Vacuum Gas Carburizing with Acetylene - Gas Phase Modeling of a Bench Scale Reactor

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Abstrac

Vacuum gas carburizing is an important industrial process used for hardening the steel parts. The addition of carbon to the steel parts is accomplished by the pyrolysis of gaseous hydrocarbons. The gas phase composition is very important in vacuum gas carburizing to control the process. Pyrolysis of gaseous hydrocarbons is a complex process because of large number of reactions which lead to the formation of large number of species. To model such processes special software tools have been developed which can be used with detailed kinetics models. The present work focuses on modeling the gas phase reactions in a bench scale reactor used for vacuum gas carburizing of steel with acetylene.

Key words: Acetylene, Pyrolysis, Modeling, Simulation, Vacuum Carburizing

Introduction

Gas carburizing of steel is most commonly used at commercial scale but the in- terest in vacuum gas carburizing process is also increasing at commercial scale because some advantages are associated with this process. The formation of soot and higher hydrocarbons during gas carburizing is higher as compared to vacuum gas carburizing. Similarly the hardening of steel parts using vacuum gas carburizing provides more uniform and repeatable results as compared to gas carburizing [1,2]. Vacuum gas carburizing process was initially developed using methane as a carburizing gas but later on propane, ethylene and acetylene were also used. The previous investigation revealed that acetylene is more suitable for vacuum gas carburizing processes [3].

In spite of its advantages, control of vacuum gas carburizing process is difficult as compared to gas carburizing process. Gas carburizing process is accomplished under thermodynamic equilibrium and activity of carbon can be measured using sensors in the gas atmosphere. The required activity on the surface of steel parts is controlled by the introduction of fresh carburizing gas [4]. On the other hand, in case of vacuum gas carburizing there is no thermodynamic equilibrium and no sensors can be used to monitor the carbon activity on the surface of steel parts since the pyrolysis of carburizing gas results in large number of hydrocarbons. The process conditions need to be optimised to control the gas phase composition for the desired results. Due to this reason gas composition modeling is very helpful for the development of vacuum gas carburizing process.

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Since the pyrolysis of carburizing gas is accompanied by large number of reactions and species, it is very difficult to consider all the reactions and species in the gas phase modeling because of computational efforts required to solve such models. There are different modeling approaches for such systems. In formal or global ki- netic modeling approach, the kinetic parameters are fitted to the experimental data and the extrapolation of the results for others process conditions may not be reli- able. However the global kinetic mechanisms are desirable for computational fluid dynamics (CFD) modeling of reactive flows in complex geometries [5]. The other modeling approach is using detailed kinetic mechanism using elementary reactions. Although in this approach the detailed chemistry is considered, the flow field is as- sumed to follow the ideal flow models e.g. Plug flow, CSTR etc in order to reduce the computational efforts.

In the present work the detailed kinetic mechanism coupled with the ideal flow model has been used for modeling the gas phase composition in the bench scale reactor.

