

AMMONIA SYNTHESIS GAS GENERATION  
FROM CATTLE FEEDLOT MANURE

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## ABSTRACT

A pilot-scale partial oxidation reactor system has been constructed and operated for the production of synthesis gas from cattle feedlot manure. Current pilot scale data (25-50 lb raw manure/hr) confirm that an ammonia synthesis gas can be produced, as demonstrated in earlier investigations using a bench-scale reactor (0.3-1.0 lb manure/hr). The pilot-scale investigations indicate that ethylene and other C<sub>2</sub> hydrocarbons potentially can be produced in the range of 50-180 lb per ton manure (daf), depending upon operating conditions. The partial oxidation reaction of manure has been studied at atmospheric pressure over an approximate average reactor temperature range of 600°C to 800°C. Cattle feedlot manure and air are the reactants in the partial oxidation, and steam is employed as a fluidizing medium. Experimental results and operating experience with the pilot-scale reactor are discussed.

## Introduction

Approximately twenty million head of feedlot cattle are marketed annually in the United States to meet the demands of the beef consumer. Although the market is subject to wide fluctuations, the number of cattle fed-out in any given year is still significant. The service area of one utility company in West Texas reflects both the high volume and the fluctuations of the cattle feedlot industry. In 1974, approximately 4 million head were fed-out compared to a high of nearly 5 million head in 1973 (SWPS, 1975; SWPS, 1974). The actual production in 1975 is expected to be less than 4 million head.

The most negative aspect of this red meat production is the generation of a solid by-product, bovine solid waste or manure, since each cow produces 5 to 9 pounds of dry manure per day (Halligan and Sweazy, 1972). The frequent result of this by-product production, particularly in the vicinity of facilities with capacities exceeding 60,000 head, is large piles of manure beside the feedlot (Whetstone, et.al. 1973).

Halligan, et.al. (1975) have discussed production of an ammonia synthesis gas from this supply of manure and reported on bench-scale investigations of a partial oxidation (thermal) reactor design. The generation of an ammonia synthesis gas was chosen on the basis of thermochemical calculations and the general proximity of anhydrous ammonia plants to the cattle industry and its associated grain crops.

This report is on the preliminary operation of a scaled-up version of a partial oxidation reactor for the production of ammonia synthesis gas as well as hydrocarbons (Peterson, 1975). Because the projected deficiency of future hydrocarbon feedstocks for the United States has increased the

value of hydrocarbons. This report will discuss both ammonia synthesis and hydrocarbon production from a large-scale, partial oxidation reactor using manure as a feedstock.

### Experimental Facilities

A flow diagram of the pilot plant reactor system used in these studies is shown in Figure 1. During operation, manure was fed to the top of the reactor and fell countercurrent to a stream of input and generated gases and liquids. The input gases, which were steam and air, were introduced at the bottom of the reactor through a distribution plate. The fluid phase products and unreacted input gases exited at the top of the reactor, along with some entrained solids. This fluid product stream was stripped of entrained solids in a cyclone, followed by a two-stage condensation of tars plus oils and water. The solid-free, dry gas was then sampled and the flowrate measured. The solid product was a char which was removed from the bottom of the reactor through a port in the gas distribution plate and stored in a batch hopper.

The reactor was constructed from Schedule 40, 316 stainless steel pipe with an average diameter of seven inches and an approximate height of eight feet. The diameter of the upper part of the reactor had a cross-sectional area which was 1.78 times that of the lower section. This diameter increase was provided to decrease the fluid velocity and to allow some separation of the solid and gas phases. The inlet, gas distribution plate of the reactor consisted of a 3/8 plate with 1/16 inch concentric holes evenly distributed around a 1 inch center port for the discharge of char product.

