

PRODUCTION OF HYDROGEN FROM POST-CONSUMER WASTES

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Abstract

At present, the commercial production of hydrogen is essentially carried out by catalytic steam reforming of hydrocarbons: natural gas and naphtha. However, the instability of the prices of natural gas makes the use of other raw materials increasingly attractive. This research focuses on the development of a technology for producing hydrogen from alternative resources, specifically from two types of waste post-consumer materials: plastics and "trap grease". The concept proposed for plastics is a two-stage process: fast pyrolysis to convert polymers to a gas/vapor stream of monomers and other low-molecular weight compounds followed by catalytic steam reforming of this gas to yield hydrogen and carbon oxides. "Trap grease", a waste material recovered from traps on sewer lines, does not require a depolymerization step and can be directly steam reformed to produce hydrogen. To prove the process concept, we employed a two-stage micro-scale reactor interfaced with a molecular-beam mass-spectrometer. Samples of plastics were pyrolyzed in the bottom part of the reactor then the created gases and vapors were steam reformed in a fixed bed of a commercial catalyst located in the upper part of the reactor. The product gas was analyzed by mass spectroscopy. Preliminary tests showed that at process conditions similar to those used for reforming natural gas, polymers were almost completely converted to hydrogen and carbon oxides. "Trap grease", after washing and filtering, was catalytically steam reformed in a 2"-diameter fluidized bed reactor using the same commercial nickel catalyst. At 850°C, using steam-to-carbon ratio 5, and with a space velocity of 1000 h⁻¹, hydrogen was produced with a yield of 25 g per 100 g of grease during 135 hours of continuous testing. This yield could be increased to over 28 g H₂/100 g grease (85% of the stoichiometric potential) if CO were further converted by water-gas shift.

Introduction

At present, hydrogen is mostly produced by catalytic steam reforming of hydrocarbons: natural gas and naphtha. However, processes using other raw materials to produce hydrogen, especially wastes and by-products can also become attractive because of promising economics and environmental benefits. The goal of this research is to develop a technology for producing hydrogen from two types of waste post-consumer materials: plastics and “trap grease”. Plastics, especially polyolefins, have significant potential but are not yet used as a resource for hydrogen production. Plastics account for 8-9% of today’s waste stream, or about 30 billion pounds annually [1], that are mostly landfilled. Potentially, the waste plastics could be used to generate 12 billion pounds (6 Mt) of hydrogen per year. Waste grease is widely available throughout the country. It is recovered from two main sources: traps installed in the sewage lines of restaurants and food processing plants (from which it is pumped into trucks) and wastewater treatment plants, where it flows through municipal sewage systems. So far, this material has not found any economically viable application and is mostly disposed of; for example, grease trap pumping companies in the Boston area discharge pump trucks at processing facilities that charge tipping fees of 11 ¢/gallon. The average amount of the recovered waste grease in the U.S. is 13 lbs/person/year [2], which has the potential to produce 1 billion pounds of hydrogen annually (0.5 Mt/year). If successful, the proposed technology would save natural gas, generate regional industries, and substantially reduce the waste streams, adding environmental benefit to the process. The challenge is to efficiently convert plastic polymers and the constitutive molecules of “trap grease” (predominantly free fatty acids and glycerides) to hydrogen at a cost similar to that for the existing natural gas-based technologies.

The proposed technology for producing hydrogen from plastics includes two steps: pyrolysis of plastics and catalytic steam reforming of pyrolysis gases and vapors. Pyrolysis of plastics to produce hydrocarbons has been demonstrated at a PDU scale using different reactor configurations; e.g. BP/University of Hamburg - fluidized bed [3] and Conrad Technologies – auger reactor [4]. The product composition depends on the feedstock as well as on the process conditions. For example, pyrolysis of polyethylene at 700°C generates over 50% gaseous, non-condensable hydrocarbons and 40% condensable (liquid) hydrocarbons. Increase in the process temperature results in higher gas yields. In most cases the product is a mixture of a large number of compounds and isolating specific monomers is not practical. However, the mixed hydrocarbon product can be used as a feedstock for the catalytic steam reformer to produce hydrogen.

