1.2 grams of water per gram of coal. The gasification of #1 shale produced only 0.19 milligram of NH_3-N per gram of shale. Comparing the amount of ammonia-nitrogen output per unit heating value shows that the #6 shale out produces the coal with optimum operating conditions in the gasifier, although the difference is not significant at the ≤ 5 percent level. The ammonia-nitrogen production when #1 shale was gasified was less than 10 percent of the ammonia produced by either coal or #6 shale. The ammonia-nitrogen outputs are compared in Figure 11, normalized to a unit heating value of the fuel gas produced.

Other nitrogen species were also found in the wastewater. Table 13 relates the concentrations of nitrate and nitrite found in the wastewater. The differences in nitrate concentrations were significant at the ≤ 1 percent level between the #1 shale and #6 shale, and the #1 shale and coal. The nitrite differences were insignificant at the ≤ 5 percent except for between coal and the #1 shale. The concentrations of nitrate- and nitrite-nitrogen were low compared to ammonia. The gas was analyzed for NO_x species, and no NO_x was detectable at ≥ 1 ppm (lower range of sensitivity).

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The total organic carbon produced from the gasification of coal was significantly greater (at the $<$ 1 percent level) than the production from gasification of either of the two shales, compared on a unit mass basis. Figure 11 shows the differences in production of TOC when gasifying coal or shale at different water inputs. When the TOC production was compared on a unit heating value basis, the #6 shale produced significantly greater (at the $<$ 1 percent level) amounts of TOC than did either of the other two samples gasified.

Several samples were collected to determine whether mutagens were being created by the gasification process. The samples, consisting of both water and dimethyl sulfoxide (DMSO), were taken from a cold trap through which the process condensate and a gas stream had passed. These samples were analyzed through use of the Ames test (Ames et al. 1975). Several of the samples (from coal and #6 shale) yielded a positive response on two of the tester strains. This indicates that mutagens were created by gasification. These mutagens probably consist of the highly mutagenic larger polynuclear aromatics (Klein and Barker 1978). Since approximately 90 percent of all mutagens are also carcinogens (Ames et al. 1975), this finding strongly indicates that carcinogens are being created through use of this process. None of the samples were concentrated or separated into individual constituents; so the mutagens present were not specifically identified.

The trace elements found in the process condensate after gasification are a function of the composition of the sample and the volatility of the trace element. The form of a trace element in the gas stream determines if

the trace element will be separated from the gas stream by the quenching system.

The volatilization of the trace elements that was occurring in the gasification process was estimated by determining the composition of the samples before gasification and the composition of the ash. The data in Table 14 indicate the trace element content of the samples, the volatility of the trace elements, the concentration of trace elements in the process condensate, and the estimated amount of trace elements exiting the gasifier and requiring removal.

Arsenic and selenium were not detected in the process condensate. The coal and shale samples were not analyzed for arsenic and selenium concentrations. The volatility of Cr and Zn was much higher than the estimated volatility presented in Table 4 (greater than 60 percent volatile versus less than 15 percent). The coal contained smaller amounts of the trace elements than did either of the shales. The amount of chromium was quite comparable for all of the samples when compared with a typical coal having 15 ppm (see Table 4). When one accounts for coal versus shale requirements in a typical gasification facility, the shales have a greater output of trace metals than will coal (see Table 14). Most of the cadmium, mercury, and zinc in the gas stream was accounted for in the process condensate; however, there was no correlation between sample concentrations and process condensate concentrations of lead and chromium. This anomaly may be explained as experimental error or the trace element species formed by gasification may not be susceptible to collection by an acid solution and may have exited the cold trap in the gaseous phase.

Table 14. Trace metals analysis results from gasification experiments.