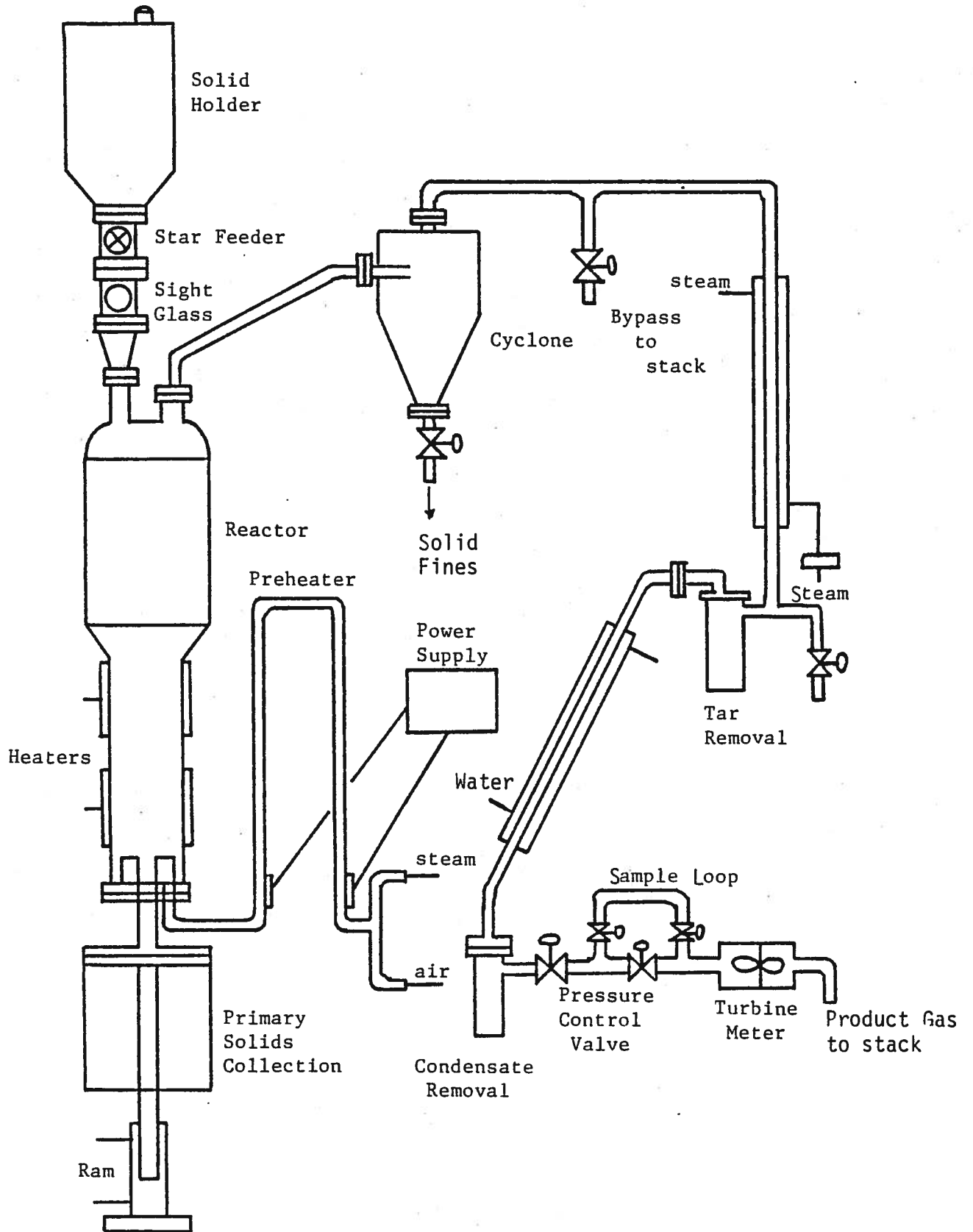


FIGURE I. SCHEMATIC DIAGRAM OF SGFM PROCESS

The lower part of the vessel was heated using 24-inch sections of preformed, electrical heaters manufactured by the Lindberg Co. (Model 50752, Type 77-1CSD; temperature limit to 1200°C). These heaters were used for start-up and steady-state heat demands. Each of the heater sections was rated for 40 amps, 206 volts. An induction preheater was used to heat the input air-steam mixture to 200-300°C.

Type K thermocouples were used to measure the temperature profile within the reactor and were monitored using a Northrup, 24-point recorder (Model 547). These thermocouples were unshielded and were spaced at 6-inch intervals along the entire reactor length. Temperature measurements were also made at key points along the gas separation equipment train and were recorded on the same multipoint recorder. Reactor temperature was controlled from a wall temperature measurement using silicone controlled-rectifiers to adjust heater input.

Standard equipment was employed downstream to separate entrained solids, organic tars (in liquid form), and water from the gas product, in that sequence. A cyclone was designed according to the recommended design procedure by Porter (1973) using an estimated particle size distribution from a filtered sample. The cyclone was approximately 5 feet high with a diameter of 15 inches and was operated at a 300-350°C to prevent condensation of tarry liquid products. Thus operating temperature permitted a free-flowing solid to be discharged from the cyclone. The rest of the gas separation unit consisted of a commercial demister to condense tar products (100°C to 150°C) and a standard double-pipe heat exchanger for removing water (25°C-100°C).

Following these separation steps, a final filter system (cotton or asbestos) was used to clean the dry gas (saturated at standard conditions) before gas samples were collected and the gas flowrate was measured. A Rockwell, TP-4, 2 inch turbometer was used to measure gas flow. Gas samples were collected using on-line 250 ml sample bottles that were purged 15 minutes or more with product gas.

Gas composition was measured for  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $H_2$ , and CO using a dual column gas chromatograph. The gas composition was qualitatively verified using an infrared scan and injecting enriched product samples (e.g., pure  $C_2H_4$  was added to a reactor sample to confirm that the expected chromatograph peak would show an increase). The gas analysis was also confirmed by using two different instruments which were calibrated and operated by two different operators. A Varian Aerograph chromatograph was used with a 50/80 mesh Poropak Q column (12 ft, 1/8 in. diameter) followed by a 48 inch length of Poropak R to measure hydrogen, methane, carbon dioxide, ethylene, and ethane. A 12 ft., 1/8 inch diameter molecular sieve column (45/60 mesh, 5 Å) was used to determine hydrogen, oxygen, nitrogen, methane, and carbon monoxide. The two columns were related using methane as the common signal. A minimum of six air samples were used prior to, and after, two product gas sample injections to standardize the gas analysis. At least two injections were run for each unknown product gas sample.

Any oxygen present in a given sample was assumed to be due to sample contamination and was subtracted out along with a corresponding amount of nitrogen because reactor feed conditions and temperature should have been sufficient to assure complete reaction of the oxygen. This adjusted

gas composition has been verified by comparing the results to strict pyrolysis experiments (Young, 1976) and by completing a nitrogen balance on the large-scale reactor system.

Manure feedstock was obtained from a local, commercial feedlot whose typical composition has been estimated to be 35.1-39.6%C, 5.3-5.9%H, 2.5-3.1%N, 0.4-0.6%S, and 23.5-29.2% on a dry basis (Halligan, et al., 1975). Moisture content generally ranged from approximately 10% to 30% with a gross heating value of 5750-6730 BTU/lb on a dry basis. The manure feedstock was generally selected from fresh, loose piles in the commercial feedlot and then ground using 1-inch screens in a standard farm hammermill. For runs 1, 6, 7, and 8, this ground manure was sieved through 3/8 inch screen to remove large particles. The last two runs were completed using manure sieved through 1/8 inch screens. The sieved manure feedstock was fed from a hopper to the reactor using a calibrated, star feeder (Beaumont Birch Co., Model 122-653) coupled to a variable speed drive.

