Influence of Catalysts on the Production Cost of Some Polyolefins and Polydiolefins, with Reference to New Catalysts Based on 4 and 5 f Group Elements of the Periodic Table

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Technical-economical aspects of polymerization processes of the first terms of mono- and diolefins, and benefits potentially achievable by catalysts based on elements of the 4f and 5f groups of the periodic table are dealt with.

Introduction

This paper reviews the impact that catalyst systems based on 4 and 5 f group elements could have when applied to industrial processes.

The catalyst systems themselves are only outlined, whereas the process advantages attained by using improved catalysts are discussed in some detail.

The paper is limited to the general technical–economical aspects of industrial processes and to the benefit potentially achievable by catalysts based on elements of the 'hidden face' of the Periodic Table.

The Main Items of Cost of a Chemical Process

The main items of cost of a chemical process are shown in Fig. 1. The first item is that of raw materials: in a polymerization process, for example, this item encompasses the catalyst system, monomer(s), and auxiliary materials such as solvents, processing aids, polymer stabilizer and so on.

SOME IMPORTANT ITEMS OF COST IN
A CATALYTIC CHEMICAL PROCESS AFFECTED
BY CATALYST SYSTEM

VARIABLE COSTS	RAW MATERIALS
	UTILITIES
FIXED COSTS	LABOR
	PLANT DEPRECIATION

Fig. 1.

The second item of cost is that of utilities and, in particular, energy. Energy is also required in spontaneous processes, *i.e.* in processes in which the free energy is negative. For example, energy is necessary for enhancing the mass translation throughout the plant, for enhancing the diffusion of monomer onto the catalyst center, for improving the withdrawal of reaction heat. Operations of stirring, pumping, cooling, separating and conveying are also necessary in spontaneous processes, such as most polymerization processes.

The third item of cost is that of labor, the fourth is depreciation. Raw materials and utilities are variable costs in a process whereas labor and depreciation are fixed costs, because they run independently from the plant productions. Therefore they affect the unit product cost to a larger extent when the plant is running under capacity.

These considerations are summarized in Fig. 2, under the heading: 'in which way an innovation of the catalyst system (and in particular catalyst systems based on lanthanides and actinides) can decrease the cost of a chemical process?'

In the last few years a huge amount of research has been directed toward an improvement of the activity of the polymerization catalyst systems and of their specificity. This effort has been successful and nowadays the cost of the catalyst system is just a small fraction of the total production cost.

For example, in the case of a typical plastic (high density polyethylene) the cost of catalyst accounts for less than 0.5% of the production cost of the

IN WHICH WAY AN INNOVATION OF CATALYST SYSTEM CAN DECREASE THE COST OF:

- RAW MATERIALS
- UTILITIES
- LABOR
- DEPRECIATION

IN A CHEMICAL PROCESS?

Fig. 2.

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polymer. In the case of a typical synthetic rubber (high cis polybutadiene) it is less than 1%.

By taking into account this fact, it could be erroneously inferred that a further improvement of the catalyst system is useless, as far as the economic aspects of the process are concerned.

This conclusion is wrong, because the catalyst system can also affect other cost items of the process, which now have an increasing relevance in the process economy.

The search for improved catalyst systems therefore maintains its validity, provided that a catholic approach is used, *i.e.* by taking into account all the manifold, indirect effects of catalyst on the process economy. This approach is made possible only by a strict cooperation between the researchers looking into the fundamental aspects of catalysis and the researchers aware of all the multifaceted economical and technical problems of a modern chemical process.

Raw Materials

In Fig. 3 this item has been split into several sub-items, *i.e.* catalyst, monomer and so on.

RAW MATERIALS

- CATALYST SYSTEM
- MONOMER
- MOLECULAR WEIGHT MODERATOR
- POLYMERIZATION MEDIUM
- AUXILIARY POLYMERIZATION CHEMICALS (SHORT STOP, SURFACTANTS ...)
- POLYMER STABILIZERS AND ADDITIVES (ANTIOXIDANT, ANTI-OZONE, UV ABSORBER, ACIDITY SCAVENGER ...)

Fig. 3.

Catalyst

As mentioned above, the direct impact of catalyst on the total production cost of typical, large consumption plastics and rubbers is marginal, less than 1%.

