STANISŁAW KUDŁA*), HANNA MACIEJEWSKA*),
MARIA UHNIAT*), ZDZISŁAWA MAJCHRZAK*),
MARIA KURKOWSKA**) ADAM WIŚNIEWSKI**),
ANDRZEJ BAŃKOWSKI**)

Research and engineering at the Polski Koncern Naftowy S.A. polypropylene plant at Płock

Summary — The propylene polymerization (30 000 ton PP/year) installations run on Ziegler—Natta generation I and II catalysts were modernized by using generation III and IV catalysts, which are highly active and stereoregular. The installations were modernized by eliminating the methanol-water wash step and the methanol recovery step. In the hexane used as solvent, fraction recyclates were used, 28 and 42%. The production capacity was raised to 100 000 ton PP/year. The old and the modernized block diagrams are shown (Figs. 1, 2), polymerization runs over seven catalyst systems are summarized (Tables 1, 2, 4) and physicochemical property data are given for the polymers obtained (Table 3).

Key words: polymerization of propylene, Ziegler—Natta generation III and IV catalysts, plant and process modernization.

The polypropylene facilities PPI and PPII at the Polski Koncern Naftowy S.A. (formerly Petrochemical Works Płock SA), each with a design capacity of 30,000 metric tons PP per year, are based on the process bought from the Mitsui Petrochemical Industries. The propylene polymerization process is carried out in a hexane fraction and in the presence of a generation I catalytic system, $TiCl_3 \cdot 0.33\ AlCl_3$ and dichloroethylaluminum modified with potassium hexafluorotitanate. The block diagram of the plant presented in Fig. 1.

The research cooperation between the Petrochemical Works Płock SA and the Institute of Heavy Organic Synthesis (ICSO) was established even before the plant start-up and has been continued until now. The joint efforts covered the tests of catalysts, commercial test runs and engineering studies. This cooperation has resulted, for example, in the use of a domestic organoaluminum cocatalyst, the use of generation II titanium catalyst and most recently in the expansion of PP production by 40—50%.

In the early 1990s, we were facing the challenge of making prices of Polish PP competitive to those of imported PP, *i.e.*, reducing the cost and consumption figures for the monomer, catalyst(s), utilities, and auxiliary materials. We planned to achieve this goal by introducing high-activity generation III and IV catalytic systems (*e.g.* $Ti\text{-}Mg/AlEt_3$/donor) into propylene polymerization. Modernization of the plant became necessary. This comprised primarily modifications in engineering and in process equipment to adapt the production facility to make use of the newest generation catalysts. Prior to commercial tests, laboratory evaluation was carried out of the polymerization runs carried out over supported titanium catalysts supplied by US and Japanese manufacturers. The catalysts are designated with letters **A**, **B**, **C**, **D**, **E**, **F**, and **G**. In the laboratory polymerization test runs use was made of 500-mL and 350-mL reactors and a hexane fraction taken from the PP I plant. Triethylaluminum was used as cocatalyst and cyclohexylmethyldimethoxysilane (CMDMS) served as an external donor, except for the **F** catalyst, where *N*-propyltrimethoxysilane was used as cocatalyst. The data obtained from the propylene laboratory polymerizations run over the high-activity catalysts are listed in Table 1. On the basis of the data collected, the catalysts **A**, **B** and **D** were selected for commercial tests. The first commercial test (Table 2) with the **A** was organized in June 1994. The catalyst was very active so that the methanol-water wash could be omitted in the catalyst deactivation section, because there was no need to remove its residue from the polymer. For comparison, Table 2 lists the data collected in a polymerization process run over a generation II catalyst. Commercial production over 1 g of the high-activity catalyst is seen to be five times that available from the generation II catalyst. Although the deactivation and washing section was not operated, the polymer yielded from catalyst A had the ash content of only 40—70 ppm. This level was compa-

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*) Institute of Heavy Organic Synthesis, 47-225 Kędzierzyn-Koźle, Poland