“Trap grease” does not require depolymerization and can be converted to hydrogen using a one-step process. Initial work on direct reforming of “trap grease” and glycerol-rich wastes from a bio-diesel plant performed at our laboratory [5] brought very encouraging results that warrant further investigation. In this paper we report on the results of preliminary plastics pyrolysis/reforming tests and more advanced work of reforming “trap grease”

Experimental

Pyrolysis/Reforming of Plastics

The tests were carried out in a vertical, dual-bed quartz reactor interfaced with a molecular beam mass spectrometer (MBMS), as shown in Figure 1 [6]. The micro-reactor was housed in a tubular furnace with four independently controlled temperature zones. An outer flow was allowed for calibration purposes as well as for the dilution of samples with helium gas to obtain

an adequate molecular beam and high signal-to-noise ratios. Steam was generated in situ in the reactor by vaporizing water injected with a HPLC pump through the bottom inlet. Samples of plastics were fed in batches through the side inlets and pyrolyzed in a preheated mixture of helium and steam. The released vapors and gases were steam reformed on catalyst beds in the upper part of the reactor. After reforming, the gas expanded through an orifice, which lead to the formation of a molecular beam of the reaction products. These product molecules were then ionized and analyzed by a quadrupole mass spectrometer.

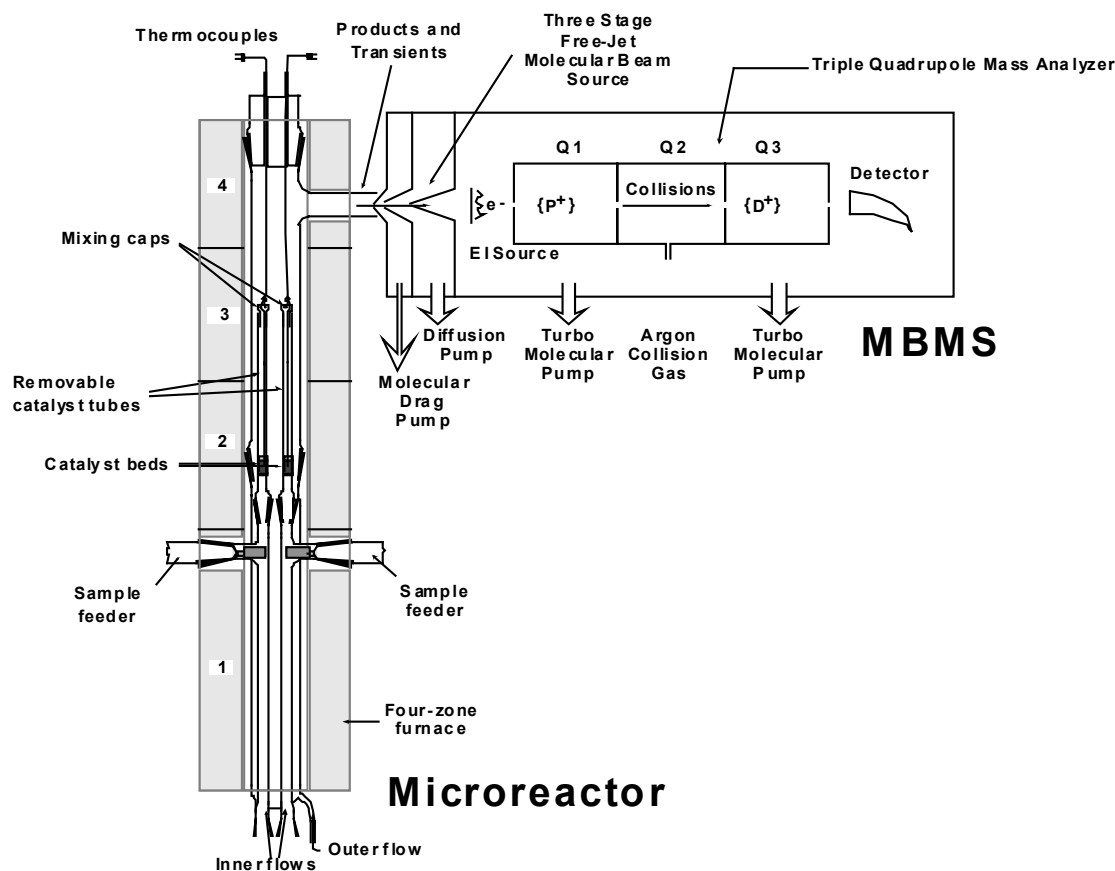


Figure 1. Schematic of MBMS-pyrolysis/reforming reactor system.