Parameter	Process Condensate Concentration			Sample Concentration			Ash Concentration			% Volatility		
	Coal μg/g	#1 Shale μg/g	#6 Shale μg/g	Coal ppm	#1 Shale ppm	#6 Shale ppm	Coal ppm	#1 Shale ppm	#6 Shale ppm	C	#1	#6
As	<0.8	<0.8	<0.8	—	—	—	—	—	—	—	—	—
Cd	0.30	2.3	0.32	0.4	3.6	<0.4	3	<0.4	<0.4	44	96+	—
Cr	0.90	2.60	0.70	91.2	91.2	91.2	41.8	65	22.6	97	77	87
Hg	0.70	0.52	15.52	1.22	0.64	16.0	0.58	0.46	0.08	96	77	99+
Pb	0.44	0.52	0.43	1.6	8.4	3.2	6.8	0.2	1.8	0.68	99+	69
Se	<0.8	<0.8	<0.8	—	—	—	—	—	—	—	—	—
Zn	21.4	140	52	26.2	148	64.4	138.8	18.6	26.2	60	96	78

See Table 6 for analytical techniques and references.

SUMMARY AND CONCLUSIONS

Large areas of Southern and Eastern Utah were found to have carbonaceous shale deposits. The carbonaceous shales were found along side coal deposits and ranged widely in quantity according to the amount of inorganic material intermixed with their carbon content. Samples were found as overburden at abandoned coal mines and as separate deposits, not observed as being part of a coal seam, found on the ground surface or in road cuts. The ash content of the shales was considerably higher than that of the coal.

Synthesis gas was produced by laboratory gasification of the carbon-shales and of a selected Utah coal. The heating values of the shales sampled varied from 282 to 4240 Kcals per kg of sample.

The coal sample used for comparison had a heating value of 6840 Kcal per kg of coal. The total heating value of the fuel gas produced was found to be a function of the quantity of water input into the reactor. The quantity of shale needed to produce a unit heating value by gasification also depends on the quality of the fuel gas desired; a high quality fuel gas, consisting primarily of methane gas, requires a substantial amount of the lower grade shales. Less energy can be obtained from the lower grade shales than from coal. The amounts obtained can be increased by larger water inputs.

The quantity of phenols, total organic carbon, and ammonia was significantly greater in the process condensate from the gasification of coal than that from the #1 shale (the shale with the highest heating value) process condensate. When the pollutant output was compared based on unit heat output, the coal and #6 shale produced significantly greater amounts of phenols, total organic carbon, and ammonia than the #1 shale. The results from the Ames test concluded that mutagens were present in the process condensate of coal and the #6 shale.

The experimental results supported the following conclusions:

1. A synthesis gas, comprised primarily of carbon monoxide, hydrogen, carbon dioxide and methane, can be produced by gasification of high-volatile bituminous coal, carbon-shales, and municipal sludge.

2. Carbonaceous shales were found in the same regions in Utah that coal deposits are known to exist.

3. The carbonaceous shales contain substantially greater quantities of ash than does the coal. In the samples taken, the coal contained 7.12 percent ash whereas the #1 shale contained 32.14 percent ash and the #6 shale contained 52.45 percent ash.

4. The optimum process water amounts (that maximizing heating value from the gas produced) in the experimental gasifier for coal, #1 shale, and #6 shale were, respectively, 1.2, 1.2, and 0.7 grams water per gram of sample.

5. The heating values of the fuel gas produced from coal, #1 shale, #6 shale, and sludge at their respective optimum operating conditions were, respectively, 7140, 5540, 2210, and 725 Kcal/kg of sample gasified.

6. The total heating value of the gas produced from the gasification of coal and #1 shale increased, significantly, at the 1 percent level, when increasing the water input from 0.0 to 0.7 and from 0.7 to 1.2 grams of water per gram of sample.

7. The total heating value of the gas produced from the gasification of #6 shale increased, significantly, at the 1 percent level, when the water input was increased from 0.0 to 0.7 gram of water per gram of sample. There was no significant increase in the total heating value of the synthesis gas when the water input was increased to 1.2 grams of water per gram of sample of this carbonaceous shale of higher ash content and lower potential heating value.

