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Resolving inconsistencies in measurements of hydrogen cyanide in syngas

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HIGHLIGHTS

- Large discrepancies in measuring HCN in syngas were investigated.
- Acetone and acidic solutions intended to sample other compounds also remove HCN.
- Ammonia and HCN should not be sampled in series from a gas stream.
- HCN in syngas has frequently been underestimated by orders of magnitude.

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ABSTRACT

Syngas from biomass and coal gasification contains ammonia (NH_3) and hydrogen cyanide (HCN) that originate from fuel bound nitrogen (FBN). Despite being minor constituents of the syngas, they are of great interest. They represent NO_X precursors when the syngas is burned for process heating or IGCC applications and catalyst poison if the syngas is to be converted to fuels or chemicals. Measuring NH_3 and HCN via wet chemical methods can be challenging and laborious, which may account for the relative paucity of NH_3 and HCN measurements reported in the literature. Three frequently cited studies report HCN yields that are insignificant regardless of operating conditions and biomass feedstock types. These studies have been cited by other authors as justification for not measuring HCN in studies of nitrogen evolution during gasification. Other authors have reported much higher yields of HCN, on the order of a few tens of percent. Tellingly, sample collection methods are distinctive for these two ranges of HCN measurements. The present study investigated the analytical methods underlying these results, and found the lower numbers to be the result of flawed sampling methodologies.

1. Introduction

Nitrogen compounds in biomass-derived syngas are considered minor constituents in terms of their concentrations, but play an outsized role in determining the quality of syngas. Ammonia (NH_3) and hydrogen cyanide (HCN) represent NO_X precursors when syngas is burned [1], and they can poison catalysts during chemical synthesis [2].

1.1. Methods of measuring HCN

The most common method of measuring HCN in syngas is the wet chemical technique, which entails bubbling syngas through a basic solution, usually dilute sodium hydroxide (NaOH). Upon exposure to the base, HCN dissolves into the aqueous phase as cyanide ion (CN^-). Analysis of the aqueous solution is then conducted off-line. By measuring the volume of syngas bubbled through the solution, the concentration of HCN in the syngas can be accurately determined.

Though laborious, the wet chemical technique has excellent sensitivity. Relatively low concentrations of HCN in the syngas can be detected by simply bubbling a larger volume of syngas through the liquid. Once the HCN is captured in aqueous form as CN^-, it is easily detected via an ion chromatograph (IC). This wet chemical technique is robust and tolerates relatively dirty gas streams. Steam in the syngas poses no problems as it can simply condense into the solutions. Some char and tar can also be tolerated. The char and part of the tar are insoluble in the collection solution and can be filtered out while preparing the samples for analysis.

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It is also possible to measure HCN in syngas using Fourier transform infrared spectroscopy (FTIR) [3,4] and gas chromatography in combination with a nitrogen chemiluminescence detector (NCD) [5]. These methods are advantageous because they allow direct measurement of HCN in the gas phase, avoiding the propagation of error that can arise from the multiple analytical steps associated with wet chemical methods. Direct measurement can also improve statistical power since more frequent sampling of the gas can be conducted. In contrast, wet chemical techniques are often too slow and laborious to allow collection of more than a few samples. Nevertheless, direct measurement of HCN can require sophisticated and expensive analytical instrumentation. Rigorous gas stream cleanup of tar and char must be conducted to avoid damaging instruments. Calibration of gas analysis instruments for HCN also presents a serious safety concern since calibration gases toxic to humans are required. The U.S. National Institute for Occupational Safety and Health (NIOSH) has designated HCN as "Immediately Dangerous to Life and Health" (IDLH) at concentrations of only 50 ppm [6]. In comparison, the IDLH of carbon monoxide (CO) is 1200 ppm [7]. A calibration standard containing cyanide ion (CN^-) is also required for analysis of aqueous samples, but the small amounts of aqueous sodium cyanide standard required can be handled with relative ease and safety. Despite the attractive aspects of direct measurement, most measurements of HCN in syngas are made via the wet chemical technique due to its safety, high sensitivity, and robustness.

1.2. Approaches to sampling NH_3 and HCN

When syngas is burned, the NH_3 and HCN are both precursors to NO_X formation. It is very common to measure both in thermochemical studies of nitrogen compounds. NH_3 and HCN are captured in aqueous solutions, although NH_3 requires an acidic solution and HCN requires a basic solution. Either two complete sampling trains are required, or NH_3 and HCN must be collected in turns. Collection in turns is commonly done to avoid the complexity of operating two sampling trains, but this doubles run time for experiments. Another disadvantage of collection in turns is that the syngas quality can drift between the two collection sessions.

