Household Cooking Fuel Hydrogen Sulfide and Sulfur Dioxide Emissions from Stalks, Coal and Biogas

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ABSTRACT

The indoor air pollution resulting from combustion of household cooking and heating fuels is increasingly recognized as a major detrimental influence on health. A pilot-scale study of hydrogen sulfide and sulfur dioxide concentrations in cooking areas was conducted in Henan Province, People's Republic of China. Data were collected in cooking areas utilizing crop stalks, coal, and biogas generated from family-scale anaerobic digesters and a large, distillery residue system. Although biogas was not scrubbed in any case, no recordable levels of hydrogen sulfide were detected in any of the areas. Sulfur dioxide levels in cooking areas where coal and stalks were used were found to average about four times higher than for biogas. The differences were statistically significant for coal but not for stalks. Problems and considerations for related studies and the aspects of biogas in ameliorating indoor air pollution are discussed.

Key words: anaerobic digestion, Henan Province (PRC), household fuels, hydrogen sulfide (H_2S) , indoor air pollution, sulfur dioxide (SO_2) .

INTRODUCTION

Pollutant emissions from household fuel combustion

The World Health Organization has now concluded that respiratory diseases are the chief cause of mortality in developing countries and that acute respiratory infections are a major cause of infant mortality in the same areas. While there are numerous factors involved, one of the most

likely causes is the exposure to the pollutant emissions from household

cooking and heating fires.

De Koning et al. and Smith offer excellent introductions to the range of considerations regarding emissions from household fuel combustion and health in developing countries. The emissions figures presented in Table 1 are 'typical, not average'. As noted elsewhere, 'Actual efficiencies and emissions depend on fuel quality and combustion conditions'. Since these efficiency figures are based on heating stoves under conditions in the USA, the emissions would certainly be much higher from the far less efficient combustion which occurs in most developing country situations. Emissions from direct combustion of crop stalks and dung might be expected to be in the range of those from wood.

TABLE 1
Comparison of Air Pollutant Emissions from Energy-Equivalent Fuels in Residential Situations (kg)

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Fuel	Wood	Coal	Distillate oil	Natural gas ^a
Efficiency under US	(40)	(50)	(85)	(85)
conditions (%) Fuel equivalent to 1 million MJ delivered	144 metric	69 metric	32 900 liters	$30\ 000\ m^3$
Suspended particulate	tonnes 2 170	tonnes 520	11	7
matter Sulfur oxides Nitrogen oxides Hydrocarbons Carbon monoxide	86 110 1450 18790	1 200 270 430 2 380	1 170 71 4 20	Neg. ^b 38 4 10

Data adapted from De Koning et al.3

Pollutant emissions considerations for biogas

While the financial and economic viability of biogas systems may still be arguable, these installations do provide undeniable benefits in the areas of household fuel supply, organic material and plant nutrient conservation, and sanitation. Another range of benefits lies in the 'cleanliness' of biogas relative to the direct biomass or coal combustion which it generally replaces in China. 'Cleanliness' is indicated by cooking vessels that are not blackened with soot while cooking with biogas. The general

^aReferences 4 and 5.

^bNeg., Negligible.

reduction in pollutant emissions from cooking fires and the reduced exposure of cooks and children to these emissions is likely to be of great

significance.

Biogas, produced by the microbial decomposition of organic materials, is composed of a mixture of gases. The exact composition depends on numerous factors, such as the substrate digested, impurities in the dilution water, the length of the digestion period, digester tank integrity, the general state of digester health, and various other parameters of digestion (temperature, moisture content, pH, digestible carbon/nitrogen ratio, etc.). In general, methane (CH₄) is the chief component, generally varying from 50 to 70%, occasionally higher, but typically about 60%. The gas is useful for combustion with common burners when the methane content is greater than 50%. Carbon dioxide (CO₂) is the other primary component of biogas and generally varies within a range of 30–40%. These two gases usually comprise well over 90% of the biogas.