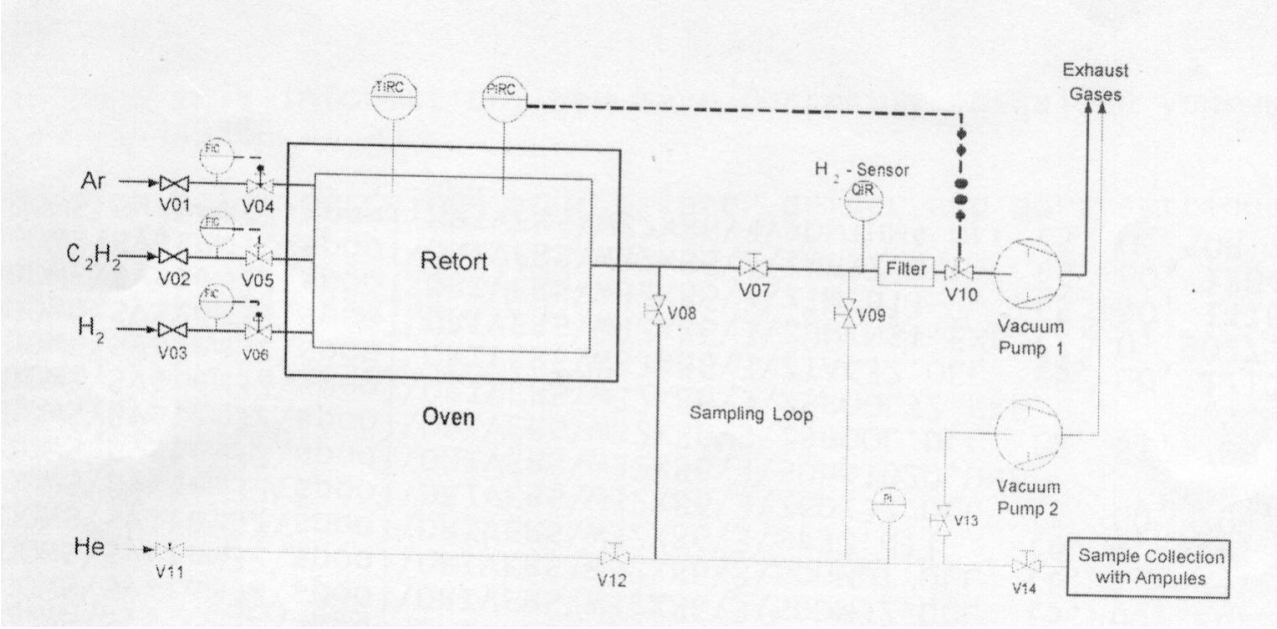


Fig. 1. Flow diagram of Vacuum Reactor

Experimental

The flow diagram of the system is shown in the Fig.1. The apparatus consists of an oven (Xerion XRetort 1150/80) with electric heating for temperatures up to 1150 oC. There are also temperature, pressure and flow controllers (Eurotherm 2408) simultaneously for three gas streams. After passing through the reactor, the gas flows into an analysis unit, with which different analyses of the exhaust gases can be performed at reduced pressure and at ambient pressure.

The required pressures are achieved with an oil-free Scroll pump (BOC Edward GVSP30). The unlubricated operating pump is required since with a conventional lubricated rotary vane pump oil diffuses towards the furnace and is found in the gas analysis. Gas analysis is continuously performed in the vacuum range with a H2-Sensor (WLD detector), a carbon -FID to measure the carbon content of the exhaust gas and a gas

sample system for glass ampoules, developed at the Institute. With this sample system gas samples can be collected at the intervals of 2-minutes. The representative gas samples collected in the glass ampoules are analyzed with an external gas chromatograph for hydrocarbons by means of GC-FID. Apart from this quasi-continuous measurement of the pyrolysis product gases, the carbon content of the carburized steel samples is measured gravimetrically after completion of the experiment.

The reactor is made of a high temperature nickel alloy (Nicrofer HT 6025) and is heated in a horizontal furnace over a length of 400 mm by an electric resistance heating. Before the start of experiments, the reactor is sufficiently carburized to avoid any loss of carbon resulting from the carburization of the reactor itself. As shown in the Fig. 1, there are three inlets for the feed gases (V01 - V03) and a discharge opening for the exhaust or product gases (V08). There is also a connection for the pressure and for the temperature measurement (V06, V07). In order to protect the seal of the flange connection against thermal damage, the front part of the reactor is cooled by a cooling jacket with a glycol/water mixture (V04, V05). The reactor has an inside diameter of 135 mm and a length of 680 mm with a wall thickness of 3 mm. Radiation protection shields are located in the front as well as in the end part of the reactor. The piping consists of 3/4 inch high-grade steel and is heated to approximately 200 0C, in order to prevent the condensing of higher hydrocarbons. For taking gas samples via glass ampoules a defined gas volume can be locked with pneumatic driven ball valves [6,7].

Operating Conditions

Operating parameters for the pyrolysis of acetylene in the Vacuum Reactor are summarized in table 1. Pyrolysis of acetylene was performed at two different tem- peratures 980 and 1050 0C. The pyrolysis of acetylene was studied at flow rates of 6.3, 9 and 12 lit/hr (NTP) and at the total pressure of 10 mbar i.e the reactor is operated under vacuum without any dilution with inert gas.