Product char was removed from the reactor through a center port in the inlet gas distribution plate. The solid char was free-flowing and the pressure drop between the reactor and the char hopper was sufficient for flow. The rate of the center port discharge was achieved using an air-operated ram. The ram served as a valve to control the solids flow as well as provide a scouring action in the discharge piping. The ram was operated to permit solids flow for 3 seconds every 13 seconds.

#### Operation of Reactor System

Only data from runs 1, 6, 7, 8, 9, and 10 are discussed in this report because other runs were too short to provide reliable results. These short

runs (2, 3, 4, and 5) were due to electrical heater failures and plugged, solids removal filters. This filter pluggage was the major reason for installing the cyclone shown in Figure 1.

A run was initiated by heating the reactor to the desired, nominal temperature and holding it at this level until the temperature of auxiliary equipment reached a steady level. This heat-up time was normally four to seven hours during which an air purge of 3 SCF/min was passed through the reactor. Once a thermal steady-state had been achieved, a helium purge of the feed hopper was initiated to prevent steam from condensing in the inlet feedstock lines and starfeeder (Note: In a full-scale operation, a part of the product or waste gas could be diverted for this purpose; helium was chosen for this purpose because it was the carrier gas in the gas chromatograph. The desired steam and air flow rates for an actual run were then established and stabilized. After stable operation of the water-gas separation system was achieved, manure feed was introduced. The system was permitted to reach a new steady-state at a controlled reactor temperature. This new steady-state was generally achieved in 15 minutes to 30 minutes. Gas, tar, and char samples were then collected for analysis at 15 to 30 min. intervals. Reactor operation with manure feed generally ranged from 30 min. (first run) to two hours; total heated reactor time generally ranged from six to nine hours, excluding cooldown.

#### Discussion of Experimental Results

The data from the initial operation of the large-scale reactor are given in Table I. In general, these results indicated that dry gas yield and gas composition per unit of manure feed were largely independent of the air and

TABLE I  
OPERATING CONDITIONS AND PRODUCT GAS DATA

Operating Conditions	Run Number									
	1	6a	6b	7	8	9	10			
Manure Feed Rate, lb daf/hr <sup>(a)</sup>	11.5	15.9	35.6	28.6	29.2	28.0	18.2			
Manure Feed Rate, lb ar/hr	17.1	23.3	52.0	41.8	39.8	39.7	25.9			
Air Feed Rate, SCF/hr	40.5	60.0	52.5	67.2	49.5	15.0	27.0			
Steam Feed Rate, lb/hr	12	10	10	8	6.8	6	8.2			
Particle Size, in	<3/8	<3/8	<3/8	<3/8	<3/8	<1/8	<1/8			
Average Temperature, °C	711	695	641	617	629	668	628			
Product Gas Data <sup>(b)</sup>										
Total Dry Gas, SCF/lb daf <sup>(c)</sup>	19.1	(10.7)	9.3	6.5	7.3	(11.5)	5.1			
Heat Value (HHV), BTU/SCF	321	328	426	380	396	295	376			
Gas Composition, vol %										
H <sub>2</sub>	25.2	22.2	20.0	28.2	17.4	15.1	20.9			
N <sub>2</sub>	14.6	27.8	15.1	23.2	26.7	36.8	24.2			
CH <sub>4</sub>	12.8	7.7	12.6	9.2	14.1	8.9	11.7			
CO	11.6	15.3	21.3	16.4	21.2	20.3	22.4			
CO <sub>2</sub>	30.8	20.7	22.1	15.4	14.1	14.2	14.8			
C <sub>2</sub> H <sub>4</sub>	4.7	6.4	8.5	4.9	5.8	4.2	5.5			
C <sub>2</sub> H <sub>6</sub>	0.3	0.5	0.4	2.7	0.7	0.5	0.5			∞

(a) daf = dry, ash-free; ar = as-received

(b) All data are average values from at least two samples. Individual gas samples were analyzed on the gas chromatograph using at least two injections.

(c) Values in parentheses are back-calculated values using a nitrogen balance.

steam feedrates, over the ranges indicated. Reactor temperature was the only consistent variable which would order the data. This is in agreement with the results reported by Halligan, et.al. (1975) for a bench scale apparatus. These correlations and interpretations are discussed below, using an average reactor temperature as a correlating variable. The average temperature for the large-scale reactor was defined as the average along the reactor length, as calculated from Simpson's rule. The value given for the bench-scale unit was the arithmetic average of two measurements.

It is important to note that the oxygen in the air feed is a key reactor parameter because the partial oxidation of the manure supplies part of the heat duty required to heat the manure feedstock to reaction temperature. This exothermic reaction is indicated by comparing the average temperature of runs 8 and 9 of Table I. Run 9 was operated with three times the air flow of run 8 with the same electric heat input in the apparent oxidation zone and the average reactor temperature was 39°C higher. The significance of this temperature increase is indicated by noting that the total temperature range of Table I is 93°C.

The yields of total gas, ultimate hydrogen ( $H_2 + CO$ ; see discussion below) and ethylene are given in Table II and presented as a function of average temperature in Figures 1, 2, and 3 respectively (the correlation line through each data set is a least-squares fit). Comparison data from the bench-scale experiments of Halligan, et.al. (1975) are also shown in these plots. Because the slopes of these three data sets agree well with the bench-scale data, the general interpretation is that reactor temperature must be considered a key scale-up variable for the partial oxidation of manure as developed in these studies.

