

# CHARACTERIZATION AND CATALYTIC CONDITIONING OF SYNTHESIS GAS PRODUCED BY BIOMASS GASIFICATION

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## 1. INTRODUCTION

Synthesis gas (syngas) is a mixture of carbon monoxide and hydrogen used as a feedstock for methanol, higher alcohols, and Fischer Tropsch hydrocarbon synthesis. Syngas generated by thermal biomass gasification (referred to as biosyngas in this paper) represents a renewable feedstock because alcohol/hydrocarbon combustion returns the carbon and hydrogen to the atmosphere as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . These are converted back into plant material during photosynthesis when new biomass is cultivated. Biomass gasification in this respect is a form of solar energy conversion.

Syngas from biomass gasification cannot be used directly for fuel synthesis because it contains particulate matter, methane,  $\text{C}_2$  hydrocarbons, and tar.<sup>1</sup> These impurities cannot be tolerated by downstream catalytic fuel synthesis processes. Unprocessed biosyngas is also unacceptably rich in CO for most syngas chemistry; for example a  $\text{H}_2/\text{CO}$  ratio equal to 0.7 is typical in biosyngas but methanol synthesis stoichiometry requires that  $\text{H}_2/\text{CO}$  be equal to 2 (in industrial methanol synthesis some  $\text{CO}_2$  is also added).

The most cost effective way to prepare biosyngas for fuel synthesis is by syngas conditioning.<sup>2-4</sup> This is a direct on-stream process that destroys tars, reduces the level of methane and other low molecular weight hydrocarbons and simultaneously adjusts the  $\text{H}_2/\text{CO}$  ratio. Excess steam from gasification is used to catalytically reform tar and methane and simultaneously adjust the  $\text{H}_2/\text{CO}$  ratio *in-situ*.

A fluidized bed syngas conditioning process using a proprietary catalyst, designated DN-34, is currently being developed in a joint effort between the National Renewable Energy Laboratory (NREL) and Battelle Columbus Laboratory (BCL).<sup>4,5</sup> DN-34 is active for tar destruction, exhibits water-gas shift activity and contains no nickel. DN-34 has also been tested for more than 50 hours on stream in a gasifier slip-stream reactor at BCL without detectable deactivation.<sup>5</sup>

The effectiveness of DN-34 in syngas conditioning was recently confirmed using the NREL transportable molecular beam mass spectrometer (TMBMS). DN-34 was tested in a slip-stream fluidized bed catalytic reactor attached to the BCL 9 tonne/day indirectly heated biomass gasifier. Real time mass spectra were obtained for unprocessed syngas and syngas processed over DN-34. In addition to methane and other permanent gases, the unprocessed syngas contained aromatic hydrocarbons including benzene, naphthalene, methylnaphthalenes, phenanthrene/anthracene and pyrene, as well as oxygenated aromatic compounds such as phenol and cresol. The oxygenated compounds were essentially eliminated by syngas conditioning, however, some benzene, naphthalene and smaller amounts of higher molecular weight aromatic hydrocarbons remained. This is qualitatively consistent with the results from two separate 50-hour microscale lifetime tests with DN-34 and other, previous, microscale experiments.<sup>4</sup>

This paper discusses the performance of DN-34 measured with the TMBMS and compares these results with the results of microscale tests performed in the laboratory.

## 2. EXPERIMENTAL METHODS

### 2.1 Syngas Analysis by Mass Spectrometry

A transportable molecular beam mass spectrometer (TMBMS) has been designed by NREL that can be moved by common carrier to a pilot plant or other engineering scale biomass conversion facility. The instrument weighs about 500 kg and there are about 200 kg of supporting electronics and ancillary instrumentation. The footprint of the TMBMS is approximately 1 m deep by 2 m wide by 1.5 m tall. The TMBMS uses a 1-750 Da quadrupole mass spectrometer with a differentially pumped molecular beam sampling interface and is computer controlled. The TMBMS is based on molecular beam mass spectrometry (MBMS) which uses extractive sampling and mass spectrometric analysis to identify chemical compounds in complex, highly reactive, high temperature process streams and systems.<sup>6</sup> In addition to reactive systems, particle laden streams can also be sampled.

A sample transfer system was constructed from stainless steel tubing and fittings to interface the TMBMS to the BCL gasifier. Figure 1 shows the transfer line design concept. The combined length of transfer line tubing was about 11 m (36 ft) when installed on the gasifier. Separate laboratory experiments were performed prior to the BCL work to test for possible artifacts in sampling. Based on the results of that work both the raw and conditioned syngas from the BCL gasifier were diluted with nitrogen preheated to 300°C at a ratio of 5:1, and the residence time in the transfer line system was kept to less than one second.

