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Reduction of Ammonia and Tar in Pressurized Biomass Gasification

Keywords: Biomass Gasification, Ammonia, Tar, Hot Gas Cleaning

Introduction

Modernized biomass gasification for power generation has attracted increasing interests as an attempt to reduce our reliance on fossil fuel. Bioenergy from biomass is sustainable and environment-friendly featured by its low emissions of SO_2 and NO_x while producing no net CO_2. The gasification technology is favored due to the high electricity efficiency, low emissions to the environment and economic benefits at small scales. Pressurized gasification system with hot gas cleaning is an advance concept, which can provide higher efficiency and have less serious tar issues (Ståhl et al. 2000a). At present R&D works are needed to improve the performance of the system to meet future utilization.

The main problematic contaminants in a producer gas from pressurized gasification are ammonia and tar. Ammonia forms primarily from the fuel-bound nitrogen (fuel-N) and can be converted to NO_x when combusted in gas turbine. A 50-90% conversion of ammonia to NO_x was reported by Leppälahti et al. in combustion of gas containing 3.5% CH_4 (Leppälahti 1993). Tars are organic contaminants formed in gasification. Tar can deposit and block filters, pipes, valves and turbochargers, leading to a decrease in performance and increase in the need for maintenance (Reed et al. 1999).

The amounts of ammonia and tar formed in gasification are affected by the fuel type and the gasification conditions. There are some studies discussing the influences of different parameters on the formation of tar and ammonia. The formation of tar was reported to decrease with increasing air-to-fuel ratio (Narvaez et al. 1996, Gil et al. 1999, Eurkela et al. 1992). Both increasing freeboard temperature (Narvaez et al. 1996, Eurkela et al. 1992) and increasing bed temperature (Narvaez et al. 1996) were found to reduce the amount of tar in the producer gas. The amount of steam or the ratio between H and C of feedstock also affected tar amount (Narvaez et al. 1996). Ammonia formation in biomass gasification is primarily related to fuel-bound nitrogen (Zhou et al. 2000, Leppälahti et al. 1995). The effects of temperatures are complicated. Zhou et al. reported that at high temperatures significant decreases of ammonia were found (Zhou et al. 2000). Leppälahti et al. reported high freeboard temperature decreased the formation of ammonia especially with the introduction of secondary air (Leppälahti et al. 1995). However, they also suggested that more ammonia could be formed with increasing temperatures until most of the volatile matters were released. Increase of air-to-fuel ratio seemed to be positive (Leppälahti et al. 1995), but was observed to be insignificant by Zhou et al. (Zhou et al. 2000). In general, the investigations reported mostly on a few parameters and did not make quantitative modeling. Therefore, it is valuable to carry out more systematic parametric study based on our pilot-scale gasifier, and perform

quantitative analysis of the results. Though quantitative analysis, formations of ammonia and tar are likely to be suppressed by optimized the operating parameters.

Though equilibrium values of ammonia and tar under the gasification conditions are very low, much high content of ammonia and tar was always reported due to slow thermal decomposition of ammonia in the gasifier (Leppälahti 1993, Wang et al. 1999, Zhou et al. 2000). In many cases, due e.g. to fuel-N rich feedstock, the levels of ammonia and tar are high comparing with the requirements of the subsequent applications. Thus, catalytic reductions of ammonia and tar are usually necessary in order to lower their content efficiently. Among the catalyst, Ni-based catalysts are widely employed because of their high removal efficiencies. A Ni-catalyst was tested by the producer gas from our gasifier to investigate the catalytic performance and the effect of the operating conditions.

Objective

The present paper intended to present the results of parametric study of the formation of ammonia and tar under pressurized gasification conditions. By the use of multivariate data analysis, the effects of operating parameters were determined and their influences could be quantified. In order to deal with cases in which high levels of ammonia and tar were produced, study of catalytic hot gas cleaning was performed, aiming to discuss the removal efficiency and test catalysts.

