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ENHANCED GASIFICATION OF WOOD IN THE PRESENCE OF MIXED CATALYSTS

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by
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SUMMARY

Experimental results obtained in laboratory investigations of steam gasification of wood in the presence of mixed catalysts are presented in this paper. These studies are designed to test the technical feasibility of producing specific gaseous products from wood by enhancing its reactivity and product specificity through the use of combined catalysts. The desired products include substitute natural gas, hydrocarbon synthesis gas and ammonia synthesis gas. The gasification reactions are controlled through the use of specific catalyst combinations and operating parameters.

A primary alkali carbonate gasification catalyst impregnated into the wood combined with specific commercially available secondary catalysts produced the desired products. A yield of 50 vol % methane was obtained with a randomly mixed combination of a commercial nickel methanation catalyst and silica-alumina cracking catalyst at a weight ratio of 3:1 respectively.

Steam gasification of wood in the presence of a commercial Si-Al cracking catalyst produced the desired hydrocarbon synthesis gas. Hydrogen-to-carbon monoxide ratios needed for Fischer-Tropsch synthesis of hydrocarbons were obtained with this catalyst system.

A hydrogen-to-nitrogen ratio of 3:1 for ammonia synthesis gas was achieved with steam-air gasification of wood in the presence of catalysts. The most effective secondary catalyst system employed to produce the ammonia synthesis gas included two commercially prepared catalysts formulated to promote the water-gas shift reaction.

The data generated from these studies give significant support for catalyst systems and operating parameters needed to produce specific gas products.

INTRODUCTION

The diminishing supplies of low-cost fossil fuels has urged energy planners to initiate developments with renewable energy sources such as biomass. Biomass is the term coined for these renewable energy sources and includes materials such as wood, wood residue, agricultural residues (stalks, stems, shells, cobs, husks), algae, kelp, animal wastes, municipal sewage and energy crops.(1) Wood residues from the logging industry are currently estimated to total 120 million dry tons annually.(2) The approximate heating value of this residue is 17 million BTU per dry ton.

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(1) Superior numbers refer to similarly-numbered references at the end of this paper.

One of several methods for utilization of biomass currently under development is gasification in the presence of mixed catalysts and steam. When wood containing volatile matter is initially subjected to steam at an elevated temperature, a series of complex physical and chemical changes occur in the wood's structure which result in devolatilization of the wood. Following devolatilization, steam gasification of the carbonaceous residue occurs at a slow rate relative to the initial devolatilization.

In a program funded by DOE, Battelle-Northwest (BNW) is investigating the technical and economic feasibility of catalyzed biomass gasification to produce valuable gaseous products. The study is being conducted at the laboratory and process development scale. In this paper, we present results of laboratory studies on the production of methane, hydrocarbon synthesis gas, and ammonia synthesis gas.

EXPERIMENTAL SYSTEM

The experimental reactor employed for this study is shown in Figure 1. The main portion of the continuous wood feed reactor is constructed of quartz. The reactor system is designed for atmospheric pressure operation and is quite flexible with respect to control of experimental variables including: 1) wood feed rates, 2) steam flow rates, 3) temperatures up to 850°C, and 4) auxiliary gas addition.

Wood samples are prepared by solution impregnation of alkali carbonate catalyst on predried wood samples. A concentration of 17 wt % K_2CO_3 (3×10^{-3} g mole of K per gram of wood) was consistently employed for the studies to be presented. The alkali carbonate has been reported to catalyze steam gasification of coal chars.(3,4,5,6,7,8,9)

Experiments are conducted by placing a weighed amount (usually 30-40 g) of impregnated wood into the wood feed hopper, which is purged with nitrogen to remove oxygen. The reactor is maintained at a predetermined temperature and purged with nitrogen before the desired steam flow is established. After steam flow is established, the wood feed system is started to initiate the experiment. Total gas volume generated and gas composition are determined during the experiment.

Experiments are between 1 and 1 1/2 hours in duration. At the end of the experiment, the char residue is burned with oxygen and the evolved gases are measured and analyzed to determine the weight of carbon remaining.

RESULTS AND DISCUSSION

Methane Generation Studies

Experiments were conducted to screen potential methanation catalysts with emphasis being placed on development of a consistent method for catalyst activation and on finding catalysts that do not require preactivation. Laboratory results obtained from these studies have produced up to 50% methane by volume in the product gas.

Conditions must be carefully controlled to effect methanation. Thermocouples located in the catalyst bed indicated that the reactions in the bed gave a temperature gradient as high as 350°C between the inlet (650°C) and the outlet (300°C). This broad temperature gradient gave favorable yields of methane. The combined catalyst studies have shown that nickel, a well known hydrogenation and methanation catalyst, combined with silica-alumina, a highly acidic cracking catalyst, is an effective combination for methane production under the proper reactor conditions. It is postulated that a sequential or propagating type reaction mechanism is occurring. This mechanism might consist of a step wise hydrogenation and cracking of the pyrolyzed wood products followed by methanation. Methanation would be the terminal step with no further cracking.

