High-temperature pyrolysis of plastic waste 1995 - 1997

Contractor:	Montan Univertity of Leoben Institute for Chemistry of Plastics Institute for Process Technology and Industrial Environmental Protection Institute for Physical Chemistry and Theoretical Metallurgy
Customer:	Styrian Provincial Government - Specialised Division 1c Federal Ministry f. Science, Research and Art Federal Ministry f. Agriculture and Forestry, Environment and Water Management Federal Ministry f. Economic Affaires
Participants:	VOEST - Alpine Plant Construction
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1. Summary

In the course of this research project, the following diploma theses and theses were written:

Diploma Theses:

- **Alfred Friedacher**
  Hochtemperaturpyrolyse von Kunststoffabfällen - Aufbau einer Apparatur und erste Vorversuche, Oktober 1996 High-temperature pyrolysis of plastic waste - building instrumentation and first preliminary tests, October 1996
- **Barbara Groß**
  Thermodynamische Berechnungen zur Hochtemperaturpyrolyse, November 1996
  Thermodynamic calculations for high-temperature pyrolysis, November 1996
- **Robert Dallavia**
  Hochtemperaturverwertung der Shredderleichtfraktion, April 1997
  High-temperature use of the shredder light fraction, April 1997
- **Jürgen Klarner**
  Verfahren zur Pyrolyse von Kunststoffabfällen und Methodik zur Untersuchung des Hochtemperaturverhaltens von Kunststoffen, November 1996
  Process for the pyrolysis of plastic waste and methodology for studying high-temperature behaviour of plastics, November 1996
- **Michael Steinwender**
  Hochtemperaturpyrolyse von Kunststoffabfällen - Systematische Untersuchungen des Pyrolyseverhaltens von Polyethylen, Shredderleichtfraktion und Polyvinylchlorid in verschiedenen Gasatmosphären, Juni 1997
  High-temperature pyrolysis of plastic waste - systematic investigations into the pyrolysis behaviour of polyethylene, shredder light fraction and polyvinylchloride in different gas atmospheres, June 1997
- **Stephan Pichler**
  Messungen der Oberflächentemperaturen der Kunststoffe während der Hochtemperaturvergasung , Februar 1998
  Measurements of the surface temperatures of plastics during high-temperature gasification , February 1998

Theses

- **Eva Maria Kern**
  Hochtemperaturverwertung der Shredderleichtfraktion im Elektrolichtbogenofen, 1998
  High-temperature use of shredder light fraction in the electric arc furnace, 1998
- **Peter M. Höllwarth**
  Modellierung des Vergasungsvorganges bei der Hochtemperaturpyrolyse mit numerischen Methoden, 1998

Modelling of the gasification process at high-temperature pyrolysis by using numerical methods, 1998

2. Starting Position

Several types of plastics, such as duroplasts, multi-layer compound foils, plastic-metal compounds and soiled plastic waste can no longer be recycled by means of melting after their use. This is, for example, true for thermoplasts. In order to find ways in the sense of recycling in spite of this, a project group at the "Montanuniversität Leoben" is to study high-temperature pyrolysis more closely.

The process for high-temperature pyrolysis might be important for recycling such types of problematic plastic waste as

- shredder light fraction from the recycling of motor vehicles
- printed circuit boards (PCB's) and plastic residues from electronic waste
- plastic waste with special disposal problems,(e. g. high chlorine or fluorine content)
- plastic bundles with hazardous residual substances

if efforts to gain the scientific bases in the fields of process technology and thermodynamics in order to design a large-scale waste disposal facility in laboratory experiments are successful.

A priori, high-temperature pyrolysis of plastics seems particularly advantageous in connection with metallurgical processes running at very high temperatures. For this, there are already several technological approaches:

- the Corex Process
- the blast furnace
- metallurgical car recycling
- the HTK Process (HTK - Hochtemperatur-Konversionsverfahren - High-Temperature Conversion Process) of VOEST-ÖMV
- the Thermoselect Process.

3. Goals

The project was aimed at elaborating a basic study that was to determine what conditions at high-temperature pyrolysis in vacuum or in different gas atmospheres were suitable for use at variable pressures and what quantities of pyrolysis gas, pyrolysis oil and pyrolysis soot were produced.

In concrete terms it was a question of determining

- for what types of plastics the process of high-temperature pyrolysis was principally suited
- whether the pyrolysis products and the developing waste materials were less hazardous in the sense of toxicology and eco-toxicology than those produced at customary processes
- whether and how the behaviour under high-temperature pyrolysis was influenced by admixing other types of plastics or other organic and anorganic substances
- whether and how high-temperature pyrolysis of plastics could be optimised by adjusting defined gas atmospheres in order to reduce the development of solid residues
- to what extent a clean separation of the fractions and their recycling were possible

The project was made in close cooperation with the Plant Construction of VOEST-Alpine. In this context, it was also a question of studying the possibiliteis of large-scale use.

