Producing carbide using plastic waste

A new process begins normal operation

Carbide is an important base material for production of fertilisers, manufacturing raw iron and in other products for the chemical industry. A chemical company from Southern Germany has developed a new process which allows plastic waste to be used to produce carbide. The carbon in the plastics is used in the carbide synthesis. That means that part of the black materials coke and coal used for the production can be replaced by the secondary raw material SCS (=synthetic carbon sources).

„The positive experiences in the operating phase have revealed that plastics can be used as carbon sources in our production process. We are therefore very confident that we can recycle around 1,000 tonnes a month in 2011. Delivery is made by rail or truck,“ explains Jürgen Franke, responsible for material flow management in the AlzChem plant in Hart, Upper Bavaria. Specific requirements are made of SCS. In addition to compliance with quality parameters, the physical form is key. The Hart plant can currently use three-dimensional plastic waste, pellets or fluff. Material flows from commercial and industrial plastic processing sectors are particularly suitable for recycling.
High quality and purity standards apply to SCS. It must be shredded and preselected. AlzChem Trostberg GmbH works with selected suppliers who guarantee constant high quality. Even plastic fractions with a chlorine content of up to 10 per cent by weight can be used. The majority of the chlorine is found as uncritical calcium chloride in furnace dust. For this reason, the AlzChem experts don’t have to worry if the SCS is not separated by type on delivery. In addition, it is even possible to use SCS which would have otherwise been extremely difficult to recycle in an environmentally-friendly manner.

**Plastic instead of coal**
Spread out over the year, the company uses up to 100,000 tonnes of various types of coal and coke. Originally high-grade coal used to be processed from deposits in the Saar and Ruhr regions. However, since the decline of German coal mining, the Hart facility has processed coal imported not only from the Ukraine and Poland but also from Australia and South Africa. In future, the production is to be expanded using roughly 15,000 tonnes of plastics.
In the last five years, several million euros have been invested in the development and installation of new technologies at the Hart facility in Upper Bavaria, combined with a sophisticated emissions reduction programme. Around 220 members of staff work in carbide production at this AlzChem facility.

**Sufficient secondary raw materials are available**
In 2007, before the studies began, a market research institute examined whether a sufficient supply of waste plastics could be guaranteed from the immediate vicinity of the production facility. The management was delighted with the result. The result was that roughly 300,000 t of high-calorie plastics are available each year in Bavaria and Baden-Württemberg. The plastic fractions are largely from the commercial waste sector.
In the meantime, as many plastics are recycled for energy in alternative fuel power plants or waste incinerators, SCS of guaranteed quality have become particularly rare on the market.

**Simple chemistry – complex process**
The reaction equation on which carbide production is based is:

\[ 3 \text{C} + [\text{CaO}]_{\text{melt}} \rightarrow [\text{CaC}_2]_{\text{melt}} + \text{CO}; \Delta H = +464.3 \text{ kJ} \]

Calcium oxide, also known as burnt lime, reacts with carbon to form calcium carbide and carbon monoxide. Though the chemical process is easy to describe, its technical implementation on a large scale in closed electric low-shaft furnaces is highly complex.

The term carbide furnace is inappropriate, as people generally associate furnaces with combustion processes. However, no combustion takes place in the reactor for carbide manufacturing. Carbide manufacturing is a production process in which the main product calcium carbide and the by-product furnace gas are created.

The carbide furnaces are charged with burden, a mixture of lime and various coals and cokes, and, in the new process, supplemented with SCS. The burden drops through feed pipes arranged in a circle into the furnace chamber with its fire-proof lining. A water-cooled lid seals the furnace gas-tight. Electrodes are submerged in the burden in the centre of the furnace. The melting process takes place at the tips of the electrodes. A high flow of current between the electrodes warms the mixture until a chemical reaction
occurs with the calcium carbide. As a co-product, carbide furnace gas, consisting of the main components carbon monoxide and hydrogen, is created.

A special electrode design, hollow electrodes, has proven itself for decades. The finely grained burden is fed to the tips of the electrodes through them, where it is converted directly to calcium carbide. This has great advantages for process management.