At this stage the tests were carried out in a qualitative mode. Samples of several types of plastics such as polyethylene, polypropylene, polystyrene, poly(ethyleneterephthalate), nylon, polyurethane, polyvinylchloride were pyrolyzed at 550-750°C. Pyrolysis was followed by steam reforming of vapors in a fixed bed of C11-NK catalyst (provided by Süd-Chemie) at 750-800°C. The composition of the product gas (mass spectrum) was observed for different values of the steam-to-carbon ratio and space velocity that changed depending on the size of plastic samples. At $S/C=5$ and $G_{C_1}VHSV=5000h^{-1}$ (defined as the volumetric gas flow that would be observed if all carbon in the feed was in the form of CH_4 per unit volume of the catalyst) the gas obtained from all those plastics contained only hydrogen and carbon oxides as shown in Figure 2. At lower S/C and higher $G_{C_1}HSV$ small amounts of methane and aromatic hydrocarbons were also produced. More aromatic compounds were obtained from polystyrene and PET than from polyethylene. While polyethylene volatilized completely within 20-30s, PET and

PET/Cotton blends left 5-10% carbonaceous residues that slowly gasified (>5 min) showing slow release of CO₂. The nitrogen containing polymers (polyurethane, nylon, polyacrylonitrile) were totally converted to hydrogen, carbon oxides, and nitrogen with only traces of benzene detected at the reactor outlet. HCl released from PVC was first adsorbed in the catalyst bed then slowly desorbed. After the contact with HCl the catalyst almost completely lost activity. As expected, processing plastic mixtures containing PVC will require a trap to remove HCl from pyrolysis gas before it can be reformed.

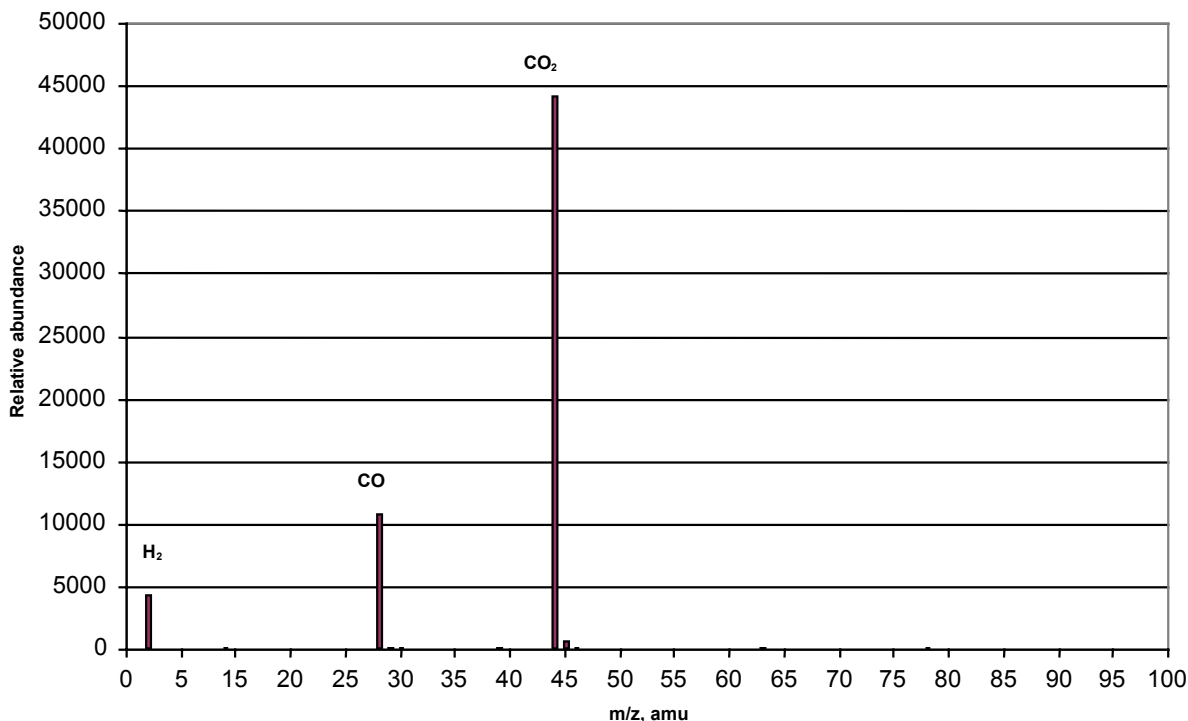


Figure 2. Mass spectrum of the product gas from pyrolysis/reforming of polyethylene-terephthalate; $t_{pyr.}=700^{\circ}C$, $t_{ref.}=800^{\circ}C$, $S/C=5.2$, $G_{C1}VHSV=5300\text{ h}^{-1}$

Reforming of “trap grease”

“Trap grease” that was obtained from Pacific Bio-Diesel had been collected from 40 different sites of the United States. The grease samples contained both saturated and unsaturated C₁₆ and C₁₈ fatty acids, fats, and small amount of solids. The grease was a dark-colored liquid of very high viscosity at room temperature. However, at 45°C its viscosity decreased to ca. 80 cP, which made it easy to pump. The overall elemental analysis of the grease showed 75.7%C, 11.9%H, and 13.3%O, with ash content of 0.05%. Before reforming “trap grease” was washed with hot water and filtered to remove solid impurities.