However, a further improvement of activity of the catalyst system seems still possible, albeit not so economically relevant.

In fact, looking to the extremely high activity reached by the catalysts for ethylene polymerization (*i.e.* up to 8 million moles of monomer is polymerized by 1 atom of transition metal), it seems that there is still room for improving the catalyst activity at least in the polymerization of dienes.

In a catalyst based on lanthanides, about 60,000 moles of butadiene are polymerized by 1 atom of transition metal. However, it seems that only 0.4–8% of the transition metal is acting as an active polymerization center [1], so that a further tenfold improvement of the already high activity of this catalyst can be envisaged. Costwise, in a Ziegler Natta catalyst system the co-catalyst (*i.e.* aluminium alkyl) is more important than is the transition metal compound.

Large amounts of aluminium alkyls, with stoichiometric ratios from 20 up to 200 with respect to the transition metal, are used in order to obtain active catalysts [2]. These huge amounts of aluminium alkyls can be hardly justified by the stoichiometry of the catalyst center.

Therefore, a further research effort in understanding the reason of the co-catalyst/catalyst stoichiometry (beside those of MW control and impurities scavenging action) seems justified.

Monomer

The increased cost of petroleum and of its derivatives has swollen the economic importance of monomer in respect to other items of production cost. The monomer cost accounts for as much as 75% of the production cost of a high density polyethylene (e.g. plastics) and 56% of a high cis polybutadiene, (e.g. synthetic rubbers).

At first glance, the monomer cost seems 'incompressible' in a chemical process. However, by looking more carefully to the monomer consumption, it is possible to see that a small (albeit economically important) fraction of monomer is lost.

Part of this loss is due to side reactions which, even if present in limited amount, can jeopardize the process economy. For example, a loss of just 1% of ethylene (with formation of ethane, waxes *etc.*) costs more than the total catalyst system. The same consideration holds for a polybutadiene process in which the catalyst cost is less than the cost of a loss of 3% of monomer (dimerization to vinylcyclohexene, oligomers formation, *etc.*).

From the above figures can be extracted the importance which the catalyst system can have (indirectly) on the process economy, by affecting other apparently-independent cost items such as monomer consumption.

Another part of monomer loss is due to physical, unavoidable loss by the plant equipment (blanketing, purges *etc.*). Also in this case, the catalyst system can affect the result. In fact, any process simplification achievable by using improved catalysts, can delete operations of purification, of recycle and so decrease the monomer loss.

Molecular Weight Moderator

The next sub-item of cost is the molecular weight moderator. This typical ingredient of polymerization recipes is a chain transfer agent: its function is that of moderating the length of polymer chains and of re-initiating a new chain, in order to avoid any loss of polymer yield (at difference with a polymerization stopper). Hydrogen is used for mono-olefins. Various types of chemicals are instead used for dienes.

Again, the catalyst system can affect this item of cost, because some catalyst systems are more sensitive than others to chain transfer agents and to their deactivating effect toward the catalyst.

A low requirement of a transfer agent can also improve the economy of the process, by allowing a higher concentration of monomer to be attained (case of ethylene and hydrogen) and consequently higher kinetics and plant output.

Polymerization Medium

The next sub-item is the polymerization medium, *i.e.* the medium in which the polymerization takes place and in which the polymer dissolves (solution processes) or precipitates (slurry processes). In principle, the polymerization medium is completely recyclable. However, in practice, a loss is unavoidable which can account for 2% of the polymer production cost in the case of a solution process.

One way of reducing or eliminating this item of cost is by designing a process which does not require any polymerization medium. This is possible, for example, by performing the polymerization in a gas phase (polyethylene) [3] or in a liquid monomer (polypropylene) [4].

These innovations in the process design cannot be attempted effectively without a catalyst suitable for the demanding conditions imposed by the new process design.

Polymer Additives

Polymer additives account for 2–3% of the production cost of the polymer, approximately the same cost as the catalyst system. The nature of the catalyst system, and in particular the transition metal used in the catalyst, can affect the cost of one of the main additives, *i.e.* the antioxidant.

In fact some transition metals such as vanadium, cerium and cobalt are powerful oxidation agents and consequently require a proper stabilization system and a generous additivation. Other transition metals such as titanium and nickel are less dangerous.

