GASIFICATION OF WASTE GASES

Keywords: Gasification, Recycling, Off-Gases, VOCs, United Treatment

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ABSTRACT

A feasibility study of united treatment of waste gases via the gasification process was investigated in the present work. Gasification of main components in refinery off-gases and VOCs were conducted in a laboratory-scale gasifier. Condensation by-products from these gasification experiments were not detectable. Experimental data of the laboratory-scale waste gases gasification were served as the basis for the scale-up of this technology, which was also refined with simulation calculations. The material and energy balances of the united treatment of petrochemical waste gas streams were calculated. In addition to the hydrogen generation, approximately $3.65 \times 10^9$ J/hr of thermal energy may be recovered from the waste gas gasification process. The cold gas efficiency of the gasification is 67%.

INTRODUCTION

Recently, with more restrictive environmental regulations, hydrogen requirements in the refinery begun to exceed the normal supply. The requirement for refinery hydrogen is increasing due to stricter product specifications and a decline in the quality

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of crude available for processing. For example, a 10% aromatic specification in diesel requires approximately 27 m$^3$ of hydrogen per barrel of feed processed (1-5). Many refiners have focused on the hydrogen balance around the plant in order to minimize the consumption of natural gas in steam reforming. The off-gas (waste) streams produced from process units such as the fluid catalytic cracking (FCC), residue catalytic cracking (RCC), hydrotreating (HT), and delayed coking (DC) have been considered as potential raw materials for hydrogen production (1-5). However, most of these waste streams contain high concentrations of nitrogen and carbon oxides, olefins, sulfur, VOCs and low concentrations of hydrogen, making it very difficult to produce or recover the hydrogen by conventional technologies (2-7).

Gasification has been known as one of the effective technology options for the utilization of a renewable energy resource (5,6). Since the gasification process generates essentially no NO$\_x$ or SO$\_x$ emissions, air pollution control equipments, such as selective catalytic reduction (SCR) unit on a stack (8-10), are not required. In addition, a wide variety of waste gas streams would be accepted as feedstocks of gasification without any pretreatment (5,6,11,12).

Many interesting studies concern the gasification of wastes from the view points of gasifier types, fuel used, and product properties and utilizations (1,4-6,11,12). These contributions have provided a valuable understanding of the gasification process and its sensitivity to geometric changes in the gasifier, fuel characteristics and general operations. However, there presently are few gasifiers operating exclusively on refinery waste gas streams (1-5).

The air pollution control units (using conventional technologies) for the treatment of refinery waste gases were reported to have technical or economical difficulties (2,3). Therefore, a feasibility study of united treatment of waste gases via the gasification process was investigated. Gasification of main components in refinery off-gas and VOCs streams were also studied to ensure an effective process developed.
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EXPERIMENTAL

The gasification experiments were conducted in an isothermal, isobaric flow reactor (approximated operationally plug-flow behavior). The product gas was analyzed using a gas chromatography (Perkin Elmer, Model 5100) equipped with a TCD/FID and on-line FTIR spectroscopy (gas cell). Infrared spectra were recorded on a Digilab FTIR spectrometer (FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm⁻¹.

Identification of the condensation by-products (collected at 77 K and extracted with a n-hexane solvent) of gasification at 700-900 K was accomplished using gas chromatography (hp Model 5890A) with a Model 5972 mass selective detector. A hp Ultra 2 capillary column (50m/0.32mm/0.17um) capillary column separated the sample constituents.

RESULTS AND DISCUSSION

In most gasification processes, the oxygen present reacts with the fed carbon in a highly exothermic manner supplying heat to keep the endothermic reactions with steam going. In a commercial gasifier, temperatures are usually much higher than 1000 K and CO is the major product. The net reaction is recognized as: 3C + O₂ + H₂O → 3CO + H₂. The CO shift reaction (CO + H₂O → CO₂ + H₂) is limited by the amount of steam present in the gasifier. The relative importance of these reactions depends upon the concentrations of the gases and the conditions prevailing in the gasifier (4).

Sulfur in the feed is primarily converted into hydrogen sulfide, which is easily removed from the syngas by conventional cleanup methods and then recovered as elemental pure sulfur. Nitrogen in the feed is converted into molecular nitrogen, with minor traces of ammonia. Generally, these small amount of ammonia readily dissolve in the process water and neutralize acidic feed components such as chlorides. It should
be noted that because of the chemically reducing atmosphere in the gasifier, no NO\textsubscript{x} or SO\textsubscript{x} are formed (2,3).

The typical infrared spectra of the syngas generated from gasification of chloroform and chlorophenol in the laboratory-scale gasifier are shown in Fig. 1. The stretching band of CO\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O gases are observed at 2200, 2340, and \textasciitilde3600 cm\textsuperscript{-1}, respectively, indicating a partial oxidation reaction occurred. As expected, the infrared band of the HCl (\textasciitilde2900 cm\textsuperscript{-1}) is also observed. It should be noted that aromatics at 3000-3100 cm\textsuperscript{-1} were found in Fig. 1(a), indicating an incomplete reaction involved in this low temperature (600 K) gasification of 2-chlorophenol experiment.

