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Polyolefin waste and its utilization in Polski Koncern Naftowy ORLEN SA

Summary — The results of the Environmental Compliance Program started in Polski Koncern Naftowy ORLEN SA in 1997 have been described. Realization of the Program allowed to reduce SO₂ annual emission from 38 kt to 16 kt, to decrease wastewater volume from 15·10⁶ m³/y to 6.6·10⁶ m³/y and to decrease the phenol content in wastewater from 8.2 to 3.8 kg/day. By-products and waste products created in polyolefins units have been described, especially atactic polypropylene and other kinds of wastes from various points of the PP and PE-LD plants. As a results of application of a new generation catalysts for propylene polymerization, atactic PP amount decreased from about 10 to 1.5 wt. %. Method of its application as a component of bitumens has been developed.

Key words: Polski Koncern Naftowy Orlen SA, environmental pollution reducing, polyolefin wastes, atactic polypropylene, utilization.

Polski Koncern Naftowy ORLEN SA was created in 1999 in the merger of Petrochemia Płock SA (the greatest Polish refinery and petrochemical complex) and Centrala Produktów Naftowych SA (the greatest Polish wholesale and retail distributor for petroleum fuels and lubricants). As a result, the greatest Polish refinery and petrochemical production as well as distribution company has been created. In 2000, the amount of crude oil processed reached up to 12 millions t/y. ORLEN SA supplies about 70% of domestic automotive fuels production. As for the production potential in Płock, both the refinery and petrochemical parts include up to 70 processing units altogether. Due to wide application of hydrogenation processes, the yield of white products reaches up to 83% of total production scope.

PKN ORLEN SA is the manufacturer of PE-LD and PP, moreover supplies the Polish market with such petrochemical products as: ethylene, propylene, ethylene oxide, glycol, butadiene, benzene, phenol and acetone. They form the feedstock base for both domestic chemicals and plastics production industry. PKN ORLEN covers almost the whole range of polyolefin production in Poland.

This production activity contributes to environmental impact of the whole refinery and petrochemical complex, therefore in 1997 there was introduced Environmental Compliance Program, including 28 modernization and investment tasks aiming the protection of all the components of natural environment.

So far, 16 tasks have been completed bringing significant environmental benefits, 10 tasks are in progress, and 2 are going to commence in 2002. One of the most important was the erection of the new Vacuum Residue Hydrodesulfurization Plant for sulfur removal from the fuel to our power plant. It enabled major SO₂ emission decrease from 38 kt/y in 1999 to only 16 kt/y in 2000.

Other indicators showing reduction of the environmental impact are as follows:

- percentage of sulfur removal during crude oil processing: increase from 33% to 58%,
- wastewater quantity: decrease from 15 mil. m³/y to 6.6 mil. m³/y,
- phenol content in wastewater: reduction from 8.2 kg/d to 3.8 kg/d,
- water intake from the Vistula River in 2000: increase by 5.6%,
- cooling water circulation: increase by 20%,
- wastewater discharged to the Vistula River: decrease by 29%.

The ambient emission monitoring system consists of four automatic monitoring stations for hydrocarbons, CO, SO₂, NO_x, H₂S, O₃. No excessive pollutant concentration has been detected at any of these stations. In most of the points no measurable concentration of aromatic hydrocarbons was detected.

Among the investments for environmental protection the following are of greatest importance:

- catalytic hydrogen vapors combustion units installed at wastewater treatment plant;

- plant for contaminated soil biodegradation;
- ground water quality monitoring system.

Also, all the new and modernized petrol stations in ORLEN SA network are equipped with all the latest technologies warranting high level of environment protection. The solutions applied include double walled fuel storage tanks with the permanent leak control or the control wells system for constant monitoring of ground pollution.

From the organizational activities for the environment protection in ORLEN SA, the most important is the implementation of environment management system according to ISO 14001 standard and participation in the Responsible Care program, understood as form of our activities for environment protection in our neighborhood. In 1999, after the certifying audit, ORLEN SA was awarded a certificate from the program co-ordinating office.

The environmental impact resulting from polyolefin production is not as significant as from other petrochemical products and automotive fuels. At polyethylene and polypropylene production units there are not operated furnaces, polluting the atmosphere with dust and sulfur or nitrogen oxides. Both the feedstock and the products are not liquid hydrocarbons as in the refinery part of the facility, which can pose a potential danger for ground water contamination with hydrocarbon products. However, both in the production stage and the packaging stage there appear some material wastes which are the subjects of activities aiming their reduction and ensuring their proper utilization.