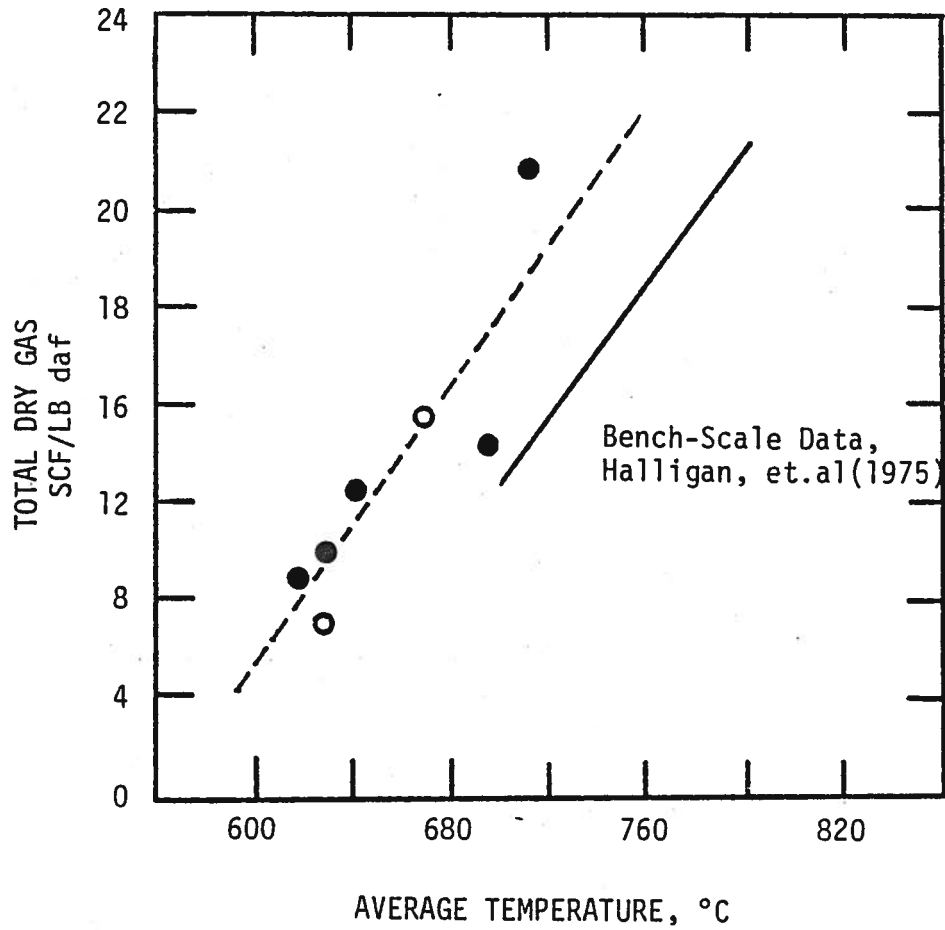


FIGURE 1. INFLUENCE OF REACTOR TEMPERATURE ON DRY GAS YIELD

Closed circles indicate particle size  $<3/8$  in;  
open circles are  $<1/8$  in.

A preliminary analysis of the operating characteristics of the reactor has shown, however, that another parameter, volume fraction of solids, may be important because this parameter could affect heat transfer as well as alter the reaction history of particles. Such a factor may account for part of the scatter in the data, but sufficient detail has not yet been developed to identify the influence of this effect. The preliminary analysis of reactor characteristics is given as an appendix to this paper.

The apparent absence of oxygen or combustion effects on the product gas rate or composition may be explained in part by the high temperature of the reaction and the relatively low rate of oxygen feed. At the temperatures in the reactor, complete reaction of oxygen within 1-2 feet of the air inlet may be expected because the rate of feed is much less than stoichiometric. Confirmation of this is indicated by a detailed comparison of runs 8 and 9 discussed above.\* In addition, the volume of combustion products is small because calculations (Peterson, 1975) have shown that combustion products only contribute 15-40% of the total CO and CO<sub>2</sub> composition.

Figure 2 and Table II illustrate the potential for the production of an ammonia synthesis gas from manure. As discussed by Halligan, et.al. (1975), ultimate hydrogen is defined as the sum of H<sub>2</sub> + CO, assuming the CO is shifted as now accomplished in commercial ammonia plants (CO + H<sub>2</sub>O = CO<sub>2</sub> + H<sub>2</sub>). In addition reformed hydrogen is defined as the ultimate hydrogen plus the hydrogen that would result from the complete partial oxidation of CH<sub>4</sub> and other hydrocarbons (e.g., C<sub>2</sub>H<sub>4</sub> + 2H<sub>2</sub>O = 2CO + 4H<sub>2</sub>); the steam reforming step is also accomplished commercially using methane as a feedstock. These results (Table II) show that the necessary H<sub>2</sub>:N<sub>2</sub> molar ratio of 3:1 can be realized from the partial oxidation of manure over the range of conditions.

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\* A detailed comparison of temperature profiles in runs 8 and 9 shows that all of the temperature increase occurred within 2 feet of the air inlet.