**) Polski Koncern Naftowy S.A., 7, Chemików, 09-411 Płock, Poland

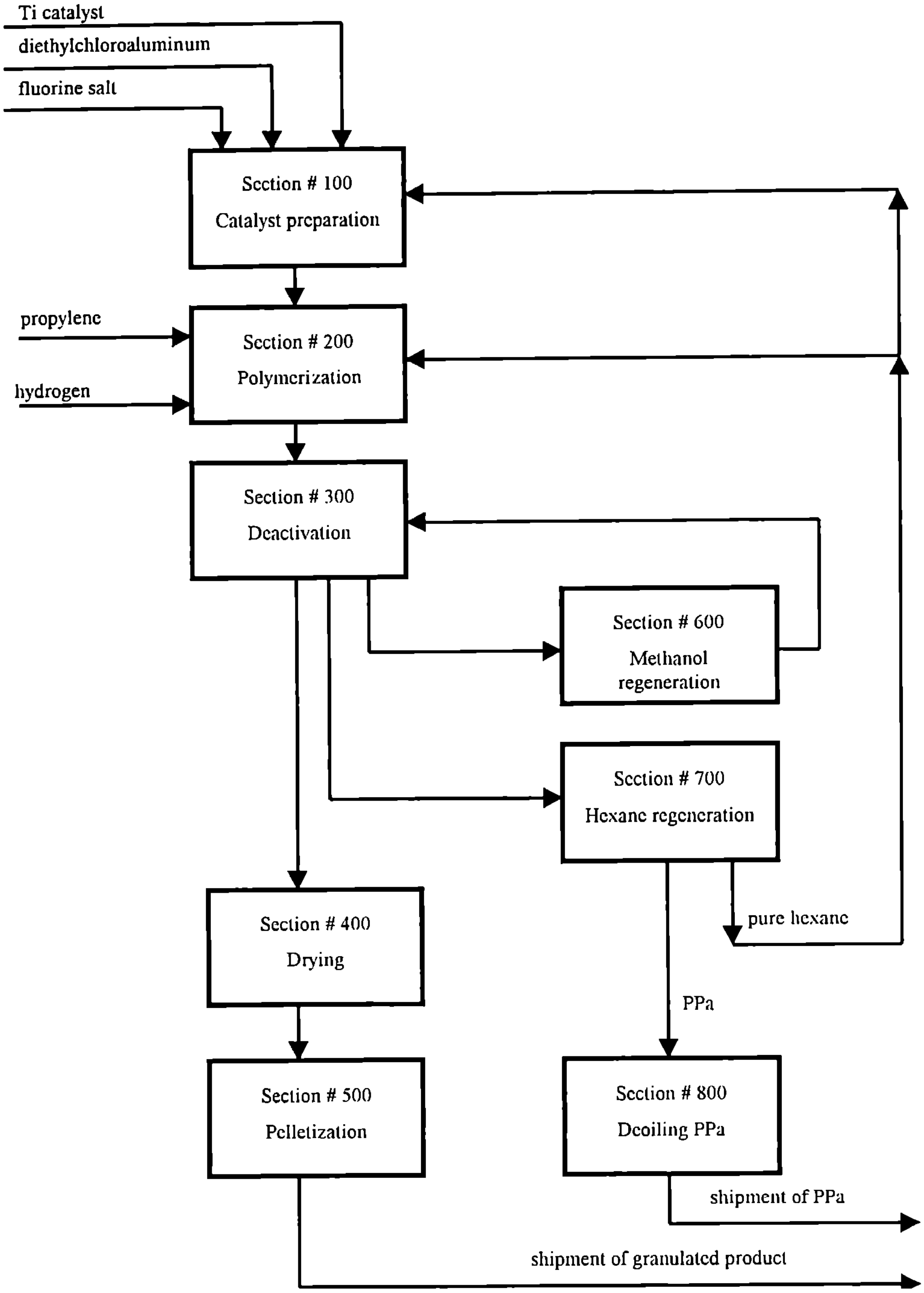

Fig. 1. Block diagram of PP plant before modernization

rable with that available for the generation II catalyst with the methanol-water wash employed.