The liquid calcium carbide melt flows out of tap holes at the base of the furnace chamber into carbide trays and hardens to form a block there. After a cooling period of approx. 30 hours, the block created is broken down.

After sieving, re-crushing and grinding, the grain is produced to the sizes required.

Until now, a lot of energy has been used. In order to reach the reaction temperature required which is over 2,000 °C in the main reaction zone, currents of up to 140,000 amperes flow between the electrodes. Approx. 3,200 to 3,500 kWh are required to manufacture a tonne of carbide from roughly 1,000 kg of lime and around 600 kg black materials.

Calcium binds chlorine

Until now, plastic waste was not used in electric low-shaft furnaces. Therefore, a number of questions had to be answered regarding the new process: How does the product quality change, what changes in emissions are to be expected, in particular if chloric materials are used? It was not possible to answer these questions at a laboratory scale, the experts had to implement their field tests at a production level.

After modifications to one of the company’s two carbide furnaces, the tests started with successive increases of the quantities of plastic added. All material flows and emissions were documented precisely. The tests focused in particular on the chloric substances, which can form toxic dioxin compounds in combustion processes. By adding specific amounts of polyvinyl chloride (PVC), the experts increased the chlorine content in the plastic up to 12% in multiple steps. There were no notable effects on the carbide process, the end product and the emissions. As expected, the chlorine is largely bound in the dust of the furnace gas as calcium chloride. As a result, no increase in the dioxin values is measurable in the exhaust gas of the electric low-shaft furnace. The heavy metal proportions are also largely bound in this dust, which is separated by a filter system. Thus, the heavy metals are concentrated in a comparably small quantity flow of the process and can be disposed of.

As a result of the positive results, the company obtained the patent rights in key economic countries and applied for approval per the German Federal Immission Control Act, which was granted on 23/06/2010.

Furnace gas becomes more valuable

The chemical reaction on which carbide production is based turns one third of the carbon used into carbon monoxide. This co-product is by no means waste. It is used as a valuable input material for chemical processes and as fuel.

Adding plastics to the burden changes both the quantity and the composition of the furnace gas. In addition to the carbon monoxide and hydrogen, it now also includes increased levels of methane and other hydrocarbons. „More and higher quality carbide furnace gas is produced than previously,“ explains Jürgen Franke. „While the gas quantity increases 30%, the heating value also increases by 20%.” The furnace gas is cleaned thoroughly, compressed and forwarded to company facilities and other external customers. There it is used as a synthesis and heating gas for material and thermal applications.

In order to use the furnace gas more efficiently, the technical feasibility of using gas motors is currently under investigation. In comprehensive test series, the engineers are cooperating with industrial partners to adapt the technology of such motors to the properties of the furnace gas.
Recycling to increase

“The market for coal and coke has changed dramatically over the past few years,” observes Dr. Klaus Holzrichter, plant manager at AlzChem in Trostberg. Former coal exporting countries such as China and India have since become importers themselves, and coal prices are increasing constantly on the global market.

By substituting coal with plastics in order to recycle the carbon contained in them not just for energy-related purposes but also to use the material for new products, AlzChem now has a unique selling proposition worldwide.

The waste policy classification was described by Dr. h. c. Karl J. Thomé-Kozmiensky as follows at the Berlin Energy Conference 2011: “From a point of view of environmental policy it is beneficial to use the carbon in plastic not just as energy but also as a raw material. Thus, the process is to be classified as a higher priority in the Waste Framework Directive than incineration of waste plastics as alternative fuels.”

In a new project, the company also intends to facilitate recycling for the chlorine in PVC. “In order to reach this goal, we utilise a well-known property of PVC – it emits hydrogen chloride at temperatures above approx. 250 °C,” explains Dr. Hans-Hermann Niemeyer, head of the project. “At the same time, a carbon-rich ‘PVC coke’ is produced, which can partially replace conventional black materials for carbide manufacturing in future.” Of course, the “PVC coke” will be tested thoroughly in the carbide process. For this purpose, a test furnace – the technical laboratory carbide furnace – is under construction.

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