Investigation of the Pyrolysis of Chlorinated Hydrocarbons in an Argon Plasma Jet

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Abstract

Experimental and theoretical investigations of the pyrolysis of chlorinated hydrocarbons were carried out using a thermal arc argon plasma as heat source. A complete reactor, built of a 15 kW Argon thermal plasma source, a mixing and reacting chamber, a quenching section and an exhaust gas cleaning device, was set up and tested. First experiments were done with trichlorethylene, a typical model substance. The exhaust gases were analyzed with promising results.

In parallel a mathematical quasi 1D flow model of the system was developed, including a simulation of the complex reaction mechanisms. The whole reactor from the point of injection down to the quenching section is simulated.

Introduction

Modern industrialization has created a considerable public liability in the form of toxic waste. As waste regulations become more comprehensive, more advanced methods of waste treatment and disposal are necessary to reduce or eliminate the hazardous inherent in these waste materials. Especially for the treatment of the chlorinated hydrocarbons, which are not suited for combustion due to their low heating value, new innovative techniques are necessary. A very promising method is the decomposition in high enthalpy plasma beams followed by controlled conversion of the substances into lass toxic products.

To investigate the technical potential of this method for commercial applications a test stand was set up in the laboratory of Institut für Raumfahrtsysteme (IRS) at Stuttgart University during the last year. The exhaust gas measurements were supported by the Institut für Dampfkesselwesen und Verfahrenstechnik (IVD) at Stuttgart University. The

aim of the development is a small mobil unit to convert liquid halogenated hydrocarbons into environmental digestible end products.

Experimental Setup and Process Description

A test stand was set up to investigate the advanced decomposition method for chlorinated hydrocarbons. For the first experiments, which are described here, the typical chlorinated hydrocarbon trichlorethylen is injected into a thermal argon plasma. The type of plasma is a DC arc- generated thermal plasma, produced by a plasma torch derived from the arc jet thrusters for space applications and plasma wind tunnels that were developed and investigated since several years at the IRS [1]. The plasma torch is a coaxial device with a cathode manufactured from 2 % thoriated tungsten and with a constrictor of 5 mm in diameter and 5 mm in length. Three elements of the 6 MW IRS power supply, which is a current regulated tyristor rectifier, may be used as the current source with a maximum value of 1500 V and 1000 A, respectively. The plasma gas and the added reaction gases were taken from the IRS laboratory gas feeding system.
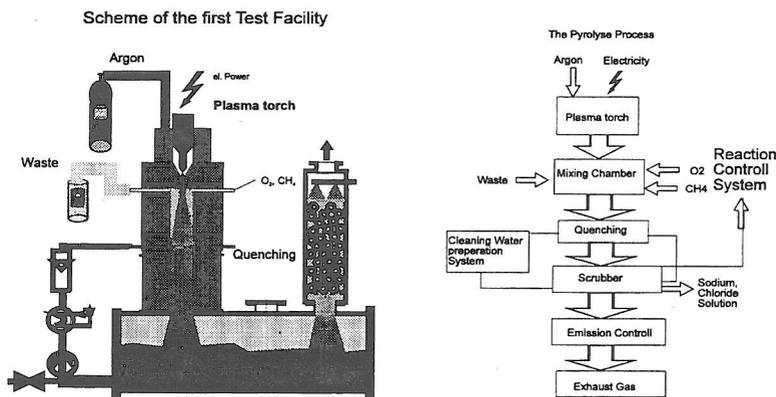

Figure 1: Scheme of the Investigated Process

The argon plasma is injected into the reaction zone downstream of the plasma torch. Here the pyrolysis of the hydrocarbons takes place. Additionally, the pyrolysis gas is mixed with a reduction and an oxidation partner to ensure the complete conversion of carbon to carbon monoxide and carbon dioxide and of chlorine to hydrogenchloride gas. The oxygen mass flow is adjusted until complete conversion is achieved. After the reaction chamber, the reacting gases are quenched with water. The mixture of the beam at the end of the pyrolysyis and reaction section is predominantly CO_2, CO, H_2, HCl, H_2O and Argon. Before the quenching section, gas probes for further analysis are extracted from the beam. Flowing through the reaction channel, the mixture is cooled down by heat flux to the wall. If the mixture is allowed to cool slowly down below 800°C, reverse reactions are likely to occur to form dioxins and furans. Therefore, the chemical

composition is freezed at the end of the reaction step by rapid quenching to temperatures below 100 °C using a direct contact spray.