Vriesman et al. [8] attempted simultaneous measurement of NH_3 and HCN in syngas from the gasification of miscanthus using one sampling train with NH_3 and HCN impingers arranged in series. The acidic impingers for trapping NH_3 were placed upstream of the basic impingers used to trap HCN. The raw syngas was lightly conditioned by removing particulate via hot ceramic filters before entering the impinger trains. There is no mention of tar removal upstream of the impingers.

Yu et al. [9] also performed simultaneous sample collection of NH_3 and HCN in their gasification study of three different biomass feedstocks. Like Vriesman et al. [8], acidic impingers were used to capture NH_3 followed by basic ones to capture HCN. Although no provisions for removing char and tar upstream of the impingers are described, the temperature of the slipstream line (200–250 °C) was probably cool enough that some heavy tars dropped out prior to reaching the impingers. A relatively high gasification temperature was employed as well (900 °C), which would have minimized char and tar yield.

The series configuration employed by these two groups simplified and accelerated the process of collecting nitrogen samples, but also allowed the possibility of HCN being unintentionally collected by the acidic solution used to capture NH_3. If this occurred, it would lead to underestimation of the true HCN concentration.

A third study by Zhou et al. [10] also employed acidic and basic impingers in series to capture NH_3 and HCN, respectively, along with extensive gas cleaning before the impingers. After removing particulate matter via a high temperature sintered metal filter, tars were removed via an acetone rinse. The syngas was then cooled using a heat exchanger before collection of NH_3 and HCN in impingers. The acetone scrubbing undoubtedly resulted in cleaner, tar-free nitrogen samples, but also introduced additional risk that HCN might have been removed by the acetone wash or by water condensation in the heat exchanger.

1.3. Evidence of unintentional removal of HCN

Evidence of unintentional removal of HCN in the studies by Vriesman et al. [8], Yu et al. [9], and Zhou et al. [10] is found by comparing their results to five similar gasification studies that measured HCN in isolation from acidic solutions and polar solvents (Table 1). From Table 1 it is clear that studies using acidic solutions prior to HCN sampling consistently reported much lower yields of HCN. The highest HCN yield reported in the three studies that used acidic impingers ahead of HCN sampling (Vriesman et al. [8], Yu et al. [9], and Zhou et al. [10]) was only 0.22%. In contrast, the three studies that avoided use of acidic impingers or solvent scrubbers ahead of HCN sampling (Kurkela et al. [11] and Abelha et al. [12,13]) reported HCN yields that were one to two orders of magnitude higher. de Jong et al. [3,4] used a third approach that directly measured HCN concentrations in syngas via FTIR and found HCN yields as high as 14%, far exceeding the yields reported when acidic impingers preceded HCN sampling.

Under reporting of HCN has been noted by Tan and Li [14]. Although they had previously used acidic and basic impingers in series [15], their more recent work acknowledged that HCN was sufficiently soluble in the acidic solutions to seriously underestimate HCN yield. No further information was given regarding the severity of this problem. Inspection of the HCN yields reported in their earlier work [15] varied from 1% to 22%, which does not obviously support or refute their concern about sampling errors.

We have performed a series of experiments to better understand the discrepancies in HCN measurements reported in the literature for gasification studies. We hypothesize that acidic and acetone impingers upstream of HCN sampling can dramatically reduce the amount of HCN reported for the gasification of nitrogenous feedstocks.

2. Materials and methods

2.1. Feed system and reactor

A fluidized bed gasification reactor with an inner diameter of 38 mm and a height of 380 mm was used to generate syngas at nearly atmospheric pressure to study HCN collection techniques. The reactor included a volumetric feed system equipped with a two-auger system. The first auger was used to accurately dispense fuel and the second was operated at high rotational speed to stoke the fluidized bed. A small stream of inert gas purged the feed system to keep the injection auger and its contents cool. Switchgrass fuel was utilized for this study, which was prepared by drying followed by grinding and sieving the material to 212–500 μm in size. Ash content was measured using a Mettler Toledo TGA/DSC 1 Thermo-Gravimetric Analyzer. Analysis of carbon, hydrogen, and nitrogen content was conducted with an Elementar vario MICRO cube analyzer. Oxygen content was found by difference. Moisture content was determined by heating samples for 72 h at 95 °C in a Fisher Scientific IsoTemp Oven. The analysis results are shown in Table 2.

A perforated plate and heated plenum below the fluidized bed preheated and distributed incoming fluidizing gas. The plenum, bed, and freeboard of the reactor were enclosed in Watlow ceramic fiber heaters that provided both temperature-controlled heating