Steam reforming tests of “trap grease” were carried out using a bench-scale fluidized bed reactor system shown in Figure 3. The tubular two-inch-diameter inconel reactor was supplied with a perforated gas distribution plate and was externally heated by a three-zone electric furnace. The reactor contained 250-280g of commercial nickel-based catalyst (C11-NK) developed by Süd_Chemie for reforming moderately heavy petroleum fractions. The catalyst obtained as pellets was ground to a particle size of 300-500μ, which allowed for uniform fluidization while avoiding entrainment from the reactor. Before reforming, the catalyst in the

reactor was activated in H_2/N_2 stream at process temperature for approximately 2 hours. This resulted in reducing NiO to Ni and in the weight loss of about 7%. The catalyst was then fluidized using superheated steam, which is also a reactant in the reforming process. Steam was generated in a boiler and superheated to $850^\circ C$ before entering the reactor.

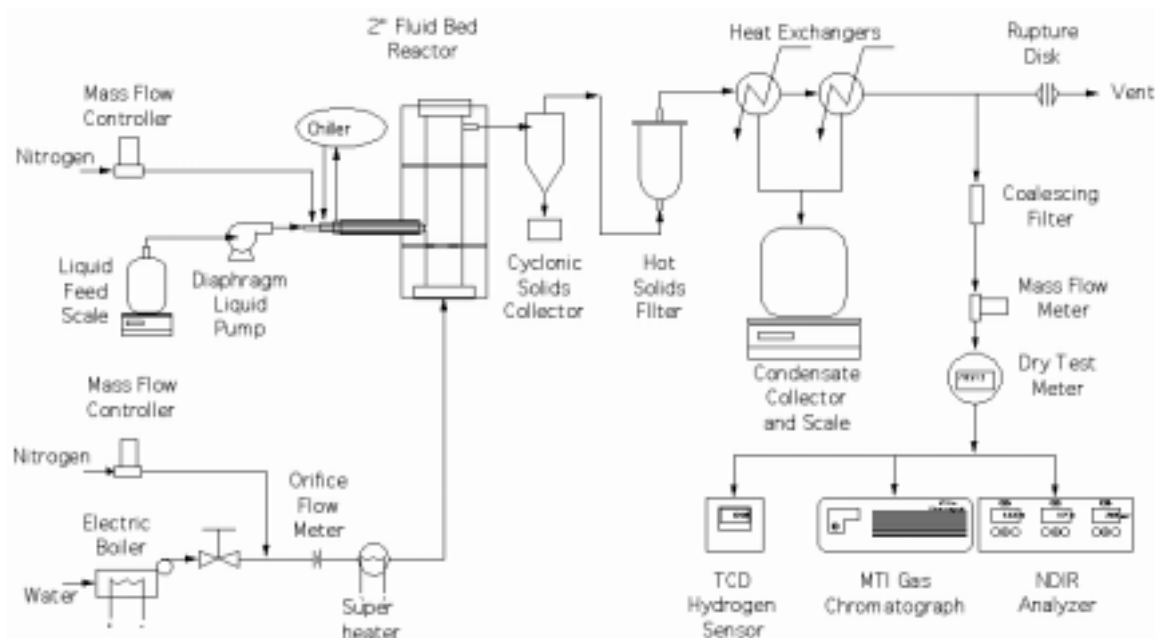


Figure 3. Schematic of the 2" fluidized bed reactor system

The "trap grease" was fed using a diaphragm pump. Because of its very high viscosity, the feed had to be preheated and the feeding lines were heat-traced and maintained at $60-80^\circ C$ to facilitate the liquid flow and atomization. A specially designed injection nozzle was used to spray liquids into the catalyst bed. The injector was jacketed to allow us to control the temperature of the feed entering the reactor. The product collection line included a cyclone and a hot-gas filter to capture fine catalyst particles and, possibly, char generated in the reactor. It also contained two heat exchangers to condense excess steam. The condensate was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter. The concentrations of CO_2 , CO , and CH_4 in the product gas were continuously monitored by a non-dispersive infra-red analyzer (NDIR Model 300 from California Analytical Instruments) and that of hydrogen by a thermal conductivity monitor TCM4 (Gerhard Wagner, Germany). In addition, the gas was analyzed every 5 minutes by an on-line MTI gas chromatograph, which provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen as a function of time. The temperatures in the system as well as the flows were recorded and controlled by an OPTO data acquisition and control system. Total and elemental balances were calculated as well as the yield of hydrogen generated from the feed.