Approach

Reduction of ammonia and tar was investigated by a 90kw$_{th}$ pilot-scale gasifier and a bench-scale fixed-bed reactor. The pilot-scale gasifier was a pressurized air-blown fluidized-bed reactor (Figure 1). It consisted of three parts, a fluidized-bed reactor, a hot gas filtration unit and a catalytic reactor. The whole system was located in pressurized vessels that had a design limit of 25 bar. The annular space between the outer shell and the inner parts was filled with furnaces and insulation material. To avoid leakage, the annular space was pressurized by nitrogen to a pressure that is 0.5 bar higher than that in the gasifier. The fluidized-bed reactor was a high-temperature steel tube with a diameter of 10 cm and a length of 3.3 m. Feedstock was introduced 30 cm from the bottom. There were five thermocouples and two pressure taps along the reactor (Figure 1). Air was fed into the reactor at the bottom with a rate of 300 to 500 Nl/min. Calcined magnesite was employed as bed material. The gas filter was a high-temperature SiC candle filter, operated at a set point of 650°C. The catalytic reactor was not filled with catalyst. Instead, tests of catalysts were performed by the fixed-bed reactor using a slipstream of the producer gas from the gasifier.

Gasification experiments were carried out under bubbling fluidized conditions, at around 850°C, 12 or 16 bar. Biomass was fed into the system at a rate of about 20 kg/h. Sampling of the producer gas and tar was taken when gasification reached steady state. The steady state was indicated by a uniform temperature profile and relatively constant temperatures in the reactor. The slipstream of the producer gas was quenched in a tar sampler (Nader et al. 2000) and then analyzed with MS and FTIR gas analyzers. The amount of tar per unit volume of the producer gas was determined by gravimetric method. By our sampling method, the tar collected was mostly hydrocarbons from naphthalene. The FTIR and MS analyzer provided measurements of CH_4, H_2, CO, CO_2, H_2O, N_2, O_2, H_2S, NH_3, HCl, C_2H_4, C_2H_6, C_2H_2, C_3H_8, benzene, toluene, and styrene.

With sawdust as the basic fuel, recycled cardboard, recycled plastic, waste textile and bark were tested by adding up to 30%wt. From feedstock analysis it can be found that cardboard waste is very similar to sawdust (Table 1). Textile waste and bark were high in fuel-bound nitrogen content. Plastic waste and the textile waste comprised mainly of

synthetic materials that lack oxygen. The effect of the compositions of the different feedstock on the formation of tar and ammonia will be discussed.

The effects of operating parameters on the formation of tar and ammonia were conducted by parametric study and multivariate data analysis. The operating parameters or the descriptors included in this study were the equivalence ratio (ER), the temperatures at different locations of the reactor (from bottom to top: T2, T7, T8, T9, T5), the pressure (P), the gas residence time (ts), the particle size of sawdust (dp) and the amount of protective nitrogen that leaks into the system (fN) (Table 2). The fuel carbon conversion (C%), amount of tar (tar), fuel nitrogen conversion (N%) and amount of ammonia in the producer gas (NH_3) were chosen to be the responses (Table 2). The fuel carbon and nitrogen conversions were prepared by making mass balances on the basis of gas analyses. The amount of carbon and nitrogen in tar and char was neglected.

The experimental results formed a big data matrix. In order to clarify the relationship between the variables, multivariate data analysis was employed using a partial least squares (PLS) method (Carlson 1992). In the PLS analysis, the descriptors and the responses were correlated through projecting experiment points to so-called PLS components in reduced spaces. Each PLS components was a linear combination of the variables. By using the projection method, the number of variables could be greatly reduced, e.g., from 12 to 2 in our study.

Catalytic hot gas cleaning of ammonia and hydrocarbons was studied by the fixed-bed reactor that was connected to a slipstream of the effluent (Figure 2). A Ni-based catalyst was tested at 800-900°C, 12-16 bar. The efficiencies of the catalyst for ammonia and tar were investigated. The effect of catalyst on the producer gas and deactivation of the catalyst was also discussed.

Project Description

The present paper is the result of one EU project "Advanced combustion and gasification of fuel blends and diagnostics of alkali and heavy metal release (JOF3-CT95-0010)" and a multi-client project "Gasification of fuel blends from biomass and wastes" financed by the Swedish Energy Agency and seven companies.

