

Design and Implementation of a Novel Quench Flow Reactor for the Study of Nascent Olefin Polymerisation

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A novel stopped flow reactor system is described in the current work, along with the underlying design philosophy. While the concept of stopped flow technology is not recent, this system is the first to be designed with the objective of studying particle morphology, and to work at extremely short (40 ms) residence times. It is shown that traditional chemical engineering principles are required to properly design and operate this type of reactor, and that when correctly design, it is a very flexible tool for the study of nascent polymerisation of olefins.



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Introduction

It is well known that heterogeneous olefin polymerisation catalysts undergo a dramatic change of morphology during the very early stages of the polymerisation reaction, and the mastery of these changes is of fundamental importance for performing successful polymerisations. A typical heterogeneous (or supported) catalyst consists of active sites dispersed on a highly porous, rigid solid support with particle diameters in the range of 10 to 100 microns. The most common examples of commercial catalyst systems include Ziegler-Natta (TiCl_4 supported on MgCl_2), Phillips (oxides of chromium or vanadium dispersed on silica), and metallocene catalysts (complex

active sites supported on silica). The support material is designed to be strong enough that the catalyst particles can be manipulated at the plant site and injected into the reactor. However they must also be friable enough that, upon injection into the reactor the polymer that forms inside the pores can provoke just enough stress that the original support fragments and the particle becomes a continuous matrix of polymer in which the fragments containing the active sites are dispersed. It is now fairly well accepted that fragmentation is one of the most important steps the development of catalyst activity and particle morphology.^[1]

In spite of its recognized importance, the catalyst fragmentation phenomenon is still not properly described, and despite certain recent efforts, much work remains to be done to understand and model the different steps in the development of particle fragmentation and morphology. To a large extent, these problems persist because of the difficulties associated with the experimental studies at the fragmentation scale:

- Fragmentation is very rapid. Typically fragmentation is complete in much less than one second in the case of Ziegler-Natta catalysts.
- The polymerisation reactions are extremely rapid (polymer is produced at rates of 10^2 – 10^5 gram of polymer per gram of support per hour during the initial instants of the reaction) which implies the need for precise control of residence times
- Commercially, the reaction takes place at pressures from 8 to 30 bar of monomer (slightly lower pressures can be used in cases where prepolymerisation is used), which means that one needs specialised equipment to run the polymerisations.
- $MgCl_2$ is destroyed upon contact with air or polar solvents, so if we are to examine the evolution of particle morphology and to follow the fragmentation process, the equipment must be designed with the constraint of being able to recover the particles intact.

The stopped flow technique by which a reaction can be carried out within an extremely short period seems to be the most likely candidate for overcoming these limitations. Associated with specific on-line recording spectroscopic detectors, it has been extensively applied to homogeneous catalysis to obtain information concerning active species, intermediate states and kinetic parameters.^[2] In its “basic” configuration, the stopped flow technique consists of two syringes that can be actuated manually or automatically to allow two reactant streams to be accelerated together and rapidly mixed, and the resulting flow is abruptly stopped by use of a third syringe. This technique has been refined to a large extent: research on stopped-flow instrumentation has focused on devel-

oping efficient mixing systems, minimizing the amount and the manipulation of the reagents, automating the different steps of the process from sample handling to data acquisition and evaluation (from stopped-flow reactions signals). In the last decade, automated micro stopped-flow apparatus for routine measurements were developed and were marketed by Applied Photophysics Ltd., Kin Tec Corporation or Bio-Logic Science Instrument among others.^[3]

It has also been shown that this method seems to be suitable for the study of the kinetics of heterogeneous Ziegler-Natta (ZN) olefin polymerisation during short intervals by Keii and Terano,^[4] who were the first to attempt to use it to evaluate specific parameters in the polymerisation of propylene with an $MgCl_2$ -supported catalyst. Their group has carried out a variety of investigations using the stopped flow method for olefin polymerisation with ZN catalysts.^[5–10] Despite its extensive use for kinetic studies (under fairly mild conditions), it must be pointed out that this method has never been used to characterise morphological development of nascent structures during olefin polymerisation. In fact the authors in these (and other papers not cited here) used ethanol or methanol solutions to stop the reaction. These are effective poisons, but destroy the structural integrity of the supports, making it impossible to study particle morphology and fragmentation.

We have therefore proposed a modified stopped-flow reactor which we call a “high-pressure quenched-flow reactor”, combining in its basic configuration, a mixer module, a delay line (allowing controlled reaction times from a few milliseconds to several seconds) and a poisoning module (cf. Figure 1). This set-up is designed to allow us to study rapid polymerisation reactions on supported catalysts suspended in an alkane (heptane) slurry at very short times, and under conditions that approximate those found in industry. It is common practice to inject a slurry of catalyst similar to this in commercial processes.