Because of the humid digester environment, the biogas is generally saturated with water vapor (H_2O) . Other gases may include varying amounts of carbon monoxide (CO), hydrogen (H_2) , nitrogen (N_2) , ammonia (NH_3) , a few larger hydrocarbons $(C_{2-4}H_{6-10})$, and hydrogen sulfide (H_2S) . Hydrogen is a normal product of the first phase of the digestion process and, in some systems, may comprise more than 5% of the total gas produced.⁸ The presence of nitrogen or oxygen in the gas generally indicates a leakage of air into the digestion tank. Nitrogen and ammonia can result from a low carbon/nitrogen ratio in the substrate. Hydrogen sulfide, most commonly known as the smell of rotten eggs, is usually present in the gas at levels less than 10 ppm but tends to increase with any upset in the digestion process.⁹ High levels of natural sulfates in

the substrate or dilution water may also result in higher levels.

The flame temperature of biogas with a composition of 60% CH₄ and 35% CO₂ is about 1200°C. With reasonably complete combustion at this temperature, the carbon dioxide and water vapor would be unchanged; the methane, other hydrocarbons and any carbon monoxide, hydrogen or oxygen would form water vapor and carbon dioxide. Some of the nitrogen would be unchanged while some would likely result in nitrogen oxides (although less than with natural gas), and the hydrogen sulfide would be converted to sulfur dioxide (SO₂) and perhaps a small amount of sulfur trioxide (SO₃). Thus, air pollutant emissions from biogas combustion would be most similar to those from natural gas — suspended particulate matter and hydrocarbons would likely be lower since there are so few larger hydrocarbons in biogas; nitrogen oxides would likely be lower due to the lower flame temperature; carbon

monoxide would likely be about the same; and only sulfur oxides would likely be higher.

Henan Province

Henan Province lies largely in the plains south of the Yellow River in central China. It is one of China's most populous provinces with over 77 million human inhabitants of which about 85% live in rural areas. The area annually experiences over 200 frost-free days and only 3–4 weeks of hard frost.¹⁰

The total rural energy consumption (not including animate energy) is about 25×10^6 Mg coal equivalent of which over 80% is consumed in the household sector. Biomass fuels provide for over 80% of these household needs. Around 21×10^6 Mg of crop stalks (about 70% of total production) and 12×10^6 Mg of wood (about 47% of total production) are burnt annually. Coal is the primary household fuel in urban areas but only about 4×10^6 Mg year $^{-1}$ are consumed in rural areas. 11

The Chinese biogas program appears to have shifted away from concentration on locally available materials and traditional construction techniques which were quite inexpensive but resulted in digester lifetimes often less than 3–4 years. Current emphasis is on quality, concrete construction and systematic operation. Labor and material costs for a household system at the time of this study were around 200 yuan (about US\$60) but reliability is greatly improved and expected lifetimes are over 10 years. Cash subsidies, previously covering about a quarter of system costs, are being phased out. Thus, government support now comes primarily from the institutional and research infrastructure developed over the last two decades. There were about 40 000 of the improved digester systems installed in Henan during the sixth Five Year Plan (1981–85).¹⁰

It is perhaps due to the great quantities of crop residues burnt directly as cooking fuel that livestock populations are comparatively low in Henan. Since there is insufficient animal residue for adequate biogas production, digesters in this area are charged primarily with crop stalks and operated in a batch mode. The feed mix recommended by researchers at the Henan Academy of Science's Energy Research Institute is about 15 parts stalks to 1 part manure. With three batches per year, these six or eight cubic meter systems provide gas for lighting throughout the year, for cooking three meals a day for six months, and for cooking one or two meals a day for four more months. With the biogas system, most of the stalks which were previously burnt directly are available for other uses.