Reforming of "trap grease" was studied in the temperature range of $600-850^\circ C$. Other important process parameters: the molar steam-to-carbon ratio (S/C) varied from 2.75 to 5 and the methane-equivalent gas space velocity ($G_{C1}VHSV$) was in the range of $950-1400 h^{-1}$. At $600^\circ C$ after 1 hour the concentration of hydrogen in the product gas from "trap grease"

reforming started decreasing while that of methane and ethylene rapidly increasing as showed in Figure 4.

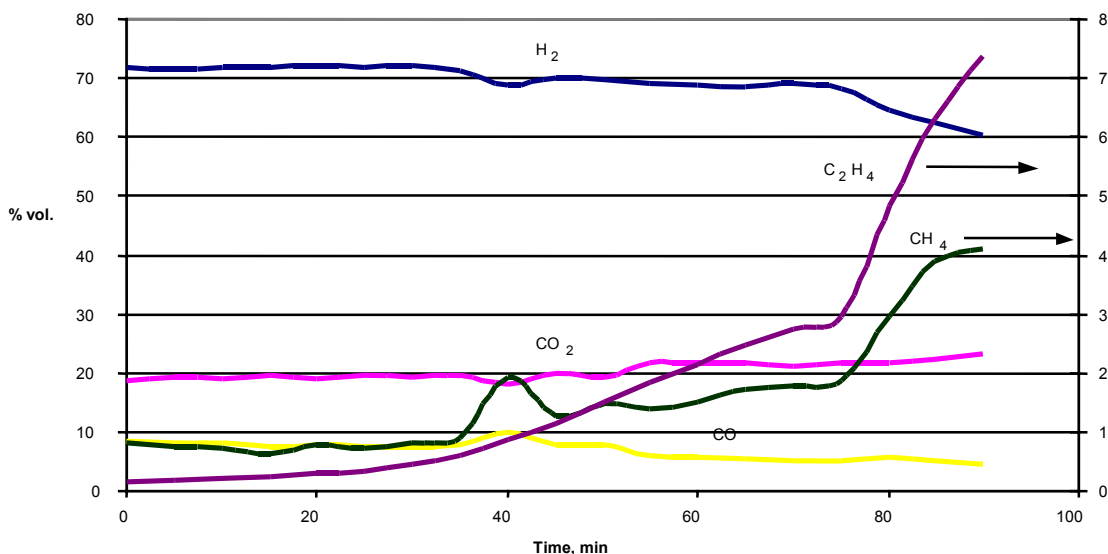


Figure 4. Composition of product gas from reforming of “trap grease”; $t=600^{\circ}\text{C}$, $S/C=2.75$, $G_{C1}VHSV=1150\text{ h}^{-1}$.

Though the extent of thermal decomposition of the grease at 600°C could be less than at higher temperatures, the resulting hydrocarbons were not efficiently converted to hydrogen and carbon oxides at these conditions.

The yield of hydrogen was 70% at the beginning but decreased to 40% of the stoichiometric potential after only 70 minutes of the process (Figure 5). The upper curve shows the yield of hydrogen that would be obtained if all CO were completely converted to CO₂ by water-gas shift. Also conversion of carbon in grease to gas was less than 70%. The remaining 30% formed carbon deposits on the catalyst, thus reducing its activity, and larger molecular weight compounds recovered in the condensate. At higher temperatures and S/C and lower space velocity the catalyst performed much better. For example, at 750°C the carbon to gas conversion was higher than 96% and the yield of hydrogen was above 70% of the stoichiometric potential for 16 hours of the operation. At 850°C , $S/C=3.5$, and $G_{C1}VHSV$ of 1300 h^{-1} the yield of hydrogen was greater than 80% of the stoichiometric potential and carbon to gas conversion was greater than 99% for six hours of processing.

A long-duration test of catalyst performance was carried out at 850°C , $S/C=5$, and initial $G_{C1}VHSV$ of 970 h^{-1} (effective space velocity increased during the test due to the progressive catalyst losses from the reactor). Also, similar to the reforming natural gas, a small amount of hydrogen (<10% of the hydrogen produced) was introduced with steam to prevent oxidation of the catalyst at the bottom of the reactor. In the first 15 hours of the operation the concentration of hydrogen slightly decreased and that of hydrocarbons increased. However, the gas composition remained stable throughout the next 120 hours of the process as shown in Figure 6 and 7.