Results
Parametric study of the formation of tar and ammonia

The effects of operating parameters such as equivalence ratio, reactor temperatures, pressure, gas residence time, sawdust particle size and sawdust-based feedstock were systematically studied.

Plot the amount of tar in the producer gas against the equivalence ratio (Figure 3) showed similar results regarding the trend and the amounts of tar as it was previously reported (Narvaez et al. 1996, Gil et al. 1999, Kurkela et al. 1992). Increasing ER from 0.2 to 0.5, regardless of the type of the feedstock, generally caused a decreasing amount of tar in the producer gas. However, as Gil et al. observed, the data points were quite scattered (Gil et al. 1999). The two-dimensional plot was not capable of accounting for the effect from other operating parameters. Similarly plot the tar amount against the other parameters suggested that the amount of tar was also affected by these parameters. However, it was difficult to reveal the relations by two- or three-dimension plots.

Figure 4 showed the relation of ammonia in the producer gas to the content of fuel-bound nitrogen. Obviously, the ammonia produced was proportional to the content of fuel-N, as it was well known. However, at lower range the scatter was extensive (Figure 4b).

Both for tar and for ammonia, the results indicated that a more powerful data-analyzing tool was needed to obtain a thorough evaluation.

<u>Data evaluation and modeling by multivariate data analysis</u>

The variables that were investigated were listed in Table 2. The table provided the detailed information about the 10 descriptors for operating parameters as well as 2 responses for tar or ammonia. The PLS method was employed to treat the problem involving such a large number of variables. The PLS analysis quantitatively associated the formation of ammonia and tar with the operating parameters. Two-component PLS model was found to be significant both for tar and for ammonia according to cross validation. Figures 5 and 6 compared the known values of tar and ammonia with the calculated values by the PLS model.

The data points in Figure 5 covered gasification tests of sawdust, and sawdust mixed with cardboard, plastic or textile wastes. The two-component model accounted for 62% (50% for the first component and 12% for the second component) of the variance for the carbon conversion and the tar level.

The data points in Figure 6 accounted only for the experiments for sawdust as feedstock. For feedstock with wastes, the determinant factor became the fuel-N content, as it was shown in Figure 4a. In order to better explain the scattered data points in Figure 4b, the experiments with wastes were excluded. The two-component model accounted for 76% (63% for the first and 13% for the second component) of the variance for the nitrogen conversion and the ammonia level.

The results of the quantitative PLS analysis will be discussed below. The details of the PLS model are available for interested readers.

In the PLS analysis the significance of the descriptors was graphically present by combined loading plots (Figures 7 and 8). On the plots the significance of the variables was visualized by the distance to origin along the PLS axes. The significant variables located away from the origin. The points in the opposite directions indicated that these variables were negatively related.

The amount of tar was negatively associated with the fuel-carbon conversion (Figure 7). Increasing equivalence ratio and all the temperatures resulted in decreasing amount of tar. The temperatures above the feeder (T8) and the freeboard temperature (T5) seemed to be of more importance. The observations were in accordance with those found by Kurkela et al., Gil et al. and Narvaez et al. (Kurkela et al. 1992, Gil et al. 1999, Narvaez et al. 1996). Comparing with ER and the temperatures, the pressure and the gas residence time were of secondary importance since they were along the PLS2 that accounted for 12% of the variance, comparing with 50% for PLS1. High pressure or long residence time favored the reduction in tar formation. The impact of residence time could easily be understood, since long residence time in the gasifier helped tar cracking. The influence of the pressure and residence time might also be caused by the fact that the pressure, the residence time and the temperatures were associated. The particle size of sawdust was not found to have significant effect on tar formation. Do clear difference was obtained when applying the PLS analysis to the experiments with or without wastes. Usually more tar could be observed in the producer gas when plastic was added to the feedstock. This indicated that additions of synthetic materials such as plastic and textile wastes were not found to have significant impact on tar formation. The change in tar amount was more likely to be attributed to the decrease in equivalence ratio with addition of plastic.