A CLOSER LOOK AT SULFUR EMISSIONS

Hydrogen sulfide from biogas digesters

Hydrogen sulfide is classified as a highly toxic gas with a Threshold Limit Value for prolonged exposure of 10 ppm.¹³ Its distinctive odor of rotten eggs can be noticed at concentrations of less than 1 ppm, but it quickly fatigues; the sense of smell sensitivity varies with the individual. At low concentrations (<10 ppm) it irritates the eyes and respiratory tract. Exposure to moderate concentrations (10–50 ppm) may result in headache, dizziness, clouded vision, nausea and vomiting.^{13,14} 'Slight symptoms' certainly appear after several hours' exposure to 70–150 ppm; the maximum concentrations that can be inhaled for 1 h without serious effects is 170–300 ppm; exposure to 400–700 ppm for 30 min is 'dangerous'; and concentrations of greater than 700 ppm are fatal in 30 min.¹³ While the greatest danger is from acute exposure, there is some clinical experience indicating undesirable and cumulative health effects from repeated low-level exposure.¹⁵

Biogas almost always contains a noticeable amount of hydrogen sulfide and, in some situations, the concentration may be very high. Digesters on some eastern US dairy farms tend to produce gas with H₂S concentrations as high as 6000 ppm.¹⁶ While there are several methods for scrubbing H₂S from the biogas, they all involve added expense. In none of the information on Chinese digestion systems reviewed by the author over the last 10 years has there been any mention of H₂S scrubbing for small systems. Even when the biogas is used in internal combustion engines, scrubbing does not appear to be considered necessary.^{8,17}

While the auto-ignition temperature of H₂S is only 260°C,¹³ it would appear that the users of biogas may experience a chronic exposure to some level of H₂S. Because of the highly toxic nature of this gas, a study was undertaken to investigate this possibility in the spring of 1987.

The raw biogas produced by several household digesters in two villages, by a very large distillery digester in the city of Nanyang, and two institutional research digesters was tested for H₂S content. This was done with H₂S detector ampules which are designed for immersion in the gas for 10 min and report a range of 0–20 ppm through a change in color.¹⁸ In one village (five samples), at the distillery (five samples) and for one of the research digesters, concentrations appeared to be less than 10 ppm. The gas from a large research digester fed only with chicken manure appeared to have a concentration of around 17 ppm. In the other village, the gas from all four digesters tested immediately

blackened the ampules, thus indicating a H₂S level very much greater than 20 ppm. More exact determination was not possible. (The reason for these high levels was not determined, but one very likely possibility is high levels of sulfur compounds in the local water supply.)

In an effort to determine whether any H_2S remained after combustion of the biogas, 8-h diffusion dosimeter tubes with a range of 0-50 ppm were employed. (All of the diffusion tubes used in these tests have an accuracy of $\pm 25\%$.¹⁹) The tubes were hung 0·5-1 m above the biogas burners (generally about 1·75 m above the floor) during the day's peak cooking period. (Personal monitoring was considered but the main point here was to determine if any H_2S was surviving combustion. Therefore, the tubes were placed where they would be most likely to record its presence.) Although the odor of H_2S was almost always noticeable during ignition of the gas, in no case was there any indication of H_2S levels within the threshold limits of the testing tubes.

Sulfur dioxide

Sulfur dioxide is classified as an irritant gas and is the primary component of sulfur emissions from combustion of fossil and biomass fuels. It is generally present in the atmosphere of industrial and urban centers at 1 ppb–1 ppm (1 ppm $SO_2 = 2620~\mu g~m^{-3}$) and in remote areas at 50-120 ppt (parts per trillion). Symptoms of upper respiratory irritation have been reported at levels of 2–5 ppm, and concentrations above 20 ppm have noticeable irritant, choking and sneeze-inducing effects. Higher concentrations promptly result in coughing and nasal discharge and can cause suppurative bronchitis and asthma- and influenza-like symptoms. Very high levels may cause asphyxia leading to death or the development of chemical broncho-pneumonia which may also be fatal in a few days. Chronic exposure has been widespread in certain industries but studies suggest only a low degree of chronic toxicity. 20