Because of the large temperature gradient in the catalyst bed, the effect of temperature on gas composition was studied with the different secondary catalyst systems. Each secondary catalyst system was tested at temperatures ranging from 250°C to 650°C. Poor methane yields were achieved at both extremes. The optimum methanation temperature for most of the commercial catalysts evaluated was about 350°C. Methane concentrations at this temperature were about 40 vol %.

Experimental results indicate that the addition of cracking catalysts, which were employed successfully when the catalyst bed temperature gradient ranged from 650-300°C, did not improve methane yields when the catalyst bed temperature remained isothermal at 550°C. For isothermal operation at 550°C a Harshaw Ni-3210 and Harshaw Ni-3266 produced the highest methane concentration of the catalysts studied; however, the concentrations were only 20%.

A summary of the major findings of the methane studies is presented below:

- Optimum methanation temperature for most Ni catalysts tested is 300-400°C.
- Poor yields of methane are achieved with a catalyst bed temperature below 300°C and above 550°C.
- A combined secondary catalyst system of Harshaw Ni-1404 and Strem Si-Al at a weight ratio of 3:1 respectively produced the maximum methane yields.
- A catalyst bed temperature gradient ranging between 700° and 300°C from inlet to outlet was the optimum system evaluated for methane production.
- Steam rates greater than 25 wt % of the input wood feed decrease methane concentrations significantly.
- Harshaw Ni-1404, Ni-3266, and Ni-3210 were the only catalysts that demonstrated methanation activity above 500°C.
- Laboratory results show that for isothermal operation a maximum methane concentration of about 25% is obtained at a catalyst bed temperature of about 550°C operating at atmospheric pressure.

Hydrocarbon Synthesis Gas Studies

A number of catalyst systems have been evaluated for the production of hydrocarbon synthesis gas. Most experiments were conducted at temperatures between 750 °C and 850°C with recycle of the product gas at a rate of 0.2 l/min. Product gas was generated at 0.5 to 0.7 l/min. Under these conditions, the wood and steam feed rates were optimized to produce a gas having a H_2/CO ratio of 2 to 1, suitable for Fischer-Tropsch synthesis.

Steam gasification of wood in the presence of a commercial Si-Al cracking catalyst produced a synthesis gas with a hydrogen:carbon monoxide ratio of 2:1 at both 750°C and 850°C.

Major results of the hydrocarbon synthesis gas studies are:

- A reaction temperature of 850°C was the maximum temperature employed and was more effective than 750°C from both a gas composition and production standpoint.
- The concentration of CO in the final product gas increased more rapidly than the concentration of H_2 with increased temperature.
- The amount of steam required to produce the desired 2:1 H_2 to CO ratio at a reactor temperature of 750°C was approximately 75 wt % of the wood feed.
- At 850 °C the wood feed to steam ratio required to maintain the 2:1 H_2 to CO concentration was 1 to 1.
- The amount of CO_2 in the product gas decreased significantly as the temperature increased.
- A Strem Si-Al cracking catalyst mixed with approximately 10% Ni catalyst proved to be a proper catalyst system for the production of a 2:1 H_2 to CO hydrocarbon synthesis gas.

Ammonia Synthesis Gas Studies

The major objective of these studies was to produce a product gas having a H_2:N_2 ratio of 3 to 1 which would make the gas suitable as feedstock for an ammonia plant. This was accomplished by reacting air/steam and wood in the presence of catalysts. Parameters investigated were steam rate, air/steam mixtures, temperatures, and secondary catalyst compositions and concentrations.

The most effective catalyst system evaluated for ammonia synthesis gas production consisted of 17 wt % K_2CO_3 impregnated in the wood and gasified in the presence of Girdler G-93 cobalt-molybdate catalyst formulated to promote the CO shift reaction or Girdler G-3 chromium promoted iron oxide catalyst commonly used for the water gas shift reaction and a silica-alumina cracking catalyst. Both secondary catalyst systems produced similar results.

From the CO concentrations obtained in these studies, increasing the steam rate decreases the CO concentration via the water gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ and that a gas consisting almost entirely of H_2, N_2, and CO_2 was produced. Carbon monoxide yields ranging between 2 to 3% were obtained by increasing steam rates. The increased steam rate magnified the water gas shift reaction thus producing more H_2 and CO_2, and less CO. These data established that the production of ammonia synthesis gas in the presence of combined catalysts is technically feasible. Major conclusions of the ammonia synthesis gas studies are summarized below.