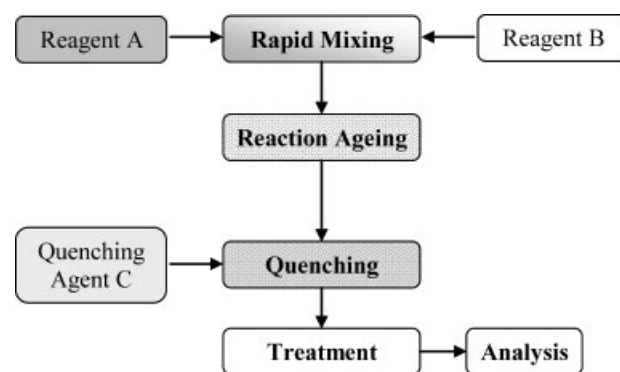


Figure 1. Block diagram of a stopped flow, or quenched flow reactor.

Analyses are off-line performed after sufficient quenched aged-mixture was collected. As this equipment is flexible, it is possible to make it evolve according to our needs in terms of monomer concentration, pressure, temperature, pre-contact time, reaction time, poisoning conditions, etc. In the following research note we will present results of the steps and analyses performed in the design of a version of the Quenched Flow Reactor from specifications to starting phase of tests and control of the equipment.

Reactor Development

The question of how to design the reactor begins with an examination of the specifications to be set.^[11]

- (i) mixing of the catalyst slurry should be efficient in order to avoid temperature and concentration gradients;
- (ii) flow velocity must be constant during the polymerisation to avoid deviation of the polymerization time within one run;
- (iii) monomer conversion must be kept low (i.e. less than 10%) in order to avoid significant changes in monomer concentration and polymerisation temperature of the polymerization mixture in the delay lines;
- (iv) the polymerization must be stopped immediately and completely in order to avoid deviation in polymerization time;
- (v) sufficient amounts of polymer must be obtained to perform all analytical measurements required;
- (vi) the particle morphology must not be damaged by the experimental, and especially quenching procedure;
- (vii) the residence time in the reactor, or delay line, should be as short as possible (and highly reproducible) to allow us to explore the rapid evolution of catalyst activation and particle morphology.

Specifications (i) through (v) were suggested by Liu et al. as being necessary for performing kinetic studies cited above. It should be noted that in points (i) and (iv), time scales play a major role. For example, if we want to carry out the reaction in such way that we have <5% of the reaction time in unsteady conditions, then if you need 0.01 seconds each for both mixing and killing than polymerisation time should not be below 0.5 seconds, if we want to assure for example <5% of unsteady regimes. Thus one needs to be very careful about using very short reaction times to look at kinetic data (see for example Di Martino et al.^[12]). The last two specifications are additional constraints imposed by the desire to be able to study particle fragmentation and

morphology in addition to the reaction kinetics (see e.g. Di Martino et al.^[13,14]). In order to be able to effectively study particle fragmentation, it is desirable that the polymerization in a quenched-flow or stopped-flow reactor can be performed in short times; if possible, much less than the one second that is typical of the average lifetime of the growing polymer chains on MgCl₂-supported ZN catalysts. We therefore want to: (i) build a reactor system capable of operating at pressures and temperatures representative of industrial conditions; (ii) have the shortest possible reaction times (≤ 0.1 s); (iii) recover our polymer particles undamaged in order to study fragmentation. The design of the apparatus that was settled upon is shown in Figures 2 and 3, and is comprised of:

- (i) Two special pressure-resistant flat-bottomed cylindrical tanks (A) and (B) (0.5 L, 7 cm inner diameter) manufactured in 360 stainless steel to resist against corrosion. Each tank is equipped with heating jackets. Holes through the lid allow us to pass a mixing shaft and impeller (only one shared motor but two driving belts), two side taps (one to feed the tank in monomer and the other for the pressure sensor and to make the internal pressure equal), a thermometer pocket, a vent nozzle, an outflow tube (the orifice of the tube is placed very close to the impeller at the bottom of the tank), and a load tap with a larger internal diameter.
- (ii) A T-mixer (C) where the two streams from A and B impinge.
- (iii) The quench vessel (D) is a simple 1 L 360 stainless steel vessel (10 cm inner diameter), the top of which is equipped with a load tap, a sampling tube, a vent nozzle connected with the over-flow valve, a central hole for the reaction tube, a CO₂ sparger, a pressure measurement tap, and a thermometer pocket.
- (iv) The reactor (D) is a 4 mm inner diameter (6 mm outer diameter) flexible tube made of Polyamide-11,12 (Manuril/Tecalan®). The maximum service pressure is 23 bar at 20 °C and 11 bar at 80 °C (bursting pressure: 100 bar at 20 °C and 45 bar at 80 °C).
- (v) The temperature in the quench and upstream reservoirs is monitored with a standard Type K clad thermocouple and the pressure via a 0–25 bar sensor (accuracy: 0.25%; maximum pressure: 75 bar; service temperature: 0–70 °C; with a 4–20 mA (2 wires) output).
- (vi) The gas storage tanks are equipped with dual stage regulators: e.g. ethylene feedstock: first stage 0–300 bar, second stage 0–80 bar; or single stage regulator: e.g. argon feedstock: only one stage 0–25 bar (accuracy: 2.5%).
- (vii) The upstream–downstream pressure difference is controlled via the use of an overflow pressure regulating valve. The device used here is a special