Green plants are far more sensitive to SO_2 than humans and animals.²⁰ Average concentrations of 0.010-0.025 ppm during the growing season have been found to adversely affect numerous agricultural crops. In mixtures with other pollutants, even lower concentrations of SO_2 have resulted in negative foliar and growth effects.²¹

The US Environmental Protection Agency's (EPA) National Primary Air Quality Standard — the level judged to be necessary to protect public health — for SO_2 is 0.03 ppm as an annual arithmetic mean and 0.14 ppm as a maximum 24 h concentration not to be exceeded more

than once a year. The secondary standards, which are to protect the public from any known or anticipated adverse effects, are 0.02 ppm for the annual mean, 0.1 ppm for the 24-h maximum, and 0.5 ppm as a 3-h maximum not to be exceeded more than once a year.²⁰

In an effort to discover the levels of SO_2 resulting from combustion of the H_2S in biogas, similar dosimeter tubes for SO_2 with an 8-h range of 0-25 ppm were hung next to the H_2S tubes. The recorded 8-h average concentrations in the 16 biogas-burning kitchens varied from 0 ppm in several households of one village to 3.9 ppm in one of the households using the very high H_2S -content gas. The mean of 0.86 ppm (s=1.12, where s is the sample standard deviation) was notably higher than the US EPA's once-a-year 3-h maximum.

To obtain some idea of the comparative importance of these high SO₂ levels resulting from biogas, pairs of tubes were placed at comparable spots in several kitchens where other fuels were used. Unfortunately, during the season in which these data were collected, very little wood is burnt in the area of the study. Data were collected, however, in kitchens where crop stalks were being utilized in one village (five samples) and where coal was being utilized in two cities (15 samples). Outdoor levels in one of the cities varied from 0.4 to 0.8 ppm SO₂ at two different sites. The five stalk-burning village kitchens had widely varying 8-h averages ranging from 0 to 13 ppm, with a mean of 3.2 ppm (s = 5.5). Levels in the 15 coal-burning kitchens varied from 1.7 to 9 ppm, with a mean of 3.5 ppm (s = 2.29). (As might be expected, there was no recordable level of H₂S in any of these kitchens.) Both stalks and coal resulted in about four times higher SO₂ levels than biogas. (A test in one natural-gas burning city kitchen showed a SO₂ level of 1·3 ppm.) The data are summarized in Table 2.

TABLE 2
Recorded 8-h SO₂ Levels in Cooking Areas

Fuel type	Location	n	Range (ppm)	Mean (ppm)	s^a
Biogas	All sites	16	0-3.9	0.86	1.12
Coal	All sites	15	1.7-9	3.5	2.29
Stalks	Zhu Yuan	5	0-13	3.2	5.5
Biogas	Zhu Yuan	5	0-3	0.60	1.34
Coal	Nanyang	5	1.7-4	2.4	0.93
Biogas	Nanyang	5	0.4-0.9	0.52	0.22

^a s, Sample standard deviation.

This level of difference continues when disaggregating the data from separate villages and cities. For the five samples each for stalks and biogas in one village, the mean for biogas-generated SO_2 is 0.60 ppm (s=1.34) compared to 3.2 ppm (s=5.5) for stalks. The five samples each of coal and biogas from Nanyang had a mean for biogas-generated SO_2 of 0.52 ppm (s=0.22) compared to 2.4 ppm (s=0.93) for coal.

Two new 5000 m³ digesters have just been built at the distillery and the gas-handling system is under construction. It would be interesting to investigate the effects of this system on the entire city's air pollution problem when the gas begins to replace coal for a projected 20000

households — about 15–20% of the total population.