Uranium among 5 f elements and neodimium among 4 f elements are very satisfactory also in this respect owing to their stable valency [5], so that the polymer can be easily stabilized with small amounts of conventional antioxidants.

Also a lower potential acidity in the catalyst system can allow saving of acidity scavengers, with advantage to the process economy and the product quality.

Utilities

This item has also been subdivided into subitems: electric energy, high pressure steam, low pressure steam, and so on (Fig. 4).

UTILITIES

- ELECTRIC ENERGY
- HIGH PRESSURE STEAM
- LOW PRESSURE STEAM
- COOLING WATER
- PROCESS WATER
- NITROGEN (FOR BLANKETING)

Fig. 4.

Utilities can account for 5% of the production cost of a high density polyethylene and as much as 18% of the production cost of a high *cis* polybutadiene. The order of the first items of the Figure, which are different forms of energy required by a process, is in function of increasing entropy content of the energy source or of decreasing cost per energy unit.

The energy consumption of a chemical process, and in particular of a polymerization process, is significantly affected, although indirectly, by the catalyst system.

Energy is required for example by refrigerating machines, when the characteristics of the catalyst system does not allow the polymerization to be performed at temperatures higher than about 60 °C. In fact, above this temperature, the refrigeration can be in general provided by cooling water. Energy is required for recycling polymerization diluents whose amount, in several polymerization processes, can be as high as 4 and even 9 tons per ton of final product. Catalyst systems able to perform at high monomer concentration or in volatile aliphatic solvents allow relevant saving of energy.

Energy is required for moving the reacting polymerization mass throughout the polymerization train, and for stirring the reactors in order to ease the access of monomer onto the catalyst center and to remove the polymerization heat.

Both these operations of mass translation and stirring are affected by the viscosity of the polymerization mass. Hence, polymerization and catalyst systems able to operate also in a condition in which the polymer formed separates as a solid (slurry and gas phase processes) are in general favoured in this respect, in comparison to solution processes, which have to deal with very viscous solutions, related to the macromolecular nature and to the concentration of the solute.

Energy is required for purification of feeds and of recycles. Therefore, catalyst systems less sensitive to impurities allow the energy required for rectifying those streams to be saved and a simplification of the process to be achieved.

The purification cost is affected also by the ability of the catalyst systems to avoid the formation of byproducts. For example, a polymerization catalyst able to avoid the formation of oligomers, beside decreasing the monomer consumption (as already mentioned) also allows a purification of recycles to be avoided.

Energy is required for purification of the polymer from the catalyst residues, when they are harmful for the polymer properties. Therefore a catalyst system which can be left in the polymer and does not require a washing step of the polymer solution (or polymer slurry), or a steam stripping of the same (or both) allows a significant saving of energy and, in general, of utilities.

Moreover, such a catalyst system does not require a section of plant for drying monomer and polymerization medium contaminated by water.

The considerations made so far on the possible influence of the catalyst system on the cost of utilities are sufficient for understanding why some elements of group 4 of the periodic table and uranium can be so interesting in comparison with conventional transition metals in the polymerization of dienes.

The high polymerization temperature allowed by some elements of the 4 f group [5, 6], the possibility of reducing the recycle energy by using low boiling aliphatic solvents, the limited toxicity of some elements of the 4 f group and of uranium toward the polymer ageing [5], owing to the stability of their valence, are all important elements in favour of actinides and lanthanides as polymerization catalysts.

Labor and Plant Depreciation

Certainly the important process simplifications made possible by improved catalyst systems should have an influence in reducing the labor and the plant cost.

A rough idea of the plant simplifications recently introduced, and based on a quantum jump in catalyst technology, are shown in Fig. 5 referring to the polymerization of high density polyethylene.

In Fig. 6 the cost advantages of a technology of butadiene polymerization with lanthanide catalysts to high *cis* polymer are compared with a conventional technology based on titanium catalysts.

Conclusions

– The increase of cost of petroleum and of energy have boosted the importance of monomer and utilities in polymerization processes.

– The improvement of catalysis has kept down the cost of the catalyst system, so that in some cases catalysts account for a mere 1% or less of the polymer production cost.