After having passed the quenching section, the gas stream is led through a cleaning column to extract the HCl. The investigated process is illustrated in Fig 1.

For the described demonstration experiments, the exhaust gas was analyzed with a FID to measure the hydrocarbons. Also, measurement devices were used to determine the oxygen, CO and the CO2 concentration in the exhaust gas before the quenching section. First investigations were carried out to determine the HCl concentration. More detailed analysis of the reaction products will be done using a gaschromatograph at the IVD and the mass spectrometer of the IRS.

Results and Discussion

The first demonstration experiments were performed using model substances. With Isopropanol, first experiments were made including the qualification of the plasma source. In the next step, the chlorinated hydrocarbon trichlorethylene, allowing the simulation of all decomposition and reaction problems, was injected into the Argon beam. Additionally to this substance, oxygen and methane, as a carrier of hydrogen, were injected into the reaction chamber. Fig. 2 shows a typical result of the exhaust gas analysis. The mass flows were 0,72 g/s trichlorethylene with 2 g/s Argon plasma and 0.06 g/s methane. The amount of oxygen is varied from 0,6 g/s that was slightly overstoichiometric to 0,35 g/s that was understoichiometric. The low concentration (> 1 ppm) of the hydrocarbons in the exhaust gas could not be determined due to instrument limitations of the used FID. The contribution of the exhaust gas shows the typical behavior for the oxidation of carbon. First analysis of the hydrochlorine gas indicates that nearly all chlorine is converted into hydrogenchlorine gas and solubilized in the water.
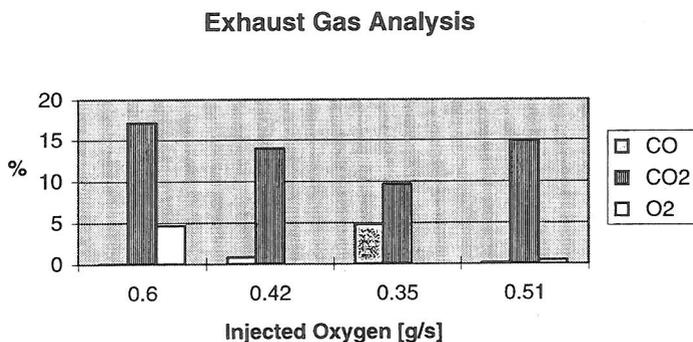
Exhaust Gas Analysis

Figure 2 Exhaust gas measurements for different amounts of oxygen

Numerical Analysis

The Chemistry
Chlorinated hydrocarbons are well investigated as heat transfer medium, yet little is known of their high temperature chemistry. A representative species, methane, which is a reaction product of the pyrolysis of hydrocarbons, is chosen for initial studies and for the verification of the calculation model.

The chemical nonequilibrium of the complex reaction mechanism for an argon, methane, hydrogen and oxygen mixture, containing the 39 most important reactions is implemented into the flow model. The rate constants are given in the Arrhenius form and were taken from [2,3,4,5,6,7]. The reaction mechanism is illustrated in Fig. 3.

Figure 3 The investigated reaction mechanism

Physical Model of the Injection and the Flow
In parallel to the experiments, a numerical simulation of the processes in the reactor was developed. In order to obtain a general impression of the physical behavior of the flow a onedimensional flow model under the assumption of constant pressure was implemented. This model includes a complex chemical reaction scheme, the injection of the waste, the quenching of the hot gas stream and the heat transfer to the wall. The actual geometry of the flow tube was considered as well. The simulation is based on a finite difference method using the conservation equations of mass and energy.