In order to examine more thoroughly the condensed by-products especially the chloronated aromatics from gasification of a compound selected from the group of refinery off-gases and/or VOCs such as ethane, propane, benzene, chlorobenzene, and chloroform, we intentionally conducted the experiments (laboratory-scale) at temperatures somewhat lower than 1200 K so that the by-products or intermediates of gasification could be detected. Chlorophenols were also gasified at 873 K to obtain detectable quantities of organic reaction intermediates. Samples were collected at 77 K and extracted with a n-hexane solvent. Gas chromatography-mass spectrometry analyses of these extracts did not reveal the presence of dibenzofuran, dibenzo-p-dioxin, or related compounds as a product. However, we tentatively identified an iron carbonyl species by searching the computer library of mass spectra and selecting the one that best matched its mass spectrum. Iron carbonyls, formed frequently in a CO environment, are very toxic and decomposed at 473-773 K. Note that commercial gasifiers provide a high-temperature, well-mixed gaseous environment in which the partial oxidation reactions take place. At the gasification temperatures, typically between 1200 and 1700 K, essentially no complex organic species can survive and the only hydrocarbon detectable, is methane.

The feasibility for the united treatment of refinery waste gas streams which renders it suitable for extensive applications in destruction of VOCs was investigated.
Experimental data of the laboratory-scale waste gases gasification were served as the basis for the scale-up and applications of this technology in the united treatment of waste gases, which is also refined with simulation calculations. The gasifier pressure is based on the pressure required for the delivery of the ultimate product to its end use. In general, operating pressure in commercial, chemical and refinery applications range from 200 to 1200 psig. For example, the optimal operating pressure for hydrogen generation is often determined by the refinery hydrogen header pressure. In the present feasibility study, the material and energy balances of the united treatment of petrochemical waste gas streams were calculated (Fig. 2). Six petrochemical waste gas
FIG. 2 Material and energy balances for united treatment of refinery waste gases by gasification with product hydrogen recycling.

streams (including the VOCs) are fed to the high pressure gasifier as feedstock and the hydrogen product stream generated is designed to recycle to the petrochemical complex for consumption. Since the feed rate of these waste gas streams may be unpredictable, waste oils and natural gas are used as supplementary fuels to keep a steady state gasification operation. Table 1 indicates that at least 83 mol% of CO and H\textsubscript{2} are produced from co-gasification of waste gases, natural gas, and heavy oil at 1673 K and 42 atm. In addition to the hydrogen generation, approximately $3.65 \times 10^9$ J/hr of thermal energy may be recovered from the waste gas gasification process. The cold gas efficiency (CGE) is 67%.

Gasification produces virtually no sulfur or nitrogen oxides emissions and water usage is minimal. Thus, the refinery waste gas streams can be fed to the gasifier without pretreatment. In the united treatment of these waste gases, individual air
Table 1
Composition of Syngas Produced from Gasification of Waste Gases

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<tr>
<td>CO</td>
<td>49.0</td>
<td>(mol%)</td>
<td></td>
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<tr>
<td>CO₂</td>
<td>11.8</td>
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<tr>
<td>H₂</td>
<td>36.4</td>
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<tr>
<td>H₂S</td>
<td>2.7</td>
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<tr>
<td>COS</td>
<td>0.1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cold Gas Efficiency</td>
<td>67.0%</td>
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pollution control unit can be eliminated. This permits considerable flexibility in adapting to existing refineries and chemical plants as well as in adapting to new installations where high-purity hydrogen is needed at high pressure. The economics, for instance, a developing FCC off-gas gasification process for hydrogen generation were reported to save on capital investment of 25-30% over conventional hydrogen supply processes (steam reforming) (3).

CONCLUSIONS

The feasibility for the united treatment of refinery waste gas streams via partial oxidation gasification reaction was investigated. GC/MS analysis of the syngas produced from gasification of Cl-containing compounds at 873 K did not reveal the presence of dibenzofuran, dibenzo-p-dioxin, or related compounds. However, an iron carbonyl species was tentatively identified. Experimental data of the laboratory-scale waste gases gasification were served as the basis for the scale-up and applications of this technology in the united treatment of waste gases, which is also refined with simulation calculations. In addition to the hydrogen generation, approximately $3.65 \times 10^9$ J/hr of thermal energy may be recovered from the waste gas gasification process. The cold gas efficiency of the gasification is 67%.
ACKNOWLEDGMENTS

The financial support of the National Science Council of Taiwan, R.O.C. (NSC84-2211-E-006-022 and NSC85-2621-P-006-003) is gratefully acknowledged.

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*Date Received: February 10, 1997*

*Date Accepted: March 28, 1997*