While these sample populations are admittedly quite small and most certainly not random, the results are at least suggestive. A statistical *t*-test of means for all samples indicates a significant difference between biogas and coal kitchen SO₂ concentrations at the 99% confidence level. The large standard deviation and small sample of stalk-burning kitchens combine to produce no significant difference between SO₂ concentrations from stalks and biogas even at the 90% confidence level. (The author would suggest, based on Table 1 and the previous discussion of pollutant emissions from biogas, that more extensive tests would be likely to show such a difference.)

DATA COLLECTION AND ANALYSIS

Perhaps the greatest problem in attempting to determine levels of the indoor air pollutants and their causes and effects is the great number of variables which may affect the situation.²² For each of the cooking areas in this study, the data collected in addition to fuel type, H₂S and SO₂ levels included location, kitchen area, number of burners or stoves, number of hours the burner or stove was used, color of the cooking flame, number of open windows (assuming one open door at the time of year), and use of exhaust fans. For the homes with biogas, further data were collected concerning the type of digester, digester feed composition, method of operation, months since the last digester cleaning, and biogas lamp type, number and hours of use. Except for the gas concentrations, all information was obtained by observation or in response to a brief questionnaire.

All data were collected in Henan Province in the late spring. Coal data were collected in Zhengzhou (population $> 1000\,000$) and Nanyang (population $\sim 3-400\,000$); stalk data were collected in Zhu Yuan village ($\sim 140\,$ households, $> 100\,$ with digesters), and biogas data were

collected in Zhengzhou, Nanyang, Zhu Yuan and Bei Zai village (~60 households).

Village kitchens all had areas of 9.5 m² or more. City kitchens were all much smaller with areas of 4 m² or less. In retrospect, 'kitchen volume' would have been a much more appropriate measurement.

The only biogas burner used in this area is the Beijing Model 4 which is said to give 60% efficiency with gas at 8 cm of water pressure. All kitchens had only one burner or stove except for the five Nanyang biogas kitchens and four of the five Zhu Yuan stalk kitchens which had two. In the latter cases, it was not determined whether both were operated during the reported hours of use.

Presumably, the number of hours of stove use would be one of the most important variables in predicting SO_2 levels. Reliance on participant response for these figures in situations of little 'clock consciousness' is, however, somewhat problematic. During discussions with biogas users, all claimed a reduction in cooking time when using the gas. However, the data showed average hours of use to be $2\cdot17$ ($s=0\cdot72$) for biogas, $2\cdot53$ ($s=0\cdot57$) for coal and $1\cdot65$ ($s=0\cdot36$) for stalks. The reported number of hours of use is further complicated by the fact that biogas can be turned on and off instantly, while stalks and coal require more time for starting and continue burning for some time after cooking is completed.

Since the color of the cooking flame gives some indication of the efficiency of combustion, it was anticipated that there might be some correlation between this color and SO_2 levels, especially for the biogas. However, all biogas burners were apparently well adjusted and flame color depended completely on the fuel type — biogas burning blue, coal yellow-blue, and stalks orange.

For simplicity, windows in the kitchens were classified as open, halfopen or closed. A more useful approach might have been to obtain the actual area of the window openings and to have included measurements of other passive ventilation openings as well.

Exhaust fans were noted in several of the 10 coal-burning kitchens investigated in Zhengzhou. In the three kitchens where these fans were in use, the mean SO_2 level was $2\cdot1$ ppm $(s=0\cdot35)$ compared to $4\cdot9$ ppm $(s=2\cdot7)$ in the others. This was in an area where the outdoor SO_2 levels of $0\cdot4-0\cdot8$ ppm were recorded.

The information on digester type, feed mix, mode of operation and months since last cleaning was collected in an attempt to ascertain whether there would be any relationship to H₂S levels in the biogas. The village systems were either 6 m³, buried, domed tanks with exterior 0.75 m³ gas storage drums, or 8 m³ tanks with internal gas storage. The

feeds included maize stalks, rice and wheat straw, wheat hulls, and pig, cow, chicken and human manure. The systems were operated in either batch or semi-continuous fashion and from one to nine months had passed since the last cleaning. The distillery system included two 2000 m³, thermophilic, plug-flow digesters and was operated continuously on the residues from distillation of sweet potatoes. Unfortunately, the sample size in this study was far too small to draw any conclusions regarding possible correlations between digester-operating parameters and H₂S levels. The most notable information obtained through this effort was the very high H₂S levels in the biogas produced by all digesters in Bei Zai village.