8. The percent of fuel-carbon in the gas increased, significantly, at the $\leq$ 1 percent level, when increasing the amount of water input to the gasification reactor.

9. There was no difference, significant at the $\leq$ 5 percent level, in process water requirements between the gasification of coal and the #1 shale. There was a significant difference between the water requirements of the #6 shale and either coal or the #1 shale.

10. The quantity of coal needed to produce a unit heating amount of energy was substantially less than the amount of #1 shale which was substantially less than the amount needed using #6 shale.

11. The cooling water required was greatest for the gasification of #6 shale due to the ash-quenching water demand. The #1 shale required less cooling water than did the #6 shale but more than coal.

12. The greatest heating value from the gas produced per unit of water consumed can be realized utilizing the indigenous coal.

13. On a mass basis, coal gasification produced significantly greater quantities of total organic carbon, phenols, and ammonia-nitrogen at the $\leq$ 1 percent level, than did gasification of either the #1 or #6 shales.

14. The #6 shale, at the optimum operating conditions, produced more total organic carbon and ammonia-nitrogen, significant at the $\leq$ 1 percent level, than did either coal or #1 shale. The #6 shale produced greater amounts of phenols than did the #1 shale, significantly, at the $\leq$ 1 percent level. There was no significant difference between the phenolic output of coal and the #6 shale at the $\leq$ 5 percent level.

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RECOMMENDATIONS FOR FURTHER STUDY

The results from this study were derived from a batch operated, laboratory scale gasifier. The energy requirements for sustaining reactions within the gasifier were supplied by a tube furnace. Different results, significantly so but not by orders of magnitude, can be expected from commercial processes. Commercial production should be monitored, particularly when fuel sources are changed, for pollutant problems, and attention should be given additional constituents not measured here, such as cyanide, polynuclear aromatics, and dissolved gases.

For refined system design (or for evaluating new potential fuels for gasification in an existing system) one should:

1. Verify the quantity of carbonaceous shale required to produce a unit heating value, and use this to determine economic feasibility.

2. Determine the composition of the product gas.

3. Determine the optimum process steam requirements.

4. Determine the phenol, ammonia-N, and total organic carbon production in the process condensate, and adopt necessary treatments.

5. Determine the type and quantity of mutagens in the process condensate.

6. Determine the relationship, if any, between the carbon associated with the volatile fraction of the sample and the production of ammonia and phenols.

7. Determine the relationship, if any, of "in place" gasification of shale on the water balance found here.

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APPENDIX A

Gas Data

Table A-1. Volume of synthesis gas produced per gram of sample.

Sample	Run No.	Water Input grams/gram sample	Volume (Correct to STP)
Coal	131	0	1110
	132		1260
	72		1170
	133	0.7	2190
	134		1820
	135		2010
	141		1980
	140		1950
	136	1.2	2490
	137		2510
	138		2535
	145		2700
	144		2535
	143		2390
	142		2353
#1 Shale	70	0	940
	68		910
	69		910
	112	0.7	1850
	113		1630
	114		1680
	115		1720
	106	1.2	2110
	108		2290
	109		2270
	110		2150
	111		1950
#6 Shale	117	0	790
	118		730
	120		725
	121		715
	122		720
	125	0.7	960
	127		980
	126		1025
	130	1.2	1080
	129		1210
	119		1080

Wastewater Characteristics

Ammonia-N

Table A-2. Results from ammonia-nitrogen analysis.

Sample	Water Input grams/gram sample	Run No.	Ammonia-N (mg/g)
Coal	0.7	139	1.09
		140	1.44
		141	1.52
	1.2	142	2.64
		143	3.14
		144	2.88
#1 Shale	0.7	161	0.29
		162	0.28
		163	0.30
	1.2	156	0.18
		157	0.19
		158	0.19
#6 Shale	0.7	146	0.90
		148	0.99
		149	1.22
	1.2	152	0.81
		153	1.00
		154	0.87
		155	0.79

Phenols

Table A-3. Results from phenol analysis.