The effect of fuel-N on ammonia formation was present in Figure 4a. The influences of the other operating parameters were illustrated in Figure 8. Ammonia formation and fuel-N conversion increased with increasing temperatures and ER, and decreasing residence time. The reason was that the relatively low temperatures in our gasifier were not sufficient to convert the fuel completely. As a result, high temperatures, particularly high freeboard temperatures (T5) and the temperatures above the feeder (T8), as well as large ER values,

which enhanced the fuel conversion, led to an increase in ammonia formation. Large particle size of sawdust resulted in low formation of ammonia. In the gasification experiments, two types of sawdust were gasified (Table 1). The sawdust that had a larger particle size contained less fuel-N. It could be seen in Figure 8, fuel-N conversion increased with particle size or decreased fuel-N content. The opposite locations of ammonia (NH3) and fuel-N conversion (N%) along the PLS2 axis indicated that fuel-N conversion to ammonia decreased with increasing fuel-N content.

In general, it was possible to adjust the operating parameters to reduce the formation of tar. The multivariate data analysis showed that the conditions of our gasifier were not sufficient to convert the fuels completely. The thermal decomposition of ammonia was not observed. On the other hand ammonia was formed by thermal cracking of tar and char in the upper part of the reactor. Consequently, suppressing formation of ammonia may not be feasible. For feedstock with high fuel-nitrogen content, the ammonia level in the producer gas is problematic.

Catalytic reduction of tar and ammonia

Catalytic hot gas cleaning of ammonia and tar by the Ni-based catalyst was tested by a slipstream of the producer gas. In our tests, ammonia was of more importance than tar. In the IGCC process tar is not a serious problem if the producer gas is combusted without cooling (Narvaez et al. 1996). Though tar can have negative effect on gas turbine, there is no clear limit as for how much tar the gas turbine can deal with. The Värnamo plant has operated up to 3600 hours with gas turbine (Ståhl et al. 2000a). With a tar level about 5 g/m3 in the producer gas, no serious tar problem was encountered.

In addition the catalyst was more effective for hydrocarbon and tar reforming than for ammonia decomposition. We found that with a level of 0.35 to 1.71% light hydrocarbons (C2 to toluene) in the producer gas, the removal efficiency for light hydrocarbons was always 90-95% (Wang et al. 2000). The amount of water vapor in the producer gas is determinant for hydrocarbon reforming. According to Bangala et al., a steam/tar weight ratio > 4 can guarantee total catalytic reduction of tar (Bangala et al. 1997). In our tests, the steam to tar weight ratios were 4 to 11, therefore, ensuring high tar removals by the catalyst.

Ammonia, on the other hand, is more problematic in the IGCC. The ammonia level was about 750 ppm for gasification of sawdust, and could increase nearly proporionaly with fuel-N content (Figure 4a). Increases in the amounts of ammonia in the producer gas will cause increasing emissions of NO_x in gas turbine combustor (Ståhl et al. 2000b). The Ni-based catalyst was found to provide 35-95% ammonia removals with ammonia concentrations between 340 to 1140 ppm (Wang et al. 2000). At high levels of hydrocarbons in the producer gas, ammonia removal efficiency dropped significantly. Ammonia was less competitive for active sites on the catalyst than the hydrocarbons. In addition the ammonia removal efficiency increased with bed temperature, ammonia level in the producer gas, and gas residence time. Ammonia concentrations at the outlet seemed to approach around 200 ppm in most cases.

Utilization of the catalyst varied the main gas composition by converting hydrocarbons and water vapor to CO and H_2. The gas composition approached equilibrium values. The heating values of the fuel gas showed no clear differences. The gasification efficiency was improved by increasing gas yield, which was probably due to tar cracking. However, note that substantial external heating must be applied to raise the temperature to 800-900°C.

No deactivations of the catalyst, such as sulfur poisoning and carbon deposition, were observed under the test conditions. It was likely to be attributed to the low H_2S concentrations of 50-150 ppm, sufficient steam/tar ratio of 4 to 11, and high temperatures of 800-900°C.

