HYDROGASIFICATION OF CATTLE MANURE TO PIPELINE GAS

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## INTRODUCTION

Growing shortages of pipeline gas and the increasing need to improve methods of waste disposal in order to minimize environmental problems prompted the Bureau of Mines to investigate the feasibility of converting solid wastes to pipeline quality gas by direct hydrogasification. A feasibility study has been published[1,2] that indicates that this means of disposing of municipal solid waste may, for larger municipalities, not only provide the lowest cost means of disposing of the solid waste but also provide a supplementary source of pipeline gas at a price lower than supplementary gas from other sources.

Of all the forms of organic solid waste, the most abundant is animal manure which amounts to at least 200 MM tons/yr of organic solids.[3] A major contributor to this manure is the modern beef cattle industry and it is in this industry that the pollution problems arising from manure disposal are most extreme. This is because the increasing size and concentration of modern feed-lots itensify manure disposal and pollution problems which range from water pollution arising from soluble nitrogen compounds in the manure to severe odor problems. But on the other hand, it is the increasing size and concentration of these feed-lots which make cattle manure a potentially attractive feed stock for pipeline gas plants because collection is simplified and larger scale plants, which allow the lowest unit cost production of pipeline gas, can be built. In addition, the areas with great concentration of feed lots such as West Texas are also areas where convenient gas transmission pipelines already exist.

In this report, experimental data are presented showing the quality and yield of pipeline gas that can be generated by directly reacting cow manure with hydrogen at gasification conditions.

## EXPERIMENTAL

### Procedure

Except for one experiment conducted with dried cow manure in a continuous free-fall dilute-phase reactor, the experiments with manure and solid wastes were conducted in a batch autoclave. A drawing of the assembled reactor is shown in figure 1. The autoclave body is fitted with a pyrex glass liner into which the autoclave charge is placed. A thermocouple well covered by a pyrex glass tube is inserted into the liner. The free volume of the assembled autoclave is 1.2 liters; the liner has a volume of 0.7 liters.

The autoclave, containing the charge, is assembled and weighed on a bullion balance. The autoclave is then installed in the electric furnace. The system is first purged with nitrogen to remove the air and then purged with hydrogen to remove the nitrogen. Oxygen in the hydrogen (usually 0.1 percent or less) is removed by passage through a vessel containing palladium on an alumina carrier. The oxygen is catalytically reduced to water which in turn is removed by passage through a vessel packed with anhydrous calcium sulfate (Drierite). The autoclave is then charged with hydrogen to the desired initial pressure. Selection of the initial pressure is governed by the pressure, at the specified reaction temperature, or by the hydrogen/solid feed ratio desired.

Upon reaching the specified pressure in the autoclave, the valve on the autoclave is closed and the rest of the system is purged with nitrogen to remove the hydrogen. The autoclave is disconnected from the purged system.

Rotation of the autoclave is started at the same time the furnace is energized. The heating rate is 8° C per minute. Reaction time is that period during which the temperature is levelled off at a specified value. For all the experiments reported here, the time at reaction temperature was one hour. Cooling is accelerated by removing the upper section of the furnace. Rotation is continued until the autoclave has cooled to 250° C or lower. The cooling rate is about 4° C per minute down to 250° C.

When the autoclave has cooled to room temperature, it is depressurized at approximately 3 scf/hr. The gas in the autoclave is first passed through a Nesbitt absorption bulb containing Drierite to remove water. The gas is then metered and several samples taken to determine the gas composition with a gas chromatograph. The absorption bulb containing Drierite is weighed to determine the yield of water and the char remaining in the autoclave is weighed and analyzed for carbon and hydrogen so that an overall material balance as well as carbon and hydrogen balances can be made.

## Results With Cow Manure

Operating results obtained from the direct hydrogasification of dried cow manure are tabulated in table 1. Ultimate analysis of the manure used in these experiments is given in table 2.