Another commercial polymerization test involving the catalyst **B** was carried out in October 1994. The catalyst deactivation and methanol-water wash section was not operated from the very beginning of the test. The ash content reached the level of 60—80 ppm (Table 2).

More prolonged commercial test runs were arranged in 1995 and 1996. The PP plant was operated with the use of **A**, **B** and **D** catalysts. Table 3 provides the properties of polypropylene materials (Malen P F-401) produced over these high-activity catalysts. As can be seen, the polymer properties are dependent on the catalyst type employed. The polymers produced in the presence of **A** and **B** had higher degrees of crystallinity than that yielded over **D**, resulting in better mechanical properties of the polymers.

The use of the high-activity catalysts made it possible to modernize the plant and to eliminate the methanol-water wash section from the polymerization process. Two polymerization lines were arranged, each comprising two reactors, instead of the previous one line composed of four reactors operated in series. The hexane, propylene and catalyst streams were charged to

Table 1. Laboratory propylene polymerizations. Polymerization conditions: temperature 70—73°C; pressure 0.6 MPa; time 1 h; no hydrogen added; reactor volumes: 500 mL and 350 mL.

Catalyst	Ti content in catalyst wt %	Concentration of Ti mmol/dm^3	Al/Ti mol/mol	Al/Si mol/mol	Yield kg PP/g cat.	Catalyst activity kg PP/g Ti	Bulk density, g/L	Isotacticity index, wt %	Polydispersity, M_w/M_n
A	3.30	0.049$^{*)}$	300	26	4.0	131.0	380	97.8—98.3	3.0
B	2.36	0.029$^{*)}$	250	16	4.7	206.0	390	98.7—99.0	3.6
C	2.67	0.043	160	20	2.1	90.0	380	96.9—97.8	7.5
D	2.36	0.040	170	20	2.3	109.0	400	96.9—97.8	7.1
E	2.10	0.020	400	10	3.7	186.0	350	96.7—97.7	4.4
F	1.95	0.037	180	17	3.6	180.0	320	99.0—99.4	5.6
G	2.21	0.037	170	14	3.0	120.0	380	98.2—99.6	4.4
generation II catalyst from USA		1.14—1.71	5—7	—	0.5—0.6	1.6—1.8	380	95.3—98.1	4.6

*) A 500-mL reactor.

Table 2. Comparison of the catalytic activities of high-activity catalysts and generation II catalyst under commercial conditions

Catalyst	Yield, kg PP/g cat.	Activity, kg PP/g cat.	Deactivation and washing section	Ash content in polymer, ppm	Polydispersity M_w/M_n
A	18.0—25.0	650—730	—	40—70	3.0
B	25.0—35.0	3000—4000	—	60—80	3.6
generation II catalyst $TiCl_3$-$AlCl(C_2H_5)_2$	5.0—5.5	16.0—17.7	+	35—76	4.6

Table 3. Physical-mechanical properties of polymers (Malen P F-401) obtained over high-activity catalyst and generation II catalyst under commercial conditions

Catalyst	Physical-mechanical properties						
	Yield point MPa	Breaking stress MPa	Ultimate elongation, %	Shore hardness °Sh D	Softening point Vicat (10 N), °C	Crystallinity (DSC), %	Polydispersity M_w/M_n
A	33.6	30.7	750	69.4	156.0	47.2	3.0
B	36.2	31.3	750	70.5	160.3	47.2	3.6
D	32.9	29.2	678	69.9	159.9	45.7	5.1
generation II catalyst	30.3	30.0	775	67.5	153.0		4.6

Table 4. The effect of recycled hexane fraction in a propylene polymerization laboratory test. Catalyst A. Polymerization conditions: temperature 72—74°C; pressure 0.6 MPa; time 1 h; reactor volume 350 mL

Reaction medium	Ti concentration mmol/dm^3	Al/Ti mol/mol	Amount of polymer, g	Yield g PP/g cat.	Activity kg PP/g Ti	Bulk density, g/L	Isotacticity index, wt %	Content of atactic fraction in hexane, wt %
Hexane fraction	0.039	190	97.4	4179	140	366	99.5	0.5
Hexane fraction with 28 vol % of recycled fraction	0.039	190	90.0	4003	136	355	99.5	1.0
Hexane fraction with 42 vol % of recycled fraction	0.043	190	95.4	3892	135	359	99.4	1.3

