Demonstration Results from Greenhouse Heating with Bio-Oil

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Abstract

Bio-oils from loblolly pine (*Pinus taeda*) and white oak (*Quercus alba*) wood were produced by the laboratory scale auger reactor located at the Department of Forest Products, Mississippi State University (MSU). The bio-oils were esterified to boiler fuel by a technology developed at MSU. The testing of esterified bio-oil combustion was performed at Natchez Trace Greenhouses located in Kosciusko, Mississippi. At the greenhouse facility an idled natural gas/diesel boiler was retrofit with a highly aerated fuel injection system. Fifteen gallons of loblolly pine esterified boiler fuel and 15 gallons of white oak boiler fuel were successfully combusted in the retrofit boiler.

Natural gas ranks second in US energy consumption after petroleum, providing 38 percent of total energy demand (US Energy Information Administration 2008). Natural gas price increases accelerated over the decade through July of 2008 with the peak price reaching a level above $14 per million British thermal units. Following this peak price, technological natural gas production advances have increased supply and the economic recession has reduced international demand for natural gas; price, therefore, declined to an approximate mean price below $3.00 by June 2012. However, long-term expectations are that price increases will resume in the following decades as the fields in which new production technology can be applied decline in number and international economic activity resumes to prerecession levels (US Energy Information Administration 2008).

Historically, the greenhouse industry has depended on natural gas as a convenient and low-cost energy resource for greenhouse heating. Energy cost ranks second, behind labor, as the largest cost for the greenhouse industry, comprising 60 percent of total production costs. Increased costs through 2008 forced a contraction in greenhouse businesses nationwide because some entities could not compete effectively because of the high level of energy costs they were required to absorb. Some greenhouse operations have converted to heating with biomass, but this source of energy is not as convenient to combust as gaseous or liquid fuels.

Development of lower cost fuels as a future supplement or replacement for natural gas is important for preserving the economic viability of the greenhouse industry. A potential alternative fuel for greenhouse heating is the use of bio-oil produced from the fast pyrolysis of biomass. Flash pyrolysis processes thermally convert biomass materials to produce a liquid fuel, generally referred to as bio-oil. In a typical pyrolysis process, biomass particles are heated to between 400°C and 550°C very rapidly in the absence of oxygen and then cooled to condense the pyrolysis vapors to a liquid. This treatment fractures plant cellular material molecular bonds converting the biomass to the final bio-oil. The yield of bio-oil can be relatively high at about 65 percent or higher on a dry weight basis depending on the production process.

Bio-oil chemical properties vary with the feedstock pyrolyzed, but woody biomass typically produces a mixture of 30 percent water, 30 percent phenolics, 20 percent aldehydes and ketones, 15 percent alcohols, and 10 percent miscellaneous compounds. As a fuel, bio-oil has environmental advantages when compared with fossil fuels emitting no SOx and half the NOx; because bio-oil is derived from biomass it is CO_2 neutral (Mulraney et al. 2002). In general, liquid fuels are more convenient to transport, store, and combust than gas or solid fuels. Thus, a primary benefit offered by fast pyrolysis is the production of a more convenient and more readily marketable liquid fuel. One drawback to bio-oil is that the chemical mix is water soluble and is, therefore, immiscible in petroleum products. This

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precludes an easy route to the use of bio-oils through mixing with diesel or gasoline to extend petroleum product supply. A method of producing a fuel from bio-oil without mixing with petroleum fuels is required.

Czernik and Bridgwater (2005) have published the most recent description of the use of bio-oil for heating fuels. They point out that limitations to the use of raw bio-oils include poor volatility and corrosiveness. These limitations are produced by the bio-oil acidity, relatively high water content, and the oxygenated nature of the bio-oil chemical compounds. Nearly all of these limitations can be eliminated if bio-oil is catalytically hydrodeoxygenated (HDO). However, catalytic HDO has proved very difficult to apply to bio-oil, mainly because of rapid catalyst coking (Czernik and Bridgwater 2005). No reports of successful commercial application of HDO to produce an upgraded bio-oil have been reported.