The purpose of these experiments was to establish the feasibility of converting manure to pipeline gas and to determine the operating conditions at which this conversion could best be carried out. These results indicate that manure is an excellent feed stock for pipeline gas synthesis. For example, in runs MH-1 and MH-2 a product gas having a heating value in excess of 1,000 Btu/scf was produced after simply scrubbing out the $CO_2$. Thus, it is possible to produce an excellent pipeline gas from manure without methanation. That this is possible is due to the high concentrations of ethane in the product gases from the manure hydrogasification. The ethane is present in such high concentrations because the high reactivity of the manure allows hydrogasification to take place at low enough temperatures for the ethane to survive in the presence of hydrogen. At the higher temperatures necessary to hydrogasify coal, most of the ethane formed is quickly converted to methane by the reaction

$$C_2H_6 + H_2 \rightarrow 2CH_4.$$

One can visualize alternate processing options available for the raw gases from manure hydrogasification. One option would be simply to shift the CO to $CO_2$ by the well-known water-gas shift reaction ($CO + H_2O \rightleftarrows CO_2 + H_2$) to get the CO level down to acceptable pipeline standards and then scrub out the $CO_2$. The resulting gas could then be placed directly in a pipeline without requiring any methanation. Another alternative would be to first separate the ethane, which could be sold separately and/or blended with the pipeline gas. In this case, the pipeline gas would be produced by methanating a mixture of CO and $CO_2$. The concentration of $CO_2$ would be adjusted by varying the amount of $CO_2$ removed during scrubbing. These options are now being investigated in a detailed process study which will be published when complete.

## Effect of Process Variables

The primary independent variables studied in the batch autoclave were the hydrogen/manure feed ratio and the reactor temperature. Since the reactions are carried out in

TABLE 1.- Summary of autoclave results for the direct hydrogasification of cow manure

| | MH-1 | MH-2 | MH-3 | MH-4 | MH-5 |
|---|---|---|---|---|---|
| Reactor temp., ° C ......... | 550 | 550 | 650 | 550 | 475 |
| Initial press., psig ....... | 150 | 150 | 150 | 150 | 150 |
| Operat. press., psig ....... | 1800 | 1630 | 2200 | 750 | 1500 |
| Solid charge, grams ........ | 80 | 80 | 80 | 20 | 80 |
| Hydrogen charge, g-moles.... | .562 | .562 | .562 | .562 | .562 |
| Solid residue, grams ....... | 38.8 | 40.6 | 37.0 | 9.3 | 39.9 |
| Carbon in charge, g-moles... | 2.363 | 2.363 | 2.363 | .591 | 2.363 |
| Gas produced, g-moles....... | .963 | .967 | 1.14 | .65 | .811 |
| Carbon gasified, % ....... | 39.9 | 40.4 | 41.4 | 50.1 | 27.0 |
| Water recovered, g-mole .... | .925 | .872 | .967 | .233 | 1.083 |
| Gas Analyses (Dry and $N_2$-Free*) | | | | | |
| $H_2$ ........................ | 13.1 | 11.3 | 14.4 | 60.2 | 30.2 |
| CO ........................ | .8 | .7 | 1.7 | 4.1 | .9 |
| $CO_2$ ........................ | 34.1 | 33.5 | 29.3 | 10.6 | 38.7 |
| $CH_4$ ........................ | 40.3 | 42.1 | 54.2 | 18.2 | 21.7 |
| $C_2H_6$ ...................... | 11.7 | 12.4 | .4 | 6.6 | 6.5 |
| $H_2S$ ....................... | - | | | .3 | .2 |
| $C_3H_8$ ..................... | - | | | | 1.8 |
| Total ..................... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

*Reported $N_2$-free because the variable amounts (usually about1% of $N_2$ were due to $N_2$ from purging sample lines. The nitrogen content of the waste is converted to $NH_3$ which is dissolved in water.

TABLE 2.- Ultimate analysis of dried cow manure

| | Wt Pct | |
|---|---|---|
| Carbon ........ | 35.4 | |
| Hydrogen ...... | 4.2 | |
| Nitrogen ...... | 0.7 | |
| Sulfur ........ | 0.2 | |
| Oxygen ........ | 23.5 | (by diff.) |
| Ash ........... | 36.0 | |
| Total ... | 100.0 | |
| Moisture ... | 2.5 | |

a batch reactor, setting the feed ratio and the reactor temperature determines, among other things, the pressure that the reactor reaches at the desired temperature. While only a few batch experiments were made, they were sufficient to establish fairly accurately the optimum temperature and roughly the range of hydrogen/manure feed ratios over which it would be reasonable to operate a plant converting manure to pipeline gas.