Conclusions

Reduction of ammonia and tar could be achieved through suppressing formation and catalytic decomposing downstream. Parametric study and multivariate data analysis showed that the equivalence ratio, the freeboard temperature and the temperature above the feeder were significant factors for the formations of tar in the gasification process. By the PLS method, the formation of tar and ammonia were quantitatively associated with the operating parameters. It was possible to adjust the operating parameters to reduce the formation of tar. However, for ammonia, the gasification conditions could not provide a complete fuel conversion. Therefore suppressing formation of ammonia by only adjusting operating parameters was not feasible. For feedstock with high fuel-nitrogen content, the ammonia level in the producer gas was problematic. Catalytic hot gas cleaning was necessary particularly for the case of ammonia. The Ni-catalyst performed well in decomposing ammonia and tar to the levels that were very likely to be sufficient for gas turbine utilization. The main gas composition of the producer gas changed, without losing the heating value.

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Figures and Tables

Table 1. Feedstock analysis.

	Sawdust small dp	Sawdust large dp	Plastic waste	Cardboard waste	Bark	Textile waste
Water, %	11	11	0.60	7.7	-	2.4
Ash, %dry	0.72	0.68	3.40	6.90	3.11	1.93
C, % dry	51.33	50.77	81.10	48.30	51.3	62.24
H, % dry	6.21	6.13	13.40	6.70	6.1	6.24
N, % dry	0.33	0.2	0.10	0	0.41	11.50
O, % dry	41.41	42.12	1.70	37.90	39.2	15.44

Table 2. Ranges of the descriptors and responses in the PLS analysis.

| Variable name	Abbreviation	Unit	For tar	For NH_3
Pressure	P	bar	11-17	11-16
Equivalent ratio	ER		0.20-0.54	0.20-0.42
Gas residence time in the reactor	ts	sec	12-16	12-16
Ratio of protective nitrogen to air input	fN		1.0-1.7	1.0-1.4
Freeboard temperature	T5	°C	770-950	770-950
Upper bed temperature	T9	°C	750-900	750-900
Temperature above the feeder	T8	°C	730-890	760-890
Temperature below the feeder	T7	°C	750-930	810-930
Lower-bed temperature	T2	°C	770-960	780-960
Particle size of the sawdust	dp	mm	0-1	0-1
Fuel-C conversion to gaseous products	C%	%	67-104	-
Fuel-N conversion to gaseous products	N%	%	-	11-63
Tar in the fuel gas	Tar	g/m^3	4.3-40	-
Ammonia	NH_3	ppm	-	200-1100
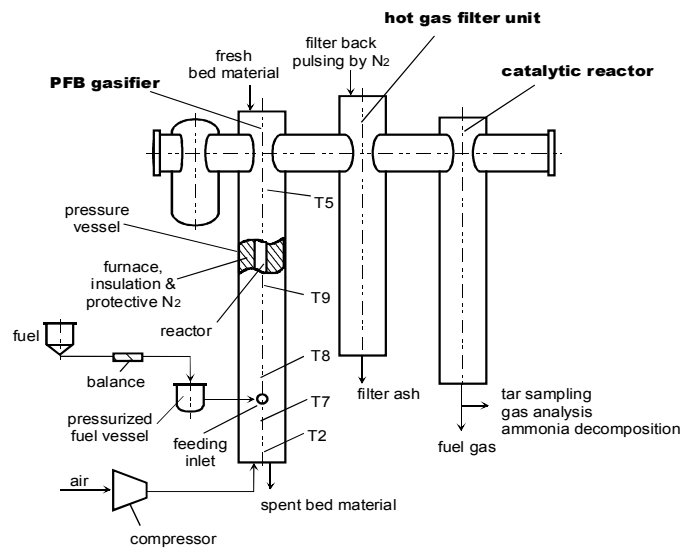
Figure 1. Schematic diagram of the pilot-scale pressurized fluidized-bed gasifier.
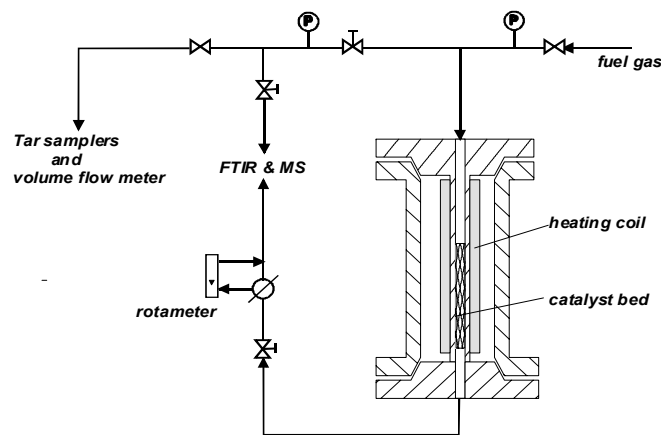