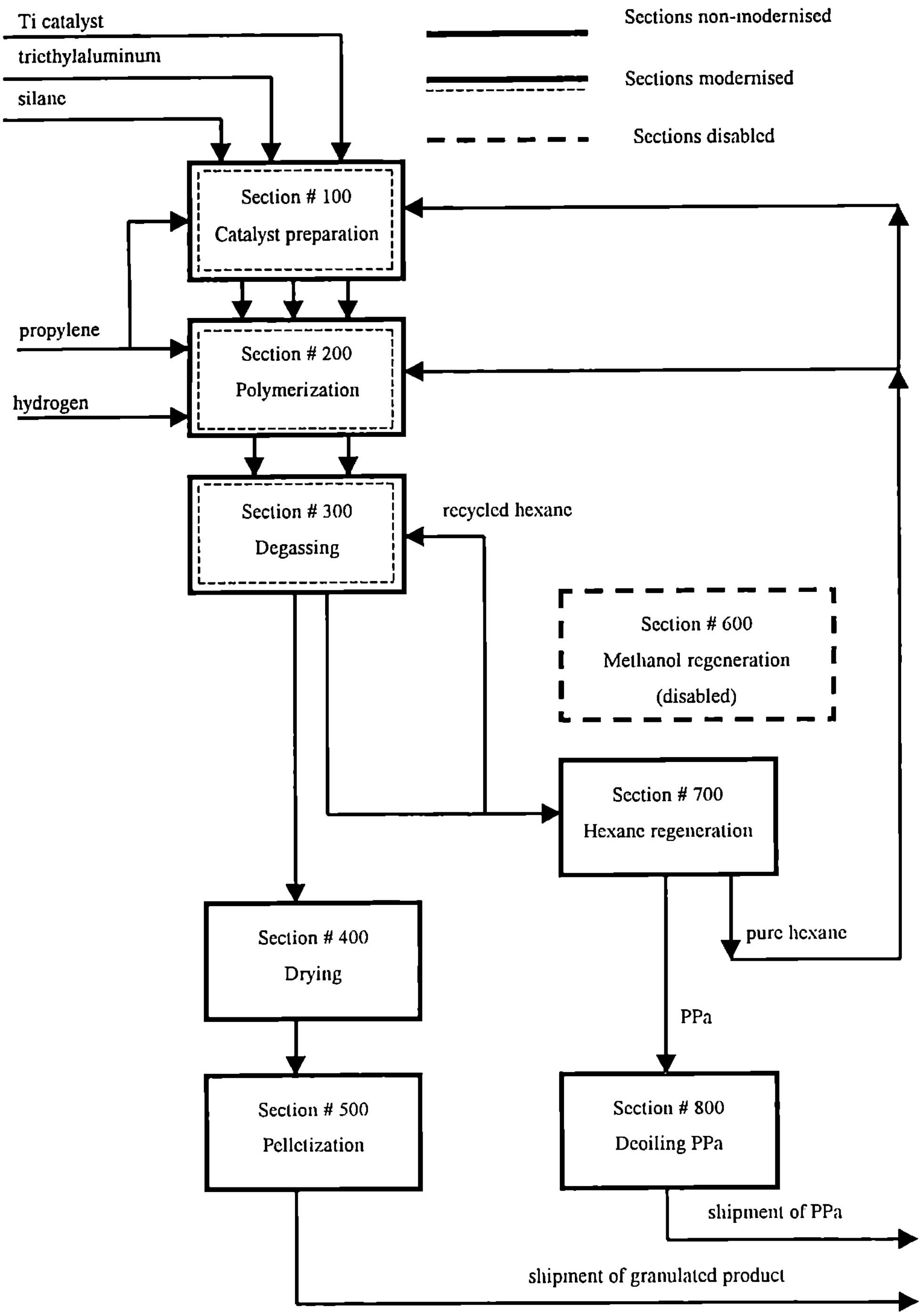

Fig. 2. Block diagram of PP plant after modernization

those lines. The engineering analysis resulted in some changes in the production equipment. Also, the catalytic system preparation section was modernized. Figure 2 presents the block diagram for the modernized propylene polymerization facility.