Temperature

Experiments were conducted at temperatures of 475,550 and 650° C. The most dramatic effect of temperature was on the fraction of carbon gasified and on the ethane yield. These trends are shown in figure 2 at a constant $H_2$/manure feed ratio of .007 g-moles $H_2$/gram manure. In addition, a single point is also shown at a $H_2$/manure ratio of .028 g-moles/gram in figure 1. As figure 2 indicates, in the batch reactor operating temperatures above 550° C are detrimental because the only effect of the increased temperature is to convert ethane to methane which consumes hydrogen and which lowers the overall thermal efficiency of the process. At this point, it should be noted that in a balanced plant in which the hydrogen is internally produced all the carbon in the manure is utilized. This requires that enough carbon should be left in the char from the hydrogasification step to produce the hydrogen. Preliminary calculations indicate that the conversion of about 40 percent of the carbon fed to the hydrogasifier will leave sufficient carbon to produce the hydrogen required for the hydrogasification step.

The water yield was not greatly affected by variations in temperature over the range studied and amounted to about 20 wt pct of the manure charged. Since the manure as charged had a moisture content of only 2.5 wt pct, most of the water was formed by release of bound water or by reaction of oxygen in the manure with hydrogen.

Water was the only liquid product formed in these tests. No tars or oils were formed in any of the experiments. Thus, the disposal of or recycle of tars should not be a problem in a.plant converting manure to pipeline gas.

Hydrogen/Manure Feed Ratio

Four of the five tests conducted with manure were made at a hydrogen/manure feed ratio of .007 g-moles $H_2$/gram-manure with a single test at an increased ratio of .028 g-moles/gram. As the data in table 1 and the single point on figure 2 indicate, increasing the hydrogen/manure feed ratio resulted in a substantial increase in carbon conversion and the yield of ethane with a less significant increase in methane yield. However, at the higher hydrogen/methane feed ratio, both carbon monoxide and dioxide would have to be methanated to produce pipeline quality gas. It is worthwhile noting that in spite of the operating pressure being considerably less in MH-4 than in the other tests, because of the greater void space in the reactor due to the smaller solid change, the hydrogen partial pressure in this test was still substantially higher than in the other tests at 550° C. However, even with this increase in hydrogen partial pressure of about 2.5 times that in the lower hydrogen/manure ratio tests at 550° F, the overall carbon conversion or methane production were not increased anywhere near in proportion to the increase in hydrogen partial pressure.

Hydrogasification of Manure in a Continuous Reactor

Because of the promising results hydrogasifying dried cattle manure in a batch reactor, a hydrogasification test was made in a free-fall dilute-phase (FDP) reactor used for our coal hydrogasification studies. This FDP reactor and the method of conducting tests in it have been described.[4] To maximize the information from the FDP reactor run, the wall temperature was changed over the course of the experiment and the response of the gas composition to the different reactor wall temperatures measured. Data from these experiments are summarized in figure 3. As figure 3 indicates in the continuous FDP reactor, the methane yield increased greatly with increasing reactor wall temperature over the range of reactor wall temperatures studied. As in the batch tests illustrated in figure 2, the ethane yield in the FDP reactor went through a maximum because, as previously mentioned, with increasing reactor wall temperature, the ratio of the (rate of ethane disappearance by hydrogenation to methane) to the (ethane formation rate) increases. In the batch tests increased methane yields with increasing temperature above 550° C were due to the hydrogenation of ethane rather than the hydrogenation of the manure. However, in the continuous tests almost all of the methane was generated from the manure over the entire range of reactor wall temperatures.