A US producer of liquid smoke from pyrolysis of wood reports the use of the noncommercial bio-oil fraction as a fuel for their 5 MWth swirl burner (Czernik and Bridgwater 2005). Space heating is provided by a heat-exchanger system incorporated into the burner. Finnish researchers have burned bio-oil in a dual-fuel burner that required only minor modifications to account for lower combustibility of the mix. A second Finnish research project tested an additional furnace configuration. Main findings were that some modifications were required to improve combustion, a secondary support fuel was required for startup, and emissions were within the environmentally acceptable range (Czernik and Bridgwater 2005).

A Canadian company, Ensyn Renewables, Inc., has developed what they term a rapid thermal process (RTP) that produces a bio-oil, a fraction of which has been marketed as liquid smoke. Recently, the company has performed successful combustion of a product they term RTP renewable fuel oil. Demonstration combustion tests have been successfully performed at three sites identified on the company's Web site (Ensyn Renewables 2011a). In addition, the company has teamed with a diesel engine manufacturer to produce a bio-oil–based diesel fuel. The fuel is scheduled for release as a marketable product in 2012 or 2013 (Ensyn Renewables 2011b). None of the Ensyn products are described as an esterified bio-oil such that there is no relationship between the RTP fuels and the Mississippi State University (MSU) esterified bio-oil.

Researchers at MSU have developed a proprietary bio-oil esterification upgrading process that increases bio-oil energy content, reduces acidity, and stabilizes the fuel over time (Steele et al. 2011). The yield of this product is 100 percent because the reaction is produced by the addition of chemicals and the reaction produces no gas or water fraction, as the HDO process does. This upgraded product is known as lignocellulosic boiler fuel (LBF). As discussed in the ''Future Research'' section at the end of the article, the initial successful combustion test performed for the current study encouraged the filing of a patent to protect multiple esterification methods developed by MSU. MSU expects to continue to produce boiler fuels by various means through its ongoing research program.

The bio-oil that is upgraded to LBF was produced by the MSU auger pyrolysis reactor. Characteristics of this auger reactor have been described in detail by Ingram et al. (2008) and further by Mohan et al. (2006). The MSU bio-oil reactor pyrolyzed wood particles produced from hammermilling wood to particles of 1 to 3 mm in diameter. The pyrolysis temperature applied was approximately 450°C, and the vapor produced during this process exited the hot reactor zone, entered into the condenser train system, and was rapidly condensed. The temperature of the vapor decreased to approximately 100°C to 110°C by the end of the first condenser, and in the second condenser it decreased to 30°C to 50°C. The bio-oil produced from loblolly pine (*Pinus taeda*) and white oak (*Quercus alba*) particles was collected from the condensers and stored at 34°F prior to use to produce the LBF. Nitrogen gas was input to the reactor at a rate of 0.75 ft^3/min to assist in reducing air infiltration into the reactor.

The Department of Forest Products performed the boiler conversion and testing in cooperation with Natchez Trace Greenhouses (NTG), located in Kosciusko, Mississippi. NTG is a medium-sized wholesale producer of plant products with 20,000 square feet of plant material under glass.

Materials

NTG provided access to an idle natural gas/diesel hot water boiler that was converted by MSU researchers to burn bio-oil. An adjustable output Peak waste oil burner was retrofit into the boiler for this purpose. The new burner was capable of combusting fuel types ranging from No. 2 heating oil up to 90-weight gear oil. The waste oil burner used compressed air produced in an attached air compressor module to accomplish fuel atomization starting at 2 psi. During the study researchers used 8 psi of compressed air pressure for atomization. The Peak burner retrofit was inserted into the existing natural gas/diesel boiler to replace the existing burner.

Methods

Thirty gallons of bio-oil was produced by the MSU auger pyrolysis reactor. The bio-oil was produced from the separate fast pyrolysis of loblolly pine and white oak feedstocks. The bio-oil was filtered with a 250-μm mesh screen.

Filtered bio-oil was upgraded to LBF by the proprietary MSU process. While proprietary, it can be disclosed that the esterification was performed by the addition of methanol with acid to catalyze the esterification reaction. The bio-oil, methanol, and acid catalyst mixture was stirred for 2 hours at a temperature of 90°C to produce the full esterification reaction. The resultant LBF for both loblolly pine and white oak were analyzed quantitatively. LBF acid value, water content, and viscosity were measured. Flue gas was collected and analyzed by gas chromatography (GC) with a thermal conductivity detector.