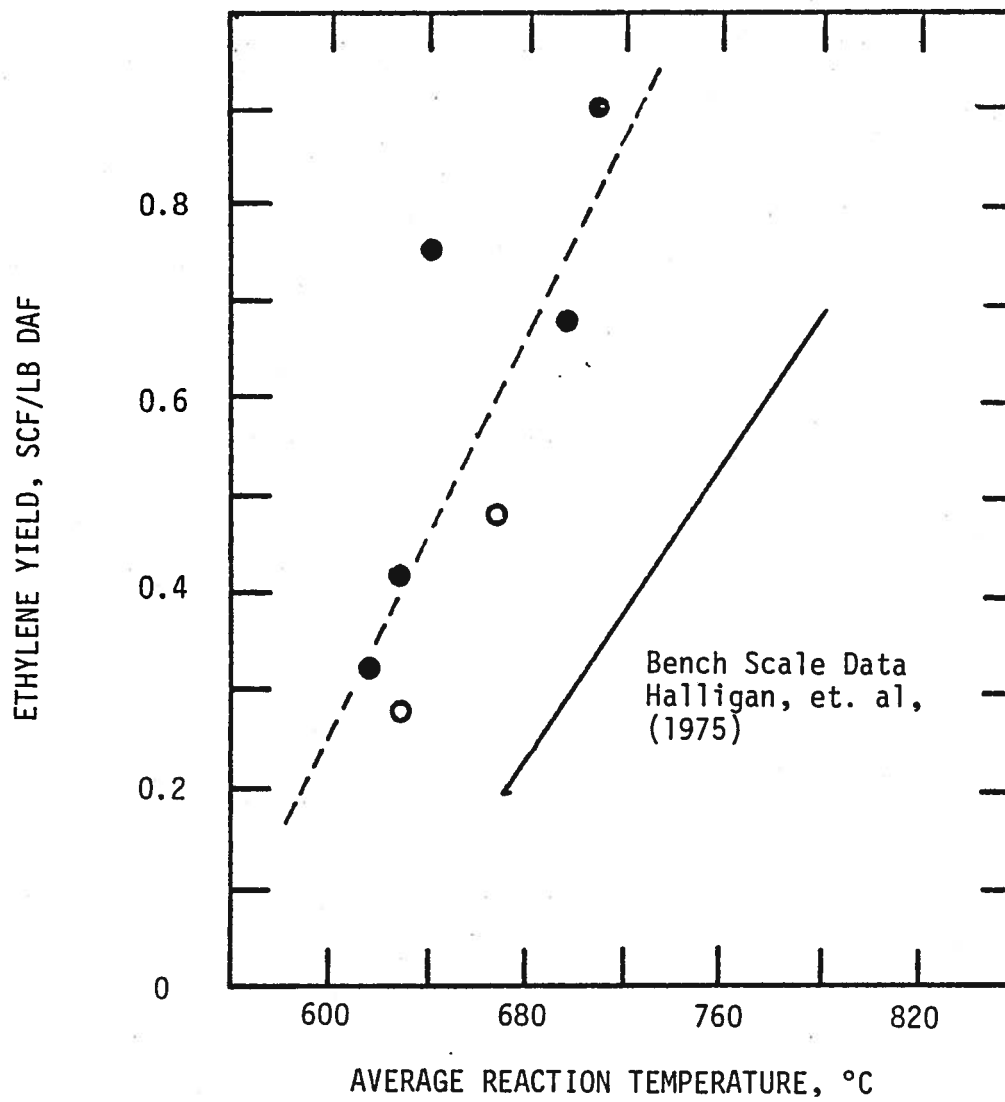


FIGURE 2 ETHYLENE YIELD AS A FUNCTION OF AVERAGE REACTOR TEMPERATURE.

Open and closed circles identified in Figure 1.

TABLE II

## CALCULATED GAS PRODUCT DATA

	Run Number									
	1	6a	6b	7	8	9	10			
Ultimate H <sub>2</sub> (H <sub>2</sub> + CO), SCF/lb daf	7.0	4.0	3.8	2.9	2.8	4.0	2.2			
Ultimate H <sub>2</sub> : (N <sub>2</sub> ) Ratio	2.5	1.3	2.7	1.9	1.4	0.95	1.8			
(Reformed H <sub>2</sub> ): (N <sub>2</sub> ) Ratio	8.0	3.8	9.5	4.7	4.9	2.6	5.1			
(Reformed H <sub>2</sub> without C <sub>2</sub> 's): N <sub>2</sub> Ratio	6.0	2.5	6.1	3.5	3.6	1.9	3.7			
Ethylene Yield, SCF/lb daf	0.90	0.68	0.75	0.32	0.42	0.48	0.28			
% C <sub>2</sub> H <sub>4</sub> without combustion products	6.8	11.0	10.3	8.7	9.9	9.5	8.7			

explored. It is recognized that the proper  $H_2:N_2$  ratio can always be achieved by simply adjusting air feed at an imposed temperature. The objective of the reactor process is to achieve maximum air input to minimize external heat duty with the constraint of  $3H_2:N_2$  ratio.

Another objective of the ammonia synthesis gas production is to exploit the  $N_2$  content of air as opposed to viewing it as a diluent which must be balanced against the cost of manufacturing oxygen. Conversely, effective nitrogen utilization from the process also means minimum product carbon. Nitrogen utilization in agricultural sectors is of equal importance, if not more so, to carbon utilization which is a common goal of many coal processes.

The ethylene yield of Figure 3 illustrates one possible key difference between the large-scale and bench-scale reactors. As noted earlier, the large scale reactor operates with a nearly complete countercurrent flow of solid and gas, with only 10-16% of the total product char (as fine particles) exiting with the gas. This flow pattern was not achieved in the bench reactor and 67-87% of the solid char product was entrained. The higher degree of hot, entrained solids (heat capacity about twice that of the gas) plus a review of the bench-scale operation indicates that product gas from the smaller reactor probably remained at temperature for a longer period of time. Thus, a lower degree of olefin cracking or pyrolysis would be expected in the large-scale unit and this interpretation is supported by a  $40^\circ C$  temperature shift in ethylene data (Figure 3) compared to a  $20^\circ C$  shift in the total gas (Figure 1) and ultimate  $H_2$  (Figure 2). The total gas or ultimate hydrogen rates would not be affected much ( $< 10\%$ ) for a 3-4% change in ethylene composition. The net ethylene production would be a strong function of time and temperature because