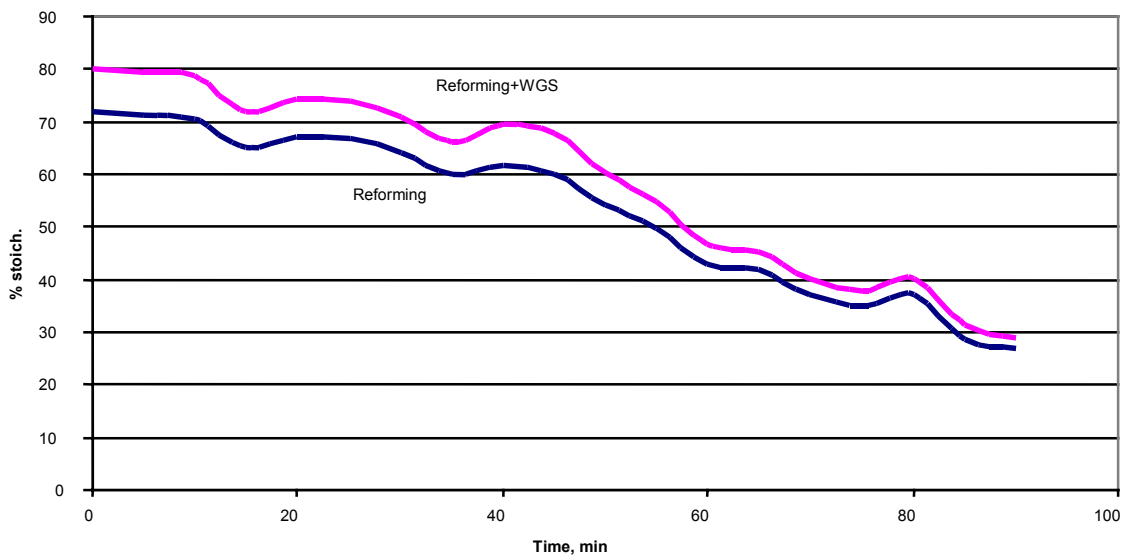


Figure 5. Yield of hydrogen obtained from reforming of “trap grease”; $t=600^{\circ}\text{C}$, $S/C=2.75$, $G_{C1}VHSV=1150\text{ h}^{-1}$.

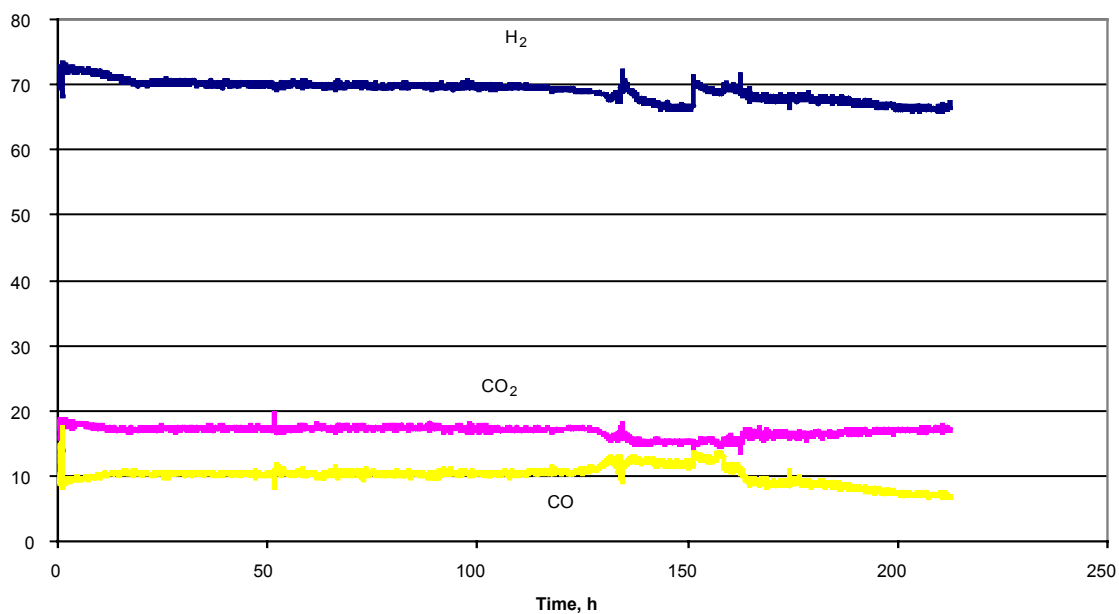


Figure 6. Composition of product gas from reforming of “trap grease”; $t=850^{\circ}\text{C}$, $S/C=5$, $G_{C1}VHSV=970\text{ h}^{-1}$.