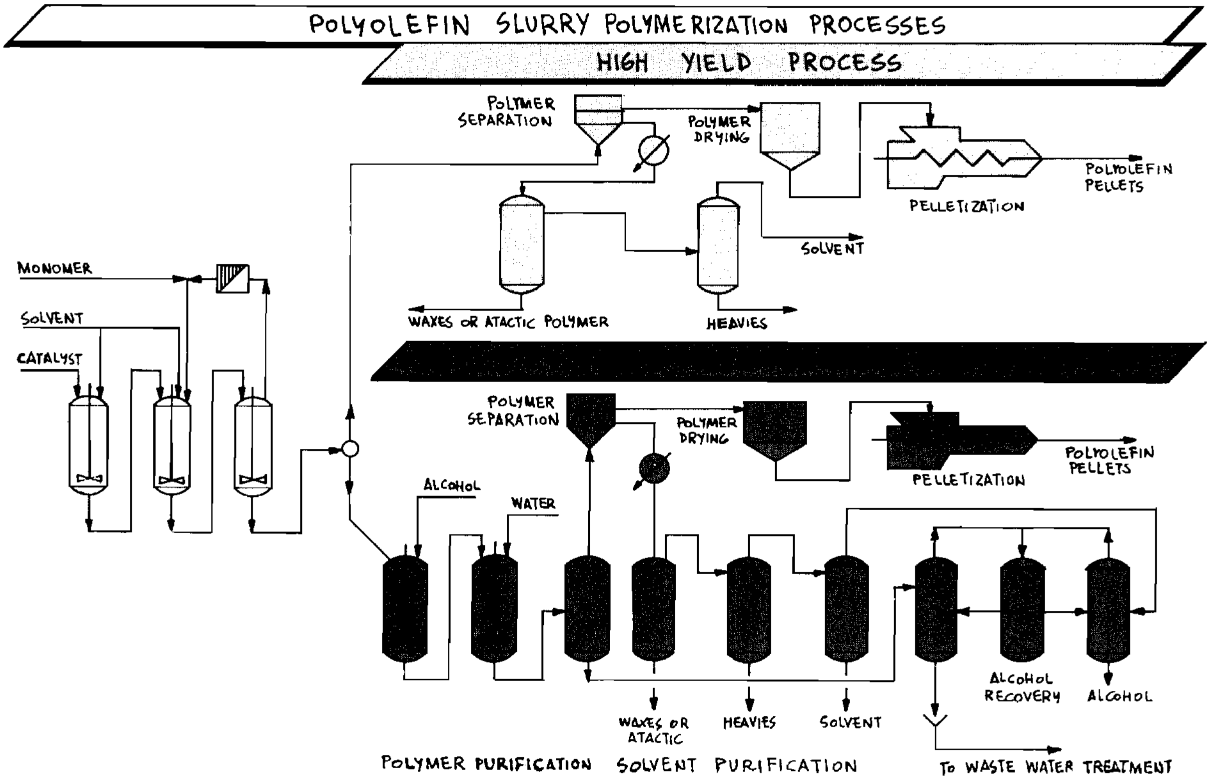
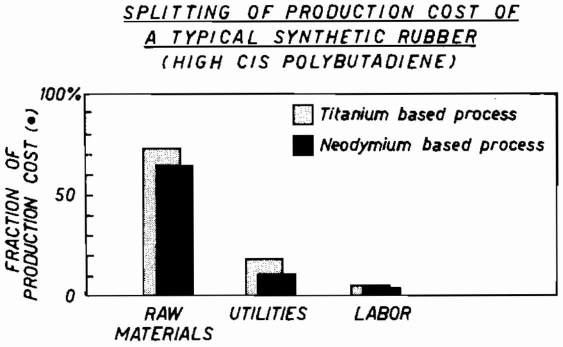


Fig. 5.



(•) costs referred to direct gate production cost of Ti process, assumed equal to 100.

Fig. 6.

– However, the catalyst system also represents nowadays the focus of the process, since it affects most of the other items of cost. Moreover, a quantum jump of technology is hardly possible without the development of a suitable catalyst.

– A catholic approach in the research on catalysis is now necessary. Any characteristics of a new catalyst should be evaluated in front of the manifold needs of a new technology.

– An effort in the organization of research also, with a stronger involvement of both fundamental and applied researchers, seems necessary for these new needs.

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