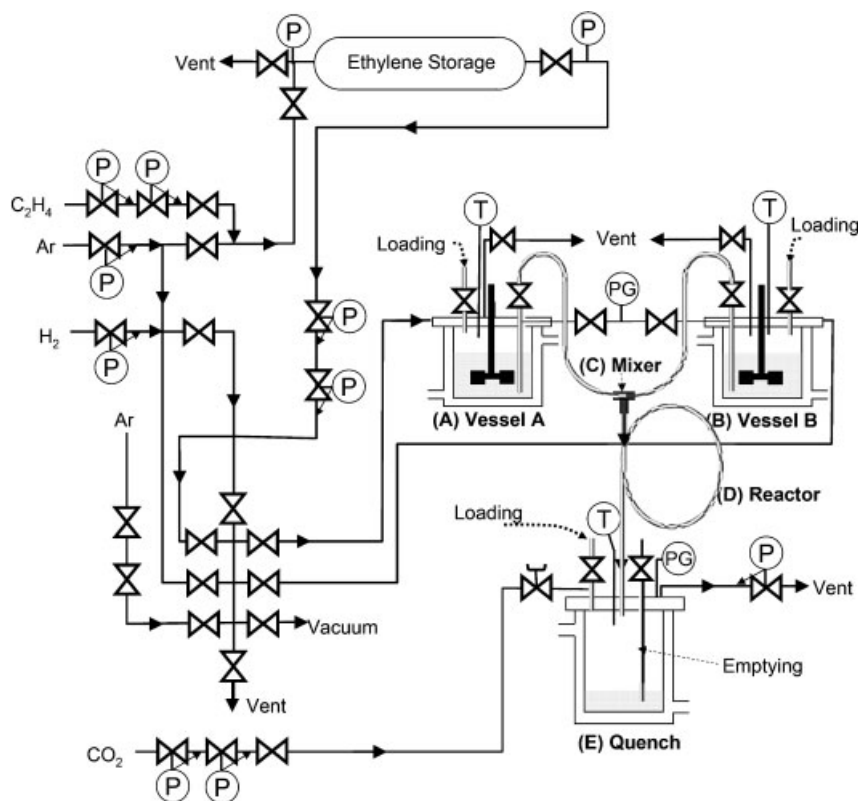


Figure 2. Schematic illustration of quenched-flow apparatus for ethylene homo-

model designed to meet our specifications of wide working pressure range (0–24 bar) with adequate sensitivity. A 35 mm diameter Viton membrane, a 7 mm long spring and a 1 mm diameter vent passage are combined to this end. Silicon seals allow us to work in a broad temperature range: usually -40°C to 80°C continuously but even down to -70°C for short periods. To keep our device in good working order it is recommended to use upstream a $25\ \mu\text{m}$ pore size stainless steel filter.

(viii) These reasoning behind these choices are outlined in the following paragraphs.

Up Stream Vessels (A and B in Figure 2)

Three principal factors influence the choice of mixing equipment for the upstream dispersion: (i) the process requirements, (ii) the flow properties of the fluid phase, and (iii) the equipment cost. The mixing equipment should maximize the flow in such a way as to enlarge the interfacial area between gas, liquid and solid phases (i.e. promotion of mass and heat transfer between the different phases) and to avoid stagnant regions in slurries via large top-to-bottom flow circulations (e.g. minimize accumula-

tion of solids behind the mixing equipment). Agitator choice simply comes down to the choice of the impeller, although mixer design usually also takes into account components such as the motor, drive and shaft. In short, the mixer motor must be properly sized to deliver the desired process result, the mixer drive must have sufficient torque for the application and the mixer shaft must be designed to withstand torque and natural vibration frequencies. Cost considerations allow us afterwards to finalize the choice of our equipment: A 4-bladed turbine with 45° pitched blades impellers seem to be a good compromise between high pumping efficiency and high shear for our process. To end, we advocate (i) to introduce the slurry when the mixer is turned on and (ii) to fix the maximum working speed at 300 rpm (however we will adapt the speed according to the ratio of particles found over the tank bottom after the slurry outflow).