- Girdler G-3 chromium-promoted iron oxide or a Girdler G-93 cobalt-molybdate CO shift catalyst combined with a 25% addition of silica-alumina cracking catalyst produced $H_2:N_2$ ratio of 3:1. These catalysts also produced the highest overall conversions (65%) to the gaseous phase at 650°C while maintaining the desired product yields.

- A maximum steam rate of 4 times the wood feed rate combined with an air rate of 40% of the wood feed produced the desired $H_2:N_2$ ratio of 3:1 with a CO concentration as low as 3%.

- Char-steam reaction rates at 550°C are too low to maintain a desired $H_2:N_2$ of 3:1 at a significant gas production rate. Constant wood feed rates are critical in maintaining a 3:1 $H_2:N_2$ product ratio.

- An increase of temperature enhanced the overall conversion to gaseous products.

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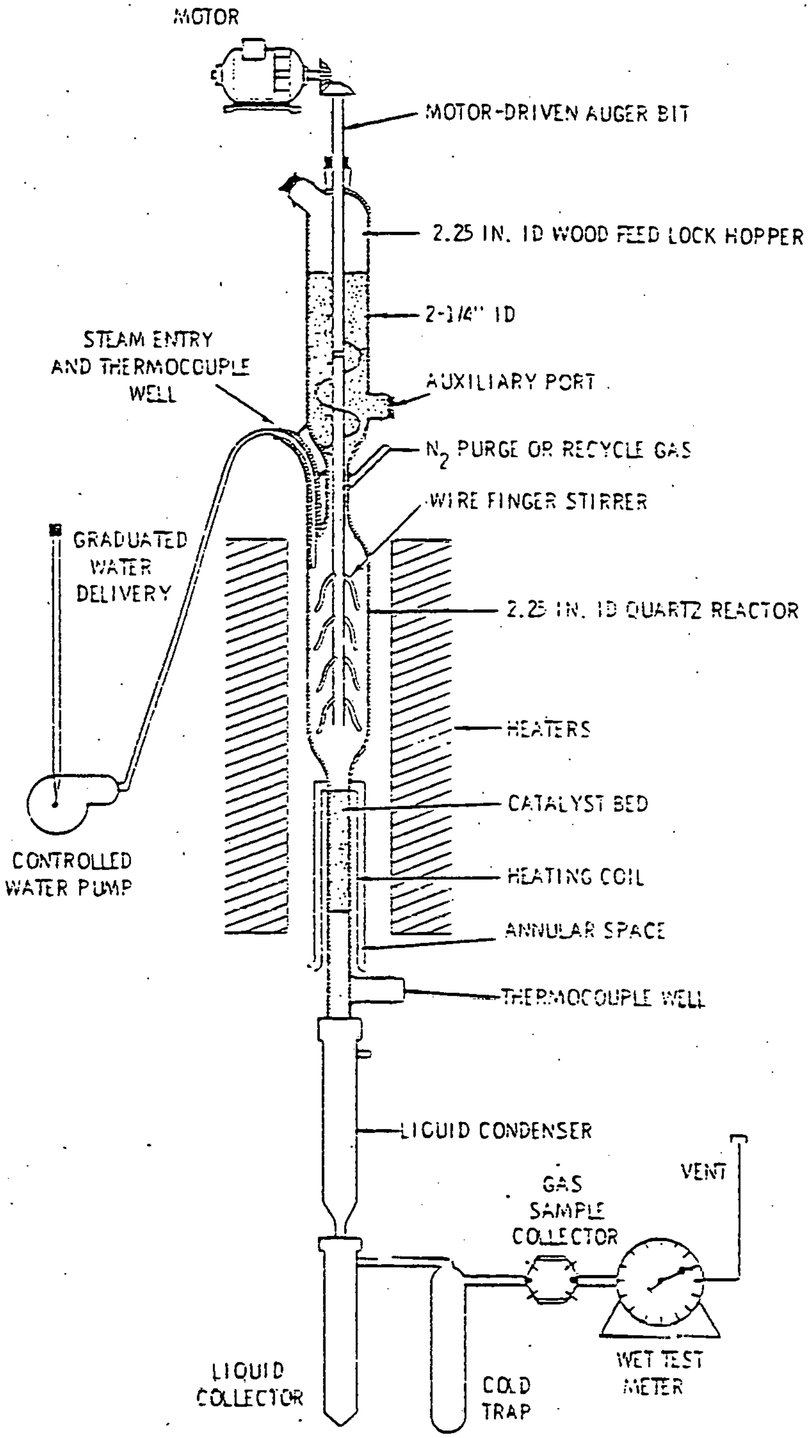

FIGURE 1. Continuous Wood Feed Quartz Reactor