Initial burn tests showed that noncombustible components of the bio-oil (chief among them was the 26% water contained in the esterified fuel) were not combusted in the bio-oil flame produced by the relatively low-energy esterified bio-oil. These noncombustible components sprayed directly through the flame,collected at the back of the burner enclosure, and formed into a sizable residual mass in a relatively short period of partial combustion. To produce a flame hot enough to either combust or evaporate noncombustible components of the esterified bio-oil, a modification was made to the three-nozzle Peak burner system. The three fuel-nozzle burner system was modified

to inject upgraded bio-oil through two injectors and diesel through the third injector. Figure 1 shows the Peak waste oil burner modified by the addition of a small diesel container. As shown, a single fuel line was retrofit onto the Peak burner with the addition of a control valve to control the percentage of diesel going to one of the three burner nozzles. The added diesel nozzle traveled through the main tank that held the bio-oil, but no diesel was released in the tank. Rather, the line passed through the tank and connected to one of the three burner ports. Figure 2 shows this detail with the center fuel line being the diesel line. Figure 3 shows the Peak three-nozzle system with two bio-oil and one diesel nozzle. The diesel nozzle is easy to identify: it is the clean, shiny nozzle.

This addition of the diesel supply to a third nozzle resolved the failure of some noncombustibles to either combust or be evaporated. The resultant flame produced by the Peak burner with this system was nearly a yard long and is shown in Figure 4. This flame combusted all components of the bio-oil spray stream, and no residual buildup in the boiler resulted after this modification. The optimal percent addition of diesel through the third injection port was determined to be 12.5 percent weight basis.

Preliminary field testing was conducted at NTG. LBF from loblolly pine and white oak biomass types were co-fed with No. 2 diesel fuel in varying ratios to yield three different fuel formulations: (1) 100 percent diesel, (2) 87.5 percent LBF from loblolly pine co-fed with 12.5 percent diesel, and (3) 87.5 percent LBF from white oak co-fed with 12.5 percent diesel. Each fuel formulation was combusted in the retrofit boiler at a rate of 4 gal/h. A total of 15 gallons of each of the loblolly pine and white oak LBF fuels were cocombusted with the addition of 12.5 percent diesel during the boiler testing. Fuel consumption and water temperature were measured periodically. The time needed to increase the boiler water temperature to 140°F was measured. Flue gas from the boiler was analyzed by GC to identify its chemical components for the fuel formulations containing 100 percent pine LBF, 87.5 percent pine LBF with 12.5 percent diesel, and 87.5 percent white oak LBF with 12.5 percent diesel. The flue gas was tested for oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide.
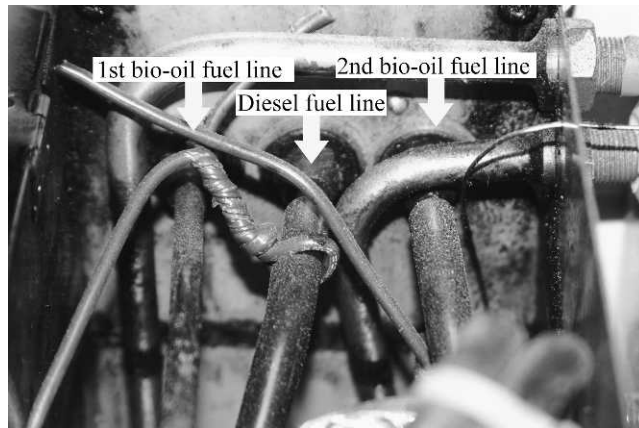

Figure 2.—Peak burner fuel lines showing their location inside main fuel tank. Both fuel lines and the single diesel fuel line are shown.

Results

Table 1 shows physical and chemical properties for both raw and bio-oil upgraded to LBF from loblolly pine and white oak biomass feedstocks. Upgrading raw bio-oil to LBF yielded a 48.8 and 59.2 percent reduction in acid value for the loblolly pine and white oak bio-oils, respectively. Respective viscosities were reduced by 63.2 and 64.2 percent for loblolly pine and white oak bio-oils. As stated previously, this reduction in acid value will reduce the corrosion issue involved when using bio-oil as a liquid fuel. Viscosity reduction will allow improved flow of the bio-oil, which tends to be difficult to feed in its high viscosity, raw condition. Bio-oil upgrading also resulted in higher heating value (HHV) increases of 5.9 and 9.2 percent and reductions in water content of 2.0 and 3.7 percent for loblolly pine and white oak biomass feedstocks, respectively. Reduction in water content was a factor in the increase in HHV for the treated LBF bio-oils in addition to the creation of esters in the bio-oil as a result of the esterification process.