Mixing Element (C in Figure 2)

The element where the streams from vessels A and B mix is the “heart” of the apparatus. It had to be designed to shorten the mixing time and mixing distance, i.e. to shorten the dead time and to localize mixing in time and space. It is well known that operation at high volume flows is expected to guarantee a short mixing due to a favourable use of turbulence induced by direct collision of the two reactant streams. Turbulent flow, by means of the chaotic eddy motion associated with local velocity fluctuations, is the preferred flow regime for mixing because it brings about uniformity of concentration and temperature, blends materials, facilitates chemical reaction, brings about intimate contact of multiple phases, and so on. As many mixers are designed for single-purpose mixing systems, there are as many mixing modules as there are specific applications. Mixers based on the “Berger ball mixer” technology,^[15] free jet^[16] and multi-capillary mixers^[17] have been proposed with commercially available stopped-flow instruments. A “T-mixer” (where the two reagent streams meet at 180° to each other) allows a symmetrical 1:1 mixing, but in limited range of flow rate. Properly designed, i.e., with due consideration given to the incoming (reagent) streams and the main resulting stream, “T-mixers” can produce high degrees of uniformity and minimize mixing time.^[18–20]

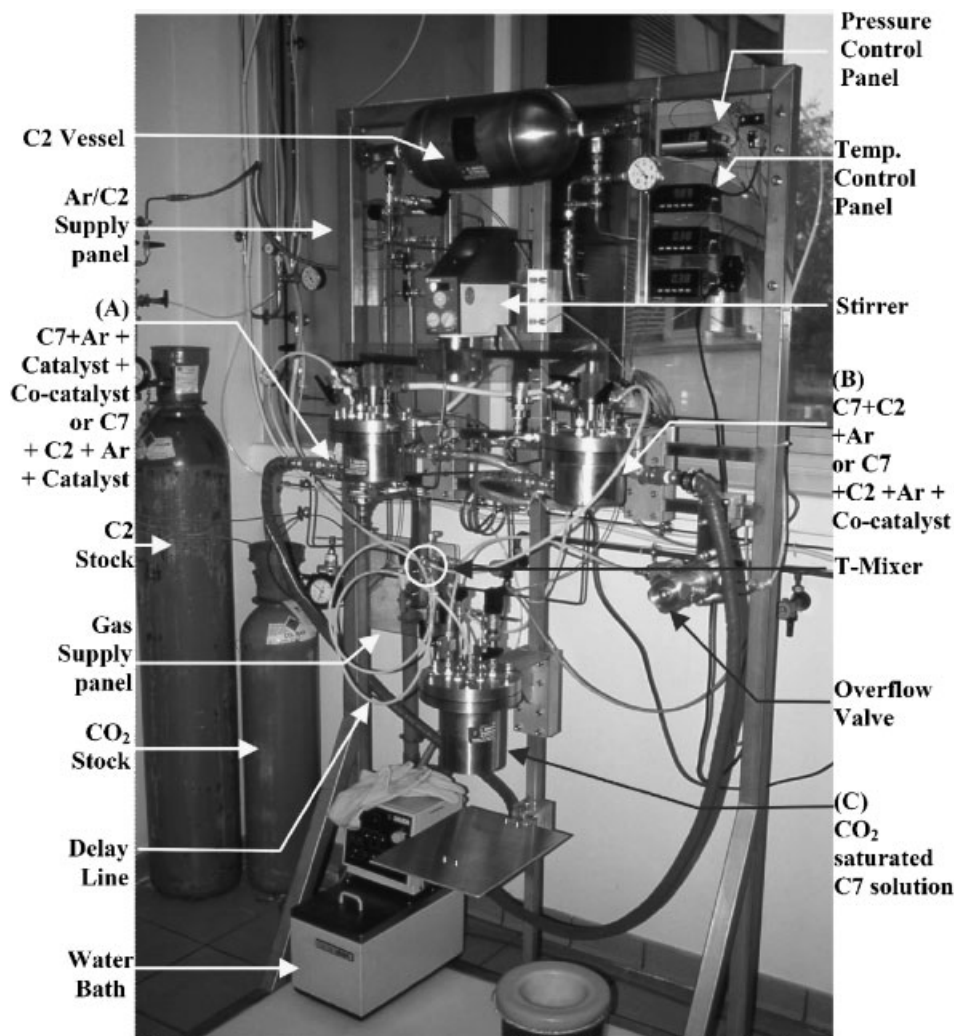


Figure 3. Photograph of the quenched-flow apparatus: this equipment was initially designed in order to supply answers to a large number of questions on particle morphology and kinetics. Thus, it is possible to use it for a wide range of monomer concentrations, total pressure, temperatures, residence times, pre-contacting times, poisoning conditions, etc.

Where slurries are concerned, it is difficult to use highly complex mixer geometries due to the solid particles themselves (especially when they are on the order of 10s of microns in diameter), and a tradeoff between mixing efficiency, life expectancy of the equipment and operating cost must be considered. A “simple” T-mixer should suit perfectly. However, the combination of slurry phase and co-catalyst solution in a T-mixer is delicate in so far as: (i) we control only some properties of the injected streams in the T; (ii) the catalyst particles properties change as soon as they are in contact with compounds such as co-catalyst, monomer, etc.; and (iii) we can not act on the geometry of the mixing cell to change the mixing itself (since we are more or less obliged to use “off the shelf” products).