### 2.2 Microscale DN-34 Lifetime Testing

Microscale tests were performed with a model biosyngas and tar to examine DN-34 deactivation during syngas conditioning. The composition of the model biosyngas is shown in Table 1. For comparison, the table also shows a typical analysis of real biosyngas from the BCL gasifier. Two 50-hour lifetime tests with DN-34 were performed at the Colorado School of Mines (CSM) using a two stage up-flow tubular reactor. The model syngas flow rate was controlled with a rotameter. Separate syringe pumps were used to meter water and model tar. The model tar was a solution of 10 wt % naphthalene dissolved in toluene. Both liquids were vaporized and mixed with the model syngas in a separate vaporizer located just before the catalytic microreactor inlet. The catalytic microreactor was a 1/2 inch O.D. quartz tube with a fritted quartz disk used to support a 2.0 gram DN-34 catalyst bed. The reactor exit lines were heated to approximately 300°C to prevent any condensation. Two gas chromatographs were used; the first to analyze unreacted model tar and the second to determine the concentration of the permanent gases and water. The conditions for the lifetime catalyst tests were: temperature = 815°C; steam in the feed = 40 vol %; and gas hourly space velocity (GHSV) =  $2000 \text{ cm}^3_{\text{gas at } 815^\circ\text{C}}/\text{cm}^3_{\text{catalyst}}/\text{hour}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 Raw Syngas Analysis by TMBMS

Figure 2 is a time trace for the benzene peak ( $m/z$  78) for the second of two raw biosyngas samples taken in real time from the BCL gasifier using the TMBMS. The figure shows how the flow rate (as measured by this trace component) fluctuated over 25 minutes. These data were taken during a shakedown run of the BCL gasifier using hog fuel as the feedstock. Considerable difficulty was encountered in feeding the hog fuel to the gasifier because a continuous dryer had not yet been installed. As a result, the wet hog fuel would bind and jam periodically in the screw feeding equipment, and we think that this is the origin of the large pulse-like fluctuations in Figure 2.

The two arrows in Figure 2 indicate the time interval used to obtain the averaged mass spectrum shown in Figure 3 (the  $m/z$  50-350 tar region for unprocessed biosyngas). The peak intensities are roughly proportional to the relative concentrations of these compounds because they are chemically similar and because the instrument was tuned so that the mass spectral response was approximately constant as a function of  $m/z$ .<sup>7</sup> Therefore, Figure 3 indicates that benzene ( $m/z$  78), toluene ( $m/z$  92), phenol ( $m/z$  94), styrene ( $m/z$  104), cresol ( $m/z$  108), indene ( $m/z$  116), naphthalene ( $m/z$  128), methyl-naphthalene ( $m/z$  142 isomer unknown) and phenanthrene/anthracene ( $m/z$  178) are among the more abundant tar compounds. The tar in Figure 3 also appears to have a greater proportion of benzene and naphthalene, and somewhat lower amounts of aromatic hydrocarbons with 3 rings or greater, or oxygenates such as phenol and cresol. This is expected because the BCL gasifier is operated at approximately 800°C.<sup>5,8,9</sup> Oxygenates and unsaturated substituted aromatic hydrocarbons (e.g. styrene,  $m/z$  104) are more abundant under conditions of less severe thermal cracking of the pyrolysis vapors formed during the initial stages of biomass gasification.<sup>8-10</sup> The exact composition of gasifier tar depends on both gasification temperature and residence time.<sup>9</sup>

### 3.2 Conditioned Syngas Analysis by TMBMS

DN-34 was tested in a slip-stream fluidized bed reactor attached to the BCL gasifier during the hog fuel shakedown run. The total slip-stream flow was about 2.8 m<sup>3</sup>/h (100 SCFH) and the catalyst was operated at a GHSV of about  $2000 \text{ cm}^3_{\text{gas at } 800^\circ\text{C}}/\text{cm}^3_{\text{catalyst}}/\text{hour}$  at a temperature of approximately 800°C. Details of the reactor configuration are reported elsewhere.<sup>5</sup>