There are two polypropylene units operating in Płock built according to the Japanese license of Mitsui Petrochemical Industries. The production bases on the slurry process of propylene polymerization in hexane using the Ziegler-Natta catalytic system. Polymerization reaction takes place in hexane environment at 70°C and under pressure up to 1 MPa. One of the basic conditions of proper process course is very high purity of monomer, solvent and hydrogen, which must be free from water compounds, sulfur, acetylene and other substances destroying the catalyst.

The major product of in the polymerization process in this unit is namely isotactic polypropylene, characterized with high molecular weight, high degree of stereoregularity and excellent mechanical properties. As the by-product atactic polypropylene of amorphous structure and the average molecular weight of about 10 000 is received, which is separated from isotactic polypropylene in hexane solution, then separated in special film condensers. Afterwards, this semi-liquid product is put into barrels and sold to customers.

Atactic polypropylene (PPA) is a major waste at the polypropylene plant due to relatively high quantity, which according to the license reach up to 10 wt. % of the isotactic polymer. Because of high scale production process, wastes utilization creates problems.

Apart from the atactic polymer there is also another waste polypropylene material, in the form of powder, quantity of 185 t/y, appearing in the process of samples taking and apparatus cleaning or from the filters. This waste material is packed into bags and sold to customers who use it for the production of extrusion elements not requiring good mechanical properties.

During polypropylene granulation and packing, other types of material waste appear as following:

- Wet polypropylene, quantity of 170 t/y, which appears during extruders start up and shut down as well as oversize grain and undersize grain from classification sieves. Its quantity depends on the frequency of extruders shut down and start up operations as well as the precision of the granule cutting.

- Fine grain polypropylene (powder), quantity of 20 t/y, being the product of PP dust extraction.

- Polymer spills, quantity of 140 t/y, produced during extruders start up in the granulation section.

- Polypropylene sweeps, quantity of about 200 t/y, from transport pipelines and storage tanks cleaning as well as from sweeps away.

- Polypropylene fibers created in the pneumatic transport from the production unit to the shipment; due to high velocity of granulate transport in the pipelines there occurred, especially in bends, lamination and creation of fibers. This waste was difficult to remove, a large portion of it was blown into the atmosphere and the remaining quantity was sent with the product to the customers.

- Waste film, quantity of 30 t/y, created in the laboratories in film tests, and left after packaging.

Total quantity of the waste material mentioned above is about 740 t/y, which is 0.6% of the total PP production.

The similar situation with waste material production is also at the two polyethylene units. First unit, built according to the ICI license, consists of two lines of 20 kt/y each. Ethylene is compressed in two-stage process up to 150 MPa. Polymerization reaction is realized in autoclave with peroxides as initiators; conversion degree is about 17%. Post-reaction mixture is separated, polyethylene is sent to extruder and pelletizer while ethylene is directed back to the process. Granulate is pneumatically sent to the homogenization section and to shipment.

The other unit licensed by ATO Chemie consists of two lines of 50 kt/y production capacity. The reaction takes place in the tubular reactor of length 810 m under pressure of 250 MPa. Oxygen is used as an initiator. The rest of the sections work according to the same technological scheme as autoclave unit.

In both of the units a waste material is created in the form of wax characterized with molecular weight 1000 to 2000 in the quantity 80 t/y. It is separated in the medium pressure recycle and put into barrels.

As in the polypropylene plant also in the polyethylene plant there is waste material created in the total

quantity of about 800 t/y, which is of about 0.55% of the total PE production.

Activities aimed to reduce the quantity of material waste include:

— Reduction of atactic polypropylene produced by the application of new generation catalysts. As a result of two subsequent upgrades of the polypropylene unit depending on introduction of the catalysts of II and III generation, PPA production was reduced to about 1.5 wt. % and in 2000 was equal to *ca.* 1700 t with PP production of 125 000 t/y. As a result of this modernization, a few separate operations resulting in heavy environmental impact were eliminated. Also, research work was started on commercial PPA, which was burned before. As a result, technologies for bitumen production with PPA were prepared. Atactic polymer addition improved their thermal and rheological properties, as well as improved homogenic structure. Atactic polypropylene is also used as additive for bitumen products such as: roofing pitch, insulation and grounding bitumen products.

— Removal of fiber created during pneumatic transport was realized by the application at transport pipelines new bends of special construction "GAMA Bend" and application of de-dusting system.

The other polymer material waste created in the production process, blending operations and pneumatic transport, namely polypropylene powder, polypropylene and polyethylene dust, spills, sweeps and waste film from both units, are utilized by our customers by re-granulation, milling or direct application as feedstock for further processing.

The non-production waste from our factory as for example post maintenance waste as wood, metal, concrete, but also paper, batteries, bottles and films, are segregated at the automatic line.

Summarizing, polyolefin production process in PKN ORLEN SA produce waste materials which are completely utilized and do not pollute the environment. Activities with the aim to reduce waste quantity by the changes in process technology and improvements in the construction have been realized.