The injection of the water droplets in the quenching section considers the acceleration, heating and vaporization of the droplets. The same formulation is used in case of the injection of liquid waste. The droplets have been assumed to be of uniform size. For the acceleration the following drag coefficient [8] is used:

$$c_D = \frac{18.5}{Re^{0.6}} \quad (1)$$

For convective cases, the surface heat flux in terms of the heat-transfer coefficient h_c can be written as:

$$h_c = \frac{\lambda}{d} \cdot Nu \quad (2)$$

The Nusselt-number is given by :

$$Nu = 1.01 \cdot \sqrt[3]{Re \cdot Pr}, \quad Re < 1 \quad (3) \qquad Nu = 0.664 \cdot \sqrt{Re} \cdot \sqrt[3]{Pr}, \quad Re \geq 1 \quad (4)$$

In order to calculate the droplet evaporation rate, the formulation of Kuo [9] is used, assuming the Lewis-number to be unity:

$$\dot{m}_F = 4 \cdot \pi \cdot r \cdot \rho_s \cdot \frac{\lambda}{c_P} \cdot \ln(1+B) \cdot \left(1 + 0.267 \cdot \sqrt{Re} \cdot \sqrt[3]{Pr}\right) \quad (5)$$

with the Spalding transfer number B.
To take the heat flux from the flow to the tube wall into account, the heat transfer coefficient is modeled using the Nusselt- number as given by [8].
With the above described equations a detailed modeling of the flow is achieved, allowing a simple analysis of the governing effects in the reactor.

Simulation Results
A typical simulation result is depicted in Figures 3 and 4. As an input parameter a mass flow of 2 g/s argon with a temperature of 7000 K is used. This temperature is derived from the calculated enthalpy of 7 kW as a product of input power and the known plasma generator efficiency. In Fig. 3 the calculated gas temperature in the reaction tube is depicted. Due to the expansion and the mixing with the cold gas the temperature decreases rapidly at the injection zone. The reaction starts at once after the injection and the methane is converted completely after a few millimeter. In the reaction tube, the temperature profile is governed by the chemical reaction energy and the heat flux to the cold wall. In the reaction zone the carbon is converted to carbon dioxide (Fig. 4). At the quenching position, the temperature decreases rapidly, quenching water is vaporized and the chemical reaction is frozned (Fig. 4).

Conclusions
With the demonstration experiments it was shown, that the use of thermal plasmas to decompose chlorcarbons is a promising method. To build a pilot plant it is necessary to develop an exhaust gas purifying system and a water purifying system, which must be adapted to this process.
The numerical analysis gives the correct trends and can be used for predicting the effects of geometric changes. Thus, expensive experiments for trials can be avoided. In the model, the determining physical effects are considered. In the next step the reaction mechanism will be modified to simulate the reactions of a typical chlorinated hydrocarbon.
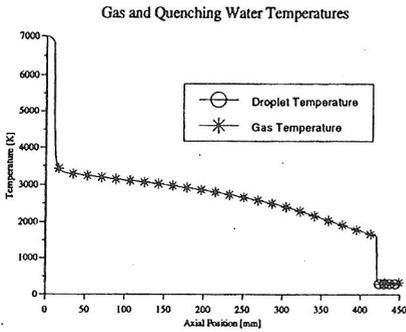
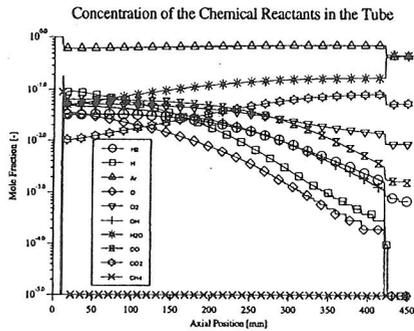Figure 3 Calculated temperature inside of the reactor tube

Figure 4 Calculated composition of the reactants inside of the reactor tube

Acknowledgment:

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