Tubular Reactor (D in Figure 2)

After the mixing step, the *delay line* allows reaction ageing from a few milliseconds to several seconds by modifying the solution flow rate and/or the delay line volume (continuous flow mode), or alternatively by including pauses in the sequence time (interrupted flow mode). To date, available commercial devices claimed to reach reaction delay times as short as 3 s.^[3] Observation times of less than a few milliseconds seemed to be unattainable with these commercial devices. It should be noted here that the minimum observation time was determined by the dead time (the time interval from initial contact of the reactants to the point at which first observations can be made) of the instrument, the length of the delay lines, the mixing efficiency and the fluid flow rates. The aged mixture is then quenched with a poison that stops the reaction as rapidly as possible.

Concerning fluid transport in the reactor, we have to consider up-flow and down-flow in vertical and curved

pipes and flow through restrictive elements (the reactor is a coiled tube). Once again where solid particles are concerned, the complexity of the operations increases and severe restrictions are imposed on the choice of equipment elements. Let us consider first the up-flow we distinguish from the down-flow. For up-flow in vertical pipes, the minimum particles conveying velocity may be estimated as twice the terminal settling velocity of the largest particles. If the flow rate we imposed is not enough to set particles in motion, the solid particles are no longer transported and may collapse the “conveying pipe”. Down-flow in vertical pipes is not a problem, but the flow in curved pipes is worth thinking about. Indeed, there are two reasons for that: (i) for flow through curved pipes, a secondary circulation perpendicular to the main flow (the Dean effect) occurs that increases the friction relative to

straight pipe flow, and (ii) as mentioned above, the catalyst surface properties change as fresh polymer was formed. Also since the particle can eventually become sticky, we will use a flexible pipe with low surface roughness, translucent in order to observe any eventual clogging, and easy and inexpensive to replace if need be.

One of the options we considered first is to lay the end of the reaction tube under the quench solution. However, if the quench occurs at temperatures below -20°C as suggested by certain authors (see below), the tube will be subjected to a local cold source at its outlet which could create a temperature gradient in the reaction section. For this reason the reactor tube ends just below the lid of the quench vessel. It should be noted that the additional time that it takes for the incoming particles to fall into the quench liquid is negligible (t estimated to be 4 ms at most; but as the fluid is sprayed in an atmosphere saturated in CO_2 , this effect diminished). Also as the residence time we aim for is for the best in the region of a few seconds, it did not appear essential to thermally insulate the tube.

As it is difficult to control the flow rate through the reactor (in order to adjust the reaction time) using additional restrictive elements of flow because of possible deposit of particles and alumina, the driving force of the assembly was used to control the flow, i.e. the pressure difference between upstream tanks and downstream quenching tank. It should be noted here that it is necessary to verify that Vessels A and B empty at the same rate.

In order to control the upstream-downstream pressure difference, it will be necessary to use calibrated pressure regulating devices. Upstream, we will use argon or monomer pressure as a piston to force the flow of our slurry and co-catalyst solutions in the reaction tube. We therefore need to maintain a nearly constant pressure level in tanks A and B although fluctuations, essentially due to gas volume expansion generated by the solution outflow, are possible. A dual stage regulator would allow us to impose a constant working pressure since the regulator element (membrane and/or spring) is sensitive and reactive enough. Downstream, to avoid and to control the increase of the internal pressure due to the reactant inflow in the quenching reactor we will use an over-flow valve. Our situation is transient in nature: indeed, the required relief rate is continually changing as the tank is filling, so the valve was designed to keep the pressure in the quench vessel (E in Figure 2) constant during the filling period (i.e. during the entire venting period). Thus, at any instant, the volumetric vent rate must be equal to the rate of liquid volume increase in the tank.

The upstream-downstream pressure difference was found solving the macroscopic mechanical energy balance of our system. To estimate the upstream-downstream pressure difference we must apply to ensure the forced flow we need, we propose to calculate the pressure drop for

each individual resistances and then to sum up for the entire system. The calculation of pressure drop involves the estimation of corresponding friction loss for each individual resistance. The detailed calculations of the pressure drop of the system are given in Appendix I. We choose here to scan a broad range of residence time by varying the length of the reaction tube (4 mm inner diameter; length: 0.5, 1, 2 and 4 m) and by varying the imposed flow rate (60 to $120\text{ cm}^3/\text{s}$). For each set of operating conditions, we obtain a residence time and the associated drop in pressure between the upstream and the downstream. It should be remembered that the values we obtained are rough estimates of the real drop in pressure, seeing that we have not considered flow through curved pipes nor the up-flow through a section of the transport and reaction tube, etc. Even so, and as Figure 4 shows, it seems that pressure drops on the order of 1–6 bar are enough to reach the residence time we aimed for (40 ms–1 s) and for that matter this trend will be confirmed below.