Since biogas lamps tend to give less efficient combustion than cooking burners, it was assumed that their use might be of consequence in predicting SO₂ levels. In this study, lamps were found only in three village kitchens and were used only briefly because of the time of day

when measurements were obtained.

Regression analysis offers one method for estimating the relative importance of numerous influences upon a given variable, in this case, the 8-h average SO₂ concentration in parts per million, 0.5-1 m above the cooking fire. Stepwise regression was conducted using Lotus 123 (Lotus Development Corporation, Cambridge, MA, USA) with the independent variables being number of hours used, kitchen area, number of open windows, number of burners/stoves, a dummy variable for exhaust fan use, hours of biogas lamp use, and two fuel-type dummies — biogas/other (BG/O) and coal/other (C/O).

Simple regression of all independent variables showed the biogas

dummy to be most predictive, the equation being:

$$SO_2 = 3.4 - 2.6(BG/O)(t = 3.1; R^2 = 0.22)$$

where t represents the Student's t and R^2 the coefficient of multiple determination. Further analysis resulted in little of real significance. Most notable was a negative correlation of SO₂ levels to the number of hours used. This is certainly counter-intuitive and difficult to explain although it may well relate to the aforementioned problems with 'clock consciousness'.

DISCUSSION

The pilot study described herein was quite small and certainly problematic as far as data collection and analysis are concerned. However, along with the literature reviewed, it does suggest that biogas systems, while being more environmentally benign than fossil fuels, may also offer the least polluting method for utilization of the solar energy stored in biomass. As mentioned previously, there is actually a very broad range of benefits offered by these systems. The control of the cycle of return through domestication of the organisms of anaerobic decomposition can provide a clean-burning household fuel while at the same time reducing human and animal enteric disease through destruction of most pathogen vectors, allowing for utilization of crop residues for the maintenance of greater numbers of livestock, and actually improving agricultural lands through the return to the soil of digested residues with their nutrient and soil amendment qualities.

Increasing the utilization of biogas systems is also benign in regard to the 'greenhouse effect' resulting from increasing atmospheric CO₂ levels. The CO₂ released during the digestion process and upon combustion of biogas is CO₂ which was taken up by plants during the growing season. Substitution of biogas for fossil fuels where possible will reduce the amount of long-stored CO₂ entering the atmosphere. While digestion generally offers many — in China's case, millions of — small contributions, it may become quite significant when utilized on the scale of the Nanyang distillery where a notable portion of the city's households will soon be switching from coal to biogas for their cooking needs.

The farmers of the People's Republic of China have a several-thousand-year history of recognition of the importance of the return of organic materials to agricultural lands. Over the last two decades, with the help of thousands of researchers and technicians, they have conducted over 10 million 'experiments' to test the practical utilization of small-scale biogas systems. Many mistakes have already been made, recognized and corrected. These developments continue among the current economic reforms and there appears to be little reticence in sharing much of this experience.

Many of the problems brought about by over-population, such as over-use of agricultural lands and biomass energy resources, which the Chinese have been facing for centuries, are now being experienced in growing areas around the world. With limited resources, a system which offers such significant potential benefits in the broad areas of renewable household energy and small-industry process energy, the maintenance of agricultural soils and increased crop production, sanitation and, it would seem, respiratory health deserves more than the shallow monetary analysis which is so commonly applied to it. Biologically and environmentally speaking, anaerobic digestion systems seem to offer the most thermodynamically efficient and healthiest means for utilization of biomass energy resources.

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