Comparing the properties of the loblolly pine bio-oil and LBF with the white oak bio-oil and LBF, we find that water content of the white oak raw bio-oil contained 21.4 percent more water and the white oak LBF contained 19.4 percent

Figure 1.—Side view of the Peak burner showing the small diesel fuel container on the right with a control valve on the line entering the main tank that holds the bio-oil.
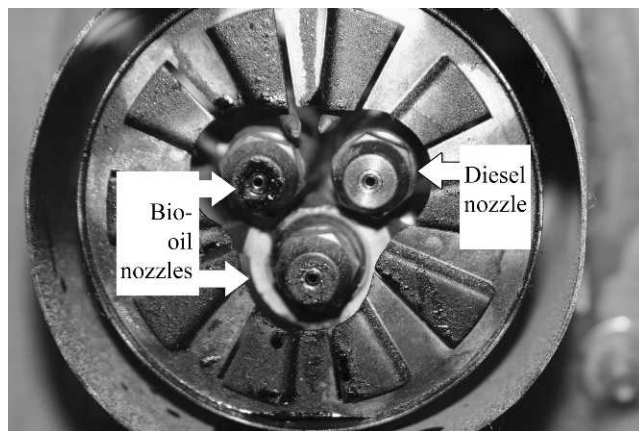

Figure 3.—Peak burner nozzles showing the two used to feed bio-oil and the single nozzle feeding diesel. The diesel nozzle is shiny and clean in comparison with the bio-oil nozzles.
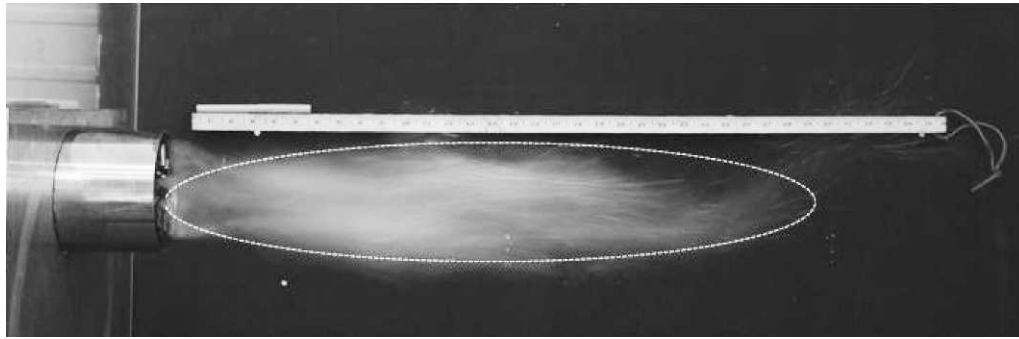
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Figure 4.—Peak burner showing combustion flame produced by two bio-oil and a single diesel nozzle. Note that flame is intense and nearly a yard long. This flame combusted, or evaporated, all bio-oil components such that no residuals built up in the boiler cavity.

more water. Higher water for hardwood bio-oils is a typical result because of the lower lignin content of hardwoods compared with pines (Ingram et al. 2008). White oak lignin content has been reported to be 24.3 (Koch 1985) compared with 28.3 for normal loblolly pine wood (not compression wood; Koch 1972). The high water content combined with the lower lignin energy value for white oak was responsible for the lower HHV values for the white oak LBF.

The actual volumes of LBF required for each species bio-oil type was compared with and without 12.5 percent diesel fuel performance. HHV was determined by calorimeter for each of the LBF fuels containing 12.5 percent diesel. Loblolly pine LBF containing diesel had an HHV of 21.2 MJ/kg compared with the 17.8 MJ/kg value for loblolly pine LBF alone. For white oak LBF, the addition of 12.5 percent diesel increased the HHV from 15.5 to 19.1 MJ/kg. The HHV resulting from the addition of 12.5 percent diesel can, therefore, be estimated to be 19.1 percent ($21.2/17.8 - 1.0 \times 100\% = 19.1\%$) for loblolly pine LBF and 23.2 percent ($19.1/15.5 - 1.0 \times 100\% = 23.2\%$) for the white oak LBF.