Figure 4 shows the mass spectral peak intensities between  $m/z$  50 and  $m/z$  350 for the conditioned syngas stream exiting the fluidized bed slip-stream reactor. Direct comparison of intensities between Figures 3 and 4 should not be made because the exact syngas flow rates in each case were unknown. Comparison of relative peak intensities within each spectrum, however, indicates the composition of tar in that sample. Figure 4 shows that the peak intensities for the aromatic hydrocarbons were reduced, and the substituted aromatic and other hydrocarbon peaks were essentially eliminated, by catalytic conditioning with DN-34. This shows that DN-34 is active for destroying many of the compounds present in biomass gasifier tar, however, benzene, naphthalene and smaller amounts of higher molecular weight aromatic hydrocarbons were detected in the outlet gas. This is consistent with previous microscale activity tests using a synthetic syngas and tar different than that listed in Table 1.<sup>4</sup> In that work, DN-34 exhibited high activity for cresol, indene, 1-methylnaphthalene and 2-methylnaphthalene destruction at 815°C, with 50 vol % steam at a GHSV = 1500 h<sup>-1</sup>, but benzene and naphthalene destruction levels were typically 30 and 50 mole % respectively.<sup>4</sup> We were not able to perform quantitative analysis of the BCL syngas with the TMBMS due to the limited time on-line so exact tar conversion levels are not reported. Future work will address quantitative analysis. Kinetic data are not yet available for DN-34, however lower space velocity operation may improve benzene and naphthalene destruction with DN-34. The small peaks at  $m/z$  55, 73, 91 and 109 in Figure 4 are from water clusters formed from the steam in the syngas sample. They form during adiabatic cooling of the sample gas in the first differentially pumped stage of the TMBMS inlet. Using hot N<sub>2</sub> to dilute the sample gas minimized their formation.

### 3.3 DN-34 Lifetime Performance and Selectivity

Two 50 hour microscale tests of DN-34 were made using a model syngas and model tar (Table 1). The results from a duplicate lifetime test were essentially identical to the first test. Toluene was not observed in these experiments but benzene (not originally in the feed) was. This is thought to be steam dealkylation of toluene to form benzene and syngas as this reaction has been observed with different catalytic systems.<sup>11</sup>

Gradual loss in benzene destruction activity was observed during the test. Benzene destruction was initially 95 mole % and decreased to 75 mole % by the end of the 50 hours. Further data were not taken, thus, it could not be determined if catalyst selectivity would continue to change. Naphthalene destruction was essentially complete during the entire 50 hours. The loss of benzene destruction activity in the microscale tests is in contrast with the lack of measurable deactivation seen in earlier slip-stream gasifier tests.<sup>5</sup> The reason for the difference is not clear at this time. While quantitative comparisons are not possible at this time, the observation that DN-34 exhibits somewhat superior performance for destroying the higher molecular weight aromatic hydrocarbons is consistent with the other microscale experiments<sup>4</sup> and with the TMBMS work discussed here. This may simply reflect the difficulty in steam reforming more stable hydrocarbons using DN-34. Current efforts in catalyst development are aimed at determining the origin of activity in DN-34 and using this information to guide the formulation improved catalysts.

### 4. SUMMARY

The NREL transportable molecular beam mass spectrometer (TMBMS) was successfully used to monitor unprocessed and catalytically conditioned biosyngas. Variations in the biosyngas flow rate were attributed to variations in the biomass feed rate. A large number of tar compounds were observed in the unprocessed syngas in addition to the known low molecular weight permanent gases (not shown) including, oxygenated and substituted aromatic hydrocarbons, and polynuclear aromatic hydrocarbons. Catalytic conditioning with DN-34 effectively destroyed the more reactive compounds, but some benzene, naphthalene, phenanthrene/anthracene and pyrene remained.

The results from the gasifier slip-stream experiment are qualitatively consistent with the results of similar experiments performed at the microscale with DN-34, that is stable hydrocarbons (e.g. benzene) are less reactive than oxygenated or substituted aromatic hydrocarbons. The 50-hour lifetime tests indicated that the conversion of benzene gradually decreased during the test period.

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Component	Gasifier Biosyngas (mole %)	Model Biosyngas (mole %)
H <sub>2</sub>	15.8	15.3
CO	23.0	22.6
CO <sub>2</sub>	9.2	8.8
CH <sub>4</sub>	9.1	8.8
C <sub>2</sub> H <sub>2</sub>	0.4	0.3
C <sub>2</sub> H <sub>4</sub>	3.0	2.9
C <sub>2</sub> H <sub>6</sub>	0.3	0.3
TAR	0.2*	1.0**
H <sub>2</sub> O	39	40

Table 1. Gasifier product gas and model syngas compositions  
 \* for average molecular weight of 100  
 \*\* 10 wt % naphthalene dissolved in toluene