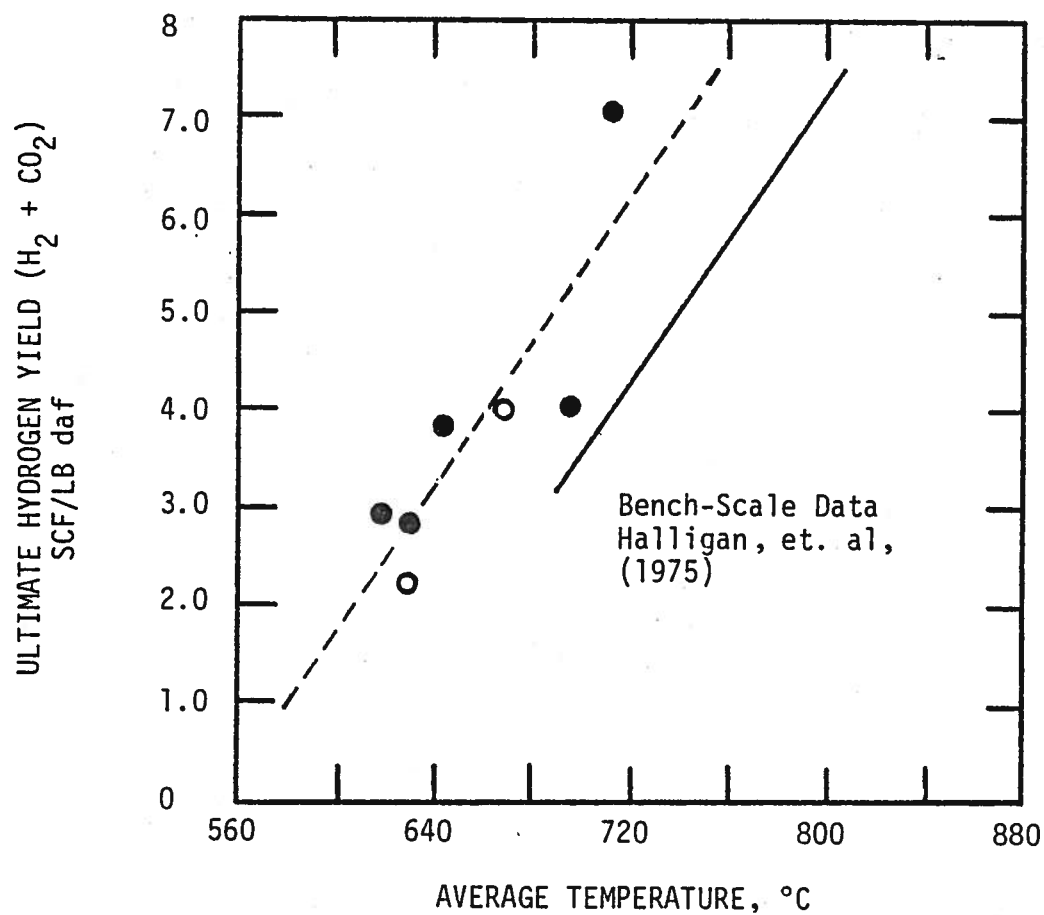


FIGURE 3 ULTIMATE HYDROGEN YIELD AS A FUNCTION OF AVERAGE REACTOR TEMPERATURES

See Figure 1 for definition of open and closed data points.

the rate of the second order decomposition kinetics at 6% (vol) and 600°C is only 0.5% the rate of decomposition at 720°C. Alternately the half-life at 600°C is 14 sec (6% vol) whereas it is only 0.15 sec at 920°C using the data of Benson and Haugen (1967).

The production of ethylene (hence its time-temperature history) is of significant practical interest because the current sales value is 10-12 cents per pound and one major manufacturer (Wishart, 1975) indicates that a 20 cent per pound price may evolve by the early 1980's. Using a value of 0.8 SCF/lb daf manure and the above current price, the ethylene in the synthesis gas has a sales value of \$12-15 per ton daf manure. The current data currently show that 125 lb  $C_2H_4$ /ton daf manure can probably be produced and limited studies indicate that reinjection of tars and oils produced in the reactor (10-30% by weight of manure fed) can raise the ethylene yield to 150-180 lb/lb daf. Because the economics of ethylene production are attractive, it is important to note that several of the runs in Table II suggest that significant quantities of both ethylene and an ammonia synthesis gas could be produced at the same reaction conditions. Our current research goals are to collaborate the reported results and maximize the production rate of both an ammonia synthesis gas and ethylene.

While the solids-fluid flow regime is considered to be important for ethylene production and overall results (see appendix), no specifics on this aspect can be given because the data are too meager. This is, the reactor cannot be characterized as either a falling-bed or a fluidized bed reactor; it may include some aspects of each. Fluid (gas) velocities were estimated to range from less than 1 ft/sec to 2 or more ft/sec along the reactor length during a given run, depending upon air and steam feed rates and the temperature

of operation. Pressure drop measurements along the reactor have not provided any definitive data to-date because normal pressure fluctuations caused by the intermittent operation of the discharge solids ram masked the readings. At most, pressure drop over the reactor ranges would appear to be less than 10 inches of  $H_2O$ , exclusive of the air-steam inlet distributor plate. The entire subject of solids-gas residence time or the flow regime remains to be investigated.

As discussed by Halligan et al. (1975), ash-fusion, the steam-carbon, and steam-hydrocarbon reactions are estimated to have a minor role at the reaction conditions. In particular, the rate of steam reactions are thought to be low because reactor pressure is 20 psia or less and average reactor temperature is generally less than  $927^{\circ}C$  ( $1700^{\circ}F$ ; see McFarland, et al. 1972 and Feldkirchner and Huebler, 1965; in Halligan, et al., 1975). Briefly, steam was added in the bench-scale experiments as a "fluidizing" medium which could be easily separated from the gas products by condensation and a similar, inert role was assumed for the larger unit. For example, without the addition of steam, the gas velocities in the larger unit would range from approximately 0.10 ft/sec to 1.35 ft/sec.