It is difficult to make comparisons between the results in the FDP reactor and those in the batch reactor because the solid residence time in the FDP reactor is, at most, a couple of seconds compared to the hour residence time at temperature in the batch reactor tests. In addition, in the FDP reactor the solids are fed in cold and heat up very rapidly as they pass through the reactor and, because the time at any one temperature is very short, it is difficult to speak of a particle temperature. The physical appearance of the manure after hydrogasification was greatly different in batch and FDP experiments. Particles from the batch reactor had the same physical appearance as the feed manure except for being blackened while those from the FDP reactor were spheres with a very porous interior indicating that they had softened upon their passage through the reactor. In appearance, they seem almost identical to the char formed by the hydrogasification of raw coal.[4] In reference 4 it was pointed out that the high reactivity of the raw coal with hydrogen in the dilute phase is due to a great extent to the porosity of the particle which exposes the entire particle volume to hydrogen. The almost identical appearance of the hydrogasified manure particles indicates a similar mechanism applies when manure reacts with hydrogen in the dilute phase. Greater hydrogen accessibility greatly increases the reactivity of the manure as evidenced by the steadily increasing carbon conversion with increasing reactor wall temperature shown in figure 3 contrasted with the leveling off of carbon conversion with increasing temperature in the batch experiments shown in figure 2. The differences in the physical structure of the particles after reaction in the batch autoclave and the FDP reactor are due to two factors. The first is the difference in heatup rates that the particles in the two types of reactors experience. In the batch autoclave, the particles take approximately an hour to reach a typical reaction temperature while, in the FDP reactor, the heatup time is on the order of tenths of a second. The second factor is the difference in particle concentration between the two types of reactors. In the batch reactor the particles are in contact with each other or the reactor walls and the void fraction is typical of that for a fixed bed. However, in the dilute phase the particles are freely falling and widely separated with a void fraction approximately 95 percent. Thus, the combination of shock heating and unconstrained expansion result in a highly expanded porous particle that is readily permeated by hydrogen and hence extremely reactive.

Since in large-scale continuous reactor systems, the particle heatup rate will be the same order of magnitude as the heatup rates in the FDP reactor, one can expect the solids from such systems to be more reactive than the solids formed in the batch exploratory tests reported here. The use of this batch data for preliminary process design is therefore probably conservative.

## SUMMARY AND CONCLUSIONS

Batch experiments show that cattle manure is readily converted to pipeline gas by hydrogasification at temperatures low enough to allow appreciable yields of ethane. It is possible to produce a SNG with a heating value in excess of 1,000 Btu/scf by simply hydrogasifying the manure, shifting a rather low (on the order of 1 to 2 vol pct) concentration of CO to $CO_2$, and scrubbing out the $CO_2$ without any need for methanation. In addition, it was found that no tars or oils were produced from manure hydrogasification in spite of the relatively low temperatures. An experiment made with cattle manure in a continuous free-fall dilute-phase reactor indicated that the manure in such a reactor system is more reactive than in the batch reactor because of the much higher heatup rates and the low concentration of particles in the dilute-phase reactor.

## REFERENCES

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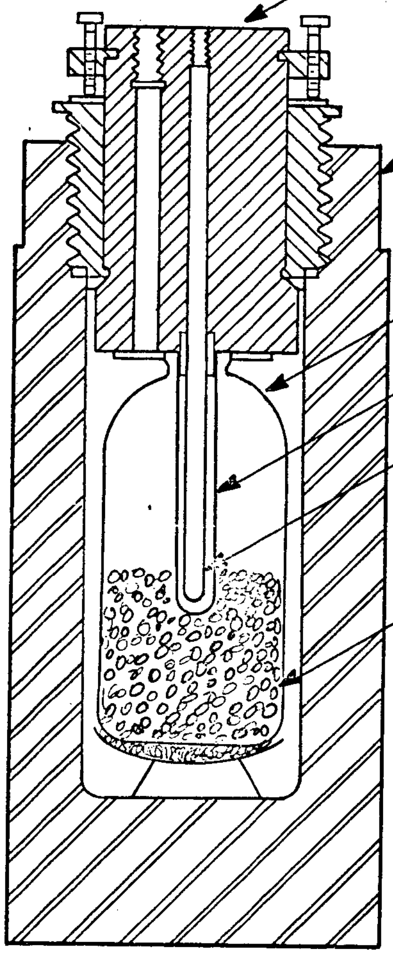


Figure 1 — Schematic diagram of autoclave.