4. Procedure

The project was subdivided into:

- theoretical deliberations, thermodynamic calculations, modelling the gasification process,
- Experiments in a small laboratory induction furnace
- Experiments in a retort or rotary tubular kiln

The thermodynamic calculations have shown for the pyrolysis of plastics that only two phases, solid carbon and the gas phase, in which two species, namely methane and hydrogen dominate, are stable thermodynamically. Higher-grade hydrocarbons and pyrolysis oil as a possible third phase have proved to be instable thermodynamically at the calculations. This finding is reflected in the results of the experiments in the retort at a temperature of 1100 °C. Here experiments with nitrogen as carrier gas show that all the hydrocarbons containing more molecules, such as methane, will be split up into hydrogen and carbon at a temperature of 1100 °C and a mean dwell time of appr. 30 seconds.

The simulation of gasification has shown that plastics will be gasified as early as at temperatures of appr. 800 - 900 K, which means that the temperature of liquid steel won't even be reached. The thermodynamic deliberations confirm this fact by predicting a ratio between hydrogen and methane for thermodynamic equilibrium that approximately corresponds to the measurements of exhaust gas at such temperatures.

Laboratory induction furnace:

A test facility allowing to throw plastics onto liquid iron or to immerge them in a bath in a wire basket was built. Such experiments were made in different gas atmospheres and with different types of plastics as well as with shredder light fraction and electronic scrap. The emerging products were subdivided into the fractions solid (soot), liquid and gaseous.

The gaseous products were characterised directly during the experiment by means of mass spectroscopy. The liquid products was coupled by means of gas chromatography and characterised by means of mass spectroscopy. Furthermore, defined mixtures of different types of plastics were compared one with another or with organic and anorganic matter (metals, metal oxides).

Among other things, the facility, which was changed several times in the course of the project, was supposed to make it possible to adjust the dosing speed for plastics. For measuring the surface temperature of the pyrolising plastics, plastic discs were equipped with thermoelements in different positions. The discs were fixed on a rod and immerged into the molten mass rapidly.

Retort:

The pyrolysis facility provided by the rotary tubular kiln at the "Institut für Verfahrenstechnik" ("Institute for Process Technology") basically consists of the main components gas station, gas preheating, rotary tubular kiln, cooling and filter systems, gas analysis as well as measuring characteristics for the pressure, temperature and flow rate and the corresponding piping. The gas station makes it possible to use pure and mixed carrier gases (hydrogen, nitrogen, carbon monoxide, carbon dioxide, synthetic air). An electrically heated rotary tubular kiln serves as a high-temperature reactor (for temperatures up to 1300 °C). This kiln is also made suitable for static operation by a special retort. The samples will get into the heated reactor via a slide. The products developing at pyrolysis and gasification, whose dwell time is adjusted by the speed of the carrier gas, pass through a cooling trap, in which components containing more molecules will be condensated and will then be analysed. The components that are still gaseous will be conducted through low-viscous oil in order to enable dust particulates to be separated before they pass through the filter system and to make it possible to continuously analyse the gas. Then they will be burned off in a reheating chamber.

At the analysis of the gas, the compounds containing few molecules will be acquired continuously:
- overall hydrocarbon content,
- methane,
- hydrogen,
- carbon monoxide,
- carbon dioxide.

5. Result / Benefits

The task to be fulfilled in this research work was to study the behaviour of plastic waste that is not accessible to recycling at high-temperature pyrolysis. At high-temperature pyrolysis running above 1000°C, a far-reaching decomposition could be expected. The experiments were, on the one hand, made in a retort and, on the other hand, in a laboratory induction furnace. This instrumentation was established in the course of the project and adapted to the requirements.

For the pyrolysis experiments, such unmixed plastics as polyethylene, polypropylene, polystyrene, polyvinyl chloride and such mixed plastic waste as shredder light fraction and electronic scrap were used.

The pyrolysis products generated in an experimental reactor were analysed and balanced. What has been shown is that large amounts of soot formed up to almost 40 % of all the existing carbon at the experiments in the laboratory induction furnace.

Accompanying thermodynamic calculations and the simulation of the gasification process were made. The calculations have shown for the pyrolysis of plastics that only two phases, solid carbon and the gas phase, in which two species, namely methane and hydrogen dominate depending on the temperature, are stable thermodynamically. Higher-grade hydrocarbons and pyrolysis oil as a possible third phase have proved to be instable thermodynamically at the calculations.

This theoretical finding is reflected in the results of the experiments in the retort at a temperature of 1100 °C. Here experiments with nitrogen as carrier gas show that all the hydrocarbons containing more molecules, such as methane, will be split up into hydrogen and carbon at a temperature of 1100 °C and a mean dwell time of appr. 30 seconds.

For a technological use, soot formation is the limiting factor. Another fact that seems problematic is the high gas development at the pyrolysis of plastic waste in contact with a molten steel bath.