The distinction between particle size of the various runs in Table I has been made because grossly unreacted solid product was observed for particle sizes exceeding 1/8-inch. To confirm the visual observation, a representative sample of the char from run 8 was sieved and the ash content of each fraction was determined. These data, which are shown in Table III, indicate that approximately one-third of the reacting mass of all particles greater than 2mm (approximately 1/12-inch), was unreacted. Some independent data (Young, 1976), show that part of the high ash content of particles smaller than 0.25 mm can be due

TABLE III  
EFFECT OF PARTICLE SIZE ON ASH CONTENT  
OF CHAR PRODUCTS<sup>(a)</sup>

<u>Particle Size</u>	<u>% Ash By Weight</u>	<u>% Reacting Mass Remaining</u>
> 2 mm	41	59
1.41 - 2.0 mm	56	44
1.05 - 1.4 mm	55	45
0.71 - 1.05	54	45
< 0.70 mm	59	41
Cyclone (< 0.70mm)	60-61	39-40
Average Feed	19.6-21.5	78.5-80.4

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<sup>(a)</sup>All data from run 8.

to separation of ash and reactable material upon grinding of manure. This effect could explain part of the shift towards a higher ash content of the two samples with the lowest particle size, i.e., approximately 55% to 60%. For convenience and to minimize the degree of carry-over (as well as the ultimate goal of minimizing feed preparation cost and investment), a 1/8-screen was chosen for additional classification. As the data show, this additional feed preparation did not affect the overall results and its effect could potentially be neglected.

The data in Table III as well as direct mass balances, show that 50-60% of the dry manure feed (including ash) was reacted. Based on wet, ash-free feed, approximately 40% of the reactable mass enters the gas phase (approximately 45% on a dry basis) with the remainder estimated to be 20-30% unreacted char and 30%-40% liquids (including feed moisture content of approximately 10%). The amount of liquid product, exclusive of water, was the most difficult to estimate because the boiling point range was from 25°C-300°C at atmospheric pressure. Due to this wide range of liquid or tar boiling points, the liquid product tended to condense along the tubing walls of the entire gas-liquid equipment sequence. This uncontrolled condensation limited overall material balances to approximately 89%. To circumvent this problem, a new single unit condenser has been designed and built. Operation with this additional piece of equipment is expected within the near future.

These limited data have demonstrated that the basic, partial oxidation technology developed from a small scale reactor can be applied to a larger scale unit to produce an ammonia synthesis gas. The potential ammonia production is  $> 0.5$  ton  $\text{NH}_3$  per ton daf manure. The results of the investigations also indicate that significant ethylene production can be achieved con-

currently with ammonia synthesis gas production. The data also suggest that the upper limit on ultimate hydrogen production, total gas yield, or ethylene production per unit of dry ash-free manure feed has not been reached.

#### Acknowledgement

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## APPENDIX

To highlight some of the operational features (not design) of the reactor discussed in the paper, a preliminary model is developed below. The model is based on several key assumptions or approximations which may not be entirely correct for design purposes or analysis of reactor dynamics, but will be sufficient for an assessment of operating features. The assumptions are noted where appropriate.

The basis for the model is the kinetic rate equation that can be used to describe the strict pyrolysis of manure particles, as developed by Young (1976) and several other investigators for other cellulose (see Wen, 1974). In the actual reactor, both pyrolysis and oxidation occur, but it is assumed that oxidation is complete within one to two feet of the air inlet (reactor bottom) because the feed air rate is much less than the stoichiometric quantity (Levenspiel, 1972). Thus, most of the reaction products of the top fed manure are assumed to be generated from pyrolysis.

For the assumed pyrolysis reaction, the rate equation is given by equations (1a) or (1b), using nomenclature similar to the above references:

$$\frac{dM}{dt} = -kM \quad (1a)$$

or

$$\frac{dX}{dt} = k(1-X) \quad (1b)$$

where  $M$  = mass of volatile or reactive manure, daf basis

$k$  = rate constant =  $k_0 e^{-E/RT}$

$k_0$  = pre-exponential factor,  $\text{time}^{-1}$

- $E$  = energy of activation, cal/mole  
 $R$  = gas-law constant, cal/mole, °K  
 $T$  = absolute temperature, °K  
 $X$  = mass conversion, mass of daf manure converted per unit  
 mass of daf manure feed  
 $t$  = time.

It is desirable, however, to express equation (1a) in terms of individual particles where  $N_p$  is the total number and  $M_p$  is the mass of an individual particle. Equation (1a) may then be written as equation (2).

$$\frac{d N_p M_p}{dt} = - k N_p M_p \quad (2)$$

If  $N_p$  is assumed to be constant (i.e., no break-up or agglomeration of particles), then using the volume of a particle,  $V_p$ , and assuming all particles are of the same size, equation (2) may be written

$$\frac{1}{V_p} \frac{d M_p}{dt} = - k C_m \quad (3)$$

where  $C_m$  = concentration of reactive mass per unit volume of particles;  $C_m = M_p/V_p$ .

Equation (3) or (4) represents a definition of reaction rate of a manure particle using the particle volume as the reaction

$$r_m = \frac{1}{V_p} \frac{d M_p}{dt} \quad (4)$$

volume (Levenspiel, 1972 b). It is noted, at this point that is it not necessary to assume that the particle volume,  $V_p$ , is a constant.

To describe the pyrolysis reaction occurring, a differential cylinder at any point in the reactor may be chosen. Then a steady-state material balance may be written as follows:

$$(-R_m) (d V_r) = F_{mo} dX \quad (5)$$

where  $R_m$  = rate of reaction based on reactor volume

$V_r$  = reactor volume

$F_{mo}$  = feed rate of daf manure, lb/hr.

For a constant number of particles,  $N_p$ , the relationship between  $R_m$  and  $r_m$  is:

$$R_m = \frac{1}{V_r} \frac{d M_p N_p}{dt}, \quad (6a)$$

$$= (V_p N_p / V_r) r_m, \quad (6b)$$

$$= \gamma r_m. \quad (6c)$$

The term  $\gamma = N_p V_p / V_r$  is the volume fraction of particles existing in the reactor at any point. Combining equations (6c) and (5), one can develop

$$(C_{mo} \gamma / F_{mo}) d V_r = -(1/k) d (\ln C_m) \quad (7)$$

where  $C_{mo}$  = initial (or feed) concentration of reactive manure per unit particle volume.