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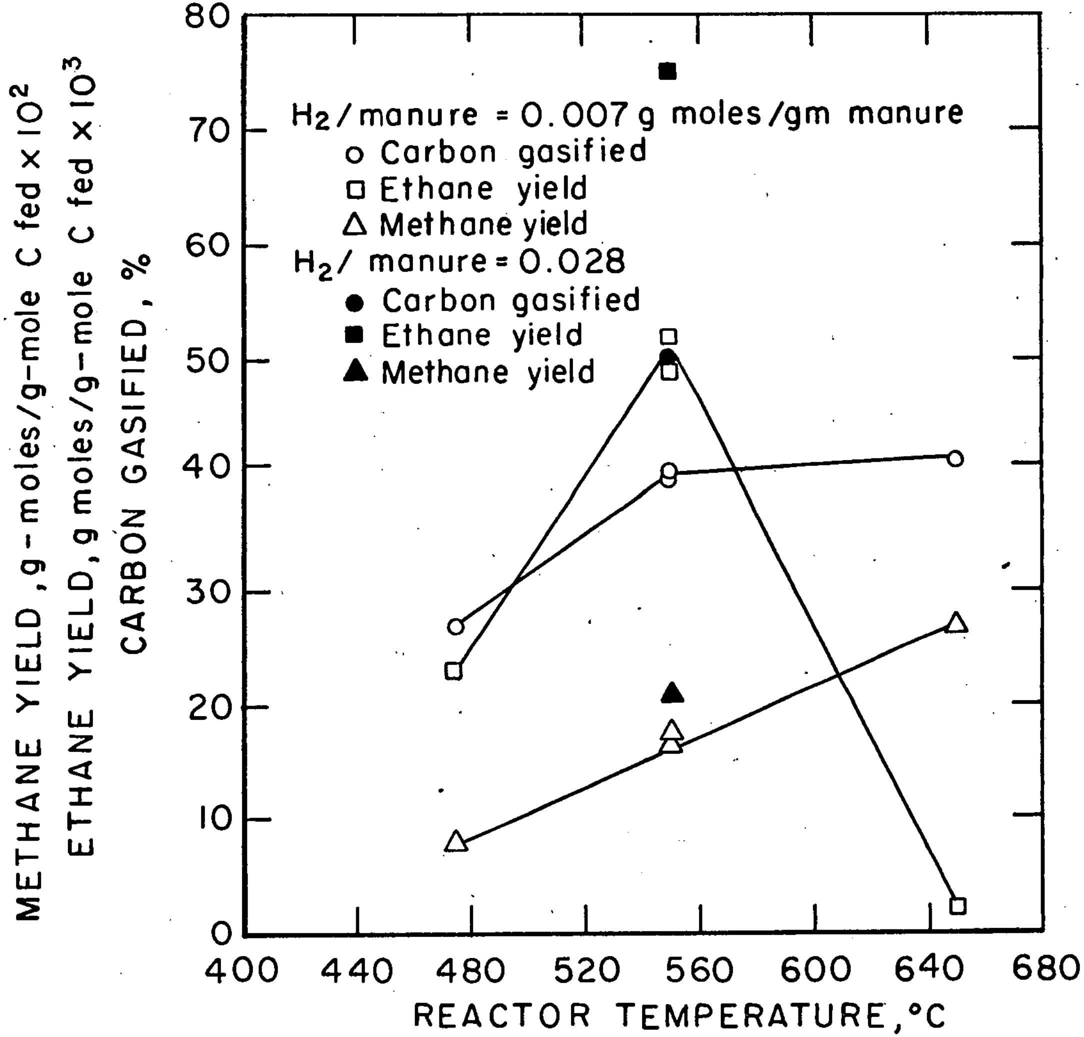


Figure 2 — Effect of reactor temperature on carbon conversion and hydrocarbon yield.