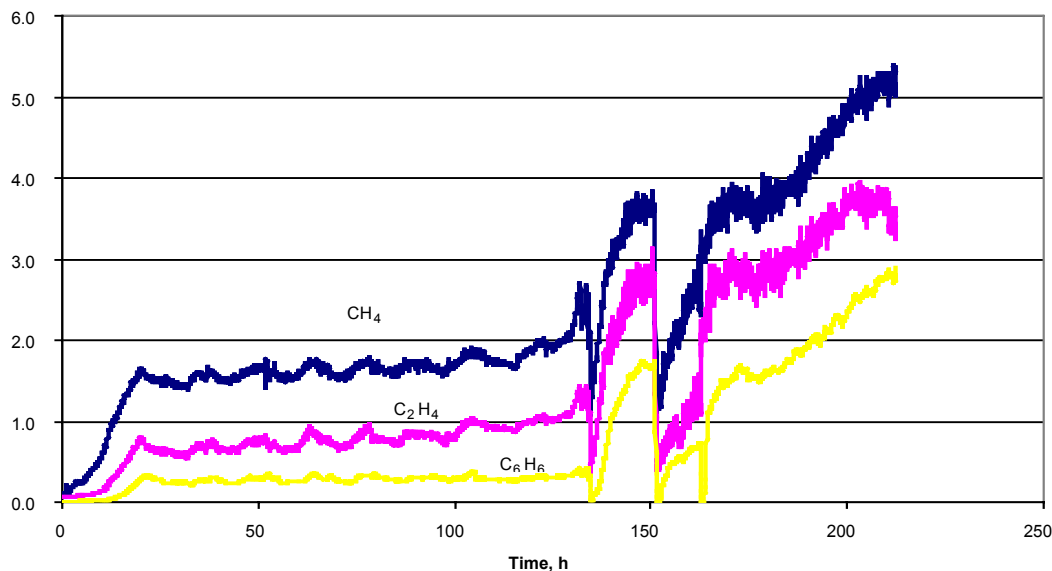


Figure 7. Concentration of hydrocarbons in the product gas from reforming of “trap grease”; $t=850^{\circ}\text{C}$, $S/C=5$, $G_{C1}VHSV=970\text{ h}^{-1}$.

The decrease in the catalyst activity during the initial period was probably due to the partial steam oxidation of Ni to NiO that later reached equilibrium. Another possible reason could be sintering of nickel crystallites and, consequently, lower active surface observed by other researchers for nickel-based catalysts [7]. After 135 hours, despite the pretreatment of the grease, an upset in feeding occurred that interrupted the operation. When the test restarted with the same catalyst a continuous decrease in hydrogen and increase in hydrocarbons was observed during the following 15 hours. We attempted to regenerate the catalyst by steam and hydrogen treatment then continued operation for the combined total 213 hours. However, the applied regeneration of the catalyst did not prove very effective and the process performance continuously deteriorated resulting in lower hydrogen and higher hydrocarbon output.

During 135 hours the hydrogen yield was 25 g/100 g grease and could increase above 28 g/100 g grease if water gas shift of CO followed the reforming. At the end, this yield decreased to 16.4 g/100 g grease (48% of the stoichiometric potential) as shown in Figure 8.

However, throughout the whole time of operation the conversion of carbon from grease to gas was 100% with the overall mass balance closure almost at 100%. No carbon deposits were detected by thermo-emission electron microscopy (TEM) on the catalyst. The main reason for the unsatisfactory performance in the latest phase of the test was probably the continuous loss of catalyst from the reactor due to elutriation leading to too high space velocity. Out of 280 g of the C11-NK catalyst at the beginning of the experiment (260 g after reduction) only 65 g remained in the reactor after the test; 77 g were recovered from the cyclone and 88 g from the filter (about 30 g were not recovered from the system). Therefore, at the end of the experiment the space velocity was four times greater than initially resulting in overloading the catalyst. The catalyst losses spread over the whole duration of the test but seemed to intensify after 135 hours on stream, possibly because of the flow upsets and weakening of the particles because of the regeneration. The catalyst losses can probably account for the low performance of “trap grease” reforming but surface deactivation effects such as carbon deposits, poisoning with

sulfur or other contaminants, or sintering of nickel crystals cannot be excluded at this time. Though the preliminary analyses (TEM, ICP) did not show any significant changes in the catalyst composition more detailed analyses are necessary to prove it.