Quenching Step (E in Figure 2)

Ideally, the poison used in this step must be able to instantaneously quench all the sites of the catalytic system and *not* interact with the support (degradation, swelling, dissolution, etc.) in order to fix the morphology of the growing macro-particles at the end of reaction. All of the quenching solutions as used in articles mentioned in the previously cited texts contain acidic alcohol that will destroy

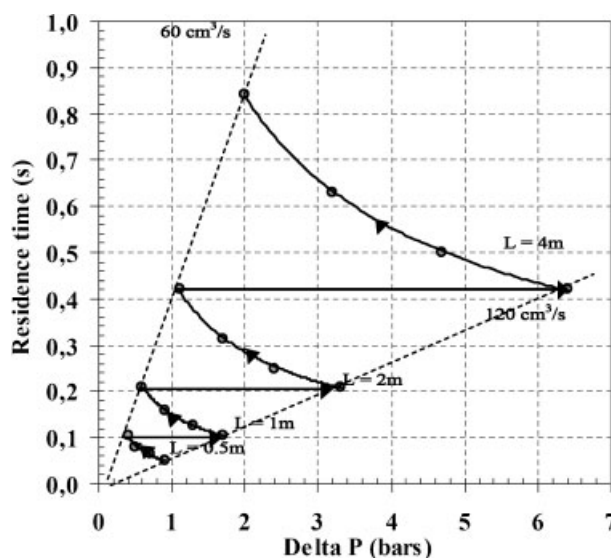


Figure 4. Estimate of the total drop in pressure of the equipment as the sum of each individual resistances to the flow we estimated. 4 lengths of reaction tube (4, 2, 1 and 0.5 m) and 4 flow rates (60, 80, 100 and $120\text{ cm}^3/\text{s}$) are tested. It seems that pressure drops on the order of 1 to 6 bar are enough to reach the residence time we aimed for (50 ms–1 s).

the catalytic support. Other poisons, such as encumbered mono-functional molecules like trimethylcyclopentadienylsilane or triphenylsilanol, macro-cycles or chelating Lewis bases like ethylene glycol dimethyl ether,^[21] are efficient poisons only if they are used in pre-treatment of the catalyst in order to strongly decrease the activity of the catalytic system. Indeed, used during the polymerization stage, a fall of activity is observed but only after interaction time of more than one minute because of the time required for the transfer and insertion of the quenching molecules between the growing chains and the active sites. Thus, large molecules that diffuse poorly through the polymer are not appropriate for our needs. Smaller quenching molecules such as CO or CO₂ are thus considered.

Poisoning by CO or CO₂ is common in studies concerned with the study of the propagation mechanism (number of propagation centre, rate constant, etc.) and transfer reactions.^[22–24] These poisoning agents react selectively with the activate transition metal-carbon bonds: the bonds referred as inactive or dead (i.e. polymer chain–aluminium bonds) are not concerned by CO or CO₂ quenching. Mejzlik et al.^[24] proposed to study the poisoning efficiency of CO and CO₂ as a function of various operating conditions such as contact time, quantity of poison (excess compared to [Ti] or not), degasification after contact or not. They pointed out that beyond certain limiting conditions, the quantity of carbonyl groups incorporated in the polymer chain (due to poisoning) no larger varied. They also noted that the carbonyl content in the polymer chain is somewhat lower after CO₂-quenching than after CO-quenching under similar conditions. Shiono et al.^[7] proposed to quench the solution with CO under various quenching temperatures, contact times, and CO concentrations in the quenching solution (fixed or at saturation). According to these last authors, the best results are those using the association of a lower temperature (–78 °C) to deactivate all the polymerization sites and of an efficient selective poison to kill irreversibly the active sites: thus one will retain first the quenching system composed of an heptane solution saturated with poison at atmospheric pressure, working at –78 °C for 1 h. Given the toxicity of CO, we chose to use CO₂ under similar conditions (saturation and low temperature) even if this system is considered as less active than CO.^[24] Thus, it seems to be essential to define the optimum or sufficient quenching conditions we need for our process by a set of poisoning tests (see below for more details).

This step was placed downstream from the reactor and consists of three principle stages:

- (i) *Gas adsorption*: the solvent is saturated in quenching CO₂ via the use of a sparger, i.e., a simple bubbler. This method allows us to disperse gas in

liquid through an open-ended pipe. Under ordinary conditions, the bubbles produce by the sparger should provide a large enough effective area of contact between gas and liquid.

- (ii) *Poisoning*: the end of the reaction tube protrudes a few centimetres into the head space of the quench vessel, and acts as a jet (a spray), allowing the fluid to extend and decelerate due to the sudden enlargement of the tube section. During this step, liquid/solid droplets may be generated taking part in the gas adsorption and thus in the quenching step. Then the suspension falls into the saturated CO₂ heptane solution and is rapidly totally quenched.
- (iii) *Agitation*: Gas sparger may also be used for simple blending and particle suspension operations when mechanical agitation is difficult or when the extra expense of mechanical agitation is not justified. The agitation produced by a stream of bubbles generates liquid flows and solid particles motion.

Validation

As mentioned above, by varying the volume of the reaction tube, and thus its length, and by varying the drop in pressure between the upstream and the downstream vessels, we are able to control the flow and thus the residence time. Figure 5 shows a representation of the precisely controlled residence times we can easily reach according to the pressure difference ΔP for 4 lengths of tube (4, 2, 1 and 0.5 m). We will choose thereafter to work with pressure drops in the range 1–6 bar to reach precisely controlled residence time in the range: 40 ms–1.5 s. Indeed as can be seen from insert in Figure 5, it is not useful to subject the equipment to ΔP higher than 6 bar because of the minimum interest brought to the level of reached residence times.