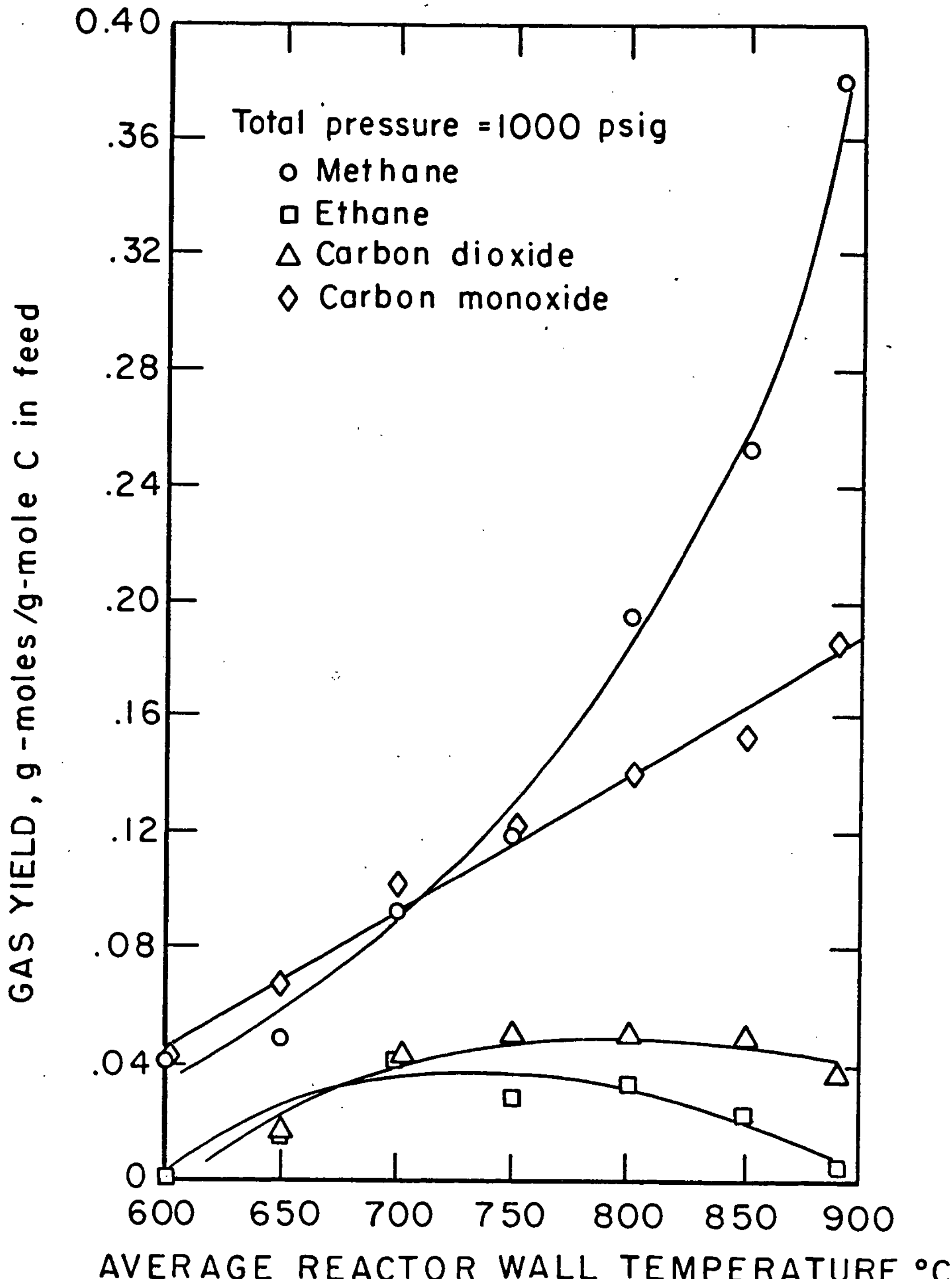


Figure 3 – Effect of reactor wall temperature on hydrogasification gas yields from dried cattle manure.



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