Table 1 Operating conditions for acetylene pyrolysis in Vacuum Reactor

Feed gas	**Temperature. *T* in ^{o}C**	**Flow rate (l/h)**	**Total Pressure (mbar)**
Acetylene	980	6.3	10
		9	
		12	
	1050	6.3	
		9	
		12	

Results and Discussions

The reactor was numerically simulated using the HOMREA software package [8,9] with a detailed reaction mechanism [10,11]. HOMREA software package solves time-dependent homogeneous reaction system. The forward reaction rate parame- ters and thermodynamic data for all species in the mechanism was provided. The other information provided to the HOMREA program includes operating tempera-ture, pressure and inlet concentration of the acetylene. The program calculates the rate constants of the backward reaction. The simulations were carried out under isothermal conditions.

Although there are many reactions in the mechanism but the following reactions were found important for the consumption of acetylene at 980 °C:

$$C_2H_2 + C_2H_2 = C_4H_4$$

$$C_2H_2 + C_2H_2 = C_4H_2 + H_2$$

$C_2H_2 + C_4H_2 = C_6H_3 + H$ $C_2H_2 + C_4H =$
$C_6H_2 + H$

The sensitivity analysis was also performed to identify the important reactions in the mechanism. The sensitivity analysis with respect to acetylene indicates that the dimerization of acetylene to form diacetyne is very important.

C2H2 + C2 H2 = C4H2 + H2

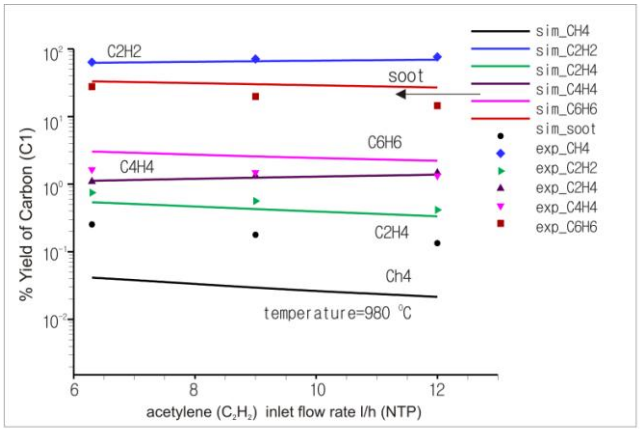
The experimentally derived carbon yields as a function of inlet flow rate are com- pared with the simulation results of the detailed kinetics model. The comparisons are shown in Fig.2 and Fig.3. The carbon yields at the reactor outlet for species other than soot and unconverted acetylene are less than 1 percent and therefore are of least importance. The experimental results are in good agreement with the sim- ulation results especially for acetylene, vinyl acetylene and soot.

Conclusion

The detailed chemical kinetic modeling which is more commonly being applied in the combustion field was applied to predict the gas phase composition of a bench scale carburizing reactor. The results of simulations were found encouraging and reveal that the approach can be further extended for the development and optimiza-

Fig. 2. Comparison of experimental measurements for percentage carbon yields at the outlet of bench scale vacuum reactor operated at a pressure of 10 mbar and simulations with detailed mechanism for pyrolysis of acetylene at 980 °C

Fig. 3. Comparison of experimental measurements for percentage carbon yields at the outlet of bench scale vacuum reactor operated at a pressure of 10 mbar and simulations with detailed mechanism for pyrolysis of acetylene at 1050 °C



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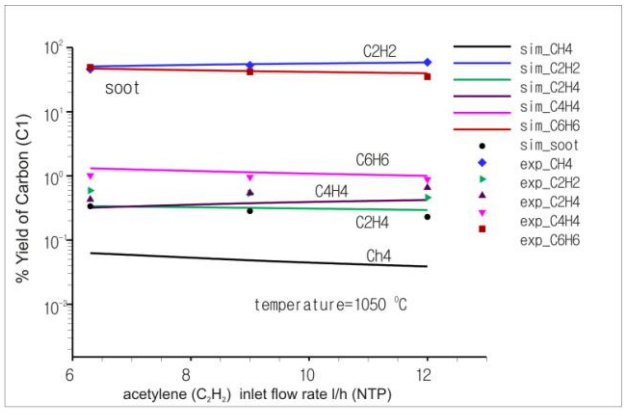

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