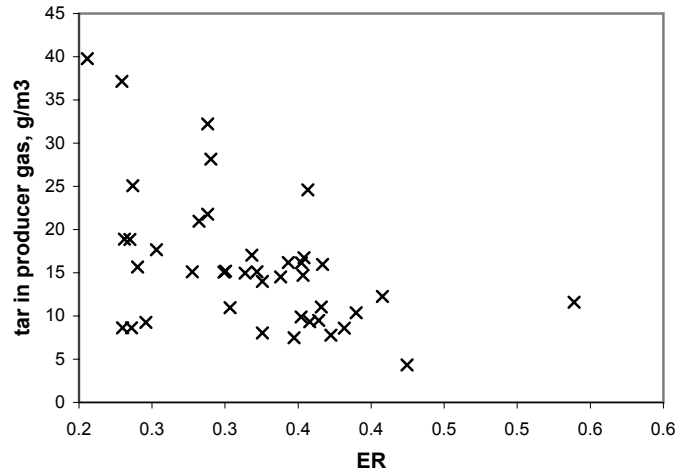Figure 1. Schematic diagram of the lab-scale pressurized fixed-bed reactor.

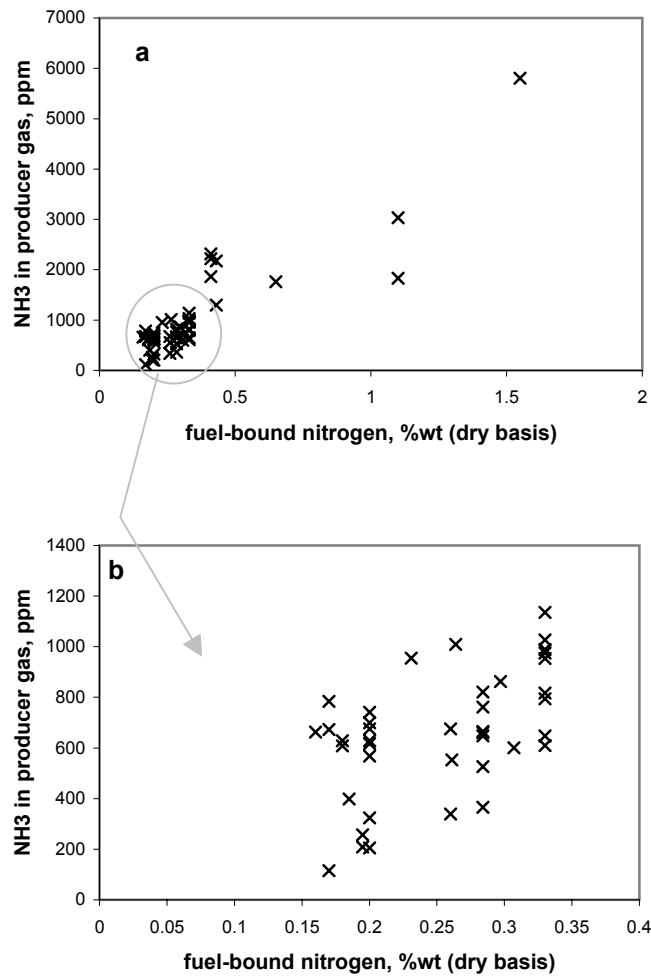Figure 3. Effect of the equivalence ratio on the amount of tar in producer gas.