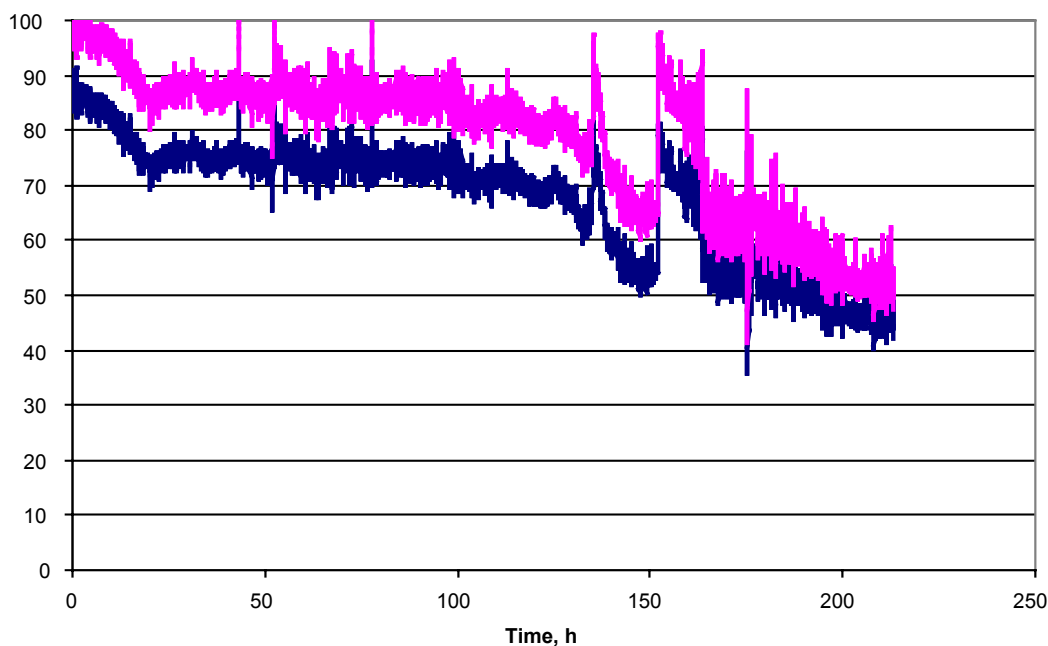


Figure 8. Yield of hydrogen from reforming “trap grease”; $t=850^{\circ}\text{C}$, $S/C=5$, $G_{C_1}\text{VHSV}=970\text{ h}^{-1}$.

Large losses of the catalyst are not acceptable in an industrial process, which clearly indicates the critical importance of developing a fluidizable attrition resistant reforming catalyst. An effort in this area that has been conducted in our laboratory already brought promising results [8]. When developed, the catalyst will be compared to and likely replace C11-NK in the “trap grease” reforming process. The alternative is to apply a circulating bed reactor that could use $80\ \mu$ particles, which are easier to produce than those of $300\text{-}500\ \mu$ used in bubbling beds.

Summary and Conclusions

1. Qualitative tests for producing hydrogen by pyrolysis/reforming of plastics showed promising results. Further experiments will continue using the MBMS-reactor system to quantitatively evaluate the process performances.
2. A fluidized bed catalytic steam reforming process for the production of hydrogen from “trap grease”, a low-cost feedstock available at food processing and sewage treatment plants, was demonstrated in a bench-scale system. The suitable process conditions are similar to those for natural gas reforming; nickel-based catalyst, temperature above 800°C , S/C 3-5, $G_{C_1}\text{VHSV}=900\text{-}1200\text{ h}^{-1}$. The hydrogen yield was about 25 g per 100 g grease, which is 74% of that possible for stoichiometric conversion, for 135 hours of the catalyst time on stream. This yield could increase to 28 g per 100 g grease if a secondary water-gas shift reactor followed the reformer.
3. The fluidized bed process performance significantly decreased after 135 hours of uninterrupted operation yielding only 16.4 g hydrogen per 100 g grease at the end of the test (213 hours). This low conversion to hydrogen was most likely due to the catalyst losses by attrition and elutriation from the reactor though some deactivation effects cannot be

excluded at this time. Development of a fluidizable attrition resistant catalyst is of critical importance to the future of the “trap grease” reforming process for producing hydrogen. Long-duration tests using catalyst formulations developed in our laboratory are necessary to demonstrate high catalyst activity over extended operation. An alternative reactor option, circulating bed that uses easier to prepare 80 μ catalyst particles can also be considered.

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