Sample	Water Input grams/gram sample	Run No.	Phenol (mg/g)
Coal	0.7	139	0.690
		140	0.700
		141	0.707
	1.2	142	0.600
		143	0.662
		144	0.698
#1 Shale	0.7	161	0.060
		162	0.064
		163	0.065
	1.2	156	0.043
		157	0.047
		158	0.046
#6 Shale	0.7	146	0.149
		148	0.145
		149	0.139
	1.2	152	0.139
		153	0.155
		154	0.110

Total Organic Carbon (TOC)

Table A-4. Results from TOC analysis.

Sample	Water Input grams/gram sample	Run No.	TOC (mg/g)
Coal	0.7	139	1.21
		140	0.81
		141	0.89
		132	0.90
	1.2	142	1.87
		143	2.39
		144	1.51
		145	1.69
#1 Shale	0.7	161	0.76
		162	0.80
		163	0.88
		115	1.16
	1.2	156	0.56
		157	0.72
		158	0.80
		106	0.56
		108	0.96
		109	0.80
		110	0.80
		111	0.80
#6 Shale	0.7	146	0.790
		148	0.768
		149	0.632
	1.2	152	1.00
		153	0.92
		154	0.66
		155	0.75
		130	0.72
		129	0.82
		119	0.82

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Table A-5. Results from Ames mutagenicity test.