Figure 4. Effect of fuel-bound nitrogen on the formation of ammonia.
a. ammonia formation in the wide range of fuel-nitrogen.
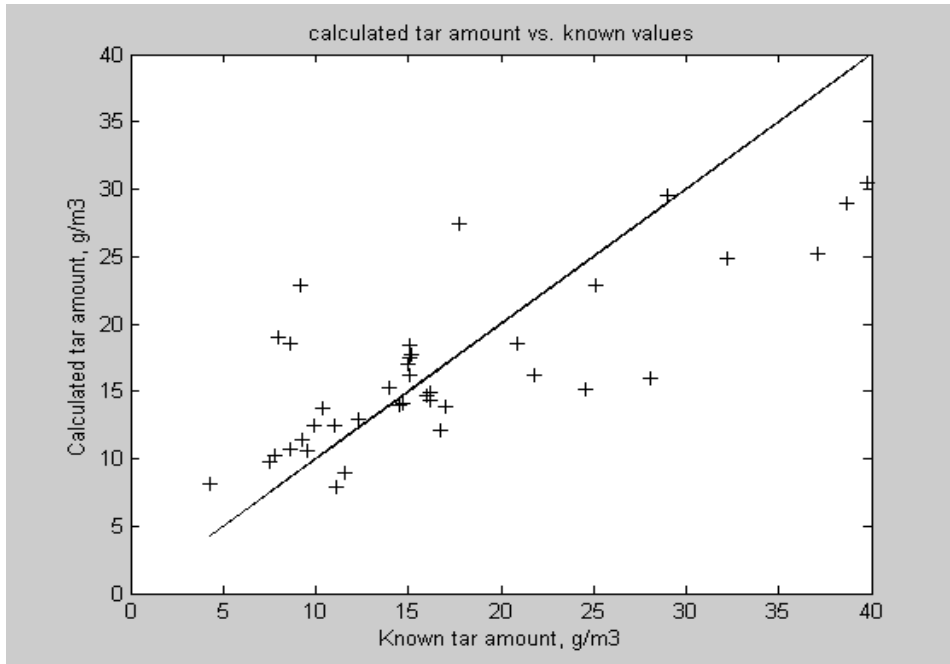b. ammonia formation in the narrow range of fuel-nitrogen.

Figure 5. Fitting results of the PLS model for tar formation.
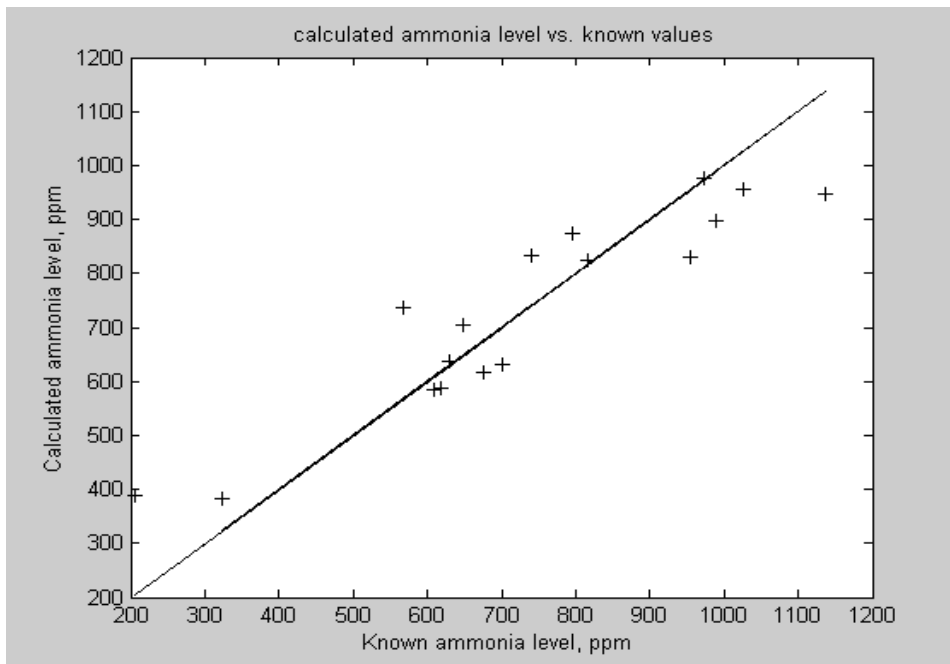The data points were from experiments of sawdust and wastes.