Polymerization Procedure

The highly active MgCl₂-supported 4th generation ZN catalyst used in this study contained 19.2 wt.-% magnesium and 2.6 wt.-% titanium. Heptane was used after drying over 3 Å molecular sieves under argon overpressure. The other chemicals (commercially obtained, research grade) are used without further purification. Each of the upstream vessels was filled with 250 cm³ of different heptane solutions. Depending on the operational mode, the solutions contained either pre-activated, or inactive catalyst.^[14] In this phase of the study, we used a pre-activated catalyst. Here, vessel A vessel contained a solution of catalyst ([Ti]: 0.1 mmol) and of TEA ([TEA]: 2.5

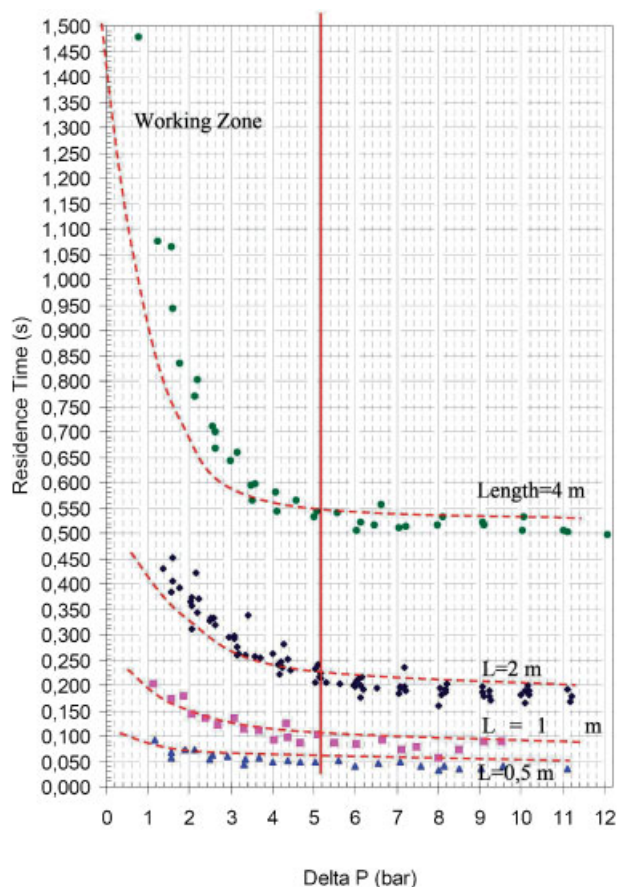


Figure 5. Representation of the residence time we can easily reach according to the upstream-downstream pressure (ΔP) we imposed for 4 lengths of reaction tube (4, 2, 1 and 0.5 m). Each point is an individual run.

mmol). Vessel B contained no catalyst, but is saturated in ethylene at the desired T and P. After the two solutions attained equilibrium conditions, they were forced to flow simultaneously through a reaction tube of various length with the pressure of argon (9 bar). When both solutions

met at the T connection, polymerisation starts and continues in the tube until the quenching step. The polymerisation mixture was quenched in 250 cm³ of CO₂-saturated heptane solution under different conditions (see below). The mixture is then degassed and gradually warmed up to room temperature before sampling for off-line analysis.

Quenching Step: Optimum Quenching Conditions

As our equipment is flexible, it is possible to use it for a wide range of monomer concentrations, pressures, temperatures, residence time, reaction times, poisoning conditions, etc. We search here to adapt the quenching conditions to suit our stated objectives by a set of poisoning tests. This was done by varying the conditions in the quenched vessel for representative reaction conditions ($L = 2$ m, $\Delta P = 6$ bar, $T_{\text{reactor}} = 80$ °C, $P_{\text{C}_2} = 8$ bar, $P_{\text{tot}} = 9$ bar, residence time $t = 200$ ms). The results are summarized in Table 1.

The quality of quench was assessed by assuming that the lower the yield was, the faster the quench was. As can be seen from Table 1 the best quenching conditions appear to be a quench vessel saturated in CO₂ at ambient temperature. It is clear that regardless of the temperature, we need to poison the active sites. Simply cooling, then degassing is not enough to stop the reaction immediately. And quenching the reaction at -30 °C, but with CO₂ seems less satisfactory while this might appear surprising, let us recall that more monomer will be absorbed by the PE at low T, and the diffusion coefficient of CO₂ in the polymer will be lower. It is therefore possible that even if the reaction stops at -30 °C, some small amount of additional polymer is formed during the degassing (stage as the particles warm up).

Thus we retain the quenching system composed of 250 cm³ of an heptane solution saturated with CO₂ under

Table 1. Effect of quenching conditions.