Sample Process Condensate	Run No.	Date	Concentration µl/plate	Activator	Response Counts				
					MNNG-POS 1535	9AA-POS 1537	2AF-POS 1538	2AF-POS 98	2AF-POS 100
Blank	–	1/17/80	–	none	13, 9, 13	18,19,20	20,17,20	20,21,21	94, 97, 93
		"		S-9	8, 8, 8	9, 9, 8	31,33,33	34,34,39	112,112,113
		"		S-9	14,14,15	7, 7, 8	29,29,28	52,52,47	141,142,140
#1 Shale	16	"	50	none	–	–	15,14,16	16,17,17	72, 72, 70
	16	"	"	S-9	–	14,14,15	34,35,35	52,53,54	98, 98, 100
	16	"	250	none	14,14,15	6, 6, 6	4, 4, 5	20,20,21	86, 86, 95
	16	"	"	S-9	8, 8, 7	12,12,12	27,27,28	59,59,60	117,121,113
#6 Shale	65	1/17/80	50	none	13,13,13	6, 8, 8	5, 5, 5	26,26,28	92, 93, 91
		"	"	S-9	6, 6, 6	16,16,16	21,27,27	30,30,30	86, 86, 84
		"	250	none	9, 9, 9	5, 5, 5	4, 4, 5	18,18,16	87, 87, 91
		"	"	S-9	16,16,16	8, 8, 8	28,27,26	42,41,44	139,138,142
Coal	C3	1/17/80	50	none	8, 8, 9	7, 7, 7	7, 7, 6	20,21,19	56, 56, 55
		"	"	S-9	7, 7, 8	7, 8, 8	21,22,20	55,55,55	109,107,105
		"	250	none	16,16,16	5, 6, 6	19,16,17	17,18,18	108,107,111
		"	"	S-9	21,22,22	28,28,28	16,17,17	41,34,39	126,139,125
Blank/DMSO	C3	1/17/80		none	14,14,14	9, 9, 9	13,13,14	20,20,19	156,151,156
		"		S-9	6, 6, 7	14,13,15	33,33,33	56,60,60	142,142,142
		"		S-9	9, 9, 7	17,19,19	40,39,42	40,40,41	99,104,104
#1 Shale/DMSO	11-12	1/17/80	50	none	19,21,21	6, 7, 8	19,19,20	28,29,32	106,106,99
		"	"	S-9	8, 9, 9	18,19,19	42,42,40	65,65,61	118,111,110
		"	100	none	19,19,18	9, 8, 8	7, 8, 9	30,29,28	73, 73, 80
		"	"	S-9	14,13,9	8, 8, 9	48,45,47	52,53,54	106,106,107
		"	250	none	13,13,9	4, 4, 4	5, 5, 5	26,26,28	92, 93, 91
		"	"	S-9	20,21,21	13, 9, 14	21,27,27	30,30,30	86, 86, 84
#1 Shale/DMSO	14-15	1/17/80	50	none	18,17,19	14,14,16	8, 6, 7	28,26,22	91, 99, 98
		"	"	S-9	6, 6, 6	17,19,19	45,44,46	79,84,81	107,112,111
		"	100	none	17,18,18	14,14,15	7, 8, 8	30,30,29	85, 93, 82
		"	"	S-9	57,57,55	18,18,18	46,45,43	45,45,44	94, 94, 91
		"	250	none	13,13,9	4, 4, 4	7,13,9	14,14,15	91, 87, 93
		"	"	S-9	20,21,21	13, 9, 14	16,16,17	39,40,42	107,107,106
#6 Shale/DMSO	61-62	1/10/80	50	none	17,17,18	19,18,18	18,18,19	65,59,59	98, 97, 97
		"	"	S-9	14,14,13	9, 9, 13	55,56,56	67,67,66	84, 87, 85
		"	100	none	15,15,15	--	16,17,15	56,56,54	112,111,110
		"	"	S-9	9, 8, 8	15,15,14	44,45,42	61,61,65	105,105,106
		"	250	none	9, 9, 9	39,40,40	13,13,9	56,53,52	92, 92, 92
		"	"	S-9	4, 4, 5	20,20,19	28,27,27	46,45,47	109,106,108
#6 Shale/DMSO	63-64	1/10/80	50	none	16,16,17	8, 8, 8	--	40,40,34	86, 86, 91
		"	"	S-9	17,17,18	14,14,13	53,54,54	66,66,67	113,113,113
		"	100	none	18,18,17	6, 7, 7	13,13,14	32,33,33	91, 85, 87
		"	"	S-9	13, 8, 8	13, 9, 9	54,55,55	58,59,59	118,119,120
		"	250	none	16,16,17	9, 9, 9	7, 8, 8	13,14,9	83, 83, 82
		"	"	S-9	14,14,14	7, 7, 7	22,22,27	34,34,35	104, 96, 100
Coal/DMSO	C1-C2	1/17/80	50	none	14,14,13	15,16,17	8, 8, 7	46,46,46	109,118,112
		"		S-9	7, 8, 8	14,13,13	46,46,52	52,52,54	109,100,106
			100	none	15,15,14	8, 8, 7	14,14,13	29,30,31	98, 99, 96
		"		S-9	13,13,14	7, 7, 8	31,31,30	--	105,100,100
			250	none	17,17,18	6, 6, 6	9, 9, 9	22,22,26	72, 72, 71
		"		S-9	14,14,15	7, 7, 6	21,21,21	31,31,30	109,109,112
		"		none	16,16,17	9, 9, 9	7, 8, 8	13,14,9	83, 83, 82
				S-9	14,14,14	7, 7, 7	22,22,27	34,34,35	104, 96, 100

APPENDIX B

Unit Conversions

Table B-1. Unit conversions for units used in the report.

English to Metric	Multiply By	Metric to English	Multiply By
acre-ft → hectare-meter	0.123	ha-m → acre-ft	8.11
Btu → Kcal	0.252	Kcal → Btu	3.97
Btu/lb → Kcal/kg	0.556	Kcal/kg → Btu/lb	1.80
Btu/scf → Kcal/scm	8.90	Kcal/scm → Btu/scf	0.112
gallons → liters	3.785	liters → gallons	0.264
gallons → cubic meters	3.78×10^{-3}	cubic meters → gallons	2.64
pound-mass → kilograms	0.454	kilograms → pound mass	2.205
scf → scm	0.0283	scm → scf	35.31
short ton → metric ton	0.907	metric ton → short ton	1.102