The development of equation (7) requires that  $V_p$  be considered a constant. This assumption is probably not a good assumption for conversion levels ex-

ceeding 80 percent, but does appear to be a reasonable approximation up to this level, especially considering the high fraction of ash in manure (20-25%; Young, 1976). The assumption of constant  $V_p$  permits equations (8) and (9) to be used in developing equation (7).<sup>\*</sup> The term,  $F_m$ , is the feed rate which corresponds to the particle concentration,  $C_m$ ,

$$X = 1 - C_m/C_{m0} \quad (8)$$

$$C_m/C_{m0} = F_m/F_{m0} = M_p/M_{p0} \quad (9)$$

in the reactor at any given point. Equation (7) may be integrated directly to obtain a result which is descriptive of a general tubular reactor containing a first order reaction. This result is given by equation (10), assuming that an average value of the product of the rate constant and the volume fraction can be defined.

$$(\bar{\gamma k}) C_{m0} V_r/F_{m0} = - \ln (C_m/C_{m0}) \quad (10)$$

where  $(\bar{\gamma k}) = [\int \gamma k d V_r]/V_r$ .

When  $\gamma$  is constant and the reaction is isothermal, the left-hand side of equation (10) can be rearranged to yield, after dividing by  $k$ :

$$\tau' = \gamma C_{m0} V_r/F_{m0} = N_p M_{p0}/F_{m0}, \quad (11)$$

where  $\tau'$  is the residence time for the ideal case of constant  $\gamma$  and  $k$  as

<sup>\*</sup>The last equality in equation (9) does not require the assumption of constant volume;  $N_p$  must, however, be constant.

noted. However, equation (10) demonstrates that  $\tau'$  is only an apparent value for the current reactor design because temperature was not constant and  $\gamma$  is not expected to remain constant.

A closer approximation to the actual  $\tau$  would be to define a term  $(\bar{k}) \tau$  and assume that  $(\overline{k\gamma}) = (\bar{k}) (\bar{\gamma})$  so that:

$$\tau = \bar{\gamma} C_{mo} V_r / F_{mo} \quad (12)$$

In other words, the actual residence time will depend upon the flow regime(s) in the reactor, through  $\bar{\gamma}$ . This result is not unexpected, but it must be appreciated because the product distribution would also be altered by a change in  $\bar{\gamma}$ . In equation 11, the rigorous average value also demonstrates the close association between reaction temperature and particle distribution within a reactor using a solid feedstock with these kinetics. It also suggests a reason for part of the differences in product distribution, at constant  $C_{mo} V_r / F_{mo}$ , between the tubular reactor developed here and that of a fluidized bed or that of a similar tubular reactor with co-current flow (Wen, 1974; G.R. & D., 1972). It is also important to realize that no attempt has yet been made to alter the flow regime in the reported reactor which would change  $\bar{\gamma}$ , and potentially alter the product rate and/or distribution.

The volume fraction term (or  $1-\epsilon$ , where  $\epsilon$  is the void fraction) can be used to illustrate a probable limiting factor of the reactor operation: heat transfer to the particle. At the temperatures involved, radiation to a particle is probably the dominant mechanism (see also, Wen, 1974). Thus, there probably exists a critical  $\bar{\gamma}$ ,  $\bar{\gamma}_c$ , beyond which the expected or desired  $X$  can no longer be achieved, as the reactor is now operated. Or, at values of  $\bar{\gamma}$  greater than  $\bar{\gamma}_c$ , all particles will not be exposed to the same radiant energy transfer

from the wall. In this case, intraparticle radiant energy transfer (or perhaps conduction/convection, if the volume fraction approaches that of a packed bed) would become a key factor. It may be argued that the effect of  $\bar{\gamma}$  would simply be reflected in the measured temperature. However, the point being discussed here is that an average temperature can probably be imposed (or held constant over a range of  $\bar{\gamma}$ ) and that  $X$  may still be altered due to the change in heat transfer from the wall surface case to intra-particle effects. Over the three-fold range of feed rates explored to date, this potential limitation does not appear to have been approached.

The  $\bar{\gamma}$  effect also suggests that the reactor performance may depend upon the manner in which the reactor is started-up. For example, if a large inventory of solids is allowed to accumulate in the reactor before solids discharge is matched to solids feed, a significant bed (large  $\bar{\gamma}$ ) could exist at steady-state which would reduce heat transfer to particles as discussed above and thereby affect  $X$ . Again, this limit does not appear to have occurred as the reactor is currently operated, over the range of data explored.

Young (1976) has also shown that at a given level of conversion over a wide range of heating rates (50°C/min to 1000°C/min), a certain fraction ( $\alpha$ ) of the mass loss will always exist as a low molecular weight gas (boiling point less than 25°C at 1 atm) when the fluid phase residence time is generally less than 2 sec. Because the operation of the pilot-scale reactor approximates these conditions, a similar effect may be expected. The gas fraction obtained from the reactor may then be expressed in terms of the  $\alpha$  fraction as follows:

$$\alpha X = \alpha \frac{M_{po} - M_p}{M_{po}} = \frac{M_G}{M_{po}} = \frac{F_G}{F_{mo}} \quad (13)$$

where  $M_G$  = mass (or SCF) of gas produced

$F_G$  = flow rate of gas produced.

This result serves to illustrate that  $F_G/F_{mo}$  is a correct correlation variable which is independent of particle volume assumptions. For this reason, the gas yield has been expressed as SCF per lb daf manure feed in Figure 1 of the text. A similar analysis may be used to demonstrate that any fraction of the produced gas should be expressed on a similar basis, as done in Figures 2 and 3.