Figure 5 shows the time required for a 140°F water temperature increase by boiler fuel type. The 100 percent No. 2 diesel fuel required 35 minutes to achieve the 140°F increase in water temperature. The 87.5 percent loblolly pine LBF and 87.5 percent white oak LBF each separately co-fed with 12.5 percent diesel required 62 and 85 minutes to reach the 140°F water temperature increase, respectively.

Figure 6 gives the rate of water temperature increase by fuel type. The 100 percent No. 2 diesel fuel yielded a water temperature increase of 4.0°F/min. The 87.5 percent loblolly pine LBF and 87.5 percent white oak LBF each separately co-fed with 12.5 percent diesel resulted in respective water temperature increase rates of 2.3°F/min and 1.6°F/min.

The values in Figures 5 and 6 provide results for LBF when combusted with 12.5 percent diesel. An estimate must be made to determine both time to target temperature and temperature rate increase that would be required if diesel were not added to the LBF fuels. The values for the HHV of loblolly pine and white oak LBF with 12.5 percent diesel fuel were calculated as indicated above to be 19.1 and 23.2 percent, respectively. Increasing time to temperature and rate of temperature increase can be adjusted by these values with the result that time to the target temperature of 140°C would be 73.8 minutes rather than 62 minutes for loblolly pine LBF; the time for white oak LBF would be 104.7 minutes rather than 85 minutes. Likewise, rate of temperature increase can be computed to be 1.9°F/min and 1.34°F/min for loblolly pine and white oak LBF, respectively, without the addition of diesel fuel.

Based on the estimated time to temperature of 73.8 minutes for loblolly pine LBF and 104.7 minutes for white oak LBF, it can be estimated that 2.1 and nearly 3 times as much, respectively, of LBF fuels would be required as compared with diesel fuel to provide the same heating capacity. It is clear that the prices per unit of energy charged for the LBF fuels must be much lower than for diesel fuel. Loblolly pine LBF will require a price less than half that of diesel, while the white oak LBF price will need to be less than one-third as high.

The heating times and heating rates in Figures 5 and 6, respectively, were adjusted to estimate the increased volumes of loblolly pine and white oak LBF required for heating without the 12.5 percent diesel supplement. It was determined that approximately 200 percent more loblolly pine and 300 percent more white oak LBF would be needed to provide the same energy as No. 2 diesel fuel alone. While additional LBF bio-oil will be required to equal the performance of No. 2 diesel fuel, it will also be true that the bio-oil fuel must be marketed at a price reflecting the reduced energy value. Therefore, the reduction in the amount of No. 2 diesel fuel allowed when used in combination with LBF will make LBF a viable environmentally friendly alternative future fuel source for greenhouse operations.

Table 2 shows flue gas emissions data from GC analysis of the combustion gases of both loblolly pine and white oak LBF fuels combined with 12.5 percent diesel. These GC results provide molar percentage volumes of oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide content in the flue gas. Examination of the relative oxygen, carbon monoxide, and carbon dioxide values in Table 2 indicates that the higher HHV value for loblolly pine LBF relative to white oak LBF has an impact on combustion

Table 1.—Physical and chemical properties of raw pine and white oak bio-oil and bio-oil upgraded to lignocellulosic boiler fuel (LBF).