Figure 6. Fitting results of the PLS model for ammonia formation.
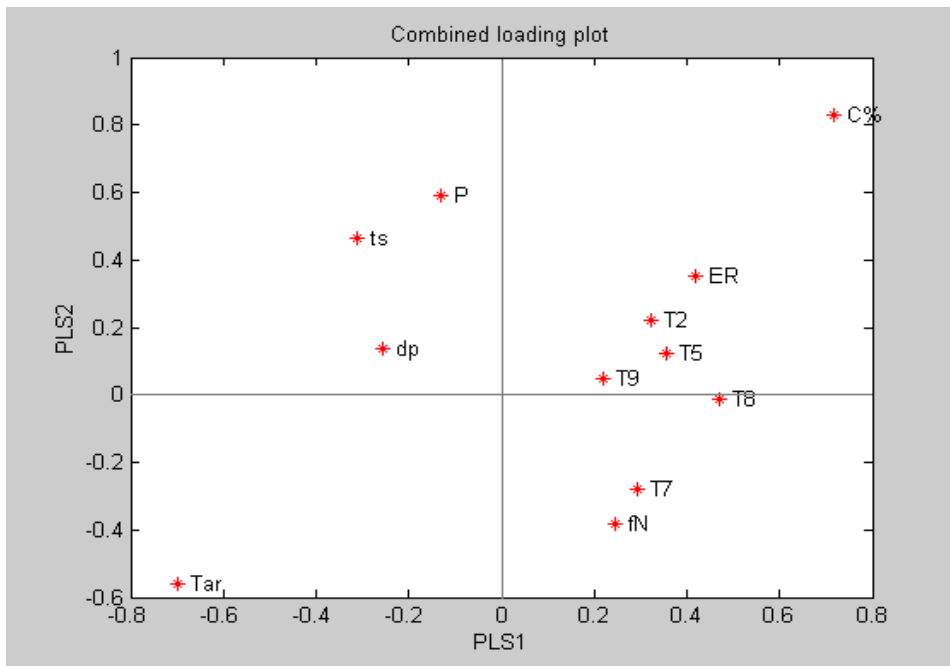The data points were from experiments of sawdust.
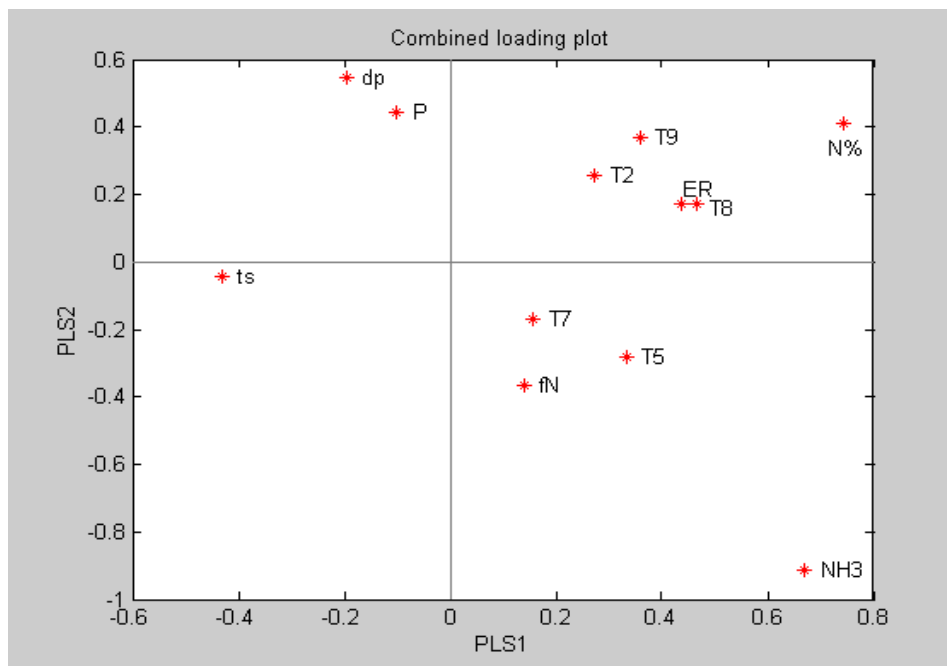
Figure 7. Combined loading plot for tar formation.

Figure 8. Combined loading plot for ammonia formation.