The use of the high-activity catalysts and the plant modernization made it possible to increase the volume of propylene homopolymer production to over 100,000 t/year. This polymer was used in injection molding and in film and fiber production. In connection with the expansion of the production capacity, it was considered that some part of "polymerization-grade" hexane fraction could be replaced in the polymerization process by the recycled hexane fraction, *i.e.* the centrifuge effluent. The idea was verified — a laboratory test was performed with the use of catalyst A and a recovered hexane fraction. Propylene polymerization was conducted in "polymerization-grade" hexane fraction and in the mixtures containing 28% and 42% of the recycled hexane fraction which was obtained from the polymerization plant where the above catalyst was employed (Table 4). The moderate percentage of the recycled fraction

(28%) did not affect adversely the catalytic activity of the system. However, with 42% of the fraction, the polymer yield per 1 g of catalyst was reduced by about 7%.

The above findings confirmed the possibility of utilizing the recycled hexane fraction in the polymerization process at the PP I facility. The first commercial test was performed in February 1997 with catalyst **A**. The amount of the recycled hexane fraction was varied within 20—50 wt %. Such levels did not change significantly the amounts of oligomers occurring in the centrifuge effluent stream (hexane fraction). No decrease was noticed in the activity of the catalytic system, either. Similar tests were arranged at the modernized plant when catalyst **B** was used with up to 60 wt % of the recycled hexane fraction introduced into each polymerization line.

The partial recycle of the hexane fraction yielded additional savings on raw materials and energy. The consumption figures of the organoaluminum catalyst and of the donor were improved and the charge to the hexane regeneration section was reduced.

Summing up the laboratory research of ICSO and the commercial tests carried out at the PP plant, it should be stressed that the solvent-based process has been modernized and the new ideas have been introduced. The result is the increased volume of production and the high quality of the product. The production exceeded 115,000 tons of polypropylene in 1998. The catalyst activity observed reached 1,300—1,800 kg/g Ti and the product polymer offered an isotacticity factor of 98.5—99.5% and a good processibility.

W kolejnym zeszycie ukażą się następujące artykuły:

— Makrocykle fenolowo-formaldehydowe w układach polimerowych. Cz. II. Otrzymywanie z wykorzystaniem polireakcji stopniowych

— Mechanochemiczna modyfikacja polietylenu trzeciej generacji bezwodnikiem maleinowym

— Homo- i kopolimeryzacja styrenu, inicjowana nadsiarczanem potasu bez użycia emulgatora, przebiegająca w warunkach statycznych. Cz. I. Homopolimeryzacja styrenu

— Spektrofotometryczna metoda oznaczania składu kopolimerów etylen/1-heksen

— Palność wulkanizatów *cis*-1,4-polibutadienu

— Procesy radiacyjne w polipropylenie modyfikowanym maleinianem rycynylo-2-oksazoliny

— Badania właściwości żywicy melaminowej modyfikowanej akryloamidem. Cz. III. Wyjaśnienie mechanizmu działania akryloamidu jako modyfikatora żywic melaminowo-acetonowo-formaldehydowych

— Nowe, ciekłe, reaktywne antypireny azotowe i azotowo-fosforowe do samogasnących poliuretanowych tworzyw piankowych. Cz. II. Zastosowanie do sztywnych pianek poliuretanowych

— Badania nad degradacją poli(tlenku etylenu) metodą wieloetapowej pirolizy sprzężonej z chromatografią gazową z zastosowaniem dozownika z programowaną temperaturą (*wersja angielska*)

— Badania nad wykorzystaniem wywaru ziemniaczanego do produkcji sztywnej pianki poliuretanowo-poliizocyjanuranowej (*wersja angielska*)