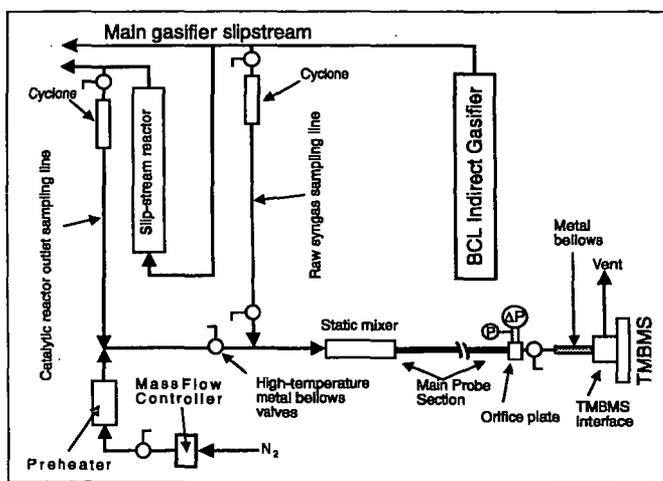


Figure 1. Schematic of TMBMS interface to Battelle gasifier

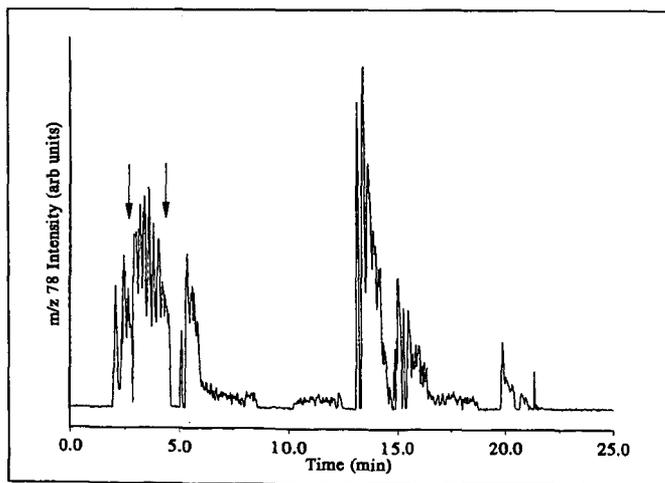


Figure 2. Benzene ( $m/z$  78) intensity vs. time for unprocessed biosyngas

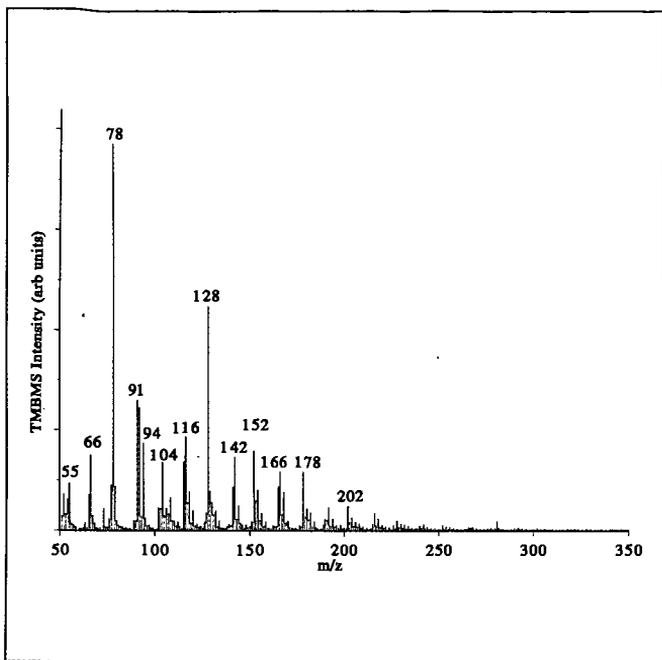


Figure 3. Mass spectrum for raw hog fuel gasifier tar

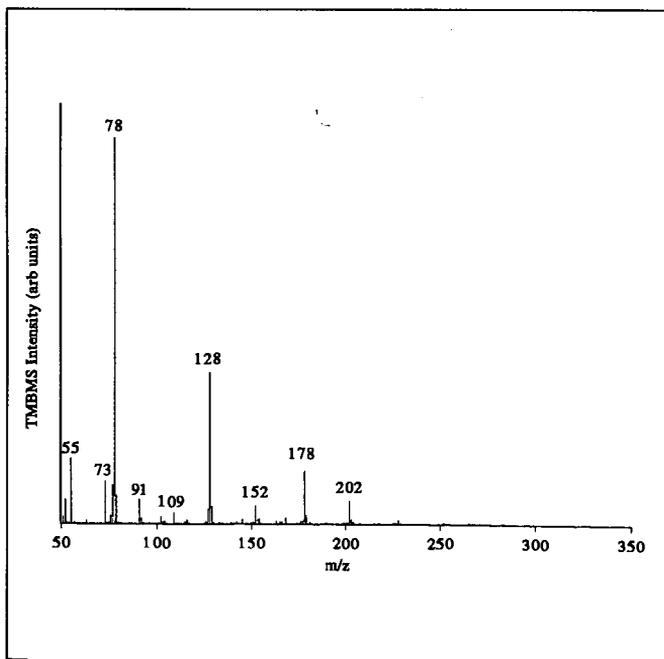


Figure 4. Biosyngas conditioned with DN-34 catalyst