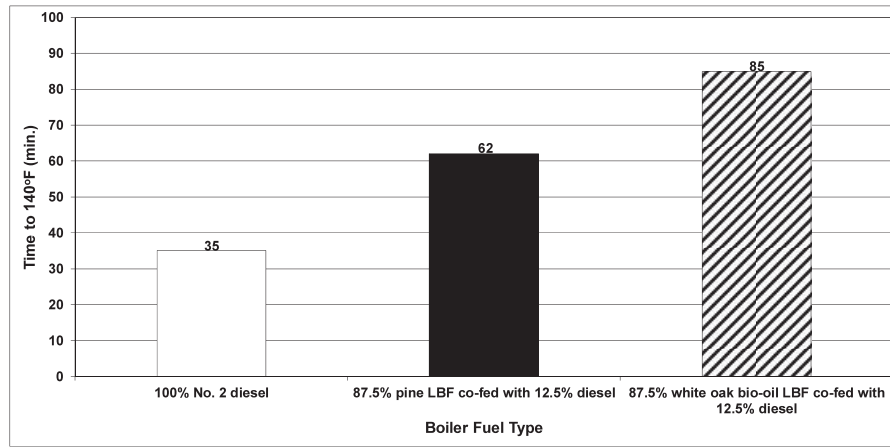| Property	Raw pine bio-oil	LBF from pine bio-oil	Raw white oak bio-oil	LBF from white oak bio-oil
Acid value (KOH mg/g)	96	49.19	109.65	44.71
Water content (%)	22.94	22.47	27.86	26.82
Viscosity (cSt)	12.16	4.64	11.06	3.96
Higher heating value (MJ/kg)	16.84	17.84	14.23	15.54

Figure 5.—Heating time required to reach 140° F water temperature by boiler fuel type.
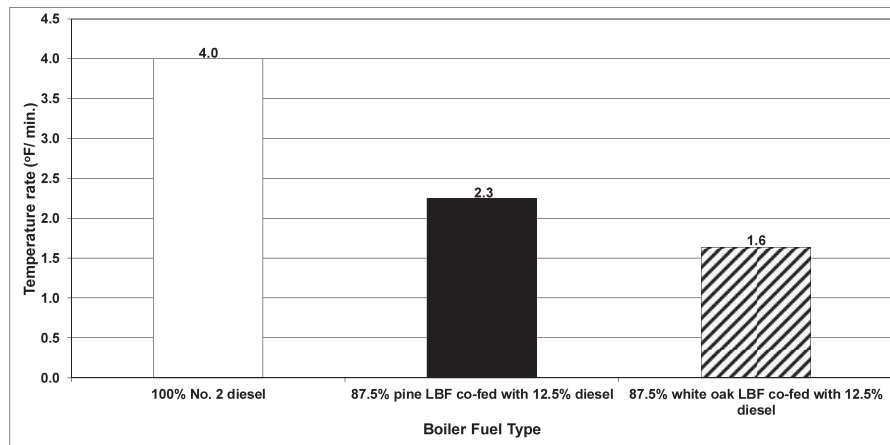

Figure 6.—Mean time to bring boiler water temperature to 140° F by boiler fuel type.

efficiency. Oxygen content in the white oak LBF flue gas was 10.2 percent higher than in the loblolly pine LBF. Higher oxygen content indicates less complete combustion for the white oak LBF. Carbon monoxide emitted by the white oak LBF was 33 percent higher than that emitted by the loblolly pine LBF. Again, higher carbon monoxide formation indicates less complete combustion for the white oak LBF. Carbon dioxide was 15 percent higher for the loblolly pine LBF than for the white oak LBF. Higher

carbon dioxide emission by the loblolly pine LBF indicates more complete combustion for this fuel compared with that for the white oak LBF.

Future Research

Following the successful combustion of the simple esterified bio-oil tested in the current study, Steele et al. (2011) filed a patent application on additional processes to produce esterified bio-oil. These methods included thermolysis with tetramethyl ammonium hydroxide, spraying an alcohol and liquid catalyst mix into the pyrolysis vapor stream to produce a vapor esterification reaction, and addition of olefins and alcohol with a catalyst to bio-oil followed by heating at low pressure. In contrast to the low HHV of 14.95 mJ/kg of initial raw bio-oil, the esterified bio-oil produced by the addition of olefins, alcohol, and catalyst had an HHV that was more than double that value, at 29.77 mJ/kg.

Acknowledgments

Table 2.—Flue gas chemical compounds produced during combustion of lignocellulosic boiler fuel (LBF) in the retrofit Natchez Trace Greenhouses boiler.

| Compound | Molar % | |
	87.5% pine LBF co-fed with 12.5% diesel	87.5% white oak LBF co-fed with 12.5% diesel
Oxygen	12.66	14.03
Nitrogen	67.41	68.62
Methane	0.00	0.00
Carbon monoxide	0.30	0.35
Carbon dioxide	6.65	5.73
Unknown	12.98	11.27
Total	100.00	100.00

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