TESTING A JET-STIRRED REACTOR UNDER ATMOSPHERIC PRESSURE FOR THE ABILITY TO PERFORM GAS-PHASE KINETIC STUDIES

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Introduction

To reduce CO_2 emissions, major efforts are undertaken to increase the use of renewable energy. However, the associated fluctuating electricity generation, particularly by wind and solar power plants, leads to a discrepancy between electricity supply and demand. Therefore, processes that are able to store energy and allow flexible and adaptable power conversion need to be developed. One concept is to store energy in chemicals, e.g. by coproduction of useful chemicals in piston engines in addition to work and heat. Conversion reactions take place at uncommon reaction conditions. These include fuel-rich mixtures, high pressures and high temperatures. In [1] for example Dagaut et al. show that a jet-stirred reactor (JSR) is well suited for gas-phase kinetic studies under different reaction conditions. Therefore a similar JSR was developed at the University of Duisburg-Essen and tested at the DLR in Stuttgart. In these initial test experiments, the experimental setup (Fig. 2 [2]) facilitates an easy junction to a time-of-flight mass spectrometer (TOF-MS) without the necessity of any construction work. In the first test period fuel-rich mixtures of the natural gas component propane are oxidized at different temperatures and ambient pressure in the JSR and product spectra are analysed by molecular beam mass spectrometry.

Methods

For the analysis of the gas-phase species after the chemical conversion a JSR is coupled to a TOF-MS. The design of the reactor is based on work by David and Matras [3] or Dagaut [4]. The JSR (Fig. 1) is a quartz sphere with an in- and outlet and an injection cross at its center, where the gas mixture enters the sphere and gets perfectly stirred. The volume is 126 ml.

Figure 1 Jet-stirred reactor

The reactor is heated by two heating wires, wrapped around the sphere. Using a nozzle-skimmer system at the reactor outlet, a gas sample is extracted into a molecular beam, ionized in the ionization chamber of the mass spectrometer and analyzed by the TOF-MS. The experimental setup at DLR in Stuttgart is shown in Fig. 2, but in the experiments presented here the high-temperature flow reactor was replaced by the JSR. [1] Since the oven is built on a linear guide unit, the setup is perfectly suited for an easy junction of the JSR without the need for any construction work. The focus of the initial experiments is on the characterization of the behavior of the JSR, e.g. to see if mixing is rapid enough, changes in composition can be observed and if radical species can be detected. The experiments were not performed under high pressure to facilitate the initial measurements. A residence time of 1 s and equivalence ratios (fuel/oxygen-ratio) between 0.5 and 2.5 in the intermediate temperature range (910 – 1030 K) were chosen. To avoid uncontrolled ignition and strong temperature fluctuations, the fuel was highly diluted with argon (98.5 %).
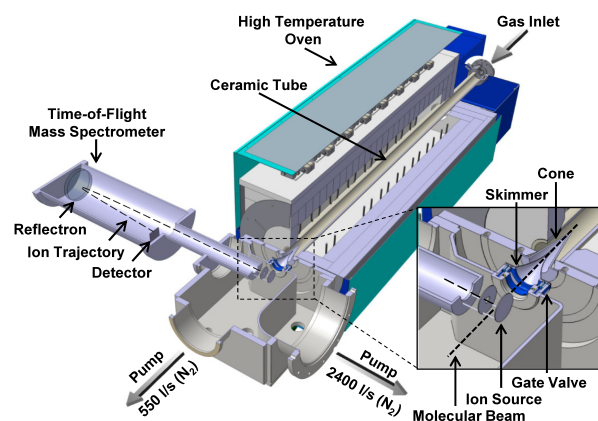

Figure 2 Experimental setup at DLR Stuttgart

Results and Discussion

Each JSR is manufactured as a unique hand-made piece of equipment and its behavior needs to be tested. The current study examines the ability of our JSR to investigate kinetic fundamentals of partial oxidation of

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propane. Special emphasis is placed on the identification of the generated species. Initially, the heating and mixing properties were investigated. With the aid of a thermocouple, which protruded into the inside of the reactor by sticking it into its outlet, the temperature stability could be confirmed. Furthermore the inner temperature corresponded to the regulated temperature of the heating wires. This suggests that the turbulence inside the JSR is very high and responsible for the excellent heat transfer. In addition to the common combustion products (CO, CO_2, H_2O) at least thirty other species were detected, especially oxygenated and higher as well as unsaturated hydrocarbons. Changes to the feed gas flows resulted in immediate responses of the signal strength confirming the rapid mixing of the gases.

Oxygenated hydrocarbons, such as formaldehyde or acetaldehyde are useful raw materials in the chemical industry and serve as precursors for many other chemical compounds. Unsaturated hydrocarbons, however, which are formed by dehydrogenation of the reactant, could be used in terms of energy storage, because their enthalpies of formation are higher compared to the enthalpy of formation of the reactants. In addition, C4 and C5 compounds were observed at higher temperatures, which indicates that C-C-coupling reactions occurred. Examples are butadiene (C_4H_6) and isoprene (C_5H_8), which both are of great industrial importance.

The results show that the yields of propene as well as C4 and C5 compounds increase with rising temperatures and higher equivalence ratios. The same applies to the oxygenated products, in which case higher temperatures play a greater role than higher equivalence ratios. In order to estimate which yields are to be expected, most detected species were quantified. Furthermore the experimental results were compared with simulations. The simulations predict species concentrations as function of temperature for the investigated conditions using the zero-dimensional reactor module of Cantera and the USC II mechanism [5]. Comparison of experimental and simulated species mole fractions yields insights into the chemical processes underlying conversion reactions.

Using the example of propane, propene and butadiene, figure 3 shows that the experimental results for propane and butadiene are in good agreement with the simulations. The slope of the experimental propene yield is much greater than the slope in the simulation while the profile shape of propane and butadiene is captured well. Quantification is performed by comparison of the measured signals to calibration curves. For these initial experiments only a few species were calibrated using the JSR setup, while the majority is quantified using older calibration data from the same mass spectrometer setup. Consequently, some deviations occur in the mole fraction data.
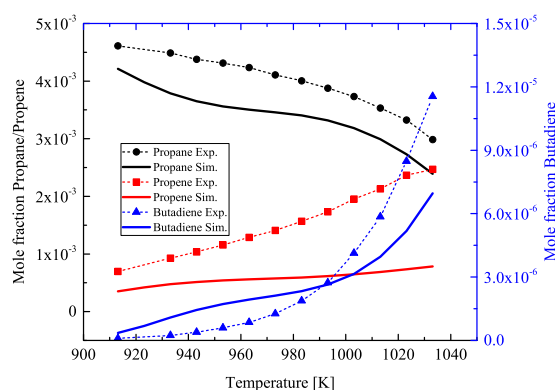

Figure 3 Yields of different species

Conclusions

The results show that the JSR, developed at the University of Duisburg-Essen, is suited for investigating the fundamental kinetics of conversion reactions under atmospheric pressure and moderate temperatures. The high turbulence inside the reactor facilitates very good mixing and heat transfer. Products of the partial oxidation of propane can be monitored. But it should be noted that these are just preliminary results give an insight into the functionality of the JSR. Further tests will not be performed with a thermocouple, stuck into the reactor, for example, as it may have a catalytic effect. Besides higher pressures and temperatures are targeted so that a special housing for the JSR has to be designed followed by further test measurements. In particular some measurements of [2] shall be reproduced in order to compare the results and validate the experimental data.

Acknowledgements

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