Degassing	Quenching conditions		Yield	
	CO ₂	Low temperature	g/g Ti	
			Sample A ^{a)}	Sample B ^{a)}
Yes	No	No/20 °C	8.169	7.833
Yes	No	Yes/ -30 °C	6.316	6.194
Yes	C7 saturated	No/20 °C	0.498	0.532
Yes	C7 saturated	Yes/ -30 °C	0.971	0.918

^{a)}Yield is determined using Mg and Ti measurement by ICP (inductively coupled plasma) associated with an optical spectroscopic detector (JY38 Type III) - see hereafter.

10 bar of CO₂ at ambient temperature because of the better results of poisoning.

Conclusion

In the present paper we have described how we have used basic chemical engineering principles to design and build a novel reactor to study the nascent polymerisation of olefins on supported catalysts. The reactor in question is flexible enough that we can measure reaction yield and rate, macromolecular properties (molecular weight distribution, crystallinity, ...). In addition, and perhaps more importantly, we can recover the particles in order to study

the evolution of particle morphology and support fragmentation at very short times, all under industrial polymerisation conditions.^[13,14]

Appendix I: Flow Regulation - Calculation of Pressure Drop

The detailed calculations of the drop pressure of the system is given in Table A1. The relationship between pressure drop, tube length and residence time is given in Table A2, and shown in Figure 4. We will briefly describe the logic behind these calculations. We can estimate the upstream-downstream pressure difference value we

Table A1. Pressure drop calculations.

(1) Vertical Down-Flow in a Straight Reaction Tube	
Internal diameter	D_i 4 mm
Length	L 200 cm
Flow	F 60 cm ³ /s
Linear flow velocity	v 4.78 m/s
Reynolds	Re 30937
Fanning friction coefficient	f 0.00596
Friction loss	L_v 135.9 m ² /s ²
Pressure drop	ΔP 92 436 Pa
(2) Other Tube Length	
Internal diameter	D_i 4 mm
Length	L 60 cm
Flow	F 30 cm ³ /s
Linear flow velocity	v 2.39 m/s
Reynolds	Re 15469
Fanning friction coefficient	f 0.0708
Friction loss	L_v 12.12 m ² /s ²
Pressure drop	ΔP 8 244 Pa
(3) Obstacles to Flow (Connections, Valves, ...)	
K_f :	
Sudden contraction	0.5
Standard 45° elbow	0.35
Standard T Connection	1
Sudden enlargement	1
Friction loss	L_v 9.13 m ² /s ²
Pressure drop	ΔP 6 207 Pa
(4) Gravity	
Pressure drop	ΔP 10 006 Pa
Upstream-downstream pressure difference we must apply to force the flow in the reaction tube	116 893 Pa or 1.16 bar

Table A2. Tube length, pressure drop and residence time for the quenched flow reactor.

Tube length m	Flow rate cc/s	Residence time ms	$\frac{\Delta P}{\text{bar}}$
4	60	840	2
	80	630	3.2
	100	500	4.7
	120	420	6.4
2	60	420	1.1
	80	314	1.7
	100	250	2.4
	120	210	3.3
1	60	210	0.6
	80	160	0.9
	100	125	1.3
	120	105	1.7
0.5	60	105	0.4
	80	80	0.5
	100	65	0.7
	120	50	0.9

needed by solving the macroscopic mechanical energy balance of our system using Bernoulli's theorem, Equation (A1).

$$\frac{1}{2}v_2^2 + gh_2 = \frac{1}{2}v_1^2 + gh_1 - \int_{P_1}^{P_2} \frac{dP}{\rho} - \delta W - L_v \quad (\text{A1})$$

where v is the linear velocity, g the local acceleration due to gravity, P the absolute static pressure, ρ the density, and h the height above any arbitrary horizontal datum plan. For liquids, the integral $\int_{P_1}^{P_2} dP/\rho$ becomes simply $(P_2 - P_1)/\rho$ where ρ is substantially constant (incompressible fluid). To estimate the upstream-downstream pressure difference we must apply to ensure the forced flow rate we need, we can calculate the pressure drop for each individual resistances with regard of the algebraic sign and then to sum up for the entire system. The calculation of pressure drop involves the estimation of corresponding friction loss for each individual resistance (N.B. we will assume that δW , external work, is equal to zero).

The friction loss L_v is given by:

$$L_v = \frac{2v^2 f L}{D_i} = \frac{32f L q^2}{\pi^2 D^5} \quad (\text{A2})$$

where D_i = duct internal diameter, L = duct length, v = fluid velocity, q = volume rate of flow, and f = fanning factor, dimensionless. The Fanning friction factor f is a

function of the Reynolds number Re and the roughness of the channel inside surface ε (for commercial steel material $\varepsilon = 0.0457$ mm). In turbulent flow ($3000 < Re < 10^5$), for smooth pipes ($\varepsilon/D_i \rightarrow 0$) and for specified flow rate, the friction factor can be conveniently computed from the Blasius equation:

$$f = 0.0791/Re^{1/4} \quad (\text{A3})$$

The constants and standard approach to calculating the pressure drop $(P_2 - P_1)/\rho$ can be found in the literature.^[25]

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